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Modulated differential scanning calorimetry – VII: Interfacial macromolecular diffusion in core-shell latex particles[1]

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Abstract

The recent introduction of modulated-temperature differential scanning calorimetry (M-TDSC) has greatly extended the power of calorimetry as a characterization technique for polymers. A method which can be used to study macromolecular diffusion in the interfacial phase of core-shell latex particles after film formation has been derived. Here, the extent of macromolecular diffusion with time of annealing at 150°C in a poly(methyl methacrylate) (PMMA) and poly(vinyl acetate) (PVAc) core-shell latex has been studied by means of modulated-temperature differential scanning calorimetry (M-TDSC). By measuring the change of increment of heat capacity in the glass transition region, the total interface content can be determined. For film integration of core-shell latices, M-TDSC gives quantitative information on the formation of a diffusion interface. According to the M-TDSC measurements of the weight fraction, interfacial thickness and its development with time can be determined. With increasing time, the interfacial thickness between the core and shell phases decreased. The PMMA diffusion coefficient is approximately $4 \times 10^{-14} cm^2/s$. Reptation behaviour of macromolecular diffusion in phase separation was confirmed experimentally. © 1997 Elsevier Science B.V.

Keywords: Core-shell latex; Diffusion; Modulated-temperature differential scanning calorimetry; Phase separation

1. Introduction

Film-forming latices are widely used to formulate water-based coatings. The development of cohesive strength in the film can be achieved by diffusion of polymer molecules across the interface between particles and particle rearrangement, which is referred to as "further coalescence". A qualitative description of the phenomenon has been given based on (1) small-angle neutron scattering (SAN) observations, (2) transmission electron microscopy (TEM), (3) atomic force microscopy (AFM), (4) fluorescence spectra, and (5) dynamic mechanical thermal analysis (DTMA).

The study of molecular interdiffusion in latex films is important, both theoretically and in applications such as coatings, welding and crack healing. There are two basic methods of studying the diffusion of polymer molecules across the boundary between particles in a latex system; SANS (1) and fluorescence techniques (4). The advantages of SANS lie in its high sensitivity and its ability to determine readily the diffusion coefficient and chain interpenetration depth [1]. Hahn et al. [6] used a *n*-butyl methacrylate-containing copolymer and Linne et al. [7] used polystyrene to study chain interdiffusion of broad molecular weight distribution polymers by SANS. They found an increase in the radius of gyration of polymer chains during the course of film annealing, which provided evidence of interdiffusion between latex particles. Yoo

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et al. [8,9], also using polystyrene and the SANS technique, worked out the relationship between the increase in mechanical strength and the interdiffusion depth during film formation. Their results were consistent with Wool's crack-healing theory [10] based on the de Gennes reptation model [11]. The other powerful method utilizes fluorescence spectroscopy and has been applied to latex film formation by Winnik and Wang [4]. In this technique, latices are prepared in two different batches. In one batch, the chains contain a donor group, while in the other, an acceptor group is attached. The interdiffusion of polymer chains between neighbouring latex particles was then studied by direct non-radiative energy transfer measurements.

AFM and TEM can give information about the change of particle size. Goh et al. [3] have studied the integration of a latex film based on polybutylmethacrylate using AFM. They calculated the diffusion coefficient based on the classical diffusion model and found it to be 10^{-13} cm^2/s, which was three orders of magnitude larger than that obtained by the fluorescence technique [1] (10^{-16} cm^2/s). This difference was attributed [1] to the extra driving force from the surface energy, which causes faster diffusion near the surface [3] than in the bulk with the AFM technique being more sensitive to surface diffusion.

DMTA has been used extensively [5,12,13] for the characterization of latex films. The temperature dependence of the moduli has been satisfactorily fitted using the Kerner equation [5] between a two-component composite. Correlations between the transition widths and morphology of the two phases have been proposed [5]. At the same time, an extensive qualitative description of the effect of thermal annealing on the final thermomechanical behaviour of polymer films has been provided by O'Connor and Tsaur [14]. These latex films exhibit dramatic changes in their dynamic mechanical response after annealing [5] arising from phase rearrangement. In addition, from dynamic micromechanical analysis spectra, local segmental mobility has been measured in dried latex film by Richard and Wong [2].

Molecular interdiffusion in core-shell latex film has been studied [15]. The core-shell latex [15] was (polybutylmethacrylate) (core) - poly(butylmethacrylate-co-butylacrylate) (shell). Because of miscibility between the core and shell components, interdiffusion between core and shell phases occurred. The volume fraction of mixing and the interparticle penetration distance increased with annealing time [15]. However, in other core-shell latex films, perhaps phase separation may occur during annealing at high temperatures because of lower critical solution phase behaviour.

In this paper, modulated-temperature differential scanning calorimetry (M-TDSC) was used to investigate interfacial macromolecular diffusion in films formed from a core-shell latex.

2. Experimental

2.1. Latex preparation

The PMMA/PVAc (50/50, wt/wt) core-shell latices were prepared by sequential emulsion polymerization using the following chemicals. Ammonium persulfate (AP) and sodium dodecylbenzenesulphonate (SDBS) were obtained from Aldrich and were used as supplied. Azoisobutyronitrile (AIBN) was supplied by BDH. Methyl methacrylate (MMA) and vinyl acetate (VAc) from Aldrich were purified by passing through a column packed with inhibitor remover. The water used was deionized.

2.1.1. Stage I. Synthesis of PMMA core

The reaction vessel equipped with stirring was kept in a water bath maintained at 80°C. To this, 250 ml water and 0.3 g SDBS were added and the vessel purged with nitrogen for 20 min. Then 0.3 g AP and 30 ml MMA were added and allowed to react for 30 min. Thereafter, 90 ml MMA and 0.3 g AP dissolved in 30 ml water were pumped separately into the reaction vessel over a 2 h period. After the monomer addition was complete, the reaction was allowed to post-react for 1 h to ensure the completion of polymerisation.

2.1.2. Stage II. Synthesis of PVAc shell

The reaction vessel, which only contained 100 ml water, was maintained at 67°C. To this 100 ml PMMA latex was added and purged with nitrogen while being stirred. Then, 0.1 g AIBN was added and a pre-emulsion of 30 ml VAc, 0.3 g AIBN, 0.3 g SDBS and 30 ml water were pumped into the reaction vessel over a 4 h period.

2.2. *Latex film preparation*

Latex films were prepared by casting the latices and evaporating the water under ambient conditions. They were then dried under vacuum for at least 20 days at room temperature. Samples were annealed in the M-TDSC cell at 150°C under a nitrogen flow of ~30 ml/min.

2.3. *Instrumentation*

A TA Instruments M-TDSC apparatus was used in this study. An oscillation amplitude of 1.5°C and an oscillation period of 60 s, with a heating rate of 3°C/min, respectively, were used for the measurements of heat flow and heat capacity.

A review of M-TDSC theory has been published by Reading [16]. Currently, the type of perturbation used is a sine wave and the mathematical analysis is a combination of a Fourier transformation and an averaging process. The basic equation for temperature is as follows.

$$T = T_0 + bT + B\sin(\omega t) \qquad (1)$$

T_0 is the starting temperature, b the heating rate, B the amplitude of the sine wave, ω the frequency of modulation, and t the time.

From M-TDSC experiments [16], the following signals can be obtained:

1. Total heat flow (as for conventional DSC)
2. Reversing heat flow
3. Non-reversing heat flow
4. Heat capacity

In this paper, we are chiefly concerned with the principles of glass transition measurement.

The total heat flow from M-TDSC [17] is given by Eq. (2).

$$\begin{aligned} \mathrm{d}Q/\mathrm{d}t = bC'_\mathrm{b} + f(t, T) + \omega BC'_\omega\cos(\omega t) \\ + C\sin(\omega t) \end{aligned} \qquad (2)$$

$bC'_\mathrm{b} + f(t, T)$ is the underlying signal component, after the cyclic component $\omega BC'_\omega\cos(\omega t) + C\sin(\omega t)$ has been filtered out by averaging over the period of the modulation. Single-primed quantities, C'_b and C'_ω denote reversing heat capacities. C is the amplitude of the change in heat flow due to the effect on $f(t, T)$ of the temperature modulation. This equation may be expressed [17] entirely in terms of heat capacity.

$$\mathrm{d}Q/\mathrm{d}t = b(C'_\mathrm{b} + C_\mathrm{E}) + \omega BC^*_\omega \mathrm{e}^{i\omega t} \qquad (3)$$

Here, C_E, defined as $f(t, T)/\mathrm{b}$, is the apparent excess heat capacity as a consequence of the frequency response of the sample. $C^*_\omega = C'_\omega + iC''_\omega$, where C''_ω, defined as $C/\omega B$, is the out-of-phase or kinetic heat capacity. For many processes such as simple irreversible chemical reactions, C''_ω is small [17] and also

$$C'_\mathrm{b} = C'_\omega = K_\mathrm{cp}\langle H_\mathrm{FA}\rangle/\omega B \qquad (4)$$

K_cp is the heat capacity calibration constant and $\langle H_\mathrm{FA}\rangle$ the average value of maximum heat flow amplitude. The deconvolution is done by continued integration, averaging and smoothing over several cycles. Under these conditions, the non-reversing component, C_E, can be found by substituting C''_ω from the underlying $C'_\mathrm{b} + C_\mathrm{E}$ value. The situation, when considering the glass transition, is more complex because C'_b and C'_ω are functions of heating rate and ω, respectively. Here, we have chosen the condition [17] such that

$$C'_\omega \gg C''_\omega \qquad (5)$$

and

$$H_\mathrm{NR} = \int_T (C_\mathrm{b} + C_\mathrm{E} - C''_\omega)\mathrm{d}T \qquad (6)$$

H_NR is the non-reversing heat flow.

2.4. *Atomic force microscope*

The morphological observations of the latex film were made using a Topometrics Explorer atomic force microscope in the contact mode.

3. Results and discussion

Fig. 1 is an atomic force micrograph of the latex film which shows a high degree of surface order. The particles are narrowly distributed in size with a mean diameter of 200 nm.

Fig. 2 shows heat capacity vs. temperature data for the PMMA/PVAc core-shell latex film after different annealing times at 150°C. In the glass transition regions, the heat capacity traces are different for

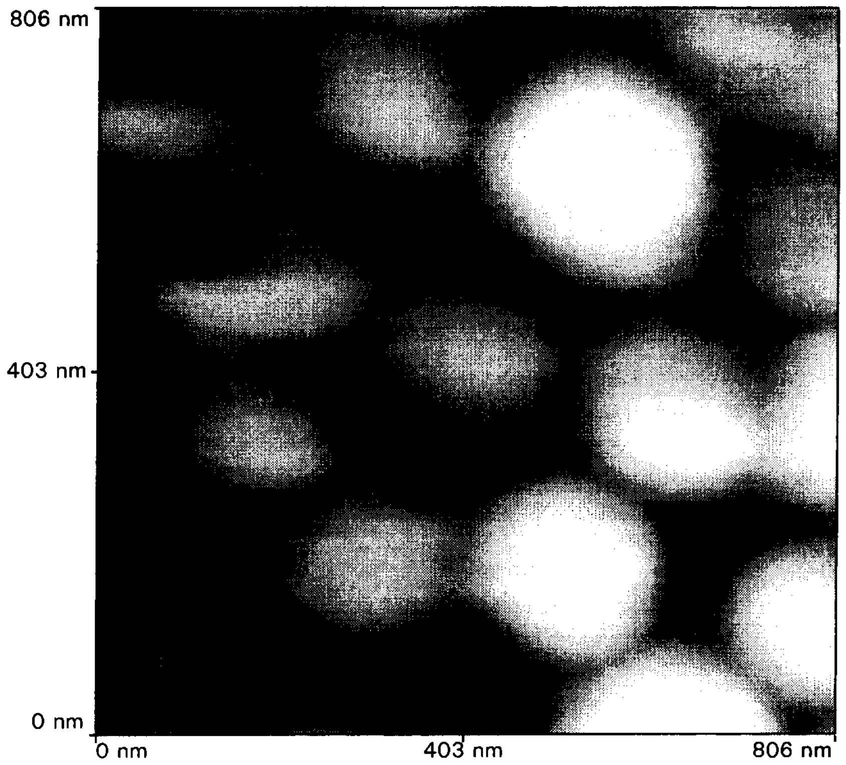

Fig. 1. Atomic force micrograph of cast latex film.

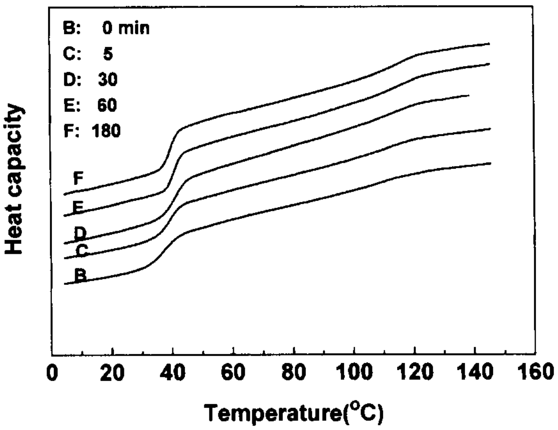

Fig. 2. Heat capacity vs. temperature for the PMMA/PVAc core-shell latex film at different annealing times at 150°C.

different annealing times. However, it is difficult to draw more detailed information from these traces. Fig. 3 shows the differential of heat capacity signal, dC_p/dT, vs. temperature for these different annealing times. Fig. 4 is an enlargement of part of Fig. 3. With increasing time, the dC_p/dT vs. temperature signal obviously changes significantly. The magnitude of the dC_p/dT signals for the pure PMMA and PVAc phases increases, which implies that the ΔC_p value increases. This indicates that the PVAc and PMMA phases become larger.

The miscibility and phase behaviour of PMMA and PVAc blends have been studied by DSC [18], M-TDSC [19], light scattering [20,21], FTIR spectroscopy [22] and solid-state NMR [23] techniques. The system was reported [18,22,23] to be miscible under certain conditions. Other researchers [19–21] indicate that the system is at least partially miscible. The system exhibits lower critical solution temperature phase behaviour [18]. On increasing the temperature, phase separation occurs [18–22].

For the core-shell latex investigated in the study, the particle morphology can be considered as consisting of three parts: the core, A, an interface between core and shell, AB, and the shell, B as shown in Fig. 5. It is

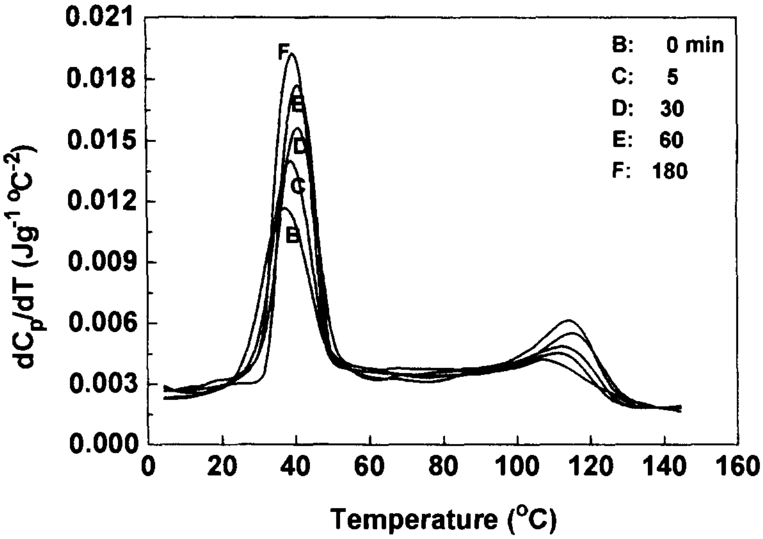

Fig. 3. dCp/dT vs. temperature for the PMMA/PVAc core-shell latex film at different annealing times at 150°C.

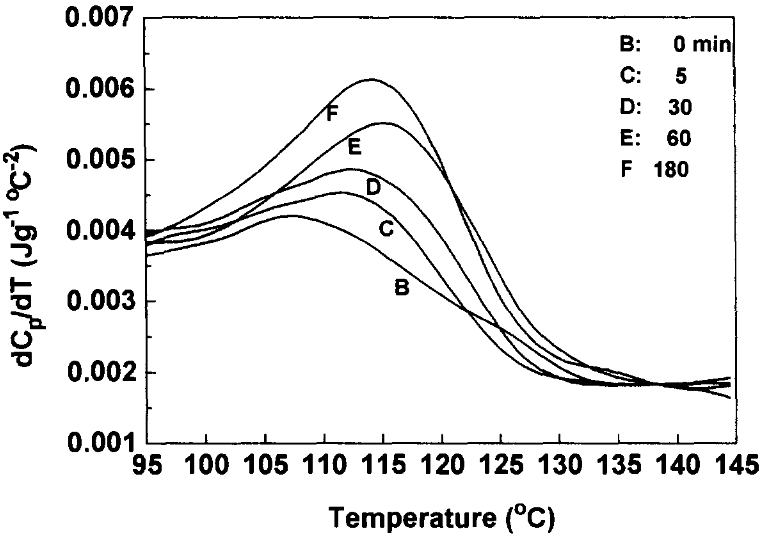

Fig. 4. An enlargement of part of Fig. 3.

assumed that the core phase is totally surrounded by the shell phase. The interfacial phase, AB, exhibits phase separation at high temperatures. It is assumed that during the phase separation of the interfacial phase, neither polymer A in the core nor polymer B in shell diffuses into AB phase.

By measuring the change of increment of heat capacity in the glass transition region, the total interface content and its change with time can be determined [24].

When the system exhibits an interface [20], the following equations apply;

$$\Delta C_\mathrm{p} = \Delta C_{\mathrm{p_a}} + \Delta C_{\mathrm{p_b}} + \delta C_\mathrm{p} \quad (7)$$

$$\Delta C_{\mathrm{p_a}} = w_\mathrm{a} \Delta C_{\mathrm{p_{a0}}} \quad (8)$$

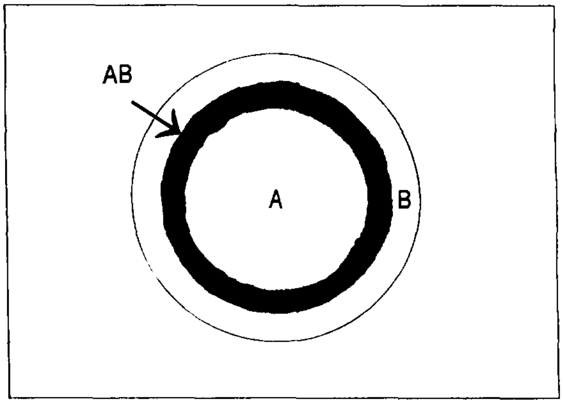

Fig. 5. Particle model for this core-shell latex.

and

$$\Delta C_{p_b} = w_b \Delta C_{p_{b0}} \qquad (9)$$

$\Delta C_{p_{a0}}$ and $\Delta C_{p_{b0}}$ are the increments of heat capacity T_{g_i} for pure core and shell, δCp the increment of heat capacity of the interface in its glass transition region and, w_a and w_b are the weight fractions of PMMA in the core and PVAc in the shell, respectively. The weight fractions, δ_a and δ_b, of the PMMA and PVAc in interfacial phase can then be obtained.

$$\delta_a = 0.5 - \Delta C_{p_a} / \Delta C_{p_{a0}} \qquad (10)$$

and

$$\delta_b = 0.5 - \Delta C_{p_b} / \Delta C_{p_{b0}} \qquad (11)$$

Fig. 6 shows that, at increasing annealing times at 150°C, the weight fraction of the interface decreases. Fig. 7 shows the total change of lost weight fraction of interface, ω_{lost}, which is diffusing out of the interface with time. The change with time can be described by following relationship.

$$\omega_{\text{lost}}(t) \propto t^{1/2} \qquad (12)$$

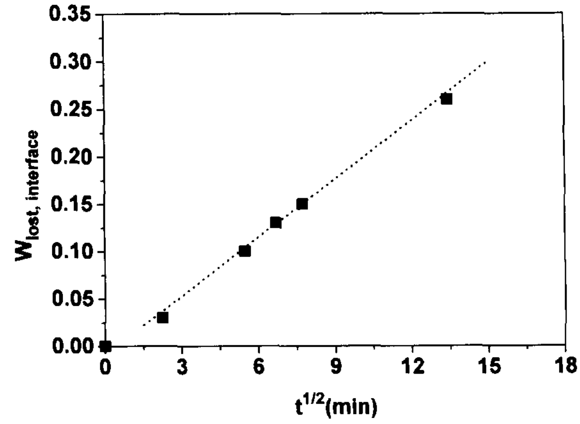

Fig. 7. Change of lost weight fraction of the interface with time.

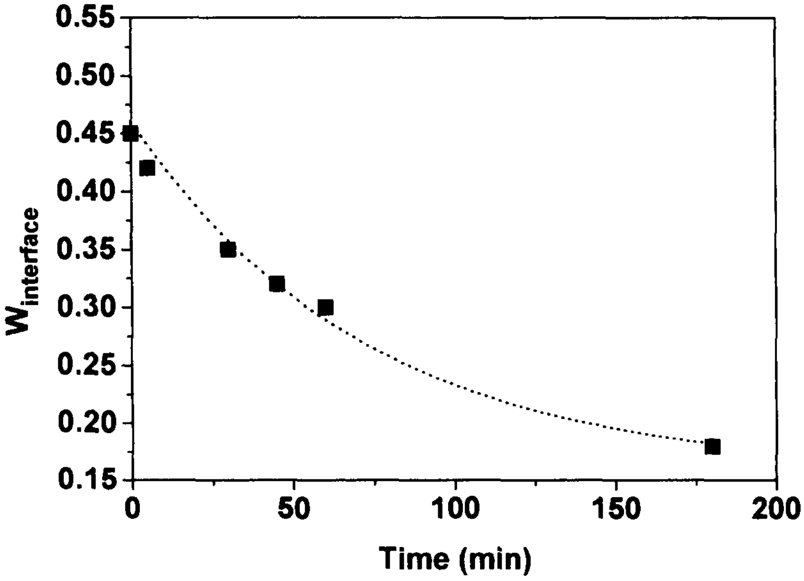

Fig. 6. Change of weight fraction of the interface with annealing time at 150°C.

Eq. (12) describes reptation behaviour [25]. Therefore, it has been confirmed here experimentally that macromolecular diffusion during phase separation can be described by the reptation model. The mechanism of macromolecular diffusion in phase separation is the same as found [24] during interdiffusion between two compatible polymer films.

Densities of PMMA and PVAc are ~1.19 and 1.192 g/cm^3, respectively [26]. For an ideal PMMA/PVAc core-shell latex particle, one with no AB interfacial zone, the volume relationship between core and shell phases is as follows:

$$\int_{R}^{R+\Delta R} 4r^2 \mathrm{d}r = 4/3R^3 \tag{13}$$

R and ΔR are the radius of core and the thickness of shell, respectively. From Eq. (13), the following relation holds:

$$3R^2\Delta R + 3R\Delta R^2 + \Delta R^3 = R^3 \tag{14}$$

For the PMMA/PVAc core-shell latex films, $R + \Delta R$ was measured to be 100 nm. Then, R was 79 nm and ΔR 21 nm.

Based on the M-TDSC measurements, the weight fraction of the interface in the PMMA/PVAc core-shell latex particle is about 45%. Obviously, the quantity is quite large, which is not surprising because the system has been reported [19–21] to be at least partially miscible. The weight fractions of the PVAc and PMMA in the interfacial phase are ~16% and 29%, respectively. When an interfacial phase exists, the shell phase will be thin and the radius of the core phase will decrease. The interfacial region has a thickness of ~28 nm. This implies taking the zero annealing time as being a reflection of the morphology in the particle state. With increasing film annealing time, the interfacial thickness will decrease.

The change of interfacial thickness with time, d(t), can be estimated approximately according to following equation:

$$\mathrm{d}(t) = 28(\delta_a + \delta_b)/0.45\,(\mathrm{nm}) \tag{15}$$

Fig. 8 shows the change of the interfacial thickness.

Assume $C(r,t)$ and $E(r,t)$ are the concentrations of PMMA and PVAc diffusing into core and shell phases, respectively.

According to Fick's second diffusion law [27]

$$\nabla(DC) = \partial C/\partial t \tag{16}$$

$$D_{\mathrm{A}}(\partial^2 C/\partial r^2 + 2/r\partial C/\partial r) = \partial C/\partial t \tag{17}$$

$$D_{\mathrm{B}}(\partial^2 E/\partial r^2 + 2/r\partial E/\partial y) = \partial E/\partial t \tag{18}$$

with the following initial conditions:

$$C(r, 0) = C_0 \tag{19}$$

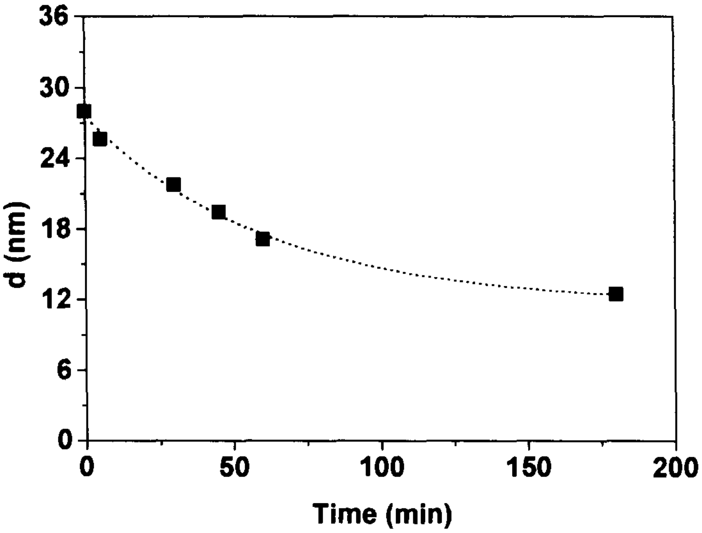

Fig. 8. Change of the interfacial thickness with time.

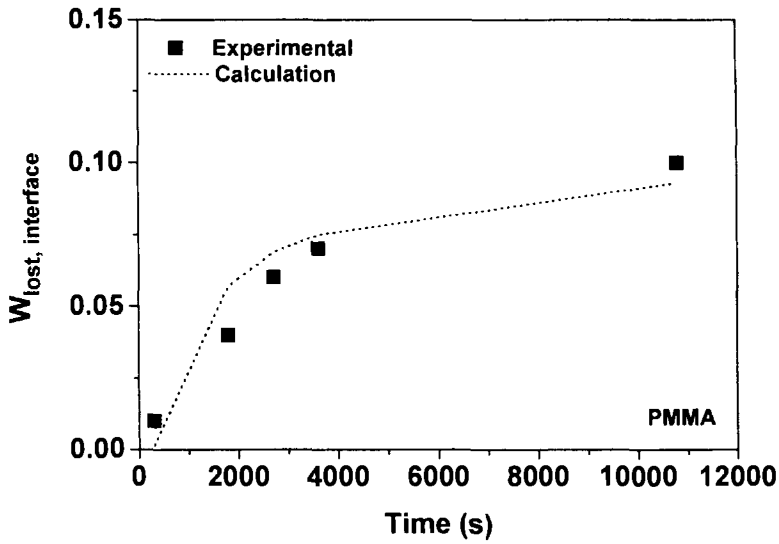

Fig. 9. Weight fraction of the PMMA diffused into the core phase vs. annealing time at 150°C.

and

$$E(r, 0) = E_0 \tag{20}$$

D_A and D_B are the diffusion coefficients of PMMA and PVAc, respectively.

Let $C = rY$, then

$$D_A \partial^2 Y/\partial r^2 = \partial Y/\partial t \tag{21}$$

$$Y(r, 0) = 0 \tag{22}$$

and let $E = rZ$, then

$$D_B \partial^2 Z/\partial r^2 = \partial Z/\partial t \tag{23}$$

$$Z(r, 0) = 0 \tag{24}$$

Using a Laplace transformation [27], the weight fraction of the PMMA, $F(t)$, which has diffused into the core phase at time t can be obtained as follows:

$$F(t) = A\{R/(\pi D_A t)^{1/2} \exp[-R^2/(4D_A t)] - \mathrm{erf}(R/(4D_A t)^{1/2}) + 1\} \tag{25}$$

where A is a constant. Eq. (25) can be used to estimate the diffusion coefficient for the PMMA.

Fig. 9 gives a comparison of the calculated (Eq. (25)) and experimental results. D_A was found to be $4 \times 10^{-14} \mathrm{cm}^2/\mathrm{s}$. This value is similar in magnitude to that obtained [20] for PMMA/PVAc by the light scattering technique.

4. Conclusions

A quantitative M-TDSC method which can be used to study macromolecular diffusion in the interfacial phase of core-shell latex particles after film formation has been developed.

According to the M-TDSC measurements, the weight fraction, the interfacial thickness and its development with time can be determined. The reptation behaviour of macromolecular diffusion during phase separation was confirmed experimentally.

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