

Rigid Backbone Polymers. XVI. Random Copolyamides

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Synopsis

Several homologous families of random copolyamides containing aromatic rigid elements and aliphatic or aralkyl flexible elements were prepared and characterized. Lyotropic liquid crystallinity was observed in all such polymers where over 50% of the aromatic residues belonged to rigid elements whose axial ratio surpassed a critical value of $5 < x < 6$. The point where $5 < x < 6$ is reached depends on the nature of the flexible comonomers. The higher their basicity or flexibility, the higher the concentration of rigid monomers in the copolymer at the point of $5 < x < 6$. In concentrated ternary systems of polymer 1/polymer 2/solvent, a single anisotropic phase containing both polymers can be obtained when each polymer can form an anisotropic solution in the solvent. When either polymer is too flexible to form an anisotropic solution by itself, it will then separate from the ternary system into an isotropic phase, leaving the more rigid polymer in the coexisting anisotropic solution.

INTRODUCTION

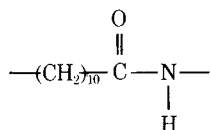
There appeared in the recent literature several examples of polymers exhibiting a well-defined thermotropic liquid crystalline behavior while containing in the main chain substantial amounts of both rigid and flexible elements.¹⁻⁵ This indicates that high backbone rigidity, approaching rodlike behavior, is too stringent a requirement and may be relaxed. A step in this direction was recently taken by Flory,⁶ who proposed from theoretical considerations that polymeric chains appearing as rods connected by flexible joints should behave as liquid crystals once the rodlike elements surpass a characteristic minimal length. Defined in terms of axial ratio x , the minimal length of the rodlike elements for anisotropy to appear in the bulk polymer occurs when the value of x is 6.70.⁶ A later, more exact treatment by Flory and Ronca⁷ yielded a critical value of $x = 6.417$ for the appearance of anisotropy in the neat mesogenic liquid. We assume that in cases of lyotropic mesomorphism of such polymers, the dilution will dictate that $x \geq 6.4$ for anisotropy to appear, and definitely not $x < 6.4$. In the following work an attempt will be made to experimentally test the value of x at the point when mesomorphic behavior becomes apparent.

There are two ways of determining the critical value of x . The first is through the synthesis of well-defined —*ABABAB*— copolymers whose alternating elements are rigid and flexible. By having the flexible elements *A* long enough to prevent direct interactions between two adjacent rigid elements *B*, and by changing the length of the rigid elements *B*, a homologous family of such polymers may be prepared with increasing x values of the rigid elements. From the known structure of the polymers showing mesomorphism, the critical value of x can be determined. In fact, in a forthcoming article in this series,⁸ the preparation and characteristics of such alternating copolyamides will be described.

The second approach useful in determining the critical value of x involves the preparation of random copolymers from rigid and flexible comonomers. By the change of the molar ratio of the comonomers in a series of copolymers, different average values of x can be obtained. The determination of these values of x may be performed by means of spectroscopy. The critical value of x is then obtained from the lyotropically or thermotropically mesomorphic random copolymer having the least amount of rigid residues in it. In this paper only the second approach is discussed.

For the sake of clarity, two flexible residues were studied. One such residue contained a single $-\text{CH}_2-$ group, forcing a turn of about 108° in the direction of the backbone per residue. Two monomers supplied such flexibility to the chain: *p*-aminophenylacetic acid producing the *p*-phenylacetamide residue, and *p*-carboxybenzylamine producing the *p*-benzylamide residue. Throughout this paper the rigid residues were *p*-benzamide ones, originating from *p*-amino benzoic acid. Homologous families of copolyamides were prepared with the composition of the comonomers changing in increments of 10 mole %. For clarity, the copolyamide families are denoted by Roman numerals followed by the mole % rigid comonomer and mole % flexible comonomer. Thus a copolymer of 70 mole % *p*-aminobenzoic acid and 30 mole % *p*-aminophenylacetic acid is denoted I, 70:30; and a copolymer of 90 mole % *p*-aminobenzoic acid and 10 mole % *p*-carboxybenzylamine is denoted III, 90:10.

Because a single $-\text{CH}_2-$ group attached to an aromatic moiety in a flexible element is not expected to allow a large measure of mobility to the rigid elements attached to it, a copolyamide family containing highly flexible elements was also prepared. In this family, denoted as family II, the flexible elements originate from ω -aminoundecanoic acid so that each flexible



element contains the highly mobile undecanoamide residue. The rigid elements consist of sequences of varying lengths of *p*-benzamide residues. Because of the high flexibility of the undecanoamide residues, it appears that copolyamides of family II may be closer than members of either family I or III to the theoretical rigid/flexible polymers envisioned by Flory.⁶

It was recently demonstrated by this author^{9,10} that highly concentrated solutions containing two rigid polyisocyanate polymers form a single anisotropic phase. This is in agreement with the prediction of Abe and Flory.¹¹ A part of the present work was directed, therefore, toward finding whether the observations above^{9,10} can be generalized to polymers such as random copolyamides, and at what level of chain flexibility blends of such polymers may start phase separating.

EXPERIMENTAL

Monomers and reagents were used as received. Solvents used for the synthesis were stored over molecular sieves. Solvents for light scattering were filtered through 220-nm millipore filters prior to use, and then again during sample

preparation. Concentrated sulfuric acid (96%) for dilute solution viscosity and ultraviolet (UV) studies, was used as received. All solvents were reagent grade or better.

The polymers were prepared following the procedure of Yamazaki et al.¹² using a solution of 5% (w/v) LiCl in *N,N*-dimethylacetamide (DMAc/5% LiCl) as the preferred solvent. In a typical run there were 100 ml DMAc, 5.0 g LiCl, and 50 ml pyridine mixed in a 500-ml r.b. flask equipped with a stirrer and a nitrogen inlet. The mixture was brought up to the desired polymerization temperature, within the 80–120°C temperature interval, and a complete dissolution of the LiCl effected. At that point a total of 0.1 mole monomers were introduced and dissolved, and 0.12 mole triphenyl phosphite added. The reaction was usually continued for two hours from the moment the triphenyl phosphite was added. For a given polymer composition, batches of decreasing molecular weight M were obtained by running the reaction for shorter durations. Precipitation or gelation commenced within a number of minutes depending mostly on the nature of the monomers present, and much less on the temperature at which the reaction was run. After the reaction was completed, the products were suspended in a large excess of methanol. When the product was in the form of a gel, it was comminuted in a blender and resuspended in methanol. After three thorough washings in methanol and two in acetone, the polymers were dried under vacuum at 115°C.

Dilute solution viscosities were determined using Cannon-Ubbelohde glass viscometers. The solvents were reagent grade concentrated (96%) H₂SO₄ for determinations at 25°C, and DMAc/5% LiCl for determinations at 25°C and at elevated temperatures. Concentrated solution viscosities were measured in DMAc/5% LiCl solutions by means of a constant shear rate Nametre Direct Readout Viscometer operating at about 4060 sec⁻¹. All dilute and concentrated solution viscosities at variable temperatures, were measured on DMAc/5% LiCl solutions. Once a solution reached apparent equilibrium, the viscosity values were the same, independent of whether the sample was in a heating or cooling cycle. The time to reach apparent equilibrium depended on the viscosity, ranging from minutes in dilute solutions to several hours in concentrated ones. In all instances where viscosities were measured at elevated temperatures (up to 150°C), the samples were allowed to cool to 25°C and their viscosity measured after 8 hr. In all cases the viscosity, after the heat cycle, was found to be, within experimental error, the same as the viscosity of the solution prior to heating.

Light scattering measurements were carried out with a Brice-Phoenix light scattering photometer, on dilute solutions of the random copolyamides in 96% H₂SO₄ or in DMAc/5% LiCl. Weight-average molecular weights M_w of several polymers were thus determined in the usual manner from Zimm plots of the light scattering data.

The molar composition of all copolyamides was determined by means of Varian T-60A proton NMR scans of isotropic solutions of the copolyamides [$< 5\%$ (w/v) concentration] in deuterated sulfuric acid. Within experimental error, there was no difference in the composition of different molecular weight batches of the same copolymer. A bias favoring the aliphatic content appeared in the NMR measurements with increased chain rigidity and polymer concentration in the scanned sample.

Room temperature and hot-stage cross-polarized light microscopy was con-

ducted using a Reichert microscope operating at $100\times$ magnification. Ultra-violet spectra were obtained from dilute solutions of the polymers in concentrated H_2SO_4 , using a Cary model 118CX spectrometer. The spectra were used to calculate the length of the aromatic amide rigid elements (poly-*p*-benzamide) containing no aliphatic residues. The assignments of the absorbance maxima were confirmed through the use of model compounds containing sequences of one, two, three, four, and longer phenylene rings attached to one another by amide bonds in the para position. In all nonpolymeric model compounds, the aromatic amide rigid elements were bracketed by aliphatic residues so that no free amine or acid existed in them. The sequence length compositions in the random copolyamides were calculated based on the linear absorbance of the two limiting homopolymers and a final correction for the relative absorbance of individual sequences extrapolated to constant concentration of all aromatic residues in each random copolyamide. All UV data were obtained under identical instrument conditions and samples concentration.

RESULTS

The Yamazaki et al.^{12,13} polymerization procedure, which we adopted for the purpose of this work, is extremely facile in that it proceeds at moderate temperatures and utilizes free amines and acids, eliminating the need for the acid chlorides necessary for low temperature polycondensations such as, the Schotten-Baumann reaction. In agreement with Yamazaki et al.¹² it was found in this work that the molecular weight of any given copolymer changes with the polymerization temperature, passing through a maximum at about 85°C . It was further found that the molecular weight of any copolyamide polymerized at any temperature T within the interval $80 < T < 135^\circ\text{C}$ reached its maximum within the first hour of polymerization and remained almost unchanged when the polymerization was continued isothermally for up to 6 hr.

While being very versatile, the Yamazaki polymerization procedure does not yield molecular weights sufficiently high to impart to the fabricated product commercially acceptable mechanical properties.¹⁴ Because of this, it was suggested by Preston and Hofferbert¹⁴ that the Yamazaki procedure be used in screening and preliminary polymerizations, and polymers meant for commercialization be prepared by Schotten-Baumann-type polymerizations. The results of the present work support the above suggestion.

Polymers belonging to families I, II, and III were prepared with 10 mole % incremental changes in their composition. Mass balance indicated the yields to be over 90% of theory in all cases, and approaching 100% in most of them. The minor decreases in yield appeared to go hand-in-hand with the increases in the comonomers other than *p*-aminobenzoic acid. When performed on dilute solutions (< 5%), NMR scans yielded polymer compositions reasonably close to the feed compositions. For instance, the compositions of I, 80:20 and I, 50:50 were found by NMR to be 84:16 and 54:46, respectively, and those of II, 70:30 and II, 60:40 were determined by NMR to be 68:32 and 57:43, respectively. Hence, for the purpose of this study, it was assumed that there exist no gross deviations in the molar composition of the polymers from the molar composition of the feedstock.

The intrinsic viscosity $[\eta]$ of the polymers was moderate, indicating a modest

molecular weight M . A typical behavior of $[\eta]$ as a function of polymer composition is shown in Figure 1. Here members of families I, II, and III, all polymerized at 100°C for 2 hr after the addition of the triphenyl phosphite, show a drop in $[\eta]$ as the mole % *p*-benzamide residues decrease. The change of viscosity with composition may reflect two things: (a) the value of $[\eta]$ drops with decreased rigidity, and (b) the monomers containing aliphatic amine are more basic and do not undergo polymerization readily, resulting in decreased degree of polymerization as a function of the concentration of these monomers. The slight rise in the viscosity of the two members of family II richest in undecanoamide residues is not understood at present.

Light scattering experiments were performed on three members of family I: I, 90:10, I, 70:30, and I, 50:50. It was found that the polymers rich in rigid residues, I, 90:10 and I, 70:30, tended to form molecular aggregates in DMAc/5% LiCl. These aggregates appeared to be immune to heating at $\sim 85^\circ\text{C}$ for several hours. Therefore, the light scattering measurements of I, 90:10 and I, 70:30 were repeated in 96% H_2SO_4 solutions obtained by shaking the pulverized polymer in the acid for 16 hr at ambient temperature. The light scattering data were plotted in the conventional Zimm plots and the values of M_w thus obtained are tabulated with the corresponding intrinsic viscosities in Table I. The number of samples studied by light scattering, and the span of $[\eta]$ covered by them, were too small for a determination of the magnitude of the coefficient a in the Mark-Houwink equation $[\eta] = KM^a$ relating $[\eta]$ to M . Therefore, a direct measure of the polymers' backbone rigidity, as obtained from the size of coefficient a , was not feasible. However, to demonstrate that the main chain of polymers of family I is rather rigid down to I, 50:50, the M_w values of nylon 6 in acidic solutions were calculated according to the Mark-Houwink relationship of nylon 6 appearing in the literature,¹⁵ for $[\eta]$ values corresponding to those actually measured for our copolyamides. The large M_w values obtained for the flexible polyamide M_w

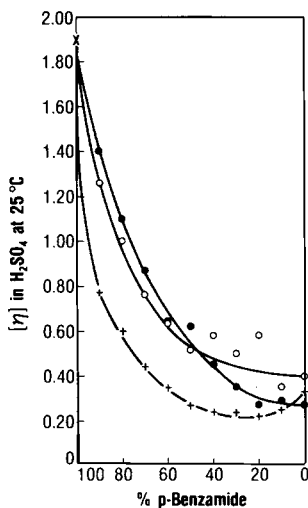


Fig. 1. Intrinsic viscosity vs. % *p*-benzamide residues in random copolyamides: Family I (●); family II (+); family III (○). [The intrinsic viscosity of I, 0:100 is in good agreement with the inherent viscosity reported for the same polymer by J. Preston and W. L. Hofferbert, Jr., *J. Polym. Sci. Polym. Symp.*, **65**, 13 (1978).]

TABLE I
 Characteristics of Four Polyamides

Polyamide	$[\eta]$ in H ₂ SO ₄ (dl/g)	M_w	M_w of nylon 6 ^b of same $[\eta]$
I, 90:10 ^a	1.55	15,400	60,200
	1.05	9,250	36,500
	0.75	8,000	23,700
I, 70:30 ^a	1.05	13,300	36,500
	0.83	8,900	27,000
	0.70	8,000	21,700
I, 50:50 ^c	0.62	7,500	18,600
I, 100:0 ^d	2.08	11,700	87,700
	1.62	10,400	63,650
	1.21	7,250	43,800
	0.88	6,800	29,100
	0.46	5,300	12,700

^a Light scattering data obtained from solutions in concentrated H₂SO₄. Batches with decreasing viscosities were obtained by running the polymerizations for shorter durations.

^b In concentrated H₂SO₄, ref. 15.

^c Light scattering data obtained from solutions in DMAc/5% LiCl.

^d In concentrated H₂SO₄, ref. 16.

values of our copolyamides of the same intrinsic viscosities, indicate that the backbone rigidity of the copolyamides of family I is far higher than the rigidity of normal flexible polymers exemplified by nylon 6 in acidic solutions. Data on polymer I, 100:0 from the literature¹⁶ are also presented in Table I. A comparison of $[\eta]$ and M_w with our copolyamides clearly indicates that I, 100:0 is more rigid than the copolymers of family I.

The intrinsic viscosity of polymer II, 0:100 in 96% H₂SO₄ was found to be 0.33 dl/g and in *m*-cresol $[\eta] = 0.35$ dl/g. Light scattering measurements of this polymer proved to be impossible because of the close values of the index of refraction of the polymer and of *m*-cresol or *o*-chlorophenol solvents. From osmometry measurements and comparison with nylon 11 of $M_n = 16,000$, the M_n value of II, 0:100 in Figure 1 was estimated to be about 3000. Condensation polymerizations yield under equilibrium $M_w/M_n = 2.0$, so that the M_w of II, 0:100 was estimated to be about 6000. This value is reasonably close to the M_w values obtained by light scattering for copolyamides of family I, tabulated in Table I. The fact that the M_w values were reasonably close while the $[\eta]$ values were so dramatically different, indicates that polymers of family I are substantially more rigid than II, 0:100. Polymers from family III are expected to exhibit about the same rigidity as those of family I. It stands to reason that members of family II containing increasing amounts of rigid residues will show an increasing degree of backbone rigidity, II, 0:100 being the most flexible member of the family.

Our results appear to be in general agreement with the observations of Ali.¹⁷ In his studies on copolymers of *p*-aminobenzoic acid and 6-aminocaproic acid^{17,18} it was found that the intrinsic viscosity of a random copolymer containing 50 mole % *p*-benzamide and 50 mole % caproamide follows the following relations: $[\eta] = 2.37 \times 10^{-4} M_w^{1.13}$ in dichloroacetic acid and $[\eta] = 13.25 \times 10^{-4} M_w^{0.99}$ in triflu-

oroacetic acid. For the parent homopolymers Ali quotes $[\eta] = 1.6 \times 10^{-5} M_w^{1.7}$ for poly-*p*-benzamide¹⁹ and $[\eta] = 2.9 \times 10^{-4} M_w^{0.78}$ for polycaproadamide,¹⁵ both in concentrated H₂SO₄. It is obvious, then, that the value of the coefficient *a* of the copolyamide is intermediate between its values for the two parent polymers. The value of *a* for nylon 11 is not known to us, but it is estimated to be somewhere in the proximity of the *a* value for nylon 6.¹⁵ An *a* value in between 0.7 and 0.8 is envisioned. The values of *a* of the copolymers of family II are expected to be higher than for nylon 11 and smaller than for poly-*p*-benzamide, i.e., $0.8 \leq a < 1.7$. Because the rigidity of the *p*-phenylacetamide residue is higher than that of the undecanoamide or caproadamide residues, the values of *a* for the copolyamides of family I are expected to be larger than for family II; that is $0.8 \ll a < 1.7$. Similar conclusions must be drawn for family III.

Another demonstration of the change in rigidity with composition was obtained by means of dilute solution viscosity measurements as a function of temperature. Solutions of several members of family I in DMAc/5% LiCl were investigated in the $25 \leq T \leq 150^\circ\text{C}$ interval. In all cases corrections accounting for changes in solvent viscosity and polymer concentration were applied. After the corrections were applied, the reduced viscosities η_{sp}/c were calculated and then extrapolated to zero concentration to give $[\eta]$. The results for η_{sp}/c at *c* = 0.50% at 25°C and some $[\eta]$ values are presented in Table II with the corresponding values of η_{sp}/c and $[\eta]$ for the same solutions at 150°C. Upon cooling to 25°C the latter samples gave essentially the same viscosities as obtained prior to heating. In light of this and the fact that isotropic solutions of copolymers of far higher concentrations behaved normally and did not produce gels, an assumption of gel formation at high temperatures may be discarded. The ratios of the reduced viscosities at 150 and 25°C give a measure of the backbone flexibility of the corresponding polymer. The more flexible the backbone chain, the easier it is to change from one rotational isomer to another and become more coiled; and the more coiled the copolyamide chain, the lower its viscosity. All copolymers in Table II behaved normally, but the viscosity of the homopolymer I, 100:0 increased with temperature instead of decreasing. This may indicate that some molecular aggregation of I, 100:0 exists at low temperatures and is destroyed upon heating. In line with the discussion above, this heating must take place at temperatures of over 85°C.

In Table II there is a single entry for a member of family II. When the ratio of its viscosities is compared with the ratio of the corresponding member of family I, that is II, 70:30 and I, 70:30, one may reach a tentative conclusion that II, 70:30 is significantly more flexible than I, 70:30.

TABLE II
Viscosities of Copolyamides as Function of Temperature

Polymer	25°C		150°C		$\eta_{sp}/c, 150^\circ\text{C}$
	$\eta_{sp}/c, c = 0.5\%$	$[\eta]$	$\eta_{sp}/c, c = 0.5\%$	$[\eta]$	$\eta_{sp}/c, 25^\circ\text{C}$
I, 100:0	2.83	1.7	4.13	2.42	1.46
I, 70:30	1.53	1.24	1.29	0.79	0.84
I, 50:50	0.83	0.78	0.57	—	0.69
I, 30:70	0.54	0.54	0.32	—	0.59
II, 70:30	0.47	0.47	0.29	—	0.62

Ultraviolet spectra were obtained²⁰ from all members of copolyamide families I and II, and from model compounds given in Table III. In the case of family II, the total area under the UV absorbance curve showed linear dependence on the mol percent of aromatic residues in the feedstock. The area under the curve extrapolated to zero, as expected, from the members of family II richest in aliphatic residues. The above indicate that, in agreement with mass balance and NMR, the amounts of comonomers in the copolyamides are about the same as in the feedstock. The raw absorbance data of family II were corrected using the band shape-intensity relationships existing in II, 100:0, II, 10:90, II, 20:80, and II, 70:30, and the corrected values were then distributed as percent of the sum among the absorption bands assigned to increasing lengths of aromatic rigid elements. The band assignments were obtained from model compounds and subsequently from aliphatic-rich members of family II, and are tabulated in Table III. From the areas under the appropriate absorption peaks of polymer families I and II, the percent of *p*-benzamide residues existing in sequence lengths of one, two, three, four, and five and over were calculated.²⁰ The results for both families of the random copolyamides are presented in Table IV.

Even though a sequence analysis of samples obtained at the end of any polymerization is not a preferred procedure, an analysis of the sequence distribution of the copolymers of families I and II presented in Table IV, was performed. Sequences of five or more *p*-benzamide residues were assumed to be of five residues only. This resulted in the copolyamides poor in *p*-benzamide yielding results closer to reality than copolyamides rich in *p*-benzamide residues. Letting r_1 be the copolymerization parameter of *p*-aminobenzoic acid and r_2 the parameter of the other comonomer, one may follow the procedure given by Vollmert²¹ and obtain for family I, $r_1 = 3.63$ and $r_2 = 0.62$, and for family II, $r_1 = 1.95 \pm 0.06$ and $r_2 = 1.22 \pm 0.12$. The numerical values should not be considered accurate, yet indicative of the fact that in order to have a given amount of long rigid elements, copolymers from family II required a larger amount of *p*-aminobenzoic acid in the feed than copolymers from family I. From the data in Table IV one calculates that in I, 50:50 and II, 70:30 the average sequence lengths of the rigid elements are 3.76 and 4.45, corresponding to axial ratios of $x \approx 3.8$ and $x \approx 4.5$, respectively. As will be shown below, at these compositions anisotropy appears.

In Figure 2 are shown the percent concentration of the long *p*-benzamide elements plotted as a function of the *p*-aminobenzoic acid in the feedstock of families I and II. The curves describing the % concentration of the long rigid elements show a sharp break at a characteristic amount of *p*-aminobenzoic acid in the polymer. For family I the break occurs at I, 50:50 and for family II the break in the curve takes place at II, 70:30. This indicates that in family I, containing the *p*-phenylacetamide, a concentration of 50% or more *p*-benzamide is sufficient in order to keep the *p*-benzamide residues predominantly in long elements of five or more aromatic rings each. In family II, containing the undecanoamide residue, a concentration of 70% or more of the *p*-benzamide is necessary in order to keep a predominance of these residues in elements each containing five residues or more. The difference between families I and II may be due to the combined effects of monomer flexibility and the difference in the reactivity of the corresponding comonomers.* These observations are in ex-

* The author is grateful to a referee for bringing this point to his attention.

TABLE III
Ultraviolet Peak Absorption of Model Compounds

Compounds	Length of rigid element in aromatic residues	Peak maximum (nm)
	1	258
	1	265
	2	291
	3	304
	4	323
	≥5	339

TABLE IV
 Percent Distribution of *p*-Benzamide Residues in Sequences of Lengths

Polymer	Absorption (nm)				
	Isolated 258-265	Two 285-290	Three 300-301	Four 320-321	Five and longer 338-339
I, 0:100	100	— ^a	—	—	—
I, 10:90	100	—	—	—	—
I, 20:80	81	8	—	—	11
I, 30:70	55	6	—	6	33
I, 40:60	25	4	7	36	28
I, 50:50	23	6	4	6	61
I, 60:40	15	11	3	3	68
I, 70:30	9	9	—	10	72
I, 80:20	4	8	—	10	78
I, 90:10	2	6	—	12	80
I, 100:0	—	—	—	—	100
II, 0:100	—	—	—	—	—
II, 10:90	100	—	—	—	—
II, 20:80	100	—	—	—	—
II, 20:70	100	—	—	—	—
II, 40:60	53	22	9	5	11
II, 50:50	25	33	6	5	32
II, 60:40	—	24	7	7	62
II, 70:30	—	17	1	2	80
II, 80:20	—	13	—	—	87
II, 90:10	3	7	—	1	89
II, 100:0	—	—	—	—	100

^a Not observed.

cellent agreement with the ability of the corresponding polymers to exhibit lyotropic liquid crystallinity.

Solutions of certain members of families I and II exhibited liquid crystalline behavior above a concentration level characteristic of each polymer. Within family I, the polymers I, 100:0 through I, 50:50 exhibited mesomorphicity in conc. H₂SO₄ or DMAc/5% LiCl, while members poorer in *p*-benzamide residues showed no lyotropic liquid crystallinity. From family II only the members richest in *p*-benzamide showed liquid crystallinity, i.e., II, 100:0, II, 90:10, II,

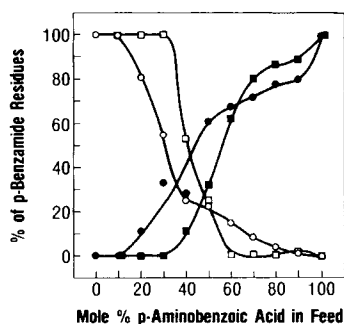


Fig. 2. Amounts of isolated rigid aromatic residues and long elements (≥ 5), presented as % *p*-benzamide residues, plotted against mole % *p*-aminobenzoic acid in the feedstock. Open symbols: isolated residues; filled symbols: long elements; ($\circ\bullet$) polymer family I; ($\square\bullet$) polymer family II.

80:20, and marginally II, 70:30. All other members of the family showed no mesomorphicity. Family III showed the same composition-anisotropy relationship as family I.

The liquid crystallinity was manifested by the opalescence of the solution. Under the cross-polarized light microscope highly birefringent regions appeared in the quiescent solution, growing in size with concentration, until the whole field of vision under the microscope was highly birefringent. In general, the shapes of the birefringent regions were illdefined and not the circular droplets exhibiting maltese crosses that exist in the biphasic region of polyisocyanate solutions.²² The liquid crystallinity of the respective solutions was further demonstrated by the characteristic behavior of the viscosity curve as a function of polymer concentration and by increases in viscosity with temperature to be discussed below.

When the observations of lyotropic liquid crystallinity and UV were compared, it was found that there existed a one-to-one correspondence between the preponderance of long rigid elements, as shown in Figure 2, and the property of mesomorphicity. It appears that once the amount of long rigid elements (of ≥ 5 *p*-benzamide residues in each) surpasses about 60–65% of all the *p*-benzamide residues in the polymer, liquid crystallinity is evident. This threshold of composition appears to be somewhat dependent on the nature of the flexible residues, but the nature of such a dependence is not known to us as yet.

Heating of the copolyamides on a hot bar indicated that, with no exception, all the copolyamides capable of lyotropic mesomorphicity started decomposing and charring without any softening. The polyamides that softened before charring were those rich in flexible residues, I, 30:70 to I, 0:100, and II, 50:50 and II, 0:100, significantly out of the ranges of lyotropic mesomorphicity of both families.

The viscosity of the polymers showing liquid crystallinity declined from $[\eta] = 1.90$ dl/g for I, 100:0 (same as II, 100:0 or III, 100:0) to $[\eta] \geq 0.60$ dl/g for I, 50:50 and $[\eta] = 0.45$ dl/g for II, 70:30. On the other hand, samples I, 20:80 with $[\eta] = 0.60$ dl/g and I, 30:70 with $[\eta] = 0.70$ dl/g did not produce liquid crystallinity even though their viscosity indicates sufficiently long chains. This leads to the obvious conclusion that it is the rigidity of the chain which dominates the ability of the polymer to form liquid crystals.

The concentration v_2^* at which each polymer first exhibited liquid crystallinity, showed a marked dependence on the rigidity of said polymer, and a much smaller dependence on its molecular weight as estimated by dilute solution viscosity measurements. Several batches of I, 100:0 varying in $[\eta]$ from 1.5 to 1.9 dl/g all showed lyotropic liquid crystallinity in H₂SO₄ at concentrations of 3 to 2% (w/v) polymer. As the composition of the copolymers changed, so did the point v_2^* . For several batches of I, 70:30, of $0.65 \leq [\eta] \leq 1.0$ dl/g, v_2^* was 3–5% and for several batches of I, 50:50 of $0.50 \leq [\eta] \leq 0.65$ dl/g; v_2^* was 15–20% polymer. Changes in v_2^* of the same nature were observed in families II and III, of course.

Viscosity runs as a function of concentration on several of the lyotropic liquid crystalline copolyamides, further indicated the existence of mesomorphicity beyond the characteristic concentration v_2^* . This is revealed by the viscosity vs. concentration curve passing through a peak at a concentration above v_2^* . For instance, the following are typical viscosity/concentration values for I, 70:30 of $[\eta] = 0.96$ dl/g: at 3.33% the viscosity η° of the whole system was 0.15 Pa sec,

at 5.5% concentration $\eta^\circ = 0.82$ Pa sec, at 10%, $\eta^\circ = 4.06$ Pa sec and at 15% concentration the viscosity dropped back to $\eta = 0.45$ Pa sec.

Even more interesting are curves of viscosity against temperature of fixed-concentration solutions of the copolyamides. When the polymer remains as a single phase throughout the studied temperature interval, then the viscosity drops with increased temperature, similar to isotropic solutions of common nonionic polymers. If, however, a biphasic system exists, then the viscosity increases with temperature, since an increasing amount of the lower viscosity anisotropic solution converts upon heating to the higher viscosity isotropic solution. If we are in the anisotropic phase very close to the biphasic region, the viscosity initially decreases upon heating; when an isotropic phase then appears, the viscosity passes through a minimum and starts increasing as the amount of isotropic phase increases at the expense of the anisotropic one. In Figure 3 there appear four viscosity versus temperature curves for 10% solutions of the denoted polymers in DMAc/5% LiCl. The figure is typical of many repeats of such measurements on many members of family I. In all cases the viscosity was corrected for the change in solvent viscosity and polymer concentration with temperature. The polymer with the highest viscosity at room temperature was I, 70:30 of $[\eta] = 0.96$ dl/g. At 10% concentration it was biphasic throughout the temperature interval. The polymer I, 80:20, of $[\eta] = 0.92$ dl/g, was fully liquid crystalline at room temperature, but an increasing amount of isotropic phase appeared with increased temperature. Hence the minimum and subsequent large increase in viscosity. The polymer I, 50:50 becomes anisotropic at concentrations higher than 10%, and I, 30:70 never becomes anisotropic. At 10% both polymers were in an isotropic state and hence the monotonically decreasing viscosity curve.

Several systems were prepared, each containing a pair of copolyamides in a single solvent. Within each system there were prepared solutions of several concentrations of both polymers in the solvent. Cross-polarized light microscopy observations indicated that when both polymers were of substantial rigidity and each capable of forming a mesomorphic solution, then they were miscible above a certain concentration level and formed a single anisotropic phase containing

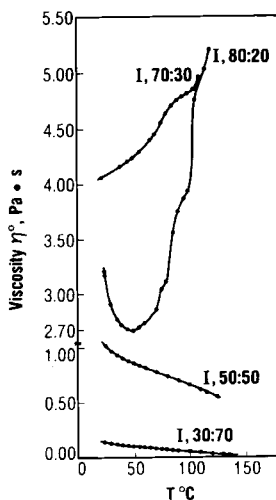


Fig. 3. Viscosities of 10% solutions of denoted polymers as a function of temperature.

both polymers. When one of the polymers was too flexible to be liquid crystalline, then a phase separation occurred and two phases, isotropic and anisotropic, coexisted. The concentration at which the phase separation occurred appears to depend on the flexibility level of the flexible polymer. Thus, a system of I, 70:30 and I, 50:50 in H_2SO_4 produced a single anisotropic phase at concentrations higher than about 30% polymer, for all polymer-polymer ratios. At concentrations below about 15% the solutions were isotropic. When the polymer I, 50:50 was replaced by nylon 6, then a phase separation and minute anisotropic droplets became evident in a solution of only 10% polymer containing only 0.5% I, 70:30. The phases never coalesced to form a single one upon increased polymer concentration or upon an increase in the ratio of nylon 6 to I, 70:30.

As was stated above, two lyotropic mesomorphic polymers can form a single anisotropic solution. A ternary phase diagram typical of such observations is presented in Figure 4. It should be noted that similar diagrams were also obtained in DMAc/5% LiCl as a solvent.

DISCUSSION

The molecular weights of the copolymers prepared by us were estimated to be of the order of $M_w \approx 10^4$. From the data in Table I, and from the osmometry measurement on polymer II, 0:100, one finds that within each family there exists a slight tendency toward lower molecular weight as a function of increased mole % of the aliphatic residue in the copolyamide. The tendency toward lower M with higher aliphatic content is in agreement with the observations of Yamazaki et al.^{12,13} that aromatic amines are more effective than aliphatic amines in the polycondensation reaction, while aromatic acids exhibit about the same level of effectiveness as intermediate chain-length aliphatic acids.

The thermotropic liquid crystalline alternating polymers prepared and described by Roviello and Sirigu,^{1,2} Skoulios and associates,^{3,5} and Griffin and

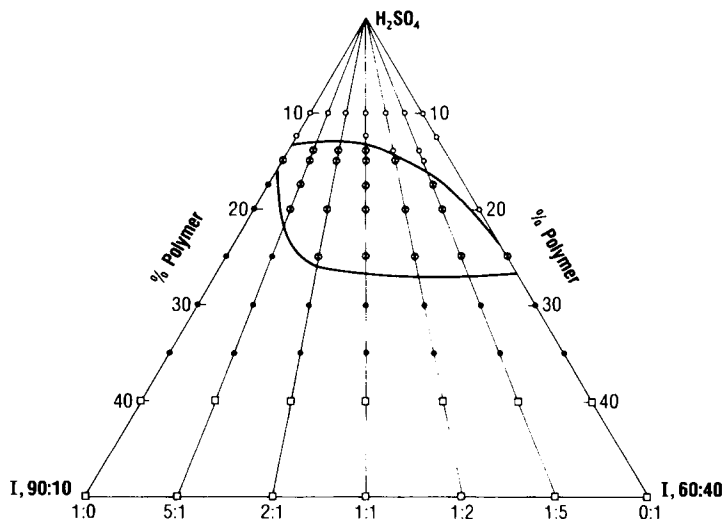


Fig. 4. Ternary phase diagram of polymers I, 90:10 and I, 60:40 in H_2SO_4 . Isotropic solution (○); anisotropic solution (●); biphasic interval containing isotropic and anisotropic solutions (⊗); concentration range containing anisotropic solution and polymeric solids (□).

Havens,⁴ are all characterized by the rigid element having a length of about four phenylene rings. This translates to a minimal axial ratio for the rigid element of about $x = 4$, for mesomorphicity to appear. This value is substantially smaller than the value of $x = 6.4$ calculated by Flory and Ronca.⁷

In the case of the *p*-benzamide residue, it was determined by several independent studies^{17,23-25} that the length of the residue in the chain direction is 0.60 ± 0.04 nm and its diameter is about 0.63 ± 0.03 nm. From the Results above, one recalls that lyotropic liquid crystallinity appeared in the random copolyamides only when over 50% of the *p*-benzamide residues existed in elements of five or more such residues. At the same time the rest of the *p*-benzamide existed in shorter sequences (Table IV). These, however, appear not to affect the onset of anisotropy. Based on this, we believe that an averaged length of rigid elements each containing five *p*-benzamide residues can be taken as the minimum length associated with the appearance of lyotropic mesomorphicity. From the dimensions of the *p*-benzamide residues, one obtains an axial ratio of $5 < x < 6$ at the point where liquid crystallinity appears. This value is somewhat smaller than the theoretical value of $x = 6.4$. In our work on alternating copolyamides⁸ it was found, in agreement with the literature,¹⁻⁵ that it was sufficient for x to be $3 < x < 4$ for mesomorphicity to appear.

The viscosity data of several of the lyotropic liquid crystalline copolyamides reported in the Results section, clearly indicate that very substantial change in the molecular weight (overall chain length) of a given copolyamide does not change the capability of the polymer to form a quiescent anisotropic liquid phase, but merely the concentration at which mesomorphicity becomes apparent.

One concludes, hence, that it is not the overall chain length which controls the formation of a liquid crystalline phase, but the average length of the rigid elements along such a chain. This also implies that substantial variations in the molecular weight distribution should not affect significantly the mesomorphic capability of a given rigid/flexible copolymer. In the case of alternating copolymers, the critical value of x is ≈ 4 , and for the random copolyamides $5 < x < 6$. For aromatic polymers with chain diameters around 0.6 nm, this translates to 2.5–3.0 nm as the minimum length of rigid elements necessary to impart liquid crystalline capability to the polymer. The strong dependence of mesomorphicity on the length of the rigid elements and not on the overall chain length is in agreement with the theoretical prediction of Flory.^{6,7} It is of interest to recognize that the shorter rigid elements, each containing four or less aromatic residues, appear not to affect the onset of mesomorphicity when they coexist with the longer rigid elements of five and more aromatic residues.

The increase in viscosity shown in Figure 3, associated with an increase in the amount of isotropic solution at the expense of the anisotropic phase, was reported in the literature for other systems as well. Papkov et al.²⁶ observed such a change in a poly-*p*-benzamide/DMAc system, while Miller and co-workers^{27,28} measured it for the system poly(γ -benzyl-L-glutamate) (PBLG) in dimethylformamide. It is of interest to note that the biphasic concentration range observed in the present work as well as in the poly-*p*-benzamide²⁶ and PBLG^{27,28} systems is far narrower than the biphasic concentration intervals previously observed in the polyisocyanate systems.¹⁰

Figure 4 is a ternary phase diagram characteristic of instances in which both random copolyamides are capable of exhibiting lyotropic liquid crystallinity.

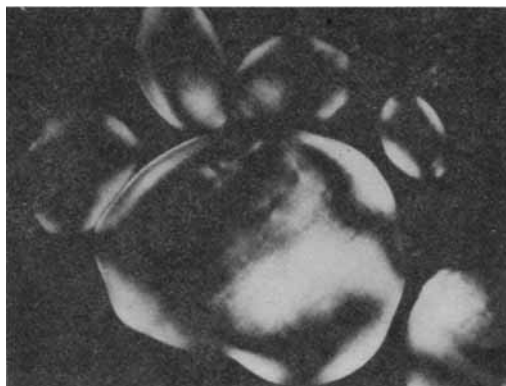
In cases where one of the copolyamides was not mesomorphic by itself, no single anisotropic solution containing both polymers was ever obtained. Figure 5 is typical of the observed pattern. In Figure 5(a), a cross-polarized photomicrograph (original magnification 58 \times) of a single anisotropic phase in a 30% solution of 1:1 I, 90:10 and I, 60:40, is shown. Upon rotation of the microscope stage by 45 $^\circ$, the dark areas in Figure 5(a) allow the passage of light and become lighter while the areas light in the figure, extinguish light and turn darker. In Figure 5(b) a single anisotropic phase is observed in a 20% solution of 1:1 II, 80:20 and II, 70:30 in H₂SO₄. The system in Figure 5(a) contains the same two copolyamides as in the ternary phase diagram in Figure 4, except for the solvent being DMAc/5% LiCl. Similar ternary phase diagrams were obtained in H₂SO₄ for the polymer pair in Figure 5(b) and for the pair II, 90:10 and II, 70:30. A ternary system containing copolyamide I, 80:20 and copolyamide III, 60:40 in H₂SO₄,



(a)



(b)



(c)

Fig. 5. Cross-polarized light micrographs of solutions containing two copolyamides each: (A) 30% solution of 1:1 I, 90:10 and I, 60:40 in DMAc/5% LiCl. (B) 20% solution of 1:1 II, 80:20 and II, 70:30 in H₂SO₄. (C) 10% solution of 1:1 I, 90:10 and I, 30:70 in DMAc/5% LiCl.

was for all practical purposes the same as the one obtained from I, 80:20 and I, 60:40 in the same solvent.

When either of the copolyamides in a ternary system was too flexible to form an anisotropic phase by itself, then a phase separation took place as is shown in Figure 5(c). Here, a 10% solution of 1:1 I, 90:10 and I, 30:70 in DMAc/5% LiCl, is clearly separated into isotropic and anisotropic phases. The phase separation persists in ever-increasing concentrations until a crystalline precipitate becomes plentiful and a solid-anisotropic-isotropic system is evident. As was mentioned before, when one of the polymers in the system is highly flexible, such as nylon 6, then the addition of even a small amount of a rigid polymer will cause a separation into a major isotropic phase and a minor anisotropic one. The observed separation of the more rigid polymer into an anisotropic phase and the more flexible polymer into an isotropic phase in Figure 5(C), and in the system nylon 6/copolyamide/H₂SO₄, is in agreement with the predictions of Flory²⁹ concerning the immiscibility of rigid and flexible polymers in a single solvent.

CONCLUSIONS

Random rigid/flexible copolyamides form lyotropic liquid crystalline phases once a preponderance of the rigid residues are in rigid elements whose critical axial ratio x is $5 < x < 6$. The point when $5 < x < 6$ is reached depends on the nature of the flexible comonomers. The higher the basicity or the flexibility of these monomers, the higher is the concentration of rigid monomers in the copolymer at the point of $5 < x < 6$.

In concentrated ternary systems of polymer 1/polymer 2/solvent, a single anisotropic phase containing both polymers can be obtained when each polymer is capable of forming an anisotropic solution in the solvent. When either polymer is too flexible to form an anisotropic solution by itself, then it will separate from the ternary system into an isotropic phase.

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