

# Diffusion and Sorption Behavior of Glycidyl Methacrylate in Styrene Butadiene Rubber

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**ABSTRACT:** In this study, the diffusion and sorption behavior of glycidyl methacrylate in styrene butadiene rubber (SBR) was investigated as a function of waste tire powder content, sulfur content (i.e., the crosslink density), and temperature by using the gravimetric sorption method. The results indicate that penetrant solubility increases as sulfur and waste tire powder contents decrease, whereas the temperature affects the solubility favorably. The results also

indicate that mutual diffusion coefficients decrease as the sulfur and waste tire powder contents increase. This behavior was interpreted in terms of free volume of the polymer and tortuosity. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 86: 2701–2706, 2002

**Key words:** diffusion; rubber; crosslink density; glycidyl methacrylate

## INTRODUCTION

Rubber has been extensively used in many applications such as tires, sporting goods, cables, and hoses, and the amount of rubber consumption increases continuously. Therefore, used rubber causes a global waste problem and recycling of used rubber has been a great concern in environmental and economic aspects. Waste rubber products have few uses; most of these products are land filled or incinerated. However, most methods are not appropriate to handle waste rubber because they result in other environmental problems such as air pollution or float to surface over time. Reutilization technology of waste rubber, especially scrap tire powder, has been widely investigated as an alternative method.

A potential use of used rubber involves the utilization of ground rubber powder as a filler in plastic compounds.<sup>1</sup> However, the incorporation of rubber powder into polymers significantly reduces the mechanical properties of the resulting composites. Poor adhesion between polymer and filler is believed to be a major factor adversely affecting the mechanical properties.<sup>2–5</sup> To overcome this problem, various surface treatments of used rubber have been proposed. McInnis et al. chlorinated waste rubber powders by a gas-solid reaction with chlorine containing gas.<sup>6</sup> Bagheri et al. used surface-modified waste rubber powders

to toughen epoxy polymers.<sup>7</sup> Redox method and grafting by  $\gamma$ -irradiation were also used to reuse waste rubber.<sup>8</sup> Recently, Kim et al. reported on the use of waste rubber powder as a polymer filler.<sup>9</sup> Rubber powder surface was photografted with acryl amide and this rubber powder was extruded with high-density polyethylene with a suitable third component.

Photografting, initiated by ultraviolet (UV) light using a photoinitiator, is an interesting alternative approach used to increase the surface activity of rubber particle. In 1978, Tazuke and coworkers photografted acrylamide onto a polypropylene surface.<sup>10,11</sup> Irradiation was carried out through a polymer film in contact with a solution of monomer and benzophenone. Zhang and Ranby developed a continuous method based on the same principle.<sup>12,13</sup> In this case, the irradiation was carried out through a thin layer of monomer, photoinitiator, and solvent of the film after dipping in the corresponding solution. On the other hand, Kubota first coated the polymer film with a thin layer of poly(vinyl acetate) containing the photoinitiator and then the irradiation was performed in the presence of a monomer solution.<sup>14,15</sup>

In these studies, possible diffusion of monomer and photoinitiator into the film was not discussed. Ruckert et al. grafted water-soluble vinyl monomers to the styrene-(ethylene-*co*-butene)-styrene (SEBS) triblock copolymer by using two different methods and taking into account diffusion phenomena.<sup>16</sup> The methods consisted of successive (I) or simultaneous (II) diffusion of benzophenone and monomer into the film followed by UV irradiation of the film. According to their experimental results, diffusion phenomena into

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the bulk of the material could not be neglected when photografting monomers onto the polymer surface was studied. Because monomer and benzophenone easily diffused into SEBS copolymer, grafting could not take place exclusively at the surface. Grafting by method I resulted in no surface modification because the photoinitiator was leached out of the superficial layer, while grafting could occur in the superficial layer in method II and had an influence on the surface properties. By grafting with method II, the depth of grafted layer could, in principle, be controlled by the diffusion time.

In this study, the diffusion and sorption behavior of glycidyl methacrylate in styrene butadiene rubber (SBR) was investigated as a function of waste tire powder content, crosslink density, and the temperature using the gravimetric sorption method.

## EXPERIMENTAL

### Sample preparation

SBR (Kosyn 1502) was kindly provided by Keumho Petrochemical Co. (Seoul, Korea) and contained 23.5% styrene and 76.5% butadiene. The waste tire powder containing about 25% carbon black (GF 120) was purchased from Rouse Co. (Portland, OR), whereas sulfur was obtained from Miwon Trading Co. (Anyang, Korea). Zinc oxide (ZnO) and stearic acid, which were used as activators, were obtained from Hanil Chemical Co. (Bucheon, Korea) and Dongsan C & G Co. (Cheonan, Korea), respectively. Glycidyl methacrylate (GMA) (98%) was purchased from Junsei Chemical Co. (Tokyo, Japan). All chemicals were used as received from producers without further purification. The ingredients were mixed homogeneously by using a Banbury mixer (Farrel Co., Ansonia, CT) at 140–150°C for a predetermined period. The samples were then prepared by hot pressing at 180°C and 5500 p.s.i. for 10 min. The compositions of samples used in this

**TABLE I**  
Composition of Vulcanized-SBR Rubbers  
Used in this Study

	SBR	ZnO	Stearic acid	Sulfur	Waste tire powder
A-1	100	5	1	1	0
A-2	100	5	1	5	0
A-3	100	5	1	11	0
A-4	100	5	1	20	0
B-1	100	5	1	1	10
B-2	100	5	1	5	10
B-3	100	5	1	11	10
B-4	100	5	1	20	10
C-1	100	5	1	1	20
C-2	100	5	1	5	20
C-3	100	5	1	11	20
C-4	100	5	1	20	20

**TABLE II**  
Physical Parameters of Materials Used in this Study

Parameter	Value
$M_n$ (g/mol)	$2.19 \times 10^5$
$V_{od}$ (cm <sup>3</sup> /mol)	194.9
$d_d$ (g/cm <sup>3</sup> )	0.73
$d_r$ (g/cm <sup>3</sup> )	0.93
$\chi$ (-)	0.44

study are provided in Table I. The physical parameters of materials used are given in Table II.

### Determination of crosslink density

Crosslink density of the vulcanized rubber was determined by swelling experiments. The rubber samples were cut into small pieces and organic ingredients in the sample were removed by using the acetone in a Soxhlet for 12 h. The samples were then dried in a vacuum oven for 1 day at 80°C and weighed. The samples were then immersed in a *n*-decane bath. After 2 days, the samples were taken out of the bath and the sample weight was measured again.

### Diffusion experiments

The rubber samples were cut into 1.6 × 5 cm pieces and the initial weight was measured. The samples were then put into a GMA bath and the weight gain of the sample was measured as a function of time. The temperature of the GMA bath was regulated by the heating element within ±0.1°C variation. The schematic diagram of the sorption apparatus is shown in Figure 1. The experiments were performed at 35, 45, 55, and 65°C, respectively.

## THEORETICAL BACKGROUND

### Determination of crosslink density

Crosslink density of the vulcanized rubbers was determined by using the Mooney–Rivlin equation as follows:

$$X_c = \frac{(Bd_rRT + C_1 - A) + [(BC_1d_rRT - A)^2 + 4ABd_rRT]^{1/2}}{2d_rRT} \quad (1)$$

$$B = \frac{2.3}{2 \times M_n} \quad (2)$$

$$C_1 = \frac{-W_sRT[\ln(1 - V_{ro}) + V_{ro} + \chi V_{ro}^2]}{2V_{od}V_{ro}^{1/3}} \quad (3)$$

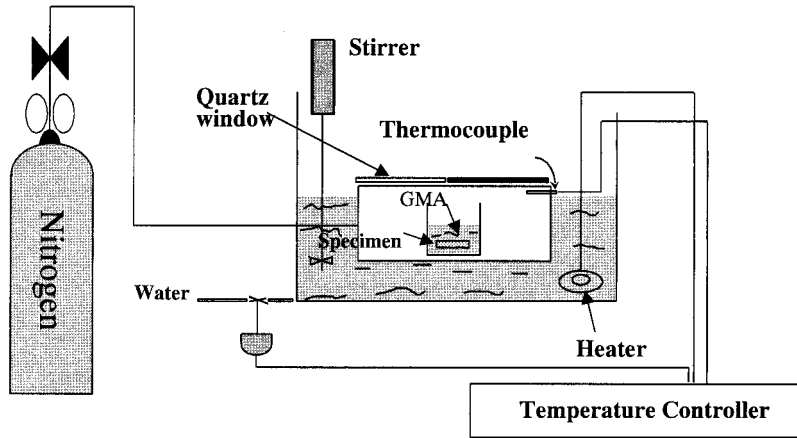


Figure 1 A schematic diagram of the sorption apparatus.

$$V_{ro} = V_r \times (0.56e^{-z} + 0.44) \quad (4)$$

where  $A$  is a constant ( $0.78 \times 10^6$ ),  $d_r$  is the density of rubber network,  $M_n$  is the number-average molecular weight of rubber network,  $W_s$  and  $\omega_c$  are the weights of the swollen sample and the weight fraction of the carbon black in the sample, respectively,  $V_r$  and  $V_{ro}$  are the volume and the corrected volume of the rubber network, respectively, and  $V_{od}$  is the molar volume of the solvent.

**Determination of diffusion coefficients**

If the diffusion coefficient is independent of concentration, the one-dimensional diffusion process is generally described by the following expression:

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} \quad (5)$$

with the following initial and boundary conditions for a film of thickness  $2l$  ( $-l$  to  $l$ ) exposed to an infinite reservoir of penetrant:

$$C = C_0 \quad \text{at} \quad 0 < x < l, \quad t = 0$$

$$C = C_1 \quad \text{at} \quad x = l, \quad t \geq 0$$

$$\frac{\partial C}{\partial x} = 0 \quad \text{at} \quad x = 0, \quad t \geq 0$$

where  $C$  is the penetrant concentration and  $D$  is the mutual diffusion coefficient. One solution of eq. (5) with these initial and boundary conditions is given by:<sup>17</sup>

$$\frac{C - C_0}{C_1 - C_0} = 1 - \frac{4}{\pi} \sum_{n=0}^{\infty} \frac{(-1)^n}{2n + 1} \times \exp \left[ \frac{-D(2n + 1)^2 \pi^2 t}{4l^2} \right] \cos \left[ \frac{(2n + 1)\pi x}{2l} \right] \quad (6)$$

In sorption experiments, the sorbed mass is obtained by integrating eq. (6) over the film thickness. If  $M_t$  denotes the total amount of penetrant that has diffused into the polymer sample at time  $t$ , and  $M_{\infty}$  is the corresponding quantity at equilibrium, the following equation can be derived<sup>17</sup>:

$$\frac{M_t}{M_{eq}} = 1 - \sum_{n=0}^{\infty} \frac{(-1)^n}{2n + 1} \exp \left[ \frac{-D(2n + 1)^2 \pi^2 t}{4l^2} \right] \times \cos \left[ \frac{(2n + 1)\pi x}{2l} \right] \quad (7)$$

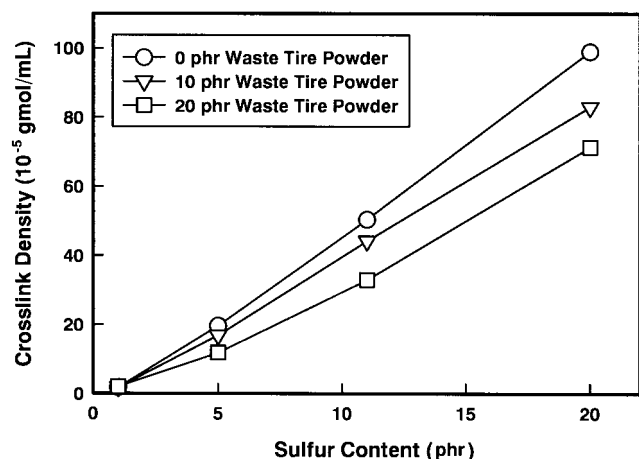


Figure 2 Effect of sulfur content on the crosslink density for waste tire powder contents.

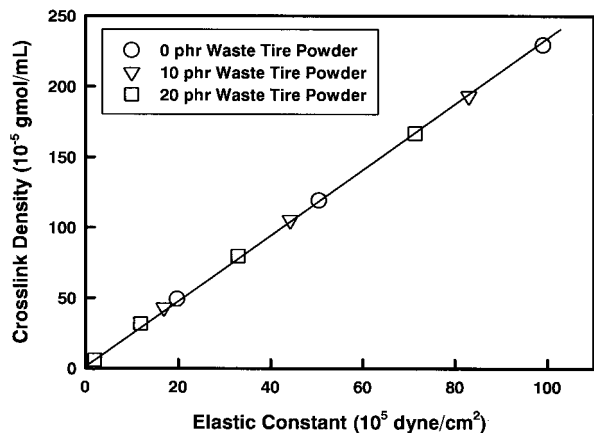


Figure 3 A relationship between crosslink density and elastic constant.

At short times, the solution can be approximated as:

$$\frac{M_t}{M_\infty} = \frac{2}{\sqrt{\pi}} \left( \frac{Dt}{l^2} \right)^{1/2} \quad (8)$$

Consequently, by plotting  $\sqrt{t}$  versus  $M_t/M_\infty$ , the diffusion coefficient can be determined from the initial slope,  $S_i$ , in accordance with the relation:

$$D = \frac{\pi}{4} S_i^2 l^2 \quad (9)$$

### RESULTS AND DISCUSSION

Dependence of crosslink density of the vulcanized rubbers on the sulfur and waste tire powder (WTP) contents is shown in Figure 2. Crosslink density increases with sulfur content as expected. For the same sulfur content, the crosslink density decreases as the WTP content increases. This is because the crosslinking reaction is inhibited in the presence of waste rub-

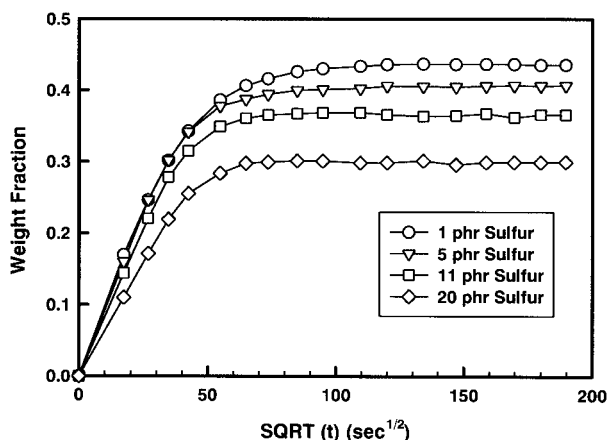


Figure 4 Effect of sulfur content on the penetrant solubility at 55°C for samples containing various amounts of sulfur.

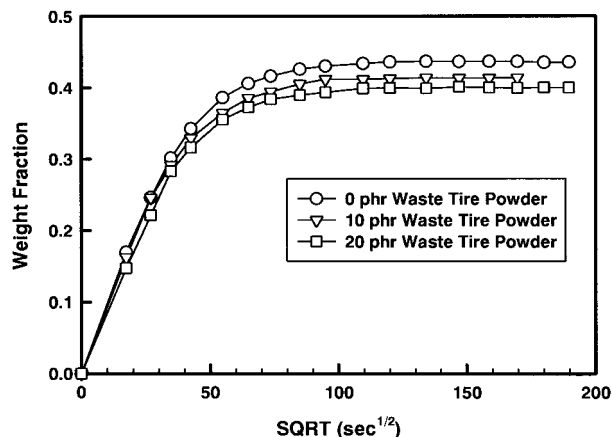


Figure 5 Effect of waste rubber powder content on the penetrant solubility at 55°C for samples containing 1 phr sulfur and various amounts of waste tire powder.

ber powder. In Figure 3, a linear relationship between the elastic constant and the crosslink density of the vulcanized rubbers is shown for various WTP contents.

The effect of sulfur and WTP contents and temperature on the solubility of glycidyl methacrylate in SBR was investigated. In Figure 4, experimental results at 55°C for the samples containing various amounts of sulfur are shown. By increasing the sulfur content (and, hence increasing crosslink density), the solubility of glycidyl methacrylate in SBR decreases. The trend is similar within the experimental temperature range and for the samples containing waste tire powder (data not shown). In Figure 5, experimental results at 55°C for the samples containing 1 phr sulfur and various amounts of waste tire powder are shown. As the WTP content increases, the solubility of glycidyl methacrylate in SBR decreases. However, the effect of WTP content on the penetrant solubility is less pronounced than the effect of sulfur content. The trend is similar at different temperatures and for the samples

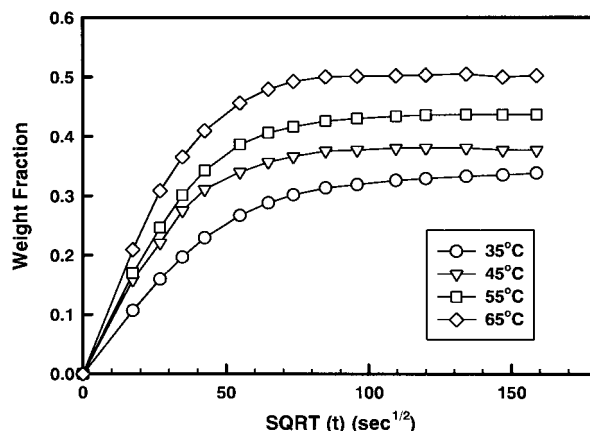
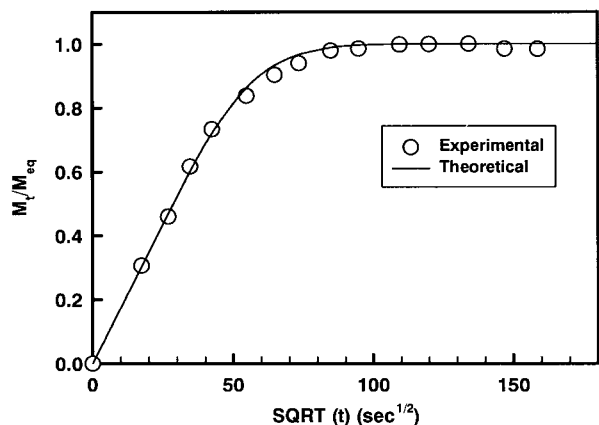


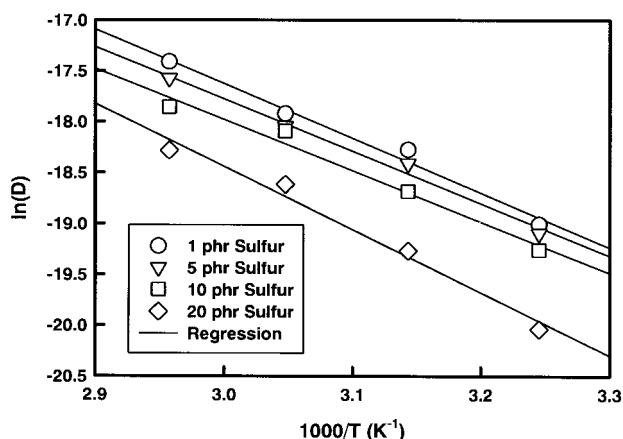
Figure 6 Effect of temperature on the penetrant solubility for samples containing 1 phr sulfur.



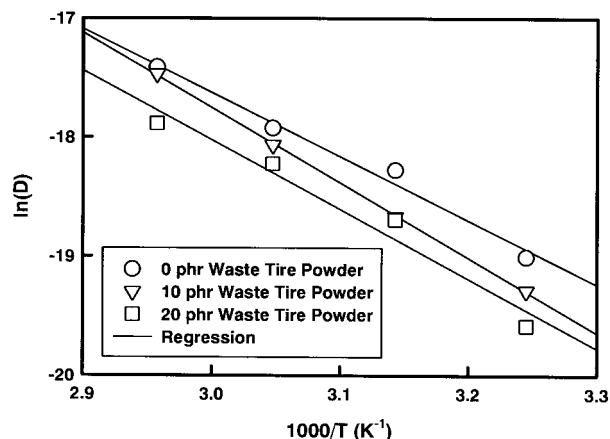
**Figure 7** Experimental results for the sorption of glycidyl methacrylate in SBR with 1 phr sulfur content at 45°C. The line represents the theoretical prediction for Fickian diffusion.

containing higher amounts of sulfur (data not shown). In Figure 6, experimental results at various temperatures for the sample containing 1 phr sulfur are shown. By increasing the temperature, the solubility of glycidyl methacrylate in SBR increases. Once again, the trend is similar for the samples containing higher amounts of sulfur and waste tire powder (data not shown).

The comparison between the un-steady-state diffusion equation and the experimental results at 45°C for the sample containing 1 phr sulfur is shown in Figure 7. The results indicate that the experimental data agree well with the Fickian diffusion model. Therefore, the conventional data analysis procedure based on the initial slope method can be used for this system. The effect of sulfur content (i.e., the crosslink density) on the diffusion coefficient is provided in Figure 8. The results show that the diffusion coefficient decreases with an increase in the sulfur content. The decrease of



**Figure 8** Effect of temperature on the diffusion coefficients as a function of sulfur content for the samples without waste tire powder.



**Figure 9** Effect of temperature on the diffusion coefficients as a function of waste tire powder content for the sample with 1 phr sulfur content.

the diffusion coefficient is more pronounced at 20 phr sulfur content. The trend is similar for the samples containing waste tire powder (data not shown).

Several researchers studied the effect of crosslink density and temperature on diffusion coefficients in rubber/solvent systems.<sup>18-22</sup> Data from all investigators showed that there was significant decrease in the diffusion coefficient with an increase in crosslink density. The addition of crosslinking into a polymer will obviously inhibit the motions of the polymer chains which occur because of thermal fluctuations. Consequently, the free volume of a crosslinked polymer will be less than the free volume of a noncrosslinked polymer and the diffusion coefficient will decrease. The activation energy for the diffusion was determined from the slope of the plot. The results imply that the activation energy increases as the sulfur content increases. Barrer and Skirrow presented diffusion data for the effect of crosslinking, temperature, and solvent type on the diffusion process for crosslinked rubbers.<sup>18</sup> They also reported that the activation energy increases with increasing the degree of crosslinking.

In Figure 9, the effect of WTP on the diffusion coefficient is shown for the sample containing 1 phr sulfur. The results show that the diffusion coefficient decreases as the WTP content increases. According to the data shown in Figure 2, the crosslink densities of the samples containing 1 phr sulfur and various amounts of waste tire powder are very similar. Therefore, the decrease of diffusion coefficient with increasing WTP content is due to the filler effect. In other words, the incorporation of the waste tire powder containing carbon black into the SBR rubber increases the tortuosity of the sample and the effective diffusion coefficient decreases. However, the effect of WTP content on the diffusion process is less noticeable than the effect of sulfur content. The trend is similar for the samples containing higher amounts of sulfur (data not shown).

## CONCLUSION

The results presented in this study show that the crosslink density increases with increasing sulfur contents and there is a linear relationship between the crosslink density and the elastic constant. The results also show that penetrant solubility and diffusion coefficient decrease with increasing waste tire powder and sulfur contents, whereas the temperature favorably affects the solubility and diffusivity. Diffusion of glycidyl methacrylate in SBR follows the typical Fickian diffusion process. The activation energy for diffusion increases as the sulfur content (and, hence the crosslink density) increases.

## References

1. Scheirs, J. *Polymer Recycling: Science, Technology and Applications*; Wiley: New York, 1998.
2. Phadke, A. A.; Chakraborty, S. K.; De, S. K. *Rubber Chem Technol* 1984, 57, 19.
3. Rodriguez, E. L. *Polym Sci Eng* 1988, 28, 455.
4. Duhaime, J. R. M.; Baker, W. E. *Plast Rubber Compos Process Appl* 1991, 15, 87.
5. Choudhury, N. R.; Bhattacharya, S. N. *Plast Rubber Compos Process Appl* 1996, 25, 448.
6. McInnis, E. L.; Bauman, B. D.; Williams, A. U.S. Pat. 5,506,283, 1996.
7. Bagheri, R.; Williams, M. A.; Pearson, R. A. *Polym Eng Sci* 1997, 37, 245.
8. Adam, G.; Sebenik, A.; Osredkar, U.; Veksli, Z.; Ranogajec, F. *Rubber Chem Tech* 1990, 63, 660.
9. Kim, J. I.; Ryu, S. H.; Lee, K. I. paper presented at International Rubber Conference '99 Seoul; Seoul, April 1999.
10. Tazuke, S.; Kimura, H. *Makromol Chem* 1978, 179, 2603.
11. Tazuke, S. *Polym Plast Technol Eng* 1980, 14, 107.
12. Zhang, P. Y.; Ranby, B. *J Appl Polym Sci* 1990, 40, 1647.
13. Zhang, P. Y.; Ranby, B. *J Appl Polym Sci* 1991, 43, 621.
14. Kubota, H. *J Appl Polym Sci* 1990, 41, 689.
15. Kubota, H. *J Appl Polym Sci* 1993, 48, 1717.
16. Ruckert, D.; Geuskens, G.; Fondu, P.; Van Erum, S. *Eur Polym J* 1995, 31, 431.
17. Crank, J. *The Mathematics of Diffusion*, 2nd ed.; Oxford: New York, 1975; pp 44–68.
18. Barrer, R. M.; Skirrow, G. *J Polym Sci* 1948, 3, 549.
19. Aitken, A.; Barrer, R. M. *Trans Faraday Soc* 1955, 51, 116.
20. Chen, S. P.; Ferry, J. D. *Macromolecules* 1968, 1, 270.
21. Hayes, M. J.; Park, G. S. *Trans Faraday Soc* 1955, 51, 1134.
22. Unnikrishnan, G.; Thomas, S. *J Polym Sci: Polym Phys Ed* 1997, 35, 725.