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The *p*-Phenylene Linkage in Linear High Polymers: Some Structure-Property Relationships*

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In a previous communication to the International Congress of Pure and Applied Chemistry[1] the chemical structure of a large number of linear condensation polymers was correlated with their physical properties and fiber-forming characteristics. It was shown that chain symmetry, interchain forces, and the presence of groupings which influence chain flexibility are the dominant factors determining crystallinity, melting point, solubility, and sensitivity to moisture. Reference was then made to the crystallinity, melting point, and fiber-forming properties of the polyesters obtained from ethylene glycol and the various isomeric phthalic acids, diphenyl dicarboxylic acids, and the naphthalene dicarboxylic acids, and the importance of a symmetrical structural unit was clearly demonstrated. Polyethylene terephthalate (Terylene), first prepared by Whinfield and Dickson,[2] has proved to be of outstanding merit as a fiber-forming polyester and the commercial production of such fibers in Great Britain (Terylene) and the U. S. (Dacron) has recently been announced. These circumstances have focused attention on the significance of the *p*-phenylene linkage in linear high polymers.

THE MELTING POINT OF CRYSTALLINE POLYMERS

Before proceeding to a detailed discussion of the influence of the *p*-phenylene linkage on polymer properties, it is appropriate to refer briefly to the measurement of the crystallite melting point. In his theory of crystallinity in high polymers, Flory[3] defined the melting point as the temperature at which equilibrium crystallinity completely disappears. This was measured[4] by direct observation of the disappearance of crystallites under the microscope. Other methods have been described, few of which are entirely reproducible with close limits.

A penetrometer method, capable of giving very consistent results, has been devised in these laboratories. The apparatus used is illustrated diagrammatically in Figure 1, and will be more fully described elsewhere.[5] A previously annealed sample of the polymer is subjected to the load of the

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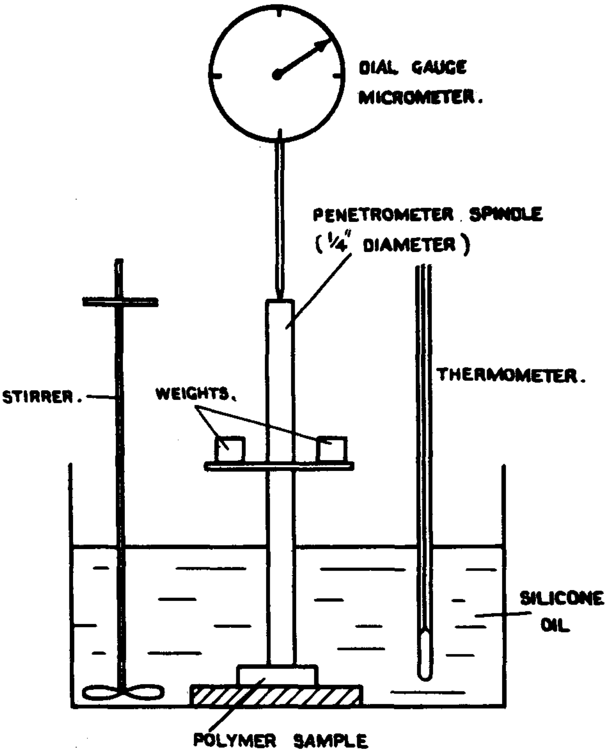


Fig. 1. Diagram of penetrometer apparatus.

penetrometer while immersed in a silicone oil bath the temperature of which is raised one degree per minute. The degree of penetration measured on a micrometer is taken at one minute intervals, and the readings are plotted against temperature, giving curves illustrated in Figure 2. Highly crystalline polymers such as polyethylene terephthalate give a sharp and precise collapse point. The melting points quoted in this communication have (with several exceptions, marked with an asterisk) been obtained by this method.

It is now well established that the melting behavior of a polymer is affected by its previous thermal history. In the case of natural rubber Bekkdahl and Wood[6] showed that the melting point depends on the temperature at which the crystallites were formed. More recently Evans, Mighton, and Flory[4] have pointed to a similar phenomenon in the case of polydecamethylene sebacate. Though similar effects have also been observed with polyethylene terephthalate, the effect is not considered to be of major consequence within the context of the present study.

The melting points obtained for various samples of polyethylene terephthalate after annealing the quenched (*i.e.*, amorphous) polymer under various conditions are shown in Table I. It will be appreciated, however, that the determination of melting point by this method provides an additional annealing treatment during the premelting period.

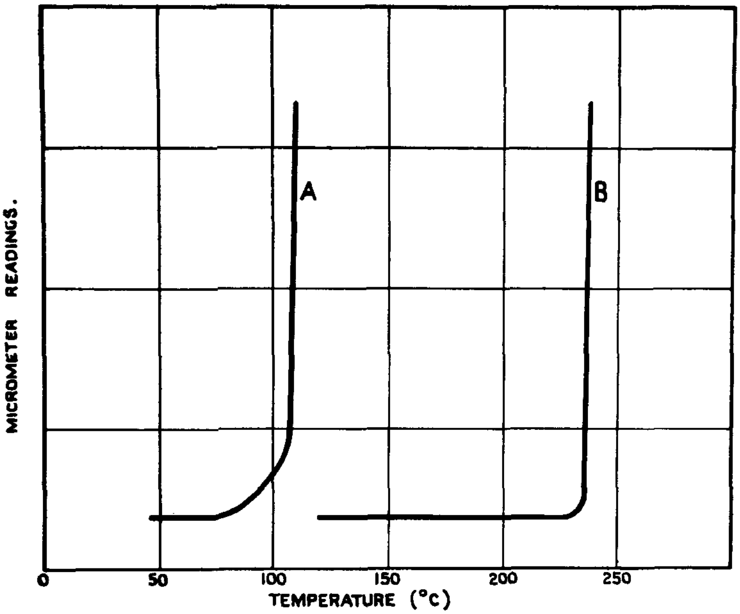


Fig. 2. Penetrometer curves: (A) polyethylene terephthalate/-adipate (50/50); (B) polyethylene terephthalate/sebacate (90/10).

TABLE I

Influence of Annealing Treatment on Melting Point

Annealing temperature, °C.	Density, g./ml.	Crystallinity, %	Melting point, °C.
120	1.370	31	—
140	1.378	38	262
180	1.390	48	261
220	1.402	58	264
260	1.411	65	265

SECOND ORDER TRANSITION TEMPERATURE

The penetrometer apparatus has also been used[5] to measure the second order transition temperature and the results cited here have been obtained in the following manner: A small tray containing the molten polymer is plunged into the silicone oil bath cooled to −80°C. and then moved into position under the foot of the penetrometer. The bath temperature is then allowed to rise at the rate of 1°C. per minute and a penetration *vs.* temperature graph obtained. As the temperature approaches the transition point some flow commences and the graph, originally horizontal, shows a gradual curve upward (Fig. 3). At a definite reproducible temperature the slope of the curve suddenly increases, and in many cases further penetration is prevented a few degrees above this point by the onset of crystallization. In the case of polyethylene terephthalate the sudden change in slope always occurred in the region 67–69 °C. in good agreement with the second order transition point measured by the dilatometric method by Kolb and Izard[7] and confirmed independently. Reproducibility was generally within ±1 °C., though for some polymers where the change of slope was less rapid there was some doubt as to the precise location of the transition point.

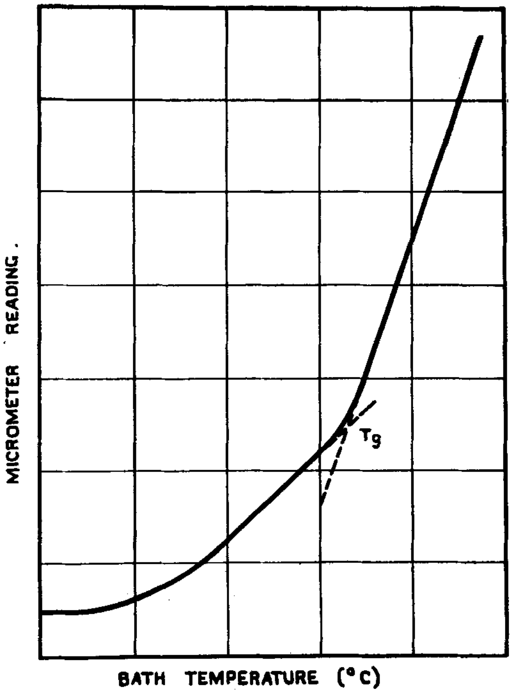


Fig. 3. Penetration curve in the determination of second order transition point.

THE *p*-PHENYLENE LINKAGE

The high melting point of the aliphatic polyamides, *e.g.*, polyhexamethylene adipamide and sebacamide, is believed to arise from the strong interchain hydrogen bonding forces. By contrast, the aliphatic polyesters are considerably lower in melting point, and it was this very fact that caused Carothers to turn away from the polyesters in favor of polyamides. The discovery of a high melting crystalline polyester—polyethylene terephthalate—was a most significant achievement which has stimulated much interest in the *p*-phenylene linkage and the principle underlying its contribution toward the properties of high polymers.

It has been suggested, possibly by analogy with the polyamides, that the high melting point of polyethylene terephthalate could imply the existence in that polymer of strong interchain forces, and several suggestions have been made as to how these might arise, *e.g.*, (*1*) by enhancement of the polarity of the ester group resulting from conjugation with the *p*-phenylene nucleus, (*2*) hydrogen bonding of the ester carbonyl groups with nuclear hydrogen atoms, or (*3*) strong attractions between the *p*-phenylene groups themselves. These hypotheses may be discussed conveniently by reference to various other polyesters which can be regarded as modifications of the polyethylene terephthalate structure. The effects of such modifications on melting point and crystallinity are shown in Table II.

The viewpoints advanced above appear to find some support in the observation that when the aromatic character of polyethylene terephthalate is destroyed by hydrogenation of the *p*-phenylene linkage there is a complete change in physical properties. Thus, polyethylene hexahydroterephthalate (Table II, 2) is completely amorphous and plastic at ordinary temperatures. This evidence is, however, inadmissible, because of geometrical isomerism in the polymer. Irrespective of whether *cis* or *trans* hexahydroterephthalic acid is used in the polyesterification with ethylene glycol the polymer is found by hydrolysis to be built up from both forms. Apparently an equilibrium mixture of the two isomers is formed during the condensation.

Trimethylene, tetramethylene, and hexamethylene terephthalate polymers (Table II, 3, 4, and 5) illustrate the effect of increasing the distance between the ester groups. As in the case of the polyamides, this brings about a slight reduction in melting point. Polyethylene 1,4-diphenoxybutane-*p,p'*-dicarboxylate (Table II, 6) provides an interesting test case wherein the spacing of the ester groups is doubled, leaving the disposition of the *p*-phenylene linkages unchanged. It is most significant that this has very little effect on the melting point.

It is now interesting to examine the effect of interrupting the conjugation of the ester groups with the aromatic nucleus by the insertion of methylene groups. Polyethylene homoterephthalate (Table II, 7) has an unsymmetrical repeat unit; therefore, unless the repeat units occur regularly in head-to-tail fashion, the distribution of the various groupings along the chain will be irregular. Further, when this polymer was prepared at a condensation temperature of 275 °C. gelation occurred, possibly due to the reactivity of the α-methylene group attached to the nucleus. Gelation did not occur at 198 °C., but the polymer so formed, though fiber-forming and giving the cold-drawing ("necking down") phenomenon, showed no significant sign of crystallinity in the mass. In the case of polyethylene *p*-phenylene diacetate (Table II, 8) the introduction of the second methylene group restores symmetry, so that crystallinity can be anticipated. Gelation was again observed when the condensation was attempted at high temperatures but was avoided by carrying out the reaction at 198 °C. The polymer so obtained was fiber-forming and crystallized readily on annealing.

The self-condensation polymers of *p*-(γ-hydroxypropoxy)benzoic acid (Table II, 9) and *p*-(β-hydroxyethoxy)phenylacetic acid (Table II, 10), respectively, provide a further example of the effect of removing the ester

TABLE II

POLYESTERS CONTAINING THE *p*-PHENYLENE LINKAGE

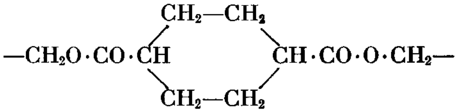
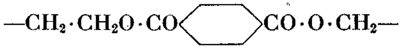
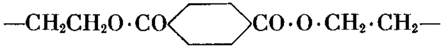
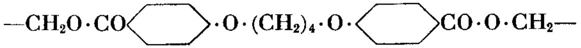
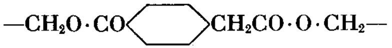
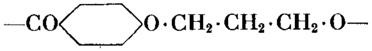
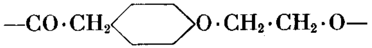
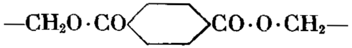
No.	Repeating unit	No. of chain atoms between *p*-phenylene linkages	Crystallite melting point, °C.	Crystallinity	Ref. No.
1		6	265	Yes	2,9
2		6	—	No	8
3		7	235	Yes	9,2(b)
4		8	230	Yes	9
5		10	155	Yes	9
6		6	252	Yes	9,10
7		7	—	No	9
8		8	137	Yes	9
9		6	185*	Yes	9,11
10		6	172*	Yes	9,12
11		6	*ca.* 300	Yes	13

TABLE III

SOME EXAMPLES OF THE *p*-PHENYLENE LINKAGE IN HIGH POLYMERS

No.	Repeating unit	Melting point, °C.	Crystallinity, solubility	Ref. No.
1	$—CH_2·CH_2·CH_2·CH_2·CH_2·CH_2—$	135*	Highly cryst. Soluble in hot toluene and xylene.	14
2		380*	Highly cryst. Insoluble except in very high boiling solvents.	15,16
3	$—CH_2O·CO·(CH_2)_4·CO·O·CH_2—$	50	Highly cryst. Readily soluble in chloroform and acetone.	18
4		264	Soluble only in phenols, or high boiling solvents.	2,9
5	$—(CH_2)_3·NH·CO·(CH_2)_4·CO·NH·(CH_2)_3—$	264	Soluble only in highly polar solvents.	19
6		>400*	Highly cryst. and insoluble.	9
7	$—(CH_2)_4CO·NH·(CH_2)_8NH·CO·(CH_2)_4—$	197*	Crystalline.	19
8		285	—	21
9	$—CO·CH_2·CH_2·CH_2·CH_2·CO·O—$	85° (98°)*	Microcrystalline powder.	22
10		>300*	Crystalline.	23

group directly away from the *p*-phenylene nucleus. Their melting points, while being lower than that of polyethylene terephthalate, are very much higher than the aliphatic polyesters. Finally, in polyhydroquinone succinate (Table II, 11), interchange of the positions of the =C=O and —O— groups of polyethylene terephthalate has produced a rise in melting point to about 300 °C.

The general conclusion to be drawn from these considerations is that the *p*-phenylene linkage has a direct, elevating effect upon melting point quite apart from any secondary effect it may have by enhancing the polarity of adjacent groupings. This conclusion is well illustrated by a comparison of polymethylene and polyphenylene-ethylene (Table III). The latter, though devoid of permanent dipoles, is very high melting and insoluble in all but a few very high boiling solvents such as acenaphthene, benzyl benzoate, and coumarin.[16] The same effect is also evident in the series: diphenyl, terphenyl, quaterphenyl, etc.,[17] where there is a sharp increase in melting point and decrease in solubility. The effect of the introduction of the *p*-phenylene linkage into other classes of polymers is shown in Table III; where strongly polar or hydrogen bonding groups are already present, the melting point is usually raised above the decomposition point of the polymer, and it is quite clear that the *p*-phenylene group has its effect independently of other groups which may be present.

If, in fact, the *p*-phenylene linkage does increase interchain cohesion this must arise from the interaction of the aromatic nuclei by the operation of the London dispersion forces. The magnitude of this effect in benzene, and the possibility of its operation in polystyrene, have been discussed by de Boer.[24] It is doubtful whether it could adequately account for the high melting point of polyethylene terephthalate, which, if it is to be attributed entirely to a high heat of fusion, would require interchain forces of the same order as the hydrogen bond.

Decisive evidence is furnished by x-ray analysis of the crystal structure of diethyl terephthalate,[25] and polyethylene terephthalate itself.[26] In the latter the molecules are nearly planar in configuration, and distances between atoms in adjacent molecules are all normal van der Waals' contact distances. There is therefore no evidence of any unusually strong forces between the molecules, and the high melting point of polyethylene terephthalate and structurally related polymers with the *p*-phenylene linkage cannot be explained on that basis. A study of the crystallite melting points of the polyethylene terephthalate copolymers, together with the second order transition points of these polymers in the amorphous state, has shown that a more adequate explanation can be found in the rigidity of the *p*-phenylene linkage.

CO-POLYESTERS BASED ON POLYETHYLENE TEREPHTHALATE

The melting point–composition diagrams for two families of copolyesters in which ethylene adipate and ethylene sebacate are the second components

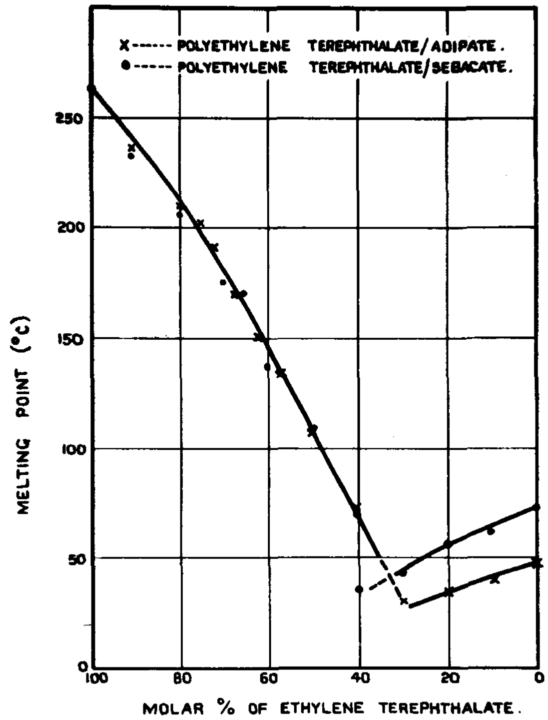


Fig. 4. Melting point *vs.* composition for polyethylene terephthalate copolymers.

are shown in Figure 4. The main feature of this diagram is that over the composition range 100–40 "mole" per cent of ethylene terephthalate the melting points in the two series lie on a common curve, *i.e.*, the melting point is determined by the "mole" fraction of ethylene terephthalate units, independently of the other component. This is in qualitative agreement with the theory of Flory.[3] X-ray diffraction photographs[27] taken on copolymers in that composition range showed that the crystallinity was due to ethylene terephthalate units, though the amount of background scattering increased, as expected, with the proportion of the second component. The copolymers containing less than 30 "mole" per cent of ethylene terephthalate units gave the x-ray diffraction pattern of the appropriate aliphatic polyester and their melting points lie on two separate curves characteristic of the aliphatic polyester.

Using the theory of melting points of copolymers,[3] the heat of fusion of polyethylene terephthalate (h_u) can be calculated from the copolymer melting points (T_m) by the equation:

$$(1/T_m) - (1/T_m^{\circ}) = -R/h_u \ln X$$

where T_m° is the melting point of the polyethylene terephthalate and X is the "mole" fraction of ethylene terephthalate in the copolymer. This relationship requires that the plot of $(1/T_m)$ *versus* $-\ln X$ should be a straight line of slope R/h_u. This plot covering the composition range $X = 1.0$ to 0.4 is shown in Figure 5. Down to $X = 0.7$ the data fit fairly well onto a straight line, but at lower values of X the melting points are lower than theory requires.

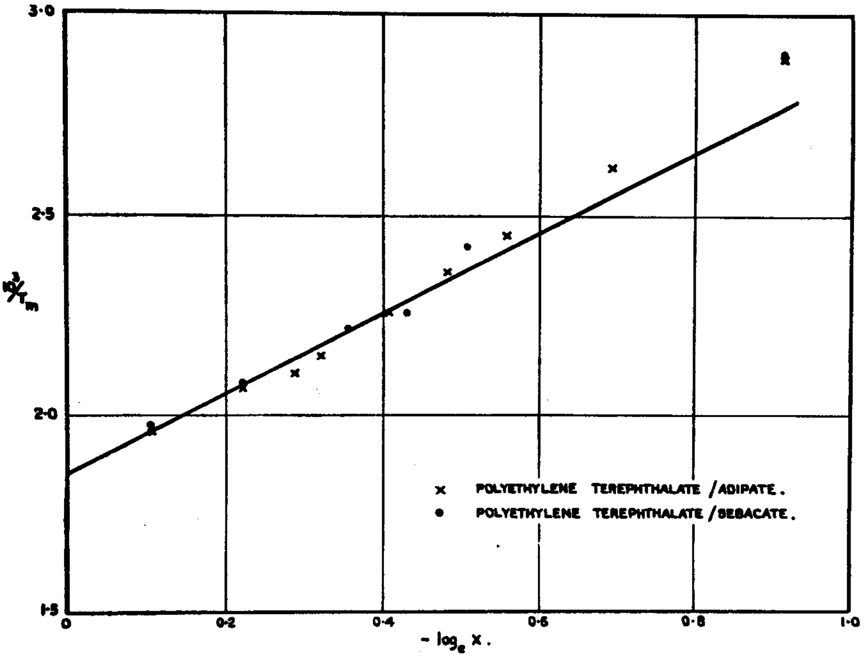


Fig. 5. $1/T_m$ *vs.* ln x for ethylene terephthalate copolymers.

From the slope of the straight line the heat of fusion per ethylene terephthalate unit is calculated to be about 2200 calories, which is less than the corresponding values for the aliphatic polyesters obtained in a similar manner. These values (together with the entropies of fusion derived from them) are shown in Table IV; they are of the same order as those found for decamethylene adipate and decamethylene sebacate by Evans, Mighton, and Flory.[4] The evidence from copolymer melting points thus indicates that the high melting point of polyethylene terephthalate is not due to strong interchain forces but to the low entropy of fusion arising from the presence of the *p*-phenylene linkage.

TABLE IV

HEATS AND ENTROPIES OF FUSION OF POLYESTERS

Polymer	Heat of fusion per repeat unit, cal.	Entropy of fusion per repeat unit, cal./degree
Polyethylene terephthalate	2200	4.0
Polyethylene adipate	3800	12
Polyethylene sebacate	3300	9.6

While discussing copolymers it is of interest to refer to copolyesters of polyethylene terephthalate in which a small proportion of the ethylene glycol is replaced by an equivalent *molar* proportion of a polyoxyethylene glycol:[28]

$$\mathrm{HO(CH_2CH_2O)_{\mathit{n}}CH_2CH_2OH} \qquad (\text{where } n = 1 \text{ to } 100)$$

It is clear that, when $n = 1$, as in the ethylene/diethylene terephthalate copolymers, the weight fraction of diethylene terephthalate in the copolymer is little different from the mole fraction, and the melting point of such a copolymer should be governed by the Flory equation. As n increases, however, the weight fraction of the poly(oxyethylene) terephthalate becomes very much greater than the mole fraction. If, for example, the polyoxyethylene glycol has a molecular weight of 4,000, then only 1 mole per cent of this component corresponds to 17% by weight, which might be expected to have considerable effect on the polymer properties. In Figure 6 the melting points of a range of ethylene terephthalate copolymers with diethylene glycol and polyoxyethylene glycol (molecular weight 4000) are presented. These results provide a striking illustration that the melting point is determined by the mole fraction of the ethylene terephthalate, and not the weight fraction.

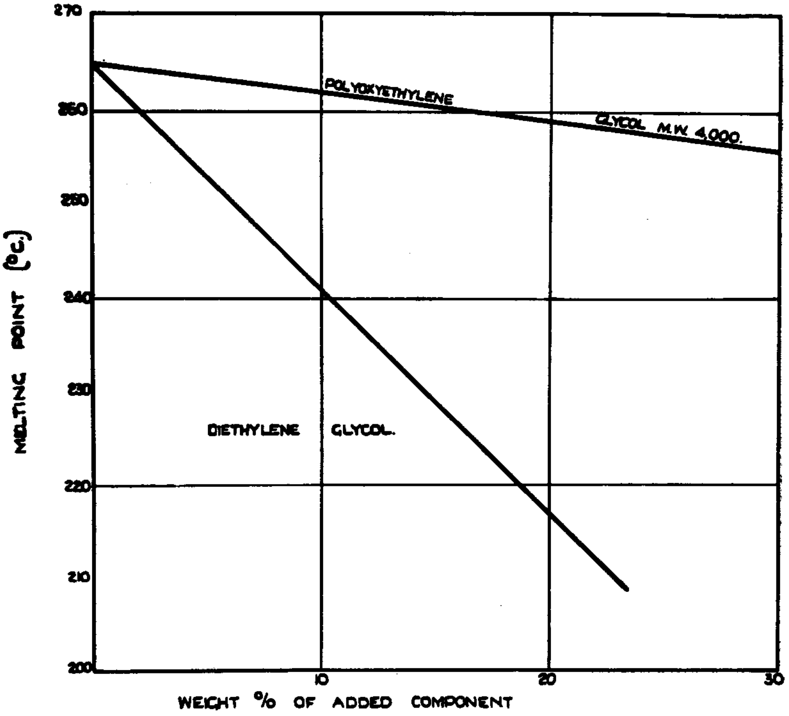


Fig. 6. Melting points of polyethylene terephthalate modified with polyoxyethylene glycols.

It is of great technical interest that substantial weight proportions (*ca.* 15%) of the high molecular weight glycols can be incorporated into the polyethylene terephthalate molecule, profoundly altering certain properties without seriously reducing the melting point. If, for example, such copolymers are melt-spun and oriented by drawing to produce fibers, all the mechanical properties of the fibers suggest that the crystalline regions are essentially the same as in unmodified polyethylene terephthalate fibers, while the amorphous regions show greatly increased absorptive capacity for water and certain dyestuffs (Fig. 7).

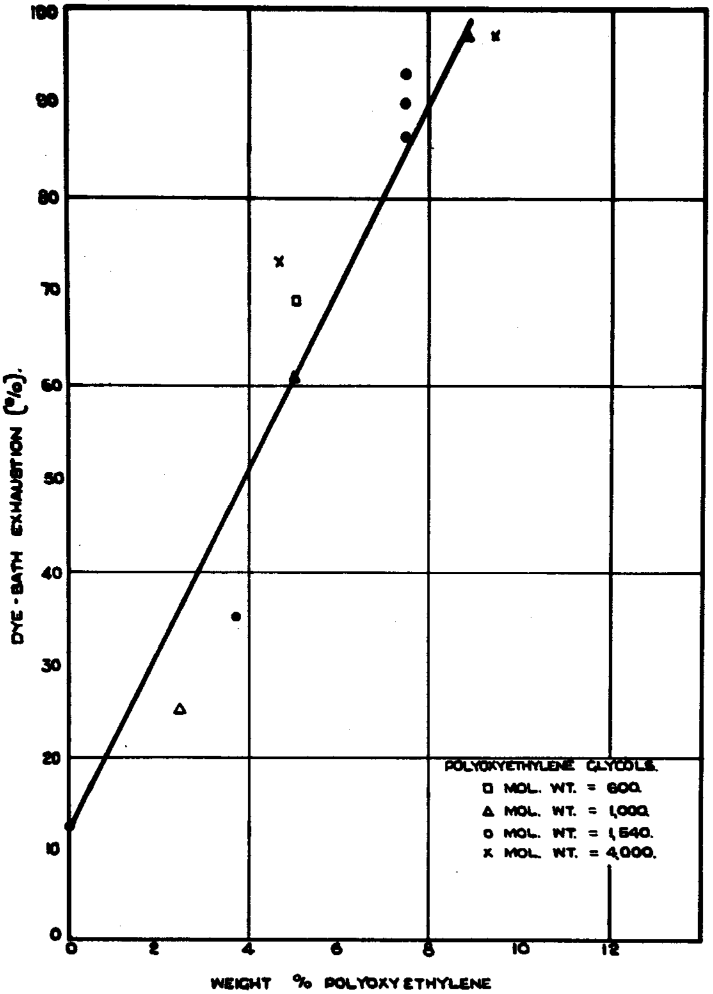


Fig. 7. Effect on dye exhaustion of the polyoxyethylene content of polyethylene terephthalate copolymers.

In a recent paper on the synthesis of macromolecules with long-chain periodicities, Mark[29] has described the ideal fiber-forming polymer as "one which has crystalline domains of a high melting point and amorphous areas of a low so-called second order transition point." He attempted to produce this structure by condensing the polyoxyethylene glycols with various dicarboxylic acids (including terephthalic acid) but the products were waxy and of low melting point. However, in the copolymers described above this "ideal" structure has been achieved, producing macromolecules consisting of alternating long stretches of polyoxyethylene and unmodified polyethylene terephthalate. The products combine the excellent mechanical properties of polyethylene terephthalate with greatly improved dye receptivity.[28]

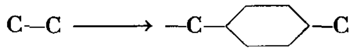
EFFECT OF THE *p*-PHENYLENE LINKAGE ON THE SECOND ORDER TRANSITION POINT

Polyethylene terephthalate differs from the aliphatic polyesters not only in melting point but also in having a much higher second order transition point. Thus, on rapidly quenching the molten polymer to room temperature it can be obtained in a transparent amorphous condition, which softens and begins to crystallize at 80–90 °C. In order to observe this type of behavior with polyethylene adipate it is necessary to quench the molten polymer to −80 °C.

The second order transition temperatures of a range of polyethylene terphthalate copolymers containing as second components oxalic, succinic, glutaric, adipic, and sebacic acids have recently been measured by the penetrometer technique.[5] It was found that, unlike the melting point, the second order transition point is determined by the weight rather than the molar composition. The transition point is lowered when the molecular proportion of the aliphatic component is increased or, at any one molar composition, when the chain length of the aliphatic component is increased. It is clear then that in these copolyesters the second order transition point is determined by the relative amounts of aromatic and aliphatic material, irrespective of whether the latter be present in many short segments (as in the succinate residues) or fewer longer segments (as in sebacate residues).

The second order transition temperature is generally regarded as a measure of the flexibility of the chain molecules; the more flexible the chains the lower the second order transition temperature. Thus the aliphatic polyesters which are believed to have very flexible chains have second order transition points of the order of −70 °C. The increase in transition point on introducing *p*-phenylene linkages into the chains may therefore be due to a stiffening effect of these groups.

Suppose that into a segment of a saturated aliphatic chain consisting of 100 chain atoms (*i.e.*, 100 single bonds) are introduced *N* *p*-phenylene linkages. For each group this can be imagined to occur by the opening of a C—C bond and the insertion of a *p*-phenylene group, thus:



If the average mass per bond in the original aliphatic polymer is m and the mass of the p-phenylene linkage is M, then the mass of the segment is increased from $100m$ to $100m + NM$. Owing to the linearity of the p-phenylene linkages, their presence does not increase the number of configurations which the segment can assume (ignoring those due merely to the rotation of the p-phenylene linkage about its axis). Hence since the segment now has a greater mass associated with only the same number of possible configurations, we can say that it is stiffer by the factor:

$$\frac{100m + NM}{100m} = 1 + \frac{NM}{100m}$$

Putting $M = 76$ (for C_6H_4) and $m = 17.2$ (molecular weight of the ethylene adipate repeat unit divided by the number of chain atoms per unit) this factor becomes $(1 + 0.044N)$.

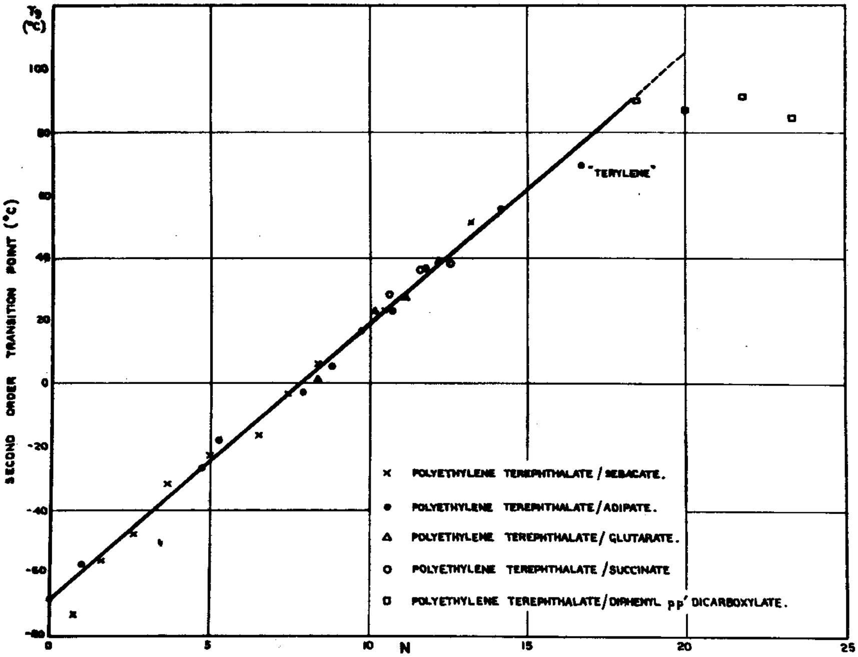


Fig. 8. Second order transition point *vs.* number (N) of p-phenylene linkages per 100 aliphatic chain atoms.

It is clear from the plot (Fig. 8) of the second order transition point against N (the number of p-phenylene linkages per hundred aliphatic chain atoms), that the relationship is linear for values of N up to 16.67 (for polyethylene terephthalate). The straight line has the equation:

$$T_g = 8.7N - 68\,°\mathrm{C}.$$

which can be written in the form:

$$T_g = \overset{\circ}{T}_g(1 + 0.042N)\,°\mathrm{K}.$$

where T_g° = 203°K., the second order transition point of polyethylene adipate. The factor $(1 + 0.042N)$ in this equation is in close agreement with the "stiffness factor" previously elaborated. It appears probable that the transition temperature can be related to the weight and number of chain bonds in the polymer. In the foregoing argument it has been assumed that chain flexibility is determined by the number of chain bonds available per unit mass of chain. This was convenient in that the mass terms employed are accurately known constants, but perhaps a theoretical study would show that units of length or volume would be preferable. Calculations of the stiffness factor using standard bond lengths and molar volumes gave equally close agreement with experiment.

In this treatment it has been assumed that throughout the variation in the spacing of the *p*-phenylene groups, the interchain forces remained constant. The alternative process of maintaining a constant spacing of *p*-phenylene groups in the chain backbone while varying the concentration of lateral groupings has also been examined, using the series of copolymers from terephthalic acid with varying proportions of ethylene and 1,2-propylene glycols. As the concentration of lateral methyl groups was increased, there was an initial drop in transition point to 45°C. for 10 mole per cent propylene terephthalate, after which it increased slowly again to 68°C. for 100% polypropylene terephthalate. The comparatively narrow range of this variation shows that the lateral groups have only minor significance, the determining factor being the inherent rigidity of the main chain.

Since both the high melting point and the high second order transition point of polyethylene terephthalate arise from chain stiffness a simple relationship between these two temperatures might be anticipated. That such a relationship exists can be illustrated by determining the ratio between melting and transition points for polyethylene adipate and terephthalate (Table V).

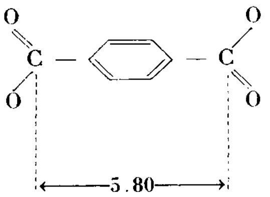
TABLE V

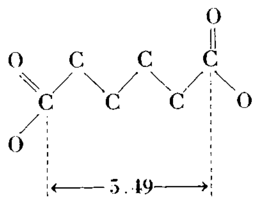
MELTING AND TRANSITION POINT RATIOS IN POLYETHYLENE ADIPATE AND TEREPHTHALATE

Temperature	Polyethylene terephthalate	Polyethylene adipate	Ratio
Melting point	537°K.	323°K.	1.67
Transition point	342°K.	203°K.	1.68

ISOMORPHISM

This review would be incomplete without reference to the possibilities which exist for isomorphism of the terephthalyl and adipyl groups in copolymers. Calculations based on standard bond lengths and angles show that the distances between the carboxyl groups in the parent acids differ by only 0.31 A.:





This close resemblance is clearly shown in the photographs of models (Fig. 9) of the carbon skeletons of the two acids.

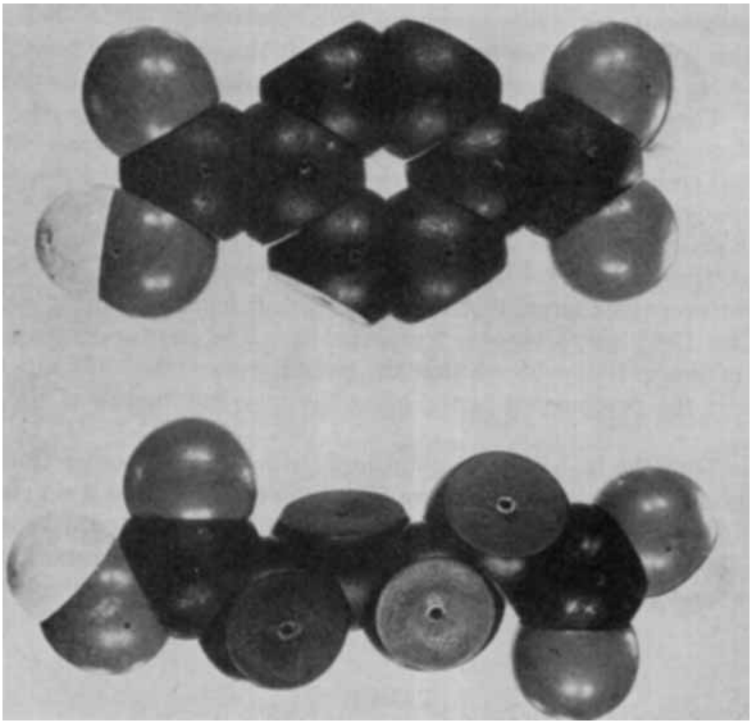


Figure 9

Evidence that this close resemblance does permit isomorphous replacement has come from a study in these laboratories by Plimmer and Reynolds[20] of the effects on melting point and crystallinity of the replacement of a part of the adipic acid in polyhexamethylene adipamide by terephthalic acid. Experimental data on this series of copolymers are given in Table VI, the densities being measured after annealing the sample at 160 °C. for 16 hours to ensure maximum crystallinity.

The melting point *vs.* composition curve (Fig. 10) differs from those of other copolyamide systems in having no minimum; the gradual introduction of terephthalic acid produces immediately a rise in melting point, until beyond the 50/50 composition the melting point is so high that the polymers could not be prepared by conventional methods without the risk of thermal decomposition. The absence of a minimum in this series may be taken as evidence that the hexamethylene terephthalamide units enter into the crystal lattice of hexamethylene adipamide without causing any appreciable disturbance. The melting point–composition curve of the polyhexamethylene sebacamide/terephthalamide copolymers on the other hand shows the minimum usually observed with copolymeric systems. Thus, as would be expected, the hexamethylene terephthalamide unit is not accommodated within the hexamethylene sebacamide lattice.

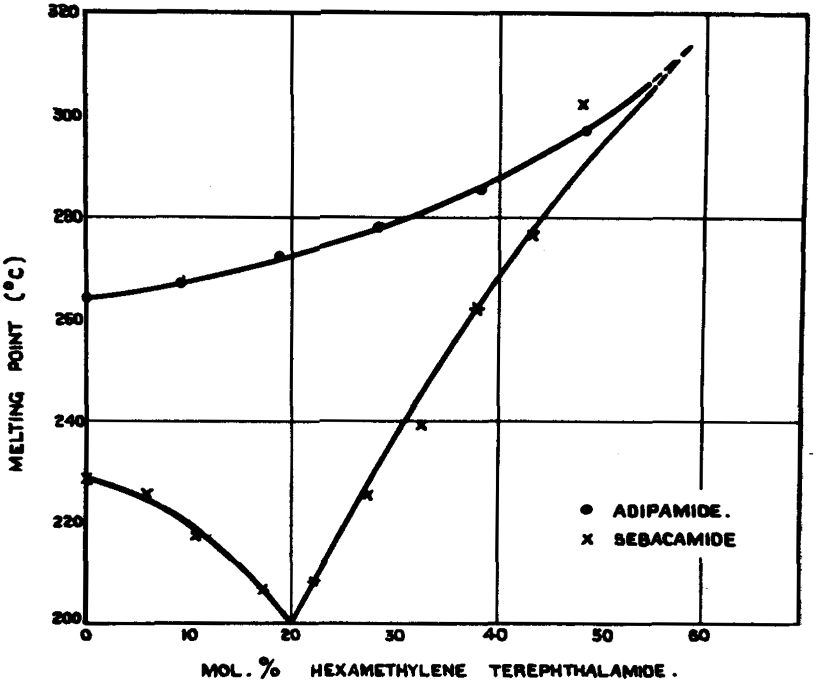


Fig. 10. Melting points of hexamethylene adipamide/terephthalamide and hexamethylene sebacamide/terephthalamide copolymers.

TABLE VI

MELTING POINT AND DENSITY OF POLYHEXAMETHYLENE ADIPAMIDE/TEREPHTHALAMIDE COPOLYMERS

Mole fraction of terephthalic component	Melting point, °C.	Density, g./ml.
0	264	1.141
0.094	267	1.149
0.128	272	1.155
0.283	278	1.157
0.383	285	1.166
0.482	296	1.172

The abnormal nature of the polyhexamethylene adipamide/terephthalamide copolymers is also revealed in the relationship between degree of crystallinity and composition. In most copolymer systems the introduction of the second component generally leads to a progressive reduction in the degree of crystallinity, frequently leading to its complete disappearance coinciding with the minimum in the melting point–composition curve. In this particular system, however, crystallinity (as indicated by density) rises continuously with increasing proportion of the terephthalamide unit (Fig. 11), thus providing further evidence of isomorphism.

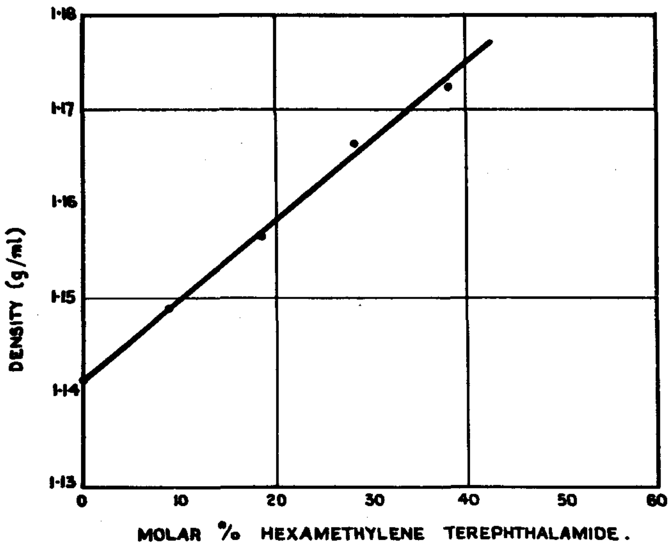


Fig. 11. Densities of polyhexamethylene adipamide/terephthalamide copolymers.

It is now interesting to inquire why such isomorphism does not also occur in the analgous co-polyester systems, *e.g.*, the polyethylene adipate/terephthalate copolymers previously described. The deep trough in the melting point–composition curve (Fig. 4) and the reduction in crystallinity in this system clearly indicate the absence of isomorphism.

This contrasting behavior between co-polyesters and co-polyamides may well be due to the powerful interchain forces existing in the latter. Owing to the zigzag form of the polyester chains (Fig. 12) the *p*-phenylene linkage in polyethylene terephthalate and its copolymers does not lie directly in the line of the chain but is slightly inclined to it. Thus, in spite of the close similarity in the lengths of the adipate and terephthalate units, the latter still interfere with regular chain packing so that isomorphism is not exhibited. By contrast, the occurrence of isomorphism in the copolyamide series is ascribed to the hydrogen bond forces which are sufficiently powerful to bring the *p*-phenylene linkage into the line of the chain.

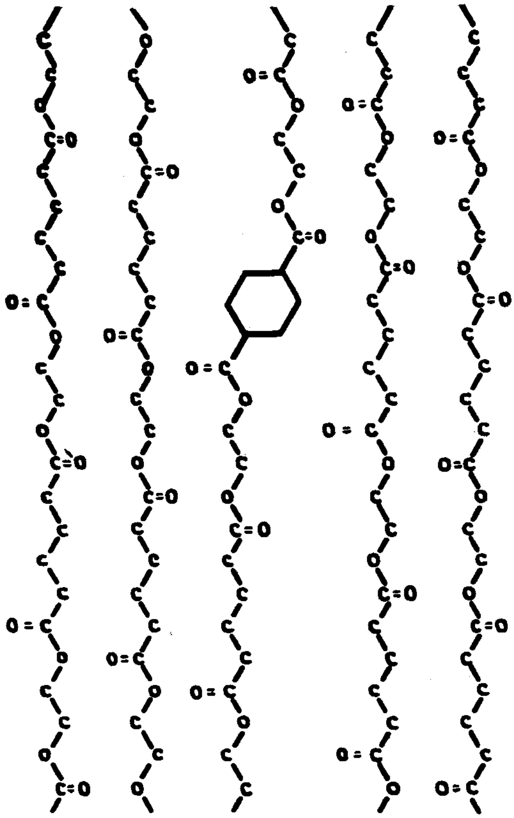


Fig. 12. Disturbance in the chain packing of polyethylene adipate/terephthalate by the *p*-phenylene linkage.

It is significant that when the *p*-phenylene linkage is introduced into polyamides and similar polycondensates, *e.g.*, polyurethans, a high melting point invariably results. This can be attributed both to the additive effects of hydrogen bonding and chain stiffness.

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Synopsis

The high crystallite melting point of polyethylene terephthalate (Terylene) compared with the melting points of the aliphatic polyesters emphasizes the significance of the *p*-phenylene linkage as an important factor determining polymer properties. A consideration of other polymer structures containing the *p*-phenylene linkage shows that its influence is independent of any polar groups which may be present. X-ray examination of the crystallite structure of polyethylene terephthalate and related substances has revealed no evidence of strong intermolecular forces.

From a study of co-polyesters based upon polyethylene terephthalate with aliphatic dibasic acids it is shown that the melting point of compositions containing more than 40 mole per cent of ethylene terephthalate is essentially independent of the aliphatic dibasic acid employed. The Flory relationship between crystallite melting point and mole fraction of the units forming the crystallites shows fair agreement with the results obtained. The calculated latent heat of fusion of polyethylene terephthalate approaches closely to that of the corresponding aliphatic polyesters, and suggests that the high melting point induced by the *p*-phenylene linkage is due to chain rigidity rather than to strong interchain attraction.

This rigidity is consistent with the second order transition temperatures of such polyesters. It is shown that second order transition temperature is a linear function of the number of *p*-phenylene linkages per unit chain length. The *p*-phenylene linkage reduces the possibilities of change of shape available to a given length of chain, so accounting for the low entropy of crystallization and high melting point of polyethylene terephthalate.

Evidence is advanced for the isomorphism of adipyl and terephthalyl linkages in linear polyamides. The absence of isomorphism in polyethylene adipate/terephthalate copolymers is ascribed to the weakness of the interchain forces.

Résumé

Le point de fusion élevé des cristallites de téréphtalate de polyéthylène (Térylène), comparé aux points de fusion des polyesters aliphatiques démontre l'importance du groupement p. phénylène dans l'établissement des propriétés polymériques. En considérant d'autres polymères de structure différente, mais contenant également le groupement p. phénylène, on constate que son influence est indépendant des groupes polaires qui pourraient être présents. L'examen aux rayons-X de la structure des cristallites du téréphtalate de polyéthylène et d'autres substances semblables ne révèle pas la présence de fortes forces intermoléculaires.

De l'étude de co-polyesters, à base de téréphthalate de polyéthylène et d'acides dibasiques aliphatiques, on voit que le point de fusion de composés, contenant plus de 40 moles pour cent de téréphtalate de polyéthylène est essentiellement indépendant de la nature de l'acide dibasique aliphatique utilisé. La relation de Flory concernant le point de fusion des cristallites et la fraction molaire des unités formant ces cristallites indique un accord remarquable avec les résultats obtenus. La chaleur calculée de fusion latente du téréphtalate de polyéthylène se rapproche étroitement de la chaleur de fusion latente des polyesters aliphatiques correspondants, et ceci suggère que le point de fusion élevé, provoqué par la présence du lien p. phénylène est dû à la rigidité de la chaîne, plutot qu'à l'attraction intermoléculaire.

Cette rigidité répond aux températures de transition de second ordre de tels polyesters. Il est montré que la température de transition de second ordre est une fonction linéaire du nombre de liaisons p. phénylène présentes par longueur de chaîne unitaire. Le groupement p. phénylène diminue les possibilités de changement de configuration pour un logueur de chaîne déterminée, ce qui rend compte de la faible entropie de cristallisation et du point de fusion élevé du téréphtalate de polyéthylène.

L'isomorphisme des polyamides linéaires, contenant des groupements adipoyle et téréphtaloyle, est mise en évidence. L'absence d'isomorphisme dans les copolymères adipate/téréphtalate de polyéthylène est attribuée à la faiblesse des forces intermoléculaires.

Zusammenfassung

Der hohe Kristallit-Schmelzpunkt von Polyäthylen-Terephtalat (Terylen) im Vergleich mit dem Schmelzpunkt aliphatischer Polyester betont die Bedeutung der *p*-Phenylen-Bindung als wichtiger, die Polymer-Eigenschaften bestimmender Faktor. Eine Betrachtung anderer Polymerstrukturen, die die *p*-Phenylen-Bindung enthalten, zeigt, dass ihr Einfluss unabhängig von allen etwa vorhandenen polaren Gruppen ist. Röntgenuntersuchung der Krystallitstruktur von Polyäthylen-Terephtalat und verwandten Substanzen zeigt keine Anzeichen von starken intermolekularen Kräften.

In einer Untersuchung von Copolyestern, die aus Polyäthylen-Terephtalat und aliphatischen zweibasischen Säuren aufgebaut sind, wird gezeigt, dass der Schmelzpunkt von mehr als 40 mol Prozent Äthylen-Terephtalat enthaltenden Verbindungen im wesentlichen von der verwendeten aliphatischen zweibasischen Säure unabhängig ist. Die Flory-Beziehung zwischen Krystallit-Schmelzpunkt und Molekularanteil der die Krystallite bildenten Einheiten zeigt recht gute Übereinstimmung mit den erhaltenen Resultaten. Die berechnete latente Schmelzwärme von Polyäthylen-Terephtalat nähert sich der von dem entsprechenden aliphatischen Polyester stark. Dies läst annehmen, dass der hohe Schmelzpunkt, der durch die *p*-Phenylen-Bindung bewirkt wird, eher durch Starrheit der Kette als durch starke Anziehung zwischen den Ketten hervorgerufen wird.

Diese Starrheit ist mit den Umwandlungstemperaturen zweiter Ordnung solcher Polyester vereinbar. Es wird gezeigt, dass die Umwandlungstemperaturen zweiter Ordnung eine lineare Funktion der Zahl der *p*-Phenylen-Bindungen pro Kettenlänge-Einheit ist. Die *p*-Phenylen-Bindung reduziert die Möglichkeiten eines Formwechsels,

der für eine gegebene Kettenlänge möglich ist, und ist so für die niedrige Krystallisationsentropie und den hohen Schmelzpunkt von Polyäthylen-Terephtalat verantwortlich.

Das Vorhandensein von Isomorphismus von Adipyl- und Terephthalylbindungen in linearen Polyamiden wird gezeigt. Die Abwesenheit von Isomorphismus in Polyäthylen-Adipat/Terephthalat-Copolymeren wird der Schwäche der Kräfte zwischen den Ketten zugeschrieben.

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