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SYNTHESIS AND PROPERTIES OF POLY(1,6-HEPTADIYNE) HAVING A BULKY AND RIGID t-BUTYLBENZOYL GROUP

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Key Words: Cyclopolymerization, Transition Metal Catalysts, Conjugated Backbone, Recurring 5-Membered Ring, Oxygen Permeability

ABSTRACT

The polymerization of 4,4-bis(t-butylbenzoylmethyl)-1,6-heptadiyne (BTBH) was carried out by group 5,6-transition metal catalysts. $MoCl_5$- as well as WCl_6-based catalysts were effective for the cyclopolymerization of BTBH. The polymer structure was analyzed to have conjugated backbone and recurring 5-membered ring by various spectroscopes. The polymer showed good solubility in common organic solvents. The polymer had good thermal stability and mechanical property. The oxygen permeability coefficient (PO_2) and permselectivity of oxygen to nitrogen (PO_2/PN_2) of poly(BTBH) with bulky and rigid t-butyl benzoyl group were 23.2 barrer and 4.63, respectively.

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INTRODUCTION

Since the discovery of polymerization of 1,6-heptadiyne using Ziegler-Natta catalysts in 1961 [1], there have been many studies on the cyclopolymerization of nonconjugated diynes giving conjugated double bonds and 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 [3-15]. 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 [3-10, 13-15].

In a recent series of papers, Masuda *et al.* reported the synthesis of mono- and disubstituted polyacetylene derivatives with various functional groups as good gas separation membranes with high permeabilities. [16-19]

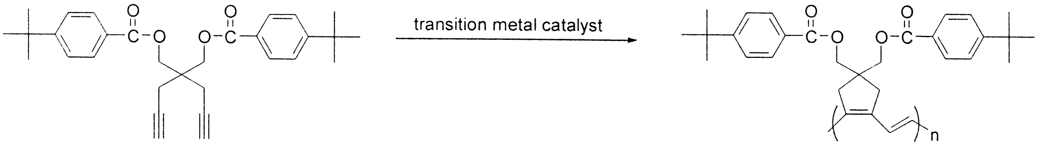
Poly(1,6-heptadiyne derivative)s was also candidated as good gas separation membrane because they had rigid backbone structure containing functional group, which could be designed for good gas separation. Thus, we have studied on poly(1,6-heptadiyne derivative)s as gas permeable membrane by introducing proper functional groups such as perfluoroalkylester and t-butyl—di-methylsiloxy group at 4-position of 1,6-heptadiyne [7, 15]. Most of these polymers exhibited moderate permeability, however, they showed low permselectivity of oxygen to nitrogen and relatively poor mechanical properties due to weak interchain attraction.

The present paper deals with the synthesis, structure characterization, and properties of poly[4.4-bis(t-butylbenzoxymethyl)-1,6-heptadiyne] poly (BTBH) containing rigid and bulky t-butyl benzoyl, which is expected to have good permeability and permselectivity due to high free volume and inhibited local motion, and superior mechanical properties (Scheme 1).

EXPERIMENTAL

Materials

Propargyl bromide (Aldrich Chem. Co., 80% solution in toluene) was dried over calcium hydride and fractional distilled. $MoCl_5$ and WCl_6 (Aldrich



Scheme 1.

Chem. Co.) were used as received. All solvents were used after purification according to conventional methods.

Preparation of 4,4-bis(t-butylbenzoxymethyl)-1,6-heptadiyne (BTBH)

Diethy dipropargylmalonate (33 g, 140 mmol) which was prepared by a literature method was dissolved in 80 mL of diethyl ether [5]. The solution was added dropwise over a period of 1 hour 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 hours. Water was added dropwise to the gray suspension until it turned white and the 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 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 ($CDCl_3$) 80.1 (≡C), 71.0 (≡CH), 66.3 (OCH_2), 42.0 (C_{quat}), 21.6 (CH_2C≡). Elem. Anal. Calcd. for $C_9C_{12}O_2$: C, 71.03; H, 7.95. Found: C, 71.01; H, 7.99. 4-t-Butylbenzoyl chloride (20 ml, 100 mmol) was put to the mixture of 7 g (46 mmol) of 4,4-bis(hydroxymethyl)-1,6-heptadiyne and 20 mL of triethylamine in THF solvent, After the mixture was refluxed for 24 hours, the reaction solution was cooled and poured into ice-water, and extracted with diethyl ether. After the organic layer was dried over anhydrous $MgSO_4$, and the crude BTBH was obtained by evaporation of ethyl ether. The resulting crude product was recrystallized in ethanol (mp: 92-93ºC 94%): ^{1}H-NMR ($CDCl_3$) δ 8.0–7.5 (d of d, 8H, aromatic H), 4.5 (s, 4H, O–CH_2), 2.6(s, 4H, C–CH_2), 2.1(t, 2H, ≡CH), 1.3 (s, 18H, -$C(CH_3)_3$): ^{13}C-NMR ($CDCl_3$) δ 178 (–C=O), 158, 130, 125, 123 (aromatic C), 78 (–C≡), 71.6 (C≡CH), 65 (OCH_2), 40 (C_{quat}), 38.9 (C_{quat}-

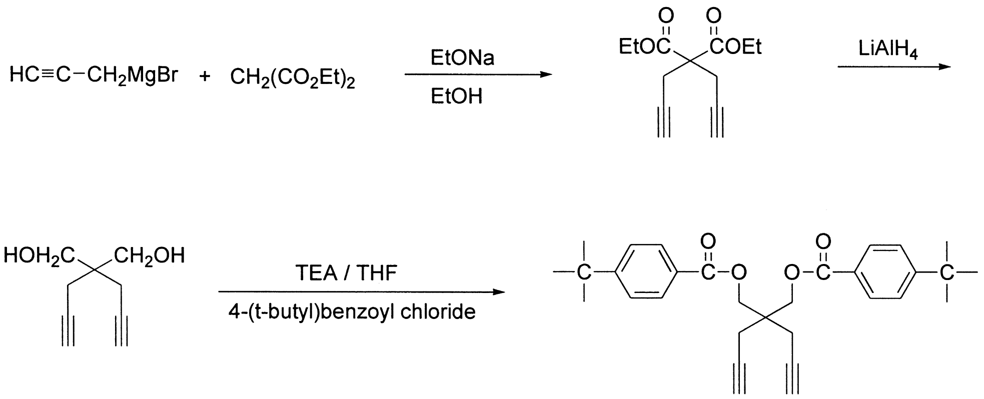
$(CH_3)_3$) 27.1 (CH_3), 22 (≡C-CH_2): IR (KBr, Cm^{-1}) 3294 (C≡C-H), 2120 (C≡C), 1718 (C=O); Anal. Calcd. for $C_{31}H_{36}O_4$: C, 78.99; H, 7.56. Found: C, 78.75: H, 7.43.

Instruments for Characterization

^1H 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 Fourier Transition 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 (Mn) 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, about 40 µm thick, were measured at 25°C with a conventional permeability apparatus, which consists upstream and down stream parts separated by a membrane. The effective area available for permeation is 5.72 cm^2. The upstream pressure was maintained constant at 5 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 flow meter 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 procedure for the preparation of catalyst systems and polymerization were carried out under dry nitrogen atmosphere. Transition-metal halides and organometallic compounds were dissolved in each solvent as 0.1M solutions before use. A typical polymerization procedure was as follows: solvent, catalyst solution, and, when needed, cocatalyst solution were injected into a 20 mL ampoule equipped with a rubber septum. When cocatalyst was used, the catalyst system was aged at 30°C for 15 minutes. Finally, monomer dissolved in each solvent was injected into the polymerization ampoule. After the mixture was allowed to react at 30°C for 24 hours, adding a small amount of methanol terminated the polymerization and chloroform was added to dissolve polymer. The



Scheme 2.

resulting solution was poured into a large amount of methanol. The polymer was filtered and dried under vacuum at 40°C for 24 hours. The polymer yield was determined by gravimetry.

RESULTS AND DISCUSSION

The results of the polymerization of BTBH by $MoCl_5$- and WCl_6-based catalysts are listed in Table 1. The organotin and organoaluminium complex have been found to be excellent cocatalysts for the polymerization of mono- and disubstituted acetylenes [13, 14]. $(Me)_4Sn$ and $EtAlCl_2$ were effective for the cyclopolymerization of BTBH by WCl_6. It was known that WCl_6-based catalysts were not effective for the polymerization of 1,6-heptadiyne derivatives containing polar functional group [6]. However, the BTBH containing ester functional group was effectively polymerized by $MoCl_5$-based catalysts as well as WCl_6-based catalysts. It can be understood that the bulky t-butylphenyl group inhibits the coordination of WCl_6-based catalyst to polar functional group in BTBH. The catalyst activities in polymerization were similar to that of poly[4,4-bis(pivaloxymethyl)-1,6-heptadiyne] with t-butyl group [20]. In order to investigate the effect of solvents on the polymerization of BTBH by $MoCl_5$, polymerization was carried out in various solvent. Aromatic hydrocarbons such as chlorobenzene, benzene and toluene were good polymerization solvents. It

TABLE 1. Polymerization of 4,4'-Bis(t-butylbenzoxymethyl)-1,6-heptadiyne by Transition Metal Catalysts[a]

Exp. No	Catalyst System (mole ratio)[b]	M/C[c]	$[M]_o$[d]	Polymer Yield (%)[e]
1	$MoCl_5$	100	0.0313	95
2	$MoCl_5$-$EtAlCl_2$(1:2)	100	0.0313	96
3	$MoCl_5$-$Sn(Me)_4$(1:2)	100	0.0313	95
4	WCl_6	50	0.125	48
5	WCl6-$EtAlCl_2$(1:2)	50	0.125	75
6	WCl6-$Sn(Me)_4$(1:2)	50	0.125	73

[a] Polymerization was carried out at 30°C for 12 hours in chlorobenzene.

[b] Mixture of catalyst and cocatalyst in chlorobenzene was aged at 30°C for 15 minutes before use as catalyst.

[c] Mole ratio of monomer to catalyst

[d] Initial monomer concentration

[e] The precipitation polymers in methanol were gravimetrically estimated.

TABLE 2. Solvent Effect in the Polymerization of 4,4'-bis(t-butylbenzoxymethyl)-1,6-heptadiyne by $MoCl_5$

Solvent[a]	Chlorobenzene	Toluene	Benzene	Dioxane	THF	Ethylacetate	DMSO	Pyridine
P. Y. (%)	95	93	92	90	89	91	0	0

[a] Polymerization was carried out by $MoCl_5$ at 30°C for 12 hours. Initial monomer concentration $[M_o]$ was 0.0313.

can be explained that aromatic solvents are good solvent for catalysts and polymer. Dioxane, THF and ethylacetate were also good solvents for this polymerizaion, however, the polymer was not obtained in pyridine and DMSO. This polymerization behavior is similar to that of other substituted acetylenes and 1,6-hepta-diyne derivatives by $MoCl_5$ [6, 13-15].

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(BTBH) 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(BTBH). The IR spectrum of the polymer showed neither the acetylenic hydrogen stretching nor the carbon-carbon triple bond stretching band. Instead, the new carbon-carbon double bond stretching band at 1600 cm^{-1}, which indicates a highly conjugated unsaturation, showed up. The ^{13}C-NMR spectra of BTBH and poly(BTBH) show the presence of olefinic carbons in the polymer backbone at 124 and 138 ppm (Figure 2). The UV-visible spectrum of the polymer obtained from chloroform solution exhibit two characteristic broad peaks (τmax =545, 585 nm) which are due to the $\pi \rightarrow \pi^*$ transition of conjugated backbone (Figure 3). In general, the polymerization of 1,6-heptadiyne derivatives gave the polymers with six- and/or five membered ring structure [21-23]. From the above spectroscopic results, we can suggest that poly(BTBH) has planar conjugated backbone and recurring five-membered ring structure than six-membered one as shown in Scheme 1, because newly formed vinylic protons appeared at 6.6 ppm in the ^{1}H-NMR and the peak of quaternary carbon showed up at 40 ppm as single sharp one in the ^{13}C-NMR spectrum.

The obtained polymer was completely soluble in various organic solvents such as chlorobenzene, toluene, benzene, chloroform, carbontetrachloride, tetrahydrofuran and diethyl ether, but insoluble in protic and nonpolar solvents such as methanol and n-hexane. GPC measurments upon poly(BTBH) prepared by $MoCl_5$ with polystyrene as calibration standard gave Mn = 152000 (Mw/Mn = 2.5). The TGA thermogram of poly(BTBH) under nitrogen atmosphere shows that the polymer is thermally stable up to 320ºC. A 5% weight loss of poly(BTBH) was observed at 350ºC and residual weight at 500ºC was 10%. Poly(BTBH) had relatively good thermal stability as compared with poly(1,6-heptadiyne derivatives).

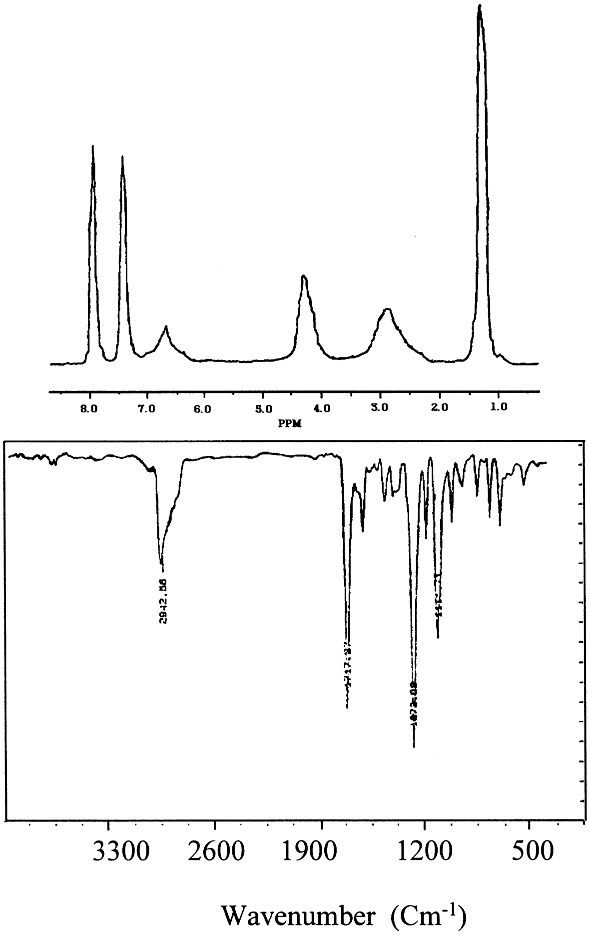


Figure 1. The ^{1}H-NMR ($CDCl_3$) and IR(KBr pellet) spectra of poly(BTBH).

The free standing film of poly(BTBH) was obtained by casting its toluene solution. The polymer film showed mechanical properties with a Young's modulus (E) of 1800 Mpa, a tensile strength (σB) of 65 Mpa, and ultimate elongation (γB) of 6.8% at a constant rate of stretching of 86%/min at 25°C. The good mechanical property of poly(BTBH) is probably due to the strong interpolymer attraction between the ester functional groups of different

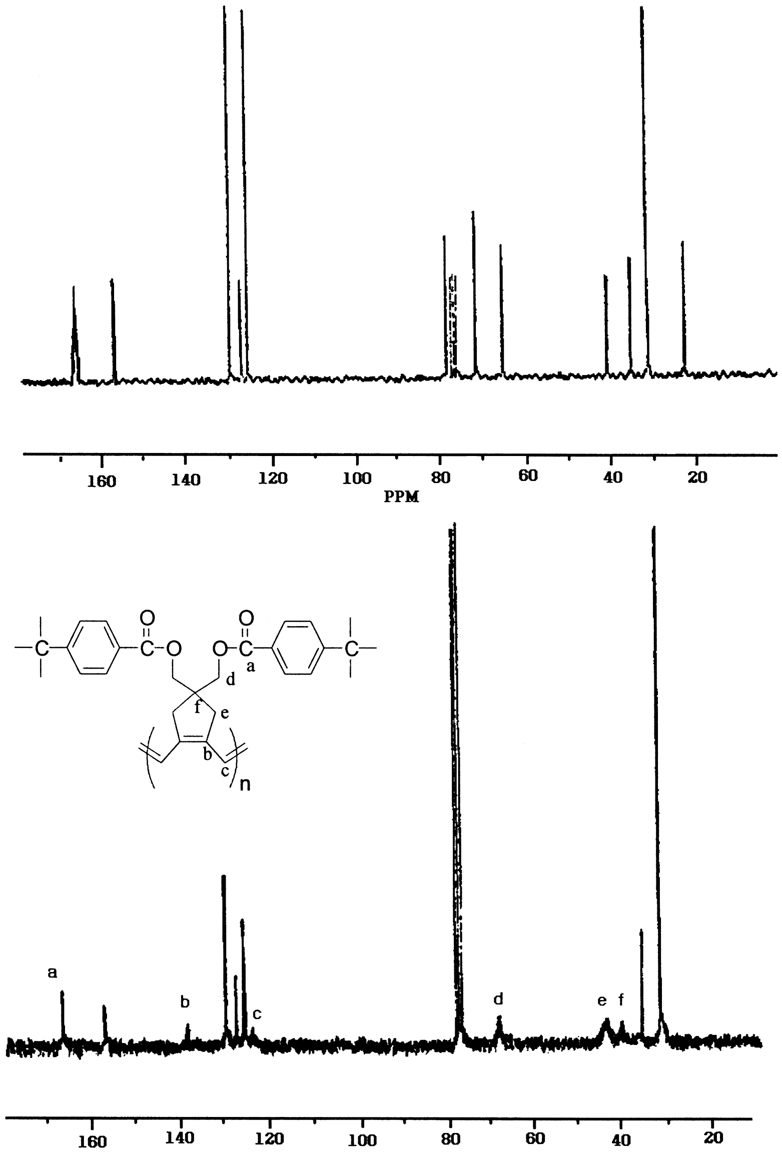


Figure 2. ^{13}C-NMR ($CDCl_3$) spectra of BTBH and poly(BTBH).

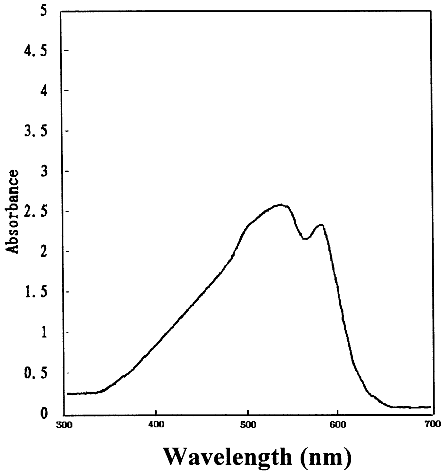


Figure 3. The UV-visible spectrum of poly(BTBH).

TABLE 3. Gas Permeation Behavior of Poly(1,6-heptadiyne Derivatives)

Polymer	P_{O_2}[a]	P_{N_2}	P_{O_2}/P_{N_2}[b]	Ref
Poly(DEDPM)[c]	3.30×10^{-10}	1.8×10^{-10}	1.8	5
Poly(TFEDPM)[d]	12.8×10^{-10}	8.2×10^{-10}	1.6	7
Poly(HFPDPM)[e]	71.4×10^{-10}	42×10^{-10}	1.7	7
Poly(DFHDPM)[f]	80×10^{-10}	28×10^{-10}	2.8	12
Poly(BTSH)[g]	320×10^{-10}	139×10^{-10}	2.3	15
Poly(BPOMH)[h]	19.7×10^{-10}	3.45×10^{-10}	5.71	20
Poly(BTBH)	23.2×10^{-10}	5.01×10^{-10}	4.63	this work

[a] In units of cm^3 (STP) $cm/cm^2 s cmHg$.

[b] Permselectivity

[c] Poly(DEDPM):poly(diethyl dipropargylmalonate).

[d] Poly(TFEDPM): poly[bis(2,2,2-trifluoroethyl)dipropargyl malonate].

[e] Poly(HFPDPM) : poly[bis(1,1,1,3,3,3-hexafluoro-2-propyl)dipropargyl malonate].

[f] Poly(DFHDPM): poly[bis(2,2,3,3,4,4,5,5,6,6,7,7-dodecafluoroheptyl) dipropargylmalonate].

[g] Poly(BTSH): poly[4,4-bis(t-butydimethylsiloxy)methyl-1,6-heptadiyne].

[h] Poly(BPOMH): poly[4,4-bis(pivaloxymethyl)-1,6-heptadiyne].

polymer chains. Table 3 shows the oxygen permeability coefficient (P_{O_2}) and separation coefficient factors of oxygen to nitrogen (P_{O_2}/P_{N_2}) of poly(1,6-heptadiyne derivatives). Poly(BTBH) with bulky and rigid t-butyl benzoyl group has relatively high permselectivity as compared with other poly(1,6-heptadiyne derivatives), though it showed slightly higher permeability and lower permselectivity than that of poly[4,4-bis(pivaloxymethyl)-1,6-heptadiyne] with t-butyl group.

CONCLUSION

We synthesized poly[4,4-bis(t-butylbenzoxymethyl)-1,6-heptadiyne] containing a bulky and rigid t-butylbenzoyl group by transition metal catalysts. The obtained polymer was completely soluble in common organic solvents. The polymer showed good mechanical and thermal stability. The polymer had good oxygen permeability and permselectivity.

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