Synthesis and Properties of Si-Containing Poly(diarylacetylene)s and Their Desilylated Polymer Membranes

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ABSTRACT: The polymerization of 1-[(*p*-trimethylsilyl)phenyl]-2-(2-fluorenyl)acetylene (**1c**) with TaCl₅– *n*-Bu₄Sn produced a high molecular weight polymer (**2c**), whose M_w reached 3.4 × 10⁶. 1-[(*p*-Trimethylsilyl)phenyl]-2-(2-phenanthryl)acetylene (**1d**) and 1-[(*p*-trimethylsilyl)phenyl]-2-(4-biphenyl)acetylene (**1e**) were also polymerized to give high molecular weight polymers (**2d** and **2e**) in good yields. In contrast, the polymerization of 1-[(*p*-trimethylsilyl)phenyl]-2-(2-anthryl)acetylene (**1f**) provided no polymer probably owing to the steric reason. The formed polymers **2c** and **2d** were soluble in common solvents such as toluene and chloroform and afforded free-standing membranes by casting from toluene solution. The onset temperatures of weight loss of polymers **2c** and **2d** in air were about 430 °C, indicating very high thermal stability. The membranes of **2c** and **2d** obtained by the casting method showed high gas permeability; e.g., their oxygen permeability coefficients (P_{O_2}) were 1650 and 460 barrers, respectively. The membranes of **2c** and **2d** were desilylated with trifluoroacetic acid to provide the membranes of poly[1-phenyl-2-(2-fluorenyl)acetylene] (**3c**) and poly[1-phenyl-2-(2-phenanthryl)acetylene] (**3d**). The desilylated poly(diarylacetylene)s exhibited even higher P_{O_2} values of 2150 and 1300 barrers, respectively. These desilylated polymers were insoluble in any solvents and showed higher thermal stability than those of **2c** and **2d**.

Introduction

Polymeric materials are one of the best candidates for separation membranes because their structure can be designed in multifarious ways to achieve high permeability and permselectivity.¹ Polyacetylenes with bulky substituents provide free-standing membranes, which generally exhibit high gas permeability. This is because they have many microvoids in the polymer matrix due to both their stiff main chain composed of alternating double bonds and the steric repulsion of bulky pendant groups.² For instance, poly(1-trimethylsilyl-1-propyne) [poly(TMSP)] exhibits the highest gas permeability among all the synthetic polymers.³ Further, the membrane of poly(1-[p-(trimethylsilyl)phenyl]-2-phenylacetylene) (Scheme 1, **2a**) also shows high gas permeability and thermal stability simultaneously, whose oxygen permeability coefficient (P_{O_2}) reaches 1100 barrers at 25 °C and its onset temperature of weight loss in air (T_0) is as high as 420 °C.⁴ The membrane of poly[1- β -naphthyl-2-(p-trimethylsilyl)phenylacetylene] (2b) is also highly permeable to gases and thermally stable (P_{O_2} 3500 barrers, T_0 450 °C).⁵

Interestingly, desilylation of the membranes of these Si-containing poly(diarylacetylene)s leads to higher gas permeability and thermal stability. Thus, the P_{O_2} values of poly(diphenylacetylene) (**3a**)⁶ and poly(1- β -naphthyl-2-phenylacetylene) (**3b**)⁵ obtained by desilylation reach up to 6000 and 4300 barrers, respectively, and their T_0 values are as high as 500 and 470 °C, respectively. High gas permeability of these polymers is explained on the grounds that the desilylation reaction generates some microvoids in polymer matrices owing to the elimination of silyl groups in the solid state. Noteworthy is that these desilylated polymer membranes are insoluble in

any solvents, and hence they cannot be obtained directly by solution casting. Their insolubility is advantageous for the separation of organic mixtures, and consequently it can be said that the desilylation reaction is an interesting method for the preparation of polymer membranes.

Here we report the polymerization of various Sicontaining aromatic disubstituted acetylenes (Scheme 1, 1c-f). Free-standing membranes were fabricated from resultant polymers, and desilylation of the membranes was accomplished with trifluoroacetic acid. Gas permeability and other properties of these novel polymer membranes were examined.

Experimental Section

General. The molecular weights of polymers were estimated by gel permeation chromatography (CHCl₃ as eluent, polystyrene calibration). IR spectra were recorded on a Shimadzu FTIR-8100 spectrophotometer. NMR spectra were observed on a JEOL EX-400 spectrometer. Thermogravimetric analyses (TGA) were conducted in air with a Perkin-Elmer TGA7 thermal analyzer. Gas permeability coefficients were measured with a Rikaseiki K-315-N gas permeability apparatus at 25 °C.

Materials. TaCl₅ as catalyst component was commercially obtained from Strem Chemicals and used without further purification. *n*-Bu₄Sn as cocatalyst was purchased from Wako Chemical and used after distillation. Trimethylsilylacetylene was donated by Shin-Etsu Chemical. Other chemicals were purchased from Tokyo Chemical Industry. Polymerization solvents were purified by the standard methods. 4-Trimethylsilyl-1-ethynylbenzene was prepared from trimethylsilylacetylene and 4-trimethylsilyl-1-bromobenzene, and the latter was prepared from *p*-dibromobenzene and chlorotrimethylsilane according to the literature methods. ⁷ 2-Ethynylphenan-threne was prepared via the same routes as in the literature.⁸ 2-Iodoanthracene was prepared according to the literature.⁹ Monomers 1c-f were synthesized as shown in Scheme 2, the details of which are stated below.

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Scheme 1. Synthesis of Si-Containing Poly(diarylacetylene)s and Preparation of Poly(diarylacetylene) Membranes



PdCl₂(Ph₃P)₂/Ph₃P/CuI

1-[(p-Trimethylsilyl)phenyl]-2-(2-fluorenyl)acetylene (1c). A 500 mL three-necked flask was equipped with a reflux condenser, a three-way stopcock, and a magnetic stirring bar and was flushed with dry nitrogen. 2-Bromofluorene (5.0 g, 20 mmol), bis(triphenylphosphine)palladium dichloride (56 mg, 0.080 mmol), cuprous iodide (93 mg, 0.48 mmol), triphenylphosphine (85 mg, 0.32 mmol), and triethylamine (150 mL) were placed in the flask. Then, 4-trimethylsilyl-1-ethynylbenzene (4.4 g, 25 mmol) in triethylamine (50 mL) solution was added. The reaction mixture was heated at reflux temperature for 5 h. After the triethylamine in the reaction mixture was evaporated, diethyl ether (ca. 300 mL) was added, and the insoluble salt was filtered off. The filtrate was washed at first with 1 N hydrochloric acid and then with water. The ethereal solution was dried over anhydrous sodium sulfate and then concentrated at reduced pressure. Purification of the crude product by flash column chromatography (eluent: hexane) provided the desired product (4.9 g, 71%) as a white solid; mp 158.0–159.0 °C, purity >99% (¹H NMR). IR (KBr): 2957, 1595, 1454, 1248, 1198, 1102, 851, 814, 756 cm⁻¹. ¹H NMR (CDCl₃, δ): 7.79-7.71 (m, 2H, Ar), 7.58-7.46 (m, 7H, Ar), 7.38-7.30 (m, 2H, Ar), 3.88 (s, 2H), 0.30 ppm (s, 9H). ¹³C NMR (CDCl₃, δ): 143.5, 143.1, 141.8, 141.0, 140.8, 133.2, 130.6, 130.5, 128.2, 127.1, 126.9, 125.0, 123.7, 121.2, 120.2, 119.8, 90.5, 89.5, 36.7, -1.2 ppm. Anal. Calcd for C₂₄H₂₂Si: C, 85.2%; H, 6.6%; Si, 8.2%. Found: C, 85.0%; H, 6.7%; Si, 8.3%.

1-[(*p*-**Trimethylsilyl)phenyl]-2-(2-phenanthryl)acetylene (1d).** This monomer was prepared by the same method as for **1c** by using 4-trimethylsilyl-1-bromobenzene and 2-ethynylphenanthrene instead of 2-bromofluorene and 4-trimethylsilyl-1-ethynylbenzene as starting materials. Yield 65%, mp >230 °C, purity 99% (¹H NMR). IR (KBr): 2957, 1595, 1462, 1250, 1105, 857, 845, 818, 758 cm⁻¹. ¹H NMR (CDCl₃, δ): 8.67 (dd, 2H, Ar), 8.10 (s, 1H, Ar), 7.88 (d, 1H, Ar), 7.51–7.78 (m, 9H, Ar), 0.30 ppm (s, 9H). ¹³C NMR (CDCl₃, δ): 1411, 133.3, 132.2, 131.8, 131.7, 130.7, 129.9, 129.8, 129.3, 128.6, 127.6, 127.5, 127.0, 126.8, 126.5, 123.5, 122.8, 121.3, 90.3, 89.9, -1.2 ppm. Anal. Calcd for C₂₅H₂₂Si: C, 85.7%; H, 6.3%; Si, 8.0%. Found: C, 85.4%; H, 6.2%; Si, 8.4%. **1-**[(*p*-**Trimethlsily**])**pheny**]-**2**-(**4**-**bipheny**])**acetylene** (**1e**). This monomer was prepared from 4-iodobiphenyl in the same way as for **1c**. Yield 75%, mp 123.0–125.0 °C, purity >99% (¹H NMR). IR (KBr): 2955, 1595, 1483, 1252, 1101, 858, 839, 764 cm⁻¹. ¹H NMR (CDCl₃, δ): 7.63–7.57 (m, 6H, Ar), 7.52 (s, 4H, Ar), 7.45 (t, 2H, Ar), 7.36 (t, 1H, Ar), 0.30 ppm (s, 9H). ¹³C NMR (CDCl₃, δ): 141.0, 140.9, 140.3, 133.2, 132.0, 131.9, 130.6, 128.8, 127.6, 127.0, 123.5, 122.1, 90.2, 89.7, –1.3 ppm. Anal. Calcd for C₂₃H₂₂Si: C, 84.6%; H, 6.8%; Si, 8.6%. Found: C, 84.5%; H, 6.8%; Si, 8.7%.

1d

1-[(*p***-Trimethylsilyl)phenyl]-2-(2-anthryl)acetylene (1f).** This monomer was prepared similarly to **1c** from 2-iodoanthracene. Yield 60%, mp 212.0–214.0 °C, purity >99% (¹H NMR). IR (KBr): 2957, 1595, 1458, 1250, 1098, 855, 839, 820, 756 cm⁻¹. ¹H NMR (CDCl₃, δ): 8.40 (s, 2H, Ar), 8.22 (s, 1H, Ar), 8.01–7.95 (m, 3H, Ar), 7.58–7.46 (m, 7H), 0.31 ppm (s, 9H). ¹³C NMR (CDCl₃, δ): 141.2, 133.3, 132.2, 132.1, 131.9, 131.1, 130.7, 128.3, 128.2, 127.7, 126.3, 126.2, 125.8, 125.7, 124.2, 123.5, 120.0, 113.3, 90.5, 89.8, –1.2 ppm. Anal. Calcd for C₂₅H₂₂Si: C, 85.7%; H, 6.3%; Si, 8.0%. Found: C, 85.5%; H, 6.4%; Si, 8.1%.

Polymerization. Polymerizations were performed in a Schlenk tube equipped with a three-way stopcock under dry nitrogen. Unless otherwise specified, the polymerizations were carried out at 80 °C for 24 h under the following conditions: $[M]_0 = 0.10$ M, $[TaCl_5] = 20$ mM, [n-Bu₄Sn] = 40 mM. A detailed procedure of polymerization is as follows: A monomer solution was prepared in a Schlenk tube by mixing monomer **1c** (0.34 g) and toluene (5.0 mL). Another Schlenk tube was charged with TaCl₅ (71 mg), *n*-Bu₄Sn (0.13 mL), and toluene (4.9 mL); this catalyst solution was aged at 80 °C for 10 min. Then the monomer solution was added to the catalyst solution. Polymerization was isolated by precipitation into a large excess of methanol, and its yield was determined by gravimetry.

Membrane Fabrication and Desilylation. Membranes (thickness ca. $30-50 \ \mu$ m) of **2c** and **2d** were fabricated by casting toluene solution of the polymers (concentration ca. 1.0-

Table 1. Polymerization of 1c-f by TaCl₅-n-Bu₄Sn^a

			polymer ^b				
run	monomer	solvent	yield (%)	$M_{ m w} imes 10^{-4}$ c	$M_{ m n} imes 10^{-4}$ c		
1	1c	cyclohexane	80	340	140		
2	1c	toluene	63	230	60		
3	1d	cyclohexane	69	70	30		
4	1d	toluene	35	30	10		
5	1e	toluene	70	$>600^{d}$	$>200^{d}$		
6 ^e	1e	toluene	64	130^{d}	30^d		
7	1f	cyclohexane	<1				
8	1f	toluene	<1				

^{*a*} At 80 °C for 24 h; $[M]_0 = 0.10$ M, $[TaCl_5] = 20$ mM, $[n-Bu_4Sn] = 40$ mM. ^{*b*} Methanol-insoluble product. ^{*c*} Measured by GPC. ^{*d*} CHCl₃-soluble part. ^{*e*} $[M]_0 = 0.050$ M.

1.5 wt %) onto a glass plate. The plate was covered with a glass vessel to slow solvent evaporation (ca. 4-6 days). Applying the same method as in the literature,⁶ the desilylation reaction of the membranes of 2c and 2d was carried out as follows: A polymer membrane was immersed in a mixture of hexane/trifluoroacetic acid (volume ratio 1:1) at room temperature for 24 h; the orange-colored membrane gradually turned dark green. To remove the remaining acid in the polymer matrix, the membrane was immersed in a mixture of hexane/triethylamine (volume ratio 1:1) at room temperature for 24 h. The color of membrane changed from dark green to red. Finally, the membrane was immersed in methanol for 24 h to remove residual impurities, washed with methanol, and dried to constant weight at room temperature for 24 h. The completion of desilylation was confirmed by the IR spectra of the polymer membranes before and after reaction; the IR spectra of the membranes of 3c and 3d exhibited no absorptions at ca. 1250, 1120, and 860 cm⁻¹, which were seen in **2c** and 2d. Upon desilylation, the weights of the membranes decreased to the values anticipated for desilylation, which also confirm the completion of the reaction (e.g., 2c: 59 mg; 3c: found, 46 mg, calcd, 46 mg).

Results and Discussion

Polymerization. The polymerization of novel monomers **1c**–**f** was investigated by using TaCl₅–*n*-Bu₄Sn as catalyst, the results of which are summarized in Table 1. The polymerization of the fluorenyl group containing monomer (**1c**) in cyclohexane at 80 °C gave a high molecular weight polymer (**2c**) in good yield (M_w) 3.4×10^6 , yield 80%) (run 1). Both M_w and yield of polymer decreased in toluene to some extent (run 2). The polymerization of the monomer having a phenanthryl group (1d) in cyclohexane also yielded polymer with relatively high molecular weight ($M_{\rm w}$ 7.0 \times 10⁵, yield 69%) (run 3). These results resemble those for other diarylacetylenes reported before (e.g., the $M_{\rm W}$ of **2b** formed in cyclohexane is 3.4×10^6 , whereas the one in toluene is 6.0×10^5).⁵ On the other hand, the polymerization of the biphenyl group containing monomer 1e produced a rather high molecular weight polymer even in toluene (run 5); however, the formed polymer did not completely dissolve in toluene, chloroform, and so forth. When the [M]₀ was reduced to 0.050 M, the $M_{\rm w}$ of polymer decreased, while the polymer yield hardly changed (run 6). The anthryl group containing monomer **1f**, in contrast, did not polymerize under the same conditions (runs 7 and 8). Owing to its planar and rigid structure, the anthryl group occupies more space than other aryl groups, and hence the propagating species from 1f suffers larger steric hindrance in the reaction with the monomer, which should lead to low polymerizability of the monomer. Similarly, 1-phenyl- $2-\alpha$ -naphthylacetylene produces no polymer, while 1-phenyl-2- β -naphthylacetylene gives a high molecular



Figure 1. TGA curves of Si-containing polymers 2c-e (in air, heating rate 10 °C min⁻¹).

weight polymer.¹⁰ Further, diphenylacetylenes with a substituent at para position polymerize, but the orthosubstituted counterparts do not.¹⁰ These observations suggest that the steric effects in monomers contribute significantly to polymerization activity.

Solubility and Thermal Stability. The solubility and thermal stability of 2c-e were examined by using the polymer samples obtained in runs 1, 3, and 6 in Table 1. The preparation of membranes of 2c-e was attempted by using the same samples. Then, desilylation of these polymer membranes was carried out, and their properties were examined.

Si-containing polymers **2c** and **2d** were totally soluble in common organic solvents such as toluene, chloroform, tetrahydrofuran (THF), benzene, chlorobenzene, cyclohexane, carbon tetrachloride, anisole, and so forth. Freestanding membranes could be obtained by casting their toluene solution. 2c and 2d were partly soluble in hexane and diethyl ether. Polymer 2e hardly dissolved in any solvents including toluene, chloroform, and THF. Thus, free-standing membrane suitable for the permeability measurement could not be prepared from polymer 2e. Desilylated polymer 3e could be obtained by using the powdered 2e. None of 2c-e dissolved in polar solvents such as N,N-dimethylformamide (DMF), dimethyl sulfoxide (DMSO), and lower alcohols. On the other hand, the desilylated polymers 3c and 3e were insoluble in any solvents. Polymer 3d slightly dissolved in toluene, chloroform, and THF. The same tendency was observed for other polymers 2a and 2b; i.e., Sicontaining polymers 2a and 2b were soluble in common organic solvent while desilylated polymers 3a and 3b were insoluble in any solvent.^{5,6}

The thermal stability of polymers $2\mathbf{c}-\mathbf{e}$ and $3\mathbf{c}-\mathbf{e}$ was examined by the thermogravimetric analysis (TGA) in air. The onset temperatures of weight loss (T_0) of $2\mathbf{c}-\mathbf{e}$ were approximately 430 °C, indicating considerably high thermal stability (Figure 1). These values are similar to those of polymers $2\mathbf{a}$ (420 °C) and $2\mathbf{b}$ (450 °C)^{5,6} and much higher than those of polymers from Si-containing aliphatic disubstituted acetylenes such as poly(TMSP) (330 °C),¹¹ indicating that the incorporation of aryl groups greatly improves the thermal stability. The weight loss of $3\mathbf{c}-\mathbf{e}$ in TGA occurred above 450 °C (Figure 2); the temperatures are somewhat higher than those for the corresponding Si-containing polymers. This suggests that the desilylation more or less enhances thermal stability of the present polymers.

Gas Permeability. As described above, free-standing membranes could be fabricated by casting toluene solution of polymers **2c** and **2d**, but a membrane of **2e**



Figure 2. TGA curves of desilylated polymers 3c-e (in air, heating rate 10 °C min⁻¹).



Figure 3. Oxygen permeability coefficient (P_{O_2}) and P_{O_2}/P_{N_2} of present polymers (25 °C).

could not be prepared because of its poor solubility. The permeability to various gases of membranes of Sicontaining polymers (2c and 2d) and desilylated polymers (3c and 3d) was evaluated. The oxygen permeability coefficient (P_{O_2}) of **2c** at 25 °C was 1650 barrers, which is slightly higher than that of polymer **2a** (1100 barrers)¹² and very large among all the synthetic polymers, although smaller than that of poly(TMSP) $(P_{O_2}, 6000-10\ 000\ \text{barrers})^{2a,3}$ (Figure 3). The P_{O_2} value of 3c obtained by the desilylation of 2c was 2150 barrers at 25 °C, which is even higher than that of 2c. Polymer **2d** also showed fairly high oxygen permeability (P_{O_2} 460 barrers). This value is close to that of poly(dimethylsiloxane),¹³ which exhibits the highest permeability among all the rubbery polymers. The P_{O_2} value of desilylated polymer **3d** was 1300 barrers and larger than that of **2d**. The reason for the high permeability of these poly(diarylacetylene) membranes seems to be that the aromatic rings cannot stack to one another owing to steric crowding, which results in the formation of large free volume. The separation factors of oxygen and nitrogen (P_{O_2}/P_{N_2}) of polymers **2c** and **3c** were 1.74 and 1.65, respectively, which are not large. The $P_{\rm O_2}/P_{\rm N_2}$ values of polymers 2d and 3d were 2.42 and 2.00, respectively, and larger than those of 2c and 3c. These findings agree with the general tendency that highly gas-permeable polymers usually exhibit low gas separation ability.

Similar tendencies were observed for other gases; i.e., the desilylated polymer membranes were more permeable to gases than the Si-containing counterparts (Table 2). In general, the membranes of polyacetylenes with trimethylsilyl group exhibit high gas permeability because of their large free volumes¹⁴ and the large local mobility¹⁵ of trimethylsilyl groups. The large free vol-

 Table 2. Gas Permeability Coefficients (P) of 2c, 3c, 2d, and 3d

polymer	He	H_2	O ₂	N_2	CO_2	CH ₄	$P_{\mathrm{O}_2}/P_{\mathrm{N}_2}$
2c	1300	3100	1650	950	6450	2000	1.74
3c	1600	3650	2150	1300	8500	2400	1.65
2d	450	900	460	190	2100	500	2.42
3d	1150	2500	1300	650	5300	1450	2.00

 a At 25 °C in the units of 1 \times 10 $^{-10}$ cm 3 (STP) cm/(cm $^2)$ (s) (cmHg) (= 1 barrer).



Figure 4. Effect of aging time on the oxygen permeability of **2c**, **3c**, **2d**, and **3d** (stored at 25 °C in air). The data of the right-hand end are for the membranes after methanol conditioning.

ume seems to be due to both stiff main chain and spherical side groups. It is noteworthy that desilylated polymers $3\mathbf{a} - \mathbf{d}$ exhibit gas permeability comparable to or higher than that of the corresponding Si-containing polymers despite the absence of spherical substituents. This finding can be accounted for by the generation of microvoids due to the elimination of trimethylsilyl groups in the solid state.

The variation of P_{O_2} values of **2c**, **3c**, **2d**, and **3d** with aging time was examined by storing the membranes at 25 °C in air (Figure 4). The P_{O_2} values of these polymers gradually decreased with time to a half of the initial values after 60 days. For instance, the P_{O_2} of membrane 3c changed from 2150 to 850 barrers after 60 days. The P_{O_2} values appear to level off after 60 days. Other disubstituted acetylene polymers such as poly(TMSP) and polymer 2a also exhibit a similar tendency.^{5,16} For instance, the P_{O_2} value of poly(TMSP) drastically changes from 5000 to 100 barrers.^{16a} Thus, it can be said that these poly(diarylacetylene) membranes maintain a relatively high gas permeability after storage for a long period of time. The lowered P_{O_2} values of these polymer membranes were restored to the initial ones by methanol conditioning; e.g., when membrane 3c, whose P_{O_2} value after 90 days was 750 barrers, was immersed in methanol for 24 h and then dried to constant weight at room temperature for 24 h, the P_{O_2} value of the membrane increased up to 2000 barrers.

Conclusions

New Si-containing poly(diarylacetylene)s $2\mathbf{c}-\mathbf{e}$ were synthesized, among which polymers $2\mathbf{c}$ and $2\mathbf{d}$ afforded free-standing membranes by casting their toluene solution. Desilylation of these membranes was achieved with trifluoroacetic acid to give membranes of $3\mathbf{c}$ and $3\mathbf{d}$, which were virtually insoluble in any solvents. Polymer $2\mathbf{c}$ showed gas permeability higher than that of poly(dimethylsiloxane). The gas permeability of desilylated polymer $3\mathbf{c}$ was even higher. Polymer $2\mathbf{d}$ was also fairly permeable to gases, and polymer $3\mathbf{d}$ was more

permeable than 2d. These polymer membranes are expected to be candidates of gas separation membrane because of their high gas permeability and high thermal stability. Furthermore, these desilylated polymers may be applied to the separation membrane of organic mixtures due to their insolubility.

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References and Notes

- (1) (a) Baker, R. W. Ind. Eng. Chem. Res. 2002, 41, 1393-1411. (b) Freeman, B. D.; Pinnau, I. Polymer Membranes for Gas and Vapor Separation; ACS Symposium Series 733; American Chemical Society: Washington, DC, 1999. (c) Kesting, R. E.; Fritzsche, A. K. Polymeric Gas Separation Membranes; Wiley: New York, 1993.
- (2)For reviews of substituted polyacetylenes, see: (a) Nagai, K.; Masuda, T.; Nakagawa, T.; Freeman, B. D.; Pinnau, I. *Prog. Polym. Sci.* **2001**, *26*, 721–798. (b) Choi, S. K.; Gal, Y. S.; Jin, S. H.; Kim, H. K. Chem. Rev. 2000, 100, 1645-1682. (c) Tabata, M.; Sone, T.; Sadahiro, Y. Macromol. Chem. Phys. 1999, 200, 265–282. (d) Shirakawa, H.; Masuda, T.; Takeda, K. In *The Chemistry of Triple-Bonded Functional Groups* (Supplement C2); Patai, S., Ed.; Wiley: Chichester 1994; pp 945-1016. (e) Costa, G. In Comprehensive Polymer Science, Eastmond, G. C., Ledwith, A., Russo, S., Sigmalt, P., Eds.; Pergamon Press: Oxford, 1989; pp 155-161.
- Masuda, T.; Isobe, E.; Higashimura, T.; Takada, K. J. Am. Chem. Soc. **1983**, 105, 7473–7474.
- (4) Tsuchihara, K.; Masuda, T.; Higashimura, T. Macromolecules 1992, 25, 5816-5820.

- (5) Sakaguchi, T.; Kwak, G.; Masuda, T. Polymer 2002, 43, 3937 - 3942
- Teraguchi, M.; Masuda, T. Macromolecules 2002, 35, 1149-(6)1151.
- (7)Aoki, T.; Nakahara, H.; Hayakawa, Y.; Kokai, M.; Oikawa,
- (i) Hold, H., Hullandi, H., Holyandidi, H., Holdin, H., Ohldin, H., Ohldin, H., Ohldin, E. J. Polym. Sci., Part A: Polym. Chem. 1994, 32, 849–858.
 (8) Musikabhumma, K.; Masuda, T. J. Polym. Sci., Part A: Polym. Chem. 1998, 36, 3131-3137.
- (9) (a) Nanjo, K.; Karim, S. M. A.; Nomura, R.; Wada, T.; Sasabe, H.; Masuda, T. J. Polym. Sci., Part A: Polym. Chem. **1999**, 37, 277–282. (b) House, H. O.; Koepsell, D.; Jaeger, W. J. Org. Chem. **1973**, 38, 1167–1173. (c) Sabourin, E. T.; Onopehenko, A. J. Org. Chem. 1983, 48, 5135-5137. (d) Haveus, S. J.; Hergenrother, P. M. J. Org. Chem. 1985, 50, 1763-1765
- (10) Kouzai, H.; Masuda, T., unpublished data.
- (11) Masuda, T.; Isobe, E.; Higashimura, T. Macromolecules 1985, 18, 841-845.
- (12) Tsuchihara, K.; Masuda, T.; Higashimura, T. J. Am. Chem. Soc. 1991, 113, 8548-8549.
- (13) Pauly, S. In Polymer Handbook, 3rd ed.; Brandrup, J., Emmergut, E., Eds.; John Wiley and Sons: New York, 1989; p VI 435.
- (14) (a) Merkel, T. C.; Bondar, V.; Nagai, K.; Freeman, B. D. J. Polym. Sci., Part B: Polym. Phys. 2000, 38, 273–296. (b) Toy, L. G.; Nagai, K.; Freeman, B. D.; Pinnau, I.; He, Z.; Masuda, T.; Teraguchi, M.; Yamprolskii, Y. P. Macromolecules 2000, 33, 2516-2524.
- (15) (a) Kanaya, T.; Teraguchi, M.; Masuda, T.; Kaji, K. *Polymer* **1999**, 40, 7157–7161. (b) Kanaya, T.; Tsukushi, I.; Kaji, K.; Sakaguchi, T.; Kwak, G.; Masuda, T. Macromolecules 2002, 35, 5559-5564.
- (16) (a) Shimomura, H.; Nakanishi, K.; Odani, H.; Kurata, M.; Masuda, T.; Higashimura, T. Koubunshi Ronbunshu 1986, 43, 747. (b) Nagai, K.; Higuchi, A.; Nakagawa, T. J. Polym. Sci., Part B: Polym. Phys. 1995, 33, 289-298. (c) Kwak, G.; Masuda, T. J. Polym. Šci., Part A: Polym. Chem. 2000, 38, 2964-2969.

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