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OFFICE OF NAVAL RESEARCH

END-OF-THE-YEAR REPORT

PUBLICATIONS/PATENTS/PRESENTATIONS/HONORS/STUDENTS REPORT

for

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Novel Side-Chain Liquid Crystalline Polymers

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1. End-of-the-Year Report

Part I

a. Papers Submitted to Referred Journals (and not yet published)

1. V. Percec, M. Lee and H. Jonsson
Molecular Engineering of Liquid Crystal Polymers by Living Polymerization. 2. Living Cationic Polymerization of 11-[(4-Cyano-4'-biphenyl)oxy]undecanyl Vinyl Ether and the Mesomorphic Behavior of the Resulting Polymers
Journal of Polymer Science, Part A, Polym. Chem. Ed., submitted
(no other support)

2. V. Percec and M. Lee
Molecular Engineering of Liquid Crystal Polymers by Living Polymerization. 3
Influence of Molecular Weight on the Phase Transitions of Poly{8-[(4-Cyano-4'-biphenyl)oxy]octyl Vinyl Ether}
Macromolecules, submitted
(no other support)

3. V. Percec and M. Lee
Molecular Engineering of Liquid Crystal Polymers by Living Polymerization. 4
A Continuous Dependence on Molecular Weight of the Mesomorphic Phases of Poly{8-[(4-Cyano-4'-biphenyl)oxy]octyl Vinyl Ether}
Macromolecules, submitted
(no other support)

4. V. Percec, D. Tomazos and A. E. Feiring
Semifluorinated Polymers. 1. Synthesis and Characterization of Side Chain Liquid Crystalline Polymers Containing Semifluorinated Oligooxyethylene Based Flexible Spacers
Polymer, submitted
(no other support)

5. V. Percec and C. -S. Hsu
Synthesis and Mesomorphic Behavior of Poly(methylsiloxane)s and Poly(methylsiloxane-co-dimethylsiloxane)s Containing Oligooxyethylene Spacers and Mesogenic Side Groups
Polymer Bulletin, in press
(no other support)

6. V. Percec, B. Hahn, M. Ebert, and J. H. Wendorff
Liquid-Crystalline Polymers Containing Heterocycloalkanediyl Groups as Mesogens. 8. Morphological Evidence for Microphase Separation in Poly(methylsiloxane-co-dimethylsiloxane)s Containing 2-[4-(2(S)-Methyl-1-butoxy)phenyl]-5-(11-undecanyl)-1,3,2-dioxaborinane Side Groups
Macromolecules, in press
(partial support from NSF)

7. V. Percec and J. Heck
Liquid Crystalline Polymers Containing Mesogenic Units Based on Half-Disc and Rod-like Moieties. 1. Synthesis and Characterization of 4-(11-Undecan-1-yloxy)-4'-[3,4,5-tri(p-n-Dodecan-1-yloxybenzyloxy)benzoate]Biphenyl Side Groups
Journal of Polymer Science; Polym. Lett., submitted
(partial support from NSF)

8. V. Percec and J. Heck
Liquid Crystalline Polymers Containing Mesogenic Units Based on Half-Disc and Rod-like Moieties. 2 Synthesis and Characterization of Poly{2-[3,4,5-tri[p-(n-Dodecan-1-yloxy)benzyloxy]benzoate]-7-[p-(11-undecan-1-yloxy)benzoate]naphthalene]methyl siloxane}
Polymer Bulletin, submitted
(partial support from NSF)

b. Papers Published in Refereed Journals

1. J.M. Rodriguez-Parada and V. Percec
Synthesis and Characterization of Liquid Crystalline Poly(N-acylethyleneimine)s
J. Polym. Sci., Polym. Chem. Ed., 25, 2269 (1987)
(partial support from Petroleum Research Fund of ACS)

2. C.S. Hsu, J.M. Rodriguez-Parada and V. Percec
Liquid Crystalline Polymers Containing Heterocycloalkane Mesogens, 1. Side Chain Liquid Crystalline Polymethacrylates and Polyacrylates Containing 2,5-Disubstituted-1,3-Dioxane Mesogens
Makromol. Chem., 188, 1017 (1987)
(no other support)

3. C.S. Hsu, J.M. Rodriguez-Parada and V. Percec
Liquid Crystalline Polymers Containing Heterocycoalkane Mesogens., 2. Side Chain Liquid Crystlline Polysiloxanes Containing 2,5-Disubstituted-1,3-Dioxane Mesogens
J. Polym. Sci., Polym. Chem. Ed., 25, 2425 (1987)
(no other support)

4. C.S. Hsu and V. Percec
Synthesis and Characterization of Liquid Crystalline Polysiloxanes Containing Benzyl Ether Mesogens
J. Polym. Sci., Polym. Chem. Ed., 25, 2909 (1987)
(no other support)

5. C. Pugh and V. Percec
Functional Polymers and Sequential Copolymers by Phase Transfer Catalysis, 29. Synthesis of Thermotropic Side-Chain Liquid Crystalline Polymers Containing a Poly(2,6-dimethyl-1,4-phenylene oxide) Main Chain
Polym. Bull., 16, 513 (1986)
(partial support from the Center for Adhesives, Sealants and Coatings of Case Western Reserve University)

6. C. Pugh and V. Percec
Functional Polymers and Sequential Copolymers by Phase Transfer Catalysis. 30. Synthesis of Liquid Crystalline Poly(epichlorohydrin) and Copolymers
Polym. Bull., 16, 521 (1986)
(partial support from the Center for Adhesives, Sealants and Coatings of Case Western Reserve University)

7. C.S. Hsu and V. Percec
Liquid Crystalline Polymers Containing Heterocycloalkane Mesogens. 3. Biphasic Side-Chain Liquid Crystalline Polysiloxanes Containing trans 5-n-Undecanyl-2-(4-Cyanophenyl)-1,3-Dioxane Side Groups
Makromol. Chem. Rapid Commun., 8, 331 (1987)
(no other support)

8. C.S. Hsu and V. Percec
Liquid Crystalline Polymers Containing Heterocycloalkane Mesogens. 4. Biphasic Side-Chain Liquid Crystalline Polysiloxanes Containing trans-5-(n-Undecanyl)-2-(4-Methoxyphenyl)-1,3-Dioxane and trans-2-(n-Decanyl)-5-(4-Methoxyphenyl)-1,3-Dioxane Mesogens
Polym. Bull., 17, 49 (1987)
(no other support)

9. B. Hahn and V. Percec
Liquid Crystalline Polymers Containing Heterocycloalkane Mesogens. 5. Synthesis of Biphasic Chiral-Smectic Polysiloxanes Containing 2,5-Disubstituted-1,3-Dioxane and 2,5-Disubstituted-1,3,2-Dioxaborinane Based Mesogens
Macromolecules, 20, 2961 (1987)
(partial support from Materials Research Group at Case Western Reserve Univ.)

10. C.S. Hsu and V. Percec
Synthesis and Characterization of Liquid Crystalline Polyacrylates and Polymethacrylates Containing Benzyl Ether and Diphenyl Ethane Based Mesogens
J. Polym. Scvi., Part A: Polym. Chem., 27, 453 (1989)
(no other support)

11. V. Percec, J.M. Rodriguez-Parada and C. Ericsson
Synthesis and Characterization of Liquid Crystalline Poly(p-vinylbenzyl ether)s
Polym. Bull., 17, 347 (1987)
(no other support)

12. V. Percec, J.M. Rodriguez-Parada, C. Ericsson and H Nava
Liquid Crystalline Copolymers of Monomer Pairs Contai[illegible] Mesogenic Units which Exhibit Constitutional Isomerism
Polym. Bull., 17, 353 (1987)
(no other support)

13. C.S. Hsu and V. Percec
Liquid Crystlline Polymers Containing Heterocycloalkanediyl Groups as Mesogens. 6. Liquid Crystalline Polymethacrylates and Polyacrylates of trans 2-[4-(11-hydroxyundecanyloxy)-3,5-dimethylphenyl]-4-(4-methoxyphenyl)-1,3-dioxane
Makromol. Chem., 189, 1141 (1988)
(no other support)

14. C.S. Hsu and V. Percec
Synthesis and Characterization of Biphasic Liquid Crystalline Polysiloxanes Containing 4-Undecanyloxy-4'-Cyanodiphenyl Side Groups
Polym. Bull., 18, 91 (1987)
(no other support)

15. V. Percec, C.S. Hsu and D. Tomazos
Synthesis and Characterization of Liquid Crystalline Copolymethacrylates, Copolyacrylates, and Copolysiloxanes Containing 4-Methoxy-4'-Hydroxy-α-Methylstilbene Constitutional Isomers as Side Groups
J. Polym. Sci., Part A: Polym. Chem., 26, 2047 (1988)
(no other support)

16. V. Percec and D. Tomazos
Liquid Crystalline Copoly(vinylether)s Containing 4(4')-Methoxy-4'(4)-Hydroxy-α-Methylstilbene Constitutional Isomers as Side Groups
Polym. Bull., 18, 239 (1987)
(no other support)

17. V. Percec
Liquid Crystalline Polyethers
Mol. Cryst. Liq. Cryst., 155, 1-35 (1988)
(partial support from NSF)

18. V. Percec
Liquid Crystalline Polymers by Cationic Polymerization
Makromol. Chem., Makromol. Symp., 13/14, 397 (1988)
(partial support from NSF)

19. V. Percec and D. Tomazos
Synthesis and Characterization of Liquid Crystalline Polymethacrylates, Polyacrylates and Polysiloxanes Containing 4-Methoxy-4'-hydroxy-α-methylstilbene Based Mesogenic Groups
J. Polym. Sci., Polym. Chem. Ed., 29, 999 (1989)
(no other support)

20. V. Percec and D. Tomazos
Transformation of a Monotropic Mesophase into an Enantiotropic Mesophase by Copolymerization of the Parent Polymers' Monomer Pair Containing Constitutional Isomeric Mesogenic Side Groups
Macromolecules, 22, 1512 (1989)
(no other support)

21. V. Percec and D. Tomazos
Synthesis and Characterization of Liquid Crystalline Polymethacrylates, Polyacrylates and Polysiloxanes Containing 4-Hydroxy-4'-methoxy-α-methylstilbene Based Mesogenic Groups
Macromolecules, 22, 2062 (1989)
(no other support)

22. V. Percec, D. Tomazos and C. Pugh
Influence of Molecular Weight on the Thermotropic Mesophases of Poly 6-[4-methoxy-(4'-oxy)-α-methylstilbene] hexyl methacrylate
Macromolecules, 22, 3259 (1989)
(partial support from ARO)

23. V. Percec, D. Tomazos and R.A. Willingham
The Influence of the Polymer Backbone Flexibility on the Phase Transitions of Side Chain Liquid Crystal Polymers Containing 6-[4-(4-Methoxy-p-methylstyryl)-phenoxy]hexyl Side Groups
Polym. Bull., 22, 199 (1989)
(partial support from ARO)

24. V. Percec and D. Tomazos
Suppression of Side Chain Crystallization and Transformation of Monotropic Mesophases into Enantiotropic Mesophases by Copolymerization of the Parent Polymers' Monomer Pairs Containing Constitutional Isomeric Mesogenic Side Groups
Polymer, 30, 2124 (1989)
(no other support)

c. Books (and sections thereof) Submitted for Publication

None

d. Book Chapters Published

1. Coleen Pugh and Virgil Percec
The Effect of the Polymer Backbone on the Thermotropic Behavior of Side-Chain Liquid Crystalline Polymers, in Chemical Reactions on Polymers, J.L. Benham and J.F. Kinstle, Eds., ACS Symposium Series 364, Am. Chem. Soc., Washington, DC, 1987, p. 97.
(partial support from the Center for Adhesives, Sealants and Coatings of Case Western Reserve University)

2. V. Percec and C. Pugh
Molecular Engineering of Predominantly Hydrocarbon Based Liquid Crystalline Polymers, in Side Chain Liquid Crystal Polymers, C.B. McArdle, Ed., Blackie and Son Ltd., Glasgow, and Chapman and Hall, New York, 1989, p. 30.
(partial support from NSF)

e. Technical Reports Published and Papers Published in Non-Refereed Journals

1. J.M. Rodriguez-Parada and V. Percec
Synthesis and Characterization of Liquid Crystalline Poly(N-acylethyleneimine)s
J. Polym. Sci., Polym. Chem. Ed., 25, 2269 (1987)
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Liquid Crystalline Polymers Containing Heterocycloalkane Mesogens. 1. Side Chain Liquid Crystalline Polymethacrylates and Polyacrylates Containing 2,5-Disubstituted-1,3-Dioxane Mesogens
Makromol. Chem., 188, 1017 (1987)
(no other support)

3. C.S. Hsu, J.M. Rodriguez-Parada and V. Percec
Liquid Crystalline Polymers Containing Heterocycoalkane Mesogens. 2. Side Chain Liquid Crystlline Polysiloxanes Containing 2,5-Disubstituted-1,3-Dioxane Mesogens
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Makromol. Chem. Rapid Commun., 8, 331 (1987)
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19. V. Percec and D. Tomazos
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J. Polym. Sci., Polym. Chem. Ed., 29, 999 (1989)
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20. V. Percec and D. Tomazos
Transformation of a Monotropic Mesophase into an Enantiotropic Mesophase by Copolymerization of the Parent Polymers' Monomer Pair Containing Constitutional Isomeric Mesogenic Side Groups
Macromolecules, 22, 1512 (1989)
(no other support)

21. C.S. Hsu, J.M. Rodriguez-Parada and V. Percec
Side-Chain Liquid Crystalline Polymethacrylates and Polyacrylates Containing 2,5-Disubstituted-1,3-Dioxane Mesogens
Am. Chem. Soc., Polym. Prepr., 27(2), 185 (1986)
(no other support)

22. C.S. Hsu, J.M. Rodriguez-Parada and V. Percec
Synthesis of Novel Side-Chain Liquid Crystalline Polysiloxanes
Am. Chem. Soc., Polym. Prepr., 27(2), 193 (1986)
(no other support)

23. C. Pugh and V. Percec
The Effect of the Polymer Backbone on the Thermotropic Behavior of Side-Chain Liquid Crystalline Polymers
Am. Chem. Soc., Polym. Prepr., 27(2), 36 (1986)
(partial support from the Center for Adhesives, Sealants and Coatings of Case Western Reserve University)

24. V. Percec, C.S. Hsu, D. Tomazos and J.M. Rodriguez-Parada
Side Chain Liquid Crystalline Copolymers of Monomer Pairs Containing Mesogenic Units which Exhibit Constitutional Isomerism
Am. Chem. Soc., Polym. Prepr., 29(1), 232 (1988)
(no other support)

25. V. Percec and D. Tomazos
Side-Chain Liquid Crystalline Polymers Containing 4-methoxy-4'-hydroxy-α-methylstilbene Based Mesogens
Am. Chem. Soc., Polym. Prepr., 29(1), 234 (1988)
(no other support)

26. V. Percec and D. Tomazos
Side Chain Liquid Crystalline Polymers Containing 4-hydroxy-4'-methoxy-α-methylstilbene Based Mesogens
Am. Chem. Soc., Polym. Prepr., 29(2), 292 (1988)
(no other support)

27. B. Hahn and V. Percec
Biphasic Side-Chain Liquid Crystalline Polymers Containing Chiral 2,5-Disubstituted-1,3,2-Dioxaborinane Based Mesogens
The Twelfth International Liquid Crystal Conference, Freiburg, W. Germany, 15-19 August 1988, Abstracts, p. 182
(partial support from NSF)

28. V. Percec and R. Yourd
Liquid Crystal Polyethers Based on Conform ational Isomerism
VI European Liquid Crystal Winter Conference, Schladming, Austria, 5-10 March 1989, Abstracts, p. 79
(partial support from NSF)

29. V. Percec and R. Yourd
Liquid Crystalline Polymers Based on Conformational Isomerism
Makromolekulares Kolloquium, Freiburg, W. Germany, 9-11 March 1989, Abstracts, p. 20
(partial support from NSF)

30. V. Percec
Conformational and Constitutional Isomerism in Liquid Crystalline Polymers
British Liquid Crystal Society, 4th Annual Meeting, 10-12 April 1989, Abstracts IV.1
(partial support from NSF)

31. J.L. Feijoo, G. Ungar, A. Keller, J.A. Odell, A.J. Owen and V. Percec
Evidence for Disclinations in the Isotropic State of Liquid Crystals forming Polymers
British Liquid Crystal Society, 4th Annual Meeting, 10-12 April 1989, Abstracts IV.4
(partial support from NSF)

32. V. Percec and D. Tomazos
Synthesis and Characterization of Liquid Crystalline Polymethacrylates, Polyacrylates and Polysiloxanes Containing 4-Hydroxy-4'-methoxy-α-methylstilbene Based Mesogenic Groups
Macromolecules, 22, 2062 (1989)
(no other support)

33. V. Percec, D. Tomazos and C. Pugh
Influence of Molecular Weight on the Thermotropic Mesophases of Poly 6-[4-methoxy-(4'-oxy)-α-methylstilbene] hexyl methacrylate
Macromolecules, 22, 3259 (1989)
(partial support from ARO)

34. V. Percec, D. Tomazos and R.A. Willingham
The Influence of the Polymer Backbone Flexibility on the Phase Transitions of Side Chain Liquid Crystal Polymers Containing 6-[4-(4-Methoxy-p-methylstyryl)-phenoxy]hexyl Side Groups
Polym. Bull., 22, 199 (1989)
(partial support from ARO)

35. V. Percec and D. Tomazos
Suppression of Side Chain Crystallization and Transformation of Monotropic Mesophases into Enantiotropic Mesophases by Copolymerization of the Parent Polymers' Monomer Pairs Containing Constitutional Isomeric Mesogenic Side Groups
Polymer, 30, 2124 (1989)
(no other support)

f. Patents Filed

None

g. Patents Granted

None

h. Invited Presentations

1. C. Pugh and V. Percec
The Effect of the Polymer Backbone on the Thermotropic Behavior of Side-Chain Liquid Crystalline Polymers
Symposium on Chemical Reactions on Polymers, ACS Meeting, Anaheim, CA., Sept. 1986
(partial support from the Center for Adhesives, Sealants and Coatings of Case Western Reserve University)

2. V. Percec
Liquid Crystalline Polyethers
Current Contributions in Polymer Science and Engineering Symposium, University of Michigan, Ann Arbor, 16-17 October 1986
(partial support from NSF)

3. V. Percec
Self-organized Polymeric Systems
University of Illinois, Urbana, October 1986

4. V. Percec
Polymers with Less than Three-dimensional Order
University of Chicago, Chicago, November 1986

5. V. Percec
Self-organized Polymers by Non-bonding Interactions
University of Massachusetts, Amherst, December 1986

6. V. Percec
Liquid Crystalline Polymers--New Synthetic Trends
Kent State University, Kent, April 1987

7. V. Percec
Liquid Crystalline Copolymers
Makromolekulares Kolloquium, Freiburg, W. Germany, March 1987

8. V. Percec
   Liquid Crystalline Polymers
   presented at Frontiers in Polymer Science, University of Akron, May 1987

9. V. Percec
   Liquid Crystalline Polymers Containing Calamitic Mesogens
   University of Lowell, May 1987

10. V. Percec
    New Trends in the Synthesis of Liquid Crystalline Polymers
    Massachusetts Institute of Technology, Cambridge, May 1987

11. V. Percec
    Liquid Crystalline Polymers based on Mesogenic Exhibiting Cinstitutiional and Conformational Isomerism
    Cornell University, Ithaca, July 1987

12. V. Percec
    Synthesis of Liquid Crystalline Polymers does not Require Rigid Rodlike Mesogens
    University of Connecticut, Storrs, July 1987

13. V. Percec
    Liquid Crystalline Polyethers
    International Conference - "Liquid Crystal Polymers"
    Bordeaux, France, 20-24 July 1987

14. V. Percec
    Liquid Crystalline Polymers by Cationic Polymerization
    8th Intwernational Symposium on Cationic Polymerization and Related Processes
    Munchen, 10-14 August 1987

15. V. Percec
    Liquid Crystalline Copolymers
    International Symposium on Copolymerization, Sydney, Australia, 23-27 August 1987

16. V. Percec
    Constitutional and Conformational Isomerism in Liquid Crystalline Polymers
    USA-Germany Symposium on Polymers, Napa Valley, CA, 7-11 September 1987

17. V. Percec
    Liquid Crystalline Polymers
    Great Lakes Polymer Conference, Detroit, 18 February 1988

18. V. Percec
    Side Chain Liquid Crystalline Polymers
    Germany-Brasil Symposium, Freiburg, W. Germany, 29 February-1 March 1988

19. V. Percec
    Liquid Crystalline Polymers
    University of Stuttgart, W. Germany, 27 July 1987

20. V. Percec
Liquid Crystalline Polymers
University of Akron, 11 May 1988

21. V. Percec and D. Tomazos
Constitutional Isomerism in Side Chain Liquid Crystalline Polymers
Sixth International Symposium on Liquid Crystals and Ordered Fluids, 31 August-4 September 1987

22. V. Percec and C.S. Hsu
Side Chain Liquid Crystalline Polymers Containing Heterocycloalkanediyl Based Mesogens
Sixth International Symposium on Liquid Crystals and Ordered Fluids, 31 August-4 September 1987

23. V. Percec, C.S. Hsu and B. Hahn
Biphasic Side-Chain Liquid Crystalline Polymers
Sixth International Symposium on Liquid Crystals and Ordered Fluids, 31 August-4 September 1987

24. V. Percec
Liquid Crystalline Copolymers
University of Bayreuth, W. Germany, 15 June 1988

25. V. Percec
Conformational Isomerism in Liquid Crystalline Polymers
University of Freiburg, W. Germany, 27 June 1988

26. V. Percec
Liquid Crystalline Copolymers
University of Marburg, W. Germany, 1 July 1988

27. V. Percec
Liquid Crystalline Polymers Based on Conformational Isomerism
University of Bristol, England, 25 January, 1989

28. V. Percec
Side Chain Liquid Crystalline Polymers
University of Bristol, England, 29 January 1989

29. V. Percec
New Liquid Crystalline Polymers
University of Bayreuth, W. Germany, 13 March 1989

30. V. Percec
Molecular Engineering of Side Chain Liquid Crystalline Polymers
The Royal Society of Chemistry, Annual Chemical Congress, University of Hull, England, 4-7 April 1989

31. V. Percec (invited main lecture)
Conformational and Constitutional Isomerism in Liquid Crystalline Polymers
British Liquid Crystl Society, 4th Annual Congress, University of Sheffield, England, 10-12 April 1989

32. V. Percec
New Liquid Crystalline Polymers, Penn State Univesity, College Station, PA, 30 April 1989

33. V. Percec
Molecular Engineering of Liquid Crystalline Polymers
University of Akron, Akron, OH, 3 May 1989

34. V. Percec
Liquid Crystal Polymers
Regional ACS Meeting, Cleveland, 31 May 1989

35. V. Percec
Molecular Engineering of Liquid Crystal Polymers
Army Technology Laboratory
Boston, 23 June 1989

36. V. Percec
Highly Decoupled Side Chain Liquid Crystalline Polymers
Liquid Crystal Polymers Conference, University of Massachusetts, Amherst, 24 June 1989

37. V. Percec
Liquid Crystalline Copolymers
Gordon Research Conference, 30 June 1989

38. V. Percec and J. Heck
Side Chain Liquid Crystal Polymers Containing Mesogenic Units Based on Half-Disk and Rod-like Moieties
Conference on Liquid Crystal Polymers, ACS, Miami Beach, FL., September 1989

39. V. Percec and D. Tomazos
Liquid Crystalline Polymers Containing Constitutional Isomeric Mesogenic Side Groups
Conference on Liquid Crystal Polymers, ACS, Miami Beach, FL., September 1989

40. V. Percec
Liquid Crystalline Polymers
University of Rochester, 25 October 1989

41. V. Percec and M. Lee
Living Polymerization of Mesogenic Vinyl Ethers
British Liquid Crystal Society, Bristol, 9-11 April 1990

1. Contributed Presentations

1. V. Percec, C.S. Hsu, D. Tomazos and J.M. Rodriguez-Parada
Side-Chain Liquid Crystalline Copolymers of Monomer Pairs Containing Mesogenic Units which Exhibit Constitutional Isomerism
ACS Meeting, Toronto, 6-10 June 1988

2. C. Percec and D. Tomazos
Sid-Chain Liquid Crystalline Polymers Containing 4-Methoxy-4'-hydroxy-α-methylstilbene Based Mesogens
ACS Meeting, Toronto, 6-10 June 1988

3. B. Hahn and V. Percec
Biphasic Side-Chain Liquid Crystalline Polymers Containing Chiral 2,5-Disubstituted-1,3,2-Dioxaborinane Based Mesogens
The Twelfth International Liquid Crystal Conference, Freiburg, W. Germany, 15-19 August 1988

4. V. Percec
Liquid Crystalline Polymers Based on Conformational Isomerism
VIth European Liquid Crystal Winter Conference, Schladming, Austria
5-10 March 1989

5. V. Percec and R. Yourd
Liquid Crystalline Polyethers Based on Conformational Isomerism
Makromolekulares Kolloquium, Freiburg, W. Germany, 9-11 March 1989

6. J.L. Feijoo, G. Ungar, A. Keller, J.A. Odell, A.J. Owen and V. Percec
Evidence for Disclinations in the Isotropic State of Liquid Crystal Forming Polymers
British Liquid Crystal Society, 4th Annual Conference, University of Sheffield, England, 10-12 April 1989

7. G. Ungar and V. Percec
Structure of Liquid Crystal Phase of a Crown Ether Side Chain Polymer
British Liquid Crystal Society, Bristol, 9-11 April 1990

8. J. L. Feijoo, G. Ungar, V. Percec and R. Yourd
Smectic and Crystalline Phases in Main Chain Copolymers with a Semi-flexible Mesogen
British Liquid Crystal Society, Bristol, 9-11 April 1990

j. Honors/Awards/Prized

None

k. Number of Graduate Students Receiving Full or Partial Support on ONR Grant or Contract

Dimitris Tomazos
Myongsoo Lee
Carolyn Ackerman

l. Number of Postdoctoral Fellows Receiving Full or Partial Support on ONR Grant or Contract

Presently none

1. End-of-the-Year Report

Part II

a. Principal Investigator
Dr. Virgil Percec

b. Cognizant ONR Scientific Officer
Dr. Kenneth J. Wynne

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d. Brief description of project

The Project "Novel Side-Chain Liquid Crystalline Polymers" is divided into two main parts: (a) synthesis of noncrystallizable side chain liquid crystalline polymers, and (b) solid electrolytes based on liquid crystalline polymers. Both topics aim toward the preparation of highly decoupled side chain liquid crystalline polymers which, however, do not give rise to side chain crystallization. This idea contradicts the previous results provided by our laboratory which showed that highly decoupled liquid crystalline polymer systems give rise to side chain crystallization. To avoid the side chain crystallization process we intend to insert kinks within the flexible spacer and attach mesogenic groups in a parallel way to the polymer backbone.

e. Significant results during last year

The results obtained during the last year can be classified into several different classes. 1) We have provided the most conclusive experiment which supports the concept of microphase separated side chain liquid crystalline polymer. It is based on the morphological analysis of the smectic copolymers containing mesogenic and nonmesogenic side groups by X-ray scattering experiments. The results are as follows: the smectic layer increases with the decrease of the content of mesogenic side groups. This is due to the microphase separation of the polymer backbone in between the smectic layers. By decreasing the content of mesogenic groups the thickness of the backbone increases and therefore the overall thickness of the smectic layer increases (Macromolecules, 23, 2092 (1990)). 2) We have synthesized the first examples of side chain liquid crystalline polymers containing semifluorinated spacers. It seems that semifluorinated spacers are very suitable for the preparation of microphase separated systems. 3) We have developed a novel method to synthesize mesogenic vinyl ethers with any spacer length and to polymerize them through a living cationic mechanism. These experiments have demonstrated that the old problem of the "polymer effect" (i.e., monomer nematic polymer smectic) will be solved. We have demonstrated that there is a continuous dependence of phase transition temperatures on molecular weight and that the difference between the slope of the nematic versus smectic phase creates this "polymer effect".

f. Summary of plans for next years work

The work for next year is dedicated to the design of monomers which contain oligooxyethylenic, fluorinated and hydrogenated spacers which can be polymerized by living cationic polymerization. We prefer to work with vinyl ethers since we have developed living cationic polymerization techniques which can tolerate a variety of functional nucleophilic and electrophilic functional qroups. So far, we have already synthesized noncrystallizable polysiloxanes containing long oligooxyethylenic spacers which exhibit a very broad range of mesomorphism. The transplant of these structures to vinyl ethers is in progress.

g. List of graduate students currently working on project

D. Tomazos
M. Lee
C. Ackerman

No postdoctoral fellows are presently working on this project.

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FIELD	GROUP	SUB-GROUP	liquid crystalline copolymers, X-ray scattering experiments, microphase separated morphology

19. ABSTRACT (Continue on reverse if necessary and identify by block number)

Oriented samples of poly(methylsiloxane-co-dimethylsiloxane)s containing 2-[4-(2(S)-methyl-1-butoxy)phenyl]-5-(11-undecanyl)-1,3,2-dioxaborinane side groups were characterized by WAXS and SAXS experiments. Both the homopolymer and the copolymers with different compositions display a S_A and a crystalline phase. The thickness of the smectic layer of the S_A phase increases with the decrease of the concentration of the structural units containing mesogenic groups. This result is consistent with a microphase separated copolymer morphology in which the polysiloxane backbone is squeezed between the smectic layers.

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Technical Report No. 28

Liquid-Crystalline Polymers Containing Heterocycloalkanediyl Groups as Mesogens. 8. Morphological Evidence for Microphase Separation in Poly(methylsiloxane-co-dimethylsiloxane)s Containing 2-[4-(2(S)-Methyl-1-butoxy)phenyl]-5-(11-undecanyl)-1,3,2-dioxaborinane Side Groups

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Liquid Crystalline Polymers Containing Heterocycloalkanediyl Groups as Mesogens. *8. Morphological Evidence for Microphase Separation in Poly(methylsiloxane-co-dimethylsiloxane)s Containing 2-[4-(2(S)-Methyl-1-butoxy)phenyl]-5-(11-Undecanyl)-1,3,2-Dioxaborinane Side Groups

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*Part 7 in this series: Reference 8

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ABSTRACT: Oriented samples of poly(methylsiloxane-co-dimethylsiloxane)s containing 2-[4-(2(S)-methyl-1-butoxy)phenyl]-5-(11-undecanyl)-1,3,2-dioxaborinane side groups were characterized by WAXS and SAXS experiments. Both the homopolymer and the copolymers with different compositions display a S_A and a crystalline phase. The thickness of the smectic layer of the S_A phase increases with the decrease of the concentration of structural units containing mesogenic groups. This result is consistent with a microphase separated copolymer morphology in which the polysiloxane backbone is squeezed between the smectic layers.

Recently, by analogy with the behavior of block and graft copolymers, we have suggested that highly or even completely decoupled side-chain liquid crystalline polymers would be realizable for systems in which the mesogenic side groups and the polymer backbone are microphase separated.[1-8] Such a morphology is particularly favorable for smectic copolymers based on flexible backbones which contain mesogenic and nonmesogenic structural units. Most probable, a microphase separated morphology like this is induced by the thermodynamic immiscibility between the random-coil polymer backbone and the rodlike mesogenic units which in the liquid crystalline phase tend to segregate into isotropic and anisotropic domains. The tendency toward microsegregation is enhanced when the polymer backbone and the side groups are, due to their chemical disimilarity, immiscible even within their isotropic phase. Such a microphase separated morphology can be best observed in copolymers containing about similar weight ratios between the polymer backbone and the mesogenic side groups.

In a previous publication[8] we have presented our investigations on poly(methylsiloxane-co-dimethylsiloxanes)s containing 2-[4-(2(S)-methyl-1-butoxy)phenyl]-5-(11-undecanyl)-1,3,2-dioxaborinane side groups with different molecular weights and compositions. Differential scanning calorimetric (DSC) and dynamic mechanical thermal

analysis (DMTA) experiments have suggested a microphase separated morphology for these copolymers. Both techniques have demonstrated that these copolymers display two glass transition temperatures. They were assigned to the independent motion of the polymer backbone, and cooperative (but independent from the polymer backbone) motion of the side groups. The dependence of the width of the isotropization peak observed on the DSC curves on both copolymer composition and molecular weight have also suggested a microphase separated morphology.

The goal of this paper is to present direct structural evidence for such a microphase separated morphology obtained from wide-angle (WAXS) and small-angle (SAXS) X-ray scattering experiments.

Poly(methylsiloxane-co-dimethylsiloxane)s with number average molecular weights higher than 18000 and different contents of 2-[4-(2(S)-methyl-1-butoxy)phenyl]-5-(11 undecanyl)-1,3,2-dioxaborinane side groups were synthesized as previously reported.[8] Scheme I presents the structure and composition of these copolymers. All copolymers display two phases. The dependence of the parameters of the two phase transitions on polymer molecular weight and copolymer composition were previously discussed in detail.[8]

X-ray scattering experiments were performed both in the wide angle [9] and small angle [10] regions on macroscopically unoriented samples. In addition, flat camera studies were performed on macroscopically oriented samples in glass

capilaries. The orientation was induced by surface interaction.

Figure 1a presents a representative WAXS pattern of the high temperature phase displayed by an oriented copolymer sample containing 56 mole% structural units with mesogenic groups. The X-ray beam was paralell to the polymer flow direction and both the beam and the flow direction were perpendicular to the equator. The mesogenic side groups are alligned perpendicular to the polymer backbone. WAXS experiments were also performed from the other two directions.This X-ray pattern is characteristic for a S_A mesophase. Figure 1b displays a representative WAXS pattern of the low temperature phase of an unoriented sample of the same copolymer.This phase is crystalline.

The thickness of the smectic layer, d, of the high temperature phase was determined (from the small angle region of the WAXS) as a function of copolymer composition and is both tabulated and plotted in Scheme I.
The calculated thickness of the smectic layer, l,(assuming an all trans conformation of the spacer) is 29Å.
The thickness of the smectic layer determined experimentally for homopolymer is 30.4Å, and is in good agreement with the calculated one. When the concentration of the structural units containing mesogenic groups from the copolymer decreases, the thickness of the smectic layer increases (Scheme I). This dependence of the thickness of the smectic layer on copolymer composition can be explained only by a

microphase separated copolymer morphology as that described in Scheme I. This morphology requires a distortion of the random-coil conformation of the flexible backbone to the extent that it can be squeezed in between the smectic layers. Therefore,the experimentally determined thickness of the smectic layer increases with the decrease of the concentration of structural units containing mesogenic units, since the volume of the flexible backbone which is available to be sqeezed between the smectic layers increases. The dependences of the smectic layer thickness, d, and of the isotropization temperature, Ti, on copolymer composition are plotted in the left corner of Scheme I. Within experimental error both plotts display, as expected, almost linear dependences on copolymer composition.

This microphase separated morphology is identical to that observed by Ringsdorf et all [11-13] in copolysiloxanes containing paired mesogens, and may represent a general morphology displayed by smectic copolymers containing mesogenic and nonmesogenic structural units and flexible backbones.

A distortion of the random-coil conformation of the polymer backbone within the smectic phase was theoretically predicted [14] and experimentally observed by small angle neutron scattering experiments [15,16], even for the case of homopolymers. Smectic polymers based on rigid backbones may display a different morphology which was discussed in a

different publication.[17]

Figure 2a presents a representative focal conic texture displayed by the S_A phase of the copolymer containing 56 mole% mesogenic units. Such a characteristic texture could not be obtained for the parent liquid crystalline homopolymer even after extensive annealing. Upon cooling into the crystalline phase the polymer displays the texture presented in Figure 2b. This texture is characteristic for a chiral smectic C (S_C*) mesophase. This texture made us assigne previously, based on optical polarized microscopy only, this phase to a S_C* phase.[4-8] The X-ray scattering experiments described in this paper have definitively demonstrated that this phase is crystalline.

This microphase separated morphology may be significant for a number of theoretical and practical reasons. First, the dynamics of these copolymers is much faster than of corresponding homopolymers. Second, this morphology may provide a novel approach to host-guest systems. This two phase system can selectivelly dissolve anisotropic and isotropic guests in its different phases.[13] Therefore, we can easily envision systems which can be thermally regulated to capture and release these guests. Third, as we can observe in Scheme I, this system provides a unique technique to molecular engineer the thickness , a, of a flexible random-coil backbone at wish. Combined systems based on more than one immiscible flexible polymer backbone and identical side groups are also of interest.

At least for these reasons it is important to further elucidate the mechanisms by which these microphase separated systems function, as well as their capabilities for some practical applications which can be considered from the above discussion. Research on these lines is in progress in our laboratory.

Acknowledgments

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References and Notes

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(9) Wide angle X-ray experiments were performed with a wide angle goniometer (D500, Siemens Erlangen) and with a flat film camera and a Kratky pinhole camera.

(10) A Kratky compact camera with a position sensitive detector was used in the small angle region. Nickel filtered Cu-Kα radiation (λ= 0.154 nm) was used in all cases. Each of these experimental setups was equipped with thermostated cells.

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(17) Percec, V.; Tomazos, D. Polymer, in press.

Figure Captions

Figure 1: a) WAXS pattern of an oriented sample of copolymer containing 56 mole% structural units with mesogenic groups, within the S_A phase. The beam was paralell to the polymer flow direction which is paralell to the equator (temperature, 75 °C).

b) WAXS pattern of the crystalline phase of an unoriented sample of the same copolymer (temperature, 20°C).

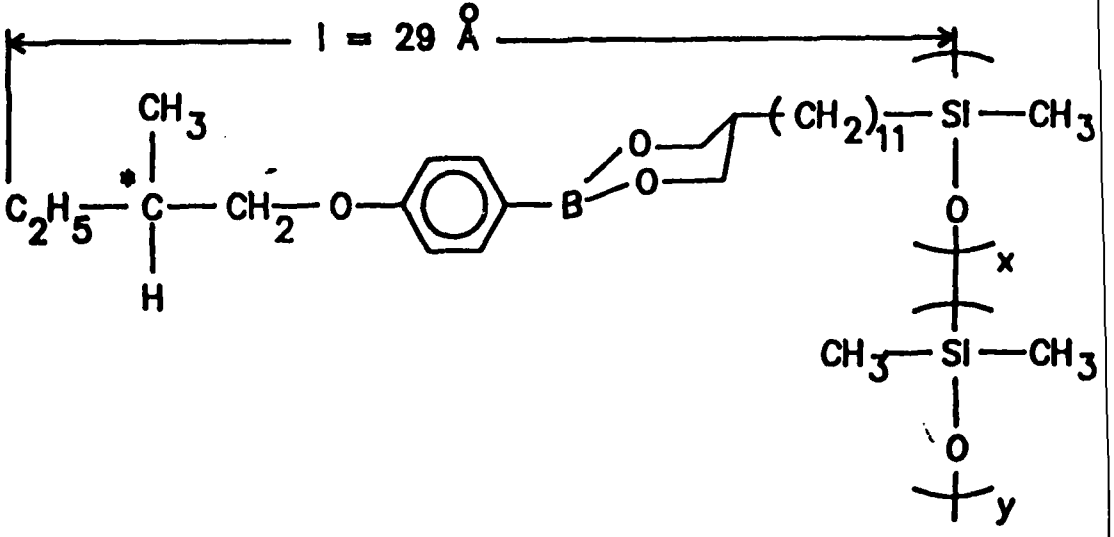
Figure 2 a) Representative optical polarized micrograph (magnification 100x) of the focal conic texture displayed by the S_A phase of copolymers (copolymer containing 56 mole% structural units with mesogenic groups; temperature, 75°C).

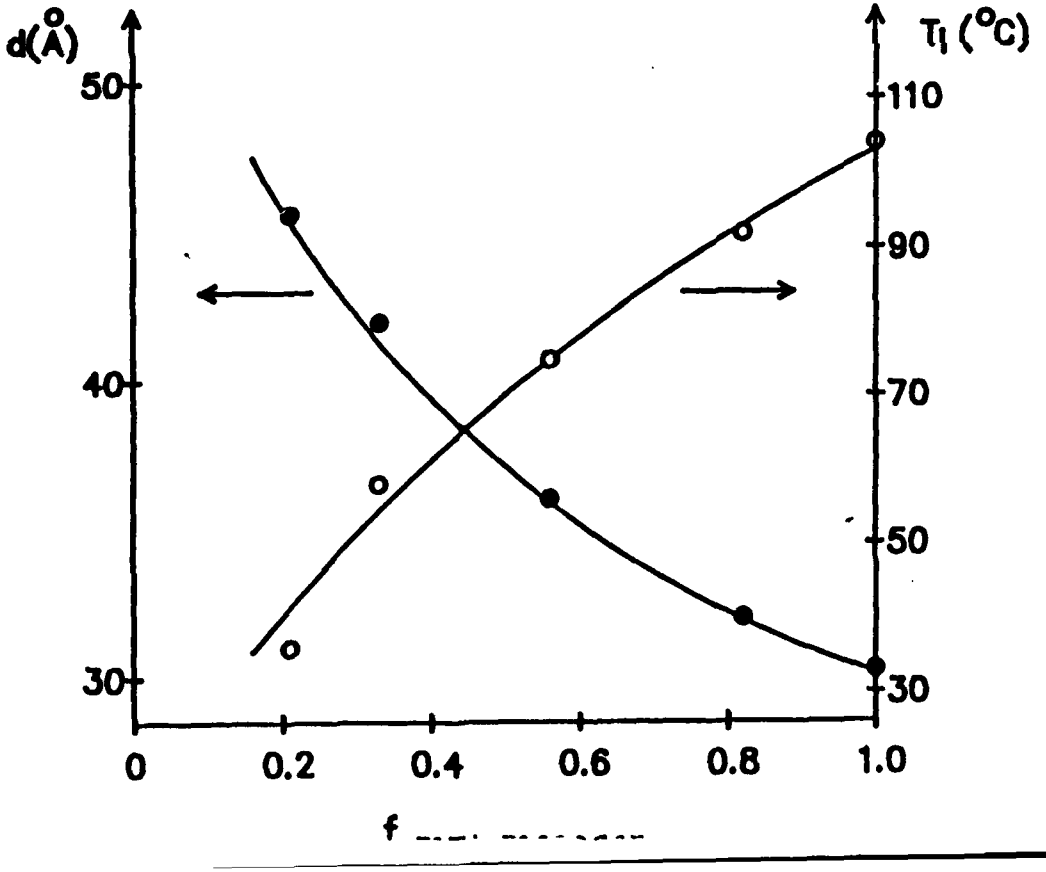
b) Representative optical polarized micrograph (magnification 100x) of the crystalline phase displayed by copolymers (copolymer containing 56 mole% structural units with mesogenic groups; temperature, 20°C).

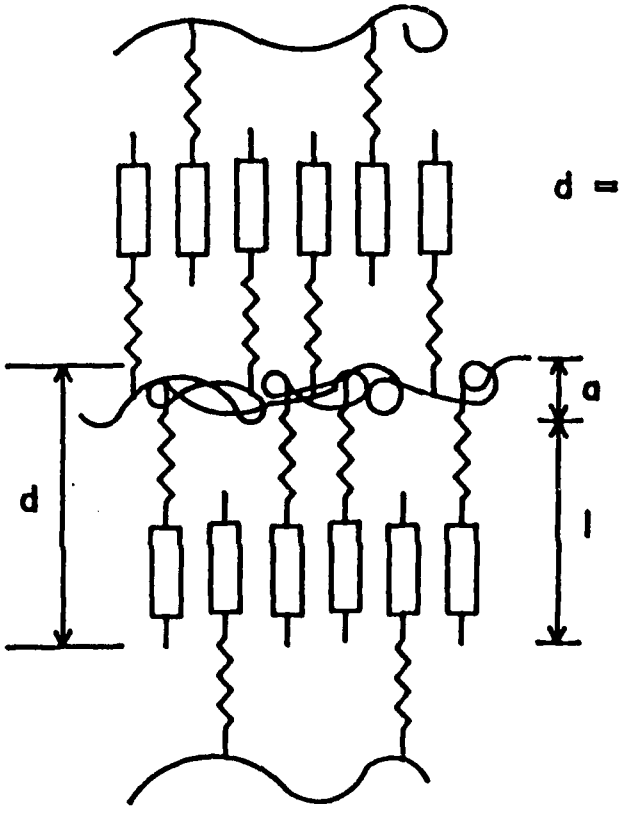
Scheme I.

Microphase Separated Morphology of Smectic Copolymers

mesogen(%)	d(Å)	a(Å)	T_I (°C)
100	30.4	1.4	104
82	32.0	3.0	92
56	36.0	7.0	75
33	42.0	13.0	58
21	45.6	16.6	36







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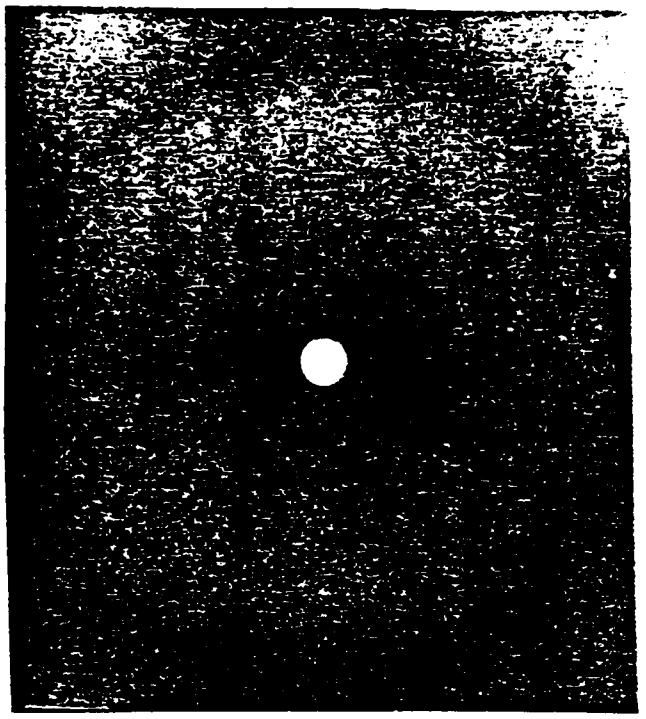

Figure 1a

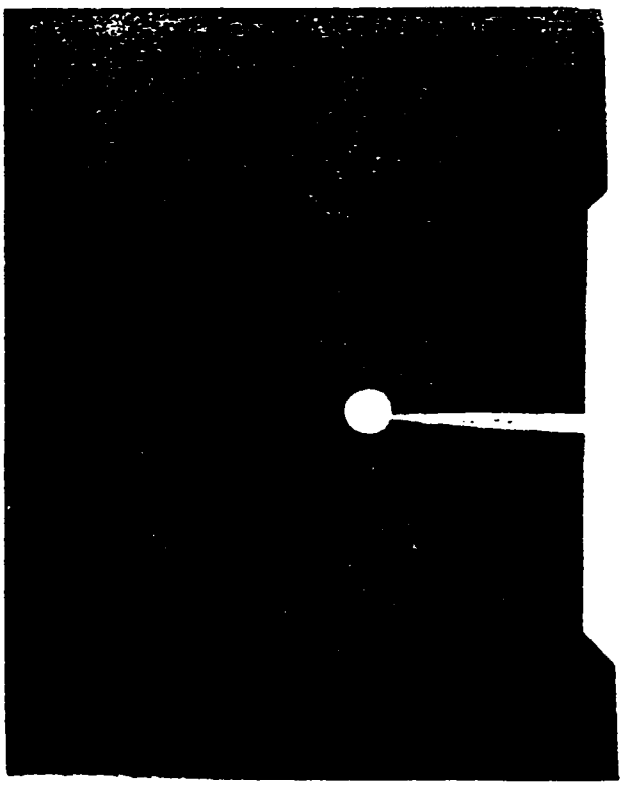

Figure 1b

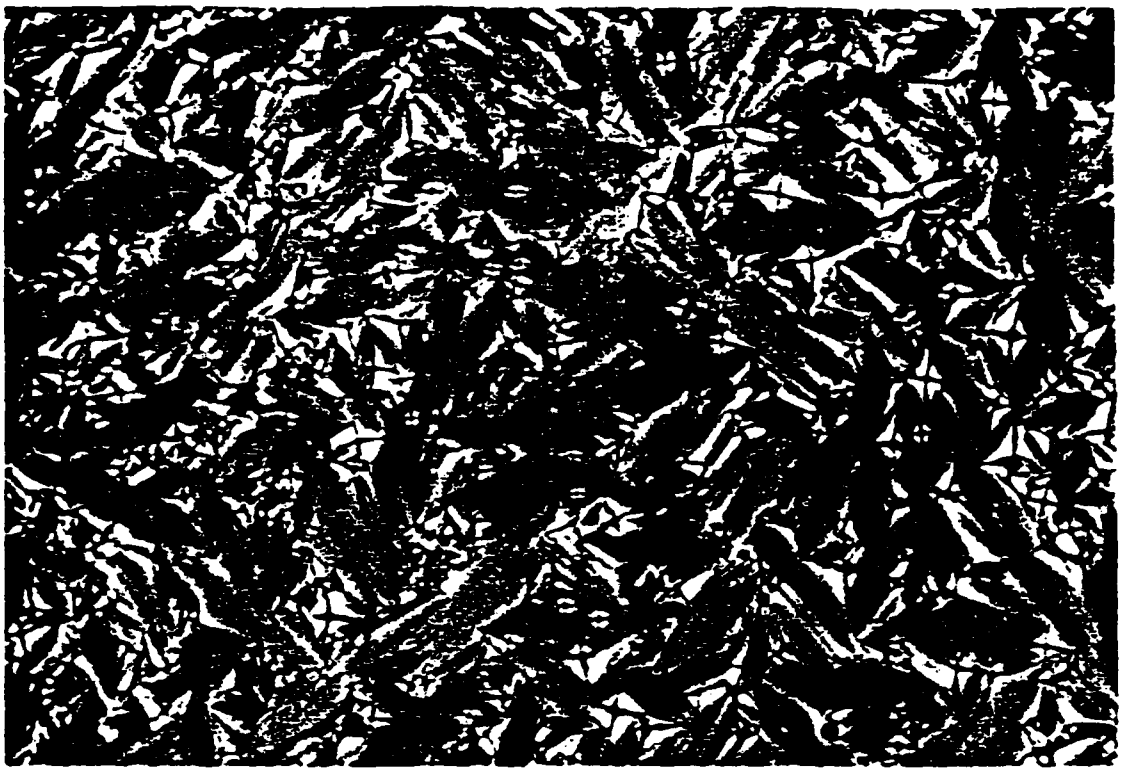

Figure 2a

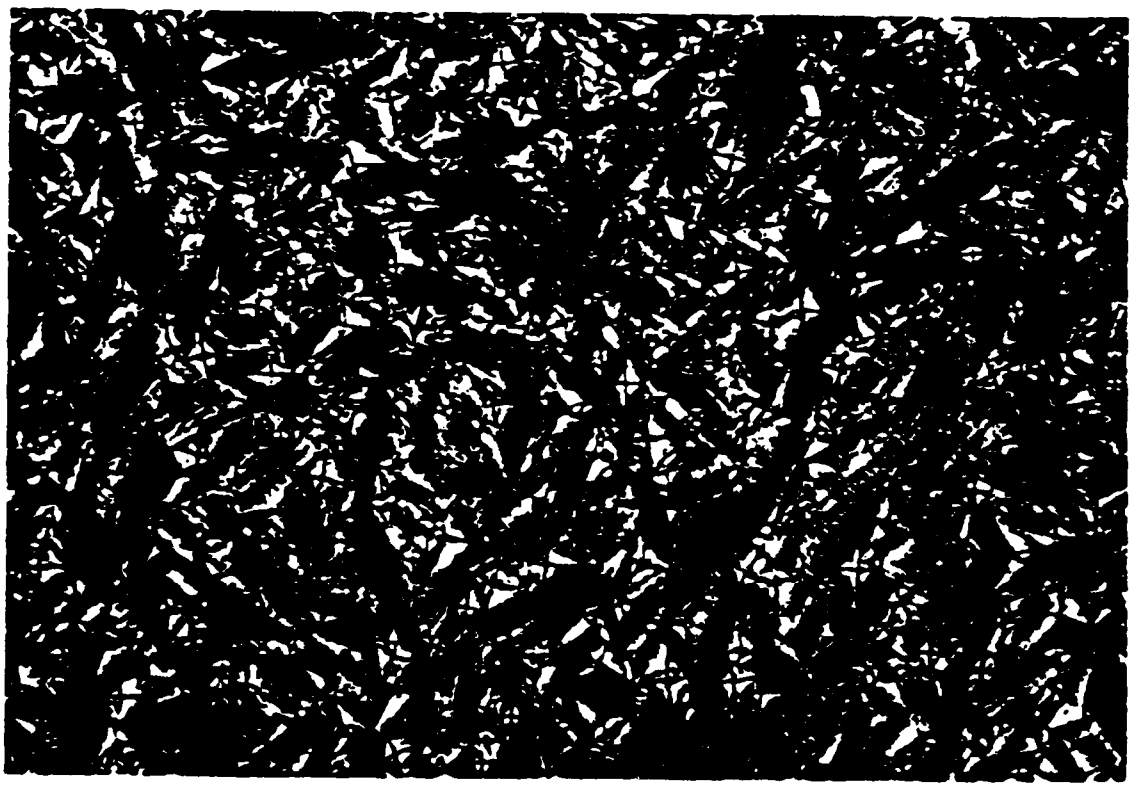

Figure 2b

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11. TITLE (Include Security Classification) Synthesis and Mesomorphic Behavior of Poly(methylsiloxane)s and Poly(methylsiloxane-co-dimethylsiloxane)s Containing Oligooxyethylene Spacers and Mesogenic Side Groups

12 PERSONAL AUTHOR(S)
Virgil Percec and Chain S. Hsu

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FIELD	GROUP	SUB-GROUP	liquid crystalline polymers, oligooxyethylenic spacers

19. ABSTRACT (Continue on reverse if necessary and identify by block number)
The synthesis and characterization of poly(methylsiloxane)s and poly(methylsiloxane-co-dimethylsiloxane)s containing either bis(ethylene oxide) or tris(ethylene oxide) flexible spacers and either 4-methoxy-4'-hydroxybiphenyl a mixture containing a 1:1 ratio of 4-methoxy-4'-hydroxy-α-methylstilbene and 4-hydroxy-4'-methoxy-α-methylstilbene, or 4-[5-(4-methoxyphenyl)-1,3-dioxan-2-yl]phenol mesogenic groups, in all combinations, is presented. All polymers and copolymers display smectic mesomorphism. The dependence of phase transition temperatures on the spacer length and copolymer composition is described.

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Technical Report No. 29

Synthesis and Mesomorphic Behavior of Poly(methylsiloxane)s and Poly(methylsiloxane-co-dimethylsiloxane)s Containing Oligooxyethylene Spacers and Mesogenic Side Groups

by

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Synthesis and Mesomorphic Behavior of Poly(methylsiloxane)s and Poly(methysiloxane-co-dimethylsiloxane)s Containing Oligooxyethylene Spacers and Mesogenic Side Groups.

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SUMMARY

The synthesis and characterization of poly(methylsiloxanes)s and poly(methylsiloxane-co-dimethylsiloxane)s containing either bis(ethylene oxide) or tris(ethylene oxide) flexible spacers and either 4-methoxy-4'-hydroxybiphenyl a mixture containing a 1:1 ratio of 4-methoxy-4'-hydroxy-α-methylstilbene and 4-hydroxy-4'-methoxy-α-methylstilbene, or 4-[5-(4-methoxyphenyl)-1,3-dioxan-2-yl]phenol mesogenic groups, in all combinations, is presented. All polymers and copolymers display smectic mesomorphism. The dependence of phase transition temperatures on the spacer length and copolymer composition is described.

INTRODUCTION

Main chain and side chain liquid crystalline polymers containing flexible spacers which are not aliphatic are of both theoretical and practical interest (1-4). Spacers of different flexibility are useful in testing the spacer concept (5). So far, the only flexible spacer, other than paraffinic considered to some extent is based on oligooxyethylene segments (1). There are, however, a few results available on the use of oligodimethylsiloxanes (2), semifluorinated (6) and perfluorinated (7) flexible spacers.

We are presently investigating various synthetic avenues leading to host-guest liquid crystalline systems. So far, oligooxyethylenic flexible spacers (8-12) or macroheterocyclic ligands (13,14) have been used. Side chain liquid crystalline polymers containing oligooxyethylenic spacers represent a novel class of host-guest systems which is intermediate between podants and macroheterocyclics from a structural point of view, i.e., they are pseudo-crown-ethers (10).

The goal of this paper is to present the synthesis and characterization of liquid crystalline side chain poly(methylsiloxane)s and poly(methylsiloxane-co-dimethylsiloxane)s containing 4-methoxy-4'-hydroxybiphenyl, 4-methoxy-4'-hydroxy-α-methylstilbene, 4-hydroxy-4'-methoxy-α-methylstilbene and 4-[5-(4-methoxyphenyl)-1,3-dioxan-2-yl]phenol mesogenic groups and bis(ethylene oxide) and tris(ethylene oxide) based flexible spacers.

EXPERIMENTAL

Materials:

All reagents were purchased from commercial sources and were used as received or purified by standard methods. 4-Methoxy-4'-hydroxybiphenyl (8), 4-[5-(4-methoxyphenyl)-1,3-dioxan-2-yl]phenol (15) and a mixture containing a 1/1 molar ratio of 4-methoxy-4'-hydroxy-α-methylstilbene and 4-hydroxy-4'-methoxy-α-methylstilbene (16) were synthesized as described in previous publications. Poly(methylsiloxane)s and (methylsiloxane-co-dimethylsiloxane)s with different

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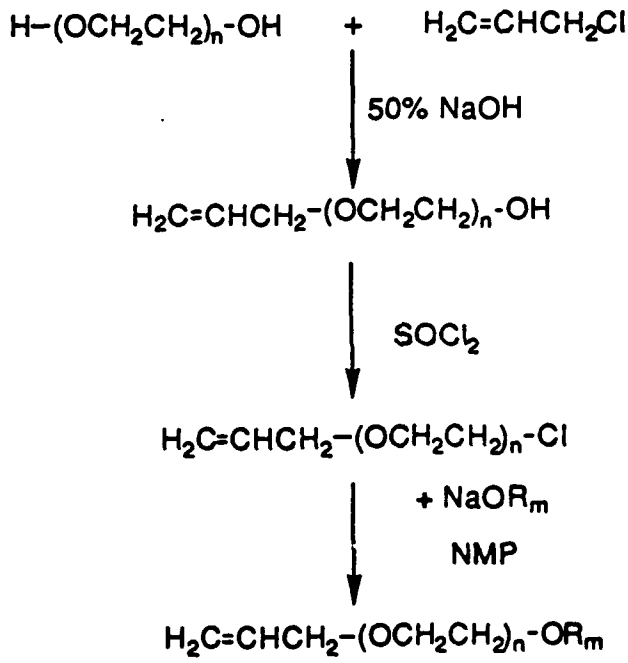
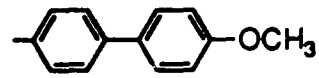
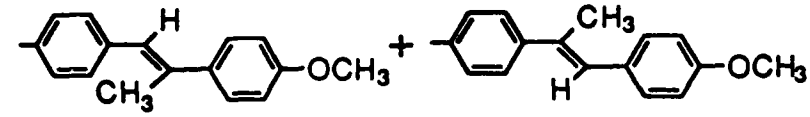
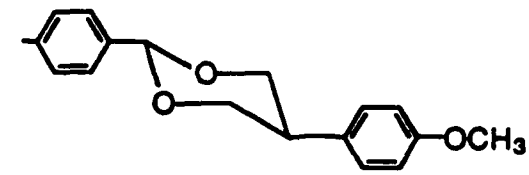
molecular weights were synthesized and characterized as described previously (17). Scheme I outlines the synthesis of monomers

Synthesis of 2-(2-Allyloxyethoxy)Ethanol and 2-[2-(2-Allyloxyethoxy)ethoxy]Ethanol.

Both compounds were prepared by the monoetherification of diethylene glycol and triethylene glycol with allyl chloride by a modified literature procedure (18,19). A representative example is presented below. A mixture of triethylene glycol (30 g, 200 mmol) and allyl chloride (4.07 ml, 56 mmol) in aqueous 50% sodium hydroxide (16 ml, 200 mmol NaOH) was heated at 100°C for 24 hr. The mixture was cooled, diluted with water and extracted with diethyl ether. The organic extracts were combined, dried over anhydrous magnesium sulfate, filtered and concentrated under vacuum. The remaining oil was distilled at 116-118°C/10 mm Hg, and further purified by column chromatography (silica gel, chloroform as eluent) to yield 3.5 g (37%) of monoallyl ether. ^{1}H-NMR ($CDCl_3$, TMS, δ, ppm): 3.66 (m , $-C\underline{H_2}O$, 8 protons), 4.03 (d, $=CH-C\underline{H_2}-O-$), 5.22 and 5.93 (m, $C\underline{H_2}=C\underline{H}-$).



Monomer	n	R_m
1M	2	R_1: 
2M	3	
3M	2	R_2: 
4M	3	
5M	3	R_3: 

Scheme I: Synthesis of Monomers

Synthesis of 2-(2-Allyloxyethoxy)Ethyl Chloride and 2-[2-(2-Allyloxyethoxy)ethoxy]Ethyl Chloride

Both compounds were synthesized by chlorination of the corresponding allyl ether alcohol with thionyl chloride. An example is presented below. 2-[2-(2-Allyloxyethoxy)ethanol] (3.5g, 18.4 mmol) was dissolved in dry methylene chloride (50 ml). Thionyl chloride (1.7 ml, 23 mmol) was added dropwise and the reaction mixture was stirred at room temperature for 2 hours. The methylene chloride and excess thionyl chloride were removed on a rotovapor and the residue was distilled at 97-99°C/12mm Hg to yield 2.8g (73%) 2-(2-allyloxyethoxy)ethyl chloride. ^{1}H-NMR ($CDCl_3$, TMS, δ, ppm): 3.66 (m, -CH_2O-, 6 protons), 3.77 (t, -CH_2Cl), 4.03 (d, =CH-CH_2-O-), 5.22 and 5.93 (m, CH_2=CH-).

Synthesis of Olefinic Derivatives 1M-5M

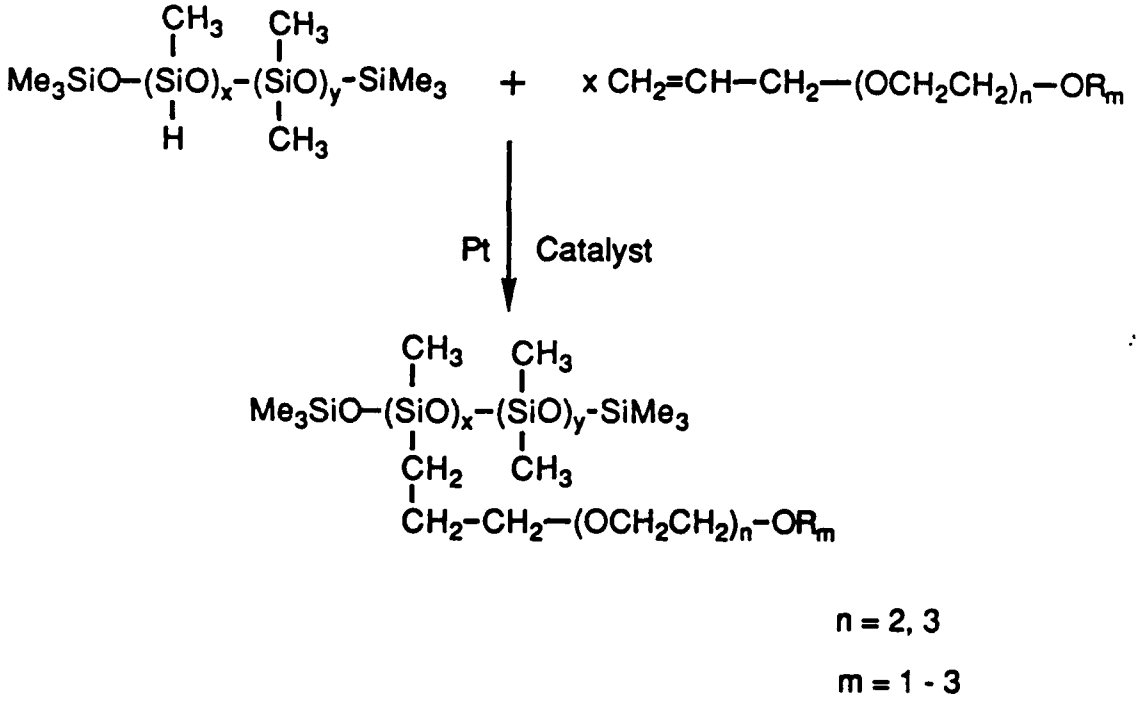
Compounds 1M to 5M were synthesized by the etherification of 4-methoxy-4'-hydroxybiphenyl (R_1), the 1/1 mixture of 4-methoxy-4'-hydroxy-α-methylstilbene and 4-hydroxy-4'-methoxy-α-methylstilbene (R_2), and 4-[5-(methoxyphenyl)-1,3-dioxan-2-yl]phenol (R_3) with either 2-(2-allyloxyethoxy)ethyl chloride or 2-[2-(2-allyloxyethoxy)ethoxy]ethyl chloride. An example is presented below. Freshly cut sodium (0.23 g, 10 mmol) was dissolved in absolute ethanol (50 ml). After the sodium was completely dissolved, 4-methoxy-4'-hydroxybiphenyl (2g, 10 mmol) was added to the reaction mixture. After ethanol was removed from the reaction mixture, dry N-methyl-2-pyrrolidinone (50 ml) was added to the residual sodium salt of 4-methoxy-4'-hydroxybiphenyl. When the sodium salt was completely dissolved, 2-[2-(2-allyloxyethoxy)ethoxy]ethyl chloride (2.29 g, 11 mmol) was added and the resulting mixture was stirred at 110 °C under a nitrogen atmosphere overnight. N-methyl-2-pyrrolidinone was removed by distillation and the residue was poured into water. The resulting precipitate was filtered, washed with dilute aqueous NaOH, water and dried under vacuum. The product was recrystallized from methanol to yield 3.0 g (81%) white crystals. Table I summarizes the melting transition(s) and ^{1}H-NMR chemical shifts of compounds 1M to 5M.

Table I: Characterization of Olefinic Derivatives 1M-5M

Compound	m.p. (°C) T_1	T_2	200 MHz ^{1}H-NMR ($CDCl_3$, δ, ppm)
1M	87	-	3.62, 3.74, and 3.87 (t. 3, -CH_2O-); 3.83 (s, CH_3O-); 4.06 (d, =C-CH_2-O-); 4.17 (t, -CH_2OPh): 5.21 and 5.91 (m, CH_2=CH-); 6.94 and 7.43 (m, 8 aromatic protons)
2M	73	83	3.66 and 3.86 (m, 5 -CH_2O-); 3.80 (s, CH_3O-); 4.00 (d, =C-CH_2O-); 4.13 (t, -CH_2OPh); 5.19 and 5.89 (m, CH_2=CH-); 6.94 and 7.46 (m, 8 aromatic protons)
3M	46	-	2.26 (s, CH_3-C=); 3.66, 3.76 and 3.90 (3t, 3, -CH_2O-); 4.05 (d, =CH-CH_2O-); 4.17 (t, -CH_2OPh); 5.25 and 5.94 (m, CH_2=CH-); 6.73 (s, Ph-CH=): 6.90 to 7.48 (m, 8 aromatic protons)
4M	35	-	2.26 (s, CH_3-C=); 3.66 and 3.89 (m, 5-CH_2O-); 3.84 (s, CH_3O-); 4.04 (d, =CH-CH_2O-); 4.15 (t,-CH_2OPh); 5.25 and 5.94 (m, CH_2=CH-); 6.73 (s, Ph-CH=); 6.90 to 7.48 (m, 8 aromatic protons)
5M	63	-	3.31 (m,- C≡CH; 3.63 to 4.34 (m, 7 -CH_2O-); 3.80 (s, CH_3O-); 5,22 and 5.91 (m, CH_2=CH-); 5.53 (s, -HC(O)(O)-); 6.87 to 7.46 (m, 8 aromatic protons)

Synthesis of Poly(methylsiloxane)s and of Poly(methylsiloxane-co-dimethylsiloxane)s

Both polymers and copolymers were synthesized by the hydrosilation of the poly(methylsiloxane) with the olefinic derivatives 1M to 5M in the presence of a Pt catalyst (Scheme II). Experimental details concerning the synthesis and purification of these polymers are identical to those used in the preparation of other liquid crystalline polysiloxanes (17-20).



Scheme II: Synthesis of Polymers

Characterization of Polymers and Intermediary Derivatives

All intermediary derivatives and polymers were characterized by a combination of HPLC, GPC, DSC, and thermal optical polarized microscopy according to standard procedures used in our laboratory (17,20). All purities are higher than 99% and are therefore not reported.

RESULTS AND DISCUSSION

Table II summarizes the phase behavior of all polymers and copolymers. The first column provides a notation based on the parameters n, m and R_m from Scheme I and x and y from Scheme II. Most of the homopolymers 1P to 5P present two thermal transition temperatures, T_1 and T_i. Some also display a glass transition temperature. In the case of 1P to 4P, T_1 seems to be a melting transition. Above T_1 all polymers display a smectic mesophase. Both T_g and T_i are lower for polymers based on the tris(ethylene oxide) spacer. Increasing the spacer length from bis(ethylene oxide) to tris(ethylene oxide) can decrease the T_i transition to below the T_g of the corresponding polymers (see 3P and 4P in Table II). Both T_1 and T_i of 5P are associated with liquid crystalline phase transitions (Figure 1).

Table II: Thermal Transitions and Thermodynamic Parameters of Polysiloxanes

Polymer					Thermal Transitions (°C), and Enthalpy Changes, ΔH(kcal/mru)[a]				
					Heating			Cooling	
No.	x	y	n	R_m[b]	T_g	$T_1(\Delta H_1)$	$T_i(\Delta H_i)$	$T_i(\Delta H_i)$	$T_1(\Delta H_1)$
1P	80	0	2	R1	33	94(–)	114(1.05)[c]	104(1.36)[c]	92(--)
2P	80	0	3	R1	–	86(0.11)	103(2.34)	94(2.25)	79(0.10)
3P	80	0	2	R2	–	42(2.13)	52(0.03)	27(2.16)	– (–)
4P	80	0	3	R2	-19	– (–)	30(0.72)	12(0.73)	– (–)
5P	80	0	3	R3	-3	67(–)	76(1.60)[c]	71(1.60)[c]	60(--)
6P	10	20	2	R1	-91	– (–)	88(2.19)	80(2.21)	– (–)
7P	10	20	3	R1	-63	– (–)	82(2.75)	72(2.73)	– (–)

a) mru = mole of repeat units; b) x, y, n and R_m according to Schemes I and II; c) overlapped transitions, $\Delta H_i = \Delta H_i + \Delta H_1$.

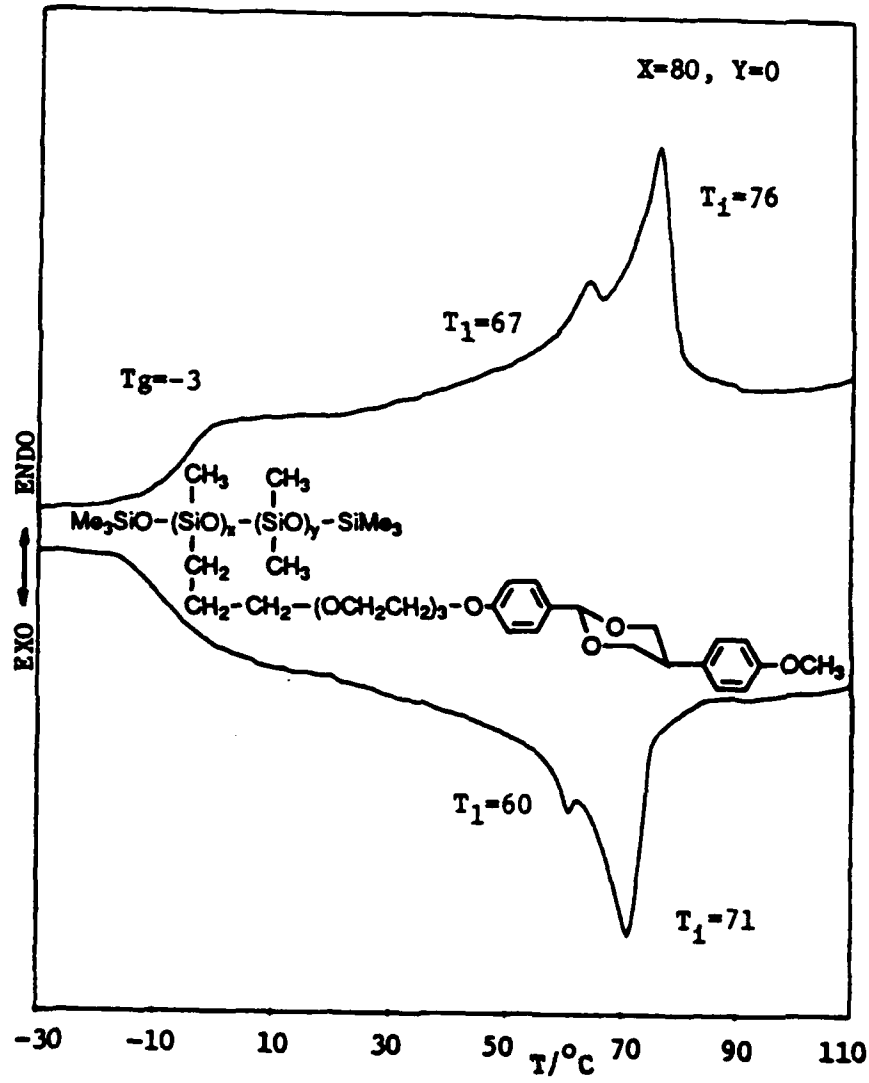


Figure 1: **Second heating and cooling DSC scans (20 °C/min) of polymer 5P.**

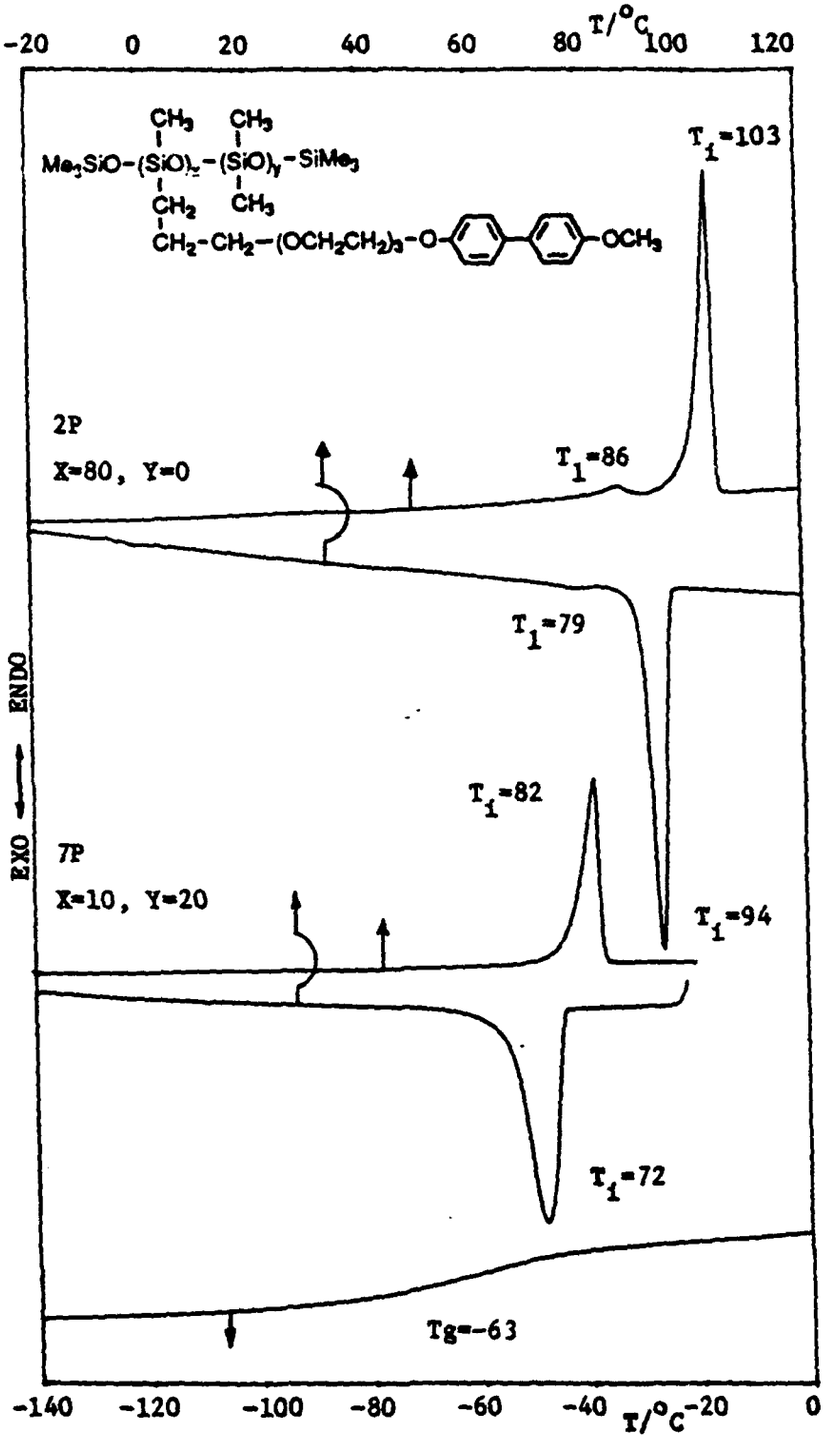


Figure 2: **Second heating and cooling DSC scans (20 °C/min) of polymers 2P and 7P.**

Figure 2 presents representative DSC traces of 2P and 7P. Copolymer 7P displays a lower T_i than the corresponding homopolymer 2P, and no T_1 transition. The T_g of 7P is very low. The same trend is observed by comparing homopolymer 1P and copolymer 6P (Table II). In contrast to copolysiloxanes containing aliphatic flexible spacers which display two glass transition temperatures (17,20), copolysiloxanes 6P and 7P display a single broad glass transition temperature (Table II, Figure 2). A representative smectic texture displayed by 2P is presented in Figure 3.

a) b)

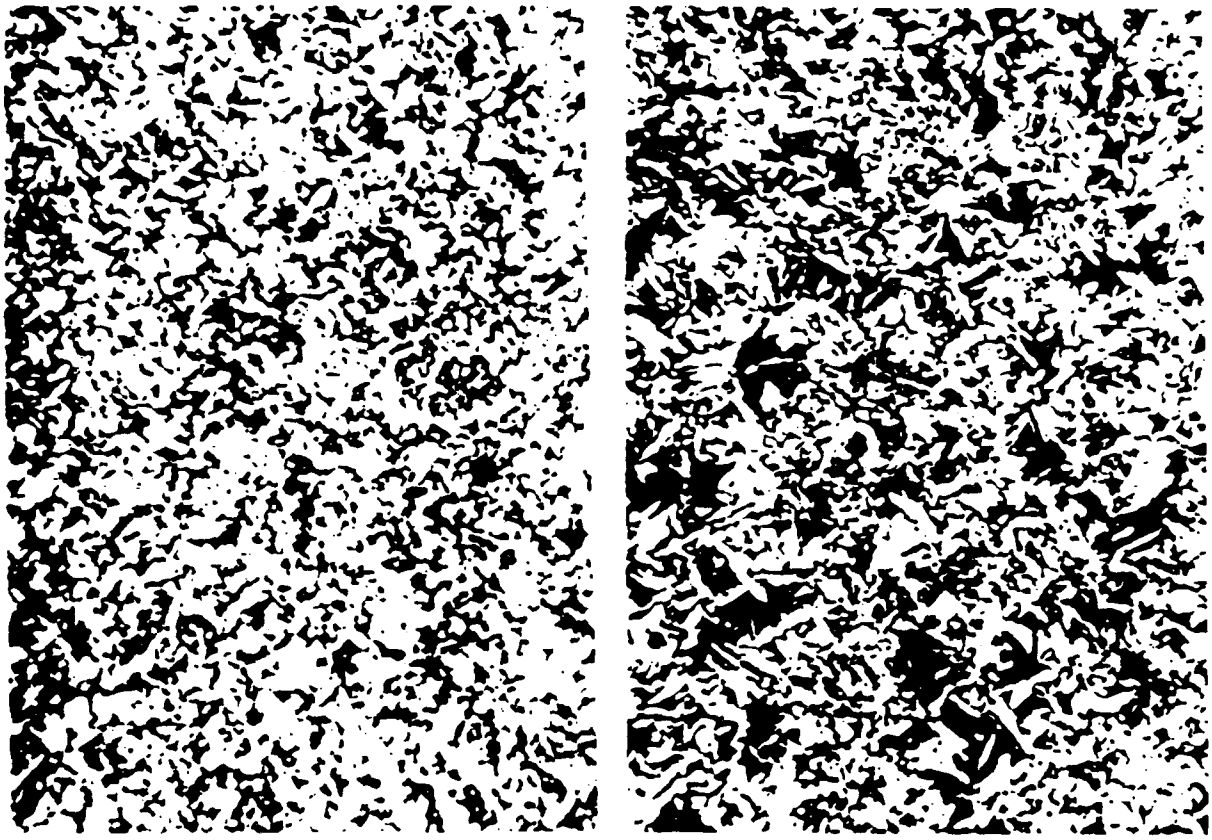


Figure 3: Optical polarized micrographs of the textures displayed by 2P upon cooling from isotropic phase: a) 98.4 °C after 1 hour; b) 98.4 °C after 12 hours.

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The synthesis and characterization of polymethacrylates, polyacrylates and polysiloxanes containing 4-methoxy-4'-hydroxybiphenyl (4-BP), 4-methoxy-4'-hydroxy-α-methylstilbene (4-MS) and 4-hydroxy-4'-methoxy-α-methylstilbene (4'-MS) mesogenic groups and a semifluorinated triad based on tetrafluorooxetane, hexafluoropropylene oxide and trifluoroethylene oxide is described. All polymers display a S_A mesophase and side chain crystallization. In the case of polymers based on 4-MS and 4'-MS the highest degree of decoupling seems to be displayed by the polymethacrylates. This result is in contrast to the behavior of the corresponding polymers containing aliphatic spacers. The polymethacrylate based on 4-BP displays an unusual "inverse" monotropic S_A mesophase which to our knowledge was not previously encountered in any liquid crystal systems. The synthesis and characterization of copolymethacrylates and copolysiloxanes containing 4-methoxy-4'-hydroxy-α-methylstilbene and 4-

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hydroxy-4'-methoxy-α-methylstilbene constitutional isomers is also described.

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Semifluorinated Polymers. 1. Synthesis and Characterization of Side Chain Liquid Crystalline Polymers Containing Semifluorinated Oligooxyethylene Based Flexible Spacers

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ABSTRACT

The synthesis and characterization of polymethacrylates, polyacrylates and polysiloxanes containing 4-methoxy-4'-hydroxybiphenyl (4-BP), 4-methoxy-4'-hydroxy- α -methylstilbene (4-MS) and 4-hydroxy-4'-methoxy- α -methylstilbene (4'-MS) mesogenic groups and a semifluorinated triad based on tetrafluorooxetane, hexafluoropropylene oxide and trifluoroethylene oxide is described. All polymers display a S_A mesophase and side chain crystallization. In the case of polymers based on 4-MS and 4'-MS the highest degree of decoupling seems to be displayed by the polymethacrylates. This result is in contrast to the behavior of the corresponding polymers containing aliphatic spacers. The polymethacrylate based on 4-BP displays an unusual "inverse" monotropic S_A mesophase which to our knowledge was not previously encountered in any liquid crystal systems. The synthesis and characterization of copolymethacrylates and copolysiloxanes containing 4-methoxy-4'-hydroxy- α -methylstilbene and 4-hydroxy-4'-methoxy- α -methylstilbene constitutional isomers is also described.

(Keywords: side chain liquid crystal polymers, semi-fluorinated spacers)

INTRODUCTION

The field of side chain liquid crystalline polymers was critically and extensively reviewed.[1-10] Nevertheless, still numerous problems remain contradictory and/or non-elucidated. One of the fundamental issues of this field refers to the mechanism by which the nature and molecular weight of the polymer backbone, and the nature and length of the flexible spacer determine the overall morphology of the resulting polymer and through it the type, the degree of order, and the dynamics of the mesophase formation.

Side chain liquid crystalline polymers containing paraffinic segments as flexible spacers are so far the most thoroughly investigated systems.[1-10] For this particular class of polymers the following general relationship seems to emerge. For polymers with molecular weights above which the phase transition temperatures are molecular weight independent,[4,9,12] the length of the flexible spacer dictates the type of mesophase displayed by the polymer[9,13-16] and the degree of decoupling.[2,17] For the same spacer length, the nature of the polymer backbone determines the thermal stability of the mesophase (i.e., the isotropization temperature), its thermodynamic stability with respect to the crystalline phase (i.e., enantiotropic, monotropic, or virtual), and the degree of decoupling.[12-16,18] The effect of the polymer backbone can be explained

based on thermodynamics.[19] Since the statistical random-coil conformation of the backbone gets distorted in the mesophase,[20,21] its ease of distortion is determined by the backbone flexibility and seems to dictate the overall dynamics of the side chain liquid crystalline polymer.[22] Therefore, the highest degree of decoupling is provided by the most flexible polymer backbones. Smectic copolymers based on very flexible backbones and containing structural units with and without mesogenic groups display a microphase separated morphology in which the polymer backbone gets microsegregated between the smectic layers.[9,23-28] Such a polymer displays two glass transition temperatures.[9,23-25] One of these two glass transitions was assigned to the independent motion of the polymer backbone, the other to the cooperative motion of the side groups which in such systems is independent of the motion of the polymer backbone. These polymer systems have the potential of providing side chain liquid crystalline polymers with very high degrees of decoupling. In such systems, by analogy to the known situation in immiscible polymer blends and microphase separated block and graft copolymers,[29,30] we assume that the miscibility of the polymer backbone with the flexible spacer and the mesogenic groups should influence the overall morphology of the system and therefore, its dynamic behavior. Based on these considerations, the investigation of side chain liquid crystalline polymers containing novel

types of flexible spacers is of both fundamental and practical interests.

So far, in addition to paraffinic groups, only oligodimethylsiloxane[2] and oligooxyethylene[2,31-35] segments were investigated as flexible spacers.

The goal of this paper is to present our first series of experiments on the synthesis and characterization of side chain liquid crystalline polymers containing semifluorinated flexible spacers based on an oligooxyethylenic triad containing trifluoroethyleneoxide, hexafluoropropyleneoxide and tetrafluorooxetane structural units. 4-Methoxy-4'-hydroxybiphenyl (4-BP), 4-methoxy-4'-hydroxy- α -methylstilbene (4-MS), and 4-hydroxy-4'-methoxy- α -methylstilbene (4'-MS) were used as mesogenic side groups, while, polymethacrylate, polyacrylate and poly(methylsiloxane) were used as polymer backbones. A copolymethacrylate and a copoly(methylsiloxane) containing 4-MS and 4'-MS side groups were also synthesized and characterized. There are some additional reasons for which side chain liquid crystalline polymers containing semifluorinated flexible spacers can be of interest. Perfluorinated alkanes are highly immiscible with their hydrogenated alkane homologues and therefore, exhibit high tendency towards microphase separation into distinct domains even when the molecular weights of the fluorocarbon and hydrocarbon segments are very low. Subsequently, semifluorinated n-alkanes display amphiphilic character and

behave as surfactants which exhibit both thermotropic and lyotropic (i.e., amphotropic) mesomorphism.[36-40] Polymerized liposomes based on fluorinated and non-fluorinated amphiphilic monomer pairs display also high tendency towards microphase separation.[3,41,42] Recently, it has been suggested that triphilic low molecular weight mesogens based on perfluorinated, paraffinic and biaryl segments may provide a new strategy towards the stabilization of a non-centrosymmetric arrangement within the layer of the smectic mesophase.[43] Therefore, polyphilic mesogens based on semifluorinated structures may also be of interest for the generation of materials displaying nonlinear optical and ferroelectric properties.[43] In conclusion, there are multiple fundamental reasons which justify the investigation of side chain liquid crystalline polymers containing semifluorinated flexible spacers.

To our knowledge this paper represents the first report on the synthesis and characterization of side chain liquid crystalline polymers containing semifluorinated flexible spacers.

EXPERIMENTAL

Materials

4-Methoxy-4'-hydroxybiphenyl (4-BP) was synthesized and purified as described previously.[31] 4-Methoxy-4'-hydroxy-α-methylstilbene (4-MS) and 4-hydroxy-4'-methoxy- α -methylstilbene (4'-MS) were synthesized by synthetic procedures developed previously.[14,15] Methyl 3-[2-(trifluoroethenoxy)-1-(trifluoromethyl)trifluoroethoxy]-tetrafluoropropionate was synthesized according to a literature procedure.[46] Poly(methylhydrosiloxane) ($\overline{DP}$=10) was synthesized as described in a previous publication from our laboratory.[25] Tetramethyldivinyldisiloxane platinum complex (Petrarch) used as catalyst in the hydrosilation reaction was diluted to 5% solution in xylene. All the other reagents were commercially available products and were used as received or purified by conventional methods.

Synthesis of Monomers and Polymers

Schemes I and II outline the synthesis of monomers.

Mesogens containing semifluorinated spacers terminated with a methyl ester group (4-BP-ME, 4-MS-ME, 4'-MS-ME)

Short notations used for these compounds are presented in Scheme I and Table I. In all cases the short notation

used for the mesogenic group is followed by ME which stands for methyl ester.

All methyl ester derivatives were prepared by the nucleophilic addition of phenolic -OH to the vinyl ether group of the fluorinated ester vinyl ether. An example is outlined below. To a solution of 5.0 g (0.025 mole) of 4-methoxy-4'-hydroxybiphenyl in 15 ml of DMF was added 0.52 g (0.0046 mole) of potassium t-butoxide. After stirring for 10 minutes, this solution was added over 1 hr to a solution of 15.1 g (0.036 mole) of methyl 3-[2-(trifluoroethenoxy)-1-(trifluoromethyl)trifluoroethoxy]tetrafluoropropionate in 10 ml of anhydrous THF while maintaining the solution temperature at 20-22°C. After addition, the solution was stirred at room temperature for 5 hrs and poured into 200 ml of ice water containing three drops of conc. HCl. The aqueous mixture was extracted with 3 x 200 ml of ether. The combined ether extracts were dried over $MgSO_4$ and concentrated on a rotary evaporator to 20.4 g of oil. Kugelrohr distillation of the oil at 0.2 mm gave, after removing a small forerun, 13.3 g (86%) of product (4-BP-ME) which distilled at a bath temperature of 160-170°C. The white solid was sufficiently pure to use directly in the next step.

Mesogens containing semifluorinated spacers terminated with an alcohol group (4-BP-OH, 4-MS-OH, 4'-MS-OH)

The short notations used for these compounds consist of the short notation used to characterize the mesogenic group, followed by OH which stands for alcohol.

All alcohol derivatives were prepared by the reduction of the corresponding methyl esters with $LiAlH_4$ in dry diethyl ether. An example is as follows. In a 500 ml three neck round bottom flask equipped with condenser, drying tube, and addition funnel, and containing 3.00 g (0.0783 mole) of $LiAlH_4$ in 50 ml dry diethyl ether, a solution of 4-BP-ME (9.74 g, 0.0157 mole) in 30 ml dry diethyl ether was added dropwise with stirring. After the addition was completed, the reaction mixture was stirred under reflux for 3 hours. The excess of $LiAlH_4$ was decomposed by dropwise addition of 50 ml of water, followed by 100 ml of 10% aqueous HCl solution. The ether layer was separated, washed with water, dried over $MgSO_4$ and evaporated to dryness to yield 8.53 g (92%) of product. m.p. 76°C (DSC). The yields, melting points, and 200 MHz ^{1}H-NMR spectral characterization of all derivatives are presented in Table I.

Mesogens containing semifluorinated spacers terminated with a methacrylate (4-BP-MA, 4-MS-MA, 4'-MS-MA) or acrylate (4-BP-AC, 4-MS-AC, 4'-MS-AC) group

Short notations for these compounds contain the notation for the mesogenic group followed by MA or AC which stand for methacrylate and acrylate respectively.

All monomers were synthesized by the esterification of the corresponding alcohol derivatives with acryloyl or methacryloyl chloride. An example is as follows. 4-BP-OH (2.50 g, 0.0042 mole) was dissolved in 30 ml of dry THF, followed by 0.68 ml (0.0049 mole) of dry triethylamine. The resulting solution was cooled to 0°C in an ice-water bath and 0.38 ml (0.0046 mole) of acryloyl chloride was added dropwise. The reaction mixture was allowed to warm up to room temperature and was kept stirring overnight. The precipitated $Et_3N.HCl$ was filtered and THF was evaporated in a rotary evaporator at room temperature. The crude product was dissolved in CH_2Cl_2, washed with aqueous $NaHCO_3$ solution, water, dried over $MgSO_4$, and purified by column chromatography (silica gel, CH_2Cl_2 eluent) to yield 2.30 g (84%) of white product. Purity > 99% (HPLC); m.p. 45°C (DSC). The characterization of all methacrylates and acrylates is summarized in Table I.

Radical polymerization and copolymerization of methacrylates and acrylates

All monomers were polymerized or copolymerized in dry benzene using AIBN as initiator at 60°C for 24 hrs. Polymerizations were carried out in Schlenk tubes under nitrogen atmosphere after monomer solutions were degassed by several freeze-pump-thaw cycles under vacuum. The monomer and initiator concentrations for the polymerization of methacrylates were 20% (w/v) and 0.5% (w/w of monomer), respectively, while those for the polymerization of acrylates were 20% (w/v) and 0.25% (w/w of monomer), respectively. After polymerization, the reaction mixture was diluted with benzene and precipitated into methanol. The filtered polymers were dried under vacuum and then were purified by successive reprecipitations from THF solutions into methanol until GPC analysis showed no traces of unreacted monomer, or oligomers. Conversions were higher than 90% in all cases. Tables II and III summarize the characterization of all polyacrylates, polymethacrylates and copolymethacrylates.

Mesogens containing semifluorinated spacers terminated with an allyl ether group (4-BP-O, 4-MS-O, 4'-MS-O)

The short notations used for these compounds consist of the short name of the mesogenic unit followed by O which stands for olefin.

All compounds were synthesized by the phase-transfer catalyzed etherification of the corresponding alcohols with allyl chloride. An example is presented below. A solution of 4-BP-OH (1.50 g, 0.0025 mole), 2.0 ml of 50% (w/v) aqueous NaOH solution, TBAH (0.086 g, 0.0003 mole), and allyl chloride (0.31 ml, 0.0038 mole) in 6 ml of solvent (benzene/DMSO, 5/1 v/v) was stirred at 60°C for 5 hours. The reaction mixture was cooled to room temperature, diluted with benzene, washed with water, dried with $MgSO_4$ and the solvent was evaporated in a rotary evaporator. The crude product was purified by column chromatography (silica gel, CH_2Cl_2 eluent) to yield 1.15 g (71%) of pure product. Purity > 99% (HPLC); m.p. 49°C. Table I presents the characterization of all allyl ethers synthesized.

Synthesis of polymethylsiloxanes and copolymethylsiloxanes

Liquid crystalline polymethylsiloxanes were synthesized using the following representative procedure. The olefinic derivative (4-BP-O), (0.80 g, 20 mole % excess versus the Si-H groups present in the polymethylhydrosiloxane) was dissolved in 30 ml of dry, freshly distilled toluene together with the proper amount of poly(methylhydrosiloxane) ($\overline{DP}$=10). The reaction mixture was heated to 60°C under nitrogen, and 100 μg of tetramethyldivinyldisiloxane platinum catalyst were then added with a syringe as solution in xylene (5%). The reaction mixture was stirred at that temperature until both IR and 200 MHz ^{1}H-NMR analyses showed that all Si-H groups were consumed (about 4-6 hrs). The white polymers were separated by precipitation into methanol, and were purified by successive precipitations from chloroform solutions into methanol until GPC analysis showed that the polymers were free of unreacted 4-BP-O derivative. To avoid contamination of the resulting polymers with polydimethylsiloxane from silicon grease, only teflon tape and teflon gaskets were used in the hydrosilation equipment. The characterization of polymethylsiloxanes and copolymethylsiloxanes is presented in Tables II and III.

Techniques

200 MHz ^{1}H-NMR spectra were recorded on a Varian XL-200 spectrometer. All spectra were recorded in $CDCl_3$ solutions with TMS as internal standard.

A Perkin-Elmer DSC-4 differential scanning calorimeter, equipped with a TADS 3600 data station, was used to determine the thermal transitions which were read at the maximum of the endothermic or exothermic peaks. Unless specified otherwise, all heating and cooling rates were 20°C/min. Glass transition temperatures (T_g) were read at the middle of the change in heat capacity. Second and subsequent heating scans and first and subsequent cooling scans were perfectly reproducible unless stated otherwise. When the second DSC heating scan differed from the first heating scan, the difference will be mentioned and attempts to explain it will be made. Both enthalpy changes and transition temperatures were determined using indium as a calibration standard. A Carl-Zeiss optical polarized microscope (magnification: 100X) equipped with a Mettler FP 82 hot stage and a Mettler FP 80 central processor was used to observe the thermal transitions and to analyze the anisotropic textures.[44,45] Molecular weights were determined by gel permeation chromatography (GPC) with a Perkin-Elmer series 10 LC instrument equipped with LC-100 column oven, LC-600 autosampler, and a Nelson Analytics 900 series data acquisition system. High pressure liquid

chromatography (HPLC) determinations were performed with the same instrument. The molecular weight measurements were made using a UV detector, THF as solvent (1ml/min; 40°C), a set of PL gel columns of 10^2, $5X10^2$, 10^3, 10^4, and 10^5 Å, and a calibration plot constructed with polystyrene standards.

RESULTS AND DISCUSSION

Scheme I outlines the synthesis of the 4-BP, 4-MS and 4'-MS derivatives containing a semifluorinated flexible spacer terminated with a methyl ester group, i.e. 4-BP-ME, 4-MS-ME and 4'-MS-ME. The introduction of the semifluorinated spacer group is accomplished through the base catalyzed addition of the phenolic -OH to the vinyl ether of the fluorinated ester vinyl ether.[46] Although nucleophilic additions to fluorinated olefins are well known,[47] few examples of the addition of -OH[48] or other nucleophiles[49] to fluorovinyl ethers have been reported. The addition reaction occurs selectively with the vinyl ether in the presence of a reactive fluorinated ester. Although the esters could be purified by column chromatography, substantial amounts of material were lost, presumably due to the hydrolysis of the ester group. Better yields were generally obtained by reduction of the crude ester to the alcohol which was easily purified.

Scheme II presents the synthesis of 4-BP-OH, 4-BP-MA, 4-BP-AC and 4-BP-O. The methyl ester derivatives were reduced to the corresponding alcohols with $LiAlH_4$-diethyl ether. The resulting alcohols were esterified with methacryloyl or acryloyl chloride to yield the corresponding methacrylate and acrylate monomers. Alternatively, they were etherified with allyl chloride under phase transfer catalyzed conditions[50] to provide the corresponding allyl ethers. The semifluorinated alcohol derivatives are more acidic than their aliphatic analogues and therefore, they can be easily deprotonated and etherified under liquid-liquid phase transfer catalyzed conditions. Under phase transfer catalyzed reaction conditions the reactivity of these semifluorinated alcohols resembles more the reactivity of phenols rather than that of aliphatic alcohols.

The acrylate and methacrylate monomers were polymerized using AIBN as a radical initiator. The allyl ether derivatives were hydrosilylated with a poly(methylhydrosiloxane) to provide poly(methylsiloxane)s containing mesogenic side groups. The structure of the polymers containing 4-BP mesogenic side groups is outlined in Scheme III. Scheme IV presents the structure of the polymers containing 4-MS and 4'-MS mesogenic side groups.

The molecular weights and the thermotropic behavior of all polymers are summarized in Tables II and III. These molecular weights were obtained by using a GPC calibration based on polystyrene standards and therefore are only

relative. Nevertheless, based on our previous experience with similar polymers containing aliphatic spacers,[12,25] with the exception of 4-BP-PS from Table II and 4-MS-PAC from Table III, all polymers have molecular weights which are higher than those below which their phase transitions are molecular weight dependent. Therefore, the phase transition temperatures and the thermodynamic parameters of polymers based on different backbones and similar mesogenic side groups, or different mesogenic side groups but identical polymer backbones can be quantitatively considered.

We will first discuss the thermotropic behavior of the polymers containing 4-BP mesogenic side groups. Representative differential scanning calorimetric traces displayed by different heating and cooling scans of these polymers are presented in Figure 1. First and subsequent heating and cooling scans of 4-BP-PMA are always identical and perfectly reproducible (curves A,C, Figure 1). On the first or subsequent heating scans 4-BP-PMA presents a melting transition at 114°C, followed by a S_A mesophase which undergoes isotropization at 124°C. On cooling 4-BP-PMA presents the isotropic-crystalline transition at 107°C. Upon quenching the polymer from the isotropic phase to -30°C, the first transition temperature shifts to a slightly lower temperature i.e. 109°C. The isotropization transition temperature remains unchanged (curve B, Figure 1). A characteristic focal conic texture displayed by the S_A

mesophase of 4-BP-PMA is presented in Figure 2A. We could not obtain a different texture for the crystalline phase of 4-BP-PMA since the motion of the polymer within this range of temperatures is frozen. The crystalline phase of 4-BP-PMA was confirmed by X-ray diffraction experiments.

The thermotropic behavior of 4-BP-PMA is quite similar to that of the corresponding polymethacrylate containing 4-BP mesogenic side groups and a paraffinic flexible spacer consisting of eleven methylenic units.[51] For example, in the case of 4-BP-PMA, the degree of supercooling of the lowest temperature transition is only 7°C while that of the isotropic-liquid crystalline phase transition is 17°C. The corresponding polymethacrylate with a paraffinic spacer exhibits two smectic mesophases. The one at lower temperature displays a degree of supercooling of 5°C while the one at higher temperature a degree of supercooling of 10°C.[51] The enthalpy change of the peaks at 114 and 124°C from the heating scan is equal to that of the peak at 107°C from the cooling scan (Table II). Therefore, the peak at 107°C is due to both isotropic-S_A and S_A-crystalline transitions which are overlapped. This behavior transforms the S_A mesophase exhibited by 4-BP-PMA into a monotropic mesophase which appears as an "inverse monotropic mesophase". In the case of polymers containing paraffinic flexible spacers or of low molar mass liquid crystals, a monotropic mesophase (i.e., thermodynamically metastable with respect to the crystalline phase) is obtained as a

result of the fact that the crystallization transition is supercooled more than the corresponding isotropic-mesomorphic transition. Subsequently, the monotropic mesophase can be observed only on cooling scans, and is thermodynamically metastable. In the case of 4-BP-PMA the situation is reversed and the mesophase can be observed only on the heating scans. 4-BP-PMA displays a high ability towards side chain crystallization. In the case of most polymethacrylates containing flexible spacers based on eleven methylenic units, the side chain crystallization process is kinetically controlled while the mesophase formation is thermodynamically controlled.[14,15] In many cases, the side chain crystallization process requires extensive annealing above the glass transition temperature of the polymer. Subsequently, most of the time no crystallization exotherm can be observed on the cooling scan. At the same time, the melting transition temperature and the enthalpy change associated with this transition are thermal history dependent. In the case of 4-BP-PMA, the melting and crystallization transition temperatures and the enthalpy changes associated to them are very little affected by the thermal history of the sample. The high rate of crystallization of 4-BP-PMA suggests that the polymer based on the semifluorinated spacer exhibits a higher degree of decoupling than the similar polymers based on aliphatic spacers. The lower degree of supercooling of the crystalline phase versus that of the S_A phase indicates that

the difference of order between the isotropic and S_A phase is higher than that between the S_A and crystalline phase. The thermodynamic data from Table II are supporting this statement.

Curves D and E in Figure 1 present representative heating and cooling DSC traces of 4-BP-PAC. First and subsequent heating and cooling scans are identical. This polymer displays also a crystalline phase followed by an enantiotropic S_A mesophase. The degree of supercooling of the crystalline phase transition is lower (8°C) than that of the S_A-isotropic phase transition (12°C). Nevertheless, the isotropization temperature of 4-BP-PAC is higher than that of 4-BP-PMA, although the enthalpy and entropy changes associated with isotropization transitions are higher for polymethacrylate than for polyacrylate. Both trends are in agreement with the behavior of the polymethacrylates and polyacrylates containing aliphatic flexible spacers.[51] Since the enthalpy changes of the transition peak from the heating DSC scan at 112°C (curve D, Figure 1) and cooling scan at 104°C (curve E, Figure 1) are equal, we would tend to assign this peak to a transition from a S_A mesophase into a highly ordered smectic mesophase rather than into a crystalline phase. However, preliminary X-ray diffraction experiments show the low temperature phase to be crystalline. A representative focal conic texture exhibited by the S_A mesophase of 4-BP-PAC is presented in Figure 2B.

Curves H and I in Figure 1 present second and subsequent heating and cooling DSC scans of 4-BP-PS. This polymer exhibits side chain crystallization and an enantiotropic S_A mesophase. The degree of supercooling of the S_A mesophase is again higher than that of the crystallization process. However, both melting and isotropization transition temperatures are lower than those of the 4-BP-PMA and 4-BP-PAC. The first heating scan of 4-BP-PS (curve G, Figure 1) or the heating scan after annealing above T_g shows only a melting transition and the S_A-isotropic transition at 91°C. This demonstrates that under equilibrium conditions the S_A mesophase of 4-BP-PS is only monotropic. At first sight, the lower isotropization and melting transition temperatures displayed by 4-BP-PS in comparison to those of 4-BP-PMA and 4-BP-PAC represent a reversed trend when compared to the influence of the polymer backbone on the phase transition temperatures of the corresponding polymers containing aliphatic spacers.[51,52] However, the spacer of 4-BP-PS contains three more methylenic units than that of the corresponding 4-BP-PMA and 4-BP-PAC. Therefore, it could be that the lower isotropization temperature of the polysiloxane is due to a combination of both longer spacer length (Scheme III) and lower polymer molecular weight (Table II).

Figure 3 presents representative heating and cooling DSC scans of 4-MS-PMA, 4-MS-PAC and 4-MS-PS. The corresponding phase transitions and thei· associated

thermodynamic parameters are summarized in Table III. All three polymers display a melting transition at about 50°C. In the case of 4-MS-PMA and 4-MS-PAC, this melting transition appears only in the first heating scan or after suitable annealing above T_g. In the case of 4-MS-PS, the melting process is very little dependent on the thermal history of the sample and appears on each heating or cooling scan regardless of their previous thermal history. All three polymers display a S_A mesophase. This mesophase is enantiotropic in the case of 4-MS-PMA and monotropic in the case of 4-MS-PS. In the case of 4-MS-PAC, the mesophase is enantiotropic when recorded from second or subsequent heating and cooling scans (curves E and F, Figure 3). However, it is only monotropic under equilibrium conditions (curves D and F, Figure 3). The side chain crystallization process of the polymers based on 4-MS and semifluorinated spacers resembles that of the corresponding polymers based on aliphatic spacers. However, the isotropization transition temperatures of the polymers based on semifluorinated spacers and 4-MS decrease with increasing flexibility of the polymer backbone. This trend is reversed in the case of the polymers based on 4-MS and aliphatic flexible spacers.[14] At the present time we do not have any good explanation for this behavior. In the case of 4-MS-PAC, the isotropization temperature is lower than that of 4-MS-PS most probably due to the fact that the molecular weight of the polyacrylate is below values where phase

transition temperatures are molecular weight independent (Table III). Figure 2C shows the focal conic texture exhibited by the S_A phase of 4-MS-PMA, while Figure 2D the formation of batonnetes on cooling 4-MS-PS from the isotropic into the S_A phase.

Representative DSC traces of 4'-MS-PMA, 4'-MS-PAC and 4'-MS-PS are presented in Figure 4. The phase transition temperatures of these polymers and the corresponding thermodynamic parameters are summarized in Table III. 4'-MS-PMA displays side chain crystallization and an enantiotropic S_A mesophase. The side chain melting process of 4'-MS-PMA is thermal history dependent (curves A, B, Figure 4). The melting peak of 4'-MS-PAC appears only on the first heating scan or after suitable annealing. Therefore, under equilibrium conditions, the S_A mesophase displayed by 4'-MS-PAC is only monotropic (curves D, F, Figure 4) although it appears enantiotropic when determined from second or subsequent heating and cooling scans (curves E, F, Figure 4). The side chain crystallization process of 4'-MS-PS is very little dependent on the thermal history of the sample (curves G, H, and I, Figure 4) and is observable in every heating scan. The S_A mesophase of 4'-MS-PS is only monotropic. As in the case of the polymers based on 4-MS, the polymers based on 4'-MS and semifluorinated spacers present isotropic transition temperatures which decrease with the increase of the polymer backbone flexibility. This result is opposite to the one obtained with the same

mesogenic group and aliphatic flexible spacers.[15] For all polymer backbones, the isotropization and melting transition temperatures of the polymers based on 4-MS mesogenic group are higher than those based on 4'-MS. These data are in agreement with those obtained with 4-MS and 4'-MS mesogens, polymethacrylate, polyacrylate and polysiloxane backbones and paraffinic flexible spacers.[14,15]

Previous experiments performed in our laboratory have demonstrated that copolymerization of the parent polymers' monomer pair containing 4-MS and 4'-MS constitutional isomeric mesogenic side groups suppresses the crystalline melting transition temperature more than the isotropization transition temperature. Therefore, these copolymerization experiments were used to transform monotropic or even virtual mesophases into enantiotropic mesophases.[18,53] This result is due to the fact that the structural units of the copolymer were isomorphic in the mesophase but not in the crystalline phase. To see whether this concept applies to the liquid crystalline polymers and copolymers based on semifluorinated spacers we have synthesized the two copolymers described in Scheme V. We can assume that the reactivities of 4-MS-MA (M_1) and 4'-MS-MA (M_2) are equal, and therefore, $r_1 = r_2 = 1$. Under these circumstances the copolymer composition is equal to the monomer feed and is independent of conversion (i.e., azeotropic copolymerization). Consequently, starting with a 1 : 1 mole ratio between 4-MS-MA and 4'-MS-MA in the reaction mixture

we obtained 4,4'(1/1)-MS-coPMA copolymer from Scheme V. Its DSC traces are presented as curves A, B and C in Figure 5. In the first heating scan (curve A, Figure 5) this copolymer displays a melting transition at 48°C followed by a S_A phase which undergoes isotropization at 107°C. Subsequent heating and cooling scans show only the enantiotropic smectic mesophase. Figure 2E presents the texture of the smectic mesophase exhibited by 4,4'(1/1)-MS-coPMA. Regardless of the thermal history of the sample, one of the parent homopolymers of this copolymer, i.e., 4'-MS-PMA, exhibits a melting transition (curves A, B, Figure 4). Therefore, for the case of polymethacrylates containing semifluorinated flexible spacers, copolymerization of the parent polymers' monomer pair containing 4-MS and 4'-MS constitutional isomeric mesogenic side groups suppresses the side chain crystallization tendency, as in the case of the copolymers based on paraffinic spacers. At the same time, this copolymerization experiment affects very little the formation of the mesophase.

However, this is not the case for the copolysiloxane 4,4'(1/1)-MS-coPS from Scheme V. Its DSC traces are presented in curves D, E and F of Figure 5. The first heating scan of 4,4'(1/1)-MS-coPS (curve D, Figure 5) displays multiple transitions which are difficult to assign. The second heating scan (curve E, Figure 5) presents a melting transition at 38°C followed by a smectic mesophase which undergoes isotropization at 44°C. On the cooling scan

we can observe only a crystallization exotherm (curve F, Figure 5). Therefore, 4,4'(1/1)-MS-coPS presents an "inverse monotropic mesophase" which resembles the one displayed by 4-BP-PMA from Figure 1 (curves A, B, C).

A previous publication from our laboratory[25] discusses the dependence of the smectic-isotropic transition peak width on the polymer molecular weight and on the composition of copolymers containing mesogenic and non-mesogenic structural units. The broadening of this peak was attributed to a higher miscibility between the polymer backbone and the mesogenic side groups in the smectic phase. These results were recently supported by additional experiments.[28,54] An inspection of the DSC traces from Figures 1, 2 and 3 shows that the isotropic-S_A transition peak width is narrower in the case of polymethacrylates than in the case of polyacrylates and polysiloxanes. Therefore, it could be that the semifluorinated oligooxyethylene flexible spacer is more miscible with the last two polymer backbones than with the polymethacrylate backbone. This different miscibility may contribute to the overall mesomorphic behavior of these polymers. The solubility of this semifluorinated oligooxyethylene spacer does not resemble that of perfluorinated paraffins. All intermediary compounds, monomers and polymers based on this semifluorinated spacer are much more soluble especially in basic solvents like tetrahydrofuran, alcohols, etc. This might be due to the presence of a very acidic proton in the

trifluoroethoxy segment of the mesogenic group (Schemes I, II, III). In addition, the formation of the textures of the polymethacrylates with semifluorinated spacers is much faster than that of the corresponding polyacrylates or polysiloxanes. At the same time, the isotropization enthalpies of polymethacrylates are higher than those of polyacrylates and polysiloxanes (Tables II, III). Therefore, the peak widths, the dynamics of mesophase formation, the isotropization transition temperatures and their corresponding enthalpy changes, suggest a higher degree of decoupling for polymethacrylates than for polyacrylates and polysiloxanes. This result is in contrast to the behavior of the corresponding polymers containing aliphatic flexible spacers.[14,15,18,22,51-54] The only two polymers which behave similar to the corresponding polymers based on aliphatic spacers[51] are 4-BP-PMA and 4-BP-PAC.

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FIGURE CAPTIONS

Scheme I. Synthesis of 4-methoxy-4'-hydroxybiphenyl (4-BP-ME), 4-methoxy-4'-hydroxy- α -methylstilbene (4-MS-ME) and 4-hydroxy-4'-methoxy- α -methylstilbene (4'-MS-ME) methyl ester derivatives containing the semifluorinated flexible spacer.

Scheme II. Synthesis of methacrylate (4-BP-MA), acrylate (4-BP-AC), and allyl ether (4-BP-O) containing semifluorinated flexible spacers and 4-methoxy-4'-hydroxybiphenyl based mesogens.

Scheme III. Polymethacrylate (4-BP-PMA), polyacrylate (4-BP-PAC), and polymethylsiloxane (4-BP-PS) containing semifluorinated flexible spacers and 4-methoxy-4'-hydroxybiphenyl based mesogens.

Scheme IV. Polymethacrylates (4-MS-PMA, 4'-MS-PMA), polyacrylates (4-MS-PAC, 4'-MS-PAC), and polymethylsiloxanes (4-MS-PS, 4'-MS-PS) containing semifluorinated flexible spacers and 4-methoxy-4'-hydroxy- α -methylstilbene or 4-hydroxy-4'-methoxy- α -methylstilbene based mesogens.

Scheme V. Copolymethacrylate [4,4'(1/1)-MS-coPMA], and copolymethylsiloxane [4,4'(1/1)-MS-coPS] containing

semifluorinated flexible spacers and a 1/1 molar ratio of 4-methoxy-4'-hydroxy- α -methylstilbene/4-hydroxy-4'-methoxy- α -methylstilbene based mesogens.

Figure 1. Normalized DSC scans (20°C/min) of: A) 4-BP-PMA, first and subsequent heating scans; B) 4-BP-PMA, heating scan after quenching the isotropic liquid to -30°C; C) 4-BP-PMA, first and subsequent cooling scans; D) 4-BP-PAC, first and subsequent heating scans; E) 4-BP-PAC, first and subsequent cooling scans; F) 4-BP-PS, first heating scan; G) 4-BP-PS, second and subsequent heating scans; H) 4-BP-PS, first and subsequent cooling scans.

Figure 2. Representative optical polarized micrographs (100X) of: A) 4-BP-PMA, after 5 min of annealing at 116°C on heating scan (below 107°C this texture remains unchanged); B) 4-BP-PAC, after 5 min of annealing at 135°C on heating scan (below 100°C this texture remains unchanged); C) 4-MS-PMA, after 10 min of annealing at 94°C on cooling scan; D) 4-MS-PS, after 1 min at 46°C on cooling scan; E) 4,4'-(1/1)-MS-coPMA, after 10 min of annealing at 90°C on cooling scan.

Figure 3. Normalized DSC scans (20°C/min) of: A) 4-MS-PMA, first heating scan; B) 4-MS-PMA, second and subsequent heating scans; C) 4-MS-PMA, first and subsequent cooling scans; D) 4-MS-PAC, first heating scan; E) 4-MS-PAC, second

and subsequent heating scans; F) 4-MS-PAC, first and subsequent cooling scans; G) 4-MS-PS, first heating scan; H) 4-MS-PS, second and subsequent heating scans; I) 4-MS-PS, first and subsequent cooling scans.

Figure 4. Normalized DSC scans (20°C/min) of: A) 4'-MS-PMA, first heating scan; B) 4'-MS-PMA, second and subsequent heating scans; C) 4'-MS-PMA, first and subsequent cooling scans; D) 4'-MS-PAC, first heating scan; E) 4'-MS-PAC, second and subsequent heating scans; F) 4'-MS-PAC, first and subsequent cooling scans; G) 4'-MS-PS, first heating scan; H) 4'-MS-PS, second and subsequent heating scans; I) 4'-MS-PS, first and subsequent cooling scans.

Figure 5. Normalized DSC scans (20°C/min) of: A) 4,4'(1/1)-MS-coPMA, first heating scan; B) 4,4'(1/1)-MS-coPMA, second and subsequent heating scans; C) 4,4'(1/1)-MS-coPMA, first and subsequent cooling scans; D) 4,4'(1/1)-MS-coPS, first heating scan; E) 4,4'(1/1)-MS-coPS, second and subsequent heating scans; F) 4,4'(1/1)-MS-coPS, first and subsequent cooling scans.

TABLE I. Characterization of monomers

Compound	Yield (%)	M.p. (°C)	200 MHz ^{1}H-NMR ($CDCl_3$, δ , ppm)
4-BP-ME	86	63	[b] 3.76 (s, CH_3O-); 3.88 (d, $-CO_2CH_3$); 5.96 and 6.14 (2s, -CHF-); 6.88-7.46 (m, 8 aromatic protons).
4-BP-OH	92	76	3.86 (s, CH_3O-); 4.06 (t, $-CH_2OH$); 5.94 and 6.21 (2s, -CHF-); 6.97-7.54 (m, 8 aromatic protons).
4-BP-MA	65	34	1.94 (s, CH_3-C-COO); 3.83 (s, CH_3O-); 4.57 (t, $-CH_2O$-); 5.64 and 6.17 (2s, CH_2=); 5.93 and 6.20 (2s, -CHF-); 6.94-7.51 (m, 8 aromatic protons).
4-BP-AC	84	45	3.86 (s, CH_3O-); 4.63 (t, $-CH_2O$-); 5.90-6.54 (m, CH_2=CH-); 5.97 and 6.23 (2s, -CHF-); 6.97-7.56 (m, 8 aromatic protons).
4-BP-O	71	49	3.84 (s, CH_3O-); 3.87 (t, -CH2-); 4.09 (bs, CH_2=CH-CH_2-); 5.23 and 5.83 (m, CH_2=CH-); 5.93 and 6.20 (2s, -CHF-); 6.94-7.51 (m, 8 aromatic protons).
4-MS-OH	78	62[a]	2.23 (s, CH_3-C=); 3.84 (s, CH_3O-); 4.04 (t, $-CH_2OH$); 5.94 and 6.21 (2s, -CHF-); 6.73 (s, Ph-CH=); 6.90-7.46 (m, 8 aromatic protons).
4-MS-MA	83	11	1.94 (s, CH_3-C-COO); 2.23 (s, CH_3-C=); 3.84 (s, CH_3O-); 4.59 (t, $-CH_2O$-); 5.67 and 6.20 (2s, CH_2=); 5.94 and 6.20 (2s, -CHF-); 6.73 (s, Ph-CH=); 6.90-7.46 (m, 8 aromatic protons).
4-MS-AC	78	15	2.23 (s, CH_3-C=); 3.84 (s, CH_3O-); 4.60 (t, $-CH_2O$-); 5.91-6.54 (m, CH_2=CH-); 5.97 and 6.21 (2s, -CHF-); 6.73 (s, Ph-CH=); 6.90-7.44 (m, 8 aromatic protons).
4-MS-O	81	19	2.24 (s, CH_3-C=); 3.84 (s, CH_3O-); 3.89 (t, $-CH_2O$-); 4.10 (bs, CH_2=CH-CH_2-); 5.27 and 5.87 (m, CH_2=CH-); 5.94 and 6.21 (2s, -CHF-); 6.73 (s, Ph-CH=); 6.91-7.46 (m, 8 aromatic protons).
4'-MS-ME	79	31[a]	[b] 2.18 (s, CH_3-C=); 3.78 (s, CH_3O-); 3.89 (d, $-CO_2CH_3$); 5.95 and 6.13 (2s, -CHF-); 6.73 (s, Ph-CH=); 6.86-7.45 (m, 8 aromatic protons).
4'-MS-OH	85	46[a]	2.27 (s, CH_3-C=); 3.86 (s, CH_3O-); 4.06 (t, $-CH_2OH$); 5.99 and 6.24 (2s, -CHF-); 6.80 (s, Ph-CH=); 6.94-7.53 (m, 8 aromatic protons).

4'-MS-MA	83	-9	1.97 (s, CH_3-C-COO); 2.29 (s, CH_3-C=); 3.88 (s, CH_3O-); 4.65 (t, -CH_2O-); 5.73 and 6.26 (2s, CH_2=); 6.01 and 6.26 (2s, -CHF-); 6.83 (s, Ph-CH=); 7.00-7.58 (m, 8 aromatic protons).
4'-MS-AC	64	3	2.26 (s, CH_3-C=); 3.84 (s, CH_3O-); 4.61 (t, -CH_2O-); 5.95 and 6.21 (2s, -CHF-); 5.91-6.54 (m, CH_2=CH-); 6.77 (s, Ph-CH=); 6.91-7.50 (m, 8 aromatic protons).
4'-MS-O	75	7	2.26 (s, CH_3-C=); 3.84 (s, CH_3O-); 3.87 (t, -CH_2O-); 4.10 (bs, CH_2=CH-CH_2-); 5.26 and 5.84 (m, CH_2=CH-); 5.93 and 6.20 (2s, -CHF-); 6.74 (s, Ph-CH=); 6.90-7.49 (m, 8 aromatic protons).

[a] $T_m = T_i$
[b] CD_2Cl_2

TABLE II. Characterization of Polymers Containing Semifluorinated Flexible Spacers and 4-Methoxy-4'-hydroxybiphenyl Based Mesogens

Polymer	$\bar{M}_n \times 10^{-3}$	$\bar{M}_w/\bar{M}_n$	Thermal Transitions (°C) and Thermodynamic Parameters [Δ H (Kcal/mru) / ΔS (cal/mru°K)][a]
4-BP-PMA	49.0	2.1	k 114(0.89/2.29) s_A 124(1.97/4.97) i i 107(2.82/7.41) k
4-BP-PMA[b]	49.0	2.1	k 109(0.79/2.06) s_A 124(1.99/5.01) i i 107(2.82/7.41) k
4-BP-PAC	15.4	2.0	k 112(1.61/4.19) s_A 142(1.38/3.33) i i 130(1.39/3.44) s_A 104(1.50/3.99) k
4-BP-PS[c]	12.7	3.1	k 91(2.55/7.00) i i 82(1.46/4.11) s_A 74(1.30/3.74) k
4-BP-PS	12.7	3.1	k 85(1.26/3.53) s_A 95(1.47/4.01) i i 82(1.46/4.11) s_A 74(1.30/3.74) k

[a] First line corresponds to heating DSC scan while second line corresponds to cooling DSC scan
[b] Heating scan after quenching to -30°C
[c] First heating scan

TABLE III. Characterization of Polymers and Copolymers Containing Semifluorinated Flexible Spacers and 4-Methoxy-4'-hydroxy-α-methylstilbene and/or 4-Hydroxy-4'-methoxy-α-methylstilbene Based Mesogens

Polymer	$\bar{M}_n \times 10^{-3}$	$\bar{M}_w/\bar{M}_n$	Thermal Transitions (°C) and Thermodynamic Parameters [ΔH (Kcal/mru) / ΔS (cal/mru°K)][a]
4-MS-PMA[b]	35.2	2.0	k 54(1.07/3.28) s_A 118(0.86/2.19) i i 99(0.84/2.26) s_A -4 g
4-MS-PMA	35.2	2.0	g 2 s_A 115(0.86/2.23) i i 99(0.84/2.26) s_A -4 g
4-MS-PAC[b]	6.1	1.2	k 50(1.71/5.31) i i 25(0.06/0.18) s_A 0 g
4-MS-PAC	6.1	1.2	g 1 s_A 37(0.26/0.82) i i 25(0.06/0.18) s_A 0 g
4-MS-PS[b]	35.4	2.4	k 50(3.31/10.23) i i 36(0.20/0.64) s_A 31(2.31/7.59) k
4-MS-PS	35.4	2.4	k 44(0.76/2.41) k 50(1.86/5.75) i i 36(0.20/0.64) s_A 31(2.31/7.59) k
4'-MS-PMA[b]	25.3	1.8	g 1 k 43(0.16/0.49) s_A 75(0.52/1.49) i i 62(0.61/1.82) s_A -5 g
4'-MS-PMA	25.3	1.8	g -3 k 54(0.05/0.15) s_A 74(0.67/1.92 i i 62(0.61/1.82) s_A -5 g
4'-MS-PAC[b]	18.0	1.7	k 48(0.66/2.06) i i 45(0.19/0.61) s_A 2 g
4'-MS-PAC	18.0	1.7	g 9 s_A 52(0.33/1.02) i i 45(0.19/0.61) s_A 2 g
4'-MS-PS[b]	36.0	2.9	k 39(2.09/6.69) i i 28(0.36/1.20) s_A 18(1.88/6.46) k
4'-MS-PS	36.0	2.9	k 26(0.15/0.49) k 34(2.03/6.60) i i 28(0.36/1.20) s_A 18(1.88/6.46) k
4,4'(1/1)-MS-coPMA[b]	31.5	2.9	g -5 k 48(0.74/2.30) s_A 107(0.89/2.33) i i 89(0.80/2.21) s_A -3 g
4,4'(1/1)-MS-coPMA	31.5	2.9	g 2 s_A 104(0.86/2.29) i i 89(0.80/2.21) s_A -3 g
4,4'(1/1)-MS-coPS[b]	43.6	2.3	k 43(2.16/6.84)[c] i i 24(1.76/5.93) k
4,4'(1/1)-MS-coPS	43.6	2.3	k 38(1.96/6.30) s_A 44[d] i i 24(1.76/5.93) k

[a] First line corresponds to heating DSC scan while second line corresponds to cooling DSC scan
[b] First heating scan
[c] Multiple endotherms
[d] Overlapped transition

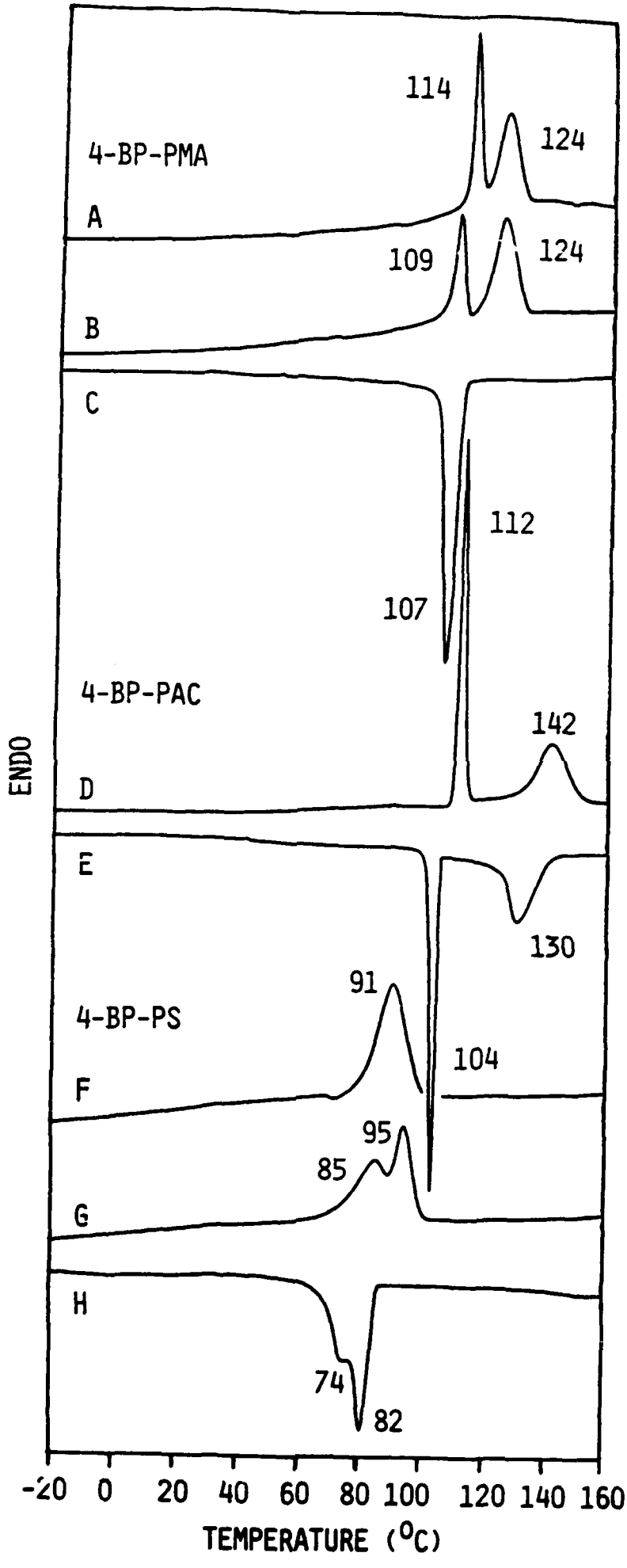
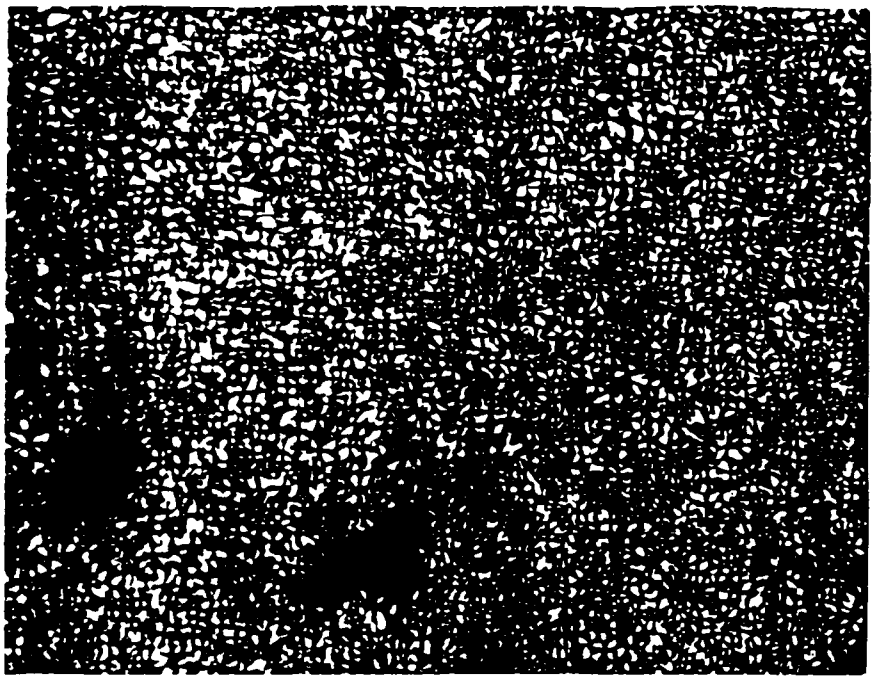
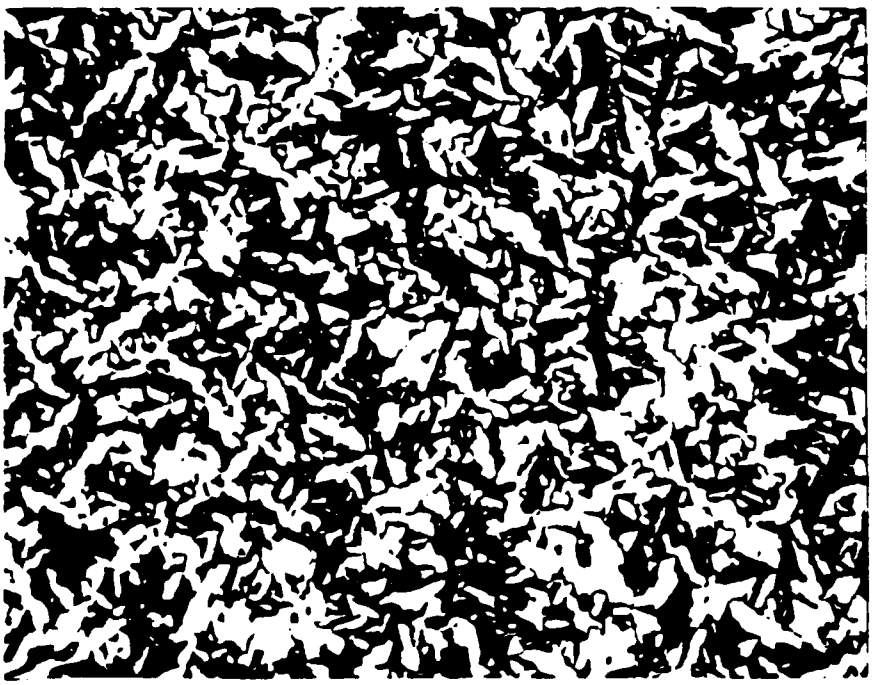

114
124
4-BP-PMA
A
109
124
B
C
112
107
4-BP-PAC
142
D
ENDO
E
130
91
4-BP-PS
104
F
95
85
G
H
74
82
-20 0 20 40 60 80 100 120 140 160
TEMPERATURE (°C)

Figure 1



(Figure 2A)



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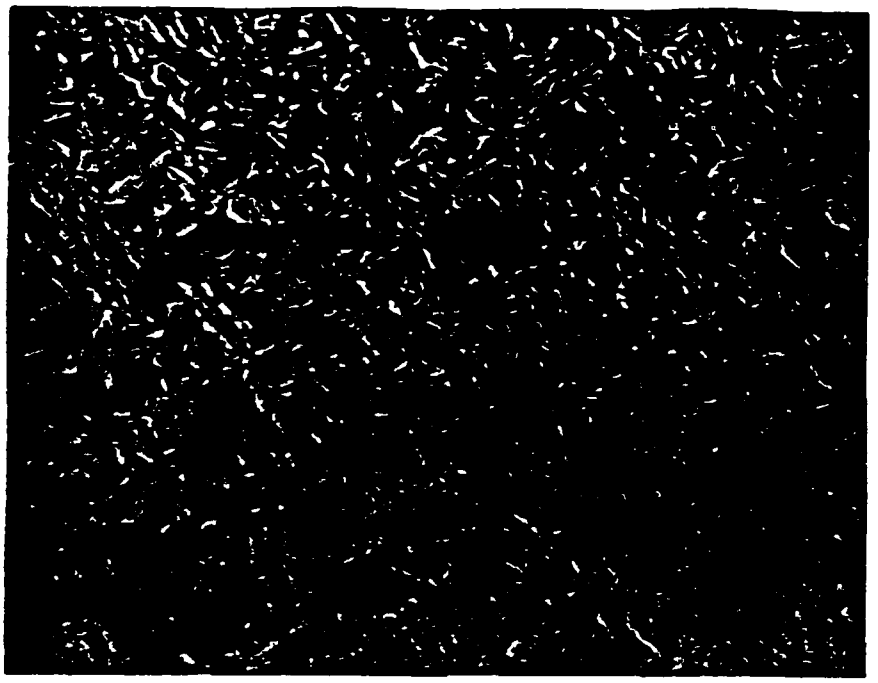

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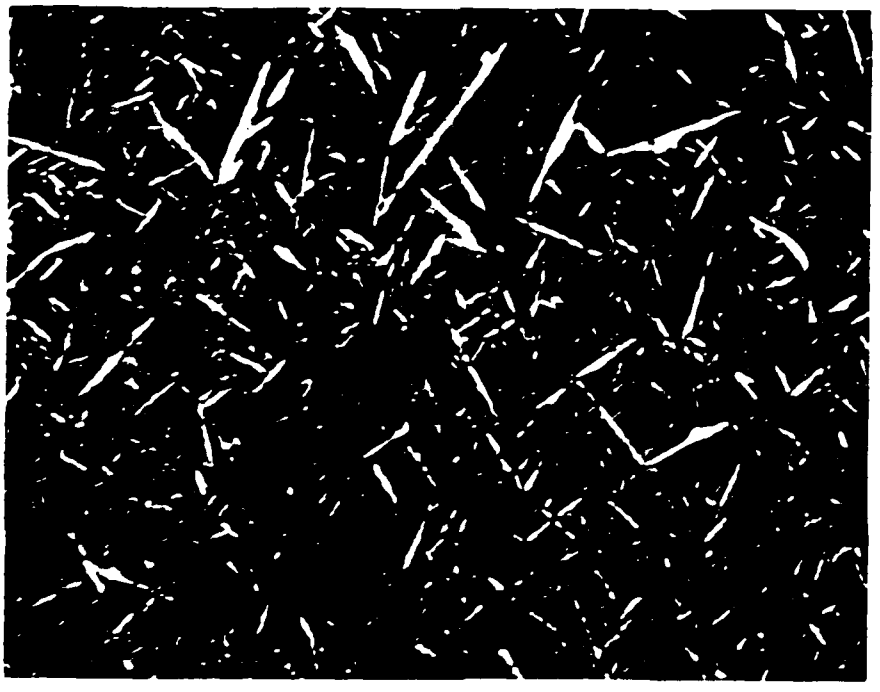
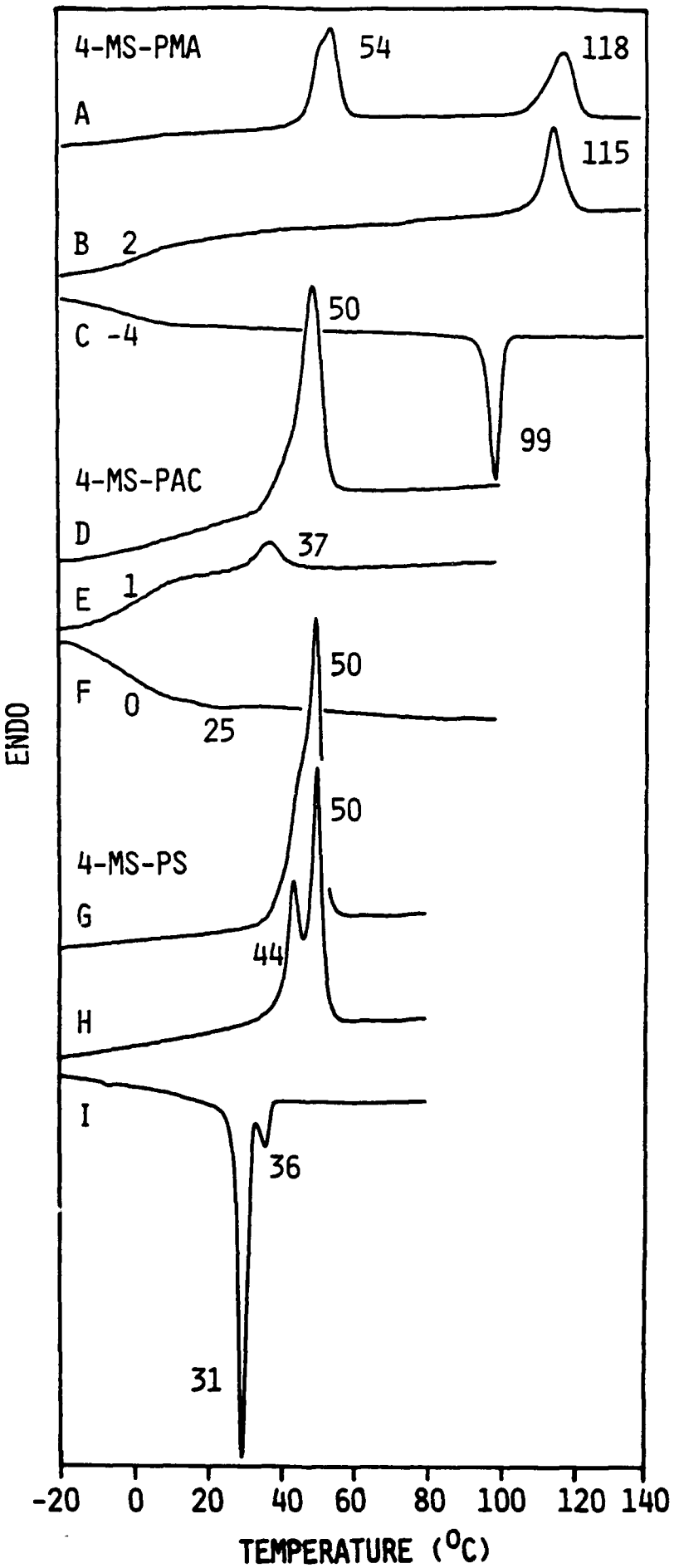


(Figure 2D)

(Figure 2E)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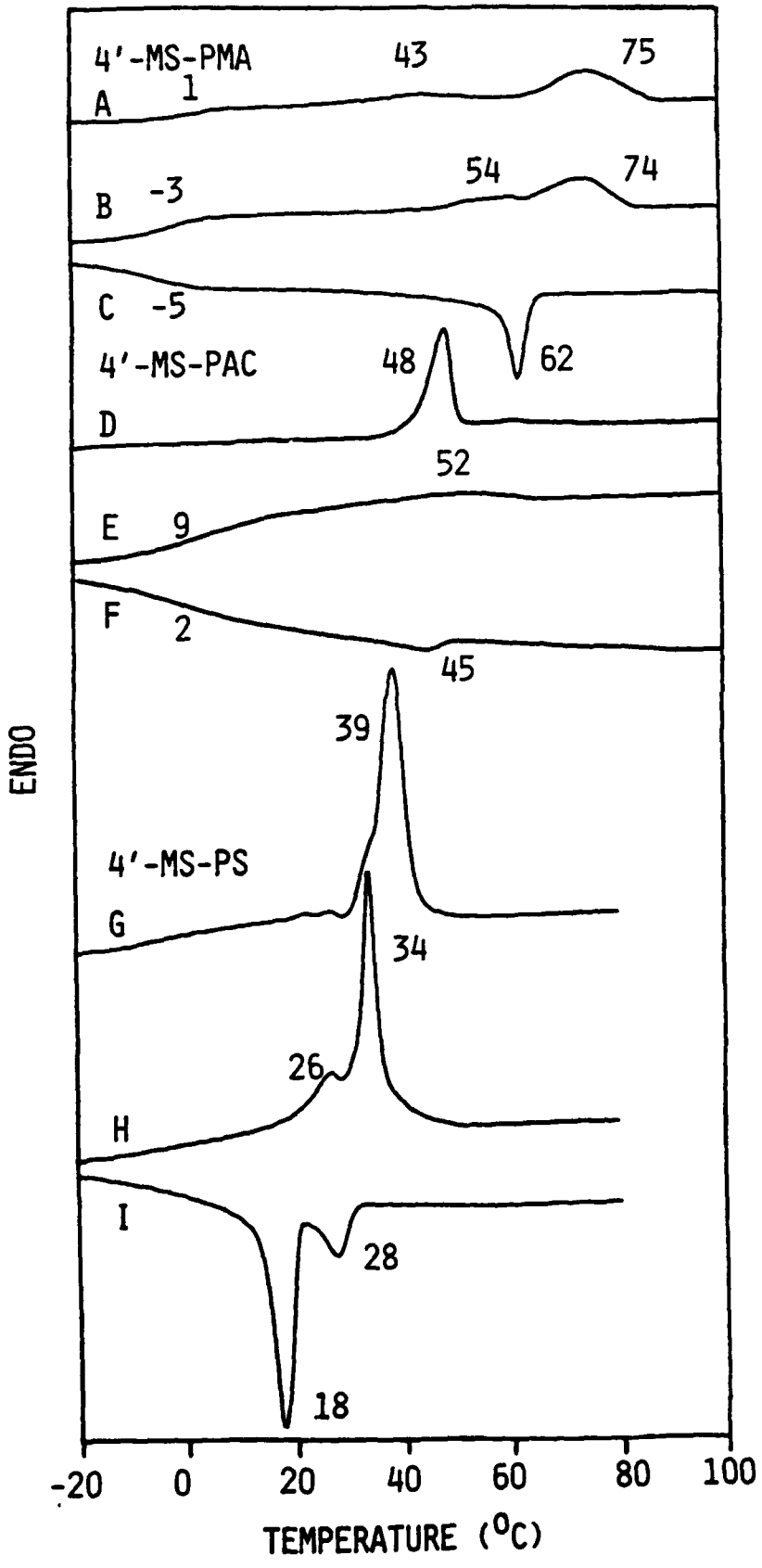
A
54
118
115
B 2
C -4
50
99
4-MS-PAC
D
37
E 1
F 0
25
50
4-MS-PS
G
50
44
H
I
36
31
ENDO
-20 0 20 40 60 80 100 120 140
TEMPERATURE (°C)

Figure 3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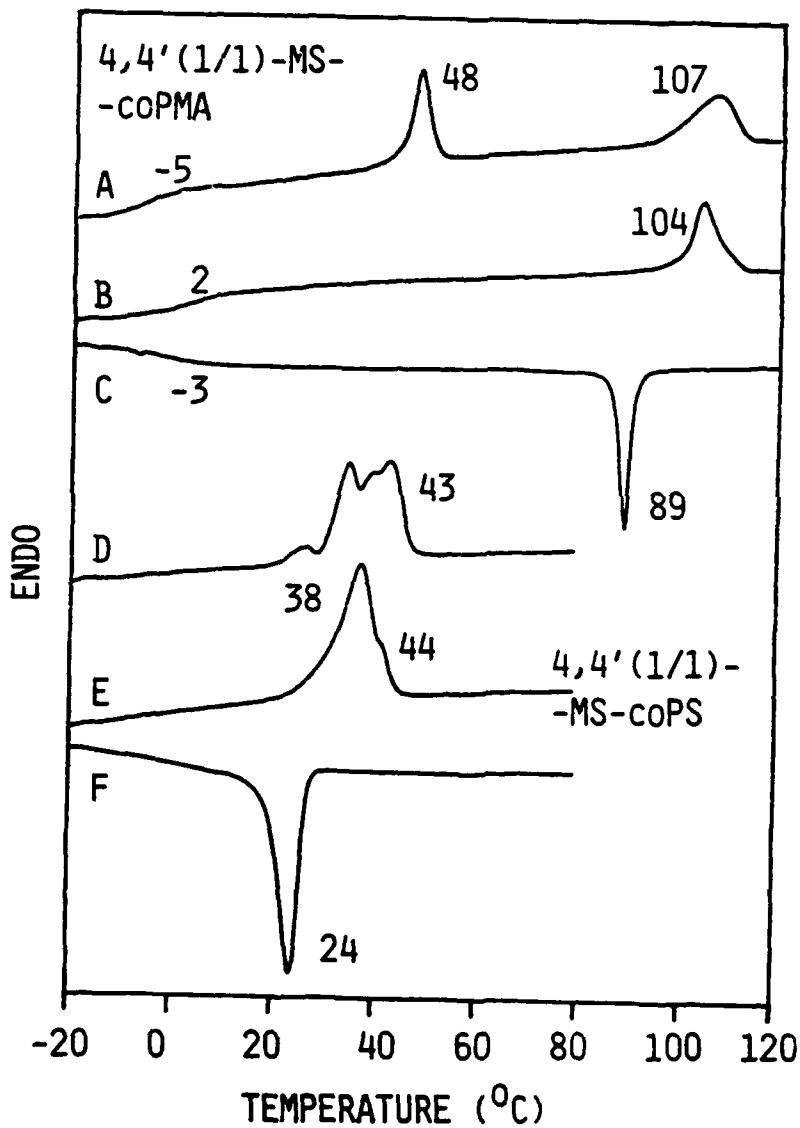
43
75
B
-3
54
74
C
-5
4'-MS-PAC
48
62
D
52
E
9
F
2
45
39
ENDO
4'-MS-PS
G
34
26
H
I
28
18
-20
0
20
40
60
80
100
TEMPERATURE (°C)

Figure 4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-coPMA
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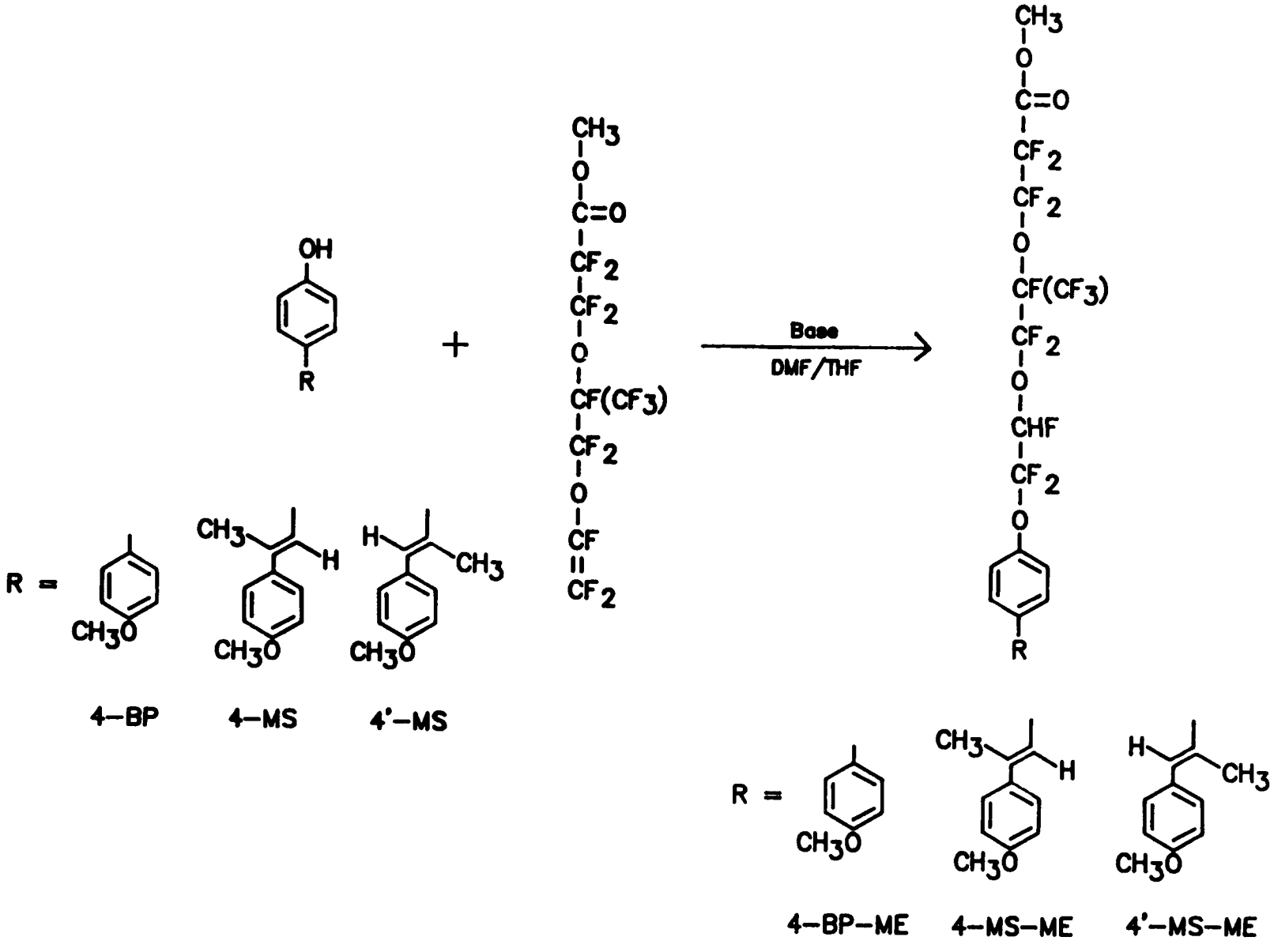
107
A
-5
104
B
2
C
-3
89
43
D
38
44
4,4'(1/1)-
-MS-coPS
E
F
24
ENDO
-20
0
20
40
60
80
100
120
TEMPERATURE (°C)

Figure 5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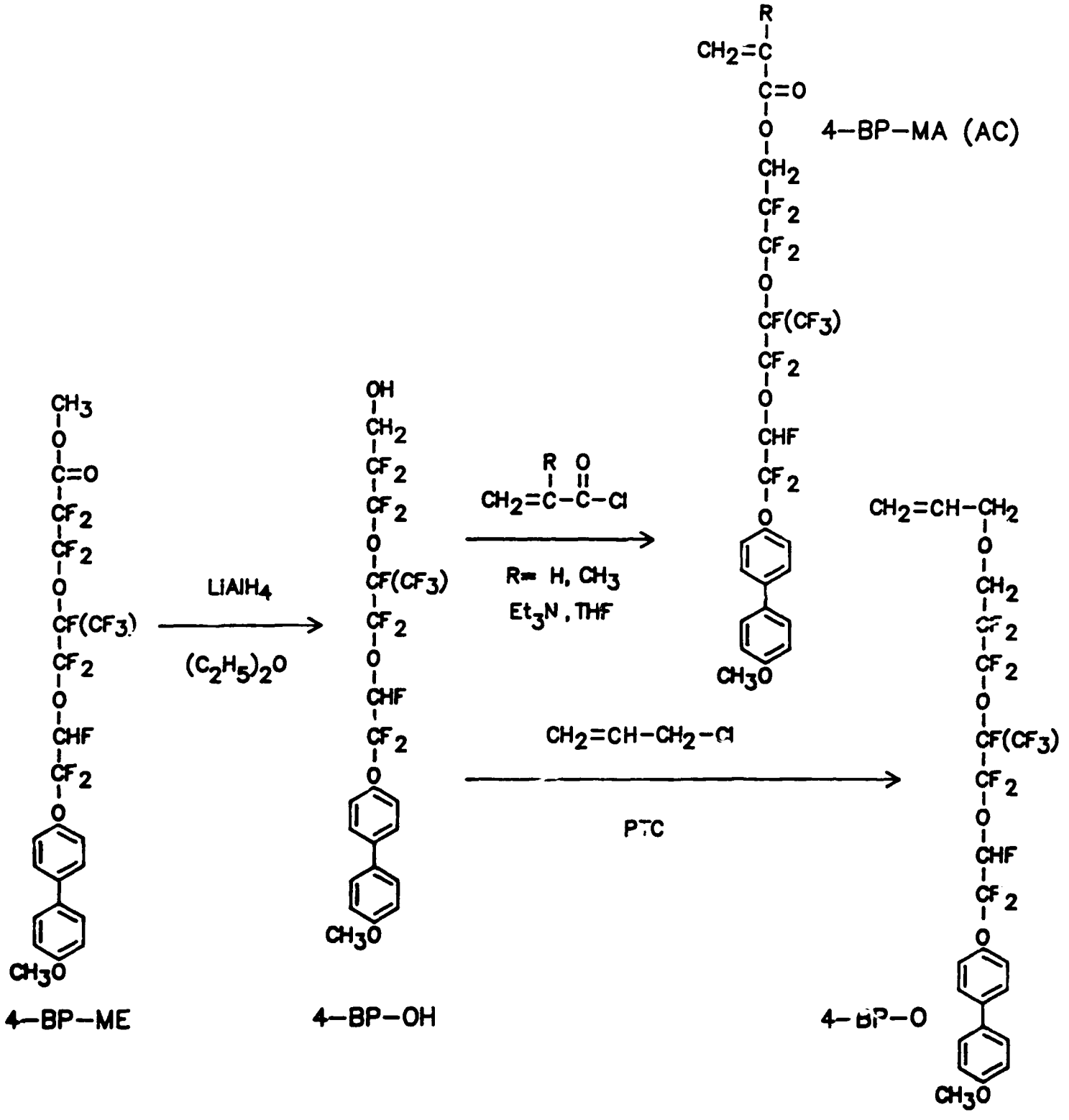
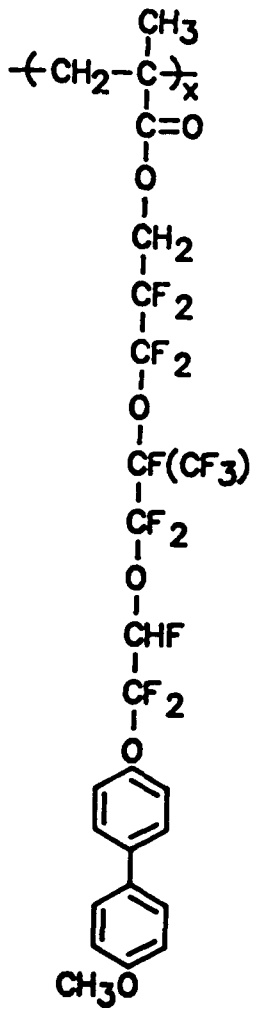
R
+
CH3
O
C=O
CF2
CF2
O
CF(CF3)
CF2
O
CF
II
CF2
Base
DMF/THF
CH3
O
C=O
CF2
CF2
O
CF(CF3)
CF2
O
CHF
CF2
O
R
R =
CH3O
CH3
H
H
CH3
4-BP
4-MS
4'-MS
R =
4-BP-ME
4-MS-ME
4'-MS-ME

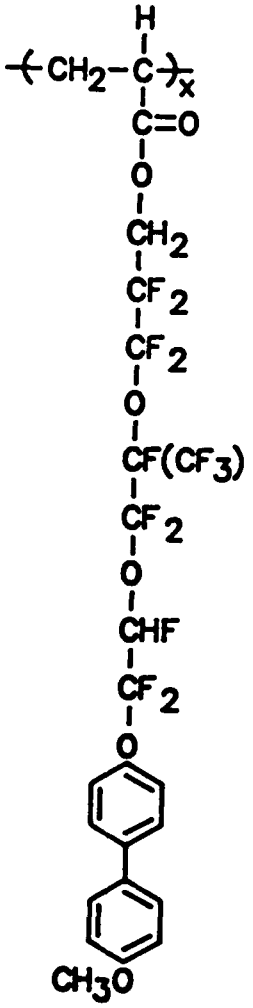
Scheme I


4-BP-ME
LiAlH4
(C2H5)2O
4-BP-OH
R= H, CH3
Et3N, THF
4-BP-MA (AC)
CH2=CH-CH2-Cl
PTC
4-BP-O

Scheme II



4–BP–PMA



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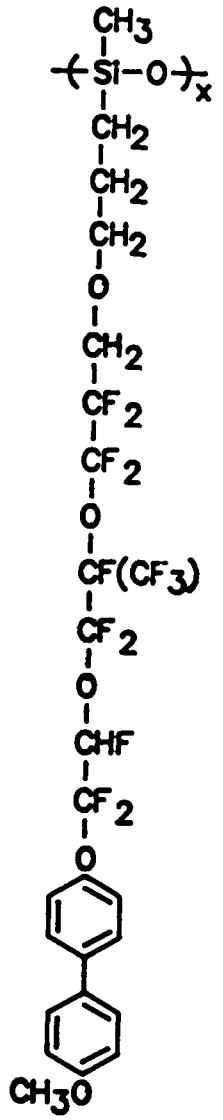
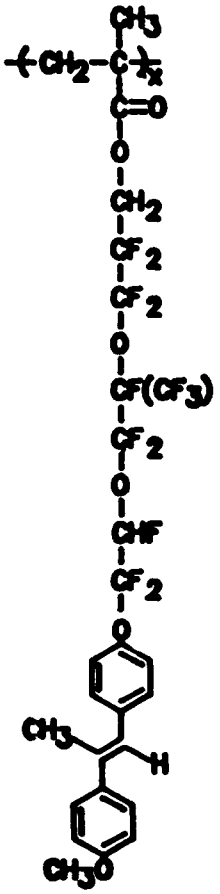
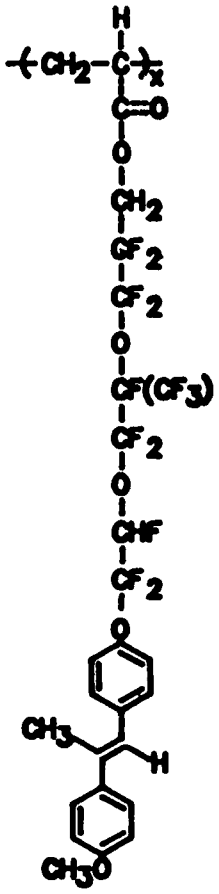


4–BP–PS

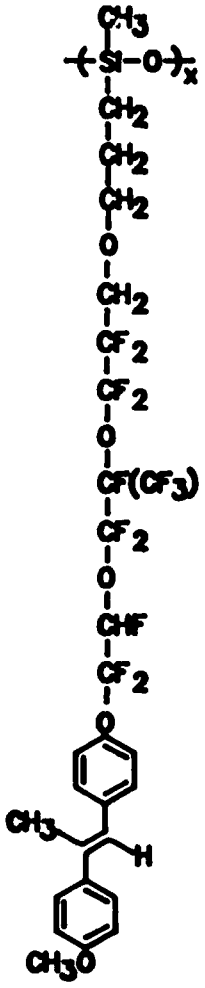
Scheme III



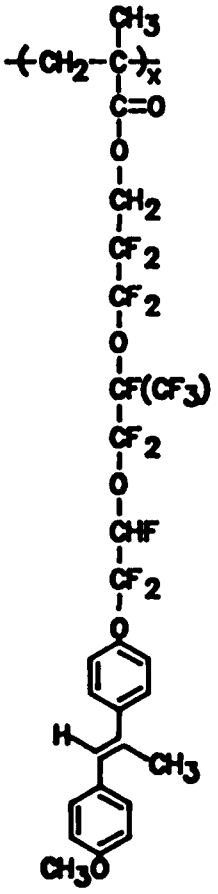
4–MS–PMA



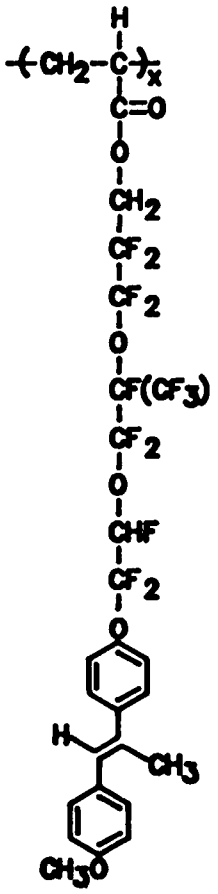
4–MS–PAC



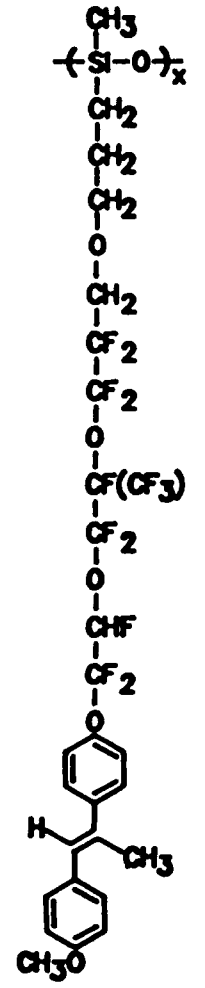
4–MS–PS



4'–MS–PMA



4'–MS–PAC



4'–MS–PS

Scheme IV

SECURITY CLASSIFICATION OF THIS PAGE

REPORT DOCUMENTATION PAGE

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Molecular Engineering of Liquid Crystal Polymers by Living Polymerization. 4. A Continuous Dependence on Molecular Weight of the Mesomorphic Phases of Poly{6-[(4-Cyano-4'-biphenyl)oxy]hexyl Vinyl Ether}

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Molecular Engineering of Liquid Crystal Polymers by Living Polymerization. 4.[a] A Continuous Dependence on Molecular Weight of the Mesomorphic Phases of Poly{6-[(4-Cyano-4'-biphenyl)oxy]hexyl Vinyl Ether}

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a) Previous paper in this series: reference12

ABSTRACT: The synthesis and living cationic polymerization of 6-[(4-cyano-4'-biphenyl)oxy]hexyl vinyl ether (6-6) is presented. The mesomorphic behavior of poly(6-6) with different degrees of polymerization and narrow molecular weight distribution was compared to that of 6-6 and of 6-[(4-cyano-4'-biphenyl)oxy]hexyl ethyl ether (8-6) which is the model of the monomeric structural unit of the polymer. Both 6-6 and 8-6 exhibit a monotropic nematic mesophase. Poly(6-6)s with degrees of polymerization from 3.3 to 7.3 display an enantiotropic s_A and an enantiotropic nematic mesophase. Higher molecular weight polymers exhibit either a monotropic or enantiotropic s_X (i.e., an unidentified smectic phase) and an enantiotropic s_A mesophase. The dependence of the phase transitions as a function of the degree of polymerization demonstrates that the transformation of the nematic mesophase of the monomer into a smectic mesophase upon polymerization is continuous.

INTRODUCTION

The elucidation of the mechanism by which the molecular weight influences the phase behavior of side chain liquid crystalline polymers represents the first step which should be considered in order to provide a molecular approach to the design of such polymers.[1] It is already accepted that the temperature range of the mesophase increases with the increase of the molecular weight of the polymer.[1-11] This dependence can be easily explained by thermodynamic principles assuming that the phase behavior of the polymer is determined by that of the monomeric structural unit.[13,14] There are only three reports in which the phase behavior of a polymer with different molecular weights was compared to that of the model compound of its monomeric structural unit.[7,11,12] In the first two cases, the mesophase which appears below the isotropization is identical to that of the model compound of the monomeric structural unit. A second mesophase appears only above a certain molecular weight.[7,11] In one case, the model compound of the monomeric structural unit and the dimer display a nematic and a s_A mesophase. The higher molecular weight oligomers exhibit a s_A mesophase while the high molecular weight polymer a s_A and a s_X (i.e., an unidentified smectic phase) mesophase. Based on these data, we have assummed that the transition from nematic to s_A should represent a continuous dependence on molecular weight.[12] However, additional examples are required in order to support this trend.

The elucidation of this dependence entails the synthesis of polymers with well defined molecular weights and narrow molecular weight distribution. So far, the techniques used to prepare well defined side chain liquid crystalline polymers are based on the group transfer polymerization of mesogenic methacrylates,[7] cationic polymerization of vinyl and propenyl ethers,[8-12,15,16] and by polymer homologous reactions.[17] For the present series of investigations we prefer to use the living cationic polymerization of mesogenic vinyl ethers.

We have selected this polymerization technique since it tolerates a large variety of functional groups,[8-10,15,16,18-21] can be performed in a polar solvent like methylene chloride and at elevated temperatures,[22,23] and provides a polymer with a flexible backbone.

This paper will describe the synthesis and living cationic polymerization of 6-[(4-cyano-4'-biphenyl)oxy]hexyl vinyl ether and the mesomorphic behavior of the resulting polymers. The phase behavior of the polymers with different molecular weights will be compared to that of 6-[(4-cyano-4'-biphenyl)oxy]hexyl ethyl ether which is the model of the monomeric structural unit of poly{6-[(4-cyano-4'-biphenyl)oxy]hexyl vinyl ether}.

EXPERIMENTAL

Materials

4-Phenylphenol (98%), 1,10-phenanthroline (anhydrous, 99%), palladium (II) diacetate (all from Lancaster Synthesis), ferric chloride anhydrous (98%, Fluka), copper (I) cyanide (99%), n-butyl vinyl ether (98%), 9-borabicyclo[3.3.1]nonane (9-BBN, crystalline, 98%), 6-chlorohexan-1-ol (97%) and the other reagents (all from Aldrich) were used as received. Methyl sulfide (anhydrous, 99%, Aldrich) was refluxed over 9-BBN and then distilled under argon. Dichloromethane (99.6%, Aldrich) used as a polymerization solvent was first washed with concentrated sulfuric acid, then with water, dried over anhydrous magnesium sulfate, refluxed over calcium hydride and freshly distilled under argon before each use. N-Methyl-2-pyrrolidone (98%, Lancaster Synthesis) was dried by azeotropic distillation with benzene, shaken with barium oxide, filtered, and fractionally distilled under reduced pressure. Trifluoromethane sulfonic acid (triflic acid, 98%, Aldrich) was distilled under argon.

Techniques

^{1}H-NMR (200 MHz) spectra were recorded on a Varian XL-200 spectrometer. TMS was used as internal standard. A Perkin-Elmer DSC-4 differential scanning calorimeter, equipped with a TADS 3600 data station, was used to determine the thermal transitions which were reported as the maxima and minima of their endothermic or exothermic peaks respectively. In all cases, heating and cooling rates were 20°C/min unless otherwise specified. Glass transition temperatures (Tg) were read at the middle of the change in the heat capacity. First heating scans differ from second and subsequent heating scans. However, second and subsequent heating scans are identical. The first heating scans can be reobtained after proper annealing of the polymer sample. A Carl-Zeiss optical polarized microscope (magnification:100x) equipped with a Mettler FP 82 hot stage and a Mettler FP 800 central processor was used to observe the thermal transitions and to analyze the anisotropic textures.[17,18] Molecular weights were determined by gel permeation chromatography (GPC) with a Perkin-Elmer series 10 LC instrument equipped with LC-100 column oven, LC-600 autosampler and a Nelson Analytical 900 series integrator data station. The measurements were made at 40°C using the UV detector . Two Perkin-Elmer PL gel columns of 10^4 and 500A with $CHCl_3$ as solvent (1ml/min) and a calibration plott constructed with polystyrene standards were used to determine the molecular weights. High pressure liquid chromatography experiments were performed with the same instrument.

Synthesis of Monomers

The synthesis of 4-cyano-4'-(6-hydroxyhexan-1-yloxy)biphenyl, 6-[(4-cyano-4'-biphenyl)oxy]hexyl vinyl ether and of 6-[(4-cyano-4'-biphenyl)oxy]hexyl ethyl ether are outlined in Scheme I.

1,10-Phenanthroline Palladium (II) Diacetate (9)

9 was synthesized according to a literature procedure.[26] mp 220°C. (lit. 26, mp 234°C).

4-Cyano-4'-Hydroxybiphenyl (5)

5 was synthesized as reported in a previous publication.[11] Purity: 99% (HPLC). mp 195-198°C. (lit. [27,28], mp 196-199°C). ^{1}H-NMR (Acetone-d_6, TMS,δ, ppm): 3.80 (1 proton, -OH, s), 7.01 (2 aromatic protons, o to hydroxy, d), 7.61 (2 aromatic protons, m to -OH, d), 7.70 (4 aromatic protons, o and m to -CN, s).

4-Cyano-4'-(6-hydroxyhexan-1-yloxy)biphenyl (7-6)

4-Cyano-4'-hydroxybiphenyl (126 g, 0.082 mol), potassium hydroxide (4.6 g, 0.082 mol) and few crystals of potassium iodide were dissolved in a mixture of ethanol-water (4/1) (450 ml). 6-Chloro-1-hexanol (12.3 g, 0.09 mol) was added to the resulting solution which was heated to reflux for 24 hr. The ethanol was removed on a rotavapor and the resulting solid was washed succesivelly with water, dilute aqueous NaOH and water. Recrystallization from methanol yielded 17 g (70.2%) of white crystals. Purity: 99.8% (HPLC). ^{1}H-NMR ($CDCl_3$, TMS, δ, ppm): 1.01-1.95 (8 protons, -$(CH_2)_4$-, m), 3.64 (2 protons, -CH_2OH, t), 4.00 (2 protons, PhOCH_2-, t), 7.01 (2 aromatic protons, -CH_2OH, t), 7.55 (2 aromatic protons, m to alkoxy, d), 7.66 (4 aromatic protons, o and m to -CN, d of d). Thermal transitions of 7-6 are reported in Table I.

6-[(4-Cyano-4'-biphenyl)oxy]hexyl Vinyl Ether (6-6)

7-6 (2 g, 6.77 mmol) was added to a mixture of 1,10-phenanthroline palladium (II) diacetate (0.27 g, 0.677 mmol), n-butyl vinyl ether (36 ml) and dry chloroform (10 ml). The mixture was heated at 60°C for 6 hr. After cooling and filtration (to remove the catalyst) the solvent was distilled in a rotavapor and the product was purified by column chromatography (silica gel, methylene chloride eluent) to yield 1.85 g (85%) of white crystals. Purity: 99% (HPLC). ^{1}H-NMR ($CDCl_3$, TMS, δ, ppm): 1.01-1.95 (8 protons, -$(CH_2)_4$-, m), 3.70 (2 protons, -CH_2O-, t), 4.00 (3 protons, -OCH=CH_2, trans and PhOCH_2, m), 4.14 and 4.21 (1 proton, -OCH=CH_2, cis, d), 6.45 (1 proton, -OCH=CH_2, q), 7.01 (2 aromatic protons, o to alkoxy, d), 7.50 (2 aromatic protons, m to alkoxy, d), 7.66 (4 aromatic protons, o and m to -CN, d of d).

6-[(4-Cyano-4'-biphenyl)oxy]hexyl Ethyl Ether (8-6)

7-6 (2.95 g, 0.01 mol) was added to a solution containing potassium t-butoxide (1.12 g, 0.01 mol) and 18-crown-6 (2.6 mg, 0.01 mmol) in 78 ml of dry tetrahydrofuran. Diethyl sulfate (1.54 g, 0.01 mol) was added and the reaction mixture was refluxed for 3 hr. After cooling, the reaction mixture was extracted with chloroform, washed with water, dried over magnesium sulfate and the chloroform was removed in a rotavapor. The resulting product was purified by column chromatography (silica gel , methylene chloride eluent) to yield 2.1 g (67%) of white crystals. Purity: 99.9% (HPLC). ^{1}H-NMR ($CDCl_3$, TMS, δ, ppm): 1.21 (3 protons, -OCH_2CH_3, t), 1.46-1.82 (8 protons, -$(CH_2)_4$-, m), 3.43(4 protons. -$CH_2OCH_2CH_3$, m), 4.01 (2 protons, -CH_2OPh, t), 7.02 (2 aromatic protons, o to alkoxy, d), 7.51 (2 aromatic

protons, m to alkoxy, d), 7.68 (4 aromatic protons, o and m to -CN, d of d). Thermal transitions of 8-6 are reported in Table I.

Cationic Polymerizations

Polymerizations were performed in glass flasks equipped with teflon stopcocks and rubber septa under argon atmosphere at 0°C for 1hr. All glassware was dried overnight at 130°C. The monomer was further dried under vacuum overnight in the polymerization flask. Then the flask was filled with argon, cooled to 0°C and the requested amounts of methylene chloride, dimethyl sulfide and triflic acid were added via a syringe. The monomer concentration was about 10 wt% of the solvent volume and the dimethyl sulfide concentration was 10 times larger than that of the initiator. The polymer molecular weight was controlled by the monomer/initiator ratio. At the end of the polymerization the reaction mixture was precipitated into methanol containing few drops of NH_4OH. The filtered polymers were dried and reprecipitated from methylene chloride solutions into methanol until GPC traced showed no traces of monomer. Table II summarizes the polymerization results.

RESULTS AND DISCUSSION

Scheme I outlines the synthesis of 6-[(4-cyano-4'-biphenyl)oxy]hexyl vinyl ether (6-6) and of 6-[(4-cyano-4'-biphenyl)oxy]hexyl ethyl ether (8-6). Two routes are presented for the synthesis of 6-6. However, we prefered the method based on the transetherification of 4-cyano-4'-(8-hydroxyhexan-1-yloxy)biphenyl (7-6) with n-butyl vinyl ether catalyzed by 1,10-phenanthroline palladium (II) diacetate.[26,29]

Table II summarizes the polymerization results. 8-6 was polymerizaed with triflic acis/dimethylsulfide initiating system. The polymerization mechanism is outlined in Scheme II. The selection of this initiating system is based on its ability to polymerize vinyl ethers through a living mechanism in methylene chloride and at 0°C.[22,23] The GPC traces of the resulting polymers are shown in Figure 1. The theoretical degree of polymerization of poly(6-6) is equal to the $[M]_o/[I]_o$ ratio and agrees very well with the degree of polymerization determined by GPC (Table II). The dependence of the number average molecular weight and of the polydispersity of poly(6-6) are plotted in Figure 2 as a function of the $[M]_o/[I]_o$ ratio. Both plotts demonstrate the living polymerization of 6-6.

Heating and cooling DSC traces of 7-6, 6-6 and 8-6 are presented in Figure 3. 7-6 displays an enantiotropic nematic mesophase. 6-6 and 8-6 display a monotropic nematic

mesophase. The nematic-isotropic transition temperatures and their corresponding thermodynamic parameters were determined by cooling the sample up to before it reaches the crystallization temperature and then reheating it (Figure 3). Both thermal transition temperatures and their corresponding thermodynamic parameters are summarized in Table I.

The DSC traces of the first heating, second heating and cooling scans of poly(6-6) are presented in Figure 4,a,b,c. All cooling scans are identical. The phase transition temperatures which are not influenced by kinetics are identical on the first, second and subsequent heating scans. Only phase transitions which are located in the close proximity of the glass transition temperature are dependent on the thermal history of the sample. Poly(6-6) with degrees of polymerization from 3.3 to 7.6 display enantiotropic s_A and nematic mesophases irrespective of the DSC scan we consider for their characterization (Figure 4a,b,c). Polymers with degrees of polymerization from 8.9 to 29.5 display a s_X (i.e., an unidentified smectic phase) mesophase in the first heating scan. Only poly(6-6) with degrees of polymerization from 23.2 to 29.5 display an enantiotropic s_X phase. The s_X phase does not appear on the second heating and cooling scans for polymer samples with degrees of polymerization ranging from 8.9 to 13.5. However, after proper annealing conditions, the s_X mesophase reappears on the first heating scan. That is, for polymer samples with degrees of polymerization from 8.9 to 13.5, under equilibrium conditions the s_X phase is "inverse" monotropic. This behavior demonstrates that mesophases located in the close proximity of the glass transition temperature are subjected to strong kinetic influences.

The phase transition temperatures collected from the first, second and cooling DSC scans are plotted in Figure 5a,b and c. The phase transition temperatures of the model compound of the monomeric structural unit (8-6), are also plotted and correspond to a degree of polymerization equal to 1. The plotts from Figure 5a,b,c demonstrate a clear trend. Both the nematic-isotropic and the s_A-nematic or s_A-isotropic as well as their reversed transition temperatures display continuous dependences of polymerization degree. Let us assume that 8-6 displays a virtual s_A mesophase. Under these conditions, the dependence of the nematic-isotropic transition temperature versus polymerization degree has a higher slope than the dependence of the s_A-nematic, s_A-isotropic transition temperature versus polymerization degree. Above the degree of polymerization where these two dependences intersect each other, the nematic mesophase should appear below the s_A mesophase and therefore it becomes "virtual". This behavior can explain the change of the highest temperature mesophase from nematic to smectic upon increasing the degree of polymerization. It is well accepted that many monomers displaying a

nematic mesophase lead to side chain liquid crystalline polymers displaying a smectic mesophase.[1] However to our knowledge this is the first experiment which demonstrated that this phenomenon is the result of a continuous dependence of phase transition temperatures on molecular weight. The formation of a second smectic mesophase by increasing the degree of polymerization has been previously observed.[7,11,12] The formation of the sX mesophase in poly(6-6) is in line with these results.[7,11,12] However, the continuous change of the mesomorphic-isotropic phase transition from nematic-isotropic to smectic-isotropic was observed for the first time in the case of side chain liquid crystalline polymers in the previous paper from this series.[12] The example described previously displayed this change at a degree of polymerization equal to 2.2 and only two data points were available to suggest such a trend. A similar dependence was recently observed in the case of main chain liquid crystalline polymers.[30]

The formation of a second smectic mesophase by increasing the molecular weight of the polymer can be explained by a simple thermodynamic scheme.[13,14] However, an explanation for the transformation of a nematic-isotropic into a smectic-isotropic phase transition by increasing the molecular weight of the polymer should also consider the different degrees of distortion of the random-coil conformation of the polymer backbone in the nematic and smectic mesophases.[1,31-35] This discussion will be presented in a different publication.

The formation of various mesophases at different degrees of polymerization has some important implications. For example, polydisperse samples of poly(6-6) and of other similar polymers may represent multiple mesophases due to the heterogeneity of the molecular weight of the sample. At the same time, the dependence of the mesophase on the polymer molecular weight should be considered in the case of copolymers based on two different mesogenic monomers or one mesogenic and one nonmesogenic monomer. Both types of copolymers are of importance in the molecular design of side chain liquid crystalline polymers.[1] All these problems will be considered in subsequent publications from this series.

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FIGURE CAPTIONS

Figure 1: GPC traces of poly(6-6). The degree of polymerization of each sample is printed on the GPC trace.

Figure 2: The dependence of the number average molecular weight (Mn) and of the polydispersity (M_w/M_n) of poly(6-6) on the $[M]_o/[I]_o$ ratio.

Figure 3: Heating and cooling DSC traces of 7-6 (a,b), 6-6 (c,d) and 8-6 (e,f).

Figure 4: DSC traces displayed during the first heating scan (a), second heating scan (b) and first cooling scan (c) by poly(6-6) with different degrees of polymerization (DP). DP is printed on the top of each DSC scan.

Figure 5: The dependence of the phase transition temperatures on the degree of polymerization of poly(6-6). DP=1 corresponds to 8-6. a) data from first

heating scan: ○ -Tg (fh); □ -Ts_A-n (fh) or Ts_A-i (fh); △ -Tn-i (fh); ● -Ts_X-s_A (fh); ◑ -Tm (fh); b) data from second heating scan: ○ -Tg (sh); □ -Ts_A-n (sh) or Ts_A-i (sh); △ -Tn-i (sh); ● -Ts_X-s_A)sh); ◑ -Tm (sh); c) data from cooling scan: ▲ -Ti-n; □ -Tn-s_A or Ti-s_A; ● -Ts_A-s_X; ■ -Tg; ◨ -Tk.

Figure 6: Representative optical polarized micrographs (100x) of: a) 8-6 at 46°C on cooling (nematic phase); b) poly(6-6), DP=5.1, 97°C on cooling (nematic phase); c) poly(6-6), DP=5.1, at 90°C on cooling (transition from nematic to s_A phase); d) poly(6-6), DP=8.9, at 101°C on cooling (nematic phase); e) poly(6-6), DP=8.9, at 95°C on cooling (s_A phase).

SCHEME CAPTIONS

Scheme I: Synthesis of Monomers and Model Compounds.

Scheme II: The Mechanism of Living Cationic Polymerization.

Table I. Thermal Characterization of 4-Cyano-4'-(6-hydroxyhexan-1-yloxy)phenyl (7-6), 6-[(4-Cyano-4'-biphenyl)oxy]hexyl Vinyl Ether (6-6) and of 6-[(4-Cyano-4'-biphenyl)oxy]hexyl Ethyl Ether (8-6).

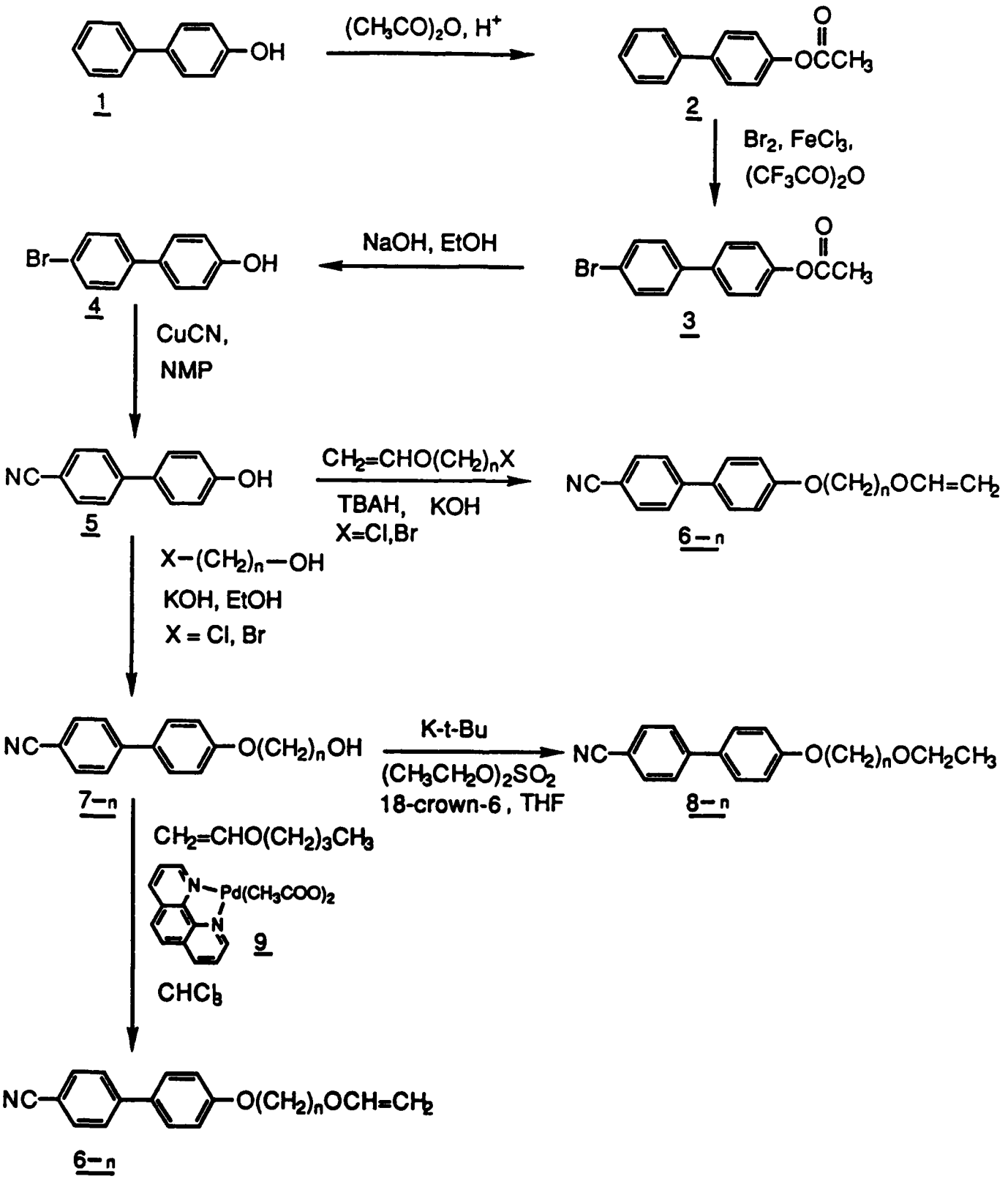
Compound	phase transitions (0^0C) and corresponding enthalpy changes (kcal/mru)	
	heating	cooling
7-6	k 93.5 (8.01) n 110.9 (0.25) i	i 107.8 (0.33) n 71.04 (5.66) k
6-6	k 75.5 (5.95) [n 75.9 (0.35)]*i	i 68.2 (0.31) n 55.8 (5.22) k
8-6	k 64.6 (8.67) [n 60.0 (0.12)]*i	i 46.7 (0.13) n 27.1 (7.21) k

*[ ] virtual data

Table II. Cationic Polymerization of 6-[(4-Cyano-4'-biphenyl)oxy]hexyl Vinyl Ether (6-6) (polymerization temperature,0°C; polymerization solvent,methylene chloride; $[M]_0$=0.311M; $[(CH3)2]_0/[I]_0$=10; polymerization time,1hr) and Characterization of the Resulting Polymers.

Sample no.	$[M]_0/[I]_0$	Polymer yield (%)	GPC			phase transitions(°C) and corresponding enthalpy change(kcal/mru)	
			$Mnx10^{-3}$	Mw/Mn	DP	heating	cooling
1	4.0	63	1.06	1.02	3.3	g 12.1 s_A 90.8 (-)* n 95.7 (0.22)*i g 12.1 s_A 91.4 (-)* n 95.1 (0.21)*i	i 91.5 (0.21)*n 86.7 (-)* s_A 3.3 g
2	5.0	67	1.65	1.03	5.1	g 16.4 s_A 98.7 (-)* n 100.8 (0.28)*i g 13.2 s_A 99.2 (-)* n 101.2 (0.20)*i	i 97.5 (0.20)*n 94.8 (-)* s_A 7.2 g
3	7.0	76	2.44	1.07	7.6	g 17.9 s_A 101.9 (-)* n 102.8 (0.25)*i g 16.4 s_A 101.5 (-)* n 102.6 (0.19)*i	i 100.7 (0.19)*n 98.8 (-)* s_A 4.8 g
4	9.0	84	2.87	1.03	8.9	g 17.7 s_X37.3 (0.21) s_A 107.8 (0.17) i g 17.5 s_A 104.0 (0.14) i	i 102.4 (0.19)*n 100.8 (-)* s_A 4.8 g
5	11.0	72	3.59	1.10	11.2	g 26.2 s_X45.6 (0.30) s_A 109.1 (0.15) i g 15.6 s_A 104.0 (0.14) i	i 105.0 (0.19) s_A 5.6 g
6	13.0	75	4.33	1.05	13.5	g 28.9 s_X47.7 (0.45) s_A 112.2 (0.15) i g 15.7 s_A 112.7 (0.21) i	i 111.9 (0.19) s_A 3.7 g
7	23.0	85	7.45	1.09	23.2	g 24.3 s_X 52.0 (0.25) s_A 117.1 (0.15) i g 23.2 s_X53.9 (0.23) s_A 117.4 (0.14) i	i 113.4 (0.18) s_A 36.2 (0.06) s_X 12.7 g
8	30.0	87	9.47	1.10	29.5	g 28.9 s_X 73.9 (0.32) s_A 124.8 (0.12) i g 29.5 s_X 67.1 (0.46) s_A 120.5 (0.15) i	i 117.6 (0.15) s_A 54.1 (0.29) s_X25.8 g

* overlapped peaks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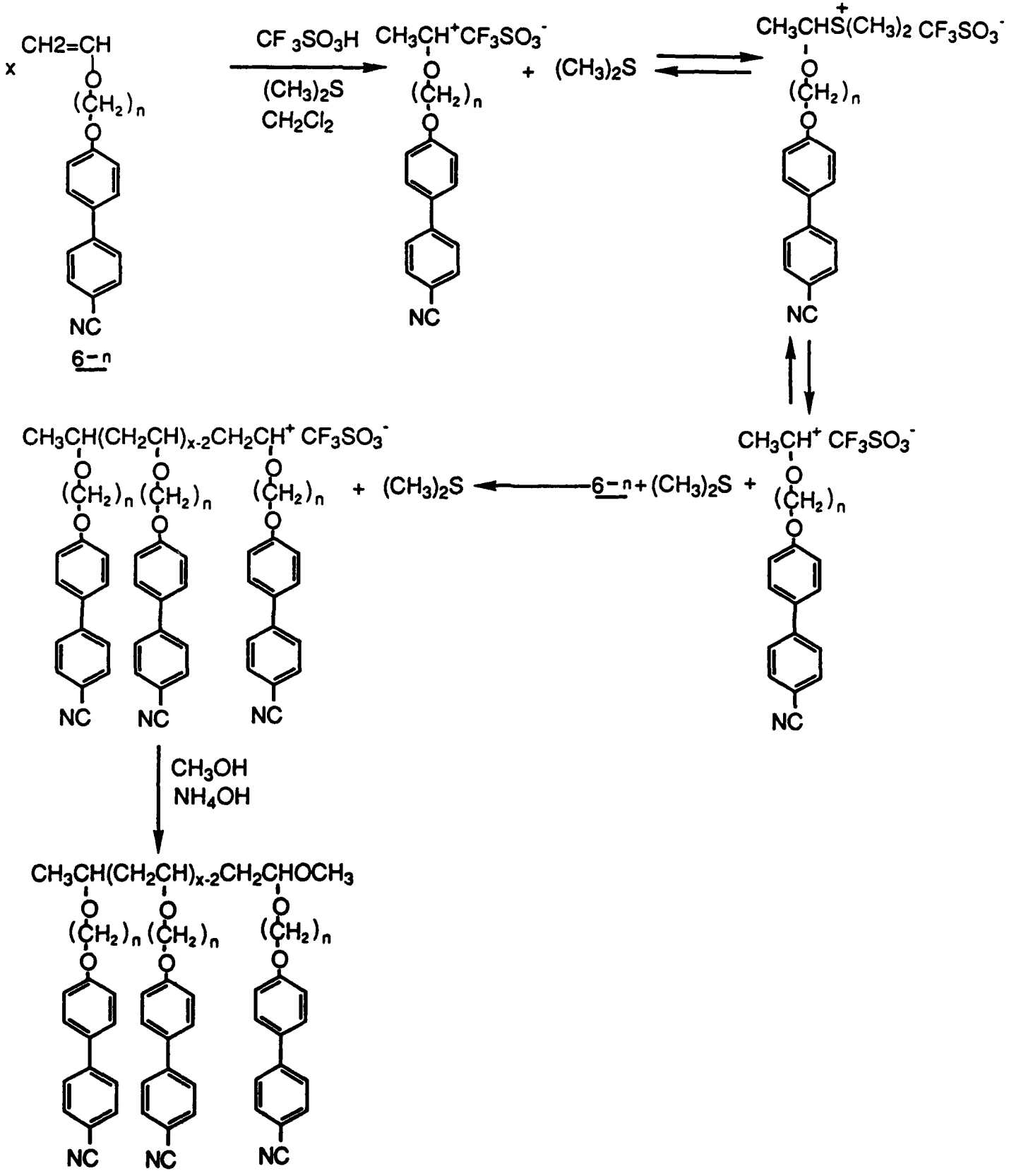
OH
1
OCCH3
O
2
Br2, FeCl3,
(CF3CO)2O
NaOH, EtOH
Br
OH
4
3
CuCN,
NMP
NC
5
CH2=CHO(CH2)nX
TBAH, KOH
X=Cl,Br
6–n
X–(CH2)n–OH
KOH, EtOH
X = Cl, Br
7–n
K-t-Bu
(CH3CH2O)2SO2
18-crown-6, THF
8–n
CH2=CHO(CH2)3CH3
Pd(CH3COO)2
9
CHCl3

Scheme I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x
(CH2)n
O
NC
6-n
CF3SO3H
(CH3)2S
CH2Cl2
CH3CH+CF3SO3-
+ (CH3)2S
CH3CHS+(CH3)2 CF3SO3-
CH3CH(CH2CH)x-2CH2CH+ CF3SO3-
+ (CH3)2S
6-n + (CH3)2S +
CH3CH+ CF3SO3-
CH3OH
NH4OH
CH3CH(CH2CH)x-2CH2CHOCH3

Scheme II

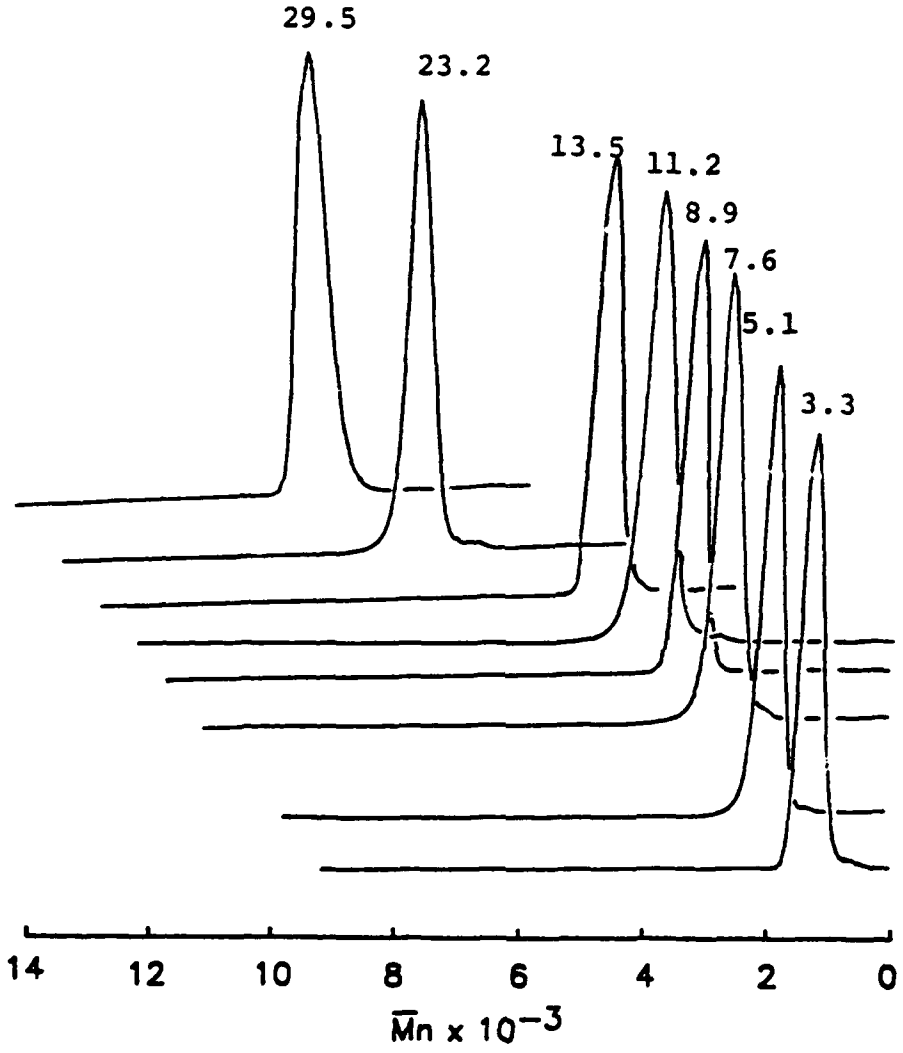
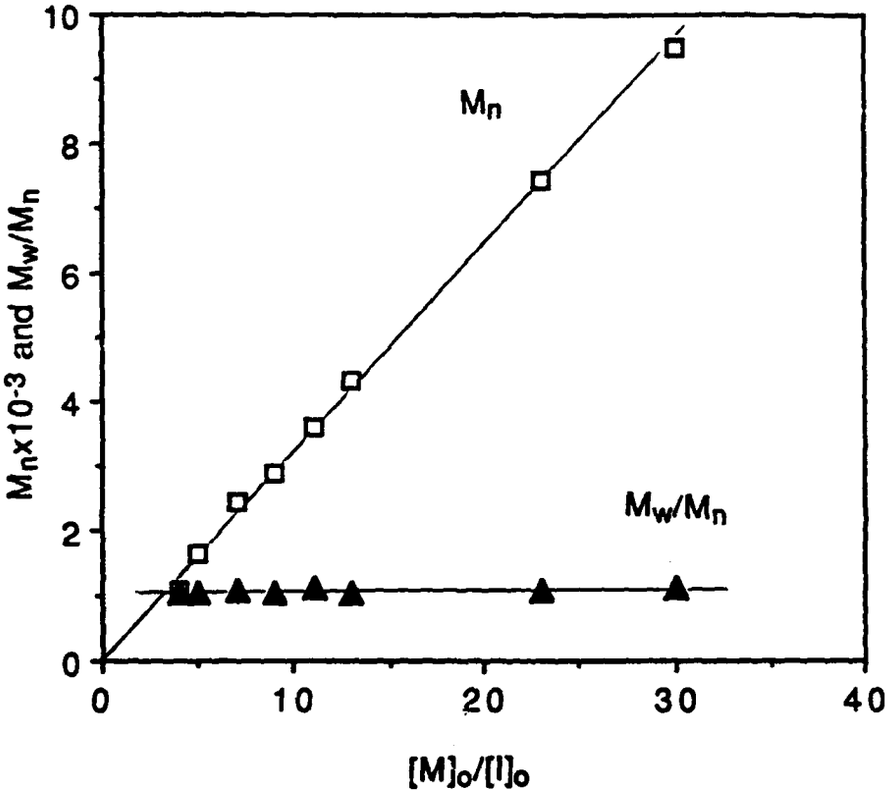


Figure 1



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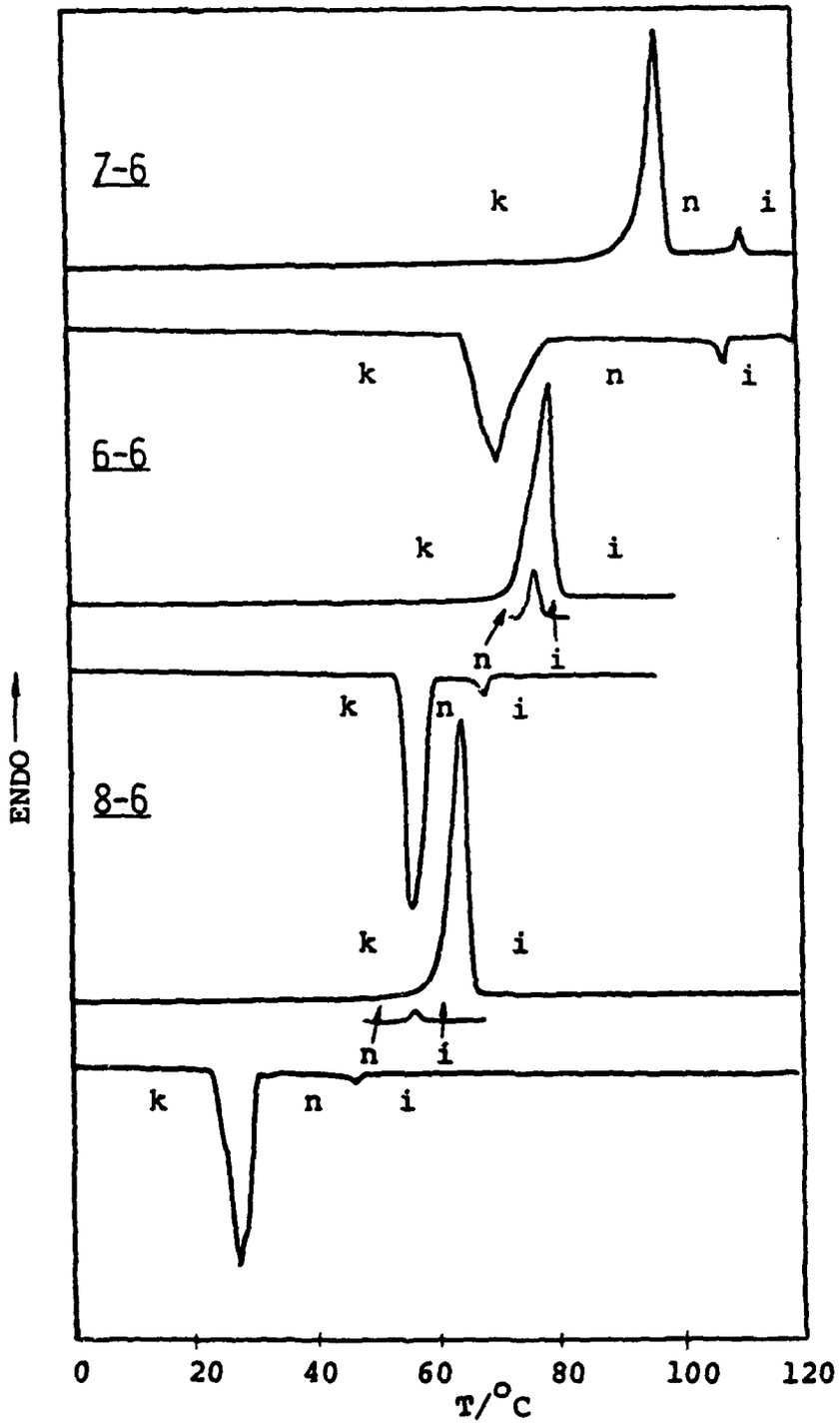

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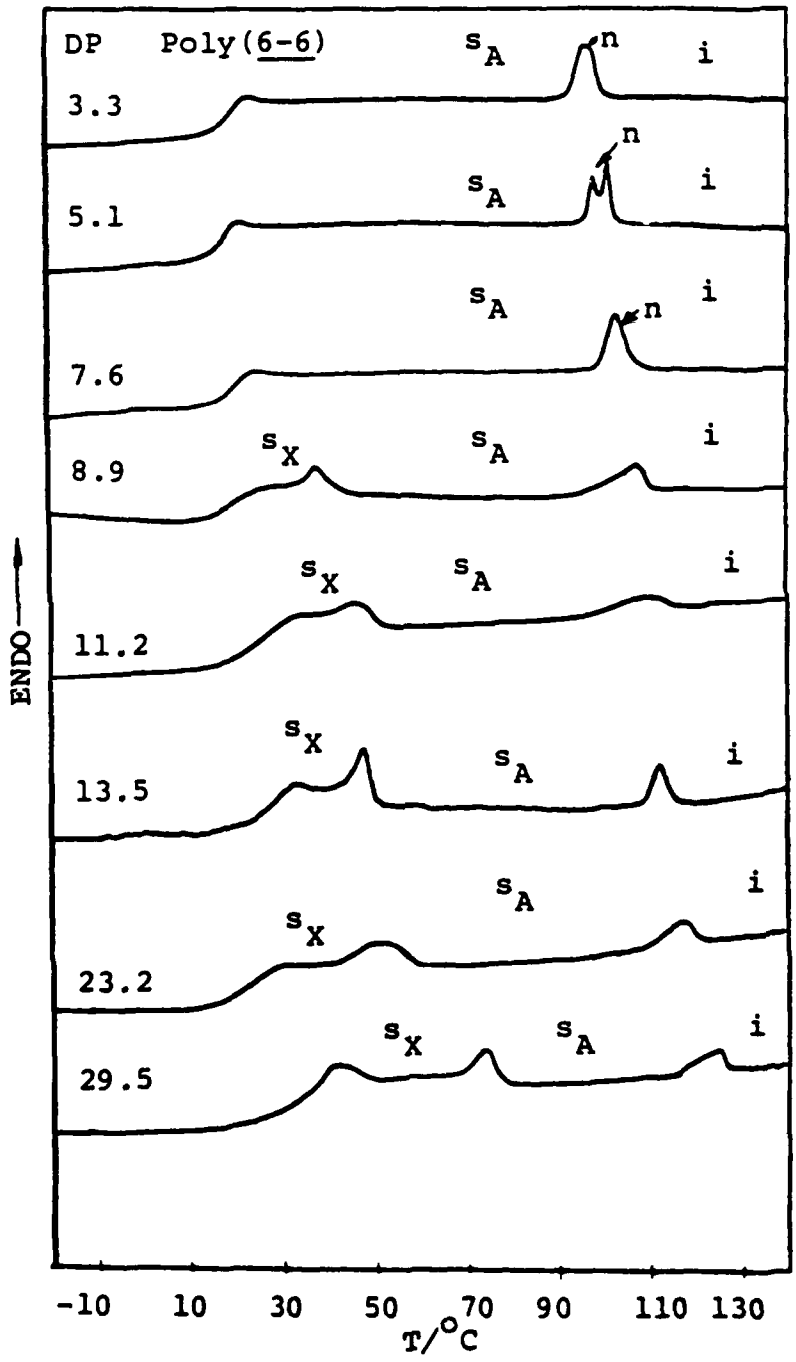
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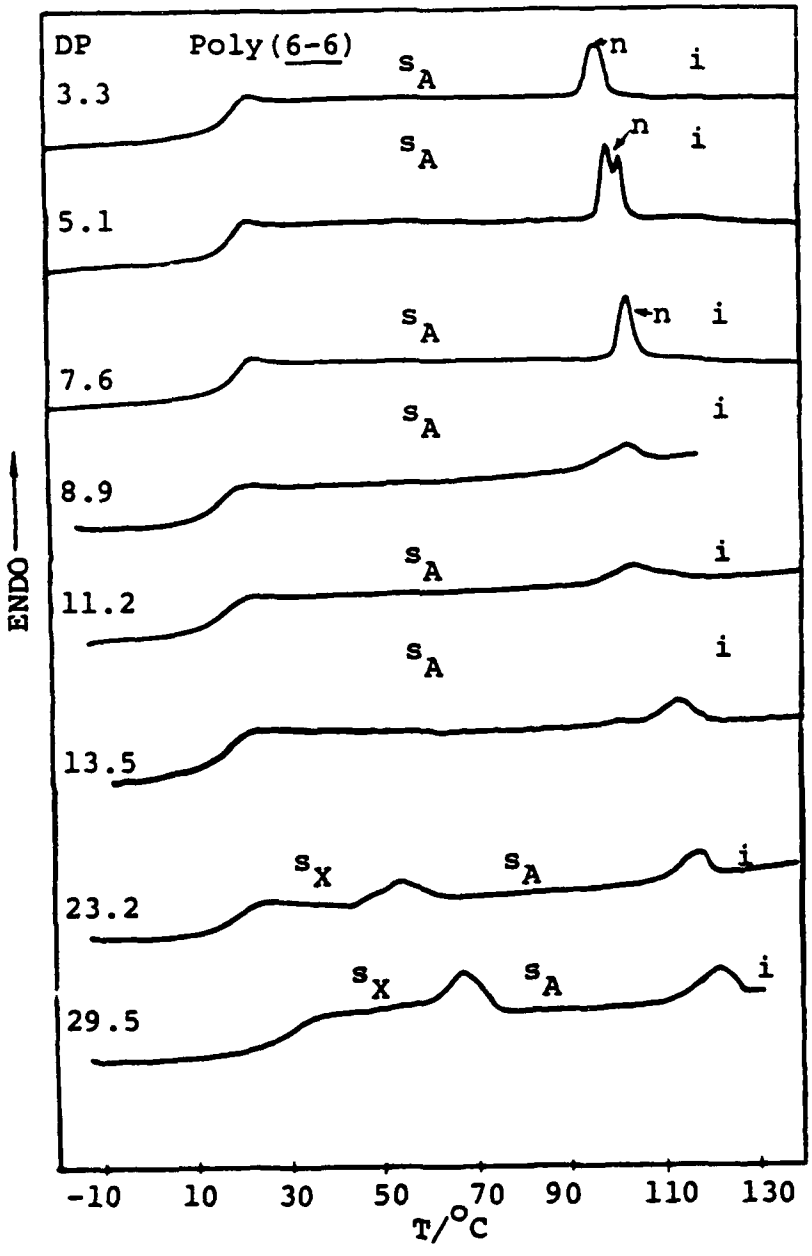
Poly(6-6)
3.3
5.1
7.6
8.9
11.2
13.5
23.2
29.5
S_A
S_X
n
i
ENDO
-10
10
30
50
70
90
110
130
T/°C

Figure 4a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3.3
5.1
7.6
8.9
11.2
13.5
23.2
29.5
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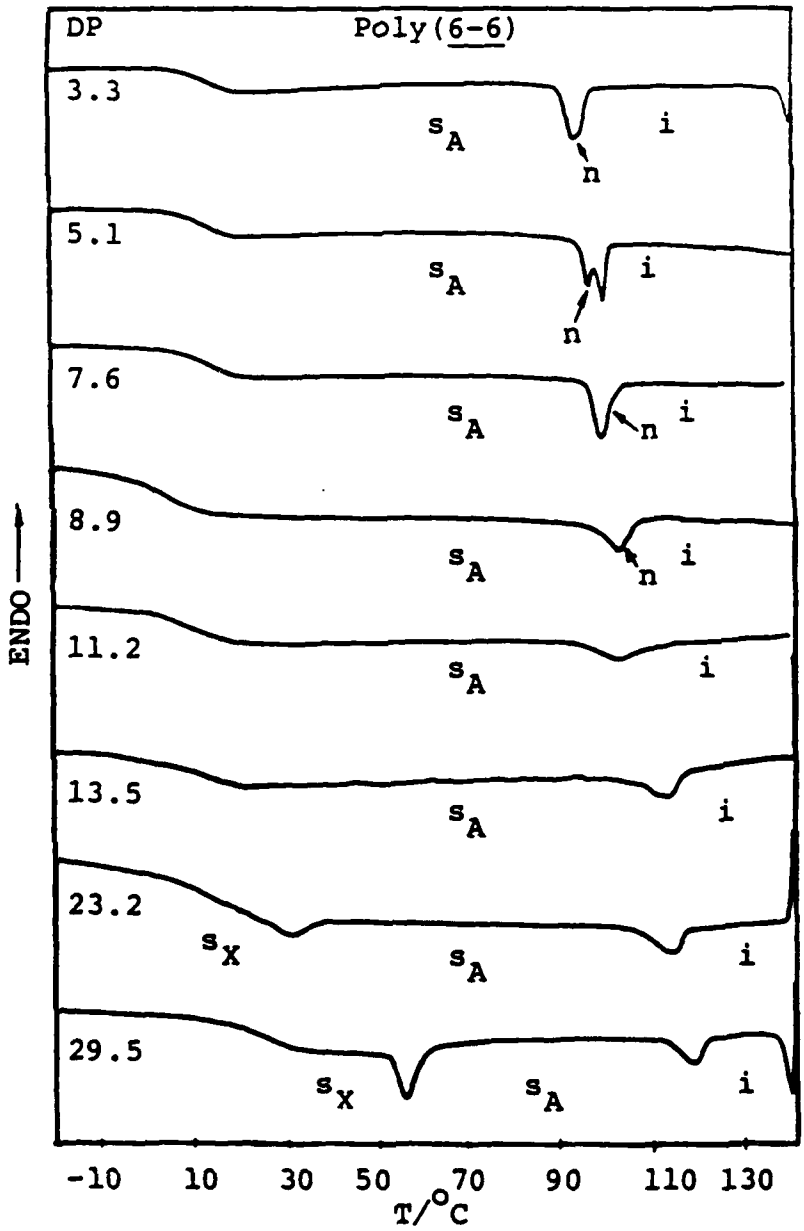
S_X
n
i
ENDO
-10
10
30
50
70
90
110
130
T/°C

Figure 4b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n
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n
i
7.6
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n
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S_A
n
i
11.2
S_A
i
13.5
S_A
i
23.2
S_X
S_A
i
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30
50
70
90
110
130
T/°C

Figure 4c

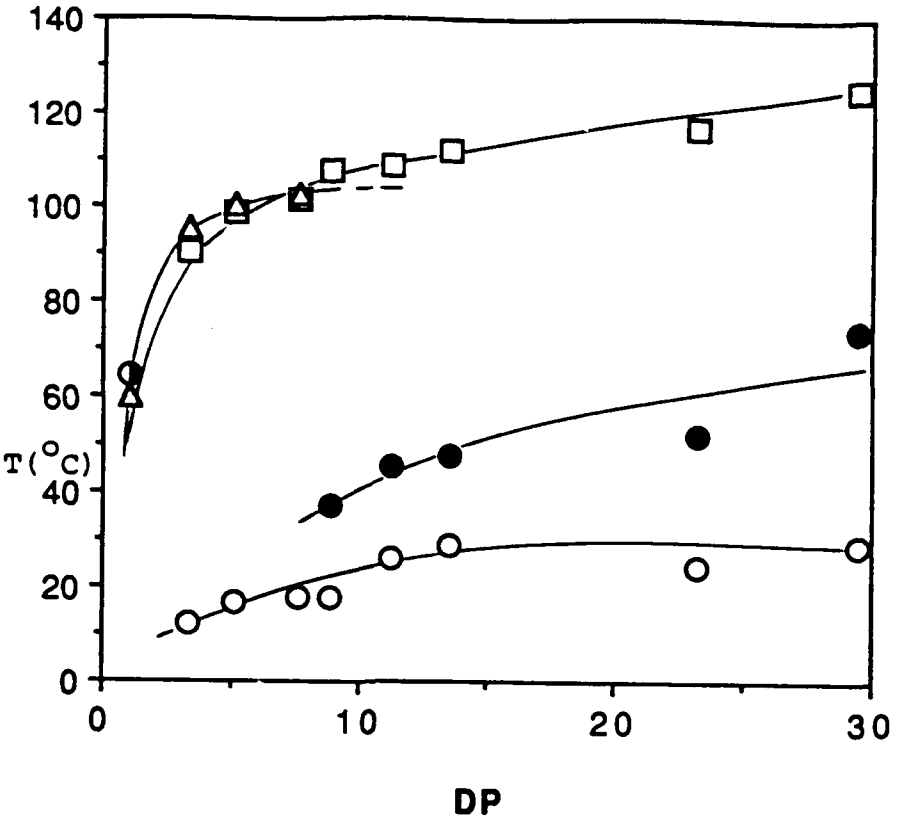

Figure 5a

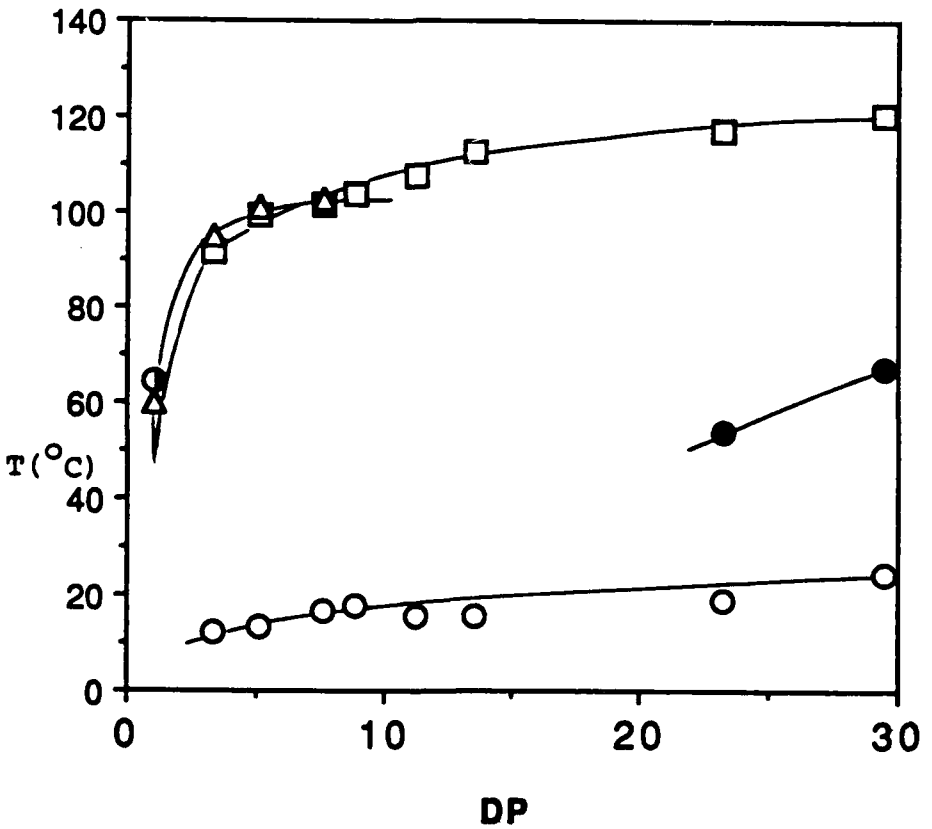

Figure 5b

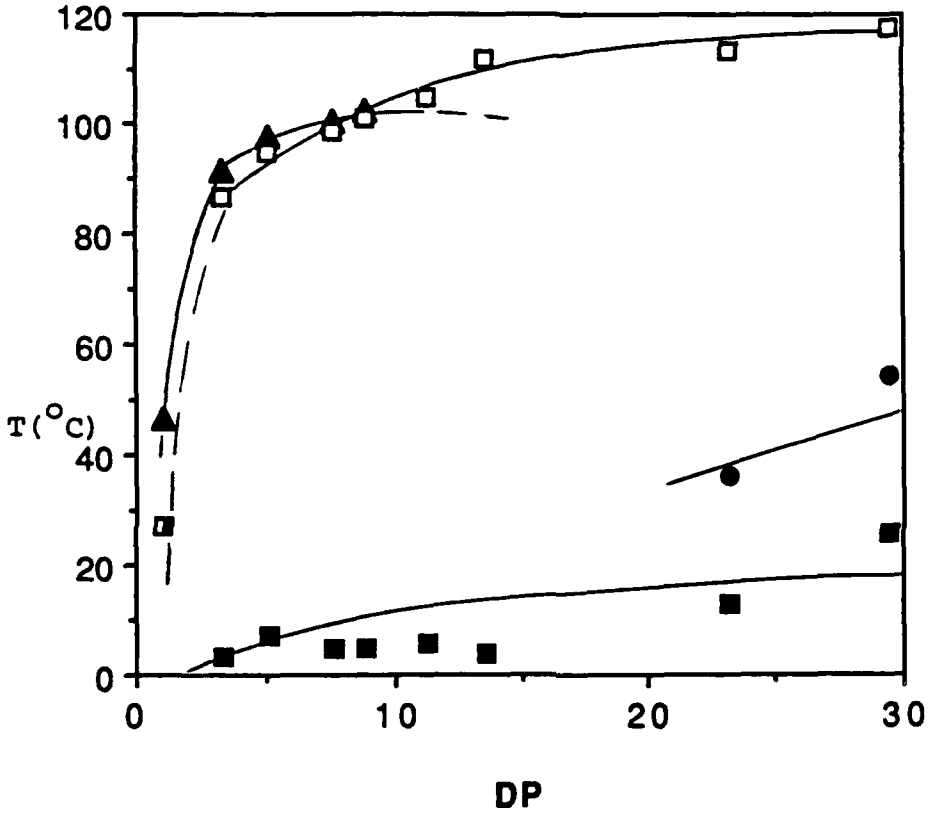

Figure 5c

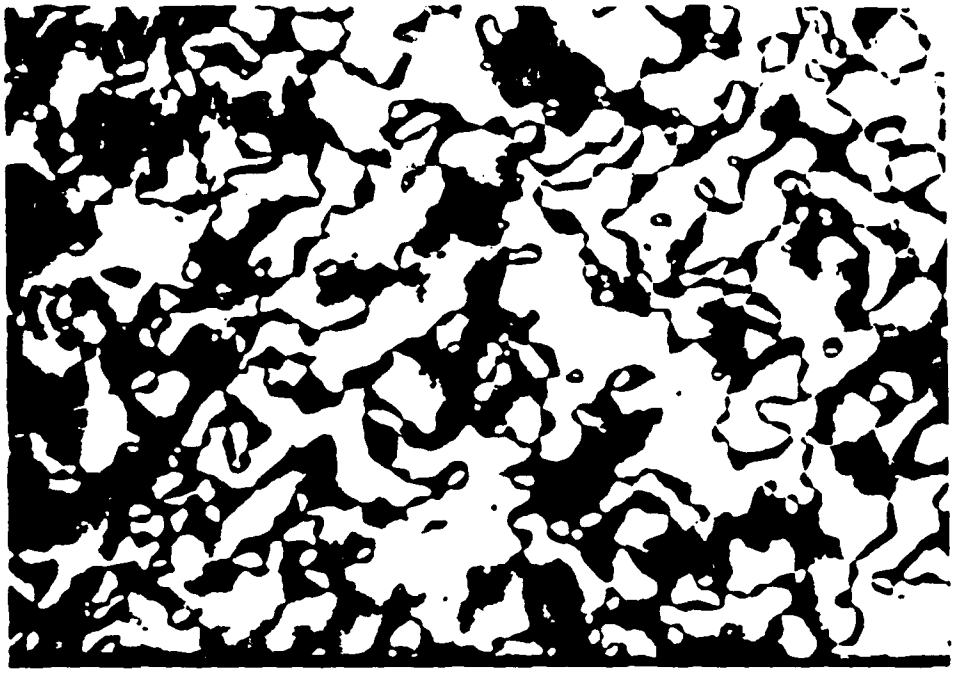

Figure 6d

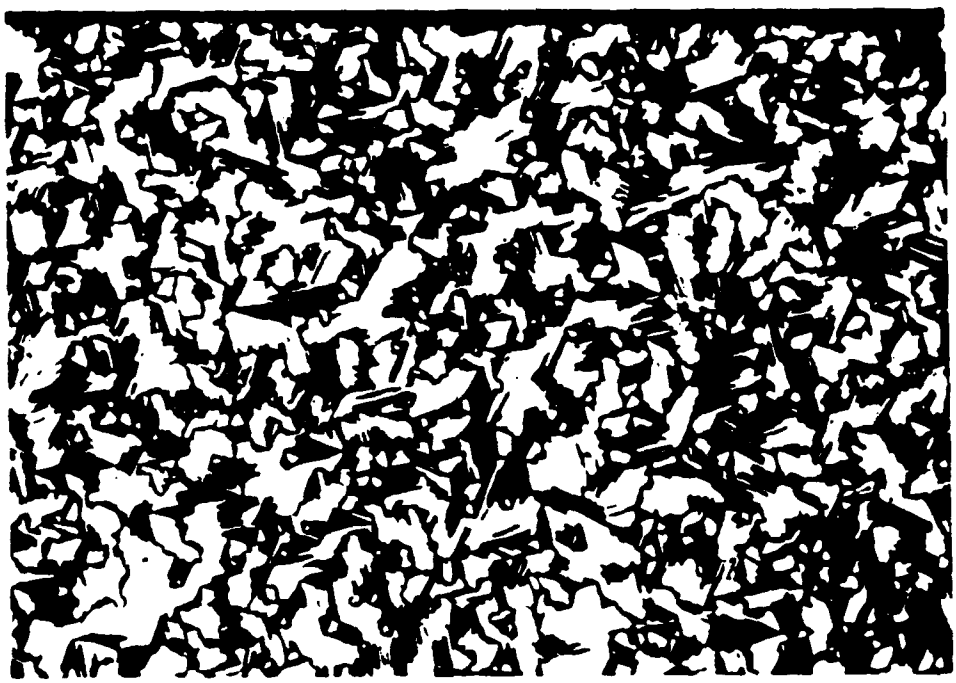

Figure 6e

Figure 6c

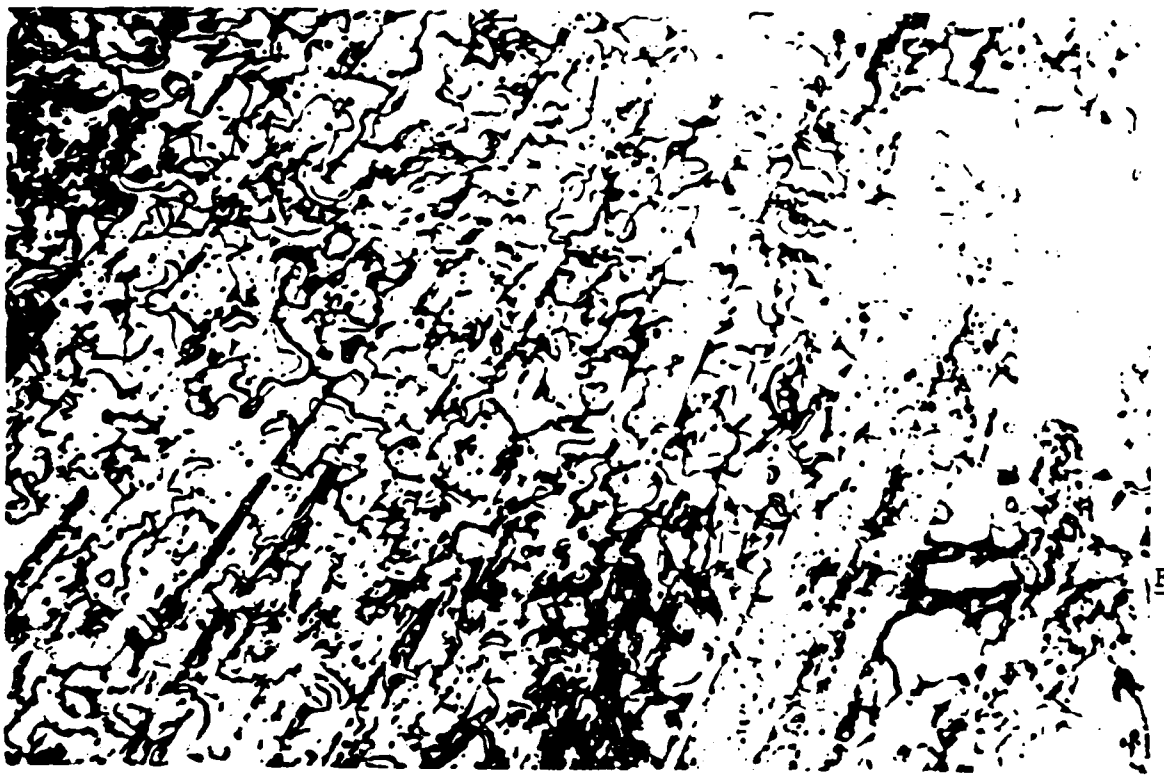

Figure 6a

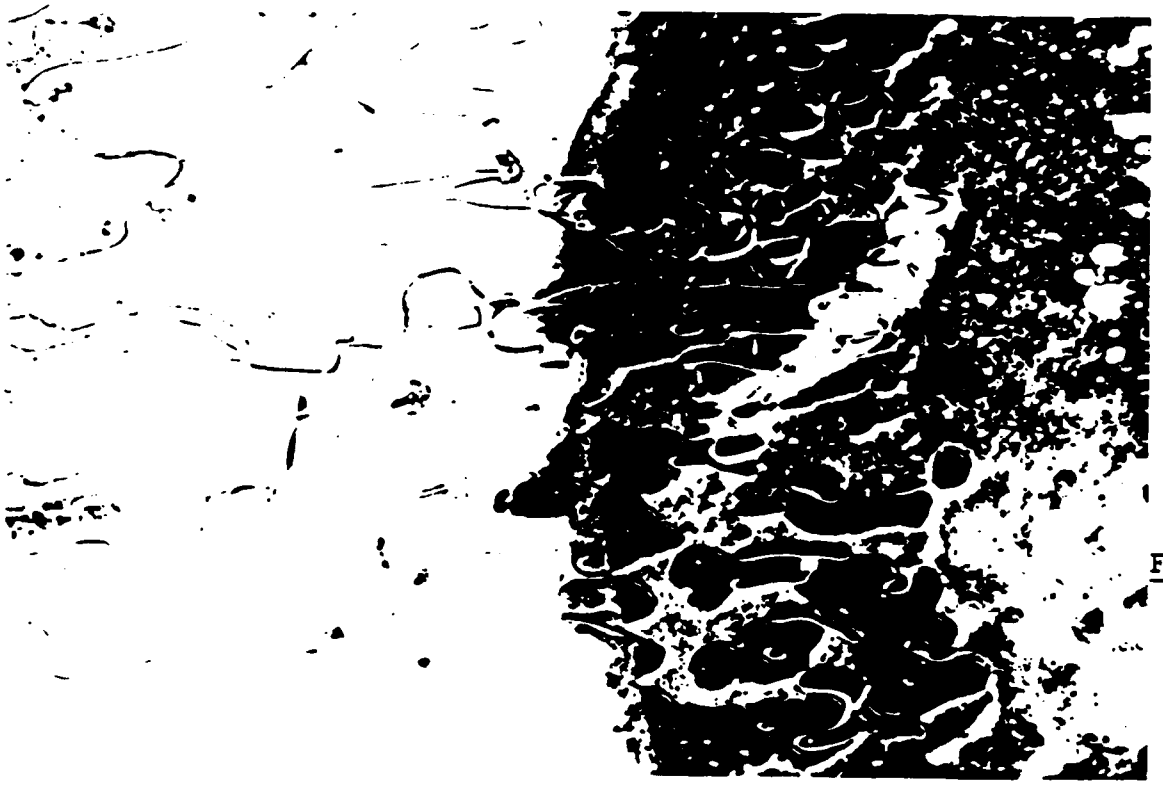

Figure 6b

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12 PERSONAL AUTHOR(S)
Virgil Percec and Myongsoo Lee

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The synthesis and living cationic polymerization of 8-[(4-cyano-4'-biphenyl)oxy]octyl vinyl ether (6-8) are described. The mesomorphic behavior of poly(6-8) with different degrees of polymerization and narrow molecular weight distribution was compared to that of the 6-8 and of 8-[(4-cyano-4'-biphenyl)oxy]octyl ethyl ether(8-8). 8-8 is the model compound of the monomeric structural unit of poly(6-8). 6-8 displays an enantiotropic nematic mesophase while 8-8 a monotropic nematic and a monotropic S_A mesophase. Poly(6-8)with a degree of polymerization of 2.1 displays an enantiotropic S_A and an enantiotropic nematic mesophase. Polymers with degrees of polymerization from 4.2 to 10.2 display an enantiotropic S_A mesophase. Poly(6-8)s with degrees of polymerization larger than 12.4 display an enantiotropic S_X (i.e., an unidentified smectic phase) and an enantiotropic S_A mesophase. Poly(6-8)s with degrees of polymerization from 1 (i.e., 8-8) to 31.1 represents the first example of

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side chain liquid crystalline polymer which shows a continuous change of the mesomorphic-isotropic phase transition (i.e., from nematic-isotropic to smectic-isotropic) on increasing its molecular weight.

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Molecular Engineering of Liquid Crystal Polymers by Living Polymerization. 3. Influence of Molecular Weight on the Phase Transitions of Poly{8-[(4-Cyano-4'-biphenyl)oxy]octyl Vinyl Ether}

by

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Molecular Engineering of Liquid Crystal Polymers by Living Polymerization. 3.[a] Influence of Molecular Weight on the Phase Transitions of Poly{8-[(4-cyano-4'-biphenyl)oxy]octyl Vinyl Ether}

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Department of Macromolecular Science
Case Western Reserve University
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a) Part 2 of this series: reference 11

ABSTRACT: The synthesis and living cationic polymerization of 8-[(4-cyano-4'-biphenyl)oxy]octyl vinyl ether (6-8) are described. The mesomorphic behavior of poly(6-8) with different degrees of polymerization and narrow molecular weight distribution was compared to that of the 6-8 and of 8-[(4-cyano-4'-biphenyl)oxy]octyl ethyl ether (8-8). 8-8 is the model compound of the monomeric structural unit of poly(6-8). 6-8 displays an enantiotropic nematic mesophase while 8-8 a monotropic nematic and a monotropic s_A mesophase. Poly(6-8) with a degree of polymerization of 2.1 displays an enantiotropic s_A and an enantiotropic nematic mesophase. Polymers with degrees of polymerization from 4.2 to 10.2 display an enantiotropic s_A mesophase. Poly(6-8)s with degrees of polymerization larger than 12.4 display an enantiotropic s_X (i.e., an unidentified smectic phase) and an enantiotropic s_A mesophase. Poly(6-8)s with degrees of polymerization from 1 (i.e., 8-8) to 31.1 represents the first example of side chain liquid crystalline polymer which shows a continuous change of the mesomorphic-isotropic phase transition (i.e., from nematic-isotropic to smectic-isotropic) on increasing its molecular weight .

INTRODUCTION

The most elementary step towards the molecular design of side chain liquid crystalline polymers represents the elucidation of the mechanism by which the polymer molecular weight influences its phase behavior. So far, the only trend which is generally accepted consists of the enlargement of the temperature range of the mesophase with the increase of the polymer molecular weight.[1-14] This dependence was recently explained based on thermodynamic principles assuming that the phase behavior of the polymer is determined by that of the monomeric structural unit.[12,13] So far there are two experiments in the literature in which the phase behavior of a polymer with different molecular weights was compared to that of the model compound of its monomeric structural unit.[7,11] In both cases the model compound of the monomeric structural unit and the polymers with different molecular weights display the same type of mesophase. A second mesophase may however appear above a certain polymer molecular weight.[7,11] This trend can be easily explained based on thermodynamics.[12,13] There are additional examples in the literature where a polymer displays various mesophases at different molecular weights.[4,9,10] However, no information is available on the phase behavior of the models of their monomeric structural units. Elucidation of this phenomenon requires the synthesis and characterization of polymers with well defined molecular weights, narrow molecular weight distributions as well as of the model compounds of

their monomeric structural units. So far, s chain liquid crystalline polymers with narrow molecular weight distribution were prepared by group transfer polymerization of mesogenic methacrylates,[7] by cationic polymerization of mesogenic vinyl and propenyl ethers[8-11,14,15] and by polymer homologous reactions.[16]

This paper will present the synthesis and living cationic polymerization of 8-[(4-(cyano-4'-biphenyl)oxy]octyl vinyl ether and the mesomorphic behavior of the resulting polymers with different molecular weights. The phase behavior of these polymers will be compared to that of 8-[(4-cyano-4'-biphenyl)oxy]octyl ethyl ether which represents the model of the monomeric structural unit of poly{8-[4(cyano-4'-biphenyl)oxy]octyl vinyl ether}.

EXPERIMENTAL

Materials

4-Phenylphenol (98%), 1,10-phenanthroline (anhydrous, 99%), palladium (II) acetate (all from Lancaster Synthesis), ferric chloride anhydrous (98%, Fluka), cooper (I) cyanide (99%), n-butyl vinyl ether (98%), 9-borabicyclo[3.3.1]nonane (9-BBN, crystalline, 98%), 8-bromo-1-octanol (95%) and the other reagents (all from Aldrich) were used as received. Methyl sulfide (anhydrous, 99%, Aldrich) was refluxed over 9-BBN and then distilled under argon. Dichloromethane (99.6%, Aldrich) used as a polymerization solvent was first washed with concentrated sulfuric acid, then with water, dried over anhydrous magnesium sulfate , refluxed over calcium hydride and freshly distilled under argon before each use. N-Methyl-2-pyrrolidone (98%, Lancaster Synthesis) was dried by azeotropic distillation with benzene, shaken with barium oxide, filtered, and fractionally distilled under reduced pressure. Trifluoromethane sulfonic acid (triflic acid, 98%, Aldrich) was distilled under argon.

Techniques

^{1}H-NMR (200 MHz) spectra were recorded on a Varian XL-200 spectrometer. TMS was used as internal standard. A Perkin Elmer DSC-4 differential scanning calorimeter, equipped with a TADS 3600 data station, was used to determine the thermal transitions which were reported as the maxima and minima of their endothermic or exothermic peaks respectively. In all cases, heating and cooling rates were 20^{o}C/min unless otherwise specified. Glass transition temperatures (Tg) were read at the middle of the change in the heat capacity. First heating scans differ from second and subsequent heating scans. However, second and subsequent heating scans are identical. The first heating

scans can be reobtained after proper annealing of the polymer sampie. A Carl-Zeiss optical polarized microscope (magnification 100x) equipped with a Mettler FP 82 hot stage and a Mettler FP 800 central processor was used to observe the thermal transitions and to analyze the anisotropic textures.[17,18] Molecular weights were determined by gel permeation chromatography (GPC) with a Perkin-Elmer Series 10 LC instrument equipped with LC-100 column oven, LC-600 autosampler and a Nelson Analytical 900 series integrator data station. The measurements were made at 40°C using the UV detector. A set of Perkin Elmer PL gel columns of 10^4 and 500 A with chloroform as solvent (1ml/min) and a calibration plott constructed with polystyrene standards was used to determine the molecular weights. High pressure chromatography experiments were performed with the same instrument.

Synthesis of Monomers

Scheme I outlines the synthesis of 4-cyano-4'-(8-hydroxyoctan-1-yloxy)biphenyl, 8[(4-cyano-4'-biphenyl)oxy]octyl vinyl ether, and of 8-[(4-cyano-4'-biphenyl)oxy]octyl ethyl ether.

1,10-Phenanthroline Palladium (II) Diacetate (9)

1,10-Phenanthroline palladium (II) diacetate was synthesized according to a literature procedure.[19] mp 220°C. (lit. 19, mp 234°C).

4-Cyano-4'-Hydroxybiphenyl (5)

5 was synthesized as reported in a previous publication.[11] Purity: 99% (HPLC). mp 195-198°C. (lit. 20,21, mp 196-199°C). ^{1}H-NMR (Acetone-d_6, TMS, δ, ppm): 3.80 (1 proton, OH, s), 7.01 (2 aromatic protons, o to -OH, d), 7.61 (2 aromatic protons, m to -OH, d), 7.70 (4 aromatic protons, o and m to -CN, s).

4-Cyano-4'-(8-hydroxyoctan-1-yloxy)biphenyl (7-8)

4-Cyano-4'-hydroxybiphenyl (5.8 g, 0.0297 mol), potassium hydroxide (1.66 g, 0.0297 mol) and few crystals of potassium iodide were dissolved in a mixture of ethanol-water (4/1) (165 ml). 8-Bromo-1-octanol (6.8 g, 0.033 mol) was added to the resulting solution which was heated to reflux for 24 hr. The ethanol was removed on a rotavapor and the resulting solid was washed succesivelly with water, dilute aqueous NaOH and water. Recrystallization from methanol yielded 5.8 g (60.3%) of white crystals. Purity: 99.9% (HPLC). ^{1}H-NMR ($CDCl_3$, TMS, δ, ppm): 1.01-1.95 (12 protons, -$(CH_2)_6$-, m), 3.66 (2 protons, -CH_2OH, t), 4.01 (2 protons, PhOCH_2-, t),

7.01 (2 aromatic protons, o to alkoxy, d), 7.66 (4 aromatic protons, o and m to -CN, d of d). Thermal characterization of 7-8 is reported in Table I.

8-[(4-Cyano-4'-biphenyl)oxy]octyl Vinyl Ether (6-8)

7-8 (4.5 g, 0.0139 mmol) was added to a mixture of 1,10-phenanthroline palladium (II) diacetate (0.55 g, 1.39 mmol), n-butyl vinyl ether (76 ml) and dry chloroform (70 ml). The mixture was heated at 60°C for 6 hr. After cooling and filtration (to remove the catalyst) the solvent was distilled in a rotavapor and the product was purified by column chromatography (silica gel, methylene chloride eluent) to yield 3.4 g (69.9%) of white crystals. Purity: 99.9% (HPLC). ^{1}H-NMR ($CDCl_3$, TMS, δ, ppm): 1.01-1.95 (12 protons, $-(CH_2)_6-$, m), 3.68 (2 protons, $-CH_2O-$, t), 4.00 (3 protons, $OCH=CH_2$, trans, and $PhOCH_2-$, m), 4.14 and 4.21 (1 proton, $-OCH=CH_2$ cis, d), 6.49 (1 proton, $-OCH=CH_2$, q), 7.01 (2 aromatic protons, o to alkoxy, d), 7.50 (2 aromatic protons, m to alkoxy, d), 7.66 (4 aromatic protons, o and m to -CN, d of d). Thermal transitions of 6-8 are reported in Table I.

8-[(4-Cyano-4'-biphenyl)oxy]octyl Ethyl Ether (8-8)

7-8 (3.23 g, 0.01 mol) was added to a solution containing potassium t-butoxide (1.12 g, 0.01 mol) and 18-crown-6 (2.6 mg, 0.01 mmol) in dry tetrahydrofuran (78 ml). Diethyl sulfate (1.54 g, 0.01 mol) was added and the reaction mixture was refluxed for 3 hr. After cooling, the reaction mixture was extracted with chloroform, washed with water, dried over magnesium sulfate and the chloroform was removed in a rotavapor. The resulting product was purified by column chromatography (silica gel , methylene chloride eluent) to yield 2.2 g(63%) of white crystals. Purity: 99.9% (HPLC). ^{1}H-NMR ($CDCl_3$, TMS, δ, ppm): 1.20 (3 protons, $-OCH_2CH_3$, t), 1.30-1.81 (12 protons, $-(CH_2)_6-$, m), 3.41 (4 protons, $-CH_2OCH_2CH_3$, m), 4.00 (2 protons, $-CH_2OPh$, t), 7.01 (4 aromatic protons, m to alkoxy, d), 7.66 (4 aromatic protons, o and m to -CN, d of d). Thermal transitions of 8-8 are reported in Table I.

Cationic Polymerizations

Polymerizations were carried out in glass flasks equipped with teflon stopcocks and rubber septa under argon atmosphere at 0°C for 1 hr. All glassware was dried overnight at 130°C. The monomer was further dried under vacuum overnight in the polymerization flask. Then the flask was filled with argon, cooled to 0°C and the requested amounts of methylene chloride, dimethyl sulfide and triflic acid were added via a syringe. The monomer concentration was about 10 wt% of the solvent volume and the

dimethyl sulfide concentration was 10 times larger than that of the initiator. The polymer molecular weight was controlled by the monomer/initiator ratio. At the end of the polymerization the reaction mixtures were precipitated into methanol containing few drops of NH_4OH. The filtered polymers were dried and precipitated from methylene chloride solutions into methanol until GPC traces showed no traces of monomer. Table II summarizes the polymerization results. Although the polymer yields are lower than expected due to losses during the purification process, the conversions were almost quantitative in all cases.

RESULTS AND DISCUSSION

The synthesis of 8-[(4-cyano-4'-biphenyl)oxy]octyl vinyl ether (6-8) and of 8-[(4-cyano-4'-biphenyl)oxy]octyl ethyl ether (8-8) is outlined in Scheme I. Although 6-8 can be synthesized by the etherification of 4-cyano-4'-hydroxybiphenyl with 8-bromooctyl vinyl ether as outlined in Scheme I,[8-12,14,23] the prefered route consists of the transetherification of 4-cyano-4'-(8-hydroxyoctan-1-yloxy)biphenyl (7-8) with n-butyl vinyl ether. This reaction is catalyzed by 1,10-phenanthroline palladium (II) diacetate.[19,22]

As shown previously,[8-10,11,14,15,24-26] living cationic polymerization of vinyl ethers tolerates a variety of functional groups. We prefer to perform this polymerization with triflic acid/dimethylsulfide initiator, since this polymerization can be carried out in methylene chloride at 0°C.[11,15,27,28] Scheme II outlines the polymerization mechanism. Under our polymerization conditions, the polyethers contain acetal chain ends (Scheme II) and therefore, they should be manipulated in the absence of acids.

The polymerization results are presented in Table II. GPC traces of all polymers are exhibited in Figure 1. The molecular weights and the molecular weight distributions are presented in Table II. All polymers display narrow molecular weight distribution. The theoretical {i.e., $[M]_o/[I]_o$} and experimental degrees of polymerization of these polymers agree very well (Table II). The dependences of the number average molecular weight (Mn) and of Mw/Mn versus the ratio between the initial monomer and initiator concentration $[M]_o/[I]_o$ are plotted in Figure 2. Both plotts demonstrate the living character of these polymerizations.

Figure 3 displays the heating and cooling DSC traces of 4-cyano-4'-(8-hydroxyoctan-1-yloxy)biphenyl (7-8), 8-[4-cyano-4'-biphenyloxy]octyl vinyl ether (6-8) and of 8-[(4-cyano-4'-biphenyl)oxy]octyl ethyl ether (8-8). 7-8 and

6-8 present an enantiotropic nematic mesophase. The model compound of the monomeric structural unit of poly(6-8), i.e., 8-8 presents a monotropic nematic and a monotropic s_A mesophase. The s_A-nematic and nematic-isotropic transitions from the heating scan of 8-8 were determined by reheating the sample in the DSC instrument from the above the temperature at which this compound crystallizes (Figure 3). All, these thermal transitions and the corresponding enthalpy changes are summarized in Table I.

Figure 3a, b and c presents the first heating, the second heating and the cooling DSC scans of all polymers. All cooling scans are identical. With the exception of the poly(6-8) which has a degree of polymerization equal to 12.4, all other polymers display first and subsequent heating scans which are almost identical. The case of poly(6-8) will be discussed later. Poly(6-8) with a degree of polymerization of 2.1 displays an enantiotropic s_A phase and an enantiotropic nematic phase which are almost overlapped on both their heating (Figure 4a,b) and cooling (Figure 4c) scans. Therefore, this dimer resemble the phase behavior of the model of the monomeric structural unit, 8-8, except that the dimer does not crystallize and its thermal transitions are shifted towards higher temperatures (Table I and II). Poly(6-8)s with degrees of polymerization from 4.2 to 10.2 display only an enantiotropic s_A mesophase. Poly(6-8) with degrees of polymerization equal and higher than 12.4 display a s_X (i.e., a smectic phase which was not yet identified) and an enantiotropic s_A phase. The s_X phase is enantiotropic in the case of polymers with degrees of polymerization from 18.1 to 31.1 and appears only on the first heating scan in the case of the polymers with a degree of polymerization equal to 12.4. This behavior is due to the kinetic effect provided by the close proximity of this phase transition to the glass transition of the polymer.

All these phase transition temperatures and their corresponding thermodynamic parameters are summarized in Table II.

The thermal transition temperatures from the first heating, second heating and cooling scans of all polymers are plotted as a function of the degree of polymerization in Figure 5a,b,c. The phase transition temperatures of the model compound of the monomeric structural unit (8-8) from Figure 3 and Table I are also included. However, the melting and crystallization temperatures are not plotted since they would overlap the other data. Nevertheless, we have to recall that both the nematic and the sA phase of 8-8 are monotropic. Figure 5,a,b,c provides us with the following conclusion. On increasing the degree of polymerizatioin from 1 to 2.1, both the nematic and s_A phase transition temperature become enantiotropic. This effect is both due to the decreased rate of crystallization of the dimer , which represents a kinetic effect, and due to the increase of the two phase transition temperatures with the increase of the molecular weight, which

represents a thermodynamic effect. However, on increasing the degree of polymerization from 2.1 to 4.2, the polymer does not display anymore the nematic mesophase. Although only from two data points, we can assume that this change represents a continuous dependence of molecular weight. This result is simply due to the fact that the slope of the dependence temperature transition of the s_A phase versus polymerization degree is higher than that of the slope relating the dependence of the nematic temperature transition versus degree of polymerization.

It is generally accepted that many nematic monomers lead to smectic side chain liquid crystalline polymers.[1] However, it is not correct to compare the phase behavior of monomers with that of the corresponding polymers since as observed from Figure 3, small changes in the structure of the monomer changes drastically their phase behavior. Most frequently, the mesomorphic behavior of the monomer is different from that of the model compound of the monomeric structural unit.[11] To our knowledge, this is the first time when is is experimentally observed that the change of the mesophase of the monomeric structural unit represents a continuous dependence of molecular weight. Such a dependence was previously demonstrated only for the case of a main chain liquid crystalline polymer.[29] A second example of this kind of dependence observed over a broader range of molecular weights of the side chain liquid crystalline polymer will be reported soon.[30]

The formation of a second mesophase at higher polymer molecular weights as is the case of the s_X phase from this example, was observed previously.[7,11] Such a dependence on polymer molecular weight can be explained by a simple thermodynamic scheme.[12,13] However, an explanation for the transformation of a nematic-isotropic phase into a smectic-isotropic phase by increasing the molecular weight of the polymer should also consider the different degrees of distortion of the random-coil conformation of the polymer backbone in the nematic and smectic mesophase.[1,31-35] This discussion will represent the subject of a further publication.

An additional trend which is observed from Figure 4a,b,c refers to the dependence of the width of the s_A-isotropic and isotropic-s_A phase transition peaks on the polymer molecular weight. This width decreases with the increase of the polymer molecular weight. Figure 6 illustrates this trend. A similar trend was observed for other two polymers based on flexible backbones and displaying a smectic-isotropic transition.[6,11] An explanation for this behavior was provided in a previous publication.[6]

Figure 7 presents some representative textures displayed by the nematic, s_A and s_X phases exhibited by 8-8 (degree of polymerization of 1) and poly(6-8) with a degree of

polymerization of 31.1. The nematic and s_A mesophases of poly(6-8) with a degree of polymerization of 2.1 exhibit the same textures as those of 8-8.

ACKNOWLEDGMENTS

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FIGURE CAPTIONS

Figure 1: GPC traces of Poly(6-8). The degree of polymerization of each sample is printed on the figure.

Figure 2: The dependence of the number average molecular weight (M_n) and of the polydispersity (M_w/M_n) of poly(6-8) on the $[M]_o/[I]_o$ ratio.

Figure 3: Heating and cooling DSC traces of 7-8 (a, b), 6-8 (c, d) and 8-8 (e, f).

Figure 4: DSC traces displayed during the first heating scan (a), second heating scan (b) and first cooling scan (c) by poly (6-8) with different degrees of polymerization (DP). DP is printed on the top of each DSC scan.

Figure 5: The dependence of phase transition temperatures on the degree of polymerization of poly(6-8). DP=1 corresponds to 8-8. Data from first heating (fh) scan are presented in Figure 5a. ○ -Tg (fh);□ -Ts_A-n (fh); △-Tn-i (fh); ● -Ts_X-s_A (fh). Data from second heating (sh) scan are presented in Figure 5b. ○ -Tg (sh);□ -Ts_A-n (sh);△ -Tn-i (sh);● -Ts_X-s_A (sh). Tm's of 8-8 from first and second heating scans are not plotted. Data from the cooling scan are presented in Figure 5c. □ -Ti-s_A;△ -Ti-n; ●-Ts_A-s_X;○-Tg;◑ -Tk.

Figure 6: The dependence of the peak width ΔT (°C) of the mesomorphic-isotropic and isotropic-mesomorphic phase transition temperatures versus the degree of polymerization of poly(6-8); □ -first heating scan; △ -second heating scan;● -cooling scan.

Figure7: Representative optical polarized micrographs (100x) of : a) 8-8 at 53°C on the cooling scan (nematic phase); b) 8-8 at 47°C on the cooling scan (s_A phase); c) poly(6-8), DP=31.1 at 150°C on the cooling scan (s_A phase); and d) poly(6-8), DP=31.1 at 60°C on the cooling scan (s_X phase).

SCHEME CAPTIONS

Scheme I: Synthesis of Monomers and Model Compounds.

Scheme II: The Mechanism of Living Cationic Polymerization.

Table I. Thermal Characterization of 4-Cyano-4'-(8-hydroxyoctan-1-yloxy)phenyl (7-8), 8-[(4-Cyano-4'-biphenyl)oxy]octyl Vinyl Ether (6-8) and of 8-[(4-Cyano-4'-biphenyl) oxy]octyl Ethyl Ether (8-8).

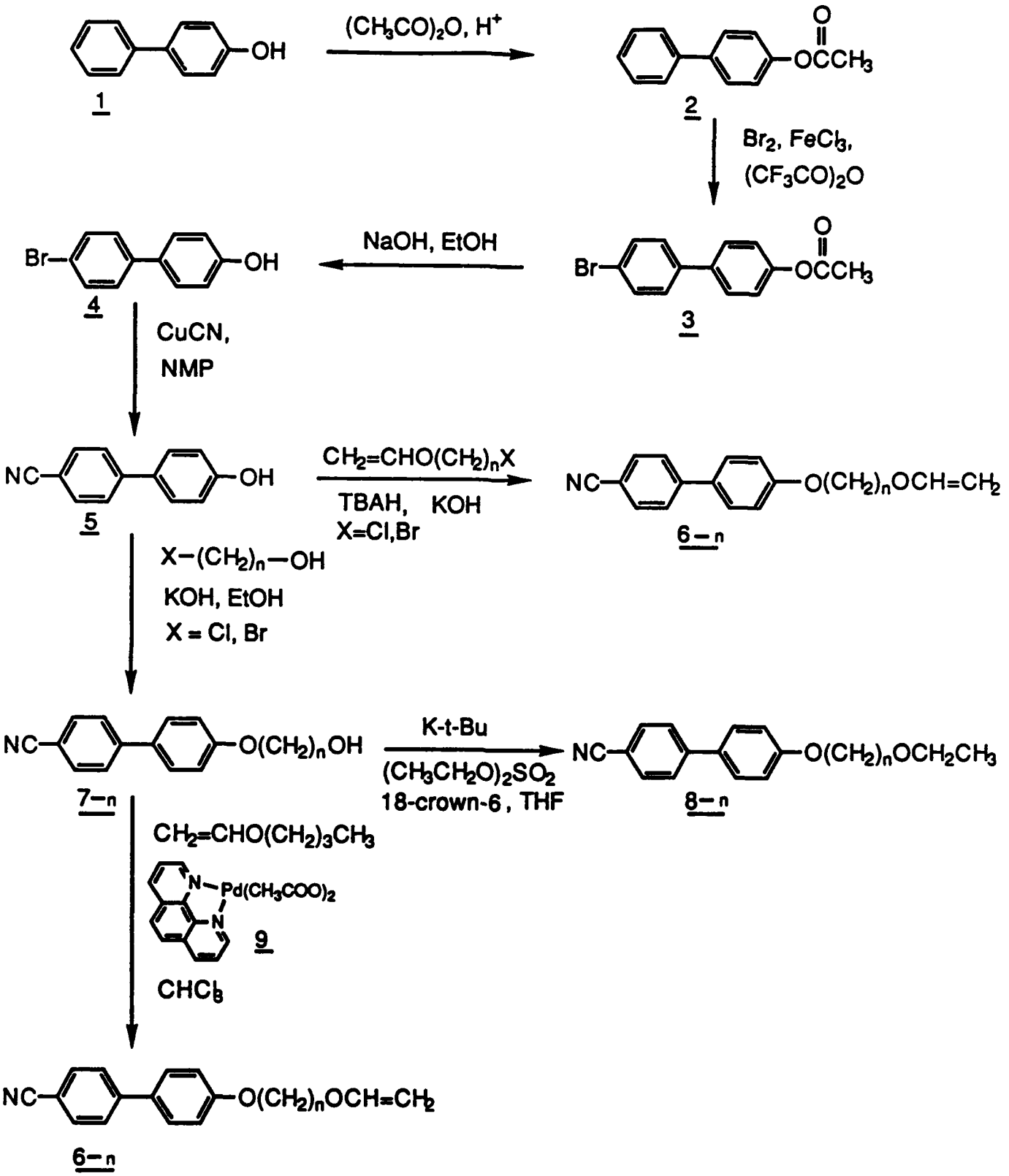
Compound	phase transitions (0^0C) and corresponding enthalpy changes (kcal/mru)	
	heating	cooling
7-8	k 87.7 (9.1) n 104.0 (0.23) i	i 100.4 (0.38) n 57.7 (6.09) k
6-8	k 54.0 (8.31) n 70.8 (0.27) i	i 67.3 (0.31) n 27.9 (4.68) k
8-8	k 62.9 (8.77)[s_A 58.5 (0.26) n 61.0 (0.39)]*i	i 53.1 (0.37) n 46.9 (0.015) s_A 23.7 (7.21) k

*[ ] virtual data

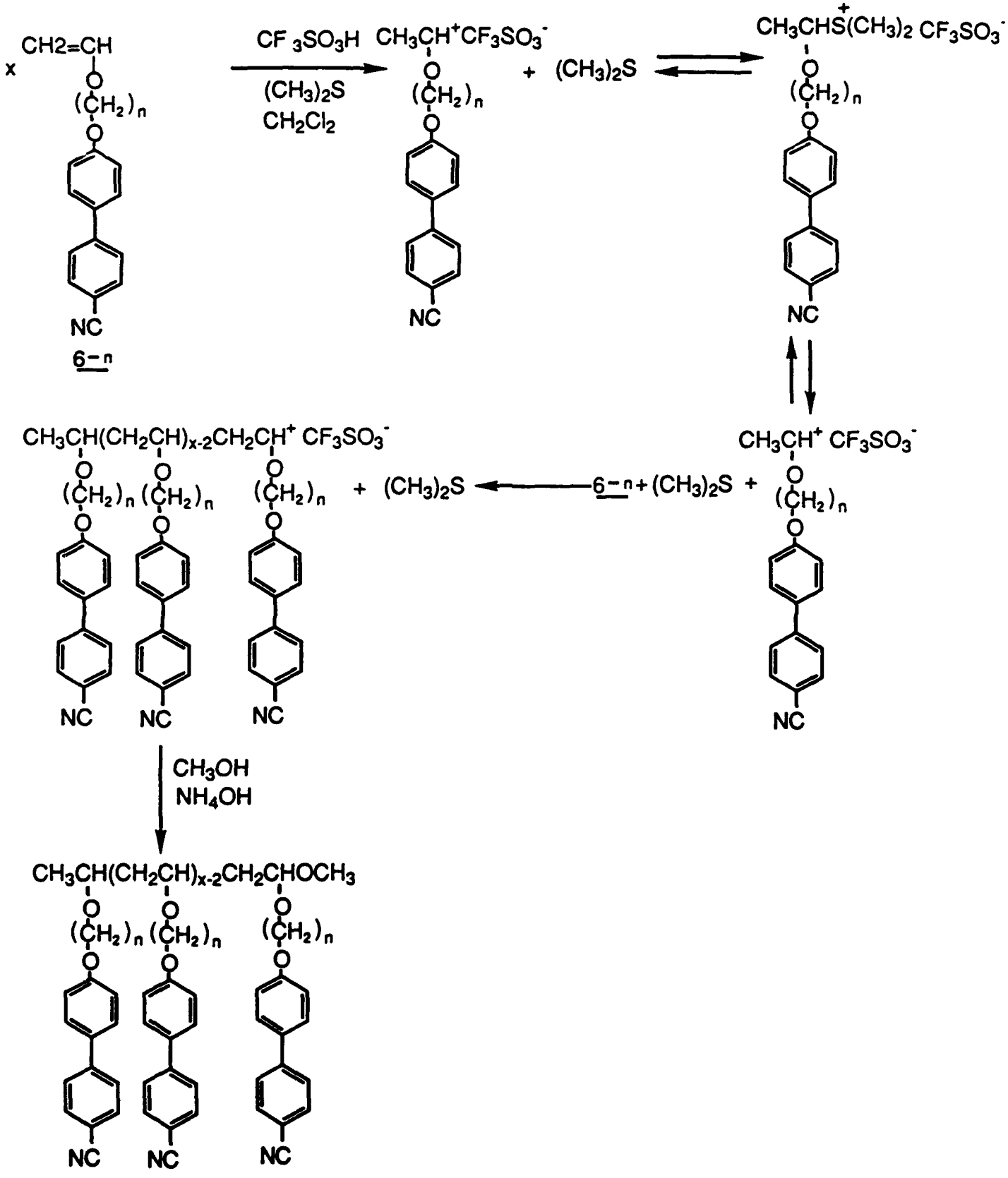
Table II. Cationic Polymerization of 8-[(4-Cyano-4'-biphenyl)oxy]octyl Vinyl Ether (6-8) (polymerization temperature,0^0C ; polymerization solvent,methylene chloride; $[M]_0$=0.285; $[(CH_3)_2S]_0/[I]_0$=10; polymerization time,1hr) and Characterization of the Resulting Polymers

Sample No.	$[M]_0/[I]_0$	Polymer yield(%)	GPC			phase transitions(^{0}C) and corresponding enthalpy changes (kcal/mru)	
			$Mn\times10^{-3}$	Mw/Mn	DP	heating	cooling
1	2.0	42.3	0.75	1.11	2.2	g-6.4 s_A65.1 (-)* n 67.4 (0.28)* i g-6.7 s_A 63.8 (-)* n 65.6 (0.31)* i	i 65.0 (0.29)* n 63.5 (-)* s_A -6.4 g
2	4.0	68.0	1.47	1.06	4.2	g 4.9 s_A 110.9 (0.48) i g 2.5 s_A 110.5 (0.47) i	i 105.6 (0.46) s_A 0.1 g
3	6.0	65.0	2.06	1.07	5.9	g 5.8 s_A 114.3 (0.51) i g 4.2 s_A 114.0 (0.51) i	i 109.2 (0.50) s_A 2.5 g
4	8.0	69.0	2.87	1.09	8.2	g 9.2 s_A 125.6 (0.47) i g 7.5 s_A 125.8 (0.47) i	i 120.5 (0.46) s_A 7.5 g
5	10.0	71.0	3.57	1.04	10.2	g 12.6 s_A 127.5 (0.43) i g 8.3 s_A 127.3 (0.43) i	i 122.8 (0.46) s_A 7.8 g
6	13.0	76.0	4.32	1.06	12.4	g 15.7 s_X 36.4 (0.31) s_A 136.4 (0.58) i g 9.2 s_A 134.8 (0.46) i	i 128.8 (0.45) s_A7.9g
7	18.0	86.0	6.31	1.11	18.1	g 23.2 sS_X 49.4 (0.27) s_A 145.0 (0.50) i g 17.5 s_X 49.1 (0.27) s_A144.9 (0.44) i	i 139.6 (0.30) s_A 40.9 (0.44) s_X12.5 g
8	23.0	85.0	7.89	1.09	22.6	g 22.5 s_X 67.1 (0.27) s_A 154.1 (0.48) i g 18.7 s_X62.1 (0.28) s_A 151.1 (0.43) i	i 141.6 (0.32) s_A 49.7 (0.40) s_X 13.3 g
9	30.0	69.0	10.88	1.11	31.1	g 22.7 s_X 69.0 (0.34) s_A 155.1 (0.41) i g 21.5 s_X67.9 (0.31) s_A 155.3 (0.40) i	i 150.0 (0.32) s_A 62.8 (0.39) s_X 19.2 g

* overlapped peaks


(CH3CO)2O, H+
OH
OCCH3
1
2
Br2, FeCl3,
(CF3CO)2O
NaOH, EtOH
Br
OH
OCCH3
4
3
CuCN,
NMP
NC
OH
CH2=CHO(CH2)nX
TBAH, KOH
X=Cl,Br
NC
O(CH2)nOCH=CH2
5
6—n
X—(CH2)n—OH
KOH, EtOH
X = Cl, Br
NC
O(CH2)nOH
K-t-Bu
(CH3CH2O)2SO2
18-crown-6, THF
NC
O(CH2)nOCH2CH3
7—n
8—n
CH2=CHO(CH2)3CH3
N
Pd(CH3COO)2
N
9
CHCl3
NC
O(CH2)nOCH=CH2
6—n

Scheme I


CH2=CH
x
(CH2)n
O
NC
6-n
CF3SO3H
(CH3)2S
CH2Cl2
CH3CH+CF3SO3-
(CH3)2S
CH3CHS+(CH3)2 CF3SO3-
CH3CH+ CF3SO3-
6-n + (CH3)2S
CH3CH(CH2CH)x-2CH2CH+ CF3SO3-
+ (CH3)2S
CH3OH
NH4OH
CH3CH(CH2CH)x-2CH2CHOCH3

Scheme II

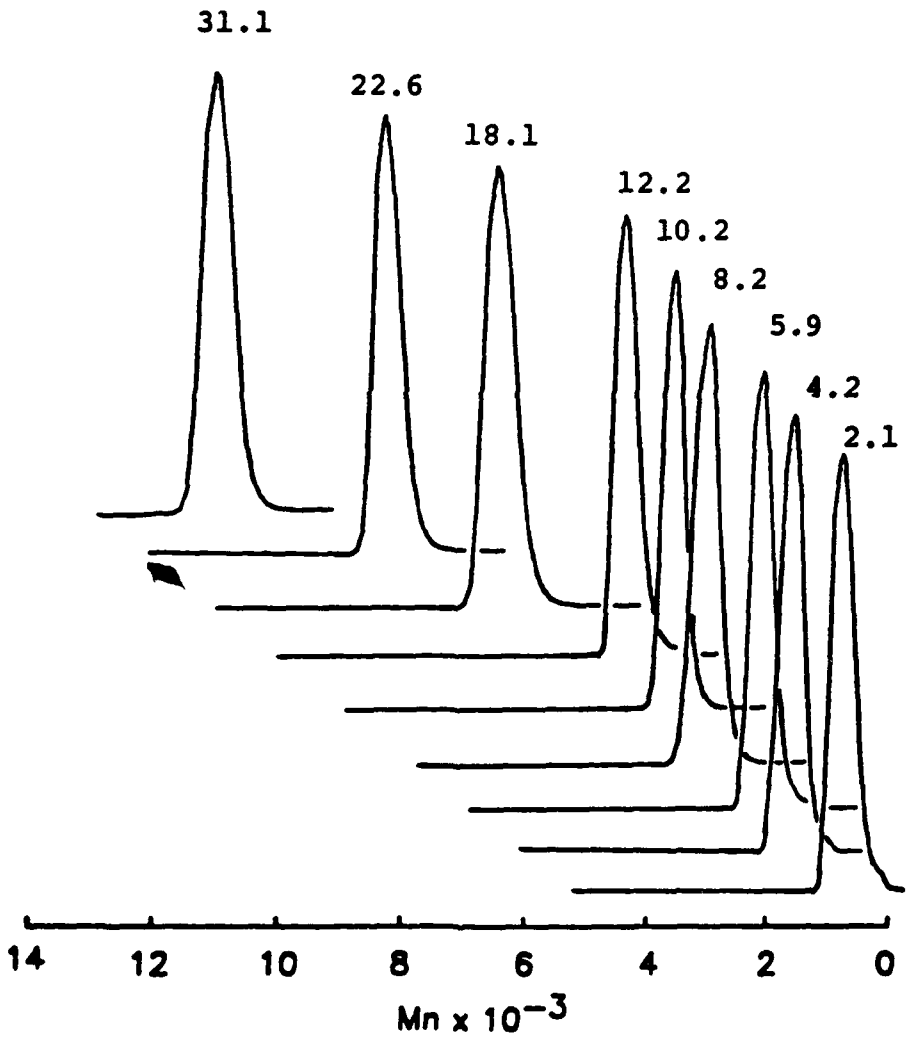


Figure 1

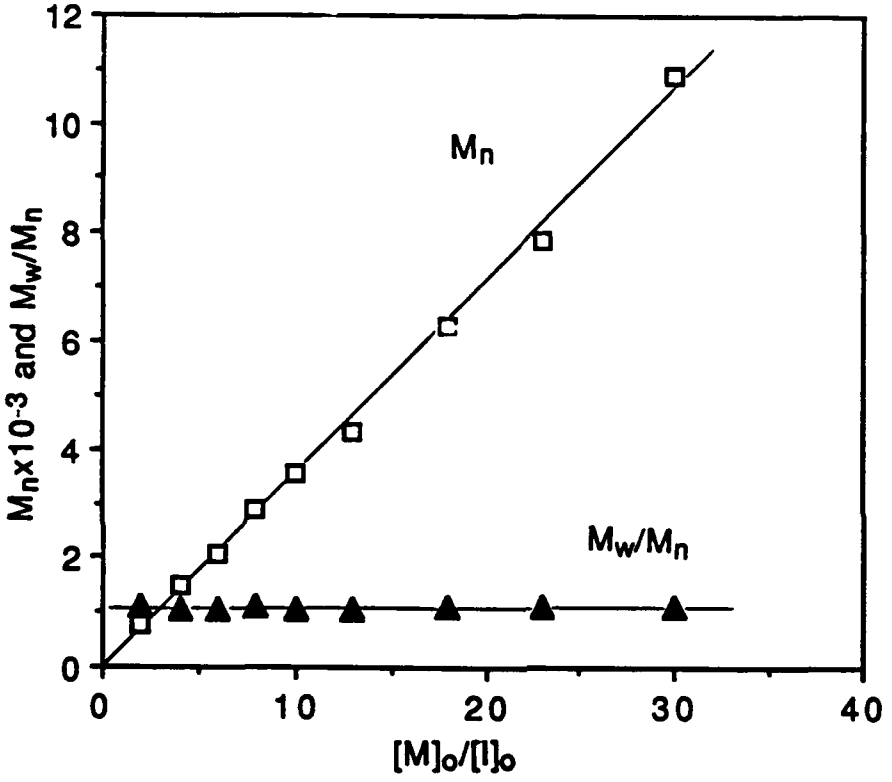


Figure 2

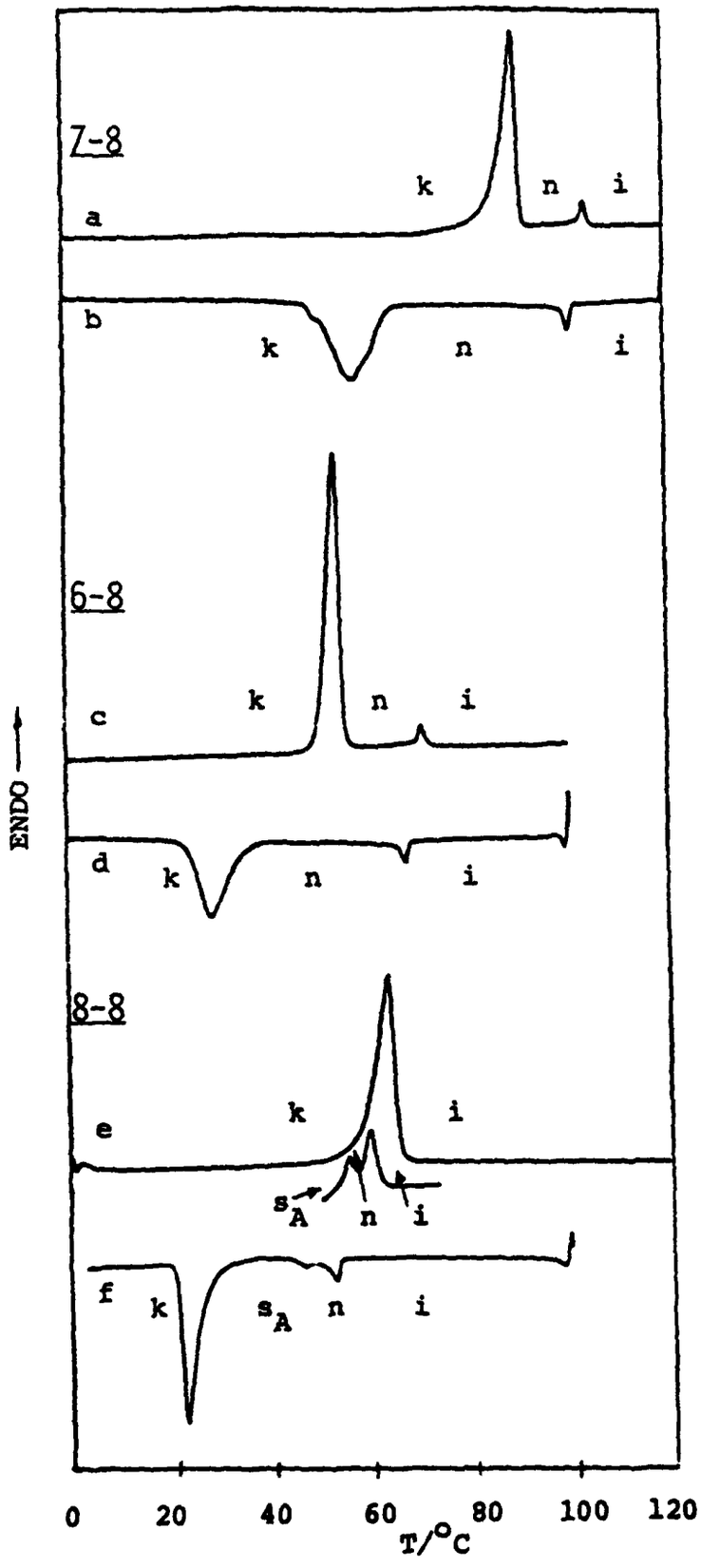

7-8
a
k
n
i
b
k
n
i
6-8
c
k
n
i
d
k
n
i
ENDO
8-8
e
k
i
s_A
n
i
f
k
s_A
n
i
0
20
40
60
80
100
120
T/°C

Figure 3

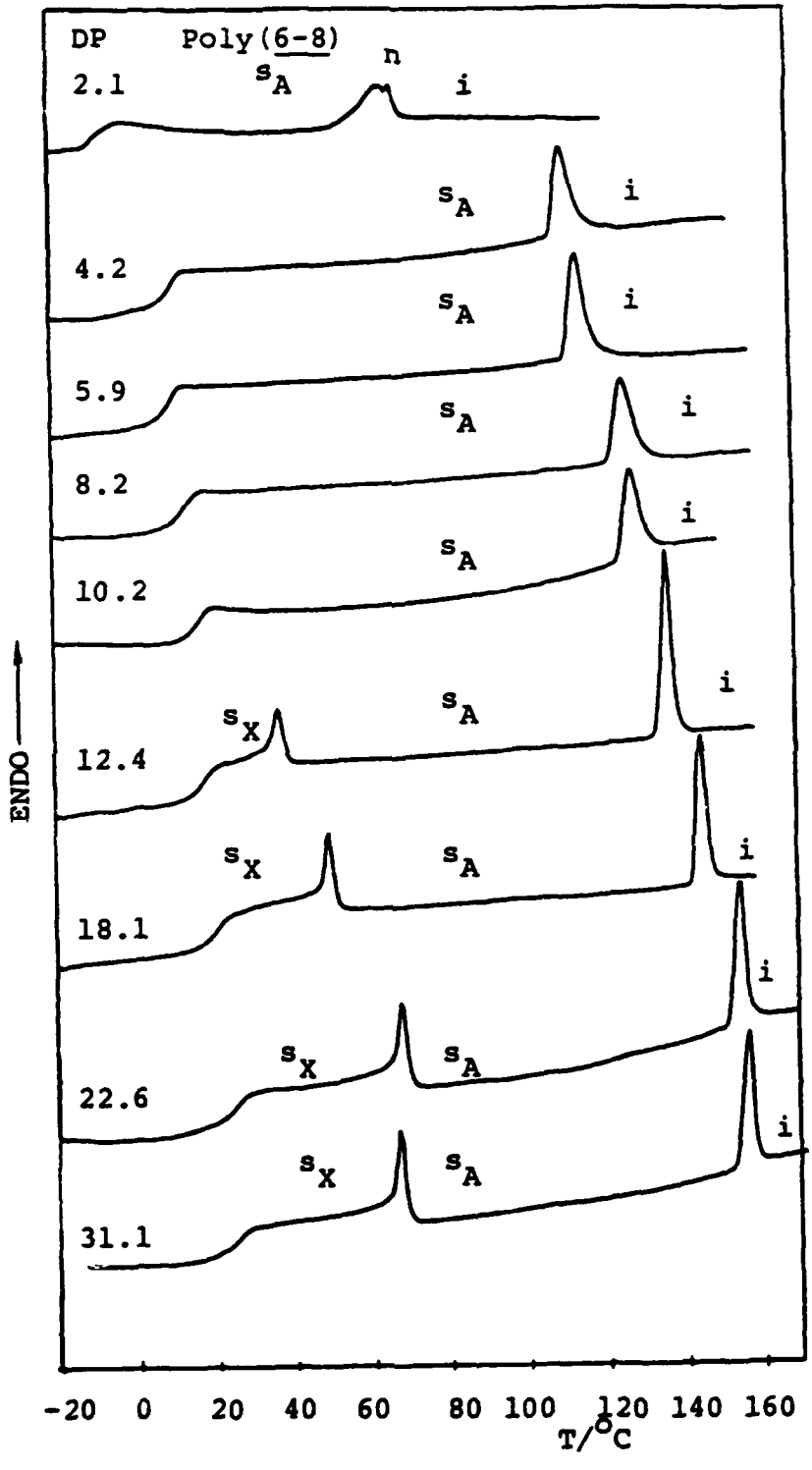

DP
Poly(6-8)
2.1
S_A
n
i
4.2
S_A
i
5.9
S_A
i
8.2
S_A
i
10.2
S_A
i
12.4
S_X
S_A
i
18.1
S_X
S_A
i
22.6
S_X
S_A
i
31.1
S_X
S_A
i
ENDO
-20 0 20 40 60 80 100 120 140 160
T/°C

Figure 4a

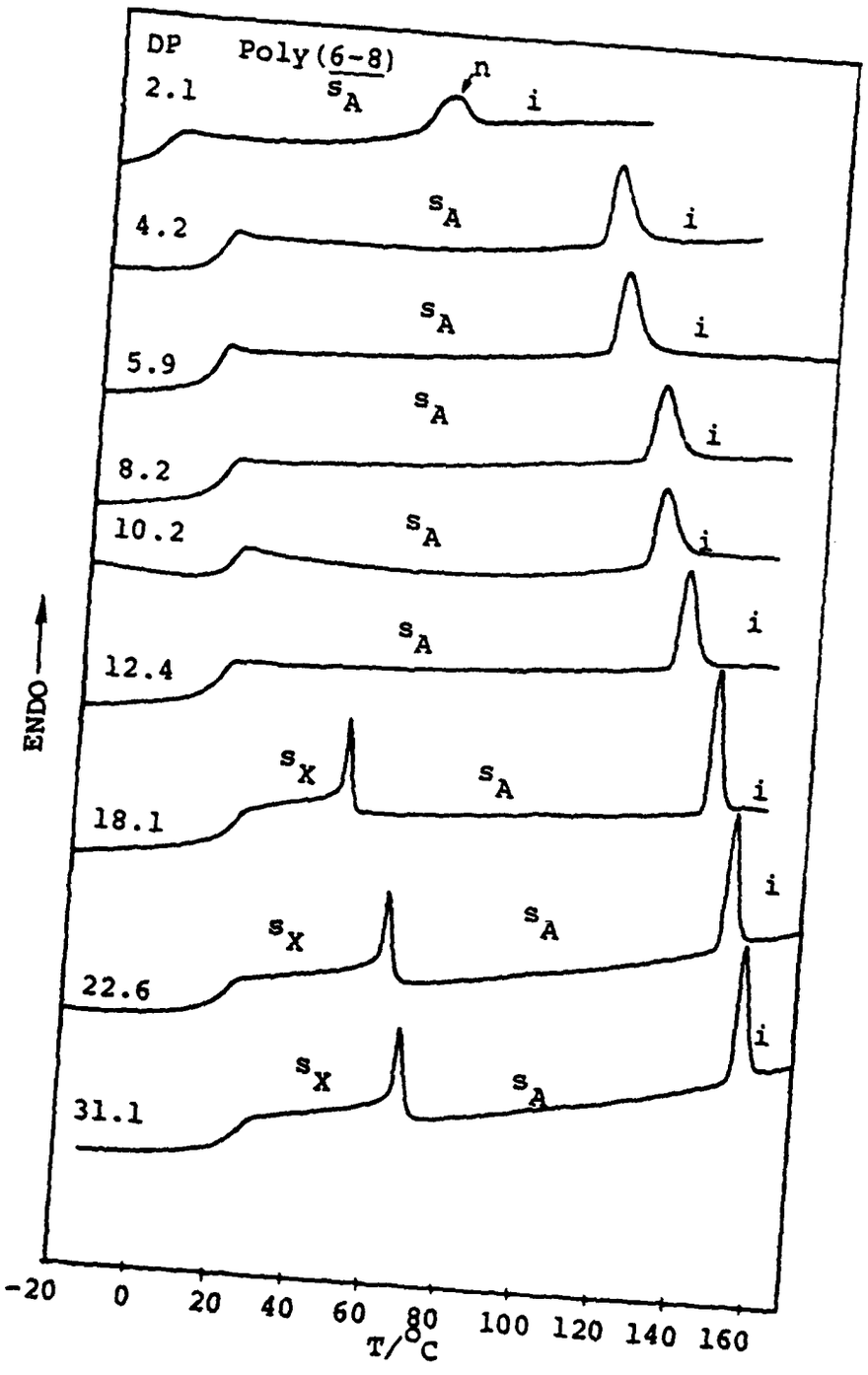

DP
Poly(6-8)
2.1
S_A
n
i
4.2
S_A
i
5.9
S_A
i
8.2
S_A
i
10.2
S_A
i
12.4
S_A
i
18.1
S_X
S_A
i
22.6
S_X
S_A
i
31.1
S_X
S_A
i
ENDO
-20
0
20
40
60
80
100
120
140
160
T/°C

Figure 4b

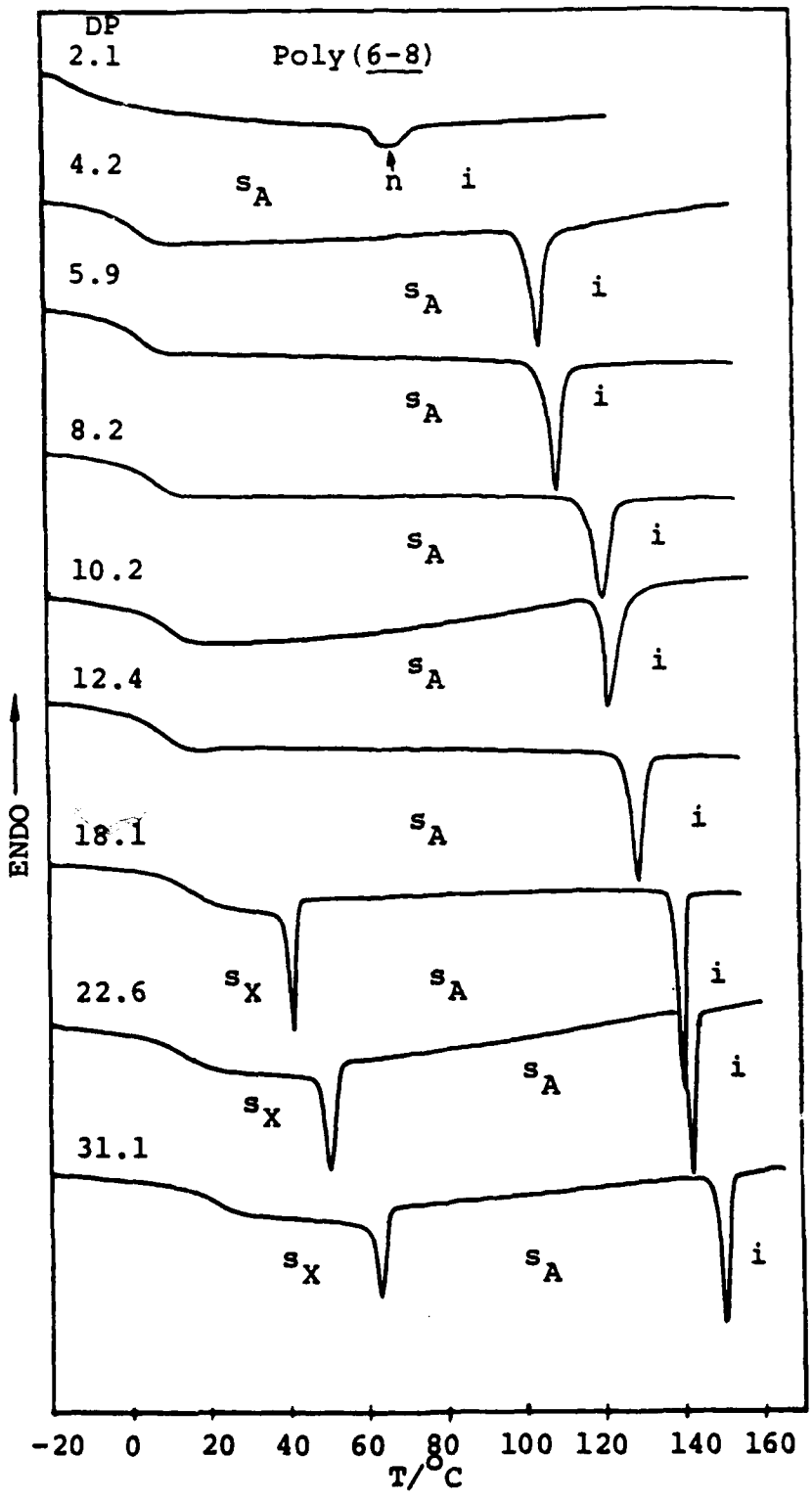

DP
2.1
Poly(6-8)
4.2
S_A
n
i
5.9
S_A
i
8.2
S_A
i
10.2
S_A
i
12.4
S_A
i
18.1
S_A
i
22.6
S_X
S_A
i
31.1
S_X
S_A
i
S_X
S_A
i
ENDO
-20
0
20
40
60
80
100
120
140
160
T/°C

Figure 4c

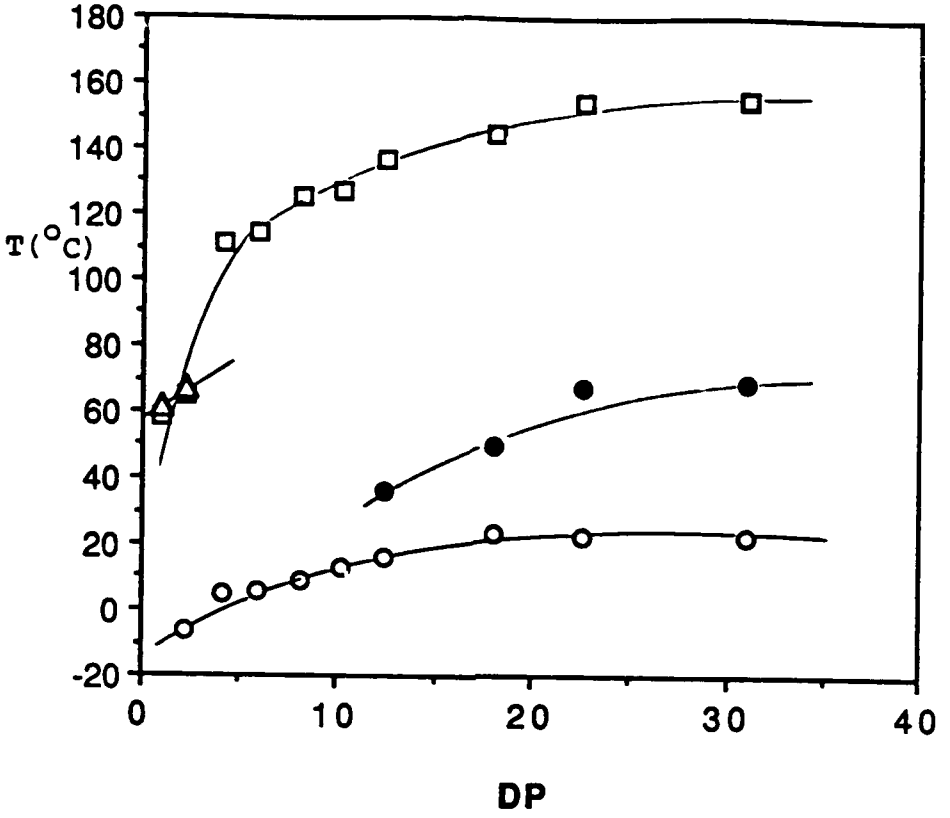


Figure 5a

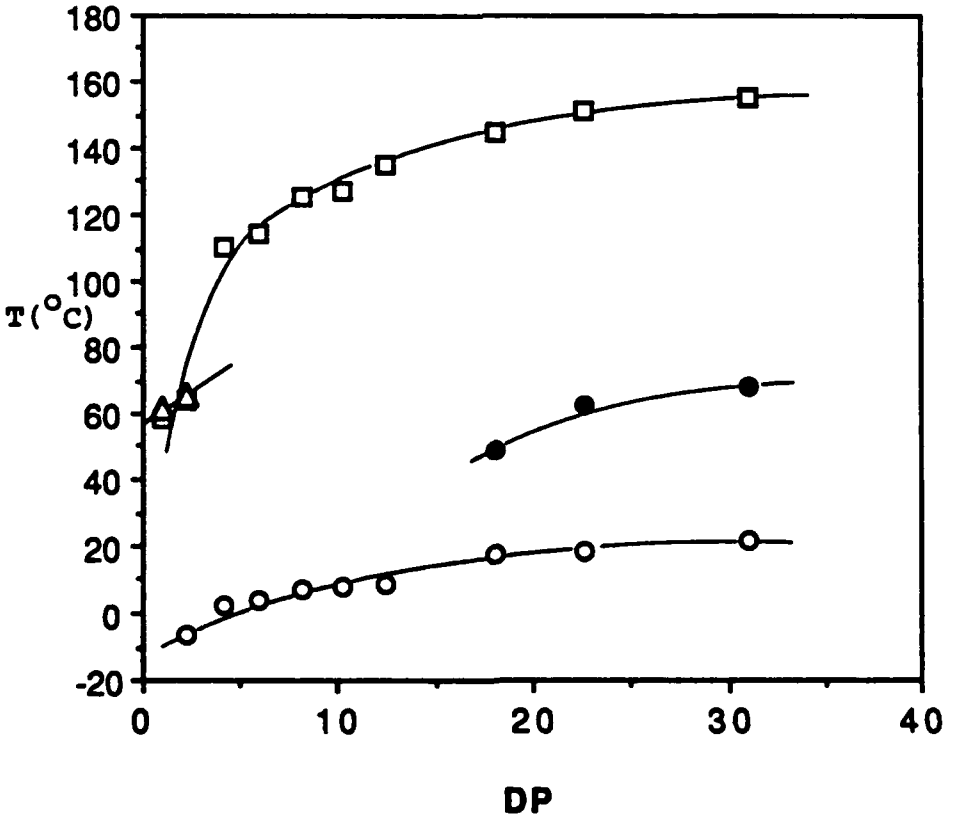


Figure 5b

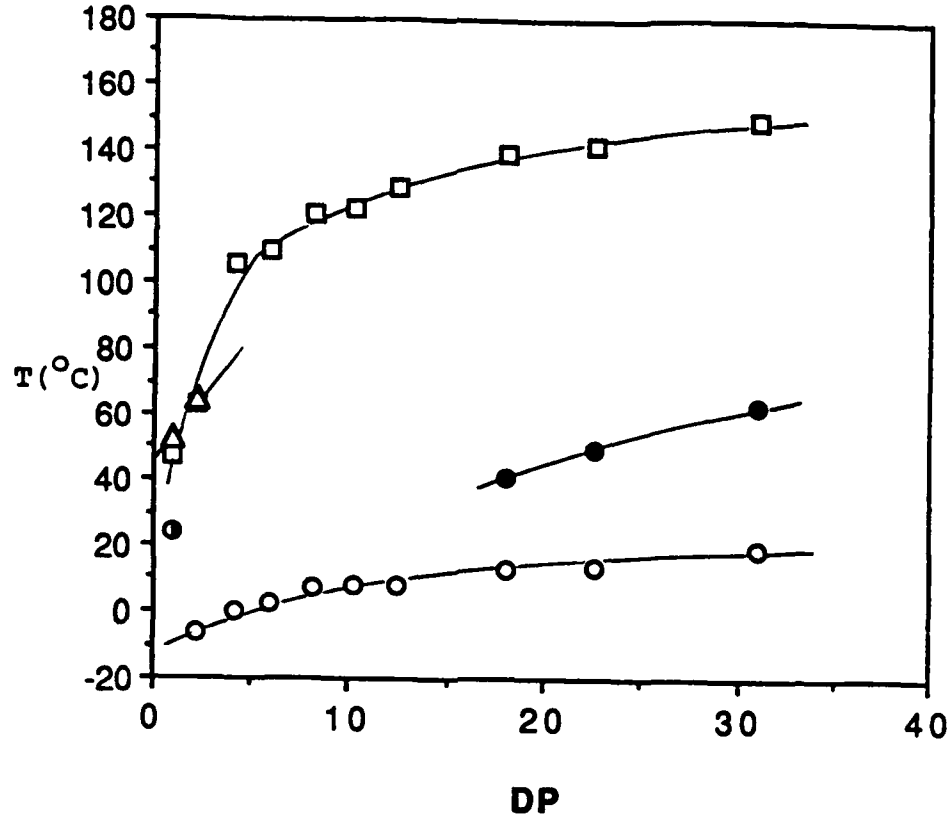


Figure 5c

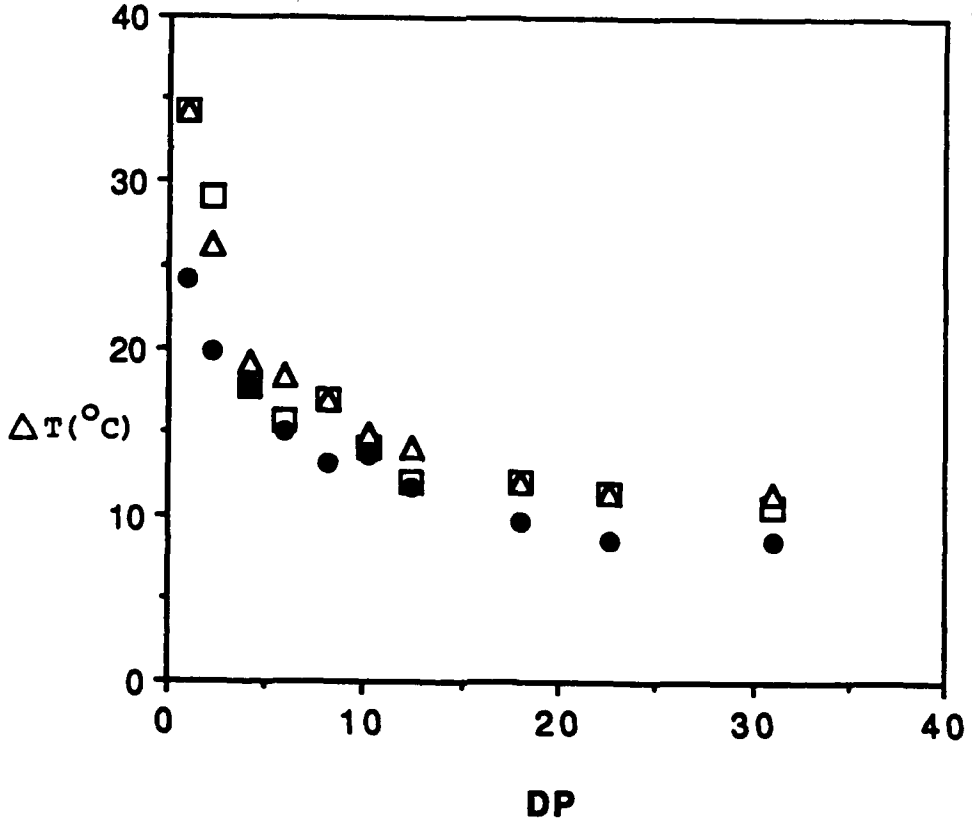


Figure 6

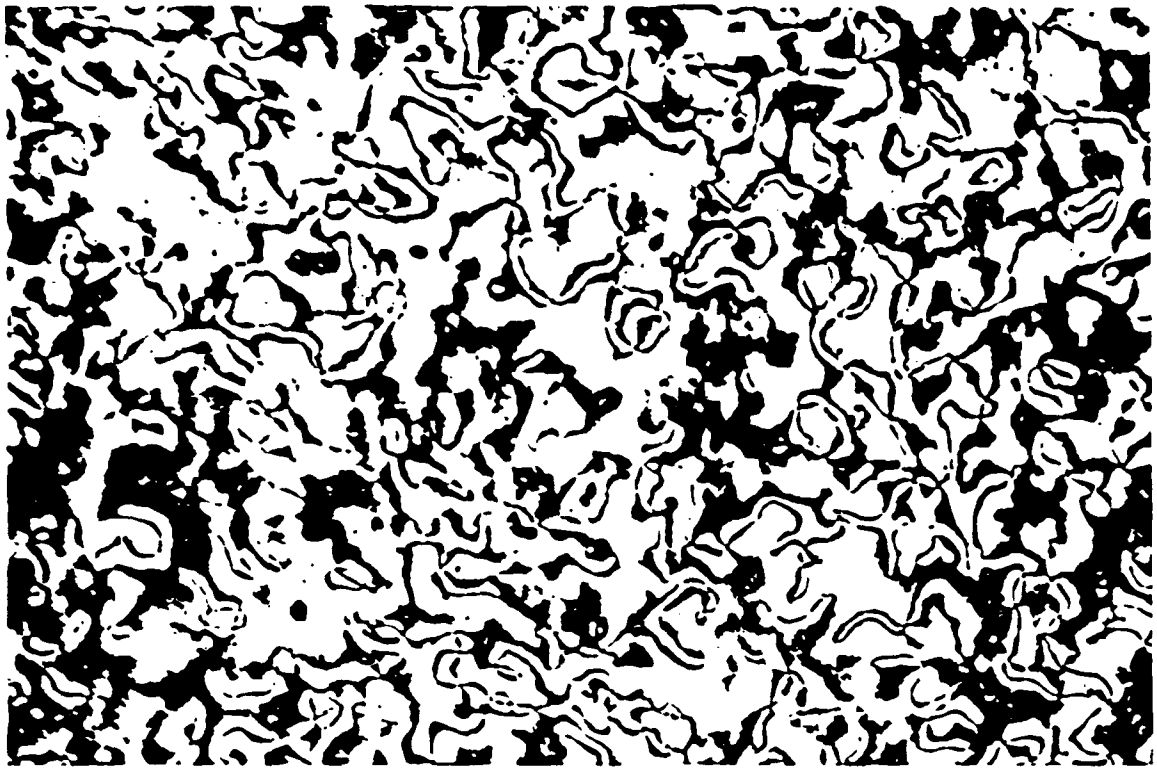


Figure 7a

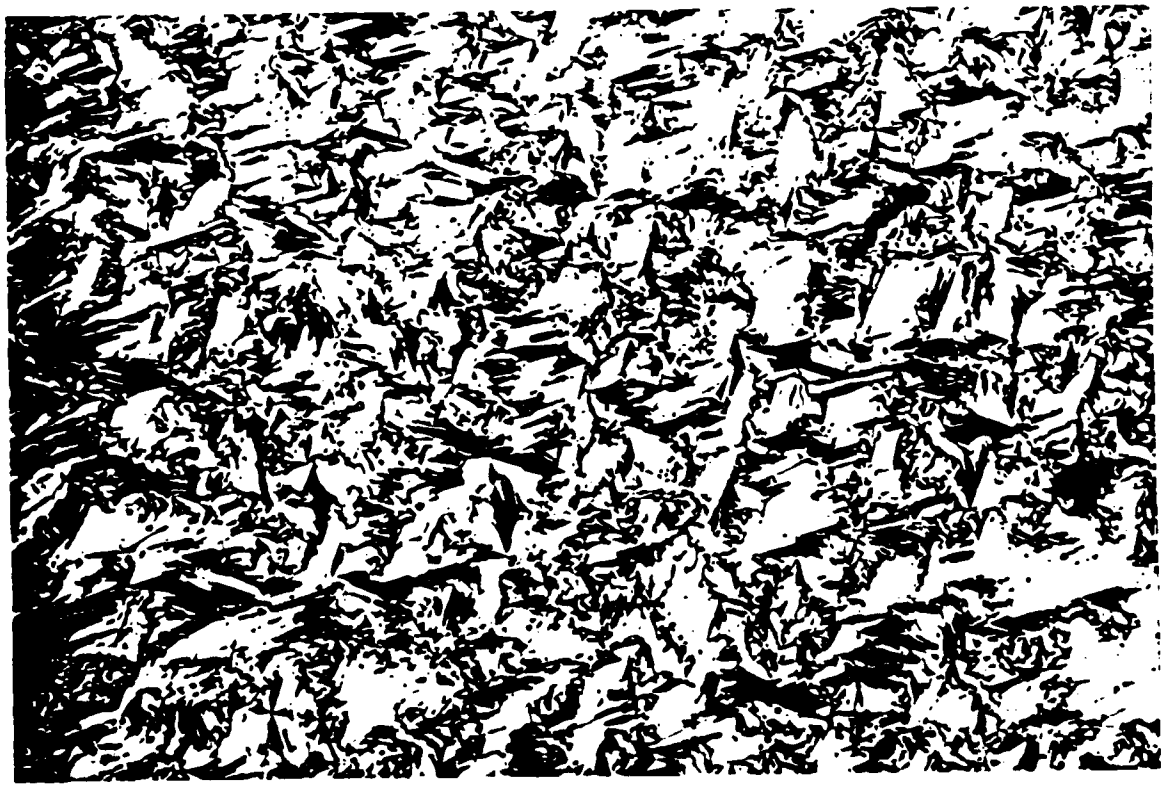


Figure 7b

Figure 7c

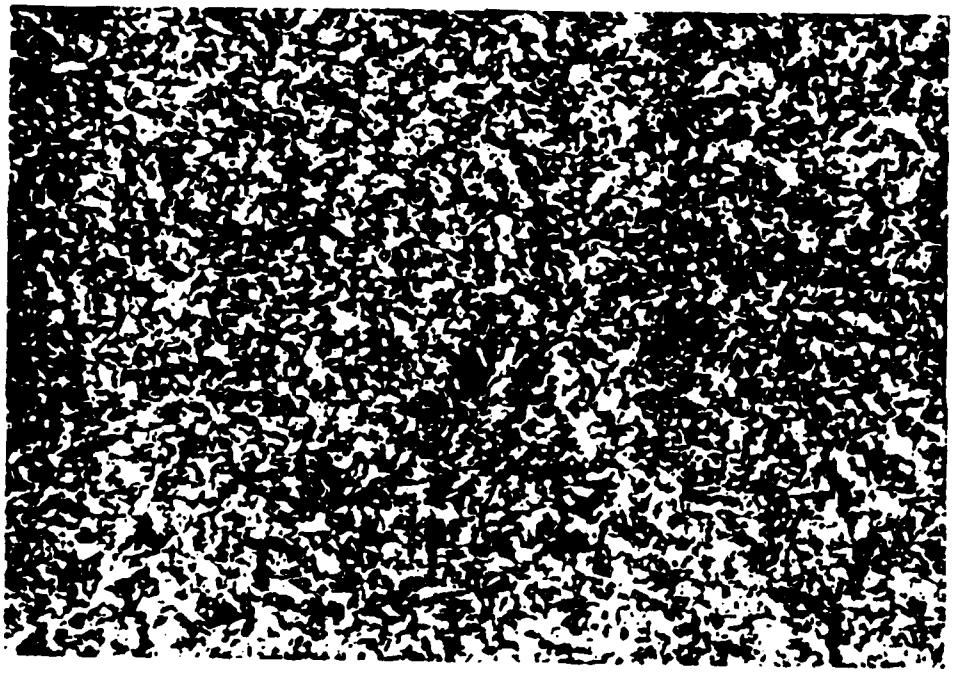


Figure 7d

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The synthesis and living cationic polymerization of 11-[(4-cyano-4'-biphenyl)oxy]undecanyl vinyl ether (6-11) are described. The mesomorphic phase behavior of poly(6-11) with different degrees of polymerization was compared to that of 6-11 and of 11[(4-cyano-4'-biphenyl)oxy]undecanyl ethyl ether (8-11) which is the model compound of the monomeric structural unit of poly(6-11). 6-11 displays a monotropic S_A and a monotropic nematic mesophase while 8-11 an enantiotropic S_A mesophase. Poly(6-11) with low degrees of polymerization exhibits an enantiotropic S_A mesophase. Poly(6-8) with high degrees of polymerization displays an enantiotropic S_X (i.e., an unidentified smectic phase) and an enantiotropic S_C mesophase. These results demonstrate that the transformation of the nematic mesophase of the monomer into a smectic mesophase after polymerization, occurs at the level of monomeric structural unit.

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Molecular Engineering of Liquid Crystal Polymers by Living Polymerization. 2. Living Cationic Polymerization of 11-[(4-Cyano-4'-biphenyl)oxy]undecanyl Vinyl Ether and the Mesomorphic Behavior of the Resulting Polymers

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Molecular Engineering of Liquid Crystal Polymers by Living Polymerization. 2.* Living Cationic Polymerization of 11-[(4-Cyano-4'-biphenyl)oxy]undecanyl Vinyl Ether and the Mesomorphic Behavior of the Resulting Polymers

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SYNOPSIS

The synthesis and living cationic polymerization of 11-[(4-cyano-4'-biphenyl)oxy]undecanyl vinyl ether (6-11) are described. The mesomorphic phase behavior of poly(6-11) with different degrees of polymerization was compared to that of 6-11 and of 11[(4-cyano-4'-biphenyl)oxy]undecanyl ethyl ether (8-11) which is the model compound of the monomeric structural unit of poly(6-11). 6-11 displays a monotropic s_A and a monotropic nematic mesophase while 8-11 an enantiotropic s_A mesophase. Poly(6-11) with low degrees of polymerization exhibits an enantiotropic s_A mesophase. Poly(6-8) with high degrees of polymerization displays an enantiotropic s_X (i.e., an unidentified smectic phase) and an enantiotropic s_C mesophase. These results demonstrate that the transformation of the nematic mesophase of the monomer into a smectic mesophase after polymerization, occurs at the level of monomeric structural unit.

INTRODUCTION

The mechanism by which the polymer molecular weight influences the phase behavior of side chain liquid crystalline polymers (LCP) represents an open subject of discussion .[1-10] The molecular weight-phase transition dependence is the first factor which should be elucidated before a molecular design of side chain LCP can be accomplished. So far, the only trend which is generally accepted consists of the enlargement of the temperature range of the mesophase with the increase of the polymer molecular weight. [1-10]

This dependence was recently explained based on thermodynamic principles assuming that the phase behavior of the polymer is dictated by that of the monomeric structural unit. However, there is only a single experiment in the literature which compares the phase behavior of a polymer with different molecular weights to that of its monomeric structural unit.[7] When the mesophases of the monomeric unit and of the polymers are identical , the overal dependence of phase transitions on molecular weight could be explained.[11,12] The least understood situation refers to polymers which display various mesophases at different molecular weights.[4,7,9-10] Elucidation of this phenomenon requires the synthesis of polymers with well defined molecular weights, narrow molecular weight distributions as well as of their model compounds. So far, side

chain liquid crystalline polymers with narrow molecular weight distribution were prepared by group transfer polymerization of mesogenic methacrylates,[7] by cationic polymerization of mesogenic vinyl and propenyl ethers,[8-10,13,14] and by polymer homologous reactions.[15]

This paper will present a novel and general procedure for the preparation of mesogenic vinyl ethers containing two or more than two methylenic units in the flexible spacer. Then it will describe the living cationic polymerization of 11-[(4-cyano-4'-biphenyl)oxy]undecanyl vinyl ether, and the mesomorphic behavior of the resulting polymers with different molecular weights. Finally, the phase behavior of these polymers will be compared to that of 11-[(4-cyano-4'-biphenyl)oxy]undecanyl ethyl ether which represents the model for the monomeric structural unit of poly{11-[(4-cyano-4'-biphenyl)oxy]undecanyl vinyl ether}.

EXPERIMENTAL

Materials

4-Phenylphenol (98%), 1,10-phenanthroline (anhydrous, 99%), palladium(II)acetate (all from Lancaster Synthesis), ferric chloride anhydrous (98%, Fluka), copper (I) cyanide (99%), 11-bromoundecan-1-ol (98%), n-butyl vinyl ether (98%), 9-borabicyclo[3.3.1]-nonane (9-BBN dimer, crystalline, 98%) and the other reagents (all from Aldrich) were used as received. Methyl sulfide (anhydrous, 99%, Aldrich) was refluxed over 9-BBN and then distilled under argon. Dichloromethane (99.6%, Aldrich) used as a polymerization solvent was first washed with concentrated sulfuric acid, then with water, dried over anhydrous $MgSO_4$, refluxed over calcium hydride and freshly distilled under argon before each use. N-Methyl-pyrrolidinone (98%, Lancaster Synthesis) was dried by azeotropic distillation with benzene, shaken with barium oxide, filtered, and fractionally distilled under reduced pressure. Trifluoromethanesulfonic acid (triflic acid, 98%, Aldrich) was distilled under argon.

Techniques

^{1}H-NMR (200 MHz) spectra were recorded on a Varian XL-200 spectrometer. TMS was used as internal standard. A Perkin-Elmer DSC-4 differential scanning calorimeter, equipped with a TADS data station was used to determine the thermal transitions which were reported as the maxima and minima of their endothermic or exothermic peaks respectively. In all cases, heating and cooling rates were 20^{o}C/min unless otherwise specified. Glass transition temperatures (Tg) were read at the middle

of the change in the heat capacity. First heating scans differ from second and subsequent heating scans. However, second and subsequent heating scans are identical. A Carl-Zeiss optical polarized microscope (magnification: 100x) equipped with a Mettler FP 82 hot stage and a Mettler FP 800 central processor was used to observe the thermal transitions and to analyze the anisotropic textures .[15,16] Molecular weights were determined by gel permeation chromatography (GPC) with a Perkin-Elmer Series 10 LC instrument equipped with LC-100 column oven, LC-600 autosampler and a Nelson Analytical 900 series integrator data station. The measurements were made at 40°C using the UV detector. A set of Perkin Elmer PL gel columns of 10^4 and 500 Å with $CHCl_3$ as solvent (1ml/min.) and a calibration plott constructed with polystyrene standards was used to determine the molecular weights. High pressure liquid chromatography experiments were performed with the same instrument.

Synthesis of Monomers

Scheme I outlines the general methods used in the synthesis of vinyl ethers.

1,10-Phenanthroline Palladium (II) Diacetate (9)

1,10-Phenanthroline palladium (II) diacetate was synthesized according to a literature procedure.[17] mp 220°C (lit. 17, mp 234°C).

4-Phenylphenol Acetate (2)

To a mixture of 70g (0.41 mol) of 4-phenylphenol in 77.4 ml (0.82 mol) of acetic anhydride were added a few drops of concentrated H_2SO_4. The resulting solution was stirred at 60°C for 1 hr, cooled to room temperature, diluted with 300 ml of cold water and left stirring overnight. The resulting white crystals were filtered, washed with cold water, dried and recrystallized from ethanol to yield 87.2 g (92%) of 2. Purity: 98% (HPLC). mp 86-87°C. ^{1}H-NMR ($CDCl_3$, TMS, δ, ppm): 2.32 (3 protons, $OCOCH_3$, s), 7.15 (2 aromatic protons, o to acetoxy, d), 7.44-7.58 (7 aromatic protons, m).

4-Acetoxy-4'-Bromobiphenyl (3)

Trifluoroacetic anhydride (14.2 ml, 0.1 mol) and $FeCl_3$ (0.2 g, 1.23 mmol) were added sequentially to an ice cooled solution of 4-phenyl phenol acetate (21.2 g, 0.1 mol) in 400 ml of dry CCl_4. Bromine (16 g, 0.1 mol) was dropwise added and the reaction mixture was stirred at 0°C for 7 hr and at room temperature for other 7 hr. The CCl_4 was removed in a rotavapor and the resulting solid was washed with methanol and recrystallized from n-hexane to yield 20.5 g (66.8%) of white crystals. Purity: 99%

(HPLC). mp 128-130°C (lit. 19, 20, mp 130°C). ^{1}H-NMR ($CDCl_3$, TMS, δ, ppm): 2.32 (3 protons, $OCOCH_3$, s), 7.18 (2 aromatic protons, o to acetoxy, d), 7.44-7.53 (2 aromatic protons, m to acetoxy, and 4 aromatic protons, o and m to Br, m).

4-Bromo-4'-Hydroxybiphenyl (4)

4-Acetoxy-4'-bromobiphenyl (20.5 g, 0.07 mol) was hydrolized by refluxing for 2 hr with a solution of 20 g NaOH in 400 ml of 80% aqueous ethanol. The ethanol was removed on a rotavapor and the obtained solid was dissolved in distilled water. The water solution was neutralized with dilute hydrochloric acid and the obtained solid was filtered, dried and recrystallized from a mixture of ethanol/water (3/2) to yield 16.5 g (94.6%). Purity: 98% (HPLC). mp 165-167°C (lit. 20, mp 196-199°C). ^{1}H-NMR (Acetone-d_6, TMS, δ, ppm) : 4.8 (1 proton, -OH, s), 6.95 (2 aromatic protons, o to -OH, d), 7.49-7.55 (2 aromatic protons, m to -OH , and 4 aromatic protons, o and m to Br, m).

4-Cyano-4'-Hydroxybiphenyl (5)

A mixture of 4-bromo-4'-hydroxybiphenyl (20 g, 0.08 mol) and CuCN (10 g, 0.11 mol) in dry N-methyl-2-pyrrolidone (68 ml) was refluxed for 6 hr. After cooling, the reaction mixture was poured into a mixture of hydrated ferric chloride (31.7 g), concentrated hydrochloric acid (8 ml), and water (47 ml), and the resulting mixture was stirred at 60°C for 20 min. The mixture was extracted with chloroform, and the chloroform solution was succesivelly washed with 5N hydrcchloric acid, 10% aqueous sodium bicarbonate, water and dried over anhydrous magnesium sulfate. The chloroform was removed in a rotavapor, the obtained solid was dissolved in a minimum volume of hot acetone and sufficient petroleum ether was added to produce turbidity. The solution was refrigerated and the crystalline product was filtered, dried and recrystallized several times from toluene to yield 11.8 g (75.3%) of 4-cyano-4'-hydroxybiphenyl. Purity: 99% (HPLC). mp 195-198°C (lit. 20, mp 196-199°C). ^{1}H-NMR (Acetone-d_6, TMS, δ, ppm): 3.80 (1 proton, -OH, s), 7.61 (2 aromatic protons, o to hydroxy, d), 7.61 (2 aromatic protons, o to hydroxy, d), 7.61 (2 aromatic protons, m to -OH, d), 7.79 (4 aromatic protons, o and m to -CN, s).

4-Cyano-4'-(11-Hydroxyundecan-1-yloxy)biphenyl (7-11)

4-Cyano-4'-hydroxybiphenyl (15.7 g, 0.08 mol), potassium hydroxide (4.5 g, 0.08 mol) and few crystals of potassium iodide were dissolved in a mixture of ethanol-water (4:1) (440 ml). 11-Bromoundecan-1-ol (22.6 g, 0.09 mol) was added to the

resulting solution which was heated to reflux for 24 hr. The ethanol was removed on a rotavapor and the resulting solid was washed succesively with water, dilute aqueous NaOH and water. Recrystallization from methanol yielded 22.7 (78%) of white crystals. mp 92°C (DSC). ^{1}H-NMR ($CDCl_3$, TMS, δ, ppm): 1.01-1.95 (18 protons, -$(CH_2)_9$-, m), 7.02 (2 aromatic protons, o to alkoxy, d), 7.51 (2 aromatic protons, m to alkoxy, d), 7.68 (4 aromatic protons, o and m to -CN, d of d).

11-[(4-Cyano-4'-Biphenyl)oxy]undecanyl Vinyl Ether (6-11)

4-Cyano-4'-(11-hydroxyundecan-1-yloxy)biphenyl (3.9 g, 0.01 mol) was added to a mixture of 1,10-phenanthroline palladium (II) diacetate (0.4 g, 1 mmol), n-butyl vinyl ether (15 ml) and dry chloroform (3.85 ml). The mixture was heated at 60°C for 6 hr. After cooling and filtration (to remove the catalyst) the solvent was distilled in a rotavapor and the product was purified by column chromatography (silica gel, CH_2Cl_2 eluent) to yield 3.8 g (91%) of white crystals. Purity: 99% (HPLC). mp 71°C (DSC). ^{1}H-NMR ($CDCl_3$, TMS, δ, ppm): 1.01-1.95 (18 protons, -$(CH_2)_9$-, m), 3.68 (2 protons, -CH_2O-, t), 4.01 (3 protons, -OCH=CH_2 trans, and $PhOCH_2$-, m), 4.15 and 4.22 (1 proton, OCH=CH_2 cis, d), 6.47 (1 proton, OCH=CH_2, q), 7.01 (2 aromatic protons, o to alkoxy, d), 7.51 (2 aromatic protons, m to alkoxy, d), 7.66 (4 aromatic protons, o and m to -CN, d of d).

11-Bromoundecanyl Vinyl Ether

11-Bromoundecan-1-ol (2 g, 7.96 mmol) was added to a mixture of 1,10-phenanthroline palladium (II) diacetate (0.32 g, 0.8 mmol), n-butyl vinyl ether (42.5 ml) and chloroform (10 ml). The mixture was heated at 60°C for 6 hr. After cooling and filtration (to remove the catalyst) the solvent was distilled in a rotavapor and the product was purified by column chromatography (silica gel, methylene chloride eluent) to yield 1.96 g (89%) of a liquid. ^{1}H-NMR ($CDCl_3$, TMS, δ, ppm) : 1.0-2.1 (18 protons, -$(CH_2)_9$-, m), 3.45 (2 protons, -CH_2Br, t), 3.71 (2 protons, -CH_2O-, t), 4.03 (1 proton, -OCH=CH_2 trans, d), 4.20 (1 proton, -OCH=CH_2 cis, d), 6.57 (1 proton, -OCH=CH_2, q).

Synthesis of 6-11 by the Etherification of 5 with 11-Bromoundecanyl Vinyl Ether

6-11 was also synthesized by the etherification of 5 with 11-bromoundecanyl vinyl ether, by following the synthetic procedure used for the preparation of 7-11. The purification of 6-11 was performed as in its previous synthesis. Yield: 60%.

11-[(4-Cyano-4'-Biphenyl)oxy]undecanyl Ethyl Ether (8-11)

4-Cyano-4'-hydroxybiphenyl (3.9 g, 0.01 mol) was added to a solution containing potassium t-butoxide (1.12 g, 0.01 mol), 18-crown-6 (2.6 mg, 0.01 mmol) and dry tetrahydrofuran (78 ml). Diethyl sulfate (1.54 g, 0.01 mol) was added and the reaction mixture was refluxed for 3 hr. After cooling, the reaction mixture was extracted with chloroform, washed with water, dried over magnesium sulfate and the chloroform was removed in a rotavapor. The resulting product was purified by column chromatography (silica gel, methylene chloride eluent) to yield 2.43 g (62%) of white crystals. Purity: 99% (HPLC). mp 51.0°C, s_A-i 60.1°C (DSC). ^{1}H-NMR ($CDCl_3$, TMS, δ, ppm): 1.20 (3 protons, -$OCH_2C\underline{H}_3$, t), 1.30-1.81 (18 protons, -$(CH_2)_9$-, m), 3.41 (4 protons, -$C\underline{H}_2OC\underline{H}_2$-, m), 4.00 (2 protons, -$C\underline{H}_2OPh$, t), 7.01 (2 aromatic protons, o to alkoxy, d), 7.51 (2 aromatic protons, o and m to -CN, d of d).

Cationic Polymerizations

Cationic polymerizations were performed in glass flasks equipped with teflon stopcocks and rubber septa under argon atmosphere at 0°C for 1 hr. All glassware was dried overnight at 130°C. The monomer was further dried under vacuum overnight in the polymerization flask. Then the flask was filled with argon, cooled to 0°C, and the requested amounts of methylene chloride, dimethyl sulfide and triflic acid were added via a syringe. The monomer concentration was about 10 wt% from the volume of solvent and the dimethyl sulfide concentration was 10 times larger than that of the initiator. The polymer molecular weight was controlled by the monomer/initiator ratio. At the end of the polymerization the reaction mixture was precipitated into methanol containing few drops of NH_4OH. The filtered polymers were dried and reprecipitated from methylene chloride solution into methanol until GPC traces showed no traces of unreacted monomer. Table I summarizes the polymerization results.

RESULTS AND DISCUSSION

The synthesis of 11-[(4-cyano-4'-biphenyl)oxy]undecanyl vinyl ether (6-11) and of 11-[(4-cyano-4'-biphenyl)oxy]undecanyl ethyl ether (8-11) which represents the model compound of the monomeric structural unit of poly(6-11) is outlined in Scheme I. 6-11 was synthesized both by the transetherification of 7-11 with n-butyl vinyl ether and by etherification of 5 with 11-bromoundecanyl vinyl ether. The novel part of this synthesis consists of the transetherification of 4-cyano-4'-(11-hydroxyundecan-1-yloxy)biphenyl (7-11) and of 11-bromoundecan-1-ol with n-

butyl vinyl ether in the presence of 1,10-phenanthroline palladium (II) diacetate (9). The vinyl interchange reaction between vinyl ethers and alcohols catalyzed by 9 can be performed under mild reaction conditions.[18,21] Experiments performed in our laboratory have demonstrated that this reaction tolerates a variety of functional groups. Therefore, this reaction can be used in the synthesis of vinyl ethers containing mesogenic groups attached through various spacer lengths. Previously, mesogenic vinyl ethers were synthesized by the phase transfer catalyzed etherification of a mesogenic phenol with chloroethyl vinyl ether.[8-10,13,22] This procedure allowed the preparation of monomers containing only two methylenic units in the flexible spacer. 1,10-Phenanthroline palladium (II) diacetate was also used to catalyze the transetherification of ω-bromoalkan-1-ols with n-butyl vinyl ether. The synthesis of 11-bromoundecanyl vinyl ether by this reaction, followed by the alkylation of 5 with 11-bromoundecanyl vinyl ether was also used in the preparation of 6-11.

As shown previously,[8-10,14,15,23-25] living cationic polymerization of vinyl ethers tolerates a variety of functional groups. We prefer to perform this polymerization with triflic acid/dimethyl sulfide initiator system, since under these conditions the polymerization can be carried out in methylene chloride at 0°C.[26] Scheme II outlines the polymerization mechanism. The resulting polymers contain acetal chain ends and therefore, they should be manipulated in the absence of acids.

Table I summarizes the polymerizatuion results. All polymers display narrow molecular weight distribution and their degrees of polymerization are almost equal to the theoretical values which are equal to $[M]_o/[I]_o$. Figure 1 presents the GPC traces of these polymers. Figure 2 presents the plotts of the dependences of the number average molecular weight (M_n) and of M_w/M_n versus the ratio between the initial monomer and initiator concentrations $[M]_o/[I]_o$. This figure demonstrates the living character of this polymerization.

The DSC traces of 4-cyano-4'-(11-hydroxyundecan-1-yloxy)biphenyl (7-11), 11-[(4 -cyano-4'-biphenyl)oxy]undecanyl vinyl ether (6-11) and of 11-[(4-cyano-4'-biphenyl)oxy]undecanyl ethyl ether (8-11) are presented in Figure 3. 7-11 displays a monotropic nematic mesophase. The transition from this nematic phase to the isotropic phase was determined by reheating the sample in the DSC instrument from a temperature which is above the crystallization temperature. 6-11 presents a monotropic nematic and a monotropic s_A phase. The parameters of these two phase transitions from the heating scans were obtained by reheating the sample before it reached the crystallization temperature. 8-11 presents an enantiotropic s_A mesophase.

Table II summarizes all the thermal transitions and their corresponding thermodynamic parameters.

Figure 4a,b,c displays the first and second heating and the cooling DSC scans of all polymers. In the first heating scan all polymers display a crystalline melting followed by a s_A phase (Figure 4a). In the second and subsequent heating scans only poly(6-11) with a degree of polymerization 2.9 presents a melting transition followed by a s_A phase. Polymers with degrees of polymerization from 4.4 to 14.7 show only the s_A phase while polymers with higher degrees of polymerization display a s_X (i.e., an unidentified smectic phase) and a s_A mesophase (Figure 4b). On the cooling DSC scans (Figure 4c) we observe the crystallization peak only in the case of the lowest molecular weight polymer (degree of polymerization 2.9). The onset of the s_X phase formation from the cooling DSC scans can be observed only for the polymers with degrees of polymerization from 19.5 to 30.6. The formation of this s_X phase continues on the heating scan. The uncovering of the s_X phase is due to the very low rate of crystallization. Nevertheless , under proper annealing conditions all these polymers crystallize again. Consequently, under equilibrium conditions, the s_X phase of poly(6-11) is only monotropic. Therefore, the kinetically controlled crystallization process influences the relative thermodynamic stability of various mesophases. This effect was observed previously for other polymer samples.[7] All these results are summarized in Table I.

Figure 5a plotts the dependence between the various phase transition temperatures collected from the first and second heating scans and the degree of polymerization of poly(6-11). The data for the model compound of the monomeric structural unit, 8-11, which corresponds to a degree of polymerization equal to one , are also included. The thermal transition temperatures collected from the cooling scan are plotted in Figure 5a. Both the enlargement of the range of temperature of the s_A phase with the increase of the degree of polymerization, and the formation of the s_X mesophase above a certain degree of polymerization are in agreement with theoretical predictions.[11,12] That is, the mesophase of the polymer is identical to that of the monomeric structural unit. This assumes that the monomeric unit should also display a virtual s_A mesophase.

It is generally accepted[1] that the polymerization of a mesogenic monomer which displays a nematic mesophase frequently leads to a polymer which displays a smectic mesophase. This is the case with the monomer 6-11 which displays a monotropic nematic and a monotropic s_A mesophase while poly(6-11) exhibits only a s_A mesophase. However, as previously mentioned[7] we believe that it is not correct to compare the mesophase displayed by polymer only with the mesophase displayed by the model compound which corresponds to the monomeric structural unit. Under these

circumstances, both the model of the monomeric structural unit 8-11 and the poly(6-11) display a s_A mesophase.

Several representative textures displayed by the s_A and s_X mesophases of poly(6-11) are presented in Figure 6.

Figure 7 plotts the dependence of the peak width of the s_A-isotropic transition peak versus the degree of polymerization of poly(6-11). The peak width decreases with increasing the degree of polymerization as can be qualitatively observed from the DSC traces from Figure 4a,b,c. This result agrees with that obtained on an other polymer displaying a smectic mesophase .[6]

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25. T. Higashimura and M. Sawamoto, in "Comprehensive Polymer Science", Vol.3, G. Allen and J. Bevington Eds., Pergamon Press, Oxford, 1989, p.684
26. B. A. Feit, C. G. Cho and O. W. Webster, 9th International Symposium on Cationic Polymerization and Related Ionic Processes, Strasbourg, June 5-9, 1989, Abstracts, p. 59

FIGURE CAPTIONS

Figure 1: GPC traces of poly(6-11). The degrees of polymerization of each sample are printed on the figure.

FIGURE 2: The dependence of the number average molecular weight (M_n) and of the polydispersity (M_w/M_n) of poly(6-11) on the $[M]_o/[I]_o$ ratio.

FIGURE 3: Heating and cooling DSC traces of 7-11 (a, b), 6-11 (c, d) and 8-11 (e, f).

FIGURE 4: DSC traces displayed during the first heating scan (a), second heating scan (b) and first cooling scan (c) by poly(6-11) with different degrees of polymerization (DP). DP is printed on the top of each DSC scan.

FIGURE 5: The dependence of phase transition temperatures on the degree of polymerization of poly(6-11). DP=1 corresponds to 8-11. Data from first heating (fh) and second heating (sh) scans are presented in Figure 5a. □ -Tk-s_A(fh); ○ -Tg(fh);△ -Ts$_A$-i(fh); • -Tk-s_A(sh); ● -Tg(sh);■ -Ts$_C$-s_A(sh);▲-Ts$_A$-i(sh). Data from the cooling scan are presented in Figure 5b. ■ -Ti-s_A;◆-Ts$_A$-k;▲-Ts$_A$-s_X;● -Tg.

FIGURE 6: Representative optical polarized micrographs (100x) of poly(6-11) with DP=30.6: a)the s_A displayed at 148°C; b) the s_X displayed at 30°C.

FIGURE 7: The dependence of the peak width△T(°C) of the s_A-I phase transition temperature versus the degree of polymerization of poly(6-11):□ -first heating scan;△ -second heating scan;● -cooling scan.

SCHEME CAPTIONS

Scheme I: Synthesis of Monomers and Model Compounds.

Scheme II: The Mechanism of Living Cationic Polymerization.

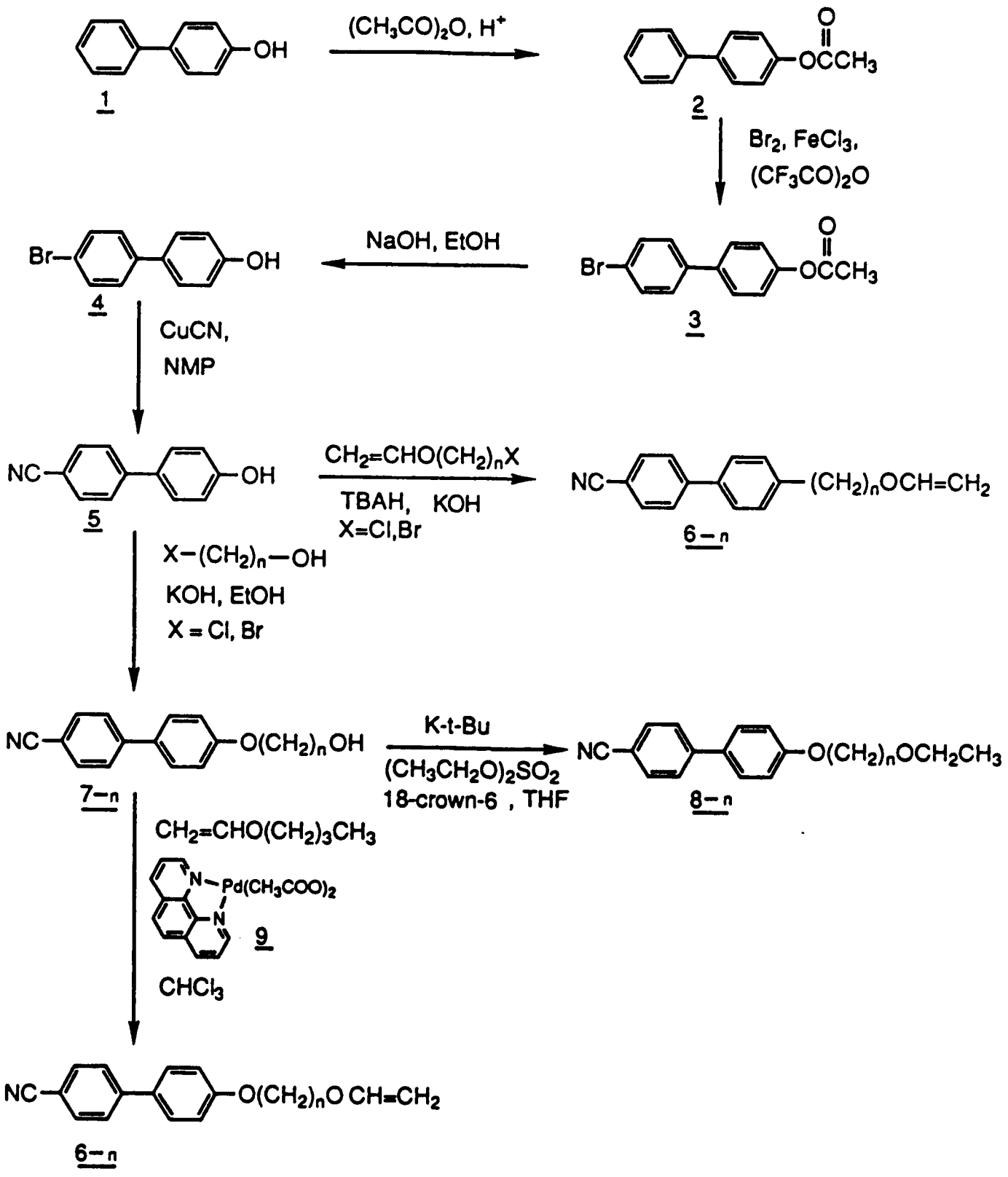
Table I. Cationic Polymerization of 11-[(4-cyano-4'-biphenyl) oxy]undecanyl Vinyl Ether (6-11) (polymerization temperature, 0^{o} C; polymerization solvent,methylene chloride; $[M]_o$=0.255M; $[(CH_3)_2S]_0/[I]_0$=10; polymerization time,1hr) and Characterization of the Resulting Polymers

Sample No.	$[M]_o/[I]_o$	Polymer Yield (%)	GPC			phase transitions (^{o}C) and corresponding enthalpy changes (kcal/mru)	
			Mn x 10^{-3}	Mw/Mn	DP	heating	cooling
1	3.0	75	1.16	1.04	2.9	k 50.1(3.75) s_A 96.4 (0.65)i g 3.6 k 67.1(3.05) s_A 90.2 (0.60) i	i 85.4(0.65) s_A 31.7 k-1.7 g
2	4.0	75	1.72	1.04	4.4	g 8.2 k 53.3 (3.33) s_A 108.3 (0.83) i g-0.10 s_A 106.5 (0.74) i	i 103.7 (0.81) s_A 0.2 g
3	7.0	71	2.72	1.08	6.9	g 12.5 k 59.7 (3.34) s_A 133.5 (0.81) i g 9.1 s_A 125.8 (0.75) i	i 115.1 (0.69) s_A 2.0 g
4	15.0	75	5.74	1.05	14.7	g 17.0 k 66.3 (3.29) s_A 155.2 (0.82) i g 14.7 s_A 150.1 (0.77) i	i 141.4 (0.78) s_A 8.3 g
5	20.0	72	7.65	1.09	19.5	g 16.0 k 65.2 (2.95) s_A 159.9 (0.82) i g 14.9 s_X 50.7 (1.68) s_A 148.7 (0.70) i	i 142.3 (0.74) s_A 19.7(0.70) s_X 9.1 g
6	25.0	81	9.83	1.04	25.1	g 19.8 k 66.0 (3.31) s_A 155.0 (0.80) i g 14.7 s_X 50.0 (0.48) s_A 146.8 (0.70) i	i 141.0 (0.78) s_A 15.0 (0.29) s_X 9.7 g
7	30.0	78	11.97	1.10	30.6	g 21.3 k 66.5 (2.76) s_A 164.9 (0.77) i g 16.7 s_X51.6 (1.03) s_A 160.8 (0.71) i	i 155.7 (0.72) s_A 19.5 (0.42) s_X11.4 g

Table II. Thermal Characterization of 4-Cyano-4'-(11-hydroxyundecan-1-yloxy)phenyl (7-11),11-[(4-Cyano-4'-biphenyl)oxy]undecanyl Vinyl Ether (6-11) and of 11-[(4-Cyano-4'-biphenyl)oxy]undecanyl Ethyl Ether (8-11).

Compound	phase transitions (°C) and corresponding enthalpy changes (kcal/mru)	
	heating	cooling
7-11	k 92.0 (12.4) [n 95.2 (0.46)]* i	i 92.3 (0.49) n 77.0 (9.36) k
6-11	k 71.3 (11.10)[s_A 60.8 (0.29) n 70.6(0.32)]* i	i 58.9 (0.55) n 54.2 s_A 39.7 (0.55) k
8-11	k 51.0 (9.80) s_A 60.1 (0.74) i	i 56.8 (0.72) s_A 27.2 (8.72) k

*[ ] virtual transitions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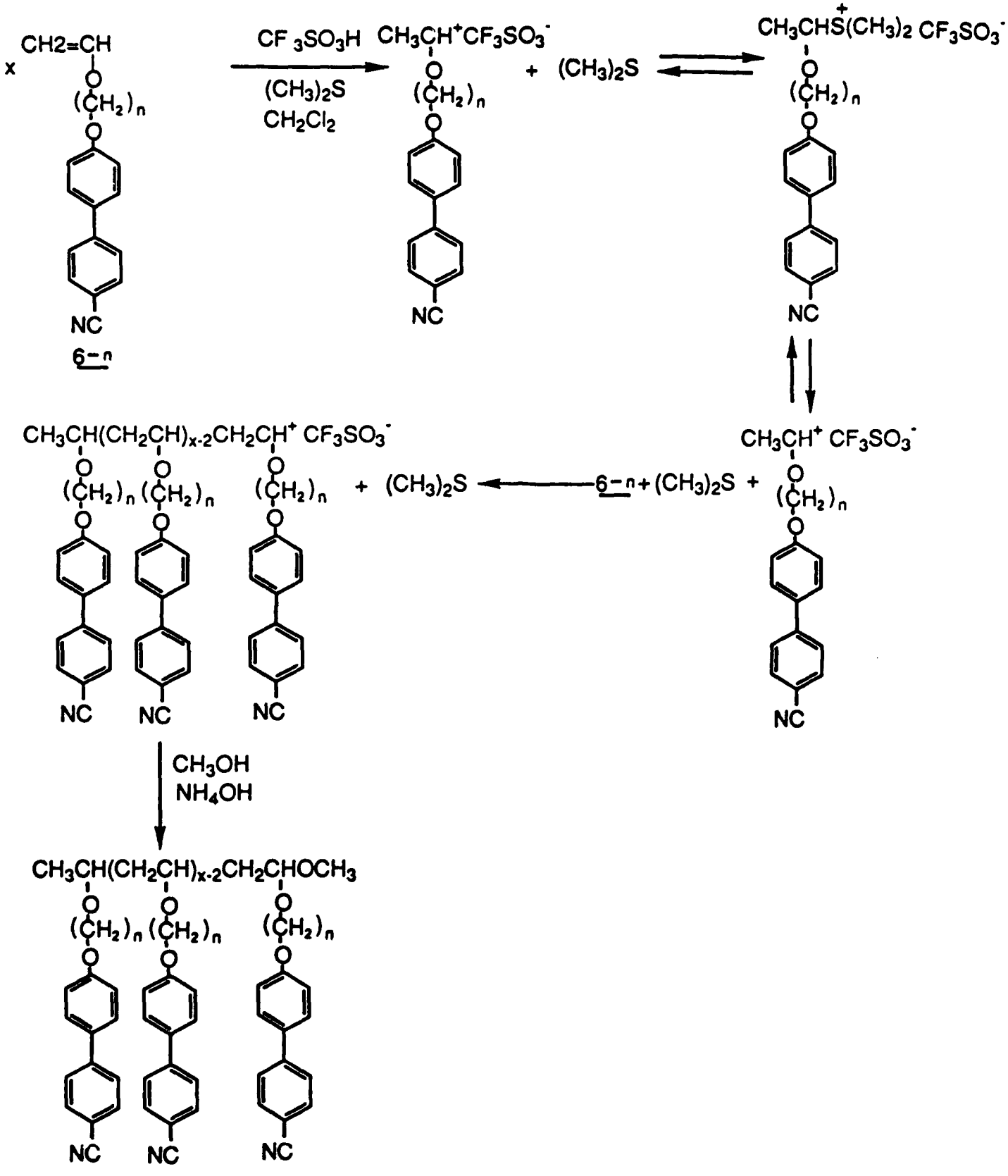
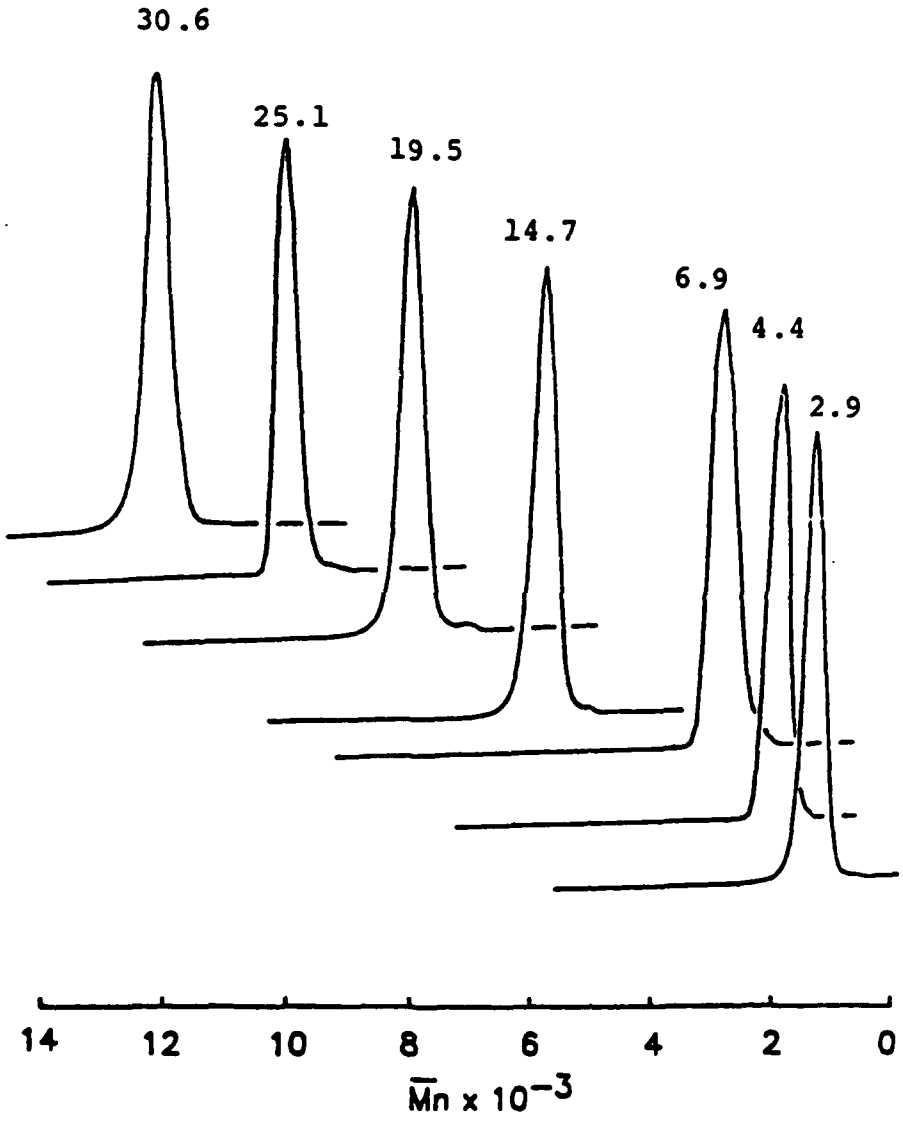
OH
1
OCCH3
O
2
Br2, FeCl3,
(CF3CO)2O
NaOH, EtOH
Br
OH
4
3
CuCN,
NMP
NC
OH
5
CH2=CHO(CH2)nX
TBAH, KOH
X=Cl,Br
6–n
X–(CH2)n–OH
KOH, EtOH
X = Cl, Br
O(CH2)nOH
7–n
K-t-Bu
(CH3CH2O)2SO2
18-crown-6 , THF
O(CH2)nOCH2CH3
8–n
CH2=CHO(CH2)3CH3
N–Pd(CH3COO)2
N
9
CHCl3
O(CH2)nO CH=CH2
6–n

Scheme I


CH2=CH
x
(CH2)n
NC
6-n
CF3SO3H
(CH3)2S
CH2Cl2
CH3CH+CF3SO3-
(CH3)2S
CH3CHS+(CH3)2 CF3SO3-
CH3CH+ CF3SO3-
6-n + (CH3)2S
CH3CH(CH2CH)x-2CH2CH+ CF3SO3-
CH3OH
NH4OH
CH3CH(CH2CH)x-2CH2CHOCH3

Scheme II



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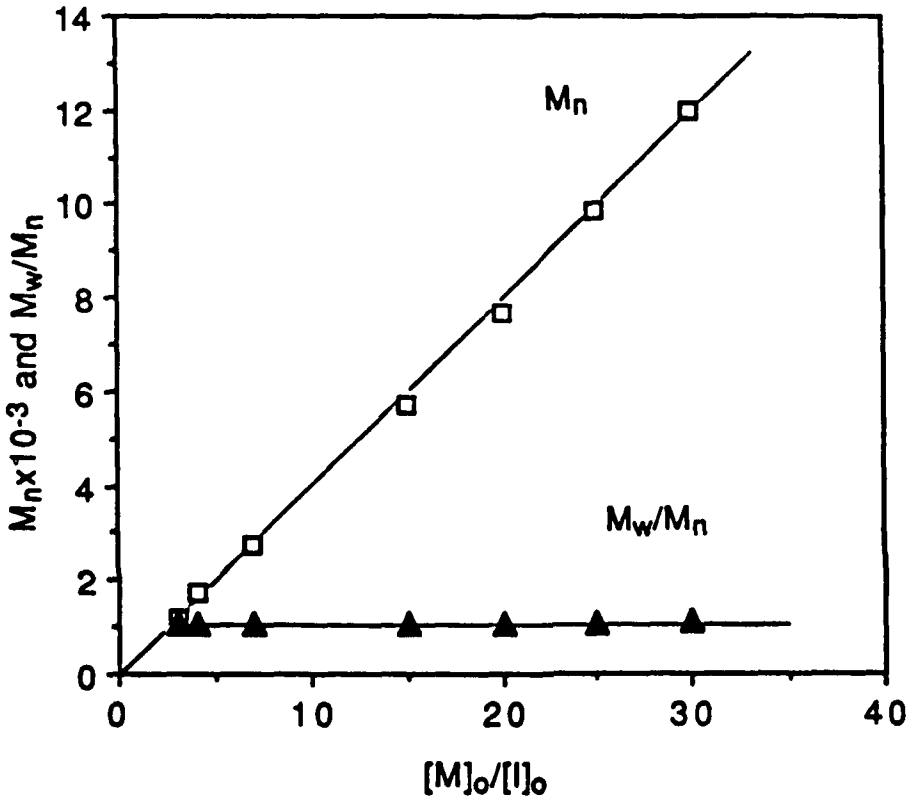

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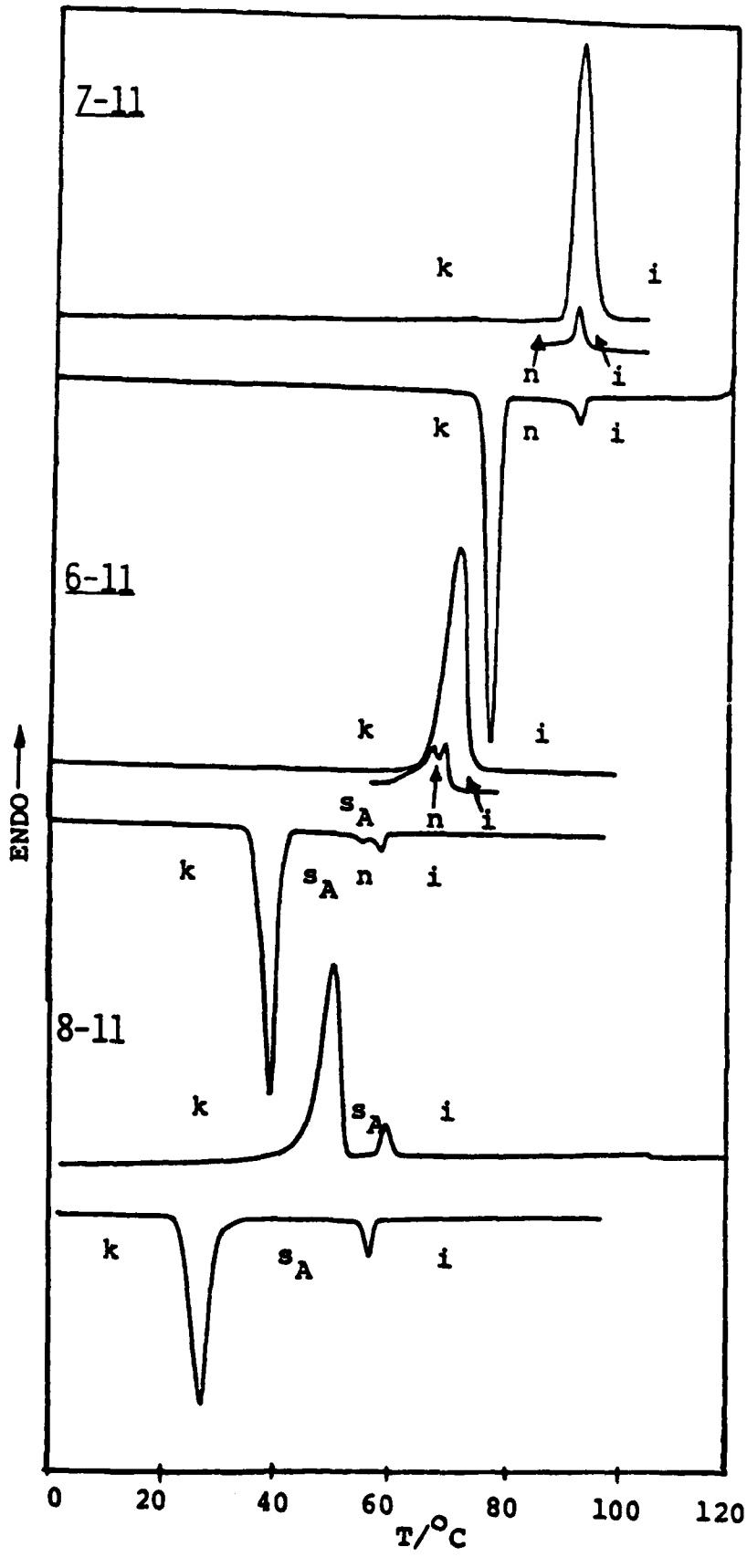
Z-11
k
i
n
i
k
n
i
6-11
k
i
s_A
n
i
ENDO
k
s_A
n
i
8-11
k
s_A
i
k
s_A
i
0
20
40
60
80
100
120
T/°C

Figure 3

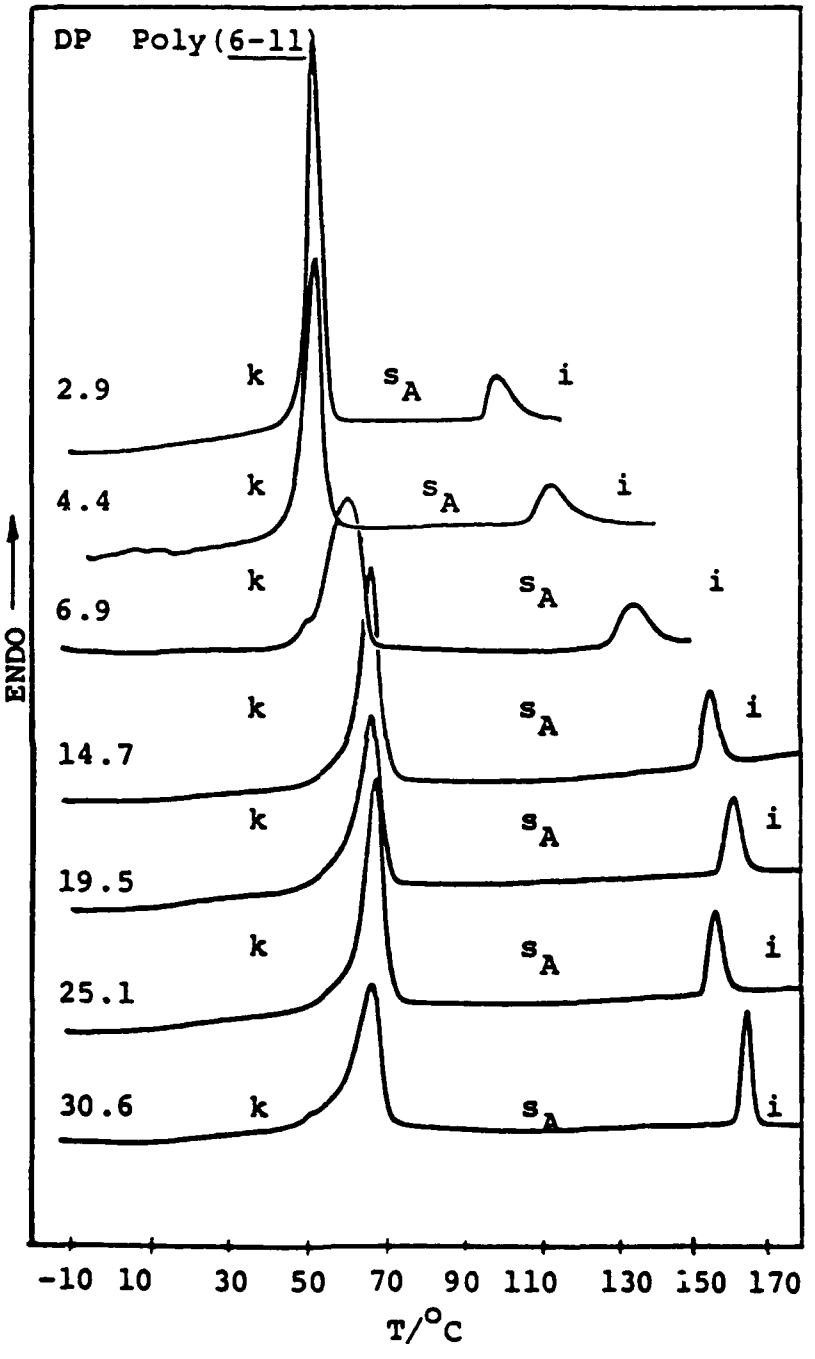
DP Poly(6-11)
2.9
4.4
6.9
14.7
19.5
25.1
30.6
k
s_A
i
ENDO
-10 10 30 50 70 90 110 130 150 170
T/°C

Figure 4a

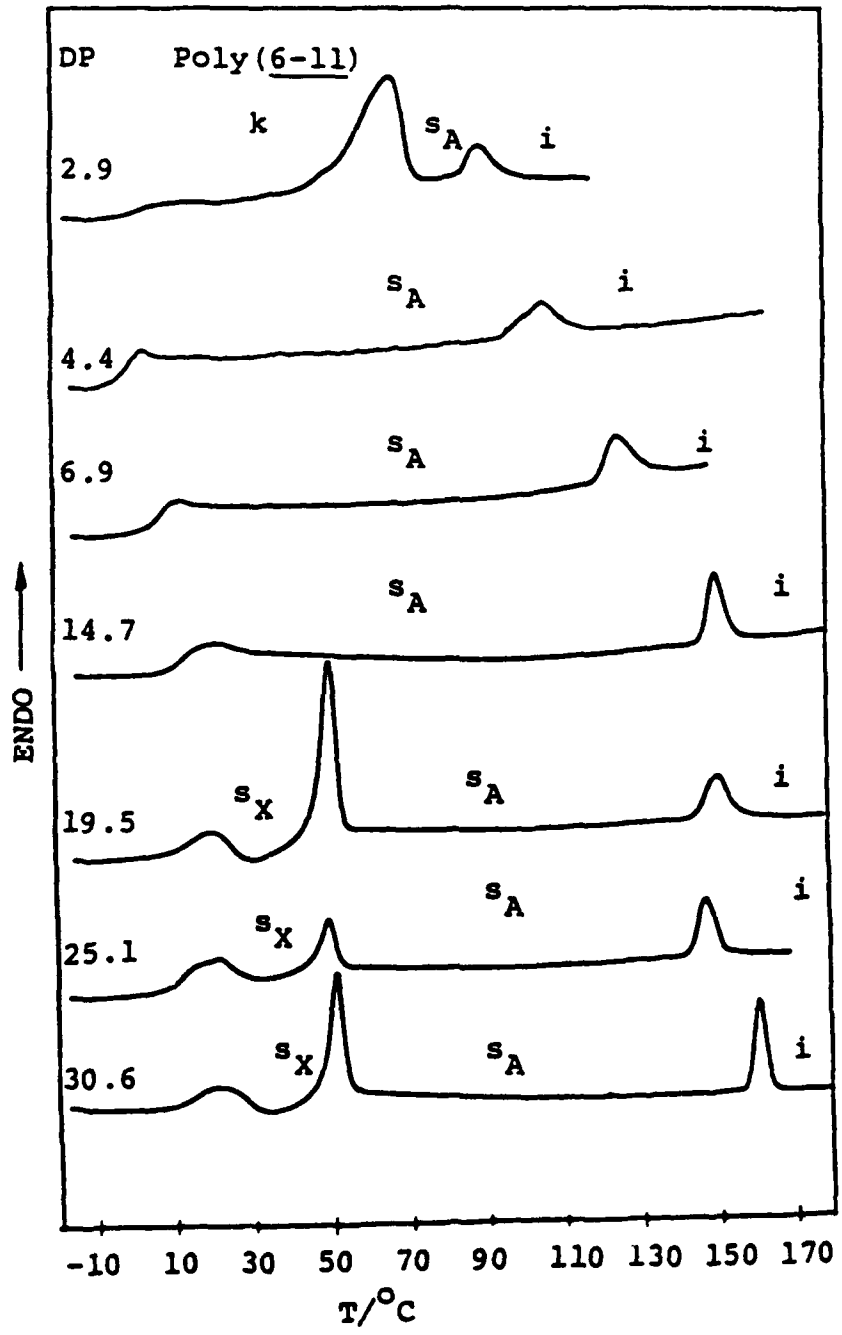
DP
Poly(6-11)
2.9
k
S_A
i
4.4
S_A
i
6.9
S_A
i
14.7
S_A
i
19.5
S_X
S_A
i
25.1
S_X
S_A
i
30.6
S_X
S_A
i
ENDO
-10
10
30
50
70
90
110
130
150
170
T/°C

Figure 4b

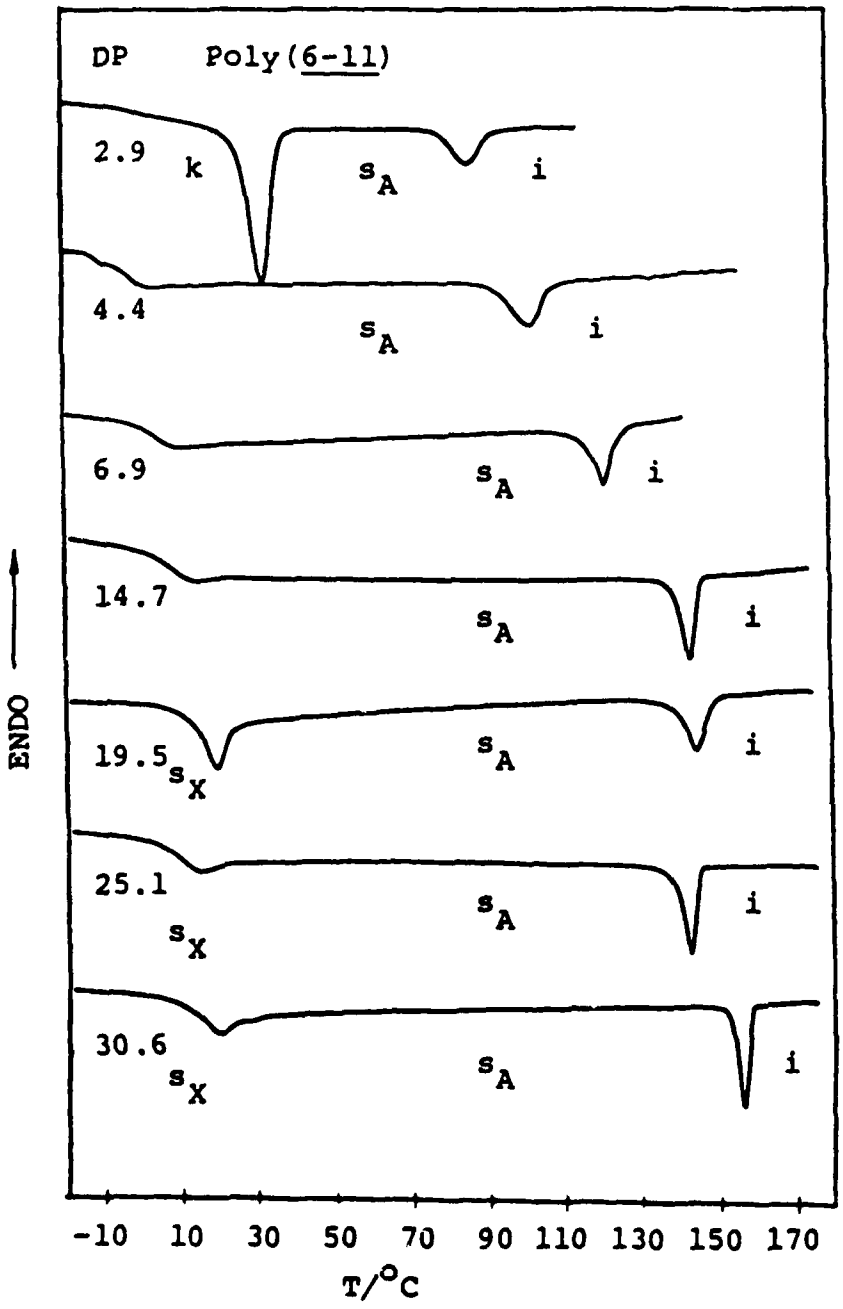
DP
Poly(6-11)
2.9
k
s_A
i
4.4
s_A
i
6.9
s_A
i
14.7
s_A
i
19.5
s_X
s_A
i
25.1
s_X
s_A
i
30.6
s_X
s_A
i
ENDO
-10
10
30
50
70
90
110
130
150
170
T/°C

Figure 4c

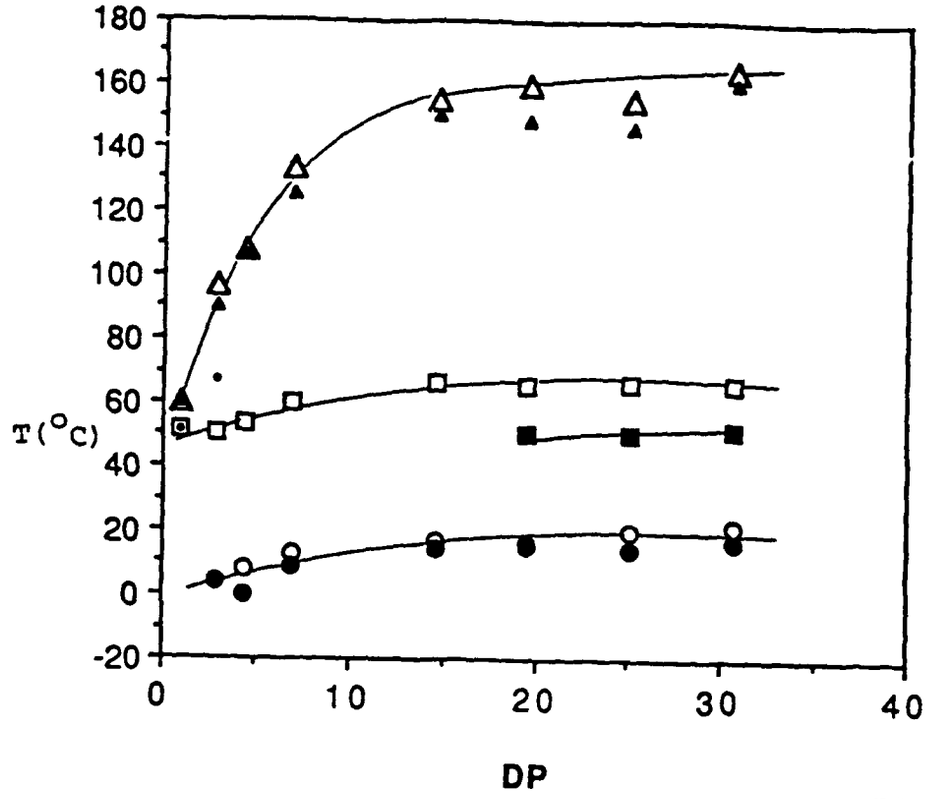

Figure 5a

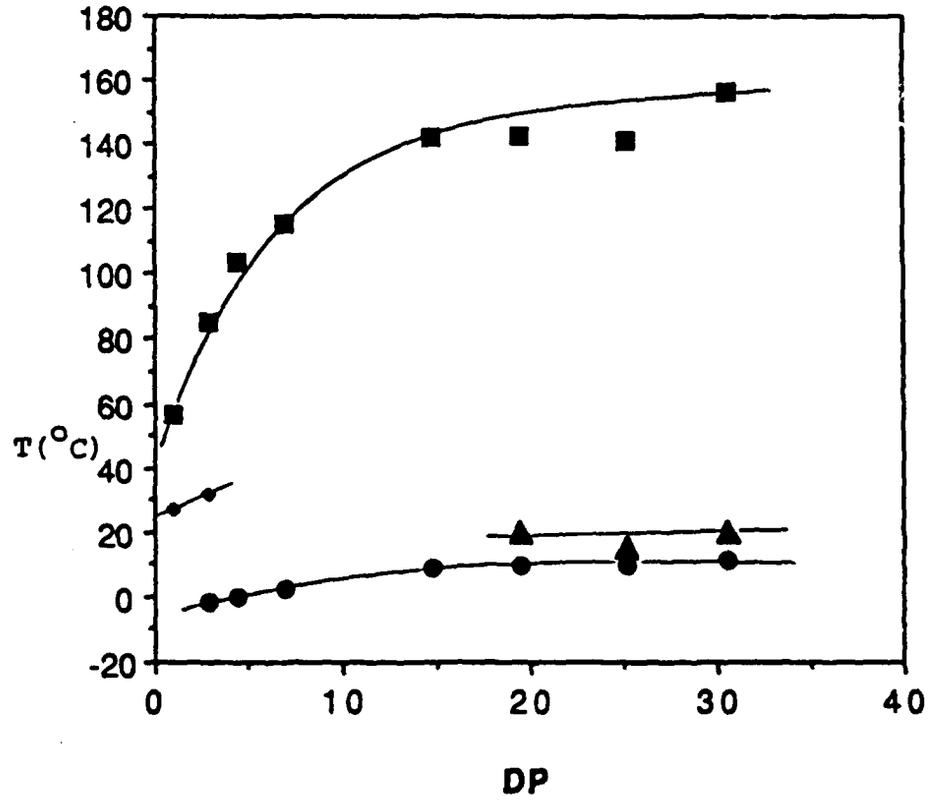

Figure 5b

Figure 6a

Figure 6b

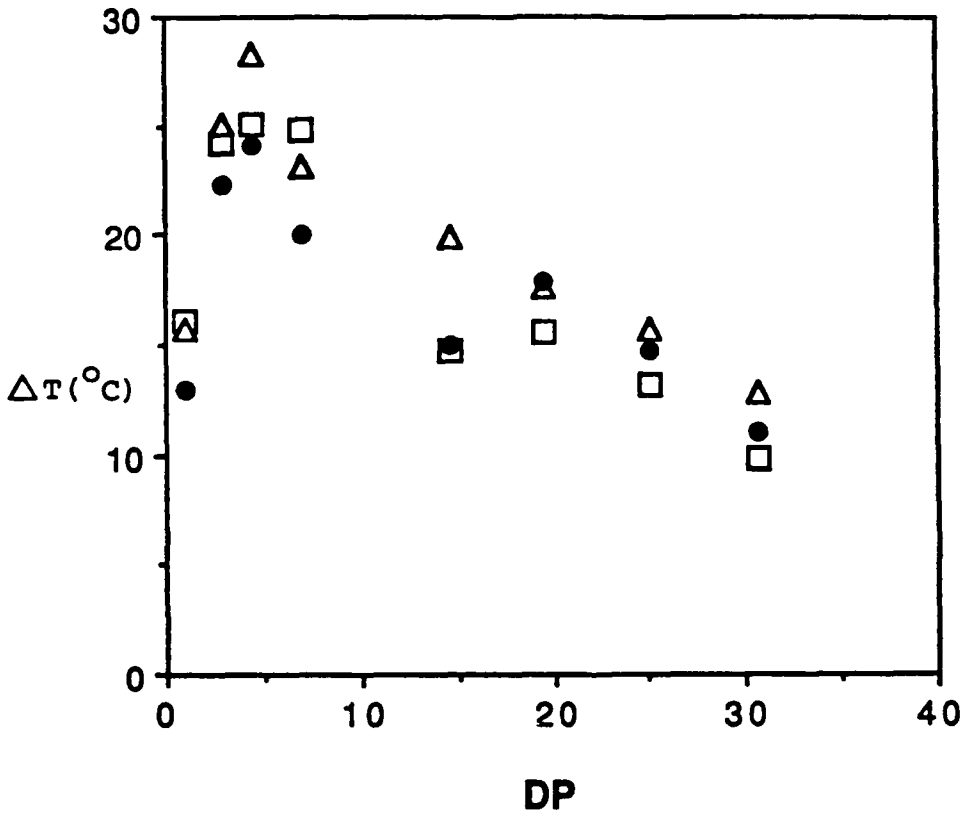

Figure 7

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The synthesis and characterization of the alkene monomer and the corresponding poly(methylsiloxane) containing 4-(11-undecan-1-yloxy)-4-[3,4,5-tri(p-n-dodecan-1-yloxybenzyloxy)benzoate]biphenyl side groups is presented.

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Liquid Crystalline Polymers Containing Mesogenic Units Based on Half-Disc and Rod-like Moieties. 1. Synthesis and Characterization of 4-(11-Undecan-1-yloxy)-4'-[3,4,5-tri(p-n-Dodecan-1-yloxybenzyloxy)benzoate]Biphenyl Side Groups

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Cleveland, OH 44106

INTRODUCTION

The concept of mesogenic unit based on combinations of disc-like and rod-like moieties was advanced by Chandrasekhar[1] as an architectural approach to the synthesis of biaxial nematic (N_b) liquid crystals. Although the first examples of lyotropic N_b were reported by Yu and Saupe in 1980[2], the first examples of monotropic biaxial nematic liquid crystals were reported by Malthete et all[3] and by Chandrasekhar et all[4]. These liquid crystals were obtained by synthesizing molecules which contain various combinations of half-disc or disc-like and rod-like moieties. Alternatively, the interconnection of two half-discs with a rod-like molecule can lead to either phasmidic[5-9] (i.e.,Φ_{ob} and Φ_h), or N_b[10] mesophases. Polymers displaying biaxial nematic liquid crystalline mesophases were synthesized so far by using a paralell attachement of the rod-like mesogens to the polymer backbone.[11,12] While our research was in progress,[13] Ringsdorf et all[14] have reported the first examples of liquid crystalline polymers containing phasmidic mesogens.

The goal of this paper is to report the synthesis and characterization of a poly(methylsiloxane) containing 4-(11-undecan-1-yloxy)-4-[3,4,5-tri(p-n-dodecan-1-yloxybenzyloxy)benzoate]biphenyl side groups.

EXPERIMENTAL

Materials

All materials were of commercial source and were used as received or purified as it will be reported at the proper place in the paper.

Techniques

The techniques used in the characterization of intermediary derivatives and polymers (200 MHz ^{1}H-NMR, IR, DSC, GPC, HPLC, thermal optical polarized microscopy) were described elsewhere.[15,16]

Monomers and Polymers

Schemes I and II outline the synthesis of monomers and polymers.

p-(n-Dodecan-1-yloxy)Benzaldehyde (3)

A solution of p-hydroxybenzaldehyde (10.0g, 0.082 mol) (recrystallized from water), anhydrous K_2C0_3 (11.87g, 0.086 mol), 1-bromododecane (21.42g, 0.086 mol) and 250 ml acetone was refluxed under nitrogen for 23 hr. Acetone was distilled in a rotavapor and

the residue was dissolved in chloroform. The chloroform solution was filtered, dried over anhydrous $MgSO_4$, filtered and the solvent was evaporated to yield 23.0g (97%) of gold-like viscous liquid. Purity, 97% (HPLC). ^{1}H-NMR ($CDCl_3$, TMS, δ, ppm): 0.88 (t, 3H, -CH_3), 1.22 (m, 18H, -$(CH_2)_9$-), 1.79 (m, 2H, -CH_2-CH_2-O-Ar), 4.00 (t, 2H, -CH_2-O-Ar), 6.97 (d, 2H, meta OHC-Ar-H), 7.77 (d, 2H, ortho OHC-Ar-H), 9.83 (s, 1H, -CHO). IR (KBr plate): 1685 cm^{-1} (νCO), 2720 cm^{-1} (νCHO).

p-(n-Dodecan-1-yloxy)Benzyl Alcohol (4)

To a solution of 3 (25.04g, 0.087 mol) in 600 ml of methanol was added dropwise 50 ml of a solution containing 3.42g (0.090 mol) of $NaBH_4$ in 50 ml of 0.45N aqueous NaOH. The reaction mixture was allowed to stir for 24 hr at room temperature after which it was poured into water. The resulting precipitate was filtered, washed with water, dried, and recrystallized three times from hexane to yield 22.45g (89%) of white crystals. Purity, 91% (HPLC). mp, 66°C. ^{1}H-NMR ($CDCl_3$, TMS, δ, ppm): 0.88 (t, 3H, -CH_3), 1.26 (m, 18H, -$(CH_2)_9$-), 1.85 (m, 2H, -CH_2-CH_2-O-Ar), 3.94 (t, 2H, -CH_2-O-Ar), 4.61 (d, 2H, -Ar-CH_2-OH), 6.87 (d, 2H, meta HO-CH_2-Ar-H), 7.32 (d, 2H, ortho HO-CH_2-Ar-H). IR (KBr plate): 3180-3500 cm-1 (ν-OH). ν-CHO and ν-C=O are absent.

p-(n-Dodecan-1-yloxy)Benzyl Chloride (5)

To a solution of 28.66g (0.098 mol) of 4 in 200 ml of dry CH_2Cl_2 was added dropwise under stirring 14.5g (0.123 mol) of $SOCl_2$. The reaction was stirred for 2 hr at room temperature. Then it was washed with water, 2% aqueous $NaHCO_3$, water, dried over anhydrous $MgSO_4$, filtered, and the solvent was distilled in a rotavapor to yield 28.4g (93%) of a white solid. Purity, 97% (HPLC). mp, 36°C. ^{1}H-NMR ($CDCl_3$, TMS, δ, ppm): 0.88 (t, 3H, -CH_3), 1.28 (m, 18H, -$(CH_2)_9$-), 1.85 (m, 2H, -CH_2-CH_2-O-Ar), 3.94 (t, 2H, -CH_2-O-Ar), 4.56 (s, 2H, -CH_2-Cl), 6.88 (d, 2H, meta Cl-CH_2-Ar-H), 7.27 (d, 2H, ortho Cl-CH_2-Ar-H). IR (KBr plate): ν-OH is absent.

3,4,5-Tri[p-(n-Dodecan-1-yloxy)Benzyloxy]Benzoic Acid (8)

A reaction mixture containing 37.05g (0.119 mol) of 5, 7.0g (0.038 mol) of methyl-3,4,5-trihydroxybenzoate, 53g (0.3841 mol) anhydrous K_2CO_3 and 300 ml of dry DMF was purged with nitrogen and then heated to 80°C under nitrogen with stirring for 18 hr. The resulting mixture was poured into water and the precipitate was filtered and recrystallized twice from ethanol. The resulting product was refluxed for 3 hr with 200 ml of a solution of 6N KOH in ethanol. The reaction mixture was poured into water, acidified with dilute HCl and the precipitate was filtered. The resulting solid was redissolved in chloroform containing 5% methanol and acidified with dilute HCl. Water was added until two layers were obtained. The organic layer was separated and washed with water, dried over anhydrous $MgSO_4$, filtered and the chloroform was distilled in a rotavapor. The

resulting solid was purified by column chromatography (silica gel, chloroform containing 5% methanol as eluent), and then it was recrystallized twice from isopropyl alcohol containing 10% methanol to yield 21.51g (57%) of white crystals. Purity: 95% (HPLC). Phase transitions are reported in Table I. ^{1}H-NMR ($CDCl_3$, TMS, δ, ppm): 0.88 (t, 9H, -CH_3), 1.27 (m, 54H, -$(CH_2)_9$-), 1.79 (m, 6H, -CH_2-CH_2-O-Ar), 3.96 (two overlapped t, 6H, -CH_2-O-Ar), 5.02 (s, 2H, -CH_2-O-Ar-COOH from para position of benzoic group), 5.05 (s, 4H, -CH_2-O-Ar-COOH from 3 and 5 positions of benzoic group), 6.75 (d, 2H, -O-Ar-H-CH_2.O-Ar-COOH from 3 and 5 positions of central benzylic unit), 6.89 (d, 4H, -O-Ar-H-CH_2-O-Ar-COOH from 3 and 5 positions of external benzylic units), 7.26 (d, 2H, -O-Ar-H-CH_2-O-Ar-COOH from the 2 and 6 positions of the internal benzylic unit), 7.31 (d, 4H, -O-Ar-H-CH_2-O-Ar-COOH from the 2 and 6 positions of the external benzylic units), 7.42 (s, 2H, -Ar-H-COOH 2 and 6 positions). IR (KBr plate): 1670 cm-1 (ν-C=O).

10-Undecen-1-ol (10)

Into a three neck flask equipped with condenser and drying tube containing 500 ml of dry THF and 12.63g (0.41 mol) of $LiAlH_4$, was added dropwise a solution of 100g (0.54 mol) 10-undecenoic acid in 100 ml of dry THF. After the addition was complete, the reaction mixture was refluxed for 16 hr and then cooled to room temperature. Water was dropwise added to the reaction mixture, followed by a solution of 50/50 (V/V) H_2O/HCl until it became acidic, and the mixture was separated into two layers. The organic layer was washed with water, dried over anhydrous $MgSO_4$, filtered and the solvent was evaporated in a rotavapor to yield 72.6g (79%) of a clear liquid.^{1}H-NMR ($CDCl_3$, TMS, δ, ppm): 1.27 (m, 12H, -$(CH_2)_6$-), 1.58 (m, 2H, -CH_2-CH_2-OH), 2.05 (m, 2H, -CH_2-CH=CH_2), 2.20 (s, 1H, -OH), 3.64 (t, 2H, -CH_2-OH), 4.95 (d, 1H, CH_2=CH-CH_2- trans), 5.03 (d, 1H, CH_2=CH-CH_2- cis), 5.84 (m, 1H, =CH-CH_2-).

10-Undecen-1-yl Tosylate (12)

To a reaction mixture containing 25.94g (0.152 mol) 10, 12.7 ml (0.157 mol) pyridine (distilled from KOH) and 30 ml of dry CH_2Cl_2 was added 32g (0.167 mol) of p-toluenesulfonyl chloride and the mixture was stirred for 18 hr at room temperature. Water (5 ml) was added and the mixture was stirred for 24 hr. Methylene chloride was evaporated in a rotavapor. Enough THF and water were added until the reaction mixture separated into two layers. The organic layer was separated, washed with water, dried over anhydrous $MgSO_4$, filtered, and the solvent was evaporated. The resulting liquid was passed through a chromatographic column (basic alumina, THF eluent) to yield 45.31g (92%) of a gold-colored liquid. ^{1}H-NMR ($CDCl_3$, TMS, δ, ppm): 1.22 (m, 12, -$(CH_2)_6$-), 1.62 (m, 2H, -CH_2-CH_2-O-), 2.01 (m, 2H, -CH_2-CH=CH_2), 2.44 (s, 3H, -CH_3), 4.01 (t, 2H, -CH_2-O-), 4.92 (d, 1H, H_2C=CH-CH_2- trans), 4.98 (d, 1H, H_2C=CH-CH_2- cis), 5.78 (m, 1H, -

CH_2-C<u>H</u>=), 7.32 (d, 2H, CH_3-<u>H</u>-Ar-SO_2- 3 and 5 positions from -SO2-), 7.76 (d, 2H, CH_3-Ar-<u>H</u>-SO_2- 2 and 6 positions from -SO_2-).

<u>4-(10-Undecen-1-yloxy)-4'-Hydroxybiphenyl (13)</u>

A mixture containing 7.70g (41.4 mmol) 4,4'-dihydroxybiphenyl, 2.54g (42.3 mmol) KOH and 100 ml methanol was refluxed for 0.5 hr. To the resulting solution was added 13.43g (41.4 mmol) of <u>12</u> and the reaction mixture was refluxed for 16 hr. The reaction mixture was filtered while hot and the filtrate was cooled to 0°C and maintained for 6 hr. The separated solid was filtered, washed with water and recrystallized twice from methanol to yield 5.03g (36%) of white crystals. Purity: 99% (HPLC). Phase transitions are reported in Table I. ^{1}H-NMR ($CDCl_3$, TMS, δ, ppm): 1.36 (m, 12H, -($C\underline{H}_2$)$_6$-), 1.85 (m, 2H, -$C\underline{H}_2$-O-Ar-), 2.09 (m, 2H, -$C\underline{H}_2$-CH=CH_2), 4.04 (t, 2H, -$C\underline{H}_2$-O-Ar-), 4.76 (s, 1H, -O<u>H</u>), 4.96(d, 1H, $\underline{H}_2$C=CH=CH_2- trans), 5.04 (d, 1H, $\underline{H}_2$C=CH-CH_2- cis), 5.87 (m, 1H, -C<u>H</u>=CH_2), 6.90 (d, 2H, HO-Ar-<u>H</u>- ortho from -OH), 7.00 (d, 2H, -CH_2-O-<u>H</u>-Ar- ortho from alkoxy), 7.42-7.62 (m, 4H, biphenyl meta from -O-).

<u>4-(10-Undecen-1-yloxy)-4'-{3,4,5-tri[p-(n-Dodecan-1-yloxy)benzyloxy]Benzoate}Biphenyl (14)</u>

A solution containing 1.0g (1.0 mmol) of <u>8</u>, 0.34g (1.0 mmol) of <u>13</u>, 1.0g (4.8 mmol) of dicyclohexylcarbodiimide and 1.0g (8.2 mmol) 4-dimethylaminopyridine in 30 ml of dry CH_2Cl_2 was stirred at room temperature for 18 hr. The resulting precipitate was filtered and the methylene chloride was evaporated in a rotavapor. Hexane was added to the resulting residue. The hexane solution was filtered, the solvent was evaporated and the resulting compound was dissolved in methylene chloride, washed with water and the solvent was again evaporated. The product was dissolved in a mixture of $CHCl_3$/CH_3OH (20/1) and precipitated in methanol. The precipitate was filtered, dissolved in chloroform and precipitated into a mixture of methanol/water (20/1). The precipitate was filtered, dried, and purified by column chromatography (basic alumina, CH_2Cl_2 eluent). The solvent was evaporated to yield 0.43g (32%) of white solid. Purity: 99% (HPLC). Phase transitions are reported in Table I.^{1}H-NMR ($CDCl_3$, TMS, δ, ppm): 0.88 (t, 9H, -$C\underline{H}_3$), 1.05-1.50 (m, 66H, -$C\underline{H}_2$-), 1.79 (m, 8H, -$C\underline{H}_2$-CH_2-O-Ar-), 2.05 (m, 2H, CH_2=CH-$C\underline{H}_2$-), 3.96 (m, 8H, -CH_2-$C\underline{H}_2$-O-Ar-), 4.96 (m, 2H, $C\underline{H}_2$=CH-), 5.05 (s, 2H, -$C\underline{H}_2$-O-Ar-COO- from para position), 5.09 (s, 4H, -$C\underline{H}_2$-O-Ar-COO- from 3 and 5 positions), 6.75 (d, 2H, -O-<u>H</u>-Ar-CH_2- from 3 and 5 positions of internal benzylic units), 6.90 (d, 4H, -O-<u>H</u>-Ar-CH_2-O-Ar-COO- 3 and 5 positions of external benzyl units) , 6.97 (d, 2H, -CH_2-O-Ar-<u>H</u>-Ar- ortho from -CH_2O-), 7.23 (d, 2H, -COO-Ar-<u>H</u>-Ar- ortho from -COO-), 7.27 (d, 2H, -Ar-<u>H</u>-CH_2-O-Ar-COO- ortho from -CH_2- of internal benzylic unit), 7.34 (d, 4H, -Ar-<u>H</u>-CH_2-O-Ar-COO- ortho from -CH_2- of external benzylic units), 7.50-7.59 (m, 4H,

biphenyl meta from -O-), 7.52 (s, 2H, -O-Ar-H-COO- ortho from -COO-). IR (KBr plate): 1730 cm^{-1} (ν-C=O).

Poly(methylsiloxane) Containing 4-(11-Undecan-1-yloxy)-4'-{3,4,5-tri[p-(n-Dodecan-1-yloxy)Benzyloxy]Benzoate}Biphenyl Side Groups (15)

To a flame dried 5 ml test tube containing a microstirring bar were added 0.5g (0.38 mmol) of 14, 0.023g (0.38 mmol) poly(hydrogenmethylsiloxane) (Mn=1500 from Petrarch), 2 ml dry toluene and three drops (about 0.06g) of platinum divinyltetramethyl disiloxane complex (from Petrarch). The reaction was purged with nitrogen and the tube was sealed with a cork stopper covered with teflon tape. The reaction mixture was heated for 24 hr at 60°C, cooled and precipitated into methanol. The precipitate was filtered, dissolved in 50 ml THF and acetone (about 400-500 ml) was dropwise added to the THF solution until the solution became cloudy. The turbid solution was allowed to stir 30 to 60 min during which time the polymer precipitated. The precipitate was filtered to yield 0.16g (32%) of white solid. Purity: 99% (HPLC). Mn=37000, Mw/Mn=1.7 (GPC with polystyrene standards).

RESULTS AND DISCUSSION

The synthesis of the intermediary compounds and of the polymer are described in Schemes I and II. Although most of the reaction steps do not require unusual synthetic procedures, the synthetic methods and the purification techniques presented in the experimental part are essential in obtaining compounds 8, 13, 14 and 15 of high purity. The mesomorphic phase behavior of 14 and 15 of lower purities than 99% differs drastically from that reported in this paper since all impurities present in these compounds consist of intermediary derivatives which display various liquid crystalline phases. Since most of these liquid crystalline phases are nonisomorphic they give rise to additional transition peaks. Alternatively, when their mesophases are isomorphic the phase transition of the studied derivative is different from that of the pure compound.

Representative DSC traces of compounds 8, 13, 14 and 15 are presented in Figure 1. The phase transition temperatures and the corresponding thermodynamic parameters of all these derivatives are summarized in Table I. Depending on the sample history (i.e., precipitation from various solvent-nonsolvent mixtures, or crystallized from various solvents), 8 displays one or more than one melting transitions followed by a hexagonal columnar mesophase which undergoes isotropization at 149°C.[9] Precipitation from various solvents or annealing under different thermal conditions can change the number of melting transitions from one to up to three. The isotropization temperature is only slightly affected

by this process. Figure 2a displays a typical fan-shaped texture displayed by 8. The columnar mesophase of 8 is realized through the dimerization of 8 through the hydrogen bonding of its carboxylic group.[9] 13 exhibits a highly ordered enantiotropic smectic phase (Figures 1 and 2). 14 displays a monotropic phasmidic mesophase. This phase transition can be observed also on the heating DSC scan when the polymer sample is reheated from above the crystallization temperature (Figure 1, Table I). This mesophase exhibits a fan-shaped texture which is characteristic of a Φ_{ob} or Φ_h phase.[5] Representative DSC traces of 15 are presented in Figure 1. Both on heating and on cooling scans 15 displays a glass transition temperature followed by a mesophase which undergoes isotropization at a temperature which is about 100°C higher than that of the corresponding monomer (149°C for 15 and 51.5°C for 14). A very small and broad melting endotherm can be observed at about 103°C only on the heating scan of 15. The fan-shaped texture of the polymer 15 (Figure 2c) resemble the one exhibited by the monomer 14. Therefore, 15 may also display either a Φ_{ob} or Φ_h mesophase. Structural studies on the definitive identification of the liquid crystalline mesophase displayed by 15 are in progress.

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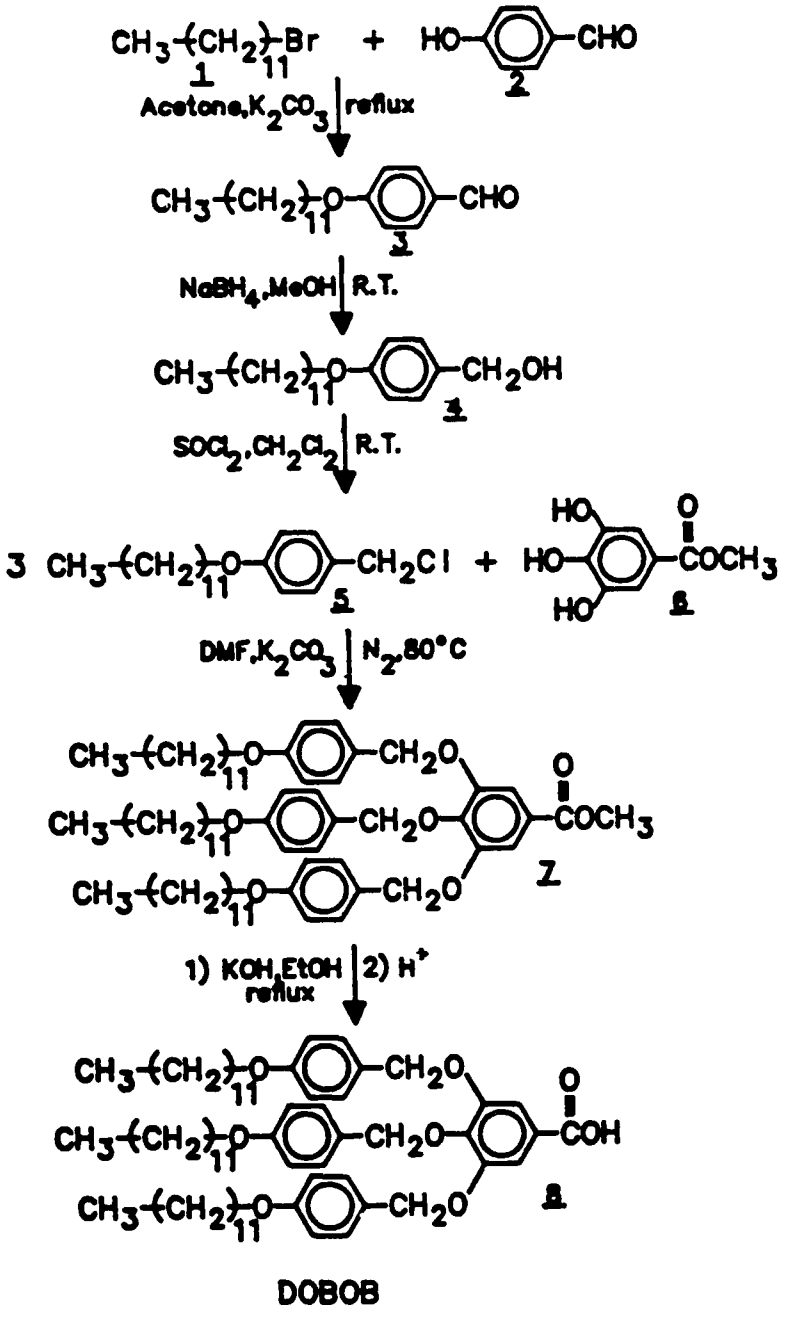
FIGURE AND SCHEME CAPTIONS

Scheme I: Synthesis of 3,4,5-tri[p-(n-dodecan-1-yloxy)benzyloxy]benzoic acid (8)

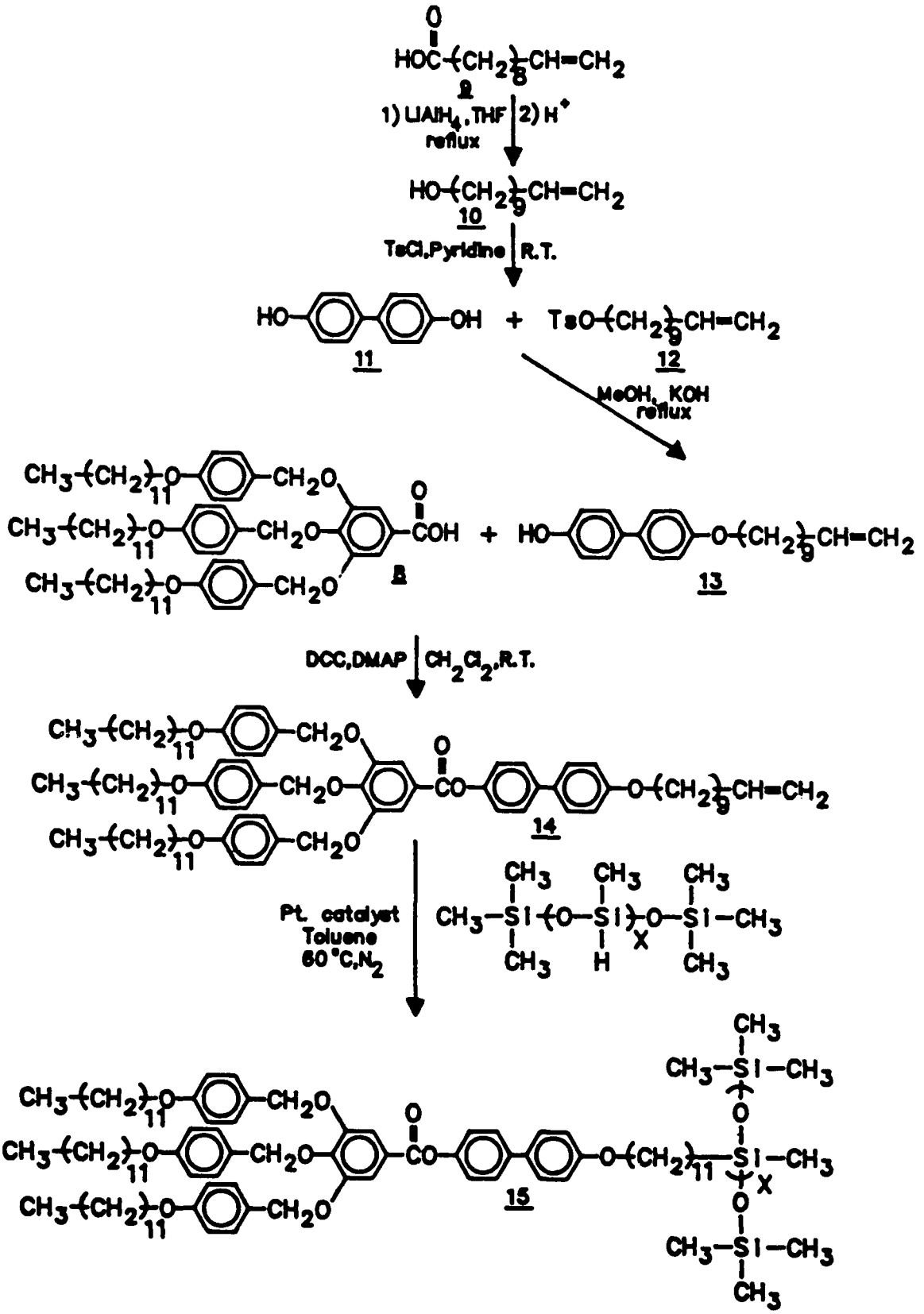
Scheme II: Synthesis of 4-(11-undecan-1-yloxy)-4'-{3,4,5-tri[p-(n-dodecan-1-yloxy)benzyloxy]benzoate}biphenyl side groups (15)

Figure 1: Heating and cooling DSC (20°C/min) traces of: 8 (a, first heating scan; b, cooling scan); 13 (c, first heating scan; d, cooling scan); 14 (e, first heating scan; f, cooling scan; g, second heating scan; h, second heating scan after cooling to 40°C); and 15 (i, first heating scan; j, cooling scan).

Figure 2: Representative optical polarized micrographs (100x) of: a) fan-shaped Φ_h mesophase of 8 after 10 min annealing at 110°C; b) smectic phase of 13 at 133°C; c)fan-shaped Φ mesophase of 15 after 5 hr annealing at 142°C.



Scheme I: Synthesis of 3,4,5-tri[p-(n-dodecan-1-yloxy)benzyloxy]benzoic acid (8)



Scheme II: Synthesis of 4-(11-undecan-1-yloxy)-4'-{3,4,5-tri[p-(n-dodecan-1-yloxy)benzyloxy]benzoate}biphenyl side groups (15)

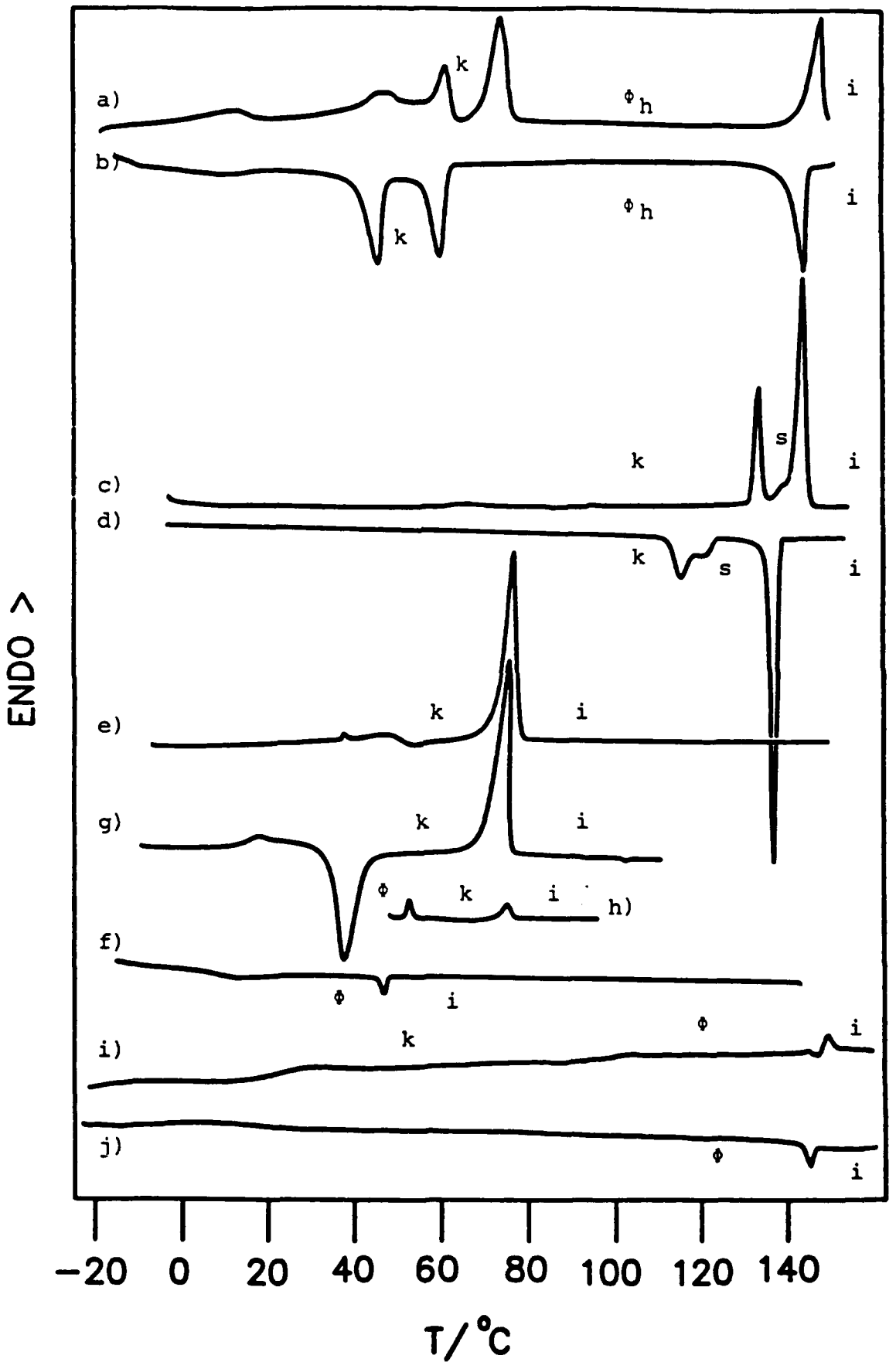


Figure 1

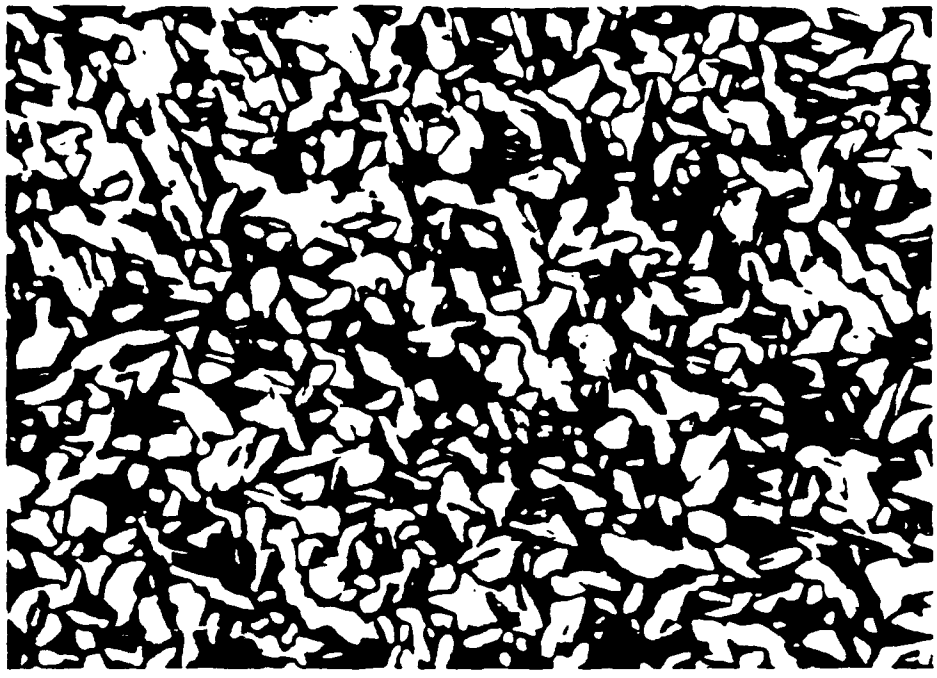


Figure 2a

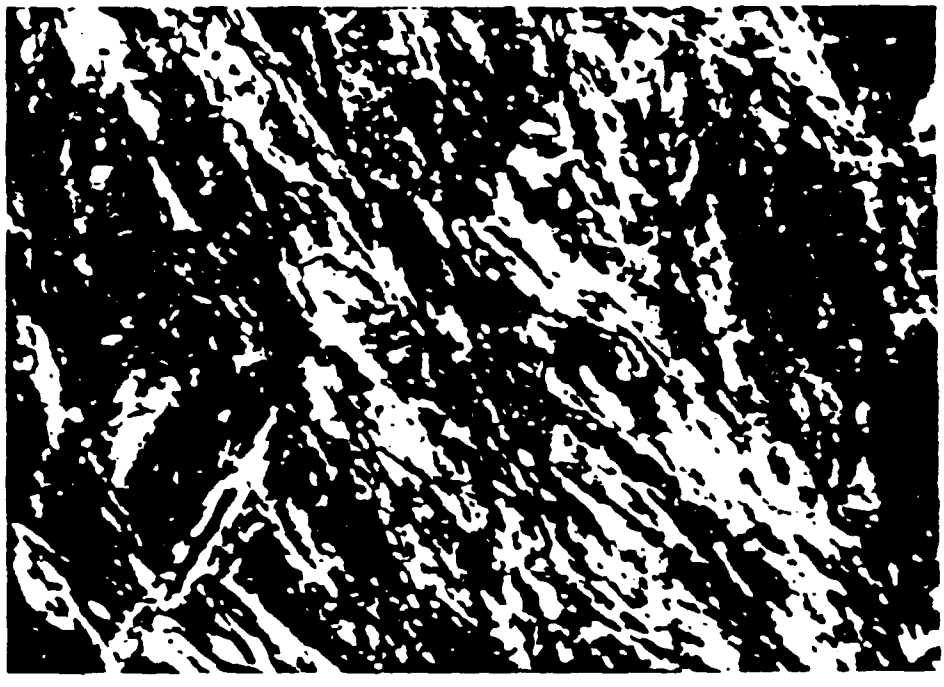


Figure 2b

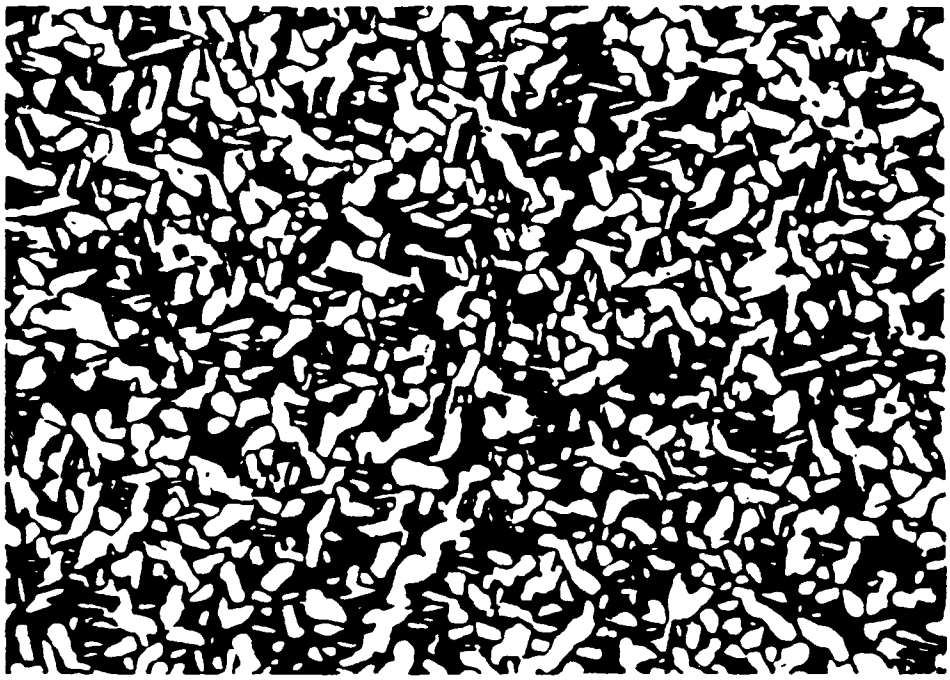


Figure 2c

Table I Thermal characterization of 8, 13, 14, 15 (g=glassy phase, k=crystalline phase,s=smectic mesophase,Φ=phasmidic mesophase)

Sample no.	GPC M_n	GPC M_w/M_n	phase transitions(^oC) and corresponding enthalpy changes(kcal/mru) heating	cooling
8	---	---	k 47,61(4.4)[a] k 73(3.6) Φ 147(12.6) i	i 138(4.2) Φ 54,40(7.2)[a] k
13	---	---	k 129(2.9) k 134 s 139(7.8)[a] i	i 131(8.3) s 115,109(3.3)[a] k
14	---	---	k 42(4.2) k 72(14.8) i	i 47(0.6) Φ 9 g
			g 15 k 17(0.3) k 38(-12.7)[b] k 73(14.7) i	
			Φ 52(0.5) k 74(0.9) i[c]	
15	37000	1.7	g 24 k 103(0.1) Φ 149(0.2) i	i 142(0.2) Φ 12 g

[a] combined enthalpy for overlapped transitions

[b] crystallization during heating

[c] heated to isotropic, cooled at 20°C/min to 40°C, and then reheated

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The synthesis and characterization of the alkene monomer and the corresponding poly(methylsiloxane) containing 2-[3,4,5-tri[p-(n-dodecan-1-yloxy)benzyloxy]benzoate]-7-[p-(11-undecan-1-yloxy)benzoate]naphthalene side groups is presented.

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Liquid Crystalline Polymers Containing Mesogenic Units Based on Half-Disc and Rod-like Moieties. 2 Synthesis and Characterization of Poly{2-[3,4,5-tri[p-(n-Dodecan-1-yloxy)benzyloxy]benzoate]-7-[p-(11-undecan-1-yloxy)benzoate]naphthalene]methyl siloxane}

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Liquid Crystalline Polymers Containing Mesogenic Units Based on Half-Disc and Rod-like Moieties. 2*. Synthesis and Characterization of Poly{2-[3,4,5-tri[p-(n-Dodecan-1-yloxy)benzyloxy]benzoate]-7-[p-(11-undecan-1-yloxy)benzoate]naphthalene]methyl siloxane}

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INTRODUCTION

Mesogenic units based on various combinations of half-disc and rod-like moieties represent a novel class of liquid crystals. Combinations of two half-disc and a rod-like moieties lead to phasmidic liquid crystals which display either phasmidic i.e., columnar oblique (Φ_{ob}) and hexagonal (Φ_h), [1-6] or biaxial nematic (N_b)[7] mesophases. Alternatively, half phasmids, or combinations of a half-disc and a rod-like moiety provide the most succesfull architectural approach to the synthesis of liquid crystals displaying N_b mesophases.[2,6,8]

The first examples of liquid crystal polymers containing phasmidic and half phasmidic mesogens were reported from our[9] and from Ringsdorf's[10] laboratories.

Both low molar mass and polymer liquid crytstals containing phasmidic or half phasmidic mesogens synthesized so far, contain a rod-like or cone-like moiety connected to the half disc part of the mesogen.[1-6]

The goal of this paper is to present the synthesis of the first example of liquid crystalline polymer based on a half-disc and a kinked-rigid moiety, i.e., poly{2-[3,4,5-tri[p-(n-dodecan-1-yloxy)benzyloxy]benzoate]-7-{p-(11-undecan-1-yloxy)benzoate]naphthalene]methyl siloxane}.

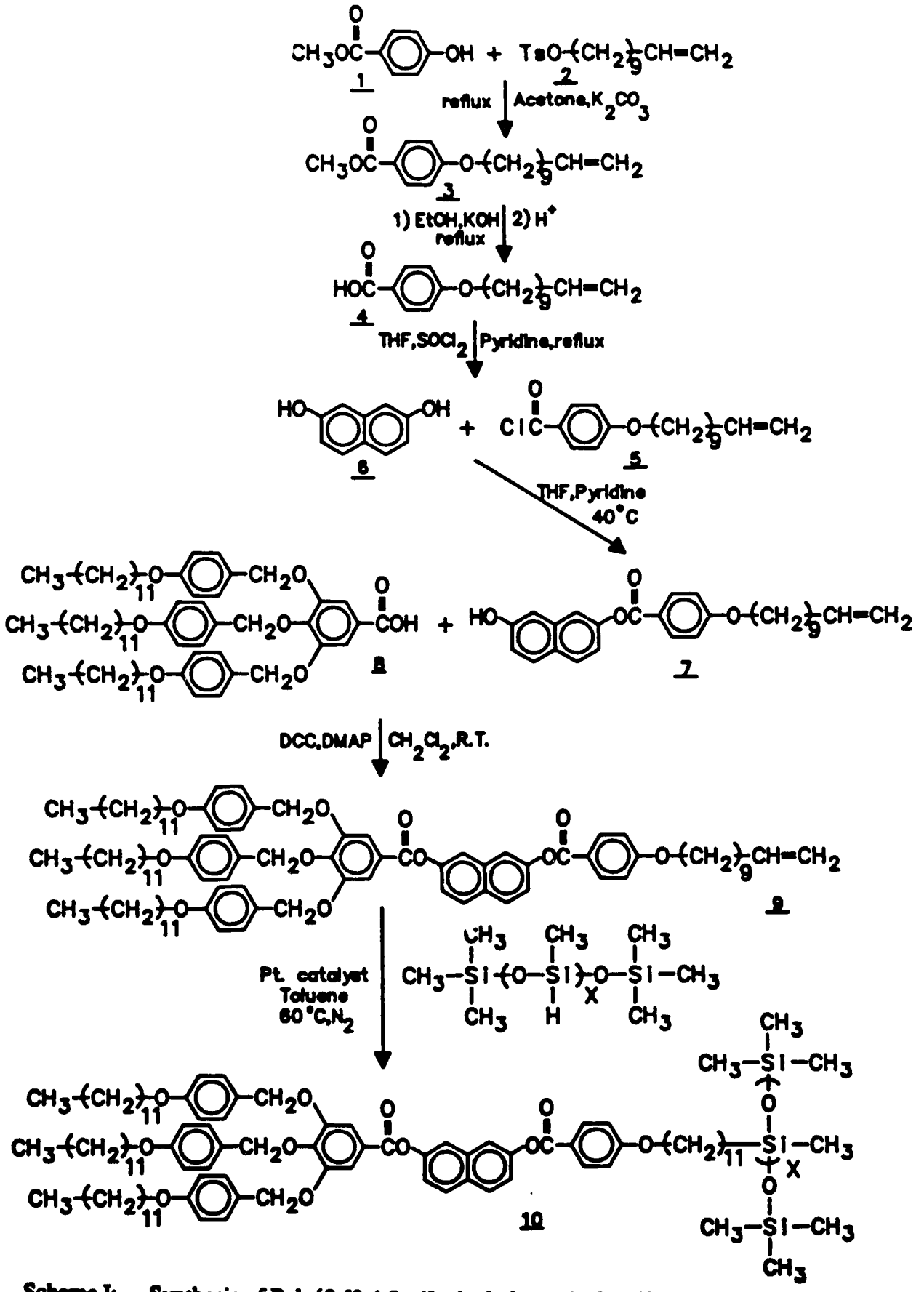
EXPERIMENTAL

Materials

All materials were of commercial source and were used as received or were purified by conventional techniques.

Techniques

The techniques used in the characterization of intermediary derivatives and of polymers (200 MHz ^{1}H-NMR, IR, DSC, GPC, HPLC and thermal optical polarized microscopy) were described elsewhere.[11,12]



Scheme I: Synthesis of Poly{2-[3,4,5-tri[p-(n-dodecan-1-yloxy)benzyloxy]benzoate]-7-[p-(11-undecan-1-yloxy)benzoate]naphthalene]methyl siloxane} (10)

Monomers and Polymers

Scheme I outlines the synthesis of monomers and polymers.

p-(10-Undecen-1-yloxy)benzoic Acid (4)

A mixture containing 16.57g (0.051 mol) of 10-undecen-1-yl tosylate,[9] 7.90g (0.052 mol) methyl-4-hydroxybenzoate, 30g (0.2 mol) anhydrous K_2CO_3 and 250 ml acetone was heated at reflux temperature for 16 hr. After cooling to room temperature, the reaction mixture was poured into water, methylene chloride was added, and the mixture was acidified with formic acid. The organic layer was separated, dried over anhydrous $MgSO_4$, filtered and the solvent was evaporated. The resulting solid was first purified by column chromatography (basic alumina, methylene chloride eluent), then it was mixed with 200 ml 1N KOH solution in ethanol and heated to reflux temperature for 2 hr. After cooling to room temperature, the reaction mixture was acidified with HCl. Water was added until a precipitate formed. The precipitate was filtered, washed with water and recrystallized from methanol/water to yield 9.45g (63%) of white crystals. Purity: 89% (HPLC). mp, 81°C. ^{1}H-NMR ($CDCl_3$, TMS, δ, ppm): 1.31 (m, 12 H, -(CH_2)-), 1.81 (m, 2H, -CH_2-CH_2-O-Ph), 2.03 (m, 2H, -CH_2-CH=CH_2), 4.02 (t, 2H, -CH_2-O-Ph), 4.93 (d, 1H, CH_2=CH-CH_2- trans), 5.00 (d, 1H, CH_2=CH-CH_2- cis), 5.80 (m, 1H, -CH=CH_2), 6.95 (d, 2H, -O-Ph-H-COOH ortho from -O-), 8.03 (d, 2H, -O-Ph-H-COOH ortho from -COO-). IR (KBr plate): 1670 cm^{-1} (ν-C=O).

2-Hydroxy-7-[p-(10-undecen-1-yloxy)benzoate]Naphthalene (7)

To a mixture containing 3.6g (0.012 mol) of 4 dissolved in 300 ml of dry THF were added 3 ml (0.037 mol) of dry pyridine and 1 ml (0.014 mol) of thionyl chloride, and the reaction mixture was refluxed for 15 min. After cooling to 0°C, 10g (0.06 mol) of 2,7-dihydroxynaphthalene was added and the reaction mixture was stirred at 40°C for 10 hr. After cooling to room temperature, water and chloroform were added to the reaction mixture. The chloroform layer was separated, dried over anhydrous $MgSO_4$, filtered and the solvent was distilled in a rotavapor. The resulting solid was passed through a chromatographic column (silica gel, chloroform eluent) and the concentrated chloroform solution was precipitated into hexane. The precipitate was stirred for 18 hr at room temperature and then was filtered and dried to yield 2.99g (54%) of a white solid. Purity: 99% (HPLC). mp, 138°C. ^{1}H-NMR ($CDCl_3$, TMS, δ, ppm): 1.33 (m, 12H, -(CH_2)-), 1.80 (m, 2H, -CH_2-CH_2-O-Ph), 2.00 (m, 2H, CH_2-CH=CH_2), 4.02 (t, 2H, -CH_2-O-Ph), 4.93 (2 overlapped d, 2H, -CH=CH_2), 5.30 (b, 1H, -OH), 5.78 (m, 1H, CH=CH_2), 6.97 (m, 4H, -COO-Nf-H-OH 6 and 8 positions, and -O-H-PhCOOH ortho from -O-), 7.17 (d, 1H, -COONf-H-OH 3 position), 7.47 (s, 1H, -COONf-H-OH 1

position), 7.70-7.81 (2 overlapped d, -COONf-H-OH 4 and 5 positions), 8.18 (d, 2H, -O-PhH-COO- ortho from -COO-). IR (KBr plate): 1705 cm^{-1} (ν-C=O), 3410 cm^{-1} (ν-OH).

2-[3,4,5-Tri(p-(n-dodecan-1-yloxy)benzyloxy)benzoate]-7-[p-(10-undecen-1-yloxy)benzoate]naphthalene (9)

A solution containing 0.41g (0.4 mmol) of 8,[9] 0.23g (0.5 mmol) 7, 0.10g (1.2 mmol) of dicyclohexylcarbodiimide and 0.15g (1.2 mmol) of 4-dimethylaminopyridine in 15 ml of dry methylene chloride was stirred for 6 hr at room temperature. The resulting precipitate was filtered and the methylene chloride solution was precipitated into methanol/water (20/1). The resulting precipitate was filtered and recrystallized from a mixture of diethyl ether/methanol. The final purification was performed by column chromatography (basic alumina, methylene chloride eluent) to yield 0.39g (68%) of white crystals. Purity: 99% (HPLC). mp, 98.1°C (DSC, 20°C/min). ^{1}H-NMR ($CDCl_3$, TMS, δ, ppm): 0.84 (t, 9H, -CH_3), 1.26 (m, 66H, -(CH_2)-), 1.74 (m, 8H. -CH_2-CH_2-O-Ph), 1.99 (m, 2H, -CH_2-CH=CH_2), 3.93 (m, 6H, -CH_2-OPh-CH_2O-), 4.02 (t, 2H, CH_2-CH_2-OPh-COO), 4.92 (2 overlapped d, 2H, -CH=CH_2), 5.03 (s, 2H, -OPhCH_2OPh-COO- from para position), 5.06 (s, 4H, -OPhCH_2O-Ph-COOH from 3 and 5 positions), 5.75 (m, 1H, -CH=CH_2), 6.77 (d, 2H, -OHPhCH_2-OPhCOO- ortho from -O- of internal benzylic unit), 6.80 (d, 4H, -OH-Ph-CH_2-OPhCOO- ortho from -O- of external benzylic units), 6.98 (d, 2H, -CH_2-CH_2-O-PhHCOO- ortho from -O-), 7.27 (d, 4H, -O-PhHCH_2O-PhCOO- ortho from -CH_2- of internal benzylic unit and 3 and 6 protons of Nf), 7.35 (d, 4H, -O-PhH-CH_2OPhCOO- ortho from -O- of external benzylic units), 7.54 (s, 2H, -Ph-CH_2OPhHCOO-), 7.64 (2 overlapped d, 2H, 1 and 8 protons of Nf), 7.94 (d, 2H, 4 and 5 protons of Nf), 8.29 (d, 2H, -CH_2-CH_2O-PhHCOO- ortho from -COO-). IR (KBr plate): 1730 cm^{-1} (ν-C=O).

Poly[2-[3,4,5-tri(p-dodecan-1-yloxy)benzoate]-7-[p-(11-undecan-1-yloxy)benzoate]naphthalene]methyl siloxane] (10)

To a flame-dried 5 ml test tube containing a microstirring bar were added 0.50g (0.35 mmol) 9, 0.0210g (0.35 mmol) poly(hydrogenmethylsiloxane) (Mn=1500 from Petrarch), 2 ml dry toluene and 3 drops (about 0.06g) of platinum divinyltetramethyldisiloxane complex (solution in xylene from Petrarch). The reaction mixture was purged with nitrogen and the tube was sealed with a cork stopper covered with teflon tape. The reaction mixture was heated for 24 hr at 60°C, cooled and precipitated into methanol. The precipitated was filtered, dissolved in THF and precipitated in acetone (by the technique described in the previous publication[9]) to yield 0.26g (52%) of white solid. Purity: 99% (HPLC). Mn=37000, Mw/Mn=1.7 (GPC with polystyrene standards).

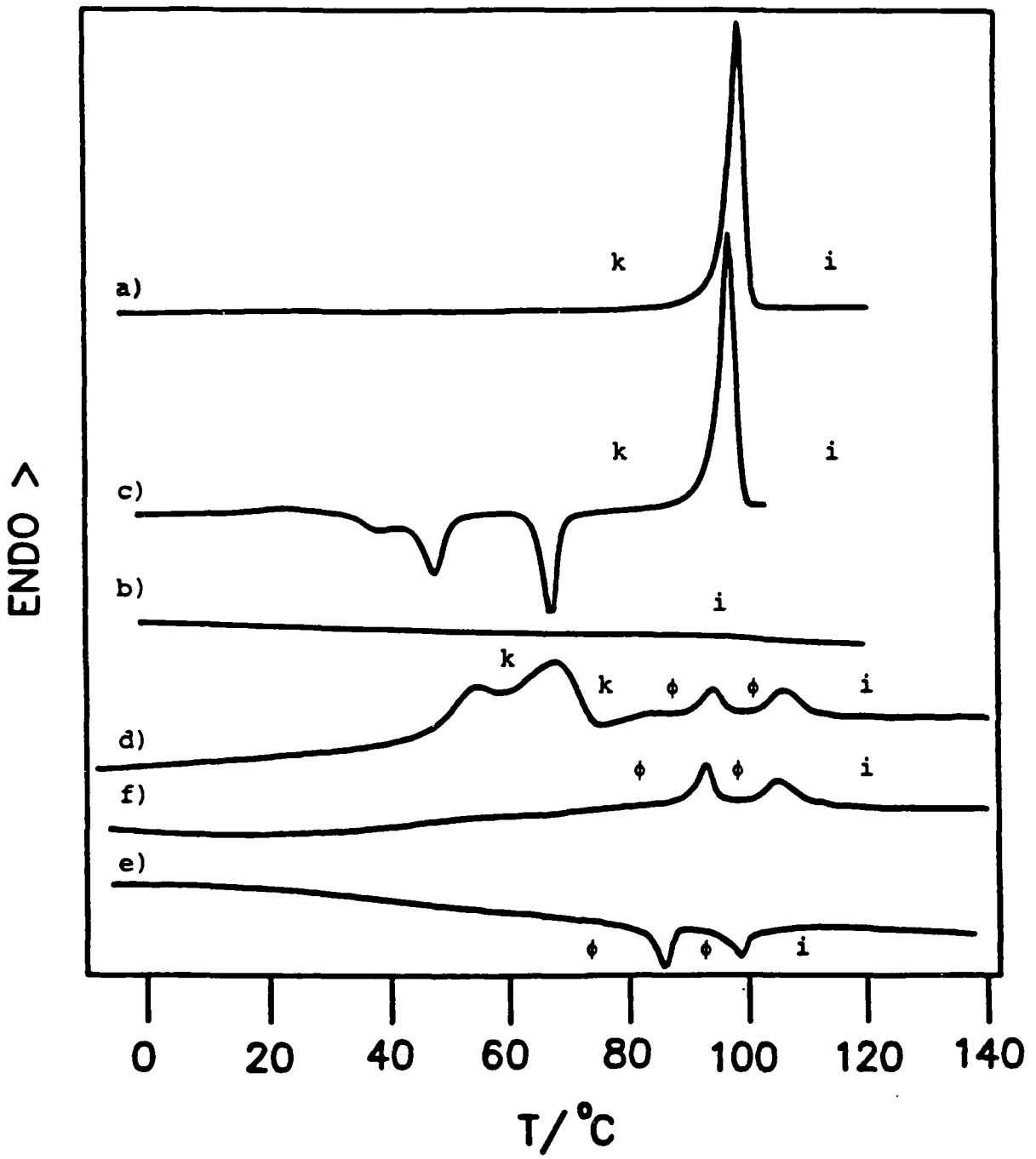


Figure 1: Heating and cooling DSC (20°C/min) traces of : 9 (a, first heating scan; b, cooling scan; c, second heating scan) and 10 (d, first heating scan; e, cooling scan; f, second heating scan)

Table I Thermal characterization of 9 and 10 (g=glassy phase, k=crystalline phase, Φ=phasmidic mesophase)

Sample no.	GPC M_n	GPC M_w/M_n	phase transitions(^{O}C) and corresponding enthalpy changes(kcal/mru) heating	cooling
9	---	---	k 98(26.3) i g 17 k 34,44(-12.0)[ab] k 64(-8.8)[b] k 94(25.1) i	i 10 g
10	37000	1.7	k 53,67(5.6)[a] k 82(0.06) Φ 93(0.4) Φ 104(0.6) i g 44 Φ 92(0.6) Φ 104(0.6)	i 99(0.6) Φ 87(0.6) Φ

[a]combined enthalpy for overlapped transitions

[b]crytallization during heating

RESULTS AND DISCUSSION

Synthesis of 9 and 10 are outlined in Scheme I. 8 was prepared as reported in the previous publication from this series.[9] Some representative DSC traces of 9 and 10 are presented in Figure 1. Table I summarizes the thermal transition temperatures and the corresponding enthalpy changes of 9 and 10. 9 melts at 98°C directly into an isotropic liquid. On cooling it does not crystallize. However, it crystallizes on the subsequent heating scan. 10 exhibits three melting endotherms at 53, 67 and 82°C, followed by two enantiotropic mesophases. The first mesophase changes at 93°C into a second mesophase which undergoes isotropization at 104°C. On subsequent heating and cooling scans, 10 exhibits only the two enantiotropic mesophases. The degree of supercooling of the phase transitions associated with these two mesophases on the cooling scan is very low. Both mesophases were characterized by thermal optical polarized microscopy. Figure 2 shows a characteristic texture displayed by 10 after annealing for 8 hr at 103°C. It exhibits a fan-shaped texture which is characteristic for Φ_{ob} and Φ_h mesophases.[1] Upon cooling below 87°C, a small change in this texture is observed. However, the texture remains fan-shape type. We can assume that 10 displays one or even two phasmidic mesophases. The discrimination between Φ_{ob} and Φ_h mesophases requires X-ray scattering experiments. Research on this line is in progress.

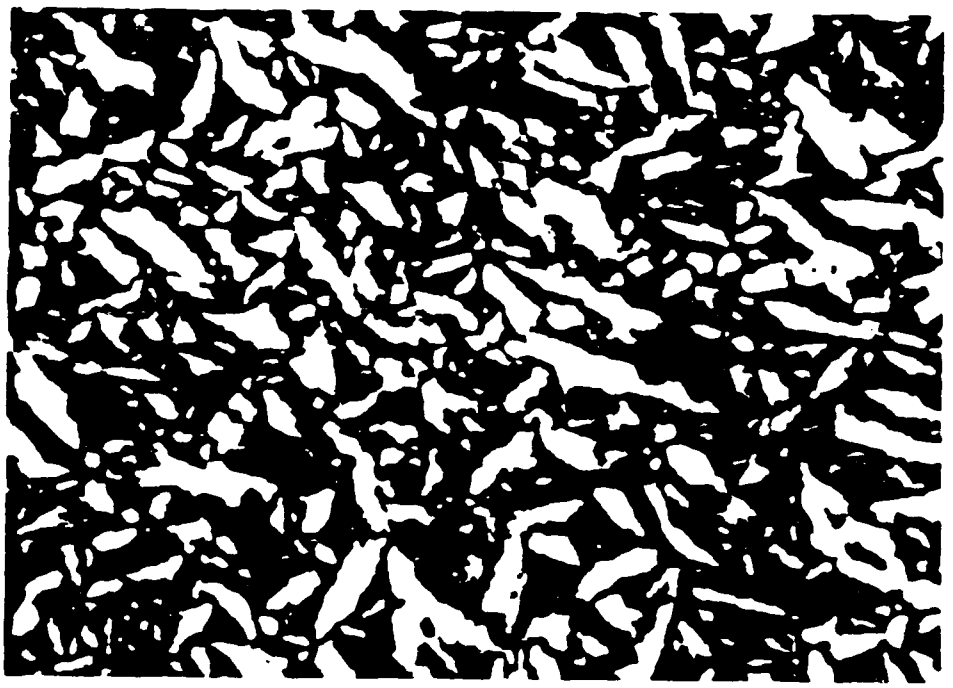


Figure 2: Representative optical polarized micrograph (100x) of fan-shaped texture of 10 after 8 hr annealing at 103°C

ACKNOWLEDGMENTS

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1. End-of-the-Year Report

Part III

a) Introductory "viewgraph" (attached)
b) A figure (attached)
c) A concluding "viewgraph" (attached)
d) A paragraph of explanatory text (attached):

MECHANISM OF FORMATION OF SIDE CHAIN LIQUID CRYSTAL POLYMERS AND OF CONTROL OF THEIR DYNAMICS

The spacer concept (Scheme I) was introduced to decouple the motions of the mesogenic side-groups from that of the random-coil conformation of the polymer backbone (Percec and Pugh, in "Side Chain Liquid Crystal Polymers", C. B. McArdle Ed., Chapman and Hall, New York, 1989, p. 30). However, recent theoretical calculations predicted that the random-coil conformation of polymer backbones containing mesogenic side groups gets distorted at the transition from the isotropic to the anisotropic phase. The degree of this distortion depends on the nature of the mesophase (smectic>nematic) and on the flexibility of the polymer backbone (Scheme II)

a) Rigid backbones (left side of bottom part in Scheme II) get elongated and provide systems which can freeze the motion of side groups below T_g.

b) Flexible backbones (right side of bottom part in Scheme II) get squeezed and therefore microsegregated between the smectic layer and can provide decoupled systems in which the motion of the side groups is less dependent on that of the main chain (Percec and Tomazos, Polymer in press).

The decoupling of these two motions can be controlled by varying the ratio between the domain size of the microsegregated backbone and side groups (i.e., by varying the ratio between the mesogenic and nonmesogenic groups in a copolymer). Scheme III demonstrates this concept. X-ray scattering experiments on such a copolymer system show that the experimentally determined smectic layer (d) increases with decreasing concentration of mesogenic groups. This is due to the increased thickness of the backbone layer (a) [Percec et al., Macromolecules, 23, 2092 (1990)].

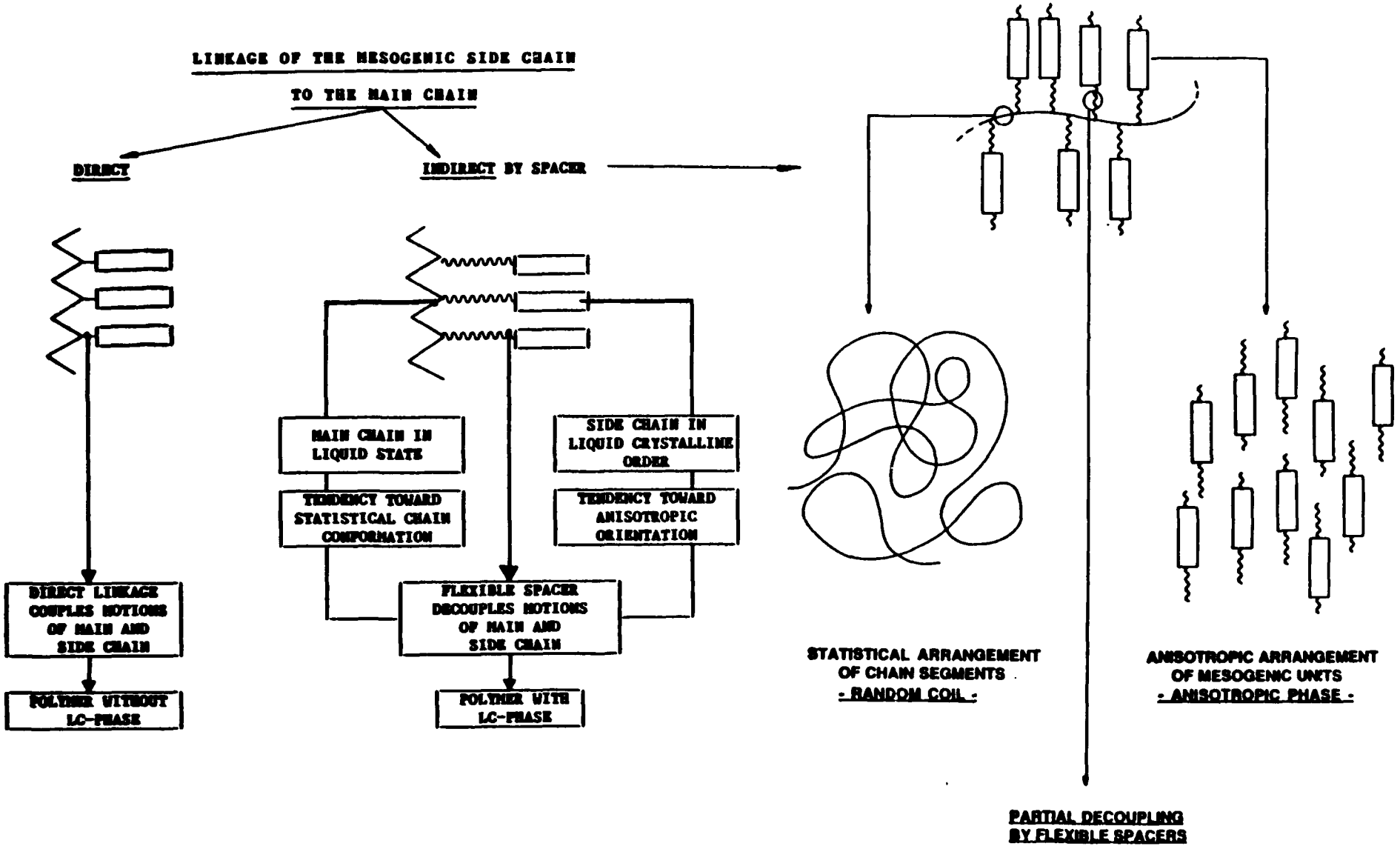
Significance: 1) Liquid crystalline homopolymers with rigid backbones are suitable for applications in which a frozen conformation of the side groups is desirable i.e., devices for storage of information; materials displaying non-linear optical properties, etc.

2) Liquid crystalline copolymers based on very flexible backbones are useful for systems in which fast dynamics are required i.e., devices based on chiral smectic C for fast displays; ionic conductors, etc.

Part III (a)
Scheme I

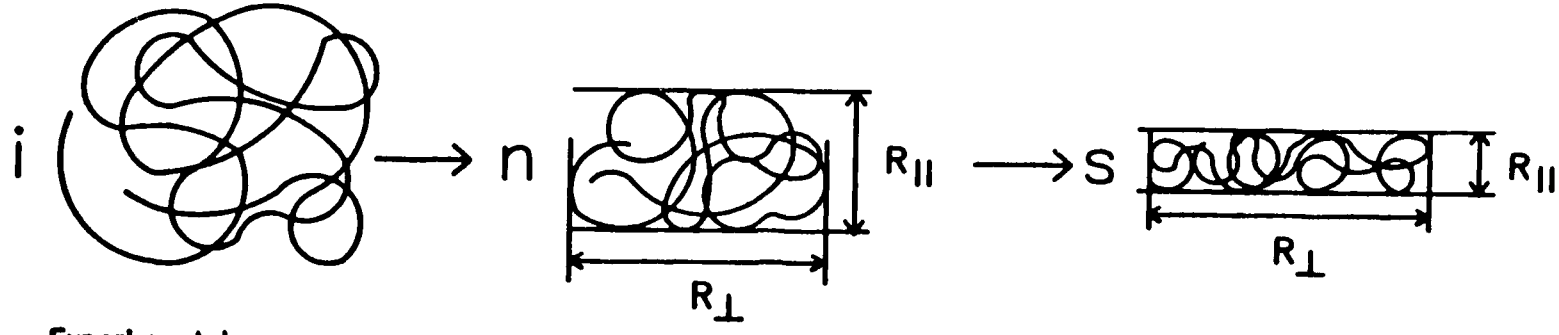
SIDE CHAIN LIQUID CRYSTAL POLYMERS

MODEL CONSIDERATIONS

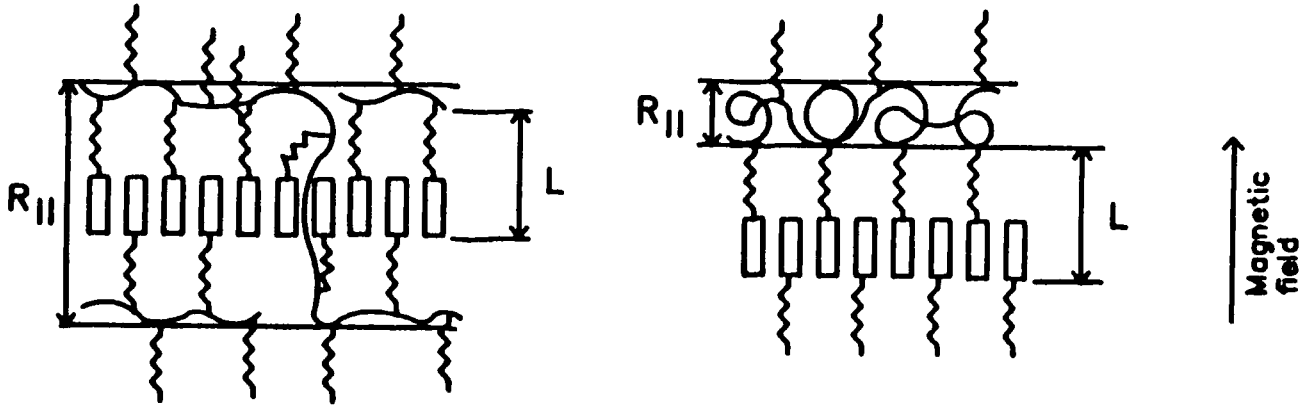


Part III (b)
Scheme II

Theoretical



Experimental

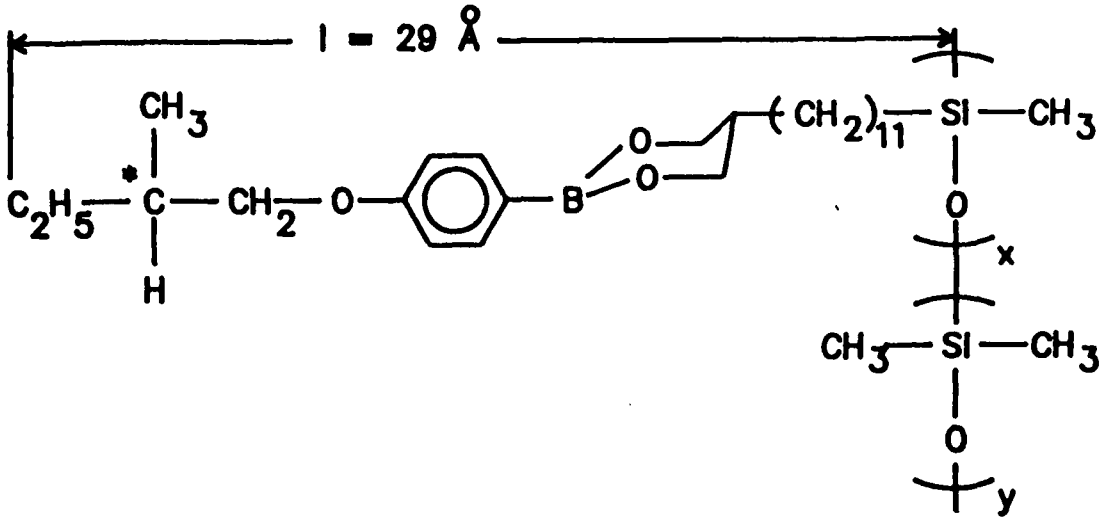


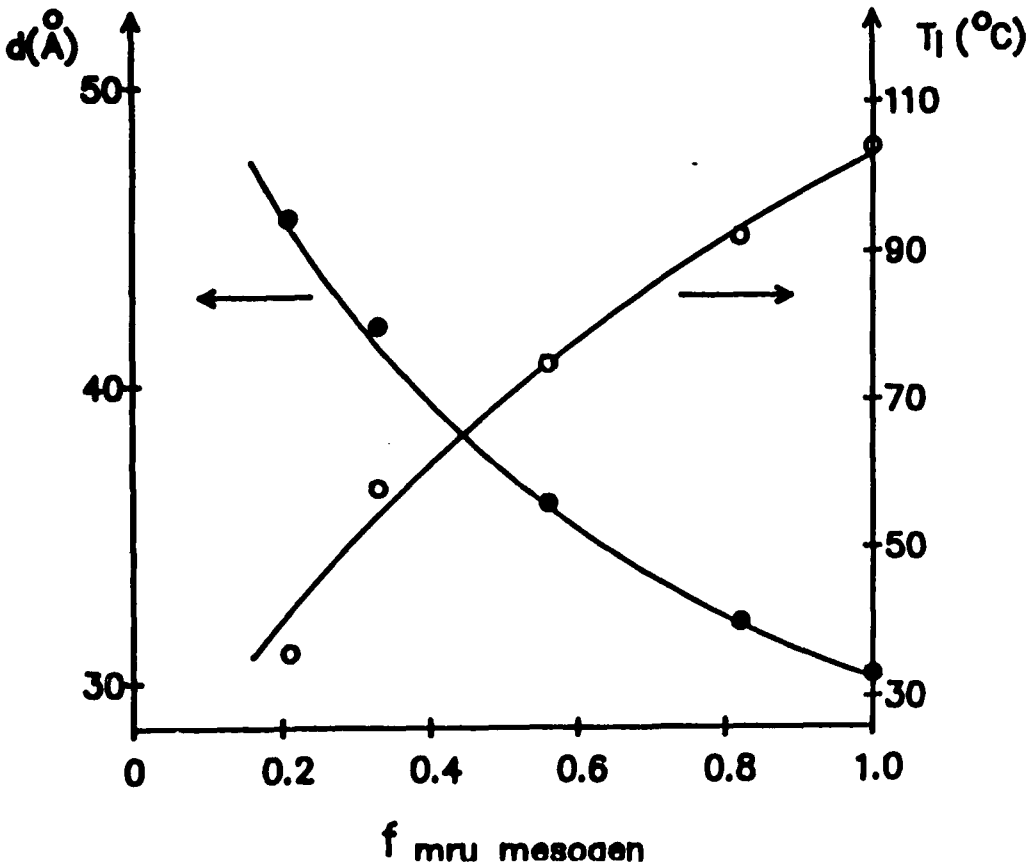
$R_{II\,PAC} \leq R_{II\,PMA}$ $R_{II\,PAC} < L_{PAC}$ $R_{II\,PMA} \geq L_{PMA}$

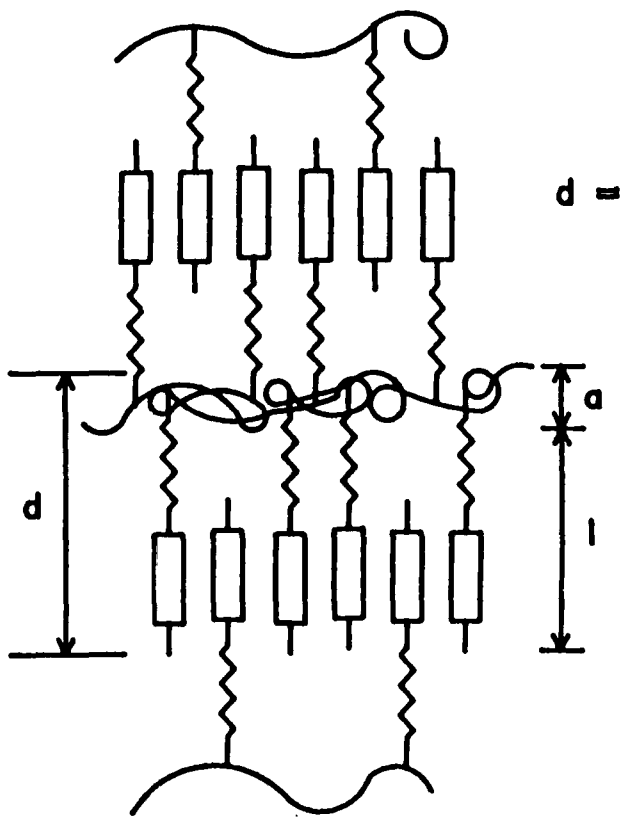
Microphase Separated Morphology of Smectic Copolymers

Part III (c)
Scheme III

mesogen(%)	d(Å)	a(Å)	T_I (°C)
100	30.4	1.4	104
82	32.0	3.0	92
56	36.0	7.0	75
33	42.0	13.0	58
21	45.6	16.6	36







d = a + l ; d > l

MECHANISM OF FORMATION OF SIDE CHAIN LIQUID CRYSTAL POLYMERS AND OF CONTROL OF THEIR DYNAMICS

THE SPACER CONCEPT (SCHEME I) WAS INTRODUCED TO DECOUPLE THE MOTIONS OF THE MESOGENIC SIDE-GROUPS FROM THAT OF THE RANDOM-COIL CONFORMATION OF THE POLYMER BACKBONE (Percec and Pugh, in "Side Chain Liquid Crystal Polymers", C. B. McArdle Ed., Chapman and Hall, New York, 1989, p. 30). HOWEVER, RECENT THEORETICAL CALCULATIONS PREDICTED THAT THE RANDOM-COIL CONFORMATION OF POLYMER BACKBONES CONTAINING MESOGENIC SIDE GROUPS GETS DISTORTED AT THE TRANSITION FROM THE ISOTROPIC TO THE ANISOTROPIC PHASE. THE DEGREE OF THIS DISTORTION DEPENDS ON THE NATURE OF THE MESOPHASE (SMECTIC>NEMATIC) AND ON THE FLEXIBILITY OF THE POLYMER BACKBONE (SCHEME II)
A) RIGID BACKBONES (LEFT SIDE OF BOTTOM PART IN SCHEME II) GET ELONGATED AND PROVIDE SYSTEMS WHICH CAN FREEZE THE MOTION OF SIDE GROUPS BELOW T_g.
B) FLEXIBLE BACKBONES (RIGHT SIDE OF BOTTOM PART IN SCHEME II) GET SQUEEZED AND THEREFORE MICROSEGREGATED BETWEEN THE SMECTIC LAYER AND CAN PROVIDE DECOUPLED SYSTEMS IN WHICH THE MOTION OF THE SIDE GROUPS IS LESS DEPENDENT ON THAT OF THE MAIN CHAIN (Percec and Tomazos, Polymer in press).

THE DECOUPLING OF THESE TWO MOTIONS CAN BE CONTROLLED BY VARYING THE RATIO BETWEEN THE DOMAIN SIZE OF THE MICROSEGREGATED BACKBONE AND SIDE GROUPS (I.E., BY VARYING THE RATIO BETWEEN THE MESOGENIC AND NONMESOGENIC GROUPS IN A COPOLYMER). SCHEME III DEMONSTRATES THIS CONCEPT. X-RAY SCATTERING EXPERIMENTS ON SUCH A COPOLYMER SYSTEM SHOW THAT THE EXPERIMENTALLY DETERMINED SMECTIC LAYER (d) INCREASES WITH DECREASING CONCENTRATION OF MESOGENIC GROUPS. THIS IS DUE TO THE INCREASED THICKNESS OF THE BACKBONE LAYER (a) [Percec et al., Macromolecules, 23, 2092 (1990)].

SIGNIFICANCE: 1) LIQUID CRYSTALLINE HOMOPOLYMERS WITH RIGID BACKBONES ARE SUITABLE FOR APPLICATIONS IN WHICH A FROZEN CONFORMATION OF THE SIDE GROUPS IS DESIRABLE I.E., DEVICES FOR STORAGE OF INFORMATION; MATERIALS DISPLAYING NON-LINEAR OPTICAL PROPERTIES, ETC.
2) LIQUID CRYSTALLINE COPOLYMERS BASED ON VERY FLEXIBLE BACKBONES ARE USEFUL FOR SYSTEMS IN WHICH FAST DYNAMICS ARE REQUIRED I.E., DEVICES BASED ON CHIRAL SMECTIC C FOR FAST DISPLAYS; IONIC CONDUCTORS, ETC.