AD-A208 845

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DOCUMENTATION PAGE

1a REPORT SECURITY CLASSIFICATION: Unclassified	1b RESTRICTIVE MARKINGS: FILE COPY
2a SECURITY CLASSIFICATION AUTHORITY	3. DISTRIBUTION / AVAILABILITY OF REPORT: Available for distribution Distribution unlimited
2b DECLASSIFICATION / DOWNGRADING SCHEDULE	
4. PERFORMING ORGANIZATION REPORT NUMBER(S): Technical Report No. 27	5. MONITORING ORGANIZATION REPORT NUMBER(S)
6a NAME OF PERFORMING ORGANIZATION: Case Western Reserve University 6b OFFICE SYMBOL (If applicable): 4B566	7a. NAME OF MONITORING ORGANIZATION: ONR
6c. ADDRESS (City, State, and ZIP Code): 2040 Adelbert Road Cleveland, OH 44106	7b. ADDRESS (City, State, and ZIP Code): Office of Naval Research Arlington, VA 22217
8a. NAME OF FUNDING / SPONSORING ORGANIZATION: ONR 8b. OFFICE SYMBOL (If applicable):	9 PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER
8c. ADDRESS (City, State, and ZIP Code): Office of Naval Research 800 N. Quincy Arlington, VA 22217	10 SOURCE OF FUNDING NUMBERS PROGRAM ELEMENT NO.: N00014-89 PROJECT NO.: J-1828 TASK NO.: 413c024 WORK UNIT ACCESSION NO:

11. TITLE (Include Security Classification)
Can the Rigidity of a Side Chain Liquid Crystalline Polymer Backbone Influence the Mechanism of Distortion of its Random-Coil Conformation?

12. PERSONAL AUTHOR(S) Virgil Percec and Dimitris Tomazos

13a. TYPE OF REPORT	13b. TIME COVERED	14. DATE OF REPORT (Year, Month, Day)	15. PAGE COUNT
Preprint	FROM ____ TO ____	May 30, 1989	

16. SUPPLEMENTARY NOTATION
POLYMER

17. COSATI CODES		
FIELD	GROUP	SUB-GROUP

18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)
side chain, liquid crystal polymers; isotropization entropy change; isotropization temperature; acrylates, polymers.

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

The relationship between the isotropization transition temperatures and the associated entropy changes of two series of side chain liquid crystalline polymers based on three different polymer backbones (polymethacrylate, polyacrylate and polymethylsiloxane) and 4-methoxy-4'-hydroxy-α-methylstilbene (4-MHMS) and 4-hydroxy-4'-methoxy-α-methylstilbene (4'-MHMS) mesogenic side groups attached to the polymer backbone through different flexible spacers is discussed. In the case of polymers containing long flexible spacers, isotropization transition temperatures, which are mostly dictated by the side groups, are higher for polymers based on flexible backbones, suggesting that they provide the highest degree of order in the mesophase. Therefore, their mesophase should exhibit the lowest entropy and the highest entropy change of isotropization. Experimentally determined entropy changes of isotropization, which refer to the overall degree of

(continued on reverse)

20 DISTRIBUTION / AVAILABILITY OF ABSTRACT ☒ UNCLASSIFIED/UNLIMITED ☐ SAME AS RPT. ☐ DTIC USERS	21. ABSTRACT SECURITY CLASSIFICATION: unclassified/unlimited
22a NAME OF RESPONSIBLE INDIVIDUAL: Virgil Percec	22b TELEPHONE (Include Area Code): (216) 368-4242 22c. OFFICE SYMBOL

DD FORM 1473, 84 MAR — 83 APR edition may be used until exhausted. All other editions are obsolete. SECURITY CLASSIFICATION OF THIS PAGE

10. ABSTRACT (continued)

order of the polymer, present however, the highest values for polymers based on the most rigid backbone. Two different mechanisms of distortion of the random-coil conformation of flexible and rigid polymer backbone are suggested to account for this contradictory result. A squeezed random-coil conformation, which in the case of smectic polymers is confined between the smectic layers is considered for flexible backbones. An extended chain conformation is considered for rigid backbones. The entropy associated with the squeezed random-coil conformation is higher than that associated with the extended conformation, and therefore, the overall order which results from the mesogenic side groups may explain the experimentally observed isotropization entropy changes. Polymers based on short flexible spacers exhibit similar entropy changes of isotropization irrespective of the nature of their backbone. This may suggest an extended backbone conformation for polymers based on short spacers and rigid or flexible backbones.

OFFICE OF NAVAL RESEARCH

Contract N00014-89-J-1828

R&T Code 413c024

Technical Report No. ~~24~~ 27

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Submitted for Publication

in

Polymer

May 30, 1989

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ABSTRACT: The relationship between the isotropization transition temperatures and the associated entropy changes of two series of side chain liquid crystalline polymers based on three different polymer backbones (polymethacrylate, polyacrylate and polymethylsiloxane) and 4-methoxy-4'-hydroxy- α -methylstilbene (4-MHMS) and 4-hydroxy-4'-methoxy- α -methylstilbene (4'-MHMS) mesogenic side groups attached to the polymer backbone through different flexible spacers is discussed. In the case of polymers containing long flexible spacers, isotropization transition temperatures, which are mostly dictated by the side groups, are higher for polymers based on flexible backbones, suggesting that they provide the highest degree of order in the mesophase. Therefore, their mesophase should exhibit the lowest entropy and the highest entropy change of isotropization. Experimentally determined entropy changes of isotropization, which refer to the overall degree of order of the polymer, present however, the highest values for polymers based on the most rigid backbone. Two different mechanisms of distortion of the random-coil conformation of flexible and rigid polymer backbones are suggested to account for this contradictory result. A squeezed random-coil conformation, which in the case of smectic polymers is confined between the smectic layers is considered for flexible backbones. An extended chain conformation is considered for rigid backbones. The entropy

associated with the squeezed random-coil conformation is higher than that associated with the extended conformation, and therefore, the overall order which results from the combination of backbone and the organization of the mesogenic side groups may explain the experimentally observed isotropization entropy changes. Polymers based on short flexible spacers exhibit similar entropy changes of isotropization irrespective of the nature of their backbone. This may suggest an extended backbone conformation for polymers based on short spacers and rigid or flexible backbones.

(Keywords: side chain liquid crystal polymers; isotropization entropy change; isotropization temperature; anisotropic backbone conformation)

INTRODUCTION

Recent results from several laboratories suggest that for a given series of side chain liquid crystalline polymers (LCP) based on a similar mesogenic group and flexible spacer but different polymer backbones, the degree of decoupling is determined by the nature of the polymer backbone.[1-4]

So far, this conclusion refers only to polymers containing rigid rod-like mesogens, which are normally attached to the polymer backbone. The situation may differ when the rod-like mesogenic group is laterally attached,[5] or when disk-like,[6] phasmidic,[7] or other bulky[8] mesogens are considered.

For polymer molecular weights above which phase transitions are molecular weight independent, the highest isotropization temperature of the LCP with normally attached mesogens is consistently obtained for polymers based on the most flexible backbones.[1,9-11] The highest ability to undergo side-chain crystallization which results in the highest melting temperatures and lowest degrees of supercooling of the crystallization temperatures, is also displayed by the polymers based on the most flexible backbone. Certainly, we may consider that on going from the isotropic to the anisotropic state, the random-coil conformation of a more flexible backbone can be distorted easier than that of a rigid polymer backbone. Therefore, it

is expected that higher melting and isotropization temperatures should be associated with higher degrees of order in the crystalline or mesomorphic phase located next to the isotropic phase. This assumes that the mesomorphic phases displayed by polymers based on the most flexible backbones are characterized by the lowest entropies. Subsequently, the entropy changes associated with the anisotropic-isotropic phase transitions of LCPs based on flexible backbones should be higher than those of LCPs based on rigid backbones.

This paper will critically discuss the entropy changes associated with the isotropic-liquid crystalline phase transitions of two series of side chain liquid crystalline polymers (LCP) based on three different polymer backbones i.e., polymethacrylate, polyacrylate, and polymethylsiloxane and 4-methoxy-4'-hydroxy- α-methylstilbene (4-MHMS) and 4-hydroxy-4'-methoxy- α -methylstilbene (4'-MHMS) based mesogenic side groups attached to the polymer backbone through different spacer lengths. As far as we know, this is the first attempt to quantitatively discuss the relationship between the entropy change of isotropization and the nature of the polymer backbone.[1-4] The entropy change of isotropization of the polymers based on long flexible spacers is always higher when the polymer is based on the most rigid backbone. This is an unexpected result which suggests that the overall degree of order of the mesomorphic phases displayed by LCPs with rigid backbones is

higher than that displayed by the corresponding polymers based on more flexible backbones. The difference between the entropy change associated with the isotropization temperature of LCPs based on different backbone flexibilities decreases with the decrease in the spacer length, and disappears for polymers based on short flexible spacers. An explanation of this behavior based on different mechanisms of distortion of the statistical random-coil conformations of the rigid and flexible polymer backbones is suggested.

EXPERIMENTAL

Polymers based on polymethacrylate, polyacrylate, and polymethylsiloxane backbones, and 4-methoxy-4'-hydroxy- α -methylstilbene (4-MHMS) and 4-hydroxy-4'-methoxy- α -methylstilbene (4'-MHMS) based mesogens were synthesized and characterized as previously described.[9,10] Scheme 1 outlines their structures. Their isotropic-liquid crystalline transition temperatures (T_i) are plotted in Figure 1. The entropy changes associated with the isotropic-liquid crystalline phase transitions (ΔS_i) were determined by differential scanning calorimetry (DSC). The DSC scans were performed with heating and cooling rates of 20°C/min. Additional experimental details were published elsewhere.[9,10] The entropy changes ($\Delta S = \Delta H/T$) plotted in Figures 2 and 3 are not affected by the difference of the

phase transition temperatures of the polymers with different backbones, since the corresponding enthalpy changes associated with these isotropic-liquid crystalline transition temperatures follow the same trend. When the polymer displays an enantiotropic mesophase, the entropy change determined from the cooling scan was always equal to that determined from the heating scan. However, since many polymers display monotropic mesophases, Figures 2 and 3 report entropy changes collected only from the cooling scans. The entropy changes reported in Figures 2 and 3 are independent of the DSC scan number they were calculated from. These entropy changes can be only very little affected by the difference between the molecular weights of these polymers. This is because the enthalpy change of isotropization of side chain liquid crystalline polymers is molecular weight independent.[12,13] Therefore, the entropy change is molecular weight dependent only over the range of molecular weights where the isctropization temperatures are molecular weight dependent. Nevertheless, with the exception of some polyacrylates, the molecular weights of most of the polymers discussed in this study are above values which can affect their isotropization temperatures.[12,13] Therefore, we can state that the relationships between polymer structure and ΔS_i plotted in Figures 2 and 3 are correct.

RESULTS AND DISCUSSION

Figure 1 plots the isotropic-anisotropic transition temperatures (T_i) for all polymers presented in Scheme 1. The molecular weights of polyacrylates are lower than of the other polymers and, in many instances, within the range of molecular weights where their T_i is still molecular weight dependent.[9,10] The molecular weights of polymethacrylates and polymethylsiloxanes are above the molecular weight range where T_i values are molecular weight dependent. Therefore, their T_i data can be compared. Polymethylsiloxanes show higher T_i than polymethacrylates.

Data plotted in Figures 2 and 3 can be considered in two different ways. For a certain polymer backbone, they provide the dependence between ΔS_i and spacer length. When the polymers are based on the same spacer length (i.e., number of methylenic units in the spacer, n), these data provide the dependence between ΔS_i and the nature of the polymer backbone. For a given polymer backbone, the dependence of ΔS_i versus spacer length derived from Figures 2 and 3 is expected. That is, ΔS_i increases with the increase in the spacer length since the degree of order of the mesophase increases with the spacer length.[2,3] All polymers containing in between three and eight methylenic units in the spacer, display ΔS_i values which refer to an isotropic-nematic phase transition. The ΔS_i of polymers

containing eleven methylenic units in the flexible spacer refer to an isotropic-smectic A phase transition.

The dependence between ΔS_i and the nature of the polymer backbone is, however, unexpected. It is well documented both from theoretical work[14] and from data obtained by small angle X-ray scattering (SAXS)[15] and small angle neutron scattering (SANS) experiments[2,3,16] that the statistical random-coil conformation of the polymer backbone gets distorted within the mesomorphic phase. This distortion is very small on going from an isotropic to a nematic mesophase and becomes larger in the smectic mesophase. Therefore, since a flexible backbone would be easier to get distorted we would expect a higher degree of order in the mesomorphic phase of a side chain liquid crystalline polymer based on a flexible backbone. This would lead to a lower entropy in the mesomorphic phase and a higher entropy change associated with the isotropization transition. Isotropization transition temperatures indeed suggest this trend.[9-11] Our thermodynamic data are, however, leading to a reversed result. With the exception of the polymers based on flexible spacers containing three methylenic units, ΔS_i values associated with polymethacrylate backbones are higher than those associated with polyacrylate and polymethylsiloxane backbones. This trend is clearly independent of the nature of the constitutional isomer of the mesogenic side group (Figures 2 and 3). In fact, most of the ΔS_i data in Figures 2 and 3

are overlapping each other when the nature of the backbone and the spacer length are identical, demonstrating that polymers based on 4-MHMS and 4'-MHMS constitutional isomeric mesogens provide almost identical results. The difference between ΔS_i displayed by LCPs with different backbones increases with the increase in the spacer length. Within instrumental error, there is no difference between the ΔS_i of the polymers containing three methylenic units in their flexible spacer. For polymers based on long flexible spacers, S_i values of polyacrylates are almost equal to those of the polymethylsiloxanes and are much lower than those of the corresponding polymethacrylates.

Let us assume that the degree of disorder in the isotropic state is identical for all polymers, independent of the nature of their backbone. Therefore, based on the thermodynamic data the mesomorphic phase of the polymethacrylates displays a higher overall degree of order than that of the corresponding polyacrylates or polymethylsiloxanes. This contradicts with the higher ability of the mesogenic side groups to get organized when the backbone they are attached to is more flexible, for at least two reasons. First, the mesogenic groups attached to a flexible backbone give rise to a mesophase which undergoes isotropization at a higher temperature than that of the corresponding mesophase of polymers with more rigid backbones. Therefore, the mesogens attached to the flexible backbone are located in a mesophase of lower entropy than

those attached to a rigid backbone. Subsequently, this assumes that the more flexible backbone would have to be distorted more than the rigid backbone. A more distorted random-coil would have to be characterized by a lower entropy than a less distorted random-coil. In conclusion both the degree of order of the mesogenic side groups and of the polymer backbone of polymers based on flexible backbones would lead to a higher entropy change associated with their isotropization transition than that of polymers based on more rigid backbones.

The only speculative explanation we can provide for these reversed results can be obtained by assuming two different mechanisms for the distortion of the flexible and rigid polymer backbones. Let us try to discuss this problem by using the illustrations presented in Scheme 2. They summarize both theoretical and experimental data related to polymer backbone conformations of LCPs. For both upper and lower parts of Scheme 2 the magnetic field has the sign shown on the right side of the scheme. The mesogenic units are considered to align parallel to the field and perpendicular to the polymer backbone. Although there is still dispute concerning the perpendicular alignment of the mesogenic groups irrespective of the nature of the polymer backbone,[16-19] for the present discussion, we will consider that this is true. Warner et al[14] have theoretically predicted that on going from the isotropic to the nematic phase the statistical random-coil conformation of the

polymer backbone becomes slightly anisotropic. This anisotropy increases in the smectic phase. Subsequently, the polymer displays two radii of gyration. One is parallel to the magnetic field ($R_{\parallel}$). The other is perpendicular to the magnetic field ($R_{\perp}$). Both in the nematic and in the smectic phase $R_{\perp} > R_{\parallel}$.

These theoretical predictions were experimentally observed by small angle X-ray scattering experiments,[15] and by small angle neutron scattering experiments performed on LCP containing deuterated backbones.[16,19] It is only a very recent result based on neutron scattering experiments[19] which provides some support for the sketch in the lower part of Scheme 2. This result concludes that for a liquid crystalline polyacrylate $R_{\parallel}$ in the smectic phase is smaller than the smectic layer, L (lower right part of Scheme 2). This means that in this case the random-coil conformation of the polyacrylate backbone is squeezed in between two smectic layers and therefore is confined between the two smectic layers. However, for a liquid crystalline polymethacrylate, $R_{\parallel}$ in the smectic phase is equal or slightly larger than the smectic layer, L (lower left part of Scheme 2).[16-19] This may mean, that for flexible backbones like polyacrylates and polymethylsiloxanes the polymer backbone is squeezed in between two smectic layers and becomes segregated without to cross the smectic layer. However, in the case of polymethacrylates the polymer backbone is stretched into an extended conformation and crosses the

smectic layer. The extended conformation of polymethacrylate backbones is also suggested by other authors.[18] Certainly, the entropy of the extended backbone from the lower left part of Scheme 2 is lower than that of the squeezed backbone from the lower right part of Scheme 2. Although when crossing the smectic layer the polymer backbone increases the entropy of the smectic layer, the overall degree of order which considers both the organization of the side groups and the conformation of the polymer backbone is higher in the case of the lower left part of Scheme 2 than in that of the lower right part of the same scheme. Therefore, the overall entropy of the liquid crystalline phase in the left part of Scheme 2 is lower than that in the right part of Scheme 2. Consequently, the entropy change associated with the transition from the left sided smectic phase to the isotropic phase should be higher than the ΔS_i from the right sided smectic phase to the corresponding isotropic phase.

Certainly, these two very general models should provide particular situations from case to case and require additional experiments to be confirmed. Nevertheless, there are reports claiming both extended and squeezed polymer chain conformations of side chain liquid crystalline polymers. The right sided sketch in the lower part of Scheme 2 resembles the microphase separated morphology observed in smectic liquid crystalline copolysiloxanes containing mesogenic and non-mesogenic structural

units,[12,20,21] and suggested for liquid crystalline polysiloxanes containing long flexible spacers.[12] Examples of the extended chain conformation model were recently reported for a smectic polymethacrylate containing flexible spacers[22a] and for a nematic polymethacrylate without flexible spacer.[22b]

The influence of polymer backbone flexibility on its conformation in the mesomorphic phase seems to vanish at short flexible spacers. It is expected,[1] that polymers based on short spacers can exhibit liquid crystallinity only when their backbone is extended. This might be the case regardless of their backbone flexibility. If the two models of Scheme 2 are correct, they may open avenues to explain the difference between the dynamics of side chain LCPs based on long flexible spacers and highly dissimilar polymer backbone flexibilities, between polymers based on long and short flexible spacers, and between the dynamics of LC polymers and copolymers.

These thermodynamic results are not particular only for the class of polymers described here. ΔS_i values calculated from the ΔH_i data reported for polymethacrylates, polyacrylates[23] and polymethylsiloxanes[24] containing 4-[5-(4-methoxyphenyl)-1,3-dioxan-2-yl]phenol and 4'-methoxy-4-biphenylol mesogens connected to the polymer backbone through a flexible spacer containing eleven methylenic units, exhibit the same trend. The same behavior can be determined upon calculating the ΔS_i values of several other

examples of polymethacrylates and polyacrylates.[25] Unfortunately, there are only very few data in the literature reporting both the polymer molecular weights and the thermodynamic parameters of their mesomorphic phase transitions. Therefore, generalization of this dependence requires additional experiments.

ACKNOWLEDGMENTS

Financial support of this work by the Office of Naval Research is gratefully acknowledged.

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Scheme and Figure Captions

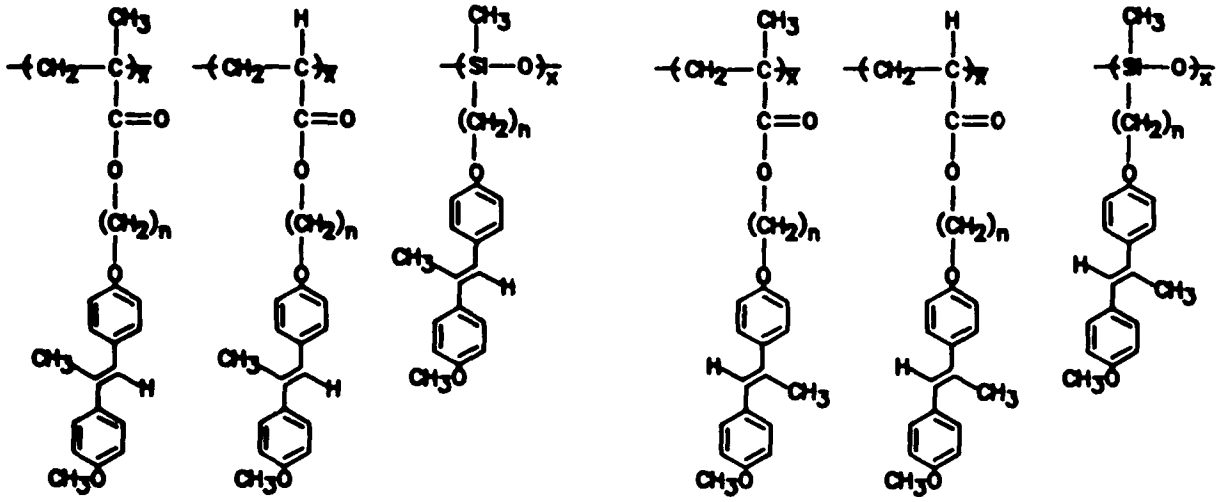
Scheme 1: The structures of the polymers based on polymethacrylate, polyacrylate, and polymethylsiloxane backbones, 4-MHMS and 4'-MHMS constitutional isomeric mesogenic side groups, and different spacer lengths. Corresponding notations used within the manuscript are labelled on the bottom part of the scheme.

Scheme 2: Schematic representation of the theoretical distortion of the statistical random-coil conformation of the polymer backbone in the nematic and in the smectic phases (upper part). Two possible modes of distortion of the random-coil conformation of a rigid (lower left part) and a flexible (lower right part) polymer backbone. $R_{\parallel}$ refers to the radius of gyration parallel ($\parallel$) to the magnetic field. The radius of gyration perpendicular ($\perp$) to the magnetic field is labelled as $R_{\perp}$.

Figure 1: The dependence between the isotropic-anisotropic transition temperature (T_i), the nature of the polymer backbone (○ , ● : polymethylsiloxane; □ , ■ : polymethacrylate; △ , ▲ : polyacrylate), and the number of methylenic units (n) in the flexible spacer for the series of polymers based on 4-MHMS (open symbols) and 4'-MHMS (filled symbols) isomers.

Figure 2: The dependence between the entropy change of isotropization (ΔS_i) determined from the cooling DSC scans, the nature of the polymer backbone, and the number of methylenic units (n) in the flexible spacer for the series of polymers based on 4-MHMS isomer.

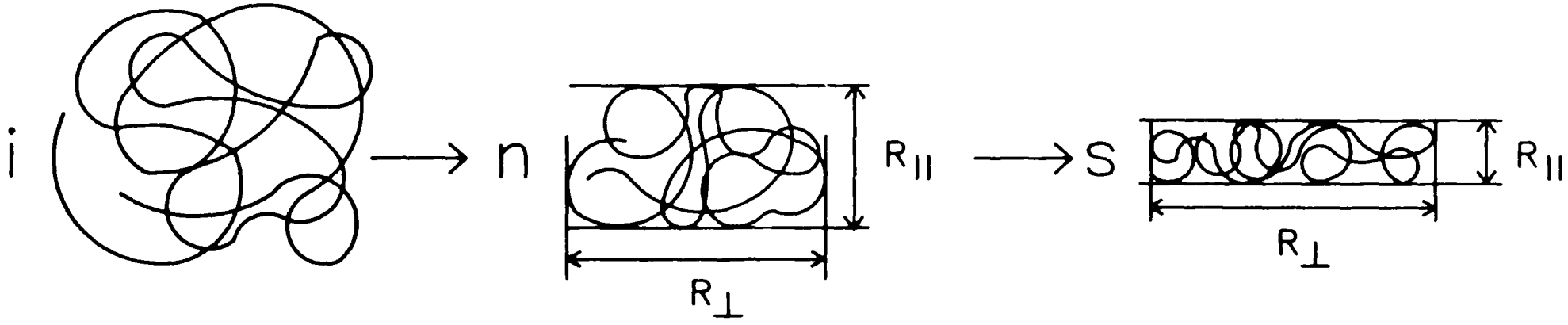
Figure 3: The dependence between the entropy change of isotropization (ΔS_i) determined from the cooling DSC scans, the nature of the polymer backbone, and the number of methylenic units (n) in the flexible spacer qfor the series of polymers based on 4'-MHMS isomer.



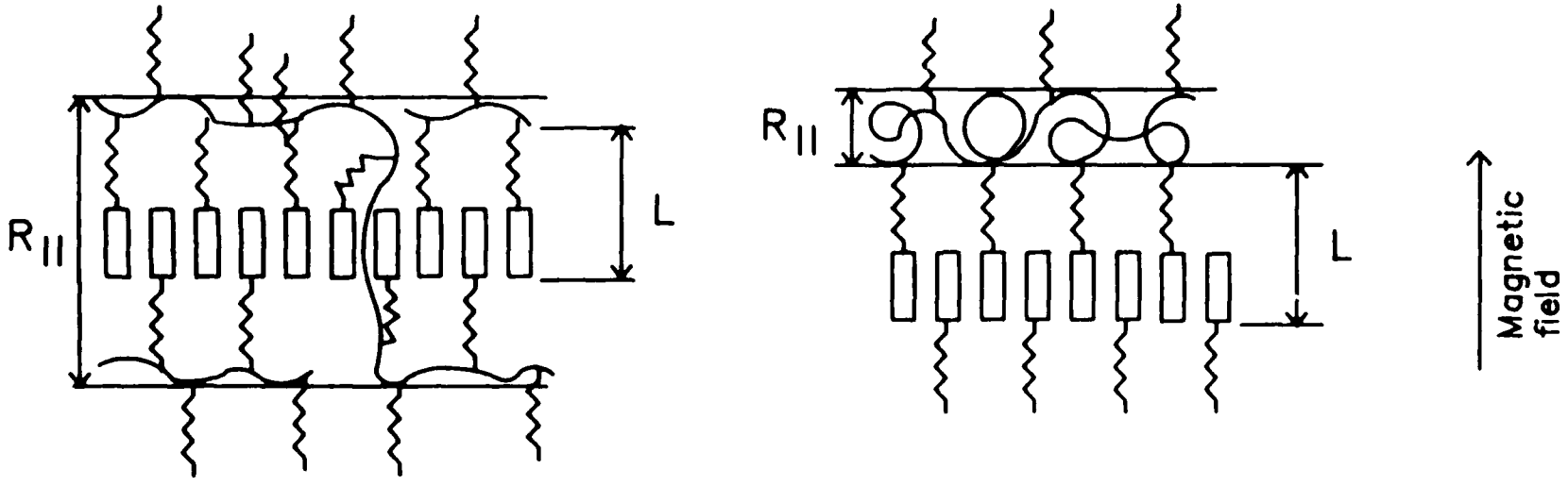
4-n-PMA 4-n-PAC 4-n-PS 4'-n-PMA 4'-n-PAC 4'-n-PS

Scheme 1

Theoretical (M. Warner)

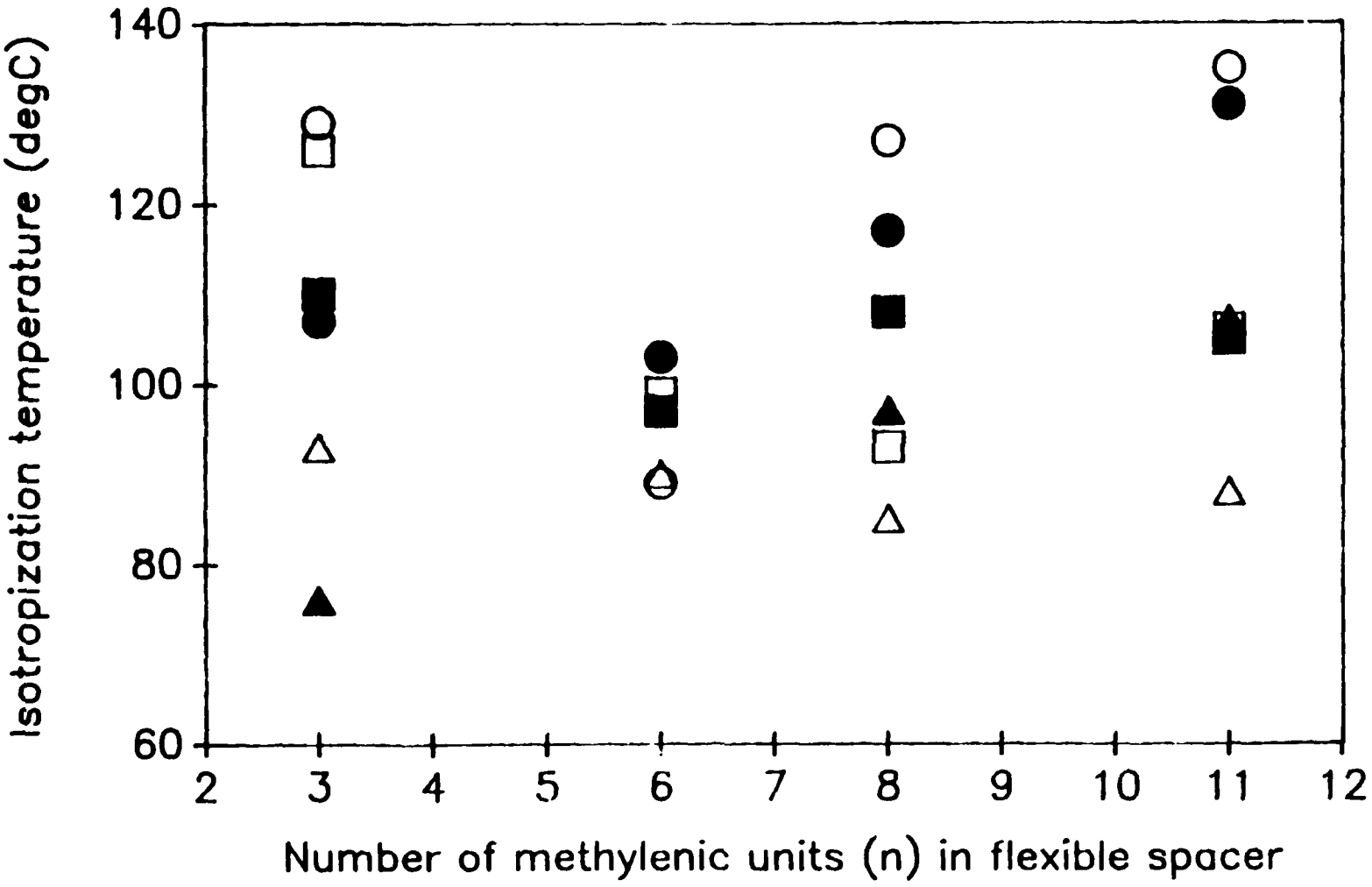


Experimental (Sacley Group)



$R_{\parallel PAC} \leq R_{\parallel PMA}$ $\quad R_{\parallel PAC} < L_{PAC}$ $\quad R_{\parallel PMA} \geq L_{PMA}$

Scheme 2


Isotropization temperature (degC)
140
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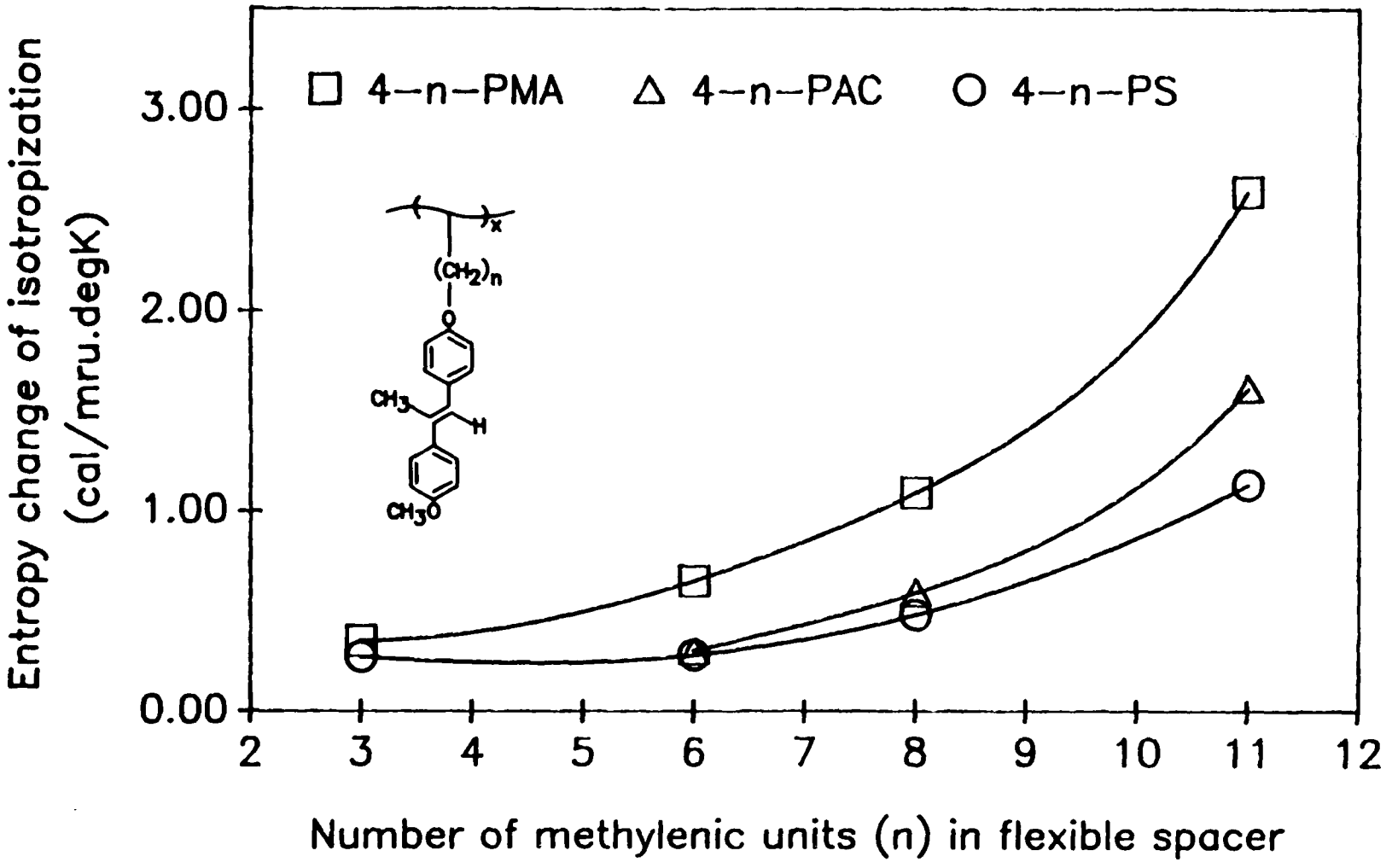
Number of methylenic units (n) in flexible spacer

Figure 1


□ 4–n–PMA
△ 4–n–PAC
○ 4–n–PS
Entropy change of isotropization
(cal/mru.degK)
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2.00
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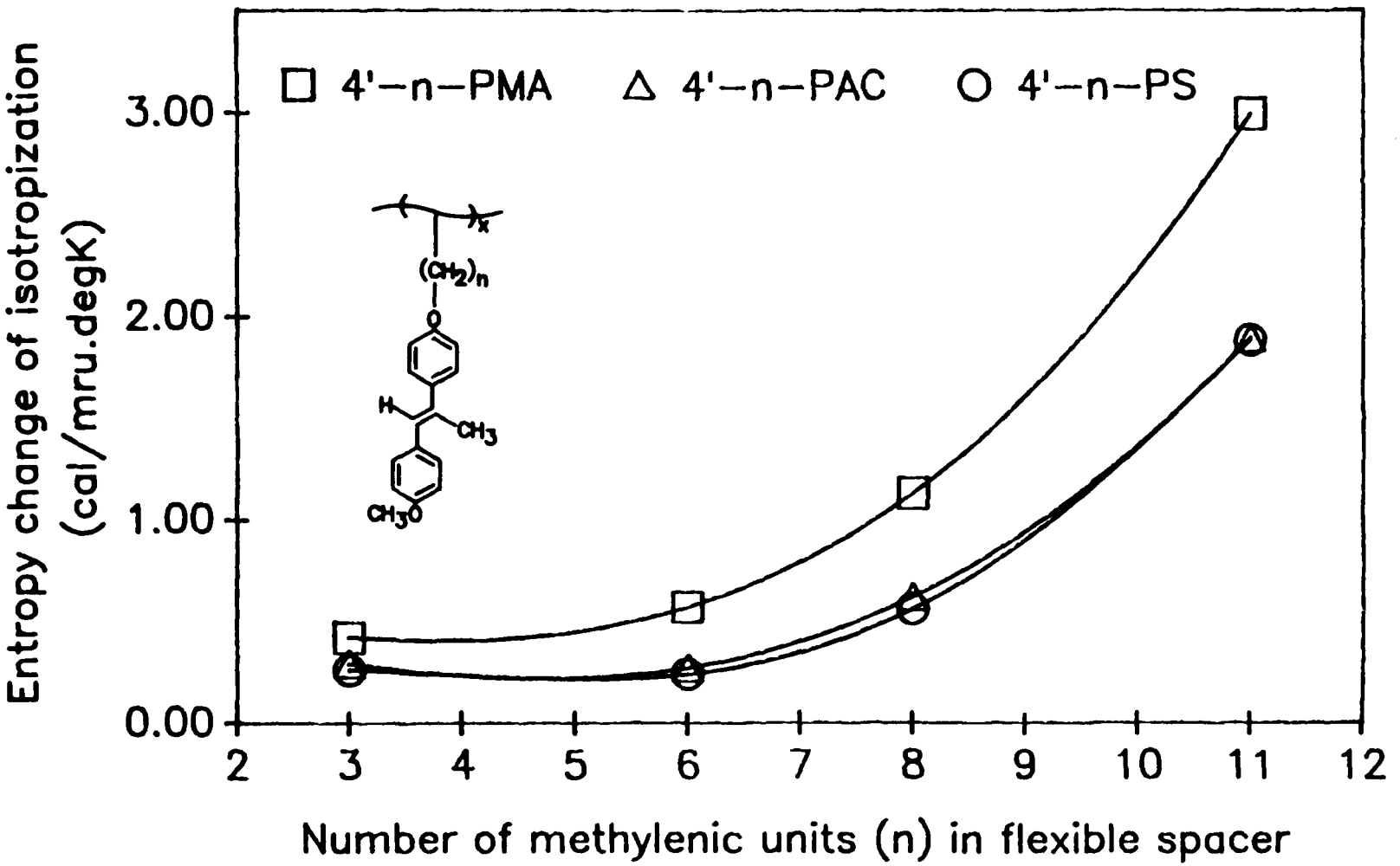
Number of methylenic units (n) in flexible spacer

Figure 2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4'-n-PAC
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Entropy change of isotropization
(cal/mru.degK)
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1.00
0.00
2
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6
7
8
9
10
11
12
Number of methylenic units (n) in flexible spacer

Figure 3