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 $[\eta_{\text{inh}} = 2.3 \log (\eta_{\text{rel}})/c]$ 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.

Acknowledgment. We wish to acknowledge the excellent technical assistance of P. Lopez and W. F. Dryden, Jr., the preparation of fibers by C. E. Smullen, and the preparation and analysis of x-ray diffraction patterns by H. G. Thielke.

References and Notes

(1) Paper presented at ACS meeting in New York City, April 1976. See *Polym. Prepr. Am. Chem. Soc., Div. Polym. Chem.*, **17**, 53–58 (1976).

(2) F. C. Bawden and N. W. Pirie, *Proc. R. Soc. London, Ser. B.*, **123**, 274 (1937).

(3) C. Robinson, *Trans. Faraday Soc.*, **52**, 571 (1956).

(4) A. Blumstein, R. B. Blumstein, S. B. Clough, and E. C. Hsu, *Macromolecules*, **8**, 73–76 (1975).

(5) H. Morawetz, "Macromolecules in Solution", 2nd ed, Wiley, New York, N.Y., 1975, p. 67.

(6) S. L. Kwolek, U.S. Patent 3 600 350 (August 17, 1971).

(7) S. L. Kwolek, U.S. Patent 3 819 587 (June 25, 1974).

(8) R. Graph and W. Langer, *J. Prakt. Chem.*, **148**, 161 (1937).

(9) E. F. Hoegger, J. R. Schaefgen, and C. W. Stephens, U.S. Patent 3 575 933 (April 20, 1971).

(10) S. P. Papkov, V. G. Kulichikhin, V. D. Kalmykova, and A. Ya. Malkin, *J. Polym. Sci., Polym. Phys. Ed.*, **12**, 1753 (1974).

(11) S. L. Kwolek, U.S. Patent 3 671 542 (June 20, 1972).

(12) P. W. Morgan and S. L. Kwolek, *Macromolecules*, **8**, 111 (1975).

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

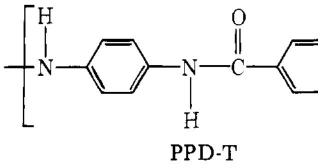
T. I. Bair,* P. W. Morgan, and F. L. Killian

Pioneering Research Laboratory, Textile Fibers Department, E. I. du Pont de Nemours and Company, Wilmington, Delaware 19898.

Received April 11, 1977

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



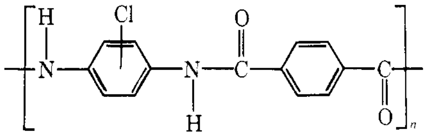
PPD-T

Chart I

Reactant, mol/L		
Diamine	Acid chloride	Polymer η_{inh}
0.095	0.095	3.4
0.190	0.190	6.1
0.595	0.595	5.6
0.720	0.720	4.8
1.05	1.05	3.1

(HMPA) [*Caution!* See ref 5] and *N*-methylpyrrolidone-2 (NMP).

Many of the para-aromatic polyamides dissolve in selected solvents to form an anisotropic (mesomorphic) phase at some critical concentration. The transition from isotropic to anisotropic phase is marked by a rapid decrease in viscosity, an opalescent cast when stirred in visible light, and a bright appearance when viewed between crossed polars. Presented here in some detail are the key factors related to forming liquid anisotropic phases with PPD-T and poly(chloro-1,4-phenyleneterephthalamide), ClPPD-T, and the distribution of polymer in both anisotropic and isotropic phases of liquid-crystalline solutions.



ClPPD-T

Experimental Section

Purification of Materials. Commercially obtained 1,4-phenylenediamine and terephthaloyl chloride were purified by vacuum sublimation to essentially white solids with sharp melting points.

2-Chloro-1,4-phenylenediamine (*Caution!* 2-chloro-1,4-phenylenediamine is unstable, see ref 6) was obtained from commercially available hydrochloride salt. The salt was dissolved in water and the solution was made alkaline to litmus paper with 50% sodium hydroxide solution. The resulting mixture was extracted with several successive portions of petroleum ether which were then combined and dried over anhydrous sodium sulfate. The petroleum ether was removed at reduced pressure and the residue was sublimed under vacuum at about 80 °C to give pale yellow needles, mp 64–65 °C.

Commercially available hexamethylphosphoramide (*Caution!* see ref 5) and *N*-methylpyrrolidone-2 were each purified by vacuum distillation over calcium hydride to clear, colorless liquids with a narrow boiling range.

Poly(1,4-phenyleneterephthalamide) Synthesis. 1,4-Phenylenediamine (11.57 g, 0.107 mol), hexamethylphosphoramide (280 mL), and *N*-methylpyrrolidone-2 (140 mL) were combined anhydrously in an oven-dried 1-L resin kettle equipped with an air-driven "egg-beater"-type stirrer and stirred for about 15 min while being cooled in a bath of ice and acetone at −15 °C. To the resulting cooled solution was added powdered terephthaloyl chloride (21.76 g, 0.107 mol) with rapid stirring. The reaction mixture became a thick, pastelike gel in about 5 min. Stirring was discontinued after a few minutes and the thick mixture was allowed to stand overnight while gradually warming to room temperature. The mixture was then worked up by agitating the contents with water in a blender to wash away solvent and the polymer was collected by filtration. This washing procedure was repeated several times with water and finally with acetone. The collected polymer was dried in a vacuum oven for about 24 h at about 85 °C. The dried polymer (24.4 g, 96% recovery) had an inherent viscosity of 6.93.

Other poly(1,4-phenyleneterephthalamide) polymers prepared by the same general procedure but at different reactant concentrations gave the data in Chart I.

Poly(chloro-1,4-phenyleneterephthalamide) Synthesis. 2-Chloro-1,4-phenylenediamine (35 g, 0.245 mol) was dissolved in 425 mL of hexamethylphosphoramide contained in an oven-dried 1-L resin kettle equipped with an air-driven stirrer. The mixture was cooled with an ice/water bath and powdered terephthaloyl chloride (49.7 g, 0.245 mol) was added with stirring. Almost immediately, a precipitate formed as a wet paste. The mixture was allowed to stand overnight and then worked up by agitating with water in a blender to wash away solvent. The polymer was then collected by filtration. This work-up procedure was repeated several times and the polymer was then dried in a vacuum oven at 78 °C. The dried polymer (60 g, 90% recovery) had an inherent viscosity of 1.13.

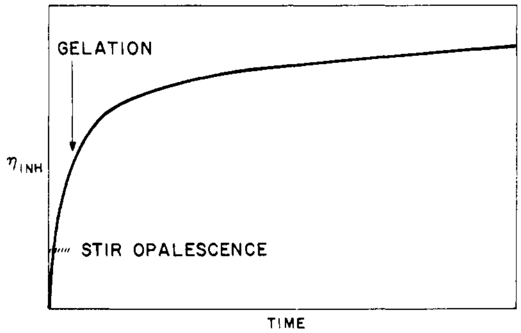


Figure 1. General schematic representation of the polymerization of poly(1,4-phenyleneterephthalamide) in HMPA–NMP showing an initial rapid increase of molecular weight and transient stir-opalescence followed by gelation and subsequent retardation of polymerization rate.

Determination of Inherent Viscosity. The inherent viscosity number [$\eta_{\mathrm{inh}} = 2.3 \log (\eta_{\mathrm{rel}})/c$] was determined at 30 °C on solutions containing 0.5 g of polymer per 100 mL of concentrated (95–98%) H_2SO_4 with a Cannon-Fenske viscometer. Results are reported in deciliters per gram.

Determination of Critical Concentration. The critical concentration is the minimum concentration of polymer in a solvent needed to yield an anisotropic phase. This concentration was determined for a given polymer–solvent combination by slowly "titrating" a liquid crystalline solution of known concentration with the given solvent while manually agitating the dope with a flat spatula. As solvent was added via a buret, the point at which light transmission under crossed polars or stir opalescence disappeared was noted. The weight fraction of polymer at the critical point was then calculated from the volume of solvent added, the solvent density, and the known composition of the original liquid.

Determination of Liquid-Phase Volume Fraction and Composition of ClPPD-T/*N,N*-Dimethylacetamide (DMAc)/LiCl Fluids. Highly liquid-crystalline solutions containing a mixture of anisotropic and isotropic phases were readily separated into a dense anisotropic phase and a lighter clearer isotropic phase by allowing the liquid to stand in a graduated centrifuge tube at room temperature for several days. Separation of the more viscous liquid-crystalline solutions was assisted by centrifuging for several hours at room temperature. The volume fraction of each phase was calculated directly from the volume readings on the graduated tube. To obtain the polymer concentration in each phase, a 5–10-mL aliquot of each phase was carefully removed with a pipet and the polymer was isolated by working up with large quantities of water in a blender. The polymer was collected on a filter, dried in a vacuum oven at 85–100 °C, and then weighed. A portion of each aliquot was viewed under crossed polars to confirm that separation was complete. Viewed in this manner, the isotropic phase transmitted no light, and the anisotropic phase showed no dark oblong bubblelike regions of isotropic liquid.

Results and Discussion

I. PPD-T Preparation. The formation of PPD-T by adding powdered terephthaloyl chloride (TCl) to a solution of 1,4-phenylenediamine (PPD) in a mixture of hexamethylphosphoramide (HMPA) and *N*-methylpyrrolidone-2 (NMP) rapidly proceeds, with stirring, through an opalescent state to a heavy thick gel at the moderately high concentrations we have studied. The gel has little reactivity and polymerization is nearly complete at this point (see Figure 1). The η_{inh} of the final polymer is dependent upon such factors as the reaction temperature, stirring rate, solvent composition, stoichiometry, and, in an interesting manner, ingredients concentration. When the polymerization was carried out in HMPA:NMP (2:1 by volume), the maximum η_{inh} was obtained when the con-

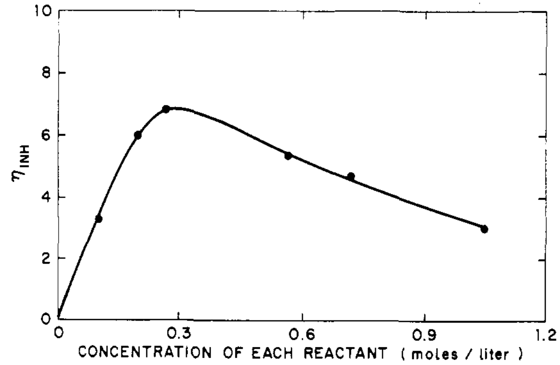


Figure 2. Maximum PPD-T inherent viscosity obtained plotted as a function of the concentration of each reactant for polymerization in HMPA–NMP (2 to 1 by volume) at −15 °C.

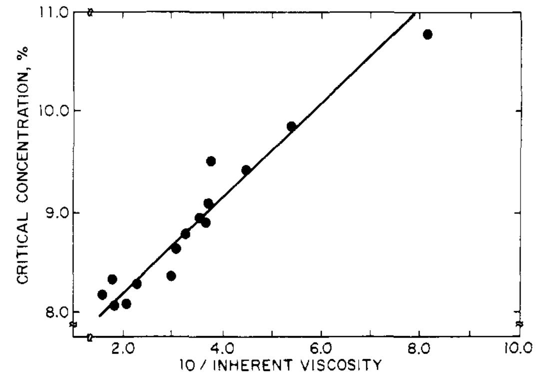


Figure 3. Plot showing minimum PPD-T concentration (critical concentration) in fuming sulfuric acid (equivalent to 100.2–100.5% H_2SO_4) needed to form an anisotropic phase at room temperature for various polymer-inherent viscosities. Liquids characterized by polymer concentrations above the line contain an anisotropic phase.

centration of the reactants was on the order of 0.25 mol/L as shown in Figure 2. The lower η_{inh} obtained at lower reactant concentration can be readily rationalized by taking into account competitive side reactions similar to those discussed by Herlinger et al.[7] for solution polymerization of aromatic diamines and aromatic dicarboxylic acid chlorides in *N,N*-dimethylacetamide (DMAc).

One possible explanation for the drop-off of η_{inh} at higher reactant concentration is reduced reactant mobility due to the onset of gelation before high η_{inh} could be reached. We would expect, therefore, that as the solvent power of the reaction medium is increased, the η_{inh} maximum would move to higher concentrations. This has been found to be the case. When the polymerization medium was100% HMPA, the η_{inh} peaked at about 0.7 mol/L reactant concentration. Another possible reason for lower polymer η_{inh} at higher concentration is an increase in the rate of side reactions as a result of greater heat generation at higher reactant concentration. A combination of both reduced reactant mobility and increased side reactions is probably the best explanation for the observed drop-off of η_{inh} at higher reactant concentration.

II. PPD-T Liquid-Crystalline Solutions. High-concentration sulfuric acid is one of the better solvents for PPD-T and in cases where the concentratin of H_2SO_4 is 98% or greater, this rigid chain polymer is sufficiently soluble to form an anisotropic phase and liquid-crystalline solution at room temperature over a wide range of polymer molecular weights. The critical polymer concentration for formation of the anisotropic phase decreases as polymer η_{inh} increases as shown in Figure 3 for PPD-T in fuming sulfuric acid. At the point of anisotropic phase formation, these liquids exhibit the stir opalescence and drop in solution viscosity described by Kwolek[8] for liquid-crystalline solutions of poly-1,4-benzamide.

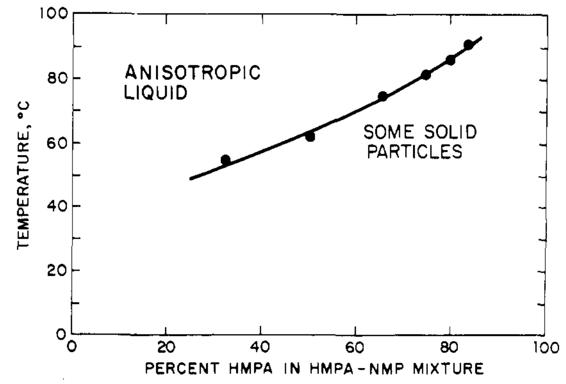


Figure 4. Temperature required to dissolve 10 g of PPD-T in 100 mL of HMPA–NMP–LiCl solvent which contains 3.6 g of LiCl per 100 mL of HMPA–NMP plotted as a function of volume fraction of HMPA. Liquids at or slightly above the solubilizing temperature contain an anisotropic phase.

PPD-T also forms an anisotropic phase with mixtures of HMPA, NMP, and LiCl. Complicated relationships exist between solvent composition, LiCl concentration, polymer η_{inh}, and temperature in the formation of these phases.[3] Treatment of all the relationships leading to an anisotropic phase is beyond the scope of this paper, but one combination of variables is shown in Figure 4 where the temperature at which a mixture of PPD-T in HMPA–NMP–LiCl solvent becomes completely fluid is plotted as a function of the amount of HMPA in the solvent mixture. PPD-T polymers generally have substantially lower critical concentrations in HMPA–NMP–LiCl solvents than in concentrated sulfuric acid, and the liquids described in Figure 4 contain a substantial fraction of anisotropic phase.

III. ClPPD-T Liquid-Crystalline Solutions. Many substituted para-aromatic polyamides also form liquid-crystalline solutions. One of the more tractable is poly(chloro-1,4-phenyleneterephthalamide) [ClPPD-T]. This polymer is considerably less symmetrical than PPD-T and forms a liquid anisotropic phase in relatively simple solvents such as DMAc–LiCl at room temperature. Further, the anisotropic phase can usually be readily separated from the isotropic phase, which allows ready analysis of the composition of the equilibrium isotropic and anisotropic phases.

A. Anisotropic Phase Formation. Plots of the critical concentrations of ClPPD-T polymers of two inherent viscosities as a function of weight percent LiCl in DMAc (Figure 5) show, as with PPD-T polymer in sulfuric acid, that the critical concentration is lower for higher η_{inh} polymer at relatively low LiCl concentration. Also, the critical polymer concentration is highly dependent upon the amount of LiCl and increases as the concentration of LiCl increases. A possible explanation for this behavior is that the effective axial ratio of the polymer chain decreases with higher LiCl content. This decrease could occur by increased solvation of the chain or by induced lateral chain-to-chain association at the higher salt levels. As will be shown later, the polymer concentration in the anisotropic phase increases with higher LiCl content supporting the chain-to-chain association concept.

Also, at relatively high LiCl content, 4% or greater for the polymers used in Figure 5, the distinction between polymers of different η_{inh} surprisingly disappears. This behavior is best explained by chain-to-chain association to the extent that differences in the effective axial ratio of polymers of different η_{inh} are leveled out. This concept is discussed further in subsection C.

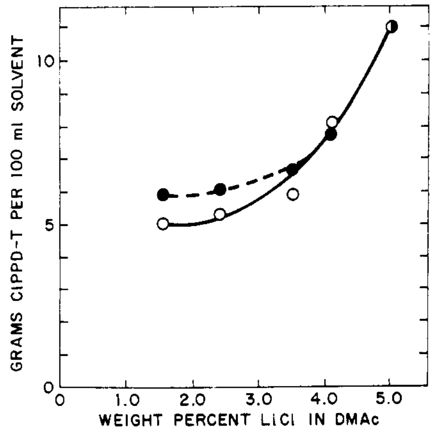


Figure 5. Critical concentrations at room temperature of ClPPD-T in DMAc–LiCl plotted as a function of LiCl concentration. Polymer η_{inh}: (●) $\eta_{inh} = 1.27$; (○) $\eta_{inh} = 2.01$. Liquids characterized by polymer concentrations above the lines contain an anisotropic phase.

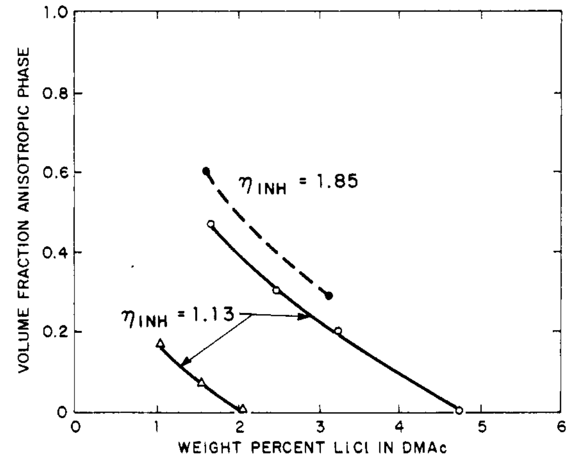


Figure 6. Volume fraction of anisotropic phase at room temperature for liquids at ClPPD-T in DMAc–LiCl plotted as a function of LiCl concentration. Amount of ClPPD-T: (△) 7.5 g per 100 mL of DMAc–LiCl; (○) 10.0 g per 100 mL of DMAc–LiCl. Solid lines are for ClPPD-T of $\eta_{inh} = 1.13$ and broken line for ClPPD-T of $\eta_{inh} = 1.85$.

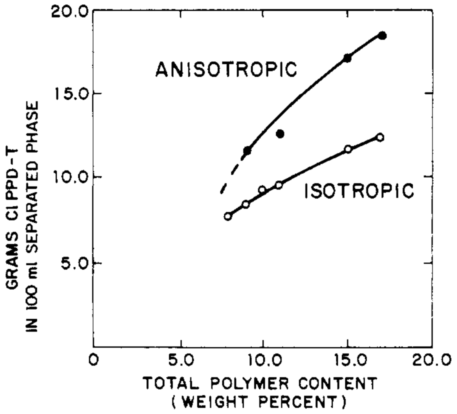


Figure 7. ClPPD-T concentration in equilibrium anisotropic and isotropic phases at room temperature of liquid-crystalline solutions prepared with various weight percent ClPPD-T ($\eta_{inh} = 1.09$) in DMAc containing 2.18% LiCl: (●) concentration of ClPPD-T in separated anisotropic phase; (○) concentration of ClPPD-T in separated isotropic phase.

B. Extent of Anisotropic Phase Formation. There are three primary factors governing the extent of anisotropic phase formation for ClPPD-T in DMAc–LiCl at a given temperature: (1) polymer content, (2) LiCl content, and (3) polymer η_{inh}. These relationships are shown in Figure 6. A greater amount of anisotropic phase is formed at lower LiCl content. (Of course, some minimum amount of LiCl is needed to dissolve a significant amount of polymer and mixtures with much less than 1% LiCl contain undissolved polymer.) The volume fraction of anisotropic phase increases with increasing total ClPPD-T polymer content as well. As expected from its lower critical concentration, higher inherent viscosity polymer yields a higher fraction of anisotropic phase at a given total polymer content in DMAc containing a modest level of LiCl. By proper selection of polymer and solvent variables, the extent of anisotropic phase formation can be varied from 0 to essentially 100%.

C. Polymer Distribution in Liquid-Crystalline Solutions. Plotting the amount of ClPPD-T polymer in the equilibrium anisotropic and isotropic phases as a function of the total ClPPD-T polymer content (Figure 7) shows the amount of ClPPD-T polymer in the anisotropic phase to be always greater than that in the isotropic phase. Thus, above the critical concentration, the anisotropic phase forms by some of the polymer and solvent molecules collapsing into a more dense, ordered arrangement leaving behind a less concentrated isotropic phase.

Interestingly, in the mixtures studied (which contain from 10 to 60% anisotropic phase), the polymer concentration in the isotropic, as well as in the anisotropic, phase increases with increasing total ClPPD-T content instead of leveling off at some constant value. This is a consequence of the polydispersity of the ClPPD-T polymer. Because the polymer is polydisperse, as more polymer is added beyond the critical point, lower molecular weight chains enter the isotropic phase, thereby increasing the critical concentration requirement (see also subsection D). However, the difference in polymer concentration between the two phases tends to increase as the total polymer content increases and the amount of isotropic phase decreases, probably because the polymer molecular weight distribution in the isotropic phase tends to narrow. In the limit, the whole solution will be converted essentially to the anisotropic phase in which the concentration will equal the total polymer content.

The effect of LiCl on the phase composition is shown in Table I. The polymer concentration in the anisotropic phase is substantially higher at greater LiCl content, which is consistent with the higher critical concentration found for ClPPD-T at higher LiCl content (see Figure 5). Interestingly, the concentration in the equilibrium isotropic phase decreases with increasing LiCl content. This behavior further supports the concept of chain-to-chain association in a manner which tends to increase the axial ratio of chains of lower η_{inh} but decreases this ratio for chains of higher η_{inh}. Thus, increasing LiCl content results in higher critical concentrations and higher polymer concentration in the anisotropic phase (both governed by the higher chains) but lower polymer concentration in the isotropic phase (governed by the lower η_{inh} chains). In effect, the effective polydispersity of the polymer in solution appears to have been lowered by increasing the LiCl content.

We might expect from a general consideration of critical points that as the inherent viscosity of the polymer is increased, the concentration in the isotropic phase would decrease. However, in the few systems studied, the ClPPD-T concentration in each phase actually appears to be independent of the polymer-inherent viscosity (see Table II). This apparent lack of sensitivity to η_{inh} is probably due to the relatively small range of inherent viscosity studied and the relatively high LiCl content (3.12 g/100 mL of solvent) used

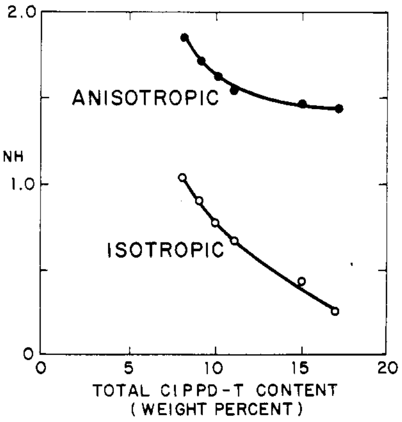


Figure 8. Inherent viscosity of ClPPD-T in equilibrium anisotropic and isotropic phases at room temperature of liquids prepared with various weight percent of ClPPD-T ($\eta_{\text{inh}} = 1.09$) in DMAc containing 2.18% LiCl: (●) η_{inh} of ClPPD-T in separated anisotropic phase; (○) η_{inh} of ClPPD-T in separated isotropic phase.

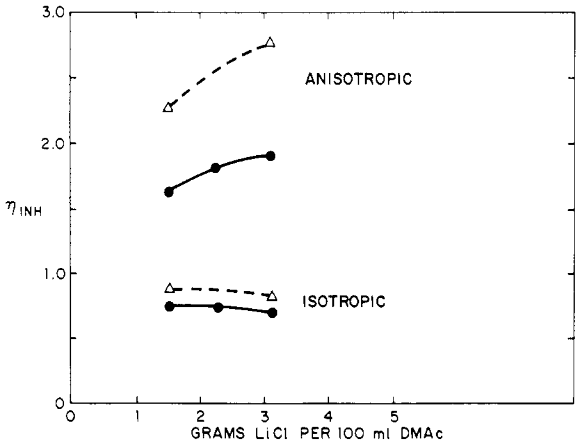


Figure 9. Inherent viscosity of ClPPD-T in equilibrium anisotropic and isotropic phases at room temperature for liquids from 10 g of ClPPD-T per 100 mL of DMAc containing various amounts of LiCl: (△) η_{inh} of unfractionated ClPPD-T is 1.85; (●) η_{inh} of unfractionated ClPPD-T is 1.13. Two upper curves show the η_{inh} of fractionated ClPPD-T in the anisotropic phase and the lower two curves the η_{inh} of fractionated ClPPD-T in the isotropic phase.

which tends to level out η_{inh} differences as discussed in subsection A.

D. ClPPD-T Polymer Fractionation. As the chain ordering and anisotropic phase formation occur, not only does the polymer distribute itself between anisotropic and isotropic phases in nonequal concentrations but, as a consequence of the polydispersity of ClPPD-T polymer, polymer molecular weight fractionation also occurs. This phenomenon has also been reported by Oster[9] for solutions of tobacco mosaic virus and by Kwolek[8] for solutions of polybenzamide and appears to be a consequence of the relative space requirements of long and short rods randomly arranged in solution.

As shown in Figure 8, the inherent viscosity of polymer in the anisotropic phase is higher than that in the isotropic phase, and the inherent viscosity of polymer in both phases decreases with increasing polymer content. Thus, fractionation occurs as a result of the highest molecular weight chains being the first to form an anisotropic phase. As more anisotropic phase is formed by adding more polymer to the mixture, lower molecular weight polymer begins to enter the anisotropic phase, thereby reducing the overall polymer η_{inh} in that phase.

Table I
Effect of LiCl on the Polymer Concentration in Equilibrium Anisotropic and Isotropic Phases [a]

LiCl concn in DMAc	ClPPD-T concn	
	Isotropic phase, g/100 mL	Anisotropic phase, g/100 mL
1.56	8.0	9.8
2.34	7.2	10.9
3.12	7.2	13.0

[a] 10 g of ClPPD-T polymer ($\eta_{\text{inh}} = 1.13$) dissolved in 100 mL of DNAc–LiCl at 25 °C.

Table II
Effect of ClPPD-T Inherent Viscosity on the Polymer Concentration in Equilibrium Anisotropic and Isotropic Phases [a]

η_{inh} of unfractionated ClPPD-T	ClPPD-T concn	
	Isotropic phase, g/100 mL	Anisotropic phase, g/100 mL
1.13	7.2	13.0
1.67	6.9	13.1
1.71	6.9	12.9
1.85	7.3	12.9

[a] 10 g of polymer dissolved in 100 mL of DMAc containing 3.12 g of LiCl at 25 °C.

When ClPPD-T of higher inherent viscosity was used to form the liquid-crystalline solution, the η_{inh} of the polymer in each phase is increased. As the LiCl concentration of the solution was increased, the η_{inh} of the polymer in the anisotropic phase became significantly higher whereas the η_{inh} of polymer in the isotropic phase changed only slightly (Figure 9) to a lower value.

In summary, the formation of a liquid-crystalline solution requires not only a polymer having a relatively high axial ratio in solution but also the proper solvent. The solvent must be capable of dissolving a fairly large amount of polymer and yet not interact with the polymer chain in such a way that the critical concentration is raised to a level above the polymer solubility. Once the critical concentration is reached, the system is converted into more and more anisotropic phase as more and more polymer is added. The anisotropic phase has higher polymer concentration than the coexisting isotropic phase and is composed of the higher molecular weight chains. The effect of changing polymer inherent viscosity or solvent is to alter both the concentration at which anisotropy begins and the composition of the two phases. This occurs, presumably, due to a change in the effective axial ratio of the polymer chains by altering the average degree of polymerization or by changing chain-to-chain association, or both.

References and Notes

(1) Presented before the Division of Polymer Chemistry at the 171st National Meeting of the American Chemical Society, New York, N.Y., March 1976.
(2) S. L. Kwolek, P. W. Morgan, and W. R. Sorenson, U.S. Patent 3 063 966 (1962).
(3) (a) T. I. Bair and P. W. Morgan, U.S. Patent 3 673 143 (1972); (b) *ibid.*, 3 817 941 (1974).
(4) A. A. Fedevov et al., *Vysokomol. Soedin., Ser. B*, **15**, 74 (1973).
(5) HMPA can cause cancer in laboratory animals. Accordingly, all experiments with it should be done in a good hood to avoid inhaling any of its vapors, and skin contact with liquid HMPA should be carefully avoided.
(6) Chloro-1,4-phenylenediamine is unstable above 135 °C and should not be heated above that temperature. Explosive decomposition was experienced during an attempted distillation under reduced pressure at about 180 °C.
(7) H. Herlinger et al., *Appl. Poly. Symp.*, **No. 21**, 201 (1973).
(8) S. L. Kowlek, U.S. Patent 3 671 542 (1972).
(9) G. Oster, *J. Gen. Physiol.*, **33**, 445 (1950).