Ultraviolet photopolymerization and performances of fast-water absorbing sodium polyacrylate

Banugul Dolat, Amatjan Sawut, Mamatjan Yimit, Ismayil Nurulla

Key Laboratory of Oil and Gas Fine Chemicals, Educational Ministry of China, School of Chemistry and Chemical Engineering, Xinjiang University, Urumqi 830046, China
Correspondence to: I. Nurulla (E-mail: ismayilnu@sohu.com)

ABSTRACT: A kind of fast-water absorbing sodium polyacrylate was prepared by UV polymerization under no crosslinker or initiator condition. Influence of factors, such as exposure time, neutralization degree, polymerization temperature, and monomer concentration on the absorption rate of the resin, were investigated. Its pH sensitivity, average absorption rate in distilled water and saline under load were also studied, respectively. The obtained resin reached to considerably high absorption rate: 4.6 g/g min and 2.6 g/g min even under 8000 Pa load in distilled water and 0.9% NaCl solution, respectively. Simultaneously, the resin displayed excellent water absorbency and water retention capacity. The impact of pH value on absorption rate reflected that the absorption rate was greatly influenced by pH. Synthesized polymer was characterized by FTIR, ^{1}H-NMR, and SEM. © 2015 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2015**, *132*, 42787.

INTRODUCTION

Acrylic acid-based superabsorbents are one of the popular polymers because of their broad sources and super water absorbency. They have been widely used not only in agriculture, horticulture, food additive but also in sanitary products, drug delivery,[1–3] and so on.

Arid soil during rain is expected to absorb rainwater quickly before evaporation. Disposable diapers, feminine napkins are required to have rapid absorption capacity.[4] Currently, majority of reports involve works pursuing the improvement of water absorption amount and gel strength of acrylic acid-based superabsorbents.[5–8] There are also some literatures that report swelling equilibrium time of polyacrylic acid: the average fastest swelling rates of which in a rather short time were less than 5 g/g min[9] (by γ-radiation crosslinking in aqueous solution), less than 10 g/g min[10] (by electron beam crosslinking), 35 g/g min[11] (by postpolymerization foaming protocol), respectively. However, some defects exist in reports mentioned above: (a) Their swelling rates in a specific short time are not fast enough; (b) The methods they adopted are time-consuming; (c) More substances were involved, which caused complex synthesis crafts. It seems to be essential to synthesize a sort of fast-swelling, uniform porous structured, less raw material typed resin.

In this study, a series of fast-water absorbing sodium polyacrylates were prepared by UV polymerization[12–14] without introducing any other substances. The optimum synthesis condition was determined by investigating the influences of corresponding factors on the absorption rate in distilled water within 30 min, with 5 min time interval. Then absorption rate of the resulted resin in various circumstances, including different pressure[13] and pH, and its structure were evaluated. To describe the absorption rate of the synthesized polymer, we chose its average absorption rate within 5 min, during which test data has stability and can reflect the fast-absorbing property of the resin in a better way. Resulted resin has the potential of industrialization because of simple process and excellent performances.

EXPERIMENTAL

Materials

Acrylic acid (AA) supplied by China Tianjin Damao Chemical Industry was used as monomer. The sodium hydroxide purchased from China Tianjin Baishi Chemical Industry was used as neutralizing reagent.

Synthesis of Fast-Absorbing Polymers

Fast-absorbing polymers were synthesized according to a procedure followed below: 5 mL of AA was introduced into a dish and partially neutralized using adequate volume of $5M$ sodium hydroxide. Then appropriate amount of water was added under
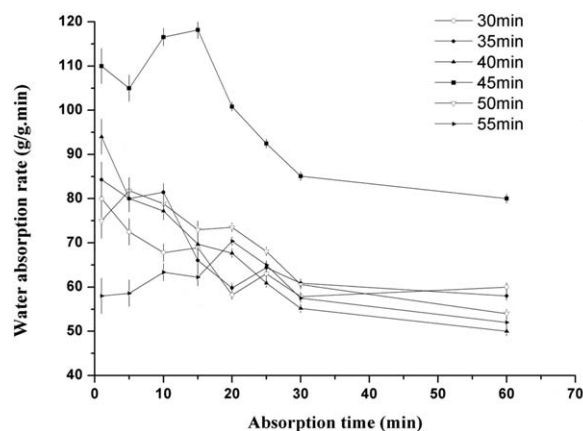
Figure 1. Effect of the reaction time on resin absorption rate.

continuous stirring condition to form well-dispersed mixture with monomer concentration adjusted to proper value. When the mixture solution was cooled down to room temperature, the dish was put into the UV polymerization equipment with 1000 W radiation power. The reaction was conducted under different polymerization times and temperatures. The formed polymers were dried at 80°C for 48 h in vacuum oven and then were smashed.

Absorbency Tests Under Unload Condition

0.1 g resin powder (40–60 mesh) was immersed in 600 mL distilled water or 0.9 wt % NaCl solution to measure its swelling equilibrium and average absorption rate within various time ranges from 1 min to 30 min, with 5 min time interval. Each of the swollen samples was filtered through a 100-mesh gauze bag by hanging it at a static state for 15 min. Absorbency and average absorption rate (v) of the resin were determined as follows:

$$Q = \frac{m_2 - m_1}{m_1} \qquad (1)$$

$$v = \frac{m_2 - m_1}{m_1 \times t} \qquad (2)$$

where m_2, m_1 are the weights of swollen and dried sample during t (min), respectively.

Absorbency Tests Under Load Condition

A porous plate ($d = 80$ mm, $h = 12$ mm) was put into a dish ($d = 160$ mm, $h = 22$ mm), then a glass cylinder, the bottom of which was covered with nylon gauze, was put on the plate. 0.1 g sample of fast-absorbing resin was placed on the surface of nylon gauze pressed by plastic tank ($d = 56$ mm, $h = 70$ mm) with different weighted loads in it. Distilled water or 0.9% NaCl solution was poured into the dish to the same height of the porous glass cylinder. The swollen sample was weighted within various time interval ranges from 1 min to 360 min. Its absorbency under load (AUL) and average absorption rate of the resin under load (ARUL) were determined as follows, respectively:

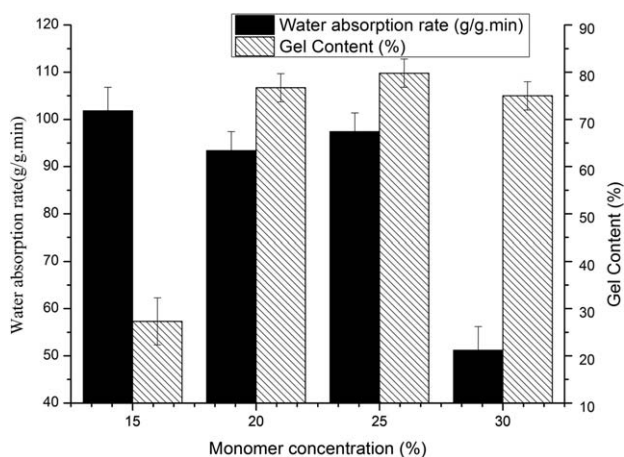$$AUL = \frac{m_2 - m_1}{m_1} \qquad (3)$$

Figure 2. Effect of monomer concentration on resin absorption rate and gel content.

$$ARUL = \frac{m_2 - m_1}{m_1 \times t} \qquad (4)$$

where m_2, m_1 are the weights of swollen and dried sample during t (min), respectively.

Measurement of Gel Content

Ample amount of sample was immersed into the mixture of 5 wt % acetone and water. Acetone was added to the sufficiently swollen sample until a group of white swollen substance appeared. After that, soluble fraction was washed away and the white swollen substance was dried to constant weight in vacuum oven. Gel content is measured as follows:

$$\text{Gel content } (\%) = \frac{m_2}{m_1} \times 100\% \qquad (5)$$

where m_1, m_2 is the weight of the sample before and after acetone treatment, respectively.

Tests of Water Retention

0.1 g swollen sample within 5 min, filtered by 100-mesh gauze bag and hanged at a static state, weighted within various time interval. Its water retention was measured as follows:
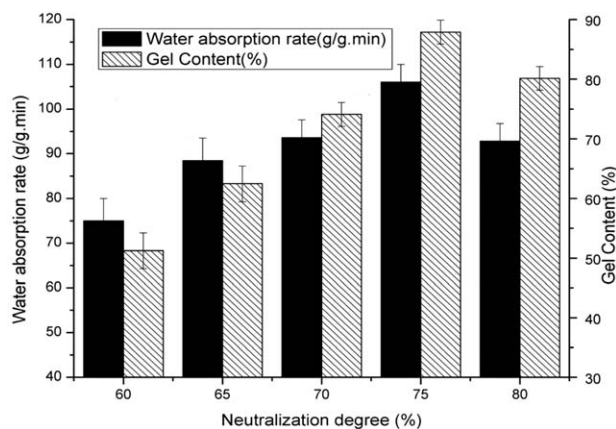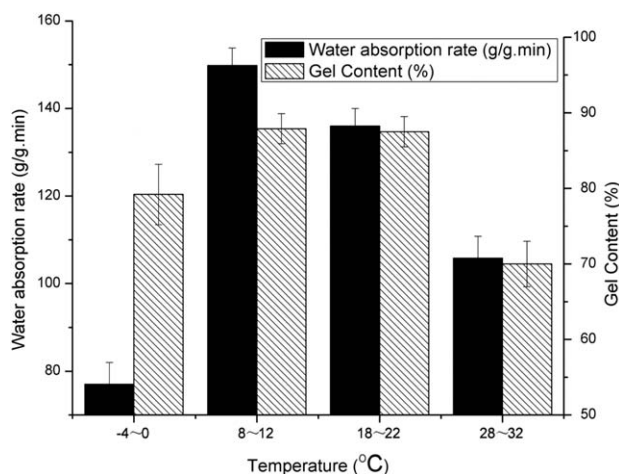

Figure 3. Effect of neutralization degree on resin absorption rate and gel content.

Figure 4. Effect of polymerization temperature on resin absorption rate and gel content.

$$W_r(\%) = \frac{m_i}{m_0} \times 100\% \qquad (6)$$

where m_0 is the initial weight of swollen water within 5 min, m_i is the weight of sample after releasing some water in different time.

Measurement of pH Sensitivity

Various pH-valued solutions were prepared with sodium hydroxide and hydrochloric acid. A series of 0.1 g samples were, respectively, immersed into 600 mL different solution with different pH. After 5 min, absorption rates of the samples were evaluated.

Analysis

The FTIR spectra was investigated on BRUKER EQUINOX-55 FTIR spectrometer in 4000–500 cm^{-1} region using KBr pellets. ^{1}H-NMR spectroscopy was carried to determine the chemical structures of the resin. Small amount of dried and milled sample was filtered through a 100-mesh sieve, then swollen in nuclear magnetic tube filled with D$_2$O for 1 h using a VARIAN INOVA-400 spectrometer (400 MHz).
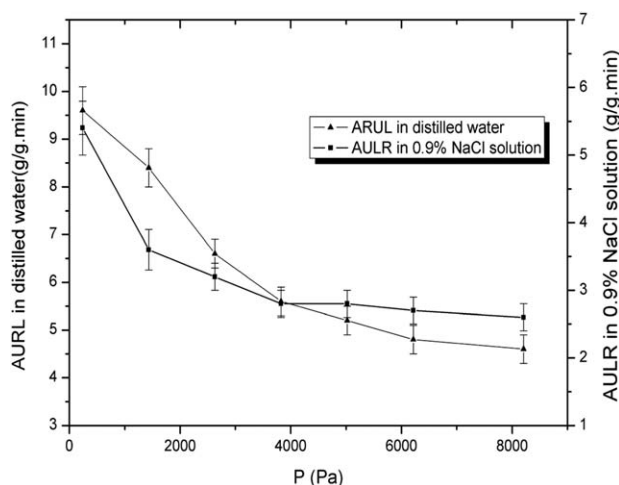
Table I. Water Retention Capacity of the Resin

Water absorption time:			5 min				
Water retention time (h)	2	6	12	24	33	48	56
Water retention rate (%)	92.9	86.8	75.2	58	44.7	28.6	21.01

The surface morphology of the resin was studied with scanning electron microscopy (SEM, JSM-5600LV, JEOL, Japan). Sample was swollen in distilled water first and frozen in liquid nitrogen and then lyophilized before investigated.

RESULTS AND DISCUSSION

Influence of Polymerization Time

Average water absorption rate (under unload condition) of the samples exposed to the UV light for different times were shown on Figure 1. Shorter or longer exposure time led to smaller absorption rate while 45 min-exposed resin displayed higher absorption rate within different time. Shorter exposure time makes monomer has no enough time to react, which cause incomplete polymerization, resulting in low absorption rate. Since UV rays play the role of initiators, longer exposure time will create macroradicals, making too intensive crosslinking density[15] and resulting in the low absorption rate. Apparently, the optimum polymerization time is 45 min.

Influence of Monomer Concentration

Figure 2 reveals the influence of monomer concentration on the resin absorption rate and gel content. At low monomer concentration, the resin resulted from the lack of effective collision chance of monomer molecular displays low absorption rate and low gel content because of unsufficient reaction[16] (semipolymerized resin has given viscosity that gives rise to the quantity of water surrounded by them, so, it seemed as if the sample had higher absorption rate at low monomer concentration, but in fact is not). At higher monomer concentration, percentages of linear polyacrylic acid within crosslinked polyacrylic acid increases, causing increased amount of soluble polymer.[17,18]

Figure 5. Absorption rate under load of the resin.
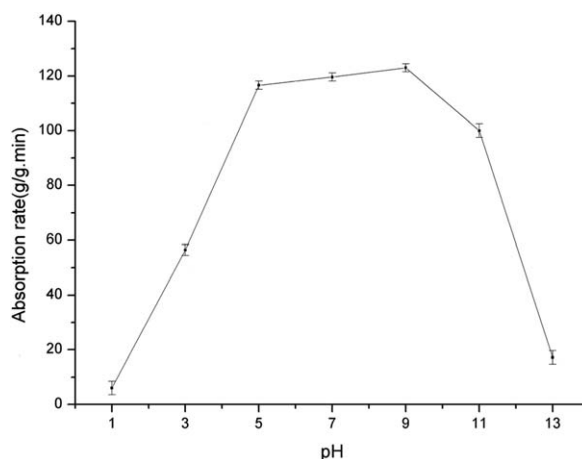
Figure 6. Effect of pH on absorption rate of the resin.
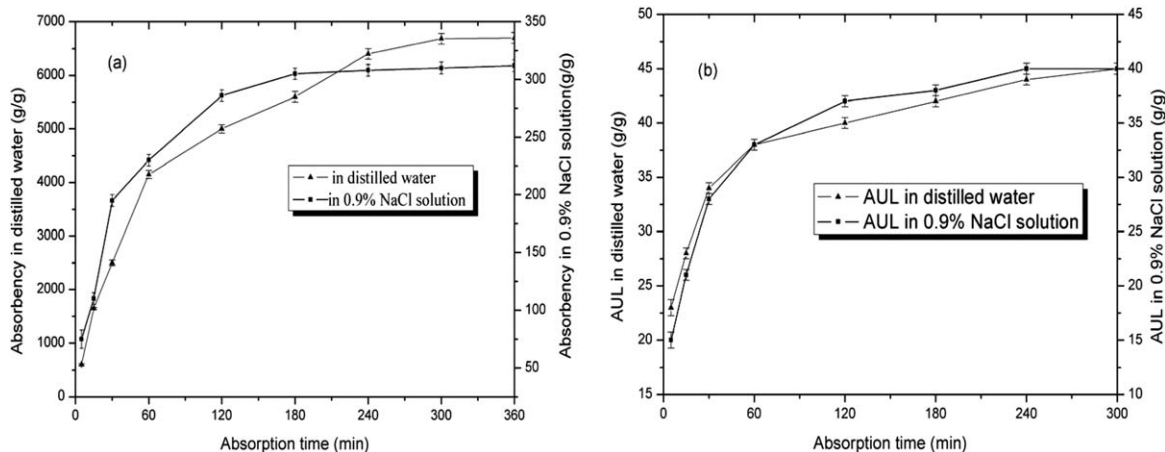
Figure 7. Swelling equilibrium (a) absorbency under unload condition in distilled water and 0.9% NaCl solution; (b) absorbency under load in distilled water and 0.9% NaCl solution.

Moreover, increase in the monomer concentration causes increase in the —COONa groups, simultaneously. And more —COO⁻, Na⁺ groups come together leads to counter ions which behave like an additional crosslinks. This fact cause decrease in pore sizes which resulted in decrease in swelling rate and degree. Obviously, the common conversion point (of absorption rate and gel content), at which monomer concentration was 25%, can be the optimal monomer concentration.

Influence of Neutralization

Neutralization degree had a great impact, as shown as on Figure 3, on gel content and absorption rate of the resins. Content of —COONa in the reaction system will change following the alternative neutralization degree. In the beginning, substitution of H in —COOH by Na+ was too limited to absorb large amount of water in a rather short time until the neutralization degree reached to 75%. Then, when the neutralization degree exceeded 75%, "charge screening effect" 15 of excess Na+ ions was turned out, resulting in the lower absorption rate and descended gel content. The analysis of these data leads to the conclusion that 75% can be the optimum neutralization degree of acrylic acid.

Influence of Polymerization Temperature

From Figure 4, it can be found that within 8–22°C, absorption rate and gel content only had small fluctuations. At too low temperature: −4–0°C, adequate polymerized polymer cannot be formed due to slower generation rate of free radicals, resulting in low absorption rate and gel content. At relative high temperature: 28–32°C, polymerized degree of the resin decreased because of partial thermal decomposition,[19] still resulting in low absorption rate and gel content. Temperature within 8–12°C favors the resin more in both of absorption rate and gel content.

Absorption Rate Under Load

Figure 5 shows the ARUL of the resin synthesized under optimal condition in distilled water and 0.9wt % NaCl solution respectively. ARUL of the sample in both of distilled water and 0.9% NaCl solution dropped down along with the increasing load and tended to the balance when the pressure added to 8000 Pa, at which condition the resin also had considerably high absorption rate (nearly about 5 g/g min in distilled water and 2.6 g/g min in 0.9% NaCl solution).

### Water Retention Capacity of the Resin

From Table I, it can be illustrated that the resin absorbed some water only for 5 min can still retain more than 20% water after 2 days.
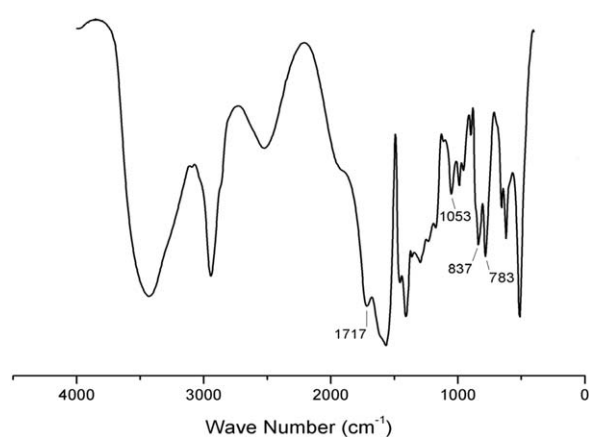
Figure 8. FTIR spectra of the fast-water absorbing resin.
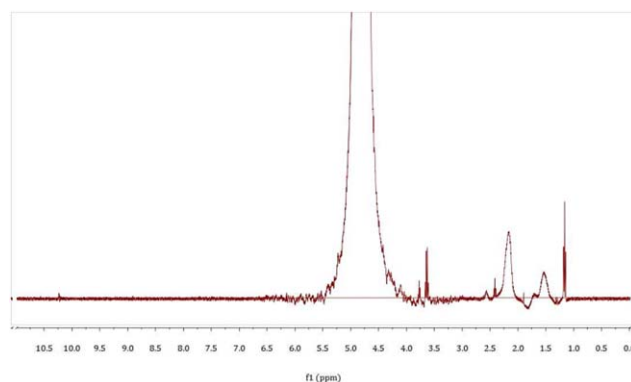
Figure 9. ¹H-NMR spectra of the fast-water absorbing resin. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
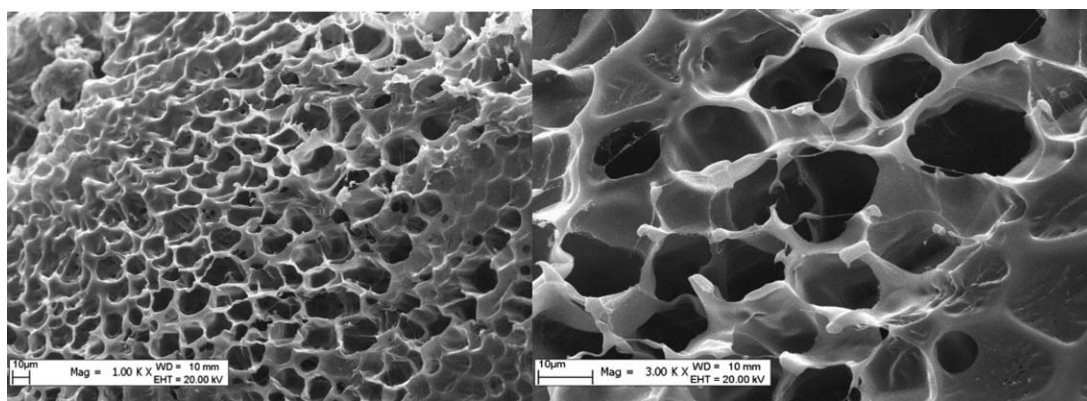
Figure 10. SEM pictures of the fast-water absorbing resin.

pH Sensitivity of the Fast-Absorbing Resin

From Figure 6, a conclusion can be made that absorption rate of the resin was heavily influenced by pH. The synthesized polymer had higher absorption rate in various pH valued solution ranges from 5 to 11.

Swelling Equilibrium

As is shown on Figure 7(a), equilibrium absorbency of the resin without load reached to 6500 g/g and 310 g/g in distilled water and 0.9% NaCl solution, respectively. Figure 7(b) shows equilibrium absorbency 45 g/g in distilled water and 40 g/g in 0.9% NaCl solution under 8000 Pa pressure and almost 50% of the whole absorbency was absorbed in 5 min.

IR Analysis of the Fast-Absorbing Resin

From IR spectra (Figure 8), the absorption peak around 1053 cm^{-1} was absorbed, which is extension vibration of C—O—C or —COO bounds. The characterization absorptions of C≡C occurred at 836 cm^{-1} and 782 cm^{-1}. The absorption peak around 1717 cm^{-1} indicated the existence of —CO bound. All of the absorption peaks described above suggested that the resins synthesized by UV polymerization possessed hydrophilic groups such as C≡C, C—O—C, and —COO.

^{1}H-NMR Analysis of the Fast-Water Absorbing Resin

Almost all of the absorbing peaks occurred at the chemical shifts before 5 cm^{-1} on Figure 9, which suggested that nearly all of the monomers turned to be polymers.

SEM Analysis of the Fast-Water Absorbing Resin

SEM pictures of samples frozen by liquid nitrogen and dried by lyophilized is shown on Figure 10. As is demonstrated on the SEM images, the resin after sufficiently swollen and dried displayed manifest network structure for the reason that it can easily loss great amount of free water on surface and portion bounded water (absorbed water) inside of it during freeze-drying process. This illustrated that polyacrylic acid has already formed uniformly distributed porous network structure which contributed to fast-water absorbing properties of the resin.

CONCLUSIONS

In this work, fast-water absorbing sodium polyacrylate was synthesized by UV polymerization, without introducing any cross-linker or initiator. The optimum synthesis condition is: 45 min exposure time, 25% monomer mass concentration, 75% neutralization degree, and 8–12°C. The absorption rate in distilled water and 0.9% NaCl solution respectively ranged from 119 g/g min to 4.6 g/g min, from 15 g/g min to 2.6 g/g min with the alternative load within 0–8000 Pa. Meanwhile, equilibrium absorbency without load in corresponding solutions reached to 6500 g/g and 310 g/g while equilibrium absorbency under 8000 Pa pressure reached to 45 g/g and 40 g/g, respectively. SEM images showed that well-distributed porous structure was formed. Owing to its simple synthesis process, excellent absorption and water retention rate, the prepared resin might be good for industrialization.

REFERENCES

1. Sharma, K.; Kaith, B. S.; Kumar, V.; Kalia, S.; Kumar, V.; Swart, H. C. *Geoderma* **2014**, *45*, 232.

2. Nho, Y.-C.; Park, J.-S.; Lim, Y.-M. *Polym. J.* **2014**, *6*, 890.

3. Sarti, F.; Javed, I.; Müller, C.; Shahnaz, G.; Rahmat, D.; Bernkop-Schnürch, A. *Anal. Biochem.* **2012**, *420*, 13.

4. Enrica Caló, V. V. K. *Eur. Polym. J.* **2015**, *65*, 252.

5. Chen, X.-P.; Shan, G.-R.; Huang, J.; Huang, Z.-M.; Weng, Z.-X. *J. Appl. Polym. Sci.* **2004**, *92*, 619.

6. Liu, C.-Y.; Zhang, M.-J.; Zhu, J.; Ma, S.-S. *J. Appl. Polym. Sci.* **2008**, *110*, 2440.

7. Sharma, K.; Kumar, V.; Kaith, B. S.; Kumar, V.; Som, S.; Kalia, S.; Swart, H. C. *Polym. Degrad. Stabil.* **2015**, *111*, 20.

8. Rui Ding, K. G. *J. Appl. Polym. Sci.* **2013**, *130*, 1098.

9. Esmaiel Jabbari, S. N. *Eur. Polym. J.* **2000**, *36*, 2685.

10. Sheikh, N.; Jalili, L.; Anvari, F. *Radiat. Phys. Chem.* **2010**, *79*, 735.

11. Ruiying Gong, N. K.; Mu, Y.; Li, J. Z.; Wan, X. *J. Appl. Polym. Sci.* **2012**, *125*, 3100.

12. Weiqing Ruan, J. Q.; Huang, Y.; Niu, A. *J. Appl. Polym. Sci.* **2004**, *92*, 1618.

13. Amatjan Sawut, M. Y.; Sun, W.; Nurulla, I. *Carbohydr. Polym.* **2014**, *101*, 231.

14. Hosseinzadeh, H.; Sadeghi, M. *Braz. J. Chem. Eng.* **2013**, *30*, 379.

15. Bardajee, G. R.; Pourjavadi, A.; Ghavami, S.; Soleyman, R.; Jafarpour, F. *Photochem. Photobiol. B: Biol.* **2011**, *102*, 232.

16. Andryushina, N. S.; Stroyuk, O. L.; Dudarenkob, G. V.; Kuchmiy, S. Y.; Pokhodenko, V. D. *Photochem. Photobiol. A: Chem.* **2013**, *256*, 1.

17. Peters, R.; Litvinov, V. M.; Steeman, P.; Dias, A. A.; Mengerink, Y.; van Benthem, R.; de Koster, C. G.; vander Wal, S. J.; Schoenmakers, P. *Chromatogr. Sci. Ser. A* **2007**, *1156*, 111.

18. Bai, M.; Wilske, B.; Buegger, F.; Esperschutz, J.; Bach, M.; Frede, H. G.; Breuer, L. *Environ. Sci. Pollut. Res.* **2015**, *22*, 5444.

19. Li, X.; Chen, Y. *J. Appl. Polym. Sci.* **2008**, *108*, 3435.