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Synthesis and Properties of Aromatic and Extended Chain Polyamides

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ABSTRACT: Three areas of research on wholly aromatic polyamides are discussed. (1) Poly(1,3-phenyleneisophthalamide) was prepared in high molecular weight in chloroform or methylene chloride with tertiary amine acid acceptors. The degree of polymerization was enhanced by the presence of added or by-product tertiary amine salts. (2) 1,4-Aminobenzoyl chloride hydrochloride as crystalline needles was polymerized to high molecular weight in the solid state at high temperature and in suspension at low temperature in inert solvents with an acid acceptor. Both procedures led to the retention of the outward needle form. The polymer was crystalline and oriented crosswise of the needle structures. (3) A variety of extended chain polyamides, e.g., those based on such units as 1,4-phenylene, 2,6-naphthylene, *trans*-cyclohexylene, and *trans*-vinylene, were prepared which will form mesomorphic or liquid-crystalline solutions. These solutions depolarize transmitted, plane-polarized light and exhibit a reversal in viscosity–concentration relationship at the anisotropic–isotropic transition. Because these liquid-crystalline solutions contain microscopic domains of aligned and extended polymer chains, they yield molecularly oriented films and fibers upon extrusion. Such products have exceptionally high strength and modulus.

In a program of discovery in chemistry, success often seems to depend on a fortunate choice of ingredients, experimental conditions, and timing. Some call it serendipity. Described here are some key features of three pieces of research on aromatic polyamides, all of which involved in varying degrees some happy circumstances, a sharp eye, and often an element of care and persistence.

These three topics are: (1) preparation of polyamides in halogenated hydrocarbon–salt mixtures; (2) preparation of poly(1,4-benzamides) by thermal and suspension methods; and (3) extended chain polyamides and their liquid crystalline solutions.

Wholly aromatic polyamides in which the amide groups are linked directly to the rings have been known in the literature only for about 20 years when such a polymer was described in a patent to Magat.[3] An interfacial procedure was used and the molecular weight was not high by current standards.

At the time of our first programs on the synthesis of wholly aromatic polyamides there was a body of lore suggesting that, in addition to low reactivity, there were some peculiar side reactions which prevented formation of high polymers. Certainly, air oxidation of some diamines in the presence of alkali was a problem. Soon, as we developed low-temperature solution polycondensation methods,[4] the importance of monomer purity and polymer swelling and solubility were recognized.[5] At about the same time, modified interfacial procedures (that is, the use of water-miscible organic solvents) were found to yield high molecular weight aromatic polyamides.[6] Of the two methods, the solution method is more broadly applicable. These syntheses are most commonly carried out with diamines and diacid chlorides or amino-substituted acid chlorides.

Discussion and Results

For any of the low-temperature procedures there are a number of common controlling factors in their successful application. The principal ones are shown in Table I. To some degree an optimum condition in relation to one factor may make up for lack in another. For example, high reaction rate may compensate somewhat for low solubility. It is not the purpose here to examine these relations in detail, but the importance of some of them will become apparent in the discussion.

Preparation of Aromatic Polyamides in Halogenated Hydrocarbons. The first low-temperature solution preparations of polyamides from acid chlorides were carried out in halogenated hydrocarbons. Some of the first polymers were based on piperazines and aliphatic or aromatic diacids.[7,8] Tertiary amines were used as acid acceptors. Now it seems not to be generally known that this is a perfectly good route to many wholly aromatic polyamides. This is the first topic.

In a typical reaction, 1,3-phenylenediamine is allowed to react with isophthaloyl chloride in chloroform in the presence of triethylamine and added triethylamine hydrochloride (see Scheme I). Both the added and by-product triethylamine hydrochloride are soluble in the chloroform. The salt presumably forms a soluble complex with polymer, aiding solution and the polymerization process in a manner similar to that of LiCl in amide solvents. Viscous spinnable solutions can be formed as shown by the first set of data in Table II.

The polymerization series is arranged in order of decreasing salt concentration and polymer η_{inh}. Only at the highest concentration does the polymer remain dissolved. The first, second, and last polymerizations, wherein the salt to polymer mole ratio is about 4, show that dilution lowers the resulting degree of polymerization. The remaining three preparations show a decrease in viscosity of the polymer as the salt concentration decreases while polymer content is kept at about the same level. At low salt concentrations, high-speed stirring is needed in order to attain maximum mixing and uniform reaction before the polymer precipitates and further reaction essentially ceases.

If one adds anhydrous triethylamine hydrochloride to a

Scheme I
Preparation of Poly(*m*-phenyleneisophthalamide)

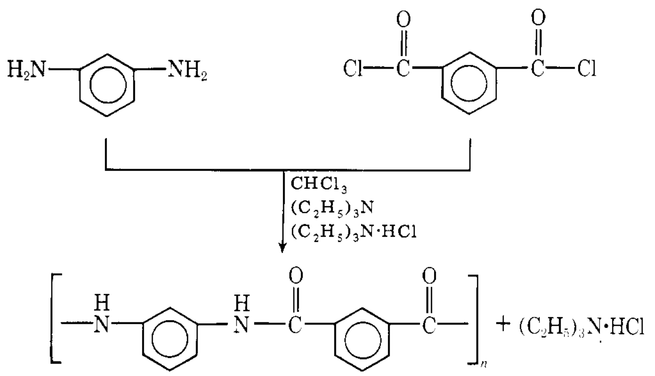


Table I
Major Factors Affecting Low-Temperature Polycondensations

Reaction rate
Purity of intermediates and solvents
Equivalence of reactants
Solubility of intermediates and polymer
Mixing
Side reactions
Temperature
Concentration

preparation completed at a low salt level, then further polymerization will occur. The result may not quite match a single-stage preparation. The new salt presumably enhances swelling of the precipitated polymer and provides mobility for further polymerization. See example in the Experimental Section.

A second series of polymerizations similar to that shown in Table II was carried out in methylene chloride (Table III). High degrees of polymerization were attained with less salt and in dilute systems. For example, polymer with an inherent viscosity of one was obtained with no salt but that produced in the reaction. The greater effectiveness of the salt in methylene chloride may be related to its lower solubility in that solvent; that is, less association with the solvent and more with the polymer.

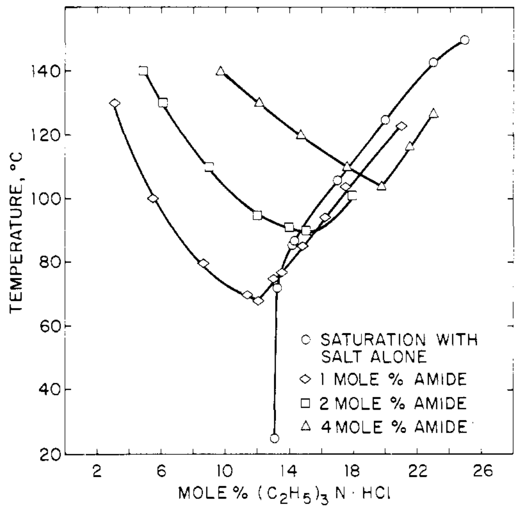


Figure 1. Solution temperatures for *N,N′*-diphenylisophthalamide in chloroform with varying amounts of triethylamine hydrochloride.

The discovery of the value of salts as aids in these polymerizations was made in a backhanded way. The only available source of pure 1,3-phenylenediamine at the time was the dihydrochloride. This was used in a polymerization with 4 mol of triethylamine and the diacid chloride. High polymer resulted. Later, when pure, free diamine became available, only low polymers were obtained. The difference was traced to the extra by-product salt.

Some insight into the behavior of the salt–solvent–polymer system can be gained by examining the solubility of model compounds. In Figure 1 are plotted the solution temperatures of different proportions of *N,N′*-diphenylisophthalamide and triethylamine hydrochloride in chloroform. (See Experimental Section for method.) The saturation line for salt in chloroform is shown by the circles. Clearly, the model amide solubility increases as the amount of salt is increased; the model solubility decreases again as the saturation region for the salt is

Table II
Preparation of Poly(1,3-phenyleneisophthalamide) in Chloroform–Triethylamine Hydrochloride[a]

Final salt concn in $CHCl_3$ system		Polymer			
g/100 mL	Mole %[b]	Mole %[b]	State	Yield, % isolated	η_{inh} in H_2SO_4
16.2	8.42	2.11	Soln	99	1.9
11.4	6.11	1.53	Soft ppt	96	1.36
7.25	4.02	0.764	Ppt	100	1.26
5.00	2.81	0.773	Ppt	99	1.21
3.75	2.12	0.779	Ppt	100	0.86
2.75	1.57	0.401	Ppt	100	0.60

[a] Polymerization at ~30 °C with triethylamine equivalent to by-product HCl. [b] For polymer–salt–solvent system.

Table III
Preparation of Poly(1,3-phenyleneisophthalamide) in Methylene Chloride–Triethylamine Hydrochloride[a]

Final salt concn in CH_2Cl_2 system		Polymer			
g/100 mL	Mole %[b]	Mole %[b]	State	Yield, % isolated	η_{inh} in H_2SO_4
4.70	2.11	0.618	Soft ppt	95	1.71
4.00	1.80	0.620	Ppt	97	1.54
3.10	1.40	0.623	Ppt	98	1.29
2.75	1.25	0.624	Ppt	100	0.98
2.62	1.19	0.595	Ppt	100	0.84
2.50	1.14	0.568	Ppt	100	0.74

[a] Polymerization at ~30 °C with triethylamine equivalent to by-product HCl. [b] For polymer–salt–solvent system.

approached. However, more salt is soluble in the presence of amide than in solvent alone. This may result because some of the salt forms a complex with the amide. Model solubility parallels solubility or swelling of the polymer and model–solvent interaction energies can be used as a tool for predicting success with polymerizations.

The amide units in phenylisophthalamide bear hydrogen substituents. This is a necessary feature for enhancement of solubility by dissolved salt. Model amides from secondary amines, which, of course, lack the NH group, show a sharp decrease in solubility upon addition of triethylamine hydrochloride to the chloroform (Figure 2). Here the effect is illustrated with amides of dimethylpiperazine and piperidine, which are not aromatic. Table IV shows several measurements with *N,N'*-dimethyldiphenylterephthalamide. Again solubility decreases as salt is added. Solution temperature rises even though the amount of amide used is decreased.

The presence of triethylamine hydrochloride in chloroform and methylene chloride markedly increases the measured dielectric constant (Figure 3). On the other hand, tetraethylammonium chloride, within the range measured, does not show such an effect. However, use of the quaternary salt does greatly increase the solubility of phenylisophthalamide and is beneficial in the preparation of poly(1,3-phenyleneisophthalamide). An earlier study of solvent media for the preparation of polyamides derived from piperazines, which are secondary diamines, showed that the degree of polymerization attained was raised as the dielectric constant of the solvent increased.[5,7,8] This effect was attributed to an enhancement of the reaction rate. No such correlation between the dielectric constant of the solvent or the solvent–salt combination and the degree of polymerization attained with primary aromatic polyamides has been found. The difference may lie in the salt association. That is, as oligomers of primary polyamides form, they associate with by-product polar salt and thus have a common environment in varying solvent media; oligomers of secondary polyamides do not associate with salt and, therefore, react in a medium consisting principally of solvent molecules.

A limited number of experiments were done on a variation of acid acceptors and amine salts (Table V). The results show that weak bases such as pyridine and diethylaniline by themselves give polymer with very low molecular weight. Ethylmorpholine provided a higher polymer in methylene chloride. When the weak bases were used in combination with triethylamine hydrochloride as a solvating agent, polymers with much higher inherent viscosities were obtained. The results with diethylaniline (pK_a in water, 6.56) and *N*-methylmorpholine (pK_a in water, 7.41)[7] with large amounts of salt were somewhat higher than that with triethylamine base–salt combination.

Preparation of Poly(1,4-benzamide). The foregoing experience has shown that high molecular weight poly(1,3-phenyleneisophthalamide), an AA–BB polymer, is formed only if there is a strong interaction between the medium and the forming polymer. This is interpreted to mean that there is provided at least a short-term solution period wherein the polymer may grow before a precipitate forms and the molecules become too associated for further rapid reaction. That is the experience with all low-temperature polycondensations. Non-polar, non-salt-dissolving media, such as hexane, carbon tetrachloride, or ether, are poor choices for attaining high molecular weight in a low-temperature solution process even when the reaction rate is high.

In Table VI are given the results of some preparations which run contrary to this conclusion.

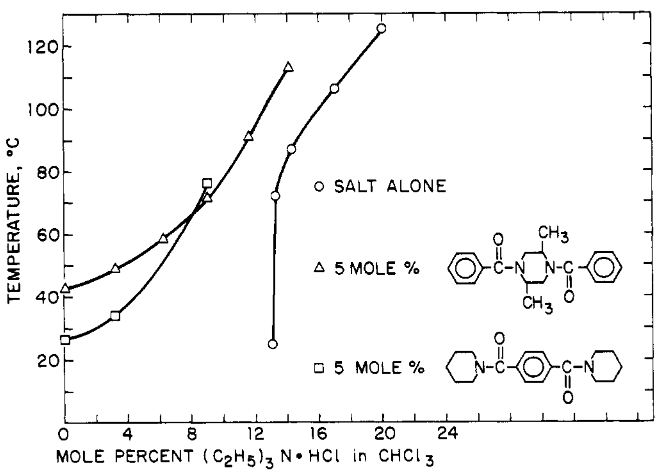
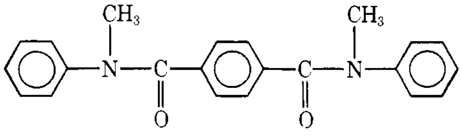


Figure 2. Solution temperatures for amides of secondary diamines in chloroform with varying amounts of triethylamine hydrochloride.

Table IV
Effect of Triethylamine Hydrochloride on the Solubility of *N,N'*-Dimethyl-*N,N'*-diphenylterephthalamide in Chloroform



Mol % amide	Mol % salt	Min. soln temp, °C
10.45		70.5
10.29	1.53	71.5
9.70	3.03	81.0

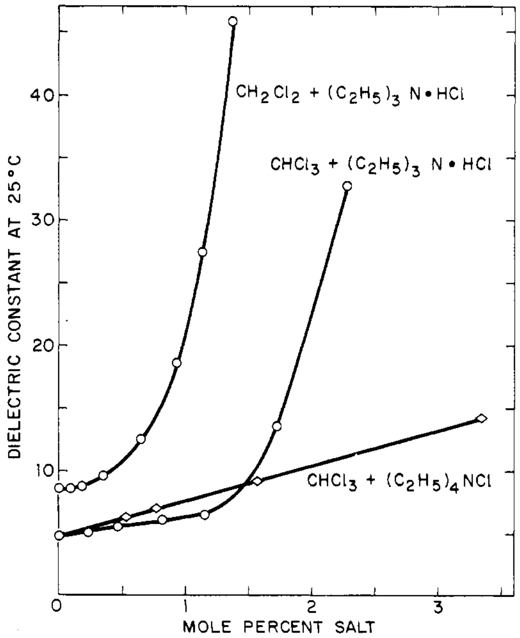


Figure 3. Effect of dissolved amine salts in chloroform and methylene chloride on the measured dielectric constant.

Poly(1,4-benzamide) can be prepared in very high molecular weight in hexane–pyridine and other selected nonsolvents from aminobenzoyl chloride hydrochloride. How can it be that high polymer forms from an intermediate with low reactivity in poor swelling media and a weak acid acceptor to yield a polymer with low solubility? First, only one intermediate is used. But that is a salt and insoluble. The answer seems to lie in an interesting and happy circumstance.

Table V
Poly(1,3-phenyleneisophthalamide) Prepared in Halogenated Hydrocarbons with Varying Acceptors and Salts[a]

Solvent	Acid acceptor	Added HCl salt, mol/mol of polymer	Polymer State	Mole %[b]	Yield, % isolated	η_{inh} in H_2SO_4
$CHCl_3$	Pyridine		Plastic	4.33	100	0.24
	Pyridine	Et_3N; 5.0	Soln	2.33	100	0.60
	Diethylaniline		Ppt	1.53	100	0.14
	Diethylaniline	Et_2NPh; 18	Soln	0.80	93	0.41
	Diethylaniline	Et_3N; 5.0	Soln	2.27	100	2.2
	Methylmorpholine	Me_3N; 3.6	Sw ppt	2.33	100	0.41
	Methylmorpholine	Et_3N; 5.0	Soln	2.33	100	2.4
	Triethylamine	Et_3N; 2.0	Soln	2.11	100	1.9
CH_2Cl_2	Diethylaniline		Ppt	0.93	57	0.17
	Ethylmorpholine		Ppt	2.83	100	0.57
	Triethylamine		Ppt	0.624	100	0.98
	Triethylamine	Et_3N; 1.4	Soft ppt	0.618	95	1.71

[a] Polymerization at 25–30 °C with tertiary amine equivalent to by-product HCl. [b] For polymer–salt–solvent system.

Table VI
Polymerization[a] of 4-Aminobenzoyl Chloride Hydrochloride in a Nonsolvent with Pyridine Acid Acceptor

Solvent	Yield, %	η_{inh} in H_2SO_4
Pentane	100	3.8
Hexane	100	4.1
Heptane	100	3.2
Cyclohexane	100	2.3
Carbon tetrachloride	89	1.5
Ether	92	1.1
Chlorobenzene	98	1.4
Freon 113	100	2.0
Acetonitrile	100	3.6
Ethyl acetate	100	1.0

[a] Polymerization recipe: solvent, 50 mL; pyridine, 10 mL; monomer, 6.4 g.

We had been working with some chlorine-substituted poly-1,4-benzamides[9] and using a solid-state thermal polymerization because low-temperature polymerization proceeded poorly. The monomer for one of these was obtained in the form of fine needles, and it could be polymerized thermally without loss of its needle shape. Our aminobenzoyl chloride hydrochloride had always appeared to be a nondescript powder, but examination of various samples turned up some which were in the form of needle-shaped crystals of microscopic size. These needles could be polymerized thermally between 100 and 300 °C with retention of shape. Figure 4 shows such a needle of poly(1,4-benzamide). The diameter is ~3.5 μm. It is hexagonal in cross-section and is highly crystalline. Refractive index measurements indicate that the polymer chains are oriented crosswise of the long axis of the needle. That is, the refractive indices parallel and perpendicular to the long axis of the needles are the reverse of like values found in highly oriented, crystalline fibers of poly(1,4-benzamide).

It may seem obvious now that the foregoing result relates to behavior in solution polymerization. Monomer needles with an organized crystalline structure are suspended in a poor solvent and treated with an acid acceptor. The latter must penetrate the solid and eventually be removed as salt. Pyridine hydrochloride does not crystallize readily and so may remain fluid or be a fluid in the presence of pyridine base. The activated monomer molecule can react with a neighbor with minimum movement. One finds that in hexane, and similar solvents, the polymer powder obtained after washing retains a roughened needle shape (Figure 5). Some disorganized material is also apparent. As in the thermal polymerization, the polymer chains are oriented perpendicular to the long needle axis. The polymer again is highly crystalline.

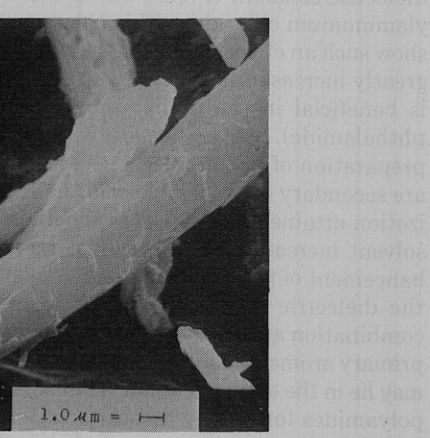


Figure 4. Photomicrograph of needles of poly(1,4-benzamide) prepared by solid-state thermal polymerization of 4-aminobenzoyl chloride hydrochloride.

Here is an easy route to relatively large units of highly organized polymer chains. They present a fascinating area for fundamental study and perhaps have some special utility, for example as compression-molded parts or reinforcing fillers.

Now let us turn to the final topic, one of the most recent developments in aromatic polyamides, extended chain polyamides, of which poly(1,4-benzamide) is an example.

Extended Chain Polyamides. Poly(1,3-phenyleneisophthalamide), which was discussed at the beginning, may be properly called a stiff chain polyamide. But there is another class which we would prefer to call extended chain polyamides, those in which the chain-forming units are linked so as to extend the chain in the same direction and wherein the amide bonds are presumed to be predominantly in a trans configuration. These polymers are part of a new class of materials which form mesomorphic or liquid crystalline solutions. Only an introductory discussion will be given here. Following papers provide a more detailed description of selected polymers.

Stephanie Kwolek was the first to prepare and describe a liquid-crystalline solution of an aromatic polyamide.[10] High performance fibers from paralinked aromatic polyamides were a goal. Liquid-crystalline solutions were a special bonus which, combined with skill and persistence, helped attain that goal.

The structures of representative extended chain polyamides are shown in Table VII. The first structure is that of poly(1,4-benzamide) which was just discussed in relation to the nee-

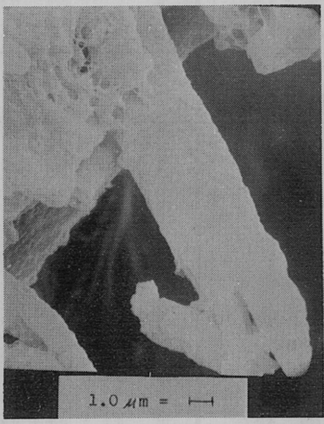


Figure 5. Photomicrograph of needles of poly(1,4-benzamide) prepared by interaction of *p*-aminobenzoyl chloride hydrochloride with pyridine in hexane.

dle-shaped crystals. In addition to 1,4-phenylene, other suitable structural units are 4,4′-biphenylene, 2,6-naphthylene, 2,5-pyridylene,[11] and *trans*-1,4-cyclohexylene.[12] The last composition indicates that an aromatic system is not required for formation of liquid-crystalline solutions. Still other useful structures are *trans*-vinylene in fumaric and muconic acids,[13] azo- and azoxybenzene,[14] and stilbene.[15] The rings may bear a variety of substituents, such as fluoro, chloro, nitro, and methyl groups.

Table VIII lists several methods of synthesis. For many of the extended chain polyamides, solution polymerization in amide solvents, such as dimethylacetamide, hexamethylphosphoramide, or *N*-methylpyrrolidone, is the most satisfactory method.[5,10,16] Solution polymerization in amide solvents will be discussed in following papers. Strongly basic diamines, such as 1,4-cyclohexanediamine, require the use of an interfacial polymerization system and strong bases as acid acceptors. Oxamides can be made in high molecular weight in an interfacial system to which the oxalyl chloride is introduced as a vapor carried by nitrogen. This method is related to a liquid–gas system used by Sokolov.[17]

Please note that hexamethylphosphoramide has been found in laboratory experiments to be a carcinogen in rats.[18] The benzidines and chloroform are also known carcinogens. Proper precautions must be taken with all such hazardous chemicals.

Formation of Liquid-Crystalline Solutions. When polymer chemists discuss linear flexible-chain polymers in solution, they commonly speak of random coils, which may

Table VII
Some Polyamides Yielding Liquid-Crystalline Solutions

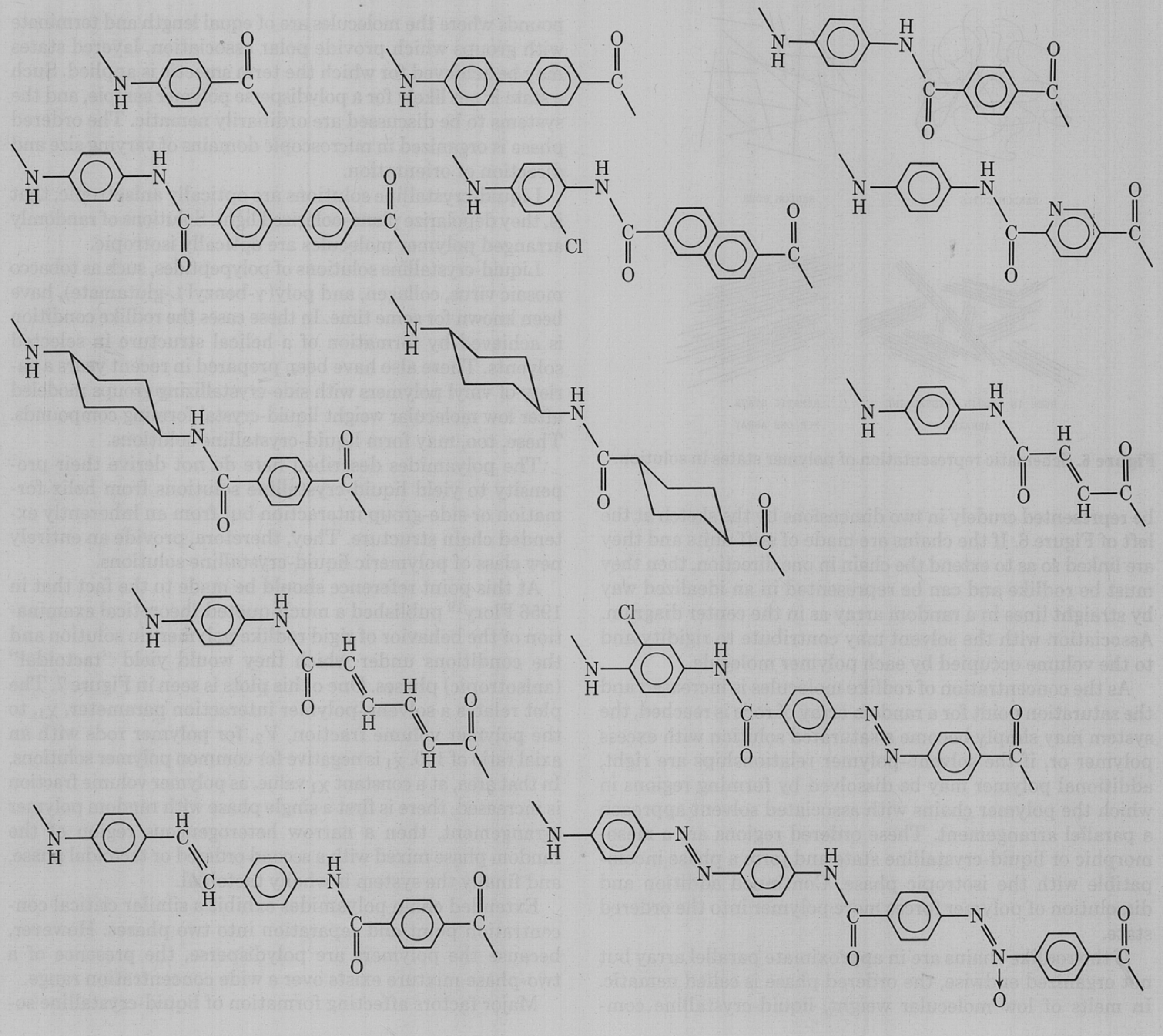
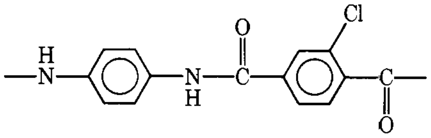
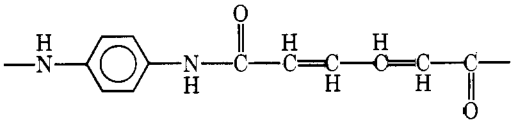
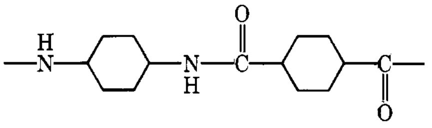
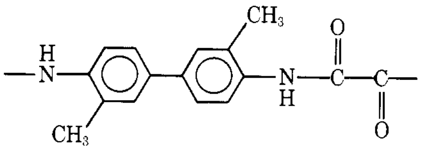


Table VIII
Polymerization Procedures for Several Types of Extended Chain Polyamides

Composition	Polymerization system	Polymer η_{inh} in H_2SO_4
	Dimethylacetamide	3.2
	Hexamethylphosphoramide[a]–*N*-methylpyrrolidone	1.3
	CH_2Cl_2–H_2O	1.1
	$CHCl_3$–H_2O with acid chloride vapor	2.2

[a] Hexamethylphosphoramide has been found in laboratory experiments to be carcinogenic in rats.

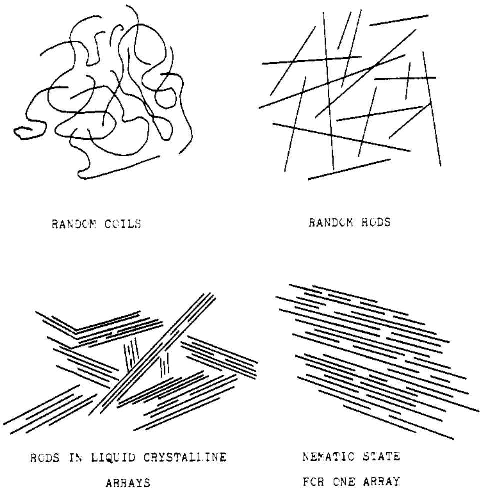


Figure 6. Schematic representation of polymer states in solution.

be represented crudely in two dimensions by the sketch at the left of Figure 6. If the chains are made of stiff units and they are linked so as to extend the chain in one direction, then they must be rodlike and can be represented in an idealized way by straight lines in a random array as in the center diagram. Association with the solvent may contribute to rigidity and to the volume occupied by each polymer molecule.

As the concentration of rodlike molecules is increased and the saturation point for a random array of rods is reached, the system may simply become a saturated solution with excess polymer or, if the solvent–polymer relationships are right, additional polymer may be dissolved by forming regions in which the polymer chains with associated solvent approach a parallel arrangement. These ordered regions are a mesomorphic or liquid-crystalline state and form a phase incompatible with the isotropic phase. Continued addition and dissolution of polymer forces more polymer into the ordered state.

If the rodlike chains are in approximate parallel array but not organized endwise, the ordered phase is called nematic. In melts of low molecular weight, liquid-crystalline compounds where the molecules are of equal length and terminate with groups which provide polar association, layered states may be achieved for which the term smectic is applied. Such a state is not likely for a polydisperse polymer sample, and the systems to be discussed are ordinarily nematic. The ordered phase is organized in microscopic domains of varying size and direction of orientation.

Liquid-crystalline solutions are optically anisotropic; that is, they depolarize plane-polarized light. Solutions of randomly arranged polymer molecules are optically isotropic.

Liquid-crystalline solutions of polypeptides, such as tobacco mosaic virus, collagen, and poly(γ-benzyl L-glutamate), have been known for some time. In these cases the rodlike condition is achieved by formation of a helical structure in selected solvents. There also have been prepared in recent years a variety of vinyl polymers with side-crystallizing groups modeled after low molecular weight liquid-crystal forming compounds. These, too, may form liquid-crystalline solutions.

The polyamides described here do not derive their propensity to yield liquid-crystalline solutions from helix formation or side-group interaction but from an inherently extended chain structure. They, therefore, provide an entirely new class of polymeric liquid-crystalline solutions.

At this point reference should be made to the fact that in 1956 Flory[19] published a much-quoted theoretical examination of the behavior of rigid rodlike polymers in solution and the conditions under which they would yield "tactoidal" (anisotropic) phases. One of his plots is seen in Figure 7. The plot relates a solvent–polymer interaction parameter, χ_1, to the polymer volume fraction, V_2, for polymer rods with an axial ratio of 100. χ_1 is negative for common polymer solutions. In that area, at a constant χ_1 value, as polymer volume fraction is increased, there is first a single phase with random polymer arrangement, then a narrow heterogeneous region of the random phase mixed with a second ordered or tactoidal phase, and finally the system is wholly tactoidal.

Extended chain polyamides exhibit a similar critical concentration point and separation into two phases. However, because the polymers are polydisperse, the presence of a two-phase mixture exists over a wide concentration range.

Major factors affecting formation of liquid-crystalline so-

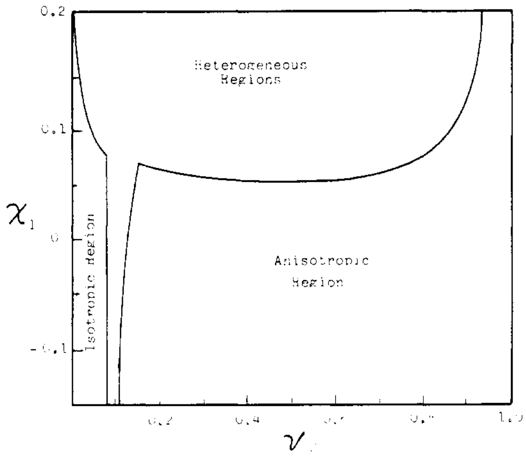
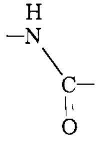


Figure 7. Diagram relating the solvent–polymer interaction parameter (χ_1) and the volume fraction (V_2) of rodlike polymer molecules with the formation of a "tactoidal" solution phase (Flory, ref 19).

Table IX
Factors Affecting Formation of Liquid-Crystalline Solutions of Polyamides

- Polymer structure
  - Extended chain
  - Trans configuration of



- Molecular weight
  - Must exceed some minimum value
  - Increasing concentration compensates to some degree for low molecular weight
- Solubility
  - Must be sufficient to exceed critical concentration
  - Dispersion by solvent can be excessive
  - Mixed solvents may have optimum ratio
- Temperature
  - Affects solubility
  - Changes liquid-crystalline range

lutions of polyamides are (1) the polymer structure, (2) molecular weight, (3) solubility, and (4) temperature (Table IX).

Polymer structure requirements have been touched upon already. The amide link is presumed from energy and steric considerations to maintain the trans configuration. In crystalline solids, such as acetanilide, the terminal bonds in the amide group deviate from parallel alignment by 12°.[20] Solvents must help maintain the trans arrangement but they may change the bond angles somewhat. Yet there presumably remains an increment of bend in each amide unit which can contribute to a gradual curvature or nonlinearity of the chain. Likewise, many of the suitable units, such as 2,6-naphthylene, *trans*-vinylene, *trans*-1,4-cyclohexylene, and azo and azoxy units, have displaced but parallel connecting bonds which contribute a crankshaft type of freedom to the polymer chain. The disorder in the liquid-crystalline solution produced by these structural features of the polymer chain is probably greatly restricted by energy requirements, by association between polymer and solvent, and by interaction of neighboring polymer chains.

The chain-forming units, such as those illustrated in Table VII, can be combined in any order provided stoichiometry is satisfied and there are enough amide links to give the needed solubility. Small substituents generally increase solubility. Copolymerization with nonconforming intermediates, such as those based on 1,3-phenylene or polymethylene units, can be tolerated to about 5 to 20 mol % depending on the nature of the component.

The average molecular weight of the polymer must exceed some minimum value. Increasing concentration compensates for low molecular weight but solubility may not be adequate to determine the lowest molecular weight which could possibly give a liquid-crystalline solution. On the other hand, association with the solvent can be so great as to maintain the polymer in isotropic solution up to the solubility limit. Mixed solvents present additional variables. For example, mixed solvents may have an optimum ratio for liquid-crystalline solution formation with a given polymer sample.

Temperatures near ambient are most convenient for many simple studies. Solubility may improve or decrease with rising temperature. In general, near the critical concentration point, raising the temperature shifts the system toward the isotropic state and lowering the temperature has the opposite effect.

Recognition of the Liquid-Crystalline State. There are several simple effects (Table X) which are characteristic of the liquid-crystalline solutions. The first three effects, opalescence, depolarization of plane-polarized light, and the critical concentration point, will be discussed briefly. Magnetic field effects are discussed in a following paper by Panar and Beste.

First, the solutions usually appear cloudy or turbid even though they contain no undissolved material. This is due to diffraction of light passing through the liquid-crystalline domains with differing direction of alignment and size. When such a system is stirred, even gently, a pearly or opalescent appearance is readily seen. This fades rapidly when stirring ceases.

A thin layer of solution, magnified between crossed polarizers in a microscope (Figure 8), exhibits colored domains (blue, green, red, yellow) which vary with the system and its history. The sample shown retains some directional character from shear. Others may be finely mottled or have far less color.

An interesting feature of the solutions of extended chain polymers is the sudden change in bulk viscosity with increasing polymer concentration at the point where liquid-crystalline order begins (Figure 9). This figure provides data on a complex system of a copolymer of chloro-*p*-phenylenediamine, *p*-phenylenediamine, and 2,6-naphthalene diacid in a mixture of hexamethylphosphoramide, *N*-methylpyrrolidone, and lithium chloride. Such complexity is not at all necessary to accomplish the effect. At the left, solution viscosity rises in the normal way for isotropic solutions and then at a critical point, the system will only accommodate more polymer if an ordered, liquid-crystalline phase can form. This occurs and is followed by decreasing viscosity and increasing amounts of ordered phase. At the minimum point in bulk viscosity the system may not be wholly anisotropic. Following papers will fill in some details on this behavior.

If one samples a solution at a point above (that is, to the right) but near the critical concentration point in Figure 9 and examines it between crossed polarizers, droplets of anisotropic solution appear against a dark background of isotropic phase (exemplified by Figure 10).

When such mixed phases are not too viscous, they may separate upon standing or be separated in a centrifuge. The ordered, anisotropic phase, being more concentrated in polymer than the isotropic phase, appears as the lower layer when the solvent density is less than that of the polymer.

There are many variables which can be studied in relation to the formation of liquid-crystalline solutions. Figure 11 shows the results of tests on the solubility and solution state for the copolymer and mixed solvent system just described.

Table X
Recognition of the Liquid-Crystalline State

- Visual observation
  - Turbidity (schlieren)
  - Opalescence upon stirring

- Depolarization of plane polarized light

- Solution Viscosity
  - Critical concentration points

- Orientation in a magnetic field

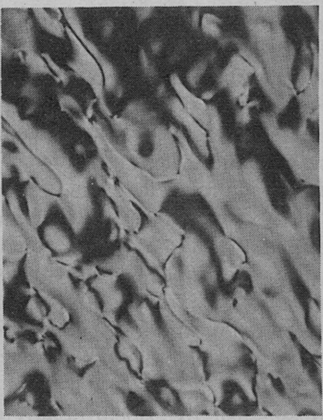


Figure 8. Texture of a liquid-crystalline solution of poly(chloro-1,4-phenyleneterephthalamide) dissolved in dimethylacetamide–LiCl; observed between crossed polarizers at about 340×.

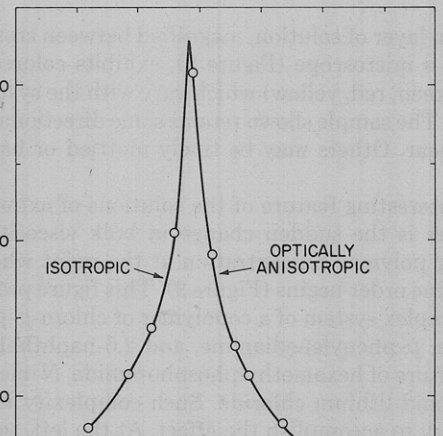


Figure 9. Effect of polymer concentration and the formation of a liquid-crystalline solution on the bulk viscosity of solutions of poly(chloro-1,4-phenylene/1,4-phenylene, 2,6-naphthalamide) (70/30) in hexamethylphosphoramide–*N*-methylpyrrolidone (1–1, v/v) containing 2.9% LiCl at 27 °C; polymer $\eta_{\text{inh}} = 2.0$. Bulk viscosity was determined with a Brookfield, Model RV, viscometer with a No. 6 spindle at 10 rpm (see following paper).

The polymer and lithium chloride concentrations are varied. At very low salt concentration, the polymer is at best only partly soluble. At about 1% salt there is a small zone in which an anisotropic solution can be formed. The zone of anisotropic solution is enlarged as the salt content goes up and then decreases again. The decreased solubility at high salt content may result from an increase in the amount of solvent associated with salt. No special ratio of salt to amide units seems to be indicated by the greatest range of anisotropic phase formation in the central area of the plot.

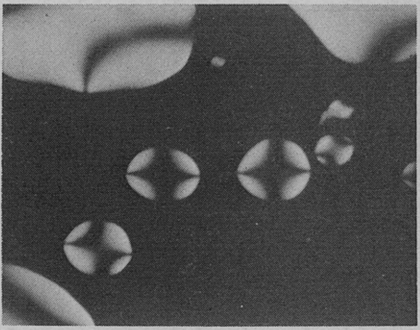


Figure 10. Droplets of a liquid-crystalline phase in a dark background of isotropic phase of a solution of poly(chloro-1,4-phenyleneterephthalamide) in dimethylacetamide–LiCl; observed between crossed polarizers at about 340×.

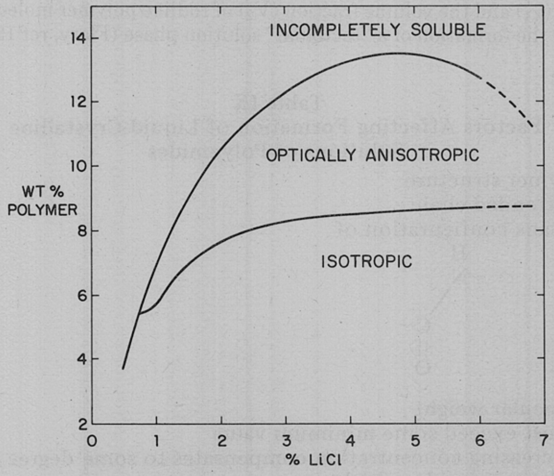


Figure 11. Effect of polymer and LiCl concentrations on the formation of a liquid-crystalline phase from poly(chloro-1,4-phenylene/1,4-phenylene-2,6-naphthalamide) (70/30) in hexamethylphosphoramide–*N*-methylpyrrolidone (1–1, v/v); polymer $\eta_{\text{inh}} = 1.75$.

The liquid-crystalline solutions of extended chain polyamides are colorful and interesting systems to work with and study, but beyond that they are also useful for preparing highly oriented fibrids, films, and fibers. The easy attainment of high molecular orientation in these unmeltable polymers has high technological importance. This effect is illustrated in the following paper by Kwolek, Morgan, Schaefgen, and Gulrich. A feature of economic importance is the formation of fluid solutions with high polymer content.

The study of aromatic polyamides has led to new understanding of polymerization systems and of polymer behavior in solution. In an industrial laboratory, primary goals are to seek new polymeric materials with superior properties, new uses for the polymers, and, of course, better processes for producing them. The aromatic polyamides are being used around the world in high-temperature applications, such as electrical insulation and protective clothing, and as high strength, high modulus fibers in straps, cables, and so on, and as reinforcing fibers for resins and rubber.

Experimental Section

Viscosity Measurement. Inherent viscosities [$\eta_{\text{inh}} = (2.3 \log \eta_{\text{rel}})/c$] were determined in 96–98% sulfuric acid at 30 °C and a concentration (c) of 0.5 g/100 mL of solution. The values are in dL/g.

Dielectric Constants. Measurements for calculation of dielectric constants were made with a Sargent Chemical Oscillometer, Model V, at 25 °C.

Solvents. Solvents used in this work were reagent or spectro grade chemicals. Chloroform was freed of alcohol stabilizer by washing re-

Table XI
Model Compounds

				Anal.					
				Calcd			Found		
Composition	Crystallization solvent	Mp, °C	Formula	C	H	N	C	H	N
N,N-Diphenylisophthalamide	Dimethylformamide–ethanol	288.5[a]							
Bis(*N*-methyl-*N*-phenyl)terephthalamide	2B ethanol	211–212	$C_{22}H_{20}N_2O_2$	76.72	5.85	8.13	76.59	5.78	8.04
N,N'-Dibenzoyl-*trans*-2,5-dimethylpiperazine	Benzene–ether	230.5[b]							
N,N-terephthaloyldipiperidine	Acetone	206.5	$C_{18}H_{24}N_2O_2$	71.96	8.05	9.33	72.05	8.01	9.50

[a] Mp 279–281 °C reported by Grimmel et al.[21] [b] Mp 228–229 °C reported by Bain and Pollard.[22]

peatedly with water and storing, after rough drying, over a mixture of calcium chloride–potassium carbonate. An alternate procedure is treatment with neutral molecular sieves.

Intermediates. Diamines and diacid chlorides were purchased or synthesized by known procedures. They were purified as necessary by sublimation and/or solvent crystallization and stored under nitrogen in dryboxes. Triethylamine was carefully distilled to free it from water and any secondary or primary amines. The hydrochloride was prepared by addition of anhydrous hydrogen chloride to an ether solution of the amine.

Model Solubility Tests. Model amides were synthesized from the appropriate amines and acid chlorides (Table XI).

Tests of solubility were made by heating measured amounts of solvent, model, and salt in sealed Pyrex tubes, while they were rotated fully submerged in a bath of silicone oil. The solution temperature, obtained with Jackson Laboratory Calibrated Thermometers (Precision Thermometer and Instrument Co., Philadelphia, Pa.), was taken at the temperature of dissolution of the last particle of solute. It was possible to observe by crystal form that the amides dissolved after the salt in the tests described here.

Unused, unmarred test tubes (125 × 15 mm) were used. The ingredients were placed in the open tube, filling not over one-third of the capacity; the lightly capped tube and contents were cooled in a dry ice pack; the upper portion of the tube was drawn down in a flame to about 1–2 mm i.d.; the pressure was reduced to 20–50 mm, and the seal was completed. The solubility tests must be conducted behind adequate shields; each set of tests must be started at room temperature; and the used sealed tubes must be handled only after returning to room temperature.

Preparation of Poly(1,3-phenyleneisophthalamide) in Chloroform Solution. A 200-mL round-bottom flask equipped with a low-speed stirrer and dropping funnel was charged with 2.163 g of 1,3-phenylenediamine, 5.62 mL of triethylamine, 5.506 g of triethylamine hydrochloride, and 36 mL of chloroform. Isophthaloyl chloride (4.06 g) in 14 mL of chloroform was added through the dropping funnel over a period of 15 min while the slowly stirred mixture was maintained at 30 °C. An additional 3 mL of chloroform was used to rinse in residues from the funnel. After 20 min, the reaction mixture, which was a clear, extremely viscous solution, was poured into a large volume of petroleum ether, yielding a fibrous precipitate. This was collected and washed thoroughly with hot water. A 99% yield of polymer having an inherent viscosity of 1.9 was obtained.

Increase in Molecular Weight of a Precipitated Polyamide by Salt Addition. 1,3-Phenylenediamine (2.163 g), 0.70 g of triethylamine hydrochloride, and 5.62 mL of triethylamine were dissolved in 100 mL of methylene chloride in a dry 1-quart blender jar. As the blender rotor was raised to a high speed, there was added from an Erlenmeyer flask over a period of about 8 s a solution of 4.06 g of isophthaloyl chloride in 90 mL of methylene chloride. Residues of acid chloride solution were rinsed in with 10 mL of solvent and the mixture was stirred for 4 min. A portion (~80 mL) of the polymer suspension was poured into a dry flask which was stoppered and shaken for 5 min, diluted with an equal volume of hexane, and then filtered. The washed and dried polymer (1.77 g) had an $\eta_{\rm inh}$ of 1.29. While the separated portion of the suspension was treated as above, there was added to the remainder in the blender 2.0 g of triethylamine hydrochloride and moderate stirring was continued for 5 min. An equal volume of hexane was added and the polymer was isolated in the same way. The polymer yield was 2.78 and the $\eta_{\rm inh}$ was 1.71. The total yield was 95%.

Preparation of Poly(1,4-benzamide) in Hexane–Pyridine. In a 100-mL tubular flask equipped with a stirrer, nitrogen inlet, and a third loosely stoppered inlet were placed 50 mL of "spectro grade" hexane and 6.4 g of 4-aminobenzoyl chloride hydrochloride. Under a flow of dry nitrogen, the stirred mixture was cooled in a pack of solid carbon dioxide. Pyridine (10 mL) was added quickly. After 15 min the flask was allowed to warm to room temperature. Total reaction time was 2 h. The polymer was collected by filtration, washed thoroughly with water, and dried. The yield was 100% and the $\eta_{\rm inh}$ was 3.7.

Preparation of Poly(2,6-dichloro-1,4-phenyleneterephthalamide) in Dimethylacetamide. In a 1-L resin kettle equipped with a basket-type stirrer, a nitrogen inlet, and a drying tube was placed 2,6-dichloro-1,4-phenylenediamine (17.70 g) and *N,N*-dimethylacetamide (410 mL). The solution was cooled with an ice bath for 15 min, after which powdered terephthaloyl chloride (20.30 g) was added with rapid stirring of the solution. The ice bath was removed after 20 min and replaced with a water bath maintained at room temperature. The solution gradually increased in viscosity. After being allowed to stand 3 days, the solution was clear and viscous. A sample of polymer was isolated by precipitation in water, washed several times with water and once with acetone, and dried at ~80 °C under vacuum. The polymer $\eta_{\rm inh}$ was 3.77. Lithium carbonate (7.39 g) was added and stirred into the clear reaction mixture, which soon became unstirrable gel. The product was isolated by combination with water and washed and dried as for the small sample. The polymer $\eta_{\rm inh}$ was then 3.84. The yield was essentially quantitative.

Caution. Halogenated aromatic diamines should not be sublimed or distilled because of the possibility of a violent reaction evolving heat, hydrogen halide, and other gases of decomposition.

Poly(*trans*-1,4-cyclohexylenechloroterephthalamide) by Interfacial Polycondensation. A solution of 17.1 g of *trans*-1,4-cyclohexanediamine and 35 g of sodium carbonate in 1500 mL of water was formed in a large blender. While this solution was stirred at high speed, there was added as rapidly as possible 35.63 g of chloroterephthaloyl chloride dissolved in 300 mL of methylene chloride. After the reaction mixture was stirred for 10 min, it was filtered to isolate the product which was collected, washed several times with water and twice with acetone, and dried in a vacuum oven at 80 °C. The polymer, obtained in nearly quantitative yield, had an $\eta_{\rm inh}$ of 1.43.

Needles of 3,5-Dichloro-4-aminobenzoyl Chloride. 3,5-Dichloro-4-aminobenzoic acid was purchased and also prepared by the direct chlorination of 4-aminobenzoic acid in glacial acetic acid. These products contained trichloroaniline, which was removed by dissolving the acid in aqueous sodium hydroxide, filtering to remove the byproduct, and reprecipitating the acid. The acid sublimes rapidly at 290 °C.

3,5-Dichloro-4-aminobenzoic acid (18 g) was refluxed with 200 mL of thionyl chloride. A solution formed in 1 h and heating was maintained for 2 additional h, after which the mixture was permitted to stand overnight. Excess thionyl chloride was removed by evaporation under slightly reduced pressure and with a bath at <50 °C to leave a yellow-brown crystalline mass. This was recrystallized from *n*-hexane/ethylene chloride (90/10, v/v) to produce a crystalline product melting at 155 °C. A portion of this material was recrystallized from methylene chloride as pale yellow needles in round clusters. These needles were dissolved in methylene chloride and anhydrous hydrogen chloride was bubbled into the solution. The yellow color was discharged and off-white needles of 3,5-dichloro-4-aminobenzoyl chloride were obtained by evaporation of part of the solvent, mp 165 °C. In some preparations the melting point was 162 °C. The melting test must be done rapidly because of a tendency for the product to polymerize.

Anal. Calcd for $C_7H_4ONCl_3$: C, 37.4; H, 1.74. Found: C, 37.3; H, 1.62.

Thermal Polymerization of 3,5-Dichloroaminobenzoyl Chloride as Needles. Into a 1-cm polymerization tube equipped with a side arm and a capillary bleed for dry nitrogen, reaching to the 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.

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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