

Superabsorbent Resin of Acrylic Acid/Ammonium Acrylate Copolymers Synthesized by Ultraviolet Photopolymerization

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ABSTRACT: A new method of synthesizing a superabsorbent resin (SAR) from an acrylic acid/ammonium acrylate copolymer by direct UV photopolymerization was studied. The effects of the degree of neutralization of acrylic acid, the photoinitiators, the crosslinking agents, and the UV-light exposure time on the water absorbency (Q) were investigated. The results showed that Q of an SAR based on Irgacure 1700 or Irgacure 1800 and Irgacure 651 was high, reaching about 1200 mL/g, but under the same conditions, Q was low for an SAR based on other photoinitiators. The UV absorption spectrum proved that the photoinitiators matched the UV light source. Among the crosslinking agents, N,N' -methylene bisacrylamide was more efficient than the others at a small concentration and a high value of Q . ^{13}C -NMR spectrometry was used to identify the mecha-

nism of the crosslinking reaction through the esterification of hydroxyethyl acrylate (HEA) and 2-hydroxypropyl acrylate with carboxylic acid group in acrylic acid/ammonium acrylate copolymerization, but the efficiency of the crosslinking reaction by esterification was lower than that of the copolymerization of vinyl groups in the crosslinking agent. Q of the acrylic acid/ammonium acrylate copolymer for the SAR reached 1255 mL/g under certain conditions (degree of neutralization of acrylic acid = 75%, Irgacure 651 concentration = 0.2 wt %, [HEA] = 0.2 wt %, exposure time = 10 min). © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 95: 546–555, 2005

Key words: copolymerization; resins; photopolymerization

INTRODUCTION

A superabsorbent resin (SAR) is an important kind of functional polymer. It is capable of absorbing large quantities of water (hundreds or even thousands of times its own weight) and has high water retention under pressure. SARs are widely used in areas such as soil amelioration, medicine, and hygiene. The traditional method of synthesizing SARs is thermal polymerization, including solution polymerization and inverse suspension polymerization.^{1–13} In comparison with thermal polymerization, photopolymerization has many merits, such as simple technology; also, it can be carried out at a normal temperature, has a very short exposure time, and produces less pollution.¹⁴ In this article, we propose a route of photopolymerization for synthesizing an SAR from an acrylic acid/ammonium acrylate copolymer, and the influence of the degree of neutralization of acrylic acid (AA) by ammonia water of the SAR is discussed. The effects of the photoinitiators, crosslinking agents, and exposure

time on the properties of the AA/ammonium acrylate copolymer SAR are also examined.

EXPERIMENTAL

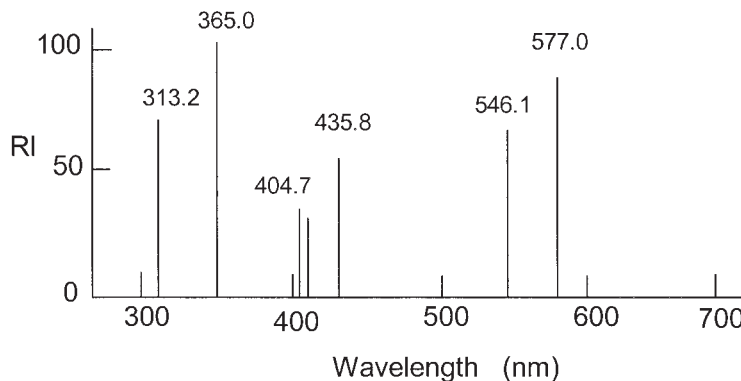
Materials

AA, hydroxyethyl acrylate (HEA), 2-hydroxypropyl acrylate (HPA), diethylene glycol diacrylate (DEGDA), triethylene glycol diacrylate (TEGDA), and poly(ethylene glycol) diacrylate (PEGDA-200) were purchased from Beijing Dongfang Chemical Factory (Beijing, China). Ammonia water and N,N' -methylene bisacrylamide were purchased from Beijing Chemical Factory (Beijing, China). Irgacure 651, Irgacure 184, Irgacure 819, Irgacure 1700, and Irgacure 1800 were provided by Ciba-Geigy Co (New Jersey).

Instrumentation

UV light (700 W, intensity = 1.1 mJ/cm²) was used at the Beijing University of Chemical Technology (the wavelength distribution of the UV light is shown in Scheme 1). A UV-260 ultraviolet-visible spectrophotometer (Shimadzu Corp., Japan) and a Bruker AV300 NMR spectrometer (Bruker Company, Germany) were

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Scheme 1 Wavelength distribution of UV light.

used (the SAR of the AA/ammonium acrylate copolymer was dried and ground into a powder for analysis by ^{13}C NMR spectrometry).

Synthesis

AA was first neutralized with ammonium water (concentration = 25%) to a certain degree of neutralization (30–95%), and this was followed by the addition of the photoinitiators (Irgacure 651, Irgacure 184, Irgacure 819, Irgacure 1700, or Irgacure 1800) and crosslinking agents (*N,N'*-methylene bisacrylamide, HEA, HPA, DEGDA, TEGDA, and PEGDA-200) and by mixing. After that, the mixture was exposed to 700-W UV light for a certain interval, and the SAR of the AA/ammonium acrylate copolymer was obtained. It was dried and ground into particles of a certain size for further characterization.

Characterization

The water absorbency (Q ; mL/g) and salt solution (0.9% NaCl) absorbency (Q_s ; mL/g) were determined by a natural filtration method:¹⁵ 0.1 g of each SAR sample was placed into a filtration bag, which was submerged in 500 mL of water (100-mL salt solution) for 10 min. Q (Q_s) was calculated from the ratio of the volume of lost water (salt solution) to the mass of SAR (the diameter of each side of each SAR sample was ca. 0.07–0.08 cm).

The crosslinking ratio (G) was determined by a natural filtration method¹⁵ (the diameter of each side of each SAR sample was ca. 0.07–0.08 cm).

The double-bond content (wt %) was analyzed by iodometry,¹⁶ which was expressed by the content of AA in the samples.

RESULTS AND DISCUSSION

Degree of neutralization

Before the UV photopolymerization, AA was neutralized with ammonia water to provide a mixture of AA

and ammonium acrylate. Figure 1 shows the effects of different degrees of neutralization on Q of the SAR. Q increased as the degree of neutralization increased from 30 to 75%; the highest value was 710 mL/g. When the degree of neutralization increased from 75 to 95%, Q of the SAR tended to decrease. This was due to two factors that determined the capacity of water absorption of the SAR: the content of hydrophilic groups (carboxylic groups) in the polymer and the osmotic pressure between the SAR and water. Therefore, Q of the SAR was determined by the joint effect of these two factors. The higher the neutralization degree was of the SAR, the greater the content was of the ammonium salt inside the SAR, and this increased the osmotic pressure and Q . However, with an increasing of degree of neutralization, the content of carboxylic groups in SAR decreased, and this reduced Q . The proper degree of neutralization of the AA/ammonium acrylate copolymer SAR was 75%. In this case, the effects of the content of hydrophilic groups

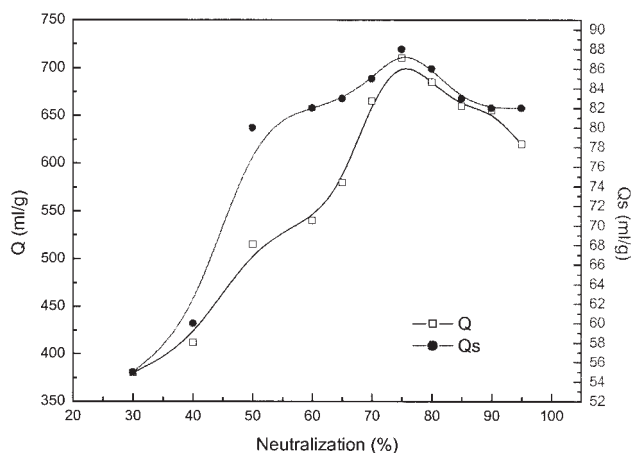


Figure 1 Effects of the degree of neutralization on Q and Q_s of SAR [photoinitiator = Irgacure 1700 (0.2 g/mol of AA/ammonium acrylate); crosslinking agent = *N,N'*-methylene bisacrylic acid (0.005 g/mol of AA/ammonium acrylate); monomer concentration = 68.9%; exposure time = 10 min].

TABLE I
Effects of the Degree of Neutralization on SAR

Degree of neutralization (%)	Monomer content (wt %)	Crosslinking ratio (%)	Double-bond content (wt %)
30	83.4	88.6	0.12
40	79.4	90.1	0.15
50	75.9	90.5	0.12
60	72.9	91.0	0.13
65	71.5	91.2	0.12
70	70.2	92.5	0.12
75	68.9	92.6	0.13
80	67.7	92.8	0.15
85	66.6	92.0	0.14
90	65.5	89.1	0.17
95	64.5	87.5	0.19

Photoinitiator = Irgacure 1700 (0.2 g/mol of AA/ammonium acrylate); crosslinking agent = *N,N'*-methylene bisacrylic amide (0.005 g/mol of AA/ammonium acrylate); exposure time = 10 min.

and the osmotic pressure were at a proper point, and Q was highest (710 mL/g). The same was true for Q_s of the SAR. When the degree of neutralization reached

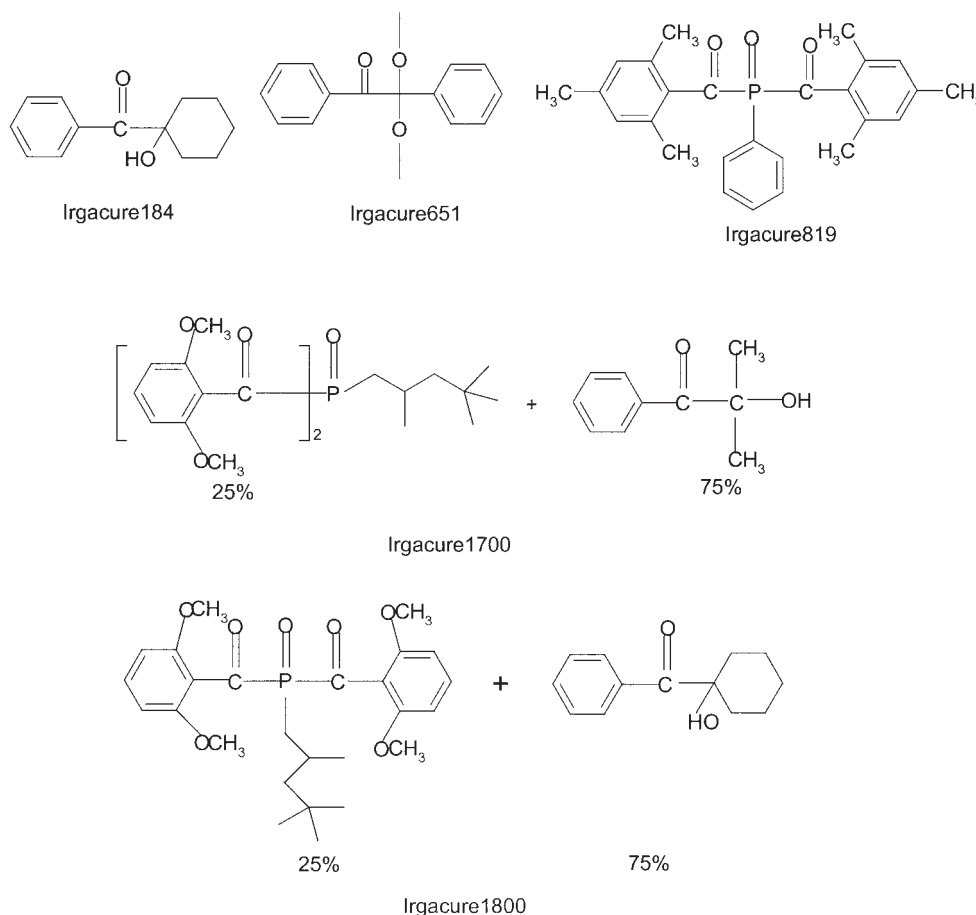
75%, the top Q_s value of 88 mL/g was obtained. The degree of neutralization should be controlled to around 75% to obtain high water absorbency characteristics of the SAR.

Table I lists the effects of the degree of neutralization on the monomer content and characteristics of the SAR. The monomer content was calculated from the mass ratio of monomers of AA and acrylate ammonium to the total material of polymerization. The higher the neutralization degree was, the lower the AA content was. A high G value (92.8%) of the SAR appeared at 70–80% neutralization. A lower double-bond content meant that the monomer polymerized to a greater extent.

Photoinitiators

Effects of the photoinitiators and exposure time

The photoinitiators played the most important role in the UV photopolymerization.¹⁷ Scheme 2 lists the molecular formulas of the photoinitiators that we used. As shown in Table II, there were five photoinitiators (Irgacure 651, Irgacure 184, Irgacure 819, Irgacure



Scheme 2 Molecular formulas of the photoinitiators.

TABLE II
Effects of the Photoinitiators and Exposure Time on SAR

Photoinitiator	Exposure time (min)	Q (mL/g)	G (%)	Double-bond content (wt %)
Irgacure 184	1	90	28.6	5.2
	5	165	87.5	0.95
	10	305	90.8	0.43
	20	325	92.1	0.36
	30	316	92.0	0.38
Irgacure 651	1	203	56.6	1.23
	5	455	90.2	0.35
	10	450	91.8	0.19
	20	446	92.2	0.16
	30	425	91.5	0.17
Irgacure 819	1	105	33.1	4.67
	5	115	58.9	1.85
	10	260	68.8	0.52
	20	380	88.3	0.32
	30	365	86.8	0.36
Irgacure 1700	1	240	63.8	0.85
	5	550	92.2	0.25
	10	555	93.1	0.18
	20	545	92.5	0.13
	30	536	91.2	0.15
Irgacure 1800	1	225	60.9	1.02
	5	520	91.6	0.25
	10	537	93.3	0.20
	20	560	93.7	0.18
	30	552	93.1	0.16

Photoinitiator content = 0.15%; crosslinking agent = *N,N'*-methylene bisacrylamide (content = 0.025%); degree of neutralization = 75%; exposure time = 10 min.

1700, and Irgacure 1800) used in synthesizing the AA/ammonium acrylate copolymer SAR. The conditions of the photopolymerization are shown in Table II. The content of the photoinitiator (crosslinking agent) of the SAR was calculated from the ratio of the mass of the photoinitiator (crosslinking agent) to the mass of the AA and acrylate monomers. The longer the exposure time was, the higher *Q* was, the higher *G* was, and the fewer double bonds there were in the SAR. Excessive exposure led to some degradation of the crosslinked copolymer. When the exposure time was greater than 20 min, *Q* and *G* of the SAR decreased a little. Table II shows that the proper exposure time of the SAR was about 10–20 min, and Irgacure 1700, Irgacure 1800, and Irgacure 651 were more efficient at initiating photopolymerization than the other photoinitiators for short exposure times, yielding high *G* values and low double-bond contents.

Effects of the content of the photoinitiators

Figure 2 shows the effects of the content of the photoinitiators (Irgacure 1700, Irgacure 1800, and Irgacure 651) on *Q* of the SAR. As the content of Irgacure 1700 increased, *Q* increased significantly. When the Irga-

cure 1700 content was 0.05%, *Q* reached 1180 mL/g. The same was true for Irgacure 1800 and Irgacure 651; the top *Q* values of Irgacure 1800 and Irgacure 651 were 1135 and 1020 mL/g, and the contents of these two photoinitiators were 0.1 and 0.25%, respectively. Figure 2 shows that the efficiency of Irgacure 1700 and Irgacure 1800 was higher than that of Irgacure 651 with small contents for top *Q* values of the SAR; their top *Q* values of the SAR were a little higher than that of Irgacure 651. Schemes 3–5 show the processes of photoinitiation fragmentation under the UV light of Irgacure 651, Irgacure 1700, and Irgacure 1800,¹⁸ including the chemical structure and photolysis mechanism of these three photoinitiators and the resultant radicals; these photopolymerization processes were radical polymerizations by nature. Irgacure 651 was able to release methyl radicals under UV irradiation, and the methyl radical had a small volume and a high capacity for diffusion, so Irgacure 651 had high activity of initiation. Irgacure 1700 and Irgacure 1800 contained acylphosphine oxides in their chemical structures, which could produce phosphonyl radicals to initiate the copolymerization of SAR. The high reactivity toward the AA/ammonium acrylate monomers could be explained in terms of the pyramidal structure of the phosphonyl radicals, which permitted the site of the unpaired electron to be approached rather easily by the AA and acrylate monomers.¹⁹

Uv spectra of the photoinitiators

Figures 3–5 show the UV spectra of photoinitiators Irgacure 651, Irgacure 1700, and Irgacure 1800. There are distinct UV absorption peaks that appear between 320 and 400 nm for each photoinitiators. With increasing exposure time (0, 10, 30, and 60 s) for every photoinitia-

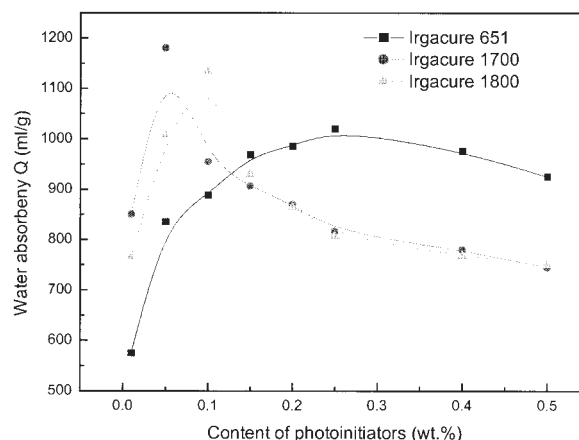
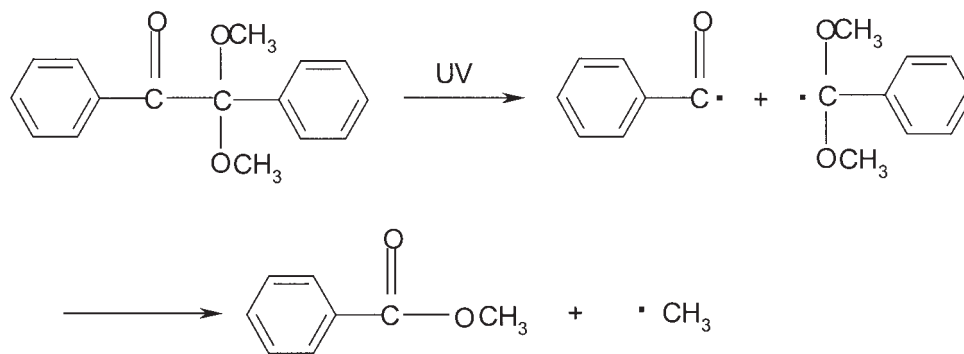


Figure 2 Effects of the concentration of the photoinitiators on *Q* of SAR [degree of neutralization = 75%; crosslinking agent = *N,N'*-methylene bisacrylamide (0.0025 wt %); exposure time = 10 min].



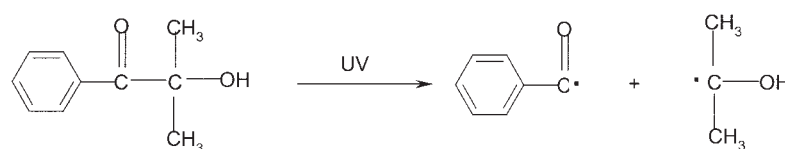
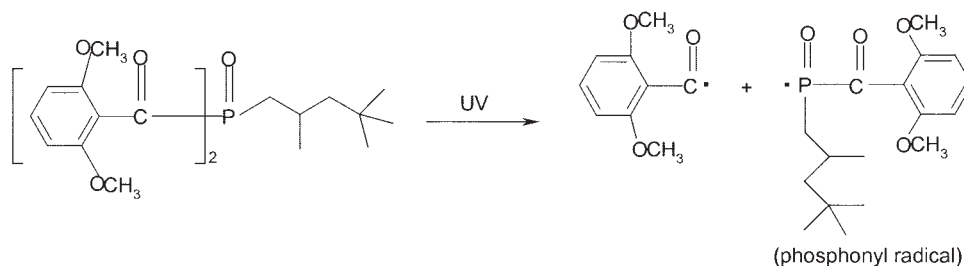
Scheme 3 Fragmentation of Irgacure 651.

tor, the height of the UV absorption peaks decreases. This means that greater exposure time led to greater fragmentation of Irgacure 651, Irgacure 1700, and Irgacure 1800. Moreover, the irradiation wavelength of the UV light that we used conformed to the UV absorption wavelength of these photoinitiators. The main irradiation wavelength of the UV light was 365 nm.

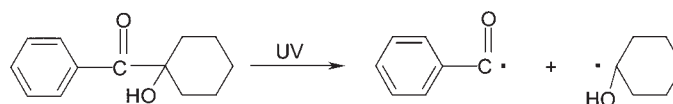
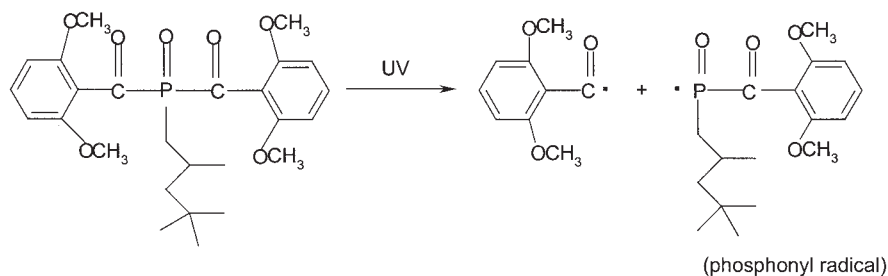
Crosslinking agents

Effects of the content of the crosslinking agents

The crosslinking agents were important factors that determined the water absorption characteristics and mechanical properties of the AA/ammonium acrylate SAR. In the AA/ammonium acrylate copolymeriza-



Scheme 4 Fragmentation of Irgacure 1700.



Scheme 5 Fragmentation of Irgacure 1800.

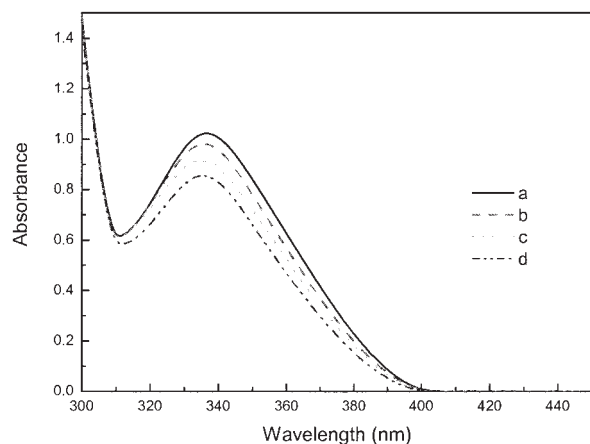


Figure 3 UV absorption spectra of Irgacure 651 (solvent = ethyl alcohol; Irgacure 651 concentration = 0.001 g/mL) with exposure times of (a) 0, (b) 10, (c) 30, and (d) 60 s.

tion, the crosslinking reactions could be performed by copolymerization and esterification. Here, different kinds of crosslinking agents (*N,N'*-methylene bisacrylamide, HEA, HPA, DEGDA, TEGDA, and PEGDA-200) were used separately.

Figure 6 shows that, when *N,N'*-methylene bisacrylamide was used as a crosslinking agent, the peak value of *Q* of the SAR was 1210 mL/g, and the respective content of the crosslinking agent was 0.001%. *G* of the SAR increased as the content of *N,N'*-methylene bisacrylamide increased. Figures 7 and 8 show that the contents of HEA and HPA were about 0.2%, and the peak values of *Q* of the SAR were 1255 and 1020 mL/g. Figure 9 shows the effects of the content of the crosslinking agents (DEGDA, TEGDA, and PEGDA-200) on *Q* of the SAR. For these three crosslinking agents, a higher value of *Q* appeared at a content of

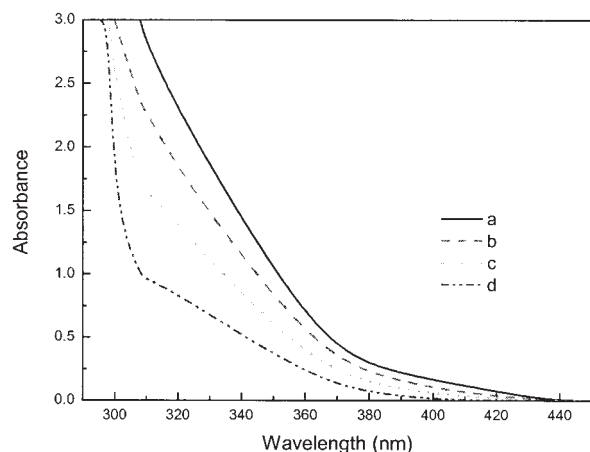


Figure 4 UV absorption spectra of Irgacure 1700 (solvent = ethyl alcohol; Irgacure 1700 concentration = 0.001 g/mL) with exposure times of (a) 0, (b) 10, (c) 30, and (d) 60 s.

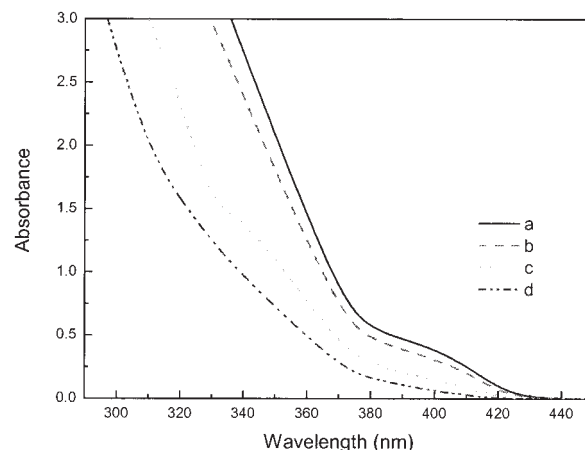


Figure 5 UV absorption spectra of Irgacure 1800 (solvent = ethyl alcohol; Irgacure 1800 concentration = 0.001 g/mL) with exposure times of (a) 0, (b) 10, (c) 30, and (d) 60 s.

approximately 0.025–0.05%. DEGDA had higher efficiency for improving the water absorption capacity of SAR than the others; its top *Q* value was 955 mL/g. Figures 6–8 and 10 show that *N,N'*-methylene bisacrylamide was most efficient because a small amount resulted in higher *Q* and *G* values. With HEA as the crosslinking agent, the top *Q* value of the SAR (1255 mL/g) was obtained.

Figures 6–9 show that the contents of HEA and HPA in the SAR were much higher than those of the other four crosslinking agents for higher *Q* values. The reason was that the crosslinking mechanisms of the crosslinking agents were different. Scheme 6 shows the molecular structures of the crosslinking agents that we used. The crosslinking reaction of *N,N'*-meth-

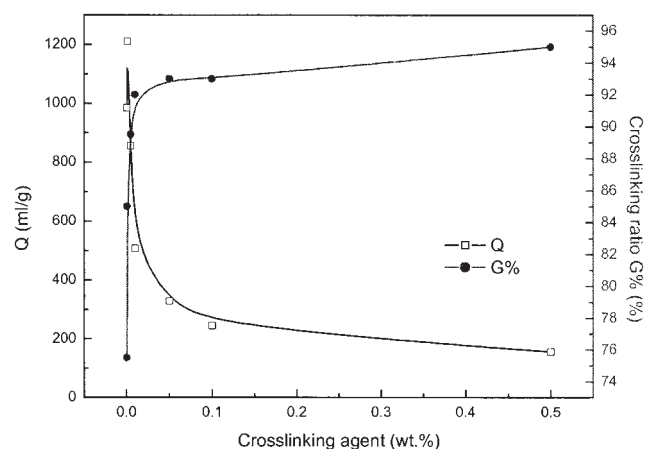


Figure 6 Effects of the crosslinking agent (*N,N'*-methylene bisacrylamide) concentration on *Q* and *G* for the AA/ammonium acrylate SAR [degree of neutralization = 75%; photoinitiator = Irgacure 651 (0.2 wt %); exposure time = 10 min].

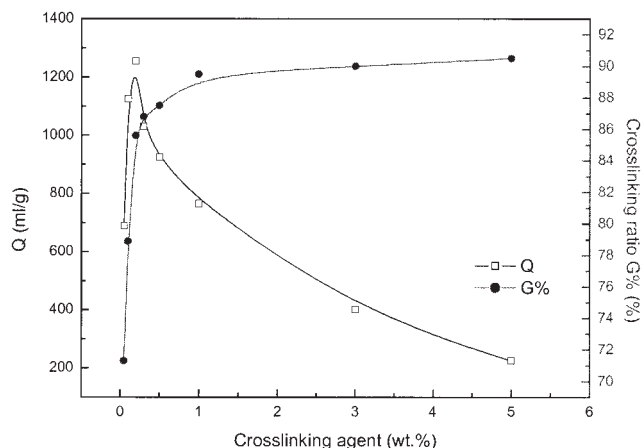


Figure 7 Effects of the crosslinking agent (HEA) concentration on Q and G for the AA/ammonium acrylate SAR [degree of neutralization = 75%; photoinitiator = Irgacure 651 (0.2 wt %); exposure time = 10 min].

ylene bisacrylamide, DEGDA, TEGDA, and PEGDA-200 was copolymerization with AA and ammonium acrylate because there were two double bonds in the molecular structures; for HEA and HPA, it was either copolymerization or esterification because there were one double bond and one hydroxyl group in the molecular structure, and the hydroxyl group could be esterified partly with the carboxyl group at the main chain of the AA/ammonium acrylate copolymer. When the copolymerization of the SAR proceeded, HEA or HPA copolymerized with AA and acrylate ammonium, and part of the hydroxyl group in HEA or HPA esterified with the carboxyl group of AA, which had copolymerized into main chains of the AA/ammonium acrylate copolymer of the SAR. However, in

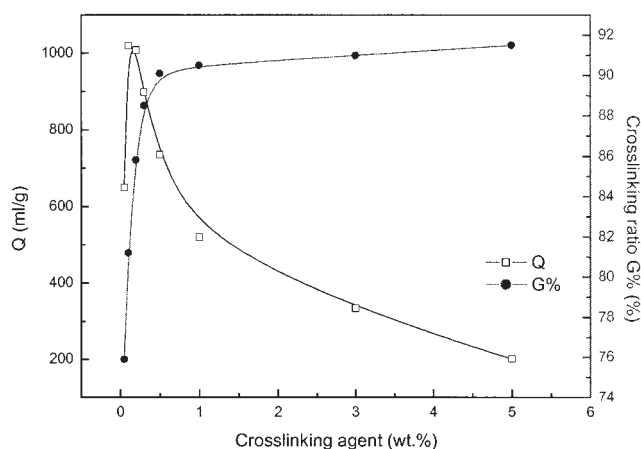


Figure 8 Effects of the crosslinking agent (HPA) concentration on Q and G for the AA/ammonium acrylate SAR [degree of neutralization = 75%; photoinitiator = Irgacure 651 (0.2 wt %); exposure time = 10 min].

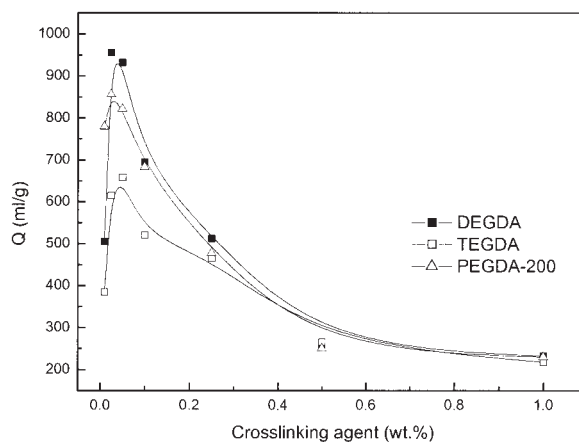


Figure 9 Effects of the crosslinking agent (DEGDA, TEGDA, and PEGDA-200) concentration on Q for the AA/ammonium acrylate SAR [degree of neutralization = 75%; photoinitiator = Irgacure 651 (0.2 wt %); exposure time = 10 min].

this water solution, the conversion percentage of esterification was low; that is, the efficiency of crosslinking by copolymerization was much higher than that of crosslinking by esterification. That was why HEA or HPA had to be added at a higher concentration than the other crosslinking agents to obtain good water absorption characteristics for the SAR.

Analysis by ^{13}C -NMR spectrometry

Scheme 7 shows the crosslinking structures of HEA and HPA in the AA/ammonium acrylate copolymer SAR. The $C\delta$ values for HEA and HPA were 62.7 and 66.9 ppm, respectively, and if there was no esterifica-

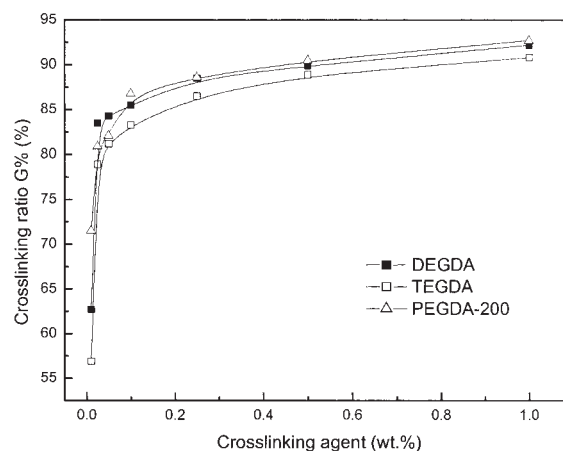
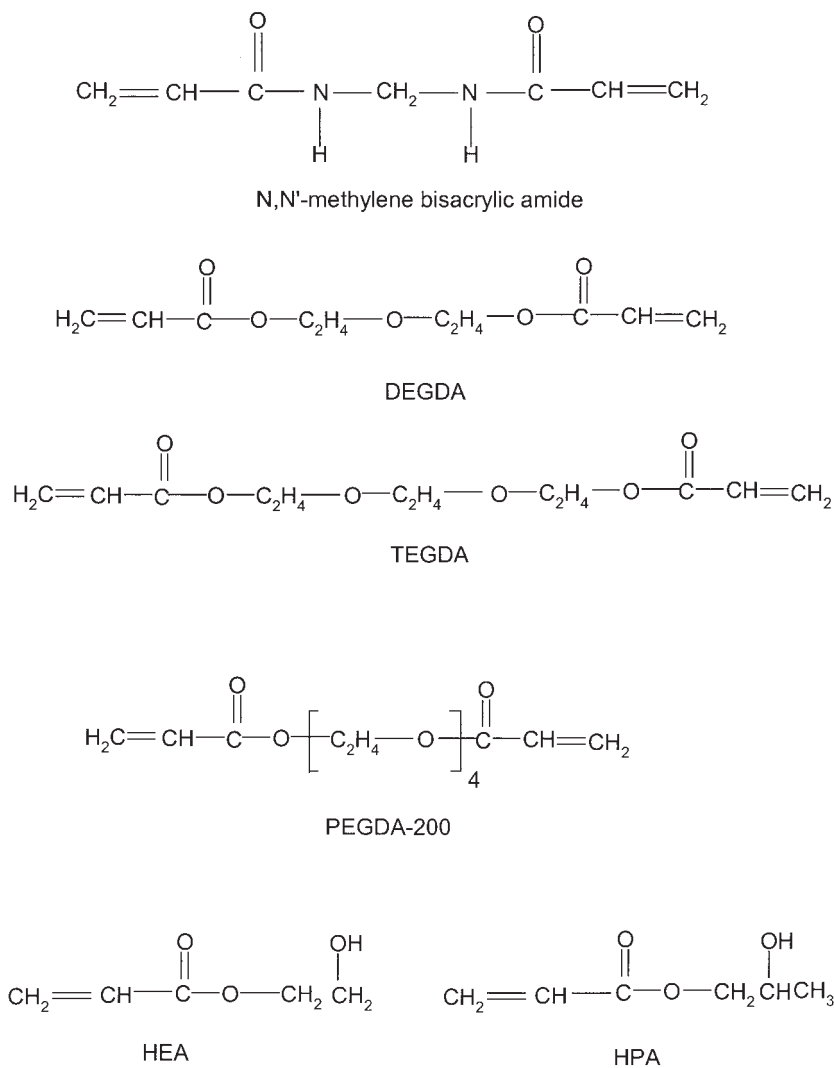


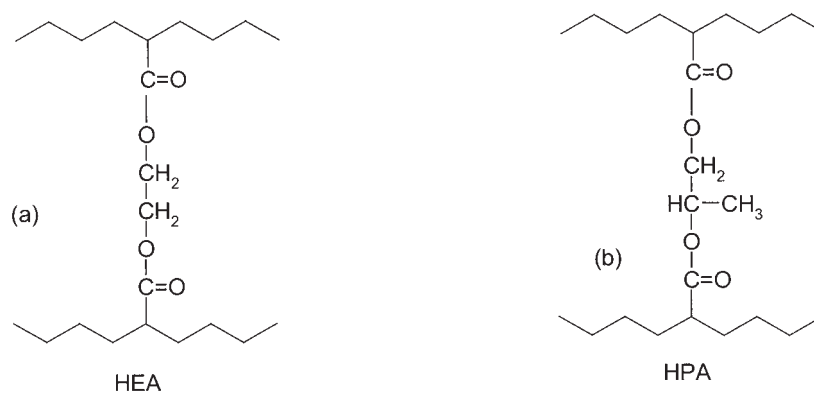
Figure 10 Effects of the crosslinking agent (DEGDA, TEGDA, and PEGDA-200) concentration on G for the AA/ammonium acrylate SAR [degree of neutralization = 75%; photoinitiator = Irgacure 651 (0.2 wt %); exposure time = 10 min].



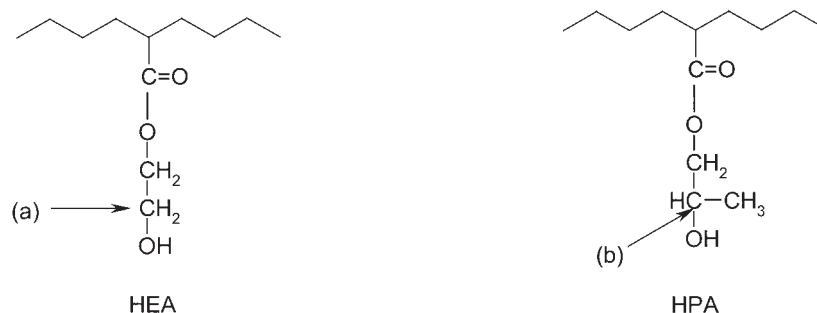
Scheme 6 Molecular structures of the crosslinking agents.

tion crosslinking reaction of HEA or HPA to the carboxyl group of AA in the copolymerization system, Scheme 8 shows the structure; and the C δ values for

HEA and HPA were 59.7 and 62.9 ppm, respectively.²⁰ Figure 11 shows the ¹³C-NMR spectrum of HEA; near $\delta = 63.8555$ ppm, there is a clear peak. For HPA,



Scheme 7 Crosslinking structures of (a) HEA and (b) HPA in SAR.



Scheme 8 Uncrosslinking structures of (a) HEA and (b) HPA in SAR.

Figure 12 shows a distinct peak near $\delta = 66.2842$ ppm. This means that the mechanism of the crosslinking reaction of HEA and HPA (esterification) that we mentioned previously is correct.

CONCLUSIONS

UV photopolymerization is a new method for synthesizing an AA/ammonium acrylate copolymer SAR. The proper degree of neutralization of AA by ammonia water for reaching higher Q values of the SAR is 75%. Irgacure 651, Irgacure 1700, and Irgacure 1800 are more efficient at initiating AA and acrylate ammonium copolymerization than other photoinitiators.

With Irgacure 651, Irgacure 1700, and Irgacure 1800 as photoinitiators and 5–10 min of UV-light exposure, good water absorption characteristics of SAR were achieved; in this case, Irgacure 1700 exhibited higher photopolymerization reactivity for a short exposure time but high G values and low double-bond contents. N,N' -Methylene bisacrylamide and HEA were highly efficient crosslinking agents for obtaining SAR with good water absorption capacity. Copolymerization and esterification are the two main mechanisms of crosslinking for HEA and HPA with AA and ammonium acrylate in synthesizing SAR. An AA/ammonium acrylate SAR with a Q value as high as 1255 mL/g was attained by UV photopolymerization un-

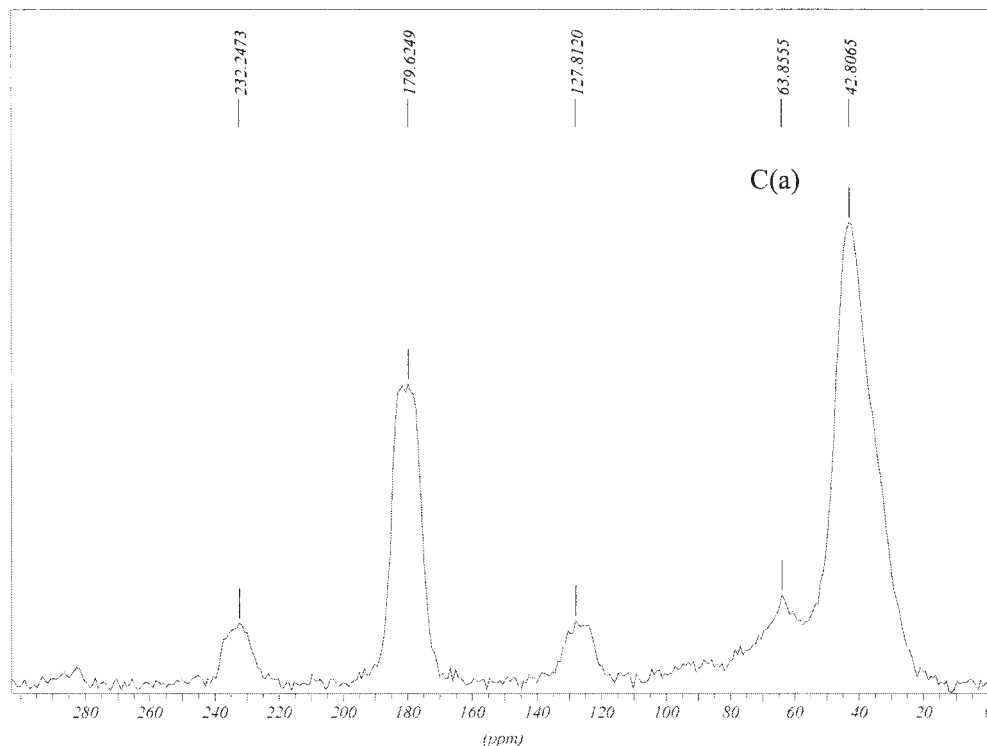


Figure 11 ^{13}C -NMR spectrum of SAR (crosslinking agent = 15 wt % HEA).

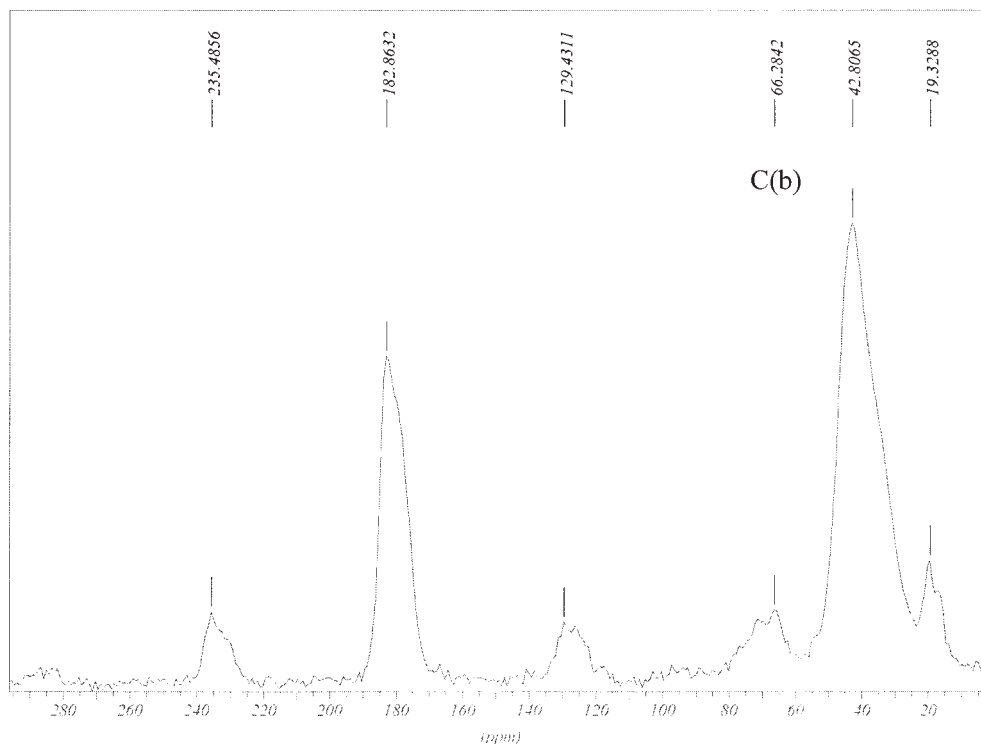


Figure 12 ^{13}C -NMR spectrum of SAR (crosslinking agent = 15 wt % HPA).

der certain conditions [degree of neutralization = 75%, photoinitiator = Irgacure 651 (0.2 wt %) crosslinking agent = HEA (0.2 wt %), exposure time = 10 min].

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