

Spin Probe Studies of Nonsolvent Penetration into Polymer Particle formed from Poly(vinyl acetate) and Poly(2-ethylhexyl methacrylate)

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SYNOPSIS

Nonaqueous dispersion (NAD) of poly(vinyl acetate) (PVA_c) particles sterically stabilized by poly(2-ethylhexyl methacrylate) were examined by ESR spectroscopy after introduction of a trace quantity of a spin probe, 3-carbomoyl-2,2,5,5-tetramethyl 3-pyrrolin-1-yloxy. ESR spectra were monitored as a function of temperature from -160 to 100°C. In spite of the complex morphology of the particle, it is found that the behavior of the probe in the NAD was essentially identical to that in a pure PVA_c matrix. Solvent penetration into (NAD) particles were studied. These colloidal particles were exposed to a dilute solution of the spin probe, and the bimodal distribution of the ESR spectra of this probe molecule 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 were interpreted as the parameter, inversely proportional to the apparent viscosity of the environment inside the PVA_c particle. The maximum amount of diffused solvent molecules (*M*_∞) into the PVA_c particle was found inversely proportional to polymer-solvent interaction through the solubility parameters. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

Accurate determination of the diffusion coefficients of small molecules in polymeric systems have important applications of phenomena 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. Using the forced Rayleigh scattering method, some researchers have measured very small diffusion coefficients.^{1,2} Recently, we have used the ESR method with organic nitroxides to determine diffusion coefficients of (*D*) solvents penetrating into nonaqueous dispersion (NAD) of poly(methyl methacrylate) (PMMA) particles sterically stabilized by polyisobutylene (PIB). *D* values were found around 10⁻¹⁵ cm²/s for various solvents.³

Stable organic nitroxides have seen wide-spread application as spin probes. Their easily identified three-line ESR spectrum has features that are sensitive to probe mobility and provides a tool to study molecular motion in polymer matrices. When nitroxides are frozen in an amorphous matrix, the observed ESR spectrum appears as a characteristic line shape^{4,5} in the case of random distribution. When molecular motion of the nitroxides in the solid is somehow activated, anisotropic parameters are averaged out if the motion is sufficiently rapid and the observed spectrum appears "isotropic," as it is from a nitroxide in a liquid of low viscosity. In the intermediate case, which commonly occurs in polymer matrices, the anisotropy is partially averaged.⁶ Therefore, it is always possible to obtain information on molecular motion by analysis of either the changes in line shape of an ESR spectrum or the changes of the line width of each peak of a spectrum.

Spin probes were first applied to the study of polymer blends by Boyer and his colleagues.⁷ They examined a variety of AB and ABA block copolymers

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and demonstrated that the nitroxide spin probe partitions between the two phases of the system, giving a superposition of signals from the two phases. Variation of the temperature elicited different responses from the two sets of signals. These responses could be related to the (high-frequency) glass transition temperature T_g of the individual phases. In some circumstances, evidence was presented for signals originating from spin probes located specifically in the interphase region.^{8,9}

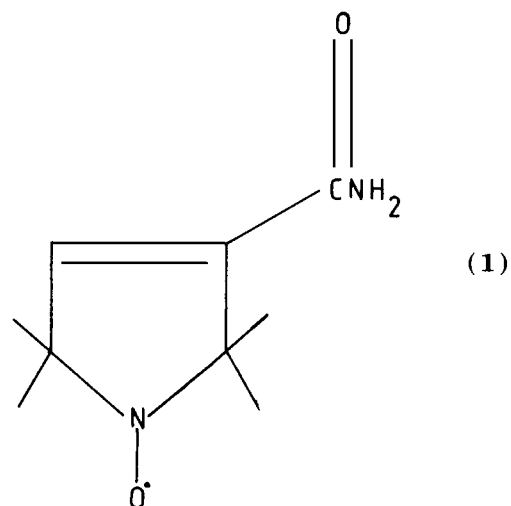
Nonsolvent penetration into nitroxide-labeled poly(methyl methacrylate) (PMMA) and polystyrene latex particles was studied by Veksli and Miller.¹⁰ They observed that, in most cases, the ESR spectra were superpositions of slow- and fast-motion components. Their results suggested that many nonsolvents penetrate at least a few hundred angstroms in a glassy, amorphous polymer and give rise to high-frequency short-range segmental backbone motion.

In this article we report the results of ESR experiments on submicron poly(vinyl acetate) (PVA_c) particles that contain 4 monomer mol % of poly(2-ethylhexyl methacrylate) (PEHMA) in the form of a PVA_c-PEHMA graft copolymer.¹¹ These particles are prepared by the technique of dispersion polymerization.¹² It was previously shown that much of the PEHMA is trapped in the interior of these particles,¹¹ and we have proposed an interpenetrating network model for the global morphology of these types of particles.¹³⁻¹⁶ The model is depicted schematically in Figure 1. This structure arises because of extensive chemical grafting between PVA_c and PEHMA during preparation of the particles.

In this work, we monitored bimodal distribution of ESR spectra of nitroxides to study solvent pen-

etration into this polymer-blend-like material. Increase in the intensity of the slow-motion nitroxide component with time was associated with the diffusion of nitroxide (i.e., nonsolvent) molecules into a glassy polymeric material.

In penetration studies, samples of particles, 0.3 μm in diameter, were exposed to a dilute solution of the spin probe (1) 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,^{17,18} we studied the behavior of the maximum amount of diffused solvent molecules (M_∞) with respect to the solubility parameter (δ). Diffusion coefficients (D) were found around 10^{-15} cm^2/s for various nonsolvents.

EXPERIMENTAL

Poly(vinyl acetate) Particles

The preparation and characterization of poly(vinyl acetate) particles as a sterically stabilized nonaqueous dispersion in isooctane medium have been described in detail.¹¹ Briefly, one carries out a free-radical (benzoyl peroxide-initiated) polymerization of vinyl acetate (ca. 50% v/v) in isooctane in the presence of poly(2-ethylhexyl methacrylate) (ca. 20% w/w based upon vinyl acetate). A milky white dispersion forms when the reaction mixture is heated several hours at 75°C. The particles formed are spherical and have a narrow distribution of sizes, with diameters in the range of 200–300 nm, de-

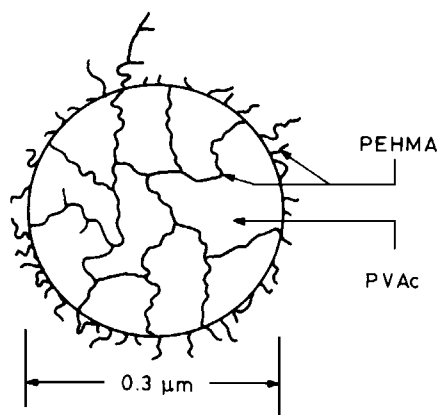


Figure 1 A representation of the bicontinuous interpenetrating networklike morphology of the PVA_c-PEHMA particle.

pending upon the reaction conditions. After the reaction, the particles are cleaned by successive centrifugation (17,000 rpm) and redispersion in spectrograde cyclohexane. Five centrifugation–redispersion cycles suffice to remove unreacted PEHMA and any residual monomer. The particles are freeze-dried, stored as a powder, and redispersed as needed.

Here, the minor rubbery component (PEHMA) serves as the steric stabilizer for the particle, which is very soluble in the kind of hydrocarbon media in which the particles are formed. The major core component (PVA_c), which is in the form of an amorphous glass, does not dissolve in the hydrocarbon media such as hexane and pentane but dissolves in polar solvents such as chloroform and ethylacetate. ¹H-NMR and UV analyses showed that colloid particles contains 8.3 wt % PEHMA.

The spin probe (3-carbomoyl-2,2,5,5-tetramethyl-3-pyrrolinlyloxy) and solvents used in the present study were obtained from Aldrich and Merck and used as received. Characteristics of the 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. Diffusion measurements were made 1 day after the preparation of samples. ESR spectra were recorded on a Varian E-L9 spectrometer operating at an *x*-band frequency (9.1–9.5 GHz) and employing a 100 kHz field modulation. The spectrometer was equipped with a variable temperature accessory along with a liquid-nitrogen system.

Before studying the diffusion, we prepared three

different samples to probe the location of nitroxide after the penetration processes is completed.

Introduction of the Spin Probe (PCL)

The spin probe was dissolved in pentane and added to the dry polymer particles. After 4 days, solvent was removed and the sample was dried under vacuum (10⁻⁴ Torr) for 7–8 h. Weight ratios of the spin probe to the powder colloid were calculated to be 10⁻⁵.

Doped PVA_c Film (PVAF)

Thin films of spin-probed PVA_c were cast from an ethyl acetate solution of PVA_c containing about 10⁻² wt % nitroxide radical. Films were dried under 10⁻⁴ Torr vacuum for about 7–8 h. The low molecular weight PVA_c samples were obtained from BDH and used as they were received. This sample was used as a model for motionally slowed ESR spectra of PVA_c.

Hexane Saturated Powder (HSCL)

After waiting 4 days, the spin-probed colloid suspension was centrifuged and hexane was removed. After removing the solvent from the ESR tube, the sample was degassed by several freeze–pump–thaw cycles at 10⁻⁵ Torr on a vacuum line and then sealed. At the end of the degassing, no free solvent could be seen in the tube. The sample resembled an aggregate of gel-like particles, which we call hexane saturated powder (HSCL).

Table I Characteristics of the Solvents

Solvents	Abbreviation	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	5.10	130
<i>n</i> -Heptane	HP	0.38	7.40	147.36	6.20	160
<i>n</i> -Pentane	PN	0.22	7.00	114.52	10.01	166
Cyclohexane	CH	0.89	8.20	107.89	2.11	80
Methylcyclohexane	MCH	0.68	7.80	127.45	4.22	110
Isooctane	IO	0.50	6.84	165.55	3.13	75

^a η = viscosity 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

Location

Since the particles are exposed passively to the spin probe, the first question is its location in the particle. Pertinent information is available through comparison of the ESR spectra of the PCL and PVAF samples, where the latter serves as a model for probe behavior in a PVA_c phase.

In the PCL sample, the line shape changes gradually with temperature. As seen in Figure 2, an increase in temperature causes an inward shift of the outer peak positions along with an increase in the intensity of the shoulder (shown with an *), which appears at about 40°C. At sufficiently high temperatures, the outer peak joins the shoulder, and the spectrum becomes isotropic with the relatively sharp, narrowed three-line pattern characteristic of the fast rotational motion of a nitroxide in a viscous liquid. The pattern observed at 80°C is similar to the spectrum of a nitroxide radical in a liquidlike environment where anisotropic parameters are av-

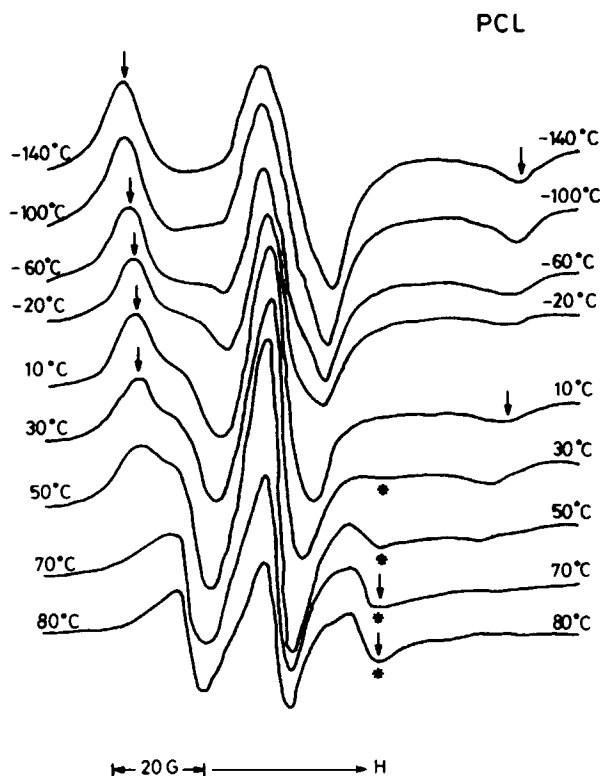


Figure 2 ESR spectra of (1) in PCL as a function of temperature. The arrows indicate the field positions of the outermost peaks and the asterisk marks the peak position of the motionally mobile component at high temperatures.

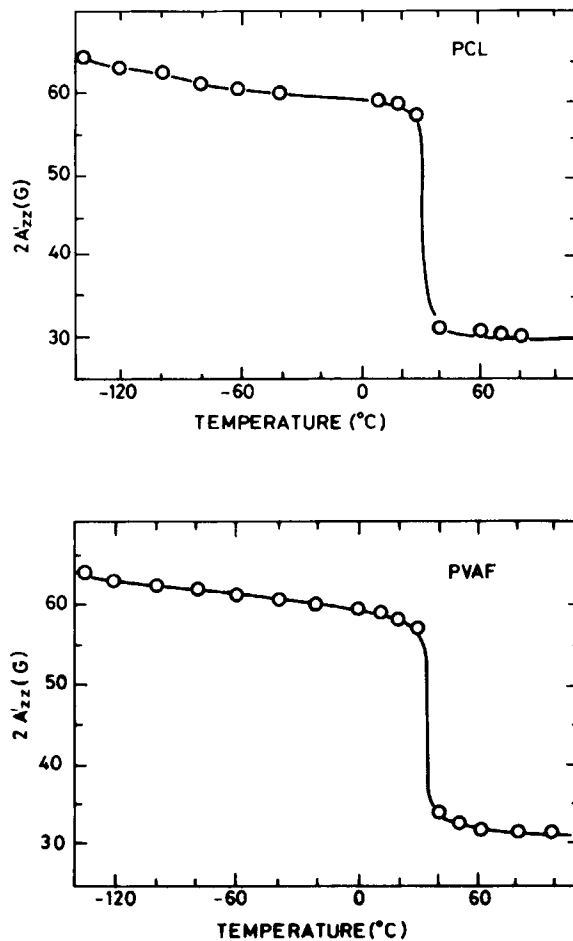


Figure 3 The temperature variation of the outermost peak-to-peak separation ($2A'_{zz}$) for (a) PCL and (b) PVAF samples. The smaller $2A'_{zz}$ values (< 40 G) indicate the fast component and the larger $2A'_{zz}$ values (> 50 G) correspond to slow components in the composite ESR spectra.

eraged out. This fact means that the molecular motion of the spin probe in the sample at this temperature is as rapid as in a nonviscous fluid. One of the characteristic measures of probe mobility is the separation, in gauss, $2A'_{zz}$, of the extrema of the ESR signal. Faster motion leads to a decrease in the outermost peak-to-peak separation. We have plotted these values as function of temperature in Figure 3 for the PCL and PVAF samples that we have examined.

The partially averaged, broadened ESR spectrum of the PCL and PVAF samples shows a small decrease in the $2A'_{zz}$ values as the samples are warmed from -140 to $+20$ °C. Above 20 °C, these values become somewhat more sensitive to temperature, with a precipitous decrease in $2A'_{zz}$ above 40 °C.

At temperatures above 30 °C, the isotropic spectra with a narrowed three-line pattern appears for PCL

and PVAF samples. As shown in Figure 2, these peaks become narrower as the temperature increases. Above this temperature, however, the line shape and the outermost peak-to-peak separation of the spectra change only slightly for both samples. The similarity of the spectral change for (1) in PVAF and in PCL suggest that most of the nitroxide free radicals were trapped in the PVA_c phase of the particles during the vacuum drying process. We conclude that the spin probe (1) in PCL is located almost exclusively in PVA_c domains.

In Figure 4 we present the temperature dependence of the ESR spectra of the HSCL sample. The line shape for the HSCL sample changes very little

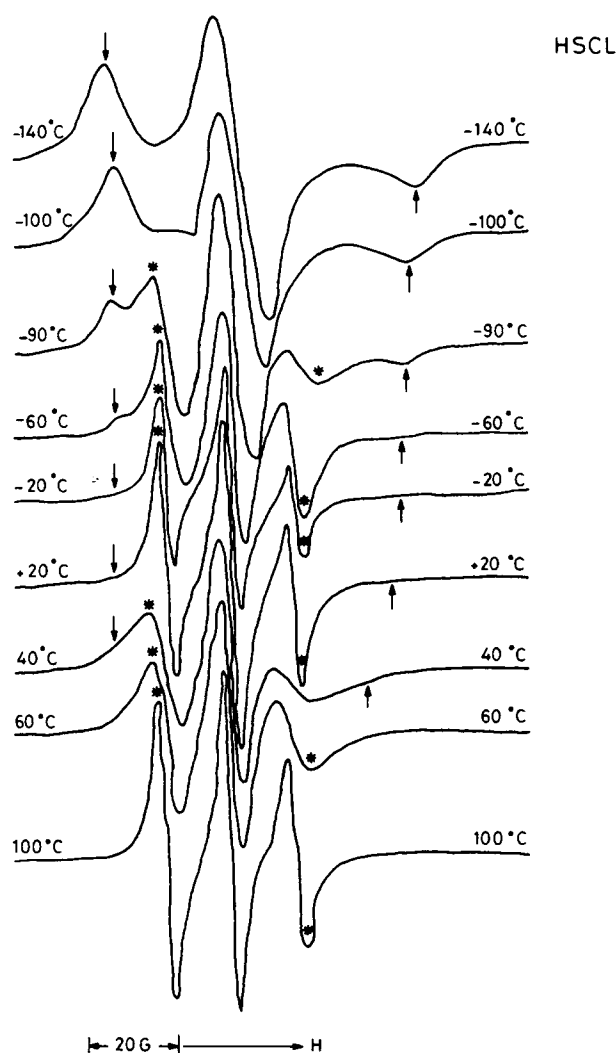


Figure 4 ESR spectra of (1) in HSCL as a function of temperature. The asterisks indicate the appearance of the motionally mobile component above -100°C . The arrows mark the motionally slowed component that disappeared above 40°C .

for temperatures below -100°C and show only the partially averaged spectra of (1) in a glassy environment. Between -100 and $+40^{\circ}\text{C}$, two components appear in the ESR spectra, indicating the coexistence of both mobile and immobile spin probes in the HSCL system.

Above 40°C , the partially averaged slow components disappeared from the ESR spectra of HSCL, leaving only the isotropic fast components. At 40°C , the HSCL spectra is similar to the spectra of a spin probe in a viscous liquid environment. These characteristics remained even when the HSCL sample was heated well above the T_g of PVA_c (28°C). Only above 100°C does the spectra for the MSCL sample become isotropic.

In Figure 5, the temperature behavior of $2A'_{zz}$ of PCL and HSCL are plotted. In the HSCL sample, at temperatures above -100°C , a composite spectra consisting of both slow and fast components appeared, yielding different $2A'_{zz}$ values obtained for these HSCL samples. $2A'_{zz}$ values of the slow part of HSCL decreased gradually above -100°C by following the $2A'_{zz}$ values of PCL. This fact may indicate that the nitroxide motion is highly immobilized in the PVA_c phase of HSCL at this temperature range. Above 40°C , the slowed part disappeared completely from the spectra, indicating that, above this temperature, virtually all the probe molecules were in environments of sufficient free volume to permit rapid rotation. Here, the question is the location of the nitroxide inside the particle. Since the chemical composition of the particles indicates that the PCA_c represents 96% of the dry volume, it would not be surprising if the probes were located predominantly in that phase. Peak-to-peak separation of immobilized component in Figure 5 is consistent with the ESR spectra of nitroxide in pure colloid powder or in pure PVA_c matrix. From here one can conclude that the spin probe in the polymer colloid, in the presence of hexane, is located exclusively in the PVA_c domain or at least at the interface where PEHMA-PVA_c segments are intermixed.

Diffusion

When PVA_c particles are in various solvents, ESR measurements were taken at each consecutive day to follow the penetration of the spin probe (i.e., nonsolvent) into the colloid particle. ESR spectra of the nitroxide in the hexane PVA_c system, which were taken on different days, are compared in Figure 6. Spectrum A was taken 1 day after the sample preparation. The peak indicated by the asterisk (*)

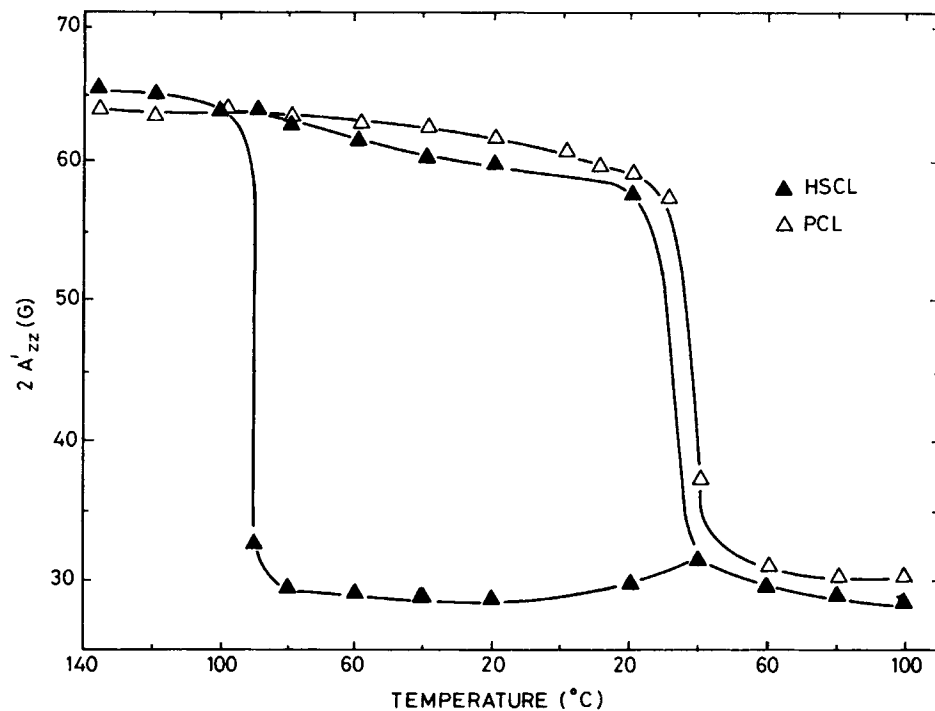


Figure 5 The temperature variation of the outermost peak-to-peak separation ($2A'_{zz}$) for ($-\blacktriangle-\blacktriangle-\blacktriangle-$) HSCL and ($-\triangle-\triangle-\triangle-$) PCL samples. The smaller $2A'_{zz}$ indicate the fast component and the larger $2A'_{zz}$ values correspond to slow components in the ESR spectra.

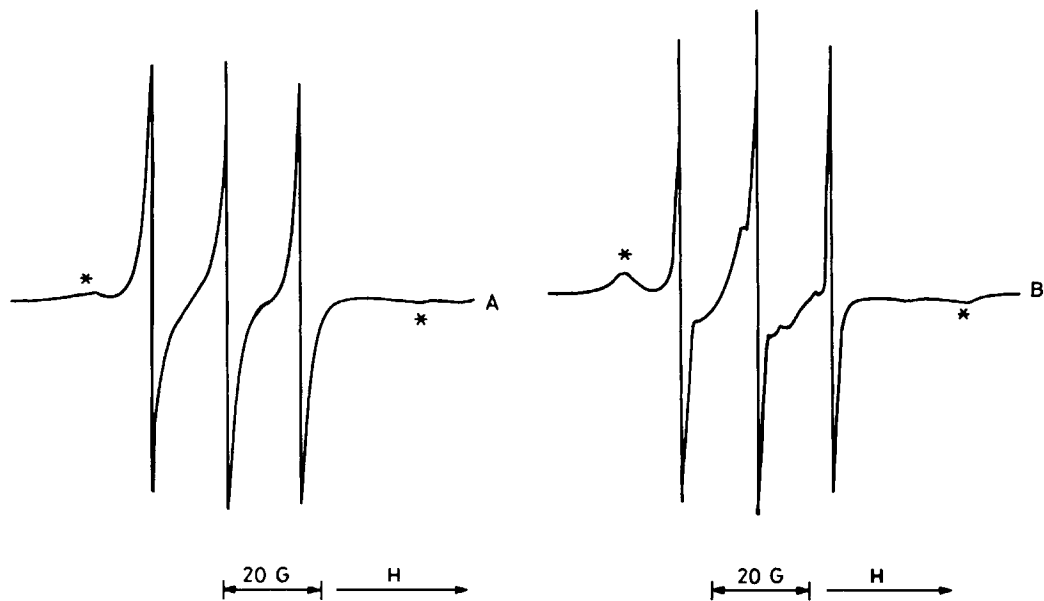


Figure 6 ESR spectra of the spin probe (1) in the hexane-PVA_c system: (A) 1 day after the sample preparation; (B) sixth day after the sample preparation. (*) indicates the immobilized component of the spin probe (1).

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 on the sixth day of the penetration process, it can be seen that diffusion of nitroxides into the colloid particle can be traced by the following ratio:

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

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. The M_t can represent the amount of nitroxide (or nonsolvent) molecule diffused into the particle at time t . To introduce a model to the penetration problem, we assumed that the PEHMA phase forms a randomly distributed, interconnected network inside the spherical PVA_c matrix, so that the Fickian diffusion of the spin probe through PEHMA channels, across the parti-

cle, can be fitted to a spherical model. Such diffusion is described by the following equation¹⁹:

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

Here, M_∞ is the value of M_t at $t = \infty$; a , the maximum distance over which diffusion can occur; and D , the diffusion coefficient. In our experiments, we considered only the first term in the summation on the rhs of eq. (2) and let a equal the radius of the colloid particle; then, eq. (2) becomes

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

Plots of eq. (3) are presented in Figure 7 for various solvents. Equation (3) was fitted to experimental results and D values were obtained for each solvent. Results are presented in Table I for the corresponding solvents.

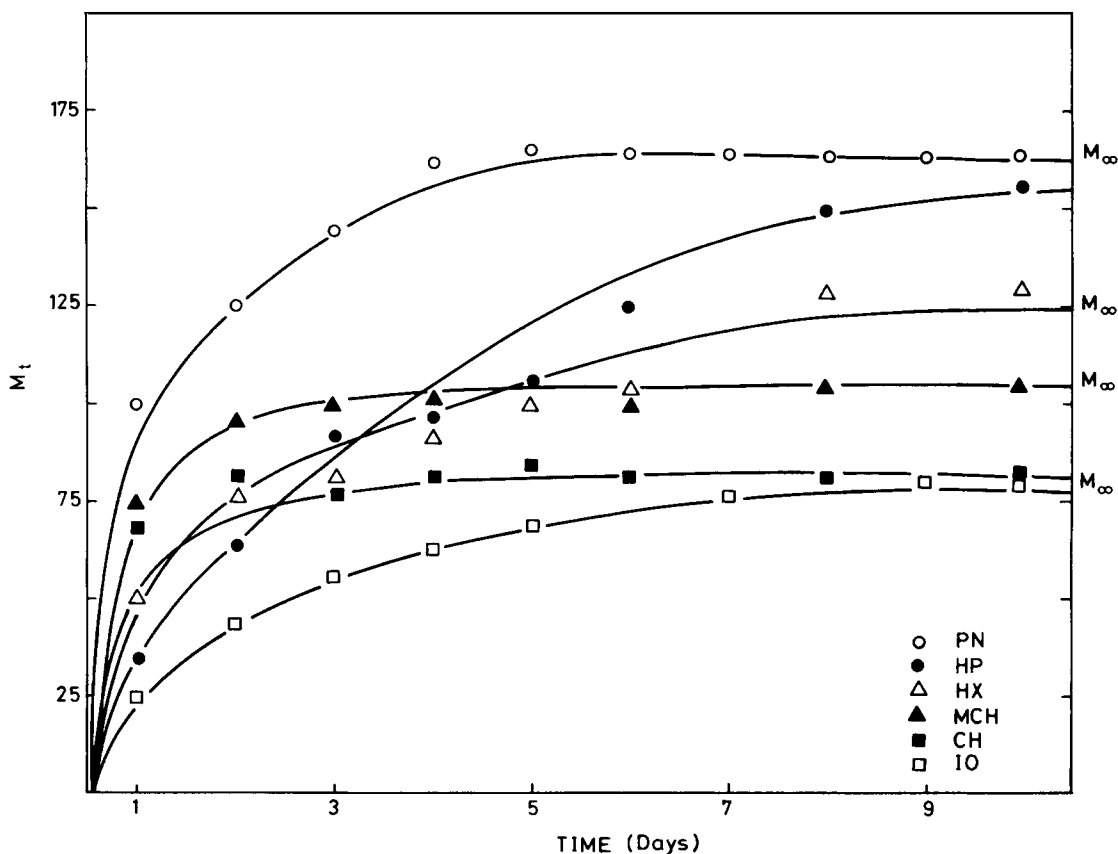


Figure 7 Nonsolvent diffusion into the PVA_c particles. M_∞ is represented the maximum amount of nonsolvent diffused into the particle.

Experimentally found D values appear to be consistent with those recently presented by Ehlich and Silescu² for the diffusion of a small molecule in polystyrene at temperatures below T_g . They measured the diffusion coefficient as approximately 10^{-15} cm²/s. Recently, using a nonradiative energy transfer technique,²⁰ we measured the diffusion coefficient of dye molecules as 3×10^{-19} and 5×10^{-13} cm²/s in PMMA at 25 and 115°C, respectively.

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

There are entropic and enthalpic contributions of solvent-induced mixing at the PEHMA-PVA_c interphase. Entropy of mixing decreases with increasing molar volume of substances and enthalpy of mixing is related to the solubility parameters.²¹ These are the thermodynamic effects that contribute to diffusion. On the other hand, solvent viscosity plays the retarding role during small molecule diffusion.

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 Boltzmann constant; T , the absolute temperature; r , the radius of the nitroxide (i.e., solvent) 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 8, where the dependence is found linear. Increase in D as η decreases is quite satisfactory. 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.¹⁷

Solution theory predicts that the polymer-solvent interaction parameter is related to the solubility parameters via the following expression²¹:

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

where V and δ are the molar volume and solubility parameter of the solvent; R , the gas constant; T ,

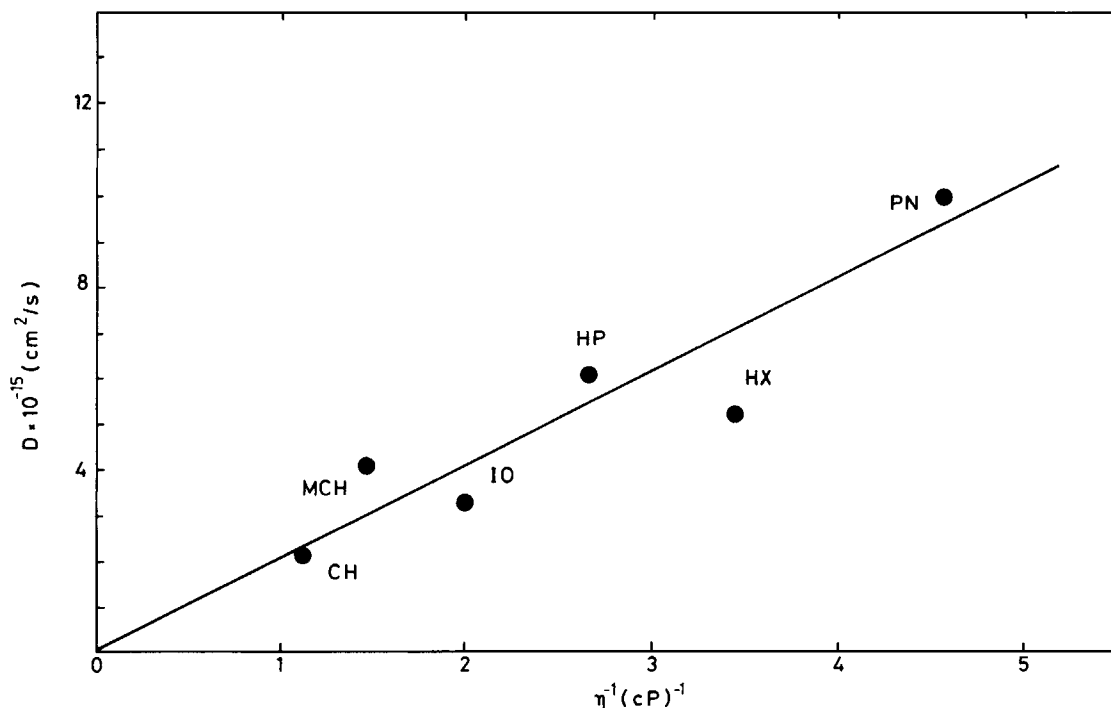


Figure 8 Plot of diffusion coefficient D vs. inverse of solvent viscosity (η).

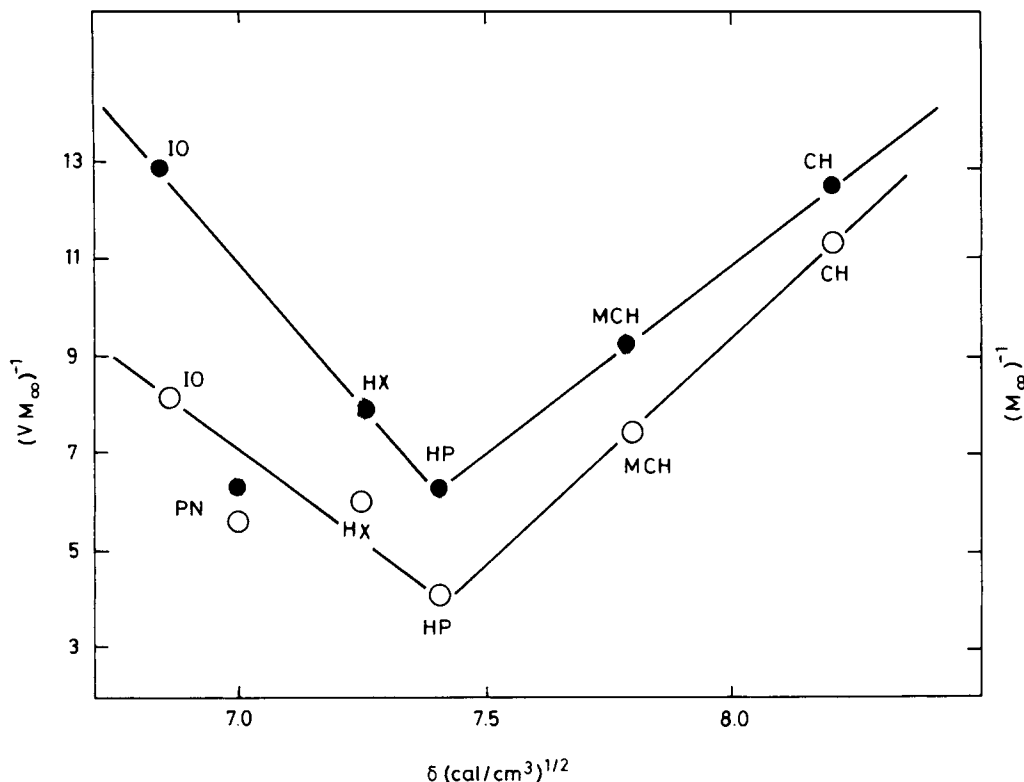


Figure 9 Plot of (—○—○—○—) $(VM_\infty)^{-1}$ vs. δ and (—●—●—●—) $(M_\infty)^{-1}$ vs. δ .

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 the Flory-Huggins parameter χ can be inversely proportional to the maximum amount of diffused solvent molecules (M_∞) into the PVA_c particle. To prove that this assumption is correct, we plotted $(M_\infty V)^{-1}$ and $(M_\infty)^{-1}$ vs. δ in Figure 9. The results are quite satisfactory; in both cases, data can be represented by two straight lines intersecting at $\delta = 7.4$ (cal/cm³)^{1/2}.

In the M_∞^{-1} vs. δ plot, the point for PN is quite off the line; however, in the $(VM_\infty)^{-1}$ vs. δ plot, the result looks much better, indicating that the volume of the solvent molecule is critical for the polymer-solvent interactions. The intersection value of δ suggests that heptane is the best solvent for the PEHMA phase or for the PVA_c-PEHMA interphase to promote penetration.

From these results, we reached the conclusion that D is strictly a kinetic quantity that mostly associates with the solvent viscosity. However, M_∞ measures the thermodynamic effects (enthalpy of mixing) between polymer and solvent molecules. Here, presumably, the

PEHMA network is responsible for the solvent penetration into the polymer particle. At the beginning of penetration, the PEHMA phase has to be swelled with the corresponding solvent; then, solvent molecules can diffuse into the PVA_c phase or the PVA_c-PEHMA interphase, where they face a medium at very high apparent viscosity in which the diffusion coefficient is found around $D = 10^{-15}$ cm²/s.

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REFERENCES

1. J. L. Xia and C. H. Wang, *J. Phys. Chem.*, **93**, 3839 (1989).
2. D. Ehlich and H. Silescu, *Macromolecules*, **23**, 1600 (1990).
3. Ö. Pekcan and Y. Demir, *J. Appl. Polym. Sci.*, **43**, 2169 (1991).
4. R. H. Sands, *Phys. Rev.*, **99**, 1222 (1955).
5. T. K. Kneubuhl, *J. Chem. Phys.*, **33**, 1074 (1960).
6. S. Morinchi, N. Nakamura, S. Shimada, H. Kashiwabara, and Sohma, *J. Polym.*, **11**, 630 (1970).
7. (a) P. L. Kumler and R. F. Boyer, *Macromolecules*,

- 9, 903 (1976); (b) R. F. Boyer and P. L. Kumler, *Macromolecules*, **10**, 461 (1977); (c) P. L. Kumler, S. E. Keinath, and R. F. Boyer, *Polym. Eng. Sci.*, **17**, 613 (1977).
8. Z. Veksli and W. G. Miller, *Macromolecules*, **10**, 686 (1977).
9. Z. Veksli and W. G. Miller, *Macromolecules*, **10**, 1245 (1977).
10. Z. Veksli and W. G. Miller, *J. Polym. Sci.*, **54**, 299 (1976).
11. L. S. Egan, M. A. Winnik, and M. D. Croucher, *J. Polym. Sci. Polym. Chem.*, **24**, 1895 (1986).
12. A. J. Barrett, *Dispersion Polymerization in Organic Media*, Wiley-Interscience, New York, 1975.
13. Ö. Pekcan, M. A. Winnik, and M. D. Croucher, *J. Coll. Interface Sci.*, **95**, 420 (1983).
14. 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.
15. Ö. Pekcan, M. A. Winnik, and M. D. Croucher, *Phys. Rev. Lett.*, **61**, 641 (1988).
16. Ö. Pekcan, S. L. Egan, M. A. Winnik, and M. D. Croucher, *Macromolecules*, **23**, 2210 (1990).
17. (a) J. E. Guillet, *Polymer Photophysics and Photochemistry*, Cambridge University Press, Cambridge, 1985; (b) X.-B. Li, M. A. Winnik, and J. E. Guillet, *Macromolecules*, **16**, 992 (1983).
18. J. Crank and G. S. Park, *Diffusion in Polymers*, Academic Press, London, 1968.
19. J. Crank, *Mathematics of Diffusion*, 2nd ed., Clarendon, Oxford, 1975.
20. Ö. Pekcan, *Turkish J. Chem.*, **15**, 294 (1991).
21. P. J. Flory, *Principles of Polymer Chemistry*, Cornell University Press, Ithaca, NY, 1953.

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