

Polymerization of Bis(3-trimethylsilyl-2-propynyl)ether and Its Copolymerization with Diethyl Dipropargylmalonate

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Abstract: The polymerization of a cyclopolymerizable disubstituted dipropargyl ether, bis(3-trimethylsilyl-2-propynyl)ether (BTPE), was attempted by various transition metal catalysts. The yield for the polymerization of BTPE was generally low, which is possibly due to the steric hindrance of bulky substituents. In general, the catalytic activities of Mo-based catalysts were found to be greater than those of W-based catalysts. The highest yield was obtained when the MoCl₅-EtAlCl₂ (1 : 2) catalyst system was used. The copolymerization of BTPE and diethyl dipropargylmalonate yielded a random copolymer with conjugated polymer backbone. However the polymers were partially desilylated, depending on the reaction conditions. The thermal and morphological properties of the resulting polymers were also discussed.

Keywords: polymerization, polyacetylene, bis(3-trimethylsilyl-2-propynyl)ether, conjugated polymer, transition metal catalyst.

Introduction

The acetylenic triple bonds have rich π -electrons, which can be used to polymerize to yield the linear conjugated polymer systems. The acetylene monomers carrying a number of functional group such as hydroxy, carboxylic acid, sulfide, amine, and esters, were prepared and polymerized by various catalyst systems.¹⁻⁵

Conjugated polymer systems obtained from acetylene derivatives have been studied as organic semiconductors,⁶⁻⁸

as membranes for gas separation and for liquid-mixture separation,⁹⁻¹¹ as materials for enantioseparation for racemates by high performance liquid chromatography,¹²⁻¹⁴ as a side-chain liquid crystal,¹⁵⁻¹⁷ as materials for chemical sensors,^{18,19} and as materials for nonlinear optical property and for photoluminescence and electroluminescence properties.²⁰⁻²⁵

Ring-forming polymerization is very interesting method for the synthesis of conjugated polymer system by the simple polymerization of diacetylenic monomer via an alternating intramolecular-intermolecular chain propagation.²⁶

Stille and Frey firstly reported the studies on the polymerization of nonconjugated diynes, especially 1,6-heptadiyne, with Ziegler-Natta catalysts.²⁷ Poly(1,6-heptadiyne)s obtained

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were dark red or black, which indicates a high order of conjugation in the polymer. However, the poly(1,6-heptadiyne) was insoluble in any organic solvent and unstable to air oxidation as like with that of polyacetylene.²⁸ Thus, various 1,6-heptadiyne derivatives were designed and polymerized. Typical examples of 1,6-heptadiyne derivatives were dipropargylmethanes having various substituents at 4-position, such as diphenyl dipropargylmethane, diphenyl dipropargylsilane, diethyl dipropargylmalonate, 9,9-dipropargylfluorene, etc.^{7,29-32}

In our previous paper,³³ we briefly reported the attempted polymerization of bis(3-trimethylsilyl-2-propynyl)ether (BTPE), a disubstituted dipropargyl derivative. This article describes the full accounts for the homopolymerization of BTPE by various transition metal catalysts and the copolymerization with diethyl dipropargylmalonate, a well-known dipropargyl monomer, and the characterization of the resulting conjugated polymers.

Experimental

Materials. Propargyl bromide (Aldrich, 80 wt% solution in toluene) was dried with calcium hydride and distilled. Propargyl alcohol (Aldrich, 99%) was dried with magnesium sulfate and distilled. Chlorotrimethyl-silane (Aldrich, redistilled, 99+%) and *n*-butyllithium (Aldrich, 2.5 M solution in hexanes) were used as received. Diethyl malonate (Aldrich, 99%) was dried over calcium hydride and distilled at reduced pressure. MoCl₅ (Aldrich, 99.9+%), MoCl₄ (Aldrich), Cp₂MoCl₂ (Aldrich, 98%), WCl₆ (Aldrich, 99.9+%) were used without further purification. Et₃Al, Et₂AlCl, and EtAlCl₂ [Aldrich, 25 wt% (1.8 M) solution in toluene] and Me₄Sn (Aldrich, 95%) were used as received. Ph₄Sn (Aldrich, 97%) was purified by recrystallizing twice from carbon tetrachloride. The solvents were analytical grade materials. They were dried with an appropriate drying agent and distilled.

Synthesis of Dipropargyl Ether. Dipropargyl ether was prepared by the reaction of propargyl bromide and propargyl alcohol using NaOH as described in the literature.^{34,35} Yield: 85%. b.p.: 67 °C/85 mmHg; ¹H-NMR (CDCl₃, δ, ppm): 2.42 (t, 2H), 4.24 (d, 4H); ¹³C-NMR (CDCl₃, δ, ppm): 56.36 (-CH₂-O-), 75.02 (≡C-H), 78.68 (CH₂C≡); IR (wavenumbers, cm⁻¹, KBr pellet): 3300, 2963, 2919, 2866, 2125, 1505, 1452, 1351, 1253, 1090, 948, 735.

Synthesis of Diethyl Dipropargylmalonate. Diethyl dipropargylmalonate (DEDPM) was also prepared by the reaction of propargyl bromide and the sodium ethoxide solution of diethyl malonate as described in the literature.^{36,37} Yield: 82%. m.p.: 46 °C; ¹H-NMR (CDCl₃, δ, ppm): 1.3 (t, 6H), 2.1 (t, 2H), 3.0 (d, 4H), 4.31 (q, 4H); ¹³C-NMR (CDCl₃, δ, ppm): 14.8 (-CH₃), 23.5 (CH₂C≡C), 56.5 (-C-), 63.0 (-CH₂-O-), 72.9 (≡C-H), 79.6 (CH₂C≡), 169.4 (C=O); IR (wavenumbers, cm⁻¹, KBr pellet): 3310, 3012, 2988, 2129, 1732, 1467, 1215, 1093, 854, 674.

Synthesis of Bis(3-trimethylsilyl-2-propynyl)ether (BTPE).³³ 250 mL two-neck flask was charged with dipropargyl ether (10.0 g, 0.11 mmol) and THF (100 mL). *n*-Butyllithium (2.5 M in hexanes, 88 mL, 0.22 mmol) was injected over a few minute to the reaction mixture at the temperature of -60 ~ -50 °C. After an additional 10 min, the chlorotrimethylsilane (27.16 g, 0.25 mmol) was added over 10 min to the clear solution with stirring while carefully keeping the temperature within this range. And then, the cooling bath was occasionally removed and the temperature was allowed to rise gradually over 1 hr to room temperature. The white suspension was poured into 300 mL of ammonium chloride solution, and then the water phase was extracted with hexane. The combined organic phase was dried with anhydrous magnesium sulfate. The product, BTPE, was isolated by distillation at reduced pressure. Yield: 82%, b.p.: 102 °C/10 mmHg; ¹H-NMR (CDCl₃, δ, ppm): 0.15 (s, 18H), 4.21 (s, 4H); ¹³C-NMR (CDCl₃, δ, ppm): -0.23 (-SiMe₃), 56.36 (-CH₂-O-), 91.98 (≡C-) 100.6 (SiC≡); IR (wavenumbers, cm⁻¹, KBr pellet): 2960, 2899, 2850, 2175, 1346, 1251, 1087, 997, 848, 760.

Polymerization of BTPE by MoCl₅. In a 20 mL ampule equipped with rubber septum, 0.70 mL (0.070 mmol, *M/C* = 30) of 0.1 M MoCl₅ solution, chlorobenzene (0.90 mL, [M]₀ = 1.0 M), and 0.5 g (2.10 mmol) of BTSE were added in that order given. And the polymerization was carried out at 80 °C for 24 hrs under nitrogen atmosphere. The polymerization seems to proceed in somewhat mild manner. A small amount of insoluble product was precipitated into the bottom of the reactor. After a given time of polymerization, 10 mL of chloroform was added to the polymerization solution. The polymer solution was precipitated into an excess of methanol, filtered from the solution, and then dried under vacuum at 40 °C for 12 hrs. The polymer yield was 10%.

Polymerization of BTPE by MoCl₅-EtAlCl₂. In a 20 mL ampule equipped with rubber septum, chlorobenzene (0.39 mL, [M]₀ = 1.0 M), 1.40 mL (0.14 mmol, *M/C* = 30) of 0.1 M MoCl₅ solution, and 1.40 mL (0.28 mmol) of 0.2 M EtAlCl₂ solution were added in that order given. After shaking the catalyst solution at 30 °C for 15 min, 0.5 g of BTPE (2.10 mmol) was injected. After a given time of polymerization, 10 mL of chloroform was added to the polymerization solution. The polymer solution was poured into an excess of methanol, filtered from the solution, and then dried under vacuum at 40 °C for 12 hrs. The polymer yield was 23%.

Copolymerization of BTPE and DEDPM by MoCl₅-EtAlCl₂. A catalyst solution of MoCl₅ (0.84 mL of 0.1 M chlorobenzene solution, 0.084 mmol), EtAlCl₂ (0.84 mL 0.2 M chlorobenzene solution, 0.168 mmol), and 5.71 mL chlorobenzene ([M]₀ = 0.5) was prepared and aged for additional 15 min at 30 °C. To this solution was added the comonomer mixture [1.00 g, BTSE/DEDPM (0.5 g/0.5 g), comonomer feed ratio: 1/1] at room temperature. Then, the polymerization was carried out at 80 °C for 24 hrs. After the polymerization

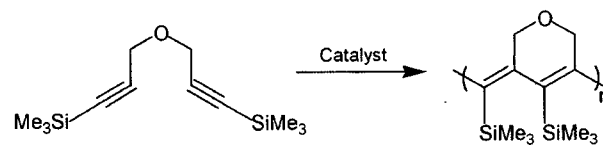
time, 10 mL of chloroform was added to the reactor. The polymer solution was precipitated into excess methanol, filtered from the solution, and dried under vacuum at 40 °C for 12 hrs. Polymer yield was 65%.

Instruments and Measurement. NMR spectra (^1H - and ^{13}C -) were recorded with the use of a Varian 500-MHz FT-NMR spectrometer (model: Unity INOVA), and chemical shifts are reported in ppm units with tetramethylsilane as an internal standard. Magic angle spinning, cross polarization ^{13}C -NMR spectra of insoluble polymer were recorded on a Bruker AM-200 spectrometer (5-s repetition time, 3.5-ms cross polarization mixing time, 8-W decoupler power, and 3.8-KHz spinning). IR spectra were obtained with a Bomem MB-100 spectrometer using a KBr pellet, and frequencies are given in reciprocal centimeters. Elemental analyses were performed with FISON S EA1110 Elemental Analyzer. UV-visible spectra of polymer solution were taken on a Shimadzu UV-3100S spectrophotometer. X-ray diffractograms were measured with a PHILIPS X-ray diffractometer (Model: XPert-APD).

Results and Discussion

The cyclopolymerization of BTPE, a typical cyclopolymerizable disubstituted acetylenic monomer, was attempted with Mo- and W-based transition metal catalysts (Scheme I).

Table I shows the results for the polymerization of BTPE by Mo- and W-based catalysts. The polymer yields were generally low. The catalytic activity of Mo-based catalysts were found to be higher than that of W-based catalysts.



Scheme I. Cyclopolymerization of BTPE.

MoCl_5 itself polymerized BTPE to give poly(BTPE) in 10% yield, whereas WCl_6 itself failed to polymerize BTPE. In our previous works, it had been shown that the catalytic activities of Mo-based catalysts was higher than those of W-based catalysts in the cyclopolymerization of 1,6-heptadiynes such as diphenyl dipropargylmethane,³⁸ diethyl dipropargylmalonate,^{37,39} and 4,4-bis((*tert*-butyldimethylsilyloxy)-methyl)-1,6-heptadiyne.⁴⁰

It was known that dipropargyl ether and 1,6-heptadiyne were explosively polymerized by the same Mo-based catalysts to produce the polymeric product with a quantitative yield.^{28,35} In that case, the oxygen atom and/or the acetylenic functional group were found to activate the molybdenum chlorides. The low yields for the polymerization of a disubstituted acetylene, BTPE, seemed to be originated from the steric hindrance of bulky trimethylsilyl substituents. Similar results were found in the polymerization of 1-phenyl-2-trimethylsilylacetylene, a disubstituted acetylene. The polymerization of phenylacetylene, mono-substituted acetylene derivative, proceeded well to give a high yield of polymer, while the polymerization of 1-phenyl-2-trimethylsilylacetylene give only a low yield of polymer (maximum polymer yield = 33%).⁴¹

Table I. Polymerization of Bis(3-trimethylsilyl-2-propynyl)ether by Various Transition Metal Catalysts^a

Exp. No	Catalyst System (mole ratio) ^b	M/C ^c	$[M]_0$ ^d	Polymer Yield ^e (%)	M_n ^f
1	MoCl_5	30	1.0	10	-
2	MoCl_5	50	1.0	0	-
3	MoCl_5	50	1.5	0	-
4	$\text{MoCl}_5\text{-Ph}_4\text{Sn}(1:1)$	30	1.5	15	6,700
5	$\text{MoCl}_5\text{-Ph}_4\text{Sn}(1:1)$	50	1.5	trace	-
6	$\text{MoCl}_5\text{-Et}_3\text{Al}(1:2)$	30	1.0	trace	-
7	$\text{MoCl}_5\text{-EtAlCl}_2(1:2)$	30	1.0	23	9,800
8	$\text{MoCl}_5\text{-EtAlCl}_2(1:2)$	50	1.0	15	6,000
9	$\text{MoCl}_5\text{-EtAlCl}_2(1:4)$	50	1.5	13	4,800
10	$\text{MoCl}_4\text{-EtAlCl}_2(1:2)$	30	1.0	21	6,200
11	$\text{Cp}_2\text{MoCl}_2\text{-EtAlCl}_2(1:2)$	30	1.0	20	4,300
12	WCl_6	50	1.5	0	-
13	$\text{WCl}_6\text{-EtAlCl}_2(1:2)$	30	1.5	10	-
14	$\text{WCl}_6\text{-EtAlCl}_2(1:2)$	50	1.5	5	-

^aPolymerization was carried out at 80 °C for 24 hrs in chlorobenzene. ^bMixtures of catalyst and cocatalyst were aged at 30 °C for 15 min before use.

^cMonomer to catalysts mole ratio. ^dInitial monomer concentration (M). ^eMethanol-insoluble polymer.

^fValues were obtained by GPC analysis with the calibration using polystyrene.

It has been reported that the addition of a small amount of reducing agents such as Ph_4Sn and $n\text{-Bu}_4\text{Sn}$ increases the polymer yield and molecular weight in the MoCl_5 -catalyzed polymerization of 2-ethynylthiophene,⁴² 2-ethynylfuran,⁴³ and 1-butyl-2-trimethylsilylacetylene.⁴⁴ And also the organoaluminum compounds such as EtAlCl_2 and Et_2AlCl were very effective cocatalysts in the polymerization of 1-ethynylcyclohexene⁴⁵ and 4-ethynyltoluene by MoCl_5 or WCl_6 .⁴⁶ In the polymerization of BTPE by MoCl_5 , the Ph_4Sn cocatalyst increased the polymer yield slightly. The EtAlCl_2 cocatalyst among the organoaluminum compounds also showed the cocatalytic activity. The best result (polymer yield = 23%) was obtained with the MoCl_5 - EtAlCl_2 (1 : 2) catalyst system. The MoCl_4 and Cp_2MoCl_2 catalyst showed similar catalytic activities with that of MoCl_5 , when the EtAlCl_2 cocatalyst was used. Especially, it was found that the effect of monomer to catalyst mole ratio (M/C) was somewhat high. In most cases, we did not obtain the polymeric products when the M/C is over 100.

We have also investigated the effect of catalyst aging time for the catalyst system of MoCl_5 - EtAlCl_2 . The best result was obtained when the aging time was 15 min. After then, the polymer yields were slightly decreased with an increase of aging time.

Figure 1 shows the time dependence curve of polymer yield for the polymerization of BTPE by MoCl_5 - EtAlCl_2 catalyst system in chlorobenzene. As shown in this figure, the polymerization proceeded slowly even at the initial polymerization time. The polymer yield was gradually increased up to 23% after 24 hrs.

In order to increase the polymer yield and the processibility of the present conjugated polymer carrying bulky substituents, we attempted the copolymerization of BTPE with DEDPM. The copolymer structure is proposed in Figure 2. DEDPM is very interesting dipropargyl monomer, which is easily

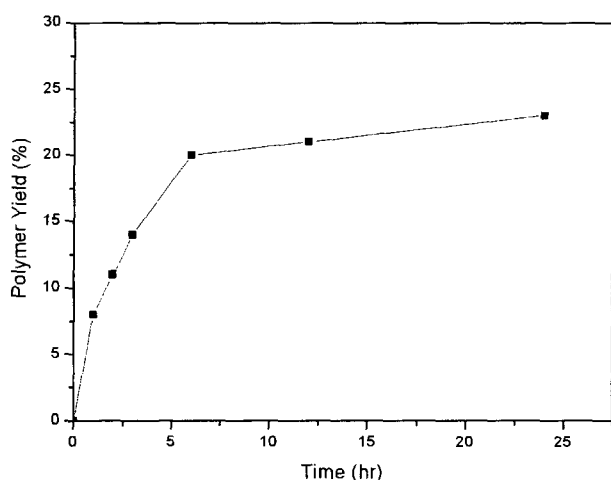


Figure 1. The time dependence curve of the polymer yield for the polymerization of BTPE by the MoCl_5 - EtAlCl_2 catalyst system.

polymerized by Mo-based catalysts to give a polymer of high molecular weight in high yields.³⁷

The copolymerization of BTPE with DEDPM (comonomer feed ratio = 1 : 1) was carried out by MoCl_5 - EtAlCl_2 catalyst system. The polymerization proceeded well and the viscosity of reaction solution increased. After 24 hrs, the polymer yield was 65%. The resulting copolymer was dark brown powder, and soluble in common organic solvents such as chloroform, chlorobenzene, and THF, whereas the homopolymer, poly(BTPE), was mostly insoluble in organic solvents. The incorporation of DEDPM moieties in the poly(BTPE) increased the polymer yield and the solubility of the resulting conjugated polymer systems. The analysis of copolymer composition by NMR and elemental analysis revealed that the feed ratio of BTPE and DEDPM at copolymer was 37 : 63. The number-average molecular weight (M_n) and the polydispersity (M_w/M_n) of this copolymer were 47,000 and 2.8, respectively.

The chemical structure of the resulting conjugated polymers was characterized by various instrumental methods. It was very difficult to identify the exact polymer structure with solution state because of the insolubility of poly(BTPE) homopolymer. Thus, we measured the IR and solid-state ^{13}C -NMR spectra of poly(BTPE) homopolymer.

Figure 3 shows the IR spectra of BTPE and poly(BTPE) in KBr pellet. In the IR spectrum of poly(BTPE), the acetylenic $\text{C}\equiv\text{C}$ bond stretching peak at 2175 cm^{-1} was mostly disappeared. However, a small amount of acetylenic $\text{C}\equiv\text{C}$ stretching peak was also observed, which means that the present polymer contains the pendant acetylenic functionality in the conjugated polymer main chain. And also, the $\text{C}=\text{C}$ double bond stretching frequency peak of conjugated polymer backbone at 1640 cm^{-1} was newly observed. We measured the UV-visible spectrum of slightly soluble poly(BTPE) in THF (Figure 4). As shown in this figure, a characteristic broad absorption peak at the visible region, which is originated from the $\pi \rightarrow \pi^*$ conjugation band transition of the polyene main chain, was observed. The absorption peak of poly(BTPE) tailed up to 650 nm.

Figure 5 shows the solid-state ^{13}C -NMR spectrum of poly(BTPE). This spectrum exhibited the new vinyl carbon peaks of conjugated polymer backbone of poly(BTPE) at 118-165 ppm broadly, which had not been observed in the ^{13}C -NMR spectrum of monomer (BTPE). It also showed two broad peaks due to the methylene carbons adjacent to conjugated

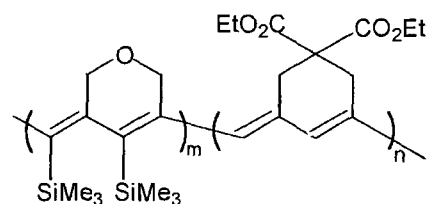


Figure 2. The proposed structure of poly(BTPE-co-DEDPM).

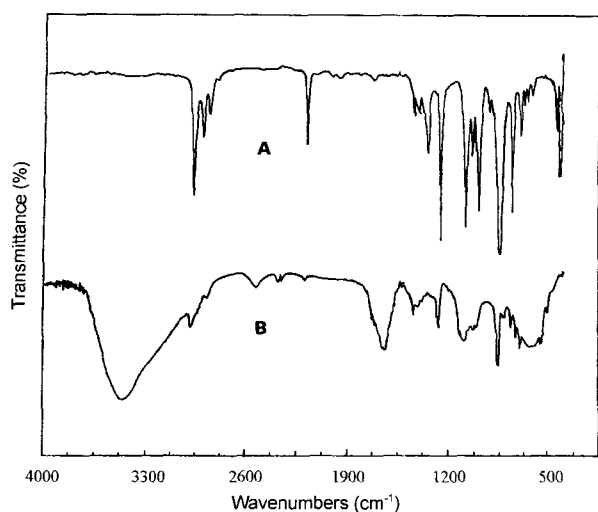


Figure 3. FT-IR spectra of BTPE (A) and poly(BTPE) (B) in KBr pellet.

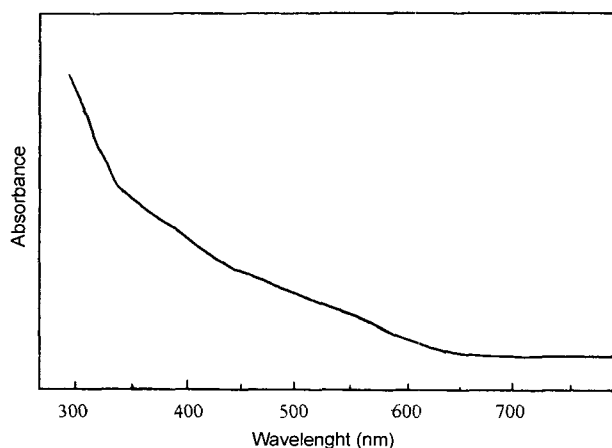


Figure 4. UV-visible spectrum of slightly soluble poly(BTPE) in tetrahydrofuran.

double bonds and the trimethylsilyl carbons at 32–63 ppm and –23~15 ppm, respectively.

We also attempted to measure the $^1\text{H-NMR}$ spectrum of slightly soluble poly(BTPE) sample (highly diluted one). From the $^1\text{H-NMR}$ peak integration of methylene and trimethylsilyl protons, it was found that the poly(BTPE)s are partially desilylated. The same observations on the desilylation phenomenon of trimethylsilyl group-containing disubstituted conjugated polymer were also observed in the systems of poly(1-aryl-2-trimethylsilylacetylene)s.⁴¹ In the present time, it is not clear that the desilylation occurs during the polymerization process and/or the work-up process.

It has been reported that the conjugated cyclic polymers obtained by both a classical metathesis catalyst and a well-defined alkylidene initiator produce five- and six-membered

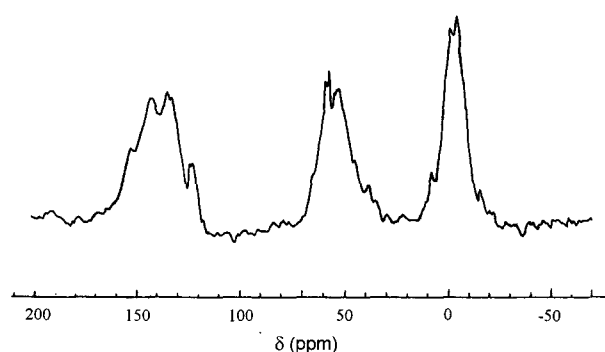


Figure 5. Solid-state $^{13}\text{C-NMR}$ spectrum of insoluble poly(BTPE) sample.

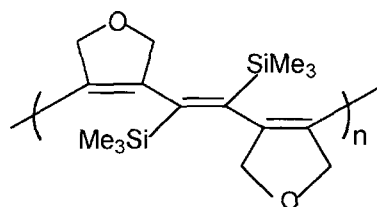


Figure 6. Sterically more favorable structure of poly(BTPE).

rings of a certain ratio, which depended on the polymerization conditions and kinds of catalysts used.^{47,48} The effect of size and type of substituents on the fine and conformational structure for this potentially interesting class of cyclic polyenes was systematically performed.⁴⁹ It was known that the ratio of five-membered ring to six-membered ring was increased as the increase of the size and number of substituents at monomer because of the α -addition of alkylidene complex to the acetylene monomer. The six-membered structure (Scheme I) obtained by the β -addition mechanism of alkylidene complex to acetylene functionality is sterically unfavorable structure because of the steric hindrance of bulky substituents. Thus, the five-membered polymer structure (Figure 6) was judged to be the most favorable one in the viewpoint of its stability and probability associated with the transition state in the cyclopolymerization.^{50,51}

Figure 7 shows the $^1\text{H-NMR}$ spectrum of the poly(BTPE-co-DEDPM) in CDCl_3 . This copolymer was mostly soluble in such organic solvents as chloroform, benzene, chlorobenzene, THF, etc, whereas the poly(BTPE) homopolymer was mostly insoluble in organic solvents. It shows the trimethylsilyl protons at –0.25~0.40 ppm. And also, the methyl and methylene protons of ethyl substituent were observed at 0.95~1.41 ppm and 3.75~4.29 ppm, respectively. The proton peaks for two ring methylenes of poly(BTPE) and poly(DEDPM) moieties were also seen at the 2.55–3.65 ppm for poly(DEDPM) moieties and the 4.29–5.00 ppm for poly(BTPE) moieties. From the integration of two ring methylene proton peaks, it was found that the feed ratio of BTPE and

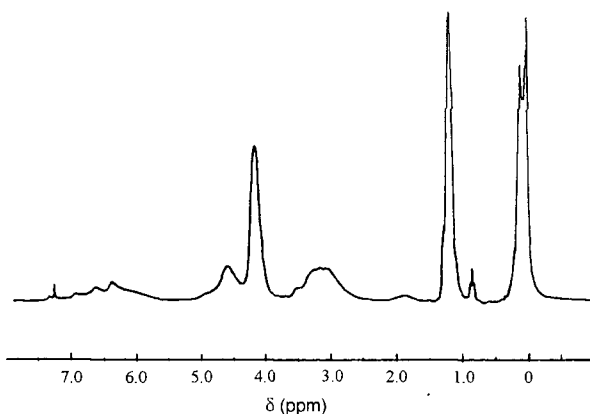


Figure 7. $^1\text{H-NMR}$ spectrum of poly(BTPE-co-DEDPM) in CDCl_3 .

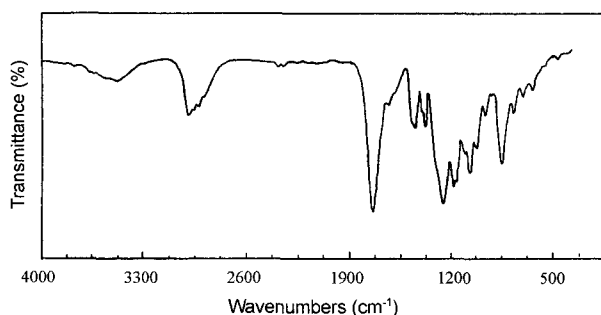


Figure 8. FT-IR spectrum of poly(BTPE-co-DEDPM) in KBr pellet.

DEDPM in the copolymers was 37 : 63. This spectrum distinctly shows the vinylic protons in the conjugated polymer backbone at 5.60-7.00 ppm.

Figure 8 shows the IR spectrum of the poly(BTPE-co-DEDPM) in KBr pellet. It did not show the acetylenic $\text{C}\equiv\text{C}$ stretching frequencies at 2175 cm^{-1} of BTPE and 2129 cm^{-1} of DEDPM and the acetylenic $\equiv\text{C-H}$ stretching frequency at 3310 cm^{-1} of DEDPM. Instead, the weak and broad peak at $1600\text{-}1680\text{ cm}^{-1}$, resulting from the conjugated double bonds of the polymer backbone, was observed. The strong peak at 1731 cm^{-1} is due to the $\text{C}=\text{O}$ stretching frequencies of ester functional group.

Figure 9 shows the UV-visible spectrum of the poly(BTPE-co-DEDPM) in THF. This spectrum was very similar to that of poly(DEDPM) homopolymer. It showed the characteristic broad band at 525 nm due to the $\pi\rightarrow\pi^*$ transition of conjugated polyene backbone.

The morphologies of poly(BTPE) and poly(BTPE-co-DEDPM) were also investigated by X-ray diffraction analysis. The peaks in the diffraction pattern are broad and the ratios of the half-height width to diffraction angle ($\Delta 2\theta/2\theta$) are greater than 0.35,⁴ indicating that the present polymers are amorphous.

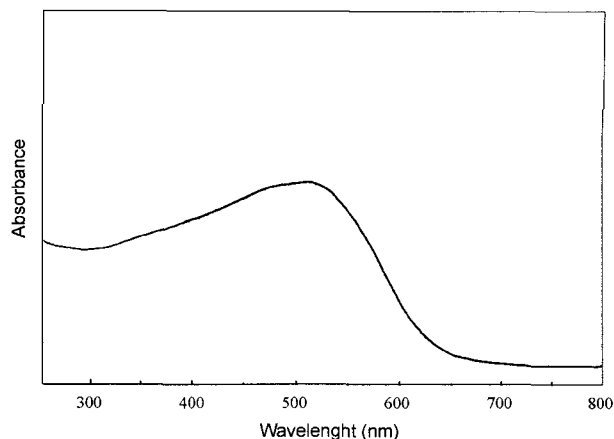


Figure 9. UV-visible spectrum of poly(BTPE-co-DEDPM) in tetrahydrofuran.

Conclusions

The ring-forming polymerization of BTPE, a trimethylsilyl group-containing disubstituted acetylene, was attempted with various transition metal catalysts. In general, the polymer yield was low due to the steric hindrance of the monomer. The catalytic activity of Mo-based catalysts were found to be greater than that of W-based catalyst systems. The best result was obtained when the $\text{MoCl}_5\text{-EtAlCl}_2$ catalyst system was used (polymer yield = 23%). However, the resulting poly(BTPE) had a partially desilylated structure, and was mostly insoluble in organic solvents. The soluble conjugated cyclopolymer having trimethylsilyl group was obtained by the copolymerization with DEDPM. The structural characterization by various instrumental methods confirmed the conjugated polymer backbone with cyclic recurring units. The X-ray diffraction data indicated that the present polymers are mostly amorphous.

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