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Water-compatible dendritic macrophotoinitiator containing thioxanthone

Xuesong Jiang[a], Wenfeng Wang[b], Hongjie Xu[a], Jie Yin[a,*]

[a] *Research Institute of Polymer Materials, School of Chemistry and Chemical Technology, State Key Laboratory for Composite Materials, Shanghai Jiao Tong University, Shanghai 200240, PR China*
[b] *Shanghai Institute of Applied Physics, Chinese Academy of Sciences, Shanghai 201800, PR China*

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Abstract

Water-compatible dendritic macrophotoinitiaors containing thioxanthone (TX), DAB-16-TX and DAB-64-TX, were synthesized by introducing a certain amount of TX moieties into the periphery of poly(propylene imine) (PPI). These photoinitiators have the similar UV–vis absorption to thioxanthone. Compared with DAB-16-TX, the fluorescence emission and the lifetime of the excited triplet state for TX in DAB-64-TX decreased, and polymerization rate of acrylamide (AAM) initiated by DAB-64-TX increased. With the increase of water content in the mixed solvent, the fluorescence emission intensity and the lifetime of the triplet state for TX of DAB-64-TX decreased, and the polymerization rate of AAM initiated by DAB-64-TX increased.

Keywords: Water-compatible; Dendritic macrophotoinitiator; Thioxanthone

1. Introduction

Photopolymerization science has become an increasing interesting subject because of its widespread applications [1,2]. In the development of this technology, photoinitiator systems play a very important role. In order to get photoinitiator systems of high performance, one of the effective ways is to develop macrophotoinitiators, which has some advantages derived from macromolecular nature, in comparison with low-molecular weight analogues [3–10]. At the same time, water-borne photoinitiator systems have been obtaining much attention because of their prominent superiority in environment protection [11–13]. Therefore, it is of much interest to prepare water-compatible polymeric photoinitiator systems.

Water-compatible photoinitiators derived from thioxanthone are widely used in processes such as printing inks, coatings, microelectronics and photoresists, and their photoinitiation activity can be promoted by the presence of coinitiator amine [14–16]. Dendritic poly(propylene imine) (PPI) is a highly branched, well-defined, water-soluble macromolecule with a number of interesting characteristics and can be used as coinitiator because of its high density of amino groups [17–19]. Dendritic macrophotoinitiator can be synthesized through introducing thioxanthone into PPI, which makes thioxanthone photoinitiators hydrophilic, and needs no low-molecular amine as coinitiator.

Recently, dendritic macrophotoinitiator containing thioxanthone was synthesized in our lab and can photoinitiate the polymerization of acrylamide (AAM) in DMSO solution more efficiently than its low-molecular weight counterpart [20]. In this text, we further synthesized the water-compatible dendritic macrophotointiator through introducing a certain amount of thioxanthone moieties into periphery of PPI (generation 3.0 and 5.0), and investigated photochemical and photophysical properties of these water-compatible photoinitiators in the aqueous solutions. Then the polymerization of AAM in different aqueous solutions initiated by these photoinitiators, were studied to evaluate the effect of solvent on photopolymerization.

2. Experimental part

2.1. Materials

Poly(propylene imine) (generation 3.0 and 5.0, named as DAB-16 and DAB-64, respectively, from Aldrich). Acrylamide (AAM) (from Chinese Machine Group). 2-(2,3-

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* Corresponding author. Tel.: +86 21 54746215; fax: +86 21 54747445.
E-mail address: jyin@sjtu.edu.cn (J. Yin).

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Epoxy)propoxylthioxanthone (synthesized according to Ref. [14] in our lab). Other chemicals are of analytical grade except as noted.

2.2. Synthesis of water-compatible dendritic macrophotoinitiators DAB-16-TX and DAB-64-TX

A mixture of 1.0 g (3.52 mmol) of 2-(2,3-epoxy)propoxylthioxanthone, 1.14 g (0.9 mmol) of DAB-4 or 0.40 g (0.232 mmol) of DAB-64, and 40 mL of chloroform was stirred at 40 °C for 12 h, and then filtered through a thin layer of activated charcoal after cooling. The chloroform solution was poured into 10-fold benzinum. The precipitate was filtered to give product, which was dried in vacuo to obtain dendritic macrophotoinitiators.

DAB-16-TX: yield ratio: 91%; UV, $\lambda = 403$ nm, $\varepsilon = 4196\ \mathrm{L\,mol^{-1}\,cm^{-1}}$. Elemental analysis, Calcd. C 64.68, H 9.07, N 14.8, S 4.53, found: C 64.25, H 9.23, N 14.53, S 4.64; ^{1}H NMR ($CDCl_3$, 400 MHz): $\delta = 8.55$–7.11 (7H, aromatic), 4.20–3.98 (3H, –OCH_2, –OCH), 2.82–2.25 (31H, NH–CH_2, N–CH_2), 1.78–1.60 (15H, –CH_2–). FT-IR (KBr): 3419 (O–H, N–H), 2933 (C–H), 1630 cm^{-1} (C=O).

DAB-64-TX: yield ratio: 89%; UV, $\lambda = 404$ nm, $\varepsilon = 3895\ \mathrm{L\,mol^{-1}\,cm^{-1}}$. Elemental analysis, Calcd. C 64.15, H 10.13, N 14.95, S 4.30; found: C 63.60, H 9.97, N 15.25, S 4.13; ^{1}H NMR ($CDCl_3$, 400 MHz): $\delta = 8.31$–6.99 (7H, aromatic), 4.20–3.98 (3H, –OCH_2, –OCH), 2.82–2.25 (33H, NH_2–CH_2, NH–CH_2), 1.78–1.50 (15H, –CH_2–). FT-IR (KBr): 3419 (O–H, N–H), 2933 (C–H), 1630 cm^{-1} (C=O).

2.3. Photopolymerization

Kinetic studies of photopolymerization were performed dilatometerically in a recording dilatometer, which is put in the water bath of constant temperature (according to Ref. [21]) by irradiating about 12 mL of 1.0 M AAM aqueous solution at 30 °C (deionized water used as solvent, HCl and NaOH used to adjust pH of aqueous solution). The concentration of photoinitiator is 0.001 M, and all the solution is neutral (pH 7). The polymerization rate (R_p) was determined below 10% conversion where R_p is almost independent of the conversion. The produced polymer was precipitated with methanol, filtered and dried in vacuo.

2.4. Analysis

^{1}H NMR spectra were recorded on a Mercury Plus 400 Hz spectrometer with $CDCl_3$ as solvent.

FT-IR spectra were recorded on a Perkin-Elmer Paragon1000 FTIR spectrometer. The samples were prepared either as KBr pellets or as liquid films between KBr discs.

Elemental analysis was conducted on an Elementar Varioel apparatus.

UV–vis spectra were recorded in aqueous solution by Perkin-Elmer Lambda 20 UV-vis spectrophotometer.

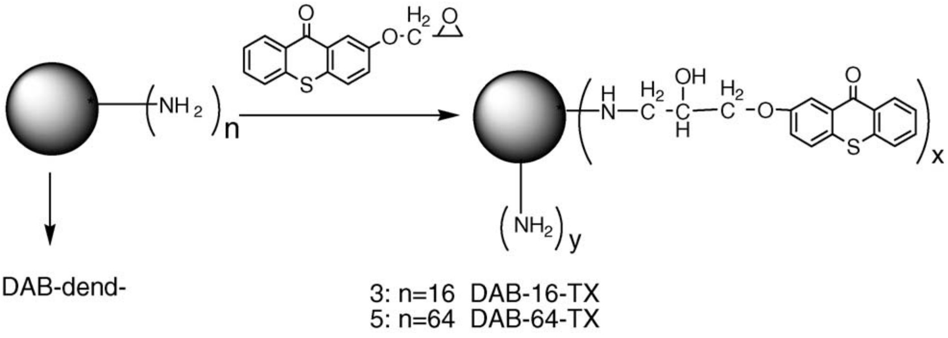
Fluorescence spectra were recorded by Perkin-Elmer LS50B luminescence spectrophotometer.

Transient absorption spectra were determined using a Nd:YAG laser, which provides 355 nm pulses with a duration of 5 ns and a maximum energy of 120 mJ per pulse. The laser and analyzing light beam passed perpendicularly through a quartz cell. The transmitted light entered a monochromator equipped with a R955 photomultiplier. The signals were collected using an HP54510B digital oscillograph and then transferred to computer to be treated.

3. Results and discussions

Dendritic photoinitiators were synthesized according to Ref. [20] (seen in Scheme 1) and confirmed by ^{1}H NMR, FT-IR and elemental analysis. Water-compatible dendritic photoinitiators can be synthesized, if less than one-third of the peripheral primary amine in the dendritic PPI is end-capped by thioxanthone moieties. In this experiment, we found that x:y is about 1:3 according to ^{1}H NMR spectra and elemental analysis (nitrogen content/sulfur content).

UV–vis spectra of three dendritic macrophotoinitiators in aqueous solution are shown in Fig. 1(a). They exhibit the usual characteristic absorption of thioxanthone and the maximum of absorption is about 404 nm, which shows that the dendritic structure has no significant influence on the UV–vis absorption of thioxanthone moieties. Although both dendritic macrophotoinitiators have the similar maximum of emission at 475 nm, the emission intensity of DAB-64-TX is weaker, according to Fig. 1(b), which shows more effective energy transition between the excited state TX and the coinitiator amine. This may be ascribed to dentritic and polymeric effects [4,22] and also can



Scheme 1.

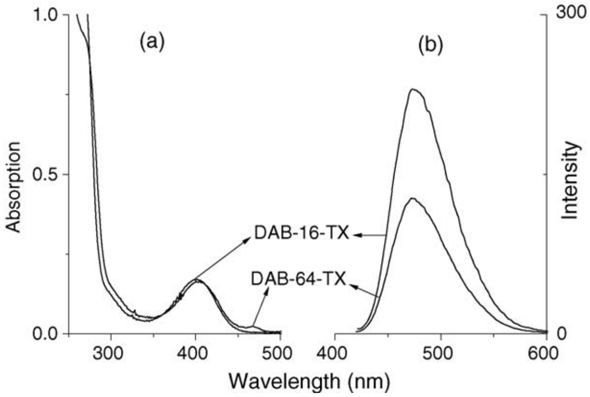


Fig. 1. (a) UV–vis absorption spectra (concentration = 5×10^{-5} mol L^{-1} in terms of thioxanthone moieties); (b) fluorescence spectra (concentration = 2×10^{-5} mol L^{-1} in terms of thioxanthone moieties, λ_{ex} = 400 nm) for DAB-16-TX and DAB-64-TX in aqueous solution.

be seen from Fig. 2, which is the transient absorption of DAB-64-TX (a) and the triplet decay of both dendritic photoinitiators (b) in aqueous solution. The maximum of absorption is about 600 nm and similar to the triplet–triplet absorption of other TX derivatives. Compared with DAB-16-TX, the lifetime of triplet state (τ) of TX in DAB-64-TX is shorter, which shows that the triplet state of thioxanthone is quenched by amine more effectively in DAB-64-TX. As to DAB-16-TX, the molecular weight of DAB-64-TX is larger, and the dendritic and polymeric effect becomes more obvious. The peripherial hydrophobic thioxathone may enter the interior of high amine intensity in dendrimer, which has cavities inside, just like a "dendritic box" [17,20,23,24]. This may result in a higher local amine concentration in the microenvironment of TX moieties in DAB-64-TX. Therefore, the fluorescence emission and the lifetime of triplet state decreased.

In the presence of coinitiators such as amine, the photolysis of thioxanthone leads to the formation of radical produced from a carbonyl compound (ketyl-type radical) and another radical derived from the coinitiator amine, through reaction between the excited triplet state TX of and coinitiator amine. The photopolymerization of vinyl monomers is usually initiated by the amine radicals and the ketyl radicals are usually not reactive toward vinyl monomers due to the steric hindrance and the delocalization of unpaired electron [25]. The overall mechanism of the photoinitiation is presented in Scheme 2, from which we can know the quantity of amine radical determines the photopolymerization rate. Fig. 3 shows conversion of AAM versus time for both dendritic photoinitiator systems. As can be seen, the polymerization rate of DAB-64-TX is greater. This may be ascribed to the more effective energy transition in DAB-64-TX. The larger local amine concentration accelerates the energy transfer between the excited state TX of and amine in DAB-64-TX (also can be seen in Figs. 1 and 2) to generate a larger amount of amine radicals, which results in the higher conversion rate of AAM polymerization in DAB-64-TX.

Polymerizations of AAM photoinitiated by DAB-64-TX in DMSO/H_2O mixed solvent were also investigated. The polymerization rate increases with the water content in DMSO/H_2O mixed solvent (Fig. 4). This may be ascribed to the different efficiency of DAB-64-TX in the different solvent. The fluorescence spectra of DAB-64-TX in the DMSO/H_2O mixed solvent

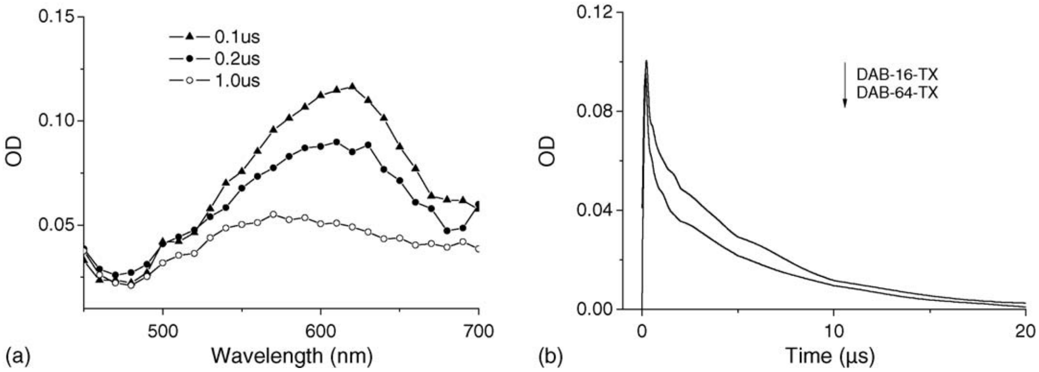
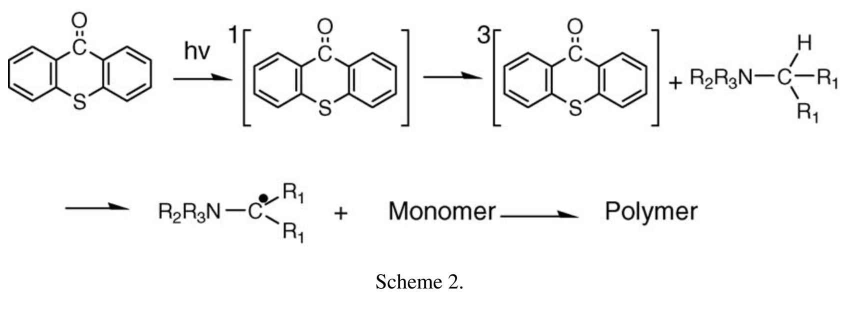


Fig. 2. (a) Transient absorption spectra obtained from 355 nm laser flash photolysis of DAB-64-TX, recorded different time after the laser pulse. (b) Triplet decay of DAB-16-TX and DAB-64-TX, monitored at 600 nm, in aqueous solution (concentration = 5×10^{-4} mol L^{-1} in terms of thioxanthone moieties).



Scheme 2.

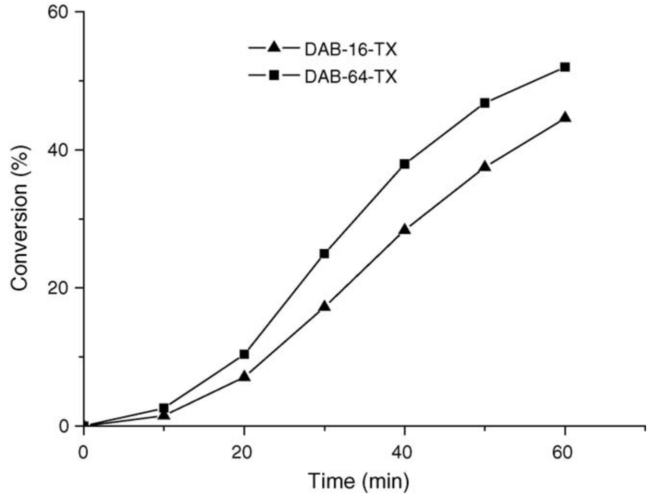


Fig. 3. Conversion vs. time curves for the polymerization of AAM in aqueous solution, photoinitiated by DAB-16-TX and DAB-64-TX at 30 °C. The photoinitiator concentration is 0.001 M in terms of thioxanthone moieties and [AAM] is 1 M.

are shown in Fig. 5, which shows that the decrease of emission intensity and the red-shift of λ_{max} increase with the water content in the mixed solvent. The lower emission intensity indicated the more efficient energy transition between the excited state TX and amine. This also can be seen from the triplet decay of DAB-64-TX in the mixed solvent (Fig. 6). The τ for triplet state became shorter with the increase of water content. Because of the higher water content in the mixed solvent, the peripheral hydrophobic thioxathone can be "forced" into the interior of high amine intensity in dendrimer, resulting in that the exited singlet and triplet state of TX can be quenched by coinitiator amine more efficiently. Thus, the DAB-64-TX photoinitiator can produced more amine radicals, which leads to the higher polymerization rate in mixed solvent of the higher water content.

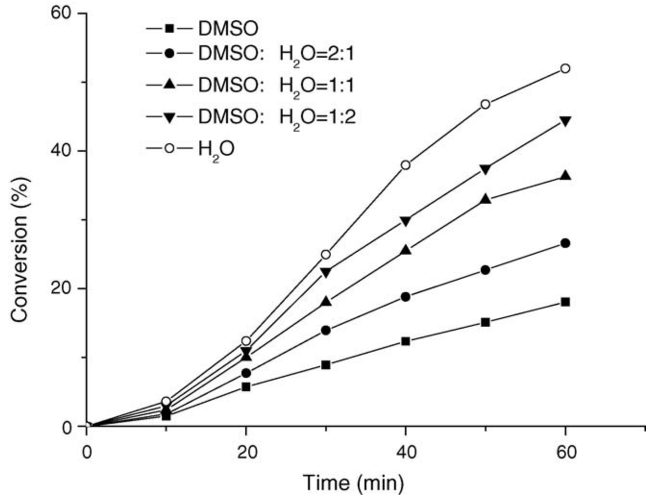


Fig. 4. Conversion vs. time curves for the polymerization of AAM in DMSO/H_2O mixed solvent (DMSO/H_2O is v/v) photoinitiated by DAB-64-TX at 30 °C. The photoinitiator concentration is 0.001 M in terms of thioxanthone moieties and [AAM] is 1 M.

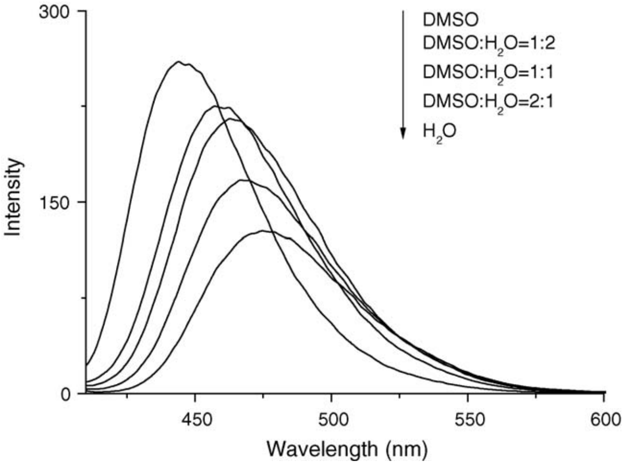


Fig. 5. Fluorescence spectra (concentration = 2 × 10^{-5} mol L^{-1} in terms of thioxanthone moieties, λ_{ex} = 400 nm) for DAB-64-TX in DMSO/H_2O mixed solvent (DMSO/H_2O is v/v).

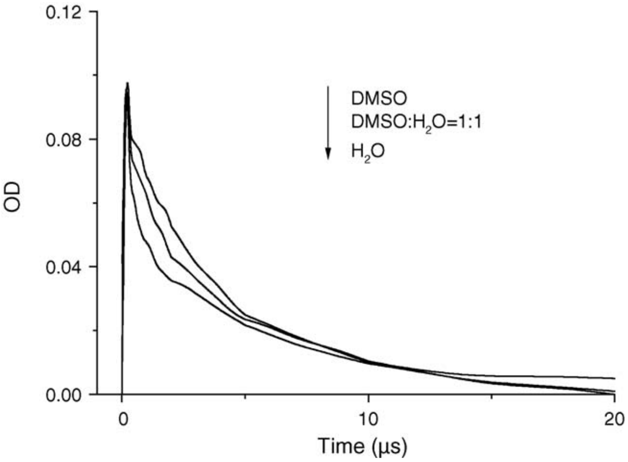


Fig. 6. Triplet decay of DAB-64-TX in DMSO/H_2O mixed solvent, monitored at 600 nm (DMSO/H_2O is v/v, concentration = 5 × 10^{-4} mol L^{-1} in terms of thioxanthone moieties).

In conclusion, water-compatible dendritic photoinitiators were synthesized by introducing a certain amount of TX into periphery of PPI dendrimers. Compared with DAB-16-TX, the fluorescence emission and the lifetime of excited triplet for TX in DAB-64-TX decreased, and the polymerization rate of AAM initiated by DAB-64-TX in aqueous solutions increased. With the increase of water content in the mixed solvent, the fluorescence emission intensity and the lifetime of the triplet state for TX of DAB-64-TX decrease, and the polymerization rate of AAM initiated by DAB-64-TX increases.

Acknowledgements

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References

[1] J.P. Fouassier, Photoinitiation, Photopolymerization, and Photocuring Fundamentals and Applications, Hanser, New York, 1995.

[2] C. Decker, Prog. Polym. Sci. 21 (1996) 593.

[3] L. Angiolini, D. Caretti, E. Salatelli, Macromol. Chem. Phys. 201 (2000) 2646.

[4] T. Corrales, F. Catalina, C. Peinado, N.S. Allen, J. Photochem. Photobiol. A: Chem. 159 (2003) 103.

[5] A.M. Sarker, K. Sawabe, B. Strehmel, Y. Kaneko, D.C. Neckers, Macromolecules 32 (1999) 5203.

[6] L. Angiolini, D. Caretti, E. Corell, C. Carlini, P.A. Rolla, J. Appl. Polym. Sci. 64 (1997) 2247.

[7] A. Ajayaghosh, Polymer 36 (1995) 2049.

[8] M. Degirmenci, G. Hizal, Y. Yagci, Macromolecules 36 (2002) 8265.

[9] L. Angiolini, D. Caretti, C. Carlini, E. Corell, E. Salatelli, Polymer 40 (1999) 7197.

[10] V. Castelvtro, M. Molesti, P. Rolla, Macromol. Chem. Phys. 203 (2002) 1486.

[11] L. Maria, E. Rodrigo, J. Polym. Sci. Part A: Polym. Chem. 40 (2002) 901.

[12] H.D.-G. Jacqueline, D. Keith, D. Henk, Biomacromolecules 2 (2001) 1271.

[13] F. Catalina, C. Peinado, M. Blanco, T. Corrales, N.S. Allen, Polymer 42 (2001) 1825.

[14] J.W. Yang, Z.H. Zeng, Y.L. Chen, Polym. J. Sci. Part A: Polym. Chem. 36 (1998) 2563.

[15] L. Robert, Polym. J. Sci. Part A: Polym. Chem. 40 (2002) 1504.

[16] T. Corrales, F. Catalina, N.S. Allen, C. Peinado, J. Photochem. Photobiol. A: Chem. 169 (2005) 95.

[17] A.P.H.J. Schenning, E. Peeters, E.W. Meijer, J. Am. Chem. Soc. 122 (2000) 4489.

[18] K. Tsuda, G.C. Dol, T. Gensh, J. Hofkens, L. Latterini, J.W. Weener, E.W. Meijer, F.C. De Schryver, J. Am. Chem. Soc. 122 (2000) 3445.

[19] A. Salmon, P. Jutzi, J. Organometal. Chem. 637 (2001) 595.

[20] X.S. Jiang, J. Yin, Macromolecules 37 (2004) 7850.

[21] X.S. Jiang, J. Yin, Macromol. Rapid Commun. 25 (2004) 748.

[22] F. Vogtle, S. Gestermann, R. Hesse, H. Schwierz, B. Windisch, Prog. Polym. Sci. 25 (2000) 987.

[23] F. Zeng, S.C. Zimmerman, Chem. Rev. 97 (1997) 1681.

[24] M.T. Morgan, M.A. Carnahan, A.A. Ribeiro, et al., J. Am. Chem. Soc. 125 (2003) 15485.

[25] D.G. Anderson, R.S. Davidson, J.J. Elvery, Polymer 37 (1996) 2477.