Copolyester Studies. V. Preparation and Characterization of Tetramethylene Terephthalate–Poly(tetramethylene Oxide) Random Block Copolymers

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Synopsis

Random block copolymers of tetramethylene terephthalate and polytetrahydrofuran (PTHF) were prepared by melt polycondensation. Five different molecular weights of PTHF were used in the polymerizations with up to 30% by weight incorporation. The copolymers so obtained were characterized in terms of their molecular weight by means of endgroup analysis and solution viscometry. Compositions were established by nuclear magnetic resonance spectroscopy. Thermal properties were studied by differential scanning calorimetry and dynamic mechanical methods. Melting and glass transition temperatures are discussed in terms of the structural differences, particularly the effect of polyether composition and block size on chain flexibility.

INTRODUCTION

In previous articles[1-4] the preparation and characterization of tetramethylene terephthalate–tetramethylene sebacate copolymers have been reported. Their melting and crystallization behavior, mechanical behavior, and dyeing behavior of drawn and undrawn fibers were discussed in terms of the change in structure and properties consequent to the incorporation of sebacate units into a terephthalate chain.

We now report studies on the random block copolymer systems prepared from the polymeric diol poly(tetramethylene oxide) (PTHF) in admixture with butane diol and dimethyl terephthalate. Such systems have been previously described and studied.[5-10] This study extends that work in a systematic manner and is concerned with the effects of both the block length of the initial PTHF and the copolymer composition on physical, mechanical, and dyeing properties.

EXPERIMENTAL

Materials

Butane-1,4-diol was supplied by BDH Ltd. and was purified by vacuum distillation (bp 90°C/0.1 mm Hg) not more than one day prior to use. Dimethyl terephthalate was supplied by BDH Ltd. and purified by vacuum distillation (bp 210°C/0.55 mm Hg). Tetraisopropyl *ortho*-titanate was supplied by Eastman–Kodak and used as received. Succinic anhydride, 1-methylnaphthalene,

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1,1',2,2'-tetrachloroethane, benzyl alcohol, acetic anhydride, AR phenol, and perchloric acid were supplied by BDH Ltd. With the exception of phenol and perchloric acid, which were used as received, the remainder were purified by vacuum distillation prior to use.

Tetrahydrofuran (THF) was supplied by BDH Ltd. and was purified in the following manner. THF (500 g) was shaken with lithium aluminum hydride (10 g) and was then distilled under nitrogen onto freshly cut sodium metal. Resublimed naphthalene (5 g) was then added and the mixture boiled under reflux until the green-black color of the sodium naphthalene complex was observed. The THF was then distilled into the vessel used for polymerization. Polymerization was effected using the catalyst system acetic anhydride/perchloric acid by the method reported by Hachihama and Shona.[11]

At the end of the polymerization period the catalyst was neutralized with 2% aqueous sodium hydroxide solution, and the viscous solution was dissolved in ether and washed with alkali and then with water until alkali free. The ether layer was separated and dried and the ether removed, yielding PTHF with acetoxy endgroups as shown by infrared analysis. These materials were converted to the hydroxyl-ended polymers by reaction with alcoholic potassium hydroxide. The course of hydrolysis was monitored by observing the disappearance of the absorption due to the acetate grouping at 1740 cm^{-1} in the infrared spectra. The waxy product obtained after removal of the alcohol by distillation was dissolved in ether and washed free from alkali, and the ether was removed by rotary film evaporation. The polymer was finally dried at 50°C/1 mm Hg for 24 hr prior to characterization or use in polymerization studies.

Commercial polytetrahydrofurans (PTHF) were obtained from du Pont and Quaker Oats as "Teracol" and "Polymeg" at nominal molecular weights of 1000 and 2000, respectively. These samples, together with those prepared in the laboratory, were characterized by endgroup analysis[12] and intrinsic viscosity studies in AR benzene at 25° ± 0.01°C. Table I reveals the results obtained together with the molecular weight dependence on catalyst concentration.

Copolymerization

The random block copolymers were prepared by standard melt polymerization procedures[13] from 1:2.2 molar ratios of dimethyl terephthalate with butane diol/PTHF admixtures so that copolymers containing up to 30 wt % of PTHF blocks of molecular weight 1000–5000 were obtained.

TABLE I
Characterization of PTHF Samples

Molecular weight[a]	Intrinsic viscosity	Catalyst concentration[b]	
		Acetic anhydride	Perchloric acid
1012	0.07	c	—
1984	0.14	d	—
2995	0.21	7.43	0.20
4095	0.28	6.76	0.19
4960	0.34	6.31	0.18

[a] Determined by endgroup analysis.[12]
[b] Percent based on monomer weight.
[c] Teracol.
[d] Polymeg.

The reactants were heated together with the catalyst (0.08% by weight on total reactants weight) in an atmosphere of dry nitrogen ("white spot") (1) at 197°C/1 atm for 3 hr to eliminate methanol, and (2) at 255°C/0.05 mm Hg for 2.5 hr to remove surplus butane diol and to effect polymerization by ester interchange.

Molecular Weight Determination

Molecular weights were determined from the carboxyl endgroup contents found after succinoylation with succinic anhydride in distilled 1-methyl-naphthalene under nitrogen at 197°C/5 hr using a modification of the method of Conix.[14] 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 mixture by weight of phenol and 1,1',2,2'-tetrachloroethane at 25°C (±0.02°C) and correlated with the values calculated from the endgroup analysis (Table II).

Composition of the Copolymers

Compositions were calculated from the initial weights of reagents using the equation derived by Shivers.[15] However, in order to confirm that loss of the volatile components during preparation did not produce significant changes in composition and that PTHF did not degrade under the polymerization conditions, the composition of each system was determined by NMR spectroscopy. Spectra were obtained from polymers as 20% solutions in trifluoroacetic acid (spectroscopic grade from BDH Ltd.), using a Varian HA-100 MH_z spectrometer. 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.

TABLE II
Number-Average Molecular Weights and Intrinsic Viscosities of the Copolymers

Polymer code	wt % PTHF[a]	$\overline{M}_n$[b]	$[\eta]_0$
4GT/PTHF 1000	10	17,800	0.96
4GT/PTHF 1000	20	16,600	0.95
4GT/PTHF 1000	30	18,800	1.02
4GT/PTHF 2000	10	23,600	1.12
4GT/PTHF 2000	20	13,100	0.77
4GT/PTHF 2000	30	23,400	1.09
4GT/PTHF 3000	10	14,300	0.87
4GT/PTHF 3000	20	22,500	1.10
4GT/PTHF 3000	30	13,500	0.79
4GT/PTHF 4000	10	13,800	0.81
4GT/PTHF 4000	20	16,100	0.90
4GT/PTHF 4000	30	21,100	1.04
4GT/PTHF 5000	10	16,000	0.83
4GT/PTHF 5000	20	18,800	0.99
4GT/PTHF 5000	30	15,300	0.82

[a] Calculated from the Shivers equation.[15]

[b] Endgroup analysis.

TABLE III
PTHF Melting Temperatures

Polymer code	$\overline{M}_n{}^a$	Melting point, °C
PTHF 1000	1012	28
PTHF 2000	1984	32
PTHF 3000	2995	34
PTHF 4000	4095	36.5
PTHF 5000	4960	38

ª From endgroup analysis.

Thermal Properties

Melting temperatures of the PTHF samples used in preparation of the block copolymers, together with those of the block copolymers, were determined using a Perkin–Elmer differential scanning calorimeter, model DSC-2. PTHF samples were studied in the as-prepared state. The block copolymers were studied in the as-prepared state and as melt-pressed films which were prepared from vacuum-dried (60°C/1 mm Hg for 16 hr) polymer shavings (5 g) as previously reported.[1] The films produced were dried at room temperature/1 mm Hg over phosphorus pentoxide. Samples ($\simeq$5 mg) were encapsulated in aluminum pans and an empty pan acted as the inert reference material. Disc samples ($\sim$5 mg) (0.3 mm thick and 6 mm in diameter) cut from melt-pressed films were studied at 20°C/min under argon at a flow rate of 20 ml/min. High-purity tin and indium samples (from Perkin–Elmer Corporation, mp 156.8 and 232°C) were used as temperature calibration standards. The data obtained for the PTHF samples are given in Table III and that for the block copolymers in Table IV.

TABLE IV
Copolymer Melting Temperatures

Polymer code	T_m, °Cª Polyester segment	T_m, °Cª Polyether segment
4GT/PTHF 1000 10%	219	—
4GT/PTHF 1000 20%	216	—
4GT/PTHF 1000 30%	211	—
4GT/PTHF 2000 10%	222	—
4GT/PTHF 2000 20%	221	—
4GT/PTHF 2000 30%	219	—
4GT/PTHF 3000 10%	223	29.7
4GT/PTHF 3000 20%	222	30.2
4GT/PTHF 3000 30%	221	30.5
4GT/PTHF 4000 10%	224	31.0
4GT/PTHF 4000 20%	223	31.2
4GT/PTHF 4000 30%	221	31.5
4GT/PTHF 5000 10%	225	32.0
4GT/PTHF 5000 20%	224	32.5
4GT/PTHF 5000 30%	222	32.0

ª Determined by DSC on melt-pressed films.

Glass Transition Temperature

Glass transition temperatures were obtained using a Rheovibron direct-reading dynamic viscoelastometer, model DDV II, using a heating rate of 1°C/min from −20 to 140°C. Samples (2.5 cm long × 0.5 cm wide × 0.25 mm thick) prepared from dried, quenched, melt-pressed films were subjected to an oscillating frequency of 3.5 cycles/sec. The results obtained for loss maxima temperatures of the polymers are recorded in Table V.

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 is based on the work of Marrs et al.[1] and was shown to be tenable in preliminary studies on this system.

Molecular Weight

By plotting the results obtained from endgroup analysis and intrinsic viscosity on a logarithmic scale, a linear relationship should be obtained. However, if the data given in Table II are treated in this manner, they show a marked degree of scatter. This can be ascribed to the difficulties associated with the endgroup analysis method as described previously.[1]

Copolymer Composition

During the first stage of polymerization some dimethyl terephthalate is lost from the melt. In addition, PTHF has been reported to degrade at temperatures greater than 150°C even under nitrogen.[16] In order to establish composition, a NMR method was chosen because of its simplicity and ease of use.

The method used is an adaptation of the method used previously for random

TABLE V
Copolymer Loss Maxima Temperatures

Polymer code	E''_{max}, °C	tan δ_{max}, °C
4GT	77	70
4GT/PTHF 1000 10%	58	50
4GT/PTHF 1000 20%	23	22
4GT/PTHF 1000 30%	9	4
4GT/PTHF 2000 10%	60	53
4GT/PTHF 2000 20%	42	40
4GT/PTHF 2000 30%	40	28
4GT/PTHF 3000 10%	65	56
4GT/PTHF 3000 20%	64	55
4GT/PTHF 3000 30%	59	50
4GT/PTHF 4000 10%	66	60
4GT/PTHF 4000 20%	65	57
4GT/PTHF 4000 30%	60	53
4GT/PTHF 5000 10%	68	66
4GT/PTHF 5000 20%	66	59
4GT/PTHF 5000 30%	64	55

copolymers of 4GT and tetramethylene sebacate[1] and has been reported in detail elsewhere.[17]   The 100 MHz spectra obtained from 4GT, PTHF, and a typical copolymer are schematically represented in Figure 1.   The 4GT shows three sets of equivalent protons, PTHF shows two sets of equivalent protons, and the copolymers show five sets of equivalent protons, all of which show singlet absorptions.   The chemical shift data, together with their interpretation, are given in Table VI.

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.   Table VII shows the percentage of PTHF in the copolymers.   These results indicate that the copolymers are of similar composition to that calculated using the Shivers equation and that no significant changes in composition occur due to loss of volatile components or by PTHF degradation.

Thermal Properties

The melting temperatures for the five PTHF homopolymers used to prepare the random block copolymers are given in Table III.   The melting points increase with increasing molecular weight and are similar to those reported by Ghaffar[18] for the same molecular weight range.

The melting temperature of the polyester and polyether segments of the copolymer are shown in Table IV.   The incorporation at random of low-melting polyether segments decreases the melting temperature of the polyester.   In addition, as the polyether content increases, the melting temperature further decreases.   However, at the same percentage incorporation an increase in
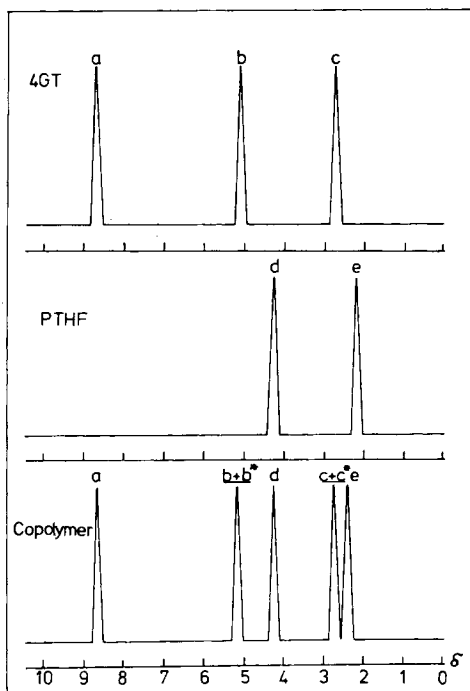

Fig. 1. NMR Spectra of 4GT, PTHF, and a typical copolymer.

TABLE VI
Chemical Shifts of Protons in the Polymers

Polymer	Proton type[a]	Group	δ
4GT	a	aromatic	8.68
	b	$\begin{matrix} O \\ \parallel \\ -C-O-CH_2- \end{matrix}$	5.10
	c	$-CH_2-CH_2-$	2.62
PTHF	d	$-O-CH_2-$	4.30
	e	$-CH_2-CH_2-$	2.26
Copolymer	a	aromatic	8.68
	b + b*	$\begin{matrix} O \\ \parallel \\ -C-O-CH_2- \end{matrix}$	5.10
	d	$-O-CH_2-$	4.30
	c	$-CH_2-CH_2-$	2.62
	e	$-CH_2-CH_2-$	2.29
	c*	$\begin{matrix} O \\ \parallel \\ -C-O-CH_2-CH_2- \end{matrix}$	2.62

[a] See ref. 17.

polyether block length results in an increase in melting temperature of the polyester phase.

The polyether component also shows a very small increase in melting temperature with increase in molecular weight and with increased percentage incorporation. Flory[19] has shown that a reduction of melting temperature occurs on random copolymerization, and this is accompanied by a reduction in crystalline content and a broadening of the melting temperature range. Figure 2

TABLE VII
Copolymer Compositions from NMR[a]

Polymer code	Theoretical wt % PTHF	% PTHF		
4GT/PTHF 1000	10	10.02[b]	9.94[c]	10.11[d]
4GT/PTHF 1000	20	21.14	—	—
4GT/PTHF 1000	30	30.54	—	—
4GT/PTHF 2000	10	9.91	9.85	9.97
4GT/PTHF 2000	20	19.56	19.56	19.05
4GT/PTHF 2000	30	30.26	30.30	30.01
4GT/PTHF 3000	10	10.33	10.39	10.23
4GT/PTHF 3000	20	18.65	—	—
4GT/PTHF 3000	30	29.40	—	—
4GT/PTHF 4000	10	10.19	10.07	9.92
4GT/PTHF 4000	20	19.76	—	—
4GT/PTHF 4000	30	29.33	—	—
4GT/PTHF 5000	10	10.28	10.16	10.25
4GT/PTHF 5000	20	19.25	—	—
4GT/PTHF 5000	30	30.89	—	—

[a] See ref. 17.
[b] Calculated from an equation derived for the proton ratio $(b + b^*)/d$.
[c] Calculated from the proton ratio total aromatic/d-type protons.
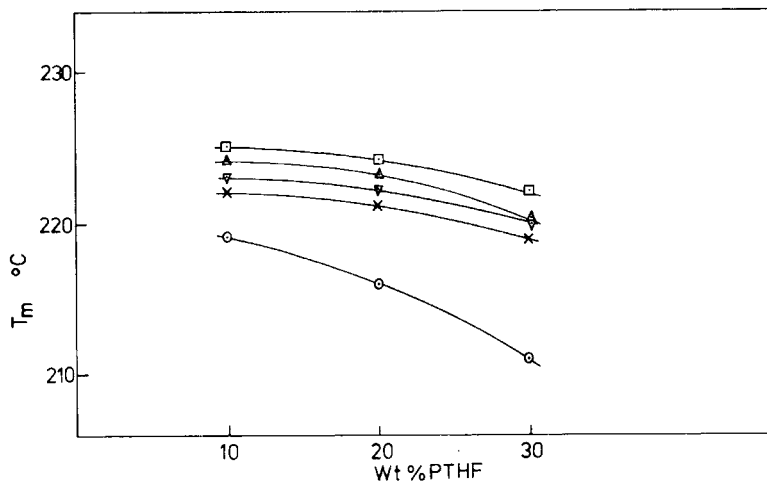[d] Calculated from the proton ratio total aromatic/total aliphatic.

Fig. 2. Melting temperatures of the polyester phase as a function of composition for different PTHF block lengths: (□) 4GT/PTHF 5000; (▽) 4GT/PTHF 4000; (▲) 4GT/PTHF 3000; (×) 4GT/PTHF 2000; (⊙) 4GT/PTHF 1000.

shows the reduction in melting temperature consequent to copolymerization in these systems as a plot of melting temperature versus percentage PTHF incorporation for each PTHF system studied.   In Figure 3 the melting temperature is plotted versus the polyether molecular weight for fixed-percentage polyether incorporation of 10%.   As can be seen, the melting temperature increases with increasing molecular weight, and thus the depression on copolymerization is less for blocks of higher molecular weight.

As shown in Table IV, DSC yielded no evidence for melting of a crystalline phase associated with PTHF blocks of molecular weight 1000 and 2000, suggesting that the polyether segments in copolymers containing these units are in the amorphous condition.   If there is a crystalline phase associated with the
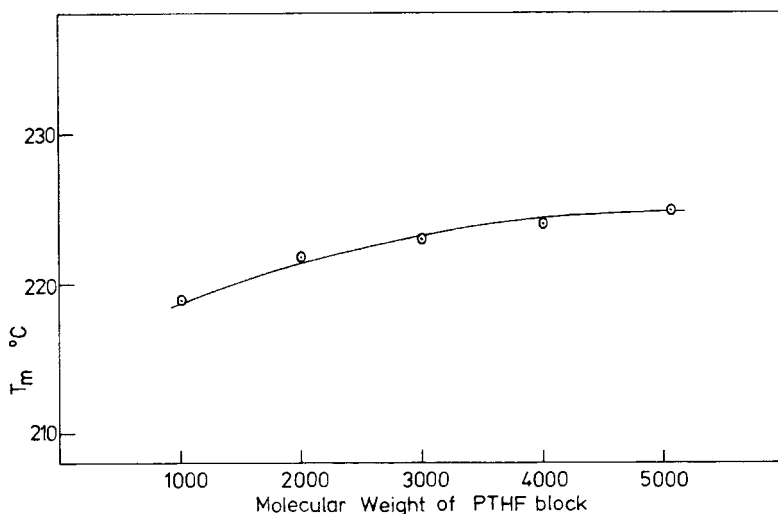

Fig. 3. Effect of molecular weight of the PTHF block on the melting temperature of the polyester phase for 10% PTHF incorporation.

PTHF 1000 and 2000 contained within the copolymers, this may be difficult to detect by DSC. This may arise because of the low degree of polymerization of the PTHF involved (14, 28) and the low percentage incorporation which may result in the formation of limited quantities of small and imperfect crystals.

The melting temperatures of the polyether segments in the remaining copolymers vary with composition, but such variation is so small that copolymers with the same block lengths have melting points which are similar. The melting temperatures of the PTHF segments within the copolymers are lower than the corresponding homopolymer samples from which they were derived (Table IV). Such a depression is probably related to the close packing of the polyether segments which is impeded by the presence of polyester segments. Similar overall results have been reported on the poly(hexamethylene terephthalate)/PTHF copolymer system[18] and the poly(hexamethylene terephthalate)/poly(ethylene oxide) copolymer system[20] and in studies of block copolyester–urethanes[21] and polyester–polyethers.[22]

The depression in melting point of random copolymers is dependent on the mole fraction of the second component in the copolymer as given by the Flory equation[19]

$$\frac{1}{T_m} - \frac{1}{T_m{}^*} = \left(-\frac{R}{\Delta H_F}\right) \ln X_A$$

where T_m is the observed copolymer melting temperature, $T_m{}^*$ is the observed melting point of homopolymer A, X_A is the mole fraction of homopolymer A, ΔH_F is the latent heat of fusion of homopolymer A, and R is the gas constant.

When the data obtained for the copolymers are plotted as $1/T_m$ vs. $-\ln X_A$, a straight line was observed of slope $R/\Delta H_F$, as typified by the 4GT/PTHF 1000 copolymers (Fig. 4). A typical heat of fusion value of 2098 cal/mole is obtained for the 4GT repeating unit. This value is similar to those obtained previously by Liw[21] and Rashid,[22] 2460 and 1982 cal/mole, respectively. However, Marrs et al.[1] in their studies on random copolyesters of 4GT and tetramethylene seb-
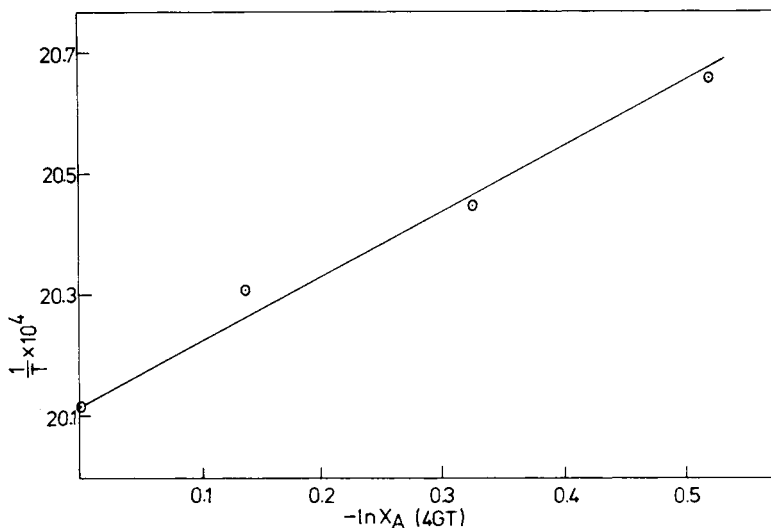

Fig. 4. Determination of the heat of fusion of the 4GT repeating unit.

acate obtained a value of 3870 cal/mole when equilibrium melting temperatures were used in the Flory equation.

Equilibrium melting temperatures were evaluated for the two copolymer systems containing PTHF 2000 and 5000, as shown in Table VIII. The ΔH_F calculated using these values, 3650 and 3600 cal/mole, was similar to that obtained by Marrs et al.[2] However, the values obtained by this method are significantly lower than that obtained by Conix and Van Kerpel,[23] who used a method based on melting point depression by diluents. The results obtained by Marrs et al.[1,24] suggest that the comonomer unit renders 4GT units adjacent to it noncrystallizable, thus resulting in an incorrect assessment of the mole fraction in the Flory equation, which leads to low values for ΔH_F.

For all these copolymer systems multiple melting endotherms were observed on the DSC traces in a similar manner to those reported by Marrs et al.[1,24] In the present study three peaks were observed and they were designated peaks I, II, and III. Peak I is small and occurs 5–10°C above the crystallization temperature T_c. Peak II occurs above a certain crystallization temperature and increases in melting temperature as the crystallization temperature T_c is increased. Peak III always occurs at the same temperature. At relatively low crystallization temperatures, peak III is of a large size; but with increasing T_c, peak II increases in size and peak III decreases. The increase in area of peak II is approximately equal to the decrease in area of peak III.

The equilibrium melting point $T_m{}^0$ was estimated using the Hoffman and Weeks equation[25] by plotting $T_{m(obs)}$ vs. T_c. It was obtained from the intersection of this line with the line $T_{m(obs)} = T_c$. $T_{m(obs)}$ was taken to be the peak temperature of peak II because only this peak exhibited the behavior expected from the Hoffman and Weeks theory, as also found by Marrs et al.[1,24] in their studies.

Dynamic Mechanical Properties

The T_g values obtained by dynamic mechanical methods are shown in Table V and decrease in the manner expected as a result of incorporation of a more flexible unit into the chain. Figure 5 shows that the glass transition temperature of the copolymers decreased as the polyether content increases, indicating an increase in segmental mobility with increase in polyether content. Figure 6 reveals that the T_g increases as the molecular weight of the polyether increases, and this can be attributed to an overall increase in crystallinity of the copolymers as shown from x-ray studies.[26]

TABLE VIII
Equilibrium Melting Points of Representative Block Copolymers

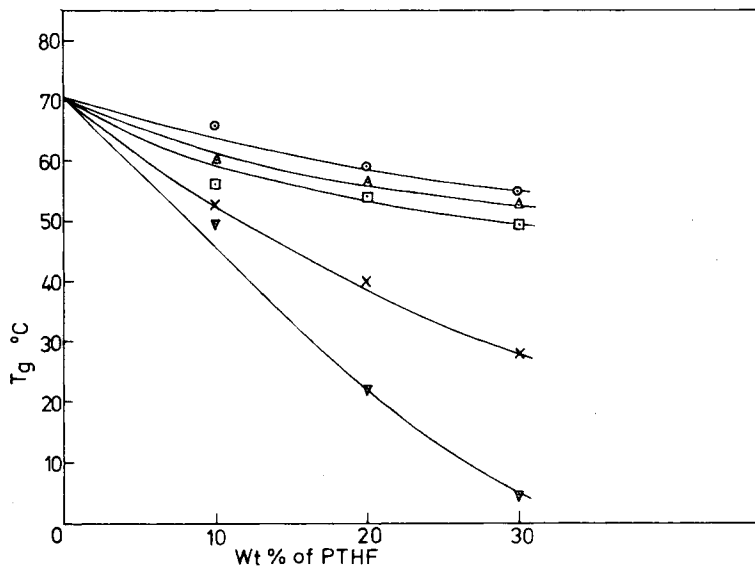| Polymer code	Theoretical wt % PTHF	$T_m{}^0$, °C
4GT/PTHF 2000	10	240
4GT/PTHF 2000	20	238
4GT/PTHF 2000	30	236
4GT/PTHF 5000	10	242
4GT/PTHF 5000	20	240
4GT/PTHF 5000	30	237

Fig. 5. Effect of PTHF block length on the glass transition temperature of the polyester phase:
(⊙) PTHF 5000; (△) PTHF 4000; (□) PTHF 3000; (×) PTHF 2000; (▽) PTHF 1000.

The different values obtained for the T_g of 4GT by various workers are reviewed by Marrs et al.[1] and are due to the difficulty in standardizing the method of producing films and the resultant differences in crystallinity of the samples used.   The results reported in this study are however in general in accord with previous work.

Lewis[27] has derived empirical equations relating the frequency of the dynamic glass transition temperature to the apparent activation energy of the glass transition process and refers to sterically restricted and nonsterically restricted polymers.
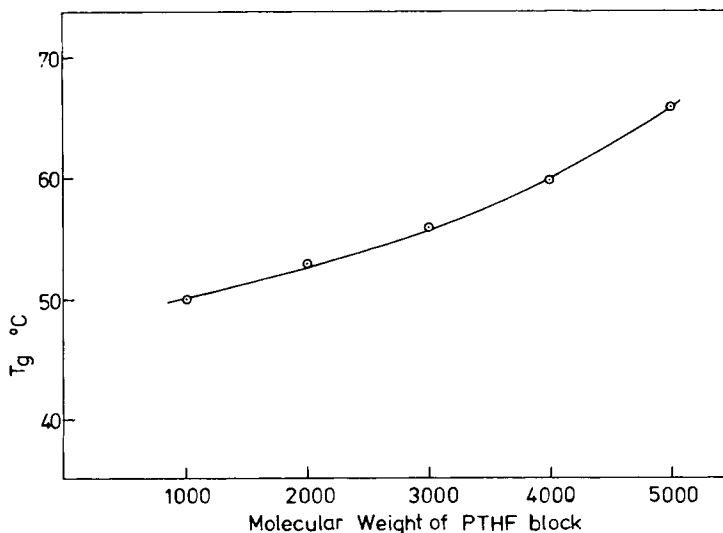

Fig. 6. Effect of molecular weight of the PTHF block on the glass transition temperature of the polyester phase for 10% polyether incorporation.

TABLE IX
Observed and Calculated Values of T_g from the Lewis Equation[27]

Polymer code	T_g	From Lewis equation	
4GT	70	55.6[a]	73.9[b]
4GT/PTHF 1000 10%	50	35.7	51.9
4GT/PTHF 1000 20%	22	0.3	10.8
4GT/PTHF 1000 30%	4	−13.4	−5.3
4GT/PTHF 2000 10%	53	37.8	53.9
4GT/PTHF 2000 20%	40	19.4	32.8
4GT/PTHF 2000 30%	28	17.4	30.5
4GT/PTHF 3000 10%	56	43.0	59.8
4GT/PTHF 3000 20%	55	42.0	58.6
4GT/PTHF 3000 30%	50	36.8	52.7
4GT/PTHF 4000 10%	60	44.0	61.0
4GT/PTHF 4000 20%	57	43.0	59.8
4GT/PTHF 4000 30%	53	37.8	53.9
4GT/PTHF 5000 10%	66	47.0	63.4
4GT/PTHF 5000 20%	59	44.0	61.0
4GT/PTHF 5000 30%	55	42.0	58.6

[a] Assuming polymers to be sterically restricted.
[b] Assuming polymers to be nonsterically restricted.

Table IX shows values for T_g calculated from the Lewis equations compared with those obtained by dynamic mechanical methods (E''_{max}). It is obvious from these results that when the polymers are considered as nonrestricted, the calculated value of the glass transition temperature is closer to E''_{max}. The Lewis equation for nonrestricted polymers thus gives a reasonable fit for the present copolymer system.

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