

Polyamides From 1,4-Cyclohexanebis(ethylamine) and Aliphatic Dicarboxylic Acids

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Synopsis

A homologous polyamide series of 1,4-cyclohexanebis(ethylamine) (CBEA) was prepared with C₆ to C₁₂ linear, aliphatic dicarboxylic acids. Polymer and fiber properties were found to be quite dependent upon the cis and trans structure of the cycloaliphatic ring. Polyamides based on *trans*-1,4-CBEA had higher melting and higher glass transition temperatures than their cis analogs. In addition, trans polyamides were quite crystalline, whereas the cis polymers were almost completely amorphous. The boiling water shrinkage, tenacity, and moisture regain of the fibers reflected the differences in molecular fit between the cis and trans polyamides.

INTRODUCTION

Polyamides containing cyclohexylene linkages have not been studied as extensively as those with phenylene linkages. Moreover, the influence of the cyclohexane ring upon polymer and fiber properties is complicated by the existence of cis and trans isomers. Interconversion of these isomeric forms can occur during melt polymerization, which dictates careful selection of intermediate materials and analysis of polymeric products. Isomerization of cis to trans structure during thermal polymerization has been reported to occur where the carboxyl group is joined directly to the cyclohexane ring.^{1,2} Carboxyl groups separated from the ring by a methylene linkage do not cause isomerization under thermal polycondensation,³ nor do amino groups, whether attached to the ring⁴ or separated by a methylene link.⁵

Investigations of the cyclohexylene linkage have been concentrated primarily upon the development of heat-resistant fibers, most of which employed cyclohexane amino acids as the starting monomer. Polyamides prepared from simple cycloaliphatic diacids and diamines have been limited primarily to diaminocyclohexane,^{4,6} hexahydrophthalic acids,^{1,7} and 1,4-cyclohexanebis(methylamine).⁵ Unfortunately, many polyamides based on these materials are unsuitable for melt polymerization because the polymer melting points are too high.

Most studies of cyclohexylene polyamide properties have been limited to melting point, solubility, or thermal stability. While such data are quite valuable, a broader investigation of structure-property relationships would be helpful.

This paper describes structural effects of 1,4-cyclohexanebis(ethylamine) (CBEA) upon polymer and fiber properties for a homologous polyamide series.

EXPERIMENTAL

Materials

The dicarboxylic acids were obtained from commercial sources. *Cis-trans*-1,4-cyclohexanebis(ethylamine) (CBEA) was prepared by high-pressure hydrogenation of *p*-phenylenebis(ethylamine) with a ruthenium dioxide catalyst. After removal of the catalyst, vacuum distillation gave the purified product, bp 122–126°/4 mm. The neutral equivalent was 86.6 (theoretical 85.2). Confirmation of structure was obtained by NMR. By vapor phase chromatography, the product was found to consist of 39.4% trans isomer, 58.9% cis, with 1.7% impurities.

Methods

Preparation of Amine Salts. The amine salts were generally prepared by a slow addition of the diamine to a 30–60% aqueous slurry of diacid in a 1:1 molar ratio. The mixture was warmed until solution was attained. The solution was then treated with activated carbon and Celite filter aid, and filtered. The solution was cooled at 0–5°C for 24 hr and the precipitated, crude trans salt was filtered. (In some cases, ethanol was added to induce crystallization.) One recrystallization from water, or water-alcohol, was sufficient to reduce to trace quantities any cis salt remaining. The filtrate from the initial salt crystallization was evaporated to dryness and recrystallized from appropriate solvents to give the cis salt.

Yields averaged 80–90% of theoretical (based upon the initial isomer ratio in the amine) for the trans salts and 60–80% for cis salts. Purity and isomer content of the salts were obtained by vapor-phase chromatography. The salt melting points were taken on a Thomas-Hoover capillary melting point Apparatus. Data on the salts are shown in Table 1. Salts of *c*-CBEA-6, *t*-CBEA-7, *t*-CBEA-11 and *c*-CBEA-11 were obtained from their respective diamines instead of the mixed diamine. These diamines were obtained by dissolving *c*-CBEA-12 or *t*-CBEA-12 salt in hot water, followed by acidification with 50% hydrochloric acid. The precipitated dodecanedioic acid was removed and the solution made basic with 50% aqueous sodium hydroxide. The basic solution was then extracted with ether using a continuous extractor. The ether was removed under vacuum, and the diamine distilled under reduced pressure. The trans diamine analyzed as 99.8% *t*, 0.2% *c*; the cis analyzed as 96.6% *c*, 3.4% *t*. Salts were then prepared as before.

Although many of the salts were contaminated slightly with small amounts of the unwanted isomer, the concentration was so low that polymers prepared from such salts would not exhibit any appreciable effect in physical properties attributable to the impurity.

TABLE I
Salts of 1,4-Cyclohexanebis(ethylamine) (CBEA) with Aliphatic Dicarboxylic Acids

Acid	Salt	Recrystallization medium	Melting point, °C	Gas-chromatographic analysis
Adipic	<i>t</i> -CBEA-6	H ₂ O-EtOH	201.0-203.0 dec.	93.7% <i>t</i> , 6.3% <i>c</i>
Adipic	<i>c</i> -CBEA-6	MeOH-EtOH	199.0 dec.	96.5% <i>c</i> , 3.5% <i>t</i>
Pimelic	<i>t</i> -CBEA-7	H ₂ O- <i>n</i> -BuOH	197.0-199.0 dec.	>99.8% <i>t</i> , <0.2% <i>c</i>
Pimelic	<i>c</i> -CBEA-7	MeOH-EtOH	188.5-190.5	>99.0% <i>c</i> , <1.0% <i>t</i>
Suberic	<i>t</i> -CBEA-8	H ₂ O-H ₂ O/EtOH	228.0-229.0 dec.	99.7% <i>t</i> , 0.3% <i>c</i>
Suberic	<i>c</i> -CBEA-8	MeOH- <i>n</i> -BuOH	157.5-159.5	98.9% <i>c</i> , 1.1% <i>t</i>
Azelaic	<i>t</i> -CBEA-9	H ₂ O	209.0-211.0 dec.	100% <i>t</i>
Azelaic	<i>c</i> -CBEA-9	MeOH-EtOH/Et ₂ O	154.0-155.0	98.8% <i>c</i> , 1.2% <i>t</i>
Sebacic	<i>t</i> -CBEA-10	H ₂ O	209.0-211.0 dec.	99.2% <i>t</i> , 0.8% <i>c</i>
Sebacic	<i>c</i> -CBEA-10	MeOH-Et ₂ O	147.0-149.5	96.0% <i>c</i> , 4.0% <i>t</i>
Undecane-dioic	<i>t</i> -CBEA-11	H ₂ O-EtOH	205.0-205.5 dec.	>99.8% <i>t</i> , <0.2% <i>c</i>
Undecane-dioic	<i>c</i> -CBEA-11	MeOH-EtOH (strike medium), recrystallized from isopropanol	117.0-118.5	97.0% <i>c</i> , 3.0% <i>t</i>
Dodecane-dioic	<i>t</i> -CBEA-12	H ₂ O	199.0-201.5 dec.	99.8% <i>t</i> , 0.2% <i>c</i>
Dodecane-dioic	<i>c</i> -CBEA-12	H ₂ O-EtOH	143.0-144.5	96.6% <i>c</i> , 3.4% <i>t</i>

Polymerization. A 75% aqueous slurry of salt was added to a stainless-steel, high-pressure autoclave which had been purged of air with purified nitrogen. The temperature and pressure were slowly raised to 220°C and 250 psig, respectively. Then, the temperature was further increased to 243°C while the pressure was maintained at 250 psig, during which time there was the continuous removal of steam condensate. The pressure was then gradually reduced to atmospheric over a 25-min period. The polymer melt was allowed to equilibrate for 30 min at about 15°C above the melting point. However, the minimum temperature employed was always at least 270°C. This finished polymer was spun directly from the autoclave through a single-hole spinneret into a quench bath of water, and the fiber was then taken up on a bobbin with a Leeson winder. This fiber was then drawn to approximately five times its original length over a hot pin at 60–90°C.

Polymer Melting Point. The melting point was determined by observing filaments of drawn fiber between crossed Nicol polarizers on an electrically heated hot-stage microscope. The melting point T_m was taken as the temperature at which the last trace of birefringence disappeared. In several cases, such a melting point could not be obtained because of a lack of fiber birefringence, so the temperature at which the polymer began to flow was taken as T_m .

Molecular Weight. The intrinsic viscosities in *m*-cresol ranged from 1.3 to 1.6 for the trans polyamides and 1.2 to 1.9 for the cis polyamides. The distribution of values was random. No particular pattern was discernible between viscosity and polymer fiber properties.

Moisture Regain. Moisture regain was determined on unoriented fiber which was dried at 60°C in a vacuum oven at about 10 mm Hg for 4 hr, then exposed at 25°C for 48 hr in air having a relative humidity of 65%. The fiber was weighed and then desiccated in a vacuum oven at 60°C for 24 hr and weighed again. The difference in weight is the amount of moisture in the fiber at 65% R.H. This value was then converted to a percentage of moisture in the fiber.

Boiling Water Shrinkage. The boiling water shrinkage was determined on fibers which had been drawn approximately five times. The fibers were immersed in boiling water for 5 min. A comparison of the original and final length gives the boiling water shrinkage, which is expressed as a percentage of original length.

Denier. Fiber deniers were determined with a Vibrascope.

Tenacity, Elongation, and Modulus. The tenacity, elongation, and modulus values of the drawn fibers were determined on an Instron tester at a rate of extension of 100%/min with the use of a 1-in. gauge length and a chart speed varied according to the particular sample measured. Young's modulus of elasticity was calculated from the initial slope of the stress-strain curve. All measurements were made at 65% R.H., 21°C.

Glass Transition Temperature. The glass transition temperatures were determined on the Vibron (Toyo Instrument Company, Tokyo, Japan),

a direct-reading dynamic viscoelastometer instrument. The glass transition temperature was taken as the maximum in the $\tan \delta$ peak. The $\tan \delta$ curve was obtained from the plot of the loss modulus (E'') divided by the dynamic modulus (E') as a function of temperature ($\tan \delta = E''/E'$). Measurements were made at 11 cps at 0.03 g/den load on drawn samples at 0% R.H.

RESULTS AND DISCUSSION

Melting Point

Analysis of the salt melting points does not show any interesting trends. The trans salts do not appear greatly affected by an increase in the aliphatic character of the diacid component. The exception is *t*-CBEA-8 salt, which unaccountably melts much higher than any of the other salts. The cis salts, on the other hand, display reduced melting points as the aliphatic character of the diacid increases. Neither the trans nor the cis salts have a zigzag odd-even melting point relationship with increased chain length in the diacid.

However, the polymer melting points do display the characteristic odd-even zigzag pattern (Fig. 1). The results are as expected for a homologous series.⁸ The even-number methylene polyamides melt higher than the adjacent odd-number methylene polymers. For example, CBEA-8

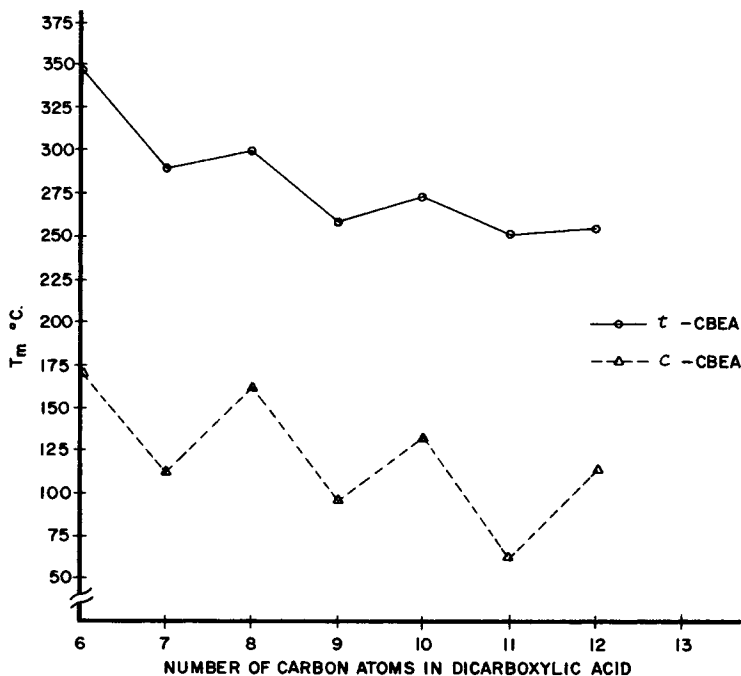


Fig. 1. Relationship of CBEA fiber melting points to carbon atom content of dicarboxylic acid.

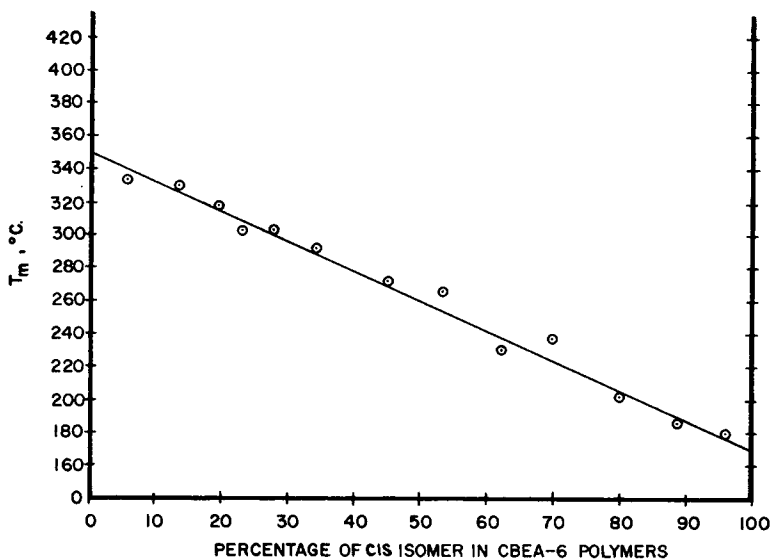


Fig. 2. Melting points of copolyamides of *cis*- and *trans*-1,4-cyclohexanebis(ethylamine) with adipic acid.

melts higher than either CBEA-7 or CBEA-9. The melting points, in general, decrease with increased chain length in the diacid. (The melting points of the CBEA-6 fibers were taken from extrapolated points in Fig. 2).

Rubin⁹ has attributed melting point trends in polyamides to those of their salts. Examination of the salt melting points in Table I does not support this thesis. No clear tendency of odd-even fluctuation exists in the CBEA salt series, while there is no question of such melting trends in the polyamides.

As found with polyamides of 1,4-cyclohexanebis(methylamine),⁵ the *cis* fibers melted lower than the *trans* fibers. The *cis*-CBEA melting points were surprisingly low, however. This low melting is attributed to the poorer ability of the *cis*-CBEA ring to accommodate itself in the polymer chains. In fact, the melting points of the *cis* polyamides were really flow points. Attempts to determine melting points through birefringence loss were unsuccessful because of the low birefringence in the fibers. The fibers began to soften at, or slightly above, the temperature where the very weak birefringence disappeared. Examination of the fibers by differential thermal analysis (DTA) showed no endothermic peak corresponding to melting, whereas the *trans* fibers displayed endothermic melting. Such behavior indicated that the *cis* fibers were highly amorphous. The amorphous nature of the *cis* polyamides was reflected also in their appearance. *Cis* fibers were transparent, while those from the *trans* material were translucent. X-Ray diffraction indicated that the *trans* fibers were quite crystalline, while the corresponding *cis* fibers were of very low crystallinity. Crystallinity could not be developed in the *cis* polymers by annealing.

The *cis*,*trans* polyamides with adipic acid melt at temperatures between those derived from the pure isomers. No evidence of a melting point eutectic occurs (Fig. 2). The lack of a melting eutectic does not imply isomorphism,¹⁰ but, considering the characteristics of the *cis* polyamides, suggests that there may be a gradual change in the crystal lattice of *t*-CBEA-6 as *cis* content increases. Surprisingly, x-ray diffraction showed that a 47% *trans*-, 53% *cis*-CBEA-7 fiber possessed about the same degree of crystallinity as *t*-CBEA-7. This result suggests at least partial isomorphism of *cis* and *trans* structures similar to that found in CBMA-polyamides.¹¹

Boiling Water Shrinkage

Fiber boiling water shrinkage relates to the molecular fit within a polymer.¹² High fiber shrinkage can indicate low crystallinity, poor chain packing, or reduced hydrogen bonding. A plot of shrinkage versus methylene content (Fig. 3) shows a similar pattern to that obtained with melting points. The polyamides with even number of methylene carbons have less shrinkage than the adjacent odd methylene polymers. Differences are small, which indicate relatively minor variations in molecular fit within a series. As expected, *cis* polyamides possess far higher shrinkages than their *trans* counterparts because of their amorphous nature. No trends are noted as far as an increase in aliphatic character is concerned.

The opening of the *trans* structure through *cis* substitution is shown in Table II. Shrinkage progressively increases as *cis* content rises. Accordingly, this property is quite sensitive to chain packing disturbances.

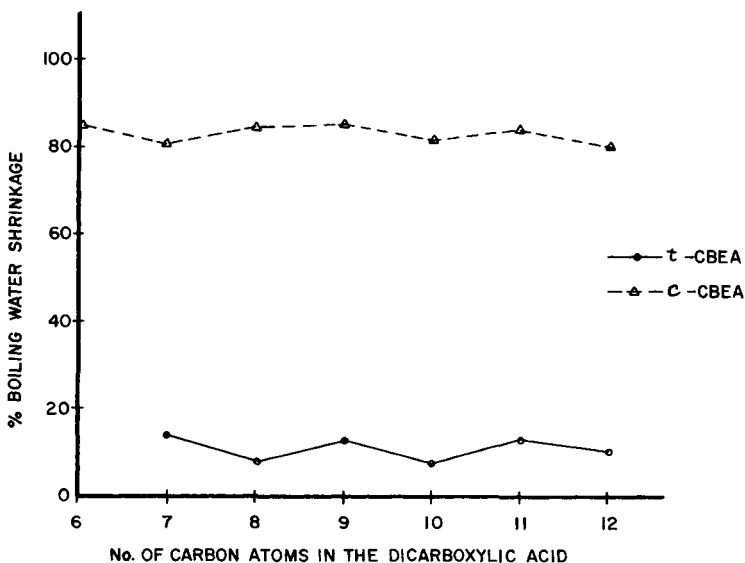


Fig. 3. Relationship of CBEA fiber boiling water shrinkages to carbon atom content of dicarboxylic acid

TABLE II
Boiling Water Shrinkage of *Cis*, *trans*-CBEA-7

Polymer	% Boiling Water Shrinkage
<i>t</i> -CBEA-7	14
51% <i>t</i> , 49% <i>c</i> -CBEA-7	29
47% <i>t</i> , 53% <i>c</i> -CBEA-7	35
<i>c</i> -CBEA-7	81

The *cis*-CBEA polyamides exhibit unusual behavior with respect to heat or boiling water. Exposure to 90°C or more (dry or wet) heat causes the drawn yarn to contract. The *cis* fibers appear to return completely to the spun (unoriented) state. This phenomenon is easily observed by partially drawing a fiber and noting the changes at the neck between the drawn and undrawn portions. Exposure to heat contracts the drawn portion such that the neck disappears. The fiber can then be redrawn as before, and the process repeated—a fiber with “plastic memory.” This shrinkage is not that normally seen in polyamides.

It is interesting to note that the odd-even relationship holds even for drawn fibers based on *cis* isomers, despite “plastic memory” effect.

Glass Transition Temperature

The glass transition temperature T_g generally increases with increased ring concentration in both *trans*- and *cis*-CBEA fibers. There is no evidence of an odd-even alternating effect in either *t*-CBEA (Fig. 4) or *c*-

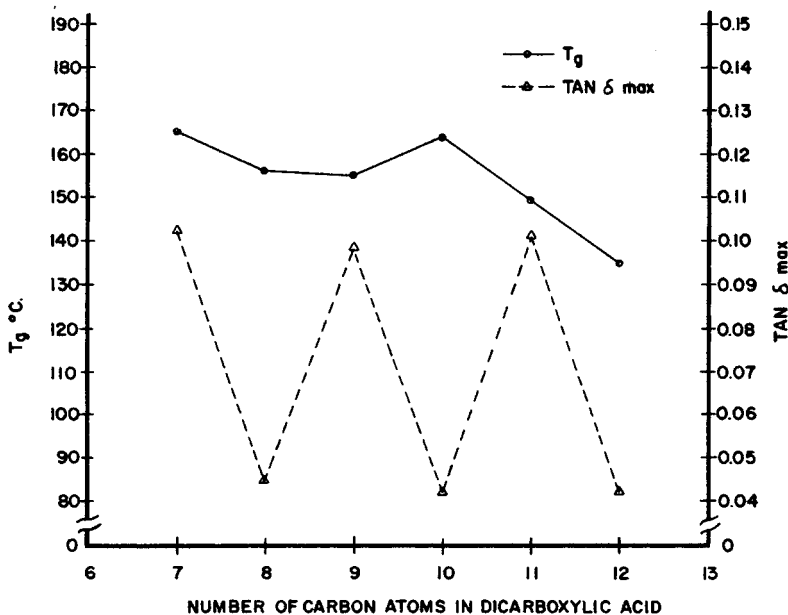


Fig. 4. Dynamic mechanical properties of *t*-CBEA polyamides at 0% R.H.

TABLE III
Glass Transition Temperatures and $\tan \delta_{\max}$ of *cis*-CBEA Polyamides (0% R.H.)

Polymer	T_g , °C	$\tan \delta_{\max}$
<i>c</i> -CBEA-6	>110	>0.550
<i>c</i> -CBEA-7	100	0.850
<i>c</i> -CBEA-8	>100	>1.550
<i>c</i> -CBEA-9	>80	>0.029
<i>c</i> -CBEA-10	95	0.600
<i>c</i> -CBEA-11	>70	>0.155
<i>c</i> -CBEA-12	80	1.600

TABLE IV
Glass Transition Temperatures and $\tan \delta_{\max}$ of *cis,trans*-CBEA Polyamides (0% R.H.)

Polymer	T_g , °C	$\tan \delta_{\max}$
<i>t</i> -CBEA-7	165	0.102
51% <i>t</i> , 49% <i>c</i> -CBEA-7	130	0.190
47% <i>t</i> , 53% <i>c</i> -CBEA-7	122	0.256
<i>c</i> -CBEA-7	100	0.850
66% <i>t</i> , 34% <i>c</i> -CBEA-6	162	0.110
11% <i>t</i> , 89% <i>c</i> -CBEA-6	115	0.370
3% <i>t</i> , 97% <i>c</i> -CBEA-6	>110	>0.550

CBEA (Table III) polymers. These results resemble those observed for polyamides containing the *p*-phenylene linkage.¹³

The *cis* polyamides shrank excessively during T_g measurement, with the result that T_g values are essentially those of unoriented fibers. In several cases, shrinkage was so severe that $\tan \delta_{\max}$ could not be measured. Note the high $\tan \delta_{\max}$ values, which indicate very low crystallinity and orientation.^{14,15} Accordingly, a direct comparison of the effects of *cis* versus *trans* ring systems is not possible, although the *cis* ring would be expected to produce lower T_g than the *trans* structure.

An indication of the differences between *cis* and *trans* ring structures is shown in Table IV. The presence of *cis* isomers depresses T_g from that for the all *trans* materials.

The $\tan \delta_{\max}$ of *t*-CBEA polyamides displays the odd-even alternating effect observed with melting points (Fig. 4). Interestingly, this effect did not occur in aliphatic polyamides,¹⁶ nor was it observed within homologous series of polyamides of *trans*-1,4-cyclohexanebis(methylamine) (*t*-CBMA), *p*-phenylenebis(ethylamine) (PBE), or *p*-xylylenediamine (PXD).¹⁷ Furthermore, the $\tan \delta_{\max}$ (γ -dispersion peak) does not appear to increase in height with increasing methylene group content, as was also reported by Kawaguchi.¹⁶ While the differences between the aliphatic polyamides and those of *t*-CBEA might be explained by the difference in sample type (the aliphatic polyamides consisted of undrawn monofilaments), the *t*-CBMA, PBE, and PXD fibers were drawn similarly to those to *t*-CBEA. The $\tan \delta_{\max}$ heights show that molecular order is best when even-number methyl-

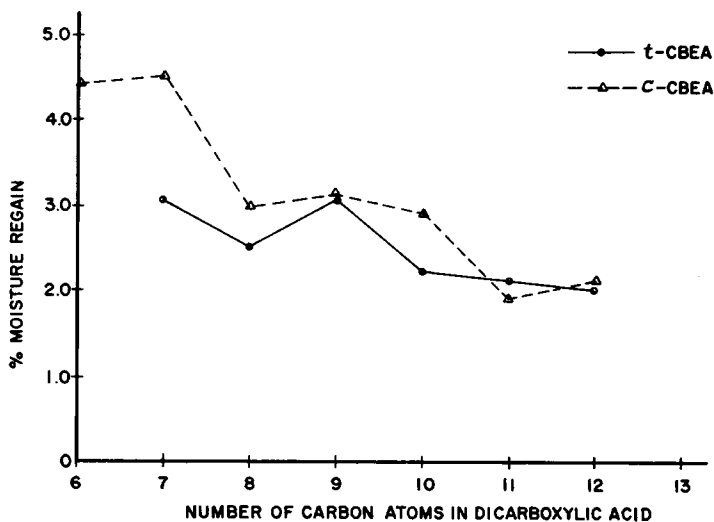


Fig. 5. Relationship of CBEA fiber moisture regain to carbon atom content of dicarboxylic acid.

enedicarboxylic acids are used. This result correlates well with the fiber melting point data, which show maximum melting points for *t*-CBEA polyamides based on even-number diacids.

Although there may be differences in molecular fit among odd and even numbers of a homologous series, T_g does not reflect them. Such results indicate that T_g is insensitive to minor changes in fit, whereas other properties may vary greatly.

Moisture Regain

The 65% R.H. moisture regains of the CBEA fibers show that regain is least in polymers with high aliphatic content (Fig. 5). Both the *trans* and *cis* polyamides show an indication of property alternation in accord with the odd-even effect of molecular structure. Polymers containing odd methylene groups tend to have higher regains than adjacent polymers with even methylenes. Little difference between *cis* and *trans* structures is noted, however.

Tenacity, Elongation, and Modulus

Fiber tensile properties are subject to a number of variables besides crystallinity, orientation, molecular fit, and hydrogen bonding. These include: molecular weight, draw ratio, elongation, drawing method, and overall spinning conditions. These conditions have such an influence upon fiber property response that comparisons are crude and subject to considerable variation. Fiber tensile properties are included only to illustrate basic trends within the series.

TABLE V
Fiber Properties of CBEA Polyamides

Fiber	Trans		Fiber	Cis	
	Tenacity, gpd	Elongation, %		Tenacity, gpd	Elongation, %
CBEA-12	4.3	37	CBEA-12	4.0	44
CBEA-11	5.3	13	CBEA-11	2.8	50
CBEA-10	7.0	14	CBEA-10	2.8	18
CBEA-9	5.0	14	CBEA-9	3.4	15
CBEA-8	5.3	21	CBEA-8	3.4	18
CBEA-7	4.7	13	CBEA-7	1.7	17
			CBEA-6	3.3	22

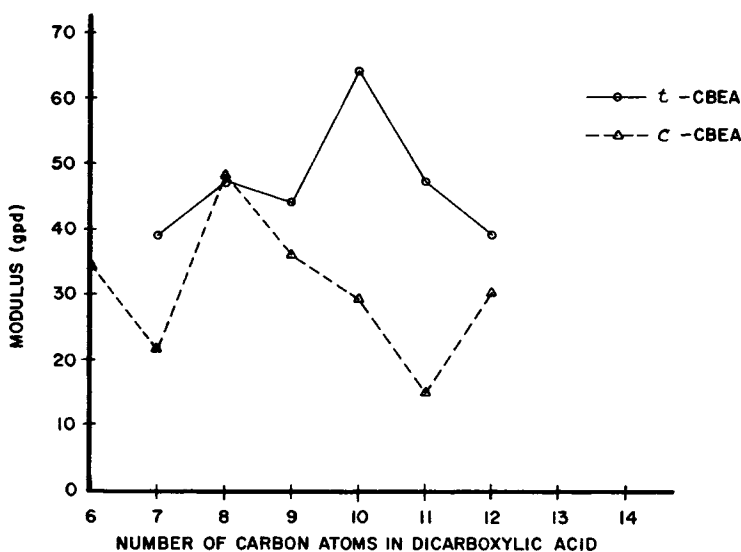


Fig. 6. Relationship of CBEA fiber modulus to carbon atom content of dicarboxylic acid.

The trends in fiber physical properties do tend to mirror molecular fit, although some data scatter is evident. For trans polyamides, tenacity tends to be higher for the even methylene group fibers over the adjacent odd-methylene structures (Table V). Similar trends occur with fiber initial modulus (Fig. 6). In the case of the cis polymers, trends are less clear. Nevertheless, the data show low strength and modulus for the amorphous cis fibers. Note that elongation does not account for tenacity and modulus relationships with cis versus trans structure.

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