



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	( $\eta$ 25°) H <sub>2</sub> SO <sub>4</sub> (Conc.)
90/10	82/18	77.1	0.159
70/30	78/22	74.3	0.166
50/50	64/36	77.9	0.174
30/70	32/68	81.9	0.183

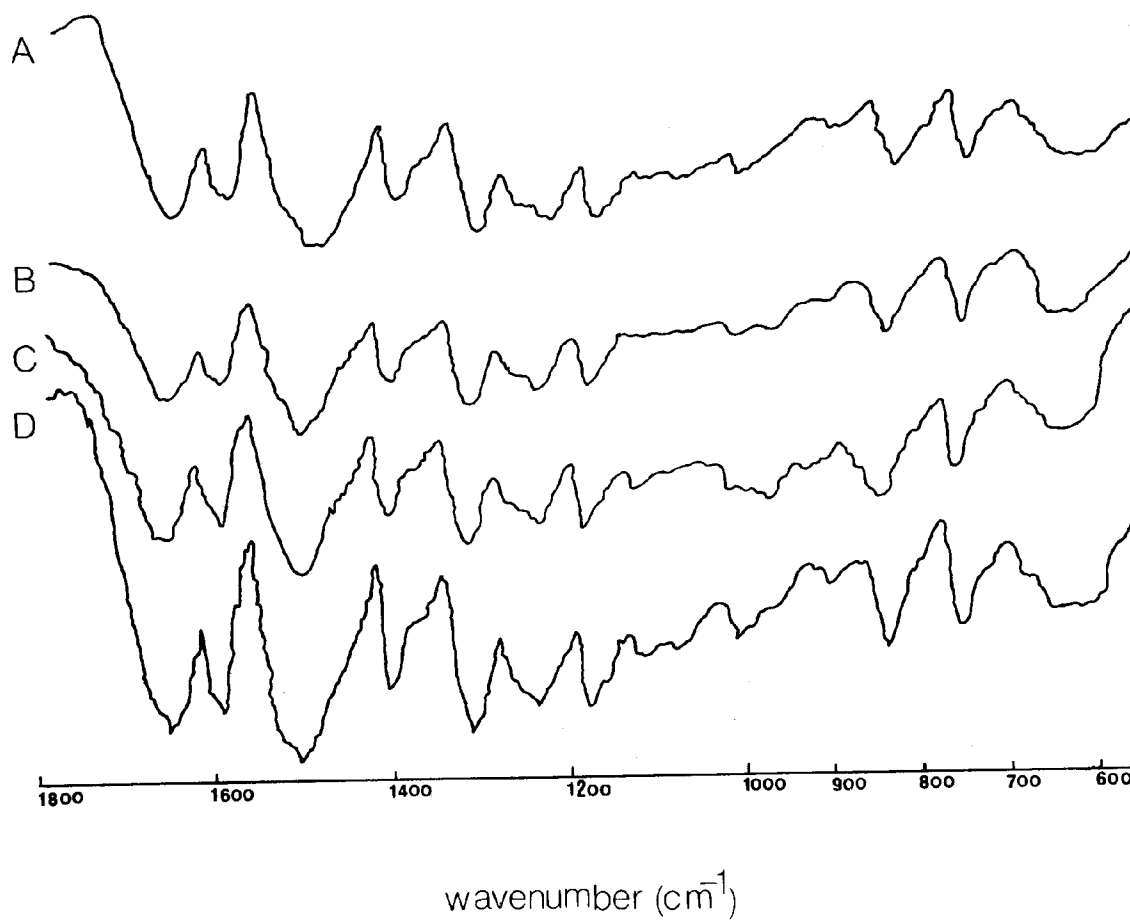


Figure 1. IR Spectra of Copolyamides From ABA and AHA. Molar Ratio [ABA]/[AHA]: (A) 90/10; (B) 70/30; (C) 50/50; (D) 30/70.

### Results and Discussion

The intrinsic viscosity,  $\eta$ , 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  $\eta$  with increase in

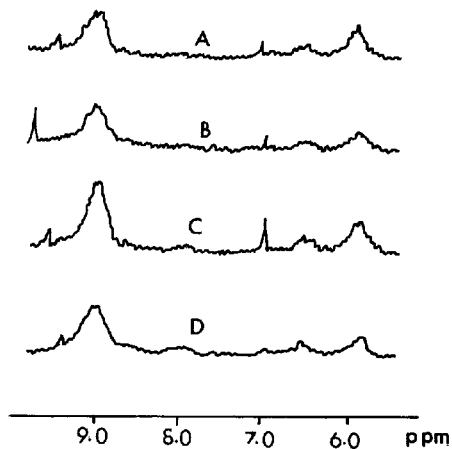


Figure 2. NMR Spectra of Copolyamides Formed From ABA and AHA. Molar Ratio [ABA]/[AHA]: (A) 90/10; (B) 70/30; (C) 50/50; (D) 30/70.

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 al<sup>7</sup>, though the observed absorptions in the 1200-600  $\text{cm}^{-1}$  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.

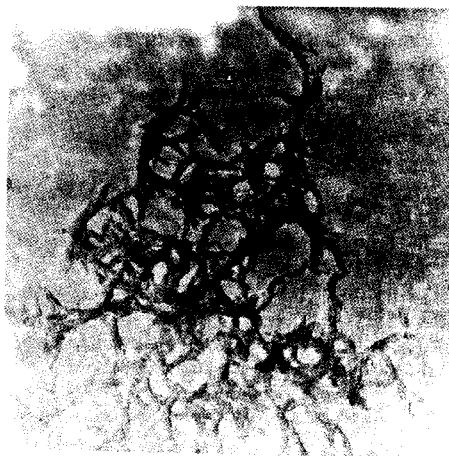


Figure 4. Electron Micrograph of Copolyamide From [ABA]/[AHA]: 90/10 Grown From 0.5% Solution in DMA (contg. 3% LiCl)/Propionic Acid in the Ratio of 70:30 X 43,000.

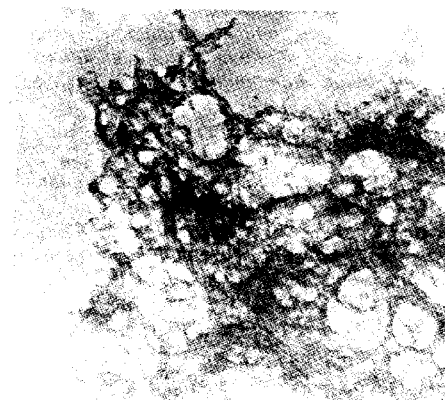


Figure 5. Electron Micrograph of Copolyamide From [ABA]/[AHA]: 50/50 Grown From 0.5% Solution in DMA (contg. 3% LiCl)/Propionic Acid in the Ratio of 50:50. X 43,000.

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

Molar Ratio (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	—	—	+	+

+ : Precipitation  
— : No precipitation

(ABA) and (AHA) are shown in Figure 1. Strong absorption at 1650  $\text{cm}^{-1}$  is the band characteristic of the amide group, associated with stretching of the C=O bond. Absorption bands at 840-750  $\text{cm}^{-1}$  are indicative of aromatic rings, bearing both -NH and -CO groups at para position. The strong absorption peaks at 1500-1150  $\text{cm}^{-1}$  are due to -CH<sub>2</sub> groups. The absorption peaks at 3000-2500  $\text{cm}^{-1}$  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. H<sub>2</sub>SO<sub>4</sub> 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 -CH<sub>2</sub> 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 obtained<sup>8</sup>. On the other hand, the aromatic polyamides such as poly (p-benzamide) are so

rigid that they are rod-like molecules even in solutions<sup>9,10,11</sup>. 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.

#### References

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