# Cyclopolymerization of Fluorinated Dipropargylmalonate and [(*tert*-Butyldimethylsilyl)oxy]-1,6-heptadiyne and Characterization of the Polymers

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*Received July 16, 1992; Revised Manuscript Received December 29, 1992*

ABSTRACT: Bis(2,2,3,3,4,4,5,5,6,6,7,7-dodecafluoroheptyl) dipropargylmalonate (DFHDPM) and 4,4-methyl-[(*tert*-butyldimethylsilyl)oxy]-1,6-heptadiyne (MSHDY) were polymerized by $MoCl_5$- and $WCl_6$-based catalysts to give new polymers. A high polymer yield was obtained in the presence of $MoCl_5$-based catalyst. Both polymers were amorphous violet solids, dissolved in common organic solvents, and their maximum number-average molecular weights reached ca. $1.0 \times 10^5$ and $5.8 \times 10^3$, respectively. The poly(DFHDPM) was film-forming, and its $P_{O_2}$ and $P_{O_2}/P_{N_2}$ values were 80 barrer and 2.8, respectively.

## Introduction

Recently, Gibson et al.[1] reported that the polymerization of 1,6-heptadiyne using the Ziegler–Natta catalyst [$Ti(OBu)_4/Et_3Al$] leads to insoluble polymer films. We reported in our previous works[2–7] that the $MoCl_5$- and $WCl_6$-based catalyst systems are highly effective in cyclopolymerization of the dipropargyl derivatives which are organosoluble polymers. Generally, fluorine- or silicon-containing polyacetylenes are expected to show unique properties and functions not only because of the alternating double bonds along the main chain but also because of the effect of the fluorine and silicon atoms in the side chain. Also, these polyacetylene membranes are known to show high permeability for oxygen.[7,8]

We have been interested in the effect of fluorine atoms and bulky siloxyl groups on the permeability for oxygen.

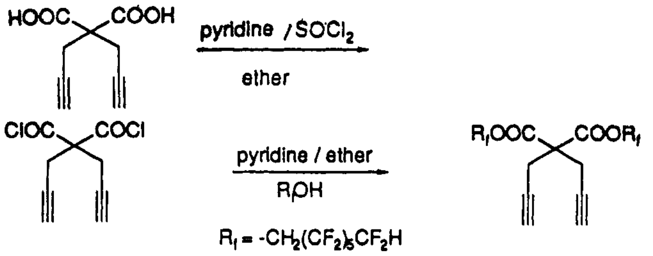
In this paper, we report the cyclopolymerization of fluorinated dipropargylmalonate and a siloxylated 1,6-heptadiyne derivative by $MoCl_5$- and $WCl_6$-based catalysts and the permeability of poly(DFHDPM). The polymeric products are characterized by $^1$H-NMR, $^{13}$C-NMR, and IR spectroscopic methods.

## Experimental Section

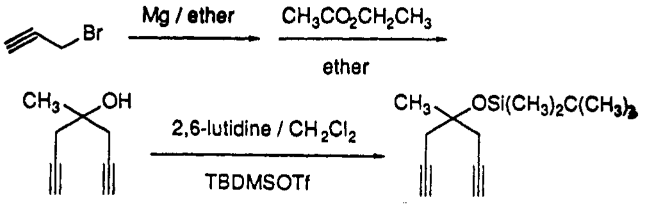
**Materials.** Commercial grades of transition-metal compounds and organometallic cocatalysts were used without further purification. 1,4-Dioxane and other polymerization solvents were purified by standard methods. Special care was taken to ensure complete removal of moisture and oxygen.

**Monomer Synthesis.** Bis(dodecafluoroheptyl) dipropargylmalonate (DFHDPM) was synthesized as follows (Scheme I). Dipropargylmalonic acid, the starting compound, was prepared as described in the literature.[7] To a flask charged with an ether solution (100 mL) of dipropargylmalonic acid (18 g, 0.1 mol) under a nitrogen atmosphere was added pyridine (15.8 g, 0.2 mol) dropwise at room temperature. Thionyl chloride (35.7 g, 0.3 mol) was added dropwise to the reaction mixture, which was kept at −30 °C for 2 h. The reaction was completed by stirring the mixture at room temperature for 10 h. After the reaction mixture was filtered and evaporated, the crude product was distilled twice at reduced pressure to give dipropargylmalonyl dichloride [yield 60% (12.9 g), bp 54–55 °C (1 mmHg)]. Under a nitrogen atmosphere, a flask was charged with an ether solution (100 mL) of 2,2,3,3,4,4,5,5,6,6,7,7-dodecafluoroheptanol (66.2 g, 0.2 mol), and pyridine (15.8 g, 0.2 mol) was added to it at room temperature. Upon completion of the addition, a mixture of dipropargylmalonyl dichloride (21.6 g, 0.1 mol) and ether (100 mL) was added dropwise at 0 °C for 2 h. Then the reaction was completed by stirring the mixture at room temperature for 12 h. Water was added dropwise and then the organic phase was extracted with ethyl ether. After the solvent was removed by a rotatory evaporator, the residue was distilled twice at reduced pressure to give bis(2,2,3,3,4,4,5,5,6,6,7,7-dodecafluoroheptyl) dipropargylmalonate (DFHDPM): yield 50% (40 g); bp 110–112 °C (1 mmHg); $^1$H NMR ($CDCl_3$) $\delta$ 2.07 (t, 2 H), 3.1 (d, 4 H), 4.6 (t, 4 H), 5.8–6.2 (t of t, 2 H); $^{13}$C NMR ($CDCl_3$) $\delta$ 22.5 ($CH_2$ of $CH_2C{\equiv}CH$), 56.8 (>C<), 60.8 ($CH_2$ of $OCH_2(CF_2)_6H$), 72.6 (${\equiv}CH$), 77.4 ($-C{\equiv}$), 107–110.9 ($(CF_2)_6$), 166.4 (C=O); $^{19}$F NMR ($CDCl_3$) $\delta$ −112 to −131 (12 F, $(CF_2)_6$); IR (NaCl) 3307 (${\equiv}CH$), 2130 ($C{\equiv}C$), 1765 (C=O) cm$^{-1}$. Anal. Calcd for $C_{23}H_{10}F_{24}O_4$: C, 34.18; H, 1.48; F, 56.41. Found: C, 34.04; H, 1.34; F, 56.61.

**Scheme I**



**Scheme II**



4,4-Methyl[(*tert*-butyldimethylsilyl)oxy]-1,6-heptadiyne (MSHDY) was prepared as follows (Scheme II). Dipropargylmethylcarbinol was prepared by Grignard reaction of propargylmagnesium bromide and ethyl acetate. To a vigorously stirred solution of 0.4 mol of magnesium turnings in ether was added a mixture of propargyl bromide and ether in 2 h. Stirring was continued for 1 h. Then a mixture of ethyl acetate and ether was added to the Grignard reagent solution during 1 h at −30 °C. Then the reaction mixture was quenched with saturated $NH_4Cl$ solution and extracted with ethyl ether. The extract was dried over anhydrous $MgSO_4$. The solvent was removed by rotary evaporator and the dipropargylmethylcarbinol was isolated by fractional distillation [yield 52% (12.7 g); bp 62 °C (10 mmHg)]. (*tert*-Butyldimethylsilyl)trifluoromethane sulfonate (TBDMSOTf)[9] (6 g, 0.023 mol) was added dropwise to a stirred solution of the carbinol (1.3 g, 0.015 mol) and 2,6-lutidine (3.2 g, 0.03 mol)

0024-9297/93/2226-2485$04.00/0

Table I. Polymerization of DFHDPM by $MoCl_5$- and $WCl_6$-Based Catalyst[a]

| no. | catalyst syst | M/C[b] | yield (%)[c] | $\bar{M}_n/10^4$ [d] |
|---|---|---|---|---|
| 1 | $MoCl_5$ | 50 | 90 | 9.3 |
| 2 | $MoCl_5$ | 100 | 82 | 9.5 |
| 3 | $MoCl_5$ | 200 | 77 | 10.2 |
| 4 | $MoCl_5$–$(n\text{-}Bu)_4Sn$ | 50 | 68 | 9.2 |
| 5 | $MoCl_5$–$EtAlCl_2$ | 50 | 60 | 11.0 |
| 6 | $WCl_6$ | 50 | trace | |
| 7 | $WCl_6$–$(n\text{-}Bu)_4Sn$ | 50 | trace | |
| 8 | $WCl_6$–$EtAlCl_2$ | 50 | trace | |

[a] Polymerization was carried out at 60 °C for 24 h in ethyl acetate; $[M]_0 = 0.25$. [b] Mole ratio of monomer to catalyst. [c] Yield of hexane-insoluble polymer. [d] Determined by GPC, polystyrene equivalent.

in 15 mL of methylene chloride (1 M solution of alcohol) at 25 °C for 30 min. Then the reaction mixture was quenched with water and extracted with *n*-pentane. The extract was dried over anhydrous $MgSO_4$. The *n*-pentane was removed by rotary evaporator, and the MSHDY was isolated by fractional distillation: yield 80% (1.9 g); bp 50 °C (3.5 mmHg); $^1$H NMR ($CDCl_3$) $\delta$ 0.03 (s, 6 H), 0.8 (s, 9 H), 1.3 (s, 3 H), 1.9 (t, 2 H), 2.4 (d, 4 H); $^{13}$C NMR ($CDCl_3$) $\delta$ 32 ($CH_2$ of $CH_2C{\equiv}CH$), 70.5 (${\equiv}CH$), 82 ($-C{\equiv}$), 74 (COSi); IR (NaCl) 3300 ($C{\equiv}CH$), 2121 ($-C{\equiv}C-$) cm$^{-1}$. Anal. Calcd for $C_{14}H_{24}SiO$: C, 71.12; H, 10.23; Si, 11.89. Found: C, 70.94; H, 10.05; Si, 12.12.

**Polymerization.** Catalyst preparation and polymerization were carried out under a dry nitrogen atmosphere. Transition-metal halide and organometallic compounds were dissolved in each solvent to make a 0.2 M solution before use. A typical polymerization procedure was as follows: Solvent, catalyst solution, and, when needed, cocatalyst solution were injected into a 20-mL ampule equipped with a rubber septum in the order given. When cocatalyst was used, the catalyst system was aged at 30 °C for 15 min. Finally, monomer dissolved in each solvent was injected into the polymerization ampule. After the reaction mixture was allowed to react at 60 °C for 24 h, the polymerization was terminated by adding a small amount of methanol. The resulting polymer was dissolved in ethyl acetate and precipitated with a large excess of hexane. The polymer was filtered from the solution and dried under vacuum at 40 °C for 24 h. The polymer yield was determined by gravimetry.

**Characterization.** $^1$H and $^{13}$C NMR spectra were recorded on a Bruker AM-300 spectrometer. $^{19}$F NMR spectrum was recorded on a Varian FT T-80A spectrometer using trifluoroacetic acid (TFA) as an external standard. Infrared spectra were taken on a Bomem MB-100 FT-IR spectrometer in film and a NaCl cell. UV–visible spectra were obtain with a Beckman DU-6 spectrometer. Thermogravimetric analysis (TGA) was performed with a Du Pont 951 TGA in a nitrogen atmosphere at 10 °C/min. Number-average molecular weights ($\bar{M}_n$) were determined in THF solution with a Waters GPC-150C calibrated with polystyrene standards. X-ray diffraction analysis was performed on a JEOL X-ray diffractometer with Cu K$\alpha$ radiation at a scan speed of 4°/min. Elemental analyses were performed with a Perkin-Elmer 240DS elemental analyzer. Gas permeabilities for the polymer membrane, about 40 $\mu$m thick, were measured with a conventional permeability apparatus, which consists of upstream and downstream parts separated by a membrane. Upstream pressure was maintained constant at 5 kg/cm$^2$ of either pure $O_2$ or $N_2$ during the experimental period, and the downstream was opened to the atmosphere. A bubble gas flowmeter was employed to measure permeated flux at the steady state, from which the gas permeability was calculated.

## Results and Discussion

**Polymerization of DFHDPM.** The polymerization of DFHDPM was examined with $MoCl_5$- and $WCl_6$-based catalysts, and results are summarized in Table I. When the mole ratio of DFHDPM to the catalyst is relatively low, the polymer yield is high. As shown in Table I, $WCl_6$ exhibits markedly lower catalytic activity than $MoCl_5$.

Table II. Polymerization of DFHDPM by $MoCl_5$ in Various Solvents[a]

| no. | solvent | yield (%)[b] | no. | solvent | yield (%)[b] |
|---|---|---|---|---|---|
| 1 | chlorobenzene | 95[c] | 3 | ethylacetate | 90 |
| 2 | toluene | 85[c] | 4 | 1,4-dioxane | 92 |

[a] Polymerization was carried out at 60 °C for 24 h; $[M]_0 = 0.25$, M/C = 50. [b] Yield of hexane-insoluble polymers. [c] Polymer insoluble in any organic solvents.

Table III. Polymerization of MSHDY $MoCl_5$- and $WCl_6$-Based Catalyst[a]

| no. | catalyst syst | M/C[b] | yield (%)[c] | $\bar{M}_n/10^3$ [d] |
|---|---|---|---|---|
| 1 | $MoCl_5$ | 50 | 80 | 4.2 |
| 2 | $MoCl_5$ | 100 | 67 | 4.8 |
| 3 | $MoCl_5$ | 200 | 30 | 5.2 |
| 4 | $MoCl_5$–$(n\text{-}Bu)_4Sn$ | 50 | 76 | 4.1 |
| 5 | $MoCl_5$–$EtAlCl_2$ | 50 | 77 | 5.8 |
| 6 | $WCl_6$ | 50 | trace | |
| 7 | $WCl_6$–$(n\text{-}Bu)_4Sn$ | 50 | trace | |
| 8 | $WCl_6$–$EtAlCl_2$ | 50 | trace | |

[a] Polymerization was carried out at 60 °C for 24 h in THF; $[M]_0 = 0.25$ M. [b] Mole ratio of monomer to catalyst. [c] Yield of methanol-insoluble polymer. [d] Determined by GPC, polystyrene equivalent.

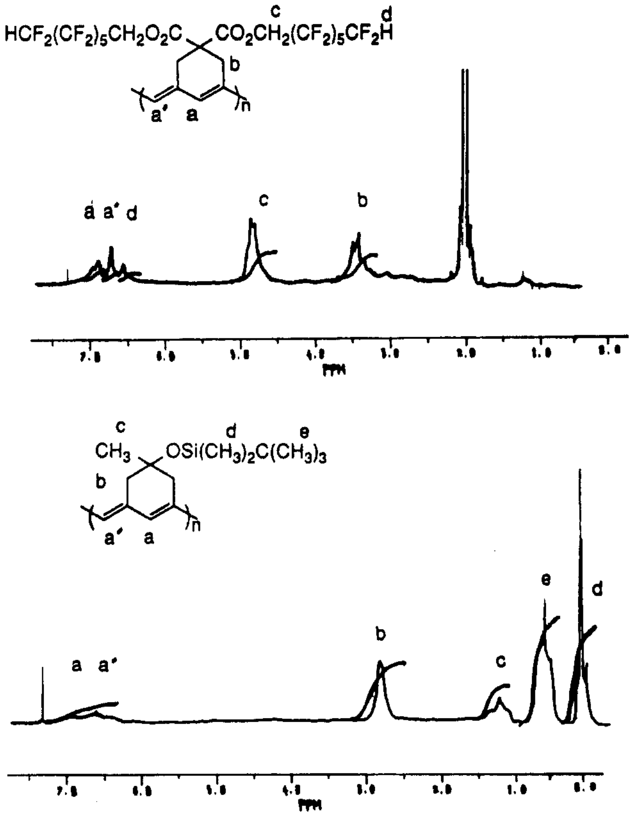


Figure 1. $^1$H-NMR spectra of poly(DFHDPM) in acetone-$d_6$ and poly(MSHDY) in $CDCl_3$.

$EtAlCl_2$ hardly affects the polymer yield, but its presence leads to higher number-average molecular weights ($\bar{M}_n$).

As it was found that $MoCl_5$ is an effective catalyst for the polymerization of DFHDPM, the influence of solvent was examined by using $MoCl_5$. As shown in Table II, poly(DFHDPM) is obtained in good yields in various solvents such as chlorobenzene, toluene, ethyl acetate, and 1,4-dioxane. Chlorobenzene and toluene, however, give insoluble polymer. These results are similar to those reported for the polymerization of propiolic acid derivatives.[10]

**Polymerization of MSHDY.** Table III lists the results of the polymerization of MSHDY by using $MoCl_5$- and

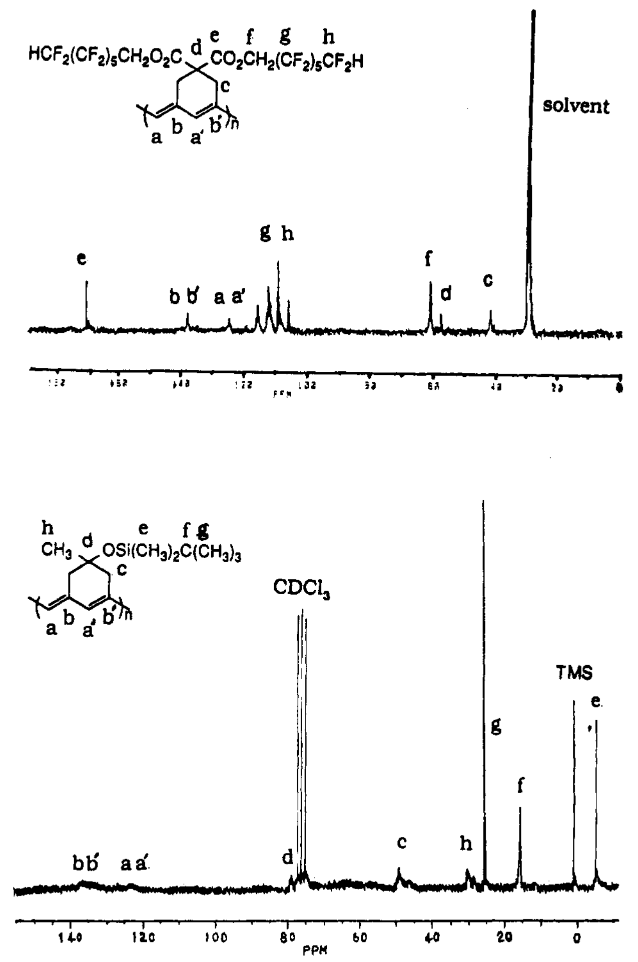


Figure 2. $^{13}C$-NMR spectra of poly(DFHDPM) in acetone-$d_6$ and poly(MSHDY) in $CDCl_3$.

$WCl_6$-based catalysts. The catalytic activity of $MoCl_5$ is greater than that of $WCl_6$. These results are similar to the polymerization of DFHDPM (Table I). The solvent effect on the polymer yield for the polymerization of MSHDY is similar to that for the polymerization of DFHDPM. Poly(MSHDY) was obtained in lower yield in solvents such as chlorobenzene and toluene, and these solvents gave insoluble polymer. Oxygen-containing solvents such as 1,4-dioxane, THF, and ethyl acetate gave higher yields of soluble polymer.

**Polymer Structure.** The analytical data of poly(DFHDPM) and poly(MSHDY) did not depend on the polymerization conditions. The data stated below have been obtained with the polymer samples from Tables I (no. 1) and III (no. 1). The $^{1}H$-NMR spectra of poly(DFHDPM) and poly(MSHDY) are shown in Figure 1. Vinylic protons of poly(DFHDPM) appear at $\delta$ 6.6–7.0 with the terminal protons of a dodecafluoroheptyl group. The $^{1}H$-NMR spectrum of poly(MSHDY) shows the vinylic protons as a broad signal at $\delta$ 6.2–7.0 having a small integral ratio relative to other proton peaks, and acetylenic proton peaks of MSHDY that should appear at $\delta$ 1.9 are not seen in the $^{1}H$-NMR spectrum of poly(MSHDY).

Figure 2 shows the $^{13}C$-NMR spectra of poly(DFHDPM) and poly(MSHDY). In the $^{13}C$-NMR spectrum of DFHDPM were observed two acetylenic carbons at $\delta$ 72.6 and 77.4. Instead, the carbon peaks from the conjugated double bond of poly(DFHDPM) appear at $\delta$ 124 and 137. The olefinic carbon peaks of poly(MSHDY) appear broadly at $\delta$ 123 and 136, and acetylenic carbon peaks of MSHDY that should appear at $\delta$ 70.5 and 82 are not seen in the $^{13}C$-NMR spectrum of poly(MSHDY).

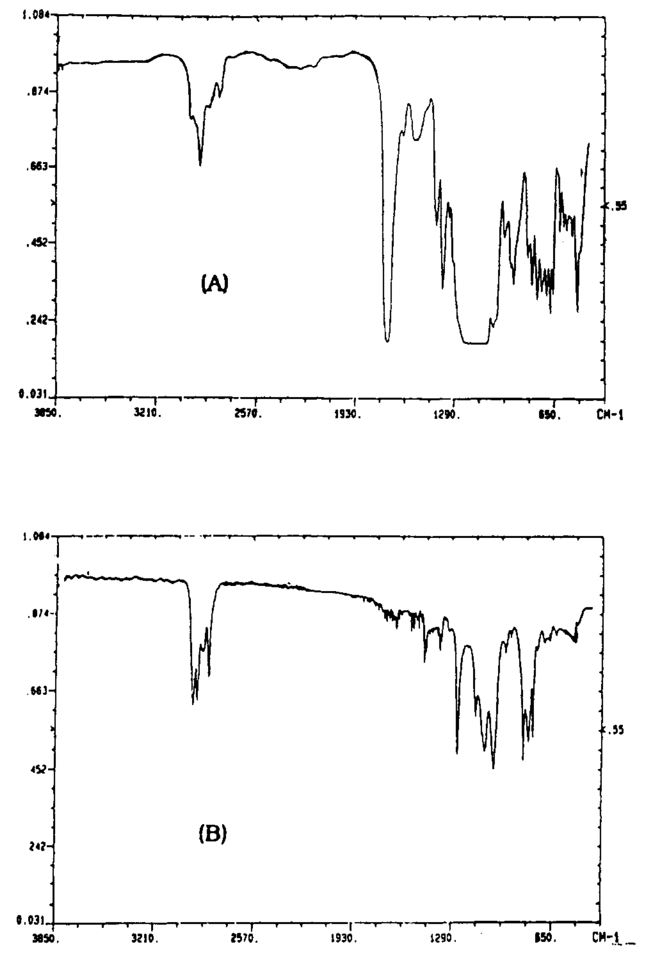


Figure 3. IR spectra of poly(DFHDPM) in film (A) and poly(MSHDY) in a NaCl cell (B) (solvent, chloroform).

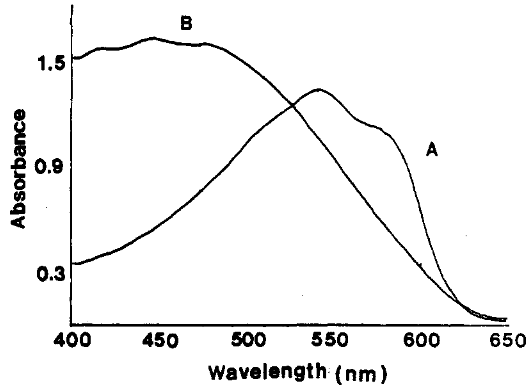


Figure 4. UV–visible spectra of poly(DFHDPM) (A) and poly(MSHDY) (B) in THF (1% solution; cell path length, 1 cm).

Figure 3 shows the IR spectra for poly(DFHDPM) and poly(MSHDY). The infrared spectra of the polymers show neither the acetylenic carbon–hydrogen stretching nor the carbon–carbon triple-bond stretching present in the IR spectra of the monomers at 3300 and 2120 cm$^{-1}$, respectively.

The UV–visible spectra of poly(DFHDPM) and poly(MSHDY) obtained in THF (Figure 4) exhibit a characteristically broad peak at 400–600 nm which is due to the $\pi$–$\pi^*$ transition of a conjugated polyene. The $\lambda_{max}$ values of the present polymers are 550 and 450 nm, respectively. The $\lambda_{max}$ value of poly(MHSDY) is lower than that of poly(DFHDPM) because of its lower molecular weight ($\bar{M}_n$) and degree of polymerization.

The data for the elemental analysis of the present polymers are as follows. Anal. Calcd for poly(DFHDPM)

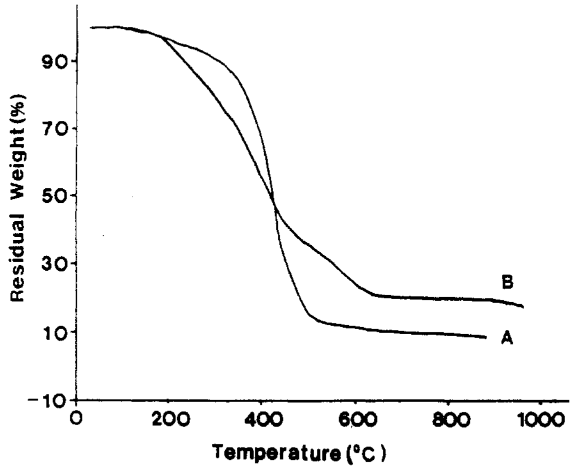


**Figure 5.** TGA curves of poly(DFHDPM) (A) and poly(MSHDY) (B) (10 °C/min in $N_2$).

$(C_{23}H_{10}F_{24}O_4)_n$: C, 34.18; H, 1.48; F, 56.41. Found: C, 33.98; H, 1.05; F, 56.89. Anal. Calcd for poly(MSHDY) $(C_{14}H_{24}SiO)_n$: C, 71.12; H, 10.23; Si, 11.89. Found: C, 70.86; H, 10.00; Si, 12.17. The values found agree well with the theoretical values.

**Polymer Properties.** Both poly(DFHDPM) and poly(MSHDY) have the form of a violet solid irrespective of polymerization conditions. Poly(DFHDPM) is completely soluble in acetone, 2-butanone, ethyl acetate, 1,4-dioxane, and THF but is insoluble in hexane, chlorobenzene, and methanol. The solubility of poly(MSHDY) is different from that of poly(DFHDPM). Poly(MSHDY) is completely soluble in ethyl acetate, 1,4-dioxane, THF, chlorobenzene, and hexane but is insoluble in polar solvents such as acetone and methanol.

A tough, free-standing film is accessible from poly(DFHDPM) by casting its ethyl acetate solution. In contrast, poly(MSHDY) is rather brittle and does not form a film. This property of poly(MSHDY) is attributable to its lower molecular weight.

Poly(DFHDPM) and poly(MSHDY) began to lose weight at about 285 and 245 °C, in thermogravimetric analysis (TGA) in a nitrogen atmosphere (Figure 5). This means that the thermal stability of these polymers does not stand very high among various substituted polyacetylenes.[11]

Table IV lists the electrical conductivities of $I_2$-doped and undoped polymers. When the film-type polymer (DFHDPM) and pellet-type polymer (MSHDY) are exposed to iodine vapor, the electrical conductivities increase from $10^{-11}$ to $10^{-3}$–$10^{-4}$ S cm$^{-1}$.

The data of X-ray diffraction analysis are as follows: poly(DFHDPM), $2\theta$ ($\Delta 2\theta/2\theta$) = 19.45 (0.41); poly(MSHDY), $2\theta$ ($\Delta 2\theta/2\theta$) = 21.30 (0.39). Because the peaks in the diffraction pattern are all broad, the ratios of the half-height width to diffraction angle ($\Delta 2\theta/2\theta$) are all greater than 0.35. In general, crystalline diffraction peaks are sharp, and hence their values of $\Delta 2\theta/2\theta$ are usually smaller than 0.05.[12] Consequently, it can be said that the present polymers are amorphous.

**Table IV. Electrical Conductivity of Poly(DFHDPM) and Poly(MSHDY)[a]**

| polym | compositn of polym[b] | conductivity (S cm$^{-1}$)[c] |
|---|---|---|
| poly(DFHDPM) | $(C_{23}H_{12}O_4F_{22})(I_2)_0$ | $5.8 \times 10^{-11}$ |
| poly(DFHDPM) | $(C_{23}H_{12}O_4F_{22})(I_2)_{0.25}$ | $1.6 \times 10^{-3}$ |
| poly(MSHDY) | $(C_{13}H_{24}OSi)(I_2)_0$ | $2.3 \times 10^{-12}$ |
| poly(MSHDY) | $(C_{13}H_{24}OSi)(I_2)_{0.5}$ | $8.1 \times 10^{-4}$ |

[a] These polymers were doped by exposure to the vapor of iodine in vacuum (1 mmHg) for 6 h. [b] The extent of doping was obtained by the weight uptake method.[13] [c] Measured with the four-point probe DC method.[14]

The following mechanical properties of the poly(DFHDPM) film were obtained with tensile measurements at a constant rate of stretching of 86%/min at 20 °C: Young's modulus ($E$), 700 MPa; tensile strength ($\sigma_B$), 20 MPa; ultimate elongation ($\gamma_B$), 9%.

The oxygen permeability coefficient ($P_{O_2}$) of a poly(DFHDPM) membrane at 35 °C was 80 barrer (1 barrer = $1 \times 10^{-10}$ cm$^3$ (STP) cm cm$^{-2}$ s$^{-1}$ cmHg$^{-1}$), and the separation factor of oxygen and nitrogen ($P_{O_2}/P_{N_2}$) was 2.8. The $P_{O_2}$ and $P_{O_2}/P_{N_2}$ values are greater than those for poly(dipropargylmalonate) ($P_{O_2}$ = 3.3 barrer, $P_{O_2}/P_{N_2}$ = 1.8).[7] This result is consistent with the fact that many fluorinated compounds show high solubilities for oxygen.

**Acknowledgment.** We gratefully acknowledge the support of this work by the Korea Science and Engineering Foundation.

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