

ESR Studies of Solvent Penetration into Polymer-Blend-Like Material: Particles Formed from Poly(methyl Methacrylate) and Polyisobutylene

ÖNDER PEKCAN* and YUSUF DEMIR

Department of Physics, Istanbul Technical University, Maslak Istanbul 80626, Turkey

SYNOPSIS

Solvent penetration into nonaqueous dispersions (NAD) of poly(methyl methacrylate) (PMMA) sterically stabilized by PIB were studied by ESR spectroscopy. These colloidal particles were exposed to dilute solution of spin probe 3-carbomoyl 2,2,5,5-tetramethyl 3-pyrrolin-1-yloxy and the bimodal distribution of ESR spectra of this probe molecules were carefully monitored as a function of time. Fickian type diffusion of spin probes into the particles was observed and a spherical model was employed to obtain the diffusion coefficients (D) in various solvents. D values were found around 10^{-15} cm²/s, and interpreted as the parameter, inversely proportional to the apparent viscosity of the environment inside the colloid particle. Maximum amount of diffused solvent molecules (M_{∞}) into the PMMA particle was found inversely proportional to polymer-solvent interaction through the solubility parameters. The interconnected network of PIB was found to be responsible for the penetration of spin-probe (i.e., solvent) molecules into the glassy PMMA phase and/or PIB-PMMA interface.

INTRODUCTION

Because of their easily identifiable three line spectrum in which the line widths and shapes are determined by their mobilities in the environment stable organic nitroxides have had wide spread application as spin probes.¹⁻⁶

When the nitroxide radicals are in solution of low viscosity, e.g., common organic solvents, rapid Brownian rotational motion occurs. This results in the averaging of the isotropic g value and isotropic hyperfine coupling constant and the ESR spectrum shows a triplet line with equal components of equal intensities. In viscous media, however, the rotational motion is hindered and tumbling rates of the nitroxide decrease.^{1,2} This gives an increase of the hyperfine coupling constant and a broadening of observed spectra.

Nitroxide radicals were first applied to study of polymer blends by Boyer³⁻⁵ and his colleagues. They

examined a variety of block copolymers and demonstrated that the spin probe partitions between the two phases of the systems, giving a superposition of signals from the two phases.

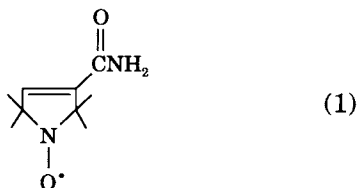
Nonsolvent penetration into nitroxide-labeled poly(methyl methacrylate) (PMMA) and polystyrene latex particles was studied by Veksli and Miller.⁶ They observed that, in most cases, the ESR spectra were superpositions of a slow and fast motion components. Their results suggested that many nonsolvents penetrate at least a few hundred angstroms in a glassy, amorphous polymer and give rise to high frequency short-range segmental backbone motion.

Accurate determination of the diffusion coefficients of small molecules in polymeric systems have important applications of phenomenas such as permeation, thermal printing, and controlled release of drugs. Unfortunately, at temperatures below T_g these diffusion coefficients can become quite small (10^{-15} cm²/s) and therefore difficult to measure. Recently using the forced Rayleigh scattering method, some researchers have measured very small diffusion coefficients.^{7,8}

* To whom all correspondence should be addressed.

In this work, we monitored bimodal distribution of ESR spectra of nitroxides, to study solvent penetration into the polymer-blend-like material. Increase in the intensity of slow motion nitroxide component with time was associated with the diffusion at nitroxide (i.e., solvent) molecules into a glassy polymeric material. Here the polymer-blend material was composed of graft copolymer of polyisobutylene (PIB) and poly(methyl methacrylate) (PMMA). This material is prepared as a hydrocarbon stable dispersion of colloidal polymer particles in which a thin surface shell of PIB serves as the steric stabilizer. This material is typical of many nonaqueous dispersions (NAD) with important industrial applications. In our samples, PMMA serves as the glassy phase. Previous fluorescence quenching studies⁹⁻¹¹ have shown that these particles have an interesting morphology with cylindrical threads of PIB forming a continuous network, penetrating throughout the particle.^{12,13} This structure arises because of extensive chemical grafting between PMMA and PIB during the preparation of the particles.

In penetration studies, samples of particles, 1–3 μm in diameter, were exposed to a dilute solution of the spin probe in various solvents:



The spherical model was used to study the Fickian type of diffusion of solvent molecules into the colloidal particles. Since it has been recognized that

the penetration of solvent into glassy polymers is controlled not only by the diffusion, but also by the solubility,^{14,15} we studied the behavior of the maximum amount of diffused solvent molecules (M_∞) with respect to the solubility parameter (δ).

EXPERIMENTAL

The PMMA-PIB polymer particles were prepared in a two-step process in which methyl methacrylate (MMA) in the first step was polymerized to low conversion in cyclohexane in the presence of PIB. The graft copolymer produced served as a dispersant in the second stage of polymerization, in which MMA was polymerized in a cyclohexane solution of the copolymer. Details have been reported elsewhere.¹⁶ A stable spherical dispersion of polymer particles was produced ranging in radius from 0.5 to 1.5 μm . ¹H-NMR studies of solutions of this material in CDCl_3 indicated a mole ratio composition of PIB/PMMA monomer units of 13/100. The material was freeze-dried from cyclohexane and stored as a powder. The spin probe (3-carbomoyl-2,2,5,5-tetramethyl 3-pyrrolin lyloxy) and solvents used in the present study were obtained from Aldrich and Merck and used as received. Characteristics of solvents are listed in Table I.

Nitroxide concentrations in all solvents were kept around 10^{-3} mol/L and volume ratios of solvent to powder colloid were taken as 1. Samples prepared in ESR tubes were degassed by several freeze-pump-thaw cycles at 10^{-5} torr on a vacuum line and then sealed. Measurements were made a day after the preparation of samples. ESR spectra were recorded on a Varian E-L9 spectrometer operating at x-band frequency (9.1–9.5 GHz) and employing 100 kHz field modulation.

Table I

Solvents	Shorthand	η^a (cP)	δ^b (cal/cm ³)	V^c (cm ³ /mol)	$D^d \times 10^{15}$ (cm ² /s)	M_∞ (in Arbitrary Units)
<i>n</i> -Hexane	HX	0.29	7.24	130.57	8.28	200
<i>n</i> -Heptane	HP	0.38	7.40	147.36	7.25	200
<i>n</i> -Pentane	PN	0.22	7.00	114.52	16.70	215
Cyclohexane	CH	0.89	8.20	107.89	3.10	140
Methylcyclohexane	MCH	0.68	7.80	127.45	3.80	200
Isooctane	IO	0.50	6.84	165.55	3.85	75

^a η = viscosity in centipoise (cP).

^b δ = solubility parameter in (cal/cm³)^{1/2}.

^c V = molar volume in cm³/mol.

^d D = diffusion coefficients, found in this work in cm²/s.

^e M_∞ = maximum amount of diffused solvent into colloid particle.

RESULTS AND DISCUSSION

Measurement of all samples were taken at each consecutive day to follow the penetration of the spin-probe (i.e., solvent) into the colloid particle. ESR spectra of the nitroxide in the hexane-colloid system, which were taken in different days, are compared in Figure 1. The spectrum A was taken 1 day after the sample preparation. The peak indicated by the asterisk (*) belongs to the nitroxides immobilized in the solid matrix. Sharper triplet lines, however, represent the nitroxides that are mobile in the hexane solvent. In spectrum B, taken at the sixth day of the penetration process, the immobilized component became dominant to the mobilized component. Here the question is the location of the nitroxide inside the particle or the nature of the solid matrix. Since the chemical composition of the particles indicates that the PMMA represents 96% of the dry volume, it would not be surprising if the probes were located predominantly in that phase. Peak to peak separation (64 G) of immobilized component in Fig. 1, is consistent with the ESR spectra of nitroxide in pure colloid powder or in pure PMMA matrix¹⁷ (See Fig. 2). From here one can conclude that the spin probe in polymer colloid, in the pres-

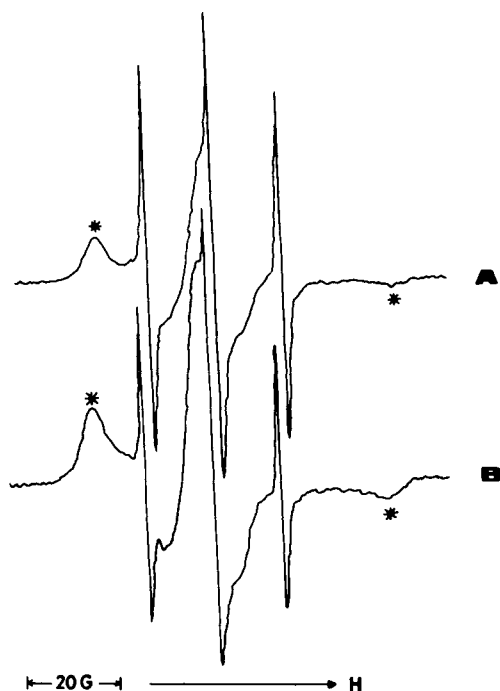


Figure 1 ESR Spectra of the spin-probe 1 in the hexane-colloid system: (A) 1 day after the sample preparation; (B) sixth day after the sample preparation. (*) indicates the immobilized component of the spin-probe 1.

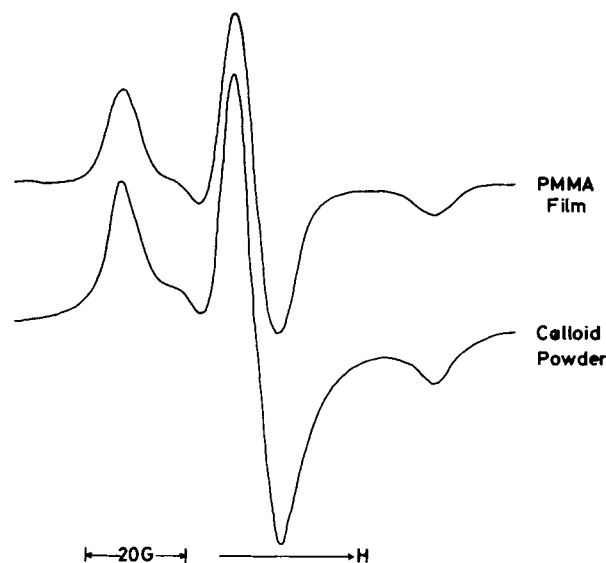


Figure 2 ESR Spectra of the spin-probe 1 in (A) pure PMMA Film and in (B) colloid powder.

ence of hexane, is located exclusively in the PMMA domain or at least at the interface where PIB-PMMA segments are intermixed.

Diffusion of nitroxides into colloid particle can be traced by the following ratio:

$$M_t = \frac{I_i}{I_i + \sum_{m=1}^3 I_m} \quad (1)$$

where I_i is the peak height of the immobilized component and I_m is the peak height of each mobile component of the nitroxide. Then M_t can represent the amount of nitroxide (or solvent) molecule diffused into the particle at time t . In order to introduce a model to the penetration problem, we assumed that PIB phase forms a randomly distributed, interconnected network inside the spherical PMMA matrix, so that the Fickian diffusion of the spin-probe through PIB channels, across the particle, can be fitted to a spherical model. In Figure 3 a model colloid particle is presented. Such diffusion is described by the following equation¹⁸:

$$\frac{M_t}{M_\infty} = 1 - \frac{6}{\pi^2} \sum_n \frac{1}{n^2} \exp\left(-\frac{D\pi^2 n^2}{a^2} t\right) \quad (2)$$

Here M_∞ is the value of M_t at $t = \infty$, a is the maximum distance over which diffusion can occur, and D is the diffusion coefficient. In our experiments, we considered only the first term in the summation

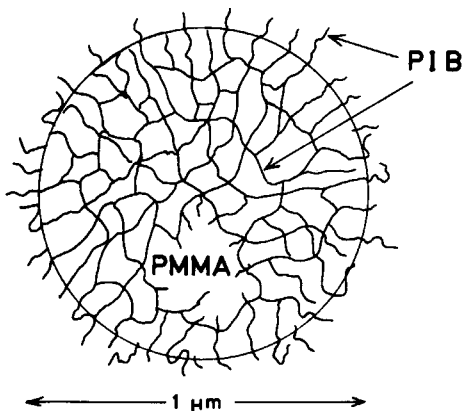


Figure 3 A cartoon representation of the interconnected network of a colloid particle.

on the rhs of eq. (2) and let a equal the radius of the colloid particle; then eq. (2) becomes

$$\frac{M_t}{M_\infty} = 1 - \frac{6}{\pi^2} \exp\left(-\frac{D\pi^2 t}{a^2}\right) \quad (3)$$

Plots of M_t and its normalized form M_t/M vs. t are presented in Figures 4(a) and 4(b), respectively, for various solvents. Equation (3) were fitted to experimental results in Figure 4(b) and D values were obtained for each solvent. Results are presented in Table I for the corresponding solvents.

Our experimentally found D values appear to be consistent with those recently presented by Ehlich and Sillescu⁸ for the diffusion of a small molecule in polystyrene at temperatures below T_g . They measured diffusion coefficient approximately 10^{-15} cm²/s. Recently, using a Nonradiative energy transfer technique,¹⁹ we measured the diffusion coefficient of anthracene molecule as 5×10^{-13} cm²/s in PMMA at 115°C.

It is important to note that diffusion of nitroxide into the PMMA particle in the presence of the solvent substantially depends upon hydrocarbon employed. The challenge is to figure out whether kinetic effects associated with the solvent viscosity (η) or the thermodynamic effect (polymer solvent interaction) are responsible for the small particle diffusion into PMMA phase or PIB-PMMA interphase.

According to Stokes-Einstein, the diffusion coefficient D is given by the following relation:

$$D = -kT/6\pi r\eta \quad (4)$$

where k is the Boltzman constant, T the absolute temperature, r the radius of the nitroxide (i.e., sol-

vent) molecule, and η the viscosity of the medium. One then expects that the inverse of the solvent viscosity (η) should be proportional to the D values. The plot of D vs. $1/\eta$ is presented in Figure 5, where the dependence is not linear but the tendency of increase in D as the decrease in η is quite satisfactory. The lack of linearity is not surprising, since the viscosity is not the only factor that effects the environment in which nitroxide resides; polymer solvent interaction is also a very important factor controlling the diffusion. The solubility is a convenient measure of solvent quality, i.e., polymer solvent interaction.¹⁴

Solution theory predicts that polymer solvent interaction parameter is related to the solubility parameters via the following expression²⁰:

$$\chi = \frac{V}{RT} (\delta - \delta_p)^2 \quad (5)$$

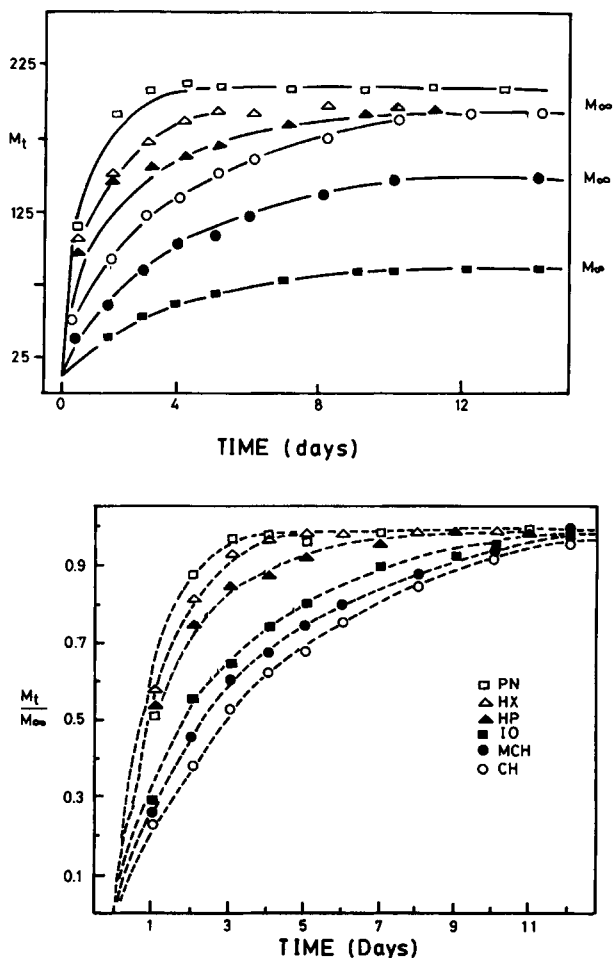


Figure 4 Solvent penetration into the colloid particle: (a) M_t vs. time t , (b) M_t/M vs. time t can be fitted to eq. (3) to obtain diffusion coefficients D .

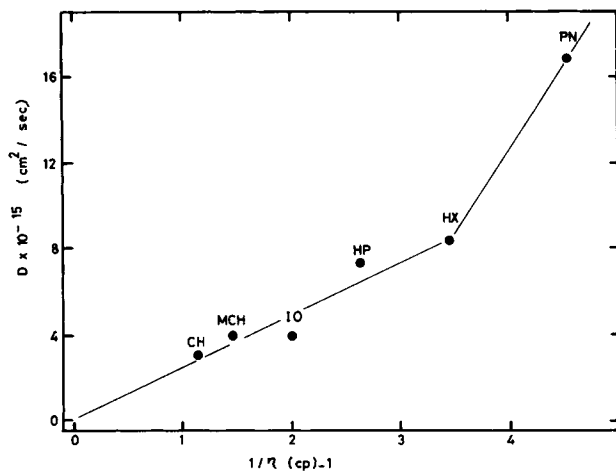


Figure 5 Plot of diffusion coefficient D vs inverse of solvent viscosity (η).

where V and δ are the molar volume and solubility parameter of the solvent, R is the gas constant, T the temperature, and δ_p the solubility parameter of the polymer. This theory leads to the conclusion that polymers dissolve in small molecular liquids only if $\Delta\delta$ is very small. Interrelation between M_∞ , V , and δ in Table I suggest that Flory-Huggins parameter χ can be inversely proportional to the maximum amount of diffused solvent molecule (M_∞) into the PMMA particle. In order to prove that this assumption is correct, first we plotted M_∞ vs. V in Figure 6. Except CH and HP, other hydrocarbon liquids obey the relation in eq. (5), i.e., if the molecule is small, it can penetrate into the polymer matrix more easily. Second, to see the relation between χ (i.e., M_∞^{-1}) and $\Delta\delta$ we plotted $(M_\infty V)^{-1}$ vs. δ in Figure 7. The result is quite satisfactory, data can be represented by two straight lines intersecting at $\delta = 7.6$ (cal/cm^3)^{1/2}, which approximately corre-

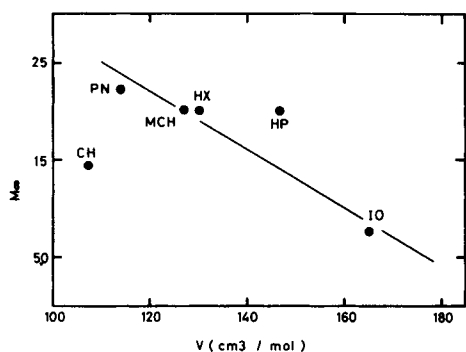


Figure 6 Plot of M_∞ , the maximum amount of diffused solvent molecules in PMMA particle, vs. V , the molar volume of solvent molecules.

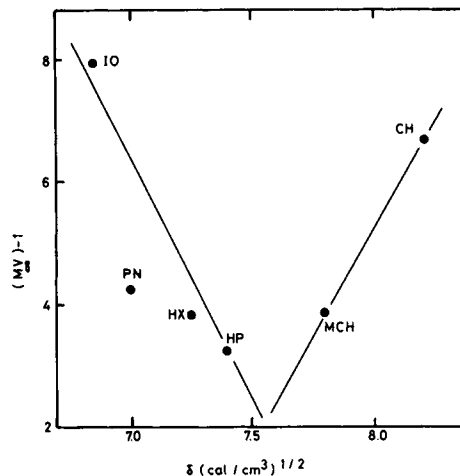


Figure 7 Plot of $(M_\infty V)^{-1}$ vs. solubility parameter δ of solvents.

sponds to the average of several literature values for δ_p of PIB.²¹

All these results suggest that D is strictly a kinetic quantity which mostly associates with the solvent viscosity. However, M_∞ measures the thermodynamic effects (enthalpy of mixing) between polymer and solvent molecules.

Here the basic conclusion we reached is that the PIB network is responsible for the solvent penetration process into the PMMA particle. At the first stage of penetration PIB phase has to be swelled in the corresponding solvent; at the second stage solvent molecules can diffuse into the PMMA phase or the PIB-PMMA interface where they face a medium at very high apparent viscosity in which they can diffuse with a coefficient of $D = 10^{-15}$ cm^2/s .

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REFERENCES

1. R. H. Sands, *Phys. Rev.*, **99**, 1222 (1955).
2. T. K. Kneubuhl, *J. Chem. Phys.*, **33**, 1974 (1960).
3. P. L. Kumler and R. F. Boyer, *Macromolecules*, **9**, 903 (1976).
4. R. F. Boyer and P. L. Kumler, *Macromolecules*, **10**, 461 (1977).
5. P. L. Kumler, S. E. Keinath, and R. F. Boyer, *Polym. Eng. Sci.*, **17**, 613 (1977).
6. Z. Vekslı and W. G. Miller, *J. Polym. Sci.*, **54**, 299 (1976).
7. J. L. Xia and C. H. Wang, *J. Phys. Chem.*, **93**, 3839 (1989).

8. D. Ehlich and H. Sillescu, *Macromolecules*, **23**, 1600 (1990).
9. Ö. Pekcan, M. A. Winnik, and M. D. Croucher, *J. Coll. Interface Sci.*, **95**, 420 (1983).
10. M. A. Winnik, in *Polymer Surfaces and Interface*, J. Feast and H. Munro, Eds., Wiley, London, 1987.
11. M. A. Winnik, Ö. Pekcan, and M. D. Croucher, *Fluorescence Techniques in the Study of Polymer Colloids*, R. H. Ottowill Ed., NATO ASI Series 1988.
12. Ö. Pekcan, M. A. Winnik, and M. D. Croucher, *Phys. Rev. Lett.*, **61**, 641 (1988).
13. Ö. Pekcan, S. L. Egan, M. A. Winnik, and M. D. Croucher, *Macromolecules*, to appear.
14. (a) J. E. Guillet, *Polymer Photophysics and Photochemistry*, Cambridge Univ. Press, Cambridge, 1985; (b) Xiao-Bai Li, M. A. Winnik, and J. E. Guillet, *Macromolecules*, **16**, 992 (1983).
15. J. Crank and G. S. Park, *Diffusion in Polymers*, Academic, London, 1968.
16. M. A. Winnik, Ö. Pekcan, S. L. Egan, and M. D. Croucher, *Macromolecules*, **16**, 699 (1983).
17. Ö. Pekcan, Y. Kaptan, Y. Demir, and M. A. Winnik, *J. Colloid Interface Sci.*, **111**, 269 (1986).
18. J. Crank, *Mathematics of Diffusion*, 2nd ed., Clarendon, Oxford, 1975.
19. Ö. Pekcan and M. A. Winnik, to appear.
20. P. J. Flory, *Principles of Polymer Chemistry*, Cornell University Press, Ithaca, NY, 1953.
21. J. Brandrup and E. H. Immergut, *Polymer Handbook*, 3rd ed., Wiley, New York, 1989.

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