Novel Thermotropic Polyesteramides

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ABSTRACT

A series of wholly aromatic, *para*-linked, thermotropic polyesteramides has been synthesized from various aminophenols, 2-trifluoromethyl terephthalic acid, and 2,2'-trifluoromethyl-4,4'-biphenyl dicarboxylic acid. The polymers exhibit good solubility and, in most cases, low mesophase transition temperatures. Oriented films of these materials show a high degree of optical anisotropy. The infrared dichroic behavior of the amide carbonyl was used to calculate orientation as well as a new value for the angle of the ester carbonyl vibrational transition moment.

INTRODUCTION

Numerous chemical classes of main-chain liquid-crystalline polymers (LCP's) have been reported to date. While polyamides and polyesters dominate this field, several other types of LCP's have been prepared including poly(β-thioester)s [1], polyethers [2], polyketones [3], poly(ether sulfone)s [4], polyurethanes [5, 6], and polycarbonates [7]. Polyesteramides, hybrids of polyamides and polyesters, have received more attention than any of the other aforementioned polymer classes. Several patents in the field of anisotropic, aromatic polyesteramides have been issued in the past few years, and among the more notable are those concerning p-acetamidobenzoic acid-modified PET and the 6-hydroxy-2-naphthoic acid-based family of thermotropic poly-

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esteramides [8]. In addition, a variety of semiflexible polyesteramides has
been prepared by a number of authors [9, 11].

Recently, we published a series of papers on the synthesis and characteriza-
tion of *para*-linked, aromatic polyamides [12, 13] and polyesters [14, 15]
which contain 2,2'-disubstituted biphenylene units. These polymer systems
were investigated because of their high inherent polarizability, rodlike geom-
etry, and orientability which gives rise to unusually high birefringence values.
Films of such materials are useful in a number of optical devices which have
been previously described [16-18].

Many of the polyamides display very good optical clarity and high bire-
fringence when oriented (Δn up to 1.0 when extrapolated to 100% orientation
[19]). A significant drawback of these materials is that films must be fabri-
cated by extrusion or casting from solution since they do not soften sufficient-
ly for melt processing. These polyamides, in spite of their high solubility, do
not form lyotropic solutions and, consequently, processing from the meso-
phase cannot be used to achieve higher degrees of orientation.

In contrast, a series of the structurally similar aromatic polyesters, synthe-
sized in our laboratory, display thermotropic liquid-crystal behavior. They
are highly amorphous and enter the nematic phase at temperatures (150-
200°C) which are sufficiently low to permit melt processing. However, their
optical quality and extrapolated birefringence values are not quite as high as
those obtained with the polyamides.

In order to combine these desired optical and processing properties, a series
of 2,2'-disubstituted biphenylene-containing polyesteramides was prepared,
and the results are presented here.

EXPERIMENTAL

Monomer Synthesis. *p*-Aminophenol and 2-methyl-4-aminophenol (Ald-
rich) were purified by sublimation prior to use. The preparations of 2-(tri-
fluoromethyl) terephthalate and 2,2'-bis(trifluoromethyl)-4,4'-biphenyl di-
carbonyl chloride have been described elsewhere [14]. 2-Trifluoromethyl-
4-aminophenol was synthesized from 2-methoxy-5-nitrobenzotrifluoride
(Aldrich) according to the procedure of Filler et al. [20].

Polymerization. The polyesteramides were prepared by a modification
of procedures described in the literature [21, 22]. The following is an illus-
trative example.

A solution of *p*-aminophenol (1.636 g; 15 mmol) and Et_3N (4.5 mL) in

dry dimethylacetamide (DMAC) (12.5 mL)/CH_2Cl_2 (10 mL) was cooled to 0°C in an ice/salt bath under N_2. To this solution a mixture of 2-(trifluoro-methyl)terephthaloyl chloride (4.06 g; 15 mmol) in CH_2Cl_2 (15 mL) was added dropwise by syringe while the reaction temperature was maintained at 0-5°C. After stirring for 3 h, the reaction was allowed to come to room temperature, DMAC (25 mL) was added, and the clear, viscous solution was precipitated into methanol. The white, fibrous polymer was filtered, washed with methanol, and dried for 24 h under vacuum at 80°C (5.91 g, 95%).

Polymer Characterization. Thermal analyses were performed on a Perkin-Elmer DSC-7 and Du Pont 1090 (TGA). Glass transitions are reported as the midpoint of devitrification and TGA temperatures as the onset of decomposition. Samples were run under N_2 at rates of 20°C/min unless otherwise specified. Liquid-crystal behavior was observed on a Zeiss 9902 Pol microscope equipped with a Leitz hot stage. The temperature ranges reported are taken at the onset of a flowing birefringent melt.

Inherent viscosities were determined in DMAC and THF (Cannon-Ubbelhode dilution viscometer) of 0.5% (w/v) polymer solutions at 30°C.

Films cast from DMAC under N_2 were heat-stretched in a unidirectional stretcher. Orientation was determined by IR dichroism (Perkin-Elmer 580), and the birefringence was calculated by measuring the respective refractive indices by the Brewster angle technique (633 nm). FTIR spectra were recorded on a Beckman FT 1100.

X-ray diffraction patterns were recorded on Kodak no-screen x-ray film in a Warhus flat film camera using Ni-filtered CuK_α radiation.
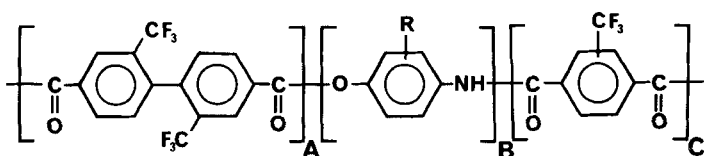
RESULTS AND DISCUSSION

Synthesis and Solubility

All of the polyesteramides listed in Table 1 were prepared by the procedure described in the Experimental section in relatively high yields (85-95%). Additional experiments were carried out where the tetrahydrofuran was substituted for CH_2Cl_2, and no pronounced effects on either polymer yield or viscosity were observed.

Aromatic *p*-aminophenols and diacids were utilized in order to control the amide/ester (A/E) bonding sequence. The incorporation of diamines and diols into these polymers would result in blocky structures, which are difficult to characterize thoroughly and would obfuscate the structure-property relationships. The amino termini react first to yield a dihydroxydiamide

TABLE 1. Structures and Abbreviations of the Aromatic Polyesteramides

Polymer[a]	CF_3,[b] A	AP,[b] R, B	TCF_3,[b] C
I (CF_3/AP)	1	H, 1	0
II (AP/TCF_3)	0	H, 1	1
III ($CF_{3/0.5}$AP/$TCF_{3/0.5}$)	0.5	H, 1	0.5
IV ($CF_{3/0.3}$AP/$TCF_{3/0.7}$)	0.3	H, 1	0.7
V ($CF_{3/0.5}$MAP/$TCF_{3/0.5}$)	0.5	CH_3, 1	0.5
VI (MAP/TCF_3)	0	CH_3, 1	1
VII ($CF_{3/0.5}$MAP$_{/0.5}$AP$_{/0.5}$$TCF_{3/0.5}$)	0.5	H, 0.5	0.5
VIII (CF_3/CF_3AP)	1	CF_3, 1	0
IX ($CF_{3/0.5}$$CF_3$AP/$TCF_{3/0.5}$)	0.5	CF_3, 1	0.5
C (CF_3AP/TCF_3)	0	CF_3, 1	1

[a]Repeat unit sequence (CF_3-biphenyl/aminophenol(s)/CF_3-terephthaloyl). Subscripts indicate the molar ratios.

[b]CF_3: 2,2'-CF_3-disubstituted biphenyl; TCF_3: CF_3-terephthaloyl; AP: 4-aminophenol; MAP: 3-methyl-4-aminophenol; CF_3AP: 2-trifluoromethyl-4-aminophenol.

intermediate which, in turn, reacts with the diacid chloride to form ester linkages. The resulting predominant bonding sequence, E/A/A/E, is a consequence of the higher reactivity of the amino groups, as was demonstrated by Preston [23]. No attempt was made to alter this sequence by changing the structure of the tertiary amine acid acceptor [24].

In general, the viscosities attained are indicative of moderately high molecular weight. Polymer III, for instance, with an intrinsic viscosity of 3.14 dL/g (THF, 30°C) has a corresponding M_n of 23 500 (by membrane osmometry,

TABLE 2. Solubility[a] of the Polyesteramides[a]

Polymer	η_{inh}, dL/g	Acetone	THF	CH_2Cl_2	Dioxane
I	3.41	Sw	S	Sw	Sw
II	1.04	I	I	I	I
III	2.96	I	S	Sw	Sw
IV	1.87	I	Sw	Sw	Sw
V	2.28	I	Sw	I	Sw
VI	0.44	Sw	Sw	I	Sw
VII	2.06	I	I	I	I
VIII	1.88	S	S	I	S
IX	1.28	S	S	I	S
X	0.76	S	S	I	Sw

[a]S = soluble, I = insoluble, Sw = swells.

THF, 30°C). Furthermore, the viscosity behavior of this polymer and the other polyesteramides displays very little dependence on solvent and temperature. The inherent viscosities of Polymer III in THF and DMAC are 2.96 and 2.65 dL/g, respectively, and a plot of $[\eta]$ (in THF) versus temperature has a very small (0.01) slope. Both of these results are supportive of the rod-like nature of these polyesteramides.

The solubility properties of wholly aromatic, *para*-linked polyesteramides are normally quite similar to those of rodlike, aromatic polyesters and polyamides. Typical solvents are strong acids, halogenated phenols, and salt-containing amide solvents. The biphenyl-containing polyesteramides described here are soluble in these types of solvents as well as in a number of more common organic solvents (Table 2). This enhanced solubility has also been observed in disubstituted biphenylene-containing polyesters [15] and polyamides [12, 13] which we have previously reported. The effect of the biphenylene content on the solubility can be seen by comparing polyesteramides I-IV and VI. When all of the CF_3-biphenyl monomer units in I are replaced with TCF_3 units (II), the polymer is no longer soluble in the solvents listed in Table 2. All of the examples listed in Table 2 are soluble in amide solvents like DMAC and DMF, both with and without added halide salts. The fact that

TABLE 3. The Effect of the CF_3-Group on the Solubility in Tetrahydrofuran

Polymer	Maximum solubility, % w/v	Streaming birefringence[a]
CF_3/AP (I)	32.8	+
$CF_{3/0.5}AP/TCF_{3/0.5}$ (III)	17.7	+
CF_3/CF_3AP (VIII)	59.0	+
$CF_{3/0.5}CF_3AP/TCF_{3/0.5}$ (IX)	52.0	+

[a]When these solutions were stressed and viewed between crossed polars, streaming birefringence was observed for those indicated with a +.

the solubility is regained when 50% of the diacid units are substituted biphenylenes is quantitatively demonstrated in Table 3. The solubility-enhancing role of the trifluoromethyl groups themselves is demonstrated by comparing the solubility differences between I and III and VIII and IX. The streaming birefringence observed under mild stress in all of these concentrated solutions is again indicative of their rodlike nature, but in no case was lyotropic liquid-crystal behavior observed.

Solid and Liquid-Crystal Properties

Thermal data for these polyesteramides are listed in Table 4 along with their respective inherent viscosities for comparison purposes. The thermogravimetric results indicate that those polymers which exhibit a crystalline melting point are slightly more stable than the amorphous examples. These decomposition temperatures are in the same range as those previously reported for structurally related wholly aromatic polyamides [12]. A comparison of I vs VIII, II vs X, and III vs IX reveals that the introduction of an additional trifluoromethyl group into the aminophenol portion of the chain diminishes the thermal stability. Previously reported results indicate that the introduction of fluorine into aromatic polyamides improves their hydrolytic stability in acidic media and concurrently reduces the thermal stability [25, 26]. This decrease in stability has been attributed to the formation of HF at elevated temperatures, which, in turn, accelerates the degradation. The reduction is greatest when trifluoromethyl groups are *ortho* to the amide linkages [26]. This effect is not so pronounced in our polyesteramides due to the

TABLE 4. Thermal Properties of the Polyesteramides

Polymer	η_{inh}, dL/g	TGA, °C[a]		DSC, °C[b]		T_{lc}, °C[c]
		N_2	Air	T_g	T_m	
I	3.41	451	450	175	350	350
II	1.04	452	451	172	358	358
III	2.96[d]	431	419	217	—	280
IV	1.87	420	418	200	—	260
V	2.28	422	410	205	—	285
VI	0.44	430	400	—	252	252
VII	2.06	417	395	203	—	270
VIII	1.88	400	390	213	—	265
IX	1.28	395	375	198	—	235
X	0.76	400	378	155	—	230

[a]Taken as the onset of decomposition.

[b]Glass-transition temperatures are reported as the midpoint of the transition, and melting temperatures are the peak values of the first-order crystal/liquid crystal transitions.

[c]Temperature at which the solid deforms easily under mild stress and forms a mobile nematic phase when viewed under a polarizing microscope.

[d]Number-average molecular weight of 23 500 by membrane osmometry in THF.

meta orientation of the majority of the CF_3 groups and to the presence of an equal amount of ester linkages.

The glass-transition temperatures of the noncrystalline polymers (III-V, VII-X) are 90-100°C higher than the related thermotropic, aromatic polyesters [15]. Repeated heating and annealing of these samples does not induce crystallinity or appreciably alter T_g. X-ray diffraction patterns also support the lack of crystallinity in these systems. The example shown in Fig. 1 is that of a solution-cast film of Polymer III at room temperature. The pattern and *d*-spacings of 12.9 and 4.8 Å are typical for a nematic mesophase. The pattern does not show any appreciable amount of crystallinity. The role
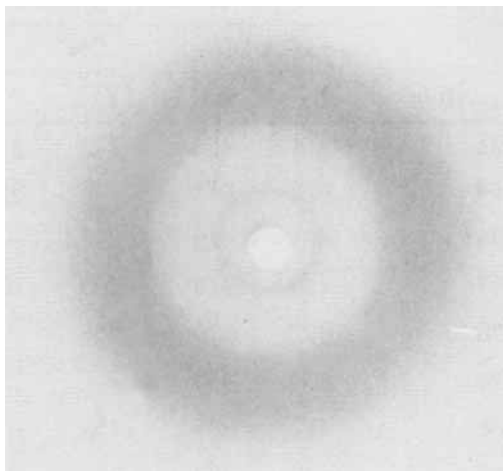
FIG. 1. X-ray diffraction pattern of an unoriented film of Polyesteramide III.

of the noncoplanar biphenylenes and substituted phenylenes in preventing crystallinity has been previously discussed [12-15]. This role has been further elucidated by FTIR spectra which indicate the presence of a significant proportion of NH groups that are not hydrogen bonded. A detailed study of this observation in polyesteramides and related polyamides will be the subject of a forthcoming publication.

The crystalline polyesteramides (I, II, and VI) enter the mesophase above their respective T_m's. On the other hand, the amorphous examples slowly become birefringent when viewed under polarized light as they are heated above T_g. Above their respective T_{lc}'s, the polymers flow when slight pressure is applied, exhibit shear opalescence, and have standard threaded nematic textures. The mesophase persists for all 10 of the examples in Table 4 until decomposition; that is, no clearing points are observed. This behavior is congruent with that of the 2,2'-disubstituted biphenylene-containing polyesters [15].

As mentioned earlier, the colution viscosity results are indicative of moderate to high molecular weight. Polyesteramide III was prepared in a number of molecular weights, and a plot of T_g vs η_{inh} (Fig. 2) shows that the glass transition temperature has nearly attained a constant value. The mesophase temperatures are lower than most of those reported for wholly aromatic polyester-
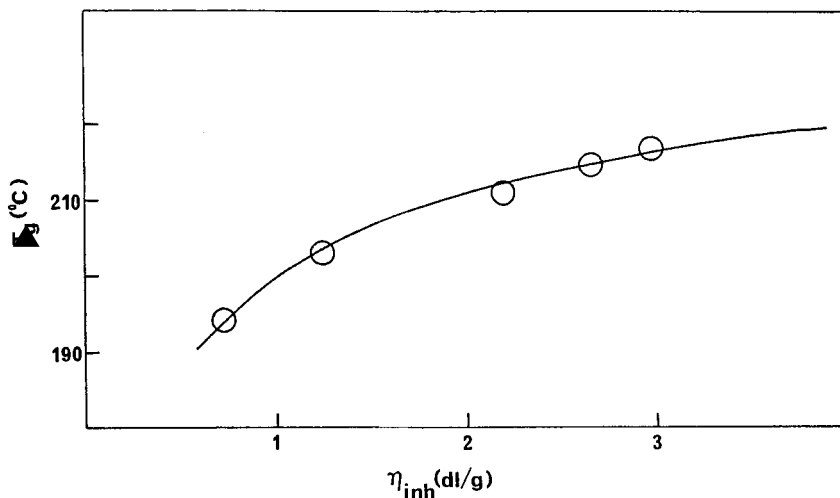
FIG. 2. Plot of T_g versus inherent viscosity for Polyesteramide III.

amides, with the exception of an example presented by McIntyre and Milburn [10], a polymer synthesized from p-aminophenol and methoxyterephthalic acid, reported to soften at 155°C. This result is probably due to the low molecular weight of the sample (η_{inh} 0.48). The authors also reported that the softening points of their polyesteramides are less than those of corresponding polyesters, in spite of their hydrogen-bonding ability [10]. We believe that this observation is also due to molecular weight effects since in our systems, where hydrogen bonding is diminished (see above discussion), the softening points are consistently higher for the polyesteramides.

The appearance of solution-cast films of the polyesteramides also parallels that of the polyesters, namely, the films range from slightly scattering to opaque, depending on solvent choice and drying conditions. It is believed that the scattering is caused by voids. However, clear films can be obtained by coagulating a cast solution of the polymer in 5% LiCl-containing DMAC in isopropanol. After all of the salt is removed by successive washings (H_2O/ isopropanol 10/90), a gel-like film is obtained which can be stretched. This behavior was observed for a series of biphenylene-containing aromatic polyamides prepared in our laboratory [12]. The polyesteramides do differ slightly, though, in that the resulting films are opaque if only water is used as the coagulating bath, while clear gels of the polyamides are obtained when either
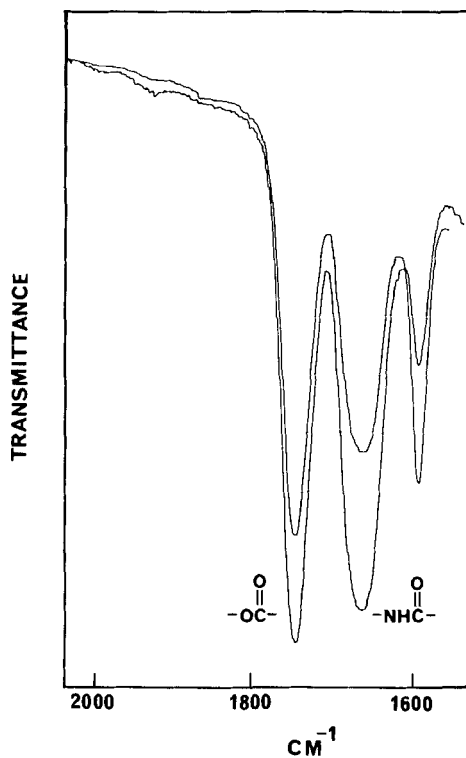
FIG. 3. IR dichroism of the carbonyl region of an oriented sample of Polyesteramide III.

water or isopropanol is utilized. This difference is a consequence of the presence of ester linkages since the polyesters themselves do not form such gel-like structures when subjected to the above conditions.

Films of these materials can be stretched (with heat or from the gel state) to give highly birefringent oriented samples. Samples of Polymer III ($CF_{3/0.5}$-AP/$TCF_{3/0.5}$) were heat-stretched at $230°C$ to various draw ratios, and their birefringence as a function of orientation was monitored. The order parameter, as determined by infrared dichroism, can be calculated from the dichroic ratio of either the amide or the ester carbonyl band (Fig. 3) at 1670 and 1752 cm^{-1}, respectively. When these calculations are performed by utilizing the reported vibrational transition moment angles (with respect to the chain axis)

of 81° [27] for the amide carbonyl and 76° [28] for the ester, the order parameters differ by a factor of almost 2, with the ester carbonyl yielding the lower value. One of the angles used must be in error since the amide and ester linkages are attached to the same phenyl ring and, therefore, experience the same orientation. Given the high birefringence values obtained (0.5-0.8) and the sound basis of the 81° angle for the amide carbonyl vibrational transition moment, the higher-order parameters calculated from the 1670 cm^{-1} band were judged correct. When a plot of birefringence vs order parameter was extrapolated to perfect orientation, a birefringence maximum of 0.95 is obtained. This is slightly lower than those obtained for the related series of aforementioned polyamides [12] and close to that calculated for the polyesters [15]. On the assumption that the orientations of the amide and ester carbonyls are equivalent, a new vibrational transition moment angle of 66° is calculated for the 1752 cm^{-1} band.

This new value for the transition moment angle was then utilized to recalculate the order parameters for the series of previously synthesized polyesters, which have been referred to throughout this paper [15]. These polymers also exhibit high birefringence values (0.5-0.70) for corresponding order parameters of 0.3-0.4 (when using an angle of 76°). When the angular value of 66° was used, order parameters of 0.6-0.7 were obtained. The corresponding extrapolated birefringence (0.91) was in better agreement with those obtained for the polyamides and polyesteramides.

CONCLUSION

A series of novel, thermotropic, wholly aromatic polyesteramides with relatively low mesophase transition temperatures has been described. These temperatures are low enough to permit melt processing from the mesophase by standard techniques. These polymers also display good solubility, a property not normally associated with wholly aromatic, *para*-linked materials. The solubility is facilitated by the presence of the noncoplanar biphenylene units and trifluoromethyl groups, which frustrate interchain interactions, thereby suppressing crystallinity.

The rigidity and high polarizability of the polyesteramide chains permit high degrees of orientation to be obtained, accompanied by large birefringence values. These characteristics, coupled with the amorphous nature of the polymers, lead to unique optical properties which can be taken advantage of in a variety of applications.

Finally, as a result of the study of the orientation and optical properties

of these polyesteramides, a value for the angle of the aromatic ester carbonyl vibrational transition moment has been calculated which differs from those previously reported. This new angle, which was calculated from the amide carbonyl orientation data, has been useful in explaining data obtained for an analogous series of wholly aromatic polyesters.

ACKNOWLEDGMENT

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