since there is a statistical disorder caused by right- and left-handed, up- and downward helices. Therefore we assume that the crystallites are built up of double-stranded helices of the same kind and are randomly disordered by other double-stranded helices.

Conclusion

From the energy calculations and X-ray diffraction data we conclude that it-PMMA crystallizes as a double-stranded 10/1 helix. A stereoview of the double-stranded right-handed upward 10/1 helix of it-PMMA is shown in Figure 6. In the triclinic, pseudoorthorhombic cell, two equal double-stranded helices are placed, shifted about $c/2$ along the fiber axis with respect to each other, and lattice disorder is mainly attributed to distortions of the first kind, i.e., to statistical incorporation by other helix types.

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Dielectric Relaxation Studies on Bisphenol A Bis(cumylphenyl) Carbonate/Lexan Polycarbonate Solid Solutions

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ABSTRACT: The dielectric relaxation spectra of solid solutions of bisphenol A polycarbonate/bisphenol A bis(cumylphenyl) carbonate have been obtained as a function of composition. T_g varies continuously with composition and can be described by either a T_g–$\bar{M}_n^{-1}$ or polymer–diluent correlation. The former indicates that the low molecular weight material is a better model system for polycarbonate than bisphenol A diphenyl carbonate studied previously. Up to 87.5 wt % small molecule, the T_g relaxations are Arrhenius activated. The T_g activation energy is composition independent above 25 wt % small molecule. This observation correlates with the disappearance of the β relaxation of the polymer and indicates that localized motion of the polymer backbone is intimately related to the energetics of longer chain motion at T_g.

Introduction

The effect of additives on polymer properties is the basis for many industrial applications. These additives can provide polymer films that are homogeneous or phase separated on a microscale. Dielectric relaxation studies provide a method to study such systems and obtain information on the modes of relaxation as well as any specific interactions that may occur in polymer blends. We have been particularly interested in the effects of small molecular dopants on the relaxation behavior of polycarbonate (PC), in particular the sub-T_g relaxations and their interrelationship with the glass transition activation energy. Three systems have been studied thus far: bisphenol A diphenyl carbonate/PC,[1] bis[(diethylamino)phenyl]phenylmethane/PC,[2] and *n*-butyl 4,5,7-trinitrofluorenone-2-carboxylate/PC.[3] The latter two systems represent mixtures of dissimilar molecules whereas the first was studied to assess the effect of a molecule similar to the PC backbone. The first two systems show that elimination of the first sub-T_g relaxation of PC by the addition of the small molecule results in a composition-independent T_g activation energy. The fluorenone derivative–PC mixtures could not be used in those comparisons as they showed specific polymer–monomer interactions, which did not allow a clear interpretation of the sub T_g relaxations. The first two systems indicate that localized backbone motions in the polymer system play an important role in the T_g activation energy.

The bisphenol A diphenyl carbonate (MLEX) (see Figure 1) was originally chosen as a model monomer system to study the effects of a bimodal polymeric distribution on the relaxation processes of the system. It was shown,[1] however, that the MLEX/PC mixture T_g's could be represented better by polymer–diluent formulas such as the Fox equation[4] rather than the T_g–reciprocal molecular weight equation of a homopolymeric system. Part of the reason for this observation may have been the selection of such a "short" molecule that end groups played an important role in determining T_g. We have, thus, synthesized a longer polycarbonate model system, bis-

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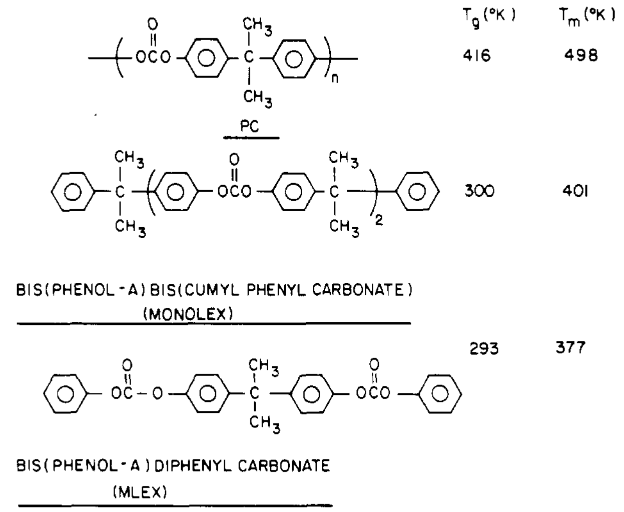

Figure 1. Composition and thermal properties for polycarbonate, bisphenol A bis(cumylphenyl) carbonate (MONOLEX), and bisphenol A diphenyl carbonate (MLEX).

phenol A bis(cumylphenyl) carbonate, to ascertain its effects as a diluent for PC. We also investigated its compatibility with PC to provide a dynamic study of a bimodally distributed system with high and very low molecular weight fractions. The following is the result of that study.

Experimental Section

The structure and thermal properties of the systems used in this study are shown in Figure 1. Thermal data were obtained on a Perkin-Elmer DSC-II at a scanning rate of 10 K/min. The polycarbonate used had $\bar{M}_n$ = 10 600 and a molecular weight distribution of 2.5 and will be referred to as PC. The bisphenol A bis(cumylphenyl) carbonate (MONOLEX) (molecular weight 705) synthesis is given below.[5]

***p*-Cumylphenyl Chloroformate [*p*-(2-Phenylisopropyl)-phenyl Chloroformate].** To a stirred solution of 116.1 g (1.175 mol) of phosgene in 100 mL of dry toluene at −10 °C was added over a period of 1 h a cold (−10 °C) solution of 84.8 g (0.40 mol) of *p*-cumylphenol in 380 mL of dry toluene containing 60.6 g (0.500 mol) of *N*,*N*-dimethylaniline. The latter solution was made by addition of the amine to the phenol solution at 5 °C over a 1-h period. The reaction mixture was stirred 1 h at 0 °C and overnight at room temperature, purged wth nitrogen for 2 h at room temperature and at 80 °C for 2 h, cooled to room temperature, and washed twice with 10% HCl and thrice with water, and dried over Na_2SO_4. Removal of the solvent left 104.1 g (95%) of an amber liquid, which was used without further purification.

Bisphenol A Bis(*p*-cumylphenyl) Carbonate. To a stirred solution of 11.4 g (0.0500 mol) of bisphenol A in 20 mL of pyridine and 75 mL of dry benzene was added dropwise over 1 h a solution of 30.3 g (0.110 mol) of *p*-cumylphenyl chloroformate. The reaction mixture was stirred overnight and then washed twice with water, twice with 10% HCl, and four times with water. Diethyl ether (200 mL) was added during the last two washes to help break up the emulsion. The solution was dried over Na_2SO_4 and taken to dryness to yield a pale yellow syrup, which when crystallized from benzene/hexane afforded 27.7 g (79%) of colorless solid, mp 119–124 °C. Successive recrystallizations from ethyl acetate/ethanol twice and from ethyl acetate/hexane twice followed by benzene/hexane yielded colorless crystals, mp 124.8–126.0 °C (capillary). Anal. Calcd for $C_{47}H_{44}O_6$: C 80.09; H 6.29. Found: C, 80.26; H, 6.40.

Films for dielectric studies were prepared by casting 10% (grams of solids/milliliters of solvent) CH_2Cl_2 solutions of components on ball-grained aluminum. The samples were air-dried and then vacuum-dried (10^{-3} mmHg, 313 K) for at least 24 h. Gold electrodes were evaporated onto the exposed surfaces of the approximately 10-μm films. Samples were isolated from the environment with a stainless steel cell sealed with Teflon. A spring-loaded configuration was used. A thermocouple was mounted within a centimeter of the sample to monitor temperature. Two dielectric devices were used: a scanning dielectric device described previously[1-3] and a General Radio 1615A capacitance bridge with accessories. The former permits continuous acquisition of data from 90 to ~473 K at variable scanning rates. Program rate for these experiments was 0.9 K/min. The latter instrument was used to obtain data for line shape analysis and a transition map plot.

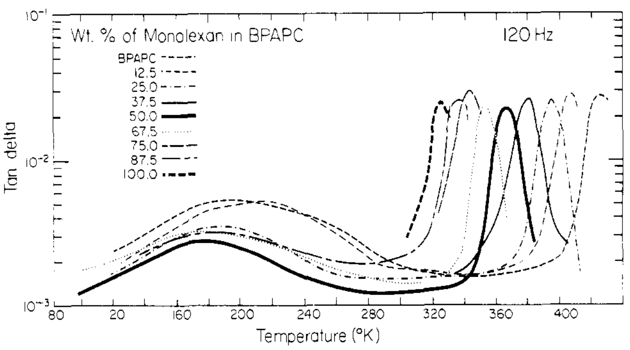

Figure 2. tan δ vs. temperature for solid solutions of MONOLEX/PC at 120 Hz.

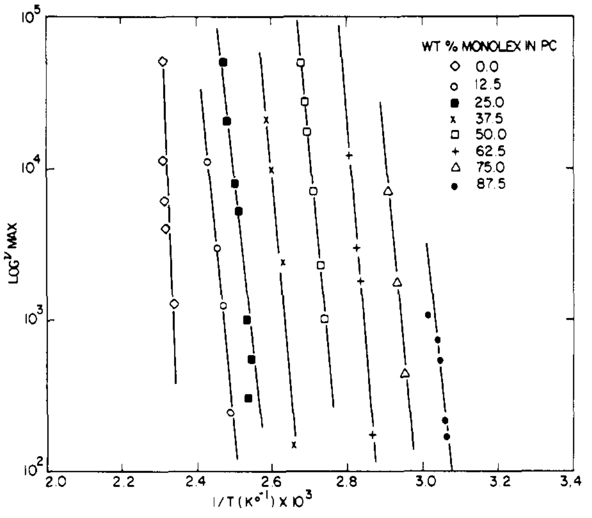

Figure 3. log ν_{max} vs. $1/T$ (K^{-1}) for the glass transition of various mixtures of MONOLEX and PC. Compositions are in weight percent.

DSC data indicate stable solid solutions of these materials within the time frame of our experiments for compositions up to ~85% MONOLEX. A single T_g was observed that did not change within the accuracy of our measurements and the time frame of these experiments (1–2 weeks). The propensity for MONOLEX to crystallize in the pure form precluded isothermal acquisition of dielectric data for the glassy phase in the glass transition region.

Results and Discussion

tan δ vs. temperature curves for the solid solutions studied are shown in Figure 2. Three dielectric relaxations are observed in PC at low frequencies, ~100 Hz: the α (420 K), the β (~220 K), and the γ (~160 K). The β and γ relaxations provide an asymmetric relaxation function in the temperature domain at constant frequency, with the weaker β relaxation producing a high-temperature skewedness in the γ-relaxation process. With few exceptions[1] this merged relaxational process is observed in PC. Dielectric,[5-7] dynamic mechanical,[8-10] and NMR[11,12] measurements indicate that the α relaxation is due to micro-Brownian motion associated with T_g, the β relaxation is a combined phenyl ring–carbonyl motion, and the γ relaxation is a carbonyl motion. We were unable to obtain low-temperature data on MONOLEX, but a previous study[2] indicates that similar relaxations should occur. A transition map for the T_g of the solid solutions is shown

Table I
T_g Activation Energies (MONOLEX/PC)

wt % MONOLEX	E_a, kcal/mol	wt % MONOLEX	E_a, kcal/mol
0.0	200 ± 30	62.5	130 ± 6
12.5	114 ± 8	75.0	115 ± 5
25.0	105 ± 10	87.5	82 ± 20
37.5	120 ± 20	100.0	
50.0	110 ± 5		

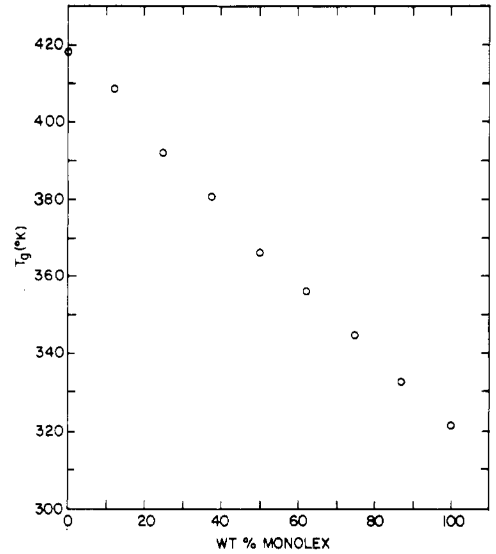

Figure 4. T_g vs. composition. T_g obtained from dielectric tan δ at 120 Hz.

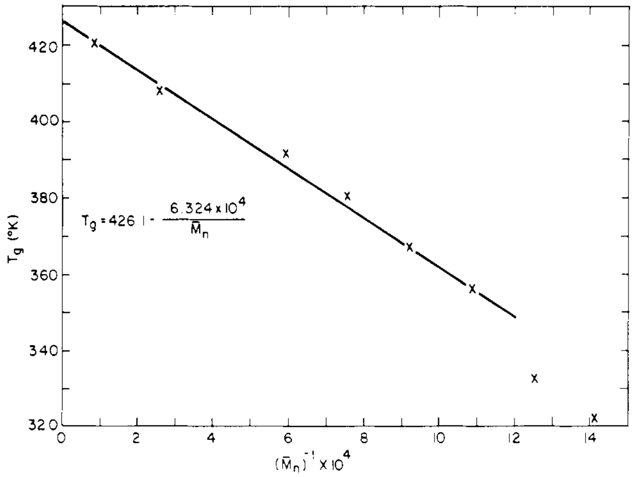

Figure 5. T_g vs. $\bar{M}_n^{-1}$ for solid solutions of MONOLEX/PC.

in Figure 3. All compositions exhibit apparent Arrhenius behavior in the temperature–frequency regime studied. The activation energies are shown in Table I. T_g vs. composition is shown in Figure 4.

The data in Figure 2 indicate one glass transition for the mixed systems over the entire composition range. These data are similar to those of our previous study on a model monomer system for PC[2] and indicate correlated motion for the mixed system. It is seen in Figure 4 that T_g varies continuously and almost linearly over the entire composition range.

If MONOLEX is a good model for PC, a plot of T_g vs. $\bar{M}_n^{-1}$ should be linear. In Figure 5 a linear correlation occurs in the 0–75% MONOLEX composition range, with some deviation above this composition. A plot of the Fox equation (an expected correlation for polymer–diluent systems) is shown in Figure 6, where it is seen that a linear correlation is obtained over the entire composition range. For the volume fraction calculated a density of 1.2 g/mL was used for PC[13] and 1.0 g/mL for MONOLEX. The data are also fit by an exponential correlation reported recently.[14] These results, when compared with bisphenol A diphenyl carbonate (MLEX)/PC results reported earlier,[1] indicate that MONOLEX is a better "model" monomer system than MLEX but that in the high-composition MONOLEX range the system behaves more as a polymer–diluent system.

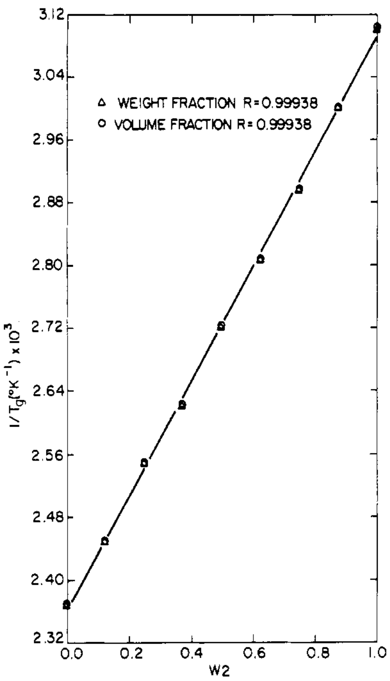

Figure 6. T_g^{-1} vs. volume percent MONOLEX in MONOLEX/PC solid solutions.

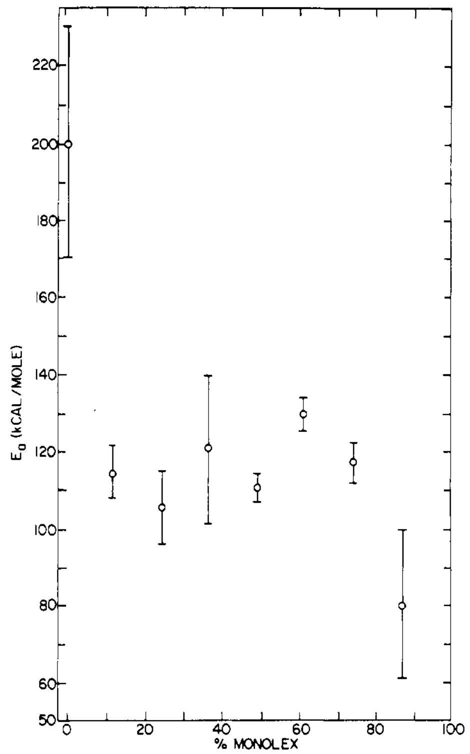

Figure 7. Apparent E_a at T_g vs. weight percent MONOLEX in MONOLEX/PC solid solutions.

In our earlier work, a correlation between the β relaxation and the T_g activation energy was reported.[1,2] In those

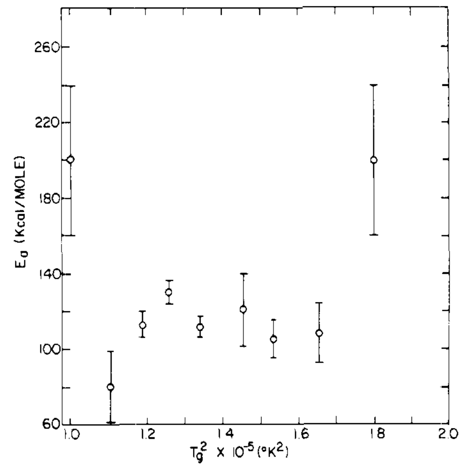

Figure 8. E_a vs. T_g^2 for solid solutions of MONOLEX/PC.

studies the activation energy for T_g was shown to become almost constant in the region where the β relaxation for PC was no longer observed with increasing monomer content. With the exception of an 87.5 wt % MONOLEX sample, the MONOLEX/PC systems demonstrate identical behavior (see Figures 2 and 7). The β relaxation is no longer observed in the blends above 12.5 wt % MONOLEX, and in this composition regime the T_g activation energy is constant (within the measurement limits of error at ~120 kcal/mol). The result indicates an intimate relation between the first sub-T_g relaxation of PC (the isolated combined phenyl–carbonyl motion) and the overall chain dynamics of the glass transition. The characteristics of the β–γ temperature regime with composition are also similar to those observed in the MLEX/PC case.[1] Initial addition of MONOLEX to PC causes the β relaxation to plasticize and the γ relaxation to decrease in intensity slightly. At high levels of small molecule, however, the γ intensity begins increasing and at 87.5 wt % MONOLEX begins showing indications of the β asymmetry. This observation would indicate that (1) the MONOLEX and MLEX have similar relaxational spectra and (2) addition of PC to the monomer affects the β relaxation of MONOLEX in a fashion similar to that of addition of MONOLEX to PC.

The T_g activation energy data can be considered in terms of the WLF formalism.[15] The activation energy can be calculated via

$$E_a = 2.303RC_1{}^\circ C_2T^2/(C_2{}^\circ + T - T_0)^2 \qquad (1)$$

where R is the universal gas constant, T_0 is an arbitrary reference temperature (usually T_g), T is the absolute temperature, and $C_2{}^\circ$ and $C_1{}^\circ$ are functions of the fractional free volume and coefficients of expansion of the system being studied. At T_g eq 1 becomes

$$E_a = 2.303RC_1T_g{}^2/C_2 \cong T_g{}^2R\alpha_f/f_g{}^2 \qquad (2)$$

where f_g is the fractional free volume at T_g and α_f is the coefficient of expansion of f. Equation 2 predicts a linear relationship between E_a and $T_g{}^2$. In Figure 8 it is seen that E_a is constant over a large portion of the composition range or that

$$RT_g{}^2\alpha_f/f_g{}^2 = K \qquad (3)$$

or

$$T_g{}^2 \simeq Kf_g{}^2/\alpha$$

If the square relationship between T_g and f_g governs eq 3, this data would indicate a direct correlation between T_g and f_g and, since the β relaxation has disappeared in this composition region, a correlation between the free volume and short-range motion of the polymer backbone.

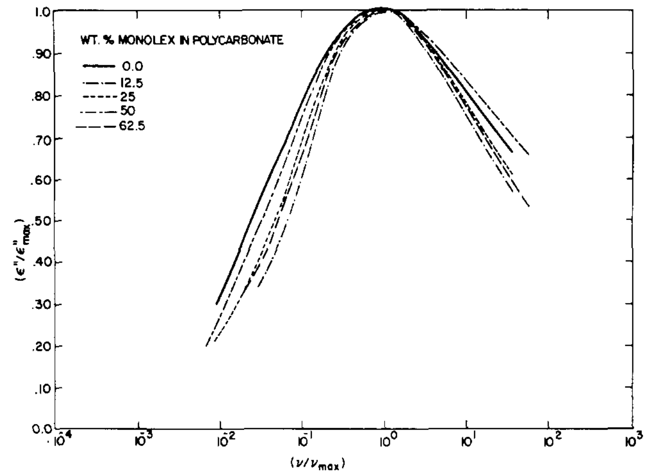

Figure 9. $\epsilon''/\epsilon''_{max}$ vs. ν/ν_{max} at various compositions of MONOLEX/PC.

Line shape analysis of the observed T_g relaxations provides further insight into underlying relaxation at T_g. Figure 9 is a plot of reduced loss vs. reduced frequency for the systems studied. Individual samples produced superimposable results, indicating that the distribution of relaxation times did not change with temperature. It was noted, however, that above 50 wt % MONOLEX, the intensities of the relaxations increased with increasing temperature. It is seen in Figure 9 that increasing the MONOLEX concentration results in a general decrease in the high-frequency skewing of the relaxation envelope. Such behavior was also noted in the MLEX/PC system and indicates a more liquid-like behavior with increasing MONOLEX content, as might be expected. The results appear quantitatively similar to the MLEX/PC results.

Conclusion

The dielectric relaxation spectra of solid solutions of bisphenol A polycarbonate/bisphenol A bis(cumylphenyl) carbonate have been obtained as a function of composition. T_g varies continuously with composition and can be described by either a T_g–$\bar{M}_n{}^{-1}$ or polymer–diluent T_g correlation. The former indicates that the low molecular weight material is a better model system for polycarbonate than bisphenol A diphenyl carbonate studied previously. Up to 87.5 wt % small molecule, the T_g relaxations are Arrhenius activated. The activation energy is composition independent above 25 wt % small molecule. This observation correlates with the disappearance of the β relaxation of the polymer and indicates that localized motion of the polymer backbone is intimately related to the energetics of longer chain motion at T_g.

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Time-Resolved Fluorescence and Emission Depolarization Studies on Polystyrene: Photochemical Processes in Polymeric Systems. 9[1]

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ABSTRACT: The prompt fluorescence emission from polystyrene has been studied in the solid phase (thin film) and in dilute CH_2Cl_2 solution. Measurements of lifetime and polarization have been performed as a function of wavelength in the region 278–380 nm. These studies demonstrate that two emissive species may be characterized in this wavelength range, the monomer (isolated single phenyl groups), emitting at wavelengths shorter than 320 nm, and the excimer, emitting in the range 300–380 nm. Emission in the wavelength region 335–380 nm is characterized by a single-exponential decay in dilute solution as well as in the solid state. No measurable delay is observed in time evolution of any emission. Steady-state polarization measurements show that the fluorescence excimer emission from pure films recorded at 330 nm is essentially completely depolarized. These steady-state measurements are in agreement with polarization measurements on the prompt fluorescence. Total prompt fluorescence following the laser flash is similarly completely depolarized at 335 and 365 nm. Excimer emission from oriented (stretched) films was also found to be depolarized. Polystyrene films that were photodegraded showed less depolarization.

Introduction

Kinetics of decay of singlet excimers are frequently complex and require functions with two or three separately variable exponents for acceptable fits for several polymers in which chromophores are farther apart than the optimal distance required for the formation of 1,3 excimers.[2-6] Guillet and co-workers[2-5] analyzed excimer emission kinetics to obtain rates of dissociation and formation of excimers in several of these systems. In these systems, it is commonly observed that (1) formation of excimers in fluid solution is delayed, the rise time approximately corresponding to the rate of rotation of the pendant groups, and (2) the rate of singlet energy migration is relatively slow, as monitored by the gradual rise in the acceptor's fluorescence over more than 100 ns in poly(1-naphthyl methacrylate). Since the rate of rotation of pendant groups in these systems is fast relative to the rate of excited singlet energy migration in fluid solution, it is to be anticipated that the predominant mechanism of excimer formation involves rotational alignment of an excited state to a neighboring chromophore.

It is our contention that polymers capable of forming 1,3 excimers belong to a distinct class, at least in terms of their photophysical characteristics. Thus in poly(1-vinylnaphthalene)[6] and poly(vinylcarbazole)[7,8] the kinetics of decay of excimer fluorescence are best interpreted in terms of formation of multiple excimer species, which once formed, do not revert back to the monomeric state prior to deactivation. Formation of excimers is observed to be rapid relative to the rate of rotation of pendant groups, even in fluid solution, being essentially complete within 2 ns. In pulse radiolysis experiments on P1VN films doped with anthracene[10] it was found that transfer of singlet excitation of anthracene was complete within 5 ns, an observation that yielded a lower limit of the rate of singlet energy migration in this system. Thus, energy migration to "preformed" parallel pairs of chromophores may be viewed as the major contributor to excimer formation in these systems; rotational alignment subsequent to excitation plays a minor role.

Polystyrene would be expected to belong to the second group of polymers; hence we proposed to investigate two crucial features of the photophysical behavior of this polymer. Specifically, we attempted to determine if the prompt fluorescence from the singlet excimer is depolarized, since observation of depolarized fluorescence from the excimer would strongly indicate energy migration prior to excimer formation.[9] Measurements of polarization as a function of time in the 0–100-ns range would also (a) yield estimates of the rate of energy migration and (b) verify whether a sequential rotational alignment mechanism proposed to interpret data on energy transfer to acceptors[11] can operate in the solid state. The other aspect of the photophysics we report here is the kinetics of fluorescence emission in fluid solution as well as in the solid state. We found a single well-characterized (in terms of spectral resolution of emission) excimer in both cases, decay of which may be satisfactorily fitted to a single-exponential decay function and the formation of which is complete within 2 ns following the laser pulse. Data reported by Ghiggino[12] indicate that the rate constant of excimer formation is greater than or equal to $k = (3\ \text{ns})^{-1}$, consistent with our results and with expected rates of singlet energy transfer in this system.

In general, two different experimental approaches have been utilized in order to seek evidence of singlet energy

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