Polymer 51 (2010) 4058–4062

Contents lists available at ScienceDirect

Polymer

journal homepage: www.elsevier.com/locate/polymer

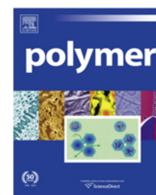


Photo-induced crosslinking of water-soluble polymers with a new photobase generator

Cheng Bo Cao [a,b,**], Chen Zhou [a], Xun Sun [b], Jian Ping Gao [b], Zhi Yuan Wang [b,*]

[a] School of Chemistry and Chemical Engineering, Shandong University, Jinan 250061, Shandong, China
[b] Department of Chemistry, Carleton University, 1125 Colonel By Drive, Ottawa, Ontario, Canada K1S 5B6

ARTICLE INFO

Article history:
Received 19 May 2010
Received in revised form
25 June 2010
Accepted 29 June 2010
Available online 7 July 2010

Keywords:
Photo-induced crosslinking
Water-soluble polymers
Photobase

ABSTRACT

A strong bicyclic guanidine base, 1,5,7-triaza-bicyclo[4.4.0]dec-5-ene (TBD), is photo-generated from its tetraphenylborate salt (TBD·$HBPh_4$) and can effectively catalyze the transesterification reaction between the ester and hydroxy groups in polymers. Accordingly, with TBD·$HBPh_4$ as a photobase generator, a water-soluble polymer blend, namely poly(1-vinylpyrrolidone-co-2-dimethylaminoethyl methacrylate) and 2-hydroxyethyl cellulose, has been developed as a potential eco-friendly photoresist. This photoresist system uses only water as a solvent and as a developer, rather than organic solvents and aqueous alkaline developers. The effects of the amount of photobase generator, polymer composition and photolithographic conditions on the photo-induced crosslinking and patterning of water-soluble polymers were studied.

© 2010 Elsevier Ltd. All rights reserved.

1. Introduction

Photo-induced crosslinking of polymeric materials is an important reaction in chemistry and as well a critical technology in industry such as microelectronics [1,2], microfluidics [3,4], sensors [5], biotechnology [6], and tissue engineering [7]. The current process routinely involves a photoacid generator, organic solvents and aqueous alkaline bases as a developer [8–11], which has raised some acid-corrosion, recycling and pollution issues. Due to the increasingly strict environmental policy, development of an environment-friendly water-soluble polymer photoresist has emerged as a new research target in recent years. Water-soluble photoresists have distinct advantages over traditional hydrophobic photoresists for in-situ patterning of proteins and cells under biologically relevant conditions [12–14]. The early attempts are mainly focused on replacing organic solvents with water, including use of photosensitive water-soluble polymers as resist materials through photo-induced polarity changes [15], chemical cleavage [16] or crosslinking reactions [17] to alter solubility of resist materials in aqueous base solution. More recently, a photoresist based on photo-cleavable poly (*N*-isopropyl acrylamide) copolymers is fully processable in water and the pattern development is achieved by control of temperature [18]. However, all these photoresists are derived from photosensitive polymers, which need several steps to prepare and are not commercially available. Ideally, photoresist materials should come from commercially available polymers and can be processed and developed with water only.

Herein we report a general method for photo-induced crosslinking of water-soluble polymers and a new approach to the development of photoresist polymers using water as both the solvent and developer. As an example, a water-based photoresist is developed and composed of a photobase generator (PBG), water-soluble 2-hydroxyethyl cellulose (HEC) and poly(1-vinylpyrrolidone-co-2-dimethylaminoethyl methacrylate) [poly(VP-co-DMAEMA)]. The crosslinking proceeds via the base-catalyzed transesterification between the pendant ester and hydroxy groups in these two polymers. The catalyst for transesterification is 1,5,7-triaza-bicyclo[4.4.0]dec-5-ene (TBD), generated from its tetraphenylborate salt (TBD·$HBPh_4$), which is recently shown to be an effective PBG [19]. In this study, the effects of the amount of PBG, the ratio of two polymers, exposure time, post-exposure baking (PEB) temperature and time and development conditions on the patterning are studied.

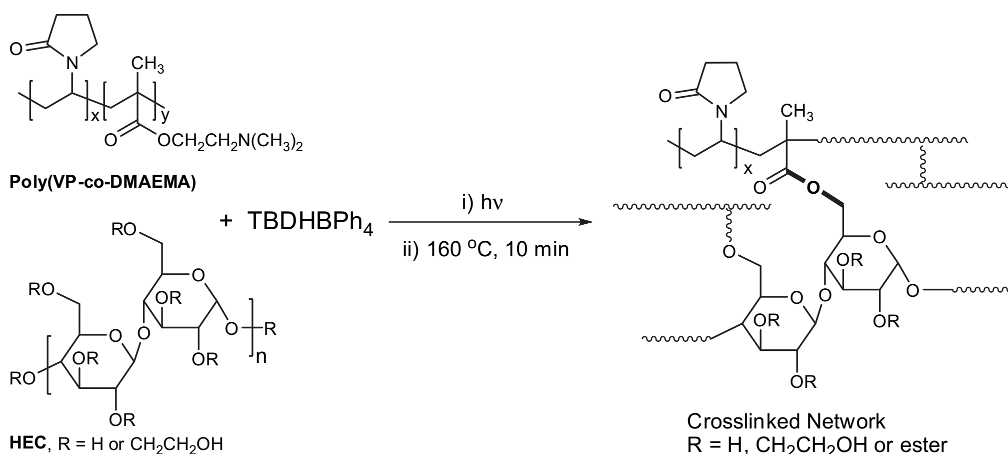
2. Experimental

2.1. Materials

1,5,7-Triaza-bicyclo[4.4.0]dec-5-ene, sodium tetraphenylborate, poly(VP-co-DMAEMA) (Mw ~1,000,000), HEC (Mv ~90,000), (3-aminopropyl)triethoxysilane and 2-methoxyethanol were

* Corresponding author. Tel.: +1 613 520 2600; fax: +1 613 520 2316.
** Corresponding author. School of Chemistry and Chemical Engineering, Shandong University, Jinan 250061, Shandong, China.
E-mail addresses: cbcao@sdu.edu.cn (C.B. Cao), wayne_wang@carleton.ca (Z.Y. Wang).

0032-3861/$ – see front matter © 2010 Elsevier Ltd. All rights reserved.
doi:10.1016/j.polymer.2010.06.052



Scheme 1. TBD-catalyzed intermolecular transesterification leading to crosslinking of HEC and poly(VP-co-DMAEMA).

purchased from Aldrich and used without further purification. TBD·$HBPh_4$ was synthesized according to the literature procedure [19]. The microscope slides from Aldrich and the silicon wafers from EMPAK were used as received.

2.2. Instruments

^{1}H NMR spectra were recorded on a Bruker Advance 300 instrument at 300 MHz. UV–vis spectra were taken on a Perkin Elemer Lambda 900. Differential scanning calorimetry and thermogravimetry were carried out on a TA instruments Q100 and Hi-Res TGA 2950 at a heating rate of 10 °C/min in nitrogen. Photo-crosslinking of polymer films was conducted by EFOS Novacure UV light source with a 100 Watt mercury vapor short arc. The light intensity (10 mW/cm^2) at 250–300 nm was determined by the built-in radiometer. Film thickness was determined with alpha-step 200 Tencor instrument.

2.3. Photoresist preparation and photo-induced patterning

The solutions of photoresist were prepared by dissolving each polymer in water (10 wt%) separately, mixing two polymer solutions at a given ratio, and adding a solution of TBD·$HBPh_4$ in acetonitrile (0.1 g/mL). The solutions were filtered through a 0.2-μm membrane filter, and then spin-coated at 2000 rpm for 1 min on silicon wafers or glass slides to form thin films. The films were dried in a vacuum oven at 80 °C overnight. The thickness of dry films was 1.0 ± 0.1 μm. The silicon wafers and glass slides were pretreated by spin-coating with 3-aminopropyltriethoxysilane in 2-methoxyethanol (1.0 wt%) for 1 min and dried in an oven at 60 °C for 10 min.

The photoresist films were irradiated (10 mW/cm^2 at 250–300 nm) in air, followed by post-exposure baking (PEB) at a given temperature in an oven. After irradiation or PEB, the films were dipped in water for 60 s at room temperature (~23 °C). The percent of insoluble fraction, defined as the ratio of film thickness of samples before and after development (dipping in water). All tests were run seven times under the same conditions. The curves were plotted using the averaged data after discarding the largest and smallest values.

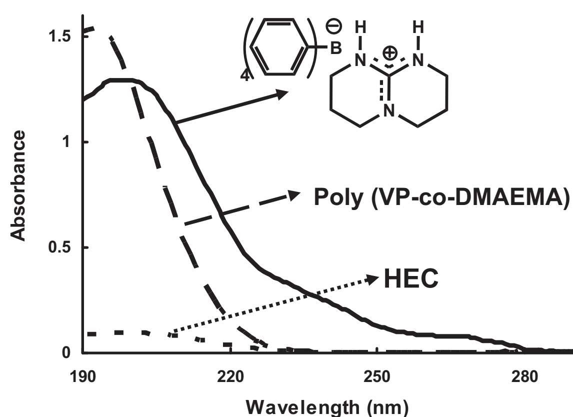


Fig. 1. Absorption spectra of TBD·$HBPh_4$ in acetonitrile with a concentration of 2.0×10^{-5} M, HEC and poly(VP-co-DMAEMA) in water with a concentration of 4.0×10^{-4} M.

3. Results and discussion

3.1. Photo-induced crosslinking of water-soluble polymers

TBD is a stronger base (pK_a of 26.03) than 1,8-diazabicyclo-undec-7-ene ($pK_a = 24.3$) and also an effective bifunctional catalyst for the transesterification reaction between an ester and an alcohol [20–22]. It can simultaneously enhance the reactivity of alcohol via hydrogen bonding and activate the ester through acyl transfer, which accelerates the transesterification much more effectively than other organic bases and acids. TBD·$HBPh_4$ is a short-wave UV PBG and able to produce TBD that catalyzes the ring-opening polymerization of ε-caprolactone [19,23]. Therefore, the photo-induced intermolecular transesterification in polymers should lead to polymer crosslinking in the presence of TBD·$HBPh_4$.

Generally speaking, any polymers containing either the pendant ester or hydroxy groups or both can be selected to formulate a photo-responsive material together with TBD·$HBPh_4$. Among many types of polymers, water-soluble polymers are of particular interest, due to their environment-friendly advantages and benefits in industrial applications. For this reason, we selected water-soluble cellulose and acrylate polymers, such as 2-hydroxyethyl cellulose (HEC) and poly(1-vinylpyrrolidone-co-2-dimethylaminoethyl methacrylate) [poly(VP-co-DMAEMA)] (Scheme 1), as an example to demonstrate a general photo-crosslinking strategy using a new PBG of TBD·$HBPh_4$ and a water-based photoresist material. The selected two polymers fulfill basic requirements of good water solubility and optical clarity in a spectral range of 200–300 nm where the PBG (TBD·$HBPh_4$) works. As shown in

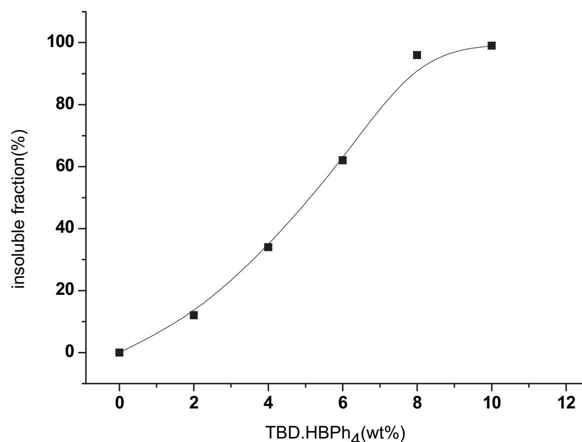


Fig. 2. Effect of the amount of TBD·$HBPh_4$ on photo-induced crosslinking of poly(VP-co-DMAEMA)/HEC film (1:1 by weight, thickness = 1.0 ± 0.1 μm). Irradiation time = 5 min, T_{PEB} = 160 °C, PEB Time = 10 min, washing with water for 60 s.

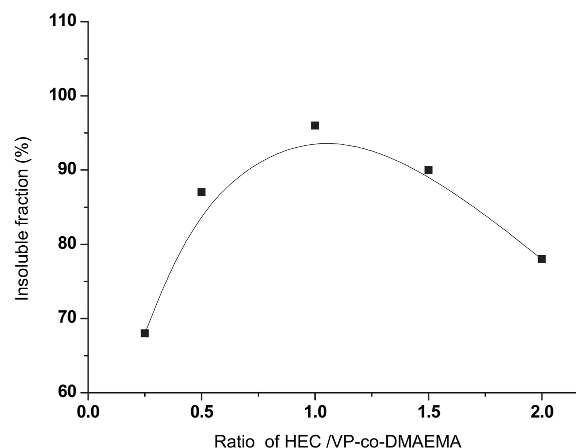


Fig. 3. Effect of polymer compositions on photo-induced crosslinking of HEC/poly(VP-co-DMAEMA) films (thickness = 1.0 ± 0.1 μm) containing 8 wt% of TBD·$HBPh_4$. Irradiation time = 5 min, T_{PEB} = 160 °C, PEB time = 10 min, washing with water for 60 s.

Fig. 1, HEC has a relatively low absorption in 190–220 nm and poly (VP-co-DMAEMA) absorbs up to 220 nm. TBD·$HBPh_4$ has a long tail of absorption from 220 nm to 280 nm. However, although an ideal wavelength range should be 220–250 nm, due to the limited availability of light source, in this study the photo-irradiation was done in a range of 250–300 nm.

Crosslinkable polymers were obtained simply by mixing HEC and poly(VP-co-DMAEMA) in water, followed by addition of a small amount of a solution of TBD·$HBPh_4$ in acetonitrile. Photo-irradiation of the cast films of polymer blend at room temperature for 5 min, followed by baking, resulted in crosslinking of polymer films as indicated by significantly decreased solubility in water.

The crosslinking is a result of the TBD-catalyzed trans-esterification of the two polymers. Upon UV irradiation, TBD is released from TBD·$HBPh_4$ within the polymer blend and catalyzes the formation of a new ester bond between the hydroxy group in HEC and the carboxylic group in poly(VP-co-DMAEMA) at elevated temperatures (Scheme 1). Thus, the degree of crosslinking also depends on the exposure time, PEB temperature and PEB time.

3.2. Effect of processing parameters on photo-induced crosslinking and patterning

To evaluate the feasibility of HEC and poly(VP-co-DMAEMA) as a potential water-soluble photoresist, effect of some of key processing parameters, including exposure time, polymer composition, PEB and developing conditions, on photo-crosslinking and patterning should be investigated. Since these variables are related to each other, orthogonal experiments should ideally be conducted. Our previous study on the photochemical reactivity of TBD·$HBPh_4$ in the solid state suggests that 5 min of exposure to UV light at 254 nm (10 mW/cm^2) at room temperature seems to be adequate for most polymer films [19]. Since the polymer crosslinking involves a base-catalyzed bimolecular reaction of the hydroxy and carboxylate on the two polymers, the amount of PBG and the ratio of the two reactive groups or ratio of the two polymers should affect the overall reaction rate and crosslinking outcome.

Fig. 2 shows the insoluble fraction of the films of the two water-soluble polymers in 1:1 ratio by weight after photo-crosslinking as function of the amount of TBD·$HBPh_4$. With an increase of PBG, the percent of insoluble fraction of the films or the degree of crosslinking increases and reaches to nearly 100% when 8–10 wt% of TBD·$HBPh_4$ is used. A similar trend was also observed when using different PEB conditions, although the maximum percent of insoluble fraction may not be as high as 100%.

With the chosen exposure time and dose and the PBG amount, the effect of polymer compositions on photo-crosslinking was further probed (Fig. 3). At first, below the 1:1 weight ratio of the two polymers, there is a tendency of increase in the degree of crosslinking with an increase of the amount of hydroxyl groups or

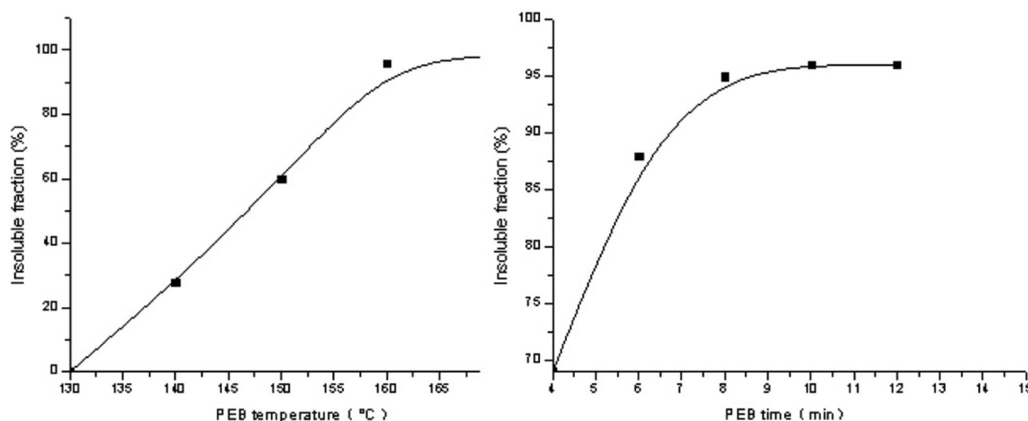


Fig. 4. Effect of PEB temperature (left) and PEB time (right) on photo-induced crosslinking of HEC/poly(VP-co-DMAEMA) film (1.0 ± 0.1 μm). Polymer composition in weight ratio = 1:1, TBD·$HBPh_4$ = 8 wt%, irradiation time = 5 min, washing with water for 60 s.

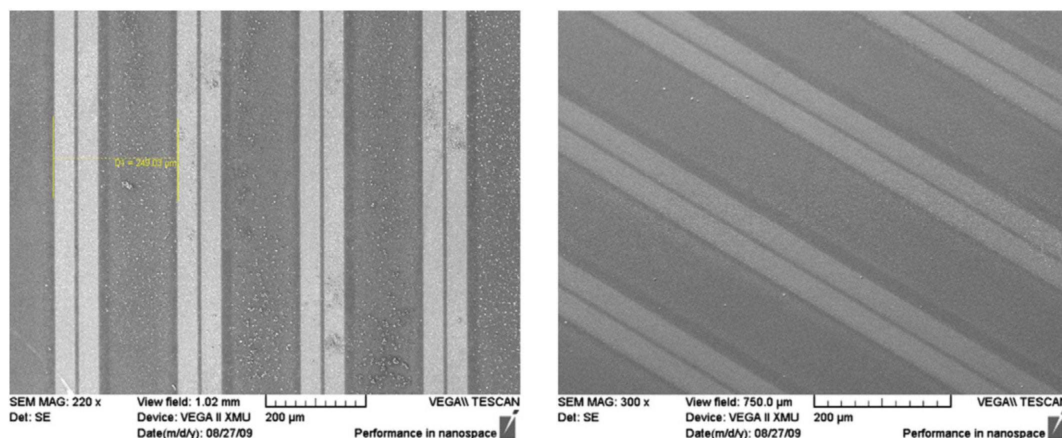


Fig. 5. Top-down (left) and cross-sectional (right) SEM pictures of negative tone images with the HEC/poly(VP-co-DMAEMA) blend film (1:1 weight ratio, thickness = 1.0 ± 0.1 μm) containing 8 wt% TBD·$HBPh_4$. Irradiation time = 5 min, T_{PEB} = 160 °C, PEB time = 10 min, washing with water for 60 s.

HEC in the blend. Over the ratio of 1.0, the amount of the insoluble fraction decreased, indicating clearly that an excess of the hydroxy groups favors the transesterification reaction and polymer crosslinking. Once again, at different PEB conditions, a similar trend was found for the effect of the polymer composition, indicating that the ideal ratio for this polymer blend should be 1.0 by weight.

Considering that the transesterification or crosslinking takes place in the solid state, chain mobility of the polymer blend is critical to ensure efficient transesterification or high degree of crosslinking. Therefore, the PEB temperature should be higher than the glass-transition temperature (T_g) of the polymers, but lower than their decomposition temperatures (T_d). The T_g of HEC and poly (VP-co-DMAEMA) are 150 and 155 °C, while the T_d are 240 and 390 °C, respectively. Accordingly, the PEB should be slightly higher than the T_g and below the T_d to avoid any possible thermal degradation. The tests were then run at the four different PEB temperatures, 130, 140, 150 and 160 °C, for the 1:1 polymer blend containing 8 wt% of PBG. As shown in Fig. 4 (left), the degree of photo-induced crosslinking of polymer blend increases with increasing the PEB temperature and reaches to a maximum at 160 °C. The PEB time was tested at a fixed PEB temperature of 160 °C Fig. 4 (right) shows that the insoluble fraction increases sharply from 4 min to 8 min and then levels off after 10 min. Therefore, 10 min of PEB is the best for our given polymer blend.

3.3. Photo-induced patterning

With all the above optimized parameters, we further demonstrated photo-induced patterning of HEC/poly(VP-co-DMAEMA) blend as a photoresist material. The spin-coated thin film (1 μm in thickness) of the photoresist on silicon wafer was irradiated through a photo-mask for 5 min with EFOS Novacure UV light source (light intensity = 10 mW/cm^2 at 250–300 nm) in air. The irradiated film was heated at 160 °C for 10 min in an oven. To develop a high-contrast pattern, a minimum of 60-s washing with water is required to yield a negative tone relief image. Fig. 5 shows a scanning electron microscopy (SEM) image of a photoresist pattern. A reverse 40-micron parallel-line pattern with a 0.9-micron film thickness is profiled and matches perfectly with the photo-mask used. Although the patterned films are thinner after development due to removal of some unreacted polymers, the 0.9-micron thick layer of crosslinked film is adequate as resist materials in most applications. Polymer swelling may hamper the patterning resolution. In our case, the swelling may come from residual hydroxyl groups in the developed photoresist films and is also related to the time of washing with water. Monitoring the films during the washing under microscope reveals that there were less than 5% swelling for 40 μm lines. As shown in Fig. 5, a thin dark line between of two thick (white) lines is of 10 μm in width, which is the same as the line width in the photo-mask.

4. Conclusions

In this work, we demonstrated a general method for photo-induced crosslinking of water-soluble polymers and a new approach to the development of eco-friendly photoresist polymers using water as both the solvent and developer in the photo-patterning process. A variety of commercially available polymers containing the hydroxy and ester group can be selected and formulated as photoresist and other photo-curable materials in the presence of a new PBG of TBD·$HBPh_4$. This PBG is simple to make and efficient to produce a strong base that can catalyze the transesterification and other useful reactions of polymers in the solid state. The blend of water-soluble HEC/poly(VP-co-DMAEMA) has been shown to be a good photoresist that is able to form 40-micron resolution negative tone images and processed with water only without the use of any other organic solvents.

Acknowledgements

We acknowledge the support from the State Scholarship Fund from China Scholarship Council and the Natural Sciences and Engineering Research Council of Canada.

References

[1] Beh WS, Kim IT, Qin D, Xia YN, Whitesides GM. Adv Mater 1999;11(12):1038–41.
[2] Nielsen CB, Angerhofer A, Abboud KA, Reynolds JR. J Am Chem Soc 2008;130 (30):9734–46.
[3] He M, Herr AE. J Am Chem Soc 2010;132(8):2512–3.
[4] Choi D, Jang E, Park J, Koh WG. Microfluid Nanofluid 2008;5(5):703–10.
[5] Anderson KD, Lu D, McConney ME, Han T, Reneker DH, Tsukruk VV. Polymer 2008;49(24):5284–93.
[6] Reynolds NP, Tucker JD, Davison PA, Timney JA, Hunter CN, Leggett GJ. J Am Chem Soc 2009;131(3):896–7.
[7] Cushing MC, Anseth KS. Science 2007;316(5828):1133–4.
[8] Driesen M, Wouters K, Puers R. Procedia Chem 2009;1:796–9.
[9] Sahaa SC, Sagbergb H, Poppeb E, Jensen GU, Fjeldly TA, Saether T. Sensors Actuators A: Phys 2008;143(2):452–61.
[10] Chatzichristidi M, Raptis I, Diakoumakos CD, Glezos N, Argitis P, Sanopoulou M. Microelectron Eng 2002;61–62:729–35.
[11] Jongsoo L, Toshiaki A, Syun'ichi K, Nobukazu M, Shigeru T, Tsuguo Y. J Polym Sci Part A Polym Chem 2002;40(11):1858–67.
[12] Doh J, Irvine DJ. J Am Chem Soc 2004;126(30):9170–1.

[13] Doh J, Irvine DJ. Proc Natl Acad Sci U S A 2006;103(15):5700–5.
[14] Katz JS, Doh J, Irvine DJ. Langmuir 2006;22(1):353–9.
[15] Taylor LD, Kolesinski HS, Edwards B, Haubs M, Ringsdorf H. J Polym Sci Polym Lett 1988;26:177.
[16] Yamada S, Mrozek T, Rager T, Owens J, Rangel J, Willson CG. Macromolecules 2004;37(2):377–84.
[17] Mihaela IA, Virgil B, Cornelia L. J Photochem Photobiol A Chem 2009;207:260–7.
[18] Leonid I, Stefan D. J Am Chem Soc 2009;131(37):13315–9.
[19] Sun X, Gao JP, Wang ZY. J Am Chem Soc 2008;130(26):8130–1.
[20] Bas G, Lohmeijie G. Macromolecules 2006;39:8574–83.
[21] Pibre G, Chaumont P, Fleury E, Cassagnau P. Polymer 2008;49(1):234–40.
[22] Ye W, Xu J, Tan CT, Tan CH. Tetrahedron Lett 2005;46:6875–8.
[23] Suyama K, Shirai M. Prog Polym Sci 2009;34(2):194–209.