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High-Conversion Polymerization Fluorescence Probes. 1. Polymerization of Methyl Methacrylate

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ABSTRACT: The effect of polymerization of methyl methacrylate on the fluorescence intensities of a series of donor–acceptor molecules ([*p*-(*N*,*N*-dialkylamino)benzylidene]malononitriles) has been investigated. The fluorescence of the probes increases gradually (1.5 times) as conversion increases to 60%. Further increase in conversion causes a sharp increase in fluorescence (20–40 times), reaching a limiting value at the limiting conversion. This sudden rise in the fluorescence occurs when the polymerization approaches the glassy state. In this region, mobility becomes restricted and internal molecular relaxation of the probes becomes controlled by the microscopic free volume provided by the polymer. This leads to a decrease in the nonradiative rate and consequently to an increase in fluorescence. Bulk polymerization of methyl methacrylate was carried at 50, 70, and 90 °C in the presence of the fluorescent probe. A correlation between the limiting fluorescence yield and the limiting conversion was found. It is assumed that these results reflect the influence of free volume on the molecular relaxation of the probes.

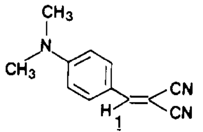
Introduction

In bulk polymerization the reaction system is converted from a low molecular weight liquid (the monomer) via solutions of the polymer in the monomer of various concentrations to the polymeric mass. This process is accompanied by dramatic physical and structural changes. As polymer concentration increases, a point is reached where appreciable chain entanglements occur and eventually a glassy-state transition may result. These physical changes often have a significant effect on both rate of polymerization and molecular weight development, which, in turn, markedly affect the kinetics of the polymerization reaction.

It is well-known that in free radical polymerization of vinyl monomers, the classical polymerization kinetics do not apply at high conversions. The deviation of the rate of polymerization from the classical kinetic behavior is usually observed after some initial conversion and this deviation is characterized by a rapid decrease of the termination rate, k_t, relative to the rate of propagation, k_p. The significant reduction in termination rate (due to polymer chain entanglement) often causes an almost "explosive" increase in radical population and polymerization rate, R_p. This process is termed autoacceleration. The extent of the autoacceleration on the rate of polymerization depends a great deal upon molecular weight development.

Despite the many theoretical and experimental contributions made on the subject,[1-7] it is quite evident that none of the proposed kinetic models can quantitatively describe free radical polymerization to moderately high conversion. Also, relative magnitudes of termination and propagation rates or evaluation of effects such as free volume and segmental and/or translation motion is virtually impossible to assess from an experimental standpoint.

Our intention in the work described here was to examine the effects of the physical changes occurring during radical polymerization of methyl methacrylate (MMA) on the flluorescence of a series of donor–acceptor (D–A) molecules, [*p*-(*N*,*N*-dialkylamino)benzylidene]malononitriles (**1–3**).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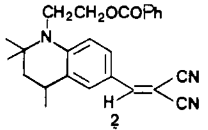
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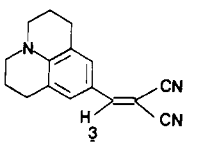
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On the basis of electrochemical and spectroscopic studies,[8] we have assigned the lowest excited singlet state of these materials to an intramolecular charge transfer (ICT) complex of the form $D^+–A^-$. The radiative decay rate, k_r, in fluid media was calculated to be 2.8×10^8 s^{-1}. The singlet lifetime is estimated to be 3–10 ps in solution, which corresponds to a nonradiative decay rate, k_{nr}, of the order of 10^{11} s^{-1}. The extremely fast deactivation rate of the singlet excited state of these materials was attributed to torsional relaxation, which is consistent with recent proposals.[8-10] We have also shown that environmental factors restricting the internal molecular rotation of dyes **1–3** lead to a decrease in k_{nr} and consequently an increase in fluorescence yield ($\phi_F = k_r/(k_r + k_{nr})$). For instance, when these dyes were embedded in a polymer matrix such as poly(vinyl acetate), ϕ_F increased by a factor of 2–6. Furthermore, the fluorescence yield approached unity in rigid glasses at 77 K (a 500-fold increase). These dyes are, therefore, excellent microscopic probes for the physical changes occurring during the course of free radical polymerization of vinyl monomer since their fluorescence yield is very sensitive to dynamic properties of the microenvironment.

The polymerization of methyl methacrylate (MMA) appears to be the most suitable system to evaluate initially, in view of the following: (1) there is a strong gel effect associated with such polymerization; (2) chain transfer reactions are unimportant; and (3) polymer chains are produced mainly by termination reactions. Hence, k_t, k_p,

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Table I
Spectroscopic Data for 1, 2, and 3 in MMA, Ethyl Acetate, and PMMA[a]

	absorption				fluorescence						
	MMA		ethyl acetate		MMA		ethyl acetate		ϕ_F in PMMA[b]		
dye	λ_{max}	log ϵ	λ_{max}	log ϵ	λ_F	$10^{-3}\phi_F$	λ_F	$10^{-3}\phi_F$	+70 °C	+23 °C	−196 °C
1	425	4.7	422	4.71	472	1.3	476	0.9	0.006	0.012	0.80
2	445	4.72	442	4.72	490	2.1	483	1.8	0.025	0.057	0.70
3	450	4.76	448	4.79	493	3.0	488	3.0	0.050	0.120	0.80

[a] λ in nm. [b] Polymerized at 70 °C.

and molecular weight are strongly interrelated.

In this paper, the photophysical behavior of the series of donor–acceptor molecules 1–3 during the free radical polymerization of MMA over a wide temperature range will be discussed.

Experimental Section

Materials. Methyl methylacrylate (Aldrich) was fractionally distilled under vacuum prior to use. [*p*-(*N*,*N*-Dialkylamino)-benzylidene]malononitriles 1, 2, and 3 were purified as described previously.[8] Bulk polymerization of methyl methacrylate was carried out in glass tubes (6-mm i.d.) at 50, 70, and 90 °C, using 0.5% by weight AIBN.

Techniques. Solutions employed for fluorescence measurements were 10^{-5} M in dye (1–3) in methyl methacrylate. The absorption spectra were measured with a Cary 17 spectrometer. The optical densities of all dyes in solution were in the range 0.8–0.9 at the absorption maximum. Fluorescence intensities were taken on a Perkin-Elmer MPF4 spectrofluorometer equipped with a differential corrected spectral unit (DCSU-2) and fitted with a special temperature-controlled copper block as sample holder. Thermal grease was employed as contact between the reaction vessel (glass tubes) and the copper block. The temperature of the copper block was controlled by circulating water which was heated to the desired temperature by a Tamson Holland bath circulator (Model TX3). The reaction temperature was monitored by using a Bailey Instruments digital meter (Model BAT8), the thermocouple probe of which was inserted into the solution so as to measure the actual polymerization temperature. The reaction temperature was controlled within ±1 °C. The fluorescence quantum yields were determined against a calibrated GG21 standard (ϕ_F = 0.494, from Helmo). The polymerization conversions were determined dilatometrically.

Results and Discussion

A description of the photophysical properties of the dyes (1–3) in methyl methacrylate (MMA) and the corresponding polymer (PMMA) matrix will be given first, with particular emphasis on the dynamic behavior of the dyes as a function of structure, viscosity, temperature, and matrix. This will be followed by a discussion of the results on fluorescence intensity changes when the dyes were incorporated into the polymerization reaction.

1. Photophysical Properties of 1–3 in MMA and PMMA. Figure 1 shows the absorption spectra of 1–3 in methyl methacrylate, which are identical with those in ethyl acetate and PMMA. The similarity of the absorption of the dyes in MMA and ethyl acetate indicates that there is no specific interaction between the double bond of the monomer and the dyes. The absorption maxima and molar extinction coefficients are given in Table I.

The $S_0 \rightarrow S_1$ transition of these compounds was previously[8] assigned to an intramolecular charge transfer state (D^+–A^-).[9,10] The shift in absorption maximum to lower energy (longer wavelength) in going from 1 to 2 to 3 reflects the decrease in the ionization energy of the donor R_2N due to increased coplanarity with the aromatic ring. The radiative rate constant, k_r, of the emitting singlet state in MMA, ethyl acetate, or PMMA was calculated for 1–3 from the integration of the absorption spectra to be 2.8×10^8 s^{-1}.

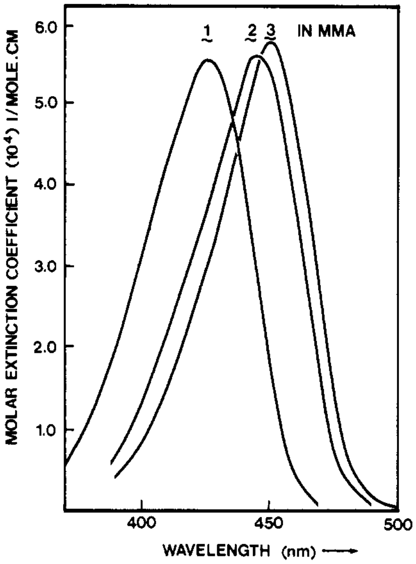

Figure 1. Visible absorption spectra of 1, 2, and 3 in methyl methacrylate.

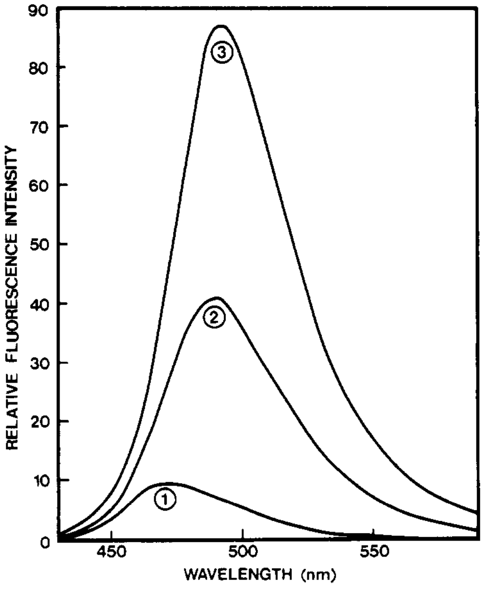

Figure 2. Fluorescence emission spectra of 1, 2, and 3 in poly(methyl methacrylate), measured at 23 °C.

The fluorescence emission spectra of 1–3 in poly(methyl methacrylate) at 10^{-6} M are shown in Figure 2. The fluorescence maxima and quantum yields in MMA, ethyl acetate, and PMMA are given in Table I. The shape and position of the fluorescence band for each of the dyes are identical in the three media (MMA, ethyl acetate, and PMMA). However, the quantum yield of fluorescence of para-substituted benzylidenemalononitriles was very sensitive to molecular rigidity, solvent viscosity, temperature, and matrix properties.

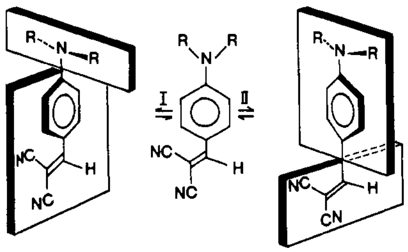

Figure 3. Schematic diagram showing the internal molecular rotation of the R_2N group (route I) and of the donor and acceptor moiety (route II).

In fluid media, the fluorescence quantum yield of **1** is consistently lower than those of **2** and **3**; i.e., ϕ_F increases with the increase in rigidity of the R_2N chromophore. Since the radiactive decay rate, k_r, of the three dyes is equal ($\sim 2.8 \times 10^8\ s^{-1}$), the increase in ϕ_F with molecular rigidity must reflect a decrease in the nonradiative decay rate, k_{nr}. The nonradiative decay rate, k_{nr}, is related to k_r and ϕ_F according to

$$k_{nr} = k_r(1/\phi_F - 1) \qquad (1)$$

From the data in Table I and the above relation, the nonradiative decay rates of excited **1**, **2**, and **3** in MMA are 2.5×10^{11}, 1.33×10^{11}, and $9.3 \times 10^{10}\ s^{-1}$. The singlet excited state lifetimes ($\tau_s = 1/(k_{nr} + k_r)$) of **1**, **2**, and **3** in MMA are 4.6, 7.5, and 10.7 ps.

The extremely short lifetime of the singlet excited state of these molecules and many intramolecular charge transfer complexes can be attributed to fast intrinsic internal relaxation.[8-10] Among the possible internal relaxation mechanisms are rotation of the R_2N group (e.g., in the case of **1**) and/or twisting around the D–A bond[10] as depicted in Figure 3. While **1** has both routes I and II available to dissipate the excitation energy, **2** and **3**, due to structural restriction, have only route II to channel the excess excitation energy. The internal rotation process with the fastest rate will control the nonradiative decay rate and consequently determine the singlet excited state lifetime in this class of materials. Internal rotation around the R_2N group ($2 \times 10^{11}\ s^{-1}$) in **1** must be faster than twisting of the large donor and acceptor moiety, leading to the very short singlet lifetime $\tau_s = 5$ ps in MMA. The increase in singlet excited state lifetime in going from **1** to **2** to **3** reflects a decrease in the internal rotation due to a blocking of the free rotation of the R_2N group coupled with an increase in mass of the donor moiety. An extrinsic mechanism involving solvent reorientation controlled by the dielectric relaxation time can be ignored since solvents such as MMA or ethyl acetate have short relaxation times at room temperature.

The quantum yield of fluorescence of **1**, **2**, and **3** increased by a factor of 10, 20, and 40, respectively, when these dyes were embedded in PMMA matrix. This remarkable increase in ϕ_F of these materials in the polymer matrix is consistent with the idea of deactivation via internal rotation, which is free-volume dependent. The importance of free volume and viscosity in the molecular relaxation processes of excited dyes has been clearly demonstrated in the case of polymethines, triphenylmethanes, and coumarin dyes.[11-19] For dyes in which rotation-dependent nonradiative decay (k_{nr}) links the excited-state conformation to the medium free volume, one can relate k_{nr} to the solvent free volume, ν_f

$$k_{nr} = k_{nr}{}^0 \exp(-\nu_0/b\nu_f) \qquad (2)$$

where $k_{nr}{}^0$ is the intrinsic rate of molecular relaxation, ν_0 is the dye van der Waals volume, and b is a constant for the particular dye. Taking $\phi_f \ll 1$, eq 1 can be substituted in eq 2 to obtain the fluorescence-dependent free volume

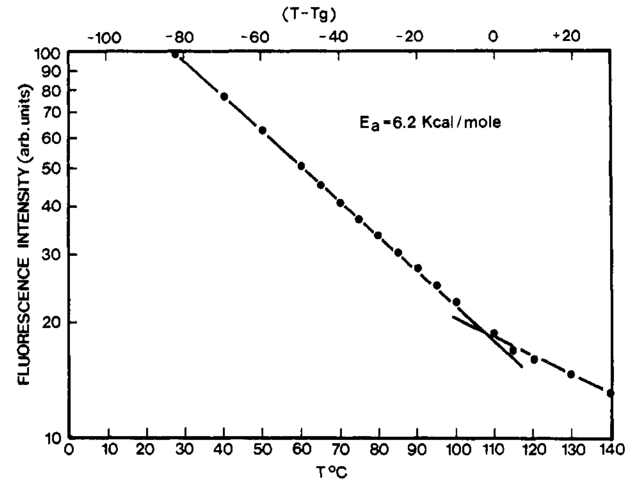

Figure 4. Dependence of fluorescence of **2** on temperature in PMMA.

$$\phi_F = (k_r/k_{nr}{}^0) \exp(\nu_0/b\nu_f) \qquad (3)$$

Since the medium viscosity, η, is free-volume dependent, the relationship between dye fluorescence yield and medium viscosity can be similarly developed[13]

$$\phi_F = C\eta^n \qquad (4)$$

where C is a constant for a particular dye and n has been found by Förster and Hoffmann to equal $^2/_3$.[13] The above relationships indicate that the fluorescence yield of dyes which exhibit rotation-dependent nonradiative decay will increase with a decrease of free volume and/or an increase of viscosity.

To test the validity of the free-volume restriction imposed by a polymer matrix on the dye internal relaxation, we studied the effect of temperature on the fluorescence yield of **2** in PMMA. The fluorescence intensity of **2** in PMMA decreased with increasing temperature, as shown in Figure 4. A break in the I_F vs. temperature plot occurs at 106 °C, the glass transition of PMMA. The activation energy for temperatures below T_g is 6.2 kcal/mol. This coincides with the activation energy to overcome van der Waals forces in translation movement of polymer chain segments.[20] The decrease in fluorescence of **2** in PMMA with increased temperature is thus due to the fact that thermal energy must be spent to create sufficient free volume for the molecular rotation to occur. The increase in free volume with temperature is provided by a polymer chain translational relaxation mechanism.

One final note on the photophysical properties of dyes **1**–**3** in PMMA is that the fluorescence yields approach unity at −196 °C. At this temperature all motions are frozen and consequently the nonradiative decay rate, k_{nr}, becomes much less than k_r, leading to the unitary fluorescence yield.

The aforementioned results show that in fluid media, the fluorescence of [*p*-(*N*,*N*-dialkylamino)benzylidene]malononitrile dyes **1**–**3** is controlled by rapid internal rotation occurring in a few picoseconds. In the case of **1** it corresponds to rotation of the NR_2 group ($2 \times 10^{11}\ s^{-1}$), while in the case of **2** and **3** it involves rotation or twisting around the bond between the donor and acceptor moieties ($(9-10) \times 10^{10}\ s^{-1}$). The driving force behind internal molecular twisting in D–A-type molecules is the reduction in energy, as was shown by ab initio and CNDO calcula-

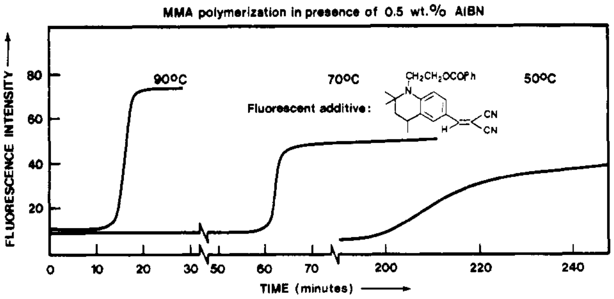

Figure 5. Change in fluorescence intensity of **2** in MMA as a function of polymerization temperature and time.

Table II
Dependence of Fluorescence Quantum Yield of Dye 2 on Limiting Conversion of PMMA

polymerization temp, °C	limiting conversion	$\phi_F{}^b$
50	85	0.038
70	90	0.057
90	95	0.080
	100[a]	0.100

[a] Sample annealed at 110 °C for 2 h. [b] Measured at room temperature.

tion.[10] Rotation of particles in fluid media is known to be viscosity, free-volume, and temperature dependent. The effect of polymer matrix on the fluorescence yield of **1**–**3** is an example of the influence of free volume on the rate of rotation. In a polymer matrix, the polymer chain translational relaxation mechanism provides the free volume needed for the dye to undergo internal twisting, which becomes the rate-determining step (2×10^{10} to 2×10^{9} s^{-1}). The larger the free volume required for the internal rotation of the probe, the greater the effect on ϕ_F. Therefore, these dyes can act as a microscopic probe to trace the physical changes occurring during polymerization reactions. The results of this investigation will be discussed next.

2. Dynamic Behavior of a Fluorescent Probe in MMA Polymerization. The polymerization reaction investigated was that of MMA with the fluorescent chromophores **1**–**3** simply dissolved in the monomer at 10^{-5} M concentration. Bulk polymerization of MMA was initiated with AIBN at the temperatures 50, 70, and 90 °C. The fluorescence intensities of the chromophores (λ_{ex} 400 nm) were continuously monitored at λ_F 500 nm at the polymerization temperature. Typical fluorescence intensity against polymerization time plots are shown in Figure 5 for dye **2** at three reaction temperatures. A unique and interesting behavior was observed. The fluorescence intensity remains almost constant for a period of time (depending on reaction temperature) until a critical moment is reached where an abrupt rise in fluorescence intensity occurs, reaching a limiting value which is dependent on the polymerization temperature. Table II lists the fluorescence quantum yield of **2** in PMMA samples prepared at these various polymerization temperatures. Recently, Marten and Hamielec[7] reported a relationship between polymerization temperature and limiting conversion. This was based on the fact that limiting conversion occurs at a point where the glass transition of the polymer/monomer equals the reaction temperature. In bulk polymerization of MMA, a limiting conversion of 85, 90, and 95% PMMA in MMA has been obtained at polymerization temperatures of 50, 70, and 90 °C, respectively. Interestingly, we find a similar relationship between the limiting fluorescence of **2** and the polymerization temperature, as shown in Figure 6, and, in turn, between limiting fluorescence and limiting conversion, which have been extrapolated to a limiting conversion of 100% to estimate the T_g (110 °C) of the polymer produced.

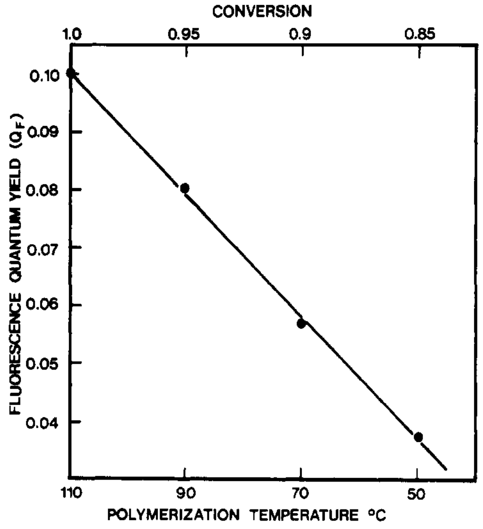

Figure 6. Correlation between the limiting fluorescence of **2** and PMMA and both the polymerization temperature and limiting conversion.

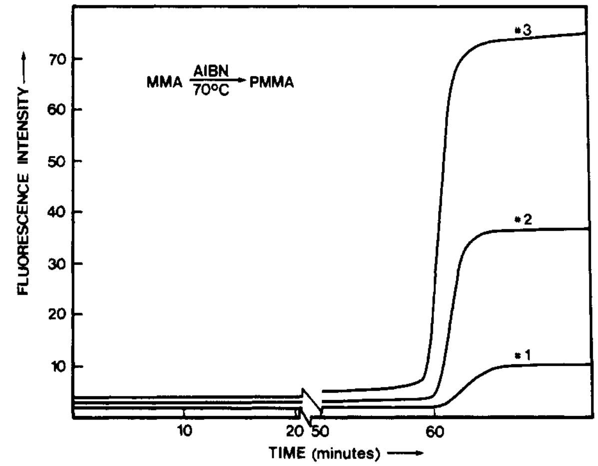

Figure 7. Dependence of the fluorescence intensity of **1**, **2**, and **3** on MMA polymerization time (polymerization carried out at 70 °C).

Figure 7 shows the change in fluorescence intensity of dyes **1** and **3** relative to dye **2** when incorporated in MMA polymerization at 70 °C. The general shape of the curves is identical in that the onset of the rise of fluorescence occurs almost at the same reaction time; however, the limiting fluorescence yield of **3** > **2** ≫ **1**. This reflects the differences in demand for free volume by each of the probes.

To quantify the fluorescence-time relationships, we simultaneously determined the polymer conversion. Figure 8 shows the conversion-time relation for MMA bulk polymerization initiated by AIBN at 70 °C. Our data agree extremely well with those reported by Balke and Hamielec,[1] implying that the added dye has no effect on the polymerization kinetics.

The plots typically have an initial gradual increase in conversion (up to 50%), followed by a section of autoacceleration (explosive region), and then a section of autoinhibition extending to the limiting conversion, where the rate of polymerization diminishes to zero when the glassy state is reached. The data are listed in Table III along with

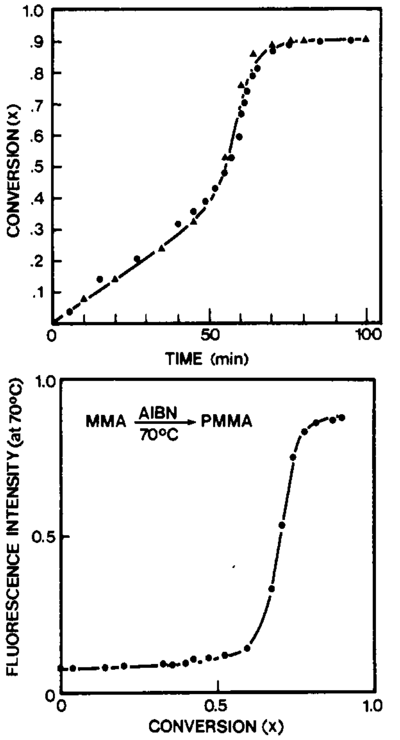

Figure 8. Plots of MMA conversion vs. time: (●) this work; (▲) from ref 1. Bottom curve shows the dependence of fluorescence of **2** on MMA conversion.

Table III
Dependence of Fluorescence Intensity of Dye 2 (at 70 °C) on MMA Conversion and PMMA Molecular Weight

reaction time, min	conversion $\bar{X}$	fluorescence intensity	$M_w \times 10^{-5}$ [a]	$M_n \times 10^{-5}$ [a]
0	0	8	0	0
5	0.04	8.2	2.68	1.17
15	0.14	8.4	2.86	1.17
27	0.20	8.5		
41	0.33	9.0	3.91	1.23
45	0.36	9.2		
49	0.39	9.5		
52	0.43	10.5		
55	0.48	11		
57	0.53	12	8.98	1.76
59	0.60	14		
60	0.67	22		
61	0.70	53		
62	0.74	75	11.8	2.24
63	0.78	83		
65	0.82	86		
70	0.87	87		
75	0.89	88		
85	0.90	88	14.5	2.7

[a] From ref 1.

the fluorescence of **2** during the course of the polymerization. Figure 8 shows the fluorescence–conversion dependence. At zero conversion, i.e., in the starting monomer, ϕ_F is very low (2×10^{-3}). An increase in conversion up to 60% only increases ϕ_F by a factor of 1.5. Obviously, at these polymer concentrations the dynamic relaxation of **2** has not changed greatly, although the macroscopic viscosity of the solution has increased by more than 2 orders of magnitude. A further increase in conversion causes a sharp increase in the fluorescence, reaching a limiting value once the limiting conversion is attained. The abrupt rise in fluorescence appears to correspond to the approach to the glass state.

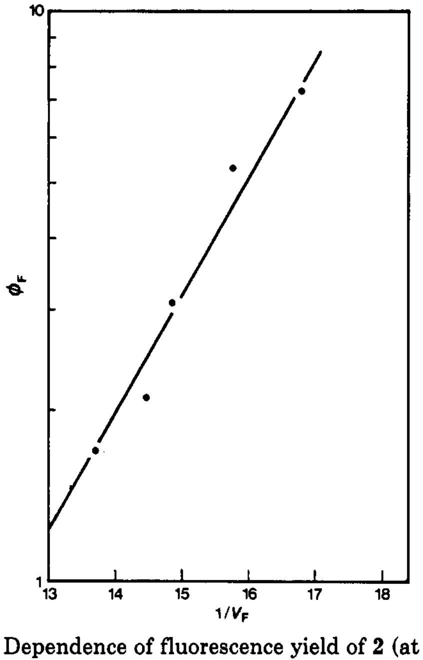

Figure 9. Dependence of fluorescence yield of **2** (at 70 °C) on PMMA/MMA mixture free volume.

To determine the link between the fluorescence intensity changes and the medium physical changes occurring during the polymerization reaction, we need to measure the change in free volume, viscosity, and glass temperature of the polymer/monomer mixture as a function of conversion. Bueche[21,22] has developed general expressions for the variation of V_f, T_g, and η of a polymer–diluent system

$$V_f = 0.025 + \alpha_p(T - T_{gp})V_p + \alpha_d(T - T_{gd})V_d \qquad (5)$$

$$T_g = [\alpha_p V_p T_{gp} + \alpha_d(1 - V_p)T_{gd}]/[\alpha_p V_p + \alpha_d(1 - V_p)] \qquad (6)$$

$$\ln (\eta_g/\eta) = 40(T - T_g)/[52 + (T - T_g)] \qquad (7)$$

where V_p is the volume fraction of polymer, η_g is the viscosity at the glass temperature ($\sim 10^{11}$ cP), and η is the polymer- or glass-forming liquid viscosity at temperature T, where $T_g < T < T_g + 120$. These relationships have been tested for several polymer–diluent systems and have been found to be reasonably accurate.[22] Application of these relations requires knowledge of the glass temperature of the polymer, T_{gp}, and the diluent, T_{gd}, as well as the expansion coefficient of the polymer, α_p, and the diluent, α_d. The value of α is very close to 4.8×10^{-4}/°C for most polymers and 10^{-3}/°C for most diluents. For the system under investigation the polymer is PMMA, which has a $T_{gp} = 110$ °C, and the diluent is MMA, whose T_{gd} is not known. However, taking $V_p = 0.90$ and $T_g = 70$ °C at the limiting conversion[7] and substituting in eq 6, we estimate a value of $T_{gd} = -102.8$ °C for MMA. This value of T_{gd} correctly predicts the T_g's for $V_p = 0.85$, 0.95, and 1.0 given in ref 7 (see Table IV). Using this value of T_{gd}, one can compute the glass temperature T_g, viscosity η, and free volume V_f of PMMA/MMA mixtures as a function of conversion; the results are listed in Table IV along with the fluorescence intensity of **2**.

According to eq 3 a plot of ln ϕ_F vs. $1/V_f$ should give a straight line, the slope of which gives ν_0/b and the intercept of which gives ln $(kr/k_{nr}{}^0)$. Figure 9 shows such a plot which gives a value of $\nu_0/b = {}^1/_2$. Figure 10 shows the dependence of the fluorescence yield of **2** on the polymerization reaction mixture viscosity. A gradual increase in fluorescence occurs as the viscosity increases from 0.1 to 10 cP. This is followed by a sharp rise in fluorescence

Table IV
Glass Temperature, Viscosity, and Free Volume of the PMMA/MMA System as a Function of Conversion (at 70 °C)

$V_p(X)$	T_g, °C	η, cP	V_f	I_F (ϕ_F)
0	−102.8			8
0.43	−46.2	0.1		10.5
0.48	−37.5	0.195		11
0.53	−28	0.45		12
0.60	−13.7	1.93		14
0.65	−3.0	7.15	0.073	17 (0.0048)
0.67	2.2	14.8	0.0695	22 (0.00625)
0.68	4.5	20.7	0.0672	32 (0.0091)
0.70	9.6	46.23	0.0634	53 (0.015)
0.72	14.2	100	0.0595	73 (0.021)
0.74	20.0	305		75
0.78	31.2	3700		83
0.82	43.2	1.2×10^5		86
0.87	59.5	1.2×10^8		87
0.89	66.4	7.5×10^9		88
0.90	70.0	1×10^{11}		88
0.95	89			
1.0	110			

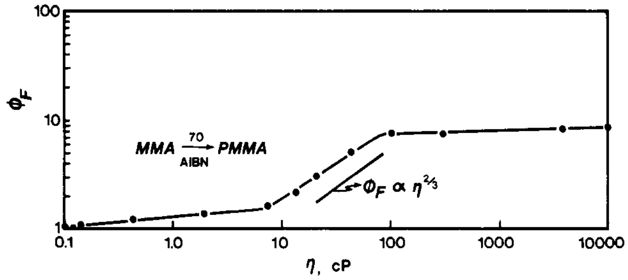

Figure 10. Dependence of fluorescence yield of **2** (at 70 °C) on PMMA/MMA mixture viscosity.

as the viscosity changes from 10 to 100 cP. The slope of this portion of the plot corresponds to $\phi_F \alpha \eta^{2/3}$, which agrees well with the Förster and Hoffmann[13] model. Further increase in conversion leads to a rapid rise in viscosity, as the glassy state is approached, with no further increase in fluorescence. The polymerization region in which fluorescence intensity increases abruptly seems to corepond to the increase of medium viscosity from fluid to rigid glass. This accounts for the abrupt increase in fluorescence until the limiting conversion is reached, at which point fluorescence levels off.

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Magic-Angle Carbon-13 Nuclear Magnetic Resonance Study of the Compatibility of Solid Polymeric Blends

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ABSTRACT: A theoretical analysis of coupled relaxation processes has been used in the quantitative interpretation of carbon-resolved, proton $T_{1\rho}$ data obtained at 15.1 MHz for a variety of solid blends of poly(phenylene oxide) and polystyrene. This analysis permits an estimate of spin-diffusion rates between different chemical species. These rates are strongly dependent on spatial proximity and hence are applicable to the determination of the homogeneity of the blends. Proton $T_{1\rho}$'s in the blends are nearly but not quite averaged to a single value by spin diffusion, indicating extensive intermixing of poly(phenylene oxide) and polystyrene chains. The proton $T_{1\rho}$ experiments are sensitive enough to distinguish between identically prepared blends made from poly(phenylene oxide) and either atactic or isotactic polystyrenes. While the bulk of both types of blends is an intimate mixture of polymer chains, there are also some small regions in the atactic polystyrene blend where the polystyrene is not uniformly dispersed.

Introduction

Magic-angle cross-polarization ^{13}C NMR of nominally homogeneous glassy polymers provides information about both structure and dynamics.[1] Resolved isotropic chemical shifts identify chemical environments, which, as for the frozen conformations of a polymer, may be unique to the solid state. Relaxation experiments exploit this high resolution so that ^{13}C T_1's and $T_{1\rho}$'s can be used to characterize individual main- and side-chain motions in the megahertz- and kilohertz-frequency ranges, respectively.

The high-resolution magic-angle techniques used to obtain ^{13}C NMR spectra in solids can also be employed