

498. Structure-Property Relationships in Polyethylene Terephthalate Co-polyesters. Part I. Melting Points.

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The melting points of polyethylene terephthalate/adipate and polyethylene terephthalate/sebacate co-polymers have been measured by a penetrometer method. The melting points of co-polymers containing more than 40 mol. % of ethylene terephthalate units were, for a given molar composition, approximately the same in the two series, and the X-ray diffraction patterns of such polymers were essentially those of polyethylene terephthalate itself but with increased amorphous scattering. Flory's relationship (*J. Chem. Phys.*, 1949, **17**, 223) between the crystallite melting point, T_m , and the "mole" fraction X , of the units forming the crystallites was found to hold for values of X between 1.0 and 0.7, though for lower values of X the melting points were lower than the calculated values. The latent heat of fusion, calculated from the slope of the $\ln X-1/T_m$ curve as X approaches unity, is similar to that for the aliphatic polyesters and indicates that the high melting point of polyethylene terephthalate is due to chain rigidity, rather than to strong interchain attraction.

THE high melting points of the polyesters obtained by condensation of glycols with terephthalic acid and other symmetrical aromatic dibasic acids (Whinfield, *Nature*, 1946, **158**, 930; Hill and Walker, *J. Polymer Sci.*, 1948, **3**, 619) are of both academic and technical interest. During the last few years we have been studying the properties of the co-polyesters between the high-melting polyethylene terephthalate (m. p. 267°) and the low-melting polymers polyethylene adipate (m. p. 47°) and polyethylene sebacate (70°). The present paper deals with the relations between melting point and composition in these co-polymers; Part II (following paper) deals with second-order transition points. These two properties taken together throw much light on the remarkable differences existing between the aliphatic and the aromatic polyesters.

The study of crystallite melting points in polymers is complicated by the fact that melting generally occurs over a temperature range which may be many degrees wide and the absolute position of which depends to some extent on the temperature at which the

crystallisation occurred. Fortunately, with the polymers studied in this work, the differences in melting point due to structural factors are so large that these other factors are of less importance. We have chosen as our definition of melting point the temperature at which the polymer collapses under the load of a penetrometer, this being the temperature of practical importance in operations such as melt-spinning and extrusion. However, Flory (*loc. cit.*) has recently defined the melting point as the upper limit of the melting range, *i.e.*, the temperature at which all equilibrium crystallinity disappears, and Evans, Mighton, and Flory (*J. Amer. Chem. Soc.*, 1950, **72**, 2018) have measured this temperature by direct observation of the disappearance of crystallites. The validity of the interpretation of our results by means of Flory's theory thus depends upon the degree to which the melting points as measured by the penetrometer method approximate to those defined by the theory. Since it is difficult to imagine the occurrence of any flow of the type observed at the penetrometer melting point whilst any appreciable degree of crystallinity remains, this approximation should in general be quite close (within 1—2°), though perhaps with co-polymers having a very wide melting range the discrepancy may be larger.

The common method of measuring the melting points of polymers by observing the temperature at which they stick when pressed on a copper block may indicate the beginning of the melting range, and we found it to be very dependent on the degree of crystallinity. In moving down the co-polymer series from 100% polyethylene terephthalate, the difference between the penetrometer melting points and the sticking points increased as the room-temperature degree of crystallinity fell. Prolonged annealing just below the melting point raised the sticking point to within a few degrees of the penetrometer melting point.

The sticking points and penetrometer melting points in the two series of co-polymers are presented in Tables 1 and 2, and the melting point-composition diagrams for the two

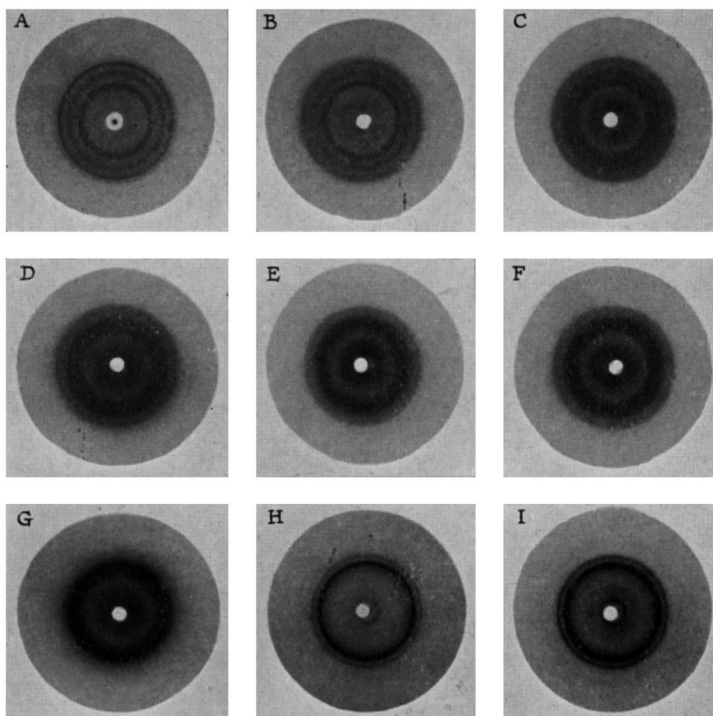
Table 1. *Polyethylene terephthalate/adipate co-polymers.*

Initial molar compn.	Final molar compn.	Sticking point *	Penetro- meter m. p.	Remarks
100 : 0	—	245°	267°	—
90 : 10	—	228	237	Hard and crystalline. Melt spins to drawable fibre
80 : 20	80.2 : 19.8	194	211	" " "
75 : 25	—	—	202	" " "
70 : 30	72.3 : 27.7	165	192	Crystalline, but softer
65 : 35	66.5 : 33.5	154	170	Crystalline, flexible, soluble in CHCl ₃
60 : 40	61.6 : 38.4	132	151	" " "
55 : 45	57.15 : 42.85	112	135	Crystallises slowly. Rubbery
50 : 50	—	103	107	" " "
40 : 60	—	58	73	" " "
30 : 70	—	<R.T.	31	Sticky "viscous" liquid Crystallises over several weeks
20 : 80	—	<R.T.	34	Crystallises very slowly
10 : 90	—	29	40	Crystalline and flexible
0 : 100	—	—	47	—

* R.T. = Room temperature.

series are shown together in Fig. 1. The most important feature of this diagram is that over the composition range 100—40 "mol." % of ethylene terephthalate the melting points of the two series lie on a common curve, *i.e.*, the melting point is determined by the molar fraction of the ethylene terephthalate units, independently of the other component. This is in agreement with the theory and with the observations of Evans, Mighton, and Flory (*loc. cit.*) in other co-polymer systems. The X-ray diffraction patterns (Plate) show that over the range in which the melting points in the two series lie on a common curve, the crystallinity is due to ethylene terephthalate units, with an increasing amount of amorphous scattering as the proportion of the aliphatic component is increased. The co-polymers containing less than 30 mol. % of ethylene terephthalate units showed the X-ray diffraction pattern of the aliphatic polyester, and their melting points lie on two separate new curves, characteristic of the aliphatic polyesters.

The ability of the ethylene terephthalate units to form crystallites when present at a



X-Ray diffraction patterns of polyethylene terephthalate/sebacate co-polymers
 [Cu-K α radiation; flat-film photographs.]

A, 100/0	B, 80/20	C, 70/30
D, 63/35	E, 60/40	F, 50/50
G, 40/60	H, 30/70	I, 0/100

molar fraction as low as 0.5 is rather remarkable. If the two kinds of repeating unit are scattered at random along the polymer chains, then when they are present in equal numbers the frequency of occurrence of long sequences of any one kind of unit must be very low, most of the units occurring singly or in groups of two or three. Thus the persistence of crystallinity at the 50/50 molar composition suggests that quite short sequences of ethylene terephthalate units can take part in crystallite formation. The other alternative is that the distribution is not random, owing to differences in the rates of condensation of the aromatic

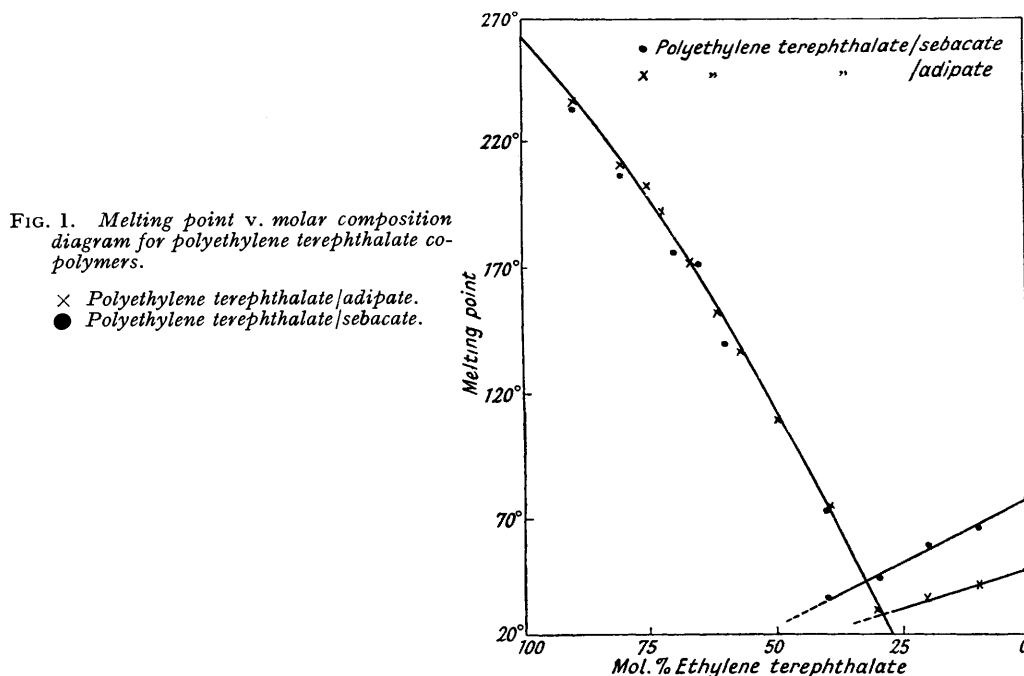


FIG. 1. Melting point v. molar composition diagram for polyethylene terephthalate co-polymers.

× Polyethylene terephthalate/adipate.
● Polyethylene terephthalate/sebacate.

and aliphatic components. It is most probable, however, that the process of ester-interchange which has been shown to occur in polyesters (Flory, *J. Amer. Chem. Soc.*, 1942, **64**, 2205) would rapidly lead to a random distribution even if the initial condensation did not.

Table 2. Polyethylene terephthalate/sebacate co-polymers.

Initial molar compn.	Inherent viscosity	Sticking point	Penetro-meter, m. p.	Remarks
100 : 0	—	—	267°	—
90 : 10	0.48	228°	233	Crystalline. Melt spins to drawable fibres
80 : 20	0.41	194	206	Crystalline. Elastic fibres
70 : 30	0.66	166	175	Elastic fibres. Soluble in CHCl ₃
65 : 35	0.69	150	170	
60 : 40	0.73	132	138	Semi-crystalline. "Rubbery"
50 : 50	0.63	98	108	Very rubbery. Crystallises slowly
40 : 60	0.81	61	{ 71 35	" " "
30 : 70	0.82	47	43	" " "
20 : 80	1.03	—	56	Crystalline. Rubbery
10 : 90	1.17	—	63	Crystalline. Flexible
0 : 100	—	—	72	—

According to Flory's theory the temperature T_m at which equilibrium crystallinity in a co-polymer disappears is related to the mol.-fraction X of the units forming the crystallites by the equation

$$1/T_m - 1/T_m^0 = - (R/h_u) \ln X$$

where T_m^0 is the melting point when $X = 1$, and h_u is the heat of fusion per repeating unit. This relation predicts that the plot of $1/T_m$ against $-\ln X$ should be a straight line of slope R/h_u , and in Fig. 2 we have plotted these quantities, using the observed data for the terephthalate/adipate and terephthalate/sebacate series of co-polymers, covering the composition range $X = 1.0-0.4$. Down to $X = 0.7$ the data fit fairly well on to a straight line, though at lower values of X , the melting points are lower than the theoretical. From the slope of the straight line in Fig. 2, the value of h_u , the heat of fusion per ethylene terephthalate unit, is calculated to be about 2200 cal., which, rather surprisingly, is less than the corresponding values for the aliphatic polyesters calculated in a similar manner. Table 3 shows the heats and entropies of fusion (S_u) of fusion of the three polyesters, the latter being calculated from the relationship $S_u = h_u/T$.

FIG. 2. Plot of $1/T_m$ against $-\ln X$ for polyethylene terephthalate co-polymers.

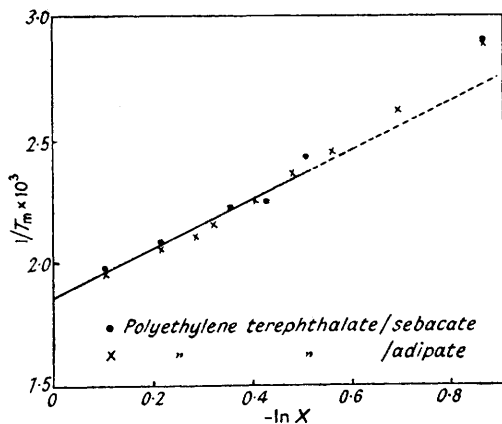
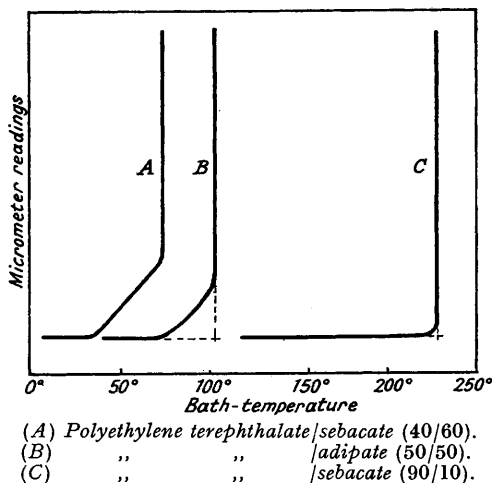


FIG. 3. Penetrometer curves.



This result indicates that the high melting point of polyethylene terephthalate is due to the remarkably low entropy of fusion rather than to the high inter-chain forces. Unfortunately, the values of the heat and entropies of fusion calculated in this way cannot be accepted without reserve. In their work on polydecamethylene adipate and polydecamethylene sebacate, Evans, Mighton, and Flory (*loc. cit.*) found that the values of h_u

Table 3. Heats and entropies of fusion of crystalline polyesters.

Polyethylene polyester	h_u , cal.	S_u per repeat unit, cal./deg.
Terephthalate	2200	4.0
Adipate	3800	12
Sebacate	3300	9.6

calculated from the melting points of co-polymers were much lower than those obtained from measurements of the depression of the melting point by the addition of simple organic compounds, or from the melting points of low-molecular-weight polymers. However, although the values in Table 3 are almost certainly too low, yet the general conclusions that the heats of fusion of the three polyesters are similar, and that the presence of the *p*-phenylene grouping greatly reduces the entropy of fusion, are probably true.

EXPERIMENTAL

Preparation of Co-polymers.—Because of the very low solubility of terephthalic acid in ethylene glycol it was not convenient to prepare the co-polymers by direct condensation of the mixed acids with an equimolar quantity of ethylene glycol. The preparations were carried out

by heating together *in vacuo* the appropriate quantities of the bis-2-hydroxyethyl esters of terephthalic acid and of either adipic or sebacic acid. These low-molecular-weight esters, which we will refer as to "monomers," were not isolated, but used as their mixtures with free ethylene glycol and probably some low polymer.

Ethylene Terephthalate "Monomer."—In a 3-l. flask fitted with a stirrer and a short, unpacked column leading to a condenser and receiver were placed 1164 g. (6.0 moles) of dimethyl terephthalate, 1116 g. (18.0 moles) of ethylene glycol, and 0.2 g. of litharge (ester-interchange catalyst). The flask was heated in an air-bath so that methanol distilled steadily with the column head at *ca.* 70° until the theoretical amount had been collected. Towards the end of the reaction the head temperature rose rapidly as glycol appeared in the distillate. Ethylene glycol (100 c.c.) was then distilled off, and the melt poured out on an enamelled tray and allowed to crystallise. The composition of the product was then calculated in terms of weight per mole of terephthalic acid.

Ethylene Adipate and Ethylene Sebacate.—In a 3-l. flask similarly equipped were placed 876 g. (6 moles) of adipic acid and 744 g. (12 moles) of ethylene glycol. The flask was heated in an oil-bath at 180—200° so that water distilled over with the column head at 100—105°. Esterification was continued until the acid value of the melt was essentially zero and the theoretical volume of water had been collected. Ethylene sebacate "monomer" was prepared in a similar manner, the adipic acid being replaced by 1212 g. (6 moles) of sebacic acid. Each preparation was assumed to contain 6 molar equivalents of the bis-2-hydroxyethyl ester.

Polycondensation.—The co-polymers were prepared by mixing suitable quantities of the two "monomers" in the desired molar ratio, in a 2-l. flask fitted with a vacuum-tight stirrer, a wide-bore take-off leading to a condenser and receiver, and a gas inlet. The flask was heated in an oil-bath at 220—260° and, when distillation of glycol at atmospheric pressure ceased, the pressure was slowly reduced to 0.2—0.3 mm. Hg. Condensation with elimination of glycol was continued under these conditions with stirring, until the melt reached a very high viscosity, usually in 6—10 hours.

It was found in the preparation of polymers containing adipic acid that, if the oil temperature exceeded 230°, the polymers were badly discoloured and small amounts of cyclopentanone collected in the solid carbon dioxide traps of the pumping system. Because of the higher m. p.s of co-polymers containing 10 and 20 mol. % of ethylene adipate, the polymerisation temperature in these cases had to be raised to *ca.* 250°, but the remaining adipate co-polymers were prepared at 220°. This difficulty did not arise in the preparation of the sebacate co-polymers, and polymers of good colour were obtained at 260°. There were signs, however (odour and, in some cases, appearance of a crystalline substance in the condenser), of a slight tendency to form cyclic ethylene sebacate, particularly in co-polymers rich in sebacate.

Polymer Characterisation.—Some measurement of molecular weights was required to demonstrate that they had been raised beyond the level at which the m. p. becomes constant (probably 2000—3000). Inherent viscosities of the polyethylene terephthalate/sebacate co-polymers were measured at 25° by using a 0.5% solution of the polymer in a mixture of phenol and tetrachloroethane (60/40 w/w). Chloroform was an unsuitable solvent because of its inability to dissolve polymers containing more than 70 mol. % of ethylene terephthalate; it also gave a very flat viscosity-molecular weight relation so that the results were of little use in deciding whether a high polymer had actually been obtained. In the terephthalate/adipate series some attempts were made to measure the molecular weights by end-group analysis. Hydroxyl end-groups were measured by acetylation with a pyridine-acetic anhydride reagent, and carboxyl end-groups by titration with 0.1N-alcoholic potash. Chloroform was used as solvent in the titrations, but again the method was limited to polymers containing less than 70 mol. % of ethylene terephthalate. Results were very erratic but served to show that the molecular weights were certainly over 5000 and probably about 10,000. The inherent viscosities quoted in Table 2 for the terephthalate/sebacate polymers give a similar assurance that the molecular weights were sufficiently high not to affect the m. p.

Gravimetric Analysis.—Some of the terephthalate/adipate co-polymers were analysed for terephthalic acid in order to determine to what extent adipic acid was lost during polymerisation through either decomposition to cyclopentanone or formation of cyclic ethylene adipate. 1.0 G. of polymer was refluxed gently with 50 c.c. of 20% aqueous potassium hydroxide until completely dissolved. The solution was acidified at the boil, then cooled, and the terephthalic acid filtered off on a weighed Jena crucible, and washed with water to constant dry weight. The results obtained are shown in Table 1, and indicate that there was no serious change in the molar ratio of the dibasic acids during polymerisation. The method was unsatisfactory when

applied to the terephthalate/sebacate co-polymers because of the low solubility of sebacic acid in water.

Melting Points.—The sticking points were determined by pressing a small piece of the polymer on a clean copper block, drilled at the side to take the bulb of a thermometer, and heated underneath by a micro-burner. The sticking point was taken as the temperature at which, when the sample was pulled away, a small spot of polymer remained behind on the block.

The penetrometer m. p.s were measured in an apparatus which consisted essentially of a vertical steel spindle 8" long and $\frac{1}{4}$ " in diameter fixed in a rigid frame so as to move freely in a vertical direction. The upper end of the spindle was pointed to give a sharp contact with the foot of a micrometer (reading to 0.0001") which was rigidly fastened to the top of the frame, and the gap was connected in series with a small torch bulb and an accumulator. The top of the spindle could thus be located accurately by screwing down the micrometer until the bulb lit. About half-way down the spindle was a circular flange to carry a weight which was adjusted so that the total weight of the spindle and its attachments was 150 g. The sample, cut in the form of a flat disc about $\frac{1}{2}$ " in diameter and $\frac{1}{8}$ " thick, with parallel sides roughened to prevent slipping, was placed on the base plate of the frame under the lower end of the spindle and the lower half of the apparatus was immersed in a silicone oil-bath. The temperature of the bath was raised at 1°/min. and micrometer readings were taken at one minute intervals.

Typical curves obtained are illustrated in Fig. 3. Highly crystalline polymers such as polyethylene terephthalate give a sharp collapse point (curve *C*) but the co-polymers in general gave more rounded curves (curves *A* and *B*) the width of which gives an indication of the broad melting range. In these cases the m. p. was taken as the intersection of the tangents to the two arms of the curve. It is noteworthy that in the case of the 40/60 terephthalate/sebacate co-polymer (curve *A*) there seem to be two distinct discontinuities, at 35° and 71°. By reference to Fig. 2 it will be seen that these are the expected m. p.s of ethylene sebacate and ethylene terephthalate crystallites, respectively, at that particular composition.

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Some of the polymers described are the subject of patent applications.

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