

Copolyester Studies. I. Preparation and Characterization of Tetramethylene Terephthalate-Tetramethylene Sebacate Copolymers

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Synopsis

Tetramethylene terephthalate-tetramethylene sebacate copolymers containing up to 20 mol % sebacate have been prepared and characterized. Molecular weights and distributions have been evaluated using viscometry and gel-permeation chromatography. Compositions have been established by NMR spectroscopy. Thermal properties have been studied by differential scanning calorimetry and dynamic mechanical methods. Melting and glass-transition temperatures and moduli are discussed in terms of the structural differences, particularly the effect of composition on chain flexibility. Density and thermal methods of crystallinity determination are critically discussed for these systems.

INTRODUCTION

The work reported in this paper forms part of a program of work in the Department on structure-property relationships in copolyester systems. Previous work has involved studies on poly(tetramethylene terephthalate) and its random block copolymers,¹ poly(hexamethylene terephthalate) and its random block copolymers,² and poly(ethylene adipate).^{3,4}

We now report studies on poly(tetramethylene terephthalate), 4GT, and its random copolymers containing tetramethylene sebacate units. Recently, 4GT has enjoyed commercial success as a molding material (Tenite, Eastman Kodak Co., and Deroton, I.C.I. Ltd.), and its properties have been extensively studied.⁵⁻⁸ It has been used as an engineering thermoplastic⁹ because of its excellent mechanical strength, chemical and corrosion resistance, and low moisture absorption.^{10,11} In addition, it has some limited use as a textile fiber.^{12,13}

The rapid crystallization rate of 4GT relative to poly(ethylene terephthalate), 2GT, makes 4GT an ideal molding material. Thus 4GT crystallizes even when quenched rapidly from the melt, whereas 2GT can be easily quenched to yield amorphous transparent films.⁵ It is reasonable, therefore, that copolymerization could reduce the crystallization rate and improve the properties of 4GT.

Apart from the work by Ueberreiter and Steiner¹⁴ on low-molecular-weight tetramethylene sebacate copolyesters and that by Weinberg,¹⁵ there is little information in the literature on random copolymers of 4GT. 4GT has, however, been extensively studied as the hard segment in polyester-polyether elastomers.¹⁶⁻²¹

In this study the effect of incorporating small amounts of tetramethylene sebacate (up to 20 mol %) into 4GT is reported. This composition range was chosen so that the useful properties of 4GT would be maintained at a suitable level.

EXPERIMENTAL

Materials

Butane-1,4-diol was supplied by BDH Ltd. and was purified by vacuum distillation (bp 90°C/0.1 mm of Hg), not more than one day prior to use. It showed no significant impurities when analyzed by gas-liquid chromatography. Dimethyl terephthalate was supplied by ICI and purified prior to use by vacuum distillation (bp 218°C, 0.5 mm Hg). Dimethyl sebacate was supplied by Eastman-Kodak Ltd and purified by vacuum distillation (bp 108°C, 0.1 mm Hg). The catalyst, tetra isopropyl *ortho* titanate was supplied by Eastman-Kodak and used as received. Succinic anhydride, 1-methyl naphthalene, 1,1',2,2'-tetrachloroethane, benzyl alcohol, and AR phenol were supplied by BDH Ltd., and with the exception of phenol, which was used as received, the materials were purified by vacuum distillation prior to use.

Polymerization

The polymers were prepared by standard melt-polymerization procedures²² from 1:2.2 molar ratios of various dimethyl ester mixtures with butane diol by heating the reactants together with catalyst (0.08% by weight on total reactant's weight) in an atmosphere of dry nitrogen ("white spot") (1) at 197°C/1 atm for 3 hr to eliminate methanol and (2) at 258°C/0.05 mm Hg for 2.5 hr to remove surplus butane diol and effect polymerization by ester interchange.

Molecular Weight Determination

The molecular weights of the 4GT homopolymer and the random copolymers were determined from the carboxyl endgroup contents found after succinoylation with succinic anhydride in distilled 1-methyl naphthalene under nitrogen at 197°C for 5 hr using a modification of the method of Conix.²³ The treated polymers were freed of excess reagent by precipitation from solution into methanol, and after intensive drying, weighed samples were titrated with a solution of potassium hydroxide in benzyl alcohol.

The intrinsic viscosities of the polymers were determined in a 40:60 w/w mixture of phenol and 1,1',2,2'-tetrachloroethane at 25°C and correlated with the values calculated from end-group analysis.

GPC analyses were carried out at RAPRA on a set of four 4 ft. \times $\frac{3}{8}$ -in. columns connected in series. These columns consisted of a Poragel column (pore size 200 Å) and three Styragel columns (pore sizes 2000–2500 Å, $1.5\text{--}5 \times 10^4$ Å, and $1.5\text{--}7.0 \times 10^5$ Å). Polymer solutions (0.2%) in *o*-chlorophenol containing Plastinox 2246 (0.025%) were passed through the column at 1 ml/min at 90°C. A standard polystyrene sample supplied by Waters Associates was used for calibration. The results obtained are shown in Table I.

Composition of the Copolymers

Composition was calculated from the initial weights of the dimethyl esters. However in order to confirm that loss of volatile components during preparation did not produce significant changes in composition, the composition of each

TABLE I
 Molecular Weight Characteristics of the Copolymers

Composition sebacate, mol %	M_n^a	$[\eta]_0$	M_n^b	M_w^b	M_w/M_n^b	M_n^c	M_w^c	M_w/M_n^c
0 ^d	17,680	0.64	26,520	48,440	1.83	29,850	53,240	1.78
5	16,890	0.64	22,530	46,160	2.05	25,520	50,830	1.99
10	21,520	0.81	28,980	77,330	2.67	32,500	83,420	2.57
15	18,160	0.77	32,570	65,450	2.01	36,310	71,070	1.96
20	20,430	0.77	22,380	48,560	2.17	25,350	53,360	2.11
100 ^e	—	0.74	20,430	42,490	2.08	—	—	—

^a From end-group analysis.

^b Calculated using a polystyrene calibration standard.

^c Calculated using the universal calibration equation (Ref. 24), assuming constants for 4GT are $K = 3.04 \times 10^{-4}$ and $\alpha = 0.77$ and for polystyrene are $K = 1.2 \times 10^{-4}$ and $\alpha = 0.70$.

^d 4GT homopolymer.

^e Poly(tetramethylene sebacate) 4G10 homopolymer.

system was determined by nmr spectroscopy. Spectra were obtained from polymers as 20% solutions in trifluoroacetic acid (spectroscopic grade B.D.H. Ltd.) using a Varian HA-100 spectrometer operating at 100 MHz/sec. Measurements were made at room temperature, and the signals were locked with the solvent. The relative intensities of the resonance peaks were determined by an electronic integration device, and 12 integrals were recorded.

Thermal Properties

Melting temperatures of the polymers were determined using Perkin-Elmer differential scanning calorimeters, models DSC1 and DSC2. Polymers were studied in the "as-prepared state" (cooled from the melt) and as quenched melt-pressed films, which were prepared from vacuum-dried (60°C, 1 mm Hg for 16 hr) polymer shavings (≈ 5 mg). The dried shavings were placed in the "window" of a thin metal "picture frame" sandwiched between two thin metal plates. Each plate was covered with a PTFE film (0.4 mm thick). The sandwich was placed in the mold at a temperature 25°C above the DSC2 melting temperature of "as-prepared material", and held under very slight pressure for 2 min. The pressure was raised to a nominal 1.5 tons, and this was maintained for a further minute. The pressure was then released, and the "sandwich" was immediately transferred to a bath of ice water.

Before use the polymer films were dried at room temperature at 1 mm Hg over phosphorus pentoxide. Samples (≈ 5 mg) were encapsulated in aluminum pans, and an empty pan acted as the inert reference material. Melting temperatures were determined using the DSC1 instrument at 16°C/min. Discs (≈ 5 mg) (0.3 mm thick and 6 mm diameter) cut from quenched, melt-pressed films were studied using the DSC2 instrument at 20°C/min under argon at a flow rate of 20 ml/min. High-purity tin and indium samples (Perkin Elmer Corp.) (mp 156.8 and 232°C) were used as temperature-calibration standards. Melting temperatures were also determined using a hot-stage polarizing microscope (HSPM) at a heating rate of approximately 3°C/min. The data obtained from such studies are reported in Table II.

TABLE II
Copolymer Melting Temperatures

Composition mol %	T_m , °C		
	DSC1 ^a	DSC2 ^b	HSPM ^a
0 (4GT)	224	222	232
5	215	215	221
10	208	208	214
15	200	199	209
20	190	190	199
100 (4G10)	65	65	66

^a Sample in "as-prepared state."

^b Quenched melt-pressed films.

Density Measurements

These were made using a density-gradient column prepared from degassed aqueous solutions of potassium iodide, which gave a linear density gradient between the limits of 1.20 and 1.39 g/cm³. The gradient was calibrated using insoluble, nonswelling floats of accurately known density. Measurements were made in accordance with the relevant British Standard.²⁶

Crystallinity Measurements

These were made by both density and thermal methods.^{25,27}

Glass-Transition Temperatures

Attempts were made to determine glass-transition temperatures using the DSC attachment of the Du Pont 900 differential thermal analyzer. Disk samples (\approx 5 mg) were prepared from quenched, melt-pressed films, and samples were also melted in the machine and quenched in liquid nitrogen. Samples were encapsulated in aluminium pans and subjected to a heating rate of 16°C/min. The results obtained are reported in Table III.

Glass-transition temperatures were also obtained using the Rheovibron direct-reading dynamic viscoelastometer, model DDVII, using a heating rate of 1°C/min. 4GT and copolymers containing up to 15 mol % sebacate were studied in the range from ambient temperature to 180°C. The 20% copolymer was studied from -40° to 180°C and 4G10 from -80°C to ambient. Samples (4 cm

TABLE III
DSC Glass-Transition Temperatures

Composition, mol % sebacate	Melt-pressed film	
	T_g , °C	% Cryst. ^a
0 (4GT)	46	6.7
5	43	6.4
10	41	9.6
15	37	3.0
20	29	0.7
100 (4G10)	-62	—

^a From density measurements.

$\times 0.45$ cm $\times 0.3$ mm thick) prepared from dried, quenched, melt-pressed films were subjected to an oscillating frequency of 3.5 cps. The results obtained for loss-maxima temperatures of the polymers are recorded in Table IV.

RESULTS AND DISCUSSION

The preparation proceeded smoothly to yield polymers of molecular weights sufficiently high to be suitable for spinning purposes and to give materials whose properties were independent of molecular weight.

The use of second-stage reaction times of 2.5 hr stemmed from preliminary studies that indicated that for all the systems the molecular weight rose to a maximum value and then fell as a result of the degradation rate exceeding propagation. In order to minimize degradation and maximize the molecular weight, a minimum time to give high-molecular-weight material was chosen. During some polymerizations the phenomenon of melt opacity was observed. This phenomenon has been reported by other workers^{15,28,29} and has been ascribed to phase separation in the systems studied. It appears that systems that show this behavior have a common feature, namely, the presence of poly(tetrahydrofuran). Although the 4GT system should not contain such units, it is of interest to note that butane diol readily dehydrates under the polymerization conditions to yield tetrahydrofuran^{30,31} and that tetrahydrofuran was found among the products when the first-stage distillate was subjected to gas-liquid chromatographic analysis.

Molecular Weight and Molecular Weight Distribution

If the logarithm of intrinsic viscosity is plotted against the logarithm of molecular weight obtained by end-group analysis, a linear relationship should be obtained. However, if the data given in Table I are treated in this manner, they show a marked degree of scatter. This can be ascribed to the difficulties associated with the end-group analysis method that make for lack of precision. With the 4GT system the limited solubility coupled with temperature sensitivity can result in precipitation of the polymer during titration, unless carefully controlled conditions are used. Molecular weights and distributions were also evaluated by gel-permeation chromatography (Table I). The data were obtained using a polystyrene-standard run under the same conditions, and they show that the polymers have molecular weights indicating that the properties will be independent of molecular weight. These values are not absolute, and it was not

TABLE IV
Loss-Maxima Temperatures

Composition, mol % sebacate	E''_{\max} , °C	$\tan \delta_{\max}$, °C	% Cryst. ^a
0 (4GT)	56	72	6.7
5	50	58	6.4
10	39	45	9.6
15	33.5	41	3.0
20	22	35	0.7
100 (4G10)	-44	-40	—

^a From density measurements.

possible to evaluate more absolute values using the universal calibration equation,²⁴ which requires the values of K and α in the Mark-Houwink equation for polystyrene (PS) and 4GT at 90°C in *o*-chlorophenol. These data are unknown, and use was made of the data for PS²⁴ and 2GT³² in *o*-chlorophenol at 25°C, leading to the values reported in Table I.

Such values, of course, are unlikely to hold for the range of materials studied, but the data indicate that the molecular weights are sufficiently high and that the distribution as recorded by the M_w/M_n ratio appears normal.³³

Copolymer Composition

During the first stage of polymerization, while methanol was being evolved, the loss from the melt of a small quantity of dimethyl terephthalate and dimethyl sebacate was observed. In order to establish composition, a nmr method was chosen because of its simplicity and ease of use, unlike more drastic hydrolytic and degradative procedures.³⁴⁻³⁷

The 100-MHz spectra obtained from 4GT, poly(tetramethylene sebacate), 4G10 and a typical copolymer are schematically represented in Figure 1 together with their structures. 4GT shows 3 sets of equivalent protons, 4G10 shows 5 sets of equivalent protons, and the copolymer shows the combined features of both. The chemical shift data together with its interpretation are given in Table V.

Since the area under the resonance peak is directly proportional to the number of protons producing the peak, this forms the basis for calculating the composition. Comparison was made of the total area due to aromatic and aliphatic protons, and this may be related to the theoretical aliphatic:aromatic ratio, which is given by $(8 + 16x)/4(1 - x)$, where x is the mole fraction of sebacate in the polymer, and 8, 16, and 4 correspond to the number of protons in the diol, sebacate, and aromatic segments, respectively. The results of such an analysis are shown in Table VI.

The results indicate that the method is accurate to $\pm 2\%$ for 4GT. The results for the copolymers suggest that they are of the same composition as the esters in the initial mixture, within experimental error, bearing in mind that the errors in measurement become greater the lower the sebacate content. Spectra were also run at 220 MHz, which allowed the resolution of peaks *f* and *g*, which coalesced at 100 MHz. In addition, an extra peak was observed in the case of the copolymer spectra. A peak was observed at $\delta = 1.91$, which increased in intensity as the amount of sebacate in the copolymer increased. This peak arises because of the structural situation shown in Figure 2. In 4GT each diol unit is flanked by a terephthalate unit, and this produces two types of methylenic proton signals. A similar situation obtains in 4G10, where each diol unit is flanked by sebacate units. Such units give rise to two types of methylenic proton signals at different field strength from those obtained for the 4GT unit. In the copolymer all four proton types must be present, but in addition, the situation shown in Figure 2, where the diol unit is flanked on one side by a terephthalate and on the other by a sebacate unit, must arise.

In this situation, four different types of methylenic protons, A-D, would thus be present. The chemical shift of the peak suggests that this is not due to A- or D-type protons. This suggests that it arises from B- or C-type protons alone or in combination. In order to resolve this matter and possibly make use of this peak for sequence determination, further studies over the whole composition range would be required at 220 or 300 MHz.

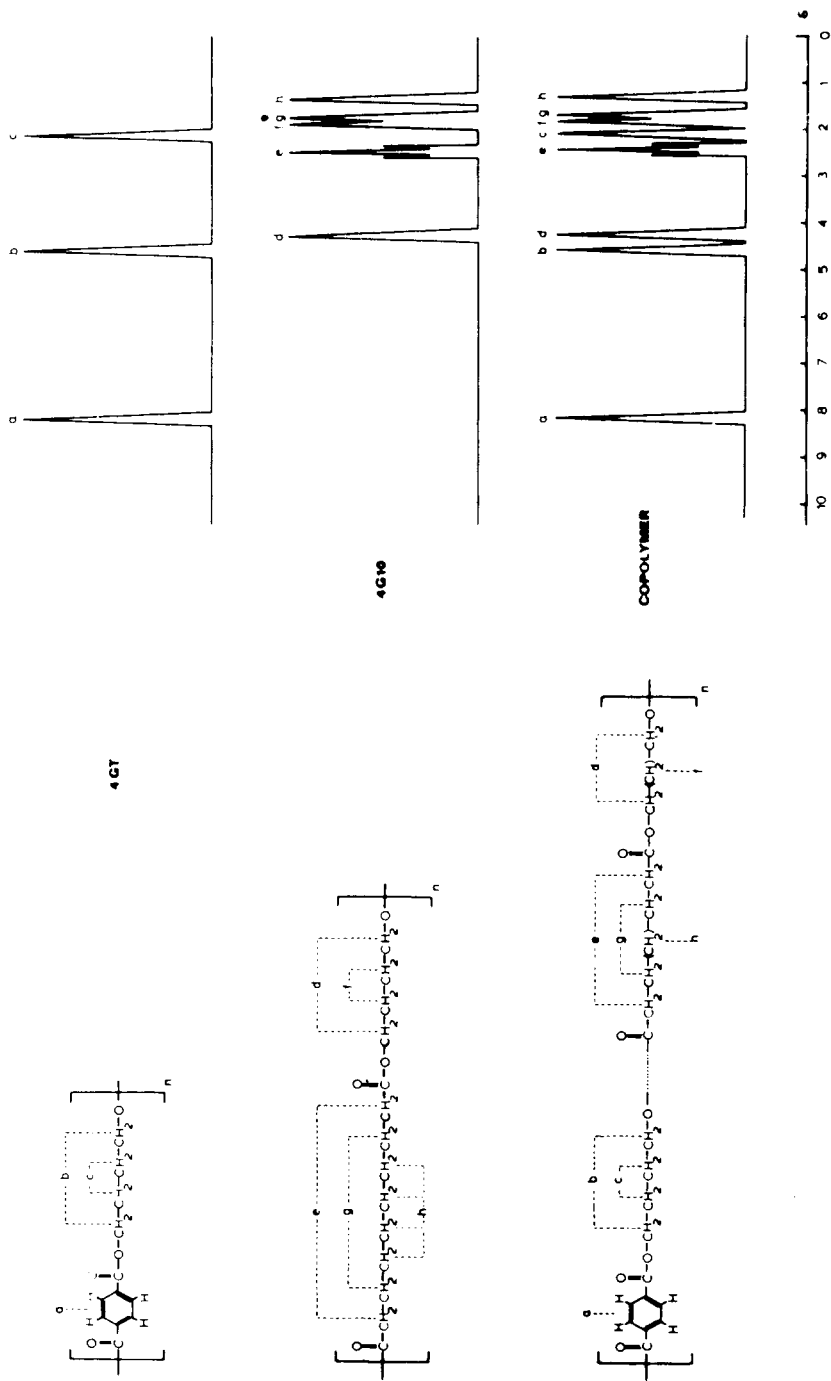


Fig. 1. Repeating structures and 100-MHz nmr spectra.

TABLE V
 Chemical Shifts of Protons in the Polymers

Polymer proton type	Group	No. protons in group	δ
4GT	a aromatic	4	8.24
	b —OCH ₂ —	4	4.64
	c —CH ₂ —CH ₂ —	4	2.16
4G10	d —OCH ₂ —	4	4.30
	e —CO—CH ₂ —	4	2.50
	f —CH ₂ —CH ₂ —	4	1.87
	g —CH ₂ —	4	1.72
	h —CH ₂ —	8	1.38
Copolymer	a aromatic	4	8.26
	b —OCH ₂ —	4	4.66
	c —CH ₂ —CH ₂ —	4	2.18
	d —OCH ₂ —	4	4.39
	e —OCCH ₂ —	4	2.53
	f —CH ₂ —CH ₂ —	4	2.04
	g —CH ₂ —	4	1.75
	h —CH ₂ —	8	1.42

 TABLE VI
 Copolymer Compositions from NMR

Copolymer composition, mol % sebacate	Aliphatic/aromatic ratio		Mole % sebacate	
	Theor.	Exptl.	Theor.	Exptl.
0 (4GT)	2.00	1.97	—	—
5	2.32	2.34	5.0	5.4
10	2.67	2.68	10.0	10.2
15	3.06	3.08	15.0	15.2
20	3.50	3.48	20	19.8

Thermal Properties

The melting temperatures obtained by DSC and the HSPM are compared in Table II. The differences can be attributed to the different methods used to evaluate the melting temperature. Thus multiple-melting endotherms were observed on all DSC curves, and the peak temperature of the major endothermic peak was taken as the melting temperature. With the optical method the disappearance of the last trace of birefringence was recorded.

The values for 4GT are similar to those reported by Smith³⁸ (221°C) and by Shulken³⁹ (223°C) by DTA, Conix⁴⁰ (230°C) by dilatometry, and Ward et al.⁴¹ (232°C) by dynamic mechanical methods. The different results obtained again can be ascribed to the different methods used for their evaluation.

It can be seen from Table II that the polymers have essentially the same melting temperature irrespective of their thermal history and thus their initial percentage crystallinity. Thus materials in the "as-prepared state" had crystallinities (measured by density studies) in the range 25%–35%, whereas the quenched melt-pressed films were in the range 0.7%–10%.

It is, however, significant that initially amorphous fibers and films of moderate crystallinity both show marked increases in density when heated in the DSC machine to specific temperatures below the melting temperature, followed by rapid cooling to ambient.

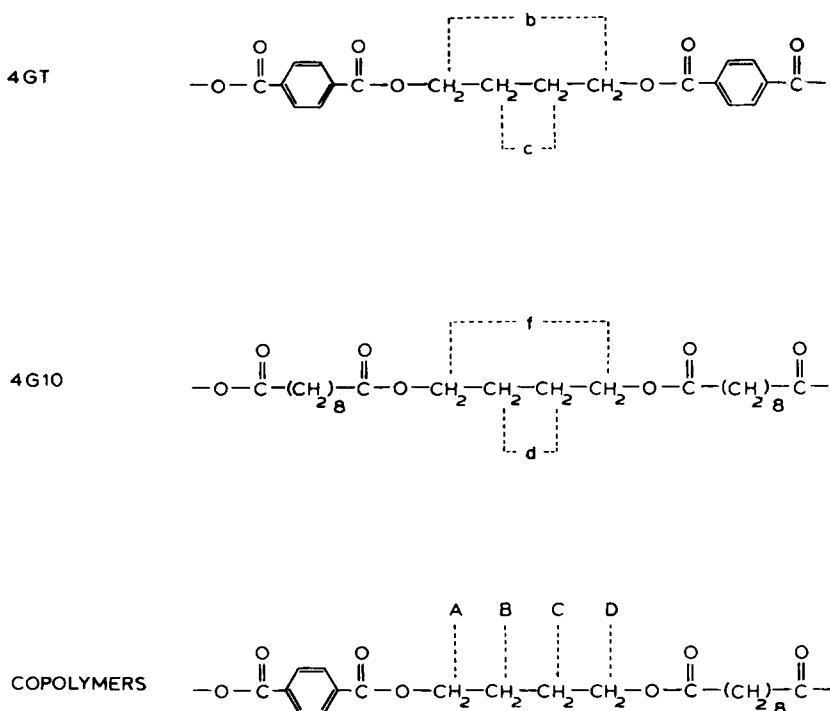


Fig. 2. Structural arrangement of the methylenic protons.

These density changes result from rapid crystallization during the heating program of the DSC run. The DSC curve obtained, however, shows no sharp exothermic peak, in contrast to that observed for 2GT⁴³ on cold crystallization. A slight exothermic drift of the base line is, however, apparent. The results shown in Table VII indicate that the previous thermal history of the sample is destroyed during the heating program, thus accounting for the melting temperatures recorded in Table II.

TABLE VII
Effect of Programmed Heating in the Differential Scanning Calorimeter on the Crystallinity of Amorphous 4GT and 4GT of Moderate Crystallinity

Temperature, °C ^a	Initially amorphous 4GT fiber		Melt-quenched 4GT film of moderate crystallinity	
	Density, g/cm ³	% Cryst. ^b	Density g/cm ³	% Cryst. ^b
Ambient	1.286	0	1.317	31.5
100	1.301	15.4	1.318	32.5
120	1.307	21.5	1.319	33.4
150	1.315	29.5	1.323	37.4
180	1.325	39.3	1.328	42.3
200	1.331	45.2	1.331	45.2

^a Sample heated to the specified temperature at 20°C/min, then cooled at 320°C/min to ambient in the DSC2 machine.

^b From density data, using 1.390 g/cm³ for the density of 100% crystalline 4GT calculated from the unit-cell dimensions reported by Pass and Hall (ref. 42), and 1.286 g/cm³ for amorphous 4GT, the value determined experimentally in this study (see Table VIII).

The observation of such density changes, together with multiple-melting behavior, suggests that the application of the thermal method of crystallinity measurement by comparison of the heat of fusion of the polymer sample with that for 100% crystalline 4GT would lead to erroneous results. In this context, application of thermal and density measurements to the assessment of the percentage crystallinities of the quenched melt-pressed films led to the data presented in Table VIII.

The crystallinity values obtained are significantly different and arise as a result of crystallization occurring during the heating program required to melt the sample. Since, however, no exothermic peak is observed under the conditions of study, the magnitude of this effect cannot be compensated for, and the situation is further complicated by the multiple-melting behavior.

On random copolymerization, only the units that are present in the major proportion crystallize. The presence of a second unit in the polymer chain should cause a reduction in crystalline content and melting temperature and a broadening of the melting-temperature range. All such effects are apparent in this copolymer series, and in addition, if the system is studied over the whole composition range, a eutectic curve is obtained with a minimum at approximately 65 mol % sebacate,⁴⁴ similar to that reported by Ueberreiter and Steiner¹⁴ for low-molecular-weight materials. In the composition range studied (0%–20%), the crystallinity arises from the terephthalate units in the polymer by analogy to the behavior found by Edgar and Ellery⁴⁵ for 2GT copolymer systems containing sebacate and adipate units.

Equilibrium melting temperature, multiple-melting behavior, and rate of crystallization studies will be reported in detail in Part II of this series.⁴⁶

Thermal methods have also been used in an attempt to measure glass-transition temperatures of the polymer. The DSC1 instrument was not sufficiently sensitive to allow reproducible detection of the transition. The DSC attachment of the Du Pont 900 thermal analyzer and the DSC2 instrument both gave reproducible results only on disk samples produced from quenched, melt-pressed films. The main problem is associated with the reproducibility of the quenching procedure and the consequent effects on the thermal history of the sample and the attendant differences in percentage crystallinity. Values recorded by this method for the film samples of 4GT and 4G10 are in accord with those in the literature.⁴⁷ The T_g value recorded for amorphous 4GT fibers is, however, 39°C.

The results shown in Table III decrease in the manner expected as a result of the incorporation of a more flexible unit into the chain.

TABLE VIII
Crystallinity Determination of Quenched, Melt-Pressed Films

Composition, mol % sebacate	Amorphous, ^a density g/cm ³	% Crystallinity	
		Density	DSC2
0	1.286	6.7	35.2
5	1.281	6.4	33.9
10	1.265	9.6	27.7
15	1.258	3.0	28.2
20	1.249	0.7	25.0

^a Determined on samples prepared by extrusion from the melt into ice water, dried, and subsequently shown to be amorphous by x-ray studies.

TABLE IX
Glass-Transition Temperatures of 4GT and 4G10 by Dynamic Mechanical Methods and DSC

Polymer	Assessment method/conditions	T_g , °C	Reference
4GT	Rheovibron/3.5 Hz ^a	66	48
4GT	Rheovibron/110 Hz	64	49
4GT	Torsional pendulum/0.24 Hz	45	49
4GT	Torsional pendulum/1.0 Hz	44	50
4GT	Vibrating reed/215 Hz	80	43
4GT	Rheovibron/3.5 Hz ^a	56	b
4GT	DTA unspecified heating rate	22	39
4GT	TMA/5°C/min	23	52
4GT	DSC/16°C/min	46	b
4G10	Vibrating reed/74 Hz	-35	51
4G10	Rheovibron/3.5 Hz	-44	b
4G10	DSC/16°C/min	-62	b

^a Samples of different degrees of crystallinity.

^b This study.

TABLE X
Copolymer T_g from the Gibbs-Di Marzio Equation

Composition, mol % sebacate	$T_{g,obs} (E''_{max})$, °C	$T_{g,calcd}$, °C
0	56	—
5	50	46.6
10	39	38.1
15	33.5	30.3
20	22	23.1
100	-44	—

TABLE XI
Loss Modulus E'' for Copolymers

Composition, mol % sebacate	Temperature of assessment, °C ^a	$E'' \times 10^8$ dynes cm ⁻²
0	77	5.539
5	70.5	2.929
10	60	1.729
15	54	1.885
20	44	2.215
100	-24.5	1.246

^a Approximately 20°C above T_g .

The T_g values obtained by dynamic mechanical methods are shown in Table IV and reflect the same trend. The T_g values, however, differ from those reported in Table III, because in each case the results are dependent on the substrate's properties and the procedural variables associated with the method of determination. The values for E''_{max} obtained are similar to those reported by other workers (Table IX).

The results shown in Table IX for dynamic mechanical methods reflect the effect of procedural variables on the determined quantity. Comparison of DSC and dynamic mechanical methods suggested that the lower results obtained by DSC correspond to the onset of motion as reflected by the onset of the E'' peak

in the dynamic mechanical spectra recorded in this work and that of Illers and Breuer.⁵⁰

The Gibbs-Di Marzio equation,⁵³ shown below, attempts to relate the effect of the chain flexibility of the individual components of a copolymer to its T_g :

$$M_A(\alpha_A/W_A)(T_g - T_{gA}) + M_B(\alpha_B/W_B)(T_g - T_{gB}) = 0$$

where M_A and M_B are weight fractions of homopolymers, W_A and W_B are weights of the homopolymer repeat units, T_{gA} and T_{gB} are the glass-transition temperatures of homopolymers, T_g is the glass transition of the copolymer, and α_A and α_B are the number of flexible bonds per monomer unit (α_A , sebacate = 16, α_B , terephthalate = 8). The glass-transition temperature calculated using the Gibbs-Di Marzio equation and the E''_{\max} values for 4GT and 4G10 are shown in Table X.

The calculated results are in good agreement with those determined experimentally. The results indicate that increasing chain flexibility plays the dominant role in determining the T_g of these systems.

In addition to the effect of composition on T_g , the effect of increasing chain flexibility on modulus is shown in Table XI.

The loss moduli are compared at a temperature consistent with the polymer being in the rubbery state. The data suggest a decrease in modulus with increasing content of the flexible unit, although the situation is further complicated by the thermal effects of the testing procedure and the related effect on percentage crystallinity.

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