

# Studies of Crosslinked Styrene–Alkyl Acrylate Copolymers for Oil Absorbency Application. I. Synthesis and Characterization

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**ABSTRACT:** The prepolymers for a novel oil absorbent were synthesized by copolymerizing styrene with 2-ethylhexyl acrylate (EHA), lauryl acrylate (LA), lauryl methacrylate (LMA), and stearyl acrylate (SA). Suspension polymerization was carried out using benzoyl peroxide (BPO) as an initiator with a varying monomer feed ratio, and the copolymers were characterized by FTIR,  $^1\text{H-NMR}$ , DSC, and a solubility test. The copolymers were random copolymers with a single phase, and their compositions were similar to those in the monomer feed. The  $T_g$  of the copolymer could be controlled by varying the styrene/acrylate ratio. Acrylates introduced the crosslinking to linear polymers as a side reaction. Crosslinked copolymers were synthesized by adding divinylbenzene (DVB) as a crosslinking agent. At a low degree of crosslinking (0.5 wt % DVB), the  $T_g$  of the crosslinked copolymers was lower than or similar to that of the uncrosslinked ones. At a high degree of crosslinking, the  $T_g$  increased with increasing crosslinking density. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 77: 903–913, 2000

**Key words:** oil absorbent; suspension polymerization; styrene–acrylate copolymer; crosslinking

## INTRODUCTION

Recently, pollution by an oil spill has been noted as a major cause for environmental pollution.<sup>1–4</sup> Its damage is tremendous and lasts a very long time. Therefore, it is very essential to clean up the oil spill efficiently at the beginning stage of the pollution in order to reduce the risk of losing invaluable marine resources.<sup>3</sup> On the occurrence of an oil-spill accident, many attempts have been made to get rid of the oil.<sup>4,7</sup> Representative methods for treatment of spilt oil are summarized in Table I. Natural cleansing, allowing oil to be degraded and removed by natural means, takes a

long time to be fully effective. This method can be enhanced by an oil dispersant or an oil sinking agent. Oil gelling agents act as a surface-tension modifier, coagulating the spilt oil, and enhance the potential for mechanical removal techniques, for example, recovery of solidified oil with a net. In both cases, there is a disadvantage in that the spilt oil cannot be reused. Therefore, recent trials of spilt oil treatment have been focused on oil absorbents. For this purpose, polypropylene fiber or nonwoven fabrics, melt-blown polyesters, and polyurethane foam sheets have been used,<sup>7</sup> but these have a serious disadvantage of bulkiness, that is, inconvenient shipping and storage. To resolve this disadvantage, an oil-recovery machine was designed, which takes advantage of an on-site foaming method.<sup>8</sup> In other words, two of the polyurethane liquid components are transported to the site of the oil spill, and polyurethane

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**Table I Representative Methods for a Treatment of Spilt Oil**

Method	Characteristics
Natural cleansing	Natural digestion by microbes Disadvantage of requiring a long time for purification
(Oil dispersant)	Emulsifying the spilt oil
(Oil sinking agent)	Sinking the spilt oil to the sea bottom
Oil gelling agent	Coagulating the spilt oil Recovery of the solidified oil
Oil absorbent	Absorbing the spilt oil Requirement of a quick treatment before the spilt oil diffuse Difficulty in shipping and storage

foams are produced by mixing the two components. However, this method also has difficulty in moving the on-site foaming machine to the site of the oil spill, and its shipping and storage are very inconvenient. Hence, quite a different approach was attempted in our study in order to achieve the objectives and resolve the disadvantages as stated above. The base material for the oil absorbent has to be a highly oil-swelling polymer. In addition, the material needs a spongelike structure and a highly shrunken volume for shipping and storage. In its shrunken state, the material does not sink into water, but stays afloat as long as it does not absorb oil. Then, when it contacts oil, it absorbs oil quickly and expands to a large size.

It is known that alkyl acrylate monomers with a long-chain alkyl group have a good affinity to oil or nonpolar solvents. Accordingly, their polymers may have a good swelling property in the oil. However, long-chain alkyl acrylate polymers have a tendency to be in a crystalline state. In this case, its oil-swelling property is reduced. To control this undesirable effect, the method of copolymerization with the second monomer is used so that amorphous copolymers can be obtained. In this study, styrene was copolymerized with various long-chain alkyl acrylates, like 2-ethylhexyl acrylate (EHA), lauryl acrylate (LA), lauryl methacrylate (LMA), and stearyl acrylate (SA). Even if copolymers are often crosslinked as a result of a side reaction, additional crosslinking is needed to have a sufficient property for oil absorbents. Divinylbenzene (DVB) was used as a crosslinking agent in this study. Copolymerization often brings about changes in the glass transition temperatures, which are one of the most important physical properties of a polymer. For control for the glass transition temperature of a copolymer, it is also important to have a com-

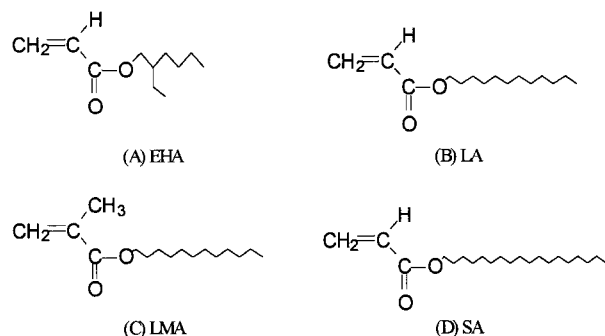
pressed spongelike structure for proper oil-absorbency application.

This article presents syntheses and characterization studies on crosslinked and uncrosslinked styrene-acrylate copolymers for oil-absorbency application. The glass transition temperatures of the copolymers were measured using differential scanning calorimetry (DSC) in order to control the physical properties of the copolymers. The structure of the copolymers was characterized through FTIR, NMR, DSC measurements, and a solubility test. The relationships between the glass transition of the styrene-acrylate copolymer and the different copolymer compositions and crosslinking agent amounts were also undertaken. A detailed study on the swelling properties of crosslinked copolymers appears in our following article.

## UNCROSSLINKED STYRENE-ACRYLATE COPOLYMERS

### Synthesis

In the synthesis of a copolymer, styrene (S, LG Chemicals, Dae-jun, South Korea), EHA (LG Chemicals), lauryl acrylate (LA, BASF), LMA (BASF) and SA (BASF) were used as monomers. Structural formulas of various acrylates and some of their properties are given in Figure 1 and Table II. Each material was washed with a 5% aqueous solution of NaOH to remove the inhibitor and washed with distilled water four times to remove the remaining hydroxyl ions. Then, it was dried over anhydrous sodium sulfate. Styrene, EHA, LA, and LMA were distilled under reduced pressure. Cuprous chloride was added to the distillation flask to inhibit polymerization during distillation. SA, which is in the solid state at room temperature, was used without further purifica-



**Figure 1** Structural formulas of various alkyl acrylates: (A) EHA; (B) LA; (C) LMA; (D) SA.

tion. The polymerization was carried out in a suspension using a free-radical mechanism with benzoyl peroxide (BPO, Chonya Fine Chemicals, Suwon, South Korea) as an initiator. BPO was dissolved in acetone and precipitated by the addition of distilled water. It was then dried under a vacuum. Poly(vinyl alcohol) (PVA, Aldrich, Seoul, South Korea) was used as a suspension stabilizer. All sample compositions used in this study are based on the weight ratios of the constituents in the monomer mixture. The exact weight ratios and the corresponding molar ratios of these samples are summarized in Table III. Various copolymers with different monomer feed ratios (wt % of styrene : wt % of acrylate) were synthesized at 90°C for 4 h. BPO, 0.5 g, was added to the monomer mixture and stirred to dissolve. The total monomer volume was 50 mL. The solution was added to 500 mL of distilled water in the reactor. The suspension polymerization was carried out using a four-blade impeller at 1600–2000 rpm in a 1-L, four-baffled reactor. The copolymer was obtained as beads. After the polymerization, the beads were decanted, suction-filtered, washed with distilled water, and dried in a vacuum oven for 2 days.

### Characterization

The characterizations of the styrene-acrylate copolymers were performed with FTIR transmission spectroscopy and <sup>1</sup>H-NMR. FTIR spectra were obtained using a Bomem MB-100 spectrometer at a resolution of 8 cm<sup>-1</sup> and 16 scans were collected. The copolymers dissolving in benzene were cast onto the KBr pellet. The <sup>1</sup>H-NMR spectra of the copolymers dissolved in CDCl<sub>3</sub> were obtained by using a JEOL JNM LA300. Tetramethylsilane was used as an internal standard material.

Figure 2 demonstrates the FTIR transmission spectra of the S-LA copolymer and the two monomers. Figure 2(A) shows the characteristic peaks of LA at 2800–3000, 1728, 1637, 1620, 1191, 985, and 965 cm<sup>-1</sup>. Figure 2(F) shows the characteristic peaks of styrene at 3000–3100, 1630, 1601, 1494, 1449, 776, and 697 cm<sup>-1</sup>. The peaks at 1637 and 1620 cm<sup>-1</sup> in Figure 2(A) and the peak at 1630 cm<sup>-1</sup> in Figure 2(F), which are due to the C=C stretching, disappeared in the copolymer as shown in Figure 2(B). In addition, the peaks at 985 and 964 cm<sup>-1</sup> in Figure 2(A), which are attributed to the vinyl twisting and wagging, disappeared in Figure 2(B). In Figure 2(B), several peaks at the 3000–3100-cm<sup>-1</sup> region are due to the CH stretching in the aromatic ring, and the peaks at 1601, 1494, 1449, 776, and 697 cm<sup>-1</sup> also originate from the aromatic ring in styrene. The characteristic peaks of the LA unit are observed at 1730 and 1160 cm<sup>-1</sup>. The very strong peak at 1730 cm<sup>-1</sup> is due to the C=O stretching in acrylate, and the less intense peak at 1160 cm<sup>-1</sup> is designated to the C—O—C stretching in acrylate. Considering Figure 2(B)–(E), it is observed that the intensity of the peaks due to LA increases with increment of the concentration of LA, but that of the peaks due to styrene decreases. Details for the peak assignments are represented in Table IV. The FTIR transmission spectra of the S-EHA, S-LMA, and S-SA copolymers are demonstrated in Figure 3. The peak assignments of these spectra are similar to those of the spectrum of the S-LA copolymer as stated above.

Figure 4 shows the <sup>1</sup>H-NMR spectrum of the S-LA copolymer dissolved in CDCl<sub>3</sub>. The peaks at (a) and (b) are assigned to the protons of the copolymer backbone from the styrene unit. The peaks at (d) and (e) are associated with the protons of the copolymer backbone from the LA unit. Especially, in comparison with the peaks at (b) and (e), the proton peaks at (a) and (d) have a

**Table II** Physical Properties of Monomers Used in This Study

Monomer	Formula Weight (g/mol)	Density (g/mL)	Molar Volume (mL/mol)
S	104.15	0.909	114.58
EHA	184.28	0.885	208.23
LA	240.39	0.884	271.93
LMA	254.42	0.868	293.11
SA	324.55	0.800	405.69

**Table III Compositions of Uncrosslinked Samples Used in This Study**

Sample	Wt % of Styrene		Mol % of Styrene		Solubility Test	
	In Feed	In Copolymer <sup>a</sup>	In Feed	In Copolymer <sup>a</sup>	Soluble <sup>b</sup>	Swelling
S/EHA						
50/50	50	46.70	63.89	60.79	Yes	Partially
60/40	60	60.18	72.63	72.78	Yes	Partially
75/25	75	73.85	84.15	83.32	No	No
90/10	90	88.67	94.09	93.26	No	No
S/LA						
20/80	20	15.28	36.59	29.39	No	Fully
40/60	40	37.06	60.61	57.61	Yes	Partially
50/50	50	44.70	69.77	65.11	Yes	Partially
60/40	60	54.88	77.59	73.73	Yes	Partially
70/30	70	67.80	84.34	82.94	Yes	Partially
80/20	80	78.91	90.23	89.62	No	No
90/10	90	89.36	95.41	95.09	No	No
S/LMA						
50/50	50	53.44	70.95	73.71	Yes	Partially
60/40	60	61.31	78.56	79.47	Yes	Partially
70/30	70	74.12	85.07	87.49	Yes	Partially
80/20	80	81.00	90.72	91.24	No	No
90/10	90	89.38	95.65	95.36	No	No
S/SA						
60/40	60	57.18	82.38	80.62	Yes	Partially
70/30	70	68.20	87.91	86.99	Yes	Partially
80/20	80	74.93	92.57	90.30	No	No
90/10	90	90.87	96.56	96.88	No	No

<sup>a</sup> Calculated from <sup>1</sup>H-NMR spectra.

<sup>b</sup> Yes: Solution is clear and transparent. It may include some swollen gels. No: Cloudy beads remain. Fully swollen gels are also classified into this.

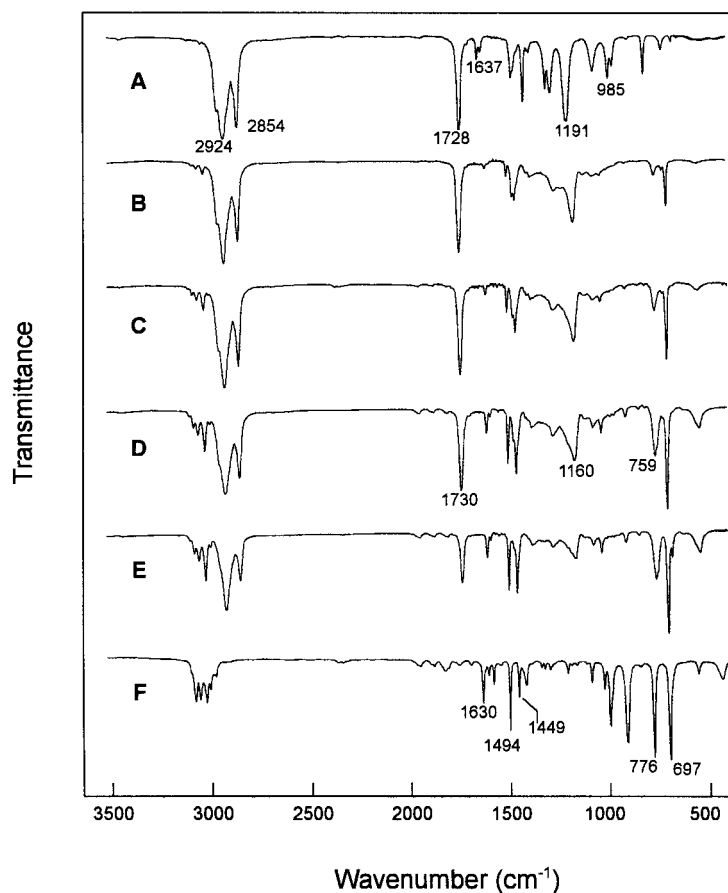
higher chemical shift due to the effect of the phenyl and ester groups. The sharp peak at about 1.5 ppm is due to water.<sup>9</sup> The several sharp peaks around 6.7 and 7.2 ppm and two doublet peaks at 5.2 and 5.7 ppm are designated to be from the unreacted styrene monomer. The calculated content of unreacted styrene from the <sup>1</sup>H-NMR peak area was less than 0.5%. On the other hand, no peaks of unreacted LA were detected. This shows that the reactivity of LA is higher than that of styrene, so that most of the remaining portion of the unreacted monomers is not LA but styrene.

<sup>1</sup>H-NMR spectra of the S-EHA, S-LMA, and S-SA copolymers are also shown in Figures 5–7. The copolymer compositions, calculated using integration from the <sup>1</sup>H-NMR spectra, are summarized in Table III. Even though the definite reactivity ratios of each monomer were not calculated, it can be expected that their reactivity differs from each other and the copolymers formed in the initial stage of polymerization will be greatly en-

riched in a certain monomer. In the S-EHA, S-LA, and S-SA copolymers, the mol fraction of acrylate in the copolymer is slightly higher than that in the monomer feed because the acrylate monomer is more reactive than is styrene. In the S-LMA copolymer, the mol fraction of methacrylate in the copolymer is slightly lower than that in the monomer feed because of the reduced reactivity of the methacrylate monomer due to the formation of resonance-stabilized radicals.<sup>10</sup> However, the gap in composition before and after the polymerization is small because the conversion of the copolymers studied in this article is over 90%. Whether phase separation caused by the different monomer reactivity occurs or not was evaluated by DSC and will be referred to in the next section.

### Glass Transition Temperatures

Although copolymerization with a functional monomer is an ideal means to functionalize a



**Figure 2** FTIR transmittance spectra: (A) LA monomer; (B) S/LA = 20/80, (C) 40/60, (D) 60/40, and (E) 80/20 copolymer; (F) styrene monomer.

polymer, this often brings about drastic changes in the mechanical and physical properties of the polymer. The most important physical property to be affected is the glass transition temperature ( $T_g$ ). The  $T_g$ 's of various uncrosslinked copolymers were determined using DSC. A TA instruments DSC2010 was used. Measurements were performed on 5-mg samples using a scanning rate of 10°C/min. The purging gas was nitrogen at a flow rate of 50 mL/min. The  $T_g$  was taken as the midpoint temperature, that is, the temperature where half of the increment in specific heat had occurred. In some cases, an enthalpy relaxation peak is superposed on the glass transition.<sup>11</sup> When this occurs, the samples were first heated up to this peak temperature, quenched, and then measured in a second run.

Fox predicted the changes of the copolymer  $T_g$  according to its composition with the Fox equation<sup>12</sup>:

$$\frac{1}{T_g} = \frac{W_A}{T_{gA}} + \frac{W_B}{T_{gB}}$$

where  $W_A$  and  $W_B$  are the weight fractions of the monomers  $A$  and  $B$  in the copolymer, and  $T_{gA}$  and  $T_{gB}$  are the respective  $T_g$ 's of the homopolymers  $A$  and  $B$ . However, this equation is very simple and many systems deviate from this. Theoretical values predicted from the Fox equation and experimental values are shown in Table V and Figures 8–10. The homopolymer  $T_g$ 's of the alkyl acrylates or methacrylates were taken from the literature,<sup>13–15</sup> except that of SA, which has not been reported yet. As shown in the figures, the theoretical values from the Fox equation somewhat deviate from the experimental values. This should be due to the difference of copolymer compositions or sequence distribution in the polymer chain, but the details are obscure.

Figure 11(A) shows the DSC thermogram of the S/LA = 80/20 copolymers. The dotted line indicates the first-run data and the solid line indicates the second-run data detected after quenching. The enthalpy relaxation peak, designated from the thermal history of slow cooling



**Table IV FTIR Spectra Peak Assignments of S-LA Copolymer and Monomers**

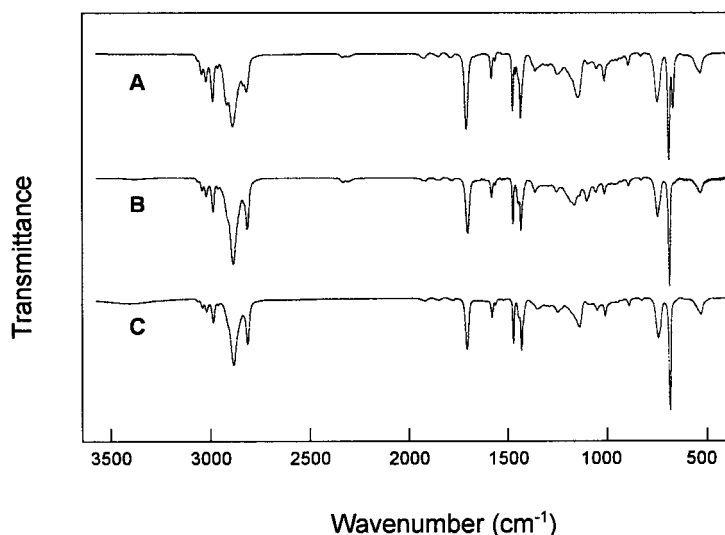
Band Positions (cm <sup>-1</sup> )	Assignments	3(A) <sup>a</sup>	3(F) <sup>b</sup>	3(D) <sup>c</sup>
3000–3100	Aromatic CH stretching		✓	✓
2960	—CH <sub>3</sub> asymmetric stretching	✓		✓
2930	—CH <sub>3</sub> symmetric stretching	✓		✓
2875	—CH <sub>2</sub> — asymmetric stretching	✓		✓
2861	—CH <sub>2</sub> — symmetric stretching	✓		✓
1728	C=O stretching (very strong)	✓		✓
1637, 1620	C=C stretching (doublet) <sup>d</sup>	✓		
1630	C=C stretching		✓	
1601	Ring quadrant stretching		✓	✓
1494	Ring semicircle stretching		✓	✓
	Ring semicircle stretching + CH <sub>2</sub> symmetric (scissors) deformation		✓	✓
1449				
1191	C—O—C stretching (less intense)	✓		
1160	C—O—C stretching (less intense)			✓
985 <sup>e</sup>	Vinyl twisting	✓		
965 <sup>e</sup>	Vinyl CH <sub>2</sub> wagging	✓		
776	Mono-substituted ring in-phase bending		✓	
759	Mono-substituted ring in-phase bending			✓
697	Mono-substituted ring out-of-plane bending		✓	✓

<sup>a</sup> LA monomer.<sup>b</sup> Styrene monomer.<sup>c</sup> S-LA copolymers.<sup>d</sup> Doublet in acrylate; singlet in methacrylate.<sup>e</sup> Two peaks in acrylate; one peak (vinyl wagging) at 940 cm<sup>-1</sup> in methacrylate.

after polymerization, disappears in the second run. All DSC thermograms of the samples in this study show a single glass transition, indicating a completely mixed random copolymer with formation of a single phase.

### Solubility Test

In radical polymerization, it is well known that chain-transfer reactions occur and often result in the formation of branches or crosslinks. Inter-



**Figure 3** FTIR transmittance spectra: (A) S/EHA = 75/25; (B) S/LMA = 70/30; (C) S/SA = 70/30 copolymer.

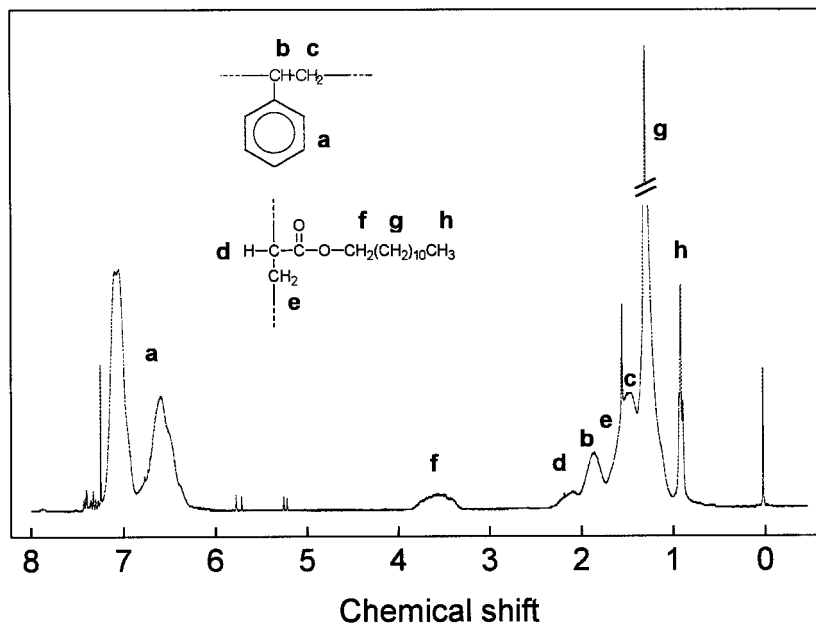


Figure 4  $^1\text{H-NMR}$  spectrum of S-LA copolymer.

lecular chain transfer to a polymer results in long-chain branches or crosslinks. It may proceed via abstraction of either a backbone hydrogen atom in a repeated unit from vinyl monomers or an atom from a substituent group.<sup>16</sup> To evaluate the degree of the chain-transfer reaction of crosslinking, temporary solubility tests were carried out. Small amounts of each sample

were dissolved in kerosene oil with magnetic stirring for about 2 days. The results are summarized in Table III. At a low concentration of acrylate, most of the sample beads remain, not dissolving in oil due to the lack of acrylate units with oil affinity. With increasing the concentration of acrylate, the copolymer includes more portions of the acrylate units. The mixture re-

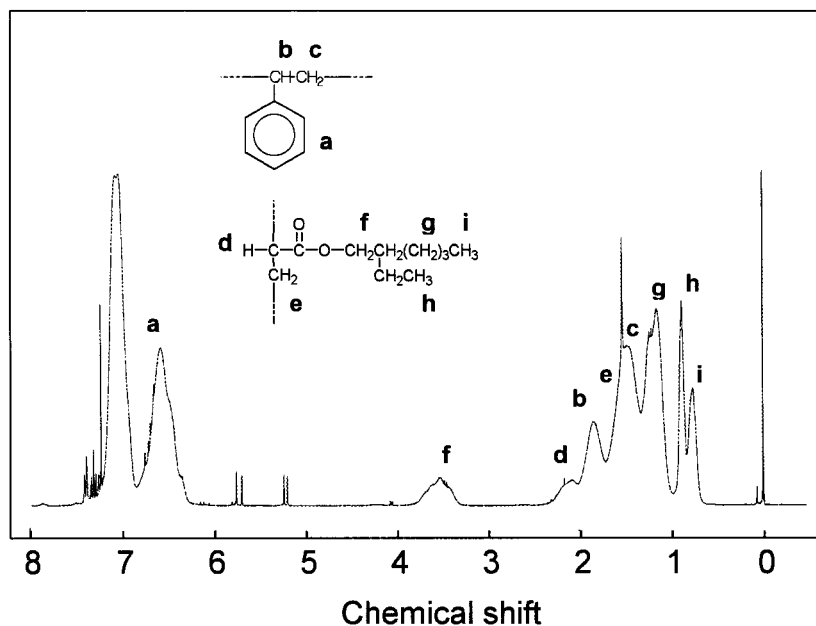


Figure 5  $^1\text{H-NMR}$  spectrum of S-EHA copolymer.

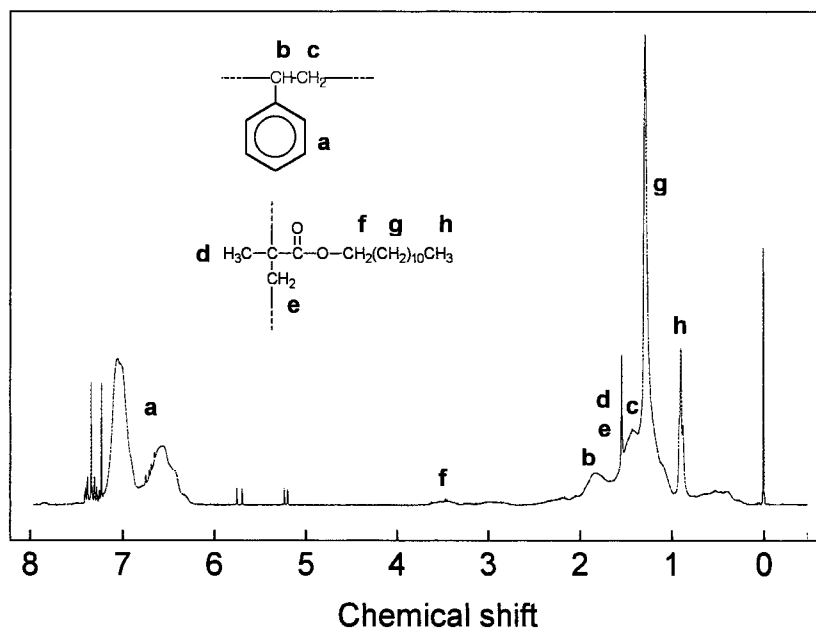


Figure 6  $^1\text{H-NMR}$  spectrum of S-LMA copolymer.

sults in a clear solution with a small amount of beads swollen. At a high concentration of acrylate (S/LA = 20/80), however, the copolymer was fully swollen in oil without dissolving. This shows that the acrylate monomers show a higher tendency toward branching and cross-linking than does styrene.

## CROSSLINKED STYRENE-ACRYLATE COPOLYMERS

### Synthesis

Additional crosslinking is needed to obtain the proper properties, high oil-absorbing capacity and

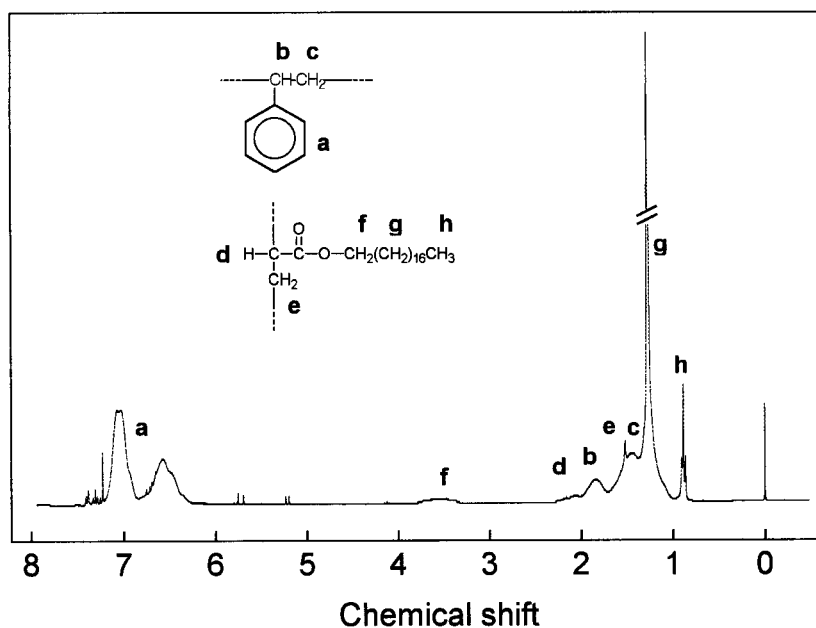


Figure 7  $^1\text{H-NMR}$  spectrum of S-SA copolymer.



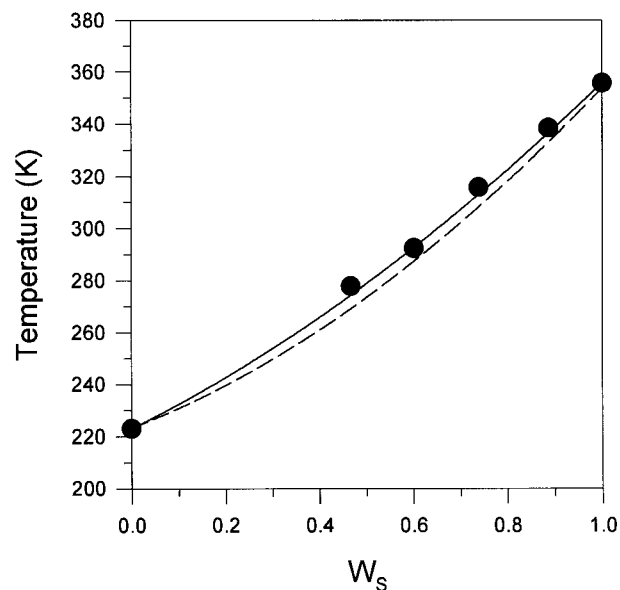
**Table V Glass Transition Temperatures of the Various Copolymers**

Sample	Polymer Composition <sup>a</sup>		$T_g$ (K)	
	Weight Fraction	Mol Fraction	Theoretical Value <sup>b</sup>	Experimental Value
S/EHA				
50/50	0.4670	0.6079	270.2	277.8
60/40	0.6018	0.7278	287.7	292.4
75/25	0.7385	0.8332	307.9	313.8
90/10	0.8867	0.9326	333.4	338.5
S/LA				
50/50	0.4470	0.6511	302.7	283.1
60/40	0.5488	0.7373	311.3	289.1
70/30	0.6780	0.8294	322.9	298.3
80/20	0.7891	0.8962	333.5	306.4
90/10	0.8936	0.9509	344.2	334.5
S/LMA				
50/50	0.5344	0.7371	267.5	261.5
60/40	0.6131	0.7947	279.2	296.1
70/30	0.7412	0.8749	300.6	297.0
80/20	0.8100	0.9124	313.6	331.8
90/10	0.8938	0.9536	330.9	338.4
S/SA				
60/40	0.5718	0.8062	—	285.8
70/30	0.6820	0.8699	—	292.6
80/20	0.7493	0.9030	—	307.5
90/10	0.9087	0.9688	—	335.0

<sup>a</sup> Weight (or mole) fraction of styrene in copolymer.

<sup>b</sup> Calculated using Fox equation.

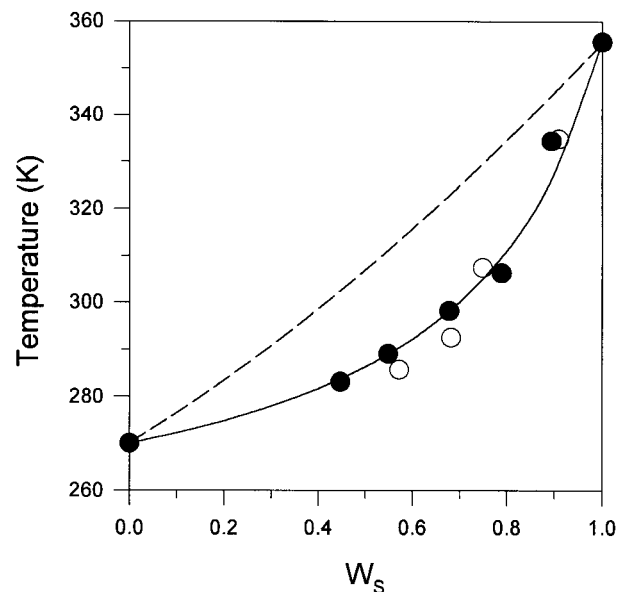
form stability, for oil absorbents. The polymeric system studied is composed essentially of a styrene backbone with varying amounts of the acrylate comonomers to provide certain hydrophobicity which improves oil affinity. The introduction of a crosslinking agent results in the formation of a three-dimensional network. A variety of crosslinked copolymers were synthesized by free-radical polymerization. The polymerization conditions and procedure were described in the previous section. DVB (BASF) was used as a crosslinking agent. It was washed with a 5% aqueous solution of NaOH, four times with distilled water, dried over anhydrous sodium sulfate, and distilled under reduced pressure. To investigate the influence of various parameters, the polymerization was carried out with varying the amount of the crosslinking agent and initiator, the monomer feed ratio (styrene/acrylate), the type of acrylate, and the polymerization temperature. Compositions, exact volumetric ratios, and corresponding molar ratios of the samples are provided in Table VI.



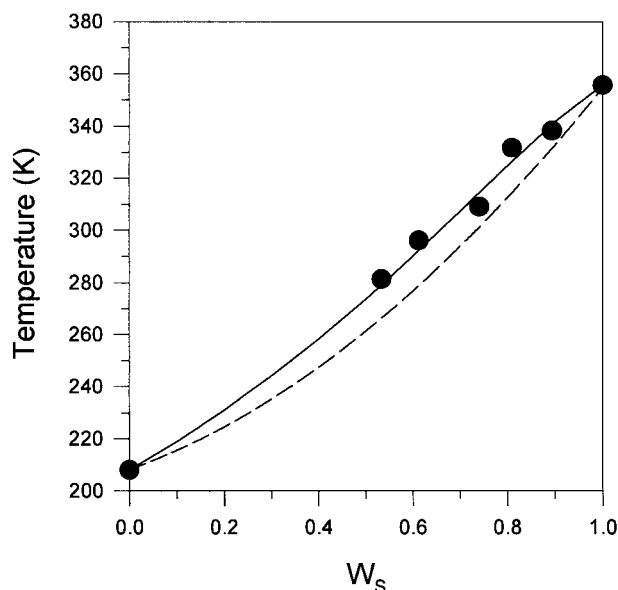
**Figure 8** Variation of  $T_g$  as a function of the weight fraction of styrene ( $W_s$ ) for the S-EHA copolymer system: (—●—) experimental points; (---) prediction curve by Fox's equation.

### Glass Transition Temperatures

In the case of crosslinked copolymers, analysis of the glass transition behavior is more complicated

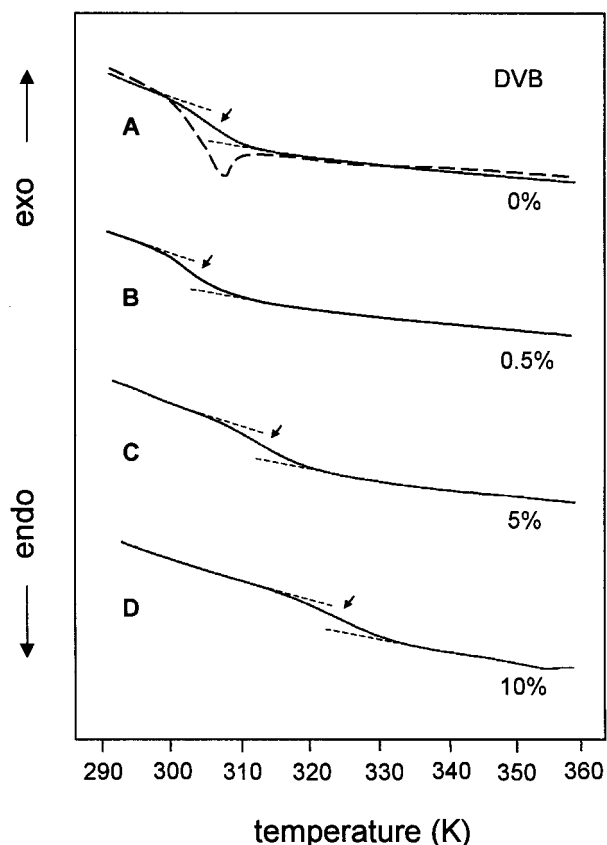


**Figure 9** Variation of  $T_g$  as a function of the weight fraction of styrene ( $W_s$ ) for the S-LA and S-SA copolymer system: (—●—) experimental points; (---) prediction curve by Fox's equation; (○) experimental point for S-SA copolymer.



**Figure 10** Variation of  $T_g$  as a function of the weight fraction of styrene ( $W_s$ ) for the S-LMA copolymer system: (—●—) experimental points; (---) prediction curve by Fox's equation.

than that of uncrosslinked copolymers.<sup>17</sup> Generally, crosslinking increases the glass transition temperature of a polymer and the change in  $T_g$  depends upon the degree of crosslinking.<sup>18</sup> In addition, the glass transition behavior becomes less evident with crosslinking as a consequence of the reduction of the linear portion in the polymer structure. Both effects could be observed by comparing the DSC traces of the crosslinked copolymer samples shown in Figure 11. The glass transition temperature increases with increase of the amount of the crosslinking agent. It can be explained by two, nearly independent, effects: the "real" effect of crosslinking and the copolymer effect. At a low degree of crosslinking, the "real" effect of crosslinking was the major effect. It increases the  $T_g$  as a consequence of reduced segmental mobility. As more and more of the crosslinking agent is incorporated into the network structure, the chemical composition of the polymer gradually changes and the crosslinking agent can be considered as a type of copolymerizing unit. Therefore, the copolymer effect becomes more influential and the shift in  $T_g$  may be very large. Table VII shows the variation of the  $T_g$  with the amount of the crosslinking agent. In case of copolymers with 0.5 wt % DVB, as shown in Figure 11(B), the  $T_g$  is almost equal to or even smaller than that of the uncrosslinked copoly-



**Figure 11** DSC thermograms of S/LA = 80/20 copolymer with different crosslinking densities: (---) first run; (—) second run; (A) control; (B) 0.5 wt % DVB; (C) 5 wt % DVB; (D) 10 wt % DVB.

**Table VI** Compositions of Crosslinked Samples Used in This Study

Copolymer	Monomer Feed Volume (mL)		Wt % of Acrylate	Mol % of Acrylate
	Styrene	Acrylate		
S/EHA				
70/30	34.72	15.28	30.00	19.15
S/LA				
50/50	24.65	25.35	50.00	30.23
60/40	29.66	20.34	40.00	22.41
70/30	34.71	15.29	30.00	15.66
80/20	39.78	10.22	20.00	9.77
90/10	44.87	5.13	10.00	4.59
S/LMA				
70/30	34.51	15.49	30.00	14.93
S/SA				
70/30	33.63	14.97	30.00	12.09

**Table VII Summary of the Glass Transition Temperatures of S-LA Copolymers with Different Compositions and Different Amounts of Crosslinking Agents**

Sample Composition S/LA	$T_g$ (K)			
	DVB			
	0%	0.5%	5%	10%
50/50	283.1	284.1	—	—
60/40	289.1	288.6	296.8	308.1
70/30	298.3	296.0	306.6	318.7
80/20	306.3	303.9	316.4	329.9
90/10	334.5	331.8	343.6	354.8

mers. When the degree of crosslinking is very low, the segmental motion in the copolymers has much the same nature as in linear flexible-chain polymers.<sup>19</sup> Infrequent crosslinks prevent achievement of the same density of segment packing as in the uncrosslinked copolymer and increase the free volume. Therefore, the  $T_g$  of the slightly crosslinked copolymer (0.5 wt % DVB) is similar to that of the uncrosslinked copolymer.

## CONCLUSIONS

Various styrene-acrylate (EHA, LA, LMA, and SA) copolymers were synthesized with and without crosslinking. Suspension polymerization was carried out using BPO as a radical initiator. The copolymers were characterized by FTIR, <sup>1</sup>H-NMR, DSC, and solubility tests.

All samples used in this study were random copolymers with a single phase, and their compositions were similar to those in the monomer feed. The glass transition temperature of the styrene-acrylate copolymers could be controlled by varying the monomer composition and the crosslinking density. The  $T_g$ -composition behavior more or less deviated from the expected values from the Fox equation due to the different copolymer compositions and sequence distribution in the polymeric chains. Acrylate monomers were often introduced branching or crosslinking in the copolymer. Especially, the S/LA = 20/80 copolymer formed a giant crosslinked network and was fully swollen in oil. Additional crosslinking was introduced to the copolymer using DVB in order to obtain the appropriate property for oil absorbents. The  $T_g$  of the copolymers increased

with increasing crosslinking density, but the  $T_g$  of the slightly crosslinked copolymer (0.5 wt % DVB) was almost similar to that of the uncrosslinked copolymer.

By controlling the crosslinking density and other reaction conditions, prepolymers with a predominant oil-absorbing capacity could be obtained. In the next part of this series, the swelling properties of crosslinked styrene-acrylate copolymers will be studied.

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