

Ultraviolet Photopolymerization Induced by a Triazine Derivative

Mingyan Jiang,¹ Kemin Wang,¹ Guiping Ma,² Lu Jian,¹ Xu Juan,¹ Qiang Yu,^{1*} Jun Nie^{2*}

¹Changzhou University, Changzhou 213164, People's Republic of China

²State Key Laboratory of Chemical Resource Engineering, Beijing University of Chemical Technology, Beijing 100029, People's Republic of China

Received 26 March 2010; accepted 18 November 2010

DOI 10.1002/app.33774

Published online 14 March 2011 in Wiley Online Library (wileyonlinelibrary.com).

ABSTRACT: 2-(3,4-Methdioxyphenyl)-4,6-bis(trichloromethyl)-1,3,5-triazine (MBTTR) was used as a photoinitiator for the polymerization of acrylate monomer. Ultraviolet–visible absorption spectroscopy was used to investigate the photochemical behavior during the photophysical process. The photopolymerization kinetics were monitored by real-time Fourier transform infrared spectroscopy. The polymerization rates of the acrylates were significantly higher than those of the methacrylates. When MBTTR induced the polymerization of trimethylol-

propane triacrylate, there was an optimum polymerization rate and the final conversion was obtained at 0.1 wt % MBTTR. MBTTR was an inefficient photoinitiator for ethyl vinyl. The final conversions of tripropylene glycol diacrylate induced by MBTTR and triazine/1,3-benzodioxole were similar. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 121: 2013–2017, 2011

Key words: FTIR; initiators; photopolymerization; UV–vis spectroscopy

INTRODUCTION

Photopolymerization is a 5E technology (efficient, enabling, economical, energy-saving, and environmentally friendly)^{1–4} that is particularly useful for industrial applications in coatings for various materials, adhesives, printing inks, photoresists, and biomaterials.^{5–8} In photopolymerization, a typical formulation consists of a vinyl monomer and a photoinitiator system. The polymerization progress is based on the use of photoinitiator systems suited to absorb the appropriate wavelength of light and to generate a primary radical to convert a monomer into a crosslinked network.⁹ Among the photoinitiating polymerization systems, acrylates and vinyl,¹⁰ 1-propenyl,^{11,12} and 1-butenyl ethers,¹³ are the most widely used monomers for free-radical and cationic photopolymerizations.

Photoinitiating systems comprising triazine (TR) derivatives have received considerable interest in the patent literature; the substituted bis(trichloromethyl)-1,3,5-triazine derivatives are used alone or in the presence of a sensitizer or/and coinitiators,

such as titanocene,¹⁴ peroxide/amine,¹⁵ or mercaptan.¹⁶ (Trichloromethyl)-1,3,5-triazines are an important class of photoinitiators and photoacid generators of HCl. Many substituted TRs have been reported. A suitable chromophore usually substitutes in the 2 position of 4,6-bis(trichloromethyl)-1,3,5-triazines, and this chromophore modifies the absorption characteristics of the unsubstituted compound to extend the wavelength range of the response.¹⁷ Grotzinger et al.¹⁸ reported that the addition of a bis(trichloromethyl)-1,3,5-triazine to a dye/amine photoinitiating system led clearly to an increased efficiency of polymerization under visible-light irradiation.

In this study, 2-(3,4-methdioxyphenyl)-4,6-bis(trichloromethyl)-1,3,5-triazine (MBTTR) was a two-component photoinitiator system used as a photoinitiator for free-radical polymerization under ultraviolet (UV)-light irradiation. MBTTR was studied via ultraviolet–visible (UV–vis) absorption spectroscopy to investigate its photochemical behavior. The photopolymerization activities were examined with real-time infrared spectroscopy.

EXPERIMENTAL

Materials

2-(2-Ethoxyethoxy)ethyl acrylate (EOEOEA), tetrahydrofurfuryl acrylate (THFA), 2-phenoxyethyl acrylate (2-PEA), 1,6-hexanediol diacrylate (HDDA), triethylene glycol dimethacrylate (TEGDMA), high-purity

Correspondence to: Q. Yu (yuqiang@jpu.edu.cn) and J. Nie (niejun@mail.buct.edu.cn).

Contract grant sponsor: Program for Changjiang Scholars and Innovative Research Team in University.

Contract grant sponsor: Changzhou Science and Technology Bureau; contract grant number: CE20090021.

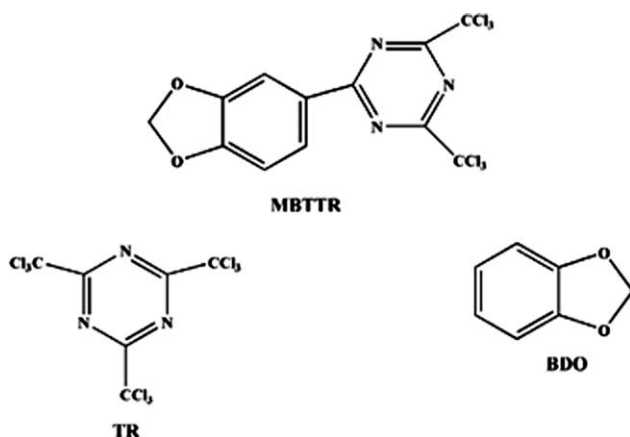


Figure 1 Chemical structures of MBTTR, BDO, and TR.

trimethylolpropane triacrylate (TMPTA), trimethylolpropane trimethacrylate (TMPTMA), tripropylene glycol diacrylate (TPGDA), tri(ethylene glycol) divinyl ether, and 1,4-butanediol divinyl ether were used as received from Sartomer Co. (Warrington, PA). 1,3-Benzodioxole (BDO) was from Acros Organics (Geel, Belgium) and TR and MBTTR were donated by Changzhou Tronly New Electronic Material Co., Ltd. (Changzhou, Jiangsu, China). All reagents were used without further purification. The chemical structures of the initiators are shown in Figure 1.

Instrumentation

Fourier transform infrared (FTIR) spectra were recorded on a Nicolet 5700 instrument (Thermo Electron Corp., Waltham, MA).

UV-vis absorption spectra were recorded in an acetonitrile solution on a Hitachi U-3010 UV-vis spectrophotometer (Hitachi High-Technologies Corp., Tokyo, Japan). A cell path length of 1 cm was used.

We used a UV spot source (EFOS Lite, 50-W miniature arc lamp, with a 5-mm crystal optical fiber, Edmonton, Canada).

Photolysis of MBTTR

The photolysis study of the MBTTR was conducted by a UV-vis spectrophotometer (Hitachi High-technologies Corporation, Tokyo, Japan). In a typical procedure, we irradiated an appropriate solution of MBTTR in acetonitrile with the UV spot source at 2-s intervals.

Photopolymerization kinetics

The initiation efficiency of MBTTR was studied by FTIR. The basic principle of FTIR spectroscopy consists of exposing the sample simultaneously to UV light, which induces the polymerization. UV photopolymerization was carried out at room temperature

in the mixture of monomer and initiator. The light intensity on the sample was 30 mW/cm^2 . The mixture of monomer and MBTTR was placed into a mold, made from glass slides and spacers $15 \pm 1 \text{ mm}$ in diameter and $1.2 \pm 0.1 \text{ mm}$ in thickness. The double-bond conversion of the mixture was monitored with near-IR spectroscopy with a resolution of 4 cm^{-1} . The absorbance change of the $=\text{C}-\text{H}$ peak area from 6101 to 6248 cm^{-1} was correlated to the extent of polymerization.¹⁹ The double-bond conversion could be expressed by the following relation:

$$\text{Double-bond conversion}(\%) = \frac{A_0 - A_t}{A_0} \times 100$$

where A_0 is the initial peak area before irradiation and A_t is the peak area at time t was calculated by the differential of conversion of double bonds versus irradiation time.

RESULTS AND DISCUSSION

UV-vis absorption spectra

The UV-vis absorption spectra obtained from MBTTR, TR, and BDO in acetonitrile at room temperature are shown in Figure 2. Three absorption peaks at 246, 292, and 351 nm were observed in the UV-vis spectrum of MBTTR, so MBTTR could be a UV-light photoinitiator. BDO had three absorption peaks at 230, 280, and 374 nm, whereas TR had two absorption peaks at 246 and 372 nm. The wavelength of maximum absorption (λ_{max}) of MBTTR was 351 nm [molar extinction coefficient (ϵ) = $1.69 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$]. The maximal absorption of the photoinitiator was important to their photochemical activity. Because of the unsaturated side chain at the 2-position of 4,6-bis(trichloromethyl)-1,3,5-triazine, MBTTR possessed a significant change in extinction coefficient of the

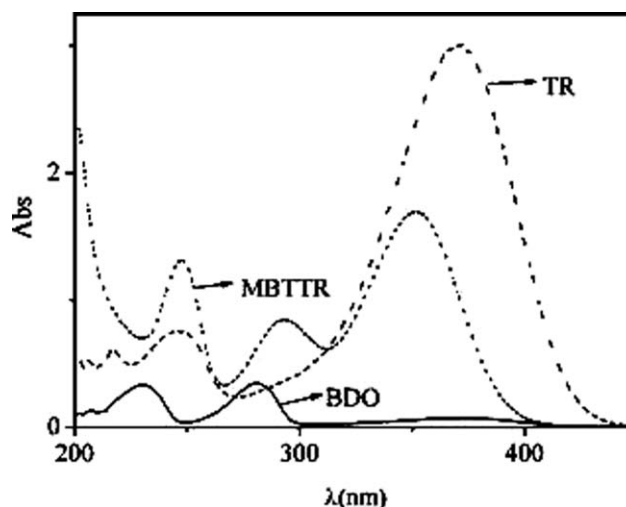


Figure 2 UV-vis absorption spectra of MBTTR, TR, and BDO in acetonitrile (10^{-4} mol/L).

TABLE I
UV Spectroscopy Absorption Data for MBTTR in Acetonitrile (10^{-4} mol/L)

λ_{\max} (nm)	ϵ ($L \text{ mol}^{-1} \text{ cm}^{-1}$)
246	1.31×10^4
292	8.45×10^3
351	1.69×10^4

long-wavelength band. Certainly, the excited singlet state of MBTTR could not be described by a locally excited configuration of the TR moiety any more, and assigning the S_1 state to an electronic configuration is not straightforward.¹⁷ λ_{\max} and ϵ at λ_{\max} are summarized in Table I. The high ϵ value made MBTTR an attractive photoinitiator.

The photodecomposition of MBTTR was monitored by the detection of UV spectra changes upon photolysis. Figure 3(a) shows the UV spectra of MBTTR in acetonitrile exposed to the UV source at intervals of 2 s. During the process of irradiation, the photoinitiator was consumed, and the absorption spectra were changed. The absorptions at 246 and 351 nm decreased significantly until diminishment, whereas the absorption at about 315 nm increased. The decrease (absorbance at 0 min minus absorbance at t) in the maximum absorbance of MBTTR at 351 nm is presented in Figure 3(b). Clearly, the observed absorption peak of MBTTR decreased dramatically. This meant that MBTTR was an attractive photoinitiator because it could absorb UV light effectively at the UV source. Thus, more free radical could be produced.

MBTTR as an initiator for UV photopolymerization

Figure 4 shows the conversion versus time plots for different acrylate monomers. THFA, EOEOEA, 2-PEA, TMPTA, and HDDA were acrylates, and TEGDMA and TMPTMA were methacrylates. The results indicate that the polymerization rates of the acrylates were significantly higher than that of methacrylates, and the functionality of the acrylates had a strong influence on both the polymerization rate and the final conversion. EOEOEA, THFA, and 2-PEA were monoacrylates whose single functional group of monoacrylate resulted in a higher double-bond conversion compared to the multifunctional monomers. The final conversions of the multifunctional monomers were lower than that of the monofunctional monomers because the early gelation of the multifunctional monomer set a limit on the extent of the unreacted double bonds. With increasing acrylate functionality, the content of residual unsaturations rose, and the resulting gel effect and higher

crosslink density set a limit on the extent of conversion.²⁰

Plots of the conversion versus the irradiation time for TMPTA incorporating different MBTTR concentrations are shown in Figure 5. The final conversion varied from 50.6 to 68.0%, whereas the MBTTR concentration increased from 0.01 to 0.1 wt %. The polymerization rate and the final conversion increased when the concentration of MBTTR continued to increase. When the concentration of MBTTR was changed from 0.1 to 1.5 wt %, the final conversion decreased from 68.0 to 63.5%. There was an optimum polymerization rate, and the final conversion was obtained at 0.1 wt % MBTTR. The higher MBTTR concentration was, the more free radical could be generated during irradiation time, which

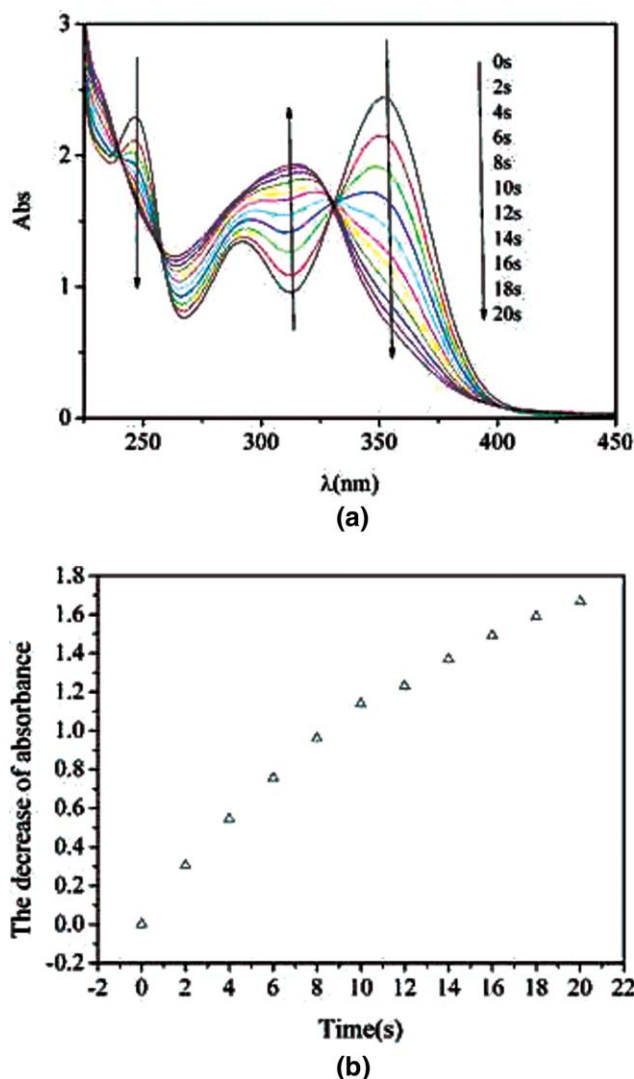


Figure 3 (a) Typical changes in the UV spectrum of MBTTR in acetonitrile with UV irradiation at 2-s intervals and (b) decreases in the MBTTR absorption band at 351 nm with UV light at 2-s intervals. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://www.interscience.wiley.com).]

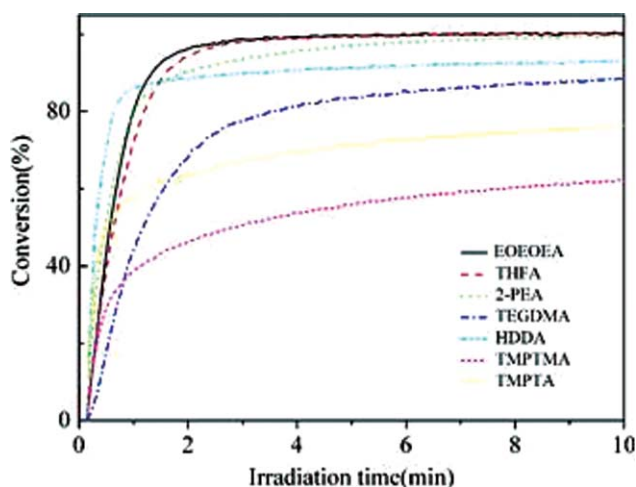


Figure 4 Double-bond conversion of different monomers ([MBTTR] = 1.0 wt %). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com]

resulted in the increase of the final conversion. However, the final conversion decreased because of the higher MBTTR concentration, which was caused by the light screening of the initiator itself and its photolysis.⁵

The effect activities of 1.0 wt % MBTTR initiating the polymerization of different monomers are shown in Figure 6. Tri(ethylene glycol) divinyl ether and 1,4-butanediol divinyl ether were ethyl vinyl ethers, and HDDA was an acrylate. The result shows that MBTTR could initiate HDDA rapidly, whereas the polymerization of tri(ethylene glycol) divinyl ether and 1,4-butanediol divinyl ether was very slow. Ethyl vinyl ethers were hard to copolymerize under free radicals, but those having different functional groups were extremely interesting for cationic polymerization and hybrid polymerization.²¹

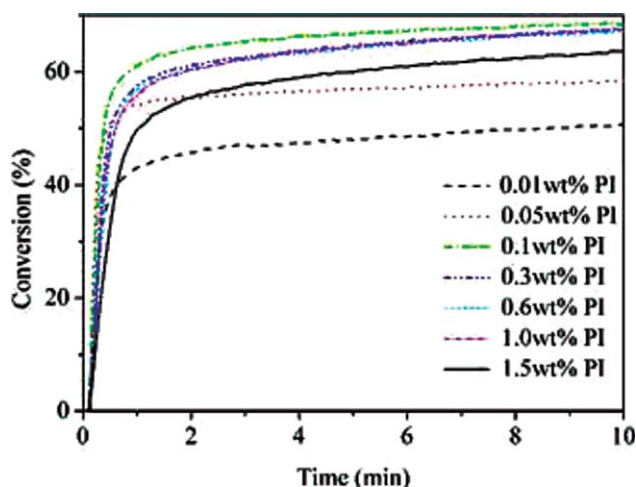


Figure 5 Effect of the concentration of the photoinitiator (PI) system on the polymerization of TMPA. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

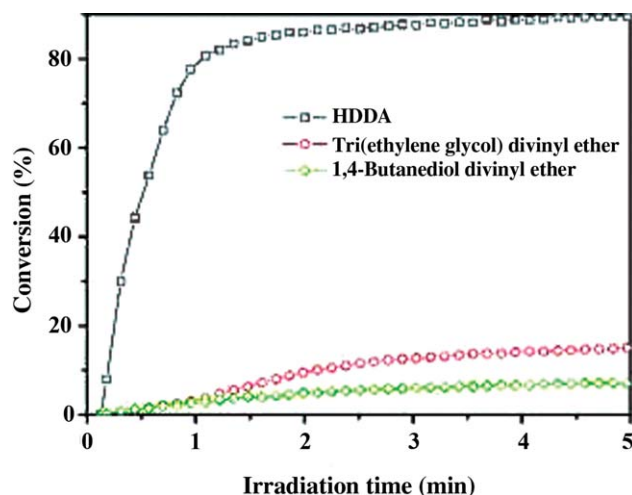


Figure 6 Polymerization kinetics of HDDA, tri(ethylene glycol) divinyl ether, and 1,4-butanediol divinyl ether initiated by 1.0 wt % MBTTR. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

The kinetics of TEGDMA polymerization initiated by different photoinitiator systems (50 $\mu\text{mol/g}$ MBTTR or 50 $\mu\text{mol/g}$ of TR/50 $\mu\text{mol/g}$ of BDO) are shown in Figure 7. The polymerization happened more rapidly with MBTTR than with BDO. Although the initiating reactivity of MBTTR was slight lower than that of TR, the curve for polymerization with the MBTTR system still indicated the approximate double-bond conversion as the TR system. BDO was a natural component from a dietary plant, and the toxicity of BDO was very low.²² Sesamin (SA), which contained cyclic acetal (BDO), could be used as a coinitiator in dental restoration, and the indirect cytotoxicity assessment of SA with mouse

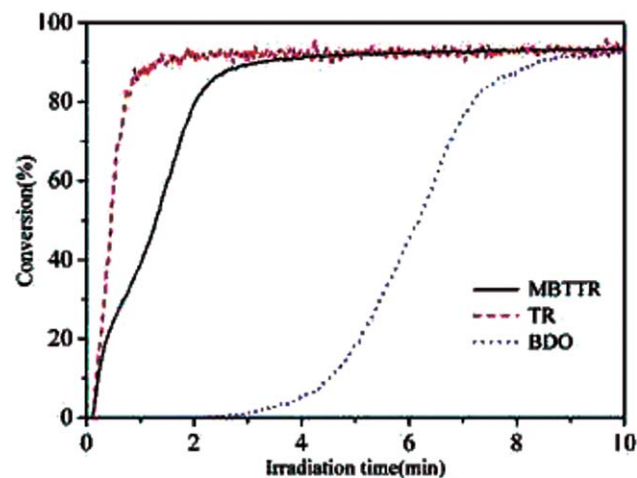


Figure 7 Kinetics of TEGDMA polymerization initiated by different photoinitiator systems: (a) 50 $\mu\text{mol/g}$ MBTTR, (b) 50 $\mu\text{mol/g}$ TR, and (c) 50 $\mu\text{mol/g}$ BDO. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

fibroblasts (L929) indicated that material showed no cytotoxicity toward the growth of the L929 cell and had good *in vitro* biocompatibility.²³ BDO-based cointiators had a satisfactory reactivity and biocompatibility and were very important for clinical applications.²⁴ So MBTTR had good biocompatibility because it contained a cyclic acetal (BDO).

CONCLUSIONS

During the process of irradiation, the absorptions at 246 and 351 nm decreased significantly until diminishment, whereas the absorption at about 315 nm increased. The polymerization rates of acrylates were significantly higher than that of methacrylates in the same polymerization situation, and the functionality of (meth)acrylates had a strong influence on both the polymerization rate and the double-bond conversion. The polymerization rate and the final conversion changed with increasing MBTTR concentration, there was an optimum polymerization rate, and the final conversion was obtained at 0.1 wt % MBTTR. MBTTR had no effect on the ethyl vinyl ethers' polymerization. The final conversions of TPGDA initiated by different photoinitiator systems (MBTTR and TR/BDO) were similar.

References

1. Decker, C. *Prog Polym Sci* 1996, 21, 594.
2. Decker, C. *Polym Int* 1998, 45, 133.
3. Andrzejewska, E. *Prog Polym Sci* 2001, 26, 606.
4. Decker, C. *Macromol Rapid Commun* 2002, 23, 1067.
5. Fouassier, J. P. *Photoinitiation, Photopolymerization, and Photocuring: Fundamentals and Applications*; Hanser: New York, 1995.
6. Mishra, M. K.; Yagci, Y. *Handbook of Radical Vinyl Polymerization*; Marcel Dekker: New York, 1998.
7. Pappas, S. P. *UV Curing Science and Technology*; Technology Marketing: Norwalk, CT, 1978.
8. Wu, G. Q.; Nie, J. *J Photochem Photobiol A* 2006, 183, 154.
9. Corrales, T.; Catalina, F.; Peinado, C.; Allen, N. S. *J Photochem Photobiol A* 2003, 159, 103.
10. Crivello, J. V.; Colon, D. A. *J Polym Sci Polym Chem Ed* 1983, 21, 1785.
11. Crivello, J. V.; Jo, K. D. *J Polym Sci Part A: Polym Chem* 1993, 31, 2143.
12. Crivello, J. V.; Lai, Y. L. *J Polym Sci Part A: Polym Chem* 1995, 33, 653.
13. Miller, C. M.; Sudol, E. D.; Silebi, C. A.; El-Aasse, M. S. *J Polym Sci Part A: Polym Chem* 1995, 33, 1381.
14. Hoechst AG. *Eur. Pat.* 364735 (1990).
15. Kawabata, M.; Kimoto, K.; Takimoto, Y. *Eur. Pat.* 211615 (1987).
16. Dietliker, K. *UV and EB Curing Formulation for Printing Inks, Coatings and Paints*; Selective Industrial Training Associates: London, 1991; Vol. III.
17. Pohlers, G.; Scaiano, J. C.; Sinta, R.; Brainard, R.; Pai, D. *Chem Mater* 1997, 9, 1353.
18. Grotzinger, C.; Dominique, B.; Jacques, P.; Fouassier, J. P. *Macromol Chem Phys* 2001, 202, 3513.
19. Decker, C.; Moussa, K. *Macromolecules* 1989, 22, 4455.
20. Mehnert, R.; Pincus, A.; Janorsky, I.; Stowe, R.; Berejka, A. *Chemistry & Technology of UV & EB Formulation for Coatings, Inks & Paints*; SITA Technology: London, 1997; Vol. I.
21. Li, S. J.; He, Y.; Nie, J. *J Polym Sci Part A: Polym Chem* 2007, 45, 191, 25.
22. Shi, S. Q.; Gao, H.; Wu, G. Q.; Nie, J. *Polymer* 2007, 48, 2864.
23. Wang, K. M.; Yang, D. Z.; Xiao, M.; Chen, X. M.; Lu, F. M.; Nie, J. *Acta Biomater* 2009, 5, 2508.
24. Shi, S. Q.; Xiao, P.; Wang, K. M.; Gong, Y. K.; Nie, J. *Acta Biomater* 2010, 6, 3071.