Synthesis and Properties of Poly(1,6-heptadiyne) Having a Bulky Siloxy Group

Yun Hi Kim, Soon-Ki Kwon,* and Sam Kwon Choi

Department of Polymer Science and Engineering & AMRI, Kyeongsang National University, Jinju 660−300, Korea, and Department of Chemistry, Korea Advanced Institute of Science and Technology, 373-1 Kusung-dong, Yusung-gu, Taejon, Korea

Received September 19, 1996
Revised Manuscript Received June 30, 1997

Introduction

Since the discovery of polymerization of 1,6-heptadiyne using Ziegler−Natta catalyst in 1961,[1] there have been many studies on the cyclopolymerization of nonconjugated diynes giving conjugated double bonds and the cyclic recurring unit in the polymer backbone. However, this catalyst leads to insoluble polymer films.[2] Recently, we have found that $MoCl_5$- and WCl_6-based catalyst systems are very effective for the cyclopolymerization of 1,6-heptadiyne derivatives.[3−14] The corresponding polymers have good solubility in common organic solvents and long term stability toward oxidation. They have also various functionalities such as electrical conductivity, nonlinear optical property, photoconductivity, and side chain liquid crystallinity by the introduction of the proper functional group.

In a recent series of papers, Masuda et al. reported the synthesis of mono- and disubstituted polyacetylene derivatives with the trialkylsilyl group which one good gas permeable membranes.[15−18] In our previous paper, we reported the synthesis and characterization of poly-(4-methyl-4-(*tert*-butyldimethylsiloxy)-1,6-heptadiyne) [poly(MTSH)].[14] However the film could not be formed from poly(MTSH), because the resulting polymer had low solubility and low molecular weight. It had been also reported that poly[4,4-bis((trimethylsiloxy)methyl)-1,6-heptadiyne] was cyclopolymerized by Schrock et al. without cleavage of the silicon−oxygen bond, which can be easily broken by transition metal catalysts.[22] However, no properties of poly[4,4-bis((trimethylsiloxy)-methyl)-1,6-heptadiyne] were reported.

In this article, we described the results on the synthesis, structure characterization, and properties of poly(BTSH) containing the bulky *tert*-butyldimethylsiloxy group, which is expected to have high gas permeability due to the bulky flexible siloxy group and higher thermal stability and solubility resulting from bulky substituents.

Experimental Section

Materials. Propargyl bromide (Aldrich Chem. Co., 80% solution in toluene) was dried over calcium hydride and fractionally distilled. $MoCl_5$ and WCl_6 (Aldrich Chem. Co., resublimed 99.9%) were used without further purification. Tetra-*n*-butyltin and ethylaluminum chloride (Aldrich Chem. Co.) were used as received. All solvents were used after purification according to conventional methods.

Preparation of 4,4-Bis(*tert*-butyldimethylsiloxy)-methyl)-1,6-heptadiyne (BTSH). Diethyl dipropargylmalonate (33 g, 140 mmol) which was prepared by a literature method[5] was dissolved in 80 mL of diethyl ether. The solution was added dropwise over a period of 1 h to a suspension of $LiAlH_4$ (8.83 g, 220 mmol) in 300 mL of diethyl ether at room temperature. The reaction mixture was refluxed for an additional 6 h. Water was added dropwise to the gray suspension until it turned white and evolution of H_2 ceased. The reaction mixture was extracted with diethyl ether, and the solution was dried over anhydrous $MgSO_4$. The ether was removed *in vacuo* to give a white solid product that could be recrystallized from ether (17.6 g, 82%). ^{1}H-NMR ($CDCl_3$): δ (ppm) 3.69 (s, 4H, OCH_2), 2.55 (brs, 2H, OH), 2.34 (d, 4H, CH_2), 2.01 (t, 2H, ≡CH). ^{13}C NMR($CDCl_3$): δ (ppm) 80.1 (−C≡), 71.0 (≡CH), 66.3 (OCH_2), 42.0 (quarternary C), 21.6 (CH_2C≡). Anal. Calcd for $C_9H_{12}O_2$: C, 71.03; H, 7.95. Found: C, 71.01; H, 7.90. *tert*-Butyldimethylsilyl chloride (15.25 g, 100 mmol) was added to the mixture of 7 g (46 mmol) of 4,4-bis-(hydroxymethyl)-1,6-heptadiyne and 200 mL of pyridine in an ice bath. After the mixture was refluxed for 24 h, the reaction solution was cooled and poured into ice−water and extracted with diethyl ether. The organic layer was dried over anhydrous $MgSO_4$. The volatile compounds were removed *in vacuo*. The resulting oilly product was distilled to afford a colorless liquid (yield 76%; bp 130−134 °C/1 mmHg). ^{1}H-NMR: δ 3.61 (s, 4H, OCH_2), 2.28 (d, 4H, CH_2C≡), 1.97 (t, 2H, ≡CH), 0.84 (s, 18H, CH_3), 0.03 (s, 12H, $SiCH_3$). ^{13}C NMR: δ 80.4 (−C≡), 70.8 (≡CH), 66.5 (OCH_2), 42.0 (quarternary C), 25.7 (C−CH_3), 21.4 (CH_2), 18.1 [Si−C(quarternary)], −5.71 (Si−CH_3). Anal. Calcd for $C_{21}H_{40}O_2Si_2$: C, 66.26; H, 10.56; Si, 14.75. Found: C, 66.22; H, 10.63; Si, 14.73.

Table 1. Polymerization of BTSH by Transition Metal Catalyst[a]

experiment no.	catalyst system[b]	initial monomer concn [Mo] (M)	polymer yield (%)	10^{-3} M_n[e]
1	$MoCl_5$	0.5	95[c]	
2	$MoCl_5$	0.125	95	156
3	$MoCl_5$	0.25	86	112
4	$MoCl_5$(*n*-Bu)$_4$Sn (1:2)	0.25	94	184
5	$MoCl_5Et_2AlCl$ (1:2)	0.25	90	105
6	$MoCl_5EtAlCl_2$ (1:2)	0.25	94	120
7	WCl_6	0.25	5	
8	WCl_6(*n*-Bu)$_4$Sn (1:2)	0.25	10[c]	
9	$WCl_6EtAlCl_2$ (1:2)	0.25	70[c]	
10	$PdCl_2$	0.5	45[d]	21

[a] Polymerization was carried out at 40 °C for 24 h in chlorobenzene. Mole ratio of monomer to catalyst (M/C) was 100. [b] Mole ratio (where applicable) is given in parentheses. Mixture of catalyst and cocatalyst in chlorobenzene was aged at 30 °C for 15 min. before use as catalyst. [c] Resulting polymer was insoluble. [d] Polymerization was carried out in dioxane. [e] Determined by GPC.

Instruments for Characterization. ^{1}H and ^{13}C NMR spectra were recorded with the Bruker AM-200 spectrometers, and chemical shifts were reported in ppm units with TMS as internal standard. Infrared spectra were measured on a Bomem MB-100 FT spectrophotometer. Thermal analysis was carried out on a DuPont TGA 9900 thermogravimetric analyzer in a nitrogen atmosphere at a rate of 10 °C/min. Number average molecular weights (M_n) were determined in THF solution with a Waters GPC-150C calibrated with polystyrene standards. Tensile tests were conducted at 25 °C with the rate of strain fixed at 86%/min on an Instron 1122. The size of the specimen was 35 × 10 × 0.2 mm. Gas permeabilities for the polymer membrane with about 40 μm of thickness were measured with a conventional permeability apparatus, which consists of upstream and downstream parts separated by a membrane.[5,7,14] The upstream part was maintained to a constant pressure of 5 kgf/cm^2 of either pure O_2 or N_2 gas during the experimental period, and the downstream part was opened to the atmosphere. A bubble gas flowmeter was employed to measure the permeation flux steady-state from which the gas permeability was calculated. Elemental analysis was performed with a Perkin-Elmer 240DS elemental analyzer.

Polymerization. All procedures for the preparation of catalyst systems and polymerization were carried out under dry nitrogen atmosphere. Transition-metal halides and or-

* To whom all correspondence should be addressed at Kyeongsang National University.

S0024-9297(96)01393-9 CCC: $14.00

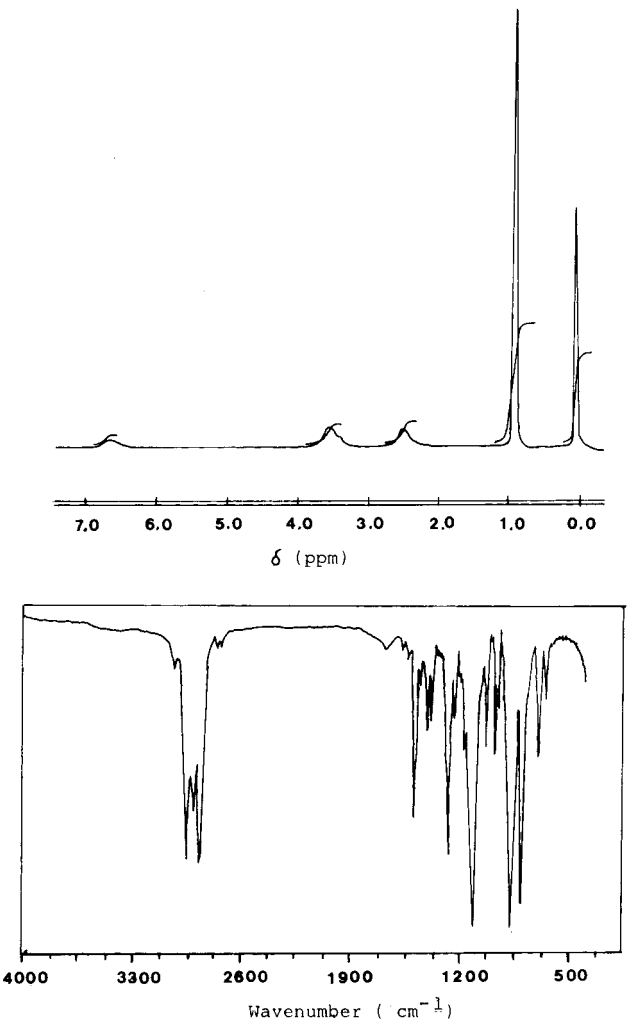

Figure 1. ^{1}H-NMR and FT-IR spectra of poly(BTSH).

ganometallic compounds were dissolved in each solvent to give 0.1 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. 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 mixture was allowed to react at 40 °C for 24 h, the polymerization was terminated by adding a small amount of methanol, and chloroform was added to dissolve the polymer. The resulting solution was poured into a large amount of methanol, and the polymer was filtered and dried under vacuum at 40 °C for 24 h.

Results and Discussion

Polymerization. Table 1 lists the results of the polymerization of BTSH by various transition metal catalysts. $MoCl_5$-based catalysts showed greater catalytic activity than the WCl_6-based one. As shown in Table 1, $(n\text{-Bu})_4Sn$ and $EtAlCl_2$ hardly exhibited a cocatalytic effect on the cyclopolymerization of BTSH by $MoCl_5$. However they were effective cocatalysts for the cyclopolymerization of BTSH by WCl_6 although they afforded an insoluble polymer. The number average molecular weight ($\bar{M}_n$) of poly(BTSH) obtained by using $MoCl_5(n\text{-Bu})_4Sn$ (1:2) was 184×10^3. These results are compared with that of 4-methyl-4-(*tert*-butyldimethylsiloxy)-1,6-heptadiyne.[14] The polymerizability of BTSH is higher than that of 4-methyl-4-(*tert*-butyldimethylsiloxy)-1,6-heptadiyne to give the polymer with a high number average molecular weight in high polymerization yield. It is believed that the bulky substituents at the 4-position cause the monomer to have the cisoid conformation, which can be easily cyclopolymerized.

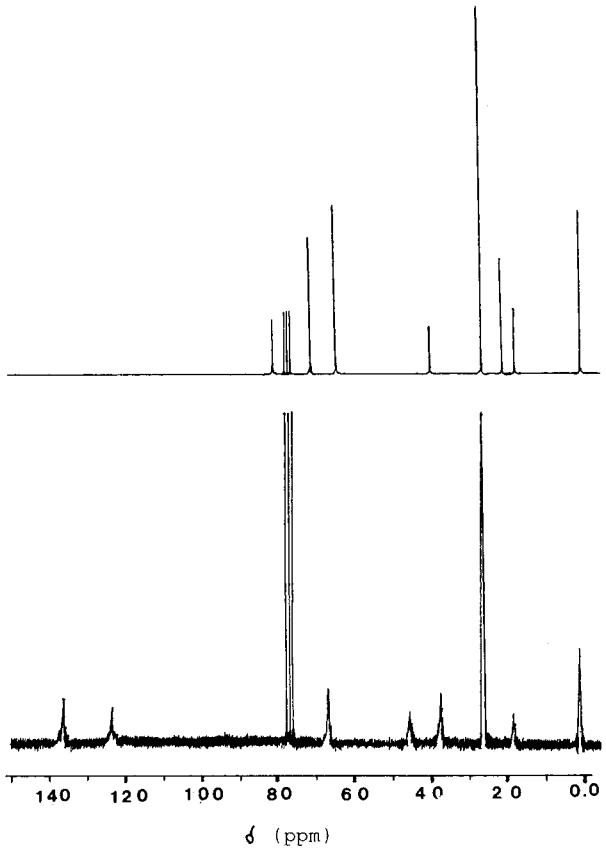

Figure 2. ^{13}C-NMR spectra of BTSH and poly(BTSH).

Polymer Structure. The polymer structure was characterized by ^{1}H-NMR, ^{13}C-NMR, IR, and UV−visible spectroscopic analysis. The ^{1}H-NMR and FT-IR spectra of Poly(BTSH) are shown in Figure 1. As the result of the polymerization, the new broad peak that is assignable to the protons on the conjugated double bond appeared at 6.6 ppm in the ^{1}H-NMR spectrum of poly(BTSH). The IR spectrum of the polymer showed neither the acetylenic hydrogen stretching nor the carbon−carbon triple bond stretching band. Instead, the carbon−carbon double bond stretching band at 1600 cm^{-1}, which indicates a highly conjugated unsaturation, showed up. The ^{13}C-NMR spectra (Figure 2) of BTSH and poly(BTSH) show the presence of olefinic carbons in the polymer backbone at 123 and 137 ppm. The UV−visible spectra of the polymer were obtained in chloroform (Figure 3). A characteristic peak of conjugated polymers, broad $\pi \rightarrow \pi^*$ absorption, appeared in the visible region ($\lambda_{max} = 600$ nm). From these spectroscopic results, we suggest that poly(BTSH) containing bulky siloxy substituents has a highly planar conjugated backbone and recurring five- and six-membered cyclic ring structures as shown in Scheme 1.[19,20] It is difficult to know the exact composition ratio for five and six-membered rings. However, we can suppose that the polymer maybe has more five-membered rings than six-membered ones, because the resulting polymer was shown to be very planar by UV−visible spectroscopy.[21]

Polymer Properties. The obtained polymer was completely soluble in chlorobenzene, toluene, carbon tetrachloride, chloroform, tetrahydrofuran, and diethyl ether but was insoluble in acetone, ethyl acetate, and

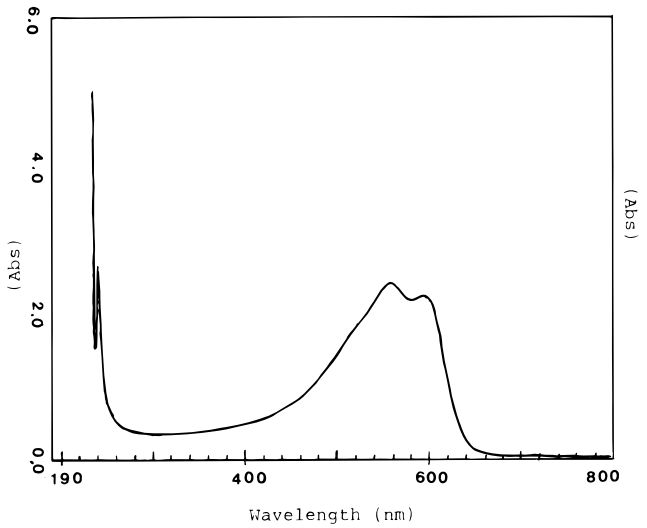

Figure 3. UV-vis spectrum of poly(BTSH).

Scheme 1

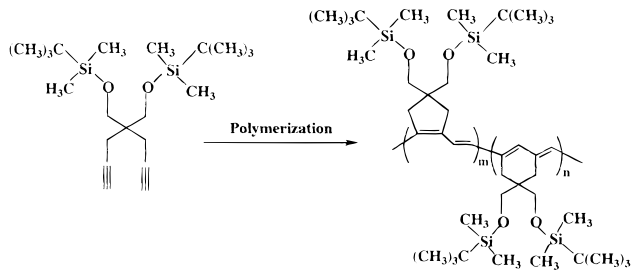

Table 2. Gas Permeation Behavior of Poly(DEDPM), Poly(TFEDPM), Poly(HFPDPM), and Poly(BTSH)

polymer	P_{O_2}[a]	P_{N_2}	P_{O_2}/P_{N_2}[b]	ref
poly(DEDPM)[c]	3.30×10^{-10}	1.80×10^{-10}	1.8	5
poly(TFEDPM)[d]	1.28×10^{-9}	8.2×10^{-9}	1.6	7
poly(HFPDPM)[c]	7.14×10^{-9}	4.20×10^{-9}	1.7	7
poly(CFHDPM)[f]	8.0×10^{-9}	2.80×10^{-9}	2.8	14
poly(BTSH)	3.2×10^{-8}	1.39×10^{-8}	2.3	this work

[a] In units of cm^3 (STP) cm/cm^2 s cmHg. [b] Permselectivity. [c] Poly(DEDPM): poly(diethyl dipropargylmalonate).[5] [d] Poly(TFEDPM): poly[bis(2,2,2-trifluoroethyl)dipropargyl malonate].[7e] Poly(HFPDPM): poly[bis(1,1,1,3,3,3-hexafluoro-2-propyl) dipropargylmalonate].[7] [f] Poly(DFHDPM): poly[bis(2,2,3,3,4,4,5,5,6,6,7,7-dodecafluoroheptyl) dipropargylmalonate].[14]

methanol. The free standing film of poly(BTSH) was obtained by casting its toluene solution. The polymer film showed mechanical properties with a Young's modulus (E) of 340 MPa, a tensile strength (σB) of 9 MPa, and ultimate elongation (γB) of 2.8% at a constant rate of stretching of 86%/min at 25 °C. Although the molecular weight of the polymer is very high, the polymer film was a little brittle. The brittleness of the polymer is probably due to the weak intermolecular force between polymer chains resulting from bulky and nonpolar siloxy substituents. Table 2 shows the oxygen permeability coefficient (P_{O_2}) and separation factors of oxygen to nitrogen (P_{O_2}/P_{N_2}) of poly(1,6-heptadiyne derivatives).[5,7,14] The P_{O_2} value of poly(BTSH) is greater than those of poly(1,6-heptadiyne derivatives). We assume that the bulky siloxy substituent makes poly(BTSH) have high oxygen solubilities and/or high free volumes. The TGA thermogram of poly(BTSH) under nitrogen atmosphere shows that poly(BTSH) is thermally stable up to 360 °C and begins to degrade at temperatures above 360 °C (Figure 4). In order to measure the air oxidation stability of poly(BTSH), IR

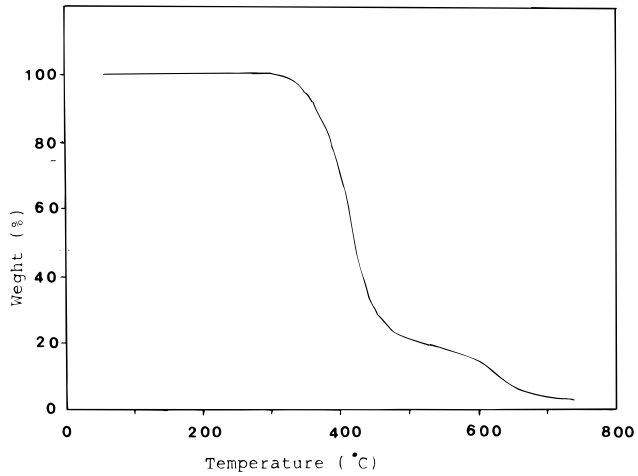

Figure 4. TGA thermogram of poly(BTSH).

spectra of poly(BTSH) exposed to air for 4 weeks in succession were measured. Because there was not any notable carbonyl absorption, which is due to the oxidation of the conjugated double bond, the polymer with bulky siloxy substituents can be said to be environmentally stable. This is due to the fact that the thermally and oxidatively susceptible conjugated double bond is shielded by the bulky substituents.

Acknowledgment. This study was supported by the Korean Ministry of Education through the Research fund for Advanced Materials in 1992−1994.

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MA961393I