

Synthesis of Superabsorbent Resin by Ultraviolet Photopolymerization

Weiying Ruan, Jinliang Qiao, Yuli Huang, Aijie Niu

College of Material Science and Engineering, Beijing University of Chemical Technology, P.O. Box 6, Beijing 100029, China

Received 11 June 2003; accepted 30 September 2003

ABSTRACT: Synthesis of superabsorbent resin (SAR) was achieved by a new method, that of direct UV photopolymerization, and in particular the synthesis of a SAR of acrylic acid–potassium acrylate copolymer by UV photopolymerization was investigated. Influences of ratio (mol) of acrylate monomer to acrylic acid monomer, photoinitiators, crosslinking agents, and exposure time of UV light on the water-absorbent properties were investigated. The results showed that the water absorbency (Q) of SAR based on Irgacure 1700 or Irgacure 1800 was 545–530 mL/g, but under the same conditions Q was 450 mL/g for the SAR based on Irgacure 651. *N,N'*-Meth-

ylene bisacrylamide, hydroethyl acrylate, and glycerol were used as crosslinking agents, of which *N,N'*-methylene bisacrylamide was the most effective. It crosslinked the molecular chains through attending the copolymerization with acrylic acid (AA) and potassium acrylate. When the exposure time was 5 min, the value of Q was 1368 mL/g (the content of *N,N'*-methylene bisacrylamide was 100 ppm). © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 92: 1618–1624, 2004

Key words: photopolymerization; radical polymerization; esterification; superabsorbent resin; photoinitiator

INTRODUCTION

Superabsorbent resin (SAR) is an important type of functional polymers. This water-absorbent polymer is capable of absorbing hundreds, even thousands, of times its own weight of water and high water retention under pressure. The traditional method of synthesis of SAR is thermal polymerization, including solution polymerization and inverse suspension polymerization.^{1–13} Compared with thermal polymerization, photopolymerization has many advantages such as simpler technology, it may be carried out at normal temperature, undergoes a very short exposure time, and produces comparatively less pollution, for example.¹⁴ In this article, we propose a method of photopolymerization for synthesizing acrylic acid (AA)–potassium acrylate copolymer SAR. We then report on the investigation of the influence of the ratio (mol) of acrylate monomer to AA monomer on the water absorbency of the SAR. The effects of photoinitiators, crosslinking agents, and exposure time on the properties of AA–potassium acrylate copolymer SAR were also investigated.

EXPERIMENTAL

Materials

AA and hydroxyethyl acrylate were purchased from Beijing Dongfang Chemical Factory (China). Potas-

sium hydroxide, sodium hydroxide, *N,N'*-methylene bisacrylamide, and glycerol were purchased from Beijing Chemical Factory (China). Irgacure 651, Irgacure 819, Irgacure 1700, and Irgacure 1800 were provided by the Ciba Company (Summit, NJ).

Instrument

We used a UV light (700 W), made at the Beijing University of Chemical Technology.

Synthesis

At room temperature, AA (7–10 g) was first neutralized by alkaline solution (KOH, NaOH) in a glass cup, to which were added photoinitiators (Irgacure 651, Irgacure 819, Irgacure 1700, or Irgacure 1800) and crosslinking agents (*N,N'*-methylene bisacrylamide, hydroxyethyl acrylate, or glycerol), after which the solution was thoroughly mixed. After exposing it under a 700-W UV light ($I = 1.1 \text{ mW/cm}^2$) for a certain interval of time, the SAR of AA–acrylate salt was obtained, after which it was dried and ground into particles of appropriate size for research.

Characterization

Water absorbency (Q , mL/g) and salt solution (NaCl: 0.9%) absorbency (Q_s , mL/g) were determined by the natural filtration method.¹⁵ The crosslinking ratio ($G\%$) [the percentage of insoluble part of SAR (whose molecule was crosslinked)] was calculated by the mass

Correspondence to: Y. L. Huang (ruankq@public.bta.net.cn).

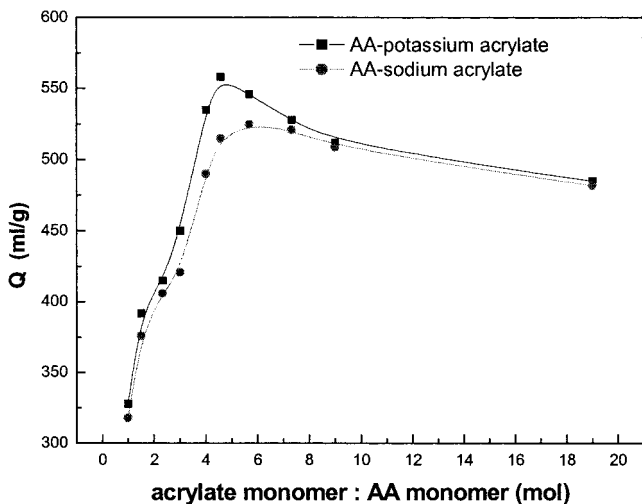


Figure 1 Effects of ratio (mol) of acrylate monomer to AA monomer on water absorbency (Q , mL/g) of SAR. Note: photoinitiator, 0.25% (weight) Irgacure 651; crosslinking agent, 0.01% (weight) N,N' -methylene bisacrylamide; exposure time, 10 min.

ratio of $M_1 : M_2$ (M_1 , mass of SAR extracted by distilled water; M_2 , mass of the SAR).

RESULTS AND DISCUSSION

Ratio (mol) of acrylate monomer to AA monomer

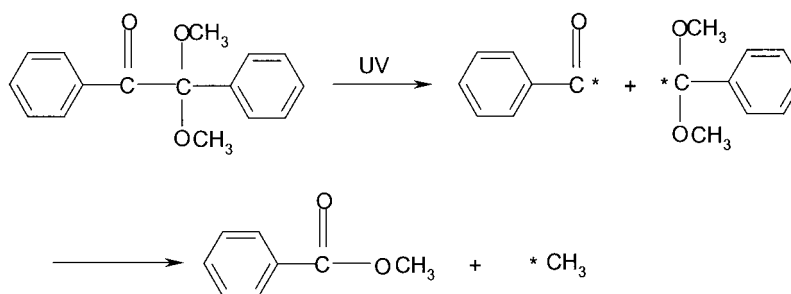
The common monomers of UV photopolymerization are AA monomer and acrylate monomer. Different

ratios (mol) of acrylate monomer to AA monomer determined the Q of SAR. Here two kinds of alkaline solutions (KOH, NaOH) were used to synthesize SAR with AA. Figure 1 shows the effects of ratio (mol) of acrylate monomer to AA monomer on the Q values of SAR. The best ratio (mol) of potassium acrylate to AA was 4.55; in the case of AA-sodium acrylate SAR, it was 5.67 (sodium acrylate : AA). From Figure 1 we can see that the water-absorption capacity of the AA-potassium acrylate SAR is slightly higher than that of the AA-sodium acrylate SAR.

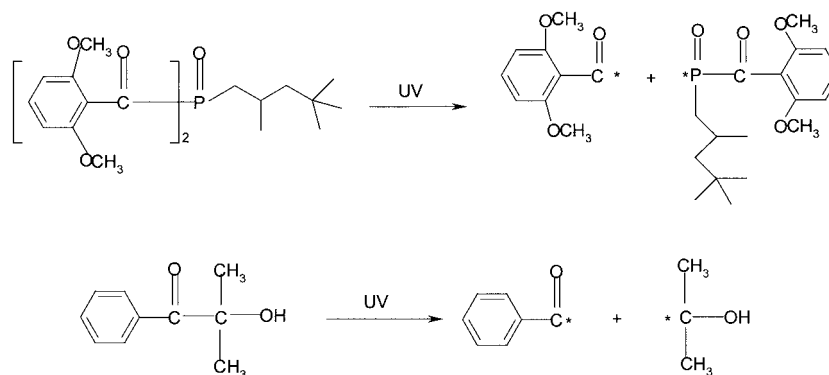
Photoinitiators

The most important factor that influences photopolymerization was the kind of photoinitiator.¹⁶ The varieties and the quantity of photoinitiators determine the water-absorption capacity of SAR. Four kinds of photoinitiators (Irgacure 651, Irgacure 819, Irgacure 1700, and Irgacure 1800) were used in synthesizing AA-potassium acrylate copolymer SAR. Schemes 1–3 show the chemical structures and photolysis mechanisms of these three photoinitiators and the resultant radicals, so these photopolymerization processes are radical polymerization in nature.

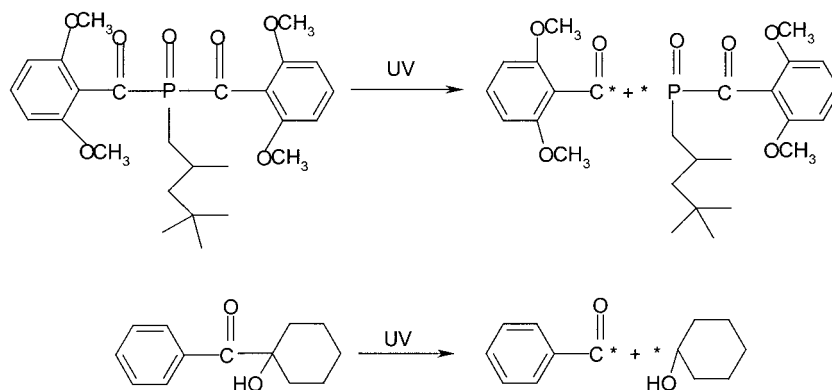
From Tables I and II we learn that different photoinitiators determined the speed of photopolymerization and the properties of SAR. When using Irgacure 651, Irgacure 1700, and Irgacure 1800 as photoinitiators, the water-absorption capacity of SAR was higher.



Scheme 1 Processes of fragmentation of Irgacure 651.



Scheme 2 Processes of fragmentation of Irgacure 1700.



Scheme 3 Processes of fragmentation of Irgacure 1800.

Irgacure 1700 was more efficient in capacity of initiation than were the others, reaching a top Q value of 545 mL/g and crosslinking ratio of 95%, with only 5 min of exposure time. Irgacure 1800 was the second most efficient after Irgacure 1700. Irgacure 1700 exhibited high efficiency of photoinitiation toward AA and acrylate monomers. This behavior can be explained in terms of the pyramidal structure of the phosphonyl radical, which allows the site of the unpaired electron to be approached rather easily by AA and acrylate monomers.¹⁷ In short, by use of Irgacure 1700 as photoinitiator to synthesize AA–potassium acrylate SAR, the speed of polymerization and the crosslinking reaction were fast and water-absorption capacity of the product was high.

Crosslinking agents

Crosslinking agents constituted another important factor that determined the water-absorption characteristics and mechanical properties of AA–potassium acrylate SAR. In AA–potassium acrylate copolymerization, the crosslinking reaction may be per-

formed by copolymerization and esterification. Here three different kinds of crosslinking agents— N,N' -methylene bisacrylamide, hydroxyethyl acrylate, and glycerol—were used separately. The crosslinking reaction of N,N' -methylene bisacrylamide was copolymerization with AA and potassium acrylate; in the case of glycerol, it was esterification between the hydroxyl group of glycerol and the carboxyl group on the polymer chain; in the case of hydroxyethyl acrylate, it was either copolymerization or esterification. Figures 2–4 show that, when using N,N' -methylene bisacrylamide, the peak value of Q of the SAR was 1368 mL/g, and the respective concentration of the crosslinking agent was 0.001%; for glycerol, the peak value of Q of SAR was 350 mL/g, whose respective concentration was 1.0%; for hydroxyethyl acrylate, the Q (885 mL/g) and the concentration (0.2%) were between those of the other two. The reason that would explain the consequences above is the crosslinking mechanism of these three kinds of crosslinking agents is different. The efficiency of crosslinking by copolymerization is much higher than that of crosslinking by esterifi-

TABLE I
Effects of Photoinitiators and Exposure Time on Water Absorbency of SAR^a

Exposure time (min)	Q (mL/g)			
	Irgacure 651	Irgacure 1700	Irgacure 1800	Irgacure 819
1	205	235	230	0
5	450	545	530	112
10	460	539	525	210
20	445	540	522	395
30	438	530	520	385

^a Potassium acrylate monomer: AA monomer (mol) 4.55; photoinitiator: 0.05% (weight); crosslinking agent: 0.01% (weight) N,N' -methylene bisacrylamide.

TABLE II
Effects of Photoinitiators and Exposure Time on Crosslinking Ratio of SAR^a

Exposure time (min)	G (%)			
	Irgacure 651	Irgacure 1700	Irgacure 1800	Irgacure 819
1	39	45	41	0.0
5	94	95	95	28
10	96	95	94	49
20	94	94	93	78
30	94	92	93	83

^a Potassium acrylate monomer: AA monomer (mol) 4.55; photoinitiator: 0.05% (weight); crosslinking agent: 0.01% (weight) N,N' -methylene bisacrylamide.

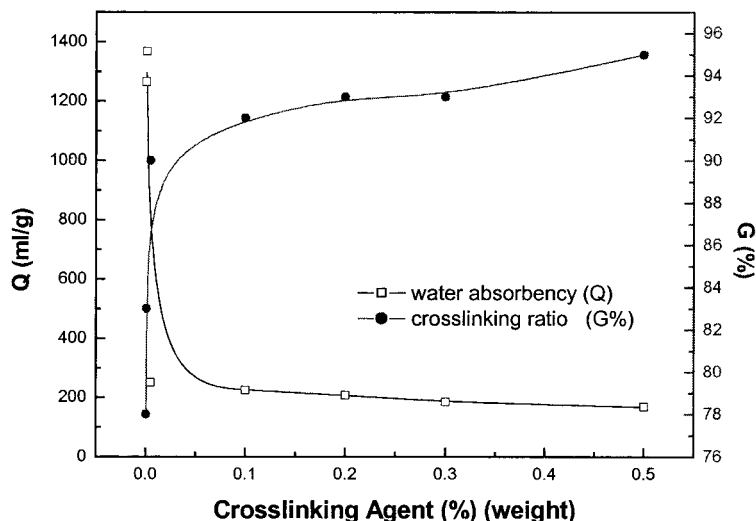


Figure 2 Effects of crosslinking agent (*N,N'*-methylene bisacrylamide) concentration on water absorbency (*Q*, mL/g) and crosslinking ratio (*G*%, %) of AA-potassium acrylate SAR. Note: potassium acrylate monomer : AA monomer (mol), 4.0; photoinitiator, 0.25% (weight) Irgacure 651; exposure time, 5 min.

cation. When polymerization proceeds, the esterification reaction of hydroxyethyl acrylate and glycerol with acid group on the polymer chain occurred. However, in the particular conditions of this water solution, the conversion percentage of esterification is low, depending on the equilibrium constant of the reaction.

Exposure time

The exposure time played an important role in determining the characteristics of SAR. We used Irgacure

651, Irgacure 1700, and Irgacure 1800 as photoinitiators to synthesize AA-potassium acrylate SAR. Figures 5–7 show the effects of exposure time on water and salt solution absorbency and crosslinking ratio of SAR. A longer exposure time resulted in higher water (salt solution) absorbency. However, excessive exposure time led to a slight decrease of water-absorption characteristics, attributed to the excessive UV radiation that caused the polymer to degrade. So from Figures 5–7 we can observe that in this condition of photopolymerization, using Irgacure 1700 and Irgacure 1800 as photoinitiators, the proper exposure time

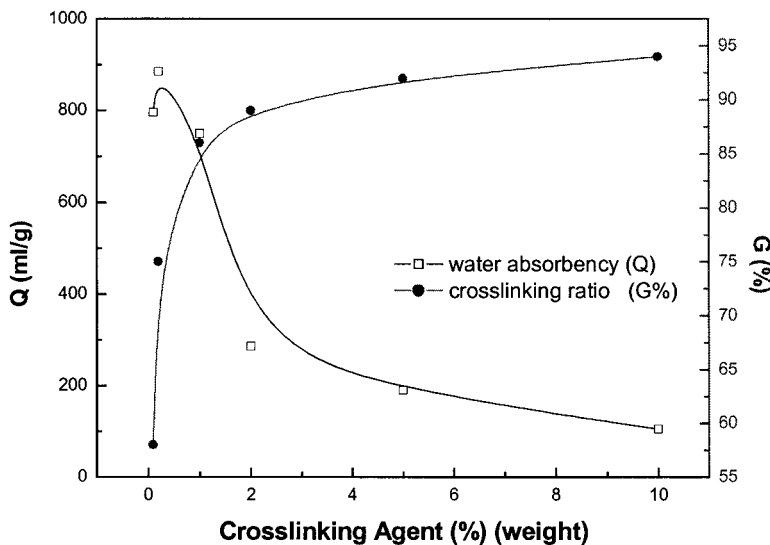


Figure 3 Effects of crosslinking agent (hydroxyethyl acrylate) concentration on water absorbency (*Q*, mL/g) and crosslinking ratio (*G*%, %) of AA-potassium acrylate SAR. Note: potassium acrylate monomer : AA monomer (mol), 4.0; photoinitiator, 0.25% (weight) Irgacure 651; exposure time, 5 min.

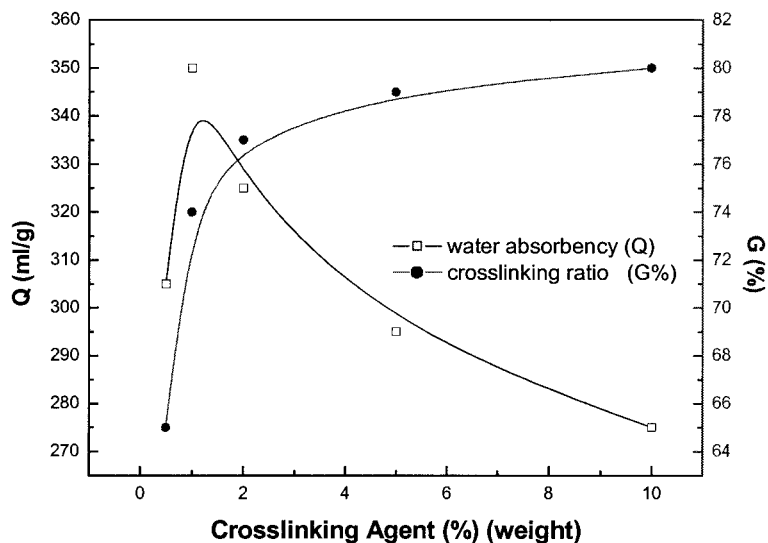


Figure 4 Effects of crosslinking agent (glycerol) concentration on water absorbency (Q , mL/g) and crosslinking ratio ($G\%$, %) of AA-potassium acrylate SAR. Note: potassium acrylate monomer : AA monomer (mol), 4.0; photoinitiator, 0.25% (weight) Irgacure 651; exposure time, 5 min.

was about 5 min. For Irgacure 651, it was about 10 min.

CONCLUSIONS

A superabsorbent resin was synthesized by a new method, that of direct UV photopolymerization. The proper ratios of potassium acrylate to AA and sodium acrylate to AA were 4.55 and 5.67, respec-

tively, for achieving a higher Q value of SAR. Using Irgacure 651, Irgacure 1700, and Irgacure 1800 as photoinitiators, and exposure time ranging from 5 to 10 min under UV light, good water-absorption characteristics of SAR were achieved. In this case Irgacure 1700 exhibited higher efficiency of photopolymerization. N,N' -Methylene bisacrylamide and hydroxyethyl acrylate and glycerol were used as crosslinking agents for preparing SAR, of which

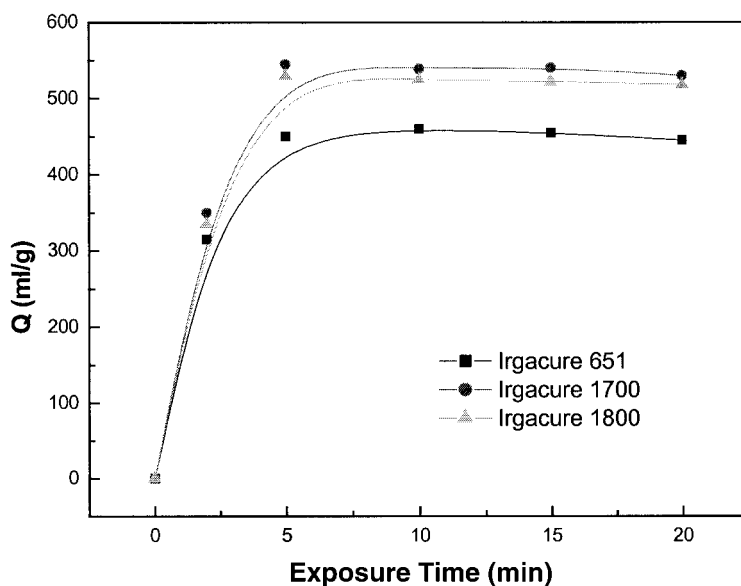


Figure 5 Effects of exposure time on water absorbency (Q , mL/g) of AA-potassium acrylate SAR. Note: potassium acrylate monomer : AA monomer (mol), 4.55; photoinitiator, 0.05% (weight); crosslinking agent, 0.01% (weight) N,N' -methylene bisacrylamide.

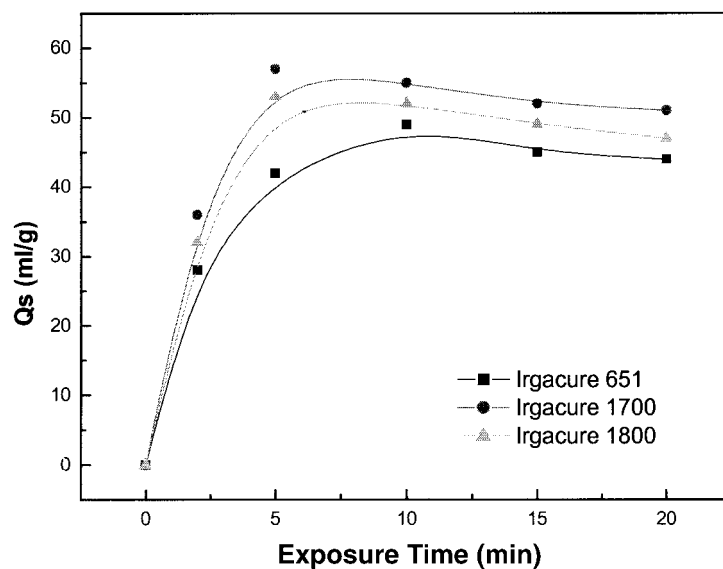


Figure 6 Effects of exposure time on salt solution absorbency (Q_s , mL/g) of AA-potassium acrylate SAR. Note: potassium acrylate monomer : AA monomer (mol), 4.55; photoinitiator, 0.05% (weight); crosslinking agent, 0.01% (weight) *N,N'*-methylene bisacrylamide.

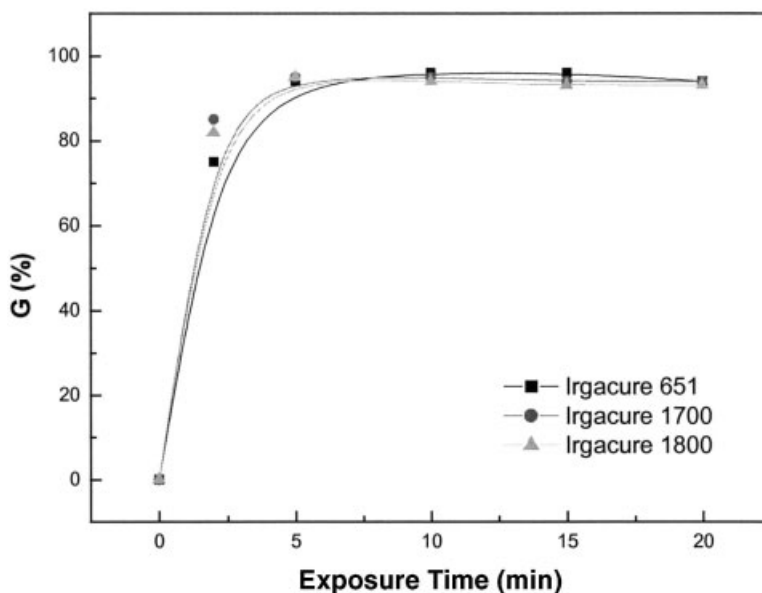


Figure 7 Effects of exposure time on crosslinking ratio (G %, %) of AA-potassium acrylate SAR. Note: potassium acrylate monomer : AA monomer (mol), 4.55; photoinitiator, 0.05% (weight); crosslinking agent, 0.01% (weight) *N,N'*-methylene bisacrylamide.

N,N'-methylene bisacrylamide was the most efficient. AA-potassium acrylate SAR with a Q value as high as 1368 mL/g was attained by UV photopolymerization (ratio of potassium acrylate monomer : AA monomer, 4.0; photoinitiator, 0.25% Irgacure 651; crosslinking agent, 0.001% *N,N'*-methylene bisacrylamide; exposure time, 5 min).

References

1. Fanta, G. F.; Burr, R. C.; Rist, C. E. *J Appl Polym Sci* 1966, 10, 929.
2. Fanta, G. F.; Burr, R. C.; Rist, C. E. *J Appl Polym Sci* 1967, 11, 457.
3. Fanta, G. F.; Burr, R. C.; Rist, C. E. *J Polym Sci* 1966, B4, 765.
4. Athawale, V. D.; Vidyagauri, L. *Carbohydr Polym* 1998, 35, 21.
5. Fujimaru, H.; Kimura, K.; Ishizaki, K.; Harada, N. *Jpn. Pat. JP 11209421 A2*, 1999.

6. Katsuhiko, K.; Nagasuna, K. Eur. Pat. EP 945143 A2, 1999.
7. Ahn, B.-m.; Park, J.-b.; Nomura, K.; Atsugi, M.; Mizutani, K. Jpn. Pat. JP 11302310 A2, 1999.
8. Dairoku, Y.; Irie, Y.; Fujino, S.; Fujita, Y.; Azumi, T.; Ishizaki, K. Eur. Pat. EP 1178059 A2, 2002.
9. Mikita, M.; Tanioku, S.; Takayasu, T. U.S. Pat. 4,703,067, 1987.
10. Aoki, S.; Yamasaki, H. U.S. Pat. 4,093,776, 1998.
11. Lin, R. X.; Huang, Y. L.; Niu, A. J. J Polym Mater Sci Eng 1999, 15, 117 (in Chinese).
12. Tian, D. T.; Guo, J. S.; Xie, L. Q. J Appl Chem 1997, 14, 15 (in Chinese).
13. Lin, R. X.; Huang, Y. L.; Niu, A. J. J Beijing Univ Chem Technol 1998, 25, 35 (in Chinese).
14. Lu, J. M.; Zhu, X. L.; Zhu, J. J Appl Polym Sci 1997, 66, 129.
15. Zou, X. X. Super Water Soluble Polymers; Chemical Press: Beijing, 1991.
16. Wang, H. D.; Jiang, L. Theory and Application of UV Curing Materials; Science Press: Beijing, 2001.
17. Sumiyoshi, T.; Schnabel, W. Macromol Chem Phys 1985, 186, 1811.