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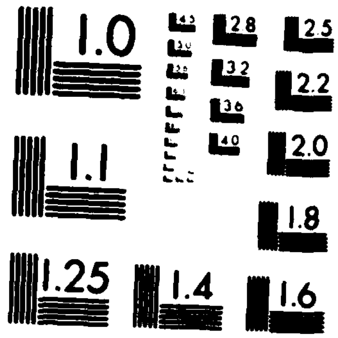

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Polymerization of Fluorinated Diacetylenes

by

Kurt Baum, Paul G. Cheng, Ronald J. Hunadi and Clifford D. Bedford

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Perfluoroalkylene diacetylenes, $HC\equiv C-(CF_2)_n-C\equiv CH$, underwent thermal polymerization at 250-350 °C to give glassy polymers stable to 450 °C. Partial polymerization of the volatile monomers gave oligomers that are processable at atmospheric pressure. Polymers with similar thermal stability were obtained by transition-metal-catalyzed polymerization of the monomers at moderate temperatures.

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Polymerization of Fluorinated Diacetylenes[1]

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Synopsis

Perfluoroalkylene diacetylenes, $HC{\equiv}C{-}(CF_2)_n{-}C{\equiv}CH$, underwent thermal polymerization at 250-350 °C to give glassy polymers stable to 450 °C. Partial polymerization of the volatile monomers gave oligomers that are processable at atmospheric pressure. Polymers with similar thermal stability were obtained by transition-metal-catalyzed polymerization of the monomers at moderate temperatures.

INTRODUCTION

There has been extensive interest in recent years on the application of acetylene-terminated monomers and oligomers for the preparation of thermally stable polymers. Systems that have been studied include polyphenylenes[2], imides[3], phenylquinoxalines[4], sulfones[5] and triazines[6]. The acetylene groups undergo thermal polymerization to give linking groups with high thermal stability.

Fluorocarbons comprised another structure class that appeared to be potentially useful for this approach. Fluoropolymers possess useful stability, dielectric, and water repelency properties, but methods for the preparation of cross-linked, castable matrices are not generally available. With the objective of providing starting materials for this purpose, we developed synthesis procedures for perfluoroalkylene diacetylenes, $HC{\equiv}C(CF_2)_nC{\equiv}CH$.[7] The preferred synthetic route for $HC{\equiv}C(CF_2)_6C{\equiv}CH$ and higher homologs is outlined below.

$$CF_2{=}CF_2 + I_2 \longrightarrow I(CF_2)_nI$$

$$I(CF_2)_nI + Me_3SiC{\equiv}CSiMe_3 \longrightarrow Me_3SiC{\equiv}C(CF_2)_nC{\equiv}CSiMe_3$$

$$Me_3SiC{\equiv}C(CF_2)_nC{\equiv}CSiMe_3 + KF \longrightarrow HC{\equiv}C(CF_2)_nC{\equiv}CH$$

The preparation of $HC{\equiv}C(CF_2)_6C{\equiv}CH$ by this method was complicated by the formation of a cyclic product, and an alternate procedure consisting of addition of the fluorocarbon diiodide to trimethylsilylacetylene, dehydrohalogenation and desilylation was used.[7]

EXPERIMENTAL

Proton and fluorine NMR spectra were obtained with a Varian T-60 spectrometer. Mass spectra were obtained using a AEI MS-9 instrument. Molecular weights were obtained with a Mechrolab vapor phase osmometer. Elemental analysis was carried out by Galbraith Analytical Laboratory, Knoxville, Tenn. or Spang Microanalytical Laboratory, Eagle Harbor, Mich. Perfluoroalkylene diacetylenes were prepared by the procedures reported previously.[7]

1H-Perfluoro-1-dodecyne

A mixture of 100 g (0.155 mol) of perfluorodecyl iodide and 58 g (0.34 mol) of bis(trimethylsilyl)acetylene was sealed in a heavy-wall glass ampule and heated at 220 °C for 48 h. Distillation gave 60 g of crude 1-(trimethylsilyl)perfluoro-1-dodecyne as a red oil, bp 150-160 °C (2 mm). This material was stirred with 100 g of potassium fluoride dihydrate in 400 mL of methanol for 16 h. The mixture was diluted with 200 mL of saturated sodium chloride solution and was extracted with 500 mL of ether. The ether solution was dried over magnesium sulfate and distilled to give 25 g (30% based on perfluorodecyl iodide) of 1H-perfluoro-1-dodecyne, bp 35 °C (2 mm), mp 24-25 °C: ^1H NMR δ 2.95 (t, J_{HF} = 5 Hz); ^{19}F NMR ϕ 86.2 (t, 3 F, J = 10 Hz, CF_3), 103 (m 2 F, $CF_2C{\equiv}C$), 123-

126 (m, 14 F, CF_2), 129 (m, 2 F, CF_2CF_3).

Anal. Calcd for $C_{12}HF_{21}$: C, 26.49; H, 0.19. Found: C, 26.26; H, 0.16.

Thermal Oligomerization of 1H-Perfluorododecyne

1H-Perfluoro-1-dodecyne (2.0 g, 3.7 mmol) was sealed in a glass tube and heated at 260 °C for 40 h. Sublimation of the material at 100 °C (0.1 mm) gave 1.1 g (55%) of a white powder, mp 90-92 °C: ^1H NMR δ 7.8 (m); ^{19}F NMR ϕ 86.0 (t, 3 F, J = 10 Hz, CF_3), 112.5 (m, 2 F, CF_2-C), 123-126 (m, 14 F, CF_2), 129 (m, 2 F, CF_2CF_3); mass spectrum m/e 1707 (tetramer M^+ - $(CF_2)_8CF_3$); MW (VPO, ethyl acetate) calcd for $C_{48}H_4F_{84}$: 2176; found: 2490.

Anal. Calcd for $C_{48}H_4F_{84}$: C, 26.49; H, 0.19. Found: C, 26.58; H, 0.17.

Catalytic Oligomerization of 1H-Perfluoro-1-dodecyne

1H-Perfluoro-1-dodecyne (1.0 g, 1.8 mmol) was sealed with 5 mg of bis(benzonitrile)palladium (II) chloride in a glass tube and heated at 110 °C for 5 h. The resulting viscous oil was dissolved in 1,1,2-trichlorotrifluoroethane and filtered to remove the catalyst. Evaporation of the solvent gave 0.95 g (95%) of viscous oil: ^1H NMR δ 7.6 (m); ^{19}F NMR ϕ 86.0 (t, 3 F, J = 10 Hz, CF_3), 114.0 (m, 2 F, CF_2-C), 124-126 (m, 14 F, CF_2), 129 (m, 2 F, CF_2CF_3); mass spectrum m/e 1613 (trimer M^+ - F), 1163 (trimer M^+ - $(CF_2)_8CF_3$); MW (VPO, 1,1,2-trichlorotrifluoroethane) calcd for $C_{36}H_3F_{63}$: 1632; found: 1483.

Anal. Calcd for $C_{36}H_3F_{63}$: C, 26.49; H, 0.19. Found: C, 26.42; H, 0.22.

Thermal Oligomerization of 1H,12H-Perfluoro-1,11-dodecadiyne

A sealed glass tube containing 0.41 g (0.9 mmol) of 1H,12H-perfluoro-1,11-dodecadiyne was heated at 250 °C for 41 h. Unreacted starting material was removed under vacuum to give 0.28 g (68%) of viscous oil: MW (VPO, ethyl acetate) calcd for tetramer $C_{48}H_8F_{64}$: 1800; found 1726. Heating the material at 260 °C for 40 h gave a yellow glassy polymer insoluble in common solvents.

Catalytic Polymerization of 1H,12H-Perfluoro-1,11-dodecadiyne

A mixture of 2.0 g (4.4 mmol) of 1H,12H-Perfluoro-1,11-dodecadiyne and 10 mg of bis(benzonitrile)palladium (II) chloride was heated in a sealed glass tube, with occasional shaking, at 120 °C for 1 h. A brown rubbery resin was obtained. An identically prepared sealed sample heated for an additional 12 h period at 150 °C gave a dark glassy polymer.

RESULTS AND DISCUSSION

Preliminary thermal polymerization studies of the fluorinated diacetylenes were carried out using $HC{\equiv}C(CF_2)_4C{\equiv}CH$, $HC{\equiv}C(CF_2)_8C{\equiv}CH$ and $HC{\equiv}C(CF_2)_{10}C{\equiv}CH$. Samples were heated in sealed tubes at 250 °C to give clear hard polymers, yellow to amber in color. DSC analysis[8] of the samples showed symmetrical exotherms at 350 °C, with no evidence of decomposition to 450 °C. Repetition of the scans showed only endotherms at 106 to 120 °C, believed to represent glass transition temperatures. TGA showed initiation of weight loss at 450 °C. The 350 °C exotherm was ascribed to the completion of polymerization of uncured sites, confirmed by the observation of acetylenic absorbtion in the IR spectra (3318 and 2145 cm^{-1}) of the original polymer. The $HC{\equiv}C(CF_2)_8C{\equiv}CH$ polymer showed a critical surface tension of 21.6 dynes/cm, and water absorbtion determination over a 6-month period was negative. A swelling experiment with Freon 113 showed 12% absorbtion in 90 hrs.[9]

Because $HC{\equiv}C(CF_2)_8C{\equiv}CH$ is more readily available in quantity than its homologs, and this material was used in subsequent work. A problem in practical applications of this diacetylene is that its volatility at the temperatures required for thermal polymerization would require the use of pressurized containers for the fabrication of samples. One way to circumvent this problem is to carry out the polymerization in sealed containers to only a low degree of completion with the objective of preparing fluid or easily processable oligomers with sufficiently low volatility that final cure can be carried out at atmospheric pressure.

The polymerization of $HC{\equiv}C(CF_2)_8C{\equiv}CH$ was controlled adequately at 250 °C in sealed tubes, and after 41 h, 68% of the monomer was consumed. Removal of the unreacted monomer under vacuum left a viscous oil with a VPO molecular weight of four monomer units. The oligomer was then cured at atmospheric pressure by heating at 250 °C for several days to give a polymer with similar appearance and thermal properties to that obtained by polymerization of the monomer in sealed tubes.

Another approach to applying the volatile diacetylene for molding or coating applications is to use catalysts to lower the polymerization temperature. The cyclotrimerization and oligomerization of 3,3,3-trifluoropropyne with metal carbonyl catalysts has been reported,[10] and a number of catalyst systems have been used for similar reactions of non-fluorinated aromatic and aliphatic acetylenes.[11] Consequently, we initiated qualitative screening studies to determine the effectiveness of some available catalysts for the polymerization of $HC{\equiv}C(CF_2)_8C{\equiv}CH$. The results are summarized in Table 1.

Table I. Catalyst Screening

Conditions: 1 wt% catalyst heated with $HC{\equiv}C(CF_2)_8C{\equiv}CH$ 4 hrs at 140 °C
++ sample solidified; + sample became viscous; - no change
Cp = cyclopentadienyl; acac = acetylacetonate

Catalyst	Result
$CpTiBr_2$	-
$CpTiBr_2/NaBH_4$	-
$Cr(acac)_3$	-
$CpMo(CO)_2PPh_3^+\ Cl^-$	-
$Mo(CO)_6$	++
$C_6H_6W(CO)_3$	+
$FeCp(CO)_2I$	-
$Fe(acac)_3$	-
$Co(acac)_3$	-
$CpCo(CO)_2$	+
$PdCl_2(PhCN)_2$	++
$Ni(acac)_2$	++
$Ni(CN)_2$	-
$NiBr_2 \cdot PPh_3$	+
$NiBr_2 \cdot PPh_3 \cdot NaBH_4$	+
$Ni(CN)_2 \cdot PPh_3 \cdot NaBH_4$	+
$NiBr_2 \cdot NaBH_4$	-
$NiI_2 \cdot PPH_3$	+
$Ni(Ph_3P)_2(CO)_2$	+

Of the catalysts tested, $PdCl_2(PhCN)_2$ was the most effective, and as little as 0.1 wt% was sufficient to promote polymerization. With a 1% catalyst level, solidification took place in 2 days at ambient temperature, in 2-3 hrs at 80 °C and in minutes at 130 °C. The catalysts, $Ni(acac)_2$ and $Mo(CO)_6$ were less effective than $PdCl_2(PhCN)_2$, but they also produced polymers with appearance similar to that of the thermally produced polymer. On the other hand, $Ni(Ph_3P)_2(CO)_2$ and $CpCo(CO)_2$ gave tarry products. Because of the effectiveness of $PdCl_2(PhCN)_2$ for our system, further work was carried out with this catalyst, which has been reported to trimerize alkynes selectively to benzenes.[12]

Cured samples of the catalyzed polymer were similar to those produced thermally in that they had a glassy appearance and were brittle. DSC curves of the two types of polymer were essentially identical. To obtain additional information about the polymeriaztion reactions, model studies were carried out using $CF_3(CF_2)_9C{\equiv}CH$. Heating a sample of this monoacetylene with $PdCl_2(PhCN)_2$ at 110 °C for 5 h gave a 95% yield of an oil, *identified by molecular weight*, elemental analysis, and mass spectroscopy as a trimer of the starting material.

Also, $CF_3(CF_2)_9C{\equiv}CH$ was heated under conditions used for the thermal polymerization of the diacetylenes, 260 °C for 40 h. The product was a sublimable solid with a molecular weight by VPO of four monomer units.

The brittleness of the polymers is attributed to the high degree of cross-linking, and would be expected to be lessened by copolymerizing a monoacetylene with the diacetylene. Mechanical properties of the palladium-catalyzed homopolymers and several copolymers were determined by the three-point bending method[13], and are summarized in Table II. Copolymers of $HC{\equiv}C(CF_2)_8C{\equiv}CH$ were obtained with $PdCl_2(PhCN)_2$ as the catalyst and $CF_3(CF_2)_9C{\equiv}CH$ as the monofunctional component. A sample based on 28 mole % monoacetylene was a hard resin similar to the diacetylene homopolymer, but somewhat less brittle. However, a sample prepared with 57 % of the monoacetylene was flexible and rubbery. Tensile moduli of the copolymers and the homopolymer are in agreement with these observations.

Tensile moduli for the homopolymer at temperatures to 200 °C were also determined. There is no significant discontinuity at the temperature of the DTA endotherm (118 °C).

Table II. Tensile Moduli

Mole % Monoacetylene	°C	Tensile Modulus (kg/cm^2)
0	25	920
28	25	796
57	25	63
0	100	550
0	130	480
0	200	540

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