when the topological restraints consist of trapped obstacles or else there is a substantial contribution from processes other than reptation, such as tube renewal,[9] when the obstacles are untrapped.

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Dielectric Relaxation Studies of Bis[4-(diethylamino)-2-methylphenyl]phenylmethane/Polycarbonate Solid Solutions. A Correlation of Sub-T_g Relaxations and the Glass Transition Activation Energy

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ABSTRACT: 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.

Introduction

The effect of plasticizers on polymer properties is important scientifically as well as industrially. The plasticizer not only can play the role of a softener[1-5] but also can have intrinsic properties that produce other valuable characteristics. An example of this latter effect is the addition of *n*-butyl 4,5,7-trinitrofluorenone-2-carboxylate to polycarbonate[4] (BPAPC). The dopant not only plasticizes the polycarbonate but also is capable of transporting electrons.[6]

The dynamics of many plasticized polymer systems have been well studied.[1-5,7-10] These studies reveal a correlated motion of both components at a mixture's T_g or an un-

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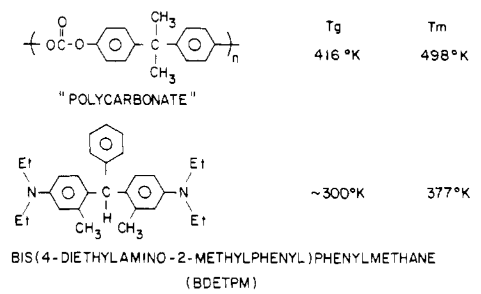

Figure 1. Structure and thermal properties of the components of the studied system.

correlated, but perturbed T_g motion of the individual components. In many of these studies, no attempt was made to observe sub-T_g relaxations in the mixed systems and correlate their behavior with those observed at the glass transition. In recent work on solid solutions of bisphenol-A diphenyl carbonate/polycarbonate, we observed a direct correlation between the sub-T_g relaxation in the mixed system and the activation energy associated with T_g.[11] It was found that the activation energy associated with T_g became compositionally independent when the β relaxation of the BPAPC disappeared. This occurred when the β relaxation was plasticized to lower temperatures than could experimentally be observed or was spread over a frequency–temperature scale so as to be undetectable with the experimental apparatus. The compositions at which this happened were 50 vol % or greater of the smaller molecule. The implication of that study was that the short-range motions of the polymer backbone (in that case the combined phenyl–carbonyl motion of PBAPC) have a great effect on the overall thermal barriers controlling the longer range molecular motions at T_g. Since this behavior had not been observed previously, we initiated the following study to ascertain if the observation was of a general nature.

Experimental Section

Dielectric results for these experiments were obtained with two devices: a scanning dielectric apparatus described previously[4,12] and a General Radio 1615A capacitance bridge with standard accessories. The former provided continuous acquisition of dielectric data from 85 to ~473 K at a variable scanning rate. The program rate for these studies was 0.9 K/min. The latter device was used to obtain isothermal data for line-shape analysis and transition map plots.

Samples for the dielectric experiments were made by casting 10% methylene chloride solutions (g of solids/mL of solvent) with an 8-mil doctor blade onto ball-grained aluminum. The samples were air-dried at ambient temperature for 2 h and then placed in a vacuum (10^{-3} mmHg) for at least 48 h. The films were approximately 10 μm thick. Gold electrodes were evaporated on the exposed surfaces of the samples and used in a spring-loaded sample cell. Samples were isolated from the environment in a stainless steel box sealed with Teflon spacers. Temperature calibration was done with a copper–constantan thermocouple mounted within a centimeter of the sample and accurate to ±2 K. The structures and thermal properties of the materials used in this study are shown in Figure 1. The bis[4-(diethylamino)-2-methylphenyl]phenylmethane (BDETPM) was graciously provided by J. Yanus of this laboratory. The polycarbonate used was reprecipitated Lexan 145 ($M_n = 10600$, $M_w/M_n = 2.5$) and shall be referred to as BPAPC.

Differential scanning calorimetry (DSC) scans of all samples were obtained and indicated the following. (1) In samples where phase separation occurred, as witnessed by the observation of a TPM melting point, a single T_g amorphous material could be generated by quenching from the melt. This effect usually occurred at high TPM loadings (>50%). (2) All other samples exhibited a single T_g, as witnessed by an apparent second-order thermal phase transition within the time frame of our experiment (1 week) and our limit of error (±2 K). These data indicated that our samples were stable solid solutions of BDETPM/BPAPC.

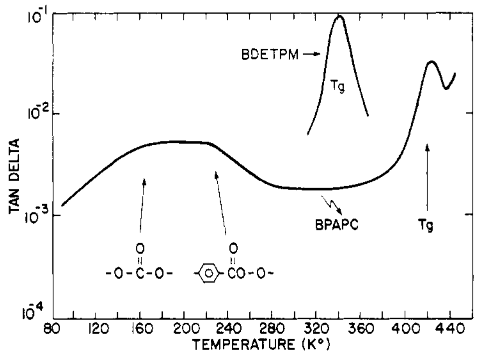

Figure 2. tan δ (120 Hz) vs. temperature for BPAPC and BDETPM. Structures associated with each relaxation are shown in the figure.

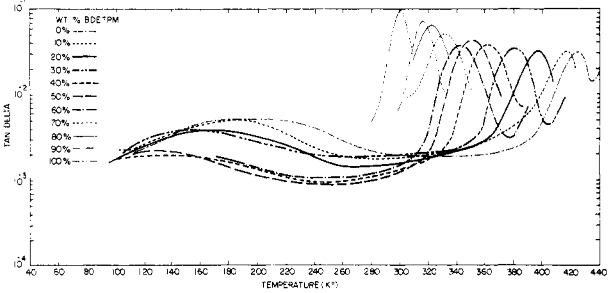

Figure 3. tan δ (120 Hz) vs. temperature for solid solutions of BDETPM/BPAPC.

Results and Discussion

Dielectric data for the pure components are shown in Figure 2, which is a plot of tan δ vs. temperature. Three relaxations have been observed for BPAPC and they are indicated on the figure: the α at 420 K, the β at ~220 K, and the γ at ~160 K. Combined NMR,[13,14] dielectric,[15-17] and dynamic mechanical[18-20] studies indicate that the α relaxation is the glass transition associated with micro-Brownian motion of the polymer, the β relaxation is a combined phenyl ring–carbonyl motion, and the γ relaxation is a carbonyl motion. These are indicated in the figure. Dielectric data for the solid solutions are shown in Figure 3. Unfortunately, low-temperature data were not obtained for systems containing 70 wt % or greater of BDETPM. With these samples, brittle fracture of the test films occurred in the low-temperature region and generated spurious results. It is interesting to note that brittle fracture did not occur until the volume loading of BDETPM was slightly above 50%, i.e., until the smaller molecule became the matrix for the solid solutions. It would appear from the data in Figure 3 that if a β relaxation occurs in BDETPM, and this should be expected based on the work of Johari and co-workers,[21] it is plasticized by the BPAPC or is of sufficiently low intensity in the mixtures that it is not observed at low temperatures.

Transition maps for the α (T_g) and sub-T_g relaxations of the solid solutions are shown in Figures 4 and 5 and the activation energies and relaxation assignments are listed in Tables I and II. Temperature positions of the observed relaxations as a function of composition are shown in Figure 6.

The α (T_g) Relaxation. It is readily seen in the data of Figure 3 that only one relaxation is observed for the glass transition of the mixed system. This is unlike the data of Hains and Williams[22] for polystyrene/di-*n*-butyl phthalate mixtures or the data of Würstlin[1] for poly(vinyl

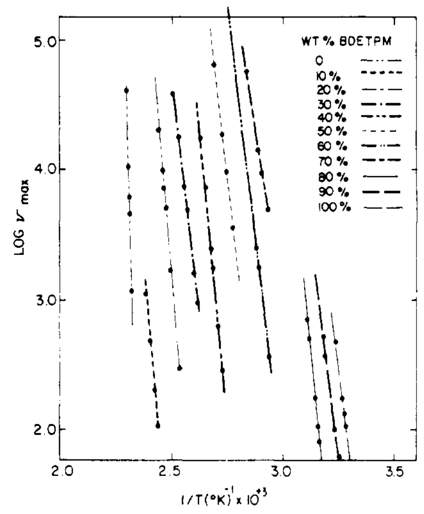

Figure 4. log ν_{max} vs. $1/T$ (K^{-1}) for the T_g relaxations in solid solutions of BDETPM/BPAPC. Compositions are in weight percent.

Table I
T_g Activation Energies for BDETPM/BPAPC as a Function of Weight Percent BDETPM Calculated from Figure 4

wt % BDETPM	$E_a(T_g)$, kcal/mol	wt % BDETPM	$E_a(T_g)$, kcal/mol
0.0	200 ± 10	60.0	70 ± 7
10.0	124 ± 20	70.0	52 ± 8
20.0	90 ± 6	80.0	78 ± 6
30.0	77 ± 8	90.0	61 ± 7
40.0	85 ± 7	100.0	55 ± 5
50.0	71 ± 5		

Table II
Activation Energies and Relaxation Assignments for the Observed sub-T_g Relaxations in BDETPM/BPAPC Solid Solutions

wt % TPM	E_a(sub-T_g), kcal/mol	relaxation assignment
0	13.1 + 1.1	comb β-γ(BPAPC)
20	5.1 ± 0.6	γ(BPAPC)
30		γ(BPAPC)
40	5.5 ± 1.4	γ(BPAPC)
50	4.0 ± 1.6	γ(BPAPC)
60	3.0 ± 1.2	γ(BPAPC)
70	0.62 ± 0.24	β(BDETPM)

acetate)/benzyl benzoate mixtures where uncorrelated, but perturbed motions of the T_g's of the individual components were observed. In those cases, it appeared that the potential fields affecting T_g of the alter components were affected by each other, but not on such an intimate level as to cause totally correlated motion of the two components. This might be viewed as microphase separation of the components into a totally amorphous system containing two concentrations of the plasticizer/polymer system. In the BDETPM/BPAPC system, the T_g relaxations are totally correlated and occur in identical frequency-temperature regimes.

The T_g-composition data of the mixture obeys the Fox equation

$$\frac{1}{T_g} = \frac{\omega_1}{T_{g1}} + \frac{\omega_2}{T_{g2}} \quad (1)$$

where T_{gi} are the glass transitions of the individual components and the ω_i are the weight fractions of these components. A plot of $1/T_g$ vs. the weight fraction of BDETPM is shown in Figure 7, where it is seen that an

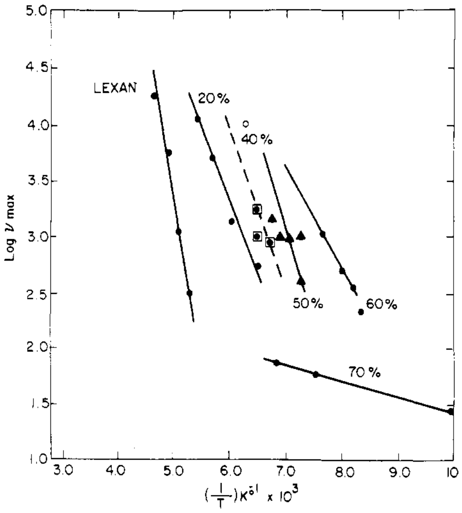

Figure 5. log ν_{max} vs. $1/T$ (K^{-1}) for the sub-T_g relaxations in solid solutions of BDETPM/BPAPC. Compositions are in weight percent.

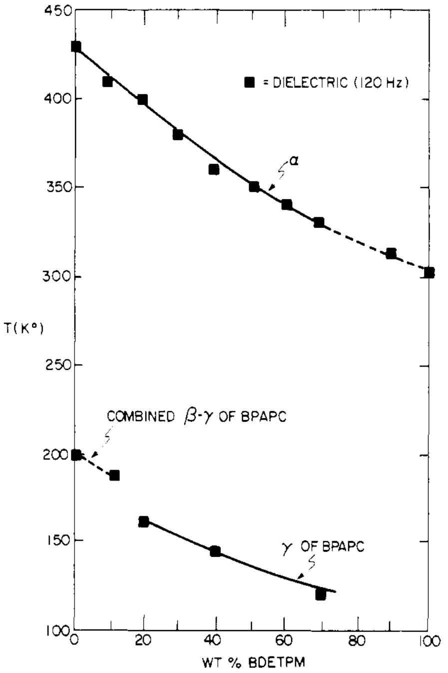

Figure 6. Temperature positions of the T_g and sub-T_g relaxations in BDETPM/BPAPC solid solutions as a function of weight percent BDETPM in the solutions.

excellent fit of the data is obtained. Equation 1 was derived assuming free-volume additivity for the components as well as free-volume dominance of the glass transition. This fit of the data to the equation indicates that the BDETPM/BPAPC system can be considered a solid solution of polymer and diluent. An excellent fit of the T_g-composition data is also obtained with a proposed logarithmic relationship.[23]

The data in Figure 4 indicate that within the frequency-temperature regime of our measurements, all T_g relaxations are Arrhenius activated and that a much higher temperature-frequency is needed to observe the WLF curvature associated with T_g.[3]

The activation energy data of Table I have been replotted in Figure 8 to show E_a vs. volume percent BDETPM in the mixtures. Volume additivity of the components and a density of 1 for BDETPM were assumed. A density of 1.2 was used for BPAPC.[24] The figure can be viewed as essentially two straight lines intersecting

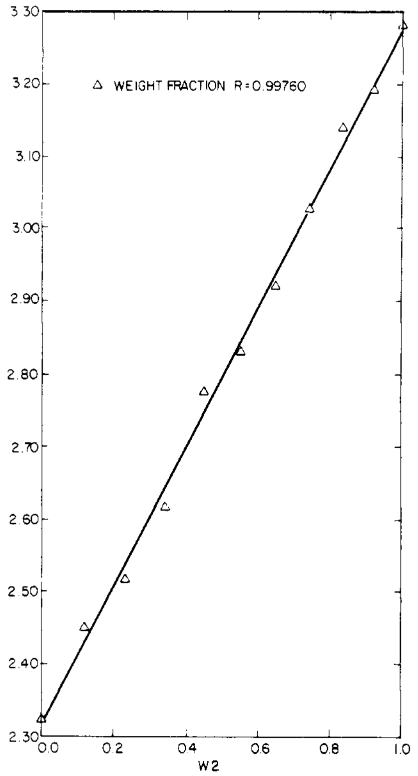

Figure 7. Inverse T_g vs. volume weight percent BDETPM in BDETPM/BPAPC mixtures. T_g is defined as the maximum in tan δ.

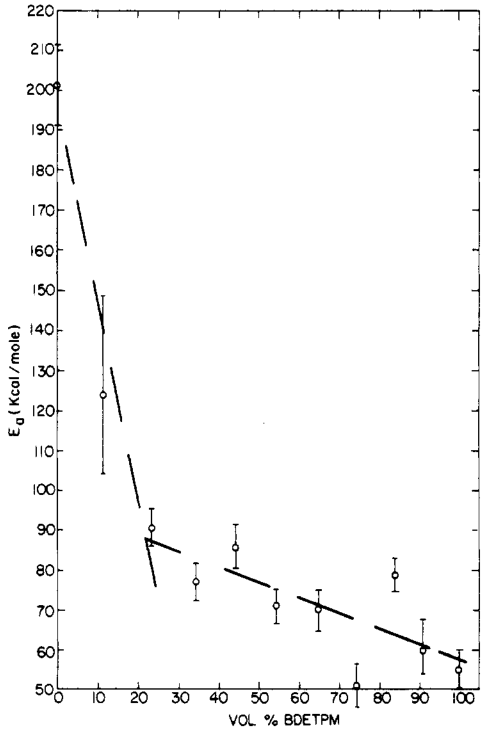

Figure 8. $E_a(T_g)$ vs. volume percent BDETPM in a BDETPM/BPAPC solid solution.

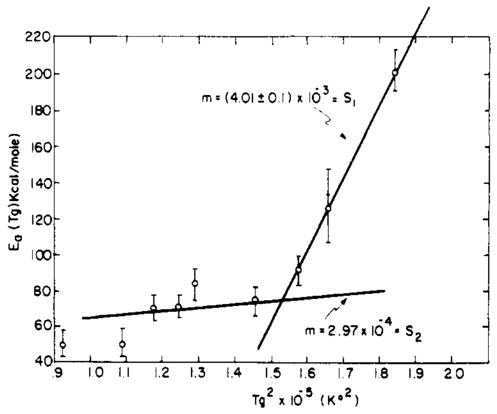

Figure 9. $E_a(T_g)$ vs. T_g^2 for solid solutions of BDETPM/BPAPC.

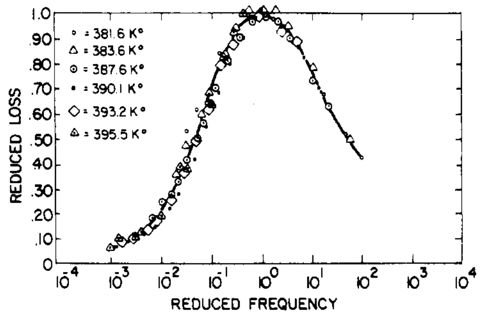

Figure 10. Reduced dielectric loss ($\epsilon''/\epsilon''_{max}$) vs. reduced frequency (ν/ν_{max}) for a 30/70 wt % BDETPM/BPAPC film.

near 20% TPM, with the composition dependence of E_a significantly greater in the 0–20% BDETPM range.

The T_g–activation energy data were considered in terms of the WLF formalism.[25] With this relationship, it can be shown that

$$E_a = 2.303RC_1^0C_2^0T^2/(C_2^0 + T - T_0)^2 \qquad (2)$$

where R is the universal gas constant, T_0 is an arbitrary reference temperature, C_2^0 and C_1^0 are functions of the fractional free volume (f_g) and coefficient of expansions (α_f) of the system, and T is the absolute temperature. At $T = T_g = T_0$, eq 2 can be rewritten

$$E_a \cong RT_g^2\alpha_f/f_g^2 \qquad (3)$$

E_a vs. T_g^2 for BDETPM/BPAPC is plotted in Figure 9. It is seen that the data can be represented by two straight lines that intersect between 20 and 30 wt % BDETPM composition. Equation 3 provides a slope equal to $R\alpha_f/f_g^2$ and a linear least-squares fit of the data in Figure 9 yields $\alpha_f/f_g^2 = 2$ for 0–20 wt % BDETPM. $\alpha_f/f_g^2 = 0.15$ for 30–100 wt % BDETPM. The data indicate that if the WLF formalism is correct, a significant change in free-volume fraction or volume coefficient of expansion between 20 and 40 wt % BDETPM has occurred. As we shall see later, these changes are intimately related to the relaxation modes of the solid solutions.

A line-shape comparison of the T_g relaxations can provide additional information concerning the molecular motions at T_g. Figure 10 is a plot of reduced loss ($\epsilon''/\epsilon''_{max}$) vs. reduced frequency (ν/ν_{max}) for a 30–70 wt % BDETPM/BPAPC film. For the temperature studied, the curves are superimposable and indicate that the distribution of relaxation times remains constant with temperature within a given sample. The data obtained for all the systems were similar, provided care was taken in the preparation of the samples. The higher percentage BDETPM films exhibited a propensity to crystallize if not dried quickly or if held at elevated temperatures for a significant time. A collective plot of reduced curves is shown in Figure 11. Unfortunately, data for the low-frequency portion of some of the curves ($\nu < \nu_{max}$) were unobtainable due to the above effects and only data with $\nu > \nu_{max}$ can be compared accurately. In this region, the data are similar to a previous system we have studied[11] and show the high-frequency skewing of the pure BPAPC being

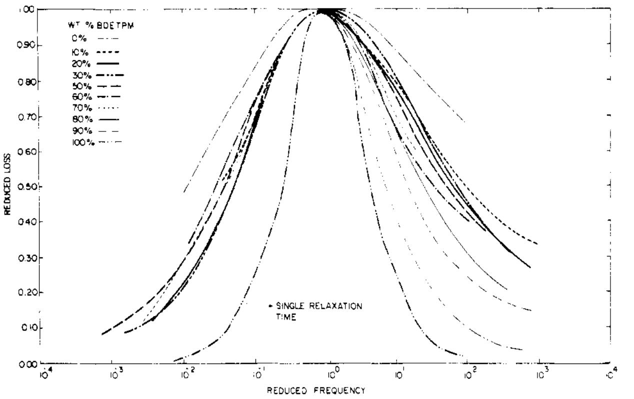

Figure 11. Reduced dielectric loss ($\epsilon''/\epsilon''_{max}$) vs. reduced frequency (ν/ν_{max}) for various BDETPM/BPAPC films. A single-relaxation time curve is shown for reference.

attentuated into a more symmetric relaxation with the addition of the BDETPM. Rather than analyze these data with a Cole–Davidson distribution function,[27] which can reproduce the observed high-frequency "skewedness" of the relaxation time distribution, a molar-averaging technique was used to study the data. This latter technique was applied since it has been shown that two or more overlapping relaxation curves with different dielectric strength can be fit via the Cole–Davidson equation.[3] The averaging equation is

$$(\epsilon''/\epsilon''_{max})_{total} = \chi_{BDETPM}(\epsilon''/\epsilon''_{max})_{BDETPM} + \chi_{BPAPC}(\epsilon''/\epsilon''_{max})_{BPAPC} \quad (4)$$

where the χ's are the mole fractions of each component. For the BPAPC this was considered the repeat-unit molecular weight of the polymer. Unfortunately, the results do not show overlap of the theoretical curve with the actual data. This result is different from our bisphenol-A diphenyl carbonate/BPAPC results, where eq 4 was used to fit the intermediate data. While the curves generated via eq 4 exhibit an almost uniform change between the two pure-component curves, the experimental data indicate that many of the intermediate compositions have similar relaxation-time distribution functions. The experimental data indicate that the BDETPM/BPAPC solid solutions cannot be considered as two independent moieties relaxing in the same temperature–frequency regime; rather they are dependent on one another. Their correlated T_g motion must involve some specific diluent–polymer interactions. Note that the BDETPM distribution is only slightly wider than would occur for a single-relaxation time process, indicating that the distribution of relaxation times is narrow and that the T_g relaxation processes for the BDETPM occur uniformly. This latter effect may be due to the rather spherical nature of the monomer structure which would preclude any orientational interaction effects in the solid solutions.

The Sub-T_g Relaxations. It is apparent, in comparing the activation energies of Table II and the temperature positions of the sub-T_g relaxations in Figures 3 and 6, that the addition of BDETPM to the BPAPC introduces apparent classic plasticization effects in the polymer. Not only does T_g of the polymer shift to lower temperatures but the strongest sub-T_g relaxation does likewise. A plot of the tan δ maximum of the sub-T_g relaxation vs. mole percent BDETPM (see Figure 12) shows a linear correlation and indicates that the observed relaxations are due only to BPAPC. A comparison of the sub-T_g activation energies produces a more complete picture of the dynamics of the solid solution. Figure 3 shows that the addition of only slight amounts of BDETPM to the BPAPC causes the β relaxation of the polymer to disappear (the relaxation shifts to lower temperatures or becomes broader on the experimental scale so as to not be detectable with the instrument resolution). This effect becomes obvious in the activation energies where an abrupt drop from ~13 to ~5 kcal/mol is observed with the addition of less than 20% BDETPM. This result indicates that the combined phenyl–carbonyl motion of the polymer is made extremely facile with the addition of small amounts of BDETPM. Beyond the 20% BDETPM range, the γ relaxation shifts to a lower temperature but remains relatively constant in activation energy. Thus, the energetics controlling the carbonyl motion of the polymer are only slightly affected by the BDETPM as compared to the significant effect the BDETPM has on the longer range motion (the phenyl–carbonyl motion). An activation energy for a sub-T_g relaxation of 70/30 BDETPM/BPAPC is also included in the data of Table II. The relaxation was barely detectable with our apparatus and has been assigned to the β relaxation of BDETPM, although there is no corroborating proof of this assignment. The activation energies observed for the combined β–γ relaxation and the γ relaxation of the BPAPC in the pure state and the mixtures are similar to those reported in the literature.[28] The γ-relaxation activation energy was consistently lower (~1 kcal/mol) than those reported in ref 11 and 28.

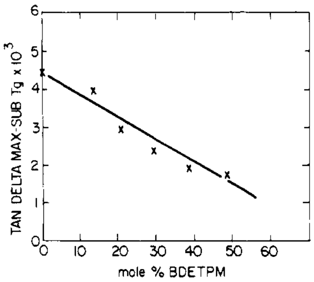

Figure 12. tan δ_{max} for the sub-T_g relaxations vs. mole percent BDETPM in BDETPM/BPAPC solid solutions.

If the T_g and sub-T_g data are compared, it is seen that there is a direct correlation between the T_g activation energies and the β relaxation. When the β relaxation of the polymer is no longer detectable with the addition of the smaller molecule, the T_g activation energy becomes much less composition independent. This is similar to our observations of solid solutions of bisphenol-A diphenyl carbonate (MLEX)/BPAPC solutions,[11] where a compositionally independent T_g activation energy was observed upon elimination of the polymer β relaxation. We had proposed that the disappearance and the composition dependence of the activation energy were related to the MLEX becoming the matrix material (>50 vol %) in the solid solutions. On the basis of these results, that original assumption is in error and it would appear that the dynamics of the T_g activation energy are related to those of the β relaxation of the BPAPC. When this relaxation is eliminated from the observable dielectric spectra, the T_g activation energy becomes less composition dependent. This indicates that in polymers where the β relaxation is found to be a localized motion of the main polymer chain (a localized T_g?), similar results for the activation would be expected with the addition of a diluent. These results also indicate that it is not the volume of diluent added that controls the dynamics of T_g in BPAPC but rather the specific polymer–diluent interactions that affect the localized motions of the main chain. The more basic (electron rich) BDETPM would be expected to interact more strongly with BPAPC than the molecularly similar MLEX and this may explain the slightly different T_g activation 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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