bottom, was placed 5.0 g of 3,5-dichloro-4-aminobenzoyl chloride needles. The polymer tube was heated in a bath maintained at 300 °C while a slow flow of nitrogen was passed through. Hydrogen chloride was evolved and the contents of the tube became opaque and more compact but did not melt. Heating and nitrogen flow were miantained for 14 h. The fibrous, needlelike poly(3,5-dichloro-1,4-benzamide) was easily removed from the tube.

A sample from the upper portion of the mass had an inherent viscosity of 0.85 dL/g and a sample from the lower portion had an inherent viscosity of 1.44 dL/g. The needles were soluble only in concentrated sulfuric acid and had a high degree of crystallinity by x-ray diffraction. A sample from another preparation had a density of 1.58 (gradient density solvent determination). Refractive index measurements, compared to those obtained from oriented fibers, indicated polymer chain orientation crosswise of the long axis of the needles.

Needles of 4-Aminobenzoyl Chloride Hydrochloride. 4-Aminobenzoic acid was dissolved in dry tetramethylene cyclic sulfone at 50–60 °C at a molar ratio of solvent to acid of at least 7/1. An excess of gaseous hydrogen chloride was bubbled into the solution to form a precipitate of the amino acid hydrochloride. The mixture was cooled below 30 °C and thionyl chloride was added with continued cooling and stirring. When the proportion of thionyl chloride was from 1 to 14 mol/mol of aminobenzoic acid hydrochloride, the resulting 4-aminobenzoyl chloride hydrochloride needles had average dimensions of 100 μm by 2 μm. When the molar amount of thionyl chloride to amino acid hydrochloride was 30/1, a solution resulted. This solution was cooled to 10 °C and two volumes of methylene chloride was added. The precipitated needles of 4-aminobenzoyl chloride had smaller dimensions (1 μm by 0.25 μm).

The acid chloride was isolated by collection on a dry sintered glass funnel and washed with an inert, dry solvent such as ether, hexane, or methylene chloride. Such moisture-sensitive intermediates must be handled and stored in dryboxes provided with an inert atmosphere and appropriate ports for manual entry and manipulation.

Thermal Polymerization of 4-Aminobenzoyl Chloride Hydrochloride as Needles. 4-Aminobenzoyl chloride hydrochloride (10.0 g), as microscopic needles, was heated in a small polymerization tube equipped with a side arm and an inlet capillary reaching to the bottom of the monomer mass and provided with a slow flow of dry nitrogen. A polymer prepared by heating the monomer gradually to 156 °C and then heating further for 6 h at 156 °C and a pressure of 0.1 mm had an inherent viscosity of 0.57 dL/g; another sample heated to 300 °C and then for 8 h at 300 °C under 0.1 mm pressure had an inherent viscosity of 3.07 dL/g. The degree of polymerization was not increased by longer heating times and the use of low pressure was not essential.

The polymers retained the external hexagonal needle shape of the monomer (Figure 4) and had the polymer chains extended and oriented crosswise of the long axis of the needles. Wide-angle x-ray diffraction showed a high degree of crystallinity and produced the same diffraction peaks found for crystalline polymer from low-temperature solution synthesis.

Acknowledgment. Advances and development of knowledge in this field have been through the contributions and interactions of many colleagues. Several, whose work has been drawn upon directly, are S. L. Kwolek, T. I. Bair, T. C. Pletcher, and F. L. Killian. W. F. Dryden, Jr., provided excellent experimental assistance.

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Synthesis, Anisotropic Solutions, and Fibers of Poly(1,4-benzamide)

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ABSTRACT: Poly(1,4-benzamide) prepared from *p*-aminobenzoyl chloride hydrochloride by low-temperature solution polymerization methods was dissolved in amide–salt solvents to form liquid-crystalline solutions which were dry spun directly into oriented fibers with tenacities >10 g/denier and moduli >500 g/denier. After heat treatment with no drawing the fibers on a weight basis were stronger than steel and had an initial modulus several times that of glass. The effects of monomer and solvent purity, monomer addition and stirring rates, temperature, added chain terminator, and added hydrogen chloride neutralizer on molecular weight of poly(1,4-benzamide) prepared by low-temperature solution polymerization were determined. Solutions of poly(1,4-benzamide) in *N,N*-dimethylacetamide–LiCl, *N,N,N′,N′*-tetramethylurea–LiCl, and hydrogen fluoride were studied for the effects of polymer concentration, polymer molecular weight, salt–additive concentration, and temperature on the critical concentration point at which liquid crystals are formed. The two phases, anisotropic and isotropic, present at the critical concentration point were separated and characterized.

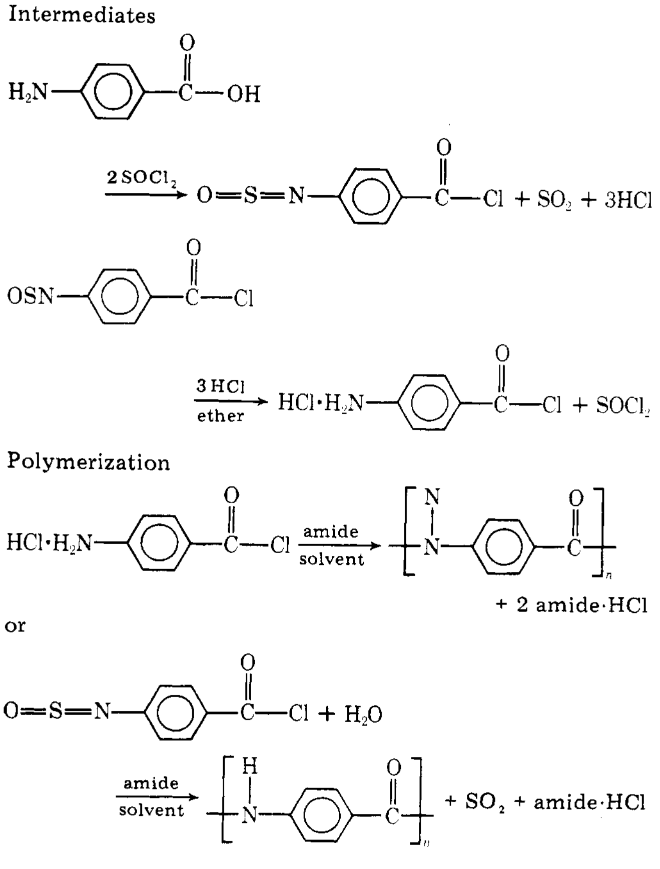
Poly(1,4-benzamide) is the first nonpeptide, synthetic condensation polymer reported to form a liquid-crystalline solution. This behavior has been observed previously with polypeptides, such as tobacco mosaic virus, poly(γ-benzyl L-glutamate), and collagen, in selected solvents and more recently with vinyl polymers containing side crystallizing groups modeled after low molecular weight liquid-crystal forming compounds.[2,3,4] Polypeptide solutions, which are generally cholesteric in nature, are unique in that the polymeric molecules behave like rigid rodlike particles of high axial ratio (length to breadth ratio) by virtue of an α helix formed by internal hydrogen bonding.[5] Poly(1,4-benzamide) forms liquid-crystalline solutions not because of helix formation as observed with polypeptides or side-group interaction but because of an inherently extended rigid chain structure produced by a combination of a paralinked benzene ring and partial double bond character of the carbon–nitrogen bond in predominantly trans amide linkages. This polymer provides an entirely new type of polymeric liquid-crystalline solution which is related directly to the preparation of high strength–high modulus oriented fibers.[6,7]

Discussion and Results

Polymer Synthesis. In order to prepare liquid-crystalline solutions of poly(1,4-benzamide), it is first necessary to synthesize a soluble polymer. This can be accomplished by preparing the latter in *N,N*-dialkylamide solvents at low temperature from *p*-aminobenzoyl chloride hydrochloride. This method produces tractable polymer with inherent viscosities up to about 5, and it can be used with solvents, such as *N,N*-dimethylacetamide and *N,N,N′,N′*-tetramethylurea, as a coupled polymerization–spinning process in which liquid-crystalline solutions formed directly during polymerization are spun. In like manner, copolymers of poly(1,4-benzamide) also can be prepared.[6,7]

The synthesis of soluble poly(1,4-benzamide) at low temperatures is somewhat more complex than the usual AA–BB condensation polymer as depicted in Scheme I. *p*-Aminobenzoic acid is reacted with thionyl chloride to form sulfinylaminobenzoyl chloride, a yellow compound which can be purified by distillation or recrystallization.[8] This compound is dissolved in ether and treated with dry hydrogen chloride to yield *p*-aminobenzoyl chloride hydrochloride which is very sensitive to moisture and heat, forming either an acid or dimer and oligomers, respectively. When this salt is dissolved in a *N,N*-dialkylamide, such as dimethylacetamide or tetramethylurea, the amine group is freed of the hydrochloride and polymerization to high molecular weight proceeds.

Scheme I
Poly (1,4-benzamide) Preparation



Sulfinylaminobenzoyl chloride also can be converted to poly(1,4-benzamide) by dissolving it in an amide solvent containing an equivalent of water. Addition of 1 equiv of a lithium base further promotes the reaction.[9]

Intermediate and polymer syntheses are described in the Experimental Section.

A number of factors influence the molecular weight of poly(1,4-benzamide) prepared from *p*-aminobenzoyl chloride hydrochloride by low-temperature solution polymerization. These are: monomer and solvent purity, monomer addition and stirring rates, temperature, added chain terminator, and added hydrogen chloride neutralizer.

The presence of impurities in the monomer, and particularly water in the solvent and surrounding atmosphere, has an adverse effect on molecular weight.

Rapid addition of monomer and a high stirring rate at the beginning of the polymerization favor high molecular weight and narrow molecular weight distribution. Side reactions between the acid chloride and *N,N*-dialkylamide solvents compete with the polymerization.

If polymerization is initiated at >25 °C, lower molecular weight polymer is formed. Above this temperature chain termination by reaction of acid chloride ends with *N,N*-dialkylamide is significant. Figure 1 shows the effect of temperature on inherent viscosity of poly(1,4-benzamide) prepared in tetramethylurea when the entire polymerization is conducted at the given temperatures. If the polymerization is initiated at low temperature and concluded at higher temperatures, much higher molecular weight polymer is obtained. For best results polymerization is conducted initially below 10 °C.

To prepare poly(1,4-benzamide) of different molecular weights, chain terminators can be used. Figure 2 shows the effect of water, benzoyl chloride, and *p*-aminobenzoic acid on chain growth in a tetramethylurea system. The effects vary because of differing reaction rates vs. the polymer-forming reaction. *p*-Aminobenzoic acid is the most effective terminator followed by benzoyl chloride and water. All three terminators allow for increase in molecular weight and tensile properties on heat treating of fibers; however, unterminated polymer reaches a higher level of inherent viscosity.

As shown in Figure 3, the polymerization of *p*-aminobenzoyl chloride hydrochloride in a *N,N*-dialkylamide solvent is initially fast but slows with the build-up of by-product hydrogen chloride. For every polymer amide group formed there are produced 2 mol of hydrogen chloride as compared to one for a diamine–diacid chloride reaction. As the polymerization proceeds, more hydrogen chloride is generated and fewer free terminal amine groups on polymer chains are available for reaction with acid chloride according to the equation:

$$\text{R-NH}_3\text{Cl} + \text{TMU} \rightleftharpoons \text{R-NH}_2 + \text{TMU} \cdot \text{HCl}$$

If a lithium base, e.g., lithium hydride, carbonate, hydroxide, etc., is added to the poly(1,4-benzamide) preparation after 1–2 h of reaction time, hydrogen chloride is neutralized, polymer amine end groups are freed, and polymerization proceeds with renewed vigor as depicted by an increase in inherent viscosity in the upper curve of Figure 3. Except when LiH is used, this reaction is limited by the slower hydrolysis of the acid chloride by water of neutralization. The neutralizer thus promotes chain extension while by-products, water, and LiCl promote chain termination and solubility, respectively.

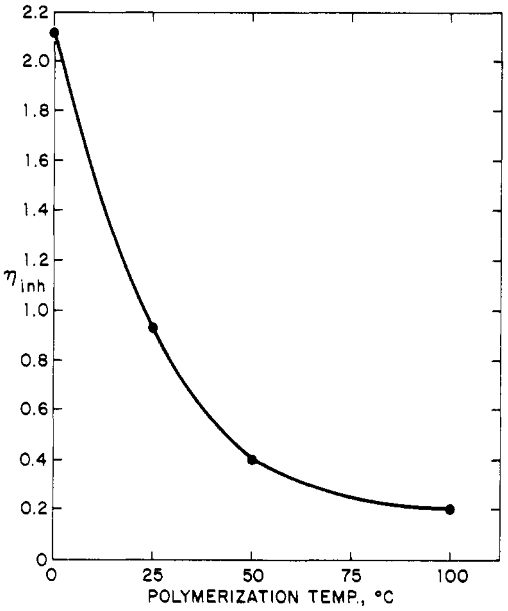


Figure 1. Effect of polymerization temperature on inherent viscosity of poly(1,4-benzamide) prepared in tetramethylurea.

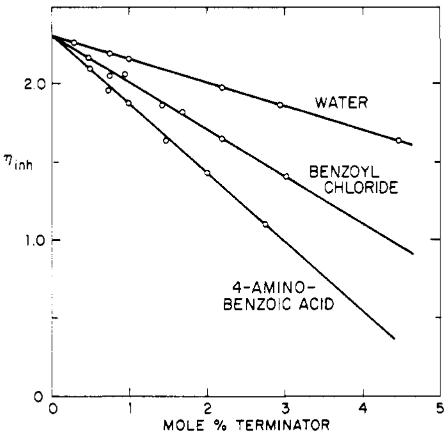


Figure 2. Terminators in poly(1,4-benzamide) preparation.

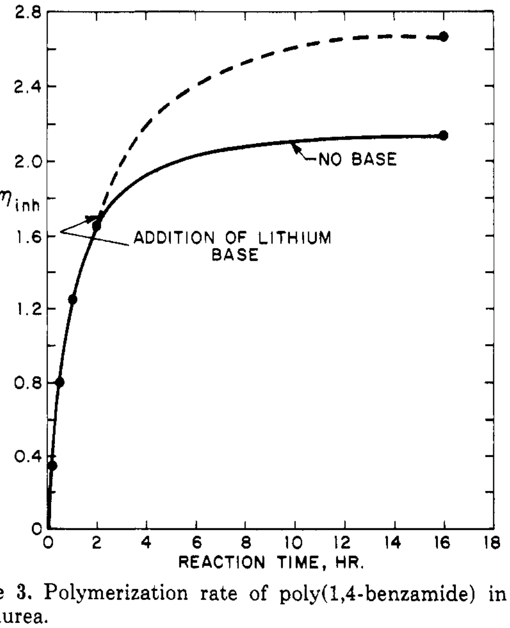


Figure 3. Polymerization rate of poly(1,4-benzamide) in tetramethylurea.

Table I
Inherent Viscosity of Poly(1,4-benzamide) as a Function of Neutralizer[a]

Neutralizer	% H_2O in dope as product of neutralization	η_{inh} Before neutral.	η_{inh} After neutral.	Soln visc, P
$LiOH\cdot H_2O$	3.6	1.65	1.80	1520
LiOH	1.8	1.75	2.24	690
Li_2CO_3	0.9	1.80	2.67	320
LiH	0	1.87	2.81	640

[a] 6% polymer (by wt) in *N*,*N*-dimethylacetamide-LiCl.

Water from neutralization in an amount of about 1.0 to 1.5% (by wt) has a stabilizing effect on polymer–dimethylacetamide solutions. With solvent systems containing low molecular weight polymer, water was necessary to prevent rapid crystallization of polymer in the solutions.

The effects of several hydrogen chloride neutralizers on polymer molecular weight and solution bulk viscosity are presented in Table I. LiH which produces no water of neutralization gives polymer with the highest inherent viscosity but lithium carbonate which produces 0.9% water in the dope gives the more desirable combination of polymer inherent viscosity, solution bulk viscosity, and solution stability for processing.

Fiber Preparation. Liquid-crystalline solutions of poly(1,4-benzamide) are useful for the preparation of high strength–high modulus fibers. These solutions may be prepared directly during polymerization or by dissolving the isolated polymer in an appropriate solvent, e.g., tetramethylurea–LiCl or dimethylacetamide–LiCl. (See Experimental Section.) Poly(1,4-benzamide) is present in solution as randomly distributed domains of extended rodlike molecules with a high degree of parallel order; extrusion through spinneret holes aligns the domains in the direction of flow with the result that fibers with high orientation are formed directly. These opalescent solutions may be spun either by evaporation of the solvent (dry spinning) or by coagulation in a nonsolvent (wet spinning).

The effect of shear in orienting polymer solutions can be illustrated by smearing a solution of poly(1,4-benzamide) across a microscope slide and then drying. There is formed a fibrillar network in which the polymer molecules are aligned with the fibril axis as seen in Figure 4. Each major strand is made up of many fiber fibrils with a very high degree of orientation as determined by electron diffraction (orientation angle = 20°).

Some results of dry spinning a tetramethylurea-LiCl solution of poly(1,4-benzamide) with varying attenuation below the spinneret are presented in Table II. Even at free fall the fibers have appreciable orientation (orientation angle = 39°), and as stretching is increased, orientation, tensile strength, and modulus of the finished fibers increase. In contrast, dry spun fibers of well-known polymers, such as cellulose derivatives, polycarbonates, polyacrylonitrile, or poly(*m*-phenyleneisophthalamide), are very little oriented, if at all, and have tenacities and moduli well below the first numbers in Table II.

As-extruded fibers with tenacities >10 g/denier and moduli >500 g/denier have been obtained by dry spinning from tetramethylurea–LiCl solutions. This tenacity–modulus level can be improved further by heat treatment.

Figure 5 shows the result of passing the last fiber sample described in Table II rapidly through a short tube with maximum temperatures indicated on the horizontal scale. The fibers are under slight tension but no drawing in the conventional sense occurs. Extension is only about 1 to 2%. There is a dramatic rise in tenacity and modulus, accompanied by an

Table II
Poly(1,4-benzamide), Properties of Undrawn Fiber by Dry Spinning

Spin stretch factor[a]	Denier	Tenacity, g/denier	Elongation, %	Initial modulus, g/denier	Orientation angle, deg
Free fall	6.0	3.2	3.7	140	39
1.90	6.1	3.9	2.7	235	37
2.42	4.8	4.2	3.4	220	38
2.56	4.5	5.5	3.3	280	26
3.83	3.1	6.9	2.9	390	22
5.11	2.3	8.6	3.0	470	22
6.39	1.9	8.0	2.8	430	19

[a] Spin stretch factor is wind-up speed/linear extrusion rate. Polymer $\eta_{\text{inh}} = 1.48$ (H_2SO_4). Spin dope = 13% in TMU–LiCl (6.54%). Fiber crystallinity is medium. Orientation angle was determined by x ray.[11]

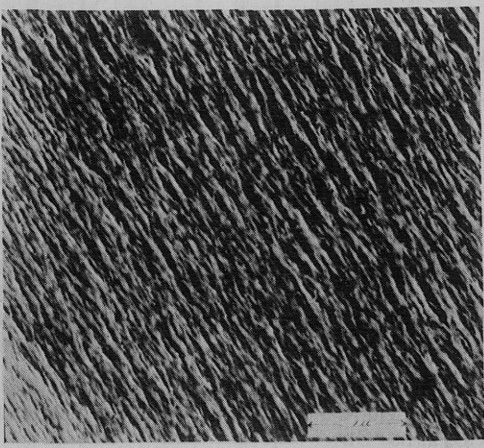


Figure 4. Smear of poly(1,4-benzamide) in tetramethylurea–LiCl solution (metal shadowed).

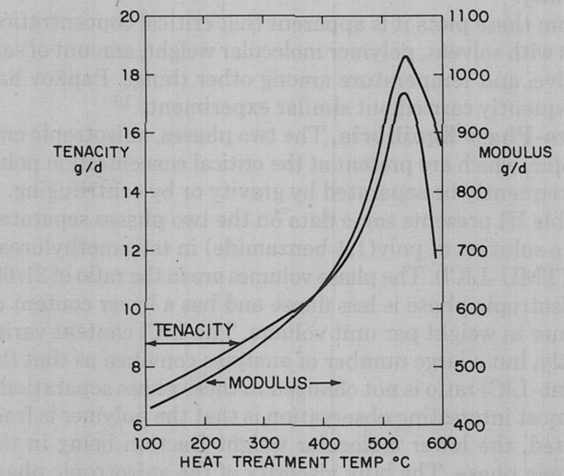


Figure 5. Effect of heat treatment on properties of poly(1,4-benzamide) fibers.

increase in density, degree of orientation, amount of crystallinity, as well as some change in crystalline arrangement. A tenacity–modulus level of about 20 g/denier (37.4 × 10^4 psi) and 1200 g/denier (2.24 × 10^7 psi) can be reached readily by heat treatment. Heat-treatment data were provided by J. T. Rivers of the Pioneering Research Laboratory. These fibers on a weight basis are stronger than steel and have an initial modulus several times that of glass.

Anisotropic Polymer Solutions. Poly(1,4-benzamide) can form *liquid-crystalline solutions in selected N,N*-dialkylamides with or without added lithium or calcium chloride depending on conditions employed and in strong acids, such as sulfuric, oleum, hydrofluoric, and chlorosulfonic.

Liquid-crystalline solutions of this polyamide are turbid in appearance, stir opalescent, and optically birefringent at rest. The turbidity is due to diffraction of light as it passes through the liquid-crystalline domains which vary in size and in direction of alignment. A solution sample placed between crossed polarizers will depolarize plane-polarized light and the bright field will change to brilliant colors under slight shear. On magnification these solutions have the nematic texture shown earlier in P. W. Morgan's paper in this series.

Poly(1,4-benzamide) readily forms liquid-crystalline solutions, since *it has an inherently extended rigid chain* structure desirable for forming such solutions. Also it can be prepared in average molecular weights high enough to exceed a minimum value for liquid-crystal formation and these polymers are sufficiently soluble to exceed the critical concentration at which liquid crystals are formed.

When a liquid-crystalline solution of poly(1,4-benzamide) is formed by dissolving increments of polymer in a solvent or by preparing a series of solutions with increasing concentrations, there occurs a sudden drop in bulk viscosity. Figure 6 shows the relationship of bulk viscosity and polymer concentration for a solution of the polymer in *N,N*-dimethylacetamide–4 wt % LiCl (DMAc/LiCl). The viscosities were determined with a Brookfield Synchro-Lectric viscometer at low shear rates. As concentration of the polymer is increased, bulk viscosity also increases. The slope of the curve, however, abruptly changes when polymer concentration reaches about 5%, i.e., at the critical concentration point. The viscosity now begins to drop and the solution consists of two phases. As more *polymer is added, viscosity drops further and the amount of* anisotropic phase increases. This continues until a saturation point is reached at about 7% when viscosity will rise again.

Curves of similar shape but with variations in critical concentration, polymer solubility range, and solution bulk viscosity have been obtained for other poly(1,4-benzamide)–solvent systems. Figure 7 presents one such example where poly(1,4-benzamide) of very high inherent viscosity (3.9) is soluble in a strong acid, hydrofluoric, at low temperature, 0 °C. The critical concentration point occurs at about 14%.

Critical concentration for a given polymer in a given solvent may be expected to vary with molecular weight. Figure 8 shows the effect of inherent viscosity of poly(1,4-benzamide) on critical concentration in *N,N*-dimethylacetamide–4 wt % LiCl. A higher concentration or volume fraction of polymer is needed to cause formation of an anisotropic phase as molecular weight of polymer decreases. This is in accord with the concept that more short chains, or chains with lower axial ratio, can be randomly fitted to a given volume of solvent than *can longer rodlike chains.*

Critical concentration also varies with amount of salt additive in the solvent. Figure 9 presents a plot of poly(1,4-benzamide) concentration versus amount of LiCl in *N,N*-

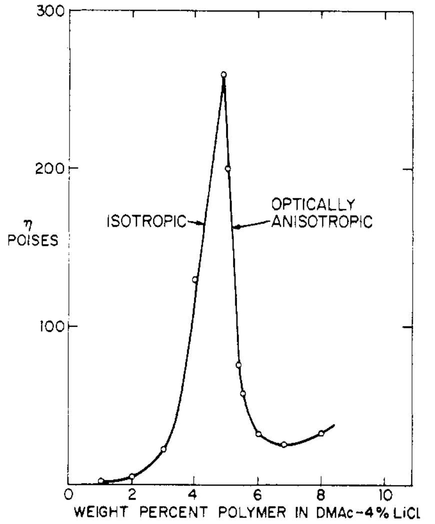


Figure 6. Critical concentration curve for poly(1,4-benzamide), η_{inh} = 2.41.

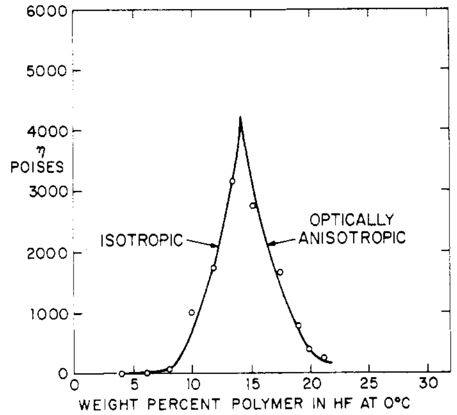


Figure 7. Critical concentration curve for poly(1,4-benzamide), η_{inh} = 3.9.

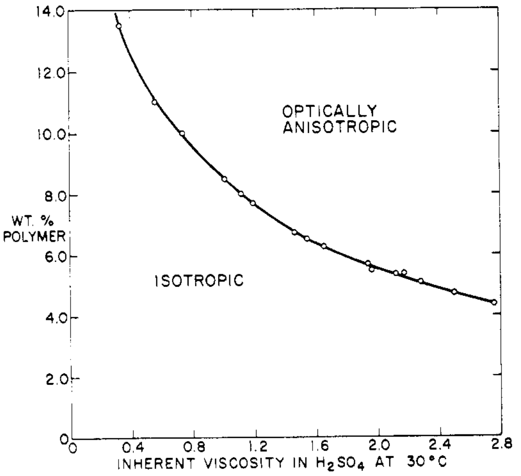


Figure 8. Effect of inherent viscosity on critical concentration for poly(1,4-benzamide) in DMAc–4% LiCl.

dimethylacetamide in which the curve represents a series of critical concentration points. As the amount of LiCl is increased, the critical point occurs at a higher polymer concentration. This behavior is most probably the result of increased polymer solubility with increased availability of LiCl for complexing up to a saturation point when additional LiCl will compete with polymer for solvent and decrease polymer solubility.

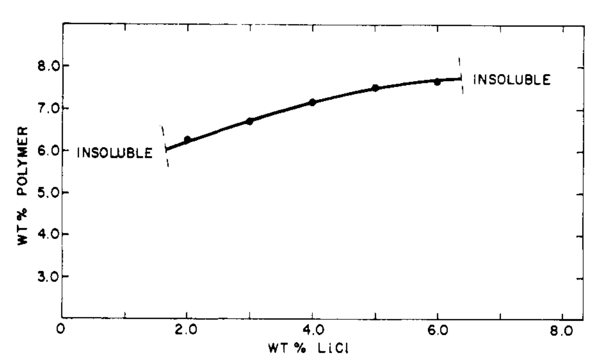


Figure 9. Effect of LiCl concentration on critical concentration for poly(1,4-benzamide), η_{inh} = 1.36, in *N,N*-dimethylacetamide at 25 °C.

Table III
Examination of the Two Phases of a Solution of Poly(1,4-benzamide) in TMU-LiCl[a]

	Isotropic phase	Optically anisotropic phase
Proportion, % by vol	31	69
Density, g/mL	1.0598	1.0664
LiCl content, g/mL	0.085	0.082
Polymer content, g/mL	0.105	0.121
Polymer η_{inh}, dL/g	0.59	0.88
Bulk viscosity, cP	~6000	3000

[a] Polymer solution prepared directly in TMU-LiCl with *p*-aminobenzoic acid as a chain terminator. η_{inh} = 0.81 (0.5 g/100 mL H_2SO_4 at 30 °C).

From these plots it is apparent that critical concentration varies with solvent, polymer molecular weight, amount of salt additive, and temperature among other things. Papkov has subsequently carried out similar experiments.[10]

Two-Phase Equilibria. The two phases, anisotropic and isotropic, which are present at the critical concentration point can frequently be separated by gravity or by centrifuging.

Table III presents some data on the two phases separated from a solution of poly(1,4-benzamide) in tetramethylurea–LiCl (TMU-LiCl). The phase volumes are in the ratio of 31/69. The isotropic phase is less dense and has a lower content of polymer in weight per unit volume. The LiCl content varies slightly, but a large number of analyses convince us that the solvent–LiCl ratio is not changed in these phase separations. The most interesting observation is that the polymer is fractionated, the lower molecular weight fraction being in the isotropic phase. The bulk viscosity of the anisotropic phase is lower than that of the isotropic phase.

When fibers are spun from pairs of separated phases under constant conditions, tenacity, modulus, and orientation are superior for fibers from the anisotropic phase. As previously mentioned, formation of two phases results in molecular weight fractionation and differences in polymer concentration. The higher concentration occurs in the anisotropic phase because of the more regular packing associated with liquid-crystal formation.

Another way to present the effect of liquid crystallinity on fiber properties is to spin fibers from polymer of the same inherent viscosity and molecular weight distribution but with polymer concentration as the only variable. As the polymer concentration increases, so does the volume fraction of the anisotropic phase. Thus we observe in Table IV the effect of amount of anisotropic phase on tenacity, modulus, and ori-

Table IV
Effect of Anisotropy on Poly(1,4-benzamide) Fiber Properties (η_{inh} = 2.1)

	Spin dope		As-extruded filaments			
Anisotropic phase in spin dope	η, P	Wt % of polymer	Tenacity, g/denier	Elongation, %	Initial modulus, g/denier	O.A., deg
None	140	4.6	4.4	10.9	182	33
Small amount	56	5.8	8.5	9.7	330	20
Larger amount	18	6.7	9.7	8.3	424	16

entation angle (O.A.). Since isotropic solutions of varying polymer concentrations yield fibers with essentially equivalent fiber properties, it is concluded that the presence of a liquid anisotropic phase is responsible for the enhanced tenacity, modulus, and orientation observed.

In this paper on poly(1,4-benzamide) the surface has barely been scratched as to the potential of polymers with extended rigid chain structures. This area has already stimulated much research work and considering the complexity of these liquid-crystalline systems should continue to do so in the future.

Experimental Section

Intermediates. *p*-Sulfinylaminobenzoyl Chloride. *p*-Aminobenzoic acid (100 g, 0.729 mol) was refluxed with 450 mL of thionyl chloride for 3 h.[8] After excess thionyl chloride was removed under vacuum, the fraction distilling at 107–113 °C (1–2 mm Hg) was collected. The latter was redistilled to give the desired product in a 95% yield with a bp of 110–111 °C (1.4 mm Hg) and a mp of 31.0–31.5 °C.

Anal. Calcd for $C_7H_4NO_2SCl$: C, 41.69; H, 2.00; N, 6.95; O, 15.87; S, 15.90; Cl, 17.59. Found: C, 42.24; H, 2.11; N, 6.82; O, 15.91; S, 15.4; Cl, 17.78.

***p*-Aminobenzoyl Chloride Hydrochloride.** Under dry conditions 100 g of *p*-sulfinylaminobenzoyl chloride was dissolved in 1800 mL of absolute ether.[8] Dry hydrogen chloride gas was conducted over the stirred yellow solution for 3 h with occasional cooling to control the exothermic reaction. The white precipitate formed during reaction was collected on a filter in a drybox, washed several times with ether on the funnel, and dried in a vacuum dessicator at reduced pressure. Yield: 93%.

Anal. Calcd for $C_7H_7NOCl_2$: C, 43.78; H, 3.67; N, 7.29; O, 8.33; Cl, 36.93. Found: C, 44.65; H, 3.87; N, 7.35; O, 8.46; Cl, 37.3.

p-Aminobenzoyl chloride hydrochloride from this preparation gave poly(1,4-benzamide) with an η_{inh} of 1.8 (H_2SO_4) and the following elemental analysis: C, 69.94; H, 4.27; O, 13.89; N, 11.6. Calcd for C_7H_5NO: C, 70.58; N, 4.23; O, 13.43; N, 11.76.

The amide solvents, hexamethylphosphoramide (*Caution!* experimental carcinogen; see paper by P. W. Morgan in this series), *N,N,N′,N′*-tetramethylurea, and *N,N*-dimethylacetamide were purified by distillation over calcium hydride through a spinning band column under vacuum and stored over molecular sieves.

Lithium chloride was dried 4 h at 450 °C.

Polymer Preparation. A. Poly(1,4-benzamide) from *p*-Aminobenzoyl Chloride Hydrochloride. 1. In Hexamethylphosphoramide. A 500-mL round-bottomed, three-necked flask equipped with a stirrer, nitrogen-inlet tube, and calcium chloride drying tube was flamed, purged with nitrogen, sealed, and placed in a drybox.

Hexamethylphosphoramide (150 mL) was poured under dry conditions in a fume hood into a dry Erlenmeyer flask which was sealed and cooled in an ice bath.

p-Aminobenzoyl chloride hydrochloride (31.6 g, 0.165 mol) was weighed in a drybox and transferred to the reaction flask which was then removed from the drybox, reconnected with the stirrer motor and nitrogen line in a fume hood, and cooled in an ice bath.

Hexamethylphosphoramide was poured rapidly into the stirred *p*-aminobenzoyl chloride hydrochloride and the resulting solution was stirred with cooling for 1 h. The ice bath was removed and stirring was continued overnight; however, if gelation had occurred, the reaction mixture was left to stand. The reaction mixture was pulverized in water in a blender and filtered, and the collected solid was washed three times with water and once with alcohol. The polymer was dried overnight at 80–90 °C in a vacuum oven with a nitrogen bleed. Inherent viscosity of the white polymer was as high as 2.3 (H_2SO_4) and yield was nearly quantitative.

2. In Tetramethylurea. The same precautions for handling of intermediates were taken as described under subsection 1.

Tetramethylurea (352 mL) was combined with the chain terminator, *p*-aminobenzoic acid, in a flamed and nitrogen-purged 1-L "resin" kettle equipped with a Teflon poly(tetrafluoroethylene)-coated shear-disk stirrer, calcium chloride drying tube, and nitrogen-inlet tube. The solution was cooled to 5 °C and *p*-aminobenzoyl chloride hydrochloride (69.132 g) was added rapidly. The reaction mixture was stirred ½ h at 5–10 °C and 1.5 h at 10–35 °C. At 2 h of reaction lithium hydroxide (17.244 g) was added and an oil bath at about 125 °C was inserted under the "resin" kettle. After an additional hour of stirring a readily spinnable solution was obtained. Polymer prepared with 1.0 mol % of *p*-aminobenzoic acid had an inherent viscosity of 1.60 (H_2SO_4).

3. In *N,N*-Dimethylacetamide. The same precautions for handling of intermediates were observed as described under subsection 1. All equipment exclusive of the air driven motor was dried in an oven at 110 °C prior to use.

In a 1-L "resin" kettle equipped with a nitrogen-inlet tube, drying-outlet tube, and an egg-beater type stirrer was placed 500 mL of *N,N*-dimethylacetamide. While the latter was cooled in an ice bath, 51.0 g of *p*-aminobenzoyl chloride hydrochloride was placed in a plastic bag attached to a standard tapered joint. When the temperature of the solvent had reached 0–5 °C, the plastic bag was removed from the drybox and was fitted to an outlet in the "resin" kettle. The stirring rate was increased and the monomer was added as rapidly as possible. The polymerization was allowed to proceed at a reduced stirring rate for 1.5 to 3.0 h (to gel formation) while the temperature of the reaction was allowed to increase slowly to about 30 °C. The stirring rate was again increased and lithium carbonate (19.6 g) was added. In about 10 min the solution became fluid and stir opalescence was observed if the inherent viscosity of the polymer reached about 2.3.

B. Poly(1,4-benzamide) from *p*-Sulfinylaminobenzoyl Chloride.[9] In a dry three-necked reaction flask equipped with a nitrogen-inlet tube, drying-outlet tube, and stirrer were placed *p*-sulfinylaminobenzoyl chloride (32.2 g) and 100 mL of tetramethylurea. While this solution was stirred, a mixture of lithium hydroxide (3.84 g, 0.16 mol) and lithium chloride (2.08 g, 0.049 mol) was added. This was followed by 25 mL of tetramethylurea and 5 mL of a solution of water in tetramethylurea (formed by adding 1.92 mol of water to 1 L of solution). The viscous solution was stirred for 20 min at about room temperature and 10 min at 130 °C. Another 15 mL of tetramethylurea was added and stirring at 130 °C was continued for an additional 30 min. The cloudy, viscous yellow dope was suitable for spinning. The polymer inherent viscosity was 1.0 (H_2SO_4).

Spinning Solution Preparation from Isolated Polymer. 1. In Tetramethylurea. Into a heavy-walled cylindrical flask equipped with an air-driven shear-disk stirrer was placed 20.0 g of poly(1,4-benzamide) (η_{inh} = 1.35) and 180 g of tetramethylurea/lithium chloride solution containing 6.5% by wt of the salt. This mixture was stirred and heated at about 130 °C by means of an oil bath. An extremely viscous gelatinous mass resulted which was cooled in solid carbon dioxide for about 1 h. The heating and cooling cycles were repeated several times until a smooth, stir-opalescent solution was obtained. The amount of heating and cooling required to form a spinnable dope varies with polymer inherent viscosity, concentration, crystallinity, particle size, and effectiveness of stirring action.

2. In *N,N*-Dimethylacetamide. In a "resin" kettle equipped with a condenser, drying tube, and shear-disk stirrer were combined a solution of 250 mL of *N,N*-dimethylacetamide with 15 g of lithium chloride and 30.0 g of poly(1,4-benzamide) (η_{inh} = 1.50). This mixture which contains 10.7 wt % of polymer and 5.3 wt % of salt was stirred first at room temperature and then at 100 °C (oil bath) until a solution suitable for spinning was produced.

Polymer Solution Viscosity. Bulk viscosities of stirred polymer solutions were measured with a Brookfield Synchro-Lectric Viscometer (Model RV, Brookfield Engineering Laboratories, Inc.,

Chart I

Deg of crystallinity	Sharpness of spots	Diffuse scatter
Low	Broad	Considerable
Medium	Intermediate	Some
High	Narrow and sharp	Essentially absent

Staughton, Mass.) using No. 4 and No. 6 spindles obtained from the above cited manufacturer. Viscosity calculations were made at different concentrations by correlating the viscometer dial readings (obtained with various spindle settings which establish spindle speeds and, therefore, shear rates) with the tabulated figures provided in the "Brookfield Factor Finder". The viscosity determinations were made with an uncalibrated viscometer–spindle system in vessels which were not of optimum dimensions; while relative viscosity determinations for the dopes are accurate, absolute values are not necessarily correct.

Bulk viscosities in Figure 6 were determined with a No. 6 spindle (diameter 14 cm) at 10 rpm and with a polymer solution sample contained in a vial of 25-cm diameter.

Bulk viscosities in Figure 7 were determined with No. 4 and No. 6 spindles and with a polymer solution sample contained in either a polyallomer test tube (3.82-cm diameter × 10.2-cm deep, nearly transparent) equipped with a Teflon TFE–fluorocarbon cap through which a viscometer spindle extends into the dope or a polyethylene bottle (about 4.45 cm in diameter × 10.8 cm deep) equipped with a cap through which a viscometer spindle extends.[7]

X-Ray Diffraction. Wide angle x-ray diffraction patterns were obtained with a Warhus pinhole camera and Phillips x-ray generating unit No. 12045 having a copper fine-focus diffraction tube and a nickel β filter. The distance from sample to film was 50 mm. The arc length in degrees between the half-maximum intensity points of a principal equatorial diffraction spot is reported as the orientation angle of the sample.[11] The degree of crystallinity was estimated by visual examination and use of the terms in Chart I.[12]

Dilute Solution Viscosity. The inherent viscosity number $[\eta_{inh} = 2.3 \log (\eta_{rel})/c]$ was determined at 30 °C on solutions containing 0.5 g of polymer per 100 mL of concentrated sulfuric acid with a Cannon-Fenske viscometer. Results are reported in deciliters per gram.

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Poly(1,4-phenyleneterephthalamides). Polymerization and Novel Liquid-Crystalline Solutions[1]

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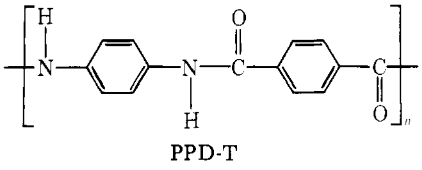
ABSTRACT: Para-aromatic polyamides were prepared and the factors leading to their novel solution behavior were studied. Preparation of high molecular weight poly(1,4-phenyleneterephthalamide) in HMPA–NMP showed a strong dependence between inherent viscosity (η_{inh}) attained and reactant concentration used. In 2:1 (by volume) HMPA–NMP, the highest η_{inh} was obtained when each reactant was at about 0.25 mol/L; lower and higher concentrations yielded polymer of lower η_{inh}. When dissolved in high strength sulfuric acid or HMPA–NMP–LiCl solvents, poly(1,4-phenyleneterephthalamide) formed unique liquid-crystalline "solutions" composed of liquid isotropic and anisotropic (mesomorphic) phases. The effect of polymer η_{inh} on the critical concentration needed to form the anisotropic phase was determined. Similarly, liquid-crystalline solutions were formed with poly(chloro-1,4-phenyleneterephthalamide) in DMAc–LiCl solvents. In this case, the liquid-crystalline solutions were readily separated into the component isotropic and anisotropic phases. The distribution of polymer in each of these phases was studied and found to be dependent upon polymer concentration, polymer η_{inh}, and LiCl content. The anisotropic phase always contained a greater amount of polymer than the isotropic phase and the η_{inh} of this polymer was greater as well. Thus, formation of an anisotropic phase occurred by the highest molecular weight polymer chains packing into an ordered, more dense fluid. By proper selection of polymer and solvent variables, the extent of anisotropic phase relative to isotropic phase could be varied from 0 to essentially 100%.

The study of para-aromatic polyamides is occurring at an accelerating rate in laboratories across the world. This interest arises in part from the novel "liquid-crystalline solutions" [liquid mixtures of isotropic and anisotropic (mesomorphic) phases] they yield. One of the simpler members of this class of polymers, poly(1,4-phenyleneterephthalamide), PPD-T, was first prepared in high molecular weight by solution polymerization several years ago.[2] Since then, many of the key polymerization factors required for obtaining high molecular weight polymer have come into better focus.[3,4] In this paper, we present data relating one of the major factors, reactant concentration, to polymer molecular weight obtained for polymerization in a mixture of hexamethylphosphoramide



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