1582 Macromolecules 1980, 13, 1582-1587

tivation energy composition effects at high small-molecule loading.

Summary

The dielectric relaxation spectra of solid solutions of bis[4-(diethylamino)-2-methylphenyl]phenylmethane (BDETPM)/polycarbonate (BPAPC) solid solutions have been studied as a function of composition. The T_g of the system is a continuous function of composition and has been interpreted in terms of a free-volume additivity equation. The polymer and monomer exhibit correlated motion at T_g. The activation energies of T_g are Arrhenius activated over the temperature–frequency regime of the experiments. These activation energies show a composition dependence made up of two linear portions which intersect between 20 and 30 wt % BDETPM. This intersection is directly correlatable to the disappearance of the BPAPC β relaxation and indicates a change in the dynamics of the T_g reorientation process with the elimination of the β relaxation. The results are discussed in terms of previously studied small-molecule/polymer solid solutions.

It is shown that the sub-T_g relaxations of BPAPC are affected by the addition of BDETPM. The β and γ relaxations are plasticized and decrease in intensity. The β relaxation "disappears" between 20 and 30 wt % BDETPM, while the γ intensity is a direct function of composition. Little evidence for the β relaxation of BDETPM is observed.

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Studies on New Polyesters. Transition Temperatures of Poly[*p*-benzoyl(1,1-dimethyl-2-ethyl)oxy]

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ABSTRACT: A new polyester, poly[*p*-benzoyl(1,1-dimethyl-2-ethyl)oxy], has been synthesized by polycondensation of either *p*-(1,1-dimethyl-2-hydroxyethyl)benzoic acid or its methyl ester. This polyester is linear and semicrystalline, melts at about 250 °C, has a glass transition temperature of about 120 °C, and exhibits excellent film- and fiber-forming characteristics. This unusual combination of the main transition temperatures is assumed to be related to a preferred conformation of the structural repeat unit, which in turn may result from an interaction between the *gem*-dimethyl and ester carbonyl moieties. The polymerization behavior of the acetyl derivative of the monomer and the dependency of the glass transition temperature on both the functional group contribution and the composition of the respective copolymers indicate that this interaction is an intracatenary rather than an intercatenary one.

Introduction

The causality characterizing the relations between transition phenomena observed in polymers and polymer properties has been well recognized.[1] Though several different transitions have been observed in polymeric materials, the glass–rubber transition (T_g) and the crystalline melting point (T_m) are the two principal ones. They have received extensive phenomenological consideration particularly with regard to determining the effects of structural parameters, mainly constitutional ones, on the temperatures at which these transitions occur. Ample evidence indicates a reciprocal relationship between these transition temperatures and what may be considered the intrinsic flexibility of the corresponding macromolecule. Though most of the published reports are concerned with effects of polymer structure on T_g, it is quite apparent that also T_m is primarily a function of the chain structure. This is reflected in the value for the ratio T_g/T_m which has been found to be in the range 0.5–0.8 and about 0.67 for most of the known semicrystalline polymers.[2-4] Awareness of the interrelation of the transition temperatures and chain flexibility characterizes the approaches to "high-T_g polymers", which entail mostly the synthesis of stiff macromolecules of the types best represented by most of

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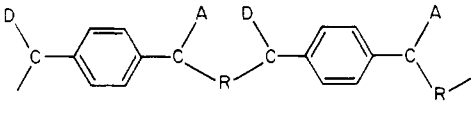
the thermally stable polymers developed during the last 2 decades.[5,6] These materials are generally characterized by structural units composed of aromatic moieties that are either condensed to each other or interlinked by simple short linkages. Thus, whereas intercatenary forces such as hydrogen bonding may be present, the stiffness of the entire macromolecule is primarily the result of the covalent bonds responsible for the direct catenation of the rigid backbone units. Consequently, introduction of flexible linkages will result in lower transition temperatures, particularly in the absence of intercatenary forces. If these linkage segments, however, are capable of reversible, temperature-dependent, intrasegmental interactions such that a specific conformation of the interlinking unit results at temperatures below T_m, then the macromolecule may be characterized by considerable stiffness. In this state there may be resistance to molecular motions that comprise nonelastic displacements of chain segments. The corresponding macromolecule may thus require a higher temperature for the onset of large-scale segmental motions—a process commonly referred to as the glass transition—without necessarily affecting proportionally the melting point of the crystalline polymer. This means that the temperature difference $T_m - T_g$ decreases and the ratio T_g/T_m shifts to higher values when compared to that of a polymer incapable of the considered intracatenary interaction. The formation of a specific conformation of the interlinking unit may result from interactions that may involve nonbonding forces (an electron density potential, van der Waals forces), coordinate covalent bonds, or hydrogen bonds.

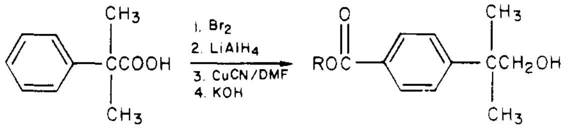
A polymer which illustrates the above concept may be represented by general structure 1, where the *p*-phenylene rings constitute the rigid segments, R is part of a flexible linkage, and A and D are functions capable of mutual interaction. If this interaction is an intramolecular one, then a cyclic structure must be considered for the conformation of the interlinking units.



1

In this paper we shall demonstrate the presented concept on poly[*p*-benzoyl(1,1-dimethyl-2-ethyl)oxy], a new polyester which may be considered a member of the group represented by general structure 1.

This polymer was formed by polycondensation of either *p*-(1,1-dimethyl-2-hydroxyethyl)benzoic acid or its methyl ester, which were obtained by the sequence of reactions shown in the following scheme:



I

II, R = H
III, R = CH$_3$

Experimental Section

Monomer Synthesis. *p*-(1,1-Dimethyl-2-hydroxyethyl)benzoic acid (II) or its methyl ester (III) can be obtained by the procedure reported by Heck and Winstein[7] or by the route we preferred, entailing conversion of *p*-(1,1-dimethyl-2-hydroxyethyl)bromobenzene to *p*-(1,1-dimethyl-2-hydroxyethyl)cyanobenzene and subsequent hydrolysis to II.

***p*-(1,1-Dimethyl-2-hydroxyethyl)cyanobenzene.** *p*-(1,1-Dimethyl-2-hydroxyethyl)bromobenzene (148 g, 0.646 mol) was added to a flask fitted with a reflux condenser, magnetic stirrer, and oil bath. Dimethylformamide (350 mL) and cuprous cyanide (69.4 g, 0.775 mol) were then added to the flask. The heterogeneous mixture was heated to gentle reflux, whereupon it became somewhat more homogeneous and could more easily be stirred. The mixture was heated at reflux for 5 h. While hot, the mixture was cast into 1 L of water and the flask was washed with 100 mL of hot DMF. The precipitated residue was stirred by hand as well as possible and allowed to settle, and the greater portion of the water was decanted and discarded. A freshly prepared solution of 340 g of ferric chloride, 85 mL of concentrated HCl, and 510 mL of water was added to the residue to destroy copper complexes. The mixture was heated with good stirring at 60–70 °C for 20–30 min. The crude nitrile was then extracted with three 200-mL portions of benzene. The benzene extracts were combined and dried over anhydrous potassium carbonate for 0.5 h. Benzene was removed in a rotoevaporator, and the resultant yellowish oil crystallized easily when cooled to room temperature. The yield was 102 g (90%); mp 70–82 °C. The product was recrystallized as follows: the crude material was dissolved in about 100 mL of carbon tetrachloride, and the resultant solution was decolorized with activated charcoal, filtered, and heated to reflux after about 400 mL of *n*-heptane had been added. Pure cyano alcohol crystallized upon cooling to room temperature: mp 84–85 °C; NMR ($CDCl_3$) δ 1.33 (s, CH_3), 2.38 (s, OH), 3.58 (s, CH_2), 7.50 (s, phenyl), in a ratio of 6:1:2:4; IR (neat) 2255 ($C{\equiv}N$) cm^{-1}; mass spectrum (CH_4/NH_3 probe), *m/e* 176 ($M + H^+$), 193 ($M + NH_4^+$), 204 ($m + C_2H_5^+$).

Anal. Calcd. for $C_{11}H_{13}NO$: C, 75.39; H, 7.48; N, 7.99. Found: C, 75.36; H, 7.46; N, 7.77.

***p*-(1,1-Dimethyl-2-hydroxyethyl)benzoic Acid.** *p*-(1,1-Dimethyl-2-hydroxyethyl)cyanobenzene (75 g, 0.43 mol) was dissolved in a solution of ethylene glycol (150 mL) and water (50 mL) at 80 °C. The above solution was then heated in an oil bath with good stirring to 135–140 °C. A solution of 50% aqueous NaOH (140 mL) in 150 mL of water was added dropwise at such a rate that a gentle reflux was maintained. After addition of the base the clear solution was allowed to reflux until no more ammonia could be detected with moist pH paper. The solution was then diluted while still hot with 500 mL of water and allowed to cool to room temperature. The cooled solution was extracted twice with 100-mL portions of ether and the ether layers were discarded. The aqueous layer was heated on a steam bath to remove any trapped ether, cooled to 0 °C, and acidified with concentrated HCl. The precipitated acid was filtered, washed with 150 mL of ice-cold water, and dried in a vacuum oven at 50 °C. The crude yield was 80 g (96%); mp 154–156 °C. The material was recrystallized once from ca. 1100 mL of 3:1 (v/v) water–methanol and three more times from boiling water: final mp 156–157 °C (lit.[7] mp 158–159 °C); NMR (CD_3COOH) δ 1.38 (s, CH_3), 3.78 (s, CH_2), 7.58–8.24 (AA′BB′, phenyl), in a ratio of 6:2:4; IR (KBr pellet) 1685 (C=O), 2520, 2645 (COO*H*), 1280 (C—O), 1360, 1382 (*gem*-CH_3) cm^{-1}; mass spectrum (CH_4/NH_3 probe), *m/e* 177 ($M + H^+ - H_2O$), 195 ($M + H^+$), 212 ($M + NH_4^+$); neutralization equivalent calcd 194.22, found 194.41.

Anal. Calcd for $C_{11}H_{14}O_3$: C, 68.02; H, 7.26. Found: C, 68.02; H, 7.21.

Methyl *p*-(1,1-Dimethyl-2-hydroxyethyl)benzoate. The method which follows eliminates any possibility of formation of oligomeric polyesters.

The following reagents were placed in a flask equipped with a magnetic stirrer, oil bath, and reflux condenser protected with a guard tube containing Drierite: *p*-(1,1-dimethyl-2-hydroxyethyl)benzoic acid (20 g, 0.103 mol), sodium bicarbonate (9.4 g, 0.112 mol), *N,N*-dimethylacetamide (100 mL), and methyl iodide (28.4 g, 0.2 mol). The mixture was heated at 80 °C for 2.5 h, cooled to room temperature, and filtered to remove any unreacted hydroxy acid. The clear solution was then poured into 600 mL of water and stirred for 10 min. Fifty milliliters of 5% aqueous sodium bicarbonate was added and the resultant solution extracted three times with 120-mL portions of ether. The ether layers were combined, washed with dilute aqueous bicarbonate, dilute aqueous sodium thiosulfate, and finally water, and dried over anhydrous potassium carbonate. The ether solution was evaporated to give a colorless liquid which crystallized upon standing at room temperature; yield 99%. The compound was purified by distillation [bp 135–140 °C (0.3–0.5 mm)] followed by recrystallization from

1:4 (v/v) ether–pentane at −20 °C: mp 44–45 °C (lit.[7] mp 42–43.5 °C); NMR ($CDCl_3$) δ 1.33 (s, *gem*-CH_3), 2.03 (br, s, OH), 3.60 (s, CH_2), 3.87 (s, CH_3OOC), 7.39–8.06 (AA′BB′, phenyl), in a ratio of 6:1:2:3:4.

Anal. Calcd for $C_{12}H_{16}O_3$: C, 69.20; H, 7.74. Found: C, 69.29; H, 7.88.

***p*-(1,1-Dimethyl-2-acetoxyethyl)benzoic Acid.** The above hydroxy acid (9.71 g, 0.05 mol) was dissolved in 1,2-dimethoxyethane (25 mL) containing acetic anhydride (20.42 g, 0.20 mol). Anhydrous pyridine (20 mL) was added and the solution was refluxed for 2 h. The solvent and excess anhydride were removed on a rotoevaporator and the residue was taken up in benzene. The benzene solution was washed with 5% aqueous HCl and water and then dried over anhydrous sodium sulfate. The solvent was removed on a rotoevaporator. The crystalline residue was recrystallized twice from 1:4 (v/v) benzene–heptane to give 4.5 g of white needles: mp 102–103 °C; NMR ($CDCl_3$) δ 1.40 (s, *gem*-CH_3), 2.02 (s, CH_3OOC), 4.20 (s, CH_2), 7.42–8.20 (AA′BB′, phenyl), 12.40 (s, $COOH$), in a ratio of 6:3:2:4:1.

Anal. Calcd for $C_{13}H_{16}O_4$: C, 66.08; H, 6.83. Found: C, 65.80; H, 6.96.

Methyl *p*-(2-Hydroxyethoxy)benzoate. This compound was prepared from *p*-hydroxybenzoic acid according to the published procedure.[8] The intermediate hydroxy acid was purified by decolorization with activated charcoal followed by recrystallization from water; mp 179–180 °C. This material was converted to the methyl ester, which was purified by recrystallization from carbon tetrachloride: mp 66–68 °C; NMR ($CDCl_3$) δ 3.25 (br s, OH), 3.84 (s, CH_3OOC), 4.04 (m, CH_2), 6.82–8.01 (AA′BB′, phenyl), in a ratio of 1:3:4:4.

Anal. Calcd for $C_{10}H_{12}O_4$: C, 61.21; H, 6.16. Found: C, 61.44; H, 6.13.

Polymer Synthesis. Poly[*p*-benzoyl(1,1-dimethyl-2-ethyl)oxy] (from the Hydroxy Acid). A typical melt polycondensation was conducted as follows: a 30-mL polymerization tube equipped with a glass capillary tube reaching to the bottom and a vacuum side arm was charged with 9 g of the monomer containing 0.002 g of antimony triacetate catalyst. The tube was then placed in a vapor bath at 222 °C (methyl salicylate) and, after the monomer had melted, nitrogen gas flow was applied to the capillary. Subsequently, vacuum was applied to the side arm gradually over a 25-min period. The final pressure was 1–3 mm. These conditions were maintained for 1 h, whereupon the tube was transferred to a vapor bath at 275 °C (triethylene glycol) without interruption of the inert-gas flow or vacuum. The pressure was lowered to 0.5–1.0 mm and the conditions were maintained for 3 h. The tube was then removed from the bath and was either allowed to cool slowly under vacuum or quenched rapidly in cold water.

The polymer, which was isolated as a hard glassy plug, is soluble in many solvents, among which are α-methylnaphthalene, hexafluoroisopropyl alcohol, 60:40 (w/w) phenol–*sym*-tetrachloroethane, and trifluoroacetic acid, and could be purified by the usual precipitation techniques with ethanol as the nonsolvent. The reduced viscosity of the above polymer was 0.4 dL/g (phenol–TCE). An IR spectrum was obtained from a thin film which was cast from hexafluoroisopropyl alcohol; the following characteristic bands were observed: 2980 (*gem*-CH_3), 1720 (ester C=O) cm^{-1}. The NMR spectrum (CF_3COOH) showed broad signals characteristic of polymeric material: δ 1.50 (s, CH_3), 4.55 (s, CH_2), 7.56–8.10 (AA′BB′, phenyl), with a ratio of 6:2:4.

Anal. Calcd for $(C_{11}H_{12}O_2)_n$: C, 74.97; H, 6.86. Found: C, 74.65; H, 7.00.

The structure of the polymer was further confirmed by saponification in refluxing 3 N 50/50 aqueous alcoholic potassium hydroxide. The product isolated from the hydrolysate by acidification with dilute HCl was identified as the monomer. A mixture melting point with authentic pure monomer showed no depression in the melting point and the NMR spectrum was identical with that of the authentic sample.

Strong fibers could be pulled quite easily from the polymer melt, and tough transparent films could be cast from hexafluoroisopropyl alcohol. The bulk material showed a T_g of 123 °C and a T_m of 250 °C (DSC and microscopy).

The polymer was also prepared by the technique described above without the addition of antimony triacetate. In this case the reduced viscosity was 0.33 dL/g, and the material was in all respects identical with that prepared with catalyst.

Poly[*p*-benzoyl(1,1-dimethyl-2-ethyl)oxy] (from the Methyl Ester). Methyl *p*-(1,1-dimethyl-2-hydroxyethyl)benzoate (5 g) was charged into a small polymerization tube equipped with a narrow gas-inlet tube and a side arm connected to a small vacuum trap. Distilled tetra-*n*-butyl orthotitanate (0.005 g) was added through the inlet tube as a 10% solution in chloroform. With the system vented to the atmosphere through an oil bubbler, argon gas was admitted through the inlet tube and allowed to purge for 0.5 h. The monomer was then melted in a Wood's metal bath at 120–150 °C under a moderate argon flow. These conditions were maintained until no more methanol collected in the trap (about 1.5 h). The temperature was then slowly raised to 250 °C over a 2-h period, during which time the material became more viscous. These conditions were maintained for an additional hour. Without interruption of heat or argon flow, the oil bubbler was removed and the system evacuated slowly to a pressure of about 2 mm. The temperature was then raised to 260–265 °C, and subsequently the pressure was lowered to 0.5 mm by decreasing the argon flow rate. After 1.5 h under these conditions, the temperature was raised to 270–280 °C and maintained for 0.5 h. At this point, the material in the tube was so viscous that it would hardly flow. The tube was removed from the bath and allowed to cool slowly under vacuum. There was obtained about 3 g of an extremely hard and transparent polymer plug which was almost water white. The reduced viscosity was 0.8 dL/g (phenol–TCE). Polymer was also prepared from the methyl ester as in the above example without the use of titanate catalyst; however, longer condensation times were required and materials of lower η_{sp}/c resulted. With the exception of the molecular weight, the polymers derived from the methyl ester were identical with those derived from the free hydroxy acid.

Copolymers with Methyl *p*-(2-Hydroxyethoxy)benzoate. A mixture of methyl *p*-(1,1-dimethyl-2-hydroxyethyl)benzoate (2.12 g, 0.01 mol) and methyl *p*-(2-hydroxyethoxy)benzoate (6.26 g, 0.032 mol) was placed in a polymerization tube constructed as in the previous example. A solution of 0.0084 g of tetra-*n*-butyl orthotitanate in 0.1 mL of chloroform was added and the temperature slowly raised to 220 °C with continuous argon flow over a 3-h period. The temperature was then raised to 250 °C and the system evacuated to 0.7 mm. These conditions were maintained for 1 h, whereupon the temperature was raised to 280 °C and the pressure adjusted to 0.4 mm. After 1.5 h, the reaction was terminated. The copolymer was then dissolved in trifluoroacetic acid (10% solution) and precipitated into 10 volumes of methanol. The white polymer solid was washed with methanol and dried in a vacuum oven; yield 6.1 g; η_{sp}/c = 0.32 dL/g (phenol–TCE). The copolymer composition was determined by ^1H NMR spectroscopy with CF_3COOD as solvent. The same technique was used to prepare other copolymer compositions of these monomers.

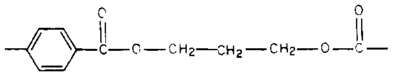
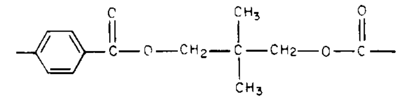
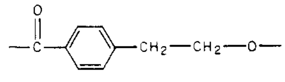
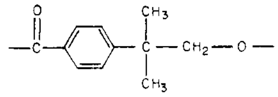
Copolymer with Bis(2-hydroxyethyl) Terephthalate. A mixture of methyl *p*-(1,1-dimethyl-2-hydroxyethyl)benzoate (2.05 g, 0.01 mol) and bis(2-hydroxyethyl) terephthalate (8.04 g, 0.032 mol) was placed in a polymerization tube along with 0.0383 g of tetra-*n*-butyl orthotitanate in chloroform. The polymerization was then conducted as described for the previous copolymer example. The yield of copolymer after precipitation from trifluoroacetic acid solution in methanol was 6 g; η_{sp}/c = 0.79 dL/g (phenol–TCE). Other copolymer compositions were prepared in a similar manner.

Attempted Polymerization of *p*-(1,1-Dimethyl-2-acetoxyethyl)benzoic Acid. This acetyl derivative failed to undergo melt polycondensation in the presence of either magnesium metal or antimony triacetate. In all cases the monomer eventually distilled from the polymerization tube in essentially pure form, leaving no residue.

Transition temperatures (T_g, T_m) for the prepared polymers were determined by differential scanning calorimetry on a Du Pont 990 instrument in argon at a heating rate of 20 °C/min. In some cases these values were confirmed by hot-stage polarized light microscopy at a heating rate of 10 °C/min. The disappearance of stress birefringence afforded the value for T_g.

Reduced viscosities were measured in the specified solvents at a concentration of 0.5% by weight at 25 °C.

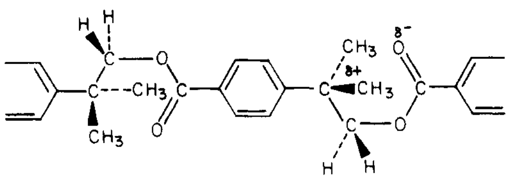
Table I
Structure and Melting Points of Some Polyesters

structure	T_m, °C
 VI	220
 V	140
 VII	185
 IV	250

Results and Discussion

The polycondensation of either II or III resulted in the expected polyester (IV), which was found to be crystalline with a melting point of about 250 °C and a glass transition temperature of about 120 °C. This combination of transition temperatures is unusual since the crystalline melting point of a semicrystalline polymer with a glass transition temperature of about 120 °C is normally expected to be above 300 °C. On the other hand, the observed melting point is at variance with a generally prevailing phenomenon, namely, that the introduction of substituents usually decreases the melting point of the polymer. This can, for instance, be seen in Table I for the polyesters derived from terephthalic acid and either 2,2-dimethylpropanediol (V) or 1,3-propanediol (VI), which have melting points of 140 and 220 °C, respectively. However, as can be seen, this does not hold for the present polymer (IV), which has a distinctly higher melting point than the corresponding unsubstituted polyester (VII). It is furthermore well-known and has been reviewed recently[9] that introduction of side chains results generally in a decrease of the glass transition temperature.

The "apparent anomaly" of polyester IV with respect to its main transition temperatures can hardly be attributed to simple steric factors since molecular models did not indicate hindrance to free rotation for the intrinsically flexible unit that interlinks the benzene rings. The phenomena observed point to a preferred conformation of this interlinking unit such as shown in structure 2, which obviously results from an interaction between the *gem*-dimethyl moiety and the ester carbonyl. This intracatenary interaction may entail either polar (as indicated) or van der Waals forces or both.



2

Though intercatenary interactions are also conceivable, the postulated intracatenary one appears thermodynamically more favored since the considered ring structure is essentially strain free. The intensity of the interaction and thus the stability of the corresponding ring structure were reflected by the behavior of the acetoxy derivative of II. This derivative was prepared since it was expected to polymerize with elimination of acetic acid in complete analogy to the process reported by Economy et al.[10] for the successful polymerization of *p*-hydroxybenzoic acid. No polymerization, however, occurred at temperatures between 200 and 275 °C, in either the presence or the absence of an ester-interchange catalyst. Upon application of vacuum the acetyl derivative distilled unchanged and quantitatively.

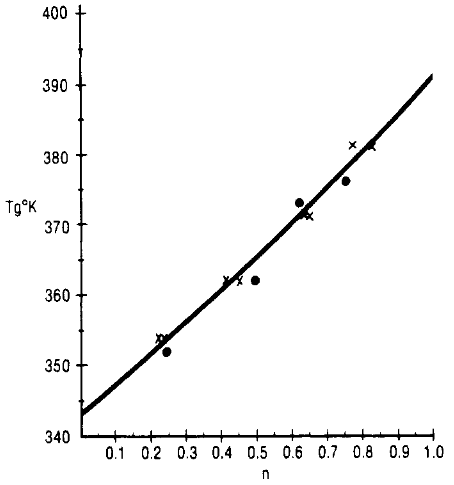


Figure 1. Glass transition temperature as a function of copolymer composition.

Copolymerization of III with either methyl *p*-(2-hydroxyethoxy)benzoate or bis(hydroxyethyl) terephthalate yielded what may be considered essentially random copolymers. Their structures and compositions were verified by NMR analysis, and their glass transition temperatures were determined by DSC techniques. Both poly(ethylene terephthalate) and poly[benzoyl(2-hydroxyethyl)oxy], the corresponding homopolymers of the comonomers employed, have essentially the same glass transition temperature of about 70 °C. It is well-known that for a copolymer in which the monomer units are randomly distributed, properties such as polarity and chain stiffness have approximately average values of those of the individual homopolymers, provided that the equilibrium conformation of the particular structural units is the same in both the copolymer and the corresponding homopolymers. In such cases T_g can be predicted readily if the copolymer composition and the glass transition of the homopolymers are known. Widely used for this purpose have been simple empirical equations such as (1), where n is in this case a mole fraction.

$$1/T_g = n_1/(T_g)_1 + (1 - n_1)/(T_g)_2 \qquad (1)$$

Figure 1 shows a plot of T_g vs. the mole fraction n of the *p*-benzoyl(1,1-dimethyl-2-ethyl)oxy units in copolymers containing co-units of either *p*-benzoyl-2-ethyloxy (●) or ethylene terephthalate (×). The solid line represents values calculated according to eq 1 with $(T)_g)_1 = 391$ K (poly[*p*-benzoyl(1,1-dimethyl-2-ethyl)oxy]) and $(T_g)_2 = 343$ K (T_g of either of the corresponding homopolymers), and the symbols are the respective experimental data.

The obviously very good agreement between the calculated and experimental values over the entire range of compositions is indicative of strict adherence to the additivity concept and this in turn indicates that the conformation of the particular individual structural units is the same in both homopolymers and copolymers. Thus, if the glass transition temperature observed for the poly[*p*-benzoyl(1,1-dimethyl-2-ethyl)oxy] would have been related to a conformation that was due mainly to inter-

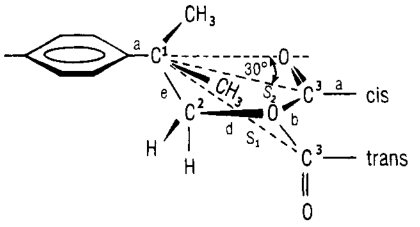


Figure 2. Structure of interlinking unit.

catenary interactions entailing the interlinking units, then the different environment for these units in a copolymer should have resulted in different contributions to the T_g of the copolymer. Intracatenary interactions of the type considered earlier should be quite independent of adjacent polymer chains and the particular units should contribute to the T_g of the copolymer in direct proportion to their concentrations. According to the results shown in Figure 1, this seems to be the case for the systems considered.

Approaches to correlate the chemical structure and the glass transition temperature of polymers have resulted in a number of empirical relationships. They are usually based upon the assumption that the functional groups in the repeating unit contribute to the glass transition temperature in direct proportion to their respective concentrations. van Krevelen[11] has proposed the simple relationship (2), where Y_g is the functional group contribution

$$T_g = \sum_i Y_{gi}/Z \qquad (2)$$

and Z is the number of atoms in the backbone of the repeating unit. He demonstrated that for many polymers there was good agreement between experimental and calculated values. Thus, with values for functional group contributions[11] of 1850 for C_6H_4, 640 for COO, 170 for CH_2, and 280 for O, values for T_g of 345 and 347 K are calculated for the poly(p-benzoyl-2-ethyloxy) and poly(ethylene terephthalate), respectively, which agree well with the experimentally determined value of about 343 K for either of the two polyesters. Obviously, the assumption made for formulating eq 2, namely, that the contribution of a given functional group is independent of the nature of adjacent groups, is valid for these two polymers. Employing the same values for the corresponding group contributions and the value of 226 for $C(CH_3)_2$[11] results in a calculated value for the glass transition temperature of poly[p-benzoyl(1,1-dimethyl-2-ethyl)oxy] of 360.75 K, which differs considerably from the experimentally obtained value of about 391 K. The lower (calculated) value could in all probability be expected if the polymer chain were characterized by a trans structure of the interlinking unit such as indicated in Figure 2 with the distance S_1 between the carbon atoms C^1 and C^3. Constructing a chain segment with molecular models showed that for the interaction considered for the dimethyl and carbonyl moieties the resulting cis structure involves a displacement of about 30° for the carbon atom C^3 with respect to the axis formed by the para carbon atoms of the benzene ring and the carbon atom C^1, resulting in the distance S_2 between C^1 and C^3. To take into account the effect of the conformation of the interlinking unit, it appears reasonable to consider the contribution of this unit a direct function of its dimension, keeping in mind that a shortening of it results in an increase in T_g. Thus, eq 2 may now be written as

$$T_g = [Y_B + Y_I(S_1/S_2)]/Z \qquad (3)$$

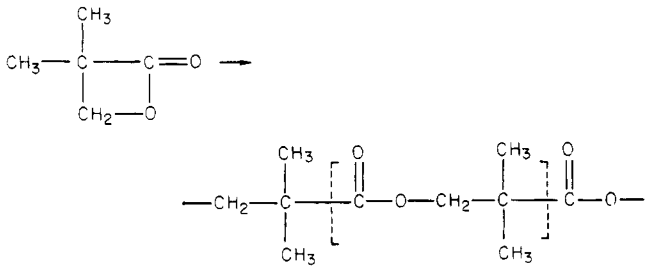
where Y_B and Y_I stand for the group contributions of the benzene ring and the interlinking unit, respectively. Values of 3.6 and 2.9 Å for S_1 and S_2 were calculated according to Figure 2, using the following bond distances and bond angles: e, 1.54 Å; d, 1.44 Å, b, 1.31 Å; $\measuredangle ae$, 108.5°; $\measuredangle ed$, 111.5°; $\measuredangle db$, 112.0°; $\measuredangle ba$, 109.0°. Substitution into eq 3 yields

$$T_g = [1850 + 1036(3.6/2.9)]/8 = 392 \text{ K}$$

which agrees very well with experimentally determined values that were in the range 391–394 K.

Though the arguments presented here have caused us to favor the cis structure as the prevailing conformation of the interlinking unit, we realize that the evidence is somewhat circumstantial. More definitive structural information may be derived from an analysis involving variable-temperature C^{13} NMR studies, which may show subtle differences in the chemical shifts for both the CH_3 and C=O carbon atoms of the corresponding cis and trans conformers. Necessitating synthesis and analysis of appropriate (low molecular weight) model compounds, however, places such a study beyond the scope of the present paper.

Examining the chemical structure of poly[p-benzoyl-(1,1-dimethyl-2-ethyl)oxy], one readily recognizes that the unit which interlinks the benzene rings is identical with the structural unit of the polymer that can be obtained by ring-opening polymerization of α,α-dimethyl-β-propiolactone, commonly called pivalolactone



Poly(pivalolactone) has been described in the literature together with some accounts of its characterization with regard to the prevailing chain conformation. On the basis of X-ray diffraction data Perego et al.[12] and Carazzolo[13] have proposed for the polylactone a chain model characterized by a (ttgg)$_2$ chain conformation. Though such a conformation would not accommodate the intramolecular interaction considered for the interlinking unit of our new polyester, it is interesting that both polymers have about the same melting point, 245 and 250 °C, whereas their glass transition temperatures are quite different, −10 and +120 °C, respectively. It appears thus possible that the collapse of a structure resulting from either inter- or intramolecular interaction between the gem-dimethyl and carbonyl moieties occurs within a rather narrow temperature range, regardless whether or not other structural elements are present. Incorporation of a rigid segment such as a benzene ring merely reduces the segmental mobility as it is reflected in an increase of the glass transition temperature. This increase, however, is not paralleled by a proportional increase in the melting point.

On the basis of this observation one may speculate that it may be possible to synthesize a series of polymers characterized by rather different physical properties as a consequence of different repeating units but all having essentially identical melting points of about 250 °C when these units are interlinked by 2,2-dimethylethylene carboxylate linkages.

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Influence of Solvent Size on the Concentration Dependence of Polymer–Solvent Diffusion Coefficients

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ABSTRACT: The effect of the size of the solvent on the concentration dependence of the diffusivity for polymer–solvent systems at low solvent concentrations is examined both theoretically and experimentally. From a new version of the free-volume theory of diffusion, it is shown that both the ratio of solvent to polymer specific hole free volumes and the solvent size strongly influence the variation of the diffusivity with concentration. The theory predicts that solvents which differ significantly in size will exhibit markedly different concentration dependences for the diffusivity even if they have comparable free-volume characteristics. Diffusivity data on six polymer–solvent systems provide direct experimental verification of the size effect, and the measured concentration dependences for the diffusivities of these systems are in reasonably good agreement with the predictions of the theory.

It has been observed experimentally that mutual diffusion coefficients for many polymer–solvent systems exhibit a strong dependence on concentration at low solvent concentrations.[2,3] The dramatic increase in the mutual diffusion coefficient can be explained by the fact that the mobilities of molecules in the mixture are sensitive to the average specific hole free volume of the system. The specific hole free volume of a solvent is usually much greater than that of a typical polymer, and the addition of solvent leads to an increase in the average specific hole free volume of the mixture and to a loosening of the polymeric structure. However, diffusivity data on water–polymer systems[2,4] exhibit a weak concentration dependence for the mutual diffusion coefficient even though it would appear that the increase in free volume is sufficient to lead to a substantial concentration dependence. Consequently, some other factor besides the change in free volume must play an important role in determining the concentration dependence of the diffusivity in polymer–solvent systems. In this paper, we further investigate[5,6] the influence of one such factor, the size of the solvent, on the variation of the diffusivity with concentration.

The concentration dependence of the mutual diffusion coefficient, D, for polymer–solvent systems in the limit of zero solvent concentration can be characterized by the quantity k_D which is defined as

$$k_D = [\{\partial(D/D_0)/\partial\rho_1\}_{T,p}]_{\rho_1=0} \tag{1}$$

Here, D_0 is the mutual diffusion coefficient at zero solvent concentration and ρ_1 is the mass density of the solvent. From a new version of the free-volume theory of diffusion,[5-9] the following expression can be derived for k_D at a given temperature and pressure if the usually negligible thermodynamic, volumetric, and volume change on mixing contributions are omitted:

$$k_D = \frac{\gamma \hat{V}_1{}^\circ(0)}{f_2}\left[\frac{M_1}{M_j}\,\frac{\hat{V}_{FH}(1)}{\hat{V}_{FH}(0)} - 1\right] \tag{2}$$

In this equation, $\hat{V}_{FH}(0)$ is the specific hole free volume of the pure polymer at the temperature of interest, $\hat{V}_{FH}(1)$ is the specific hole free volume of the pure solvent, M_1 is the molecular weight of the solvent, M_j is the molecular weight of a polymeric jumping unit, and f_2 is the fractional hole free volume of the pure polymer. Also, $\hat{V}_1{}^\circ(0)$ is the specific volume of the equilibrium liquid solvent at 0 K, and γ is an overlap factor which is introduced because the same free volume is available to more than one molecule. For this study, we consider only solvents which jump as single units,[9] and, for the present, we ignore any possible differences in the overlap factor γ for different materials.

The experimental observation of a strong concentration dependence for $D(k_D \gg 1)$ at low solvent concentrations is consistent with the predictions of eq 2 when $M_1 \approx M_j$ since the specific hole free volume of the solvent is usually significantly greater than that of the polymer at the same temperature $[\hat{V}_{FH}(1) \gg \hat{V}_{FH}(0)]$. However, for small molecules of low molecular weight $(M_1 \ll M_j)$, it is evident from eq 2 that relatively low values of k_D can be predicted even if the solvent contributes substantially more free volume than the polymer. Consequently, it is reasonable to expect significantly less concentration dependence for D for small solvents than is observed for solvents of higher molecular weight. This result is due to the fact that there

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