

The solid state structure of polycarbonate blends with lead phthalocyanine

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Abstract

The physical properties of polycarbonate blends containing the nonlinear optical dye lead tetracumylphenoxy phthalocyanine were characterized. Blends with up to 20 wt% dye were prepared and characterized in terms of density, refractive index, glass transition temperature, loss modulus, subambient relaxation behavior, and free volume hole size from positron annihilation lifetime spectroscopy. The dye strongly affected the physical properties of the blend. The initial 0.1 wt% dye produced a dramatic increase in the density. A similar trend in the refractive index was accounted for by the change in density using a relationship between density and refractive index derived from the Lorentz–Lorenz equation. Increasing the dye content to 8 wt% led to a large reduction in the glass transition temperature. An increase in E' and a decrease in the subambient γ -relaxation intensity accompanied the large decrease in T_g . This behavior fit the conventional concept of antiplasticization, which has been described for other low molecular weight diluents in PC. Recognizing that the dye was present as a mixture of monomer, dimer and higher aggregates, it was shown that the monomer form was responsible for the antiplasticization. In the glass, dimer and higher aggregates were viewed as nanoparticle fillers. It was confirmed that the antiplasticization effect was due to a reduction in excess hole free volume of the polymer.

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1. Introduction

Incorporating electronic or optical functionality into a high molecular weight polymer is an attractive approach to realize the miniaturization and robustness that are possible with a solid state device. In some cases it is also a means to reduce exposure to toxic dyes. Phthalocyanines [1,2], cinnamic acid [3], and rhodamine [4,5] have been incorporated into a polymer matrix for applications as nonlinear optical limiters, photo-patternable films, and solid state lasers, respectively. The requirements of the polymer matrix include excellent clarity, dimensional

stability at ambient conditions, and melt processability. Because they meet these requirements, and are of relatively low cost, polycarbonate, polystyrene and poly(methyl methacrylate) are frequent choices. Both copolymerization and physical blending have been employed to incorporate the functionality.

In order to employ the polymers in optical applications and devices, for example, both the optical and mechanical properties must be characterized. Furthermore, blending or copolymerization must conserve, or even enhance, the functionality of the small molecule. Phthalocyanines are an important class of optical materials and coloring agents that show good solubility in polycarbonate. They have been used in applications such as optical limiters [6], laser dyes [7], and photoreceptors in color copiers [8]. The large excited-state absorption cross-sections and relatively long excited-state lifetimes responsible for the useful optical properties of phthalocyanines reside

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primarily in the monomer [9]. Formation of dimer and higher aggregates may negatively impact their nonlinear optical properties.

In a recent study of lead tetracumylphenoxy phthalocyanine ($\text{PbPc}(\beta\text{-CP})_4$) blends, we found that PC functions as a polymeric solvent in much the same way as chloroform functions as an organic solvent [10]. The concentration effect was analyzed according to the monomer/dimer equilibrium, and correspondence was found between the equilibrium constants in PC and chloroform. However, the monomer concentration at ambient conditions could be orders of magnitude higher in a PC blend than in chloroform. By quenching the blend from the melt, the equilibrium monomer concentration established at the melt temperature, which favored the monomer, was preserved in the nonequilibrium glass.

Addition of small molecule diluents to glassy polymers usually results in plasticization. Plasticizing molecules are seen as occupying the space between polymer chains, thereby reducing the resistance to large-scale chain motions. As a consequence, the glass transition shifts to lower temperatures and the modulus decreases. However, a lower glass transition temperature also leads to lower excess hole free volume, and in some cases this has a so-called antiplasticizing effect [11]. Antiplasticizer is a term applied to diluents that reduce the glass transition temperature of the polymer matrix, but increase the modulus and the brittleness. The phenomenon of antiplasticization is frequently observed with polycarbonate [12,13] and other polymers that contain rigid polar groups and stiff chains [14–16]. Diluents that act as antiplasticizers are typically miscible, relatively planar, and many contain polar atoms [12]. The dye molecule $\text{PbPc}(\beta\text{-CP})_4$ meets these criteria. In order to determine whether the dye indeed acts as an antiplasticizer, we examined the effects of the dye on the physical properties of polycarbonate.

2. Materials and methods

Lead tetracumylphenoxy phthalocyanine ($\text{PbPc}(\beta\text{-CP})_4$) in powder form was obtained from Sigma Aldrich Inc. Its chemical structure is shown in Fig. 1. Polycarbonate (Calibre 200-14) was provided as pellets by the Dow Chemical Company. The dye powder was mixed with polycarbonate by solution blending in chloroform to a target concentration of 20 wt%. Chloroform was evaporated by drying under vacuum at 60 °C for 6 h. The dried blend was further mixed by passing it

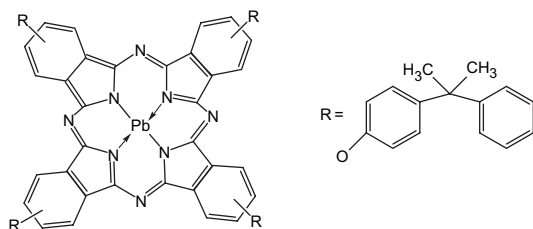


Fig. 1. Chemical structure of lead tetracumylphenoxy phthalocyanine ($\text{PbPc}(\beta\text{-CP})_4$).

through a mini twin screw extruder at 270 °C. The residence time in the extruder was 3 min. The extrudate strand was quenched in dry ice and pelletized. The 20 wt% master blend was diluted by dry blending with polycarbonate pellets and passing the mixture through the extruder at 270 °C. Blends with target concentrations of 0.01, 0.05, 0.1, 0.5, 1, 2, 4, 8, 10, 12 and 16 wt% were made by this method. Polycarbonate without dye was passed through the extruder under identical conditions and used as the control. The final dye content was determined by UV–vis spectroscopic analysis of the blends dissolved in dilute chloroform solution, Table 1. The procedure was described previously [10].

Thin films of about 50 μm thick were prepared by melting a pellet in a DSC pan. The specimen was subjected to 270 °C for 5 min in the DSC, and then removed and quenched in dry ice. These films were used for density, refractive index and positron annihilation lifetime spectroscopy. Thicker films of about 200 μm thick for dynamic mechanical analysis were prepared by heating the blend in a press at 270 °C before quenching in dry ice. Polycarbonate films prepared under identical conditions were used as control. Conservation of the characteristic UV–vis spectrum in the dissolved blend and in the molded film confirmed that the dye was not degraded.

A density gradient column was constructed from a solution of calcium nitrate and water in accordance with ASTM D Standard 1505 Method B. The column was calibrated with glass floats of known density. Small pieces of film ($\sim 25 \text{ mm}^2$) were placed in the column and allowed to equilibrate for 30 min at ambient temperature before the measurements were taken. An average of four measurements was reported, Table 1.

Refractive index was measured using a 2010 Metricon prism coupler equipped with a 532 nm laser. Measurements were carried out at 23 °C.

Positron annihilation lifetime spectroscopy (PALS) employed a fast–fast coincident method with a time resolution of 230 ps, which has been described in detail elsewhere [17], at a count rate of approximately 1×10^6 counts h^{-1} . The positron lifetimes were determined by PATFIT software. The positron annihilation spectrum was fit to three exponentially

Table 1
Characteristics of polycarbonate blends with $\text{PbPc}(\beta\text{-CP})_4$

$\text{PbPc}(\beta\text{-CP})_4$, nominal (wt%)	$\text{PbPc}(\beta\text{-CP})_4$, measured (wt%)	Density (g cm^{-3})	Refractive index	T_g (°C)	Monomer (wt%) Ref. [10]
0	0	1.1928	1.5895	161	0
0.01	0.01	1.1930	1.5900	—	0.01
0.05	0.05	1.1934	1.5905	—	0.05
0.10	0.10	1.1938	1.5907	160	0.10
0.50	0.50	1.1948	1.5912	159	0.48
1.00	0.94	1.1958	1.5917	156	0.85
2.00	1.85	1.1975	1.5922	154	1.48
4.00	3.85	1.2001	1.5950	150	2.46
8.00	7.76	1.2054	1.5979	144	4.19
10.0	9.73	1.2083	1.5991	143	4.48
12.0	11.6	1.2105	1.6000	142	4.87
16.0	15.5	1.2208	1.6035	141	5.58
20.0	19.5	1.2265	1.6080	—	6.05

decaying lifetime components. The longest-lived component τ_3 corresponded to the pickoff annihilation of *o*-Ps in the free volume holes of the polymer matrix, from which the mean hole radius r was calculated.

Dynamic mechanical thermal analysis (DMTA) measurements were carried out using the Polymer Laboratories DMTA. Measurements were made at a frequency of 1 Hz with a heating rate of $3\text{ }^\circ\text{C min}^{-1}$.

3. Results and discussion

3.1. Density and refractive index of PC blends with $\text{PbPc}(\beta\text{-CP})_4$

Blending $\text{PbPc}(\beta\text{-CP})_4$ with PC led to an increase in density, Fig. 2a. A very small amount of $\text{PbPc}(\beta\text{-CP})_4$, about 0.1 wt%, substantially increased the density. Adding more dye increased

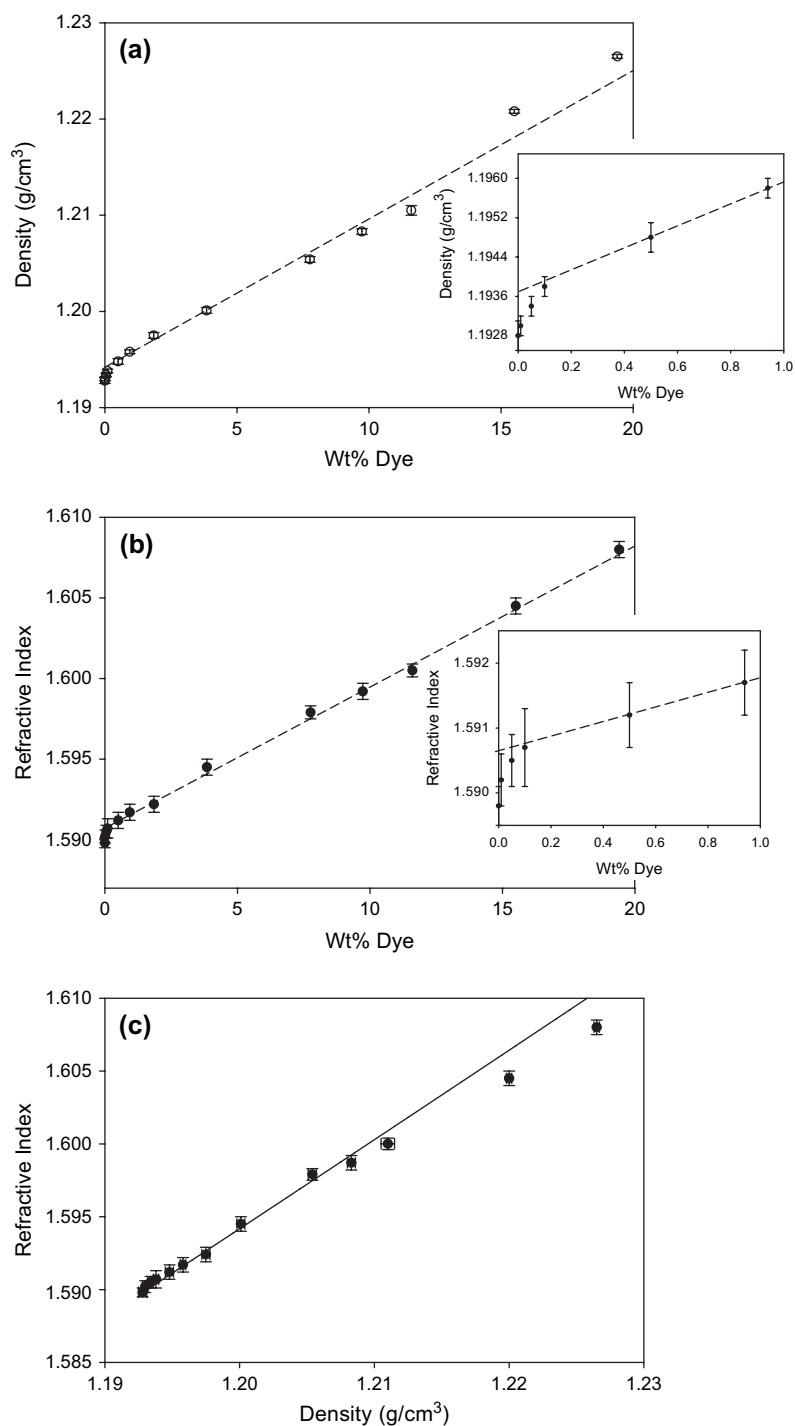


Fig. 2. Effect of dye content on density and refractive index of PC blends: (a) density; (b) refractive index measured at $\lambda = 532\text{ nm}$; and (c) the relationship between density and refractive index. The dashed lines in (a) and (b) are only to guide the eye; the solid line in (c) is the Lorentz–Lorenz prediction from Eq. (2) with $C_{\text{PC}} = 0.283\text{ cm}^3\text{ g}^{-1}$.

the density further, but with a much weaker dependence on the dye content.

The surprisingly large increase in density imparted by only 0.1 wt% dye suggested that the dye molecules filled the space in the glass that otherwise would have contributed to the free volume. This was tested by calculating the density assuming that the dye molecules were accommodated without a change in the volume. For low dye content,

$$\rho = (1 + W_{\text{dye}})\rho_{\text{PC}}^0 \quad (1)$$

where ρ_{PC}^0 is the density of PC without dye and W_{dye} is the weight fraction of the dye. The density calculated according to Eq. (1) corresponded well with the measured density of blends with up to 0.1 wt% dye and density 1.1940 g cm^{-3} , but deviated at higher dye content, Table 2.

It appeared that a small amount of dye was accommodated without a change in volume. The $\text{PbPc}(\beta\text{-CP})_4$ molecule is shaped like a shuttlecock with a height of 2.37 \AA and a diameter of about 14 \AA [18]. The molecules stack to form dimers, trimers, etc. Approximating the shape as a disk with the given height and diameter, the volume occupied by the monomer is 400 \AA^3 . The volume required to accommodate 0.1 wt% dye is estimated to be about 0.5% of the excess hole free volume of the glass, which is reported in the range of 3–6% [19–21]. Consequently, the initial 0.1 wt% dye blended with PC has a very small effect on the amount of excess hole free volume of the glass, but a large effect on the density.

Addition of $\text{PbPc}(\beta\text{-CP})_4$ qualitatively affected the refractive index in the same way as it affected density, Fig. 2b. Thus, the initial 0.1 wt% dye increased the refractive index of PC substantially. The effect of dye on the refractive index could be accounted for by the change in density using a relationship between density and refractive index derived from the Lorentz–Lorenz equation

$$n = [(1 + 2C\rho)/(1 - C\rho)]^{0.5} \quad (2)$$

where C is a material constant related to the dielectric constant. For PC at 532 nm , $C_{\text{PC}} = 0.283 \text{ cm}^3 \text{ g}^{-1}$ was obtained from the measured values of n and ρ . Eq. (2) satisfactorily described the relationship between n and ρ for blends with up to 8 wt% $\text{PbPc}(\beta\text{-CP})_4$ with C taken as C_{PC} , Fig. 2c. Although the density change dominated the index variation at lower dye concentration, the dye will contribute when the concentration is high enough, and indeed the data deviated from Eq. (2)

Table 2
Density of polycarbonate blends with small amounts of $\text{PbPc}(\beta\text{-CP})_4$

$\text{PbPc}(\beta\text{-CP})_4$ (wt%)	Measured density (g cm^{-3})	Calculated density from Eq. (1) (g cm^{-3})
0	1.1928 ± 0.0003	1.1928
0.01	1.1930 ± 0.0002	1.1929
0.05	1.1934 ± 0.0002	1.1934
0.10	1.1938 ± 0.0002	1.1940
0.50	1.1948 ± 0.0003	1.1988
0.94	1.1958 ± 0.0002	1.2040

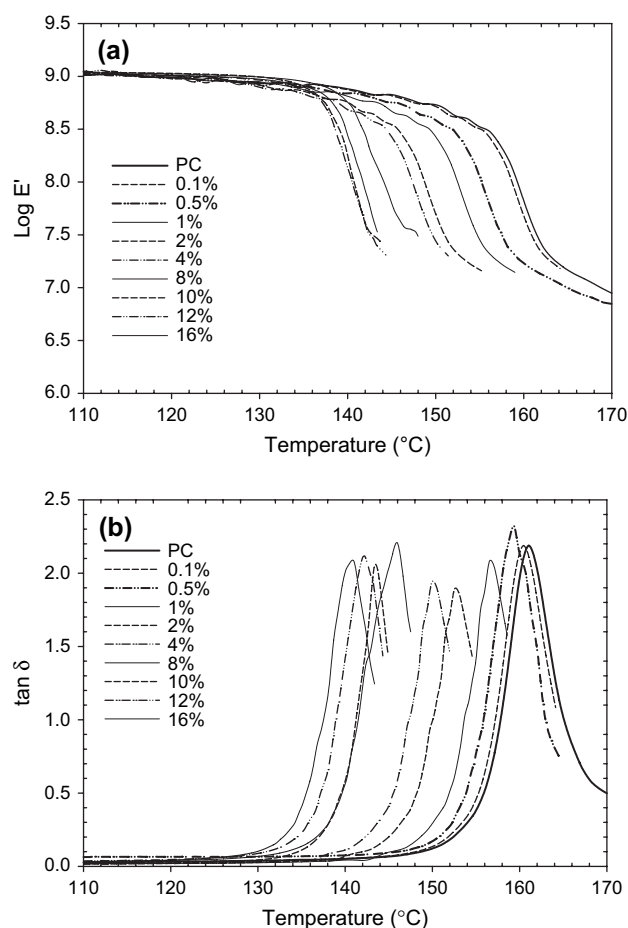


Fig. 3. Effect of dye content on the dynamic mechanical relaxation behavior in the temperature range of the glass transition: (a) E' ; and (b) $\tan \delta$.

above 8 wt% dye. An effective medium theory usually models the index of such a composite material.

3.2. Glass transition of PC blends with $\text{PbPc}(\beta\text{-CP})_4$

The relaxation behavior of $\text{PbPc}(\beta\text{-CP})_4$ blends is shown in Fig. 3 as the temperature dependence of $\log E'$ and $\tan \delta$. A drop in E' of almost two orders of magnitude accompanied the glass transition. The T_g was taken at the maximum in $\tan \delta$ and is plotted as a function of dye concentration in Fig. 4a. The T_g decreased significantly as the dye content increased from 0 to 8 wt% and continued to decrease, but more slowly, as the dye content increased further. The relationship between dye content and T_g was quite different from the almost linear dependence that is often observed for a polymer–diluent system [15,16,22,23].

The dye is not present in PC as a unique species, but as a mixture of monomer, dimer and higher aggregates [24]. The equilibrium condition at the melt temperature determines the fraction of each species. The monomer fraction was measured previously [10], and the wt% monomer in the blend is included in Table 1. If only the monomer is considered as the diluent, the effect on T_g is qualitatively closer to that expected of a polymer–diluent system, Fig. 4b. Considering only monomer as diluent, the concentration dependence can be described as [25]

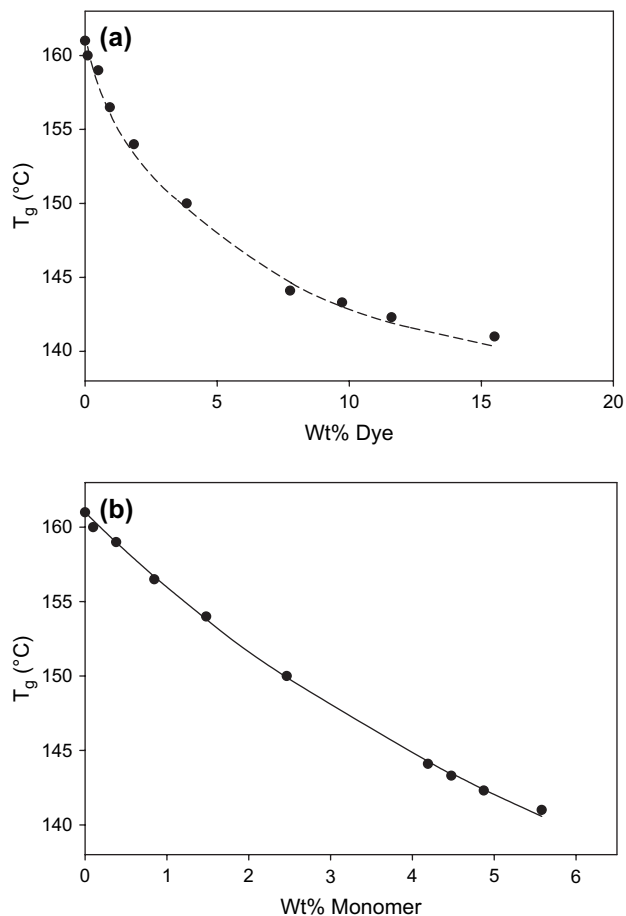


Fig. 4. Effect of dye on the glass transition temperature from $\tan \delta$ at 1 Hz: (a) dependence on total dye content; and (b) dependence on dye monomer content. The dashed line in (a) is only to guide the eye, the solid line in (b) is the predictions from Eq. (3) with $T_{g,PC} = 434$ K, $T_{g,m} = 379$ K, and $K = 10$.

$$T_g = \frac{W_{PC}T_{g,PC} + KW_mT_{g,m}}{W_{PC} + KW_m} \quad (3)$$

where W_{PC} is the weight fraction of PC, W_m is the weight fraction of monomer, and $T_{g,PC}$ and $T_{g,m}$ are the glass transition temperatures of PC and monomer, respectively, and K is a constant. For the measured $T_{g,PC} = 434$ K, a reasonable fit was obtained with $K = 10$ and $T_{g,m} = 379$ K, Fig. 4b. Thus it appeared that monomer was primarily responsible for the decrease in T_g . It followed that in the glass, dimer and higher aggregates were not closely associated with the polymer chains and acted essentially as nanoparticle fillers.

In spite of the fact that the T_g decreased with the addition of dye, and the polymer should have become softer, the polymer glass became stiffer, Fig. 5a. The increase in E' occurred over the same composition range, 0–8 wt% dye, as the large decrease in T_g , Fig. 5b. Furthermore, over the same concentration range, there was a strong decrease in the intensity of the subambient γ -relaxation of PC, Fig. 6. The γ -relaxation of PC is associated with the ductility of glassy PC [26]. Suppression of the γ -relaxation motions by antiplasticizers leads to an increase in the brittleness [27]. Indeed, in routine handling of the blends,

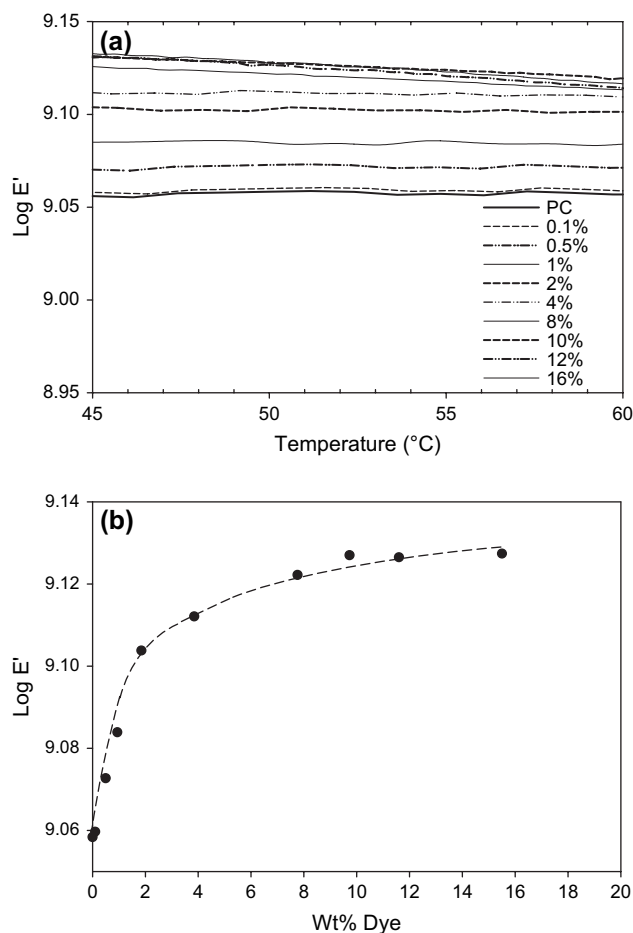


Fig. 5. Effect of dye on E' of the glass: (a) the temperature dependence; and (b) the effect of dye content measured at 50 °C.

it was apparent that they became more brittle. A decrease in T_g , accompanied by increased stiffness and embrittlement, fits the conventional concept of antiplasticization.

3.3. Free volume of PC in blends with $PbPc(\beta-CP)_4$

The antiplasticization effect of low molecular weight diluents is attributed to a reduction in excess hole free volume of the polymer. Recently, positron annihilation lifetime spectroscopy (PALS) has been employed to measure the size and number density of free volume holes, and to make direct correlations with plasticization and antiplasticization [22,23].

The free volume hole size V_h as measured by PALS decreased markedly over the same composition range as the largest decrease in T_g , Table 3. At higher dye concentrations, the hole size remained constant. The specific excess hole free volume ν_f is given as

$$\nu_f = N_h V_h \quad (4)$$

where N_h is the number density of excess free volume holes. The number of free volume holes has been related to the parameter I_3 in the PALS spectrum [22]. No systematic dependence of I_3 on dye concentration was observed, and N_h was

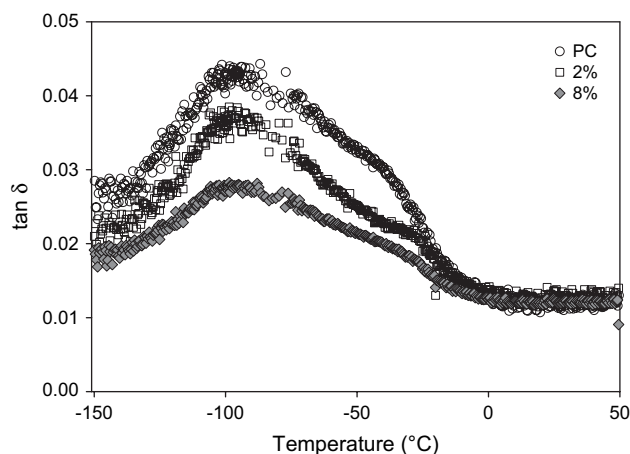


Fig. 6. Effect of dye content on $\tan \delta$ in the temperature range of the γ -relaxation.

assumed to be constant. The reported value of $5.12 \times 10^{20} \text{ g}^{-1}$ [28] was used to calculate ν_f in each blend.

It is usual to report the fractional free volume FFV defined as

$$\text{FFV}(\%) = \frac{\nu_f}{\nu} \times 100 \quad (5)$$

Considering only PC as possessing excess hole free volume

$$\text{FFV}(\%) = \frac{\nu_f}{\nu_{\text{PC}}} \times 100 \quad (6)$$

In order to obtain the fractional free volume from PALS, the specific volume of PC ν_{PC} was considered to consist of additive contributions from the occupied volume ν_{occ} and the excess hole free volume ν_f

$$\nu_{\text{PC}} = \nu_{\text{occ}} + \nu_f \quad (7)$$

where ν_{occ} was obtained from the results of PC without dye as $\nu_{\text{occ}} = (1.1928)^{-1} - 0.0507 = 0.7876 \text{ cm}^3 \text{ g}^{-1}$. Then for PC in the blends

$$\nu_{\text{PC}} = 0.7876 + \nu_f \quad (8)$$

Table 3
Free volume of polycarbonate blends with $\text{PbPc}(\beta\text{-CP})_4$

$\text{PbPc}(\beta\text{-CP})_4$ (wt%)	Free volume hole radius r_h (Å)	Free volume hole size V_h (Å ³)	FFV _{PALS} (%)	FFV _{T_g} (%)
0	2.87 ± 0.01	99 ± 2	6.05	6.05
0.10	2.85 ± 0.02	97 ± 2	5.93	6.00
0.50	2.82 ± 0.02	94 ± 2	5.76	5.96
0.94	2.81 ± 0.03	93 ± 3	5.70	5.83
1.85	2.77 ± 0.02	89 ± 2	5.47	5.74
3.85	2.76 ± 0.03	88 ± 3	5.41	5.56
7.76	2.74 ± 0.02	86 ± 2	5.29	5.30
15.5	2.74 ± 0.02	86 ± 2	5.29	5.16

where ν_f is obtained from Eq. (4) taking V_h from Table 3. The fractional free volume from PALS calculated from Eq. (6) is included in Table 3 as FFV_{PALS}.

The decrease in hole size is attributed to the reduction in T_g of PC. According to free volume concepts, decreasing the glass transition temperature should result in a reduction of the excess hole free volume of the PC [29–31]. This effect can be expressed in terms of the change in specific volume

$$\Delta\nu_f = \Delta T_g \Delta\alpha \quad (9)$$

where $\Delta\nu_f$ is the change in specific excess hole free volume of PC resulting from a change ΔT_g in the glass transition temperature, and $\Delta\alpha$ is the difference in thermal expansivities of the glass and rubber taken as $3.9 \times 10^{-4} \text{ cm}^3 \text{ g}^{-1} \text{ K}^{-1}$ [32].

The FFV can be calculated from the change in T_g as

$$\text{FFV}_{T_g}(\%) = \frac{\nu_f^\circ - \Delta\nu_f}{\nu_{\text{PC}}^\circ - \Delta\nu_f} \times 100 \quad (10)$$

where ν_f° and ν_{PC}° refer to the values for PC without dye. The values of FFV_{T_g} are in reasonably good agreement with the values of FFV_{PALS}, Table 3.

3.4. Dispersion of $\text{PbPc}(\beta\text{-CP})_4$ in PC blends

The nonlinear optical dye $\text{PbPc}(\beta\text{-CP})_4$ shows good solubility in PC. However, the dye monomer has a tendency to form dimer and even higher aggregates in solution. When in the melt, the fraction of each species is determined by the melt temperature and the total dye concentration. The monomer/dimer equilibrium established in the melt is conserved when the blend is quenched to the glass. In this regard, $\text{PbPc}(\beta\text{-CP})_4$ differs from most polymer diluents which exist as a single monomeric species. It is seen that $\text{PbPc}(\beta\text{-CP})_4$ monomer and dimer affect the blend properties in different ways. Thus, in interpreting the experimental observations, the amount of the individual species must be considered, rather than the total dye content.

A small amount of monomer, about 0.1 wt%, is incorporated into PC without a change in volume. These monomer molecules are thought to occupy space in the glass that otherwise would be free volume. The contribution of this space to the overall excess hole free volume of PC is very small. However, because the dye molecules do not make a volumetric contribution, they impart a substantial increase in density.

Monomer is the dominant species in blends with up to about 8 wt% dye, Table 1. It is speculated that the monomer is miscible with PC and produces the typical characteristics of an antiplasticizer, including a decrease in T_g , but suppression of the secondary γ -relaxation motions and increased rigidity. According to free volume concepts, decreasing the glass transition temperature should result in a reduction of the excess hole free volume of the PC. This is confirmed by a decrease in the PALS hole size over the corresponding range in dye content, and the correspondence between FFV_{PALS} and FFV_{T_g}. Because higher dye concentrations produce little or no change in T_g and no decrease in excess free volume hole size, it is

Table 4
Calculated densities of polycarbonate and PbPc(β -CP)₄ in blends

PbPc(β -CP) ₄	ρ_{PC} (g cm ⁻³)	ρ_{dye} (g cm ⁻³) from Eq. (12)
0.94	1.1956	1.222
1.85	1.1967	1.244
3.85	1.1989	1.231
7.76	1.2023	1.244
9.73	1.2029	1.262
11.6	1.2034	1.268
15.5	1.2040	1.322

concluded that dimer and higher aggregates are not closely associated with the polymer chains in the glass and act essentially as nanoparticle fillers. The size of the dimer nanoparticle is estimated to be approximately 800 Å³ (twice the size of the monomer).

Under these circumstances, a simple two-phase model with constant densities of PC and dye was not expected to describe the blends. Indeed, this was confirmed. For constant ρ_{PC}^0 of 1.1928 g cm⁻³, the dye density ρ_{dye} calculated from the measured blend density according to

$$\frac{1}{\rho_b} = \frac{W_{PC}}{\rho_{PC}^0} + \frac{W_{dye}}{\rho_{dye}} \quad (11)$$

improbably decreased from 1.71 to 1.37 g cm⁻³ with increasing dye content. A more reasonable formulation of the additive relationship considered densification of the PC

$$\frac{1}{\rho_b} = \frac{(W_{PC} + 0.001)}{\rho_{PC}} + \frac{(W_{dye} - 0.001)}{\rho_{dye}} \quad (12)$$

where ρ_{PC} as given in Table 4 was obtained from ΔT_g according to Eq. (9), W_{PC} and W_{dye} are the weight fractions of PC and dye, respectively, and the adjustment of 0.001 accounts for the small amount of dye that is accommodated without a change in volume. For dye concentrations up to 8 wt%, where most of the dye was in the monomer form, ρ_{dye} from Eq. (12) averaged 1.24 g cm⁻³ with no systematic trend, Table 4. For higher dye concentrations, where a larger fraction of the dye took the form of dimer and higher aggregates, ρ_{dye} systematically increased to 1.32 g cm⁻³ for the blend with 20 wt% dye. For comparison, the density of the solid dye from Bondi volume equivalents assuming 30% free volume is 1.48 g cm⁻³ [33]. The intermediate values of ρ_{dye} seem reasonable for combinations of the various dye species.

4. Conclusions

As polymers become increasingly important as matrices for functional molecules, there is a need to understand the functionality of the small molecule in the polymer matrix as well as how the small molecule alters the physical properties of the polymer. Here, we address the latter concern by characterizing polycarbonate blends containing the nonlinear optical dye PbPc(β -CP)₄. The dye is revealed to strongly affect the

physical properties, including the density, refractive index and glass transition temperature. The initial 0.1 wt% dye produces a dramatic increase in the density. A similar trend in the refractive index is accounted for by the change in density using a relationship between density and refractive index derived from the Lorentz–Lorenz equation. Increasing the dye concentration leads to a reduction in the glass transition temperature. In spite of the fact that T_g decreases, and the polymer should become softer with the addition of dye, an increase in E' and a decrease in the subambient γ -relaxation intensity accompany the large decrease in T_g between 0 and 8 wt% dye. This behavior fits the conventional concept of antiplasticization, which has been described for other low molecular weight diluents in PC. Recognizing that the dye is present as a mixture of monomer, dimer and higher aggregates, it is shown that the monomer form is responsible for the antiplasticization. Dimer and higher aggregates are viewed as nanoparticle fillers in the glass. The antiplasticization effect is usually attributed to a reduction in excess hole free volume of the polymer. This is shown to be the case by correlating direct measurements of excess free volume hole size from PALS with the bulk measurement of excess free volume from the reduction in T_g .

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