Probing Interphase Domains in Blend-Like Polymer Particles by Transient Fluorescence Technique

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SYNOPSIS

Small molecule (1-naphthylmethyl pivalate) (NMP) diffusion into poly(methyl methacrylate) (PMMA) particles sterically stabilized by polyisobutylene (PIB) were studied by the transient fluorescence technique. Mean lifetimes of NMP increased as it diffused into the interphase region indicating that diffusion is accompanied by quenching of excited NMP molecules by PIB phase. A delayed Fickian diffusion model is fitted to experimental data and a diffusion coefficient is measured around 10^{-19} cm^2/s at room temperature. PIB density distribution in the interphase domain is found to be Gaussian. A supporting experiment is performed in Anthracene labelled PMMA particles using the direct-energy transfer method. Reversed Gaussian distribution is detected for the PMMA density in the interphase domain. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

For about a decade the transient fluorescence technique has been used to examine the internal morphology of blend-like poly(methyl methacrylate) (PMMA) particles.[1-5] These particles are spherical and usually prepared by dispersion polymerization of methyl methacrylate (MMA) in cyclohexane in the presence of butyl rubber.[6] The major component in this type of particle, PMMA homopolymer of broad molecular weight distribution, is present at about 95–97% by weight. During the reaction, grafting occurs between the butyl rubber and the growing PMMA chains. Most of the graft copolymer is buried in the particle interior where it forms an interconnected network[2,4] of polyisobutylene (PIB). Some graft copolymer forms a monolayer on the particle surface, which serves as the steric stabilizer. Thus these particles have an interpenetrating network like global morphology. This global feature of the morphology has been of interest and studied carefully.[2-4]

In this manuscript, our emphasis will be focused on the nature of the interface between the PIB and PMMA phases where they mix and form an interphase domain. Here transport experiments involving fluorescence quenching and energy transfer were prepared with PMMA–PIB particle dispersion in an aliphatic hydrocarbon liquid with a fluorescence dye. Since this solvent does not swell PMMA itself, we inferred that PIB penetrated throughout the particle, exposing the interior of the particle to solvent and the fluorescence dye. In this work a naphthalene derivative was used as the fluorescence dye with lifetimes of 43 ns and 49 ns in PIB and PMMA, respectively. After the evaporation of liquid we waited for days and measured the variation in life times from 43 ns to 46 ns, to probe the interphase domain as dye molecules diffuse slowly into the particle interior. Two types of PMMA particles with different PIB content are used and it was observed that the distribution of PIB phase in PMMA showed a Gaussian type distribution. A supporting experiment with Anthracene (An) labelled PMMA particles was performed to check the distribution of PMMA phase in PIB. Energy transfer between diffusing naphthalene and An in the PIB–PMMA interphase domain was detected. A decrease in naphthalene lifetimes in each consecutive day suggested that PMMA is distributed in PIB in a reversed Gaussian way.

EXPERIMENTAL

The polymer particles were prepared in a two-step process.[1] Polyisobutylene of nominal molecular weight 10,000 was added to a cyclohexane solution of MMA containing azobisisobutyronitrile (AIBN) as a free-radical initiator. The solution was refluxed for several hours to induce polymerization of the methyl methacrylate. The growing PMMA chains were added across double bonds present in the polyisobutylene to give a graft copolymer soluble in cyclohexane. Polymerization was terminated before the copolymer became insoluble in the cyclohexane solvent. This material, the dispersant, was collected and purified by precipitation with methanol. The dispersant was then added to a second reaction vessel containing MMA, and AIBN in cyclohexane. This solution was refluxed overnight. It became increasingly turbid as the reaction progressed. The particles were separated from solvent and unreacted monomers by repeated cycles of centrifugation, decanting the supernatant liquid, and redispersing the particles in fresh solvent. Dispersions in cyclohexane could be freeze-dried and stored as a powder. The powders could be redispersed by subjecting their suspensions in alkane solvents to a few seconds exposure to an ultrasonic cleaning bath.

These particles formed transparent solutions in ethyl acetate and in deuterochloroform. NMR spectra of these latter solutions permitted the composition of the polymers to be determined.

Here two types of particle with different PIB content were used. We refer to them as PO3 and PO5. These particles were found to contain 3 mol % and 5 mol % of PIB per gram of polymer respectively. Anthracene-labeled particles were also prepared in the way described above. Details have been reported elsewhere.[7] NMR and UV analysis indicated that these particles contain 4 mol % monomer PIB and 0.052 mmol of An per gram of polymer. Scanning and transmission electron microscopy studies indicated that the particle diameters ranged from 1 to 3 μm.

Fluorescence decay measurements were carried out by the time-correlated single photon counting technique employing a pulsed lamp source (Edinburg Instruments, 0.5 atm of D_2 gas) and a Hamamatsu 928 photomultiplier tube. Samples were excited at 280 nm and emission was detected at 337 nm. Data were collected over three decades of decay and fitted by nonlinear least squares using the δ-function convolution method with 2,5-bis(5-tert-butyl-2-benzooxazolyl) thiophene (BBOT) in ethanol as a standard. Data analysis allowed for a

small correction because of scattered light (the scatter parameter varied between 0.1 and 1.0). The uniqueness of the fit of the data to the model is determined by $\chi^2 (\chi^2 < 1.5)$, the distribution of the weighted residuals, and the autocorrelation of the residuals. All measurements were made at room temperature.

1-Naphthylmethyl pivalate (NMP) was used as fluorescence dye for diffusion experiments. Transport experiments were prepared by weighing 0.01 g of powder particles and dispersing them in 0.1 mL methylcyclohexane (MCH) which contains 10^{-3} mol/L NMP in a 12 mm o.d. quartz tube. Then the dispersion was placed in a rotary evaporator and MCH was removed at reduced pressure (10 Torr at 25°C. In order to get rid of the excess or trapped solvent, samples were left for 24 h in the dessicator under 10 Torrs of pressure.

Samples were purged by dry nitrogen for 15–20 min to remove the oxygen. Fluorescence decay profiles were measured by exciting the samples at 280 nm and observing the emission at 337 nm. Since the samples are in powder form, they were positioned so that measurements were made at front-face geometry.

RESULTS AND DISCUSSION

Fluorescence decay profiles of NMP were fitted to the sum of two exponentials. Mean lifetimes are calculated from the relation

$$\langle \tau \rangle = \frac{A_l \tau_l^2 + A_s \tau_s^2}{A_l \tau_l + A_s \tau_s} \tag{1}$$

where τ_l and τ_s are the long and short component of lifetimes and A_l and A_s are the corresponding amplitudes of the decay curves. Lifetime measurements of NMP in the particle interior were taken on each consecutive day. Results are listed for PO3 and PO5 particles in Table I, where the lifetime of NMP in pure PIB and PMMA are also given as 43 ns and 49 ns, respectively. It is interesting to note that $\langle \tau \rangle$ values increased as time is increased indicating that NMP molecules traveled from a pure PIB region to a rich PMMA region.

Shorter lifetime in PIB compared to PMMA suggested that this polymer is a good quencher for the excited NMP molecule. The Stern–Volmer type quenching mechanism may be proposed for the fluorescence decay of NMP in PMMA–PIB interphase domain where the following law for the lifetime is satisfied.[8]

Table I   Long, Short, and Mean Lifetimes of NMP in PO3 and PO5. Lifetimes of NMP in Pure PIB and PMMA Films are also Listed. All Lifetimes are Given in (ns).

Time (Days)	PO3				PO5			
	τ_l	τ_s	A_l/A_s	$\langle\tau\rangle$	τ_l	τ_s	A_l/A_s	$\langle\tau\rangle$
PIB	44.16	18.77	9.13	43.03	44.16	18.77	9.13	43.03
1	48.54	29.24	1.62	43.30	48.71	28.16	1.66	43.40
2	49.80	29.10	1.34	43.47	49.51	27.60	1.40	43.26
3	49.53	29.42	1.60	44.08	—	—	—	—
4	50.66	30.73	1.33	44.43	49.94	28.91	1.31	43.46
5	—	—	—	—	—	—	—	—
6	52.60	33.02	1.01	45.09	48.90	24.13	1.86	43.78
7	50.42	28.33	1.81	45.17	49.63	26.84	1.98	44.63
8	—	—	—	—	—	—	—	—
9	50.39	28.33	1.74	45.01	51.04	29.23	1.44	44.81
10	—	—	—	—	—	—	—	—
11	50.85	28.29	1.68	45.17	50.45	25.34	1.77	44.88
12	52.02	30.86	1.34	45.53	51.07	28.15	1.51	44.96
13	—	—	—	—	—	—	—	—
14	50.76	26.86	1.91	45.96	51.27	27.42	1.69	45.51
15	—	—	—	—	—	—	—	—
16	—	—	—	—	—	—	—	—
17	51.39	28.44	1.61	45.53	51.39	27.49	1.62	45.45
18	—	—	—	—	—	—	—	—
19	50.56	26.93	1.91	45.42	50.42	25.87	1.97	45.35
20	—	—	—	—	—	—	—	—
21	—	—	—	—	—	—	—	—
22	—	—	—	—	—	—	—	—
23	52.21	30.61	1.30	45.50	52.54	30.55	1.13	45.42
PMMA	53.25	44.26	0.93	49.00	53.25	44.26	0.93	49.00

$$\tau^{-1} = \tau_o^{-1} + k[P]. \qquad (2)$$

Here τ_o is the lifetime of NMP in pure PMMA in which no quenching takes place, k is the quenching rate constant and $[P]$ is the PIB concentration in the region. For low quenching efficiencies $\tau_o^k[P] \ll 1$, eq. (2) became

$$\tau \approx \tau_o(1 - \tau_o k[P]). \qquad (3)$$

Mean lifetime of NMP can be obtained by using the following relation

$$\langle\tau\rangle = \frac{\displaystyle_a\!\int^r \tau \, dv}{\displaystyle_a\!\int^r dv} \qquad (4)$$

where dv is the differential volume in the interphase domain and integral is taken from a to r. Here it is assumed that the PIB phase is distributed in a cylindrical volume according to Gaussian law

$$[P] = [P_o]e^{-\alpha(r^2-a^2)}. \qquad (5)$$

We will show that this assumption is reasonable. Here $[P_o]$ is the PIB concentration at $r = a$, where a is the radius of the cylindrical PIB rich channel[4] where almost no PMMA exists and r is the radial distance from the center. α represents the distribution coefficient for PIB. According to this, NMP molecules enter the PIB rich channel early; later NMP molecules emerge from this cylinder to the PMMA rich region of interphase domain through thinner PIB channels. The whole picture is depicted in Figure 1(a).

The integral in eq. (4) for $r > a$ is calculated and found to be

$$\frac{\langle\tau\rangle}{\tau_o} = 1 - \tau_o k[P_o] \frac{(1 - e^{-\alpha(r^2-a^2)})}{\alpha(r^2 - a^2)}. \qquad (6)$$
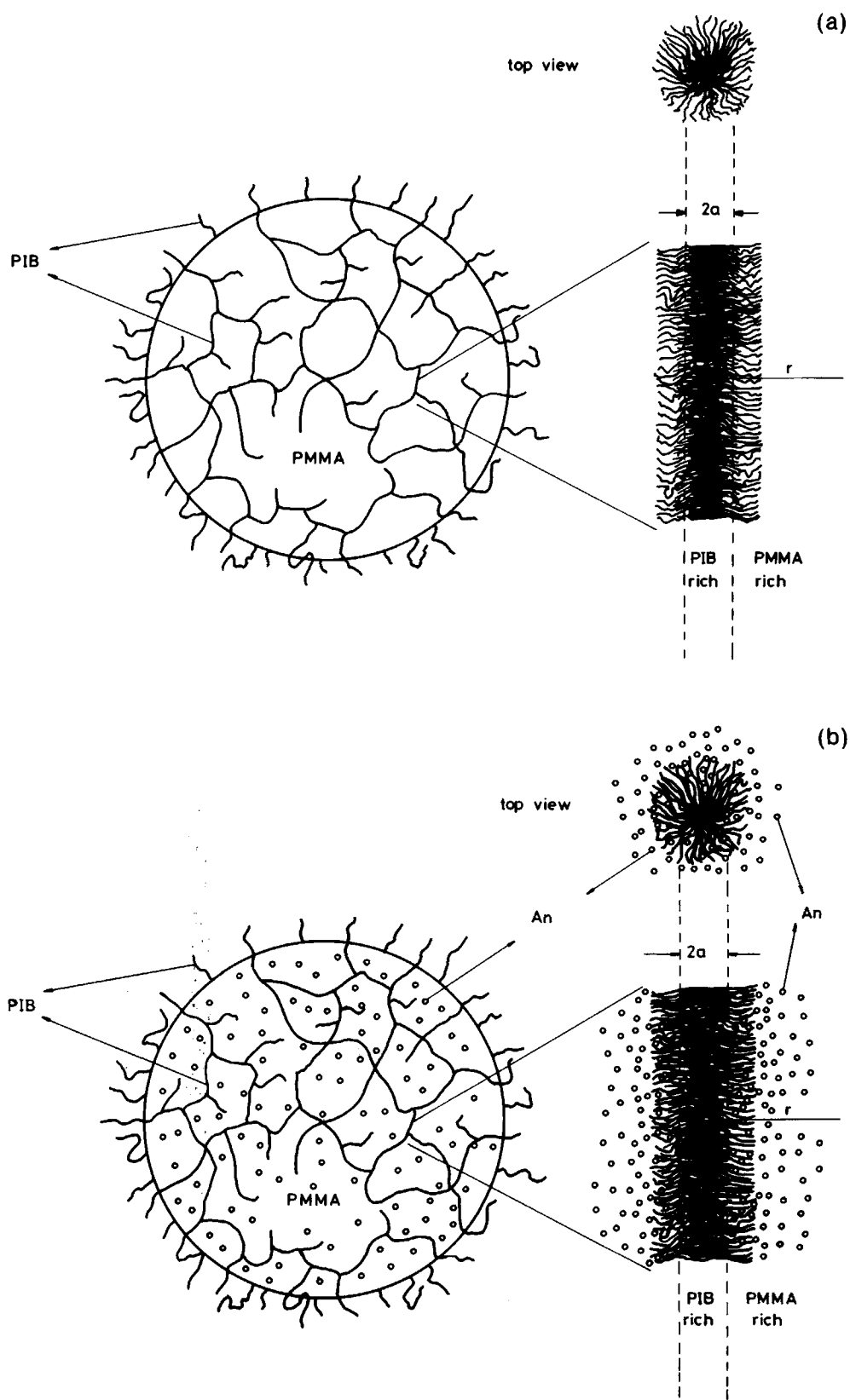
Figure 1   Cartoon representation of (a) non-labeled and (b) An-labeled. PMMA–PIB particles with the magnified part of the interphase domain.

(a)

(b)
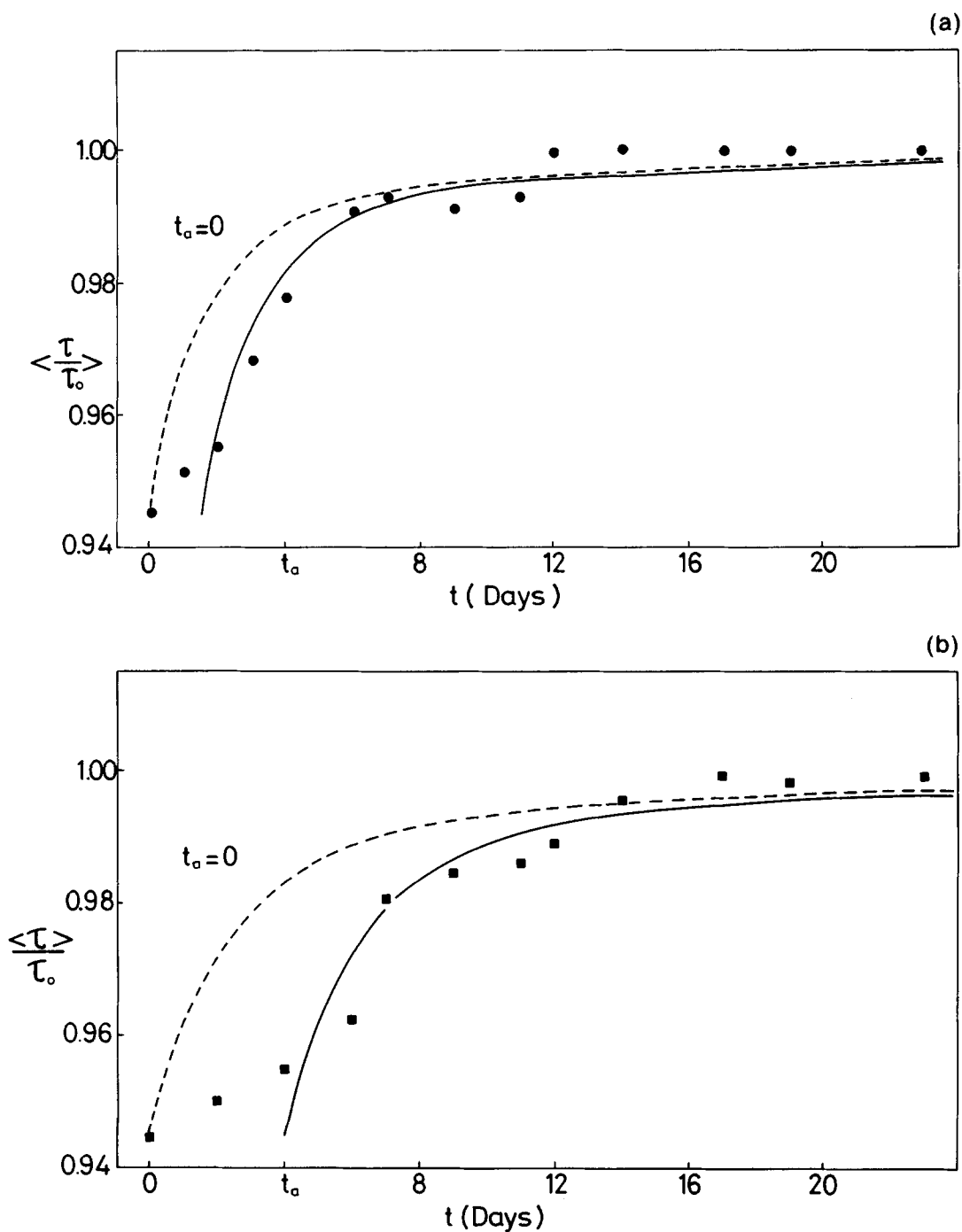
Figure 2 Fit of eq. (8) to experimental mean lifetimes (a) for PO3 and (b) for PO5 particles. Dashed lines indicate the curve for $t_a = 0$. Fitting parameters are listed in Table II.

In this picture, emerging NMP molecules from the cylindrical source can travel an average distance r at time t given[9] by

$$r = \frac{\sqrt{4Dt}}{\pi} \qquad (7)$$

where D is the diffusion coefficient for NMP molecules. Now eq. (6) is written as

$$\frac{\langle \tau \rangle}{\tau_o} = 1 - \frac{c(1 - e^{-\beta(t-t_a)})}{(t - t_a)} \qquad (8)$$
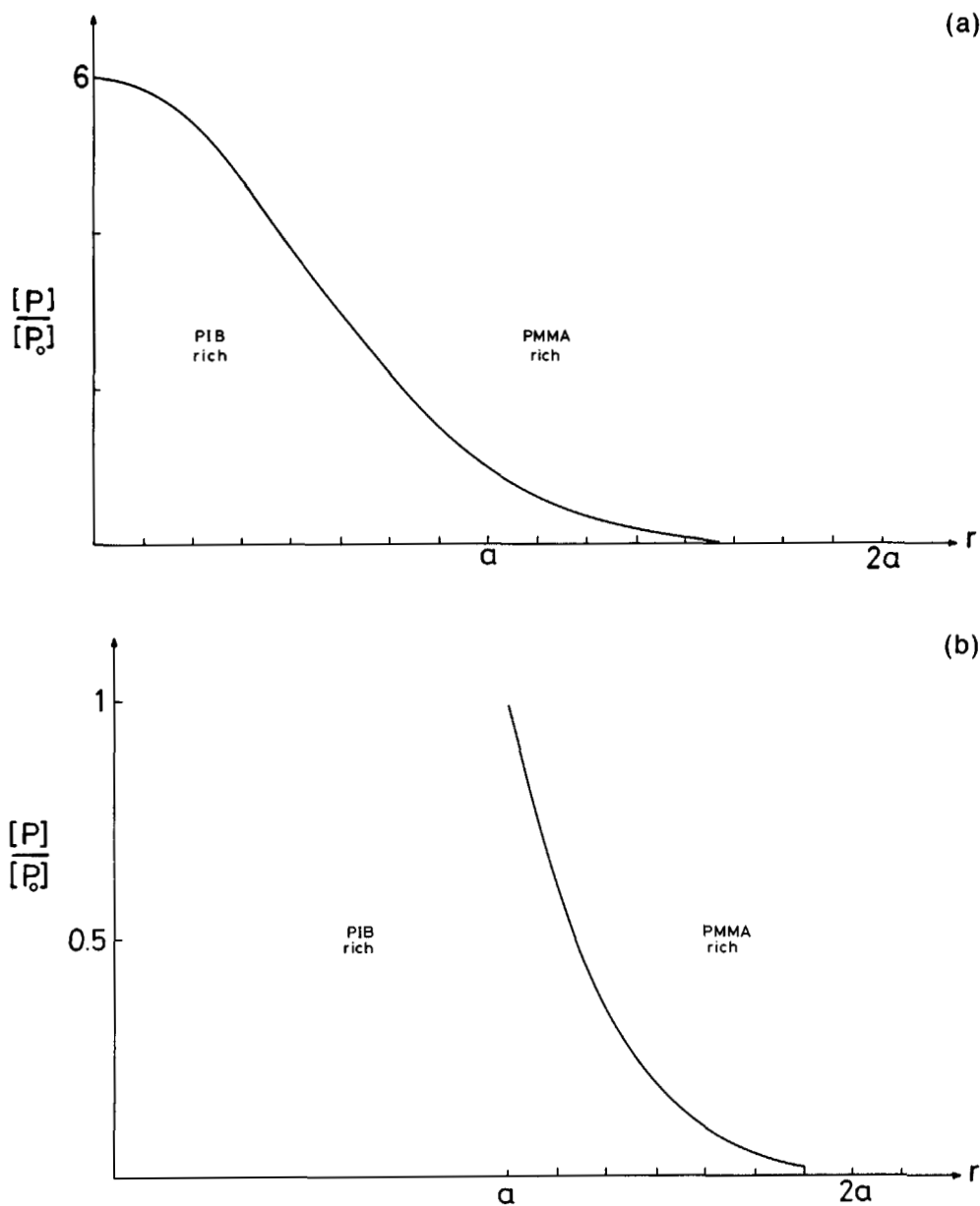
Table II

1	β (Day^{-1})	t_a (Day)	D (cm^2/s)	a (A°)	α (A°)$^{-2}$
PO1	1.2	1.5	3.78×10^{-19}	25	$1.8/a^2$
PO3	0.8	4.0	3.63×10^{-19}	40	$3.2/a^2$

β, t_a values are obtained from fitting eq. (8) to experimental mean lifetimes. D and α are calculated from eq. (9). a is estimated from ref. 4.

here

$$C = \frac{\tau_o k[P_o]}{\beta}, \quad \beta = \alpha \frac{4D}{\pi} \quad \text{and} \quad t_a = \frac{\pi a^2}{4D}. \quad (9)$$

In Figure 2(a) and (b) eq. (8) is fitted to the experimental mean lifetimes of NMP in PO3 and PO5 particles respectively. Fits are reasonably successful

(a)

(b)

Figure 3 Plot of PIB density function [eq. (5)] for PO3 particle ($\alpha = 1.8$). (a) The whole interphase domain. (b) PMMA rich region is magnified for $r > a$.

for β and t_a values given in Table II for the corresponding particles. In these fits C values were found to be close to unity, from Equation (9) quenching rate constant k, is calculated and found to be $10^6 \mathrm{sec}^{-1}\mathrm{m}^{-1}$ which corresponds to low quenching rate values. The obtained diffusion coefficients (10^{-19} cm^2/s) are quite low, which is reasonable for a small molecule diffusing into a polymeric environment at room temperature. We have previously found $D10^{-15}$ cm^2/s for a solvent molecule penetrated into nonaqueous dispersion particles of same type[10] at room temperature and $D10^{-13}$ cm^2/s for methylanthracene diffusing into a similar PMMA particle above T_g.[11]

Diffusion of an NMP molecule into a PMMA rich region starts after a certain delay in both particles. Delay time t_a is proportional to the thickness of the PIB channels. Here it is interesting to note that it took 1.5 days for the NMP molecule to completely fill the PIB rich channel, but then it took 15 days to travel into the PMMA rich region of the interphase domain of the PO3 particle.

Using eq. (5) and the experimentally obtained α value, the distribution of PIB density in the interphase domain is plotted in Figure 3(a) for the PO3 particle. The edge of the Gaussian distribution beyond α dropped quite rapidly in the interphase domain. In Figure 3(b) the PMMA rich region of the

interphase domain is magnified. Here it should be emphasized that the NMP molecule travelled in the PMMA rich region in almost 15 days. The distance is even shorter than in the PIB rich region. Since NMP diffused into very thin PIB channels in the glassy PMMA phase this situation is understandable. Cartoon representation of the whole morphology is already shown in Figure 1(a).

A supporting experiment to probe the interphase domain in An-labeled PMMA particle was also performed. Mean lifetimes of NMP molecules were measured day by day as it diffused into the interphase domain where An are labelled to PMMA. Results are plotted in Figure 4 together with the mean lifetimes of NMP in PO3. Since NMP was already quenched by PIB, corrected mean lifetimes of NMP in the An-labelled particle can be found by normalizing them with NMP lifetimes in PO3. Final results are shown in Figure 5. It is quite interesting that the curve in Figure 5 is just the reverse of the curve Figure 2(a), which suggested that as NMP travelled in the interphase domain it transfered its energy to An molecules distributed in the domain. Intuitively it is not difficult to say that the distribution of An molecules obeyed the reversed Gaussian curve. Since PMMA was labeled by An molecules one may conclude that distribution of PMMA is just the reverse
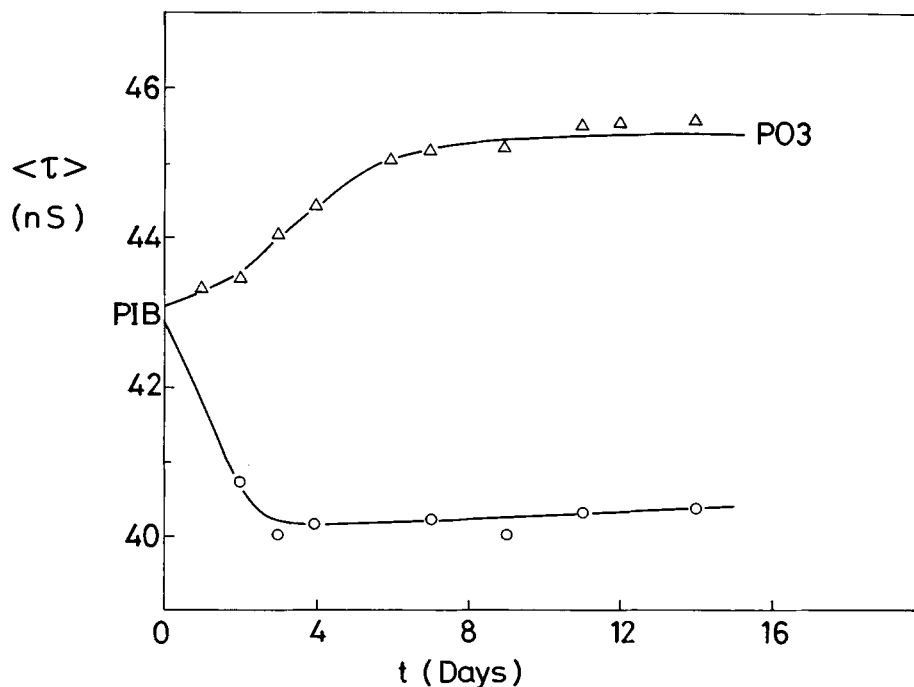
Figure 4 Mean lifetimes of NMP diffusing into ($-\triangle-$) PO3 and ($-\text{O}-$) An-Labeled PMMA–PIB particles.
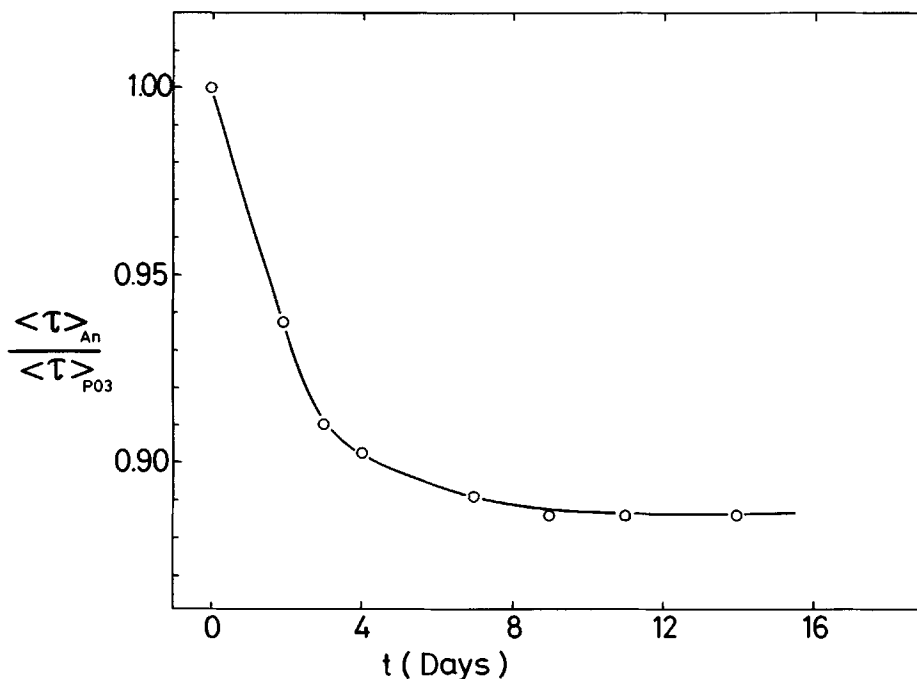
Figure 5   Normalized mean lifetimes of NMP diffusing into An-labeled particle. $\langle \tau \rangle_A$ and $\langle \tau \rangle_{PO3}$ are the mean lifetimes of NMP in An-Labeled and PO3 particles, respectively.

of PIB distribution in the interphase domain [Fig. 1(b)].

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