

# Real Time Monitoring of Latex Film Dissolution by UVV Technique

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**ABSTRACT:** UV-visible (UVV) technique is used for monitoring of polymer film dissolution. These films are formed from pyrene (P)-labeled poly(methyl methacrylate) (PMMA) latex particles, sterically stabilized by poly isobutylene (PIB). Annealing of films was performed above  $T_g$  at various temperatures for 30-min time intervals. Diffusion of solvent molecules (chloroform) into the annealed latex film was followed by desorption of PMMA chains. Desorption of P-labeled PMMA chains was monitored in real time by the absorbance change of P in the polymer-solvent mixture. A diffusion model with a moving boundary was used to quantify real time UVV data. Diffusion coefficients of desorbed PMMA chains were measured and found to be between  $2$  and  $0.6 \times 10^{-11} \text{ cm}^2 \text{ s}^{-1}$  in the 100 and 275°C temperature range. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 75: 1075–1082, 2000

**Key words:** polymer dissolution; PMMA-PIB latex; moving boundary model

## INTRODUCTION

The polymer dissolution process is very different from, and more complicated than, small molecule dissolution. The dissolution of small molecules can be explained by simple diffusion laws<sup>1</sup> and a unique diffusion rate. However, polymeric films dissolve mainly in three different stages: (a) solvent penetration, (b) polymer relaxation, and (c) diffusion of polymer chains into the solvent reservoir. A schematic representation of these three sequential steps for the dissolution of a polymer film is presented in Figure 1. In the first stage, the penetration distance of solvent molecules mainly depends on free volume, which in turn depends on the flexibility of the chains and backbone and side groups, as well as the thermal history of the polymer. These first solvent mole-

cules act as a plasticizer, and as a result these regions of the film start to swell. In the second stage, a gel layer is created by the relaxing polymer chains. This transition layer is composed of both polymer chains and solvent molecules. If the solvent-polymer interactions are more dominant than the polymer-polymer interactions, maximum swelling is obtained. This is the case when a good solvent is used during dissolution of a polymer film. In the last stage, chain disentanglement takes place, and then chains separate from the bulk and diffuse into the solvent.

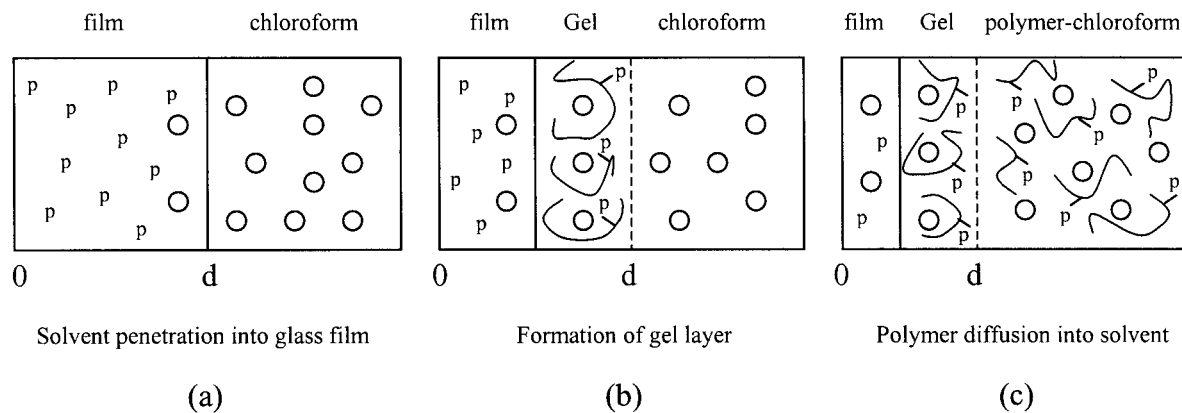
Poly(methyl methacrylate) (PMMA) film dissolution was studied using laser interferometry by varying the molecular weight and solvent quality.<sup>2</sup> Limm et al.<sup>3</sup> modified the interferometric technique and studied the dissolution of fluorescence-labeled PMMA films. By monitoring the intensity of fluorescence from the film along with the interferometric signal, the solvent penetration rate into the film and the dissolution are measured simultaneously. A real time, nonde-

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**Figure 1** Cartoon representation of polymer film dissolution.  $d$ , film thickness.

structive method for monitoring small molecule diffusion in polymer films was developed.<sup>4-8</sup> This method is essentially based on the detection of excited fluorescence dyes desorbing from a polymer film into a solution in which the film is placed. Recently, we reported a steady-state fluorescence study on the dissolution of both annealed latex film and PMMA discs using real-time monitoring of fluorescence probes.<sup>9-12</sup>

Dispersion of polymer colloid particles with a glass transition temperature,  $T_g$ , above the drying temperature are called hard latex dispersions. These particles remain essentially discrete and undeformed during the drying process. The mechanical properties of hard latex films can be enhanced by annealing after all solvent has evaporated. This process is called sintering and is an important aspect of latex-coating technology.

In this work we study the dissolution of films formed from hard latex particles labeled with pyrene (P) dye molecules.<sup>13</sup> These particles have two components: the major part, PMMA, comprises 96 mol % of the material, and the minor component, poly isobutylene (PIB) (4 mol %), forms an interpenetrating network through the particle interior,<sup>14,15</sup> which is highly soluble in certain hydrocarbons. A thin layer of PIB covers the particle surface and provides colloidal stability by steric stabilization. Film samples were prepared by annealing latex powders above  $T_g$ , at various temperatures for 30 min. Chloroform-heptane mixture was used as dissolution agents. UV-visible (UVV) experiments were performed for real time monitoring of the dissolution processes. The dissolution experiments were designed so that P-labeled PMMA chains desorbing from swollen gel were detected by the UV absorption of P. The main goal of the presented work

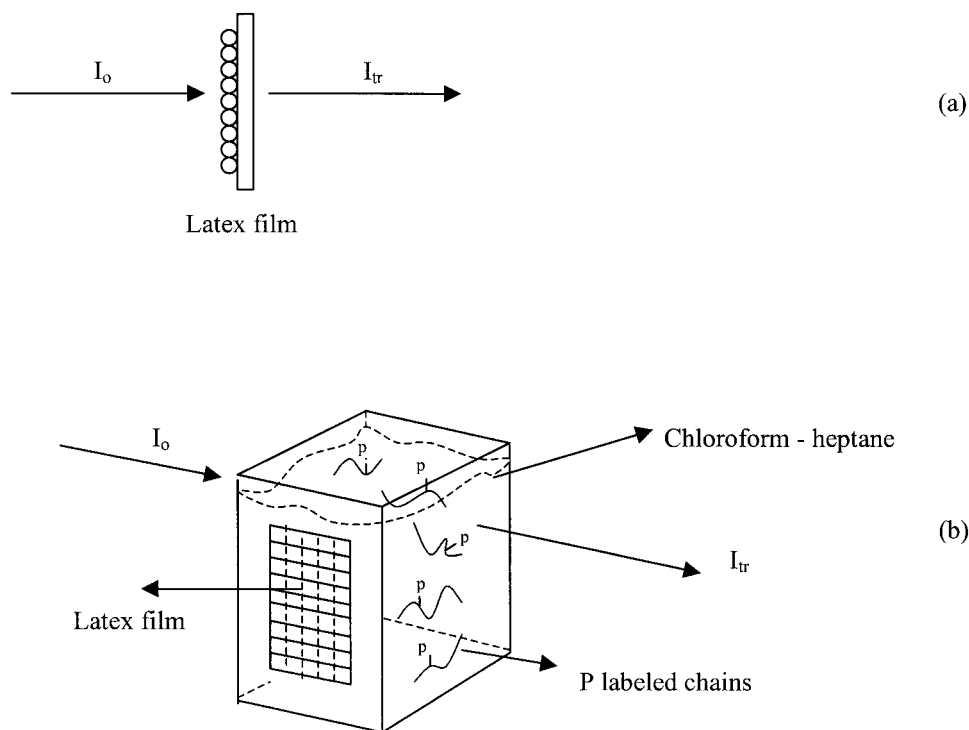
was to create transparent and mechanically strong films by annealing and then study the dissolution process by the novel UVV technique. The moving boundary model,<sup>1</sup> which was used to understand the diffusion in two distinct regions separated by a moving interface, was used to interpret the UVV data.

## EXPERIMENTAL

### Hard Latexes and Film Preparation

P-labeled PMMA-PIB latexes were prepared separately in a two-step process in which MMA in the first step was polymerized to low conversion in cyclohexane in the presence of PIB containing 2% isoprene units to promote grafting. The graft copolymer so produced served as a dispersant in the second stage of polymerization in which MMA was polymerized in a cyclohexane solution of the copolymer. Details were published elsewhere.<sup>13</sup> A stable spherical hard latex dispersion of polymer particles was produced, ranging in radius from 1 to 3  $\mu\text{m}$ . A combination of <sup>1</sup>H-NMR and UV analysis indicated that these particles contain 6 mol % PIB and 0.037 mmol P groups per gram of polymer. We refer to these particles as P (The particles were prepared in M. A. Winnik's Laboratory, University of Toronto, Toronto, Canada,

Latex film preparation was carried out in the following manner. The P-labeled PMMA-PIB particles were dispersed in heptane in a test tube. The solid content was equal to 0.5%. After complete mixing, film samples were prepared from this dispersion by placing the same numbers of drops on  $0.9 \times 3.2 \text{ cm}^2$  glass plates and allowing the heptane to evaporate. The liquid dispersion



**Figure 2** (a) Film formation and (b) dissolution cell, in Perkin Elmer Lambda 2S spectrophotometer.

from the droplets covered the whole surface area of the plate and remained there until the heptane evaporated. Samples were weighed before and after the film casting to determine the film thicknesses. The average size of the particles was taken as  $2\ \mu\text{m}$  to estimate the number of layers or the thicknesses of film samples, and the average film thickness was estimated as  $10\ \mu\text{m}$ . The films were annealed in an oven for 30 min above the  $T_g$  of PMMA, elevating the temperature to  $275^\circ\text{C}$ . The temperature was maintained within ( $2^\circ\text{C}$ ) during annealing. Stock solution for dissolution experiments was prepared from mixture of the chloroform (90%) and the heptane (10%, Solvents were purchased from Merck Co. (spectroscopically pure grade) and used as received. Because chloroform is a good solvent for PMMA, heptane is introduced into the mixtures to slow down the dissolution process.

### UVV Measurements

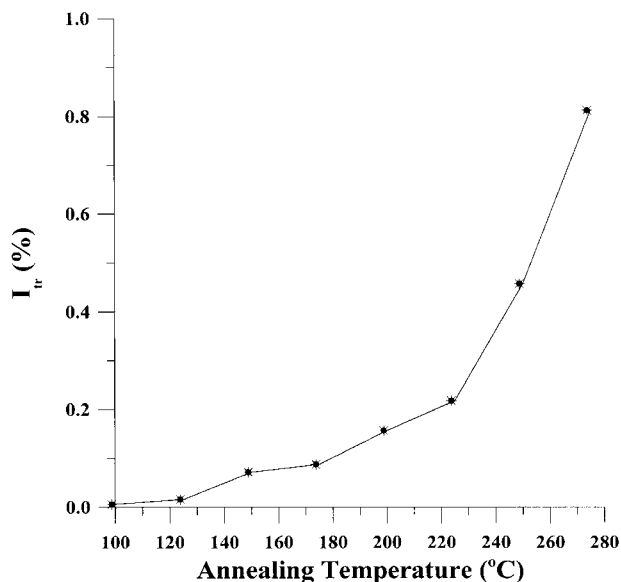
Measurements of transmitted photon intensities ( $I_{tr}$ ) during film formation and absorbance ( $A_p$ ) change during polymer dissolution were performed using a Perkin-Elmer Lambda 2S spectrophotometer (Norwalk, CT). After annealing,

each sample was placed in the spectrophotometer, and the  $I_{tr}$  of films were detected between 300 and 400 nm to monitor film formation [see Fig. 2(a)]. Dissolution experiments were performed in a  $1.0 \times 1.0 \times 4.5\text{-cm}^3$  quartz cell. Film samples were attached at one side of a UV quartz cell filled with a chloroform-heptane mixture. The cell was placed in the spectrophotometer and then illuminated with 345 nm excitation light, which is strongly absorbed by P. P absorbance ( $A_p$ ), which is proportional to the number of P-labeled chains in polymer-solvent solution change in the UV cell, was monitored as a function of time during the dissolution process, using the "time drive" mode of the spectrophotometer. The dissolution cell and the film position is presented in Figure 2(b). In dissolution experiments, film samples were dissolved in (90 + 10%) chloroform-heptane mixture. All UVV measurements were carried out at room temperature.

## RESULTS AND DISCUSSION

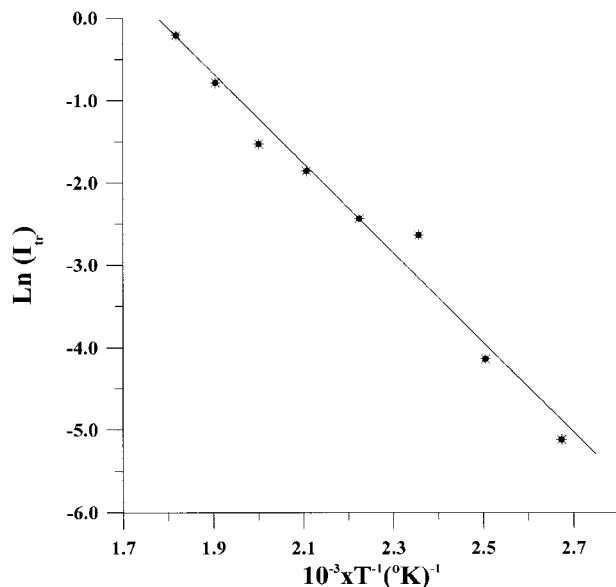
### Transparency of Films and Crossing Density

Transmitted photon intensities ( $I_{tr}$ ) were obtained and plotted versus annealing temperature

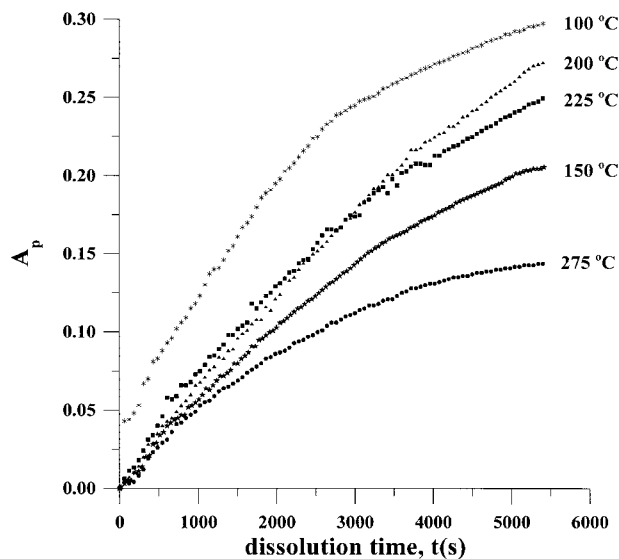


**Figure 3** Plot of transmitted photon intensity  $I_{tr}$  versus annealing temperature.

for the 30-min time interval (Fig. 3). It is seen that exponential increase in the  $I_{tr}$  was observed as the annealing temperature is increased. The increase in  $I_{tr}$  can be explained by the increase in transparency of latex film due to disappearing of particle–particle interfaces.<sup>16–20</sup> As the annealing temperature increases, some part of the poly-



**Figure 4** Fit of the data in Figure 3 to eq. (4) which produces  $\Delta E_{tr}$ .



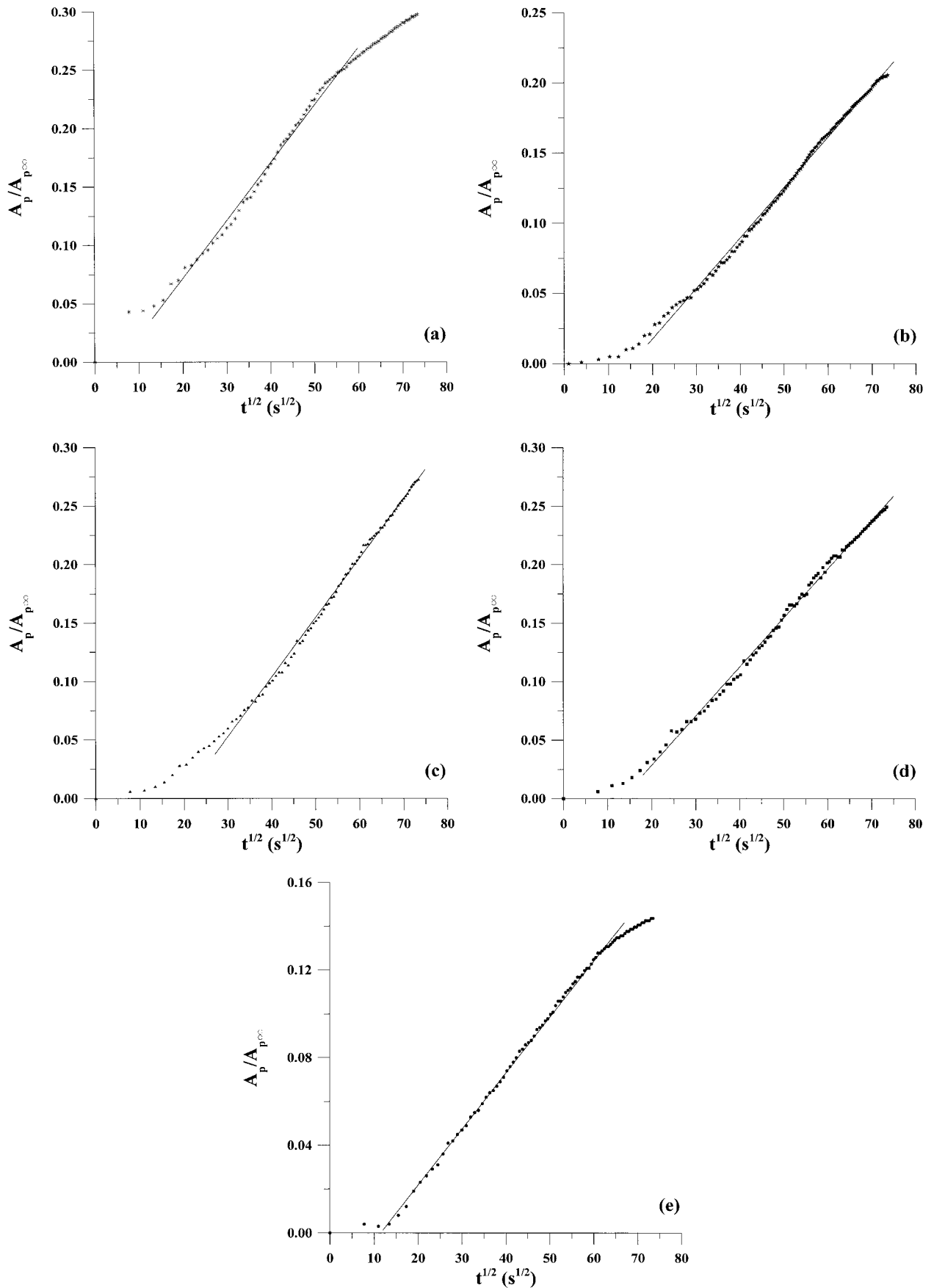
**Figure 5** P absorbance,  $A_p$ , versus dissolution time. Number on each curve indicate the annealing temperature of films. The cell was illuminated at 345 nm during dissolution experiment.

mer chains may cross the junction surface and particle boundaries start to disappear; as a result the transmitted photon intensity  $I_{tr}$  increases and the latex film becomes mechanically strong and transparent.

In order to quantify these results, the Prager–Tirrell (PT) model<sup>21</sup> for the chain-crossing density was used. These authors used de Gennes’ “reptation” model to explain configurational relaxation at the polymer–polymer junction, where each polymer chain is considered to be confined to a tube in which it executes a random back-and-forth motion. A homopolymer chain with  $N$  freely jointed segments of length  $L$  was considered by PT, which moves back and forth by one segment with a frequency  $\nu$ . The total “crossing density”  $\sigma(t)$  (chains per unit area) at junction surface was calculated from the contributions  $\sigma_1(t)$  due to chains still retaining some portion of their initial tubes, plus a remainder,  $\sigma_2(t)$ . Here the  $\sigma_2(t)$  contribution comes from chains that have relaxed at least once. In terms of reduced time  $\tau = 2\nu t/N^2$  the total crossing density can be written for small values  $\tau$  as

$$\sigma(\tau)/\sigma(\infty) = 2\pi^{-1/2}\tau^{1/2} \quad (1)$$

In order to compare our results with the crossing density of the PT model, the temperature depen-



**Figure 6** Plots of  $A_p$  values versus  $t^{1/2}$  for film samples annealed at (a) 100, (b) 150, (c) 200, (d) 225, (e) 275°C temperatures, where  $t$  is the dissolution time. Data are fitted to eq. (6) to produce  $D_1$  values.

dence of  $\sigma(\tau)/\sigma(\infty)$  can be modeled by taking into account the following Arrhenius relation for the linear diffusion coefficient:

$$\nu = \nu_0 \exp(-\Delta E/kT) \quad (2)$$

Here  $\Delta E$  is defined as the activation energy for the back and forth motion. Combining eqs. (1) and (2) a useful relation is obtained as

$$\sigma(T)/\sigma(\infty) = R \exp(-\Delta E/2kT) \quad (3)$$

where  $R = (8\nu_0 t / \pi N^2)^{1/2}$  is a temperature independent coefficient.

The increase in  $I_{tr}$  is already related to the disappearance of particle–particle interfaces, i.e., as annealing temperature is increased, more chains relaxed across the junction surface and as a result the crossing density increases. Now, it can be assumed that  $I_{tr}$  is proportional to the crossing density  $\sigma(T)$  and then the phenomenological equation can be written as

$$I_{tr}(T)/I_{tr}(\infty) = R \exp(-\Delta E_{tr}/2kT) \quad (4)$$

The logarithmic plot of  $I_{tr}$  versus  $T^{-1}$  is presented in Figure 4. The activation energy,  $\Delta E_{tr}$  is produced by fitting the data to eq. (4) as 21.61 kcal/mol. The obtained activation energy is typical for a backbone that crosses the polymer–polymer interface.<sup>22–24</sup>

### Film Dissolution and Moving Boundary Model

Labeled pyrenes in a polymer–solvent mixture in the UV cell was excited at 345 nm during dissolution experiments, and the variation in absorbance ( $A_p$ ) was monitored with the time drive mode of the spectrophotometer. P absorbance  $A_p$  is plotted in Figure 5 as a function of “dissolution time” for the film samples annealed at 100, 150, 200, 225 and 275°C temperatures. It can be seen that as the dissolution time increases, a continuous increase in  $A_p$  is observed for all film samples. It is interesting to note that film annealed at 100°C dissolved faster than the film annealed at 275°C.

Various mechanism and mathematical models were considered for the polymer dissolution. Tu and Quano<sup>25</sup> proposed a model that includes polymer diffusion in a liquid layer adjacent to the

polymer and moving out of the liquid–polymer boundary. The key parameter for this model was the polymer disassociation rate, defined as the rate at which polymer chains desorb from the gel interface. Lee and Peppas<sup>26</sup> extended this model for films to express the polymer dissolution rate where gel thickness was found to be proportional to (time)<sup>1/2</sup>. A relaxation-controlled model was proposed by Brochard and de Gennes,<sup>27</sup> where after a swelling gel layer was formed, desorption of polymer from the swollen bulk was governed by the relaxation rate of the polymer stress. This rate was found to be of the same order of magnitude as the reptation time. The dependence of the radius of gyration and the reptation time on polymer molecular weight and concentration were studied, using the scaling law,<sup>28</sup> based on the reptation model.

In this paper we considered a model in which diffusion occurs in two distinct regions, separated by a moving interface.<sup>1</sup> The moving interface can be marked by a discontinuous change in concentration as in the absorption by a liquid of a single component from a mixture of gases or by a discontinuity in the gradient of concentration, as in the progressive freezing of a liquid. The motion of the interface relative to the two regions it separates may be caused by the disappearance of matter at the interface in one or both regions, which results in a bodily movement of the matter in one or both regions relative to the interface. Discontinuities have been observed in several practical systems, for instance when two metals interdiffuse.<sup>1</sup> The sharp advancing boundary is well known in many polymer–solvent systems,<sup>29</sup> which is considered as a discontinuity for same purposes. When the diffusion coefficient is discontinuous at a concentration  $c$ , i.e., the diffusion coefficient is zero below  $c$  and constant and finite above  $c$ , then the total amount,  $M_t$  of diffusing substance desorbed from unit area of a plane sheet of thickness  $d$  at time,  $t$  is given by the following relation:

$$\frac{M_t}{M_\infty} = 2 \left( \frac{D_1}{\pi d^2} \right)^{1/2} t^{1/2} \quad (5)$$

where  $D_1$  is the constant diffusion coefficient at concentration  $c_1$ . Here  $M_\infty = c_1 d$  is the equilibrium value of  $M_t$ . If one assumes that the diffusion coefficient of polymer chains in film is negligible when compared to the desorbing coefficient,

**Table I** Desorbing Diffusion Coefficients Obtained by Fitting the Data in Figure 6 to Eq. (6) at Various Temperatures

	Annealing Temperature (°C)							
	100	125	150	175	200	225	250	275
$D_1 \times 10^{-11}$ (cm <sup>2</sup> s <sup>-1</sup> )	1.76	1.06	0.90	2.10	1.88	1.25	1.42	0.60

$D_1$  of polymer chains into solvent, then eq. (5) can be written to use our UVV data as follows:

$$\frac{A_p}{A_{p\infty}} = 2 \left( \frac{D_1}{\pi d^2} \right)^{1/2} t^{1/2} \quad (6)$$

here it is assumed that  $M_t$  is proportional to  $A_p$  at time,  $t$ .

Plots of  $A_p$  versus  $t^{1/2}$  are presented in Figure 6(a–e) for 100, 150, 200, 225, and 275°C annealing temperatures, respectively. The desorption diffusion coefficients,  $D_1$  are obtained from the linear fits in Figure 6 using eq. (6) and are listed in Table I. It is seen that  $D_1$  values are independent of the annealing temperatures of the films except at 275°C. The low value of  $D_1$  ( $0.6 \times 10^{-11}$  cm<sup>2</sup> s<sup>-1</sup>) at 275°C compared to average value of  $D_1$  ( $1.5 \times 10^{-11}$  cm<sup>2</sup> s<sup>-1</sup>) is attributed to very high annealing temperature, where mechanically strong film is obtained that is quite difficult to be dissolved. The delay in dissolution at early times is seen in Figure 6(a–e), which can be explained with the stage (b), where the gel layer is created by the relaxing polymer chains and as a result, no desorption has been showed yet. The observed  $D_1$  values are consistent with our early findings, obtained using fluorescence technique.<sup>9–12</sup> When one compares the observed  $D_1$  ( $10^{-11}$  cm<sup>2</sup> s<sup>-1</sup>) values with the backbone diffusion coefficient of the interdiffusing polymer chains during film formation from PMMA latex particles,<sup>30,31</sup> ( $\approx 10^{-16}$ – $10^{-14}$ ) 5 to 3 orders of magnitude difference can be seen. This is reasonable for the chains desorbing from swollen gel during dissolution of PMMA latex films.

In conclusion, this paper introduces a UVV technique for monitoring latex film formation and dissolution processes. It is observed that dissolution of latex film obeys the Moving Boundary model, and desorption diffusion coefficients are found to be independent of the annealing temperature. Here we have to also note that UVV tech-

nique is quite useful for measuring very small ( $=10^{-11}$  cm<sup>2</sup> s<sup>-1</sup>) diffusion coefficients.

## REFERENCES

1. Crank, J. *The Mathematics of Diffusion*, Clarendon Press, Oxford, UK, 1975.
2. Krasicky, P. D.; Groele, R. J.; Rodriguez, F. *J Appl Polym Sci* 1988, 35, 641.
3. Limm, W.; Dimnik, G. D.; Stanton, D.; Winnik, M. A.; Smith, B. A. *J Appl Polym Sci* 1988, 35, 2099.
4. Pascal, D.; Duhamel, J.; Wang, Y.; Winnik, M. A.; Napper, D. H.; Gilbert, R. *Polymer* 1994, 34, 1134.
5. Lu, L.; Weiss, R. G. *Macromolecules* 1994, 27, 219.
6. Krongauz, V. V.; Mooney, W. F., III; Palmer, J. W.; Patricia, J. J. *J Appl Polym Sci* 1995, 56, 1077.
7. Krongauz, V. V.; Yohannan, R. M. *Polymer* 1990, 31, 1130.
8. He, Z.; Hammond, G. S.; Weiss, R. G. *Macromolecules* 1992, 25, 501.
9. Pekcan, Ö.; Canpolat, M.; Kaya, D. *J Appl Polym Sci* 1996, 60, 2105.
10. Pekcan, Ö.; Ur, U.; Yilmaz, Y. *Polymer* 1997, 38, 2183.
11. Pekcan, Ö.; Ur, U. *Polymer* 1997, 38, 5579.
12. Pekcan, Ö.; Ur, U. *J Appl Polym Sci*, to appear.
13. Winnik, M. A.; Hua, M. H.; Hongham, B.; Williamson, B.; Croucher, M. D. *Macromolecules* 1984, 17, 262.
14. Pekcan, Ö.; Winnik, M. A.; Croucher, M. D. *Phys Rev Lett* 1988, 61, 641.
15. Pekcan, Ö. *Chem Phys Lett* 1992, 20, 198.
16. Pekcan, Ö.; Kemerolu, F. *J Appl Polym Sci*, 1999, 72, 981.
17. Pekcan, Ö.; Arda, E.; Kesenci, K.; Pigin, E. *J Appl Polym Sci* 1998, 68, 1257.
18. Pekcan, Ö.; Arda, E. *J Appl Polym Sci*, to appear.
19. Pekcan, Ö.; Arda, E. *Colloids; Surfaces A*, to appear.
20. Pekcan, Ö.; Canpolat, M.; Arda, E. *Polym Int*, to appear.
21. Prager, S.; Tirrell, M. *J Chem Phys* 1981, 75, 5194.
22. Canpolat, M.; Pekcan, Ö. *J Polym Sci Polym Phys Ed* 1996, 34, 691.

23. Canpolat, M.; Pekcan, Ö. *Polymer* 1995, 36, 4433.
24. Canpolat, M.; Pekcan, Ö. *Polymer* 1997, 38, 2595.
25. Tu, Y. O.; Quano, A. C. *IBM J Res Dev* 1977, 21, 131.
26. Lee, P. I.; Peppas, N. A. *J Controlled Release* 1987, 6, 207.
27. Brochardt, F.; de Gennes, P. G. *Phys Chem Hydrodynam* 1983, 4, 313.
28. Hartley, G. S. *Trans Faraday Soc* 1946, 42, B.6.
29. Papanu, J. S.; Soane, D. S.; Bell, A. T. *J Appl Polym Sci* 1989, 38, 859.
30. Winnik, M. A.; Pekcan, Ö.; Croucher, M. D. In *Scientific Methods for the Study of Polymer Colloids; Their Applications*; Candau, F.; Ottewill, R. H., Eds., NATO, ASI, Kluwer, New York, 1988; p 225.
31. Pekcan, Ö.; Winnik, M. A.; Croucher, M. D. *Macromolecules* 1990, 23, 2673.