compatibility requires a special attractive interaction between the polymers. This in turn would almost certainly be accompanied by a negative enthalpy of interaction, i.e., $\chi_H < 0$, and therefore, following eq 4, χ_{23}' would increase with T. Thus, an LCST in a compatible system would be favored both by the free volume difference between the polymers and by the specific interaction between them. In the present case, the specific interaction presumably occurs between the ether and phenyl groups of the polymer pair, and indeed χ_H for the interaction of benzene and toluene with PVME is small in Table I. Solution calorimetry shows it becomes negative for lower PVME concentration. The thermal expansion coefficients of PS[13] and PVME[14] are respectively 5.72 and 6.45×10^{-4} K^{-1} at 25 °C. Using the Prigogine–Flory theory, the free volume contribution to $d\chi_{23}'/dT$ is found to be less than 1×10^{-5} deg^{-1}. This is small compared with the experimental value of $\sim 10 \times 10^{-5}$ deg^{-1}, found from Figure 1. The LCST in the PS–PVME system seems due to the breaking-up with increasing temperature of the specific interaction between the PS and PVME chains rather than to the free-volume difference between PS and PVME.

A final point concerns the compatibility of PS and PVME in solution. Thies and collaborators[15] found that the mixture of the two polymers with each of the three solvents, benzene, toluene, and tetrachlorethene, gave a one-phase ternary solution, and a clear film is left on evaporating the solvents. On the other hand, when any of three other solvents, chloroform, dichloromethane, or trichloroethene, is used, the solution is phase separated. The turbidity remains on solvent evaporation giving a cloudy film. Recent work[16] has predicted that the compatibility of polymers in solution should reflect not only the interaction between the polymers themselves, i.e., χ_{23}', but also any difference between the interaction of the polymers with the solvent,

$$\Delta\chi = |\chi_{12} - \chi_{13}| \tag{6}$$

In the present case, the interaction between the polymers is negligible or attractive, indicating that the stable state of the film should be clear. From Table I, $\Delta\chi$ for benzene, toluene, and tetrachloroethene is respectively 0.1, 0.1, and 0.0. However, for chloroform, dichloromethane, and trichloroethene $\Delta\chi$ is respectively 1.2, 0.7, and 0.5, i.e., substantial. These results suggest that the incompatibility of PS and PVME in the second set of solvents is due to the "$\Delta\chi$ effect" which overcomes the normal PS–PVME compatibility. Further work[17] has confirmed this in the chloroform/(PS + PVME) case.

Acknowledgment. We thank the National Research Council of Canada for financial support and for a scholarship to one of us (C.S.)

References and Notes

(1) D. D. Deshpande, D. Patterson, H. P. Schreiber, and C. S. Su, *Macromolecules*, **7**, 530 (1974).
(2) C. S. Su, D. Patterson, and H. P. Schreiber, *J. Appl. Polym. Sci.*, **20**, 1025 (1976).
(3) O. Olabisi, *Macromolecules*, **8**, 316 (1975).
(4) T. K. Kwei, T. Nishi, and R. F. Roberts, *Macromolecules*, **7**, 667 (1974).
(5) T. Nishi and T. K. Kwei, *Polymer*, **16**, 285 (1975).
(6) R. P. Kambour, E. E. Romagosa, and C. L. Gruner, *Macromolecules*, **5**, 335 (1972).
(7) J. M. Braun and J. E. Guillet, *Macromolecules*, **8**, 557 (1975).
(8) J. A. Manson and G. J. Arquette, *Macromol. Chem.*, **37**, 187 (1960).
(9) D. D. Deshpande and S. L. Oswal, *J. Chem. Soc., Faraday Trans. 1*, **68**, 1059 (1972); C. Booth and C. J. Devey, *Polymer*, **12**, 309, 320 (1968).
(10) J. P. Sheridan, D. E. Martire, and Y. B. Tewari, *J. Am. Chem. Soc.*, **94**, 3294 (1972); J. Pouchlý and J. Biros, *J. Polym. Sci., Part B*, **7**, 467 (1969).
(11) J. S. Rowlinson, "*Liquids and Liquid Mixtures*", 2nd ed, Butterworths, London, 1969, p 166.
(12) (a) R. Koningsveld, L. A. Kleintjens, and H. M. Schoffeleers, *Pure Appl. Chem.*, **39**, 1 (1974); (b) L. P. McMaster, *Macromolecules*, **6**, 760 (1973).
(13) H. Höcker, G. J. Blake, and P. J. Flory, *Trans. Faraday Soc.*, **67**, 2251 (1971).
(14) R. A. Haldon, W. J. Schell, and R. Simha, *J. Macromol. Sci., Phys.*, **1**, 759 (1967).
(15) M. Bank, J. Leffingwell, and C. Thies, *Macromolecules*, **4**, 43 (1971).
(16) L. Zeman and D. Patterson, *Macromolecules*, **5**, 513 (1972); C. C. Hsu and J. M. Prausnitz, *ibid.*, **7**, 320 (1974).
(17) A. Robard, D. Patterson, and G. Delmas, *Macromolecules*, preceding paper in this issue.

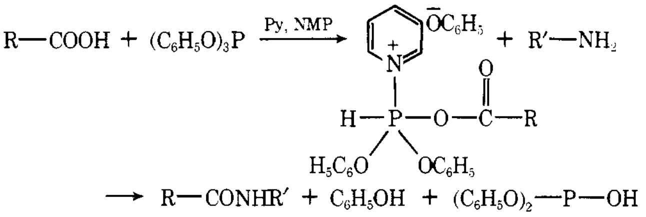
Aromatic Polyamides by a Direct Polycondensation Reaction

C. CHIRIAC[1] and J. K. STILLE*

Department of Chemistry, University of Iowa,
Iowa City, Iowa 52242. *Received January 6, 1977*

The solution polycondensation of terephthaloyl chloride with *p*-phenylenediamine or the homopolymerization of *p*-thionylaminobenzoyl chloride affords high-modulus, temperature-resistant polyamides.[2] Aromatic polyamides also have been obtained by the direct polycondensation reaction of aromatic dicarboxylic acids with aromatic diamines catalyzed by triphenyl phosphite in NMP–pyridine solution containing lithium chloride at 100 °C.[3] Trimellitic anhydride reacts with 4,4′-diaminodiphenylmethane in the presence of triphenyl phosphite at 200–210 °C in NMP to afford a polyamide–imide.[4] In this work a polyamidation reaction catalyzed by triphenyl phosphite prepared in situ from phenol and phosphorus trichloride in the presence of a large excess of pyridine is described. The proposed mechanism[3] for this polycondensation reaction involves a mixed anhydride.

$$C_6H_5OH + PCl_3 \xrightarrow[25\text{-}30\,°C]{Py} (C_6H_5O)_3P + Py{\cdot}HCl$$



Results and Discussion

Since pyridine is not a good solvent for polyaramides but is necessary for catalyst formation, the polycondensation of *p*-aminobenzoic acid (*p*-ABA) depends both on the concentration of monomer and the amount of pyridine. For a 0.4 M concentration of monomer, the necessary minimum amount of pyridine is 20% (1:4 v/v, pyridine/NMP Table I). Table II shows the effect of monomer concentration in this polycondensation reaction; the highest viscosity being obtained at 0.40 M (11%). Optimum conditions for the polycondensation reaction between isophthalic acid and aromatic diamines were obtained under the same conditions but with 50% pyridine (Table III). In each case the temperature of the reaction was increased slowly from 80–90 (2 h) to 100–105 °C, where it was held for 4 h. Temperatures higher than 100-105 °C did not improve the viscosity.

The positive influence of 3–4% lithium chloride in polycondensation reactions of aromatic polyamides is well-known.[2,3,5,6] In these reactions, low viscosities were obtained without lithium chloride, since early precipitation of the polymer occurred. Polymers 4–7 (Table IV) are lower in molecular weight, since they precipitated from the reaction solution as a result of their rigid structure.

Thus, polyamidation can be carried out simply by forming triphenylphosphite in situ. It is not necessary to isolate this

Table I
Effect of Pyridine in the Polycondensation Reaction of p-ABA[a]

Pyridine, mL (%)	NMP, mL	η_{inh}[b]
30 (60)	20	1.05
20 (40)	30	1.00
10 (20)	40	1.64
5 (10)	45	1.18

[a] Monomer concentration 0.4 M; 4 wt % LiCl. [b] H_2SO_4 at 25 °C.

Table II
The Effect of Monomer Concentration on the Polycondensation Reaction of p-ABA[a]

Solvent, mL	Monomer concn, mol/L (wt %)	η_{inh}[b]
60	0.33 (9)	1.39
50	0.40 (11)	1.64
40	0.50 (14)	1.45

[a] NMP/Py = 40/10 (vol), 4 wt % LiCl added. [b] H_2SO_4 at 25 °C.

Table III
Effect of Pyridine in the Polycondensation Reaction of Isophthalic Acid with p-Phenylenediamine[a]

Pyridine, mL (%)	NMP, mL	η_{inh}[b]
20 (50)	20	1.11
15 (37.5)	25	0.89
10 (25)	30	0.72

[a] Monomer concentration 0.5 M in NMP–pyridine with 4 wt % LiCl added. [b] H_2SO_4 at 25 °C.

catalyst since the pyridine hydrochloride by-product apparently does not affect the reaction. The success of this reaction in the synthesis of high molecular weight polymers requires, however, that the polyamides have good solubility in the solvent system.

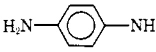
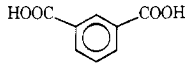
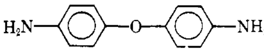
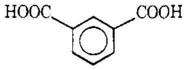
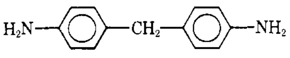
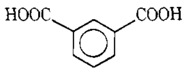
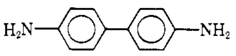
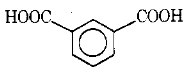
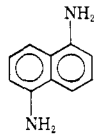
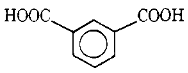
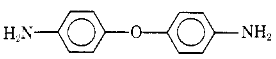
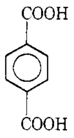
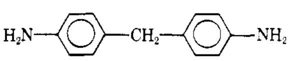
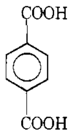
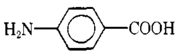
Experimental Section

The following materials were used: p-aminobenzoic acid was recrystallized from water; 4,4′-diaminodiphenyl ether, 1,5-diaminonaphthalene, and benzidine were recrystallized from ethanol; while 4,4′-diaminodiphenylmethane was recrystallized from benzene, all under nitrogen. Isophthalic acid was recrystallized from ethanol and terephthalic acid from acetic acid. NMP was freshly distilled from P_2O_5 and pyridine from KOH.

Polycondensation Reaction of p-Aminobenzoic Acid (p-ABA). To a stirred solution of 6.00 g (0.063 mol) of phenol in 10 mL of pyridine under nitrogen and cooled to 0 °C was added 1.75 mL (0.020 mol) of PCl_3. The mixture was stirred 1 h at room temperature under nitrogen then 2.742 g (0.0200 mol) of p-ABA, 2 g (4%) of LiCl, and 40 mL of dry NMP were added with stirring. This mixture was heated gradually for 2 h at 80–90 °C and then 4 h at 100–105 °C under nitrogen with stirring. The mixture was allowed to cool and the warm solution (60–80 °C) was slowly poured into a large volume of methanol (300 mL) with vigorous stirring. The fibrous white polymer was collected by filtration, washed well with methanol (3–4 times), and dried at 100 °C under reduced pressure.

General Procedure for the Preparation of Polyamides 1–8. To the reagent prepared under the same conditions in the presence of 20 mL of pyridine was added 1.661 g (0.01 mol) of isophthalic or terephthalic acid, 0.01 mol of aromatic diamine, 1.6 g (4%) of LiCl, and 20 mL of NMP. The polymers were precipitated by the work-up described above.

Table IV
Synthesis of Aromatic Polyamides by Means of Triphenyl Phosphite Prepared "in situ"[a]

	Diamine	Dicarboxylic acid	η_{inh}[b]
1.			1.11
2.			0.89
3.			0.96
4.			0.35
5.			0.48
6.			0.24
7.			0.3
8.			1.69

[a] [Monomer] = 0.4; solvent, NMP/Py = 20/20 (v/v) for all experiments, except 8, for which 40/10 was used; temperature = 2 h at 80–90 °C and 4 h at 100–105 °C; monomer/PCl_3/phenol = 1 mol/1 mol/3 mol + 6% excess. 4 wt% LiCl added. [b] H_2SO_4 at 25 °C.

Table V
The Elementary Analysis for the Polymers in Table IV

	C, %	H, %	N, %
1 Calcd	70.58	4.23	11.75
Found	69.49	4.14	11.09
2 Calcd	72.71	4.27	8.47
Found	72.09	4.42	8.34
3 Calcd	75.93	5.09	8.85
Found	74.77	4.92	8.35
8 Calcd	67.28	4.70	13.08
Found	66.33	4.63	13.17

Acknowledgment. This research was supported in part by a grant from the Army Research Office, Research Triangle, N.C.

References and Notes

(1) Senior Fullbright-Hays Scholar, U.S.–Romania.
(2) S. L. Kwolek, U.S. Patent 3 671 342; T. I. Bair and P. W. Morgan, U.S. Patent 3 673 143 (1972).
(3) M. Yamazaki, M. Matsumoto, and F. Higashi, *J. Polym. Sci., Polym. Chem. Ed.* **13**, 1373 (1975).
(4) British Patent, 1 383 480 (1973); *Chem. Abstr.*, **83**, 115, 715t (1975).
(5) German Offen, 2 460 941 (1975); *Chem. Abstr.*, **83**, 164, 847w (1975).
(6) S. L. Kwolek and P. W. Morgan, U.S. Patent 3 063 966 (1962).