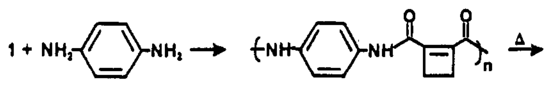
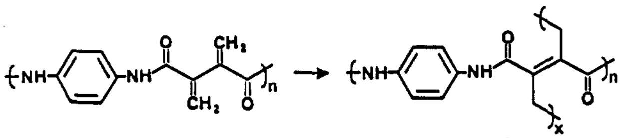
Macromolecules 1987, *20*, 703-704



7



8 9

While we have indicated a crosspolymerization structure for **9**, it is also possible for cycloadditions to lead to cross-linked and insoluble product. Additional polyamides are being synthesized, and their thermolysis chemistry and characterization are under further study.

These systems offer the unique ability to generate new polybutadienes from the model diamides. More important is the potential of cyclobutene-containing polymers to function as thermally cross-linkable components of composites and high-performance polymers.

Acknowledgment. We gratefully acknowledge an instrumentation grant from the Department of Defense for purchase of a solid-state NMR spectrometer, the Office of Naval Research for support of our composites research, and Dr. R. L. Cobb of Phillips Petroleum Co. for a generous donation of 1,2-dicyanocyclobutane.

References and Notes

(1) Bellus, D.; Sauter, H.; Weis, C. D. *Org. Synth.* **1978**, *58*, 67.
(2) Cobb, R. L.; Mahan, J. E. *J. Org. Chem.* **1977**, *42*, 1948.
(3) Bellus, D.; Bredow, K.; Hanspeter, S.; Weis, C. D. *Helv. Chim. Acta* **1973**, *56*, 3004.
(4) General procedure for preparation of model diamides: A 125-mL flask was charged with 50 mL of methylene chloride. To this were added 0.011 mol of the appropriate amine and 0.011 mol of triethylamine as acid scavenger. The reactants were dissolved with stirring, and the solution was cooled in an ice bath. The acid chloride **1b** (0.005 mol) was added quickly via syringe to the stirred solution. Stirring was continued for 15 min. The mixture was washed with successive portions of dilute HCl, dilute NaOH, and water. The solution was dried over anhydrous $MgSO_4$, and the solvent was evaporated. The solid residue was recrystallized from a minimum amount of boiling methanol. Isolated yields ranged from 30 to 80%. Spectral data and microanalyses confirmed product identities.
(5) Cobb, R. L.; Mahan, J. E.; Fahey, D. R. *J. Org. Chem.* **1977**, *42*, 2601.
(6) Tsao, J.-H.; Lenz, R. W. *J. Polym. Sci., Polym. Chem. Ed.* **1979**, *17*, 331.
(7) This polymer gave an intrinsic viscosity of 0.38 dL/g (hexafluoro-2-propanol) and a number-average molecular weight of 190 000 by size-exclusion chromatography (tetrahydrofuran with polystyrene standards).
(8) Mathias, L. J.; Ahmed, S. U.; Livant, P. D. *Macromolecules* **1985**, *18*, 616.

Lon J. Mathias* and Douglas G. Powell
Department of Polymer Science
University of Southern Mississippi
Hattiesburg, Mississippi 39406-0076

Received January 13, 1987

Novel Synthesis of High Molecular Weight Aramids from N-Silylated Aromatic Diamines and Aromatic Diacid Chlorides

Wholly aromatic polyamides (aramids) are among the oldest members of the class of thermally stable polymers, and some of them have been commercialized as high temperature resistant fibers, high-strength and high-modulus fibers, and high-performance plastics.[1] These aramids are usually prepared through the conventional diamine–diacid chloride route shown in eq 1 by either an interfacial or a low-temperature solution method.[2]

$$H_2N\text{-}Ar\text{-}NH_2 + ClOC\text{-}Ar'\text{-}COCl \xrightarrow{-HCl} [\text{-}NH\text{-}Ar\text{-}NHC(O)\text{-}Ar'\text{-}C(O)\text{-}]_n \quad (1)$$

Recently, we found that N-trimethylsilylated aromatic amines were far more reactive than the corresponding unsubstituted amines toward acid chlorides, giving excellent yields of amide compounds. The unusually high reactivity of N-silylated amines toward acid chlorides was entirely unexpected,[3] though N-trimethylsilylated aromatic diamines were prepared many years ago for the synthesis of polyamines[4] and polyureas.[5]

We now wish to communicate a novel and facile synthesis of aramids with high molecular weights by the low-temperature solution polycondensation of N-trimethylsilylated aromatic diamines (I) with aromatic diacid chlorides (II) (eq 2). Silylated diamines Ia and Ib were

$$\underset{\substack{\text{Ia, Ar} = m\text{-}C_6H_4\\ \text{Ib, Ar} = p\text{-}C_6H_4}}{Me_3SiNH\text{-}Ar\text{-}NHSiMe_3} + \underset{\substack{\text{IIa, Ar}' = m\text{-}C_6H_4\\ \text{IIb, Ar}' = p\text{-}C_6H_4}}{ClOC\text{-}Ar'\text{-}COCl} \xrightarrow{-Me_3SiCl} [\text{-}NH\text{-}Ar\text{-}NHC(O)\text{-}Ar'\text{-}C(O)\text{-}]_n \quad (2)$$

synthesized by the reaction of the corresponding diamines with trimethylsilyl chloride in the presence of triethylamine. Both Ia and Ib were purified by distillation: Ia, bp 88–89 °C (0.5 Torr);[5] Ib, bp 150–152 °C (8 Torr), mp 102–104 °C.[5]

A typical polymerization procedure is as follows: In a flask 1.263 g (5 mmol) of *N,N'*-bis(trimethylsilyl)-*p*-phenylenediamine (Ib) and 1.33 g of lithium chloride were dissolved in 16.7 mL of hexamethylphosphoramide (HMPA) and 8.3 mL of *N*-methyl-2-pyrrolidone (NMP). The solution was brought to −15 °C using an ice–salt mixture, and 1.015 g (5 mmol) of powdered terephthaloyl chloride (IIb) was added. The mixture was stirred at −10 to −5 °C under nitrogen. The polymerization proceeded in a homogeneous solution and the solution became a gel after 6 h. The reaction mixture was worked up by agitating with methanol. The polymer was collected by filtration, washed thoroughly with hot methanol, and dried at 80 °C in vacuo. The polymer weighed 1.18 g (99%) and had an inherent viscosity of 7.41 $dL\cdot g^{-1}$, measured at a concentration of 0.5 $g\cdot dL^{-1}$ in concentrated sulfuric acid at 30 °C.

It was confirmed that the low-temperature solution polycondensation proceeded according to eq 2 with elimination of trimethylsilyl chloride to afford aramids having high inherent viscosities.

Reaction conditions were examined in the polycondensation of Ib with IIb giving aramid PPTA (Du Pont's Kevlar molecule). Morgan et al.[6] reported the synthesis of high molecular weight PPTA by the polycondensation of *p*-phenylenediamine with IIb in a mixed solvent of HMPA and NMP. However, in the present investigation, addition of lithium chloride to the HMPA–NMP binary solvent was found to be advantageous, and hence a HMPA–NMP–LiCl mixture was used as the reaction medium.

The effect of reactant concentration on the inherent viscosity of PPTA formed was investigated. It was found that an inherent viscosity greater than 7.0 $dL\cdot g^{-1}$ was readily obtained when the concentration was in the range 0.1–0.2 $mol\cdot L^{-1}$. The lower inherent viscosity obtained at higher reactant concentration is attributable to reduced reactant mobility due to the onset of gelation before high inherent viscosity can be reached.

0024-9297/87/2220-0703$01.50/0

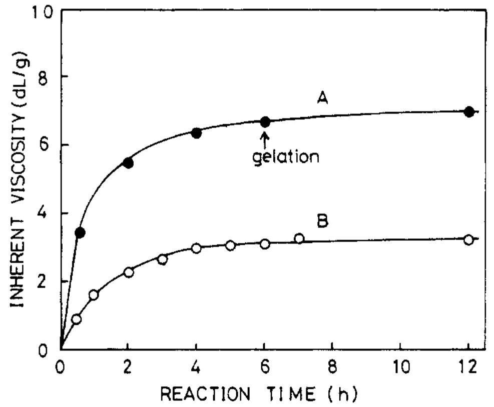


Figure 1. Time dependence of inherent viscosity of PPTA formed in the polycondensation of IIb with Ib (A) or with *p*-phenylenediamine (B) at a reactant concentration of 0.2 mol·L^{-1} in HMPA–NMP–LiCl at −10 to −5 °C.

Table I
Synthesis of Aramids by Polycondensation of N-Trimethylsilylated Aromatic Diamines with Aromatic Diacid Chlorides[a]

N-silylated diamine	diacid chloride	polymer		
		code	yield, %	η_{inh},[b] dL·g^{-1}
Ia	IIa	PMIA	99	2.41 (1.03)
Ia	IIb	PMTA	99	3.08 (0.94)
Ib	IIa	PPIA	98	2.20 (1.19)
Ib	IIb	PPTA[c]	99	7.41 (3.23)

[a] Polymerization was carried out with 5 mmol of the diamine component and with 5 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] Measured at a concentration of 0.5 g·dL^{-1} in concentrated sulfuric acid at 30 °C. 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 mmol of each reactant in 16.7 mL of HMPA, 8.3 mL of NMP, and 1.33 g of LiCl at −10 to −5 °C for 12 h.

As shown in Figure 1, the polymerization of Ib with IIb at a reactant concentration of 0.2 mol·L^{-1} in the solvent system proceeded more rapidly compared with the reaction of *p*-phenylenediamine with IIb. Although gelation occurred during the polymerization, the inherent viscosity finally reached 7.0 dL·g^{-1} after 12 h of the reaction. From the results Ib was found to be more reactive than *p*-phenylenediamine, giving higher molecular weight PPTA.

Next, the polycondensations of combinations of N-trimethylsilylated aromatic diamines (Ia and Ib) and aromatic diacid chlorides (IIa and IIb) were tried, and the results are shown in Table I. Under these reaction conditions, aramids PMIA, PMTA, and PPIA, as well as PPTA, were obtained with inherent viscosities over 2.2 dL·g^{-1}. These viscosity values were higher than those of the aramids prepared from the corresponding unsubstituted aromatic diamines by the conventional low-temperature solution method.[2]

The N-silylated diamine method developed here has several advantages over the conventional diamine–diacid chloride route. (1) High-purity N-silylated aromatic diamines can be obtained simply by distillation. (2) N-Silylated aromatic diamines are more reactive than the corresponding unsubstituted diamines, and higher molecular weight aramids can readily be formed under milder reaction conditions. (3) The polycondensation proceeds under almost neutral reaction conditions with elimination of trimethylsilyl chloride, whereas that by the conventional diamine–diacid chloride route proceeds with liberation of hydrogen chloride.

Thus, this N-silylated diamine method is a promising one and can be widely applied to the synthesis of various types of aramids from less reactive aromatic diamines[7,8] or less reactive diacid chlorides and further to the preparation of polyimides and other condensation polymers.

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) Schwarz, G.; Alberts, H.; Kricheldorf, H. R. *Liebigs Ann. Chem.* **1981**, 1257.
(4) Klebe, J. F. *J. Polym. Sci., Part A* **1964**, *2*, 2673.
(5) Klebe, J. F. *J. Polym. Sci., Part B* **1964**, *2*, 1079.
(6) Bair, T. I.; Morgan, P. W.; Killian, F. L. *Macromolecules* **1977**, *10*, 1396.
(7) Kakimoto, M.; Oishi, Y.; Imai, Y. *Makromol. Chem., Rapid Commun.* **1985**, *6*, 557.
(8) Oishi, Y.; Kakimoto, M.; Imai, Y. *J. Polym. Sci., Polym. Chem. Ed.*, submitted for publication.

Yoshiyuki Oishi, Masa-aki Kakimoto, and Yoshio Imai*
Department of Textile and Polymeric Materials
Tokyo Institute of Technology
Meguro-ku, Tokyo 152, Japan

Received November 4, 1986