Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

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To cite this Article Lee, Hyung-Jong , Choi, Sam-Kwon and Gal, Yeong-Soon(1995) 'Synthesis and Properties of Unsymmetrical Mono- and Disubstituted Poly(Diyne Ether)s by Transition Metal Catalysts', Journal of Macromolecular Science, Part A, 32: 11, 1863 — 1874

To link to this Article: DOI: 10.1080/10601329508009366

URL: http://dx.doi.org/10.1080/10601329508009366

J.M.S.—PURE APPL. CHEM., A32(11), pp. 1863–1874 (1995)

SYNTHESIS AND PROPERTIES OF UNSYMMETRICAL MONO- AND DISUBSTITUTED POLY(DIYNE ETHER)S BY TRANSITION METAL CATALYSTS

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ABSTRACT

The cyclopolymerization of 2-butynyl-propargyl ether and 3-trimethylsilyl-2-propynyl propargyl ether and its copolymerization with diethyl dipropargyl malonate (DEDPM) were carried out by various transition metal catalysts. $MoCl_5$-based catalyst was found to be very effective and gave high polymer yields. The resulting homopolymers were insoluble in organic solvents, whereas copolymers showed good solubility in organic solvents such as chloroform, tetrahydrofuran, and dimethylsulfoxide. The structure of the products was confirmed by IR, NMR, and UV-visible spectroscopies. From the spectral data it is proposed that mainly cyclized products with conjugated systems are formed. Thermal and morphological properties were also studied.

INTRODUCTION

Since the discovery of polyacetylene thin film as a highly conducting polymer [1], a number of π-conjugated organic polymers have been extensively studied because of their potential applications as organic semiconductors [2–4], third-order NLO devices [5], and membranes for gas separation [6, 7]. Many workers have developed substituted polyacetylenes with catalysts based on Groups 5 and 6 transition metals (Nb, Ta, Mo, and W) [8–11].

We recently reported that dipropargyl derivatives ($HC\equiv C-CH_2-X-CH_2-C\equiv CH$) are very effectively cyclopolymerized with Mo- or W-based catalyst systems [12–15]. It has been known that the resulting cyclized polymers with a substituent at the X-position exhibit good solubility in common organic solvents and long-term stability toward air oxidation. However, systematic studies of the cyclopolymerization of mono- and disubstituted diynes ($R-C\equiv C-CH_2-X-CH_2-C\equiv CH$) have not been investigated so far.

In this paper we introduce the first example of the unsymmetrically substituted poly(diyne ether) derivatives. This article deals with the cyclopolymerization of 2-butynyl-propargyl ether (BPE) and 3-trimethylsilyl-2-propynyl propargyl ether (TSPPE) and its copolymerization with diethyl dipropargyl malonate (DEDPM). In addition, the characterization and physical properties of the resulting products are also discussed.

EXPERIMENTAL

Materials

Tungsten(VI) and molybdenum(V) chlorides (Aldrich Chemical Co., resublimed, 99.9%) were used without further purification. Palladium(II) chloride and ethyl aluminum dichloride (Aldrich Chemical Co.) were used without further purification. 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 [16]. Propargyl alcohol and 2-butyn-1-ol (Aldrich Chemical Co.) were used without further purification. All solvents were used after purification according to conventional methods.

Instruments for Characterization

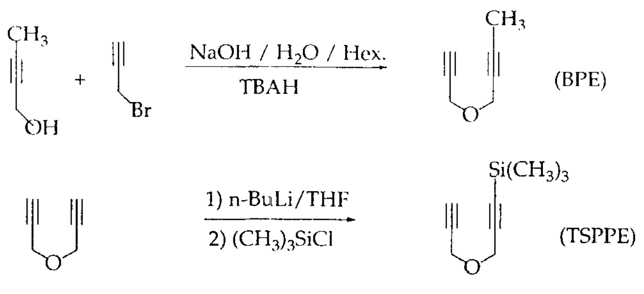
^1H- and ^{13}C-NMR spectra were recorded with the use of a Bruker AM-200 spectrometer, and chemical shifts are reported in ppm units with tetramethylsilane as the internal standard. FT-IR spectra were measured with neat oils or KBr pellets on a Bomem MB-100 spectrometer, and frequencies are given in reciprocal centimeters. A Shimadzu UV-3100S spectrometer was used for UV-visible spectral data. The molecular weight and polydispersity were determined in THF solvent with a Waters GPC-150C calibrated with polystyrene standards. Thermal analyses were carried out on a Dupont TGA 9900 thermogravimetric analyzer under nitrogen at a heating rate of 10°C/min.

Preparation of Monomers

Scheme 1 outlines the synthesis of unsymmetrical mono- and disubstituted diyne ethers

2-Butynyl-propargyl Ether (BPE). A two-phase system composed of propargyl bromide (11.9 g, 0.1 mol) in hexane (70 mL) and 2-butyn-1-ol (4.4 g, 0.06 mol), sodium hydroxide (36 g, 0.9 mol), and 0.1 g tetrabutylammonium hydrogen sulfate in water (70 mL) was stirred overnight at room temperature and heated to reflux under stirring for 0.5 hour. After the reaction system was cooled to room temperature, water (200 mL) was added and the organic layer was extracted three times with hexane (50 mL each). The product was isolated by evaporating the solvent after drying the solution over anhydrous magnesium sulfate. The crude product was purified by distillation; bp = 162°C/760 mmHg, yield = 53%. ^{1}H NMR ($CDCl_3$): δ 1.83 (t, 3H), 2.41 (t, 1H), 4.21 (m, 4H). ^{13}C NMR ($CDCl_3$): δ 3.4 ($-CH_3$), 56.0, 56.9 ($-CH_2-O-CH_2-$), 74.1 ($CH_3-C\equiv$), 74.6 ($HC\equiv$), 79.0 ($HC\equiv C-$), 83.0 ($CH_3-C\equiv C-$). IR (cm^{-1}): 3285 ($H-C\equiv$), 2229 ($C\equiv CCH_3$), 2117 ($C\equiv CH$).

3-Trimethylsilyl-2-propynyl Propargyl Ether (TSPPE). The reaction flask was charged with dipropargyl ether [17] (4.7 g, 0.05 mol) and THF (40 mL). *n*-Butyllithium (1.6 M in hexane solution, 0.05 mol) was added over a few minutes to the reaction mixture cooled to −60 to 50°C. After 5 minutes freshly distilled chlorotrimethylsilane (5.4 g, 0.05 mol) was added over a 5-minute period to the clear solution with vigorous stirring while carefully keeping the temperature within the same range. After this addition the cooling bath was occasionally removed and the temperature was allowed to rise gradually over 1 hour to room temperature. The white suspension was then poured into 250 mL ammonium chloride solution and then the water phase was extracted with hexane. The combined organic phase was dried over anhydrous $MgSO_4$. The product was isolated by distillation at reduced pressure; bp = 72°C/10 mmHg, yield = 42%. ^{1}H NMR ($CDCl_3$): δ 0.13 (s, 9H), 2.40 (t, 1H), 4.20 (m, 4H). ^{13}C NMR ($CDCl_3$): δ −0.3 ($-Si(CH_3)_3$), 56.3, 57.2 ($-CH_2-O-CH_2-$), 74.9 ($HC\equiv$), 78.9 ($\equiv C-$), 92.0 ($Si-C\equiv$), 100 ($Si-C\equiv C-$). IR (cm^{-1}): 3294 ($H-C\equiv$), 2175 ($C\equiv C-Si$), 2112 ($C\equiv CH$).



Hex. = Hexane. TBAH = Tetrabutylammonium hydrogen sulfate

SCHEME 1.

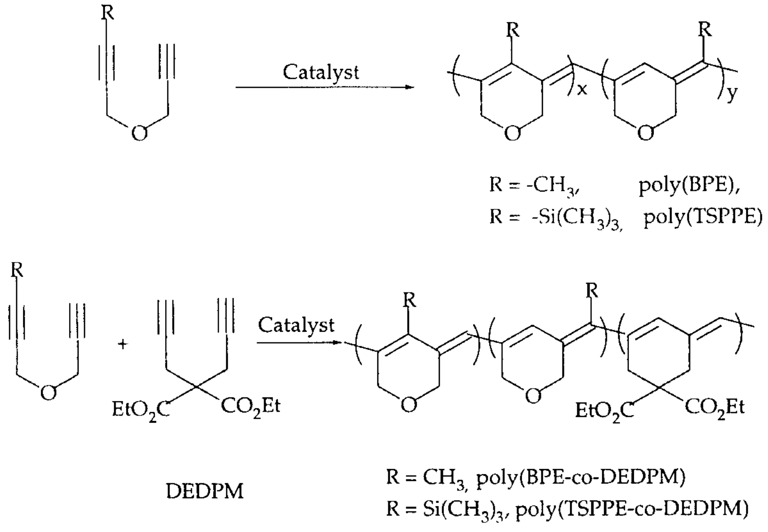
Polymerization

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 in the order given into a 20-mL ampule equipped with a rubber septum. When cocatalyst was used, the catalyst system was aged at 30°C for 15 minutes. 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 hours, the polymerization was terminated by adding ~5 mL methanol. The resulting polymer was precipitated in a large excess of methanol. The polymer was filtered from the solution and dried under vacuum at 40°C for 24 hours. The polymer yield was determined by gravimetry.

RESULTS AND DISCUSSION

Scheme 2 outlines the polymerization of the diyne ether derivative and its copolymerization with DEDPM with transition metal catalysts.

Table 1 shows the results for the polymerization of BPE bearing a methyl substituent by various transition metal catalysts. $MoCl_5$ alone gives some moderate yield of polymers. $EtAlCl_2$ was found to be a very effective cocatalyst for this polymerization by $MoCl_5$. However, WCl_6 alone and WCl_6-based catalysts were less effective than $MoCl_5$-based catalysts for the polymerization of dipropargyl ether



Catalysts = $MoCl_5$, WCl_6, $PdCl_2$
Cocatalysts = $EtAlCl_2$, $(n\text{-}Bu)_4Sn$

SCHEME 2.

TABLE 1. Polymerization of 2-Butynyl-propargyl Ether (BPE) with Various Transition Metal Catalysts[a]

Experiment	Catalyst system (mole ratio)	Polymer yield, %[b]
1	$MoCl_5$	73
2	$MoCl_5$-$EtAlCl_2$ (1:4)	82
3	$MoCl_5$(n-Bu)$_4$Sn (1:4)	64
4	WCl_6	5
5	WCl_6-$EtAlCl_2$(1:4)	37
6	WCl_6-n-Bu_4Sn (1:4)	2
7[c]	$PdCl_2$	12

[a]Polymerized in chlorobenzene at 70°C for 24 hours; mole ratio of monomer to catalyst was 50. Initial monomer concentration was 1 M.

[b]Polymer precipitated with excess methanol.

[c]Polymerization was carried out at 90°C for 24 hours in dimethylacetamide.

derivatives. $PdCl_2$ polymerized BPE to give poly(BPE) in 12% yield. The polymerization of TSPPE bearing a trimethylsilyl substituent was carried out by using $MoCl_5$- and WCl_6-based catalysts, and the results are summarized in Table 2. Similarly to the polymerization of BPE, $EtAlCl_2$ was found to be a very effective cocatalyst for the polymerization of TSPPE by $MoCl_5$. The polymerization reaction of

TABLE 2. Polymerization of 3-Trimethylsilyl-2-propynyl Propargyl Ether (TSPPE) with Various Transition Metal Catalysts[a]

Experiment	Catalyst system (mole ratio)	Polymer yield, %[b]
1	$MoCl_5$	70
2	$MoCl_5$-$EtAlCl_2$ (1:4)	94
3	$MoCl_5$-(n-Bu)$_4$Sn (1:4)	31
4	WCl_6	Trace
5	WCl_6-$EtAlCl_2$ (1:4)	15
6	WCl_6-n-Bu_4Sn (1:4)	Trace
7[c]	$PdCl_2$	12

[a]Polymerized in chlorobenzene at 70°C for 24 hours; mole ratio of monomer to catalyst was 50. Initial monomer concentration was 1 M.

[b]Polymer precipitated with excess methanol.

[c]Polymerization was carried out at 90°C for 24 hours in dimethylacetamide.

these monomers using most catalysts exhibits insolubility in organic solvents. These results are similar to poly(dipropargyl ether) [17], poly(1,6-heptadiyne) [18], and poly(dipropargyl sulfide) [19].

Cyclopolymerizations of substituted diyne ethers were characterized by ^{13}C-NMR and FT-IR spectroscopic analyses. Figure 1 shows the FT-IR spectra of BPE monomer and its polymer. The spectrum of polymer shows no absorptions at 3287, 2229, and 2117 cm^{-1} which are expected to be present for the acetylenic carbon—hydrogen stretching, disubstituted carbon—carbon triple bond stretching, and the monosubstituted carbon—carbon triple bond stretching bands of BPE, respectively. Instead, the carbon—carbon double bond stretching band in the polymer backbone is observed at about 1650 cm^{-1}.

The ^{13}C-NMR spectra of TSPPE and its polymer are shown in Fig. 2. The peaks of the methylene carbon atoms adjacent to the oxygen atom shifted from 56.3 and 57.2 in TSPPE to about 75 ppm for poly(TSPPE). TSPPE gave monosubstituted acetylenic carbon peaks at 74.9 and 78.9 ppm and disubstituted acetylenic carbon peaks at 92.0 and 100 ppm, while poly(TSPPE) did not show any peaks at those positions. The olefinic carbon peaks of the polymer backbone appeared at the 135–145 ppm region. From the above spectral data it is proposed that the polymer structure is a cyclized form as described in Scheme 2 [12–15], although it has been reported that poly(1,6-heptadiyne)s with cyclic conjugated double bonds have both five- and six-membered ring structures with a ratio which depends on the polymerization conditions and the kind of catalysts used [20].

Table 3 summarizes the results on the copolymerization of BPE or TSPPE with DEDPM by $MoCl_5$ catalyst. In general, the catalyst activity of $MoCl_5$ alone

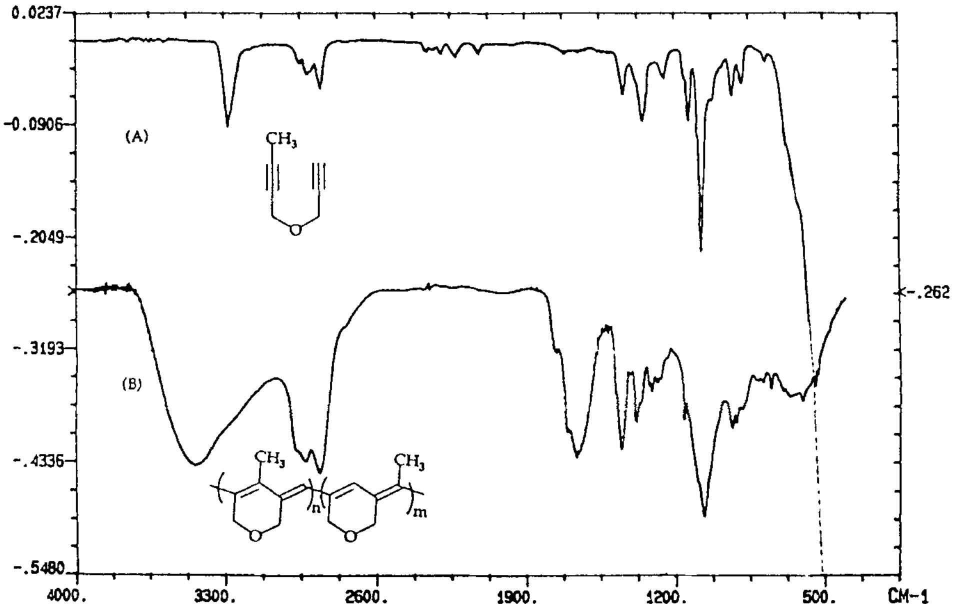


FIG. 1. FT-IR spectra of BPE (A) and poly(BPE) (B) in neat oil and KBr pellet, respectively (sample: Experiment 2 in Table 1).

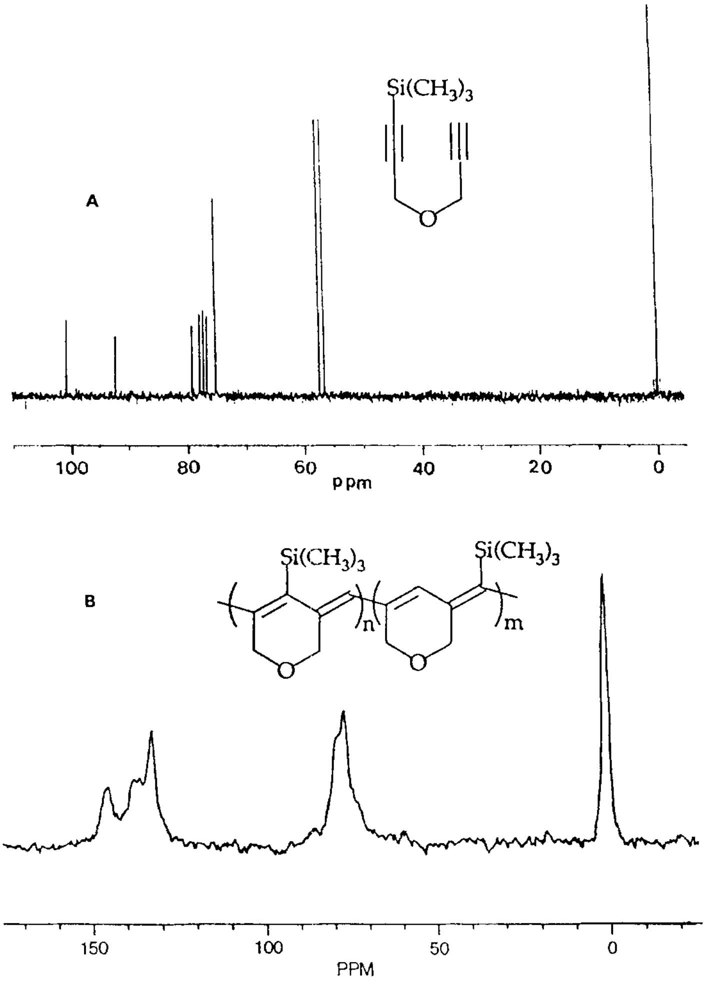


FIG. 2. ^{13}C-NMR spectrum of the TSPPE (A) and ^{13}C magic angle spinning cross-polarization NMR spectrum of poly(TSPPE) (B). (sample: Experiment 2, Table 2).

was enough and greater than that of WCl_6 in the polymerization of DEDPM and its derivatives [15, 17–19]. As shown in Table 3, the copolymer yields increased with an increase in the mole fraction of DEDPM. The resulting copolymers exhibited good solubility in such common organic solvents as THF, $CHCl_3$, DMF, and DMSO. The weight-average molecular weights ($\overline{M}_w$) of copolymers were found to be in the 0.5–4.4 × 10^4 range relative to polystyrene standards by GPC.

The copolymer structure was also identified by IR, ^1H- and ^{13}C-NMR, and UV-visible spectroscopies. Like the homopolymers, there are no absorption peaks at the acetylenic regions in the IR spectrum (Fig. 3) of copolymers (1:1) while the carbon—carbon double bond and the carbonyl stretching band appear at about 1630 and 1732 cm^{-1} respectively.

Figure 4 represents the ^1H-NMR spectra of copolymers (1:1). In both cases the broad peaks at 5.5–6.5 ppm are assigned to the protons of the conjugated double

TABLE 3. Copolymerization of BPE or TSPPE with DEDPM by $MoCl_5$[a]

Experiment	Monomer	%[b]	Polymer yield,[c] %	$\overline{M}_w$ ($\times 10^{-4}$)[d]	$\overline{M}_w/\overline{M}_n$[d]
1	BPE	20	88	4.4	2.3
2	BPE	30	79	3.5	2.1
3	BPE	50	76	1.3	2.1
4	TSPPE	30	82	4.5	3.2
5	TSPPE	50	76	1.5	3.4
6	TSPPE	70	68	0.5	1.5

[a] Polymerization was carried out at 70°C for 24 hours in chloroform. Initial monomer concentration and mole ratio of monomer to catalyst were 1 M and 50, respectively.

[b] Mole fraction (%) of diyne ether monomer in the charge.

[c] Precipitated copolymers with methanol.

[d] Values were obtained by GPC analysis with polystyrene standards.

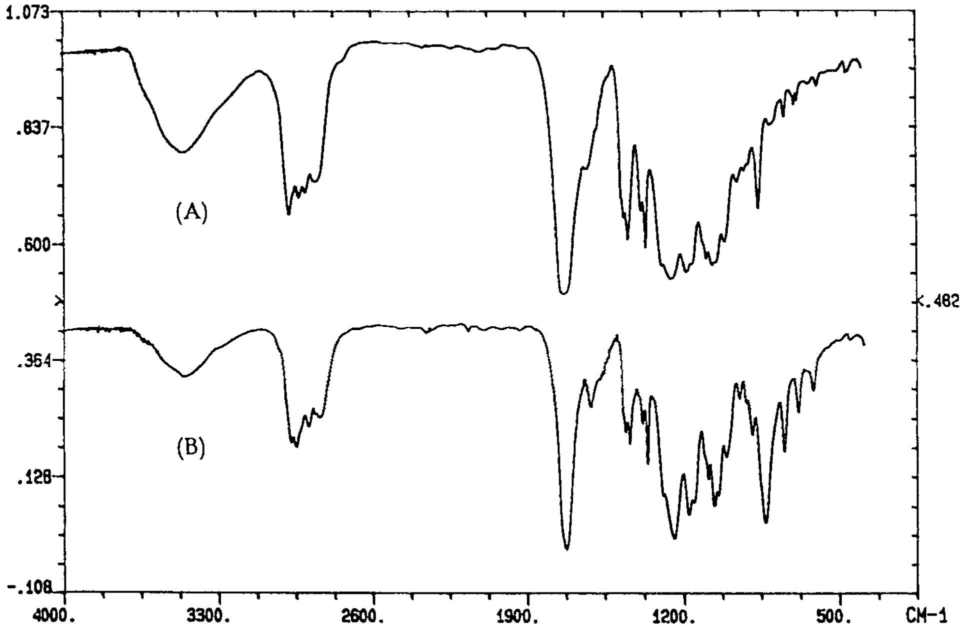


FIG. 3. FT-IR spectra of copolymers (1:1) in KBr pellet: poly(BPE-*co*-DEDPM) (A), poly(TSPPE-*co*-DEDPM) (B).

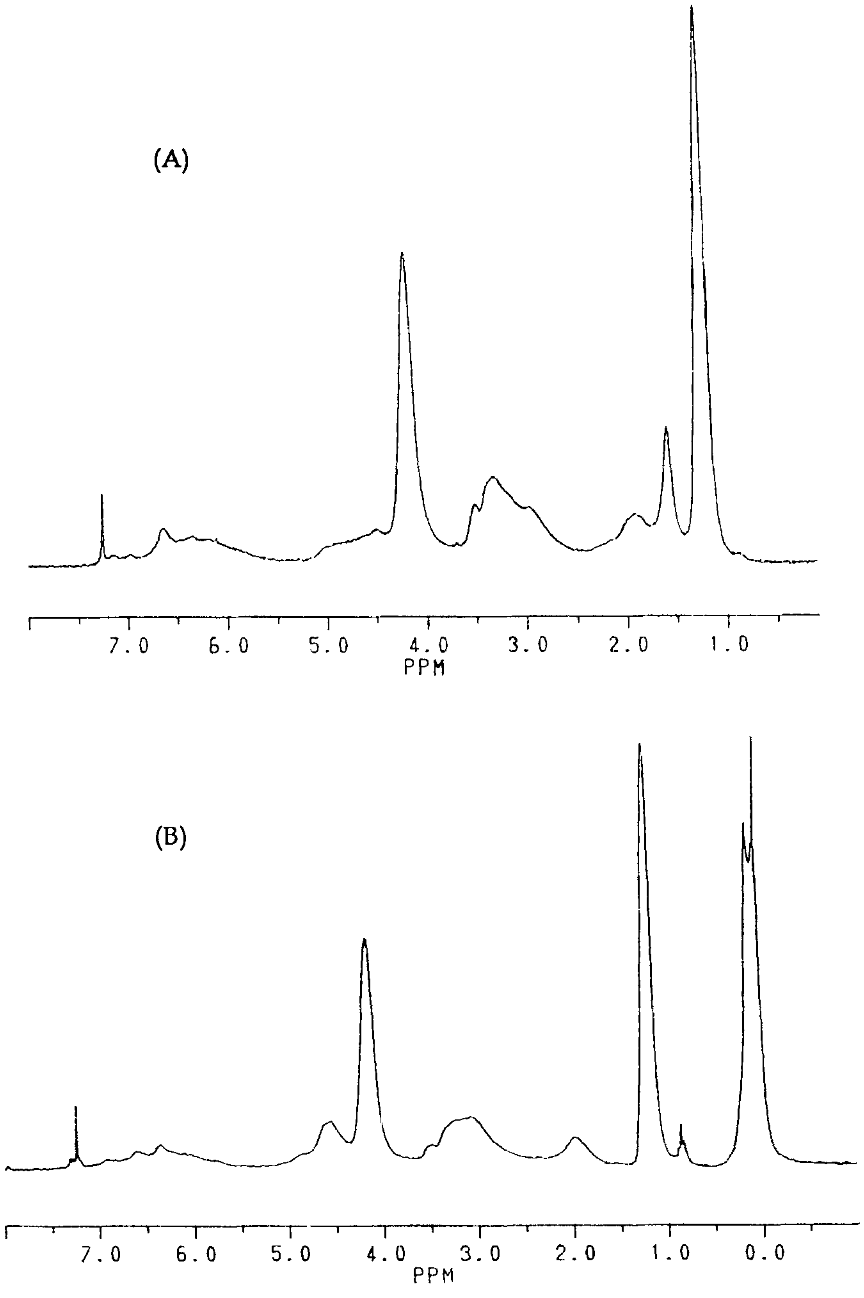


FIG. 4. ^{1}H-NMR spectra of poly(BPE-*co*-DEDPM) (A) and poly(TSPPE-*co*-DEDPM) (B) in CDCl$_3$ (sample: Experiments 3 and 5, respectively, in Table 2).

bonds. The peaks at 1.2, 4.3, and 3.4 ppm are attributed to the ethyl and methylene (cyclic ring) protons of the DEDPM portion at the copolymers. Methyl (1.6, 1.9 ppm) or trimethylsilyl proton peaks (−0.1, 0.13 ppm) of the diyne ether portion appeared as two peaks due to the presence of a geometric isomer in the copolymer as shown in Scheme 2. The compositions of the copolymers (determined by integration of ^{1}H-NMR signals) closely match the composition of the monomer feed mixture. In addition, carbonyl carbon and olefinic carbon peaks were shown at 174 and 120–140 ppm in the ^{13}C-NMR spectra, respectively.

The UV-visible spectra of the copolymers were recorded in chloroform (Fig. 5). A characteristic band of conjugated polymer appeared in the visible region; it is due to the $\pi \rightarrow \pi^*$ transition of conjugated polyene.

The thermal stability of substituted poly(diyne ether)s was evaluated by thermogravimetric analysis (TGA) under nitrogen atmosphere. TGA curves are shown in Fig. 6. Poly(BPE) and poly(TSPPE) exhibited an onset of degradation at 150 and 100°C, respectively, which is similar to unsubstituted poly(dipropargyl ether) [17]. It shows that poly(BPE) retained 90% of its original weight at 285°C, 78% at 420°C, and 60% at 600°C. Pyrolysis of poly(TSPPE) showed that 15.5% of the mass is lost at 197°C and 59.5% at 600°C.

The morphology of the resulting polymers were also investigated by x-ray diffraction analysis. The data of x-ray diffraction analysis are as follows: 2θ ($\Delta 2\theta / 2\theta$) = 18.5 (0.57) of poly(BPE), 2θ ($\Delta 2\theta / 2\theta$) = 17.8 (0.53) of poly(TSPPE).

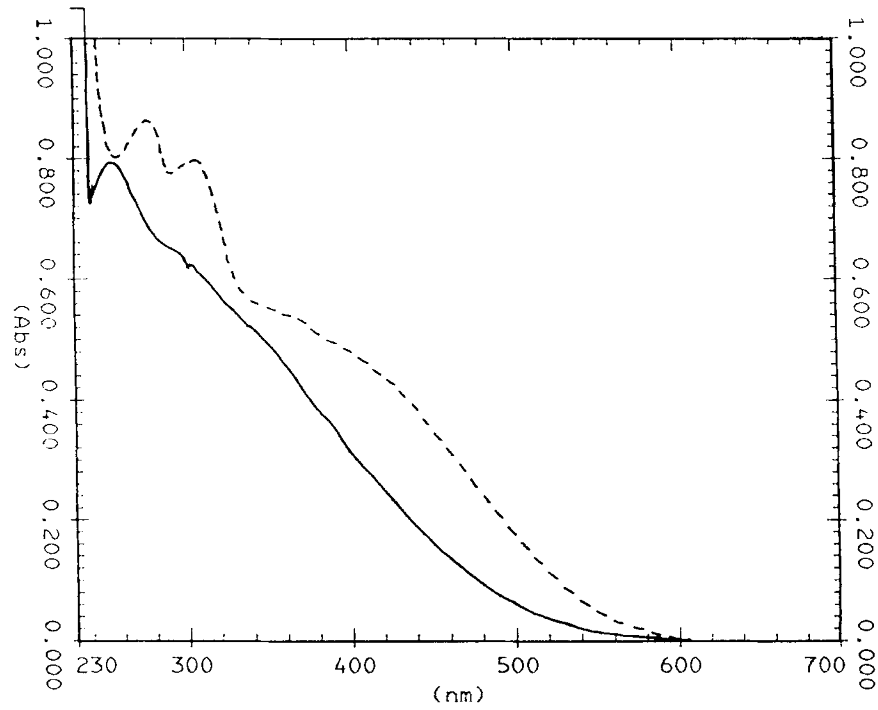


FIG. 5. UV-visible spectra of copolymers (1:1) in $CHCl_3$: poly(BPE-*co*-DEDPM) (- - -), poly(TSPPE-*co*-DEDPM) (——).

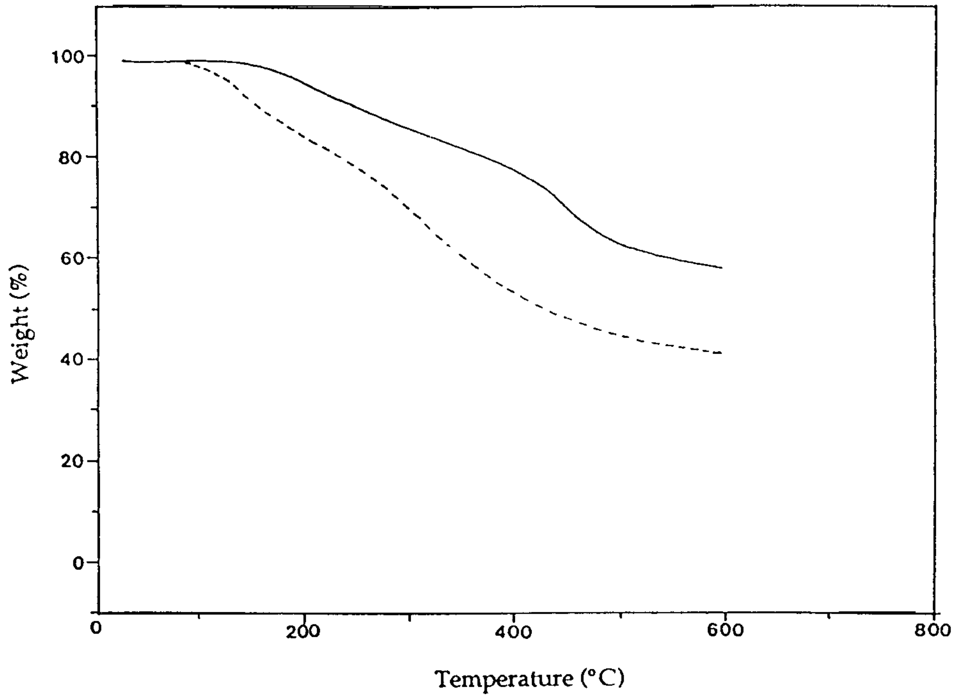


FIG. 6. TGA thermograms of the poly(BPE) (- - -) and poly(TSPPE) (——) under nitrogen atmosphere.

Because the peaks in the refraction patterns are all broad and the ratio of the half-height width to the diffraction angle ($\Delta 2\theta/2\theta$) is greater than 0.35 [10], the present polymers are amorphous.

CONCLUSION

In this paper we described the cyclopolymers of mono- and disubstituted diyne ethers prepared by various transition metal catalysts. $MoCl_5$-based catalyst was very effective and gave high polymer yields. The resulting homopolymers were insoluble in organic solvents. However, the copolymers exhibited good solubility, especially in THF, chloroform, and DMSO. The weight-average molecular weights ($\overline{M}_w$) of the copolymers were found to be in the 0.5–4.4 $\times$ 10^4 range. The polymer structure was identified by various instrumental methods to have a conjugated cyclic polyene structure in the polymer backbone. X-ray analysis showed that poly(BPE) and poly(TSPPE) are amorphous.

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Received November 1, 1994
Revision received January 26, 1995