Synthesis of Aromatic-Aliphatic Copolyamides

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Summary: Copolyamides were obtained by reacting para-aminobenzoic acid (ABA) and 6-aminohexanoic acid (AHA) by condensation in different molar ratios.

It has long been known that the incorporation of aromatic rings in linear polymers yield higher-melting, stiffer and more dimensionally stable polymers than does the incorportation of comparable amounts of aliphatic units¹. In the present paper the synthesis of a new type of aromatic-aliphatic copolyamides from paraaminobenzoic acid (ABA) and 6-aminohexanoic acid (AHA) has been reported whose light scattering and dilute solution behavior have been published elsewhere^{2,3}. The polycondensation is carried out in the presence of triphenyl phosphite in N-methyl-2 pyrrolidone (NMP)/ pyridine mixture, containing 3 wt.% LiCl by the method of Yamazaki et al4. Because of the low solubility of copolyamides, the polycondensation reaction terminates quickly and results in low molecular weight products. In order to do away with this problem, the polycondensation is carried out in the presence of LiCl5,6

Experimental

Copolyamides were obtained by reacting paraaminobenzoic acid (ABA) and 6-aminohexanoic acid (AHA) in four different molar ratios of 90:10, 70:30, 50:50 and 30:70 respectively. The copolyamides were synthesized by polycondensing para-aminobenzoic acid (ABA) and 6-aminohexanoic acid (AHA) in the presence of triphenyl phoshite in N-methyl-2-pyrrolidone (NMP)/ pyridine (Vol. ratio 80:20) solution containing 3 wt.% LiCl. The reaction mixture was heated at 80°C for 8 hours, with constant stirring under the atmosphere of nitrogen. The reaction is supposed to proceed via the N-phosphonium salts of pyridine followed by aminolysis⁴.

The copolymerization suspension was then poured into a large amount of ethanol to precipitate the resultant copolymer. The copolymer in the form of powder was washed using soxhlet extraction equipment to remove the polymerization solvents and the by-product thoroughly.

Viscosity measurements were made on solutions of copolyamides in conc. H2SO4, using Ubbelhode-type viscometer, in the concentration range of 0.1 to 0.5 g/dl at 25°C. IR spectra of the copolyamides were taken by using a JASCO IR-G spectrometer while NMR spectra of the copolyamides solution in concentrated H₂SO₄ were recorded on a JNM-PMx 60 spectrometer. Crystallization from dilute solution in solvent - nonsolvent system at room temperature was studied by mixing the solution of copolyamides (0.05%) in N,N-dimethylacetamide (DMA) containing 3% LiCl, with propionic acid. The suspension was washed with ethanol several times to remove the crystallization solvents. The suspension was spread on a carbon-coated copper sheet mesh, Pt-Pd shadowed and then observed in the electron microscope, model JEM-7 of Japan Electron Optics Laboratory.

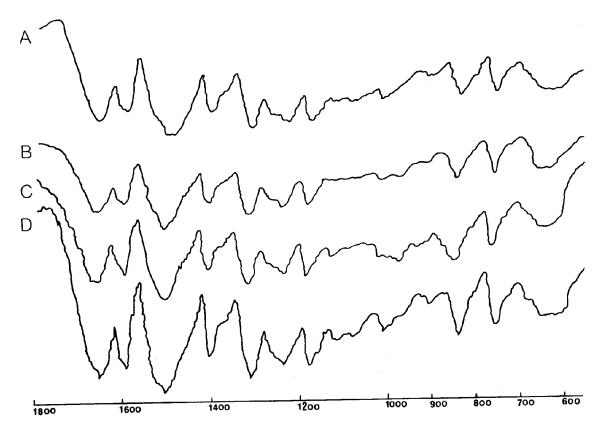
$$P(OC_6H_5)_3 + H_2NC_6H_4 COOH \xrightarrow{NMP/Pyridine} 3\% LiCl$$

$$H = P = O - CO \xrightarrow{NH_2} AHA \longrightarrow HNC_6H_4CO.NH(CH_2)_5CO$$

$$+ C_6H_5OH + OH - P - (OC_6H)_2$$

Table I. Intrinsic Viscosity and Percent Yield of Copolyamides From p-aminobenzoic acid and 6-aminohexanoic acid

Charged ratio (ABA)/(AHA)	experimentally determined ratio (ABA)/(AHA)	Yield Percent	(η 25°) Η ₂ SO ₄ (Conc.)
90/10	82/18	77.1	0.159
70/30	78/22	74.3	0.166
50/50	64/36	7 7.9	0.174
30/70	32/68	81.9	0.183



wavenumber (cm^{-1})

Figure 1. IR Spectra of Copolyamides From ABA and AHA. Molar Ratio [ABA]/[AHA]: (A) 90/10; (B) 70/30; (C) 50/50; (D) 30/70.

Results and Discussion

The intrinsic viscosity, η , and percent yield of copolyamides of four different compositions are shown in Table I. Molar ratio of (AHA) to (ABA) has a decisive influence on the molecular weight of copolyamides as evident from the increase in the η with increase in

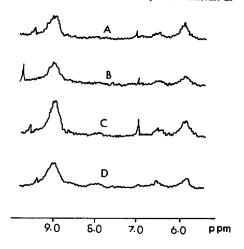


Figure 2. NMR Spectra of Copolyamides From ABA and AHA. Molar Ratio [ABA]/[AHA]: (A) 90/10; (B) 70/30; (C) 50%50; (D) 30/70.

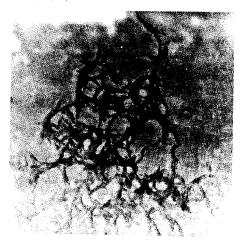


Figure 4. Electron Micrograph of Copolyamide From [ABA]/[AHA]: 90/10 Grown From 0.5% Solution in DMA (contg. 3% LiCl)/Propionic Acid in the Ratio of 70:30 X 43,000.

the molar ratio of (AHA). It is also evident from Table I that an increase in the molar ratio of (AHA) to (ABA) increase the yield which is not very consistent.

Spectra of some aromatic polyamides have been published by Mark et al⁷, though the observed absorptions in the 1200-600 cm⁻¹ range were largely too weak to be useful. The IR spectra of the copolyamides from



Figure 3. Electron Micrograph of poly (p-benzamide) Formed From 1% Solution in DMA (contg. 3% LiCl)/water. X 75,000.

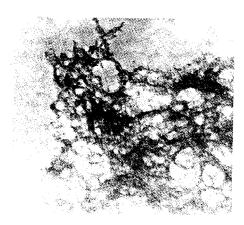


Figure 5. Electron Micrograph of Copolyamide From [ABA]/[AHA]: 50:50 Grown From 0.5% Solution in DMA (contg. 3% LiCl)/Propionic Acid in the Ratio of 50:50. X 43,000.

Table II. Solubility of copolyamides in N,N-dimethylacetamide (DMA cntg. 3% LiCl)/Propionic Acid (PA)			
Mixture at 25 ⁰ C. Copolymer conc. in DMA is 0.05%.			

(ABA)/(AHA)	Solvent Composition DMA/PA in vol. ratio				
	90/10	70/30	50/50	10/90	
90/10	_	+	+	+	
70/30	_	+	+	+	
50/50	_	_	+	+	
30/70	_		+	+	

(ABA) and (AHA) are shown in Figure 1. Strong absorption at 1650 cm⁻¹ is the band characteristic of the amide group, associated with stretching of the C=0 bond. Absorption bands at 840-750 cm⁻¹ are indicative of aromatic rings, bearing both -NH and -CO groups at para position. The strong absorption peaks at 1500-1150 cm⁻¹ are due to -CH₂ groups. The absorption peaks at 3000-2500 cm⁻¹ due to -COOH group in both the monomers are absent in the copolyamides. The complexity of the spectra of aromatic-aliphatic copolyamides means that the above tentative assignments may be used as preliminary guidelines but are not meant to be the sole basis of structural identification.

The NMR spectra of a series of copolyamides dissolved in conc. H₂SO₄ are shown in Figure 2. Three main peaks are observed. Evidently, the resonance peak at about 9ppm comes from the phenyl protons, that at and 6 ppm from -CH₂ protons. The copolymer compositions have been estimated from the relative peak areas of phenyl and methylene proton resonances, with the results given in Table I. The mole fractions of ABA in copolymer estimated from these peaks are in good accord with those of the charged monomers.

In order to study the morphology of copolyamides from aliphatic and aromatic amino acids, the crystallization was carried out from solutions of DMA (3% LiCl)/propionic acid at 25°C. The rate of crystallization was observed as a function of the solvent composition. The results are summarized in Table II. The rate of crystallization decreased with decreasing mole fraction of ABA. Also the higher the amount of non-solvent, the higher the rate of crystallization and hence the amount of precipitates.

In the crystallization of aliphatic polyamides such as nylon 6 from solution and its melts, chain-folded crystals are usually obtained⁸. On the other hand, the aromatic polyamides such as poly (p-benzamide) are so

rigid that they are rod-like molecules even in solutions ^{9,10,11}. The Copolyamides therefore, do not seem to give chain-folded crystals. A typical electron micrograph of poly-(p-benzamide) crystal grown from 1% solution in DMA (3% LiCl)/water is shown in Figure 3. The morphology of copolymer crystals is different from that of poly (p-benzamide), as is evident from Figure 4 and 5. The morphological differences may be due to different molecular rigidities between the homopolymer and copolymer. The electron microscopic studies show that the amount of lamella-crystals increases with increasing AHA fraction in the copolymer and also with increasing DMA fraction in the mixed solvent.

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