

Semi-Stiff Chain Aromatic Polyamides: New Candidates for Thermotropic Liquid Crystalline Polymers

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We would like to dedicate this paper to the memory of the late Mitchel Shen. He was a personal friend of the Institute, visited us on numerous occasions here in Lyngby and was our gracious host in California. We think that he would have enjoyed reading this paper about liquid crystalline polymers as it typifies the new areas of polymer science in which he was interested. Mitchel was, however, more than a scientific colleague. He was a good friend and we will remember fondly the pleasant afternoons at the coast north of Copenhagen as well as the exciting evenings in San Francisco. We will miss him.

A spectrum of newly synthesized polyamides have been characterized with the intent of elucidating crystalline and possible liquid crystalline behavior. The different polymers contained various rotatable linkages in the main chain as well as substituent methyl groups in some cases. These were deemed as important variables for controlling the propensity to form ordered morphologies in these polymers. Methods of characterization included: X-ray diffraction analysis, differential scanning calorimetry, and optical birefringence.

INTRODUCTION

In recent years following the discovery that ultra-high modulus fibers could be spun from nematic solutions of aromatic polyamides and polyesters, there has been considerable interest in the chemistry and physics, as well as the engineering properties, of polymers capable of forming the liquid crystalline state (1). The spinning or extrusion of the nematic phase leads to a fiber in which the polymer chains are aligned virtually coparallel with the fiber axis (2). The rupture of such a fiber, thus, entails the breaking of primary valence bonds resulting in their remarkable strength: comparable to that of steel wire on a volume basis.

Polymers capable of forming the liquid crystalline phase are built up in such a way that they either: 1) contain mesogenic monomer units (3,4) or 2) consist of an inherently rigid rod-like structure. Example of the latter are the poly- α -amino acids which form rigid helical structures and aromatic polyamides which exist in extended rod-like conformations because the backbone atoms have only a single preferred configuration.

Kevlar® is a commercial ultra-high modulus fiber which is a condensation polymer of p-phenylenediamine (p-PD) and terephthalic acid (TP) as shown in Fig. 1.

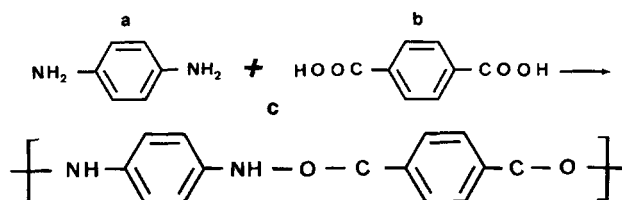


Fig. 1. The preparation and chemical structure of poly (p-phenyleneterephthalamide), Kevlar®.

Since the chain structure is both rigid and regular, it forms a highly crystalline substance with a melting point in excess of its decomposition temperature and it is thus not possible to melt spin this material. Also owing to the stable crystalline structure it is insoluble in most solvents. Lyotropic liquid crystalline solutions can be prepared in concentrated sulfuric acid, however, enabling these fibers to be solution spun in a highly complex technological process.

These difficulties have stimulated interest in other related polymers which could either be spun in the liquid crystalline phase from more conventional solvents or which would have a melting point below the decomposition temperature and thereby exhibit thermotropic liquid crystalline behavior which would enable them to be melt spun from a liquid crystalline phase.

The aim of the work communicated here was to prepare and characterize a series of polymers in which the basic rigid structure of Fig. 1 was maintained but in

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which the p-phenylenediamine monomer was replaced with various semi-flexible diamines capable of exhibiting limited internal rotational mobility. The structures of these monomers are shown in Fig. 2. They contain either an ether linkage as in the ether dianiline (EDA) or a combination of ether and sulfone linkages as in the sulfone ether diamine (p-SED). In some cases p-SED was methyl substituted. These structural variations were intended to regulate the packing efficiency of the resulting polymers and hence their crystalline and eventual liquid crystalline behavior. For similar reasons polyamides were prepared containing isophthalic acid (IP) the structure of which is shown in Fig. 3, and also with the meta-isomer of the sulfone ether diamine (-SED) as shown in Fig. 4.

Evidence of crystalline and liquid crystalline ordering was obtained by: 1) assessing room temperature solubility in dimethylacetamide, DMAC; 2) analysing thermograms obtained by differential scanning calorimetry, DSC; 3) visual observation in a microscope with crossed polarizers; 4) analysis of X-ray diffraction data.

MATERIALS

The synthesis and characterization of the monomers and polymers used in this study is described elsewhere (5).

EXPERIMENTAL

Studies were performed on either powdered polymer samples or where possible on films cast from DMAC solutions using a doctor blade technique. In some cases the effect of annealing was investigated. Polarized light microscopy observations were performed using a standard Jena NF-4 microscope at a magnification of approximately 250X. X-ray diffraction experiments were performed with a Philips X-ray diffractometry system con-

taining a PW 1050 vertical goniometer giving access to scattering angles, 2θ , ranging from 6 to 45°. The DSC thermograms were obtained with a Du Pont Thermal Analysis Unit, model 900 with the DSC attachment. Thermograms were obtained using a 20°/min heating rate under nitrogen atmosphere. Sample size varied between 2 and 4 mg.

RESULTS

The results are presented in such a way that the stiffest and most rigid polymer molecules are discussed first followed by those having progressively more flexible structures. Preliminary attempts have been made to quantify chain stiffness and relate it to the predictability of liquid crystalline formation (6).

TP/EDA

The structures of the monomers for this polyamide are shown in Figs. 1b and 2a, respectively. The synthesis and characterization of this polymer has been previously reported (7) but since the main emphasis was on the high temperature stability, we have repeated its synthesis and re-studied it within the scope of the present investigation. This polymer behaves as a typical highly crystalline polymer: The room temperature solubility in DMAC is nil; the powdered polymer is highly birefringent when visually observed in the polarizing microscope; a highly crystalline X-ray powder diffraction pattern is observed with sharp reflections at scattering angles, 2θ , of 20 and 27°; and the DSC thermogram on the virgin material exhibits a large very broad melting endotherm starting at 175°C and extending beyond 400°C. Note that the ether bond is "bent", thus removing the two-fold symmetry axis about this bond, thereby diminishing the rod-like nature of this polymer. In agreement with intuitive expectations the crystalline melting point is depressed substantially in relation to TP/p-PD and is in this case below the decomposition temperature. Additional defects must, however, be introduced if there is to be any hope of obtaining thermotropic behavior. Another point worth noting, especially in connection with the behavior of the other polymers studied in this work, is that even after slow cooling the endotherm was minimized in the second run and could be made to vanish entirely if the sample were subsequently quenched. The kinetics of crystallization is thus very important in understanding the phase behavior of these types of polymers.

TP/p-SED

The structure of the monomers for this polymer are shown in Figs. 1b and 2b, respectively with $R_1 = R_2 = R_3 = H$. This polymer was partially soluble in DMAC and two distinct fractions could thereby be obtained. While both fractions were found to be optically birefringent, neither gave evidence of crystalline reflections in the X-ray diffraction pattern. Both fractions were soluble in 96 percent H_2SO_4 so that the intrinsic viscosity of each fraction could be determined. A substantial difference was observed: 0.83 dl/g for the DMAC insoluble fraction and 0.57 dl/g for the DMAC soluble fraction.

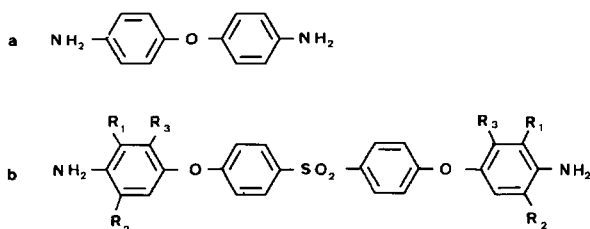


Fig. 2. Diamine replacements for p-PD: (a) EDA, and (b) p-SED.

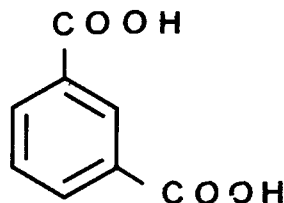


Fig. 3. The chemical structure of IP.

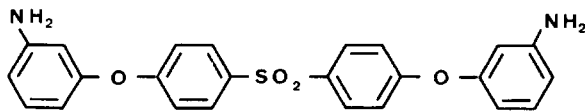


Fig. 4. The chemical structure of m-SED.

The solubility difference was thus concluded to be a molecular weight effect. The X-ray diffraction pattern indicated a very broad amorphous halo extending over 20° with a maximum occurring at about 20° .

Careful annealing under a variety of conditions could result in the appearance of an incipient peak superimposed on the amorphous halo but in no case resulting in anything close to that which would be expected for a crystalline polymer, as shown in Fig. 5. The DSC thermogram for the virgin polymer indicated, however, a small, narrow well-defined endotherm at 440°C . Calibration of the area of this endotherm with a benzoic acid standard gave an estimate of the latent heat of the transition, ΔH , to be 3.4 cal/g or 1.9 Kcal/mole of repeat unit. This was crudely estimated to be about 10 percent of that found above for the TP/EDA polymer, giving 35 cal/g or 12 Kcal/mole of repeat unit as ΔH for TP/EDA. These and subsequent estimates of ΔH for various polymers are given in Table 1. The DSC thermograms for the TP/p-SED polymers both quantitatively and qualitatively were highly non-reproducible as well as being very dependent on the mode of sample preparation. That is to say endotherms were observed as occurring as low as 200°C , and for some samples as many as three discrete endotherms were observed at different temperatures. In one case three different endotherms occurring at temperatures from 200 to 425°C had a combined ΔH of 22 cal/g or 12.4 Kcal/mole of repeat unit. In all cases, however, the samples were birefringent, but yet did not possess a crystalline X-ray diffraction pattern. The well defined endotherm invariably vanished after the first or second scan and was replaced by a second order transition, probably the glass transition, at about 250°C . Variables taken into account for the above mentioned sample preparation included: soluble and insoluble DMAC fractions, powders and cast films, rate of evaporation during film preparation, and annealing temperature. Films prepared from DMAC casting solutions with and without the benefit of vacuum to remove the solvent showed very different mechanical properties as well as DSC thermograms.

In addition to the overall birefringence of these films, a successive lightening and darkening of the films was

observed as they were rotated between the crossed polarizers, indicating a uniaxial orientation of the films. The films were prepared from 10 percent casting solutions in DMAC and required many hours for the solvent to evaporate giving ample time to relax any strain introduced during the casting procedure with the doctor blade. It is well known, however, that such types of treatment can be effective in preparing mono-domain samples of liquid crystalline material.

Methyl Substituted p-SED

Also investigated were polymers in which $R_1 = R_2 = \text{H}$ and $R_3 = \text{CH}_3$, $R_1 = \text{CH}_3$ and $R_2 = R_3 = \text{H}$, $R_1 = \text{H}$ and $R_2 = R_3 = \text{CH}_3$, and $R_1 = R_2 = \text{CH}_3$ and $R_3 = \text{H}$. These compounds were all soluble in DMAC, showed visible optical birefringence yet no crystalline reflections in the X-ray diffraction patterns. Again here, however, most of these materials showed evidences of endotherms in the DSC thermograms as shown in Table 1. Also for these materials, the endotherms gave rise to second order transitions for the second and subsequent scans. The sample for which $R_2 = R_3 = \text{CH}_3$ and $R_1 = \text{H}$ did not show a transition. These substituted materials showed a lower ΔH than films of the corresponding unsubstituted material prepared in the same fashion. The transition temperature is also depressed relative to that for the unsubstituted compound.

TP/m-SED

This polymer was also DMAC soluble, birefringent and without any crystalline features in the X-ray diffraction pattern. The film, however, did show a large endotherm at 290°C .

IP

IP polymers were prepared with p-SED, m-SED, and the four methyl substituted derivatives of the former. These all behaved as those above, being soluble, birefringent and showing only a very broad amorphous halo in the X-ray diffraction patterns. Films all showed at least one endotherm during the first scan which gave way to a second order transition during subsequent scans. These films also showed lower transition temperatures and smaller values of ΔH than the corresponding films of the all para, unsubstituted polymer, as discussed previously.

DISCUSSION

The classical study of the phase behavior of solid polymers within the definition framework: crystalline, glassy and liquid or melt polymers has generally proved to be more complicated than the corresponding phase behavior for low molecular weight compounds. The recent expansion of this framework to include liquid crystalline mesophases will surely further serve to complicate this classification. A detailed study of the phase behavior of cellulose acetate (8), a polymer of special interest because of its widespread use in the area of reverse osmosis membranes, clearly indicates some of the problems that can arise when the polymer under investigation occupies a position at the interface between well established definitions. In this regard, the term *paracrystalline* has been introduced to cover cases

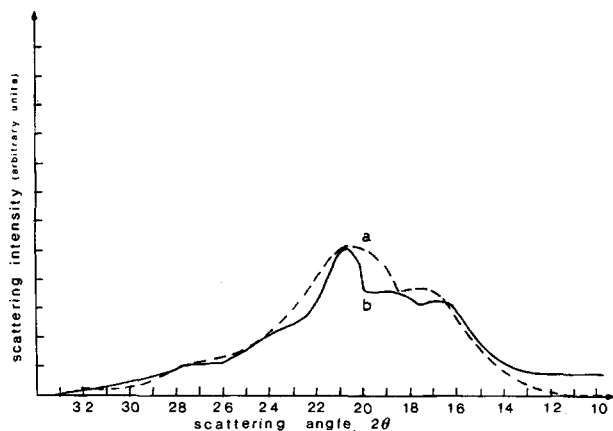


Fig. 5. The X-ray diffraction scan of the polymer TP/p-SED: (a) the virgin polymer and (b) the same polymer annealed at 425°C and slowly cooled.

Table 1. Transition Enthalpy Data for Some Selected Aromatic Polyamides and Related Compounds

Polymer	ΔH , cal/g	ΔH , Kcal/mole of repeat unit	Transition temperature, °C	Comments
TP/EDA	35.	12.0	255	Very broad transition, ΔH crudely estimated
TP/p-SED	3.4	1.9	437	Virgin material
TP/p-SED	8.1	4.5	270	DMAC insoluble fraction scanned to $T = 315^\circ$ ($T_g = 225^\circ$)
	3.3	1.8	428	second run
TP/p-SED	4.5	2.5	200	DMAC soluble fraction, vacuum dried film/70 h
	15.5	8.7	310	3 peaks
	2.2	<u>1.2</u>	427	
		$\Sigma=12.4$		
TP/p-SED	18.9	10.6	240+270	DMAC soluble fraction dried without vacuum/8 days, 3 peaks
	2.5	<u>1.4</u>	425	
		$\Sigma=12.0$		
TP/p-SED	2.9	1.6	395+420	Virgin material annealed at 425°C followed by slow cooling
TP/m-SED	6.2	3.5	290	DMAC cast film, vacuum dried
TP/p-SED, $R_3 = \text{CH}_3$	4.9	2.8	270	As above
TP/p-SED, $R_1 = \text{CH}_3$	9.6	5.5	270	As above
TP/p-SED, $R_2 = R_3 = \text{CH}_3$	nil	nil	—	As above
TP/p-SED	2.5	1.5	290	As above
IP/p-SED	5.4	3.0	280	As above
IP/m-SED	7.1	4.0	285	As above
IP/p-SED, $R_3 = \text{CH}_3$	4.6	2.6	275	As above
IP/p-SED, $R_1 = \text{CH}_3$	5.0	2.9	277	As above
IP/p-SED, $R_2 = R_3 = \text{CH}_3$	4.5	2.6	282	As above
IP/p-SED, $R_1 = R_2 = \text{CH}_3$	4.0	2.4	277	As above
Crystalline aliphatic polyamides	—	8-14	—	Ref. 13
Thermotropic azoxy and azo polyesters (mesophase-isotropic transition)	—	.3-6.4	—	Ref. 4
Thermotropic polyurethanes (mesophase-isotropic transition)	—	1.4-3.3	—	Ref. 14

where conflicting experimental evidence obtained by various means does not permit an unqualified classification of a material as either amorphous or crystalline.

A whole series of borderline cases has recently been reviewed (9,10) which imply that the concept of ordering is a continuous one which in some diffuse way connects the classical definition of the amorphous and crystalline states.

The whole area of characterizing liquid crystalline forming polymers is such a borderline area. If the observed phases are crystalline, liquid crystalline and isotropic liquid in order of increasing temperature and if the formation of the phases is reversible, then the data are readily analyzed as follows (4):

- A melting endotherm is obtained for each transition.

- Optical birefringence is maintained until the liquid crystalline-isotropic liquid transition temperature is exceeded.

- The crystalline reflections in the X-ray diffraction pattern broadens slightly at the crystalline-liquid crystalline transition and then finally is replaced by a broad featureless amorphous halo above the liquid crystalline-isotropic transition.

The analysis, however, does not have to be so simple. The polymers investigated here show a great reluctance to crystallize in the classical sense as evidenced by the lack of sharp reflections in the X-ray diffraction patterns and thus show a decided propensity to form glasses as evidenced by their DSC scans. It is well known that aromatic polyimides containing rigid, regular structures for example can only be forced to crystallize under care-

fully controlled conditions (11). The polymers studied here nonetheless are optically birefringent at room temperature and exhibit an endothermic transition at elevated temperatures. Although we were not able to study the birefringence at elevated temperatures, it is quite probable that it would disappear above the transition temperature.

We propose, therefore, that our polymers are in the nematic-glassy state at room temperature (nematic ordering would be the most probably for polymers of this type to assume). At the transition temperature the system becomes an isotropic liquid. On re-cooling at finite rates the system supercools and becomes an amorphous glass. Thermal annealing or film casting enables the order to develop, which may enhance ΔH in the DSC thermogram or lead to an incipient crystalline X-ray reflection. X-ray reflections for nematic phases are known to be diffuse (12). Transition enthalpies obtained here are small with respect to those reported for highly crystalline polyamides (13), but are similar to those reported for the nematic-isotropic transition for polymers (4,14).

CONCLUSION

A new class of polyamides have been synthesized which appear to behave as thermotropic liquid crystals. This conclusion is based on X-ray analysis, optical birefringence and differential scanning calorimetry measurements.

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