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Molecular weight effect on polymer dissolution: a steady state fluorescence study

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Abstract

In situ steady state fluorescence (SSF) technique was used to study the dissolution of disc-shaped polymer glasses in various molecular weights, M_W. The glass discs were formed by free-radical polymerization of methyl methacrylate (MMA). Pyrene (P) was introduced during polymerization as a fluorescence probe to monitor the dissolution process in chloroform. Desorption of poly(methyl methacrylate) (PMMA) chains from discs were monitored simultaneously by observing the change of P fluorescence intensity, I. Diffusion model with a moving boundary was employed to quantify the fluorescence data observed from dissolving PMMA discs made at various molecular weights. It is observed that desorption coefficient, D decreased by increasing molecular weight, M_W by obeying $D \approx M^{-1}$ law. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Dissolution; Fluorescence; Molecular weight

1. Introduction

Polymer dissolution process from bulk is very different from, and more complicated than, small molecule dissolution. The dissolution of small molecules can be explained by simple diffusion laws [1] and a unique diffusion rate. However, polymeric glass dissolve mainly in three different stages: (a) solvent penetration, (b) polymer relaxation and for formation of moving boundary and (c) diffusion of polymer chains into solvent reservoir. A schematic representation of these three sequential steps for the dissolution of a polymer glass is presented in Fig. 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, backbone and side groups, as well as the thermal history of the polymer. These first solvent molecules act as plasticizer, and as a result these regions of the film start to swell. In the second stage, the relaxing polymer chains create gel layer. This moving transition layer is composed of both polymer chains and solvent molecules. If the solvent–polymer interactions are more dominant than polymer–polymer interactions, maximum swelling is obtained. This is the case when a good solvent is used during dissolution of a polymer glass. Here the advancing boundary is formed. In the last stage, chain disentanglement takes place, then chains separate from the bulk and diffuse into the solvent, while the advancing boundary moves across the polymeric glass. The rate of dissolution can be represented by a velocity of solvent penetration, which determines the velocity of the gel front penetrating into the polymeric glass substance. The velocity of dissolution increases with stirrer frequency and decreases with increasing the chain length due to an increasing entanglement of the polymer chains.

Poly(methyl methacrylate) (PMMA) film dissolution was studied using laser inter-ferometry by varying molecular weight and solvent quality [2]. Limm et al. [3] modified the inter-ferometric technique and studied the dissolution of fluorescence labeled PMMA films. By monitoring the intensity of fluorescence from the film along with the inter-ferometric signal, the solvent penetration rate into the film and the film dissolution were measured simultaneously. A real-time, nondestructive method for monitoring small molecules diffusion in polymers films was developed [4–8]. 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. Steady state fluorescence (SSF) studies on the dissolution of both annealed latex film and PMMA discs were reported using real-time monitoring of fluorescence probes [9–12].

Recently fast transient fluorescence (FTRF) method was

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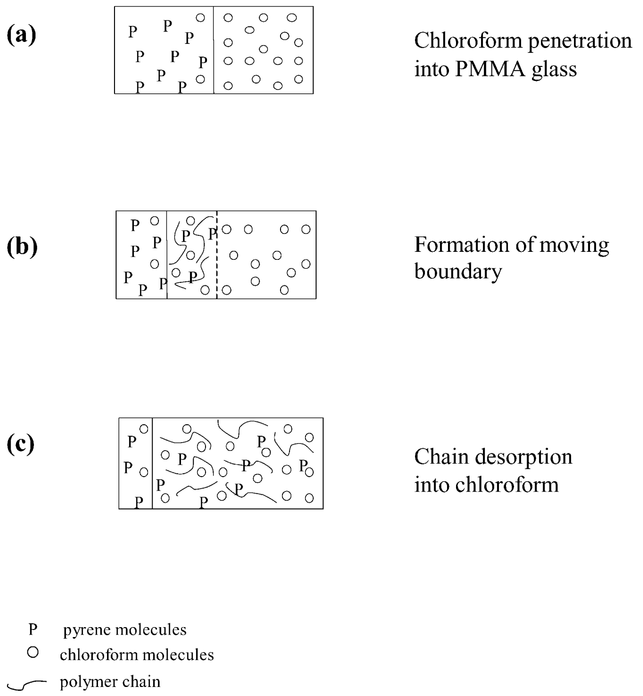

Fig. 1. Cartoon representation of the stages of polymer glass dissolution. *d* is the glass thickness.

used to monitor dissolution of polymer glasses [13,14]. The effect of γ-irradiation on latex film dissolution was extensively studied using SSF method, where two different regimes of dissolution coefficients were attributed to two different molecular weight distributions caused by scission and branching of polymer chains when they were irradiated by γ-rays [15].

In this work, SSF technique was used to study the dissolution of PMMA glasses prepared by free-radical polymerization (FRP). Pyrene (P) was simply added to the PMMA glass during FRP as a dye molecule, which is referred to as a probe. Six different glass discs were prepared with different molecular weights of PMMA using six different initiator contents. Disc thicknesses and diameter are tried to form equivalent. Chloroform was used as a dissolution agent and in situ SSF experiments were performed to monitor dissolution processes. Dissolution experiments were carried out by illuminating the chloroform reservoir and the increase in P intensity, *I*, was observed using fluorescence spectrophotometer.

2. Experimental

The monomers MMA (Merck, Germany) were freed from inhibitor by shaking with a 10% aqueous KOH solution, washing with water and drying over sodium sulfate. They were then distilled under reduced pressure over copper chloride. The initiator, 2,2′-azobisisobutyrronitrile (AIBN; Merck) was re-crystallized twice from methanol and the solvents chloroform and heptane (Merck) were used as they were received.

The radical polymerization of MMA was performed in bulk in the presence of AIBN as an initiator. AIBN and P (4×10^{-4} M) were dissolved in MMA and this solution was transformed into round glass tube of 15 mm internal diameter. Before polymerization, each solution was deoxygenated by bubbling nitrogen for 10 min. Radical polymerization of the MMA was performed at 65 ± 3 °C. Six different AIBN contents were used to prepare six different samples. After polymerization was completed the tube was broken and disc-shaped thin glasses were cut for the dissolution experiments. AIBN contents, molecular weights, disc thicknesses and their diameter are given in Table 1, Here the molecular weights, M_W were determined with size exclusion chromatography (Waters, model M-6000 A) equipped with refractive index detector using two polystyrene gel colon (500, 10,000 Å) at a flow rate of 1.0 ml/min in THF at 40 °C and using polystyrene standards.

Dissolution experiments were performed in a 1 × 1 cm quartz cell, equipped with a magnetic stirrer which was placed in the LS-50 Perkin–Elmer Spectrophotometer. Fluorescence emission was monitored at 90° angle so that the film samples were not illuminated by the excitation light. Disc-shaped samples were attached at one side of a quartz cell filled with chloroform. The cell was then illuminated with 345 nm excitation light. The P fluorescence intensity, *I*, was monitored during the dissolution process at 375 nm using the 'time drive' mode of the spectrofluorimeter. Emission of P was recorded continuously at 375 nm as a function of time until there was no observable change in intensity. The dissolution cell and the sample position are

Table 1
Experimentally observed parameters (M_W, molecular weight; AIBN, initiator; *D*, desorption coefficient; *d*, disc thickness; *R*, disc diameter)

$M_W \times 10^5$ (g/mol)	AIBN $\times 10^{-3}$ (g/ml)	Disc thickness *d* (cm)	Disc diameter *R* (cm)	$D \times 10^{-6}$ (cm^2 s^{-1})
23.2	0.5	0.20	0.81	4.4
18.2	1.0	0.21	0.81	5.1
10.6	4.0	0.23	0.80	11.3
6.4	6.0	0.21	0.82	12.0
7.5	7.5	0.23	0.80	14.2
1.9	10.0	0.23	0.80	26.6

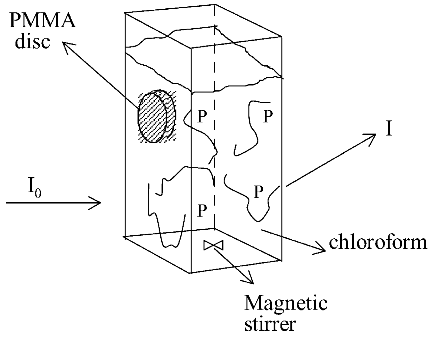

Fig. 2. Dissolution cell, in Perkin Elmer Lambda 2S spectrophotometer.

presented in Fig. 2. Six different dissolution experiments were run for different PMMA discs, which are in various molecular weights. Polymer–solvent mixture was stirred with a magnetic stirrer during dissolution process, to remove the gel layer.

3. Results and discussion

During dissolution experiments Ps in polymer–solvent mixture in the fluorescence cell were excited at 345 nm and the variation in P intensity, *I* was monitored with the time drive mode of the spectrophotometer. P intensities are plotted in Fig. 3 as a function of dissolution time, *t* for the six disc samples at different molecular weights. It is seen that as dissolution time is increased, continuous increase in *I* is observed for all disc samples. Here our aim is to interpret the increase in *I*, which most probably proportional to the number of polymer chains desorbing from PMMA disc during dissolution. Here 'formation of moving boundary' is in fact equivalent to the 'formation of a gel layer' at the surface of disc, which is known as case II diffusion [9]. Since high magnetic stirrer speed was used to gel layer can be removed immediately from the disc surface as a result dissolution of PMMA chains and P occurred simultaneously [10]. In Fig. 3, dissolution curves at early time show no indication to the formation of gel layer [9]. Under these circumstances number of P and PMMA chains in the solvent reservoir can be assumed to be proportional. Our previous findings [9–11] with P labeled and P free polymer films also supports this assumption i.e. when the high magnetic stirrer speed is used during dissolution of polymer and P behave in the same way. In Fig. 3, it is also seen that the rate of increase in *I* differs from sample to sample depending on the molecular weight of PMMA chains.

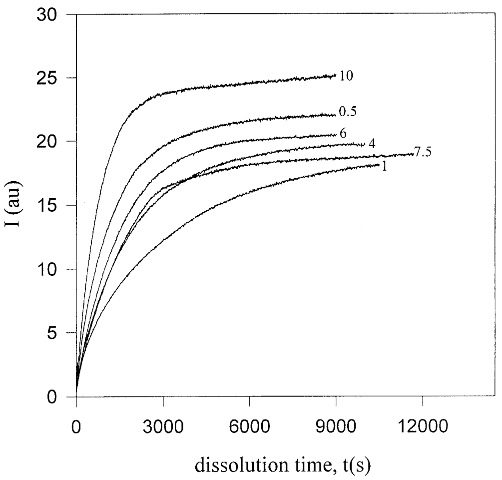

Fig. 3. Pyrene intensity, *I* versus dissolution time. Number on each curve indicate the AIBN content in g/ml × 10^{-3} at the disc samples. The cell was illuminated at 345 nm during dissolution.

Various mechanism and mathematical models were considered for the polymer dissolution. Tu and Quano [16] proposed a model which includes polymer diffusion in a liquid layer adjacent to the polymer and moving 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 [17] extended this model for films to the situations of the polymer dissolution rate where gel thickness was found to be proportional to $(\text{time})^{1/2}$. A relaxation controlled model was proposed by de Gennes and Brochard [18] 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 dependencies of the radius of gyration and the reptation time on polymer molecular weight and concentration were studied, using a scaling law [19], based on the reptation model.

In this paper, we considered a model in which diffusion occurs in two distinct regions separated by moving interface [1]. The moving interface can be marked by a discontinuous change in concentration, similar to that 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 separated by it may be caused by 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 inter-diffuse [1]. The sharp advancing boundary is well known in many polymer–solvent systems [20], 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

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

where D is 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 with compared to the desorbing coefficient, D of polymer chains into solvent, then Eq. (1) can be written to employ our fluorescence data as follows

$$\frac{I}{I_\infty} = 2\left(\frac{D}{\pi d^2}\right)^{1/2} t^{1/2} \qquad (2)$$

here it is assumed that M_t is proportional to P intensity, I at time, t.

Plots of I versus $t^{1/2}$ are presented in Fig. 4a, b and c for the disc containing 0.5, 4.0 and 10×10^{-3} g/ml AIBN, respectively. The desorption coefficients, D are obtained from the slope of linear relations in Fig. 4, using Eq. (2) and are listed in Table 1. It is observed that D values are strongly correlated with the AIBN contents in the disc samples. The linear relation of AIBN versus M_W in Fig. 5 suggest that increase in AIBN content decreases the molecular weight, M_W of PMMA chains in the disc samples. Fig. 6 presents the relation between D and M_W values, where D decreases as M_W is increased as expected. However, one would like to see the relation between D and M_W. The log D–log M_W plot in Fig. 7 shows a good linear relation except at one point i.e. at low molecular weight. The slope of the linear relation in Fig. 7 produce −0.92 which can be offer us the following relation:

$$D \approx M_W^{-1} \qquad (3)$$

between D and M_W values. Eq. (3) predicts that polymer chains reptates according to de Gennes' law [21] while

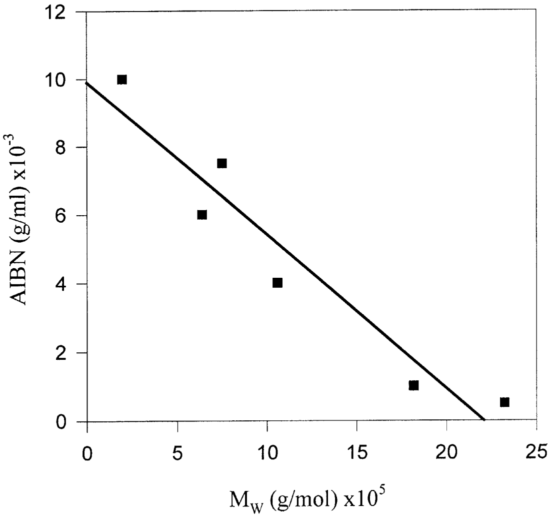

Fig. 5. The plot of AIBN content versus molecular weight, M_W of PMMA chains in disc samples.

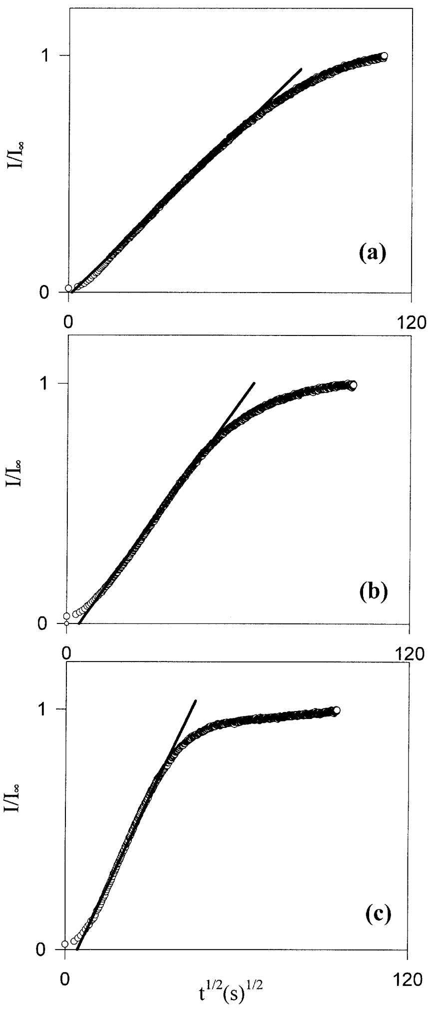

Fig. 4. Plots of I versus $t^{1/2}$ for disc samples produces with a, 0.5; b, 4.0 and c, 10.0 (10^{-3}) g/ml AIBN. Where t is the dissolution time. Data is fitted to Eq. (2) to produce desorption coefficients, D.

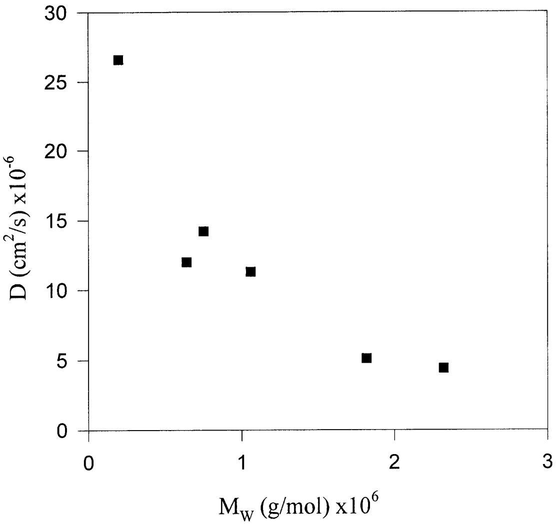

Fig. 6. The plot of desorption coefficient D versus M_W.

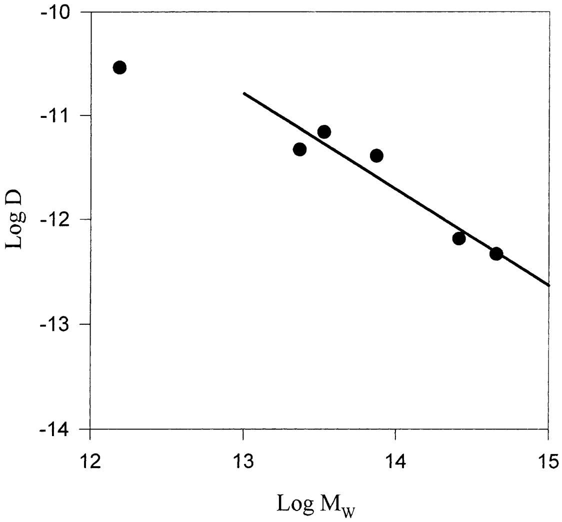

Fig. 7. Log–log plot of D versus M_W. The slope of the linear relation produce the value of -0.92.

they desorb from the glass disc. In other words when the reptating polymer chain completely escapes from its tube, it immediately desorbs into the chloroform reservoir.

In summary this work introduced the fluorescence technique to present the relation between molecular weight, M_W with the desorption coefficient, D during dissolution of polymer glasses.

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