Macromolecules

Volume 21, Number 3 March 1988

Synthesis of Aromatic Polyamides from *N,N'*-Bis(trimethylsilyl)-Substituted Aromatic Diamines and Aromatic Diacid Chlorides

Yoshiyuki Oishi, Masa-aki Kakimoto, and Yoshio Imai*

Department of Organic and Polymeric Materials, Tokyo Institute of Technology, Meguro-ku, Tokyo 152, Japan. *Received July 6, 1987*

ABSTRACT: A novel and facile method for the synthesis of high molecular weight aramids has been developed by the use of *N,N'*-bis(trimethylsilyl)-substituted aromatic diamines which were found to be more reactive toward aromatic diacid chlorides than the parent unsubstituted diamines. The low-temperature solution polycondensation of the N-silylated aromatic diamines with aromatic diacid chlorides afforded readily a series of aramids having inherent viscosities of 2.4–7.4 dL·g^{-1} with the elimination of trimethylsilyl chloride under neutral and milder reaction conditions, compared with the conventional diamine–diacid chloride method.

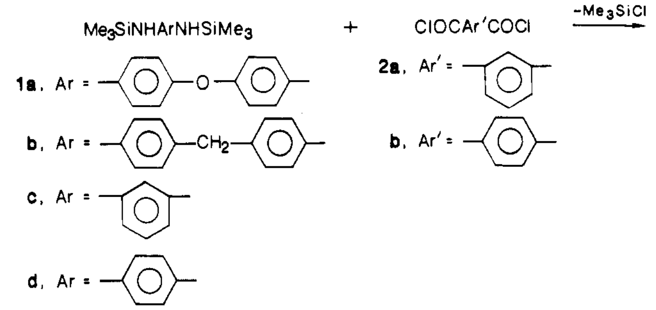
Introduction

Wholly aromatic polyamides (aramids) are members of thermally stable polymers and some are available for use as flame-resistant fibers, high-strength and high-modulus fibers, and high-performance plastics.[1] The most versatile method for the synthesis of aramids is the one starting from diamine–diacid chloride monomer pairs through either interfacial or low-temperature solution polycondensation (eq 1).[2]

$$H_2NArNH_2 + ClOCAr'COCl \xrightarrow{-HCl} -[NHArNHC(O)Ar'C(O)]_n- \quad (1)$$

In 1983, Bowser and his co-workers[3] demonstrated that aliphatic amides could be prepared in excellent yields from *N*-trimethylsilyl-substituted aliphatic amines and acid chlorides. Katsarava and his group[4] reported the synthesis of polyamides from *N*-(trimethylsilyl)lysine and diacid chlorides in 1985. More recently, we found that *N,N'*-bis(trimethylsilyl)dianilinobenzenes had higher reactivity toward diacid chlorides than the parent diamines, giving N-phenylated aramids of high molecular weights.[5,6]

These results prompted us to investigate the synthesis of simple aramids using *N,N'*-bis(trimethylsilyl)-substituted aromatic diamines. In a preceding paper, we reported the successful synthesis of high molecular weight aramids by low-temperature solution polycondensation of the N-silylated aromatic diamines with aromatic diacid chlorides.[7] This article constitutes the fourth of this series and deals with the detailed discussions on the synthesis of aramids by the N-silylation method (eq 2).



$$-[NHArNHC(O)Ar'C(O)]_n- \quad (2)$$

3

Experimental Section

Materials. Bis(4-aminophenyl) ether and bis(4-aminophenyl)methane were purified by recrystallization from tetrahydrofuran (THF) and ethanol, respectively. *m*-Phenylenediamine, *p*-phenylenediamine, isophthaloyl chloride (**2a**), and terephthaloyl chloride (**2b**) were purified by vacuum distillation. Commercial trimethylsilyl chloride and hexamethyldisilazane were used without further purification. Lithium chloride and calcium chloride were dried before use. Solvents used for the reactions were purified by distillation.

N-(Trimethylsilyl)aniline (**4**) was prepared by the reaction of aniline with hexamethyldisilazane in the presence of a trace amount trimethylsilyl chloride in THF at 60 °C for 20 h. Fractional distillation afforded the product in 80% yield; bp 114–115 °C (30 Torr) [lit.[8] 106–107 °C (24 Torr)]. The infrared (IR) spectrum (NaCl) exhibited absorptions at 1245, 840, and 750 (Si–CH$_3$) cm^{-1}.

N,N'-Bis(trimethylsilyl)-substituted aromatic diamines including *N,N'*-bis(trimethylsilyl)bis(4-aminophenyl) ether (**1a**), *N,N'*-bis(trimethylsilyl)bis(4-aminophenyl)methane (**1b**), *N,N'*-bis(trimethylsilyl)-*m*-phenylenediamine (**1c**), and *N,N'*-bis(trimethylsilyl)-*p*-phenylenediamine (**1d**) were prepared according to the method reported elsewhere[9] by the reaction of the corresponding diamines (1.0 mol) with trimethylsilyl chloride (2.4 mol) in the presence of triethylamine (3.0 mol) in dry benzene. The yields and their boiling points and melting points are summarized in Table I.

0024-9297/88/2221-0547$01.50/0 © 1988 American Chemical Society

Table I
Synthesis of N-Silylated Aromatic Diamines 1

1	yield, %	bp, °C (Torr)[a]	mp, °C[a]
1a	65	168–170 (0.5) [196–197 (1.4)]	72–74 (72–73)
1b	50	161–162 (0.5)	51–52 (52–54)
1c	47	88–89 (0.5) [130/(3.5)]	
1d	54	150–152 (8)	102–104 (103–105)

[a] The bp or mp value in parentheses is that reported in the literature.[10]

Model Reaction. Benzanilide (6) from 4 and Benzoyl Chloride (5). To a solution of 0.827 g (5.0 mmol) of **4** in 10 mL of hexane was added 0.703 g (5.0 mmol) of **5** dropwise with stirring under nitrogen. Stirring was continued at 20 °C for 6 h. Precipitation occurred during this period. The precipitate was collected, washed with hexane, and dried. It weighed 0.95 g (96%); mp 162–163 °C (lit.[11] 162 °C). The IR spectrum showed absorptions at 3340 (N—H) and 1655 (C=O) cm^{-1}.

Polymerization. Polymer 3a from 1a and 2a. In a flask, 1.723 g (5.0 mmol) of **1a** was dissolved in 10 mL of *N*-methyl-2-pyrrolidone (NMP) under nitrogen. The solution was cooled with a dry ice–acetone bath, and to this was added 1.015 g (5.0 mmol) of solid **2a** in one portion. The cooling bath was changed to an ice–salt bath, and the mixture was stirred at −10 °C for 3 h under nitrogen. The polymer was isolated by pouring the reaction solution into 500 mL of methanol. After thorough washing with hot methanol and drying, the polymer weighed 1.64 g (98%). The inherent viscosity was 3.97 dL·g^{-1}, measured at a concentration of 0.5 g·dL^{-1} in concentrated sulfuric acid at 30 °C. The IR spectrum (film) exhibited absorptions at 3300 (N—H) and 1655 (C=O) cm^{-1}. Anal. Calcd for $(C_{20}H_{14}N_2O_3)_n$: C, 72.72; H, 4.27; N, 8.48. Found: C, 72.08; H, 4.24; N, 8.46%.

Polymer 3c from 1b and 2a. A mixture of 1.713 g (5.0 mmol) of **1b** and 1.015 g (5.0 mmol) of **2a** in 10 mL of NMP was stirred at a temperature ranging from −10 to −5 °C for 3 h under nitrogen. The polymer was worked up in the same manner as described in the preceding experiment. The yield was 1.63 g (99%) and the inherent viscosity was 2.54 dL·g^{-1} in concentrated sulfuric acid. Anal. Calcd for $(C_{21}H_{16}N_2O_2)_n$: C, 76.81; H, 4.91; N, 8.53. Found: C, 75.56; H, 4.57; N, 8.31.

Polymer 3e from 1c and 2a. A mixture of 1.263 g (5.0 mmol) of **1c**, 1.015 g (5.0 mmol) of **2a**, and 0.53 g of lithium chloride in 10 mL of NMP was stirred at −10 to −5 °C for 5 h under nitrogen. The polymer weighed 1.18 g (99%) and had an inherent viscosity of 2.45 dL·g^{-1} in concentrated sulfuric acid. Anal. Calcd for $(C_{14}H_{10}H_2O_2)_n$: C, 70.58; H, 4.23; N, 11.76. Found: C, 69.99; H, 4.01; N, 11.55.

Polymer 3h from 1d and 2b. The polymer was prepared according to the method reported previously.[7] The yield was 99% and the inherent viscosity was 7.41 dL·g^{-1} in concentrated sulfuric acid. Anal. Calcd for $(C_{14}H_{10}N_2O_2)_n$: C, 70.58; H, 4.23; N, 11.76. Found: C, 70.19; H, 4.08; N, 11.60.

Measurement. IR spectra and ^{1}H nuclear magnetic resonance (NMR) spectra were recorded on a Hitachi EP-G3 spectrophotometer and a JEOL JNM-PMX60 NMR spectrometer (60 MHz), respectively.

Results and Discussion

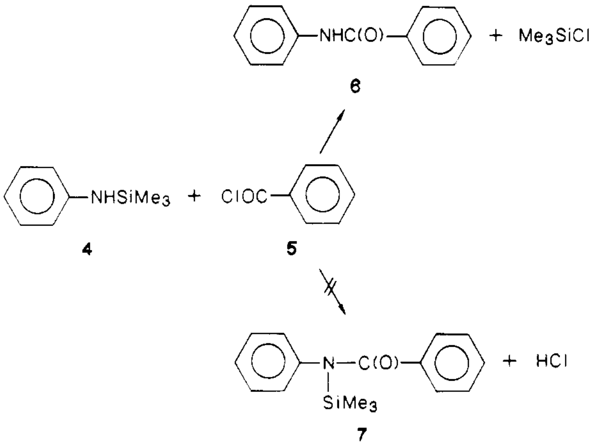
Model Reaction. Before the aramid synthesis, the model reaction of *N*-(trimethylsilyl)aniline (**4**) with benzoyl chloride (**5**) was investigated in detail. The reaction was first carried out in *N,N'*-dimethylacetamide (DMAc) at 20 °C and was followed by means of ^{1}H NMR spectroscopy. As the reaction proceeded, the peak of methyl protons (δ 0.26) of **4** disappeared, while a new singlet peak corresponding to methyl protons of trimethylsilyl chloride appeared at 0.43 ppm. The yield of benzanilide (**6**) after isolation from the reaction mixture was 98%.

In case of the reaction in chloroform or hexane, a precipitate separated out during the reaction. The precipitate was found to be **6**, since another possible product of *N*-(trimethylsilyl)benzanilide (**7**) is a liquid at room temperature.[12] The yields of **6** by the reactions in chloroform and hexane were 95% and 96%, respectively. Thus, it was confirmed that the reactions in various solvents at room temperature afforded exclusively **6** and not **7** (eq 3).[3]

Table II
Synthesis of Aramid 3a in Various Solvents[a]

solvent	polymer yield, %	polymer η_{inh},[b] dL·g^{-1}	polymer remarks[c]
chloroform	95	0.47	P
acetonitrile	94	0.31	P
nitrobenzene[d]	96	0.45	P
DMAc	99	2.28	S
NMP	99	2.87	S
HMPA	99	2.41	S

[a] Polymerization was carried out with 5.0 mmol of **1a** and 5.0 mmol of **2a** in 10 mL of the solvent at 0 °C for 3 h. [b] Measured at a concentration of 0.5 g·dL^{-1} in concentrated sulfuric acid at 30 °C. [c] Appearance of the polymerization mixture: P, polymer precipitation during the reaction; S, homogeneous solution throughout the reaction. [d] Polymerization was carried out at 10 °C.



(3)

Polymer Synthesis. Following the model reaction, the polycondensation of N-silylated bis(4-aminophenyl) ether (**1a**) with isophthaloyl chloride (**2a**) leading to aramid **3a** was investigated to optimize the reaction conditions. Table II summarizes the solvent effect on the polymerization. Since N-silylated aromatic diamines dissolve quite readily in a wide range of organic solvents, compared to the corresponding aromatic diamines, the solution polycondensation was carried out in various solvents. The polymerization in amide solvents such as DMAc, *N*-methyl-2-pyrrolidone (NMP), and hexamethylphosphoramide (HMPA) gave readily the polymer having high inherent viscosities of 2.2–2.8 dL·g^{-1}, whereas the other solvents like chloroform, acetonitrile, and nitrobenzene afforded the aramid with low viscosities of 0.3–0.4 dL·g^{-1} due to polymer precipitation during the polymerization.

The effect of reaction temperature on the inherent viscosity of the aramid was examined in NMP at a temperature between −10 and 20 °C (Figure 1). The inherent viscosity increased as the reaction temperature lowered, and the highest viscosity (4.0 dL·g^{-1}) was obtained at −10 °C.

Figure 2 shows the effect of monomer concentration on the inherent viscosity of the polymer formed by the polymerization in NMP at −10 °C. The maximum value (ca. 4.0 dL·g^{-1}) was obtained at a concentration of 0.5 mol·L^{-1}.

Figure 3 reveals the time dependence of the inherent viscosity of the aramid. The polycondensation proceeded fairly rapidly at −10 to −5 °C and gave the polymer having inherent viscosity of 2.0 dL·g^{-1} in 10 min, and the viscosity reached 4.0 dL·g^{-1} after 2 h.

From these results, the N-silylated aromatic diamine was found to be highly reactive toward the aromatic diacid

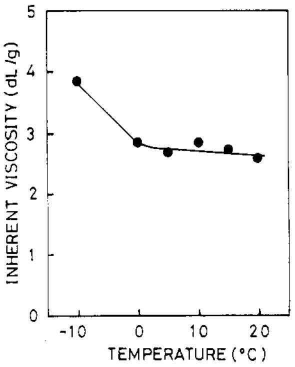


Figure 1. Effect of reaction temperature on inherent viscosity of aramid **3a** formed by the polycondensation of **1a** with **2a** at the monomer concentration of 0.5 mol·L^{-1} in NMP for 3 h.

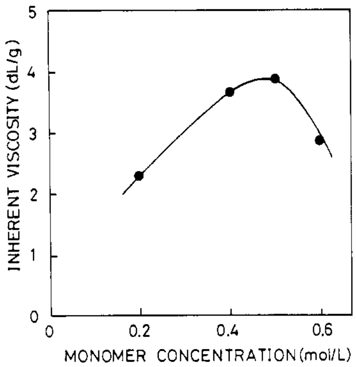


Figure 2. Effect of monomer concentration on inherent viscosity of aramid **3a** formed by polycondensation of **1a** with **2a** in NMP at -10 °C for 3 h.

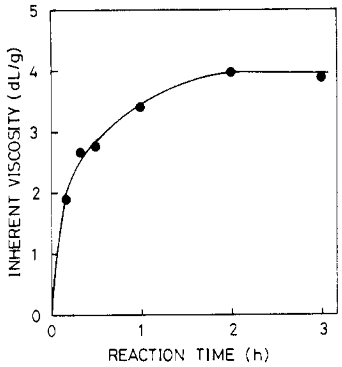


Figure 3. Time dependence of inherent viscosity of aramid **3a** formed by the polycondensation of **1a** with **2a** at the monomer concentration of 0.5 mol·L^{-1} in NMP at -10 to -5 °C.

chloride. Consequently, high molecular weight aramid **3a** with an inherent viscosity of 4.0 dL·g^{-1} could be readily prepared by the polycondensation in NMP at -10 °C for 2 h under nitrogen.

Polymerization conditions for the preparation of aramid **3e** (Du Pont's Nomex molecule) were examined in the polycondensation of N-silylated *m*-phenylenediamine (**1c**) with diacid chloride **2a**. Table III summarizes the effects of monomer concentration and reaction medium. It was found that the aramids having inherent viscosities of 2.2–2.4 dL·g^{-1} could be obtained at a concentration of 0.5–0.6 mol·L^{-1} in NMP in the presence or absence of lithium chloride.

To determine the optimum conditions for obtaining high molecular weight aramid **3h** (Du Pont's Kevlar molecule), various reaction variables were investigated in the polycondensation of N-silylated *p*-phenylenediamine (**1d**) with terephthaloyl chloride (**2b**). Morgan and his co-workers[13] reported the synthesis of high molecular weight aramid **3h** by the low-temperature solution polycondensation of *p*-phenylenediamine with **2b** in a solvent mixture of NMP and HMPA. Table IV summarizes the effect of reaction medium on the polycondensation of **1d** with **2b** giving the aramid. The polymerizations in NMP–LiCl and NMP–HMPA proceeded with precipitation of the polymer, whereas those in NMP–CaCl$_2$ and NMP–HMPA–LiCl progressed in a homogeneous solution. In particular, the polycondensation in NMP–HMPA–LiCl system was found to be the best for the preparation of the aramid with the highest inherent viscosity (7.4 dL·g^{-1}).

Two solvent systems, NMP–CaCl$_2$ and NMP–HMPA–LiCl, were employed to examine the effect of monomer concentration on the inherent viscosity of the polymer. As shown in Figure 4, the optimum concentration in the NMP–CaCl$_2$ system was 0.2 mol·L^{-1}, where the inherent viscosity reached the highest value of 4.5 dL·g^{-1}. On the other hand, the optimum concentration in the NMP–HMPA–LiCl system was 0.2 mol·L^{-1} or below, and the viscosity as high as 7.4 dL·g^{-1} was attained. The lower inherent viscosity obtained at higher monomer concentration is attributable to reduced reactant mobility due to

Table III
Synthesis of Aramid 3e in Various Reaction Media[a]

reactn med	monomer concn, mol·L^{-1}	polymer yield, %	polymer η_{inh},[b] dL·g^{-1}	polymer remarks[c]
NMP	0.5	98	2.39	S
NMP-LiCl	0.5	99	2.41	S
NMP	0.6	99	2.28	H
NMP-LiCl	0.6	99	2.45	S
NMP-LiCl	0.7	98	2.03	S
NMP-LiCl	0.8	99	2.11	S

[a] Polymerization was carried out with 5.0 mmol of **1c** and 5.0 mmol of **2a** in NMP and 0.53 g of lithium chloride at -10 to -5 °C for 5 h. [b] See footnote *b* of Table II. [c] Appearance of the polymerization mixture: S, homogeneous solution; H, turbid heterogeneous mixture.

Table IV
Synthesis of Aramid 3h in Various Reaction Media[a]

reactn med	monomer concn, mol·L^{-1}	polymer yield, %	polymer η_{inh},[b] dL·g^{-1}	polymer remarks[c]
NMP-LiCl	0.05	99	1.91	P
NMP-CaCl$_2$	0.05	98	1.34	S
NMP-HMPA[d]	0.05	98	1.84	P
NMP-HMPA[d]	0.24	99	2.60	P
NMP-HMPA-LiCl[d]	0.05	99	7.36	S

[a] Polymerization was carried out with 2.5 mmol of **1d** and 2.5 mmol of **2b** in the solvent and 5 wt % of the inorganic salt at -10 to -5 °C for 24 h. [b] See footnote *b* of Table II. [c] See footnote *c* of Table II. [d] NMP:HMPA = 1:2 by volume.

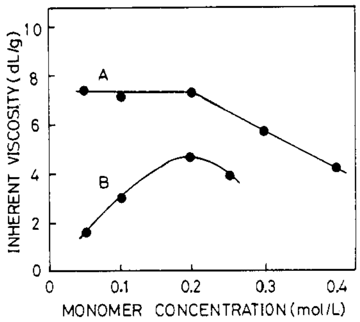


Figure 4. Effect of monomer concentration on inherent viscosity of aramid **3h** formed by the polycondensation of **1d** with **2b** at -10 to -5 ° C: (A) in MNP-HMPA-LiCl for 12 h and (b) in NMP-CaCl$_2$ for 24 h.

Table V
Synthesis of Various Aramids[a]

diamine	diacid chloride	polymer		
			yield, %	η_{inh},[b] dL·g^{-1}
1a	**2a**	**3a**	99	3.97 (2.10)
1a	**2b**	**3b**	99	3.99 (1.50)
1b	**2a**	**3c**	99	2.54 (1.15)
1b	**2b**	**3d**	99	3.21 (1.40)
1c	**2a**	**3e**	99	2.45 (1.03)
1c	**2b**	**3f**	99	3.19 (0.94)
1d	**2a**	**3g**	99	2.41 (1.19)
1d	**2b**	**3h**[c]	99	7.41 (3.23)

[a] Polymerization was carried out with 5.0 mmol of the diamine component and 5.0 mmol of the diacid chloride in 10 mL of NMP and 0.53 g of LiCl at −10 to −5 °C for 5 h. [b] See footnote *b* of Table II. The value in parentheses is that of the aramid formed by the polycondensation of the corresponding unsubstituted aromatic diamine with the diacid chloride. [c] Polymerization was carried out with 5.0 mmol of each monomer in 8.3 mL of NMP, 16.7 mL of HMPA, and 1.33 g of LiCl at −10 to −5 °C for 12 h.

the onset of gelation of the reaction mixture before the high molecular weight is reached.

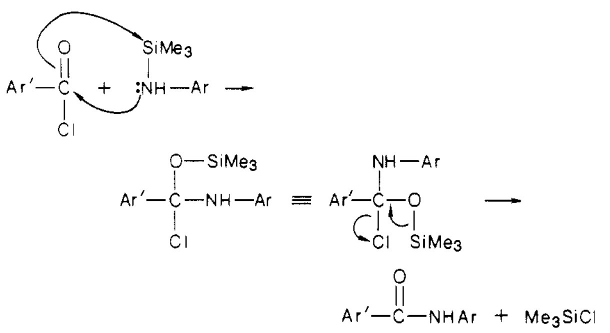
Our previous paper[7] reported that the polycondensation of **1d** with **2b** at a monomer concentration of 0.2 mol·L^{-1} in the NMP–HMPA–LiCl system at −10 to −5 °C proceeded more rapidly giving higher molecular weight aramid **3h**, compared with the polymerization of *p*-phenylenediamine with **2b**.

A variety of high molecular weight aramids **3a–h** with inherenet viscosities ranging between 2.4 and 7.4 dL·g^{-1} were successfully prepared from combinations of N-silylated aromatic diamines **1a–d** and aromatic diacid chlorides **2a** and **2b** (Table V). These viscosity values were much higher than those of the aramids prepared from the parent aromatic diamines and the diacid chlorides by the conventional low-temperature solution polycondensation method.

Discussion on Reaction Mechanism. The mechanism of the reaction of N-silylated amines with carboxylic acid chlorides is discussed here to clarify the high reactivity of the N-silylated amines compared to the parent amines toward acid chlorides. In general, the nucleophilic acyl substitution of a carboxylic acid derivative R′C(O)X with an amine RNH_2 giving an amide R′C(O)NHR proceeds through a two-step mechanism; that is, the formation of a tetrahedral intermediate by the nucleophilic addition of an amine to the carbonyl carbon on R′C(O)X and the subsequent formation of an amide with the elimination of a leaving group HX.[14]

The reaction of a N-silylated amine with an acid chloride probably follows a similar reaction mechanism. Organosilicon compounds are characterized by the fact that the silicon has a strong affinity for oxygen, fluoride, or chloride ion, and that the carbocation on the β-position to the silicon can be stabilized through the silicon σ–π effect.[15] Taking into consideration of these remarkable feature of organosilicon compounds, the following nucleophilic addition–elimination two-step mechanism is proposed for the nucleophilic acyl substitution of an acid chloride with a N-silylated amine (eq 4).

In the first step, the attraction of the carbonyl oxygen of an acid chloride to the silicon of an N-silylated amine facilitates the nucleophilic attack of the nitrogen of an N-silylated amine at the carbonyl carbon of an acid chloride, thereby quickly giving rise to the tetraherdral intermediate. In the second step, the elimination of chloride ion from the intermediate is enhanced by the presence of the β-silicon through the σ–π effect, affording the amide product along with trimethylsilyl chloride.



(4)

Conclusion

It was found that N-trimethylsilylated aromatic diamines were far more reactive than the parent diamines toward the aromatic diacid chlorides and hence higher molecular weight aramids were readily prepared by the low-temperature solution polycondensation of these monomer pairs under milder reaction conditions, compared with the aramids formed by the conventional diamine–diacid chloride route.

The N-silylated diamine method has several advantages over the conventional method: (1) High-purity N-silylated aromatic diamines can be obtained simply by distillation. (2) N-silylated aromatic diamines exhibit good solubility in organic solvents and the polycondensation can be carried out in various solvents. (3) The polycondensation proceeds under neutral reaction conditions with the elimination of trimethylsilyl chloride. (4) The trimethylsilyl chloride recovered from the polymerization system may be recycled as a silylating agent for aromatic diamines.

Thus the N-silylated diamine method is versatile and promising for the synthesis of a variety of high molecular weight aramids and can be widely used to synthesize various types of aromatic condensation polymers.

Registry No. **3a** (copolymer), 112320-04-4; **3a** (SRU), 26026-92-6; **3b** (copolymer), 112320-03-3; **3b** (SRU), 26854-93-3; **3c** (copolymer), 112320-02-2; **3c** (SRU), 25667-73-6; **3d** (copolymer), 112320-01-1; **3d** (SRU), 25667-72-5; **3e** (copolymer), 106680-81-3; **3e** (SRU), 24938-60-1; **3f** (copolymer), 106680-82-4; **3f** (SRU), 24938-63-4; **3a** (copolymer), 106680-83-5; **3a** (SRU), 24938-61-2; **3h** (copolymer), 106680-84-6; **3h** (SRU), 24938-64-5.

References and Notes

(1) Cassidy, P. E. *Thermally Stable Polymers*; Marcel Dekker: New York, 1980.
(2) Morgan, P. W. *Condensation Polymers by Interfacial and Solution Methods*; Interscience: New York, 1965.
(3) Bowser, J. R.; Williams, P. J.; Kurz, K. *J. Org. Chem.* **1983**, *48*, 4111.
(4) Katsarava, R. D.; Kharadze, D. P.; Japaridze, N. S.; Omiadze, T. N.; Avalishvili, L. M.; Zaalishvili, M. M. *Makromol. Chem.* **1985**, *186*, 939.
(5) Kakimoto, M.; Oishi, Y.; Imai, Y. *Makromol. Chem., Rapid Commun.* **1985**, *6*, 557.
(6) Oishi, Y.; Kakimoto, M.; Imai, Y. *J. Polym. Sci., Polym. Chem. Ed.* **1987**, *25*, 2493.
(7) Oishi, Y.; Kakimoto, M.; Imai, Y. *Macromolecules* **1987**, *20*, 703.
(8) Bazant, V.; Chvalovsky, V.; Rathousky, J. *Handbook of Organosilicon Compounds*; Marcel Dekker: New York, 1973; Vol. 2, p 455.
(9) Oishi, Y.; Padmanaban, M.; Kakimoto, M.; Imai, Y. *J. Polym. Sci., Polym. Chem. Ed.* **1987**, *25*, 3387.
(10) Klebe, J. F. *J. Polym. Sci., Part B* **1964**, *2*, 1079.
(11) Franzen, H. *Chem. Ber.* **1909**, *42*, 2466.
(12) Fukui, M.; Itoh, K.; Ishii, Y. *J. Chem. Soc., Perkin Trans. 2* **1972**, 1043.
(13) Bair, T. I.; Morgan, P. W.; Killian, F. L. *Macromolecules* **1977**, *10*, 1396.
(14) Beckwith, A. L. J. In *The Chemistry of Amides*; Zabicky, J., Ed.; Interscience: New York, 1970; p 75.
(15) Seyferth, D., Ed. *New Applications of Organometallic Reagents in Organic Synthesis*; Elsevier: New York, 1976; p 127.