

Synthesis and Some Properties of a Series of Polyterephthalates Having Side-Chain Branching

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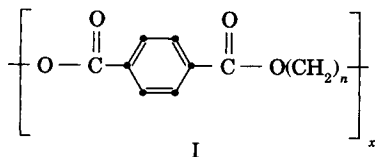
Synopsis

Polyterephthalates made from terephthalic acid and a series of cyclic alkylene carbonates to give short side-chain branching were amorphous. The T_g increased from poly(ethylene terephthalate) to poly(1,2-propylene terephthalate), and then an expected decrease in T_g resulted from a further increase in side-chain length. The initial increase in T_g was attributed to increased chain rotational energy barriers. Further alkyl substituent length increases did not significantly raise these barriers but lowered chain packing densities. New group contribution factors for polyester T_g calculations were derived from the data. Interpretations of the dynamic mechanical spectra showed an apparent decrease in *trans*-glycol unit fraction with increasing alkyl substituent length along with several interchain effects.

INTRODUCTION

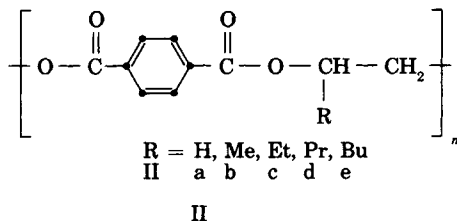
Much work has been reported previously for several series of side-chain branched polymers to establish the relationship of the glass transition temperature (T_g) to the side-chain length. There are no universally agreed upon values for the T_g for many of these materials, but the trends are the same. For the poly(1-olefins),^{1,2} the T_g first increases and then decreases. For this series, an apparent minimum value is noted for polymers with about eight or nine carbons in the side chain. For poly(vinyl ether)s, polyacrylates, and polymethacrylates, the first member of the series already contains side-chain atoms. Hence, the T_g 's simply decrease when carbon atoms are added to the side chain.^{1,2} In these series, the T_g also showed a minimum value. Results indicated that a polymer with a hexadecyl side chain had a T_g in the range of a T_g for a polymer with a methyl or ethyl side chain.

Polyesters (I) based on terephthalic acid are also known to have a decreasing T_g as n increases.^{3,4}



Interestingly, a series of polyterephthalates from 2,3-disubstituted-1,4-butanediols showed no appreciable effect on T_g by the change in side-chain length until a chain length of ca. 3 or more carbon atoms was attained.⁵

In the course of work with cyclic carbonates as synthetic equivalents of the corresponding glycols, we have discovered a facile method for producing several polyglycol terephthalates with the following general structural formula:



Poly(ethylene terephthalate) is, of course, well known. The T_g of poly(1,2-propylene terephthalate)⁶ (R = Me) is reported in the patent literature. Poly(1,2-butylene terephthalate) is named in the patent literature, but no preparation or properties are given.⁷ The other two members of the polymer series reported here appear to be new (i.e., the 1,2-pentylene and the 1,2-hexylene polyterephthalates).

EXPERIMENTAL

Terephthalic acid was obtained as high purity grade from Matsuyama Petrochemicals. Propylene carbonate and tributylamine were obtained from Eastman Organic Chemicals. The propylene carbonate was distilled prior to use (bp 104°C/8 torr). Ethylene carbonate was obtained from Union Carbide and was distilled prior to use (bp 113°C/7 torr).

The other carbonates were obtained from reaction of the corresponding diol and diethyl carbonate by using the following general procedure: 0.5 mol of diol, 236 g (2.0 mol) of diethyl carbonate, and 1.5 g of sodium metal were placed in a 500-mL round bottom flask. The mixture was refluxed, and ethanol was removed through a 12-in. Vigreux column over a period of 2 days. After this time, 5 mL of acetic acid was added to the reaction mixture, and excess diethyl carbonate was distilled to a maximum pot temperature of 130°C. The pot residue was transferred to a smaller apparatus and distilled under vacuum to obtain the cyclic carbonate.

4-Ethyl-1,3-Dioxolan-2-one. Yield 72%, bp 86°C/0.25–0.35 torr.

4-*n*-Propyl-1,3-Dioxolan-2-one. Yield 68%, bp 76–79°C/0.35–0.40 torr.

4-*n*-Butyl-1,3-Dioxolan-2-one. Yield 94%, bp 100–103°C/0.12–0.17 torr.

Structures of the carbonates were supported by IR and NMR spectra. The following preparation of poly(1,2-propylene terephthalate) is typical of the polyester series reported. In a 500-mL round bottom flask [fitted with a stainless steel stirrer (shaft and blade), and a glass head to allow volatiles removal and inert gas introduction] were weighed the following: 83.9 g (0.50 mol) of terephthalic acid, 102.0 g (1.00 mol) of propylene carbonate, and 9.25 g (0.05 mol) of tributylamine. The mixture was stirred under nitrogen, and the flask was immersed in a molten metal (Belmont alloy) bath held at 220°C. After 1 h 44 min reaction time, the melt became clear. After 2 h reaction time, the temperature of the bath was raised to 245°C, and titanium tetrabutoxide in butanol was added (100 ppm Ti in the final polymer). A

TABLE I
Polyterephthalates II

R	IV (dL/g)	T_g (K)	Density (g/cm ³)	Carboxyl number (eq/10 ⁶ g)
H ^a	0.578	351	1.335	30.0
Me	0.494	368	1.259	33.0
Et	0.404	353	1.229	36.9
Pr	0.321	340	1.197	12.2
Bu	0.341	331	1.174	46.1

^a Note that polycondensation for this experiment was carried out for 1 h at 280°C rather than the general conditions cited in Experimental.

vacuum was applied at a pressure of 0.2 torr, and the bath temperature was raised to 255°C. After 1 h 35 min polycondensation under vacuum, the bath was removed, and the polymer was cooled under nitrogen. The polymer had an inherent viscosity (60:40 phenol:1,1,2,2-tetrachloroethane, 0.50 g polymer/100 mL solvent) of 0.494 dL/g.

Glass transition temperatures were determined on a Perkin-Elmer DSC-2 instrument by using a heating rate of 20 K/min. The glass transition temperature was taken as the point of inflection of the transition. Densities were measured in a density gradient column. Dynamic properties were determined by using a DuPont DMA 980 Analyzer and a compression-molded sample 0.060 in. (ca. 1.5 mm) thick.

RESULTS AND DISCUSSION

The polyterephthalates (II), with the exception of poly(ethylene terephthalate), were clear, amorphous materials upon preparation. For $R \geq \text{Me}$, no evidence of a melting endotherm or of crystallization exotherms was observed in the DSC scans. Attempts to crystallize IIb–IIe in toluene, acetone, dioxane, ethanol, and hexane resulted in solutions in all except ethanol and hexane. No evidence of whitening was seen with either ethanol or hexane. This amorphous behavior undoubtedly arises from the disorder introduced by the side-chain substituent.

As the size of the alkyl substituent increased, the attained molecular weight (see the measured inherent viscosities in Table I) of the polyester decreased. This may be related directly to thermal stability problems with

TABLE II
Observed Versus Calculated T_g 's

R	T_g observed (K)	T_g calcd (K) ^a
H	351	341
Me	368	343
Et	353	333
Pr	340	324
Bu	331	—

^a Calculated according to Ref. 2.

TABLE III

Group contributions for polyterephthalates II		
Group	Previous work, Y_g (K g/mol) ^a	This work, Y_{gi} (K g/mol)
—CH ₂ —	2700	3700
—CH(CH ₃)—	8000	12,100
—CH(CH ₂ CH ₃)—	10,500	14,000
—CH(CH ₂ CH ₂ CH ₃)—	13,100	15,900
—CH(CH ₂ CH ₂ CH ₂ CH ₃)—	—	18,400

^a See Ref. 2.

the glycols, such as dehydration or thermal cleavage. Dehydration of an ester end group could produce a vinyl end group without forming a carboxyl group, or thermal cleavage could produce a vinyl end group and a carboxyl end group. However, NMR analysis of the final polymers failed to indicate vinyl end groups (sensitivity may have, of course, been insufficient), and the carboxyl number did not consistently increase with the increase in alkyl chain length. As the substituent chain length increased, the molecular weight probably was also decreased as a consequence of the decrease in glycol volatility.

The observed T_g 's showed the same general pattern noted for polyolefins.^{1,2} An increase in T_g was observed by going from the unsubstituted chain to a methyl substituent (Table II). The T_g was then observed to decrease as expected, as has been seen with all of the series mentioned above. Where R was octyl, the synthesis method reported here failed to produce a polymer; therefore, it was impossible to determine any possible minimum in the T_g . The initial increase in the T_g can be attributed to a chain stiffening effect from the increase in the rotational energy barrier of methyl passing hydrogen as compared to the rotational energy barrier of hydrogen passing hydrogen in the unsubstituted case. This chain stiffening effect must far

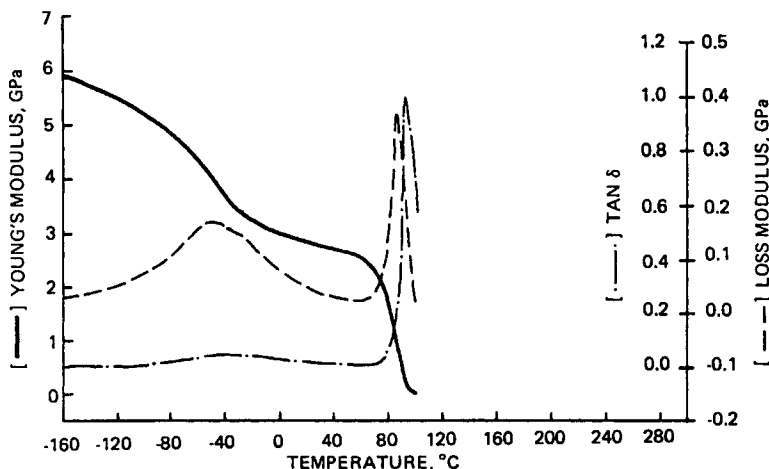


Fig. 1. Poly(ethylene terephthalate) (IIa) dynamic mechanical spectrum.

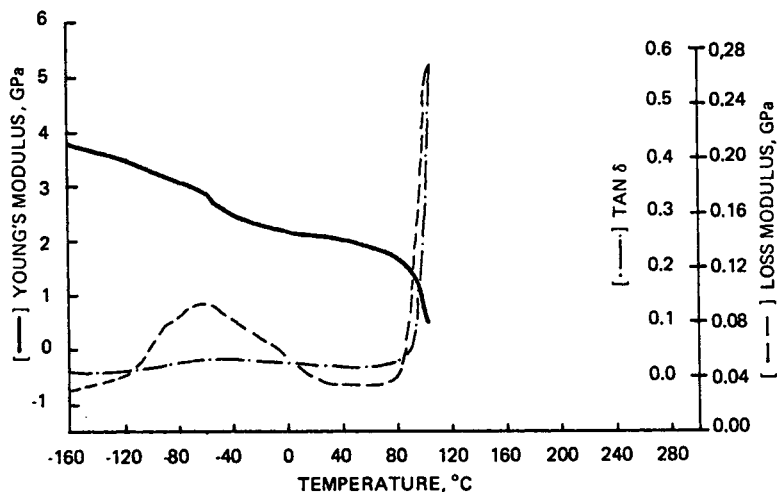


Fig. 2. Poly(1,2-propylene terephthalate) (IIb) dynamic mechanical spectrum.

exceed the effect of decreased chain packing ability. The decrease in T_g that followed as the length of R was increased must then be interpreted as a relatively small increase in rotational energy barriers accompanied by a relatively large decrease in the chain packing ability owing to an increase in steric bulk of the substituents. This was substantiated by the densities of the polymers (Table II). It should be noted that molecular weight in the range of this work was probably sufficient to yield a representative T_g since a 0.321 dL/g sample of polyester IIb had a T_g of 366 K and the 0.494 dL/g sample had a T_g of 368 K.

A correlation for predicting the T_g of a polymer via a group contribution theory² was applied to this series of polyterephthalate esters. The results (Table III) showed only a qualitatively fair correlation to the actual data. The group contribution (Y_{gi}) factors needed to correlate the observed data

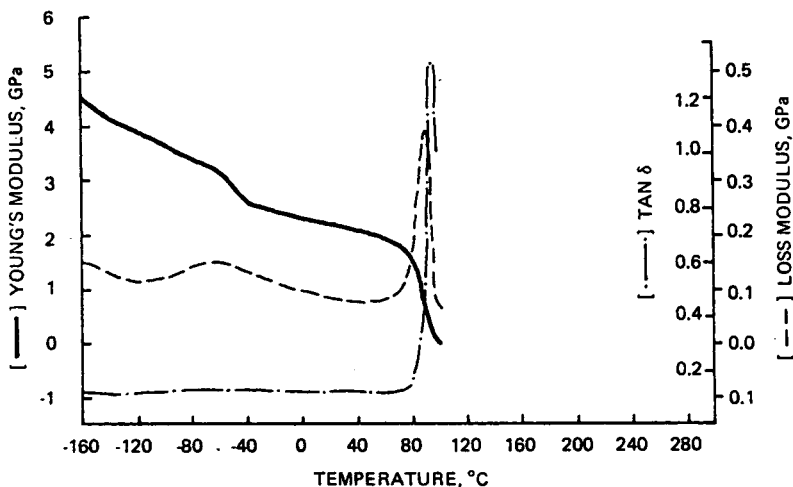


Fig. 3. Poly(1,2-butylene terephthalate) (IIc) dynamic mechanical spectrum.

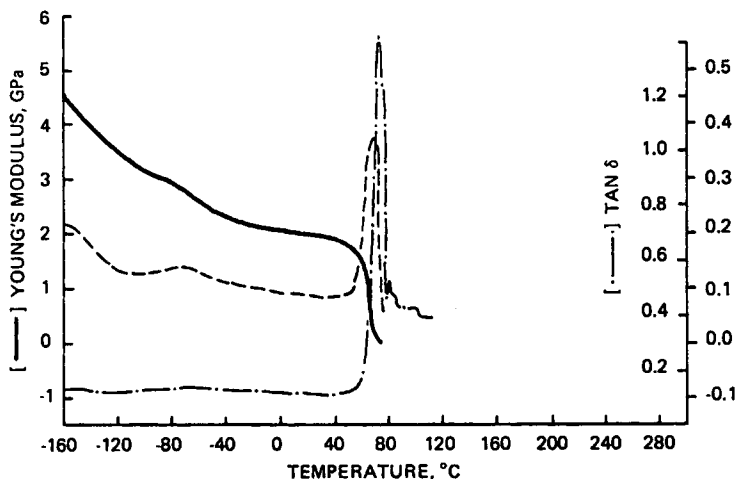


Fig. 4. Poly(1,2-hexylene terephthalate) dynamic mechanical spectrum.

(Table III) were substantially different from those previously determined for other polymers. This is not unreasonable since the original Y_{gi} factors used were derived from polymers other than polyesters.

The dynamic mechanical spectra* (Figs. 1-4) showed T_g 's consistent with those measured by DSC, with the expected shift to higher temperature due to the frequency of measurement (Table IV). The modulus G' decreased with an increase in side-chain substituent length.

Of special note was the dynamic mechanical spectra information at the β -transition (Fig. 5, Table IV). The data showed a trend towards lower peak temperature and lower relative peak area with an increase in side-chain substituent length. In this process, the β -transition peak appeared to become more symmetrical. Previous authors⁸⁻¹⁴ have looked at the dynamic mechanical properties of polyterephthalates (I) and have concluded that the β -transition in these materials is composed of several different transitions. For poly(ethylene terephthalate), two transitions have been ascribed to *trans*- and *gauche*-glycol units in the chain; the *trans*-configured units are represented by the higher temperature of the two transitions. By applying this interpretation to the polyesters of our work, we found that as the side-chain length increased, the population of *trans*-glycol units apparently de-

TABLE IV
DMA of Polyterephthalates II

R	T_a (°C)	G' at 20°C (GPa)	T_β (°C)	T_β rel area
H	93	2.85	-36	100
Methyl	104	2.15	-52	68
Ethyl	94	2.24	-52	47
Butyl	71	2.05	-74	21

* Note that the DMA spectrum for polyester IIId could not be obtained, owing to brittleness of the compression molded specimen.

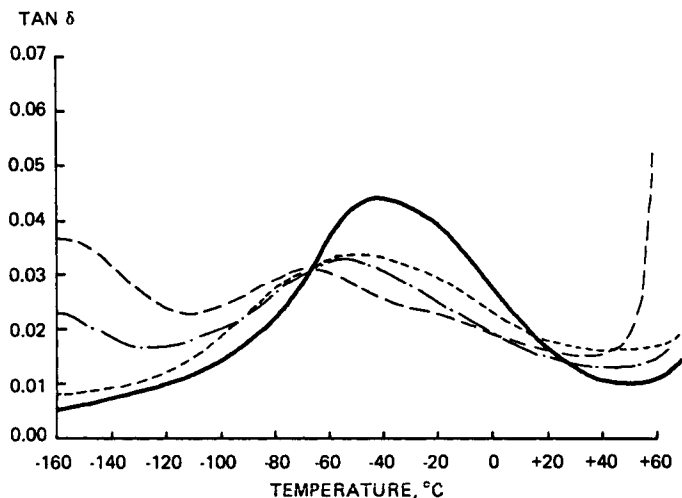


Fig. 5. Dynamic mechanical spectra: (---) IIa; (···) IIb; (—) IIc; (— · —) IIe.

creased drastically. This is reasonable since steric hinderance of the alkyl groups with the glycol oxygen (and perhaps even the carboxyl group) would be expected to be minimized by having the glycol oxygens *gauche* to each other. (The alkyl group–oxygen repulsion certainly would be expected to be larger than the oxygen–oxygen repulsion.)

The apparent diminution of the *gauche*-related peak of the β -transition, which was concurrent with the loss of the *trans*-glycol related one, could be understood as a decrease in the actual amplitude of the relaxation, which diminishes with an increase in alkyl chain length. That less energy was dissipated with the longer chains probably is an interchain steric effect. In addition to this effect, there could also be a decrease in overall peak area, owing to the loss of other transitions not considered, such as transitions involving the carbonyl groups themselves.

It should also be noted that as the alkyl chain length increased, the tail of a peak which was below -160°C began to emerge into the region above -160°C . Similar results have been seen for certain cellulose esters.¹⁵ This lower temperature peak probably has its origins in the methylene groups in the side chain. This apparent increasing restriction of the wagging (or perhaps rotation) of the methylene groups would seem reasonably to be a result of interchain interactions that restrict movement in the alkyl groups.

CONCLUSIONS

In the limited series of side-chain branched polyterephthalates reported here, the T_g increased by proceeding from $R=\text{H}$ to $R=\text{Me}$, and thereafter showed a steady decrease. This was consistent with previous work on a number of polymer series. The dynamic mechanical spectra were interpreted as showing a shift to mostly *gauche*-glycol units in the chain as a result of the steric hinderance of the alkyl group. Evidence was also apparent, that, as alkyl chain length increased, there was an increase in restricted movement of the methylene groups on the side chain.

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