

Transitions and Relaxations of Linear Polyesters Related to Poly(ethylene Terephthalate). I. Melting

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Synopsis

Observations obtained by other techniques were confirmed by DSC analyses. As the length of the methylene chain increased, T_m decreased, and crystallinity, heat capacity, and heat of fusion increased. The T_m and crystallinity of the isophthalate esters were lower than for the corresponding terephthalate esters. The values for an odd-numbered methylene sequence were lower than for the adjacent even-numbered members. A model was used to calculate the heat of fusion of theoretically 100% crystalline poly(hexamethylene isophthalate) and poly(decamethylene isophthalate).

INTRODUCTION

A study of molecular motions in polymers at various temperatures is important for an understanding of mechanical properties. One approach is to find transition temperatures, such as the melting points (T_m), which are characteristic of the crystalline regions. These are then interpreted in terms of motions of moieties of the molecule.¹ The purpose of this paper is to record relationships between chemical structure and transition or relaxation temperatures for homologous series of poly(methylene terephthalates), poly(methylene isophthalates), and equimolar random copolyesters of the two acids. The three series, except for $-(CH_2)_5-$, were limited to even numbers of methylene groups in the glycol portion of the polyesters. The experimental method involved measurements of specific heats and melting points using a dynamic calorimeter.

By far the most data are available for poly(ethylene terephthalate).² This includes heat capacities³ and some measurements using the differential scanning calorimeter. Heat capacity studies have been used to detect and explain transitions and relaxations of polymers.⁴

For the homologous series of polyesters, it has been reported^{5,6,7} that the melting points of the ethylene glycol-based polyesters are the highest. As the methylene chain length increases, the melting point passes through a minimum and increases to approach that of polyethylene. The melting points of the isophthalate-based polyesters are lower than for the corresponding

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terephthalate-based copolymers. Crystallinity could be reduced or eliminated for the lower members of the terephthalate series by quenching from the melt,^{8,9} since the rate of crystallization is low compared to that of the higher members of the terephthalate series and the members of the isophthalate series. Polymers with odd numbers of methylene groups melt at lower temperatures than those with even numbers. The heat of fusion of the isophthalate-based polyesters was higher than for the corresponding terephthalate ester⁷ crystallized from the melt. The degrees of crystallinity of the two series pass through minima at lower methylene chain lengths than do the melting points.

EXPERIMENTAL

Chemicals

Poly(tetramethylene terephthalate) Tenite Polyterephthalate (Eastman) was used as obtained.

Terephthaloyl chloride (Eastman) was purified by dissolving in hot heptane, filtering the mixture through a fluted filter to remove the insoluble terephthalic acid, and cooling the solution to permit crystallization. The crystals were dried at 40°C. Isophthaloyl chloride (Eastman) was purified the same way except that dry hexane was used. 1,10-Decanediol (Eastman), 1,6-hexanediol (Baker), and 1,5-pentanediol (Baker) were used without purification. 1,4-Butanediol (Baker) was purified by vacuum distillation at 10 mm Hg pressure, boiling point 120°C.

Polymerization

The polyesters were prepared by irreversible polycondensation in the melt^{10,11,12} and can be illustrated by the procedure used for poly(pentamethylene terephthalate). The other polyesters were prepared with changes in the experimental conditions in keeping with their respective melting and glass transition temperatures, i.e., the highest temperature was limited to 50–70°C above the expected T_m . The copolymers were synthesized using 50 mole-% of the glycol, 25 mole-% terephthaloyl chloride, and 25 mole-% isophthaloyl chloride. Polymerization times were similar in all cases.

To a 500-ml three-necked flask with a nitrogen gas inlet, a mechanical stirrer, and an exit tube for nitrogen and hydrogen chloride gases was added 81.20 g (0.40 mole) terephthaloyl chloride. This was heated to 82–84°C (melted) and 41.66 g (0.40 mole) 1,5-pentanediol in three 14-g portions added at approximately 10-min intervals, i.e., when hydrogen chloride evolution had slowed. The temperature increased to 130°C and was raised to and kept at 145–155°C for 1 hr, then to 170°C for 1 hr, the last 10 min of which was at 0.5–1.0 mm Hg pressure. The contents were cooled to 70°C for one day and broken into chips for molding. Melting points are listed in Table I.

The samples were annealed usually at 60–65°C for a week before testing. This was high enough for the isophthalate series and the higher homologues of the terephthalate series, as well as being suitable for the lower terephthalate homologues which crystallize readily, if slowly.

The intrinsic viscosity, as a measure of the viscosity-average molecular

TABLE I
 Polyesters and Their Characterization

Polyester	Code	[η]	$T_m, ^\circ\text{C}$	
			Exptl.	Literature ^{5,6,7}
Poly(ethylene terephthalate)	2GT			256, 264, 265
Poly(tetramethylene terephthalate)	4GT	1.4 ^c	226	222–223, 232
Poly(pentamethylene terephthalate)	5GT		130–135	134–140
Poly(hexamethylene terephthalate)	6GT	1.0	147, 152	148–154
Poly(decamethylene terephthalate)	10GT	0.91	127	123–127
Poly(ethylene isophthalate)	2GI			103–108, 240
Poly(tetramethylene isophthalate)	4GI	0.61	141	88–94, 152
Poly(pentamethylene isophthalate)	5GI		amorph.	76–80, amorph.
Poly(hexamethylene isophthalate)	6GI	0.70	soft. 90–95 95, 140	75–80, amorph. 75–80, 140
Poly(decamethylene isophthalate)	10GI ^a	0.72	44	34–36
Poly(tetramethylene terephthalate-co-isophthalate)	4GTCoI	0.65		
Poly(hexamethylene terephthalate-co-isophthalate)	6GTCoI	0.52 ^b		
Poly(decamethylene terephthalate-co-isophthalate)	10GTCoI	0.71		

^a Crystallized from methylene dichloride before annealing.

^b Annealed at 23°C.

^c [η] Determined in 60:40 phenol:*sym*-tetrachloroethane solvent.

weight, was determined at 25°C using a calibrated Ostwald viscometer, and the data are reported (Table I) as intrinsic viscosities since conversion to viscosity-average molecular weights was not possible in every case and the relative values sufficed for comparative purposes. The solvent was usually methylene dichloride.

Preparation of Films

The samples were dried in a vacuum oven for 3 hr at 120°C in the case of poly(tetramethylene terephthalate) and kept in a desiccator until used. Films were molded at 260°C in a laboratory press between sheets of aluminum foil coated with release agent. After allowing the sample to heat for 2–3 min, the pressure was raised to 1000 psi for 1 min and then to 5000 psi for 1 min. The samples were then cooled in various ways as described later but typically quenched by dropping the sample in the foil and the aluminum back-up plates into ice water, or annealed at 85°C for 5 hr in the foil, or annealed at 170°C for 5 hr in the foil. These procedures were varied as to time and temperature to obtain useful films from the other polymers.

Differential Thermal Analysis

Thermal analyses were performed with a du Pont Thermal Analyzer Type 990 with a standard differential scanning calorimeter (DSC) cell. For measurements of the specific heat, the cell was checked for calibration coefficient and standardized using sapphire. For determination of heats of fusion, the cell was checked for calibration coefficient and standardized using the heats of fusion of tin and indium. Sample weights were 10–30 mg, and the samples were crease free and were encapsulated immediately after preparation to minimize water absorption.

The heating rate for the DSC cell was set at 10°C/min for all measurements. Sensitivity, time base, and temperature range depended on the mass of the sample and temperature range. They were set by trial and error so that a clear thermogram and large peak area could be obtained. Liquid nitrogen was used to reduce the temperature to –160°C.

A method of putting the samples in the aluminum pans was devised. A small sample was placed in an empty pan and melted under a nitrogen atmosphere. Then a lid was crimped on by the press. A uniform thickness of the sample was obtained since the molten polymer flowed and a flat bottom was obtained. This was important in assuring reproducibility and accuracy of measurements. Otherwise, the thin aluminum pans would wrinkle when the sample was pressed.

RESULTS AND DISCUSSION

Data were obtained on T_m , degree of crystallinity, heat capacity, and heat of fusion using the DSC technique. The thermograms for the terephthalate series were similar, differing only in the location of T_m . The thermograms of poly(tetramethylene terephthalate), poly(hexamethylene terephthalate), and poly(decamethylene terephthalate) were obtained, and the T_m values were as follows: 4GT, 226°C; 6GT, 147°C; and 10GT, 127°C. The thermograms for the isophthalate series differed from those of the terephthalates. A small distinct peak was observed 30–40°C lower than the main melting transition peak which is given in Table I.

The heat of fusion and the crystallinity were calculated by measuring the area of the large peak. The smaller peak was only 5–10% of the area of the main peak and may be due to melting of metastable crystals, reorganization, or recrystallization. Multiple melting behavior¹³ was not found for either the isophthalate or terephthalate series. The data are in Table II.

Some crystallization during the experiment may have taken place when testing the terephthalate series. This is illustrated by repeated measurements on 6GT annealed at 60–65°C. The first scan shows only the main peak, i.e., only the melting peak. The second and third scans done after the sample was allowed to cool in the DSC cell before retesting showed a small second peak, presumably because the sample was not adequately annealed. The fourth scan was obtained using a sample quenched in liquid nitrogen immediately after the third scan was completed. A main peak only was observed even though the quenched sample was initially amorphous, suggesting that crystallization took place during the experiment, possibly over the tem-

TABLE II
 Data at the Melting Transition

Sample	$(\Delta H_f)_{100\%}$ calculated, cal/mol	(ΔH_f) experimental, cal/mole	Crystallinity calculated, %	Temp. above annealed temp., °C
4GT	7600	2300	30	19
6GT	8300	3400	41	40
10GT	10400, 11600	4300	41	64
4GI	10100	2351	23	37
6GI	11400, 10800	2473, 1400	22, 13	59
10GI	12000, 12900	1944, 2600 ^a	16, 20	40
4GTCoI	—	1967	—	25
6GTCoI	—	1686	—	56
10GTCoI	—	1039	—	71

^a Annealed at room temperature (25°C).

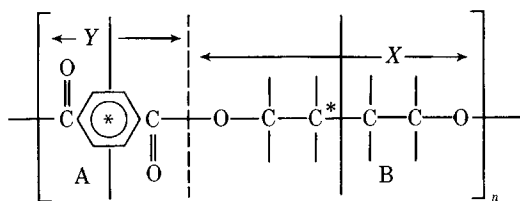
perature range between T_g and T_m . Repeating the scan after cooling the sample in the DSC cell resulted in the appearance of the small second peak again. These changes were observed also for 4GT and 10GT. The isophthalate series and the copolyester series did not seem to crystallize during the time of the experiment since no fusion peak was observed for samples quenched in liquid nitrogen.

An experiment on isothermal crystallization was carried out for the terephthalate series. The method consists of melting the samples and cooling them at 1°C/min in the DSC cell. The half-life ($t_{1/2}$) is measured by dilatometry usually, but it has been found that the $t_{1/2}$ obtained using the DSC cell is similar.¹⁴ The $t_{1/2}$ results obtained were: 4GT, 11.1 min; 6GT, 5.4 min; and 10GT, 4.7 min. The larger the glycol residue, the shorter the $t_{1/2}$. This shows that nucleation or crystallization stops sooner for the longer sequence-length polyesters. It is attributed to the longer sequence length being more difficult to crystallize into an ordered system. One would expect this since entanglements are more likely and the ability of the longer chain to acquire the trans configuration required for crystallization is reduced. Intermolecular forces are reduced for the higher homologues,¹⁵ thereby reducing the ease of crystallization. The isophthalate series and copolyester series do not have a $t_{1/2}$ within an experimental time of 1 hr. Crystallization of these polyesters takes much longer.

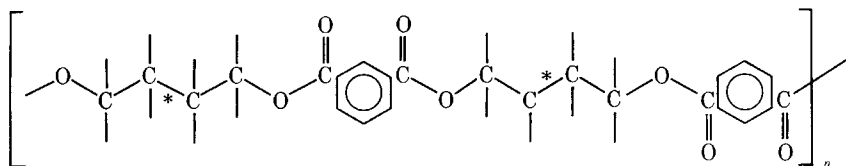
The degree of crystallinity of the polyesters was found from the ratio of the experimental heat capacity to the heat capacity for 100% crystallinity. Literature values of a 100% crystalline 4GT, 6GT, and 10GT are available.¹⁶ Except for 4GI, no literature values were found for the other samples. Conix⁷ has found the heat of fusion of poly(tetramethylene terephthalate) to be 10,100 cal/mole of repeating unit by the diluent method.¹⁷

An attempt was made to build a model for the theoretical derivation of the heat of fusion of a 100% crystallizable unit of 6GI and 10GI and the copolyesters. The degree of crystallinity of the polyesters must be known because, in comparing polymers of different chemical structure, it is necessary to know that all the samples are unoriented and have approximately the same degree of crystallinity.

The model is based on Kirshenbaum's approximation scheme¹⁶ and considers the change in entropy associated with the latent volume change upon melting¹⁸; the change in entropy due to the increase in the number of configurations a macromolecule can assume on passing from the solid to liquid state; T_m , the crystalline melting point; the heat and entropy of fusion (per mole of repeating unit), respectively, of a 100% crystalline polymer; the number of C—C linkages in the skeletal chain per repeating unit; the number of other bonds in the skeletal chain per repeating unit; and the number of stable conformations these bonds can assume with respect to the preceding bond. The last-mentioned number is 2 for —CH₂—O and the *p*-phenylene linkages. The change in entropy for the latent volume change on melting for the terephthalate and isophthalate series is assigned the value of 1, since it equals approximately 0.18 ΔV_m entropy units and ΔV_m , the volume change from solid to liquid, for 2GT is 11.5.¹⁹ Thus, the entropy change is at most 2 e.u. A calculation for 4GT yielded 15.6 entropy units, observed 15.1.⁷ To devise an empirical scheme for the isophthalate series, consider the structure



Two centers of symmetry are found in the terephthalate series, and the entropy change is due to two components, A and B. Therefore, the total entropy contributions for the terephthalate series are $Y + X$ e.u. For the isophthalate series, portion B of the repeating unit is the same as for the terephthalate series since a center of symmetry is located there:



The asterisks indicate centers of symmetry over two repeating units of 4GI. There is no center of symmetry in the *m*-phenylene group because when the group flips over, the symmetry of the chain unit is altered. Therefore, geometric isomerism exists for portion A of the skeletal chain. Since the *m*-phenylene group has twice the number of conformations of the *p*-phenylene group, the entropy contribution from portion A is twice that for the terephthalate series. Total entropy units for the isophthalate series is then $2Y + X$ e.u. If Y and X are assigned one arbitrary e.u., then 4GT has 2 e.u. and 4GI has 3 e.u. From this can be calculated an entropy change of 22.9 e.u. compared with the observed value of 23.7 e.u. for 4GI.⁷ These two pairs in agreement were accepted as sufficient grounds for trying to estimate other values.

The contributions of the increased entropy on melting is borne entirely by the *para*-versus-*meta* phenylene isomerism. Using the data available, the value for 10GI can be approximated. The entropy change was calculated to

be 39.4 e.u. and the heat of fusion, 12,000 cal/mole. Similarly, the value for 6GI was calculated to be 11,000 cal/mole.

Table II gives the values of ΔH_u for 100% crystalline samples of the polyesters involved in the experiment. A hypothetical scheme was devised for the copolyesters. Since there are four sequences available for the copolyesters, the heats of fusion were estimated empirically, but since experiments were not used to prove these models, they are not considered exact enough to record. However, since the model is adequate for 2GI and 4GI, the error involved in applying it to 6GI and 10GI should not be large enough to invalidate the estimation of the degree of crystallinity of the polymers particularly since all calculations were based on observed large peaks of carefully annealed samples.

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