1208 *Macromolecules* **1995,** *28,* 1208−1213

Synthesis of Unsymmetrically α-Substituted Poly(dipropargyl ether) Derivatives by Metathesis Catalysts

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Received January 25, 1994; Revised Manuscript Received August 15, 1994[®]

ABSTRACT: Soluble and unsymmetrically cyclized poly(dipropargyl ether) derivatives bearing α-substituents were synthesized and characterized. The monomers were propargyl α-substituted (methyl, pentyl, methyl phenyl, cyclohexyl) propargyl ethers. Polymerizations were carried out with transition metal catalysts. It was found that $MoCl_5$-based catalysts were very effective for the cyclopolymerization of α-substituted dipropargyl ethers. The solubility of poly(dipropargyl ether)s was remarkably improved by incorporation of α-substituent groups. The resulting polymers exhibited good solubility in common organic solvents such as tetrahydrofuran, chloroform, DMF. The structure of the products was confirmed by IR, UV−visible, and ^1H- and ^{13}C-NMR spectroscopy. All of the polymers were amorphous, reddish solids and their weight average molecular weights were in the range of 24.3×10^3−73×10^3. The oxidative stability was dependent on the α-substituent groups of the poly(dipropargyl ether)s. The electrical conductivities of iodine-doped poly(dipropargyl ether) derivatives were 10^{-4}−10^{-2} s/cm.

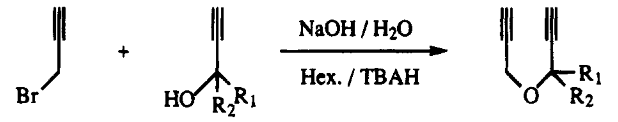
Introduction

Cyclopolymerization of nonconjugated diynes is a very interesting approach to obtain various functional polymers based on π-conjugated cyclic units in the polymer backbone. Since the discovery of the polymerization of 1,6-heptadiyne by complex metal catalysts,[1,2] there have been many studies on the cyclopolymerization of dipropargyl derivatives such as dipropargyl amine,[3] dipropargyl sulfide,[4] and dipropargyl ether[5] using various polymerization methods. The resulting polymers were found to be highly electrically conductive upon doping with I_2, but these materials are insoluble in any organic solvents and unstable to air oxidation.

Recently, we reported that dipropargyl derivatives bearing symmetric appendages are very effectively cyclopolymerized with Mo- or W-based catalyst systems.[6−11] Especially, 4,4-disubstituted poly(1,6-heptadiyne)s exhibited remarkably improved solubility in common organic solvents and long-term stability toward air oxidation.[8,9] Poly(dipropargylamine)s could also be modified by the introduction of bulky alkylamine,[3] alkanamide,[10] or *N,N*-dialkylammonium salt groups.[11] However, systematic studies to prepare soluble poly(dipropargyl ether) derivatives have not been performed so far.

In this report, we introduce the first example of the poly(dipropargyl ether)s bearing α-substitutuents to improve their physical properties and to elucidate unsymmetric cyclopolymerization. This article deals with the synthesis and cyclopolymerization of unsymmetric dipropargyl ether derivatives and the physical properties of the resulting polymers.

Scheme 1



$R_1 = R_2 = H$; DPE
$R_1 = H$, R_2 = pentyl ; POO
$R_1 = R_2$ = cyclohexyl ; POECH
$R_1 = H$, $R_2 = CH_3$; POB
$R_1 = CH_3$, R_2 = phenyl ; POP

Experimental Section

Materials. Tungsten(VI) and molybdenum(V) chlorides (Aldrich Chemical Co., resublimed, 99.9%) were used without further purification. Palladium(II) chloride and ethylaluminum dichloride (Aldrich Chemical Co.) were used without further purification, and tetrabutyltin was distilled under reduced pressure. Propargyl bromide (Aldrich Chemical Co., 80 wt % solution in toluene) was dried over calcium hydride and fractionally distilled by recommended procedures.[12] Propynol derivatives (Aldrich Chemical Co.) were used without further purification. All solvents were used after purification according to conventional methods.

Monomer Synthesis. Syntheses of unsymmetrical diacetylene ethers were carried out with propargyl bromide and propynol derivatives by phase transfer catalysis, as shown in Scheme 1.

1-(Propargyloxy)-1-ethynylcyclohexane (POECH). A two-phase system composed of propargyl bromide (22 g, 0.15 mol) in hexane (140 mL) and 1-ethynyl-1-cyclohexanol (12.4 g, 0.1 mol), sodium hydroxide (60 g, 1.5 mol), and tetrabutylammonium hydrogen sulfate in water (120 mL) was stirred overnight at room temperature and heated to reflux under stirring for 0.5 h. After the reaction system was cooled to room temperature, water (100 mL) was added, and the organic layer was extracted three times with hexane (30 mL each). The product was isolated by evaporating the solvent after drying the solution with anhydrous magnesium sulfate. The crude product was purified by distillation: bp 40 °C (0.1 Torr), yield (85%); MS, *m/e* 162 (parent), 107 (base); ^1H NMR ($CDCl_3$) δ 1.2−1.9 (m, 10H, cyclohexyl ring), 2.37 (t, 1H, *J* = 2.5, $CH_2C{\equiv}CH$), 2.48 (s, 1H, $CC{\equiv}CH$), 4.26 (d, 2H, *J* = 2.5); ^{13}C NMR ($CDCl_3$) δ 23.2, 25.7, 37.6 (cyclohexyl), 52.2 (CH_2), 73.7 (C), 75.2, 75.3 ($HC{\equiv}$), 81.4 (${\equiv}CCH_2$), 84.7 (${\equiv}CC$). Anal. Calcd for $C_{11}H_{14}O$: C, 81.44; H, 8.70. Found: C, 81.25; H, 8.61.

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[®] Abstract published in *Advance ACS Abstracts*, January 15, 1995.

0024-9297/95/2228-1208$09.00/0

3-(Propargyloxy)-3-phenyl-1-butyne (POPB). POPB was prepared from propargyl bromide and 2-phenyl-3-butyn-2-ol by the same procedure described for POECH: bp = 61 °C (0.5 Torr), yield (65%); MS, *m/e* 184 (parent), 129 (base); ^{1}H NMR ($CDCl_3$) δ 1.78 (s, 3H, CH_3), 2.4 (t, 1H, J = 2.5, $CH_2C{\equiv}CH$), 2.8 (s, 1H, $\equiv$CH), 3.8 (d of d coupling, 1H, J = 14.7, CH_2), 4.3 (d of d coupling, 1H, J = 14.6, CH_2O, 7.3–7.6 (m, 5H, phenyl); ^{13}C NMR ($CDCl_3$) δ 32.7 (CH_3), 53.1 (CH_2O), 73.7 (C), 76.4, 76.6 (HC$\equiv$), 80.1 ($\equiv CCH_2$), 82.8 ($\equiv$CC), 125.7, 128.1, 128.4, 141.3 (phenyl). Anal. Calcd for $C_{13}H_{12}O$: C, 84.75; H, 6.57. Found: C, 84.58; H, 6.30.

3-(Propargyloxy)-1-octyne (POO). POO was prepared from propargyl bromide and 1-octyn-3-ol by the same procedure described for POECH: bp 75 °C (7 Torr), yield (76%); MS, *m/e* 164 (parent), 93 (base); ^{1}H NMR ($CDCl_3$) δ 0.85 (s, 3H, J = 6.5, CH_3), 1.4 (m, 6H, $(CH_2)_3$, 1.7 (m, 2H, CH_2), 2.4 (m, 2H, HC$\equiv$), 4.2 (m, 3H, $\equiv CCH_2$, $\equiv$CCH); ^{13}C NMR ($CDCl_3$) δ 13.9, 22.5, 24.7, 31.4, 35.3 ($(CH_2)_4CH_3$), 55.7 (CH_2O), 68 (CHO), 74.2, 74.4 (HC$\equiv$), 79.4, 81.9 ($\equiv$C). Anal. Calcd for $C_{11}H_{16}O$: C, 80.44; H, 9.82. Found: C, 80.17; H, 9.65.

3-(Propargyloxy)-1-butyne (POB). POB was prepared from propargyl bromide and 1-butyn-3-ol by the same procedure described for POECH: bp 162 °C (760 Torr), yield (72%); MS, *m/e* 108 (parent), 93 (base); ^{1}H NMR ($CDCl_3$) δ 1.45 (d, 3H, J = 6.7, CH_3), 2.4 (m, 2H, HC$\equiv$), 4.1–4.4 (m, 3H, CH_2O, CHO); ^{13}C NMR ($CDCl_3$) δ 21.8 (CH_3), 55.7 (CH_2O), 63.8 (CHO), 73.6, 74.4 (HC$\equiv$), 79.2, 82.6 ($\equiv$C). Anal. Calcd for $C_{11}H_{14}O$: C, 77.75; H, 7.46. Found: C, 77.62; H, 7.35.

Dipropargyl ether (DPE). DPE was prepared propargyl bromide and propargyl alcohol by the previously reported method:[13] bp 67 °C (85 Torr), yield (85%); MS, *m/e* 94 (parent), 55 (base); ^{1}H NMR ($CDCl_3$) δ 2.48 (t, 2H, J = 2.3, HC$\equiv$), 4.26 (d, 4H, J = 2.3, CH_2O); ^{13}C NMR ($CDCl_3$) δ 55.9 (CH_2O), 74.0 (HC$\equiv$), 79.4 ($\equiv$C). Anal. Calcd for C_6H_6O: C, 76.57; H, 6.43. Found: C, 76.51; H, 6.40.

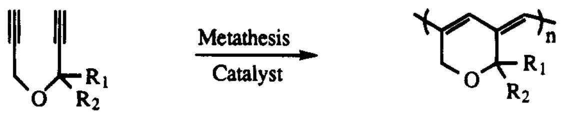
Polymerization. Catalyst solution preparation and polymerization were carried out in a dry nitrogen atmosphere. Transition metal halides and organometallic compounds were dissolved in solvent to make 0.2 M solutions prior to use. A typical polymerization procedure was as follows: solvent, catalyst solution 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, the monomer dissolved in the selected 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 chloroform and precipitated in a large excess of methanol. The polymer was filtered from the solution and dried under vacuum at 40 °C for 24 h. The polymer yield was determined by gravimetry.

Instruments. ^{1}H- and ^{13}C-NMR spectra were recorded with the use of a Bruker AM-300 spectrometer, and chemical shifts are reported in ppm units with tetramethylsilane as the internal standard. FT-IR spectra were measured with neat oils or KBr pellets on a Bomem MB-100 spectrometer, and frequencies are given in reciprocal centimeters. Mass spectra were obtained on a Hewlett-Packard 5985A GC/MS system using the electron impact method. A Shimadzu UV-3100S spectrometer was used for UV–visible spectral data. The molecular weight and polydispersity were determined in THF solvent with a Water GPC-150C calibrated with polystyrene standards. Elemental analysis was performed with a Perkin-Elmer 240DS elemental analyzer. Thermal analyses were carried out on a Dupont TGA 9900 thermogravimetric analyzer under nitrogen at a heating rate of 10 °C/min. X-ray diffraction patterns of unoriented samples were obtained on a Rigaku Geigerflex X-ray diffractometer equipped with a flat-plate camera using Ni-filtered Cu Kα radiation at a scan speed of 4°/min.

Results and Discussion

Polymerization. Scheme 2 outlines the cyclopolymerization of dipropargyl ether derivatives with transition metal catalysts. The polymerization of POPB bearing phenyl and methyl substituents was carried out with various transition metal catalysts, and the results are summerized in Table 1. $MoCl_5$-based catalysts showed greater catalytic activity than WCl_6-based catalysts. As shown in Table 1, $(n\text{-}Bu)_4Sn$ exhibited excellent cocatalytic activity compared to $EtAlCl_2$ for the polymerization of POPB by $MoCl_5$. These results are similar to other dipropargyl ether derivatives. The maximum molecular weight ($\bar{M}_w$) of poly(POPB) was ca. 26.3 × 10^3 (with $MoCl_5$–n-Bu_4Sn).

Scheme 2



Catalyst ; $MoCl_5$, WCl_6, $PdCl_2$
Cocatalyst ; n-Bu_4Sn, $EtAlCl_2$

Table 1. Polymerization of 3-(Propargyloxy)-3-phenyl-1-butyne (POPB) by Various Transition Metal Catalysts[a]

expt no.	catalyst system[b] (mole ratio)	polymer yield[c] (%)	$\bar{M}_w$[d] ($\times10^{-3}$)	$\bar{M}_w/\bar{M}_n$[d]
1	$MoCl_5$	100	24	2.4
2	$MoCl_5$–$EtAlCl_2$ (1:1)	82	15.6	2.1
3	$MoCl_5$–$EtAlCl_2$ (1:4)	78	12.7	2.8
4	$MoCl_5$–n-Bu_4Sn (1:4)	96	26.3	2.2
5	WCl_6			
6	WCl_6–$EtAlCl_2$ (1:4)	12		
7	WCl_6–n-Bu_4Sn (1:4)	trace		
8	$PdCl_2$[e]	25	9.5	3.9

[a] Polymerized in dioxane at 60 °C for 24 h. Mole ratio of monomer to catalyst was 50. Initial Monomer concentration was 1 M. [b] Mixture of catalyst and cocatalyst in chlorobenzene was aged for 15 min before use as catalyst. [c] The precipitated polymers in methanol were gravimetrically estimated. [d] Values were obtained by GPC analysis with polystyrene standards. [e] Polymerization was carried out at 90 °C for 24 h in DMF.

To investigate the effect of the α-substituent group on the cyclopolymerization, the polymerizations of α-substituted dipropargyl ethers were first carried out with $MoCl_5$, and the results are listed in Table 2. In the case of unsubstituted dipropargyl ether (DPE), the polymerization proceeded well in high concentration and the resulting polymer was a yellow-reddish insoluble powder.[13] However, the presence of α-substituents yielded very interesting results in the cyclopolymerization of dipropargyl ether derivatives. Polymerization proceeded well regardless of initial monomer concentration, and the resulting polymers were soluble in common organic solvents. The highest polymer yield was obtained in the case of POPB. The average molecular weights ($\bar{M}_w$) and the polydispersities of the polymers are also listed in Table 2. The $\bar{M}_w$ values of poly(dipropargyl ether) derivatives were in the range of 24 × 10^3–73 × 10^3 with polystyrene standards by GPC.

In the case of a relatively small substituent group such as methyl or pentyl, we found that the solubility of the resulting polymer was dependent on the initial monomer concentration. The effect of initial monomer concentration for the polymerization of POO with a pentyl substituent by $MoCl_5$ is shown in Table 3. Poly(POO)s obtained at high initial monomer concentration ($\geq$1 M) were insoluble in any organic solvents due to cross-linked gelation. However, soluble poly(POO) was obtained by dilution of the initial monomer concentration ($\leq$0.25 M). It seems that the cyclopolymerization of unsymmetric dipropargyl ethers is dependent on the

Table 2. Polymerization of Dipropargyl Ethers with Various α-Substituent Groups by $MoCl_5$[a]

expt no.	compd	R_1	R_2	$[M]_0$[b]	polym time (h)	polymer yield[c] (%)	$\bar{M}_w$[d] ($\times 10^{-3}$)	$\bar{M}_w/\bar{M}_n$[d]
1	DPE	H	H	1.5	24	100[e]		
2	POB	H	CH_3	0.5	2	84[f]	29.4	3.1
3	POO	H	pentyl	0.25	24	92	73.0	4.0
4	POPB	CH_3	phenyl	1	24	100	24.3	2.4
5	POECH	cyclohexyl		1	24	80	24.5	2.5

[a] Polymerized in dioxane at 60 °C. Mole ratio of monomer to catalyst was 50. [b] Initial monomer concentration in moles per liter. [c] The precipitated polymers in methanol were gravimetrically estimated. [d] Values were obtained by GPC analysis with polystyrene standards. [e] Insoluble in any solvent. [f] Partially insoluble in THF.

Table 3. Initial Monomer Concentration Effect on the Polymerization of 3-(Propargyloxy)-1-octyne (POO) by $MoCl_5$[a]

expt no.	$[M]_0$[b]	polym time (h)	polymer yield[c] (%)	$\bar{M}_w$[d] ($\times 10^{-3}$)	$\bar{M}_w/\bar{M}_n$[d]
1	0.125	36	81	92	4.1
2	0.25	24	92	73	4.0
3	0.5	5	69[e]	80	4.7
4	1	2	63[f]		
5	1.5	1	91[f]		

[a] Polymerized in dioxane at 60 °C. Mole ratio of monomer to catalyst was 50. [b] Initial Monomer concentration in moles per liter. [c] The precipitated polymers in methanol were gravimetrically estimated. [d] Values were obtained by GPC analysis with polystyrene standards. [e] Partially insoluble in THF. [f] Insoluble in any solvent.

steric hindrance of bulky substituents and the different reaction rates of the two different acetylene units. Generally, cyclopolymerization leads to the introduction of cyclic structures into the main chain of the polymer via an alternating intramolecular–intermolecular chain propagation.[13] It is known that the polymerization of α-unsubstituted monopropargyl ether proceeds slowly, but the polymerization of α-substituted propargyl ethers is fast.[13] At the present time, we propose that the cyclization mechanism of the unsymmetric dipropargyl ether is affected by the bulkiness of α-substituents and the different reactivity of the two acetylene groups in the monomer. In the case of POECH or POPB with a bulky substituent, it can be postulated that the α-substituted acetylene part reacts first with the Mo catalyst and then cyclizes with the other acetylene group. At this time, α-substituted acetylene complexed with Mo catalyst is thought to be difficult to react with α-substituted acetylene of the other monomers due to steric hindrance by the bulky groups. It is indicated that dipropargyl ethers bearing bulky α-substituents polymerize by an alternating intramolecular cyclization and then intermolecular chain propagation regardless of initial monomer concentration. On the other hand, for dipropargyl ethers with less hindered substituents such as a methyl or pentyl group, the propagating species of the α-substituted acetylene competes with intermolecular reaction with the α-substituted acetylene of the other monomers due to the high reactivity of the α-substituted acetylene functional group. From this consideration, we thought that the intermolecular reaction yields a small amount of noncyclized linear polyacetylene having unreacted pendant acetylene groups which, at high monomer concentration, leads to an insoluble cross-linked polymer.

Polymer Structure. Products of the cyclopolymerizations of α-substituted dipropargyl ethers were characterized by ^1H- and ^{13}C-NMR, FT-IR, and UV–visible spectroscopic analysis. The ^1H-NMR spectra of poly(POECH) (A) and poly(POPB) (B) are shown in Figure 1. As the polymerization proceeded, the two different acetylenic proton peaks at 2.3 and 2.7 ppm disappeared, and new peaks of the conjugated cyclic polyenes appeared in the region of 6.0–7.0 ppm. Also, the broad peak around 4.8 ppm is assigned to the allylic methylene protons adjacent to the oxygen atom on the ring.

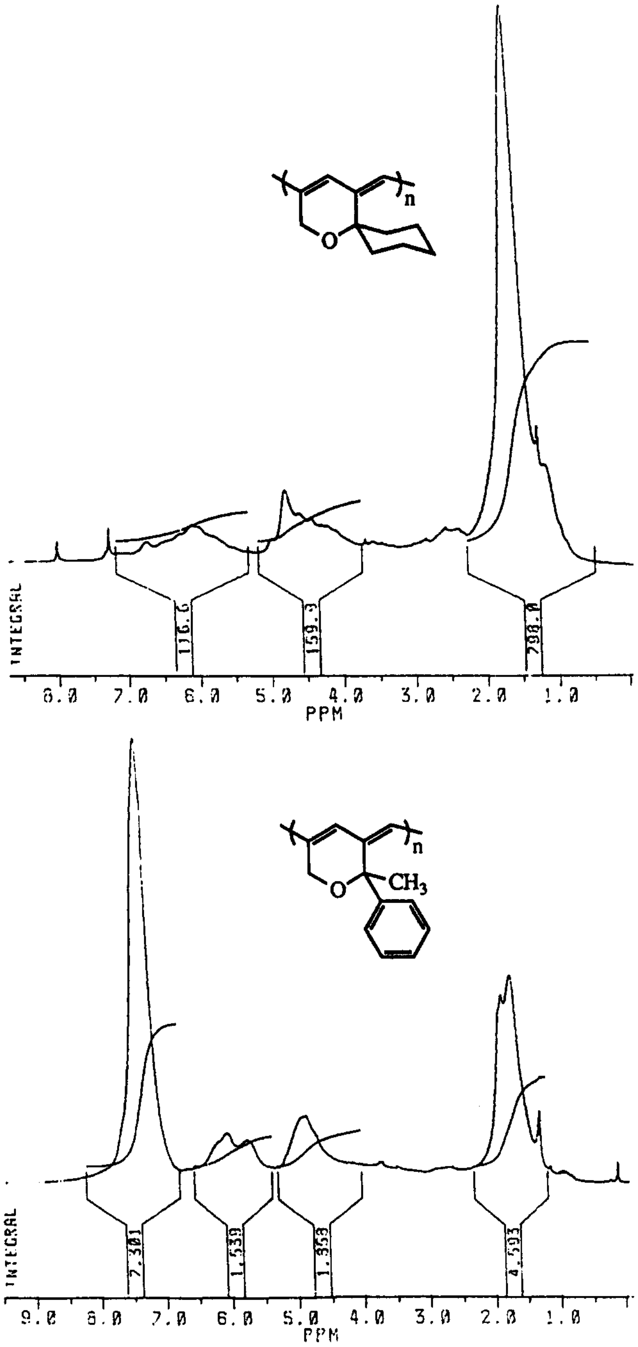


Figure 1. ^1H-NMR spectra of poly(POECH) (A) and poly(POPB) in $CDCl_3$ (samples, experiments 5 and 4, respectively, Table 2).

Figure 2 shows the ^{13}C-NMR spectra of poly(POECH) (A, A_1) and poly(POPB) (B, B_1) obtained with the DEPT 45 program, which caused disappearance of the non-

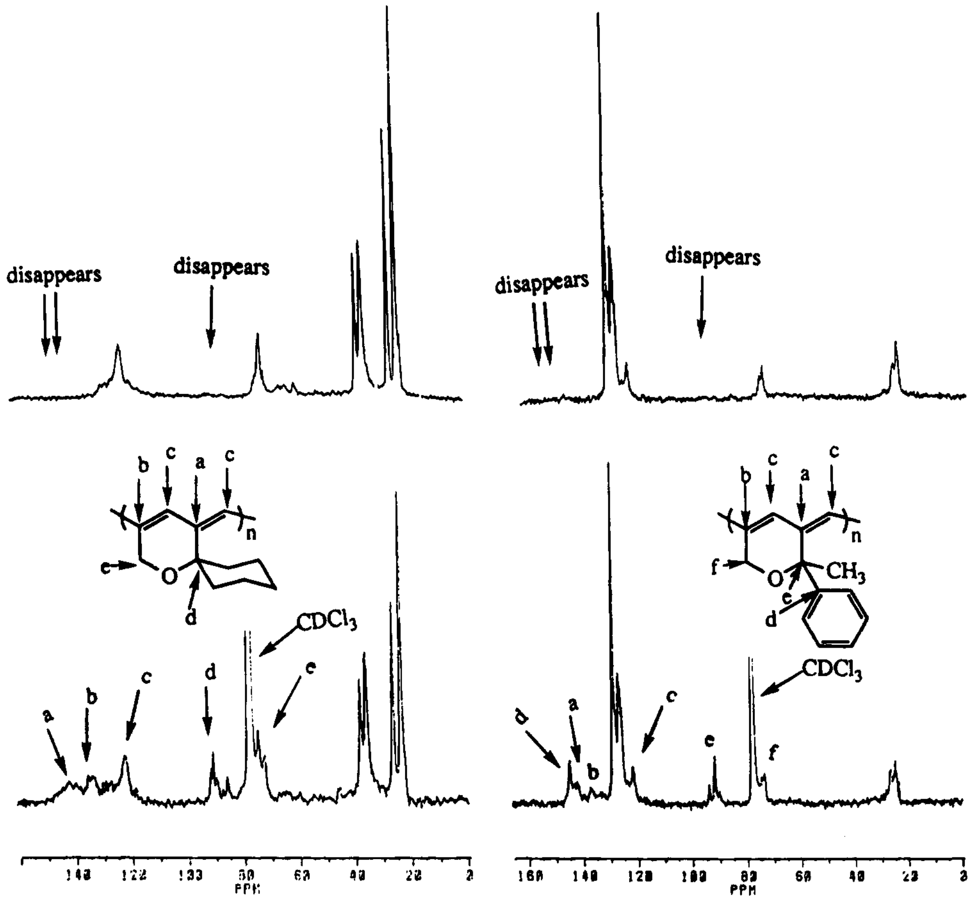


Figure 2. ^{13}C-NMR spectra of poly(POECH) (A, top left; A_1, bottom left) and poly(POPB) (B, top right; B_2, bottom right) and obtained by the DEPT 45 program in $CDCl_{13}$ (samples, experiments 5 and 4, respectively, Table 2).

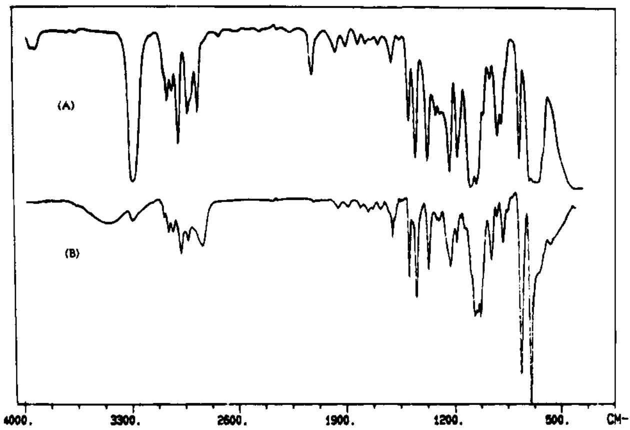


Figure 3. FT-IR spectra of POPB (A) and poly(POPB) (B) in neat and KBr pellet, respectively (sample, experiment 4, Table 2).

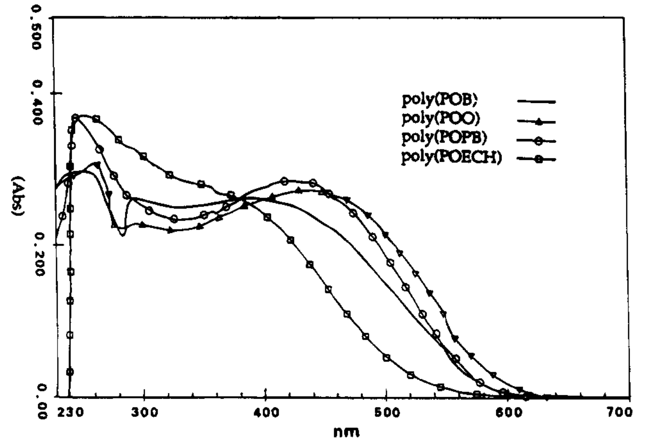


Figure 4. UV–visible spectra of poly(POB), poly(POO), poly(POPB), and pol(POECH) (samples, experiments 2–5, Table 2; 1×10^{-4} M in $CHCl_3$).

protonated quaternary carbon peaks. Four acetylene carbon peaks at 74, 76, 80, and 83 ppm of POPB disappeared, and new olefinic carbon peaks appeared at 120 and 140 ppm in the polymer. The peaks of the methylene and quaternary carbon atoms adjacent to the oxygen atom shifted from 53 and 76 ppm in the monomer to 73 and 91 ppm in poly(POPB), respectively. Quaternary vinylic carbon peaks at 91, 141, and 144 ppm disappeared in Figure $2B_1$. A similar result was observed in poly(POECH).

The FT-IR spectra of POPB and poly(POPB) are shown in Figure 3. In the case of the insoluble poly(dipropargyl ether), the IR spectrum shows no absorption at 3275 or 2150 cm^{-1}, which indicates the absence of the acetylenic functional group of dipropargyl ether. But the IR spectra of soluble α-substituted poly(dipropargyl ether)s show very weak absorptions at 3275 cm^{-1}, which suggests the presence of a small amount of unpolymerized terminal acetylene as polymer end group. The characteristic peak of conjugated polyene sequences was observed in the region of 1650 cm^{-1}.

UV–visible spectra of all polymers were obtained in $CHCl_3$ (Figure 4). The absorption spectra of the polymers exhibited a large absorption band at 320–600 nm that is due to the π–π^* transition of the conjugated polyene. The λ_{max} value of poly(POECH) was lower than those of other α-substituted polymers because of the high steric hindrance of the cyclohexyl group, which

Table 4. Solubility of Polymers[a]

solvent	poly-(DPE)	poly-(POB)	poly-(POO)	poly-(POPB)	poly-(POECH)
n-hexane	−	−	−	−	−
chloroform	−	+−	+	+	+
THF	−	+−	+	+	+
1,4-dioxane	−	−+	+−	+	+
toluene	−	−	+−	+	+
DMF	−	−+	+−	+	+
NMP	−	−	+−	+	+
methanol	−	−	−	−	−

[a] Sample, experiments 1−5 in Table 2. Key: +, soluble, +−, partialy insoluble, −+, sparingly soluble, and −, insoluble.

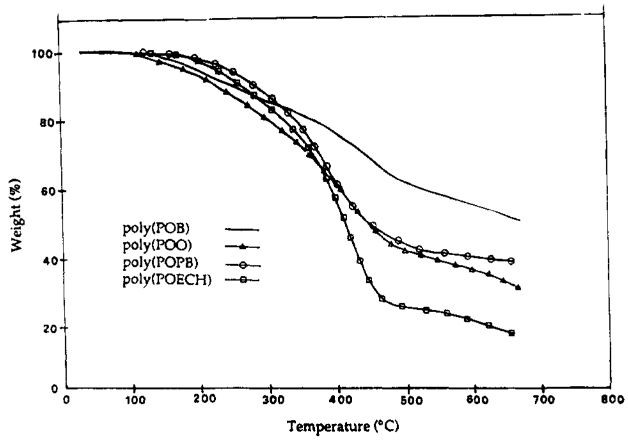
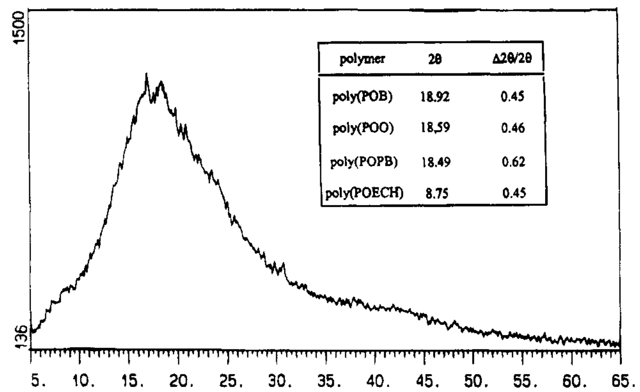


Figure 5. TGA thermograms of the poly(POB), poly(POO), poly(POPB), and poly(POECH) in N_2 (scanning rate, 10 °C/min).



polymer	2θ	Δ2θ/2θ
poly(POB)	18.92	0.45
poly(POO)	18,59	0.46
poly(POPB)	18.49	0.62
poly(POECH)	8.75	0.45

Figure 6. X-ray diffractograms of the poly(POPB) (sample, experiment 4, Table 2; scanning rate, 4 °C/min).

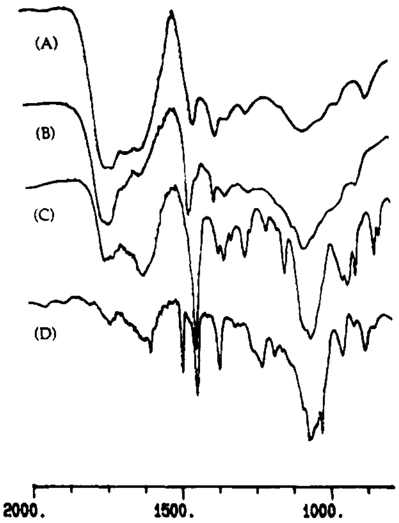


Figure 7. IR spectra for oxidative stability after 1-month exposure to air at room temperature: poly(POB) (A), poly(POO) (B), poly(POECH) (C), and poly(POPB) (D).

Table 5. Electrical Conductivity of Iodine-Doped Poly(dipropargyl ether) Derivatives[a]

polymer	polymer comp[b]	conductivity,[c] S/cm
poly(DPE)	$(C_6H_6O)_1(I_2)_{0.31}$	4.2×10^{-2}
poly(POB)	$(C_7H_8O)_1(I_2)_{0.45}$	7.3×10^{-3}
poly(POO)	$(C_{11}H_{16}O)_1(I_2)_{0.38}$	2.5×10^{-3}
poly(POPB)	$(C_{13}H_{12}O)_1(I_2)_{0.24}$	0.7×10^{-3}
poly(POECH)	$(C_{11}H_{14}O)_1(I_2)_{0.18}$	0.4×10^{-3}

[a] Pressed polymer pellets were doped by exposure to iodine vapor at vacuum (0.1 Torr) for 24 h. [b] The extent of doping was determined by the weight gains. [c] Measured with the four-point probe dc method.

disrupts the planarity of the conjugated main chain.

Polymer Properties. One of the objectives of this work was to evaluate the effect of α-substituent groups on the solubility of poly(dipropargyl ether)s. Unlike poly(dipropargyl ether), α-substituted poly(dipropargyl ether)s are soluble in common organic solvents. The solubility of the poly(dipropargyl ether) derivatives was determined for the powdery sample in various organic solvents, and the results are listed in Table 4. The solubility behavior of these polymers is strongly influenced according to the bulkiness of the substituent group. Poly(POPB) and poly(POECH) containing bulky substituents (methyl phenyl or cyclohexyl) exhibited good solubility in various common organic solvents such as $CHCl_3$, THF, and DMF. Poly(POB) and poly(POO) with less bulky substituents (methyl or pentyl) were partially soluble in organic solvents. However, unsubstituted poly(dipropargyl ether) was insoluble in any organic solvent.

The thermal stability of α-substituted poly(dipropargyl ether)s was evaluated by thermogravimetric analysis (TGA) under nitrogen atmosphere. TGA curves are shown in Figure 5. Poly(POB) and poly(POO) exhibited an onset of degradation above 100 °C, which is similar to unsubstituted poly(DPE). On the other hand, poly(POPB) and poly(POECH) with bulky α-substituents were found to be stable up to 200 °C.

We also investigated the morphology of these polymers by X-ray diffraction; the data are shown in Figure 6. In general, the X-ray diffraction patterns of amorphous polymers are broad; the ratio of the half-height width to diffraction angle ratio ($\Delta 2\theta/2\theta$) is greater than 0.35. Crystalline diffraction peaks are sharp, and their values of $\Delta 2\theta/2\theta$ are smaller than 0.05. The values of $\Delta 2\theta/2\theta$ of the present polymers are greater than 0.45. That is, all of the α-substituted poly(dipropargyl ether)s are amorphous, as shown in Figure 6.

In order to determine the air oxidation stability of α-substituted poly(dipropargyl ether)s, infrared spectra of polymers exposed to air for 1 month were measured and are shown in Figure 7. The air oxidation stability was dependent on the bulkiness of the α-substituent of the poly(dipropargyl ether)s. The infrared spectra of poly(POB) and poly(POO) exposed to air for 1 week show a carbonyl absorption peak at about 1700 cm^{-1} due to air oxidation. This instability of poly(POB) and poly(POO) to air oxidation is similar to that of poly(dipropargyl ether) itself. However, poly(POPB) was more stable to air oxidation. Even after exposing poly(POPB) to air for 1 month, only a small C=O peak in the infrared spectrum was observed.

Table 5 shows the composition and electrical conductivity of iodine-doped poly(dipropargyl ether) derivatives. The neat polymer pellets exhibited poor electrical conductivity in their undoped state ($<10^{-10}$ S/cm). When the pressed pellets of polymers were doped by I_2 for 24 h at room temperature, the electrical conductivities of the pellets were 10^{-4}–10^{-2} S/cm.

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MA940968D