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ANALYSIS OF THE MOLECULAR WEIGHT DISTRIBUTIONS OF AMINOLYZED POLY(ETHYLENE TEREPHTHALATE) BY USING GEL PERMEATION CHROMATOGRAPHY

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ABSTRACT

The molecular weight distributions of poly(ethylene terephthalate) fibers aminolyzed with selected primary amines (namely, methylamine, ethylamine, *n*-butylamine, and ethanolamine) were determined by using gel permeation chromatography. Initially the shape of the differential molecular weight distribution (DMWD) curve did not change although its peak shifted to lower molecular weights. As aminolysis continued, a shoulder appeared on the DMWD curve. Its appearance seemed to coincide with an increase in the density of the product. Ultimately, distinct molecular populations could be identified in the treated polymer depending on the severity of the aminolysis and the selectivity of the particular amine. The lowest is thought to represent primarily crystalline residues and has a peak molecular weight of 3400. The relations between $\overline{M}_n$ and ultimate tenacity and breaking strain for the aminolyzed products were linear.

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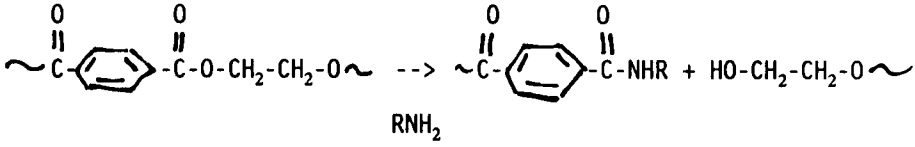
INTRODUCTION

The reaction of poly(ethylene terephthalate) (PET) with primary amines results in chain scission and the formation of an amide and a hydroxyl end group.



Research on this topic has been extensively reviewed recently [1]. The location of chain scission within the specimen has been found to vary depending on such factors as its fine structure, the basicity of the particular amine employed, the molecular weight and size of the amine, and the mode of application. Aminolysis has been used as a tool for studying the morphological structure of PET. For such studies the PET is normally aminolyzed to the point where it has no strength. However, for both theoretical and practical reasons it is equally important to study the effects of aminolysis before the product is excessively degraded so the relations between tensile properties and molecular weight properties can be elucidated. Aminolysis has been used industrially for enhancing the properties of PET.

The location of attack in a polyester filament by aqueous methylamine at room temperature has been represented by Farrow et al. [2] as a three-stage process in which the reaction occurs initially in the amorphous regions of the fiber with little change in sample weight or crystallinity but rapid fall in molecular weight. Next, increasing chain scission and rapid loss in sample weight are accompanied by an increase in density. Finally, a gradual reduction in the reaction rate occurs which has been attributed to a slower attack of the crystalline and amorphous regions of the fiber. Recent studies have supported the work of Farrow et al. [3–5]. Crystallinity has been shown to increase in PET aminolyzed by both methylamine [6, 7] and ethylamine [8].

The reduction in the viscosity-average molecular weight of PET treated with various primary amines has been used as a measure of degradation [2, 6, 7–10]. Little use appears to have been made of gel permeation chromatography (GPC) in this regard, although molecular weight distributions would provide a better picture of the changes brought about by aminolysis. GPC appears to have been confined to

analysis of the morphological characteristics of aminolyzed PET products [6, 6a]. In these studies the solvent used for analyses was *m*-cresol at 125°C, and the research was focused on the crystalline fold period. No attention was paid to tensile properties.

This study investigates the effects on the molecular weight distribution and fine structure of a single PET sample type after treatment with a set of monofunctional primary amines of increasing molecular weight; namely, methylamine, ethylamine, and *n*-butylamine, and also with ethanolamine. It also considers the relation between tensile properties and molecular weight.

EXPERIMENTAL

Materials

The starting material was a scoured heatset Dacron PET type 54 semidull fabric from Test Fabrics, Inc., Middlesex, New Jersey, made of spun yarns. Three lots of the same fabric were used; the first for the methylamine and the ethanolamine treatments, the second for the reaction with ethylamine, and the third for the *n*-butylamine treatments. The slight differences between lots, which were observed when the control specimens were characterized, were negligible and do not affect the conclusions which are drawn. The methylamine used was reagent grade, the ethylamine was practical grade, the *n*-butylamine was 99% pure, and the ethanolamine was purified grade. All other chemicals used were reagent grade.

Aminolysis

Ethylamine and n-Butylamine. The reaction conditions have been described previously for the aminolysis of PET fabric at 21°C with 70% aqueous ethylamine (EA) [8], neat *n*-butylamine (nBA) [10], and their respective controls. In all cases the reaction vessels were sealed.

Ethanolamine. PET fabric samples were treated with 1 L of 10% (w/w) aqueous ethanolamine (EoA) at 100°C (±0.5°C) in sealed containers by using the same procedure as described for 70% (aq) ethylamine [8]. PET controls were prepared by treating fabric samples in deionized water for 6 h at 100°C (±0.5°C).

Methylamine. The PET fabric samples were first washed in deionized water for 6 h at 100°C and then air dried. Each sample was next treated in 900 mL of 40% aqueous methylamine (MA) at 20°C (±0.1°C) in sealed containers. To terminate the reaction, samples were rinsed, neutralized, rinsed, and dried in the manner described for the other aminolyzed samples [8].

Characterization of Products

Gel Permeation Chromatography. Molecular weight distributions were determined at room temperature with a Perkin-Elmer (PE) liquid chromatography Series 10 unit fitted with two Water's Ultrastyragel GPC columns (sizes 1000 and 50 nm). The solvent and mobile phase was 70/30 dichloromethane/hexafluoroisopropanol. The advantages of this solvent over *m*-cresol have been described by Overton and Browning [10a]. The concentration of the PET was 0.1% (w/v), and UV detection at 254 nm was used. Data were collected and analyzed with the aid of PE CHROM2 software.

The system was calibrated by using a plot of log (M_w) versus retention time fitted by third-order polynomial regression by using four PET fractions of differing intrinsic viscosity, prepared from a broad polymer using preparative GPC, and the PET cyclic trimer [11]. The narrow calibration was verified by using a broad PET standard [12].

The molecular weight averages were calculated by using the digitized heights up to but not including the trimer peak. Without the trimer peak, polydispersity (PD) was between 2.01 and 2.47 for the whole polymer standards, whereas inclusion of the trimer caused PD to range from 3.5 up to 4.7. The validity of trimer exclusion was verified [11].

Differential molecular weight distribution (DMWD) curves were determined from the digitized chromatograms by using the method described in ASTM D-3536 [13] without the trimer area, but they are presented extrapolated past the trimer peak to a peak molecular weight of 100 only to illustrate the presence of small molecules within the PET structure. Essentially monodisperse polystyrene standards were also used to evaluate the columns for band broadening and peak skewing. Both were found to be minor in the retention times of interest, so corrections were not performed. Chromatograms were determined in at least duplicate.

Tex. Measurements of the control and aminolyzed warp yarns were made in the standard manner [14]. Weight loss was calculated from

the difference between the tex values of the control and aminolyzed specimens.

Density. Determinations were made with a density gradient column prepared with mixed xylenes and perchloroethylene and maintained at 21°C (± 2°C). Results are the average of at least four replicates.

Tensile Properties. Warp yarn tensile properties were measured by using a table model Instron Universal Testing Machine with a 7.62-cm gauge length at 2.54 cm/min constant rate of elongation for the ethylamine and *n*-butylamine treated products and 2.0 cm/min for the methylamine and the ethanolamine treated samples at 65% relative humidity and 21°C. The effect of this small difference in crosshead speed is considered negligible. Results are an average of 10 replicates.

RESULTS AND DISCUSSION

Molecular Weight Characteristics

Molecular weight averages were calculated from the GPC data (Table 1). It will be observed that aminolysis of PET resulted in a progressive reduction in number-average and weight-average molecular weights as the reaction time increased. Generally the PD of the products decreased with increasing aminolysis. Duong and Bell [6] report a PD of 1 for PET film aminolyzed with 40% aqueous methylamine for 24 h at 18°C. Their data are not comparable since they used film which does not have the same structure as fibers and their sample was more excessively degraded.

An overlay of the DMWDs of the methylamine-treated samples (Fig. 1) reveals details of the changes in molecular chain lengths. In the initial portions of the reaction, the shape of the curve did not change, but at 3 h (MA-3) a shoulder appeared at approximately 3.99 on the abscissa. This peak molecular weight (M_i) is equal to 9,700 (Table 2). The shoulder increased in size along with a decrease in the high molecular end of the curve at 4 h (MA-4), and by 5 h (MA-5) it had transformed from a shoulder to a discernible peak which caused the DMWD to emerge as bimodal.

The DMWDs for the ethylamine-treated samples (Fig. 2) resembled those of the methylamine-treated products. However, with severe eth-

TABLE 1. Molecular Weight Characteristics of Aminolyzed PET

Reaction time, h	$\overline{M}_n$	$\overline{M}_w$	Polydispersity
Methylamine (MA):			
0	15,700	34,300	2.19
1	11,900	25,100	2.10
1.5	10,500	21,200	2.02
2	9,200	18,400	2.01
3	7,800	15,300	1.96
4	6,800	13,000	1.91
5	6,400	14,000	2.17
Ethylamine (EA):			
0	14,000	34,800	2.47
4	10,400	23,000	2.22
8	7,300	15,400	2.10
16	4,300	8,400	1.93
n-Butylamine (nBA):			
0	13,800	34,100	2.47
8	12,200	30,400	2.49
16	11,200	27,900	2.49
72	8,700	19,500	2.24
Ethanolamine (EoA):			
0	15,700	34,300	2.19
2	11,600	25,300	2.10
4	7,900	17,200	2.17
5	6,100	13,400	2.19
6	6,000	12,000	2.00
7	3,700	7,600	1.97

ylamine treatment, the population distribution changed. The main peak in the DMWD of the sample reacted for 16 h (EA-16) occurs at an M_i of 3,400; a secondary peak is present at approximately an M_i of 15,900 and a very small shoulder can be observed at an M_i of 5,800 (Table 2).

The DMWDs for *n*-butylamine reacted fibers (Fig. 3) illustrate a shift to lower molecular weights, also. The same emerging shoulder observed in both methylamine and ethylamine treatments is apparent in the sample

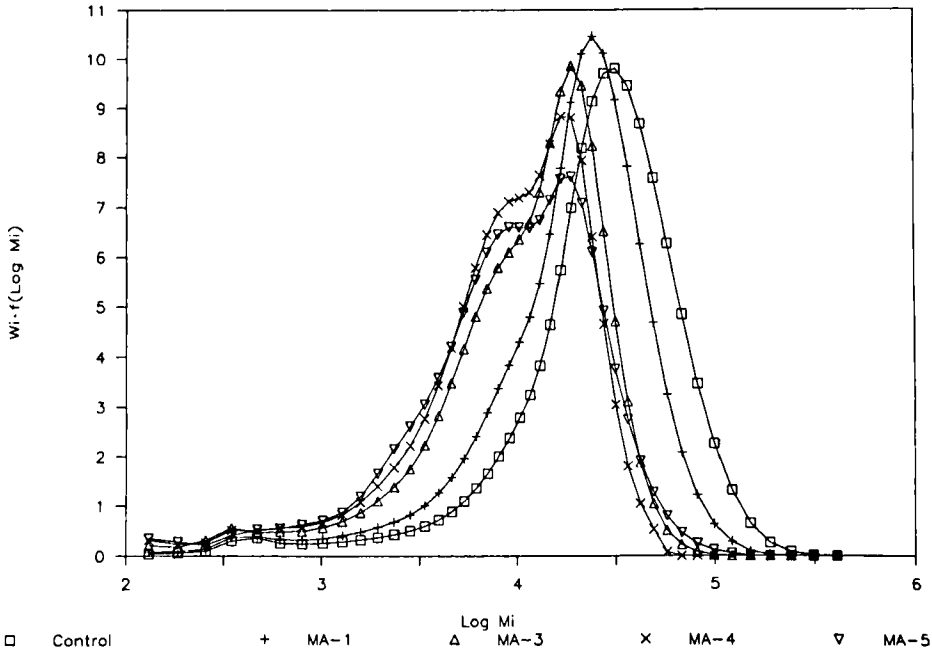


FIG. 1. Differential molecular weight distributions of control and methylamine-treated PET.

reacted for 72 h (nBA-72) at an M_i of approximately 10,800 (Table 2). In the case of the sample treated for only 8 h (nBA-8), a small reduction in the high end of the DMWD was found and a slight shift of the main peak to lower molecular weights. However, there was essentially no production of very low molecular weight material. Since the overlay of the DMWD of nBA-8 and its control were very close, nBA-8 is not shown in Fig. 3.

The DMWDs of the ethanolamine-treated PET samples (Fig. 4) also have a similar development of a shoulder after 4 or 5 h aminolysis (EoA-4 and EoA-5). At 7 h treatment (EoA-7) the DMWD reversed itself, similar to EA-16, and a lower M_i of 6,200 emerged as the major peak and a shoulder occurred at the higher M_i of 13,100 (Table 2). The low molecular weight material after the trimer peak (which was not included in molecular weight average or PD calculations) is included to

TABLE 2. Differential Molecular Weight Characteristics of Control and Aminolyzed PET Samples When Distinct Shoulder Formation Was Observed

	Peak molecular weight[a]			
Reaction time, h	M_i-1	M_i-2	M_i-3	M_i-4
Methylamine (MA):				
0	–	–	–	31,500
3	–	–	(9,700)	18,800
4	–	–	(10,300)	16,700
5	–	–	8,753	18,124
Ethylamine (EA):				
0	–	–	–	25,300
8	–	–	(10,026)	17,800
16	3,400	(5,800)	–	15,900
n-Butylamine (nBA):				
0	–	–	–	25,300
72	–	–	(10,800)	20,000
Ethanolamine (EoA):				
0	–	–	–	31,500
4	–	–	(9,400)	18,800
5	–	–	(10,300)	18,800
6	–	–	(10,200)	14,800
7	–	6,200	–	(13,100)

[a]Numbers in parentheses were interpolated from shoulders.

illustrate the much larger amount of this material in ethanolamine-treated relative to methylamine-, ethylamine-, or *n*-butylamine-treated specimens (cf Figs. 1–4).

It appears from DMWD plots that there can be up to four different molecular weight populations present in the PET sample after aminolysis (Table 2). The first is the original main peak which progressively shifts to lower molecular weight as chain cleavage occurs. Second, there is a shoulder which eventually appears on the DMWDs of all of the aminolyzed specimens and has an M_i of approximately 9–10,000. The third population is present as the major peak of EoA-7 and as a shoulder on EA-16 and has an M_i of 5,800–6,200. The fourth is present as the major population with an M_i of 3,400, only in EA-16.

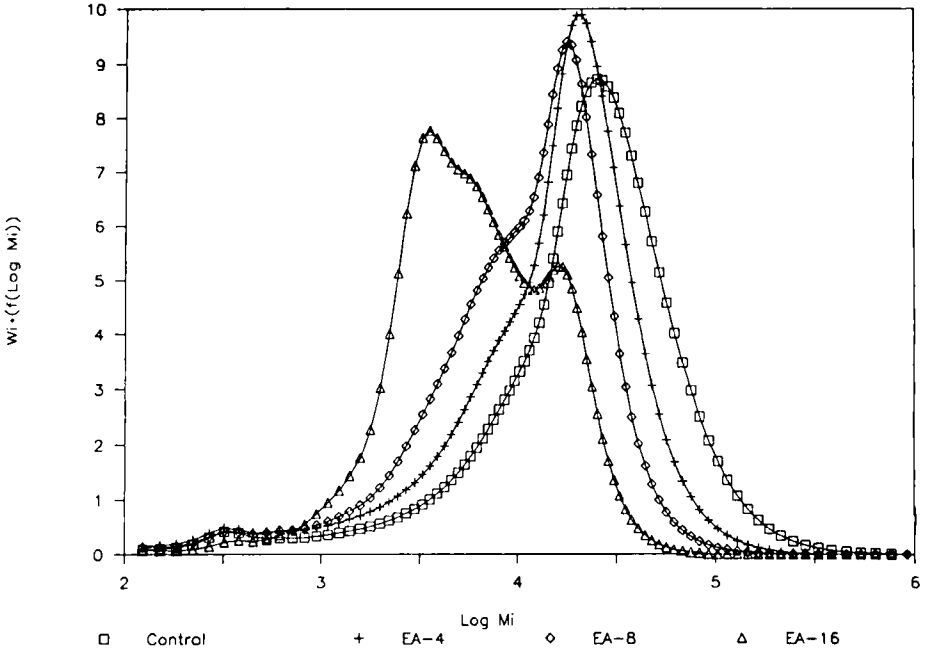


FIG. 2. Differential molecular weight distributions of control and ethylamine-treated PET.

Physical Properties

A minimum level of degradation appeared necessary before weight loss occurred in the methylamine-, ethylamine-, and ethanolamine-treated products (Table 3). With *n*-butylamine this level of degradation was not achieved. When weight loss did occur, density appeared to increase significantly. All aminolyzed products showed losses in ultimate tenacity and strain as the reaction time was extended, but initial modulus remained fairly constant until extensive degradation had occurred, when it decreased sharply.

Relations between Molecular Weights and Physical Properties

Generally, distinct shoulder formation at about a molecular weight of 10,000 on the DMWDs of the aminolyzed products was observed only when their densities began to increase (Tables 2 and 3).

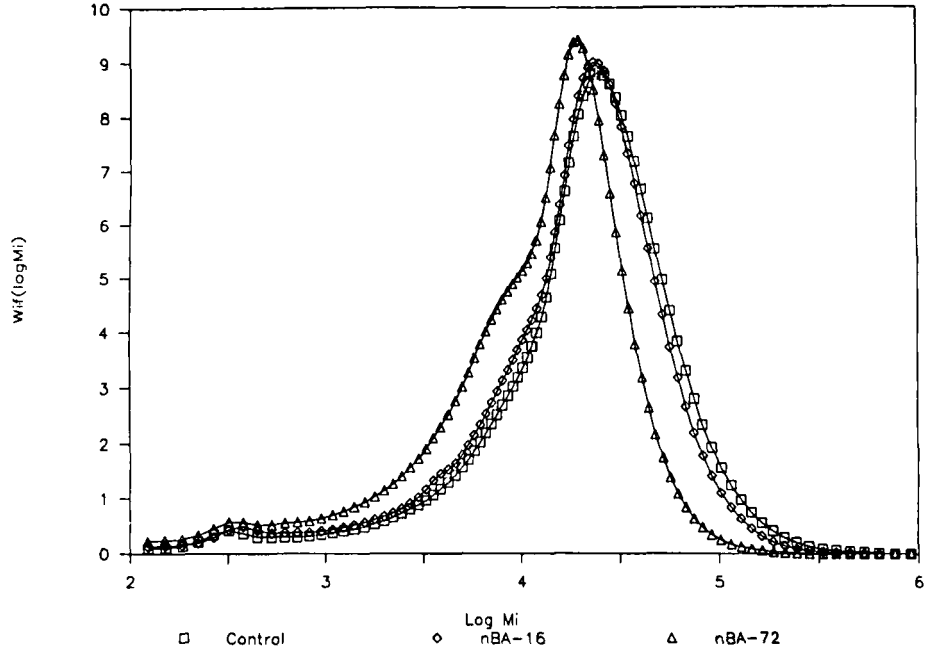


FIG. 3. Differential molecular weight distributions of control and *n*-butylamine-treated PET.

A peak molecular weight of 3,400 was obtained on the DMWD of the most severely degraded ethylamine-treated sample (EA-16). Assuming this sample consists primarily of crystalline material, then a crystalline length of approximately 20 nm is obtained, which is in the correct range for a large crystallite. There may be portions of folds left in the sample, so this value may be on the high side. Also, our sample was heat set and thus might be expected to have large crystallites. Mehta and Bell [7] degraded PET film in 40% methylamine for 24 h and calculated a value of 13 nm for the fold period of PET in unoriented film based on an $\overline{M}_n$ of 2,500. A fold period of 21.8 nm was calculated from their value of $\overline{M}_n$ equal to 3,900 for the film after annealing. Naik and Bhat [3] found values up to 10 nm for crystallites using x-ray crystallinity in PET fiber with up to 8 h treatment in 40% methylamine.

Flory [15] theoretically derived and experimentally established a straight-line relationship between tensile properties and $1/\overline{M}_n$ for high

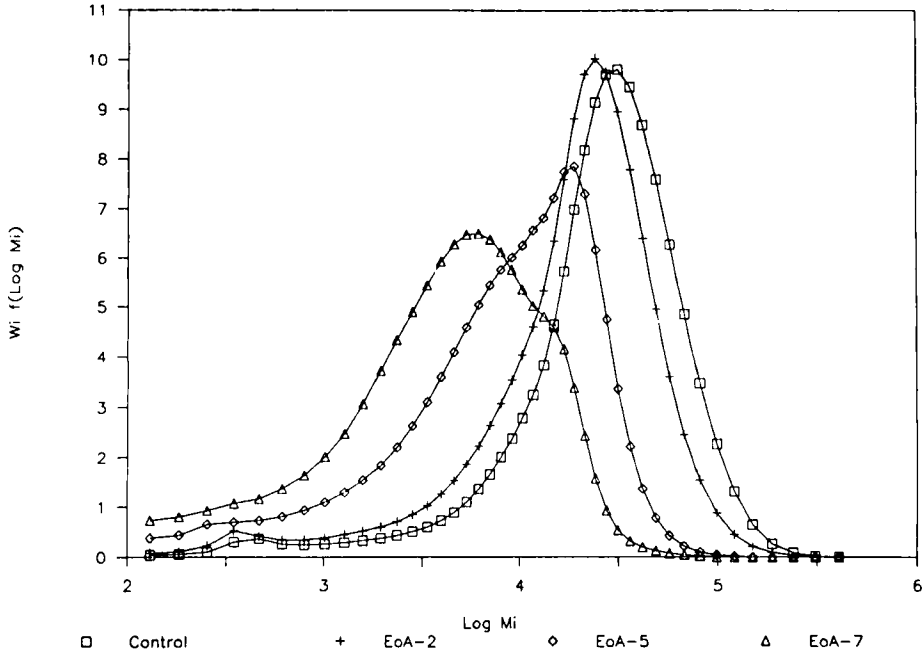


FIG. 4. Differential molecular weight distributions of control and ethanolamine-treated PET.

polymers. If the data obtained in this study are plotted as tenacity or strain versus $1/\overline{M}_n$ (Fig. 5), the relationship attained is linear only initially.

The relationship derived by Flory is not applicable for degradation experiments. Unlike his work or that of Sookne and Harris [16], where specimens of different molecular weight were formed and then tested, aminolysis does not allow any major reorganization of the polymer chains after they are reduced in length. The molecular weights determined here are for products which are of higher crystallinity than the starting polymer and are increasingly reflective of crystallite length as aminolysis progresses. On the other hand, tensile properties are affected by the number of chains between the crystalline regions. As zero tenacity is approached, the number of chains tying the crystalline regions of the aminolyzed product together become fewer. Thus it seems reasonable that if $\overline{M}_n$ is plotted against ultimate tenacity, the

TABLE 3. Physical Properties of Aminolyzed PET

Reaction time, h	Weight loss, %	Density, g/cm^3	Ultimate tenacity, kJ/kg	Ultimate strain, %	Initial modulus, kJ/kg
Methylamine (MA):					
0	0.0	1.396	252	30	1755
1	−1.2	1.393	205	23	2040
1.5	−0.3	1.397	167	20	1716
2	−1.8	1.394	131	17	1961
3	−0.3	1.399	111	14	1932
4	−0.3	1.398	76	8	2010
5	5.3	1.403	54	4	1785
Ethylamine (EA):					
0	0.0	1.401	265	30	1824
4	0.0	1.400	148	17	1902
8	4.3	1.406	68	6	1648
16	18.2	1.417	16	3	549
n-Butylamine (nBA):					
0	0.0	1.400	266	32	1647
8	−0.8	1.399	236	27	1795
16	−0.9	1.401	215	26	1638
72	−0.4	1.401	121	16	1628
Ethanolamine (EoA):					
0	0.0	1.396	252	30	1755
2	0.6	1.398	205	22	1853
3	−3.6	1.396	133	16	1775
4	1.2	1.401	102	12	1795
5	0.6	1.400	65	6	1589
6	6.8	1.407	47	3	1628
7	11.2	1.409	6	2	363

intercept at zero tenacity should give a measure of the length of the crystallites.

For both ultimate tenacity versus $\overline{M}_n$ (Fig. 6) and breaking strain versus $\overline{M}_n$ (Fig. 7), linear relationships are obtained with abscissa intercepts of 3,564 and 3,760, respectively (r = .9753 and .9671, respectively). These values are comparable to the value of the main peak on

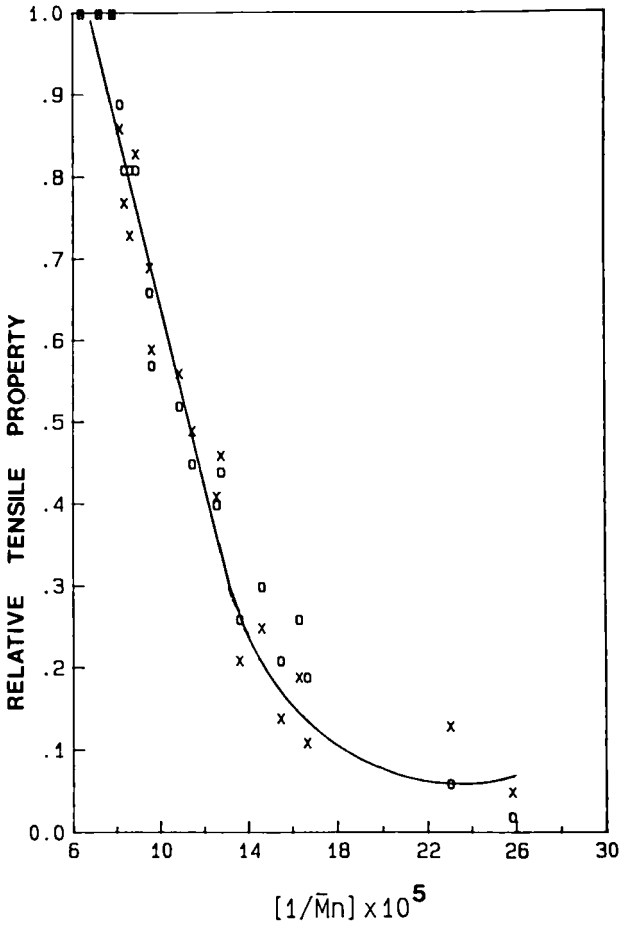


FIG. 5. Relative ultimate tenacity and relative breaking strain versus $1/\overline{M}_n$ for aminolyzed PET yarns: (X) relative ultimate tenacity; (O) relative breaking strain.

sample EA-16 with a molecular weight of 3,400. Linear relations were also obtained if the same plots were made with $\overline{M}_w$ values [11]. It is interesting to note that these relationships appear to be followed irrespective of the reactivity or penetrant size of the amine or of the reaction conditions.

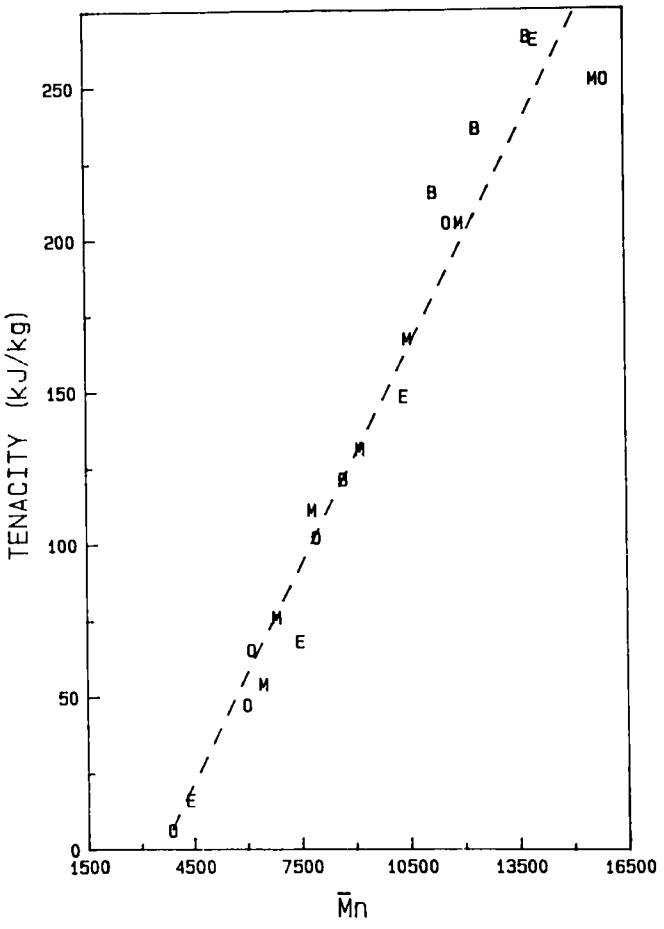


FIG. 6. Ultimate tenacity versus $\overline{M}_n$ for aminolyzed PET yarns: M = methylamine, E = ethylamine, B = *n*-butylamine, and O = ethanolamine.

Consideration of the Aminolysis of PET Fibers in Terms of Their Fine Structure

The microfibrillar model is a commonly accepted description of the crystalline regions of melt-spun semicrystalline fibers formed from polymers such as PET [17]. The semicrystalline structure in drawn fibers has been further defined by Prevorsek et al. [18] in terms of two types of amorphous domains; intermacro- or microfibrillar regions and intra-

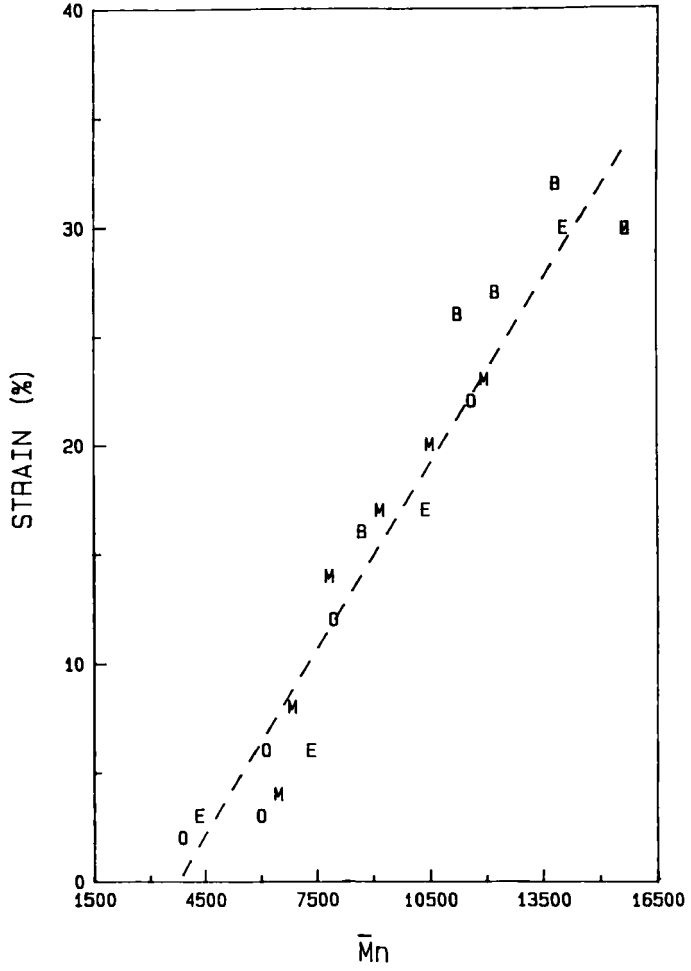


FIG. 7. Breaking strain versus $\overline{M}_n$ for aminolyzed PET yarns: M = methylamine, E = ethylamine, B = *n*-butylamine, and O = ethanolamine.

macro- or microfibrillar regions where the interfibrillar tie molecules are highly stressed and the intrafibrillar tie chains are less affected due to the drawing process. The chain ends are usually located in the noncrystalline regions.

The data we have obtained together with this hypothesis of supramo-

lecular structure permit a reevaluation and reinterpretation of the attack of PET by amines. We propose that the change in properties can be based on four stages: (1) attack of nonordered, noncrystalline regions with no loss in sample weight and no detected small oligomeric components; (2) continued attack in the nonordered noncrystalline regions with loss of sample weight and appearance of low MW components; (3) initial attack of the ordered noncrystalline regions (similar to the stressed intermicro- and macrofibrils of Prevorsek's model) and of crystallite ends; and (4) continued ordered noncrystalline and crystalline region attack. The reaction beginning at each stage is superimposed on the continued reactions of each earlier stage. Since the reagents need to diffuse into the substrate, it is envisaged that the attack at the surface may be at a higher stage than at the fiber core, and each stage would be reached faster with a more reactive amine. Therefore, a highly reactive amine would tend to achieve simultaneous reaction in all of the stages of the attack scheme more quickly than a less reactive amine.

The four major populations of the DMWDs can be interpreted in terms of semicrystalline structure and correlated to tensile properties based on the four stages defined above for amine attack. The first population change to the DMWD for all the amines is shift of the main peak toward lower molecular weights. This represents both Stages (1) and (2) attack in the nonordered noncrystalline regions of the polymer. Of all the samples, nBA-8 appears to give the only example of Stage (1). As stated previously, the DMWDs of nBA-8 and its control were very close. For this sample, tensile properties decreased and there was a small amount of weight gain, possibly due to the addition of amide end-groups (Table 3). The specimen nBA-16 has proceeded into Stage (2) with reduction at the high end of the DMWD, a decrease in peak molecular weight, and an increase of low molecular weight material (Fig. 3). Stage (3), it is speculated, occurs when cleavage of nonordered regions begins to produce a distinct distribution based on the length of interfibril chains in the amorphous portion and is reflected as a shoulder in the DMWD at an M_i of roughly 10,000 (Table 2). It appears that with the occurrence of this shoulder, all aminolyzed samples had lost a considerable amount of their strength (cf. Tables 2 and 3).

Only in the case of the aminolysis with ethylamine did a clear example of Stage (4) attack appear. After 16 h reaction the density of the ethylamine-treated sample (EA-16) had increased greatly and a large loss in weight had occurred. A new main peak population was found at M_i of 3,400 (Table 2) and a small shoulder at an M_i value of 5,800. A

residual peak of high molecular weight polymer also appeared at an M_i value of 15,900 for this sample. The highest molecular weight chains are most probably tie chains which act to conserve the remaining tensile properties. The main peak is believed to be the chains in the crystallites with fold cleavage, and the small shoulder is hypothesized to be crystallite material with folds remaining and/or crystallite plus intrafibrillar chains. The increase in density indicates noncrystalline material has been removed.

CONCLUSIONS

The linear relationship between tensile strength and $1/\overline{M}_n$ derived by Flory does not appear to hold for the reduction in tensile strength induced by chain scission. A better relationship is obtained by plotting tensile strength against $\overline{M}_n$. The differential molecular weight distributions attained after aminolysis of PET fibers can help elucidate detailed aspects of the fine structure of the material when correlated to its physical properties. The chain length of the crystallite region and possibly the interfibrillar molecules are directly attained from the DMWD in addition to the total molecular weight distribution of the PET fibers.

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