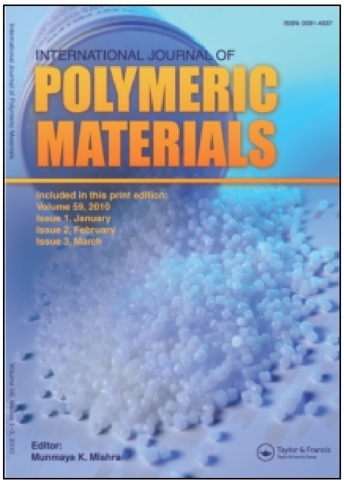

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Naphthalene-based crystalline polyamides and polyesters

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NAPHTHALENE-BASED CRYSTALLINE POLYAMIDES AND POLYESTERS

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Two families of aromatic-aliphatic poly(alkylene-1,5-naphthaleneamide)s and poly(alkylene-1,5-naphthanoate)s were prepared by means of single phase solution polymerizations. After workup and drying, the polymers exhibited very high degrees of crystallinity. Wide-angle X-ray diffraction patterns of the polymers revealed a significant similarity in the crystal structure of the polyamides and polyesters. In both of them, the naphthalene condensed rings were preferentially stacked upon one another and when the alkylene segments were sufficiently long, they were not fully extended. Infrared spectroscopy indicated that in the case of the polyamides, all the amide groups were hydrogen bonded to each other. This fact exhibited itself by the glass transition temperatures of the polyamides being higher than those of the corresponding polyesters and, especially, in the melting points of the polyamide crystals being much higher than those of the polyester analogues. Most of the polymers prepared in this work were of molecular weights too low for developing good mechanical properties, and their window for melt processing too narrow for comfort.

Keywords: poly(alkylene-1,5-naphthaleneamide), poly(alkylene-1,5-naphthanoate), polynaphthaleneamide, polynaphthalenoate, crystallinity, chain packing, melting point, glass transition point, polymerization, 1,5-diaminonaphthalene, 1,5-dihydroxynaphthalene, dimer acid

INTRODUCTION

It is well known [*e.g.*, 1–3] that in many aromatic-aliphatic main-chain liquid crystal polymers, especially in those showing smectic characteristics, the liquid crystallinity is substantially due to the long and stiff, anisotropic aromatic residues preference to associate together and align themselves more or less in parallel to one another. Once the temperature is sufficiently lowered, the main-chain anisotropic aromatic groups cease their rotational motions and by mutual attraction align themselves in register with one another to transform the polymer from the liquid crystal mesophase to the crystal phase. (A similar behavior occurs during the phase transition of side-chain liquid

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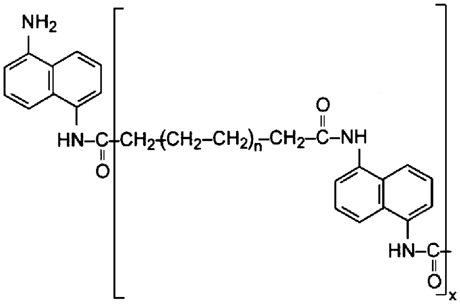
crystal polymers [*e.g.*, 4].) Once immobilized, the stiff anisotropic aromatic groups define the crystal repeat unit of the polymer, in which the more flexible aliphatic components of the chain are included too. Many other aromatic–aliphatic polymers do not pass through a mesophase upon transforming from the isotropic clear melt to the crystalline, more accurately semi-crystalline, solid. In many of these, the tendency of the aromatic residues to associate together and to align themselves in stacks seems to be driving the crystallization process and to define the molecular chain packing in the resulting crystal unit cells. Among such polymers one may find poly(ethylene oxybenzoate) [5], poly(4,4′-isopropylidenediphenylene carbonate) [6, 7], poly(ethylene-2,6-naphthanoate) [8], and several poly(alkylene terephthalate)s [9–13]. Recently, Aharoni synthesized a very large family of strictly alternating aromatic–aliphatic poly(ester amide)s that showed multi-transitional mesomorphic behavior [14]. Upon further characterization and structural analysis [15–19], it was found that inter-chain, inter-amide hydrogen bonds (H-bonds) seem to dominate the mesomorphic behavior and the crystalline structure of these polymers, wherein the aromatic rings are stacked in one direction, the H-bonds are directed in another direction, and the polymer main-chains, including the aliphatic groups, are pointing in a third direction. It was found that when the aliphatic groups in the poly(ester amide)s are not too short, they prefer to adopt conformations that are not exclusively *trans*- but contain some *gauche*- placements too [17–19].

In light of the above observations, we thought it would be of interest to find whether larger aromatic units, such as the condensed-ring naphthalene moieties, will possess stacking tendencies comparable to single-ring aromatic units, and whether H-bonds will play a significant role in determining the properties of polynaphthaleneamides. To answer these questions, we have synthesized a larger family of poly(alkylene-1,5-naphthaleneamide)s, whose generic structure is (Scheme 1):



SCHEME 1

and for comparison, a smaller family of poly(alkylene-1,5-naphthanoate)s, in which the N–H units of the amide groups are replaced by the —O-atom of the ester groups. As will be shown below, the response to both queries posed above was in the affirmative.

EXPERIMENTAL

Synthesis

All monomers, solvents and reagents were obtained from chemical supply houses in the highest available purity and used as received. Below, the procedures giving the best results are described in detail. The first two examples are for long-chain, linear alkylene groups.

(i) *Preparation of Poly(alkylene-*1,5-*naphthaleneamide) by Yamazaki-Type Procedure* [20, 21] In a 1 liter 3-neck round-bottom flask equipped with magnetic stirrer and nitrogen inlet and outlet, immersed in a thermostated hot oil bath, there were dissolved with heating and constant stirring 0.10 moles 1,5-diaminonaphthalene (15.85 g) and 0.10 moles sebacic acid (20.2 g) in 350 mL *N*-methylpyrrolidinone (NMP) with 0.2 moles tetramethylurea (TMU) (23 mL) serving as the organic base. The stirred mixture was maintained at 115°C until all solids dissolved. The temperature of the reaction mixture was then rapidly increased to 145 ± 5°C and slightly over 0.2 moles triphenylphosphite (TPP) (ca. 70 g) were added. Solids started precipitating after 25 minutes from the addition of the TPP, with larger amounts appearing about 5 minutes later. Addition of a solution of 5 wt/vol % LiCl in *N*,*N*-dimethylacetamide (DMAc) bringing the total volume of the reaction mixture to 700 mL did not dissolve the formed solids. After 3 hrs from the addition of the DMAc/5% LiCl at 145 ± 5°C, the reaction was stopped. The reaction mixture was poured in thin stream into intensely stirred 4 liters methanol. After the precipitation ceased and the temperature cooled to room temperature, the mixture was filtered through a fritted glass filter. The solids were then suspended with stirring 3 times over in 3 liters methanol and filtered through fritted glass filter. The solids were then air dried and finally dried overnight at ca. 110°C in a vacuum oven under dynamic vacuum of about 1 mm Hg. This workup and drying procedure was repeated practically identically for all polymers prepared during this work.

(ii) *Preparation of Poly(alkylene-*1,5-*naphthaleneamide) by Yamazaki-Type Procedure* The same procedure was used as in preparation (i) above, except for the use of 0.10 moles 1,10-dodecanedioic acid (23.03 g) instead of sebacic acid, and the reaction temperature kept at 120 ± 5°C instead of 145°C. The duration of reaction at the set temperature was 3 and 1/2 hours, the same as in (i). Under these conditions, the highest molecular weight polyamide in this study was obtained.

(iii) *Preparation of Short-Chain Poly*(*alkylene*-1,5-*naphthaleneamide*) *by Yamazaki-Type Procedure* In the same polymerization set-up as in examples (i) and (ii), there were dissolved with constant heating at 115°C and stirring 0.10 moles succinic acid (11.81 g) and 0.10 moles 1,5-diaminonaphthalene (15.82 g) in 350 mL NMP and 23 mL TMU. Upon complete dissolution, 62 mL TPP were added and the stirring continued at 115°C for about one additional hour. At that time, fine gels appeared in the solution and an extra 100 mL NMP were added. The reaction was terminated 90 minutes after the addition of TPP by pouring it in a thin stream into an intensely stirred large volume of methanol. After the first filtration, the solids were worked up in methanol three times and finally dried as described in procedure (i).

(iv) *Preparation of Poly*(*dimer acid*-1,5-*naphthaleneamide*) *by Yamazaki-Type Procedure* Empol 1008^R dimer acid is an aliphatic acid mixture whose approximate molecular weight is 565, containing 94% dibasic acid, 3% polybasic acid, and 3% monobasic acid [22]. It was used in the following preparation and in all other preparations in which dimer acid was a comonomer. The same reaction set-up as in procedure (i) was used in the present preparation. In 350 mL NMP and 23 mL TMU there were dissolved at 110 – 115°C with constant stirring 0.10 moles dimer acid (56.5 g) and 0.10 moles 1,5-diaminonaphthalene (15.8 g). After complete dissolution, 62 mL TPP were added, and the reaction continued for 3 additional hours at the same temperature. Although no visible solids appeared in the reaction mixture, its viscosity greatly increased to a point where, in order to allow the stirring to continue, additional 100 mL NMP had to be added at about 70 minutes from the addition of the TPP. At the end of the 3 hrs reaction time, the reaction was stopped and the mixture poured in thin stream into 4 liters of swirling methanol. After the first filtration, the solids were washed in large excess of methanol and filtered 3 times over, prior to air drying followed by drying overnight in a vacuum oven at ca. 65°C under dynamic vacuum.

(v) *Preparation of Poly*(*alkyl*-1,5-*naphthanoate*) *by Schotten – Baumann-Type Procedure* A 1.0 liter 3-neck round bottom flask equipped with nitrogen inlet and outlet, a pressure equalizing funnel, and magnetic stirrer, was immersed in a cold water bath. In it, there were dissolved at ambient temperature 0.10 moles 1,5-dihydroxynaphthalene (16.01 g) in 500 mL dichloromethane (DCM) containing about 75 mL pyridine. To this stirred solution, a solution of 0.1 moles (26.72 g) dodecanedioyl dichloride in 100 mL DCM was added dropwise from the pressure equalizing funnel over about 10 minutes. The temperature of the reaction mixture was kept below 23°C throughout the addition. All solutions, in the flask and the funnel, were kept under nitrogen atmosphere throughout the procedure. Upon completion of the addition, the reaction mixture became noticeably more viscous. It was allowed to stir at room temperature for additional 3 hours before its increasing viscosity required that the reaction mixture be poured into a very large excess of methanol. After complete precipitation, the mixture was filtered through a fritted glass filter, and the solids repeatedly washed in large excess of methanol and filtered 3 times over before finally air dried and then vacuum dried overnight at 80°C under a dynamic vacuum of less than 1 mm Hg pressure.

Characterization

Solution viscosities were determined at 25°C in 3 different solvent systems. The viscosities of the linear poly(alkylene-1,5-naphthaleneamide)s were measured in concentrated sulfuric acid (95%). The viscosities of poly(alkylene-1,5-naphthaleneamide)s containing dimer acid as the sole comonomer or in conjunction with another diacid, were measured in *m*-cresol. The reason for the improved solubility of the polyamides containing dimer acid residues is likely to be the rather large volume fraction of alkylenes contributed by the dimer acid to the main-chain of the polymer, and to the dangling side-chains which comprise an integral part of the dimer acid residue. The viscosities of the poly(alkylene-1,5-naphthanoate)s were measured in 60/40 vol/vol phenol/tetrachloroethane. Since the dissolution process of the polyesters in this solvent mixture required heating up to 135°C prior to cooling the solution to 25°C in order to determine their viscosities, it is very likely that some degradation took place and the intrinsic viscosities (I.V.) given in Table 2 below are lower than they could have been had a less destructive solvent system been found. In all cases, the viscosities were measured in Cannon-Ubbelohde internal dilution glass viscometers with efflux times not shorter than 100 seconds. As usual, solution viscosities were measured at several decreasing concentrations and the intrinsic viscosity obtained from their extrapolation to zero concentration.

Weight average molecular weight (M_w) of several poly(alkylene-1,5-naphthaleneamide)s were determined from their solutions in conc. H_2SO_4 by low angle laser light scattering (LALLS) using a Chromatix KMX-6 instrument. The scattered light intensity was collected at 25°C at several fixed angles, as is common in the art. Special care was taken to carefully filter the solvent and the solutions prior to use in order to minimize the fluorescing of the solution during the LALLS measurements, and to prevent contact with air humidity and any other moisture, whose presence reduced the polymer solubility in the sulfuric acid and produced false results.

Thermal studies were conducted in a du-Pont Differential Scanning Calorimeter (DSC) instrument model 9900, with samples of the order of 5 – 12 mg each present under slow flowing nitrogen atmosphere. The heating rate was 20 K/min. Each sample was first heated to above its melting point, then quick quenched by the addition of solid carbon dioxide to the cup in the sample cell, and then heated again. The melting point, T_m, was determined during the first heating cycle, while the glass transition temperature, T_g, was determined from the second heating cycle where the sample is less crystalline. Despite these precautions, T_g could not be clearly determined for several of the studied polymers. The number of results was sufficient, however, to draw conclusions with respect to the differences between the 1,5-naphthalene polyamides and polyesters.

Wide-angle X-ray diffraction (WAXD) patterns were obtained from samples of the powdered polymers in a Philips model PW3710 diffractometer operating in parafocus geometry and using monochromatized copper alpha-radiation. The crystallinity index was measured on the "as obtained" polymer powder samples after drying overnight at 110°C under dynamic vacuum. The degree of crystallinity was evaluated according to the procedure of Hermans and Weidinger [23].

Solid-state carbon-13 nuclear magnetic resonance (NMR) patterns of the polyamides and polyesters were obtained in order to verify their composition and structure. The patterns were obtained at 75.3 MHz using a Chemagnetics CMX 300 NMR spectrometer using standard cross polarization (CP) and magic angle spinning (MAS). There were 25000 scans obtained from each sample. Solution NMR spectra were obtained at 100.6 MHz on Varian XL-400 FT NMR spectrometer. All spectra were referenced relative to TMS. Infrared (IR) spectra of the polymers were obtained from their fine powders suspended in clear KBr pellets. The IR instrument used was a Perkin Elmer (PE) Model 983 ratio-recording double beam dispersive spectrophotometer, and the spectra deconvolution was performed by the use of a dedicated PE model 7500 computer with a PE CDS-3 Enhance software package.

RESULTS AND DISCUSSION

Synthetic Problems Unique to Symmetrically Substituted Naphthalene

Although naphthalene itself is a crystalline solid with the relatively low melting point of 81°C and is highly soluble in common organic solvents such as benzene, chloroform and ethanol, its symmetrically substituted compounds such as 2,6-naphthalenedicarboxylic acid, 1,5-dihydroxynaphthalene and 1,5-diaminonaphthalene melt at least 100 K above naphthalene, and are rather hard to dissolve in the organic solvents usually used in solution polymerizations of polyamides and polyesters. Thus, for example, it was found in the course of this work that the addition of LiCl to the aprotic amide solvents used in the Yamazaki procedure [20, 21] to create polyamides from aromatic amines, led to precipitation and gelation within minutes from the addition of the last reagent, TPP. This usually resulted in very low molecular weight products even after the reaction mixture was kept hot for hours thereafter. Such precipitation/gelation did not occur in any of the many successful polymerizations described in Ref. [21] and all the references therein. Furthermore, late addition of LiCl to the hot polymerization mixtures, toward the end of the Yamazaki procedure, have failed to exert any meaningful positive influence on the solubility of the polyamides made from 1,5-diaminonaphthalene, in stark contrast to all polyamides created from diamines with a single aromatic ring or with several aromatic rings which are not condensed together.

Because of the poor solubility of 1,5-diaminonaphthalene in *N*,*N*-dimethylacetamide (DMAc) (b.p. = 165°C) with or without LiCl, in the temperature interval of 105 – 115°C we usually have conducted the Yamazaki reaction [21], the aprotic amide *N*-methylpyrrolidinone (NMP) whose boiling point is about 200°C became the solvent of choice and was used in all the successful polyamide preparations in this work. In these, the 1,5-diaminonaphthalene had to be heated in the NMP to over 135°C to effect its complete dissolution within an acceptable time period. The use of such high temperatures compelled us to replace the organic base pyridine, whose boiling point is 115°C by the higher boiling organic base tetramethylurea (TMU) whose boiling point is 177°C. In addition to the high temperature employed in the Yamazaki reactions in which 1,5-diaminonaphthalene was used, and the observation that LiCl detracts from the solubility of both the 1,5-diaminonaphthalene monomer and polyamides containing this residue, we have found that the naphthalene-containing polyamides tended to precipitate from the reaction mixtures much earlier than polyamides not containing naphthalene moieties, even when they were kept hot and even after the addition of LiCl.

Due to its extreme insolubility, all our attempts have failed to convert by means of thionyl chloride the free 2,6-naphthalenedicarboxylic acid to the acid chloride analogue. Transamidation attempts of dimethyl-2,6-naphthalenedicarboxylate by means of 1,6-hexanediamine, aimed at creating the corresponding polyamide, were carried under inert atmosphere for several hours each in the melt at temperatures reaching 280°C and in solution in NMP at temperatures reaching up to 165°C. In both instances no high molecular weight polymer was obtained.

The condensed-rings 1,5-dihydroxynaphthalene monomer, used to create the naphthalene-containing polyester analogues of the naphthalene-polyamides, proved to be far less soluble than the dihydroxy-single-ring monomers such as hydroquinone or resorcinol. This suggested itself to interfacial polymerizations, in which a dipotassium salt of 1,5-dihydroxynaphthalene in water was reacted interfacially with aliphatic diacid chlorides in dichloromethane (DCM). The low intrinsic viscosity (I.V.) of the polymeric products indicated that the interfacial polymerizations did not proceed as well as expected. Schotten – Baumann-type polymerizations in a single phase proved to be more successful. From among these, the polymerization in a mixture of DCM and pyridine, in which the 1,5-dihydroxynaphthalene dissolves the best, turned to be the most successful and yielded the highest I.V. polyesters. When the Schotten – Baumann reactions were conducted in DMAc, the polymer yield and molecular weight were not as high as those obtained in the DCM/pyridine solvent mixture.

The naphthalene-containing polyamides turned to be poorly soluble in DMAc/5% LiCl, which is an excellent solvent for aromatic polyamides, and required the use of 95% sulfuric acid as a solvent for purposes such as solution viscosity determinations and light scattering measurements. However, when the alkylene-rich dimer acid was used as the only comonomer, or mixed with another long-chain aliphatic diacid, the naphthalene-containing polyamide product was soluble also in *m*-cresol. The polyesters, however, did dissolve in 60 : 40 phenol/tetrachloroethane at 135°C and remained in solution upon cooling to room temperature, a fact that may be attributed to their relatively low molecular weight.

The polymerization examples given in the Experimental section are each typical of the best synthesis method and conditions found for each polyamide type and for the polyesters.

Results

Nine homologues of the poly(alkylene-1,5-naphthaleneamide) family were synthesized and are presented in Table 1. Of the poly(alkylene-1,5-naphthanoate) family, only three homologues were prepared and their specifics are given in Table 2. NMR studies correctly identified the isomeric-structures and composition of the chemical repeat units and the solution viscosity results and light scattering studies clearly revealed the polymeric nature of the synthesized products. In both tables, the intrinsic viscosities of the synthesized batches, their melting points, T_m, and many of the glass transition temperatures, T_g, are also given. In Table 1 are given for three polyamides their weight average molecular weight, M_w, obtained by light scattering.

Viewed separately, the thermal transition data in each table indicate that both T_m and T_g decrease within each family of polymers as the volume fraction of the aliphatic component in the repeat unit increases. This is, of course, consistent with expectations and is similar to the reduction in T_m and T_g with increasing length of the alkylene chain-segments in polymers such as polyalkyleneterephthalates and polyalkyleneamides [15, 24 – 28]. The differences in T_m and T_g between poly(alkylene-1,5-naphthaleneamide)s and poly(alkylene-1,5-naphthanoate)s of identical alkylene lengths are very large

TABLE 1 Poly(alkylene-1,5-naphthaleneamide)s

Polymer code	*Ethylene groups per repeat unit*	*I.V. in dL/g*	T_m, °C*	T_g, °C	% *Crystallinity***	M_w
A1	1	0.12	dec. > 350	–	28	
A2	2	0.25	379.7	267	61	
A3	3	0.29	360.6 (369.2)	196.7	69	
A41	4	0.41	333.0 (346.1)	145	61	14000
A42	4	0.81	335.2 (343.2)	–	51	57000
A43	4	0.41	327.3 (340.9)	–	56	
A44	4	some gels	333.3 (340.4)	127	52	
A45	4	0.79	336.9 (346.5)	121.4	59	23000
A5	5	2.31	317.0 (332.0)	110.4	44	
A6	6	0.56	306.0 (316.6)	99.3	49	
A71	9(8 dangling)***	0.33	187.2	–	22	
A72	ditto	0.34	194.1	17.4	22	
A73	ditto	0.33	193.8	–		
A74	ditto	0.33	179.4	22.8		
A8	1:1 4 + 9(8 dngl'g)		ca. 100		12	
A9	*cis trans*-cyclohexane	0.16	133.8		24	

*Melting points in brackets indicate a secondary peak or a shoulder; **% Crystallinity plus/minus 3%; ***Dangling groups originate from dimer acid monomers.

TABLE 2 Poly(alkylene-1,5-naphthanoate)s

Polymer code	*Ethylene groups per repeat unit*	*I.V., in dL/g*	T_m, °C*	T_g, °C	*% Crystallinity***
E1	2	< 0.1	221.3	71.1	40
E21	4	0.08	117.4	–	42
E22	4	0.13	103.3	–	36
E23	4	0.17	123.8 (106.2)	5.5	51
E3	5	0.38	137.9	26.0	56

*Melting point in brackets indicates a shoulder on main melting peak; **Percent crystallinity plus/minus 3%.

and are consistent with similar differences reported in the literature [15]. Comparison of Tables 1 and 2 reveals that for polymers with two ethylene moieties in each repeat unit, *i.e.*, —$(CH_2)_4$—, the difference in T_m is 158 K, for 4 ethylene groups per repeat unit the T_m difference is more or less 215 K, and in the case of 5 ethylene groups the difference is 179 K. In the case of T_g, the poly-1,5-naphthaleneamides exhibit the transition at least several tens of degrees higher than the poly-1,5-naphthanoates of identical alkylene lengths. It is obvious that in both the T_m and T_g instances, the dramatically higher transition temperatures of the polyamides may be associated with the presence of amide groups in them, and with the fact that these amide groups may form hydrogen bonds (H-bonds) between them, in contradistinction to the polyesters wherein H-bonds are absent. H-bonding in polyamides is clearly observable by infrared (IR) spectroscopy. IR spectra of two poly(alkelene-1,5-naphthaleneamide)s, A45 and A5 in Table 1, are shown in Figure 1. These are typical of all IR spectra obtained of these polyamides. In them, the N–H stretching mode appears at about 3270 cm^{-1} and the amide I absorption band appears at about 1650–1670 cm^{-1}. These are characteristic of H-bonded secondary amide groups [29] and are frequently observed in aliphatic nylons [30] too. The corresponding "free" amide absorption bands appear at 3400–3460 cm^{-1} and 1670–1700 cm^{-1}, respectively [29, 30]. Their absence in our spectra clearly indicates that essentially all the amide residues in our polyamides are H-bonded to one another and "free" amide groups are completely absent for all practical purposes. This indicates that in the linear poly(alkylene-1,5-naphthaleneamide)s the H-bonding capabilities of the amide groups in both the crystal and amorphous phases are fully consummated. It is our belief that the full consummation of H-bondability is the dominant factor in elevating the transition temperatures of these polymers, and that amide–amide dipolar interactions are a secondary contributor to the transition temperature elevation.

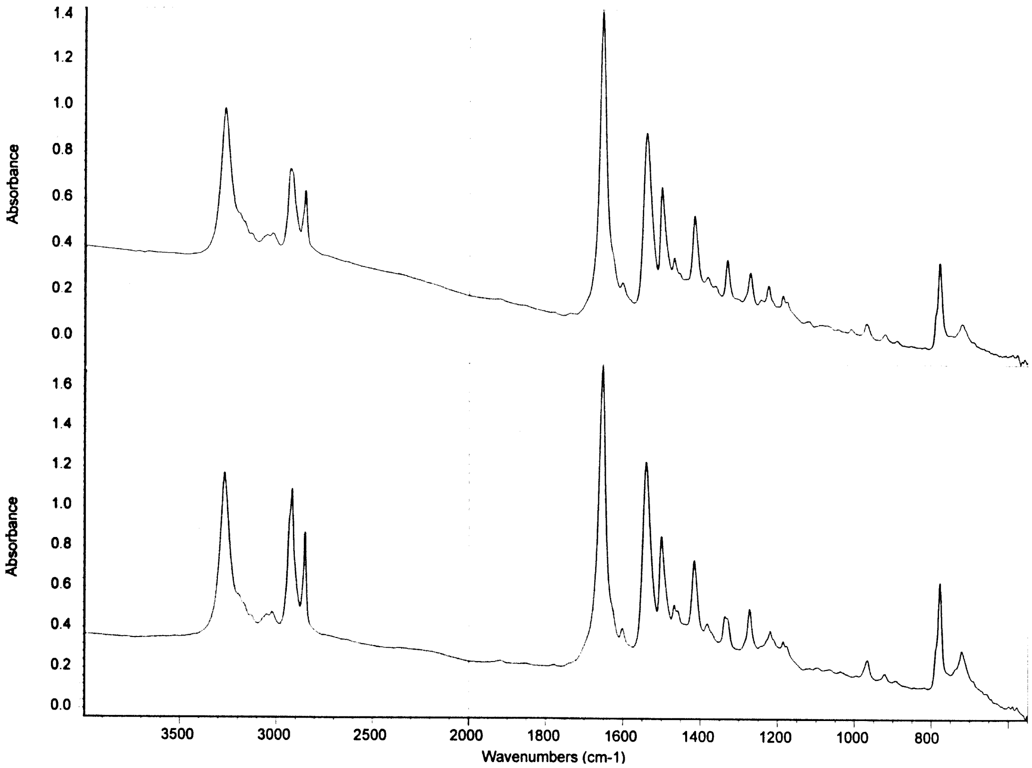


FIGURE 1 Infrared spectra of polyamide A45 (top) and polyamide A5 (bottom).

It is hard to compare the degree of crystallinity of the two polymer families because of the data paucity and scatter, but it appears that, except for poly(alkylene-1,5-naphthaleneamide)s containing dimer acid residues, the polyamides are somewhat more crystalline than their poly(alkylene-1,5-naphthanoate)s analogues. What is striking, then, in both Tables 1 and 2 is not so much the difference between the polymers, but the high degree of crystallinity both families exhibit. These high crystallinity levels, of polymers containing no dangling side-chains, reflect a high propensity towards parallel chain alignment in both the polyamide and polyester polymer families.

Typical WAXD patterns of powdered poly(alkylene-1,5-naphthaleneamide)s are shown in Figure 2 (for polyamide A5) and of powdered poly(alkylene-1,5-naphthanoate)s in Figure 3 (for polyester E23). In both figures, the X-ray reflection at $2\theta \simeq 43.5°$ originated from the aluminum sample holder and should be disregarded. As is obvious from the figures, the quality of the WAXD patterns is not sufficiently high for detailed studies, but sufficient to reveal that naphthalene condensed rings are apparently packed in stacks wherein the repeat distance is about 0.325 nm (peak at $2\theta \cong 28°$) which is an accepted repeat distance between aromatic rings stacked together. The distance between H-bonded sheets in the polyamide is about 0.36 nm. The distance between chains held together by H-bonds is about 0.472 nm (peak at $2\theta \simeq 19°$), and the distance between sheets separated only by van der Waals and dipolar interactions is about 4.05 nm (peak at $2\theta \simeq 21.9°$). The quality of the diffraction patterns is not sufficient for further refinement. The WAXD reflection associated with the repeat distance along the main-chain is rather intense for such kind of reflections. The distance increment upon going from a polyamide having, say, 4 methylene groups to the next one, having 6 methylenes along the main-chain, is significantly smaller than the 0.127 nm per methylene associated with the chain axis projection of CH_2—CH_2 bonds present in the chain in their *trans*-conformation. In fact, the distance increments along the main-chain fall in the range of 0.07 to 0.10 nm with the majority of the increments falling in between 0.07 and 0.08 nm. This indicates that once the linear aliphatic part of the main-chain contained 4 or more methylene groups, additional CH_2—CH_2 bonds preferentially adopt the *gauche*-conformation and not the *trans*-conformation. This observation is consistent with our previous observations on the conformation of alkylene segments in poly(ester amide)s [17, 19]. From symmetry considerations, we believe that upon going from 4 to 6 methylenes per repeat unit, the alkylene chain adopts a *gauche*$^+$ *trans gauche*$^-$ or *gauche*$^-$ *trans gauche*$^+$ conformations. The fully *trans*-conformation is inconsistent with the distance increments observed in our WAXD patterns. With more methylene groups added to the alkylene units, the main-chain bonds preferentially adopt the

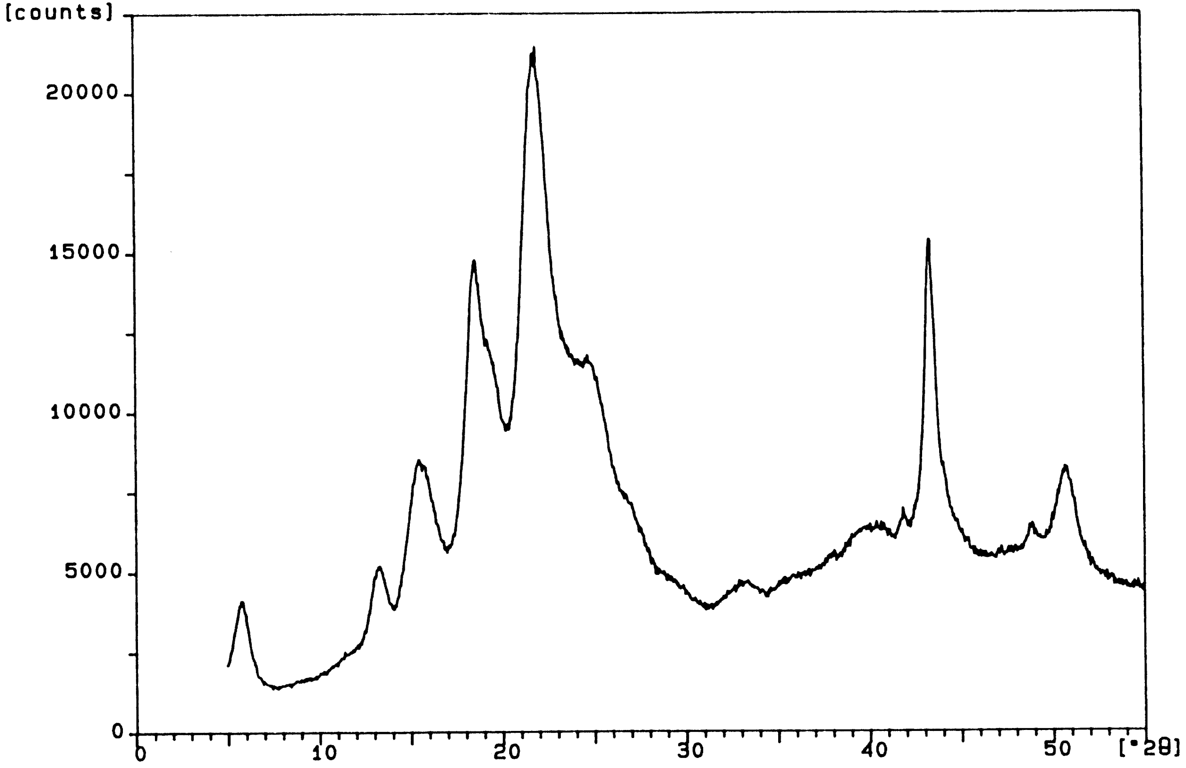


FIGURE 2 Wide-angle X-ray diffraction pattern of polyamide A5.

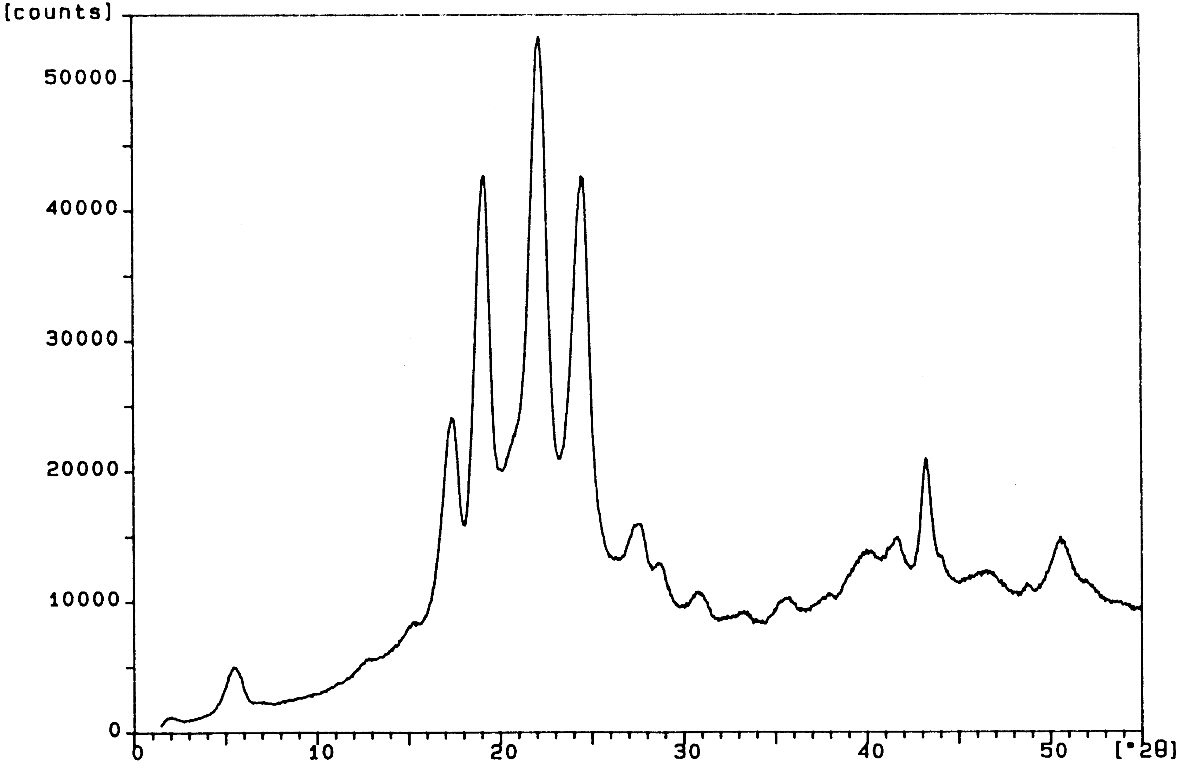


FIGURE 3 Wide-angle X-ray diffraction pattern of polyester E23.

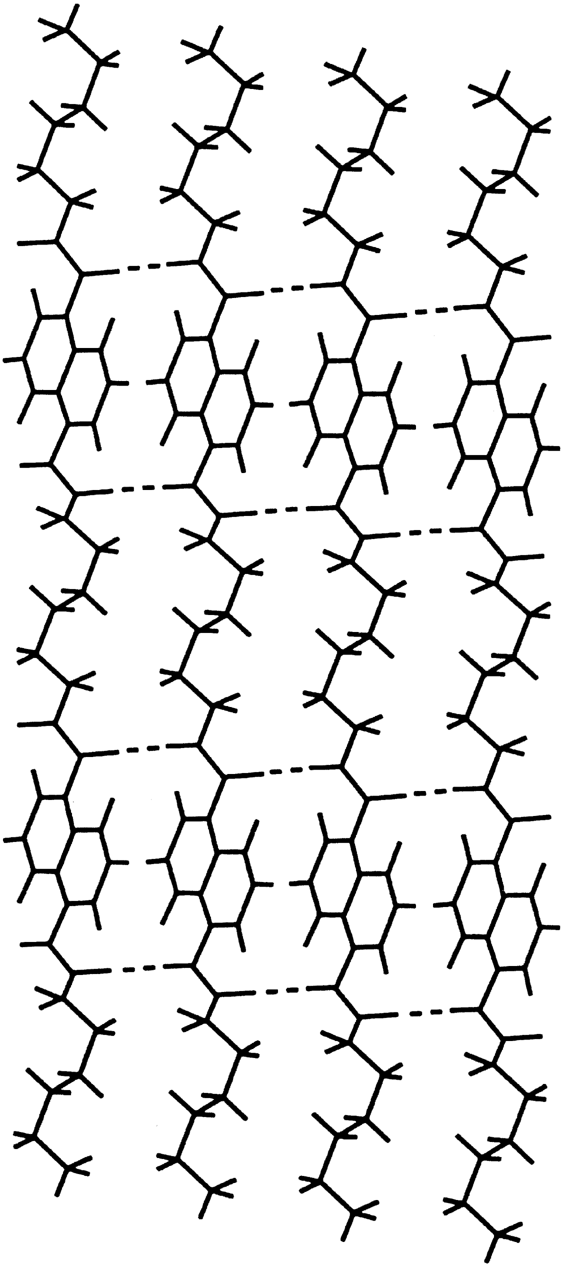


FIGURE 4 Idealized crystal structure of poly(hexamethylene-1,5-naphthalene-amide) based on our WAXD data and similar to the literature references [17, 19, 31–33].

gauche-conformation such that the majority of the alkylene main-chain bonds are in the *gauche*-conformation and a couple or so of the CH_2—CH_2 bonds end up adopting a *trans*-conformation. We do not believe, however, that the location of these few *trans*-conformers is rigidly fixed, which for sufficiently long alkylene segments leads to a system in which the majority *gauche*-conformers may dynamically interchange their locations within each segment with the minority *trans*-conformers without any energetic penalty. An idealized structure consistent with the WAXD patterns and the above discussion, of poly(alkylene-1,5-naphthaleneamide) containing 3 ethylene (6 methylene) groups in each repeat unit, is shown in Figure 4. In it we observe the stacks of the naphthalene groups growing in one direction, the amide groups H-bonds in another direction, and the alkylenes in the main-chain adopting a $gauche^{+}$ *trans* $gauche^{-}$ conformation and aligned in a third direction. The organization of the poly(alkylene-1,5-naphthaleneamide)s in the crystal phase appears to be closely related to the crystal structure of certain polyurethanes based on 1,5-naphthalenediisocyanate connected by long aliphatic diols [31 – 33]. We believe that in the case of the polyamides, the H-bonds and naphthalene stacking together greatly enhance not only the fraction of polymer ending up in the crystal state, but also the crystal stability and the resulting very high melting point.

Despite the absence of H-bonds, the poly(alkylene-1,5-naphthanoate)s show WAXD patterns strikingly similar to those of the polyamides. We believe, but can't prove at present, that the crystallinity of the polyesters is dominated by the naphthalene groups packing in stacks, as can be gathered from the intense reflection at $2\theta \simeq 28°$, and the aliphatic groups adopting similar conformations to the corresponding polyamides (note the strong reflections at $2\theta \simeq 5.5°$).

One final point: While generally being a sought-after property, in our case the very high melting points turned to be detrimental. They were so high that no useful and safe temperature interval remained in which the polyamides could be melt processed without rapid degradation. The only polyamides with sufficient thermal stability that could be melt processed safely were the ones containing dimer acid residues. These, however, could not have been prepared in molecular weights high enough to make them technologically promising. Once monomers are obtained of sufficient purity to create truly high molecular weight polymers, then polyamides created from 1,5-diaminonaphthalene and aliphatic dimer acids should be revisited.

CONCLUSIONS

Poly(alkylene-1,5-naphthaleneamide)s and poly(alkylene-1,5-naphthanoate)s are highly crystalline polymers. In the polyamides, all potential inter-amide hydrogen bonds are consummated, leading to melting and glass transition temperatures far higher than in the polyester analogues. Stacking of naphthalene condensed rings seems to be a major contributor to the high crystallinity of both families, while the H-bonds in the poly(alkylene-1,5-naphthaleneamide)s greatly increases the crystallites' stability and enhances their melting point. When the alkylene chains between naphthalene residues are long enough, they contain both *trans*- and *gauche*-conformations.

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