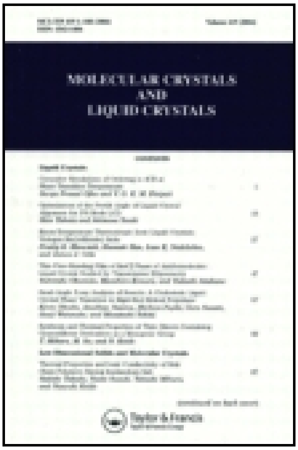

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An X-ray Diffraction Study of Glassy, Rodlike Polymers

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An X-ray Diffraction Study of Glassy, Rodlike Polymers

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Wide angle x-ray analysis of oriented and unoriented samples (including powders, films and fibers) of a wholly-aromatic, *para*-linked polyamide (I), a polyesteramide (II), and three polyesters (III–V) were performed in order to investigate the morphology of these three classes of rodlike polymers. The results indicate that four of the polymers are essentially amorphous in the unoriented state and clearly show the development of two dimensional order upon orientation. However, Polyester V is semi-crystalline. This polymer is the only one of the five which exhibits a first order DSC transition, and it is the only one containing triether substitutents which implies that these short side chains may be forming small crystalline domains.

Keywords: x-ray diffraction, glassy polymers, rodlike polymers, polymer morphology

INTRODUCTION

Over the last several years, we have published a series of papers on the subject of main-chain, rodlike polyamides, polyesters and polyesteramides containing non-coplanar biphenyls in the backbone.[1] The biphenyl moieties are forced into a non-coplanar conformation by the presence of substitutents on the 2,2′-position of the rings. A large body of experimental data indicates that these polymers exhibit a unique set of properties due primarily to the presence of the substituted biphenyls. For example, the polyamides are colorless due to incomplete overlap of the *p*-orbitals on the 1,1′-carbons adjoining the rings which disrupts multi-repeat unit conjugation; in contrast poly-*p*-phenylene terephthalamide (Kevlar) is golden yellow.[2] All of the polymers exhibit high refractive indices and high birefringence values when oriented. These properties are related to the rodlike structure and high polarizability of the groups on the backbone.[3]

Furthermore, even though polyamides and the polyesters are rodlike, e.g., persistence lengths in the 200–300 Å[1,8] range and 100–150 Å range,[4] respectively, and Mark-Houwink exponents of 1.2 and 1.0, respectively, not one of these polymers exhibits lyotropism.[5] In general, all three classes of polymers are highly soluble,

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not only dissolving in typical solvents for their class, but also many of them are highly soluble in common solvents such as acetone, THF, chloroform, etc.; the concentations attainable are far in excess of the calculated critical concentrations required for the development of a biphasic solution.

We have also reported recently that we were able to use this lack of intermolecular association for making molecular composites.[6] In these experiments, we were able to dissolve at least one member of all three classes in a vinyl monomer containing a photoinitiator. Upon irradiation, the viscosity of the polymerizing solution increased at a rate which exceeded the diffusion rate of the rodlike polymers which prevented phase separation; completely non-scattering films and molded pieces were obtained. Quite unexpectedly, identical results were obtained by dissolving the polyamides and certain very specific combinations of flexible chain polymers, e.g., polyvinylpyridine or polyvinylpyrrolidinone, in non-polymerizable solvents, e.g., pyridine, TMU, NMP, followed by evaporation of the latter.

We have suggested that the anomolous behavior exhibited by these three classes of polymers might be related to weak intermolecular associations which are imparted to each chain by the presence of the non-coplanar biphenyls. This hypothesis is supported by the finding that hydrogen bonding in highly oriented films is nearly absent[7] and more recently by Kerr constant measurements of one of the polyamides.[8] The latter experiments indicate that the polyamide does not have a permanent dipole in either the longitudinal or transverse direction relative to the main chain, but its high Kerr constant is due entirely to the high polarizability of the groups comprising each repeat unit.

Diminution of hydrogen bonding as the rodlike chains attain parallelism, uncorrelated dipoles between repeat units, and the absence of a resultant dipole for any given chain significantly disrupt interchain correlations which almost completely eliminates crystallite formation. In this paper, we present data obtained from x-ray diffraction experiments in support of this conclusion; the structures of the polymers which were investigated are shown in Figure 1.

EXPERIMENTAL

A Warhus x-ray camera which comprises a collimator and an evacuable sample chamber with four x-ray film stations at 3, 5, 17 and 32 cm was used for analysis; an x-ray wavelength of 1.541 Å was obtained from a Ni-filtered CuKα source. Precise working distances were determined by means of calibration standards: sodium fluoride (5.37 cm), and silver behenate (19.67 and 32.28 cm). After several experiments, it was determined that the 5 cm working distance gave the most useful data. Two pieces of x-ray film were used, one behind the other, for each experiment; this helped insure that each experiment would give adequate diffraction patterns since sample thicknesses varied. Exposure times were in the range of 24 to 48 hours when the source was run at 40 kV and 30 ma.

Unfortunately, image intensity was frequently very low and variable which made it impossible to obtain consistently high quality photographs suitable for publication. The x-ray defractograms presented in this paper were scanned with a Royal

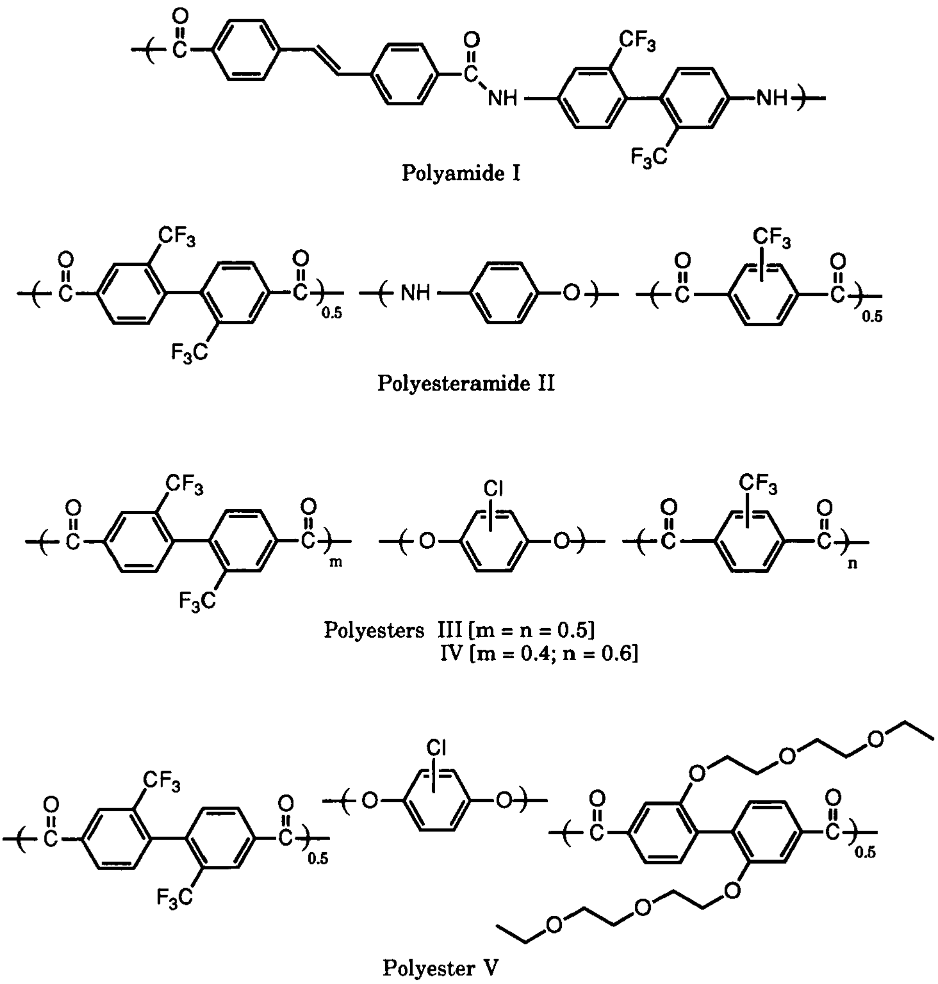


FIGURE 1 The molecular structures of the polymers used in this study.

Zenith 200-S for an output of 155 pixels per inch. Image enhancement was done on a Macintosh IIFX computer in Adobe Photoshop version 1.0.7. The hard copies were made with a Hitachi VY5000 dye diffusion thermal printer.

Estimates of *d*-spacings were made using the negatives obtained from each experiment and a Stoe light box equipped with a densitometer. The values given in Tables I–III were calculated using either the mean ring radius for samples exhibiting a diffuse ring, i.e., large radial width, or the radius of maximum intensity. The error incurred in these measurements was approximately ±5%.

Each powdered polymer sample was tamped into a glass capillary which was then sealed to prevent the sample from escaping during evaculation. Unoriented films were mounted to the sample holder with adhesive tape, and oriented samples were positioned so that their alignment direction was parallel to the meridional axis. Oriented films were obtained by stretching solvent-cast films with a mechanical stretcher while applying heat; the temperature of the stretching operation did not

TABLE I

x-ray diffraction data for Polyamide I

Sample Form	Ring or Arc #	Average Radius (cm)	2θ (°)	Azimuthal Width (°)	d-Spacing (Å)
powder	1	0.69	7.32		12.07
	2	1.16	12.18		7.26
	3	1.53	15.90		5.57
	4	2.23	22.54		3.94
un-oriented film	1	0.74	7.84		11.27
	2	1.07	11.26		7.85
	3	1.41	14.70		6.02
	4	2.06	20.98		4.23
oriented fiber	1	0.38	4.04	52.40	21.83
	2m[1]	0.72	7.63	52.40	11.58
	3m	1.10	11.57	52.40	7.64
	4m	1.46	15.20	52.40	5.82
	5m	1.90	19.48	52.40	4.56
	6e[2]	1.90	19.48	58.15	4.56

1. m - meridional arc; 2. e - equatorial arc

exceed the softening point of the polymer by more than ~30°C. Oriented fibers of the polyamide sample were obtained by wet-jet extrusion at room temperature of 5 wt/v% solutions in 5% LiCl/DMAc; water was used to coagulate the polymer and extract the salt and solvent. Oriented fibers of the polyesters were drawn from samples which were heated to about twenty degrees above their glass to liquid crystalline transition temperatures.[9]

RESULTS AND DISCUSSION

Several general observations can be made regarding the unoriented samples. In the form of powders or unoriented films, these samples typically exhibit sharp but barely discernable rings superimposed on a broad amorphous halo; Figure 2 is a typical example. In both powders and films the radii of the sharper, inner rings corresponding to the major repeat unit distances are within 1 cm (~2 Å) of each other. The average *d*-spacings correspond to sub-repeat unit distances as estimated from molecular models.

Polyester V is the only polymer examined which exhibits a sharp, isolated ring, e.g., 5.54 Å, that is not superimposed on an amorphous halo (Figure 3). DSC analysis of this polymer shows that it has a first order transition at 207°C followed at 210°C by partial clearing to an isotropic liquid.[9] These results, combined with

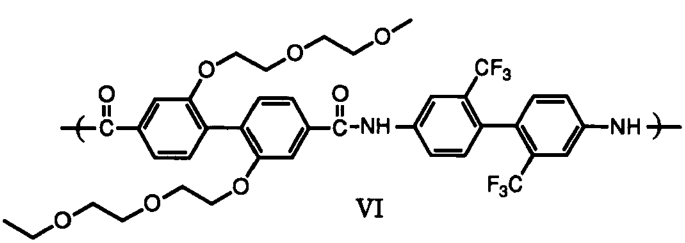
TABLE II

x-ray diffraction data for Polyesteramide II

Sample Form	Ring or Arc #	Average Radius (cm)	2θ (°)	Azimuthal Width (°)	d-Spacing (Å)
powder	1	0.63	6.69		13.21
	2	1.84	18.90		4.69
un-oriented film	1	0.60	6.37		13.86
	2	1.89	19.38		4.58
oriented film	1m	0.60	6.37		13.86
	2m[1]	1.42	14.80	28.75	5.98
	3e[2]	1.70	17.56	26.05	5.05

1. m - meridional arc; 2. e - equatorial arc

literature data on related thermotropic polyesters,[10] suggest that the triethylene oxide side chains of this polymer form crystalline domains. Interestingly, although some substituted, phenylene polyamides (no biphenyls) are thermotropic,[11] a polyamide analog of Polyester V, e.g., Polymer VI shown below, is completely amorphous and does not



VI

exhibit thermotropism. The absence of thermotropism in Polymer VI may be related to hydrogen bonding between the side chain ether groups and the amide hydrogen atoms.[7]

The results obtained from the oriented samples are much more informative. For example, an oriented fiber of Polyamide I (~60% oriented, estimated from birefringence data), exhibits four discernable meridional arcs the first of which ($d = 11.58$ Å) corresponds to half of the repeat unit (23.60 Å) (Figure 4). There is a diffuse halo with an average distance ($d = 21.83$ Å) corresponding to the full repeat unit. The large diffuse lobes along the equator represent a wide distribution

TABLE III

x-ray diffraction data for Polyesters III–V

Sample # and Form	Ring or Arc #	Average Radius (cm)	2θ (°)	Azimuthal Width (°)	d-Spacing (Å)
III	1	0.66	7.00		12.61
unoriented	2	1.42	14.80		5.98
film	3	2.48	24.78		3.59
oriented	1	0.62	6.58		13.42
film	2m[1]	1.52	15.80	36.10	5.61
	3e[2]	1.55	16.11	33.95	5.50
	4e	2.20	22.27	33.95	3.99
fiber	1m	0.60	6.37	37.40	13.86
	2m	1.50	15.60	37.40	5.68
	3m	2.16	21.90	37.40	4.06
	4e	0.72	7.63	37.20	11.58
	5e	1.57	16.29	37.20	5.44
	6e	2.36	23.71	37.20	3.75
IV	1	0.81	8.57		10.31
powder	2	1.59	16.48		5.38
	3	2.35	23.62		3.76
unoriented	1	0.65	6.90		12.81
film	2	1.53	15.90		5.57
	3	2.33	23.44		3.79
V	1	0.56	5.95		14.85
unoriented	2	1.04	10.95		8.07
film	3	1.54	15.99		5.54
	4	2.22	22.45		3.96

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1. m - meridional arc; 2. e - equatorial arc

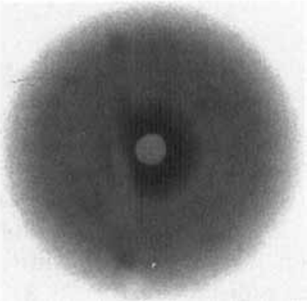

FIGURE 2 The x-ray diffraction pattern of an unoriented film sample of Polyamide I.

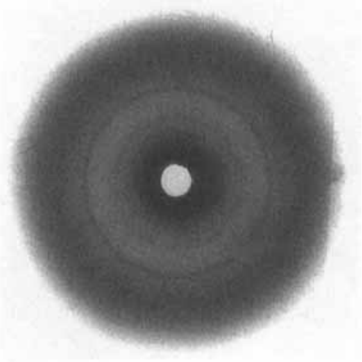

FIGURE 3 The x-ray diffraction pattern of an unoriented film sample of Polyester V.

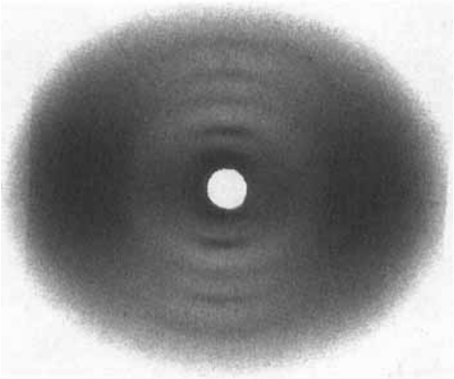

FIGURE 4 The x-ray diffraction pattern of an oriented fiber of Polyamide I.

of interchain spacings. These results suggest a two dimensional order typical of oriented non-polymeric[12] and polymeric nematics[13] and confirm the amorphous nature of the polymer.

The x-ray diffraction pattern of an oriented film of Polyesteramide II is shown in Figure 5. It has diffuse (both azimuthal and radial width) equatorial lobes in analogy to the polyamide. There is a diffuse halo with an average repeat distance of 13.86 Å which corresponds to the repeat unit length of the polymer (14.61 Å). Both the powder and the unoriented film of this polymer exhibit fairly sharp rings at this distance. Along the meridion there is a very faint arc (d = 5.98 Å) which is slightly less than half the repeat unit length. DSC analysis indicates that there are no first order transitions which strongly suggests that this polymer is also noncrystalline.

The x-ray diffraction patterns of an oriented film (~60%) and fiber of Polyester III (Figure 6, Table III) resemble its polyamide and polyesteramide analogues in that the reflections along the meridion correlate fairly well with the repeat distance estimated from molecular models (14.61 Å). However, on the equatorial axis of the fiber diffraction pattern, there is a faint, diffuse lobe (one on each side of the

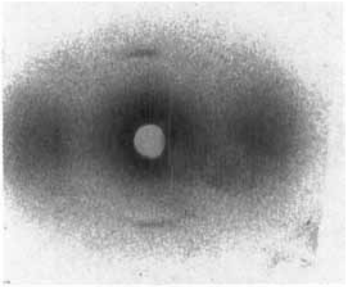

FIGURE 5 The x-ray diffraction pattern of an oriented film of Polyesteramide II.

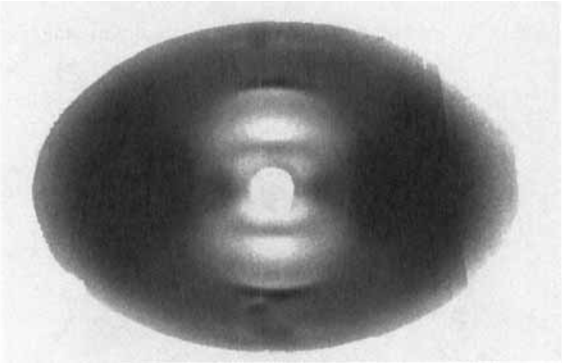

FIGURE 6 The x-ray diffraction pattern of an oriented fiber of Polyester III.

beamstop) at 11.58 Å (mean radius), a very intense diffuse lobe at 5.44 Å, and a very large diffuse arc at 3.75 Å which overlaps somewhat with the large lobe. This polymer has two second order thermal transitions according to DSC analysis; the first is indentified as a glass transition at 118°C, and the second is a glass to liquid crystalline transition at 180°C. There are no first order transitions. This data suggests that some level of three dimensional ordering is beginning to form. Polyesters containing completely random monomer sequences exhibit similar x-ray diffraction patterns and have been described simply as a nematic array of chains.[14]

The x-ray patterns exhibited by these polymers do not show any signs of crystalline order derived from regular, interchain arrays of the backbone. We suggest that the absence of crystallinity in the rodlike polymers described in this report is directly related to the presence of non-coplanar biphenyls in the backbone. Large, bulky groups such as trifluoromethyls or halogens such as bromine prevent the rings from attaining co-planarity which results in a random distribution of atropic enantiomers in every polymer chain.

Stereoisomeric randomness, however, is just one of several factors which prevent pairs of rodlike polymer molecules from associating with one another. Another factor is hydrogen bonding. Unlike poly(*p*-phenylene) terephthalamide, in which phenyl ring rotation allows the rodlike chains to approach to within 3 Å of one another for maximum interchain hydrogen bonding, rotation of one of the phenyl rings in the biphenyl pair in these polymers causes the phenyl ring to which it is bonded to rotate in unison thus preventing the relief of intermolecular steric interactions. In fact, we have demonstrated that hydrogen bonding decreases as orientation increases in biphenyl-containing polyamides.[7]

Furthermore, recent, unpublished Kerr constant measurements[8] clearly demonstrate that a permanent dipole of an individual chain is absent in these polyamides and presumably in the esters and esteramides as well. Molecular models indicate that the resultant dipole from each biphenyl pair, as well as each amide dipole, is uncorrelated with any other biphenyl or amide dipole within a given chain. Uncorrelated dipoles coupled with a large sweep diameter of the rods, 8.2 Å for polymers containing the trifluoromethyl group and 7.9 Å for the bromo substituted biphenyls, and low levels of hydrogen bonding create a rodlike polymer with a random distribution of dipoles and random surface topography. In combination, these factors significantly lower intermolecular enthalpic interactions and increase entropy. As a result, in the solid state, the inherent randomness of the polymer chains restricts their ability to correlate and pack into crystalline arrays, and consequently, these rodlike polymers exhibit good solubility and, quite surprisingly, do not form lyotropic solutions.[15]

CONCLUSION

The data strongly suggests that, with the exception of Polymer V which shows evidence of crystallite formation probably centered in the side chains, the 2,2'-disubstituted biphenyl-containing polymers examined in this study are completely non-crystalline as powders, unoriented films, and oriented films and fibers. Orientation attained by extrusion or mechanical stretching does not induce crystallinity but merely enhances two dimensional order. The morphology present in the thermotropic polyesters at temperatures below the liquid crystalline phase might be accurately described as a nematic glassy state while the aligned polyamides might be considered oriented glasses.

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