

pH-Response Superabsorbent Hydrogel Synthesized by Ultraviolet Photopolymerization

Weiying Ruan,¹ Yanqing Lian,¹ Tao Zhen,² Luning Huang,² Jinliang Qiao²

¹Institute of Polymer Science and Engineering, Department of Chemical Engineering, Tsinghua University, Beijing 100084, People's Republic of China

²College of Materials Science and Engineering, Beijing University of Chemical Technology, Beijing 100029, People's Republic of China

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ABSTRACT: A new synthesis method of pH-response superabsorbent hydrogels (SHG) was achieved by direct ultraviolet (UV) photopolymerization, and in particular, the synthesis of SHGs of acrylic acid (AA), sodium acrylate (AANa), and methacrylcholine chloride (MACC) tri-component copolymer by UV photopolymerization were investigated. The pH value responsive behavior of SHG with different monomer ratios of MACC and AA was researched, and SHG showed large swelling properties at pH value approximately 7. Influences of monomer ratio (mol) of AANa to AA, photoinitiators, crosslinking agents, and exposure time of UV light on the water absorbent properties were studied. The results showed that the water absorbent capacity of SHG based on photoinitiators:

Esacure KTO46 or Irgacure 651 can reach comparatively high, *N,N'*-Methylene bisacrylamide and diethylene glycol diacrylate (DEGDA) were high efficient crosslinking agents for its crosslinking the molecular chains through attending the copolymerization with monomers. When the exposure time was 10 min, the distilled water absorbency of SHG was 1503 mL/g under the condition: content of MACC, 14.3 wt %; monomer ratio (mol) of AANa to AA: 5.67; content of DEGDA and Irgacure 651, 0.0025 and 0.25 wt %.
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Key words: ultraviolet photopolymerization; pH-response; superabsorbent hydrogel; photoinitiator

INTRODUCTION

Superabsorbent hydrogel (SHG) is an important type of functional polymers. SHGs are lightly crosslinked hydrophilic polymers that can absorb, swell, and retain aqueous solutions up to hundreds, even thousands, of times their own weight. These materials, first originated in the United States as water retention agents in agriculture, were developed in Japan in the mid 1970s in the personal care and hygienic products (disposable diapers, sanitary napkins, surgical pads, etc.).¹ Some SHGs could respond to the stimulation from outside environment, such as pH values, variety of aqueous solutions, and the status of SHGs changed from swelling to shrinking.^{2–4} This behavior of stimulative–responsibility made pH-response SHG be widely used as healthcare products and controlled release agents for agrochemicals or pharmaceuticals. The traditional method of synthesis of SHG is thermal polymerization, including solution polymerization and inverse suspension polymerization.^{5–17} Compared with thermal polymerization, UV

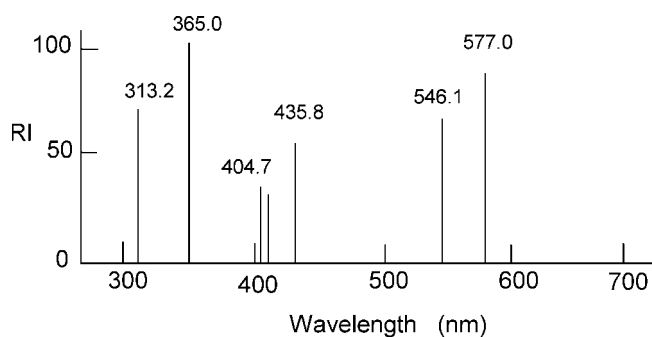
photopolymerization has many advantages such as simpler technology, it may be carried out at normal temperature, undergoes a very short exposure time, and produces comparatively less pollution.^{18–19} In this study, we propose a method of UV photopolymerization for synthesizing AA, AANa, and MACC tri-component copolymer SHGs. We then report on the investigation of the influence of the pH value responsive behavior of SHG with different monomer content of MACC, and the mol ratio of monomers AANa to AA on distilled water absorbency *Q* of the SHG. The effects of photoinitiators, crosslinking agents, and exposure time on the properties of the SHG were also investigated.

EXPERIMENTAL

Materials

Acrylic acid (AA), 2-hydroxypropyl acrylate (HPA), and diethylene glycol diacrylate (DEGDA) were purchased from Beijing Dongfang Chemical Factory (China). MACC (80% aqueous) was purchased from Tokyo Kasei Kogyo (Japan). Sodium hydroxide, *N,N'*-methylene bisacrylamide and glycerol were purchased from Beijing Chemical Factory (China). Irgacure651, Irgacure369, and Irgacure907 were

Correspondence to: R. Weiying (rwq@mail.tsinghua.edu.cn).



Scheme 1 Wavelength distributing of UV light.

provided by Ciba-Geigy Company. Esacure KTO46 and Esacure KIP ME were provided by Sartomer Company.

Instrument

UV light (high-pressure mercury light, the main wavelength distribution is shown in Scheme 1, the main wavelength of radiation is about 365 nm), 700 W, $I = 1.0 \text{ mW/cm}^2$.

Synthesis

At room temperature, AA (7–10 g) was first neutralized by sodium hydroxide aqueous solution in a beaker, to which were added MACC, photoinitiators (Irgacure651, Irgacure369, Irgacure907, Esacure KIP ME, or Esacure KTO46), and crosslinking agents (*N,N'*-methylene bisacrylamide, DEGDA, HPA, or glycerol), after which the solution was thoroughly mixed. After exposing it under high-pressure mercury light for a certain interval of time, the SHG of AA-AANa-MACC copolymer was obtained, after which it was dried and ground into particles of appropriate size for research. Scheme 2 shows the mechanism of UV photopolymerization of SHG.

Characterization

Distilled water absorbency (Q , mL/g), salt solution (NaCl: 0.9%) absorbency (Q_s , mL/g), and pH-buffer

solution (NaOH, HCl aqueous solution) absorbency (Q_b , mL/g) were determined by the natural filtration method²⁰: Put 0.1 g SHG sample into a filtration bag, then submerge the bag into 500 mL water (100 mL salt solution) for 10 min, then the Q (Q_s , Q_b) is calculated by the ratio of the volume of loss water (salt solution) to the mass of SHG. (The diameter of each sides of SHG sample is about 0.07–0.08 cm.) Cross-linking ratio (G , %) (percentage of insoluble part of SHG, the molecule of it was crosslinked, G was calculated by the mass ratio of M_1 : M_2 (M_1 : mass of SHG extracted by distilled water; M_2 : mass of the SHG) was determined by the natural filtration method.²⁰

RESULTS AND DISCUSSION

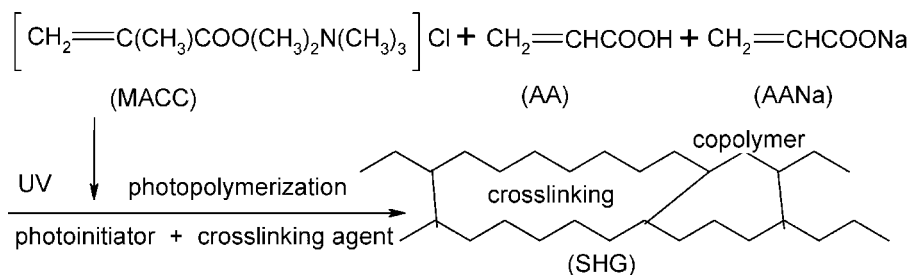
pH-responsive properties and monomer ratio (mol) of AANa to AA

Figure 1 shows the pH-responsive behavior of SHG, the effects of pH-value of aqueous solution on water absorbent characteristics of SHG. Q_b increased as the pH values increased from 1 to 7, the top Q_b can reach 1485 mL/g (content of MACC: 14.3 wt %). When the pH values increases from 7 to 13, the Q_b of SHG tends to decrease. This result explains that AA, AANa, and MACC tricomponent copolymer SHG is a kind of pH-sensitive hydrogel, and the maximum water swelling capacity of SHG appears at pH value of solution: ~ 7 . Different ratios (mol) of AANa monomer to AA monomer determined the Q of SHG. Figure 2 shows the effects of ratio (mol) of AANa monomer to AA monomer on the Q and Q_s values of SHG. When the content of MACC was 20 wt %, the best ratio (mol) of AANa to AA both in distilled water and salt solution were all 5.67, highest Q : 502 mL/g and highest Q_s : 51 mL/g were obtained separately.

Photoinitiators

Effects of photoinitiators and exposure time

The influencing factors of photoinitiator play a very important role in the UV photopolymerization of



Scheme 2 The mechanism of UV photopolymerization.

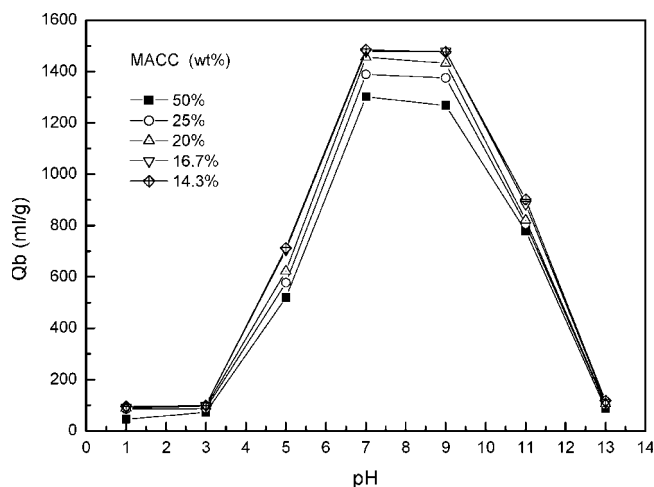


Figure 1 The pH value responsive behavior of SHG at different content of MACC. Note: monomer ratio (mol) AANa: AA, 4.56; photoinitiator, 0.5 wt % Irgacure 651; crosslinking agent, 0.005 wt %, *N,N'*-methylene bisacrylamide; exposure time, 10 min.

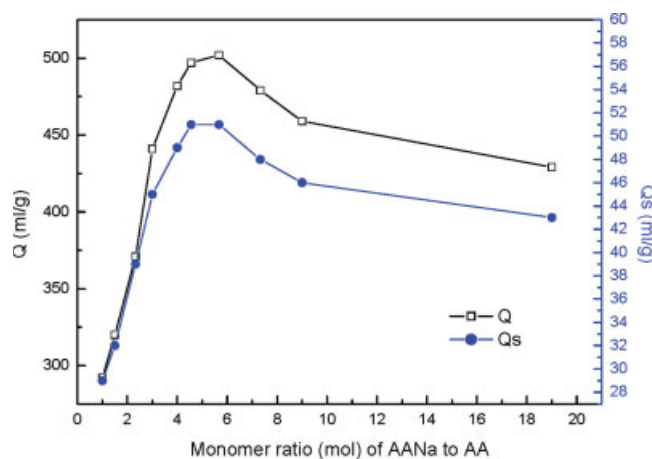
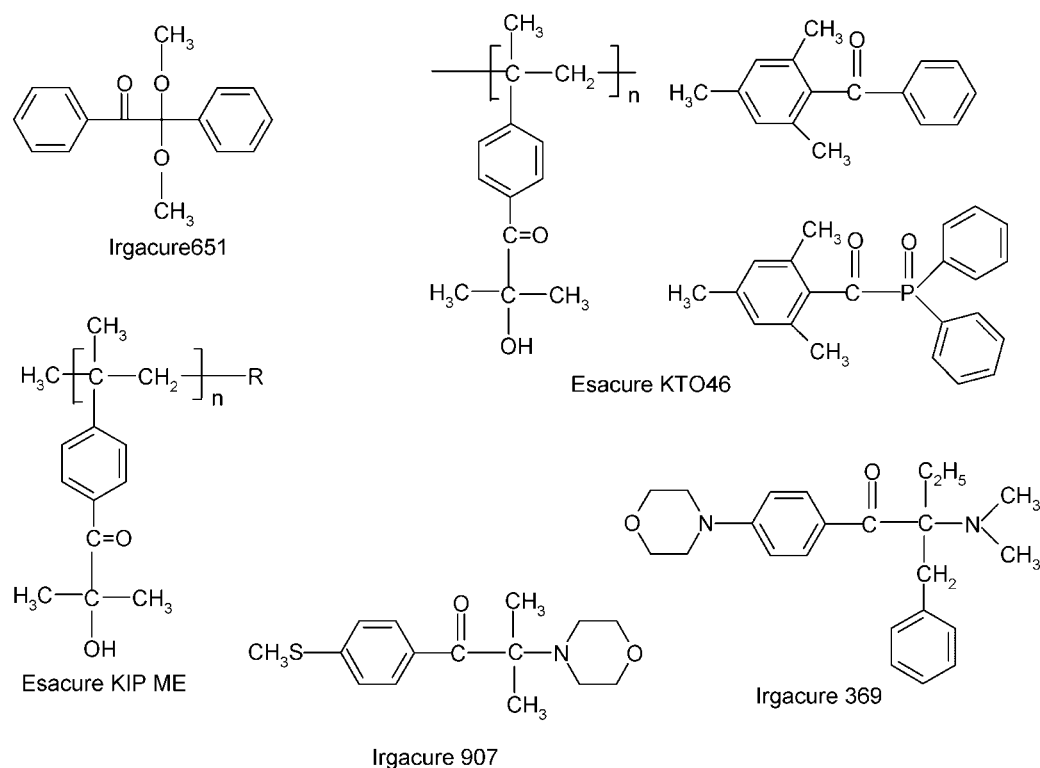


Figure 2 Effects of monomer ratio (mol) of AANa to AA on water absorbent capacity of SHG. Note: MACC, 20 wt %; photoinitiator, 0.25 wt % Irgacure 651; crosslinking agent, 0.015 wt % *N,N'*-methylene bisacrylamide; exposure time, 10 min. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

SHG.²¹ Scheme 3 lists the molecular formulas of the photoinitiators that we used. As shown in Table I, there were five photoinitiators (Irgacure651, Irgacure369, Irgacure907, Esacure KIP ME, and Esacure KTO46) used in synthesizing the AA-AANa-MACC tricomponent copolymer SHGs. The conditions of the photopolymerization are shown in Table I. The content

of the photoinitiator (crosslinking agent) of the SHG was calculated from the ratio of the mass of the photoinitiator (crosslinking agent) to the mass of the AA, AANa, and MACC monomers. The longer the exposure time, the higher was the Q , G , and Q_s in the SHG. Excessive exposure led to some degradation of the crosslinked copolymer. When the exposure time was



Scheme 3 Molecular formula of photoinitiators.

TABLE I
Effects of the Photoinitiators and Exposure Time on SHG

Photoinitiator type	Exposure time (min)	Q (mL/g)	Q _s (mL/g)	G (%)
Esacure KTO46	1	220	26.0	62.5
	5	490	51.0	92.5
	10	495	52.0	93.9
	20	490	51.5	94.6
	30	485	50.5	94.1
Irgacure 651	1	208	25.5	57.5
	5	472	49.5	91.3
	10	481	49.5	92.1
	20	479	49.0	92.5
	30	476	48.5	91.1
Esacure KIP ME	1	105	13.0	34.5
	5	125	16.0	61.7
	10	293	28.0	70.8
	20	401	41.5	90.3
	30	388	40.5	89.2
Irgacure 369	1	101	12.5	34.1
	5	125	15.5	59.9
	10	298	29.0	74.7
	20	392	39.5	90.9
	30	389	38.5	89.3
Irgacure 907	1	115	12.0	42.3
	5	132	14.5	73.2
	10	313	32.5	76.7
	20	406	41.0	91.8
	30	402	40.5	91.1

MACC, 14.3 wt %; photoinitiator, 0.15 wt %; crosslinking agent, 0.025 wt %, *N,N'*-methylene bisacrylamide; monomer ratio (mol) AANa: AA, 4.56.

greater than 20 min, *Q* and *G* of the SHG decreased a little. Table I shows that the proper exposure time of the SHG was about 10–20 min, and Esacure KTO46 was the most efficient photoinitiator among the photoinitiators we used for short exposure times, yielding high *G*, *Q*, and *Q_s* values.

Effects of content of photoinitiators

Esacure KTO46 is a kind of new style and high efficiency photoinitiator. It is a kind of three parts composition mixture of which contains acylphosphine oxides. The acylphosphine oxides in Esacure KTO46 can absorb UV light and give out phosphonyl radicals. The chemical structure of phosphonyl radical is pyramidal structure, which allows the site of the unpaired electron to be approached rather easily by AA, AANa, and MACC monomers.²² For this reason, Esacure KTO46 has high activity of initiation than other photoinitiators in Table I. Figure 3 shows the effects of content of photoinitiator, Esacure KTO46, on *Q* and *Q_s* of SHG. As the content of Esacure KTO46 increases, *Q* and *Q_s* increases significantly. When the content of Esacure KTO46 reaches 0.3 wt %, the top values of *Q* and *Q_s* are 1301 and 131 mL/g, respectively.

Crosslinking agent

Crosslinking agents constituted another important factor that determined the water-absorption characteristics and mechanical properties of AA-AANa-

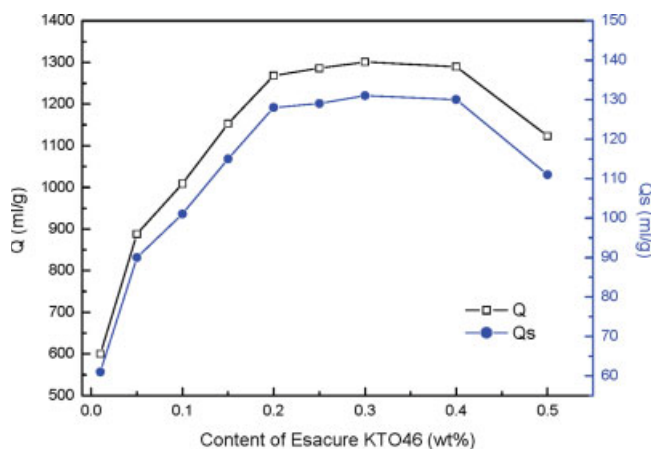
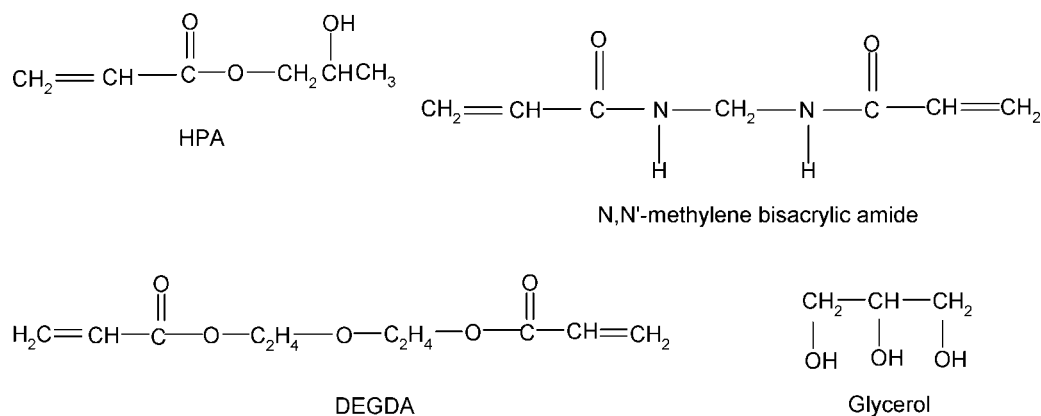


Figure 3 Effect of content of photoinitiator (Esacure KTO46) on water absorbent capacity of SHG. Note: MACC, 14.3 wt %; monomer ratio (mol) AANa: AA, 5.67; crosslinking agent, *N,N'*-methylene bisacrylamide (0.0015 wt %); exposure time, 10 min. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]



Scheme 4 Molecular structure of crosslinking agents.

MACC tricomponent copolymer SHG. Scheme 4 shows the molecular structure of the crosslinking agents that were used for this study. In AA-AANa-MACC copolymerization, the crosslinking reaction may be performed by mechanism of copolymerization and esterification. Here, three different kinds of crosslinking agents, DEGDA, HPA, and glycerol, were used separately. The crosslinking reaction of DEGDA was copolymerization with AA, AANa, and MACC. 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 HPA, it was either copolymerization or esterification. From Figures 4–6, we learn that, when using DEGDA as crosslinking agent, the peak value of Q of the SHG was 1503 mL/g, and the respective content of the crosslinking agent was 0.0025 wt %. Using glycerol as crosslinking agent, the top value of Q of

SHG was 449 mL/g, whose respective content was 1.0 wt %. Using HPA as crosslinking agent, the top Q (1309 mL/g) and the content (0.2 wt %) 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 esterification. When polymerization proceeds, the esterification reaction of HPA and glycerol with carboxyl group on the polymer chain occurred. However, in the particular conditions of this water solution, the conversion percentage of esterification is low, so the crosslinking efficiency of esterification style crosslinking agent, such as glycerol or HPA, is not as high as those of copolymerization style, such as DEGDA or *N,N'*-methylene bisacrylamide.

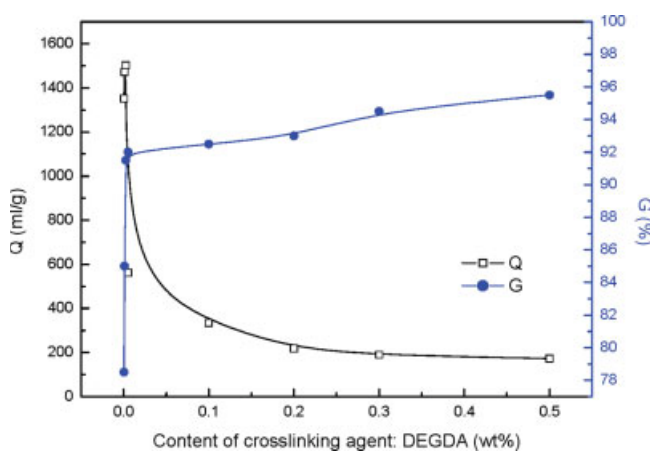


Figure 4 Effects of crosslinking agent (DEGDA) content on Q and G of AA-AANa-MACC SHG. Note: MACC, 14.3 wt %; monomer ratio (mol) AANa: AA, 5.67; photoinitiator, Irgacure 651 (0.25 wt %); exposure time, 10 min. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

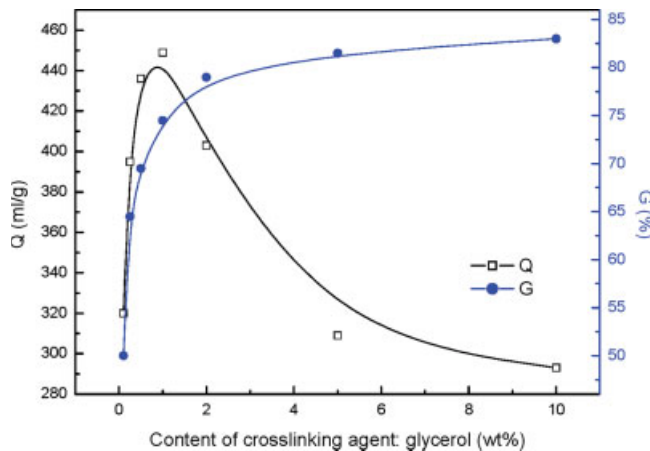


Figure 5 Effects of crosslinking agent (glycerol) content on Q and G of AA-AANa-MACC SHG. Note: MACC, 14.3 wt %; monomer ratio (mol) AANa: AA, 5.67; photoinitiator, Irgacure 651 (0.25 wt %); exposure time, 10 min. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

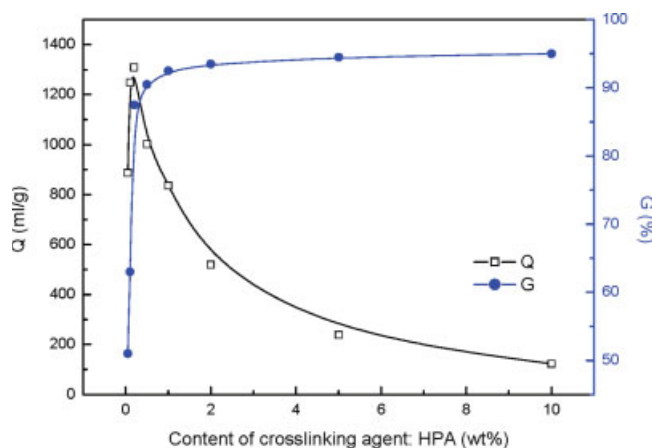


Figure 6 Effects of crosslinking agent (HPA) content on Q and G of AA-AANa-MACC SHG. Note: MACC, 14.3 wt %; monomer ratio (mol) AANa: AA, 5.67; photoinitiator, Irgacure 651 (0.25 wt %); exposure time, 10 min. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

CONCLUSIONS

Synthesis of pH-response AA-AANa-MACC tricomponent copolymer SHG by directly UV photopolymerization is a new method. The top water swelling capacity of SHG appears at ~ 7 of pH value of solution. The proper monomer ratio (mol) of AANa to AA is 5.67 for reaching higher Q of SHG. Esacure KTO46 is a kind of high efficient photoinitiator. Using Esacure KTO46 as photoinitiator and an exposure time of 10–20 min, good properties of SHG were obtained, such as short exposure time, but high Q , Q_s , and G . DEGDA and HPA were high efficient crosslinking agents for synthesizing SHG with good water absorption capacity. Copolymerization and esterification are two main mechanism of crosslinking in the reaction system of synthesis pH-response SHG, and crosslinking efficiency of copolymerization is higher than that of esterification. SHG with Q as high as 1503 mL/g has been obtained by UV photo-

polymerization under the following conditions: content of MACC, 14.3 wt %; monomer ratio (mol) of AANa to AA is 5.67; photoinitiator: Irgacure 651, 0.25 wt %; crosslinking agent: DEGDA, 0.0025 wt %; exposure time: 10 min.

References

- Buchhlz, F. L.; Graham, T. *Modern Superabsorbent Polymer Technology*; Wiley-VCH: New York, 1998.
- Sawai, T.; Yamazaki, S.; Ikariyama, Y.; Aizawa, M. *Macromolecules* 1991, 24, 2117.
- Chou, L. Y.; Blanch, H. W.; Prausnitz, J. M. *J Appl Polym Sci* 1992, 45, 1411.
- Brian, R. S.; Helen, M. C.; Brian, V. *Macromolecules* 1997, 30, 482.
- Fanta, G. F.; Burr, R. C.; Rist, C. E. *J Appl Polym Sci* 1966, 10, 929.
- Fanta, G. F.; Burr, R. C.; Rist, C. E. *J Appl Polym Sci* 1967, 11, 457.
- Fanta, G. F.; Burr, R. C.; Rist, C. E. *J Polym Sci B* 1966, 4, 765.
- Athawale, V. D.; Vidyagauri, L. *Carbohydr Polym* 1998, 35, 21.
- Fujimaru, H.; Kimura, K.; Ishizaki, K.; Harada, N. *Jpn. Pat.* JP 11209421 A2 (1999).
- Katsuhiko, K.; Nagasuna, K. *Eur Pat.* EP 945143 A2 (1999).
- Ahn, B.-m.; Park, J.-b.; Nomura, K.; Atsugi, M.; Mizutani, K.; *Jpn. Pat.* JP 11302310 A2 (1999).
- Dairoku, Y.; Irie, Y.; Fujino, S.; Fujita, Y.; Azumi, T.; Ishizaki, K. *Eur Pat.* EP 1178059 A2 (2002).
- Mikita, M.; Tanioku, S.; Takayasu, T. *U.S. Pat.* 4,703,067 (1987).
- Aoki, S.; Yamasaki, H. *U.S. Pat.* 4,093,776 (1998).
- Lin, R. X.; Huang, Y. L.; Niu, A. J. *Polym Mater Sci Eng* 1999, 15, 117 (in Chinese).
- Tian, D. T.; Guo, J. S.; Xie, L. Q. *J Appl Chem* 1997, 14, 15 (in Chinese).
- Lin, R. X.; Huang, Y. L.; Niu, A. J. *J Beijing Univ Chem Technol* 1998, 25, 35 (in Chinese).
- Ruan, W. Q.; Qiao, J. L.; Huang, Y. L.; et al. *J Appl Polym Sci* 2004, 92, 1618.
- Ruan, W. Q.; Qiao, J. L.; Huang, Y. L.; et al. *J Appl Polym Sci* 2005, 95, 546.
- Zou, X. X. *Super Water Soluble Polymers*; Chemical Press: Beijing, 1991.
- Wang, H. D.; Jiang, L. *Theory and Application of UV Curing Materials*; Science Press: Beijing, 2001.
- Sumiyoshi, T.; Schnabel, W. *Macromol Chem Phys* 1985, 186, 1811.