Characterization of Polymer Chain Interpenetration in Solution by Fluorescence after Freeze-Drying

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ABSTRACT: Solutions containing two poly(ethyl methacrylates) (PEMA) labeled with carbazole (C) and anthracene (A), respectively, were freeze-dried and pressed into pellets. Emission spectra of these samples showed that energy transfer from C to A was substantially less than in cast films with the same composition and increased with the concentration of the solution before freeze-drying. These results indicate that the extent of chain interpenetration in solution is retained on freeze-drying and that freeze-drying from highly dilute solutions leads to an assembly of compact globules of the individual polymer molecules. This concept was confirmed on systems of C-labeled PEMA and A-labeled poly(methyl methacrylate) (PMMA) diluted by different ratios of unlabeled PEMA and PMMA. When freeze-dried from dilute solution, such blends exhibited energy transfer independent of the PEMA/PMMA ratio, while energy transfer from cast films of the same composition reflected the incompatibility of PEMA with PMMA. Poly(benzyl methacrylate) (PBzMA) exhibits excimer emission in bulk but not in dilute solution; cast films of mixtures of PBzMA and PMMA show a decreasing excimer yield with PBzMA dilution, but freeze-drying such mixtures from dilute solutions yields emission spectra which do not change significantly with the composition of the blend. With blends containing 10% PBzMA excimer emission is strongly enhanced when the freeze-drying is carried out from solutions containing less than 1% polymer.

Previous publications from this laboratory[2-4] described the characterization of polymer compatibility by nonradiative energy transfer between suitably chosen fluorescent labels attached to the polymeric species. In that work films were cast from solution of the two polymers and it was reasoned that phase separation would result in a segregation of the donor and acceptor fluorophore, decreasing the efficiency of energy transfer. The data obtained confirmed the validity of this experimental approach.

Work in two other laboratories[5,6] has demonstrated that freeze-drying of solutions containing two incompatible polymers may lead to a metastable one-phase system (as characterized by a single glass transition temperature) and the same result was obtained by a rapid precipitation in a nonsolvent.[7] A. R. Shultz suggested to us that our fluorescence technique might be suitable for following the phase separation when metastable blends prepared by freeze-drying are heated above T_g, but we soon discovered that freeze-dried samples do not behave like systems exhibiting perfect mixing at the segmental level even if the original solution contained two near-identical polymeric species. This should perhaps not have come as a surprise, since Berghmans and Overbergh[8] found a few years ago that freeze-drying of dilute solutions containing two *compatible* polymers produced a system with three glass transition temperatures, corresponding to the T_g of the two polymeric species and an intermediate T_g characterizing their blend. More recently,[9] a comparison of the density of freeze-dried and bulk polystyrene has also led to the inference that freeze-drying from dilute solution leads to a system in which individual polymer chains are collapsed to globular particles rather than being intertwined.

In this study we have compared nonradiative energy transfer in systems with the same overall composition prepared by film casting or by freeze-drying from solutions of varying concentration. We have used here (a) two similar polymers carrying donor or acceptor labels, respectively, and (b) two incompatible polymers carrying the donor or the acceptor.

Another approach to the study of polymer chain interpenetration involves the use of polymers with aromatic side chains. Such polymers have fluorescence spectra exhibiting in addition to the normal "monomer" emission band excimer emission at longer wavelengths. In polystyrene solutions, the ratio of excimer and monomer emission intensity, I_e/I_m, increases with increasing polymer concentration,[10] since intermolecular chromophore interaction becomes increasingly important. Similar increases in I_e/I_m were observed for poly(2-vinylnaphthalene) dissolved in glassy films of nonfluorescing "host" polymers.[11] In a number of cases it was found[12] that excimer emission is absent at high dilution of a fluorescing polymer and that excimers can only form at higher concentration by interaction of chromophores attached to different polymer chains. Such behavior is particularly desirable for our purposes and we chose, therefore, for our study poly(benzyl methacrylate) (PBzMA), which exhibits excimer emission in bulk but not in dilute solution. Thus, in a blend of PBzMA with a nonfluorescing polymer, I_e/I_m will be an index of the interpenetration of the two polymer species.

Experimental Section

The preparation of (9-anthryl)methyl methacrylate (AMMA) and 2-(*N*-carbazolyl)ethyl methacrylate (CEMA) was previously described.[2] They were copolymerized to low conversion with methyl methacrylate or ethyl methacrylate at 65 °C in dioxane solution. The chromophore concentrations of the copolymers were obtained from UV spectra,[2] and the molecular weights were estimated from intrinsic viscosities by using the $[\eta]$–M relation of the unlabeled homopolymers. Homopolymers of methyl methacrylate, ethyl methacrylate, and benzyl methacrylate were prepared under similar conditions. Films of polymer mixtures were cast from 5–10% benzene solutions except for the PMMA–PBzMA mixtures, for which both benzene and dioxane solutions were used. To prepare freeze-dried mixtures, 25 mL or less of a benzene solution was poured slowly into a swirled flask immersed into a dry ice–acetone mixture so that the solution froze in a few seconds. The flask was immersed in an ice–water bath and connected to a rotary evaporator at a pressure of 10^{-2}–10^{-3} torr. After about 8 h of sublimation, the last traces of solvent were removed by passing a nitrogen stream for a few hours over the polymer powder. The residual benzene concentration (as estimated by UV absorption) was less than 0.01%.

Samples prepared in this manner from dilute solutions were fluffy powders, while more concentrated solutions yielded coherent elastic products. Unless stated otherwise, freeze-dried samples were pressed into pellets under a pressure of 8.5 kbar. Such pellets had densities less than 5% below those of corresponding bulk polymers. Reflectance fluorescence spectra of freeze-dried samples or cast films with the incident light at 30° and the emitted beam at 60° to the sample surface were recorded with a Hitachi Perkin-Elmer MPF-2A spectrometer equipped with a 150-W xenon lamp. Systems containing carbazole and anthracene labels were

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Table I
Characterization of Polymers Used in This Study

polymer	$[\eta]$,[a] dL/g	$10^5\bar{M}_\eta$	label
PMMA-A	1.32	9.13	0.42 mol % AMMA
PMMA	0.69	3.78	
PEMA-A	0.94	5.50	0.51 mol % AMMA
PEMA-C	1.48	9.83	0.66 mol % CEMA
PEMA-C'	0.64	3.39	0.65 mol % CEMA
PEMA	0.83	4.71	
PBzMA	0.30	2.80	

[a] In butanone at 25 °C.

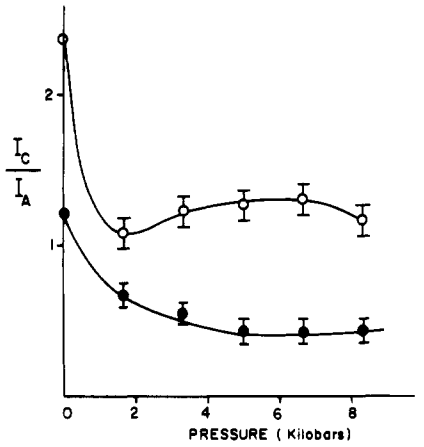

Figure 1. I_C/I_A in freeze-dried blends of PEMA-A, PEMA-C', and PEMA prepared from 1% (O) or 5% (●) solutions and compacted under varying pressures. All samples contain (C) = (A) = 9.4 mmol/kg.

irradiated at 294 nm, where the ratio of carbazole absorption to anthracene absorption is at a maximum.[2] The emission spectrum was characterized by I_C/I_A, the ratio of emission intensities of carbazole at 347 nm and anthracene at 413 nm. Systems containing PBzMA were irradiated at 250 nm and the emission was characterized by I_e/I_m, the ratio of emission intensities at 327 nm (characteristic of the excimer) to emission at 290 nm (characteristic of the "monomeric" benzyl group).

Results

Characteristics of polymers employed in this study are listed in Table I. The results obtained in the three types of systems investigated were as follows:

(a) Mixtures of Donor- and Acceptor-Labeled PEMA. The ratio of carbazole and anthracene emission intensities, I_C/I_A, in samples obtained from freeze-dried blends of carbazole- and anthracene-labeled PEMA depended on the concentration of the solution before freezing and on the pressure under which the pellets were prepared. Figure 1 illustrates this dependence on pressure for samples freeze-dried from 1% and 5% solutions.

Compacting the freeze-dried blends decreases I_C/I_A; i.e., it increases the efficiency of energy transfer. This may be interpreted either as due to a collapse of the chain molecules under pressure or as a result of the elimination of spaces between the individual polymer chains.[12b] Energy transfer is more efficient when freeze-drying is carried out from the more concentrated solution, where the chain molecules are intertwined. This suggests that the interpenetration of the polymer molecules in solution is retained during the freeze-drying process. Figure 2 illustrates the dependence of I_C/I_A on the solution concentration in more detail. The low efficiency of energy transfer in samples freeze-dried from highly dilute solutions suggests that on freeze-drying, isolated polymers collapse to globules so that many of the donor and acceptor fluorophores are too far

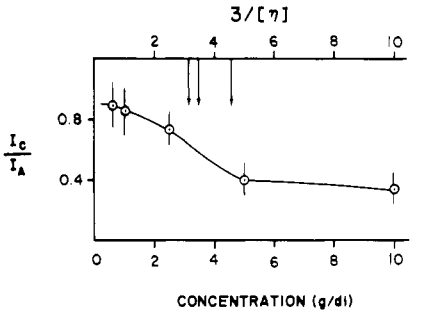

Figure 2. Dependence of I_C/I_A in PEMA-A + PEMA-C' + PEMA blends on the concentration of the solution before freeze-drying. (C) = (A) = 9.4 mmol/kg. The three arrows represent $3[\eta]$ for the three components of the system.

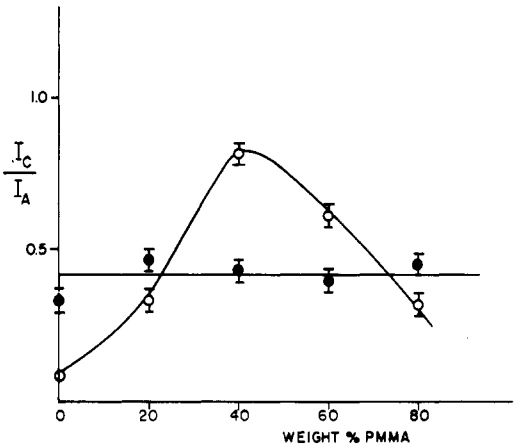

Figure 3. I_C/I_A in blends of PMMA-A + PEMA-C + PMMA + PEMA as a function of PMMA content. Samples prepared by film casting (O) and freeze-drying from 1% solutions (●). (C) = (A) = 9.4 mmol/kg.

from each other for nonradiative energy transfer. With increasing solution concentration, chain entanglements are formed which persist during the freeze-drying operation, so that energy transfer increases. However, even in the sample prepared from a 10% solution, energy transfer is very much less efficient than in cast films in which the donor- and acceptor-labeled chains fully interpenetrate each other, leading to $I_C/I_A = 0.08$.

(b) Blends of Labeled PMMA and PEMA. Figure 3 illustrates the energy transfer observed in blends of PMMA and PEMA of varying composition containing a fixed concentration of carbazole-labeled PEMA and anthracene-labeled PMMA. When a 1% solution of the mixed polymers was freeze-dried, I_C/I_A was independent of the composition of the blend. By contrast, I_C/I_A values for samples prepared by film casting rose with increasing PMMA content of the blend to a maximum at 40% PMMA and declined as the PMMA content was further increased.

Figure 4 compares the emission spectra of cast films and of samples prepared by freeze-drying from 1% solution. In Figure 4a, both donor and acceptor are attached to PEMA. In the cast film I_C/I_A is very low, since the interpenetrating chains allow for extensive energy transfer. In the freeze-dried sample this transfer is much less efficient because the donor and acceptor are segregated into microdomains. In Figure 4b, representing PMMA–PEMA blends with 40% PMMA, energy transfer is less in the cast film than in the freeze-dried sample, since phase separation to large phase domains occurs during the drying of the casting solutions containing two polymers which are known to be incompatible.[2,13]

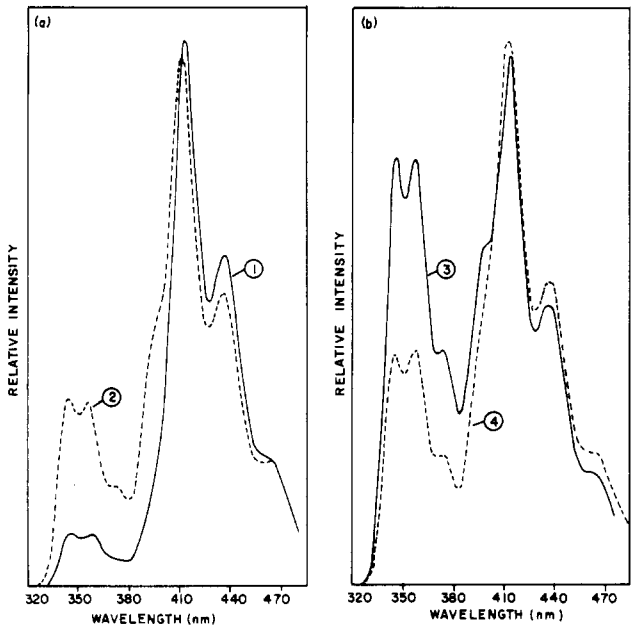

Figure 4. (a) Emission spectra of blends of PEMA-A, PEMA-C, and unlabeled PEMA prepared by film casting (1) and by freeze-drying from a 1% solution (2). (b) Emission spectra of a blend of PMMA-A, PEMA-C, and unlabeled PEMA and PMMA, containing 40% of labeled or unlabeled PMMA, prepared by film casting (3) or freeze-drying from a 1% solution (4). (C) = (A) = 9.4 mmol/kg.

We found the trend of I_C/I_A values obtained from samples freeze-dried from 5% solutions to be rather similar to that observed in cast films. It seems then that phase separation in our system is fairly extensive when solutions of this concentration are subjected to the freeze-drying process. This contrasts with the observation of Ishihara et al.,[5] who studied blends of poly(vinyl acetate) with PMMA freeze-dried from benzene solution, and Shultz and Young,[6] who studied blends of polystyrene with PMMA freeze-dried from naphthalene solution. Both these studies reported that such blends exhibited a single T_g and appeared, therefore, to be homogeneous by this criterion although incompatible polymer pairs were used.

(c) Blends of Poly(benzyl methacrylate) with Poly(methyl methacrylate). Many years ago, Hirayama[14] found that in a series of α,ω-diphenylalkanes only 1,3-diphenylpropane exhibits intramolecular excimer fluorescence. It is now known that other aromatic chromophores do not necessarily obey this "$n - 3$ rule"; e.g., intramolecular excimers were observed with pyrene residues attached to the two ends of longer, paraffinic chains[15] or polystyrene molecules[16] and intramolecular excimer emission occurs also in dilute solutions of poly(1-naphthyl methacrylate),[17] in which nearest-neighbor naphthyl residues are separated by eight bonds. Nevertheless, since phenyl excimers are much less stable than excimers formed by pyrene or naphthalene residues, it was expected that no intramolecular excimer emission would be observed in dilute systems containing poly(benzyl methacrylate), and experiment confirmed this expectation. We found that PBzMA exhibits only the normal phenyl emission at 290 nm in dilute dioxane solution, but excimer emission with a peak at 327 nm becomes increasingly prominent as the solution concentration is increased. In bulk poly(benzyl methacrylate) the ratio of the intensities of the excimer and the monomer peak, I_e/I_m, is 1.32 ± 0.2.

When mixtures of PBzMA and PMMA in different ratios are freeze-dried from a 1% solution in benzene, I_e/I_m = 1.6 ± 0.3 was observed, independent of the composition

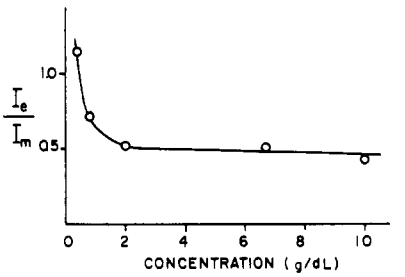

Figure 5. I_e/I_m in blends of PBzMA with 9 parts of PMMA prepared by freeze-drying from solutions of varying concentrations.

of the mixture. By contrast, when films were cast from benzene solutions of these mixtures, I_e/I_m decreased from 1.3 to 0.92, 0.85, 0.78, and 0.52 as the PMMA fraction increased from 0 to 20%, 40%, 60%, and 80%. This indicates that the PBzMA forms a separate microphase on freeze-drying from dilute solution, while film casting leads to PBzMA chains intertwined with PMMA. It should be noted that PBzMA and PMMA have been reported[13] to be incompatible although their solubility parameters are quite similar.[18] Apparently, phase separation does not take place under our conditions of film casting.

When mixtures of 10% PBzMA with 90% PMMA were freeze-dried from solutions of varying concentration, I_e/I_m increased only from 0.42 to 0.52 as the original solution concentration was reduced from 10% to 2%. However, samples freeze-dried from 0.8% and 0.4% solutions were characterized by I_e/I_m = 0.7 and I_e/I_m = 1.1, respectively (Figure 5). This indicates much less interpenetration of the two polymers at these high dilutions. On the other hand, these I_e/I_m values are still below I_e/I_m = 1.3 ± 0.2 observed for PBzMA in bulk.

Discussion

In interpreting data on energy transfer between two fluorescing chromophores, it is important to distinguish between nonradiative energy transfer by the Förster mechanism[19] and radiative energy transfer due to the absorption of the donor emission by the acceptor. In our experiments the incident beam was at 60°, while the intensity of the emitted beam was measured at 30° to the sample surface, so for a path length x of the exciting beam within the sample, the path length of the emitted beam was $3^{1/2}x$. If ϕ_D/ϕ_A is the ratio of the fluorescence quantum efficiencies of the donor and the acceptor, the ratio of their fluorescence intensities in the absence of nonradiative energy transfer on excitation of a donor–acceptor mixture should be, provided all the exciting beam is absorbed,

$$\left(\frac{I_D}{I_A}\right)_0 = \frac{\phi_D}{\phi_A}\frac{\int_0^\infty c_D\epsilon_D \exp[-(c_D\epsilon_D + c_A\epsilon_A + 3^{1/2}c_A\epsilon_A')x]\,dx}{\int_0^\infty c_A\epsilon_A \exp[-(c_D\epsilon_D + c_A\epsilon_A)x]\,dx} = \frac{\phi_D}{\phi_A}\frac{c_D\epsilon_D}{c_A\epsilon_A}\frac{c_D\epsilon_D + c_A\epsilon_A}{c_D\epsilon_D + c_A(\epsilon_A + 3^{1/2}\epsilon_A')} \quad (1)$$

where c_D and c_A are concentrations of donor and acceptor, ϵ_D and ϵ_A are extinction coefficients of donor and acceptor at the excitation wavelength, and ϵ_A' is the extinction coefficient of the acceptor at the emission wavelength of the donor. For the CEMA–AMMA pair, ϕ_D/ϕ_A = 1.05, determined by their relative emission intensity at 347 and 413 nm when irradiating their solutions of identical optical density at 294 nm. With ϵ_D = 15 400 M^{-1} cm^{-1}, ϵ_A = 600 M^{-1} cm^{-1}, ϵ_A' = 5900 M^{-1} cm^{-1}, and $c_D = c_A$, this leads to

$(I_D/I_A)_0 = 18.5$, much larger than any I_C/I_A ratio observed in our study. It may then be concluded that energy transfer by the radiative mechanism made only a minor contribution to the observed effects.

The various approaches used in this study for the characterization of the texture of freeze-dried samples gave consistent results. The conclusion that the extent of chain interpenetration depends on the solution concentration before freeze-drying is also supported by the appearance of the samples, i.e., fluffy powders obtained from highly dilute solutions as against coherent elastic samples obtained from more concentrated solutions. The notion that isolated chain molecules will collapse to compact spherical particles on sublimation of the frozen solvent is also borne out by electron microscopic studies of glassy polymers when droplets of their highly dilute solutions are evaporated.[20-22]

In recent years the transition from dilute polymer solutions to semidilute solutions, in which chain interpenetration becomes important, has been a subject of much theoretical and experimental study. This transition is generally characterized by a concentration c^*, which may be estimated by a variety of methods.[23-25] Many years ago it was pointed out that c^* should be proportional to $1/[\eta]$[26] and Ferry has recently suggested[27] that experimental data are consistent with $c^* \sim 3/[\eta]$. We have indicated this estimate of c^* for comparison with the I_C/I_A data on Figure 2.

As would be expected, the degree of chain interpenetration increases gradually with increasing solution concentration. An attempt was made some years ago[28] to characterize the interpenetration by a change in the extinction coefficient of the polymer due to a change in the polarity of its microenvironment. In this study a sharp break was reported in a plot of the optical density against polymer concentration and this was taken as characterizing c^*. However, it was never clear why such a break should be seen and recent work[29] has shown that the effect is an instrumental artifact. It is, therefore, particularly welcome to see that the technique we describe in this paper offers a spectroscopic approach to the characterization of the interpenetration of flexible chains as a function of solution concentration.

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Isotactic Polymerization of Propene: Stereoregularity of the Insertion of the First Monomer Unit as a Fingerprint of the Catalytic Active Site

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ABSTRACT: The results of the ^{13}C NMR analysis of the end groups of polypropylene samples prepared in the presence of different catalytic systems are evaluated and compared with the "enantiomorphic site" statistical model. The stereoregulating capability of the active sites for different Al alkyl cocatalysts is discussed, as well as the role of a Lewis base as a modifier of a $MgCl_2$-supported catalytic system.

1. Introduction

Isotactic polymerization of propene involves stereospecific insertion of the prochiral monomer on reactive metal–carbon bonds (active sites)[1]

$$Mt\text{–}P + C_3H_6 \rightarrow Mt\text{–}C_3H_6P$$

where Mt is the metal atom of the active site and P represents the growing polymer chain.

The chain propagation approaches the "enantiomorphic site" statistic model.[2,3] Accordingly, the ideal isotactic catalyst is a racemic mixture of enantiomorphic active sites (D-preferring sites and L-preferring sites). The stereo-

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