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Cyclopolymerization of Bis(fluoroalkyl) Dipropargylmalonate Derivatives and Characterization of the Products

Sung Ho Han, Un Young Kim,† Yong Soo Kang,† and Sam Kwon Choi*

Department of Chemistry, Korea Advanced Institute of Science and Technology, P.O. Box 150, Cheongryangri, Seoul 131, Korea

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ABSTRACT: Bis(2,2,2-trifluoroethyl) and bis(1,1,1,3,3,3-hexafluoro-2-propyl) dipropargylmalonate are polymerized by $MoCl_5$- and WCl_6-based catalysts to give new, high molecular weight polymers. High-polymer yield is obtained in the presence of $MoCl_5$-based catalysts. When $MoCl_5$–$EtAlCl_2$ is used as a catalyst, the highest number-average molecular weights ($\bar{M}_n$) of poly[bis(2,2,2-trifluoroethyl) dipropargylmalonate] and poly[bis(1,1,1,3,3,3-hexafluoro-2-propyl) dipropargylmalonate] are found to be ca. 1.1×10^5 and 3.1×10^5, respectively. The products, dissolved in common organic solvents, can be cast into films. Mechanical, thermal, and electrical properties as well as gas permeabilities of the polymers are determined in an effort to elucidate their structures.

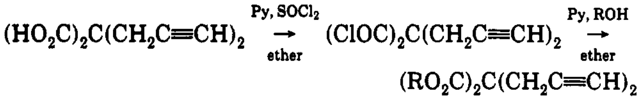
Introduction

Recently, Gibson et al.[1] reported that the polymerization of 1,6-heptadiyne by a special method using the Ziegler–Natta catalyst [$Ti(OBu)_4/Et_3Al$] leads to insoluble polymer films. In our previous work,[2–6] we reported that the $MoCl_5$- and the WCl_6-based catalyst systems are highly effective in catalyzing the cyclopolymerization of the dipropargyl derivatives, which produce organosoluble polymers. Generally, fluorine-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 atoms in the side chain.[7] In addition, many fluorinated compounds are known to show high solubility for oxygen.[8]

In this paper, the cyclopolymerization of fluorinated alkyl esters with $MoCl_5$- and WCl_6-based catalysts is investigated, and the polymer products are characterized by ^1H NMR, ^{13}C NMR, and IR spectrometry.

Experimental Section

Monomer Synthesis. Monomers were synthesized as follows.



$$(HO_2C)_2C(CH_2C{\equiv}CH)_2 \xrightarrow[\text{ether}]{\text{Py, SOCl}_2} (ClOC)_2C(CH_2C{\equiv}CH)_2 \xrightarrow[\text{ether}]{\text{Py, ROH}} (RO_2C)_2C(CH_2C{\equiv}CH)_2$$

$$R = CH_2CF_3, CH(CF_3)_2$$

Dipropargylmalonic acid, the starting compound, was prepared as described in the literature.[9,10] 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%, bp 54–55 °C (1 mmHg)]. Under a nitrogen atmosphere, a flask was charged with an ether solution (100 mL) of 2,2,2-trifluoroethanol (20 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 extracted with ethyl ether. After the solvent was removed by a rotatory evaporator, the residue was distilled twice at reduced pressure to give bis(2,2,2-trifluoroethyl) dipropargylmalonate [TFEDPM] [yield 70%; bp 69–70 °C (1 mmHg); ^1H NMR ($CDCl_3$) δ 2.1 (t, 1 H), 3.1 (d, 2 H), 4.6 (q, 2 H); ^{13}C NMR ($CDCl_3$) δ 22.5 (CH_2 of $CH_2C{\equiv}CH$), 56.5 ($\rightarrow$C–), 61.3 (q, J = 25 Hz, CH_2 of OCH_2CF_3), 73.0 (HC≡), 77.0 (–C≡), 122.2 (q, J = 175 Hz, CF_3), 166.4 (C=O); IR (NaCl) 3320, 3000, 2120, 1780 cm^{-1}; ^{19}F NMR ($CDCl_3$) δ −80 (t, 3 F). Anal. Calcd for $C_{13}H_{10}F_6O_4$: C, 43.36; H, 2.93; F, 33.12. Found: C,43.18; H, 2.75; F, 33.35]. Similarly, bis(1,1,1,3,3,3-hexafluoro-2-propyl) dipropargylmalonate [HFPDPM] was synthesized [yield 65%; mp 89 °C; ^1H NMR ($CDCl_3$) δ 2.2 (t, 1 H), 3.2 (d, 2 H), 5.8 (m, 1 H); IR (KBr) 3320, 2990, 2120, 1775 cm^{-1}; ^{13}C NMR ($CDCl_3$) δ 22.7 (CH_2), 56.8 ($\rightarrow$C–), 67.8 (CH of $OCH(CF_3)_2$), 73.4 (HC≡), 75.5 (–C≡) 120.0 (q, J = 185 Hz, CF_3), 164.6 (C=O); ^{19}F NMR $(CDCl)_3$ δ −80.7 (d, 6 F). Anal. Calcd for $C_{15}H_8F_{12}O_4$: C, 37.52; H, 1.68; F, 47.48. Found: C, 37.38; H, 1.54; F, 47.68.

Other Materials. Commercial grades of transition-metal compounds and organometallic cocatalysts were used without further purification. Dioxane and other polymerization solvents were purified by standard methods. Special care was taken to

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† Korea Institute of Science and Technology.

Table I
Polymerization of TFEDPM by $MoCl_5$- and WCl_6-Based Catalysts[a]

no.	cat.	m/c[b]	yield, %[c]	$\bar{M}_n/10^4$ [d]
1	$MoCl_5$	50	92	9.5
2	$MoCl_5$	100	82	9.8
3	$MoCl_5$	200	75	10.1
4	$MoCl_5$–$(n\text{-}Bu)_4Sn$	50	68	9.4
5	$MoCl_5$–$EtAlCl_2$	50	60	11.3
6	WCl_6	50	20	
7	WCl_6	100	12	
8	WCl_6	200	tr	
9	WCl_6–$(n\text{-}Bu)_4Sn$	50	28	
10	WCl_6–$EtAlCl_2$	50	23	

[a] Polymerization was carried out at 60 °C for 24 h in dioxane; $[M]_0 = 0.25$, [cat.] = [cocat.] = 5 mM. [b] Mole ratio of monomer to catalyst. [c] Yields of hexane-insoluble polymers. [d] Determined by GPC.

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

no.	solvent	$[M]_0$	yield,[b] %
1	chlorobenzene	0.25	95[c]
2	toluene	0.25	85[c]
3	1,2-dichloroethane	0.25	95[c]
4	ethyl acetate	0.25	90
5	dioxane	0.125	90
6	dioxane	0.25	92
7	dioxane	0.5	92
8	dioxane	1.0	95

[a] Polymerization was carried out at 60 °C for 24 h; monomer/catalyst (mole ratio) = 50. [b] Yields of hexane-insoluble polymers. [c] Insoluble polymer in any organic solvent.

Table III
Polymerization of HFPDPM by $MoCl_5$- and WCl_6-Based Catalysts[a]

no.	cat.	m/c[b]	yield, %[c]	$\bar{M}_n/10^4$ [d]
1	$MoCl_5$	50	85	21.5
2	$MoCl_5$	100	81	22.5
3	$MoCl_5$	200	75	25.5
4	$MoCl_5$–$(n\text{-}Bu)_4Sn$	50	83	23
5	$MoCl_5$–$EtAlCl_2$	50	80	31
6	WCl_6	50	tr	
7	WCl_6–$(n\text{-}Bu)_4Sn$	50	12	
8	WCl_6–$EtAlCl_2$	50	10	

[a] Polymerization was carried out at 60 °C for 24 h in ethyl acetate; $[M]_0 = 0.25$, [cat.] = [cocat.] = 5 mM. [b] Mole ratio of monomer to catalyst. [c] Yields of hexane-insoluble polymer. [d] Determined by GPC.

ensure complete removal of moisture and oxygen.

Polymerization. Catalyst preparation and polymerization were carried out under a dry nitrogen atmosphere. Transition-metal halides and organometallic compounds were dissolved in each solvent to make 0.2 M solutions 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.

Doping. The iodine doping was performed by exposing the polymer films to iodine vapor in a vacuum desiccator (initially at 10^{-1} mmHg) at 30 °C for 12 h. The dopant concentration was estimated by the weight uptake method.

Characterization. ^1H NMR and ^{13}C NMR spectra were recorded on a Varian FT-80A spectrometer and a Bruker AM-200 spectrometer. ^{19}F NMR spectra were recorded on a Varian FT T-80A spectrometer using trifluoroacetic acid (TFA) as an external standard. Infrared spectra were taken on a Perkin-Elmer 283B spectrometer in potassium bromide pellets. UV–visible spectra were obtained 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. Tensile tests were conducted at 20 °C with the rate of strain fixed at 86%/min on an Instron 1122. The size of the specimen was 35 × 10 × 0.2mm. X-ray diffraction analysis was performed on a JEOL X-ray diffractometer with Cu Kα radiation at a scan speed of 4°/min. Elemental analysis was performed with a Perkin-Elmer 240DS elemental analyzer. Gas permeabilities for the polymer membrane, about 30 μm thick, were measured with a conventional permeability apparatus, which consists of upstream and downstream parts separated by a membrane. The upstream pressure was maintained constant at 3 kgf/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 the permeate flux, steady-state from which the gas permeability was calculated. Electrical conductivities were measured by the four-point probe dc method employing a Hewlett-Packard 3435A digital multimeter.

Results and Discussion

Polymerization of TFEDPM and HFPDPM. The polymerization of TFEDPM was examined with $MoCl_5$- and WCl_6-based catalysts (Table I). When the mole ratio of TFEDPM to the catalyst is relatively low, the yield is high. As shown in Table I, $EtAlCl_2$ hardly affects the polymer yield, but its presence leads to higher number-average molecular weights ($\bar{M}_n$). WCl_6 exhibits markedly lower catalytic activity than $MoCl_5$. The highest number-average molecular weight of poly(TFEDPM) obtained is ca. 1.1 × 10^5 (with $MoCl_5$–$EtAlCl_2$ as catalyst).

As it was found that $MoCl_5$ is an effective catalyst for the polymerization of TFEDPM, the influence of solvents was examined by using $MoCl_5$ (Table II). As shown in Table II, poly(TFEDPM) is obtained in good yields in various solvents such as chlorobenzene, toluene, 1,2-dichloroethane, 1,4-dioxane, and ethyl acetate. Chlorobenzene, toluene, and 1,2-dichloroethane, however, give insoluble polymers. These results are similar to those reported for the polymerization of propiolic acid derivatives.[11]

Table III lists the results of the polymerization of HFPDPM by using $MoCl_5$- and WCl_6-based catalysts. In the polymerization HFPDPM, ethyl acetate has been used as the polymerization solvent owing to the low dissolving ability of dioxane for poly(HFPDPM). The catalytic activity of $MoCl_5$ is greater than that of WCl_6. As shown in Table III, $EtAlCl_2$ hardly affects the polymer yield, but its presence gives higher number-average molecular weights ($\bar{M}_n$). $MoCl_5$ alone catalyzes the polymerization of HFPDPM very effectively. These are similar to the results for the polymerization of TFEDPM. The highest number-average molecular weight of poly(HFPDPM) obtained is ca. 3.1 × 10^5 (with $MoCl_5$–$EtAlCl_2$ as catalyst).

Polymer Structure. The ^1H NMR spectra of poly(TFEDPM) and poly(HFPDPM) are shown in Figure 1. The peaks at 6–7.4 ppm in the ^1H NMR spectrum of poly(TFEDPM) are assignable to the protons on the conjugated double bond. Vinylic protons of poly(HFPEPM) appear at 5.8–7.4 ppm together with protons on the hexafluoroisopropyl group.

Figure 2 shows the IR spectra for poly(TFEDPM) and poly(HFPDPM). The infrared spectra of the polymers show neither the acetylenic hydrogen stretching nor the carbon–carbon triple-bond stretching present in the IR spectra of the monomers at 3320 and 2120 cm^{-1}, respec-

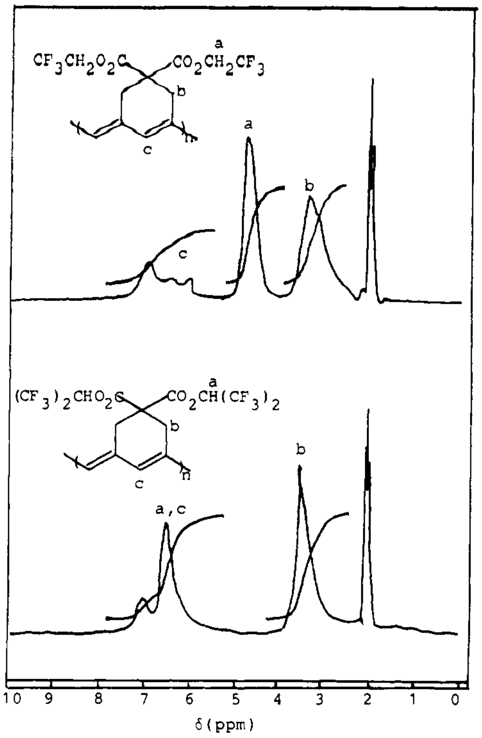

Figure 1. ^1H NMR spectra of poly(TFEDPM) and poly(HFPDPM) [sample: Table I, no. 1; Table III, no. 1; measured in CD_3COCD_3 (2.0 ppm)].

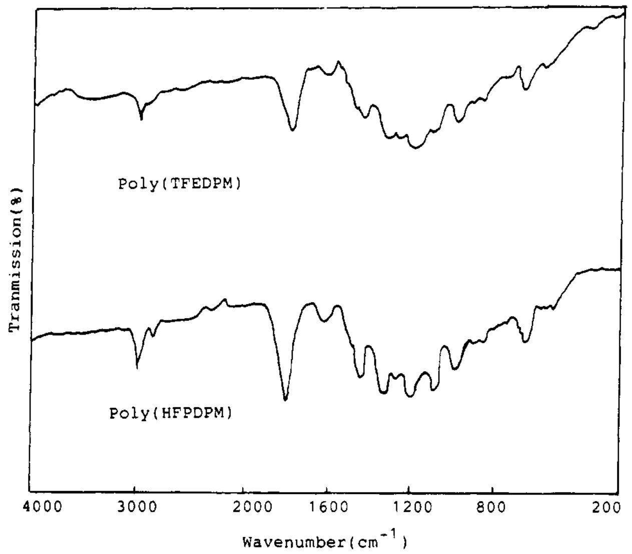

Figure 2. IR spectra of poly(TFEDPM) and poly(HFPDPM) (sample: Table I, no. 1; Table III, no. 1; KBr pellet).

tively. Instead, the carbon–carbon double-bond stretching frequency at 1600–1650 cm^{-1} indicates a highly conjugated unsaturation.

Figure 3 shows the ^{13}C NMR spectra of poly(TFEDPM) and poly(HFPDPM). Acetylenic carbon peaks that should appear between 77 and 73 ppm are not seen in these polymers. Instead, the carbon peaks from the conjugated double bond appear at 125 and 138 ppm.

The UV-visible spectra of the polymers obtained in THF (Figure 4) exhibit characteristically broad peaks at 400–600 nm, which are due to the $\pi \rightarrow \pi^*$ transition of conjugated polyenes.

The data for the elemental analysis of the present polymers are as follows: Anal. Calcd for poly(TFEDPM) $(C_{13}H_{10}F_6O_4)_n$: C, 45.36; H, 2.93; F, 33.12. Found: C, 45.10; H, 2.70; F, 33.40. Anal. Calcd for poly(HFPDPM) $(C_{15}H_8F_{12}O_4)_n$: C, 37.52; H, 1.68; F, 47.48. Found: C, 37.24; H, 1.48; F, 47.82. The values found agree well with the theoretical values.

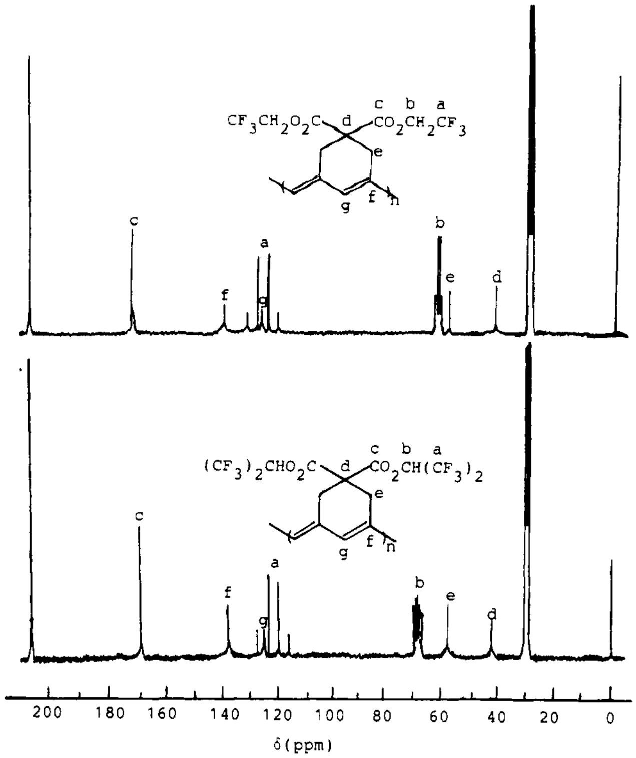

Figure 3. ^{13}C NMR spectra of poly(TFEDPM) and poly(HFPDPM) [sample: Table I, no. 1; Table III, no. 1; measured in CD_3COCD_3 (29.5, 206 ppm)].

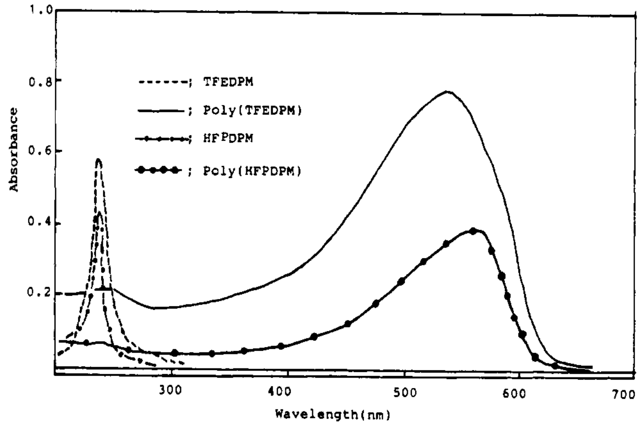

Figure 4. UV-visible spectra of poly(TFEDPM) and poly(HFPDPM) (sample: Table, no. 1; Table III, no. 1; measured in THF).

Polymer Properties. Poly(TFEDPM) and poly(HFPDPM) are completely soluble in acetone, 2-butanone, ethyl acetate, and THF but are insoluble in hexane, chlorobenzene, and methanol. The solubility of poly(TFEDPM) generally resembles that of poly(HFPDPM). One minor difference is found in that dioxane dissolves poly(TFEDPM) but not poly(HFPDPM).

Table IV lists the electrical conductivities of I_2-doped and undoped polymers. When the film-type polymers are exposed to iodine vapor, the electrical conductivities increase from 10^{-11} to 10^{-3}–10^{-2} S cm^{-1}.

Thermogravimetric analyses (TGA) of poly(TFEDPM) and poly(HFPDPM) show a 10% weight loss at 340 and 350 °C in N_2, respectively (Table V). This means that the thermal stability of these polymers does not stand very high among various substituted polyacetylenes.[12] Com-

Table IV
Electrical Conductivity of Poly(TFEDPM) and Poly(HFPDPM)[a]

polymer	comp of polymer[b]	conductivity,[c] S cm^{-1}
poly(TFEDPM)	$(C_{13}H_{10}F_6O_4)_1(I_2)_0$	4.7×10^{-11}
poly(TFEDPM)	$(C_{13}H_{10}F_6O_4)_1(I_2)_{0.4}$	1.5×10^{-2}
poly(HFPDPM)	$(C_{15}H_8F_{12}O_4)_1(I_2)_0$	5.2×10^{-11}
poly(HFPDPM)	$(C_{15}H_8F_{12}O_4)_1(I_2)_{0.25}$	7.5×10^{-3}

[a] These polymers were doped by exposure to iodine vapor under vacuum (1 mm Hg) for 12 h. [b] Extent of doping was obtained by weight uptake method. [c] Measured with four-point probe dc method.

Table V
Several Properties of Poly(TFEDPM) and Poly(HFPDPM)

parameter	poly-(TFEDPM)	poly-(HFPDPM)	poly-(DEDPM)[a]
E,[b] MPa	1160	750	4800
σ_B,[c] MPa	28	18	104
γ_B,[d] %	11.1	20	3.4
P_{O_2}[e]	1.28×10^{-9}	7.14×10^{-0}	3.3×10^{-10}
P_{N_2}[e]	8.02×10^{-10}	4.2×10^{-9}	1.8×10^{-10}
P_{O_2}/P_{N_2}	1.6	1.7	1.8
$T_{10\%}$,[f] °C	340	350	340
2θ ($\Delta 2\theta/2\theta$),[g] deg	21.3 (0.39)	20.07 (0.37)	22.03 (0.35)

[a] Data from ref 15; poly(DEDPM) = poly(diethyl dipropargylmalonate). [b] Young's modulus. [c] Tensile strength. [d] Elongation at break. [e] In units of cm^3 (STP)·cm/(cm^2·s·cmHg). [f] Measured by thermogravimetric analysis (in N_2; heating rate 10 °C/min). [g] X-ray diffraction data (Cu Kα radiation); 2θ = diffraction angle, $\Delta 2\theta$ = half-height width.

pared against poly(DEDPM) (Table V), the present polymers exhibit a lower Young's modulus, a smaller tensile strength, and a larger elongation at break. It seems that the difference in mechanical properties between the present polymers and poly(DEDPM) is due to the weak intermolecular interaction in the present polymers. Table V includes data for the X-ray diffraction analysis of the present polymers. Because the peaks in the diffraction patterns 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.[13] Consequently, it can be said that the present polymers are amorphous. Table V shows the oxygen permeability coefficient (P_{O_2}) and separation factors of oxygen to nitrogen (P_{O_2}/P_{N_2}) for poly(dipropargylmalonates). The P_{O_2} values for poly(TFEDPM) and poly(HFPDPM) are greater than those for poly(DEDPM). This result is consistent with the fact that many fluorinated compounds show high solubilities for oxygen. The P_{O_2} value for poly(HFPDPM) is greater than that for poly(TFEDPM). This agrees with the general trend that the presence of bulky substituents increases the oxygen permeability of substituted polyacetylenes.[14] It is concluded that (1) the catalytic activity of $MoCl_5$ is generally greater than that of WCl_6 in this cyclopolymerization, (2) both polymers have high number-average molecular weights ($\bar{M}_n$), and (3) both polymers are soluble and films are readily formed.

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Registry No. TFEDPM, 131236-71-0; TFEDPM (homopolymer), 131236-75-4; HFPDPM, 131236-72-1; HFPDPM (homopolymer), 131236-76-5; I_2, 7553-56-2; O_2, 7782-44-7; N_2, 7727-37-9; $MoCl_5$, 10241-05-1; $(n\text{-Bu})_4Sn$, 1461-25-2; $EtAlCl_2$, 563-43-9; WCl_6, 13283-01-7; dipropargylmalonic acid, 4431-32-7; dipropargylmalonyl dichloride, 131236-70-9; 2,2,2-trifluoroethanol, 75-89-8.