538 *Macromolecules* 1988, *21*, 538–540

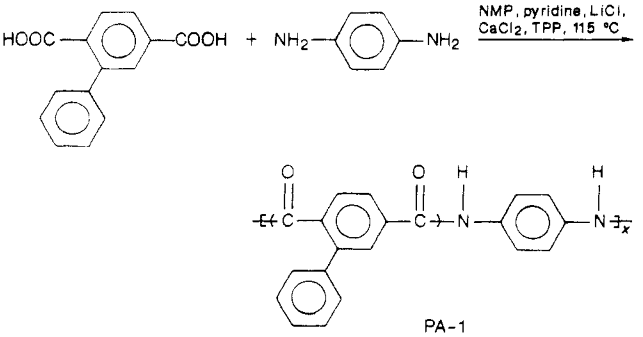
Novel Phenyl-Substituted Aromatic Polyamides

Since the commercial development of ultrahigh modulus Kevlar fiber from a lyotropic solution in concentrated sulfuric acid, the need for a para-oriented wholly aromatic polyamide soluble in organic solvents has become evident. Solubility is an extremely important factor in making anisotropic solutions of appropriate concentrations to achieve good fiber properties. Although there are several ways to increase the solubility of wholly aromatic polyamides, the unsymmetrical substitution on the benzene ring is better because rigidity, flexibility, solubility, and hydrogen bonding can be controlled with the use of a proper substituent.

The literature contains several examples of polyamides with methyl or chloro substitution, but in every case the degree of polymerization, as indicated by the inherent viscosity, is apparently adversely affected.[1-3] For example, Bair, Morgan, and Killian[4] have prepared a polyamide having inherent viscosity 2.01 dL/g in concentrated sulfuric acid by reacting 2-chloro-1,4-phenylenediamine with terephthaloyl chloride. By contrast, they reported an inherent viscosity of 6.93 dL/g when there was no chloro substituent. The polyamide with a chloro substituent was soluble up to 12% in dimethylacetamide (DMAc) containing 4% LiCl and forms an anisotropic solution. Very recently Rogers and co-workers[5,6] have made elegant attempts to prepare a para-linked polyamide using double substitution on the 2,2′-positions on the biphenyl rings of polyamides. These polymers have high solubility in organic solvents, but none of them forms an anisotropic solution due to the noncoplanar structures.[7]

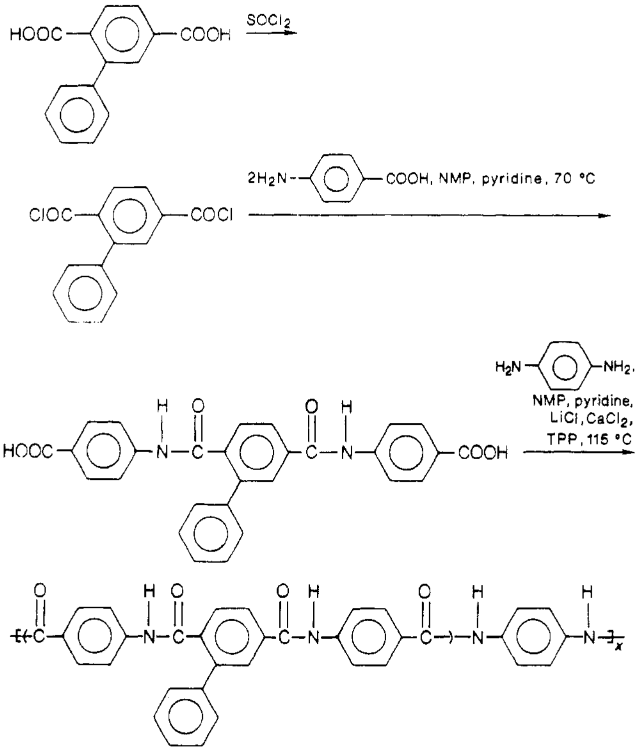
The patents of Payet[8] and Harris[9] have disclosed that introduction of a phenyl substituent in A–A + B–B aromatic polyesters is very effective in lowering the melting temperature. Krigbaum, Hakemi, and Kotek[10] have compared the efficiency of various substituent groups on the benzene rings of aromatic polyesters in depressing the crystal–nematic transition temperature. They concluded that a phenyl substituent is the most effective due to its bulkiness and degrees of rotational freedom. We therefore assumed that a phenyl substituent will be effective in increasing the solubility of rigid-rod aromatic polyamides, and two types of aromatic polyamides were prepared which will be described briefly below.

Synthesis of Phenyl-Substituted Aromatic Polyamides. 1. Phenyl Substituent Ortho to the Carbonyl Group. The first example of this class is prepared by reacting phenylterephthalic acid[11] with *p*-phenylenediamine by using Higashi's phosphorylation reaction,[12] pyridine and *N*-methyl-2-pyrrolidone (NMP) as a solvent and triphenyl phosphite (TPP) as a catalyst. This polyamide, PA-1, is similar to Kevlar except for the phenyl substituent ortho to the carbonyl group. Its inherent viscosity (Table I) in DMAc is only 1.10 dL/g. As shown in the fifth column of Table I, it is soluble up to 50% in DMAc containing 4% LiCl but does not form a liquid-crystal solution. We also tried the acid chloride + diamine route to prepare this polymer but obtained almost the same inherent viscosity. The low inherent viscosity is probably due to the bulky phenyl group which hinders reaction of the adjacent carboxylic group.



PA-1

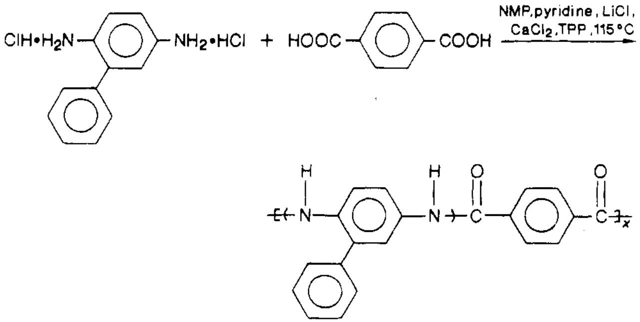
These problems can be overcome by using a monomer having preformed amide groups which enclose the less reactive acid group.



PA-2

This polyamide has a randomly positioned phenyl substituent ortho to the carbonyl on every fourth ring. Its inherent viscosity in DMAc containing 4% LiCl is 7.55 dL/g, and the maximum solubility in that solvent is 18%. The inherent viscosity in sulfuric acid is 3.28 dL/g. Light scattering measurements[13] gave a persistence length of about 150 Å. This polyamide contains 50 mol % of poly(*p*-benzamide), for which the experimental values of the persistence length range from 400 to 700 Å. We conclude that a phenyl substituent on every fourth ring is responsible for the greater flexibility. The phenyl substituent forces the adjacent carbonyl out of the plane of the ring, destroys the conjugation of the amide group with the aromatic ring, and creates a flexible link.

2. Phenyl Substituent Ortho to the Amino Group. The first example of this class is prepared by polymerizing 2,5-diaminobiphenyl hydrochloride[14] with terephthalic acid by the phosphorylation reactions:



PA-3

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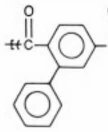
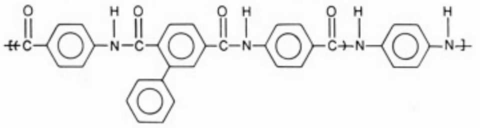
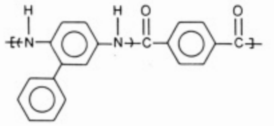
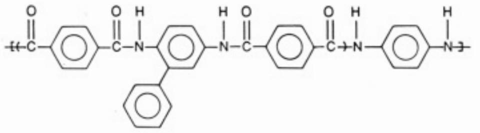
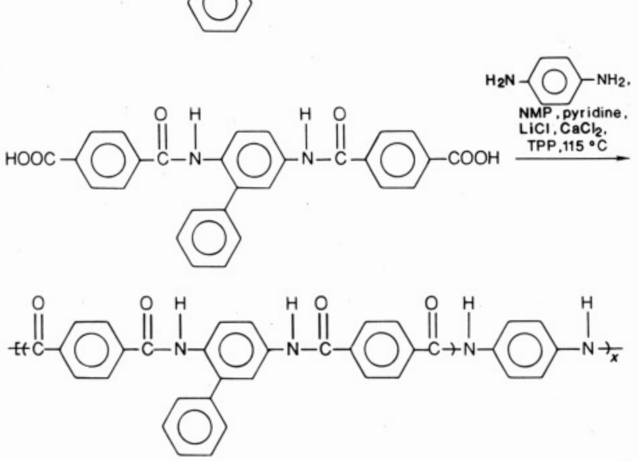
Table I
Phenyl-Substituted Aromatic Polyamides Synthesized[a]

code	repeating unit	inherent viscos η_{inh},[b] dL/g		solubil in DMAc or NMP, g/100 g[d]
		H_2SO_4[c]	DMAc[d]	
PA-1		0.61	1.10	50
PA-2		3.28	7.55	18
PA-3		1.45	2.52	20
PA-4		2.28	3.32	14–15

[a] All polymers prepared by the phosphorylation method. [b] 0.5% concentration at 25 °C. [c] 96% H_2SO_4. [d] Containing 4% LiCl.

This polymer, except for the phenyl substituent, is poly(*p*-phenylenediamine-*co*-terephthalic acid). It has an inherent viscosity of 2.52 dL/g in DMAc containing 4% LiCl and 1.45 dL/g in sulfuric acid. The solubility in DMAc/4% LiCl is 20%. It may form an anisotropic solution, but we have not as yet determined the critical concentration. We were able to maintain nearly the same solubility, while reducing the phenyl substitution, in the following polyamide. The diester monomer 2,5-bis(4-(methoxycarbonyl)benzoylamino)biphenyl was prepared by reacting 2,5-diaminobiphenyl with 4-(carboxymethoxy)benzoyl chloride.[15] This polyamide, PA-4, also resembles poly(*p*-phenylenediamine-*co*-terephthalic acid) except for the one phenyl substituent every fourth ring. Alternatively, every other *p*-phenylenediamine ring bears a phenyl substituent. The inherent viscosity of PA-4 in DMAc containing 4% LiCl is 3.32 and 2.28 dL/g in sulfuric acid. Its solubility in DMAc/4% LiCl is 14–15%. PA-4 forms a nematic solution at 10% wt/wt concentration in DMAc or NMP, both containing 4% LiCl. As shown in Figure 1, this solution exhibits characteristic nematic texture. Its solubility is due to the bulky phenyl group and the randomness introduced by the copolymer effect. The phenyl substituent ortho to the carbonyl, as compared to a phenyl substituent ortho to the amino group, is more effective in increasing solubility, but it also creates a more flexible chain.



PA-4

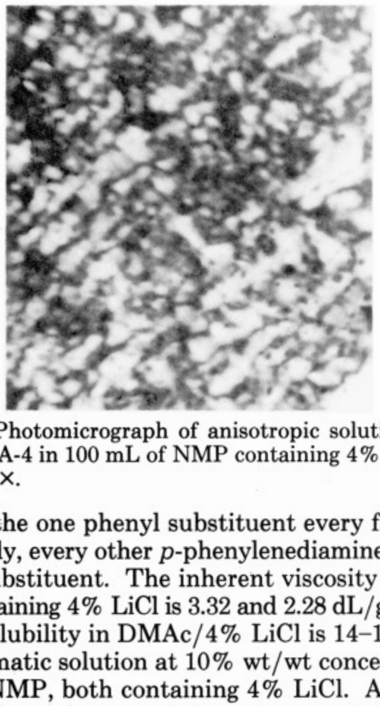


Figure 1. Photomicrograph of anisotropic solution (10 g of polyamide PA-4 in 100 mL of NMP containing 4% LiCl), magnification 63×.

The phenyl substituent not only makes the aromatic polyamides more soluble, it also depresses the melting temperature. To our knowledge, this is the first report which discloses melting transitions for wholly aromatic para-linked polyamides without substitution on nitrogen. The melting temperature and the thermal degradation temperature, both determined by DSC, are summarized for the four substituted polyamides in Table II. Aromatic polyamides without substituents decompose before reaching the melting temperature or decompose upon

Table II
Thermal Characteristics of Phenyl-Substituted Polyamides Determined by DSC[a]

	temp, °C			temp, °C	
code	T_M	PDT[b]	code	T_M	PDT[b]
PA-1	430	500	PA-3	475	510
PA-2	344, 497	520	PA-4	440, 500	530

[a] Heating rate 10 °C/min under nitrogen. [b] Polymer degradation temperature determined from DSC exotherm.

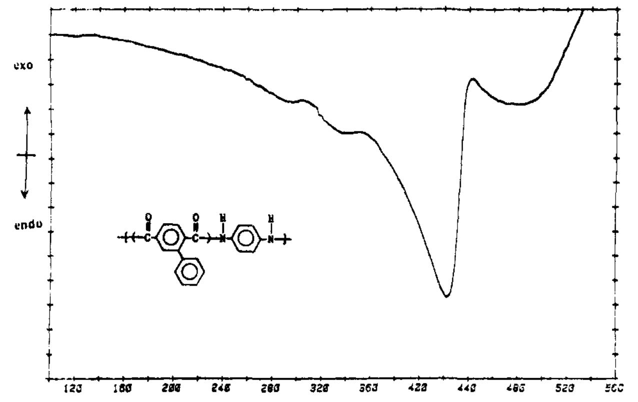


Figure 2. DSC heating curve (10 °C/min) for polyamide PA-1.

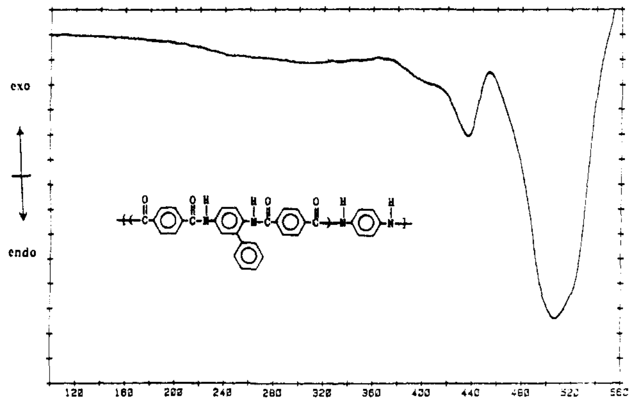


Figure 3. DSC heating curve for polyamide PA-4.

melting. Figure 2 illustrates the clear melting of polyamide PA-1. For the other three substituted polyamides, melting is followed by degradation. Polyamides PA-1 and PA-3 have a single melting transition, indicating only one crystalline form. Polyamides PA-2 and PA-4 exhibit two melting transitions, representing two crystalline polymorphs. A typical DSC thermogram for polyamide, PA-4 is given in Figure 3.

Full details of the monomer synthesis and polymerization procedures will be given in the next publication.

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Registry No. PA-1 (copolymer), 112196-94-8; PA-1 (SRU), 112269-88-2; PA-2 (copolymer), 112196-96-0; PA-2 (SRU), 112269-87-1; PA-3 (copolymer), 112196-98-2; PA-3 (SRU), 112269-89-3; PA-4 (copolymer), 112197-00-9; PA-4 (SRU), 112269-86-0.

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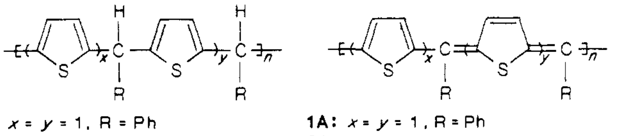
Bromine Treatment of Poly[α-(5,5′-bithiophenediyl)benzylidene] (PBTB) and Poly[α-(5,5′-bithiophenediyl)-*p*-acetoxybenzylidene] (PBTAB): A Complex Reaction

In a series of papers dealing with a clever way to implement current theoretical models for the design of degenerate ground-state conducting polymers, it was claimed that polymers **1**–**4** could be dehydrogenated by treatment with bromine vapor to low-gap polymeric semiconductors with E_g as low as 0.75 eV.[1-3] The bromination of thin films was followed by electronic and FTIR spectroscopy but no NMR experiments nor elemental analyses were mentioned.[2,3] It was also concluded that since there were no peaks due to C–Br stretching in the 500–650-cm^{-1} region, no electrophilic substitution had taken place. The products were postulated to have the general structures **1A**–**4A**[1] and more specifically structure **3A**[2,3] shown below.



1: $x = y = 1$, R = Ph
2: $x = y = 2$, R = Ph
3: $x = y = 2$, R = p-$CH_3C(O)OC_6H_4$
4: $x = y = 3$, R = Ph

1A: $x = y = 1$, R = Ph
2A: $x = y = 2$, R = Ph
3A: $x = y = 2$, R = p-$CH_3C(O)OC_6H_4$
4A: $x = y = 3$, R = Ph

In this paper we report that the reaction of both PBTB (**2**) and PBTAB (**3**) with bromine vapor depends on the phase (solid–gas versus solution–gas), and the product of either reaction condition is not the simple dehydrogenated product reported before but a brominated material containing covalently bonded as well as ionic halogen. Once the bromination product of **2** is reduced with hydrazine to remove the dopant bromide, it exhibits a bandgap of 1.53 eV (presumably dehydrogenated, partially brominated material) and not 0.83 eV as claimed before.[1-3]

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