

# Synthesis and Properties of Oil Absorption Resins Filled with Polybutadiene

Guo-Rong Shan, Ping-Ying Xu, Zhi-Xue Weng, Zhi-Ming Huang

*Institute of Polymer Engineering, Department of Chemical Engineering, Zhejiang University, Hangzhou 310027, China*

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**ABSTRACT:** Polybutadiene (PB) is used to fill an oil absorption resin as a physical crosslinker to construct a kind of 3-dimensional network with a high degree crosslinking and low crosslink density. A series of acrylic resin particles with various compositions are prepared by suspension polymerization, using benzoyl peroxide (BPO) as an initiator and ethylene glycol dimethacrylate (EGDMA) as a chemical crosslinker. The effects of the polymerization temperature, initiator concentration, monomer feed ratio, and chemical and physical crosslinker concentrations on the oil absorbency and gel fraction (degree of crosslinking) are studied. The recipe and operation conditions are optimized as follows: a mass ratio of 3:1 for styrene (St)/dodecyl methacry-

late or St/butyl acrylate, 0.5 wt % BPO, and 80°C for 7–8 h. The effect of the physical crosslinker (PB) concentration is complex. The oil absorbency increases with increasing PB at lower EGDMA concentrations. However, under this same condition, particles cannot be formed if the PB concentration is higher than a certain value. By contrast, there is an optimum PB concentration when the EGDMA concentration is higher. The oil absorption speed is also investigated. The presence of PB can speed up absorption. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 89: 3309–3314, 2003

**Key words:** oil absorption resin; methacrylate; physical crosslinking

## INTRODUCTION

High oil absorption resins usually are crosslinked copolymers that have many good properties,<sup>1</sup> such as fast oil absorption speed, convenient recovery, and resistance to water. Crosslinking is responsible for a 3-dimensional network structure, and the oil absorption process is an expansion process of this 3-dimensional network. A good network should be relaxed and easy to be penetrate with oil. A large degree of crosslinking along with a small crosslink density will meet the requirements. The degree of crosslinking is the fraction of crosslinks in a resin, which is expressed by the gel fraction. The crosslink density refers to the reciprocal of the molecular chain length between two crosslinking points of the network.

Generally, the crosslinker has two double bonds. The crosslink degree and density of the network will increase rapidly with the increase of the crosslinker. It is difficult to form a kind of relaxing network with both a high gel fraction and low crosslink density.

Hence, polybutadiene (PB) is suggested to partially replace the commonly used crosslinker. PB is a soft long-chain macromolecule containing one double bond in the monomeric unit, so its crosslinking effect

is much weaker than that of the usual crosslinkers. The introduction of PB into the crosslinked copolymer will enhance the molecular chain length between crosslinking points and increase the physical crosslink fraction via increasing the probability of entanglement and so on. The introduction of PB is expected to produce a relaxing network with a high degree of crosslinking and low crosslink density, which would finally meet the need for improving the oil absorption capacity and reversible oil-releasing ability.

Cai and Salovey<sup>2</sup> suggested that either particle clustering or a network of filler particles acted as a temporary physical crosslink relative to vulcanization of rubber. Similarly, PB is specified as a physical crosslinker here, and the commonly used crosslinker is specified as the chemical crosslinker. In this work, the effects of the polymerization conditions, including the polymerization temperature, initiator concentration, monomer mass ratio, and physical and chemical crosslinker concentrations, on the oil absorbency and gel fraction were investigated. The oil absorption speed and mainly the influence of PB were also studied.

## EXPERIMENTAL

Polymerization was carried out in a suspension process. A mixture of monomers, initiator, crosslinker, dispersant, and water at a given molar ratio was introduced into a 500-mL reactor and then polymerized at 80°C for 8 h. The copolymer was obtained as beads.

Correspondence to: G.-R. Shan (shanr@che.zju.edu.cn).

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After the polymerization, the beads were decanted, washed with distilled water, and dried in a vacuum oven for 2 days at 50°C.

### Oil absorbency

The oil absorbency ( $W$ ) was determined by the weighing method. A quantity of 0.1–0.2 g of dried sample weighed beforehand was put into a filter bag and immersed in oil at room temperature. After given time periods (24 h is needed for full oil absorbency), the filter bag with the sample was lifted from the oil and drained for 1 min. Then the sample was immediately taken out and weighed. The oil absorbency was calculated by the following formula:

$$W = (G_2 - G_1)/G_1$$

where  $G_1$  and  $G_2$  are the weights of resin before and after oil absorption, respectively. Except in special explanations, the term “oil absorbency” is specified as full oil absorbency.

### Crosslink density

The crosslink density ( $\nu$ ) was calculated by the following expression developed by Flory<sup>3</sup> and later modified by Bray and Merrill<sup>4</sup>:

$$u = \frac{1}{M_c} = \frac{2}{M_n} - \frac{(u/V_1) \{ \ln(1 - u_{2,s}) + u_{2,s} + \chi u_{2,s}^2 \}}{u_{2,r} \left\{ (u_{2,s}/u_{2,r})^{1/3} - \frac{1}{2} (u_{2,s}/u_{2,r}) \right\}}$$

where  $M_c$  is the number-average molecular weight between two crosslink points,  $u$  is the specific volume of the monomers before crosslinking,  $M_n$  is the number-average molecular weight of uncrosslinked polymer as measured by GPC,  $V_1$  is the molar volume of the oil,  $u_{2,r}$  is the relaxed polymer volume fraction,  $u_{2,s}$  is the equilibrium polymer volume fraction, and  $\chi$  is the copolymer–oil interaction parameter.

An equilibrium swelling experiment<sup>5</sup> was used to determine the polymer volume fraction before ( $u_{2,r}$ ) and after ( $u_{2,s}$ ) swelling. The volume of resin after polymerization ( $V_r$ ) was determined by measuring the displaced volume of resin in a nonsolvent (ethanol). The samples were then allowed to swell to equilibrium in vinyl trichloride for 24 h, and their volume ( $V_s$ , the volume of the resin after equilibrium swelling) was measured. Finally, the volume of the dry samples ( $V_d$ ) was measured by the same method after drying under a vacuum at 50°C for 24 h.

The values of  $u_{2,r}$  and  $u_{2,s}$  were calculated from the following equations:

$$u_{2,r} = V_d/V_r$$

$$u_{2,s} = V_d/V_s$$

The copolymer–oil interaction parameter was calculated as follows<sup>6</sup>:

$$\chi = \frac{\ln(1 - v_2) + v_2 + V_1(v/V_0)v_2^{1/3}(1 - K(v_2))}{v_2^2}$$

$$\frac{v}{V_0} = \frac{\Phi \omega_j \rho_d}{2 M_j}$$

$$\frac{1}{v_2} = 1 + \left( \frac{\omega_{sw}}{\omega_d} - 1 \right) \frac{\rho_d}{\rho}$$

where  $v_2$  is the polymer volume fraction in the swollen network,  $\rho$  is the oil density,  $\rho_d$  is the sample density (0.9–0.95 g/cm<sup>3</sup>, measured by the density method),  $v/V_0$  is the concentration of the elastic network chains at the reference state, and  $\omega_j$  is the weight fraction of the crosslinker of molar mass  $M_j$  and functionality  $\Phi$ . We assumed it is an affine network model and thus<sup>6</sup>  $K = v_2^{2/3}$ .

### Gel fraction

The gel fraction ( $G$ ) was measured by a extraction method. A weighed filter paper bag with a weighed dried sample was put into a Soxhlet extractor in a water bath at about 70°C. The sample was extracted with tetrahydrofuran for 24 h and then the filter paper bag was weighed after drying in a vacuum oven for 2 days at 50°C. The  $G$  value was calculated according to the following equation:

$$G = \frac{G_a}{G_b} \times 100\%$$

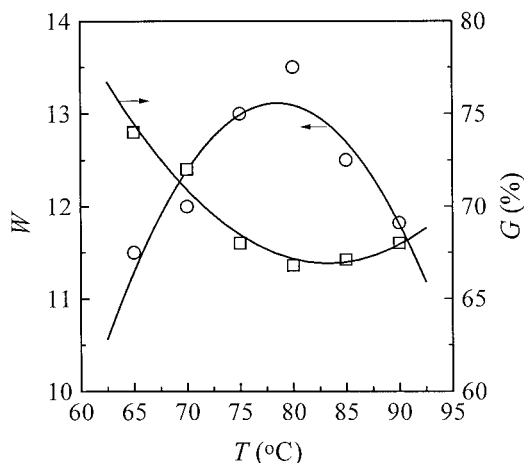
where  $G_a$  and  $G_b$  are weights of resin after and before extraction, respectively.

## RESULTS AND DISCUSSION

### Effect of polymerization temperature

In free-radical polymerization, the increase of the polymerization temperature will enhance the rates of initiation, lead to the formation of more basic chains, and then increase the crosslink density and degree of crosslinking. On the other hand, it will increase the free volume and decrease the flow activation energy of macromolecules. This provides the polymer system with enough moving space, even in the case of a higher gel fraction, and then a decrease of the crosslink density, as well as the degree of crosslinking.

The final result of these two opposite effects from the increase of the polymerization temperature is

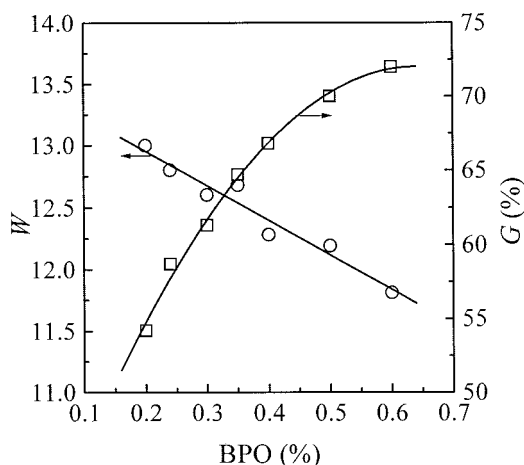


**Figure 1** The effect of the polymerization temperature on the oil absorbency and gel fraction for 3:1 St/DMA, 0.4 wt % EGDMA, and 0.5 wt % BPO.

shown in Figure 1. Polymerization was performed at various temperatures with other operation parameters at definite values. When the polymerization temperature increases, the oil absorbency will increase to a maximum first, corresponding to a minimum gel fraction at 80°C, then gradually decrease.

#### Effect of initiator concentration

The initiator concentration has great effects on free-radical crosslinking copolymerization. As shown in Figure 2, the oil absorbency is decreased and the gel fraction is increased with the increase of the benzoyl peroxide (BPO) concentration. It is known that more initiator will generate more active centers in order to increase the conversion and gel fraction and decrease the length of the basic chain in polymer systems. Moreover, the probability of an effective crosslinking



**Figure 2** The effect of the initiator concentration on the oil absorbency and gel fraction for 3:1 St/DMA and 0.4 wt % EGDMA at 80°C.

**TABLE I**  
Effect of Monomer Ratio on Oil Absorbency

Monomer	Ratio	Absorbency	
		Vinyl Trichloride	Benzene
St/DMA	2:1	15.10	5.38
	1:1	16.55	10.22
	3:1	22.00	12.30
	4:1	15.13	8.17
	3:2	14.71	8.01
St/BA	3:1	17.50	12.11
	2:1	17.23	9.98
	1:1	15.59	7.54
	1:3	12.62	6.58
	1:2	11.67	6.07

EGDMA = 0.3 wt %, PB = 2 wt %, BPO = 0.5 wt %, T = 80°C.

reaction increases when the free-radical concentration is higher. As a result, the chain length between crosslinking points of the network decreases and the crosslink density increases with the increase of the initiator concentration. Therefore, the final result is a decrease of the oil absorbency.

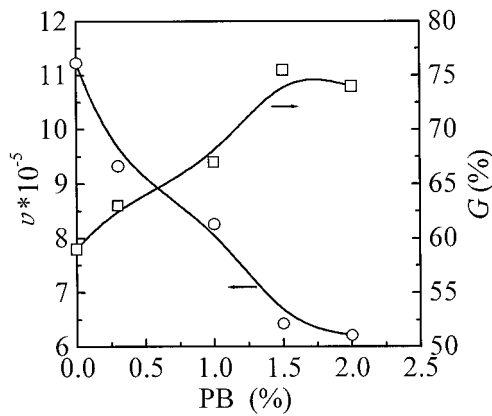
In practice, both properties of resin and conversion should be considered simultaneously. Under the conditions of a polymerization temperature (80°C) and reaction time (7–8 h), 0.5 wt % BPO (based on the total monomer weight) is optimized.

#### Effect of monomer feed ratio

The sort and ratio of monomers will affect the oil affinity of resins, the effective network volume, and so on, which influence the oil absorption process. The effects of every factor on the oil absorbency are complex, and it is hard to explain the change of  $G$  and  $\nu$  with the monomer feed ratio in detail. The experimental results are given in Table I. The polymerization was carried out at 80°C for 8 h in the presence of 0.3 wt % ethylene glycol dimethacrylate (EGDMA), 2 wt % PB, and 0.5 wt % BPO. As listed in Table I, the optimized mass ratio of styrene (St) to dodecyl methacrylate (DMA) or St to butyl acrylate (BA) is 3:1.

#### Effect of PB concentration

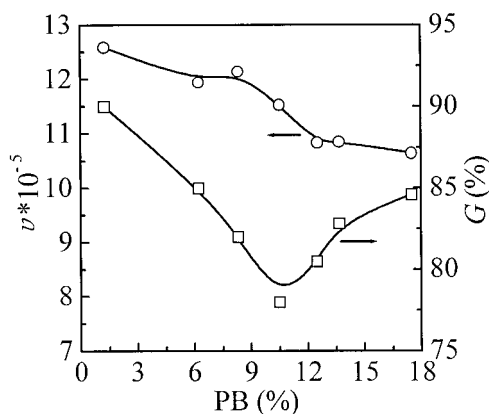
How will the introduction of PB affect the degree of crosslinking and the crosslink density? As shown in Figures 3 and 4, there are two different results for different concentrations of EGDMA in the recipe. In the case of the low concentration of EGDMA (0.3 wt %) in Figure 3, the gel fraction increases and the crosslink density decreases gradually as the concentration of PB increases. These results are desired for preparing resins with high oil absorption capacity and the reversible oil releasing ability. However, the copolymer particles could not form during the suspen-



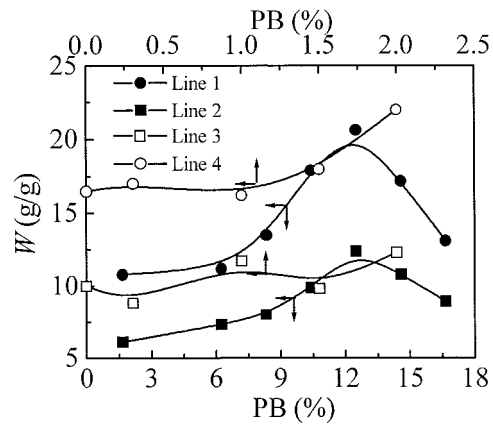
**Figure 3** The variation of the crosslink density and gel fraction with the content of physical crosslinker for 0.3 wt % EGDMA, 3:1 St/DMA, and 0.5 wt % BPO at 80°C.

sion process in the case of >2.5 wt % PB, when the concentration of EGDMA is 0.3 wt %.

With a higher concentration of EGDMA (1.25 wt %), the gel fraction decreases first, then it passes through a minimum and the crosslink density decreases slightly as shown in Figure 4. Because of the higher EGDMA concentration, the network of the resin is tightly crosslinked. Therefore, the introduction of PB mainly enhanced the quantity of physical crosslinking because the interaction of double bonds is strong. The changing of the molecular chain length between two crosslinking points of the network is very small, so the crosslink density decreases to a small degree as the concentration of PB increases. However, the gel fraction will not be enhanced by the initial introduction of PB for the tight molecular chain. Only after adding more PB is the molecular chain relaxed and the gel fraction increased. Thus, a condition of low crosslinking density and a high degree of crosslinking is achieved.



**Figure 4** The variation of the crosslink density and gel fraction with the content of physical crosslinker for 1.25 wt % EGDMA, 3:1 St/DMA, and 0.5 wt % BPO at 80°C.

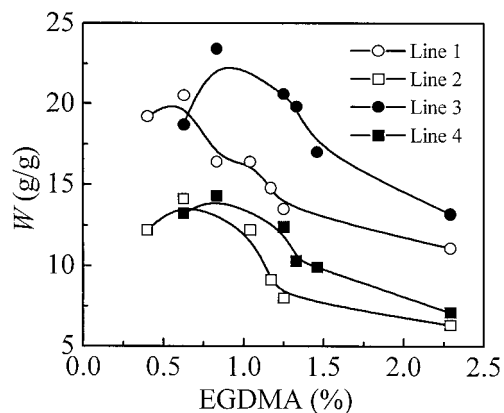


**Figure 5** The variation of the oil absorbency with the content of physical crosslinker for 3:1 St/DMA and 0.5 wt % BPO at 80°C. Lines 1 and 2: 1.25 wt % EGDMA; lines 3 and 4: 0.3 wt % EGDMA; (○, ●) vinyl trichloride; (□, ■) benzene.

Figure 5 shows the effect of the PB concentration on the oil absorbency. At a low concentration of EGDMA (0.3 wt %), the oil absorbency is increased with the increase of PB, which is due to the combined effects of the increasing gel fraction and decreasing crosslink density. A maximum oil absorbency is obtained with 1.25 wt % EGDMA, indicating that the increase of physical crosslinking makes a contribution to the relaxing network. However, the oil absorbency will decrease when the PB content exceeds 12.5 wt % because of the high viscosity within the particles.

#### Effect of EGDMA concentration

Higher concentrations of PB (8.33 and 12.5 wt %) were chosen to investigate the effect of the EGDMA concentration on the oil absorbency of the crosslinked copolymer, as shown in Figure 6. The oil absorbency first increases with the increase of EGDMA and then de-



**Figure 6** The variation of the oil absorbency with the content of chemical crosslinker for 3:1 St/DMA and 0.5 wt % BPO at 80°C. Lines 1 and 2: 8.33 wt % PB; lines 3 and 4: 12.5 wt % PB; (○, ●) vinyl trichloride; (□, ■) benzene.

TABLE II  
Oil Absorption Properties of Various Resins

	St	Monomer Ratio St/DMA				
		2:1	1:1	3:1	3:1	3:1
EGDMA (%)	0.5	0.5	0.5	0.5	1.2	2.1
PB (%)	5.8	5.8	5.8	5.8	1.7	0.8
Vinyl trichloride Absorption						
$Q_{\max}$	18.80	16.38	17.44	20.91	11.73	10.43
$Q$	9.40	8.19	8.72	10.45	5.86	5.21
$t'$ (min)	9.9	3.4	2.3	0.9	0.5	0.8
$K$ (1/min)	0.070	0.204	0.301	0.770	1.386	0.866
Benzene Absorption						
$Q_{\max}$	10.20	9.73	11.02	13.73	8.41	6.14
$Q$	5.10	4.87	5.51	6.86	4.20	3.07
$t'$ (min)	11.0	5.2	3.3	2.2	1.5	1.8
$K$ (1/min)	0.063	0.133	0.210	0.315	0.462	0.385

creases. The more PB (12.5 vs. 8.33 wt %) there is, the higher the optimum oil absorbency will be and the larger the EGDMA concentration at the maximum point (0.833 > 0.625 wt %) will be. It is known that the crosslink degree increases and the crosslink density decreases rapidly without PB; accordingly, the oil absorbency decreases rapidly with the increase of EGDMA. The existence of the soft long-chain PB macromolecule can soften the effect of EGDMA to some degree. However, it only functions at the initial stage of relatively low content of EGDMA. If the concentration of EGDMA exceeds a critical value that depends on the different content of PB, the network crosslinks so tightly that PB becomes ineffective and the oil absorbency decreases.

### Oil absorption speed

According to the 3-dimensional network kinetics of swelling for high water absorption resins, Zhou and coworkers<sup>7</sup> characterized the oil absorption speed by the the swelling kinetic constant ( $K$ ):

$$\ln[Q_{\max}/(Q_{\max} - Q)] = Kt'$$

where  $Q_{\max}$  is the maximum oil absorbency,  $Q$  is the characteristic oil absorbency, and  $t'$  is the characteristic swelling time that is defined at  $Q = 0.632Q_{\max}$ .

As is well known, oil and water absorption processes are the swelling processes of small molecules in crosslinked polymers, which have a sharper transition from the high initial rate to the slow rate and toward the end of swelling equilibrium. However, they depend on different intermolecular forces. The oil absorption process takes place by the van der Waals attractive forces between molecules, but the water absorption process depends mainly on hydrogen bonding. As a result, water absorbency is much higher than oil absorbency and the water absorption speed is also much faster than that of oil. Thus, the selection of a

characteristic oil absorbency and water absorbency should be different. For resins with lower oil absorbency, we defined  $Q = 0.5Q_{\max}$ .

From comparing  $K$  values, it is concluded that the oil absorption speed of particles with an optimum monomer mass ratio (3:1 St/DMA) is faster than that of other mass ratios (such as 2:1 St/DMA, etc.), keeping all other variables constant. The oil absorption speed is different for different kinds of oil. As listed in Table II, the vinyl trichloride absorption speed is faster than that of benzene for the same copolymer particle. Moreover, we focus on the faster oil absorption speed of particles with higher concentrations of PB when the total crosslinking quantity is equal. Toru and Tomoki's equation<sup>8</sup> is used to explain the influence of PB on the oil absorption speed.

$$t = d^2/D$$

$$D = K/F_r$$

where  $t$  is the saturated oil absorption time,  $d$  is the radius of the particle,  $D$  is the diffusion coefficient of the oil in the resin,  $K$  is the elastic modulus of the network, and  $F_r$  is the viscosity coefficient of the oil in the resin.

On the one hand, the addition of PB contributes to constructing a network with better viscoelasticity, thus increasing the value of  $K$ . On the other hand, PB can enhance the viscosity of the network, resulting in the increase of the viscosity coefficient of oil in the resin. As a whole, the increase of  $K$  is the main aspect and thus the presence of PB can speed up absorption.

The oil absorption speed may be observed directly from Figures 7 and 8. The same conclusions can also be obtained.

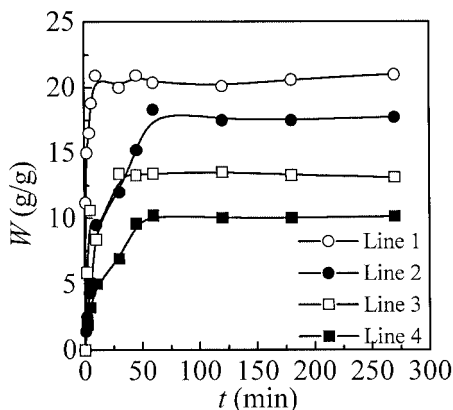
### CONCLUSIONS

Soft long-chain PB as a physical crosslinker was introduced to construct a kind of network with a high

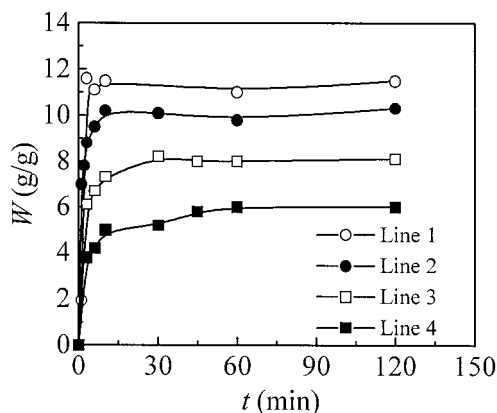
degree of crosslinking and low crosslink density for enhancing the oil absorption capacity of high oil absorption resins. The copolymer particle was prepared by suspension polymerization. The recipe and operation conditions were optimized as follows: a 3:1 mass ratio of St/DMA or St/BA, 0.5 wt % BPO, and 80°C for 7–8 h.

The effect of the PB concentration on the oil absorbency has two different results. The oil absorbency is increased with an increase of PB at a lower concentration of EGDMA (such as 0.3 wt %). However, no particles develop if the concentration of PB exceeds 2.5 wt %. With a higher concentration of EGDMA (1.25 wt %), more PB can be used and there is an optimum PB concentration of about 12.5 wt %. There is also an optimum EGDMA concentration at a certain PB concentration. For 8.33 and 12.5 wt % PB, the optimum EGDMA concentrations are 0.625 and 0.83 wt %, respectively.

The oil absorption speed depends on the copolymer composition. The oil absorption speed of particles



**Figure 7** The variation of the oil absorbency with time for 0.5 wt % BPO with 6.5% total crosslinker at 80°C. Lines 2 and 4: St; Lines 1 and 3: 3:1 St/DMA; (○, ●) vinyl trichloride; (□, ■) benzene.



**Figure 8** The variation of the oil absorbency with time for 3:1 St/DMA and 0.5 wt % BPO at 80°C. Lines 1 and 3: 1.25 wt % EGDMA and 1.67 wt % PB; lines 2 and 4: 2.08 wt % EGDMA and 0.83 wt % PB; (○, ●) vinyl trichloride; (□, ■) benzene.

from a monomer mass ratio (St/DMA) of 3:1 is faster than that from other monomer mass ratios, keeping other variables constant. Moreover, it is demonstrated that the presence of PB can speed up absorption.

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