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SYNTHESIS AND PROPERTIES OF COPOLYMERS FROM 1-[3,5-BIS(TRIMETHYLSILYL)PHENYL]-2-PHENYLACETYLENE

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SYNTHESIS AND PROPERTIES OF COPOLYMERS FROM 1-[3,5-BIS(TRIMETHYLSILYL)PHENYL]-2-PHENYLACETYLENE

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Key Words: Substituted Polyacetylene, Trimethylsilyl Group, Metathesis Polymerization, Transition Metal Catalyst, Gas Permeability

ABSTRACT

Copolymerization of 1-[3,5-bis(trimethylsilyl)phenyl]-2-phenylacetylene (*m,m*-$(Me_3Si)_2$DPA) with other diphenylacetylene derivatives and their copolymer properties were investigated. Homopolymerization of *m,m*-$(Me_3Si)_2$DPA by $TaCl_5$–*n*-Bu_4Sn (1:2) did not give the polymer due to steric hindrance. However, *m,m*-(Me_3Si)2DPA copolymerized with diphenylacetylene (DPA), 1-phenyl-2-[*p*-(trimethylsilyl)phenyl]acetylene (*p*-Me_3Si DPA), and 1-phenyl-2-[*m*-(trimethylsilyl)phenyl]acety-lene (m-Me_3SiDPA) in the presence of $TaCl_5$–*n*-Bu_4Sn at various feed ratios to give copolymers in moderate yields. The formed co-

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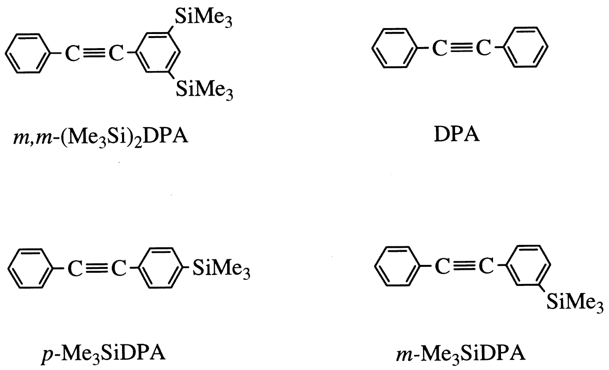
polymers were yellow to orange solids, which were soluble in common organic solvents such as toluene and $CHCl_3$. The highest weight-average molecular weights (M_w) of these copolymers reached ca. 6 × 105 and tough films could be obtained by solution casting. Their onset temperatures of weight loss in air were observed around 400°C, indicating high thermal stability. The oxygen permeability coefficients at 25°C of copoly(*m,m*-$(Me_3Si)_2$ DPA/DPA) (feed ratio 1:1) and copoly(*m,m*-$(Me_3Si)_2$DPA/p-Me_3SiDPA) (feed ratio 1:2) were 21 and 100 barrers, respectively, medium in magnitude among polymers from substituted acetylenes.

INTRODUCTION

Whereas, silicon is a group 14 element like carbon and shows properties close to those of carbon, it has vacant *d*-orbitals and hence, is more electropositive and reactive than carbon [1]. The organosilicon polymers synthesized so far [2] can be roughly classified into two categories, i.e., polymers with Si atoms in the main chain [3-5] (e.g., polysilanes, polycarbosilanes, polycarbosiloxanes, polysiloxanes, etc.) and those with Si atoms in the side chain [6]. These polymers often show interesting features such as heat resistance for flame retardant polymer, optoelectronic properties, and photoresist properties [2, 3a, 7, 8].

It is known that Si-containing polyacetylenes often exhibit unique properties, especially high gas permeabilities [9]. For example, poly[1-(tri-methylsilyl)-1-propyne] [poly(TMSP)] [10] and poly[1-phenyl-2-[4-(tri-methylsilyl) phenyl]acetylene] [poly(*p*-Me_3SiDPA)] [11] show extremely high oxygen permeability coefficients (P_{O2}) up to 4000 and 1100 barrers, respectively; the former polymer is the most permeable to gases among all the synthetic polymers. In general, it can be said that the introduction of trimethylsilyl groups enhances the gas permeability of substituted poly-acetylenes. Furthermore, poly(*p*-Me_3SiDPA) is thermally very stable, as is seen from its onset temperature for weight loss in air (T_0) as high as 430°C. These sterically crowded disubstituted acetylene polymers can be obtained by the polymerization of the corresponding acetylene monomers catalyzed by $TaCl_5$-based catalysts. The formed polymers have extremely high molecular weights (over 1× 10^6) and good film-forming ability.

It is interesting to study the polymerization behavior and polymer properties of diphenylacetylenes having more than one trimethylsilyl groups. In the present study, we used a diphenylacetylene having two trimethylsilyl groups



Scheme 1. Monomers used in the present study.

at meta position, 1-[3,5-bis(trimethylsilyl)phenyl]-2-phenylacetylene (*m*,*m*-($Me_3Si)_2$DPA) as monomer, and examined its homopolymerization and copolymerization with other diphenylacetylenes such as diphenylacetylene (DPA), *p*-Me_3SiDPA, and 1-phenyl-[2-(3-trimethylsilyl)phenyl]acetylene (*m*-Me_3SiDPA) by using $TaCl_5$–*n*-Bu_4Sn catalyst (Scheme 1). The homopolymer was not obtained but copolymers were available. Properties of the formed copolymers such as solubility, thermal stability, and gas permeability were clarified.

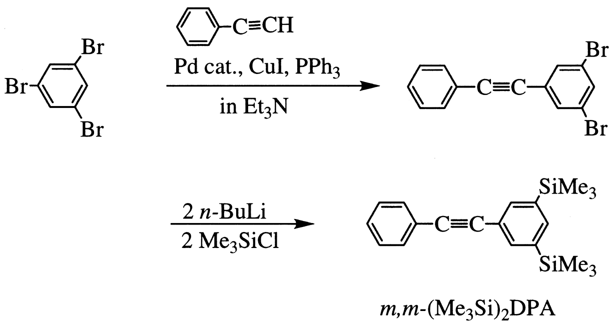
EXPERIMENTAL

Materials

$TaCl_5$ was purchased and used without further purification. *n*-Bu_4Sn was distilled twice from calcium hydride before use. Diphenylacetylene was commercially obtained and purified by sublimation. *m*,*m*-($Me_3Si)_2$DPA was synthesized with reference to the literature methods (Scheme 2) [12]. The synthesis of other monomers was reported before [13].

1-(3,5-Dibromophenyl)-2-phenylacetylene

A 1-L three-necked flask was equipped with a reflux condenser, a magnetic stirrer, and a dropping funnel, and flushed with dry nitrogen. $(Ph_3P)_2PdCl_2$ (154 mg, 0.22 mmol), Ph_3P (233 mg, 0.89 mmol), CuI (248 mg, 1.3 mmol), Et_3N (200 mL) and 1,3,5-tribromobenzene (25 g, 81 mmol) were placed in the flask,



Scheme 2. Synthesis of *m,m*-$(Me_3Si)_2$DPA.

and phenylacetylene (8.9 mL, 81 mmol) was added dropwise at room temperature with stirring. Then the reaction mixture was stirred at 60°C for 6 hours. Triethylamine was evaporated at reduced pressure. The residue was dissolved in diethyl ether and insoluble salts were filtered off. The filtrate was washed with 2N HCl aq. and water, and dried over anhydrous sodium sulfate. After evaporation of diethyl ether, the crude product was purified by flash column chromatography (Nakarai Tesque Co., silica gel 60; eluent, hexane) to afford a white solid (15 g, 55%); mp. 108.0–108.9°C

1-[3,5-Bis(trimethylsilyl)phenyl]-2-phenylacetylene (*m,m*-$(Me_3Si)_2$-DPA)

A 500-mL three-necked flask was equipped with a reflux condenser, magnetic stirrer, dropping funnel, and then flushed with dry nitrogen. 1-(3,5-Dibromophenyl)-2-phenylacetylene (5.0 g, 15 mmol) and dry diethyl ether (50 mL) were placed in the flask and cooled to –78°C. *n*-BuLi (10.3 mL, 1.6 M, 16 mmol) was added slowly and the reaction mixture was stirred at –78°C for 1 hour. Then, a solution of chlorotrimethylsilane (2.1 mL, 16 mmol) in diethyl ether (20 mL) was added dropwise. Subsequently, the reaction mixture was recooled to -78°C and monolithiation and monosilylation was repeated in the same way. The reaction mixture was warmed to room temperature and stirred for 2 hours. The reaction was quenched by the addition of water. The organic phase was washed with water and dried over anhydrous sodium sulfate. Diethyl ether was evaporated and the crude product was purified by flash column chromatography (eluent: hexane) to give the desired product as a white solid (10 g, 69%).; mp. 66.0–67.0°C, purity 99% (^{1}H-NMR). IR (KBr) 2955, 1489, 1381, 1248, 918, 862, 837, 758, and 693 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ 7.3-7.7 (m, 9H, aromatic) and 0.3 (s, 18H) ppm. ^{13}C-NMR ($CDCl_3$) δ 139.6, 137.5, 136.8, 131.6, 128.3, 128.1, 123.4, 122.0, 90.0, 89.2 and –1.2 ppm. Anal. Calcd for $C_{20}H_{27}Si_2$: C 74.45, H 8.14, Si 17.41%. Found: C 74.28, H 8.14, Si 17.58%.

Polymerization Procedure

Polymerizations were carried out in a Schlenk tube equipped with a three-way stopcock under dry nitrogen atmosphere. Monomer conversions were determined by gas chromatography (GC) using docosane as the internal standard. Polymers were isolated by precipitation into a large amount of methanol, and polymer yields were determined by gravimetry. A detailed polymerization procedure has been described elsewhere [14].

Characterization

The molecular weights of polymers were evaluated by gel permeation chromatography (GPC; polystyrene standard). GPC curves were observed with a Shimadzu LC-9A liquid chromatograph [eluent, $CHCl_3$; columns a series of Shodex K-805, K-806, K-807 (Showa Denko, Co., Japan)].

IR, UV, and NMR spectra were measured on a Shimadzu FTIR-8100 spectrophotometer, a Jasco V-530 spectrometer, a JEOL GSX-270 spectrom-eter, respectively. Thermogravimetric analyses (TGA) were carried out with a Perkin Elmer TGA-7 analyzer (in air, heating rate 10°C/min). Gas permeability coefficients were measured with a Rikaseiki K-315-N gas permeability apparatus.

RESULTS AND DISCUSSION

Polymerization

Table 1 shows the results of homo- and copolymerizations of *m,m*-$(Me_3Si)_2$DPA. A 1:1 mixture of $TaCl_5$ and *n*-Bu_4Sn was employed as the polymerization catalyst, which is the most effective catalyst for the polymerization of diphenylacetylenes. Unfortunately *m,m*-$(Me_3Si)_2$DPA gave no homopolymer. This result is attributable to the steric hindrance from the two trimethylsilyl groups at both meta positions. On the other hand, copolymerizations with DPA, *p*-Me_3SiDPA and *m*-Me_3SiDPA at a feed mole ratio 1:1 a copolymers in moderate yields (Runs 4, 9, 12). All copolymers completely dissolved in toluene and $CHCl_3$, and their M_w values were relatively high (ca. $1x10^5$–4×10^5).

TABLE 1. Copolymerization of *m,m*-$(Me_3Si)_2$DPA (M_1) with Various DPAs (M_2) by $TaCl_5$–*n*-Bu_4Sn at Various Feed Ratios[a]

Run	Feed ratio	Monomer Convn. (%)		Polymer [b]		
	M_1: M_2	M_1	M_2	Yield (%)	$M_w/10^3$ [c]	$M_n/10^3$ [c]
			Comonomer:	none		
1	1:0	34	—	0	—	—
			Comonomer:	DPA		
2	3:1	22	22	7	56	36
3	2:1	37	30	14	87	53
4	1:1	38	46	33	370	190
5	1:1[d]	19	23	11	230	140
6	1:1[e]	40	44	26	380	230
7	1:2	71	71		insoluble	
			Comonomer:	*p*-Me_3SiDPA		
8	2:1	35	29	8	48	31
9	1:1	34	42	21	200	82
10	1:2	56	59	42	440	230
			Comonomer:	*m*-Me_3SiDPA		
11	2:1	25	21	6	40	26
12	1:1	18	17	7	110	56
13	1:2	22	31	20	610	68

[a] Polymerized in toluene at 80 °C for 24 hours; $[M]_{0,total}$ = 0.40 M, $[TaCl_5]$ = 20 mM, [*n*-Bu_4Sn] = 40 mM; [b] Methanol-insoluble product; [c] Measured by GPC; [d] $[M]_{0,total}$ = 0.20 M; [e] $[M]_{0,total}$ = 1.0 M.

In general, both the molecular weight and yield of the copolymers tended to increase when the comonomer content (DPA, *p*-Me_3SiDPA and *m*-Me_3SiDPA) in the feed was increased (see Table 1). Thus, the M_w values of copoly(*m,m*-$(Me_3Si)_2DPA$/*p*-Me_3SiDPA) (feed mole ratio 1:2, Run 10), and copoly(*m,m*-$(Me_3Si)_2DPA$/*m*-Me_3SiDPA) (feed mole ratio 1:2, Run 13) reached 4.4×10^5 and 6.1×10^5, respectively. Most of the copolymers listed in Table 1 are soluble in common solvents. However, copoly(*m,m*-$(Me_3Si)_2DPA$/DPA) (feed ratio 1:2, Run 7) was insoluble in toluene, $CHCl_3$, etc, which is consistent with the result that poly(DPA) is insoluble in any solvent [15]. The M_w of copolymers obtained in Runs 4, 10, and 13 were enough to give fee-standing films by solution casting.

Polymer Structure

Figure 1 illustrates the IR spectrum of copoly (*m,m*-$(Me_3Si)_2DPA$/DPA) (feed mole ratio 1:1). A weak absorption band is observed around 1550 $\chi\mu^{-1}$, which is assignable to the stretching of the highly symmetrical tetrasubstituted ethylene structure in the main chain. Further, absorptions due to SiC–H deformation and Si–C stretching were seen around 1260 and 890–830 cm^{-1}, respectively. Figure 2 depicts the UV-visible spectrum of the copolymer. The copolymer is orange and has an absorption maximum at 430 nm and a cutoff wavelength of 500 nm. This absorption is due to the conjugated double bonds

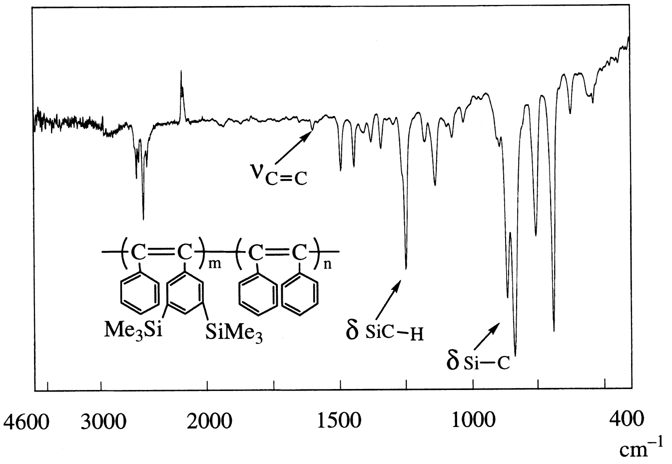


Figure 1. IR spectra of copoly(*m,m*-$(Me_3Si)_2DPA$/DPA) produced at a 1:1 feed ratio.

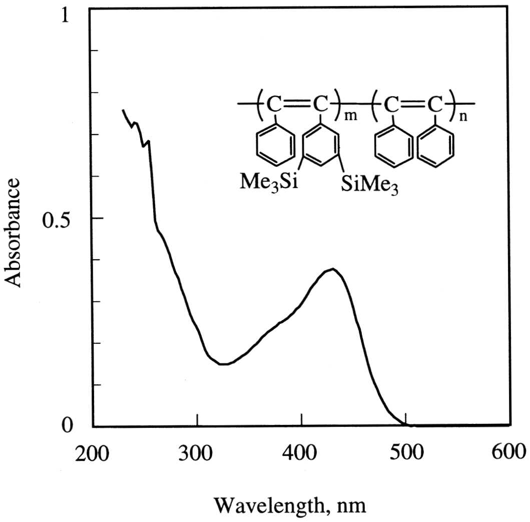


Figure 2. UV-visible spectra of copoly(*m,m*-$(Me_3Si)_2$DPA/DPA) produced at a 1:1 feed ratio (in THF).

along the main chain. These spectral data support the alternating double bond structure of the main chain for this copolymer.

Polymer Properties

All copolymers, except for Run 7 of Table 1, were completely soluble in $CHCl_3$, dichloromethane, THF, toluene, benzene, and anisole, and insoluble in methanol, DMF, DMSO, diethyl ether, and hexane.

The thermal stability of copoly(*m,m*-$(Me_3Si)_2$DPA/ DPA)s was investigated (Figure 3). In TGA runs in air, these copolymers showed fairly high thermal stability (onset temperature for weight loss (T_0) ca. 400°C), though inferior to poly(DPA) [15] (T_0 = 500°C). The T_0 values of the copolymers hardly changed with the feed ratio, while the amount of weight residue around 700°C was in the following order; Run 2 > Run 3 > Run 4. This order corresponds to the Si-content in the copolymers, suggesting that the silicon in the copolymers is converted into SiO_2.

Figure 4 shows plots of P_{O2} versus the separation factor (P_{O2}/P_{N2}) of copoly(*m,m*-$(Me_3Si)_2$DPA/DPA) (Table 1, Run 4) and copoly(*m,m*-$(Me_3Si)_2$DPA/*p*-Me_3SiDPA) (Table 1, Run 13). The P_{O2} values were 21 barrers (P_{O2}/P_{N2} = 3.4) and 100 barrers (P_{O2}/P_{N2} = 3.1), respectively. Rather opposite to our expectation, these P_{O2} values are from one to two orders of magnitude smaller

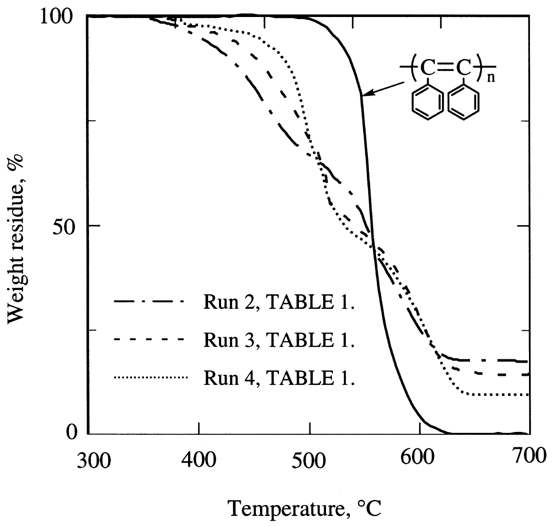


Figure 3. TGA curves of copoly(*m,m*-$(Me_3Si)_2$DPA/DPA)s produced at various feed mole ratios (heating rate 10°C/min, in air).

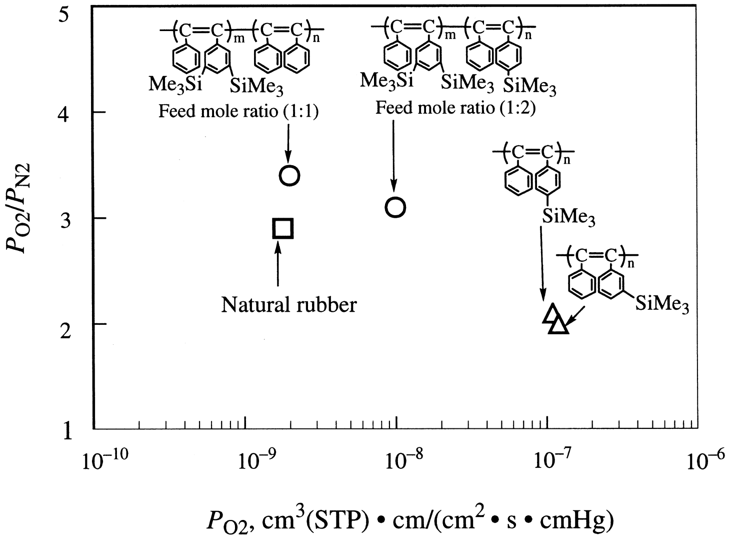


Figure 4. Oxygen permeability coefficients (P_{O2}) of copolymers from diphenylacetylenes having two trimethylsilyl groups (25°C) [1 barrer = 1 × 10^{-10} cm^3(STP)•cm/(cm^2•s•cmHg)].

than that of poly(*p*-Me_3SiDPA). A few explanations are possible for this finding. One is that there is little excess free volume due to stacking (packing) of the symmetrical *m,m*-$(Me_3Si)_2C_6H_4$ moiety. The second is that, for some reason, the present copolymers undergo physical relaxation so quickly that the gas permeability that has already decreased is observed. The third is that the low mobility of the *m,m*-$(Me_3Si)_2C_6H_4$ group in the polymer may have brought about the low gas permeability; this idea has recently been proposed by Kanaya based on the finding that there is a correlation between the P_{O2} value and local mobility of the substituents in some polyacetylenes [15]. The oxygen permeability of copoly (*m,m*-$(Me_3Si)_2DPA$/*p*-Me_3SiDPA) was also lower than that of poly(*p*-Me_3SiDPA) against expectation. Probably one of the above reasons will apply, and a study of the gas permeation mechanism is needed to clarify the proper reason.

CONCLUSION

m,m-$(Me_3Si)_2DPA$ was copolymerized with DPA, p-Me_3SiDPA, and m-Me_3SiDPA in the presence of $TaCl_5$–n-Bu_4Sn at various feed ratios to give copolymers in moderate yields. The copolymers were yellow to orange solids, which were soluble in common organic solvents such as toluene and $CHCl_3$. The highest M_w of these copolymers reached ca. $6x10^5$ and tough films could be obtained by solution casting. The oxygen permeability coefficients at 25°C of copoly(*m*,*m*-$(Me_3Si)_2DPA$/DPA) (feed ratio 1:1) and copoly(*m*,*m*-$(Me_3Si)_2$ DPA/*p*-Me_3SiDPA) (feed ratio 1:2) were 21 and 100 barrers, respectively, medium in magnitude among polymers prepared from substituted acetylenes.

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