499. *Structure–Property Relationships in Polyethylene Terephthalate Co-polyesters. Part II.* Second-order Transition Temperatures.*

By O. B. Edgar.

The application of the penetrometer technique, described in Part I,* to quenched polymers provides a new method for the measurement of second-order transition temperatures. On application of this method to co-polyesters of polyethylene terephthalate containing as the modifying component varying proportions of the polymethylenedicarboxylic acids the second-order transition temperature was found to be a linear function of the number of *p*-phenylene groups per 100 aliphatic chain atoms. Anomalies were observed when the modifying component was either 1 : 2-propylene glycol or diphenyl-4 : 4′-dicarboxylic acid. It is suggested that the *p*-phenylene groups have little effect on inter-chain forces but cause a marked increase in chain stiffness by reducing the possibilities of change of shape available to a given length of chain. This stiffening effect also accounts for the low entropy of crystallisation and consequent high melting point of polyethylene terephthalate.

The second-order transition temperature of a polymer is generally measured by studying the variation with temperature of some primary property of the polymer such as specific volume, heat capacity, or refractive index. The transition point is then indicated by a fairly sharp change in the slope of the property–temperature curve, *e.g.*, a sudden change

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* Part I, preceding paper

in the coefficient of expansion. The actual value obtained varies slightly according to the particular property chosen and to the time scale of the experiment, but such variations are usually small. Although there may be some ambiguity about the exact value of the transition point, yet it certainly indicates a temperature region in which the polymer properties undergo marked changes. For instance, below the transition range an amorphous polymer is hard, glassy, and often brittle, whereas above it, it becomes first a plastic and then at higher temperatures either a liquid or a rubber according to molecular weight. If crystallisation is possible this process will also commence a little way above the transition point. A comprehensive review of second-order transition phenomena and the theories associated with them has been made by Boyer and Spencer (" Advances in Colloid Science," Vol. II, Interscience Publishers, Inc., New York, 1946).

Polyethylene terephthalate differs from the aliphatic polyesters, not only in melting point, as discussed in Part I,* but also in having a much higher second-order transition temperature. Thus on rapid quenching of the molten polymer to room temperature it can be obtained in a transparent, amorphous condition, softening and beginning to crystallise slowly at 80—90°. In order to observe this type of behaviour with polyethylene adipate it is necessary to quench the molten polymer in a bath at —80° or below. Many of the co-polymers of polyethylene terephthalate, in which various proportions of the terephthalic acid were replaced by aliphatic dibasic acids, had transition points below room temperature, and it was impossible to make measurements on them by Kolb and Izard's dilatometric technique (*J. Appl. Phys.*, 1949, **20**, 564). Consequently, a method had to be employed which allowed the transition point to be observed immediately after quenching of the sample, before crystallisation set in.

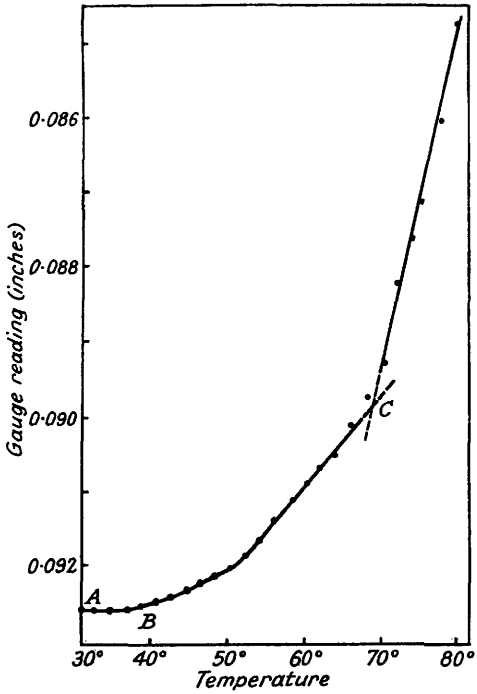


FIG. 1. *Penetrometer curve for amorphous polyethylene terephthalate.*

In Part I, the use of a penetrometer for the measurement of crystallite melting points was described. Further development of this method by F. D. Hartley and F. W. Lord in these laboratories has led to a technique whereby the apparatus can be used to measure second-order transition temperatures. In general outline the method is to plunge a small tray containing molten polymer into a silicone oil-bath cooled to at least 30° below the expected transition temperature. The foot of the loaded penetrometer is immediately placed on the quenched sample, and the bath allowed to become warm. As the bath temperature enters the transition range some flow commences and the penetration–temperature curve (Fig. 1), originally horizontal (*A*—*B*), shows a gradual curve upwards. At a definite reproducible temperature, however, the rate of penetration suddenly increases, giving a discontinuity (*C*) in the curve. In many cases further penetration was prevented a few degrees above *C* by the onset of crystallisation. With amorphous polyethylene terephthalate itself this discontinuity always occurred in the region 67—69°, which is in good agreement with the second-order transition temperature measured by the dilatometric method, both in these laboratories and by Kolb and Izard (*loc. cit.*). There is therefore some justification for regarding the discontinuity *C* in the temperature–deformation curves of other polymers as the second-order transition point.

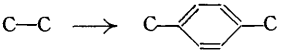
This method has been applied to the polyethylene terephthalate co-polymers containing, as second components, oxalic, succinic, glutaric, adipic, and sebacic acids, diphenyl-4 : 4′-dicarboxylic acid, and propane-1 : 2-diol, with the results presented in the table. Polyethylene sebacate itself could not be quenched, and crystallised in the bath at −80°. This also occurred with all co-polymers containing more than 40 mol.-% of diphenyl-4 : 4′-dicarboxylic acid. The reproducibility of transition points above room temperature was within ±1°, but worsened to ±5° for the very low transition points. There may also be errors up to several units % in the compositions of the polymers due to the preparative conditions, as indicated in Part I (*loc. cit.*).

Second-order transition temperatures of polyethylene terephthalate co-polymers.

Mol.-fraction of 2nd component	Second-order transition temperature						
	Oxalic acid	Succinic acid	Glutaric acid	Adipic acid	Sebacic acid	Propylene glycol	Diphenyldi-carboxylic acid
0·0	69°	69°	69°	69°	69°	69°	69°
0·1	—	—	—	55	51·5	46	90
0·2	58	38	39	36·5	23	—	87·5
0·25	36	35·5	27	23	—	—	—
0·3	—	28	23·5	16·5	5·5	47·5	90·5
0·35	—	—	—	5	−4	—	—
0·4	—	—	1·5	−3	−17	52	84·5
0·5	—	—	—	−18	−23	52·5	—
0·6	—	—	—	−27	−32	—	—
0·7	—	—	—	—	−47	61	—
0·8	—	—	—	—	−56	—	—
0·9	—	—	—	−57	−74	—	—
1·0	—	—	—	−68	(< −80)	68	—

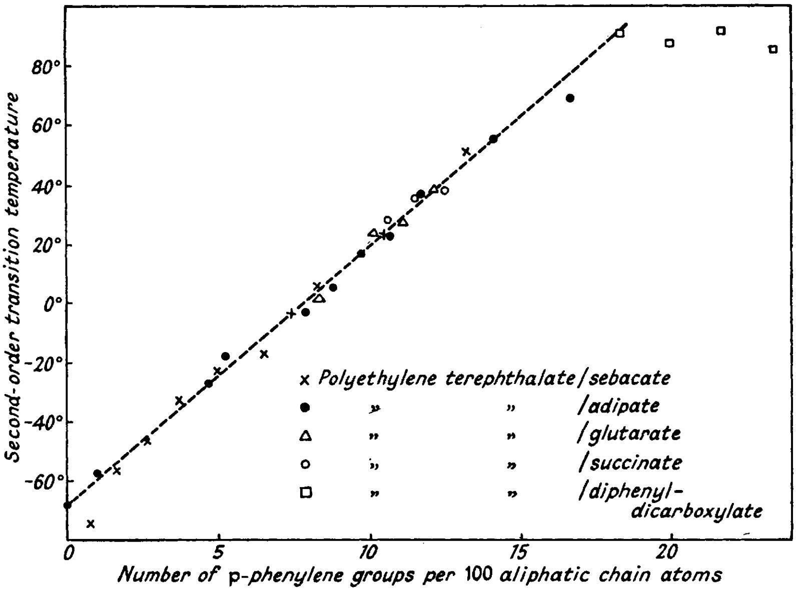
Inspection of the table shows immediately that the second-order transition temperature, unlike the crystallite melting point, is not simply a function of the molar proportions of the constituents in the co-polymer but depends significantly on the nature of the second component. In considering the co-polymers containing the aliphatic dibasic acid residues, two trends are apparent. The second-order transition point is lowered when either (*a*) the molar proportion of the aliphatic component is increased or (*b*) at any one molar composition the chain length of the aliphatic component is increased. It is clear, then, that in the polyethylene terephthalate co-polymers, the second-order transition temperature is determined by the relative amount of aromatic and aliphatic material present, irrespective of whether the latter be present in many short segments (*e.g.*, as succinate residues) or fewer longer sections (*e.g.*, sebacate residues).

The second-order transition temperature of a polymer is generally regarded as a measure of the flexibility of the chain molecules : the more flexible the chains, the lower the transition point. Thus the aliphatic polyesters, which are believed to have very flexible chains, have second-order transition points of the order of —70° (*i.e.*, in the same region as natural rubber). The increase of second-order transition temperature on introduction of *p*-phenylene groups into polyester chains may, therefore, be due to a stiffening effect of those groups, which may be accounted for in the following way. 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 groups. For each group this can be imagined to occur by the opening of a C–C bond and the insertion of the p-phenylene group, thus



If the average mass per bond in the aliphatic polyester is m and the mass of the p-phenylene group is M, then the mass of the segment is increased from $100m$ to $100m + NM$. Owing to the linearity of the p-phenylene groups, however, their presence does not increase the number of configurations which the segment can assume (the orientation of the phenylene groups about their axes being ignored). 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 $(100m + NM)/100m = 1 + MN/100m$. Putting $M = 76$ (for C_6H_4) and $m = 17{\cdot}2$ (the molecular weight of the ethylene adipate repeat unit divided by the number of chain atoms per unit), we have

FIG. 2. *Variation of second-order transition temperature with concentration of* p-*phenylene groups.*



$$\text{Stiffness factor} = 1 + 0{\cdot}044N \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

In Fig. 2 the second-order transition temperatures (T_g) of the co-polyesters are plotted against N (data for the co-polymers containing propylene glycol could not be included, since in that series N is a constant).

It is clear that the second-order transition temperature is itself a linear function of N, for values of N up to 16·67 (for polyethylene terephthalate itself), though the co-polymers containing diphenyl-4 : 4′-dicarboxylic acid, which have higher values of N, are anomalous in this respect. The straight line drawn in Fig. 2 has the equation

$$T_g = (8{\cdot}7N - 68)^\circ\,\text{C} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

which can be written in the form

$$T_g = T_0(1 + 0{\cdot}042N)^\circ\,\text{K} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2a)$$

where $T_0 = 205^\circ$ K, the second-order transition temperature of polyethylene adipate. The factor $1 + 0{\cdot}042N$ is in close agreement with the "stiffness factor" of equation (1), which strongly suggests that the second-order transition temperature is directly proportional to the mass of polymer per chain bond. (In the foregoing argument it was assumed that chain flexibility was determined by the number of chain bonds in unit mass of chain. This was convenient in that the masses of the various units in the chain are accurately known constants. It may be, however, that a theoretical examination would show that units of either volume or length would be preferable. Calculations of the " stiffness factor " by means of known bond lengths and molar volumes, which are less reliable than molecular weights, gave equally close agreement with experiment.)

According to this treatment of the experimental data, all purely aliphatic saturated chains should be equally flexible. The small differences in the second-order transition temperatures of the various aliphatic polyesters, polythene, and the rubbers indicate that this is not so, owing either to inter- or to intra-chain effects or to both. Such differences, however, are clearly of minor importance in comparison with the effect on flexibility of the *p*-phenylene groups.

A further consequence of equation (2) is that the use of diphenyl-4 : 4′-dicarboxylic acid as the second component in polyethylene terephthalate co-polymers should lead to an elevation of the transition point. This was realised with the 90/10 co-polymer, but increased proportions of diphenyldicarboxylic acid failed to raise the transition temperature above 90°. This may be due to a molecular-weight effect. In preparing these co-polymers, the polymerisation was carried out until the melt viscosity was too high for stirring with ordinary laboratory equipment, so it is possible that with these highly rigid chain polymers the maximum melt viscosity was obtained when the molecular weight was still low. Thus the series may represent a series of descending molecular weight, which would account for the approximate constancy of the transition point in that series at 90°.

In the propylene glycol series of co-polymers, the chain skeleton is the same as in polyethylene terephthalate throughout the series, the various members of the series differing only in the number of lateral methyl groups. Therefore, if equation (2) is of general application, the second-order transition temperature should remain constant in this series. This is not so, though the range of the variation of the transition point is much smaller than in the other co-polymer series. The first 10 mol.% of propylene glycol produces a remarkable fall in the transition point (about 24°), after which it rises slowly again, almost linearly, to 68° for polypropylene terephthalate. It seems likely that these variations are due to inter- rather than intra-molecular relationships. Thus the initial drop may be due to the lateral methyl groups increasing the inter-chain spacing and so reducing cohesion, and the subsequent slow rise to 68° might be due to steric hindrance between the methyl groups of adjacent chains (as, *e.g.*, in polystyrene the interaction of pendant phenyl groups leads to a high T_g).

The importance of such inter-chain effects is thus emphasised, and it becomes clear that the simple relation expressed in equation (2) was only apparent because the inter-chain forces in amorphous polyethylene terephthalate are very similar in magnitude to those of the aliphatic polyesters. As with the heats of crystallisation of polyesters (Part I, *loc. cit.*), therefore, there is again no evidence of any strong interaction between the phenylene groups of adjacent chains.

In Part I it was shown that the high melting point of polyethylene terephthalate was due to chain stiffness (*i.e.*, low entropy of fusion) rather than to an abnormally high heat of fusion. Since the second-order transition temperature is also high for the same reason, one might expect to find some quantitative relation between the two temperatures. In the following table the melting point and second-order transition temperature of polyethylene terephthalate are compared with those of polyethylene adipate, its closest aliphatic analogue. It will be seen that the replacement of the adipate by the terephthalate radical raises both the melting point and the transition point by the same factor, *viz.*, 1·69, which is very close to that calculated from equation (1).

	Polyethylene terephthalate	Polyethylene adipate	Ratio
M. p., ° K.	540	320	1·69
Transition point, ° K.	342	203	1·68

For polyethylene terephthalate, which has six aliphatic chain atoms between *p*-phenylene groups, $N = 100/6$, which gives the theoretical stiffening factor the value 1·74. Therefore, providing that the heats of fusion of the two polymers are actually equal, it seems that the entropy of fusion is inversely proportional to the number of chain bonds per repeating unit (*i.e.*, bonds about which rotation leading to change of shape can occur).

EXPERIMENTAL

Preparation of the Co-polymers.—The co-polymers containing adipic and sebacic acids were prepared as in Part I. For those containing glutaric, succinic, and oxalic acids it was found more convenient to heat the aliphatic acid directly with the bis-2-hydroxyethyl terephthalate at 200° for 5 hours. When the esterification was complete the resultant low polymer was further condensed by raising the temperature to 260°, reducing the pressure slowly to 0·3 mm. Hg, and stirring under these conditions for 6 hours.

Co-polymers containing propane-1 : 2-diol were prepared by first making low-molecular weight polymers of ethylene and 1-methylethylene terephthalate, and later further polymerising a mixture of the two in the required ratio by stirring at 270°/0·5 mm. Hg for 6 hours. This technique reduced to a minimum the risk of composition errors due to one of the glycols being more rapidly eliminated than the other. Ethylene terephthalate " monomer " was prepared as described in Part I, and converted into the low polymer by further removal of ethylene glycol at 260°/10 mm. for 1 hour. The 1-methylethylene terephthalate low polymer was prepared in a similar manner.

Co-polymers containing diphenyl-4 : 4′-dicarboxylic acid were prepared by stirring at 260°/0·5 mm. for 6 hours a mixture of ethylene terephthalate and ethylene diphenyl-4 : 4′-dicarboxylate " monomers " (*i.e.*, the bis-2-hydroxyethyl esters) in the required ratios. The latter " monomer " was prepared as follows : 59·6 G. of diethyl diphenyl-4 : 4′-dicarboxylate, 31·0 g. of ethylene glycol, and 0·02 g. of litharge were heated in an aniline vapour-bath for 7 hours and in an ethylene glycol vapour-bath for 3 hours, distillation then ceasing. When cold, the residual " monomer " was a white, microcrystalline mass; the yield was 68·0 g. (assumed to be equivalent to 0·2 mol. of bis-2-hydroxyethyl diphenyl-4 : 4′-dicarboxylate).

Measurement of Second-order Transition Temperatures.—The penetrometer was essentially the same as that described for the measurement of m. p.s (Part I), but the load on the spindle was increased to give a total load of 1000 g. Manual operation of the screw-type micrometer was found to be unsuitable, leading to erratic readings, and much smoother results were obtained by using a dial gauge micrometer reading to 0·0001″.

A small tray, 0·5″ square and 0·25″ deep, was made out of aluminium foil and placed on a copper block heated by a micro-burner. Sufficient polymer to half-fill the tray was melted in it, with a stream of nitrogen being directed on the block to avoid oxidation. When the molten sample was bubble-free, the tray was immediately plunged into the silicone oil-bath of the penetrometer, which had previously been cooled to about 30° below the expected transition point. Whilst the sample was still soft, the bottom of the spindle was allowed to rest lightly on the surface of the polymer, to ensure even contact. When the sample had attained the temperature of the bath, the full load of the penetrometer was allowed to bear on it, and the bath temperature was raised at the rate of 1°/min. The gauge readings, taken at 2° intervals, were plotted against temperature, giving the type of curve shown in Fig. 1.

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