Cis–Trans Isomorphism in 1,4-Bis(aminomethyl)cyclohexane Polyamides

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ABSTRACT: Cis–trans copolymers of 1,4-bis(aminomethyl)cyclohexane (BAMC) and adipic, sebacic, and dodecanoic acids have been prepared in isomer ratios varying from 5 to 100%. X-Ray diffraction studies have shown that isomer ratios from about 30 to 100% trans in each copolymer crystallize isomorphically. The conformation of the cyclohexane moiety in the polymer chains is believed to be a twist form which is readily accessible to both *cis*- and *trans*-BAMC residues. This is consistent with the measured structural repeat distances along the chain axes which were determined by X-ray diffraction measurements and found to be intermediate between those expected for the trans (ee) and cis (ea) isomers.

In 1965 Bell, Smith, and Kibler[1] investigated the effect of the cis–trans diamine ratio on the melting points of 1,4-bis(aminomethyl)cyclohexane (BAMC) polyadipamides. They reported a linear decrease in melting point with increasing *cis*-diamine content and a eutectic at 80 mol % cis isomer. The existence of a eutectic composition was considered to be evidence for the nonisomorphic nature of *cis*- and *trans*-BAMC residues. However, Tranter[2] has shown that the melting point *vs.* copolymer composition curve is not a valid criterion for isomorphic replacement in polyamides. As a result of X-ray diffraction studies, he concluded that in a true isomorphic system the lattice spacings should be independent of copolymer composition. The same criterion for isomorphism holds for other dissimilar molecules that have identical crystal structures.[3] One of the authors[4] has recently shown that the glass transition temperature of BAMC polyamides was independent of the diamine isomer content. Since these properties have been shown to vary with isomer content in similar systems,[5,6] we felt that isomorphism might be present in BAMC polyamides. The objective of this study, then, was to determine, using X-ray diffraction, whether these polymers crystallize isomorphically and to obtain information about chain conformation.

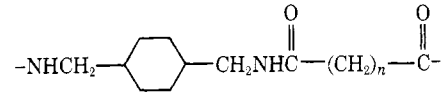
Experimental Section

We used cis and trans copolyamides that were previously prepared.[4] The diamine isomer ratios varied from 5 to 100% in copolyamides of C_6 (adipic acid), C_{10} (sebacic acid), and C_{12} (dodecanoic acid). Thus, 60/40 trans/cis BAMC–C_6 would refer to 60% *trans*- and 40% *cis*-poly(1,4-dimethylenecyclohexyleneadipamide). The isomer concentration, from analyses of the copolymers, is ±2%. X-Ray diffraction patterns were obtained on molded films using a Norelco X-ray diffractometer in parafocus geometry and crystal monochromatized copper X-radiation. The films were dusted with a thin coating of powdered sodium chloride. The sodium chloride reflections, which are accurately known,[7] were obtained with the polymer pattern. They thus served as an internal standard in that any slight shift in the polymer reflections resulting from a malpositioning of the specimen would also be observed with the sodium chloride and could be corrected. The diffraction patterns were analyzed using a Du Pont 310 curve analyzer. This permitted the more accurate determination of the position of overlapping peaks.

The 60/40 trans/cis BAMC–C_{12} film was stretched in an Instron machine at 225° to induce preferred orientation. Flat-plate X-ray diffraction patterns, with the plane of the film normal to the X-ray beam, and symmetrical transmission diffractometer patterns[8] were obtained on the specimen to assess the degree of orientation and to provide information on chain conformation. The flat-plate patterns were obtained using nickel-filtered copper X-radiation.

Results and Discussion

X-Ray diffraction patterns of polymers I were obtained.



I, $n = 4, 8, 10$

The interplanar spacings and relative intensities of the observed reflections are shown in Table I. Within each group, that is, the C_6, C_{10}, or C_{12} series, the interplanar spacings and relative intensities of the crystalline reflections, from an isomer ratio of 30 to 100% trans, are virtually identical within the experimental error of the measurement. Therefore, the crystal structures of the polymers, from 30 to 100% trans, within each series are identical and thus the polymers crystallize as isomorphic structures. Figure 1, the X-ray diffraction patterns of the C_{10} series, illustrates the isomorphism of the polymers from 30 to 100% trans.

Although the diffraction patterns of the three series of polyamides are similar, one difference is the presence of large spacings (8.45–9.45 and 16.7–19.0 Å) in the C_{10} and C_{12} series which are absent from the C_6 series. These spacings are larger in the C_{12} than in the C_{10} series. A flat-plate X-ray diffraction pattern of a film of 60/40 BAMC–C_{12}, which had been stretched in an Instron machine at 225°, showed a substantial degree of preferred orientation. Unfortunately, the orientation was not great enough to unequivocally determine the unit cell dimensions. Nevertheless, the resulting fiber pattern did reveal that the two largest spacings at 18.7 and 9.4 Å were off-meridional reflections, with the latter a second-order reflection of the first. The identity period, which is the struc-

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(3) Leonid V. Azaroff, "Introduction to Solids," McGraw-Hill, New York, N. Y., 1960.
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Table I
X-Ray Diffraction Data for BAMC Polyamides

d, Å	I/I₀	d, Å	I/I₀	d, Å	I/I₀	d, Å	I/I₀	d, Å	I/I₀	d, Å	I/I₀
					C₆ Series						
10% trans		35% trans		55% trans		67% trans		82% trans		100%/trans	
5.50	35	5.50	35	5.47	25	5.47	20	5.47	20	5.48	20
		4.72	40	4.74	20	4.74	20	4.73	20	4.73	20
4.59	100	4.55	5	4.54	10	4.55	5	4.55	5	4.55	5
4.38	20	4.36	100	4.31	100	4.31	100	4.29	100	4.30	100
		4.01	5	3.98	5	4.00	5	3.99	5	3.99	5
		3.85	30	3.83	25	3.86	25	3.86	25	3.86	25
3.72	5	3.74	15	3.72	5	3.72	5	3.72	5	3.72	5
					C₁₀ Series						
5% trans		30% trans		50% trans		60% trans		80% trans		100% trans	
16.5	15	17.4	5	17.5	10	17.6	10	17.5	10	17.9	10
8.2	15	8.4	15	8.6	15	8.5	15	8.6	10	8.6	10
5.60	15	5.60	5	5.59	5	5.53	5	5.49	10	5.47	10
5.11	15	5.22	20	5.24	20	5.21	20	5.18	25	5.15	30
4.65	100	4.69	15	4.62	20	4.65	15	4.61	5	4.58	20
4.43	20	4.51	100	4.46	100	4.44	100	4.45	100	4.44	100
3.97	15	4.16	25	4.20	50	4.19	50	4.16	50	4.16	70
3.78	10	3.78	15	3.85	20	3.83	15	3.83	50	3.86	35
					C₁₂ Series						
10% trans		35% trans		55% trans		67% trans		82% trans		100% trans	
18.8	10	19.2	15	18.7	30	18.8	20	18.9	20	18.8	20
9.8	10	10.1	25	9.4	25	9.4	25	9.4	25	9.3	25
5.64	15	5.50	15	5.47	5	5.43	15	5.42	10	5.42	10
5.11	10	5.06	20	4.98	10	4.95	20	5.03	15	5.01	15
4.85	100	4.72	15								
4.44	20	4.50	100	4.47	100	4.45	100	4.43	100	4.44	100
		4.41	20								
4.10	10	4.18	15	4.17	20	4.16	30	4.15	20	4.16	20
3.77	10	3.73	20	3.78	10	3.78	15	3.78	5	3.78	5

tural repeat distance along the chain axis,[9] corresponding to these spacings was found to be 21.2 Å. Dreiding stereomodels of the fully extended, zig-zag trans-1,4 (ee) isomer of BAMC-C_{12}, with the cyclohexane ring in the chair conformation, showed the theoretical structural repeat distance to be 24.1 Å. For the cis (ea) isomer, the theoretical structural repeat distance would be less than 21 Å because of the almost 90° angle between the cis-1,4 positions on the cyclohexane ring. Thus, it would appear that the cyclohexane ring is present in some intermediate conformation, such as a twist form,[10] or "twistmer," which is readily accessible to both cis- and *trans*-BAMC residues.

We have shown that, for a given diacid series, the interplanar spacings and relative intensities of the crystalline reflections were independent of cis–trans residue content from an isomer ratio of 30 to 100% trans. If we assume that the conformation of methylene groups along the chain is independent or nearly independent of isomer content over this range, then both *cis*- and *trans*-cyclohexane rings must adopt a similar conformation in order for the polymer chains to pack into similar lattices. One possible intermediate conformation that would be readily accessible to both cis and trans rings would be the twistmer.[10] The twist conformation(s) of the cyclohexane ring might be imposed by interchain hydrogen bonding of the NH groups on either side of the ring. An illustration of one of the possible twistmers is shown in Figure 2c and d.

The most stable chair conformation for the trans residue would be the equatorial–equatorial (Figure 2a).[10] The cis residue has only one chair conformer, the equatorial–axial (Figure 2b). It can be seen that for the structures of Figure 2c and d, the polymer chains extend from the cyclohexane ring in a linear, symmetrical fashion, whereas for the structure of Figure 2b the chains extent in an unsymmetrical manner. However, if the cyclohexane ring was in some twistmer conformation, such as is shown in Figure 2c or d, the chains would extend in a linear, symmetrical fashion for both the cis and trans residues. This would allow these two residues to crystallize in very similar lattices.

It has been shown that certain structural modifications, such as the introduction of sp^2-hybridized carbon atoms,[11] large substituents,[12] or both, stabilize the twist conformation of cyclohexanes. We suggest that the geometric restrictions imposed by the polymer backbone sufficiently lower the chair–twist energy difference of the cyclohexane ring in BAMC polyamides to allow the twistmer conformation to exist, and it is this twistmer conformation which allows cis and trans residues to crystallize isomorphically. We believe this to be the first case of cis–trans isomorphism in polyamides.

In the BAMC-C_6 series, large spacings corresponding to those generally observed in the C_{10} and C_{12} series are either not present or are very weak and diffuse. This could result from less order along the chain axis in the C_6 series or from the placement of the atoms in the C_6 unit cells. Less order along the chain axis could result from strain induced in the polymer

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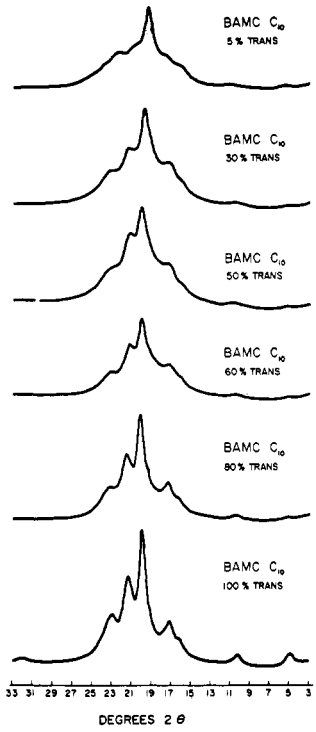
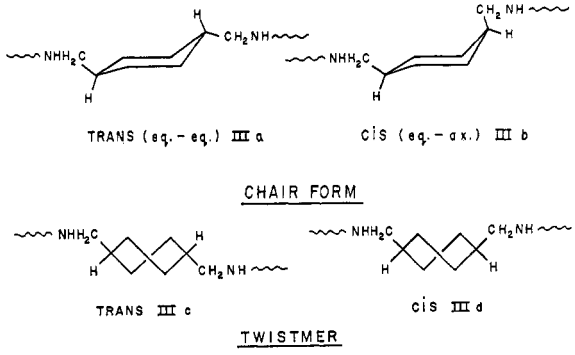


Figure 1. X-Ray diffractometer patterns of the BAMC C_{10} series.



SCHEME 3

Figure 2. Possible chain conformers and proposed twistmer for BAMC copolyamides.

crystals by the intermediate twistmer conformation. Rotation about the C–C bonds would serve to dissipate this strain. The polyadipamides have four fewer $-CH_2-$ groups than the C_{10} series and six fewer than the C_{12}. This results in a more rigid chain and, consequently, less possibility for the release of strain. A placement of the atoms in the unit cell giving rise to weak off-meridional reflections is also a possibility. Unfortunately, this cannot be tested by structure factor calculations because of our inability to unequivocally index the reflections.

TABLE II
CRYSTALLINITY OF BAMC POLYAMIDES (±5%)

C_6 series		C_{10} series		C_{12} series	
% trans	Crystallinity	% trans	Crystallinity	% trans	Crystallinity
10	21	5	20	10	24
35	36	30	20	35	23
55	38	50	23	55	26
67	43	60	26	67	29
82	55	80	39	82	28
100	61	100	49	100	35

The other spacings in the fiber diffraction pattern of the 60/40 BAMC–C_{12} were found to be equatorial or nearly equatorial reflections and, consequently, are related to directions perpendicular or nearly perpendicular to the chain axis. It is not surprising then, that these reflections and thus the packing of the chains are quite similar in all the polymers, since the structural repeat distance within a given series was independent of isomer ratio, and the different series, C_6, C_{10}, and C_{12} are homologs.

One other explanation for the isomorphous crystallization of the BAMC polyamides which should be considered would be isomerization during melt condensation to an equilibrium cis–trans mixture. If this occurred, all would have the same residue content. However, it has been shown that cyclohexylamines do not isomerize during melt condensation.[13] We have also confirmed that BAMC does not isomerize when subjected to the conditions of polymerization.[4]

In the C_6, C_{10}, and C_{12} series, the polymers containing less than 30% trans content crystallize in a somewhat different crystal structure than the isomorphic structures. We feel that this results from the perturbing effect on the structure of almost 100% cis isomer. As mentioned above, the geometry of the cis (ea) isomer is such that there is almost a 90° angle between cis-1,4 positions on the cyclohexane ring. It is our opinion that such a configuration would not readily crystallize. However, the measured crystallinity of the polymers which are essentially 100% cis is about 20%. We feel that the ability of the high cis polymers to crystallize is additional evidence for an intermediate cyclohexane ring conformation, although with a somewhat different twist angle than the isomorphic structures.

The per cent crystallinity of the various polymers was determined from the X-ray diffractometer patterns of the films. The results are presented in Table II. In the C_6 series there is a pronounced increase in per cent crystallinity with increasing trans residue content. For the C_{10} and C_{12} series, the differences among the individual values are not great and are close to experimental error.

Acknowledgment. We thank Mr. Donald W. Richardson and Mr. Donald Kyser of this laboratory for their assistance in obtaining the X-ray diffraction data. We also thank Professor Samuel Krimm for several helpful suggestions.

(13) F. Wallenbergen, U. S. Patent 3,472,818.