Materials Chemistry and Physics 131 (2011) 393–399

Contents lists available at SciVerse ScienceDirect

Materials Chemistry and Physics

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

Photo-polymerization of photocurable resins containing polyhedral oligomeric silsesquioxane methacrylate

Ho-May Lin[a,b,*], Shi-Yin Wu[b], Feng-Chih Chang[a], Ying-Chieh Yen[a]

[a] *Department of Applied Chemistry, National Chiao Tung University, 30010 Hsinchu, Taiwan*
[b] *Material and Chemical Research Laboratories, Industrial Technology Research Institute, 31040 Chutung, Taiwan*

ARTICLE INFO

Article history:
Received 21 March 2011
Received in revised form
20 September 2011
Accepted 27 September 2011

Keywords:
Polyhedral oligomeric silsesquioxanes (POSSs)
Photocurable resins
Hydrogen bonding
Acrylate monomer

ABSTRACT

Photocurable resins, bisphenol A propoxylate glycerolate diacrylate (BPA-PGDA, containing two hydroxyl) and bisphenol A propoxylate diacrylate (BPA-PDA), with fixed photoinitiator (Irgacure 907) concentration and various contents of methacrylisobutyl polyhedral oligomeric silsesquioxane (MI-POSS) were prepared and characterized by FTIR spectroscopy, scanning electron microscope and differential photocalorimetry. The MI-POSS molecules form crystals or aggregated particles in the cured resin matrix. The BPA-PGDA series photocurable resins show higher viscosity and lower photo-polymerization reactivity than the BPA-PDA series resins. The photo-polymerization rate and conversion of BPA-PGDA series are improved with increasing MI-POSS content. On the contrary, the photo-polymerization behavior of BPA-PDA series photocurable resins remains nearly unchanged by the addition of MI-POSS. Hydrogen-bonding interaction between the hydroxyl of BPA-PGDA and the siloxane of MI-POSS tends to attract and concentrate these acrylate double bonds around MI-POSS particles and thus enhances the photo-polymerization rate and conversion.

1. Introduction

Photocurable resins have been utilized since 1960s, and are extensively applied in coatings, adhesives, inks, electronics, optics, microfabrications, and biomedical materials [1–8]. Reactive (meth)acrylate monomers and free radical type photo-initiators are the main components of general photocurable resins. For processing efficiency, several approaches have been used to raise curing rate, such as adding photosensitizer or using highly reactive monomers. The mechanistic theories to account for the enhanced reactivity of (meth)acrylate monomers have also been widely discussed such as hydrogen abstraction [9], hydrogen bonding [10–13], dipole moment [14], and ionic contribution [15]. Hydrogen abstraction has the profound influence on the photo-polymerization rate via the substitution at the α carbon. Hydrogen bonding is able to promote double bond pre-aligned to increase radical propagation rate. Dipole moment increases monomer reactivity by influencing the termination rate constant and partial ionic contribution enhances the reactivity of propagation active center.

Polyhedral oligomeric silsesquioxanes (POSSs) contain inner inorganic cage made up of silicone and oxygen where outer surface is substituted by organic groups. The POSS organic–inorganic hybrid nanocomposites can be easily achieved by being copolymerized with various monomers or blended with other common polymers. Polymers incorporating POSS generally possess improved thermal stability [16], dimensional stability [17], high glass transition temperature [18] and low dielectric constant [19,20] that have attracted considerable interest in several applications. Several POSS-based photocurable resins have also been studied, such as epoxy [21], cinnamate [22], methacrylate [23], coumarin [24], and thiol-ene [25] functionalized POSS systems. In our previous study [26–29], we have observed the existence of hydrogen bonding interaction between the siloxane of the POSS moiety and the hydroxyl groups. Accordingly, we developed POSS-containing negative-type photoresist materials for UV-lithography and indicated that even small amount of POSS is able to substantially enhance the photo-polymerization [30a]. However, the composition of negative-type photoresist is too complicated to investigate the relationship between the molecular structure and photo-polymerization.

In this study, we prepare two series of photocurable resins, bisphenol A propoxylate glycerolate diacrylate series and bisphenol A propoxylate diacrylate series, containing various POSS contents but fixed photo-initiator concentration [30b]. The investigation of hydrogen bond interaction was carried out by Fourier transform infrared spectroscopy (FT-IR). The morphology of the cured resin was observed using scanning electron microscope (SEM).

---

* Corresponding author at: Department of Applied Chemistry, National Chiao Tung University, 30010 Hsinchu, Taiwan. Tel.: +886 3 5131512; fax: +886 3 5131512.
E-mail address: LillianHMLin@itri.org.tw (H.-M. Lin).

0254-0584/$ – see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.matchemphys.2011.09.061

The exotherm and conversion for the photo-polymerization of photocurable resins were studied by photo-differential scanning calorimetry (photo-DSC).

2. Experimental

2.1. Chemicals

Bisphenol A propoxylate diacrylate (BPA-PDA, Aldrich), bisphenol A propoxylate glycerolate diacrylate (BPA-PGDA, Aldrich), methacrylisobutyl polyhedral oligomeric silsesquioxane (MI-POSS, Hybrid Plastics), 2-methyl-1-[4-(methylthio) phenyl]-2-(4-morpholinyl)-1-propanone (Irgacure 907, Ciba), tetrahydrofuran (THF, TEDIA), and hydroquinone monomethyl ether (HQME, TCI) were used as received.

2.2. Characterizations

MI-POSS/BPA-PDA and MI-POSS/BPA-PGDA blends were dissolved in THF, coated on potassium bromide plate, heated at 800 °C for 30 min to remove the THF, and then the corresponding IR spectra were recorded on a Bio-Rad FTS 3000 FT-IR Spectrometer.

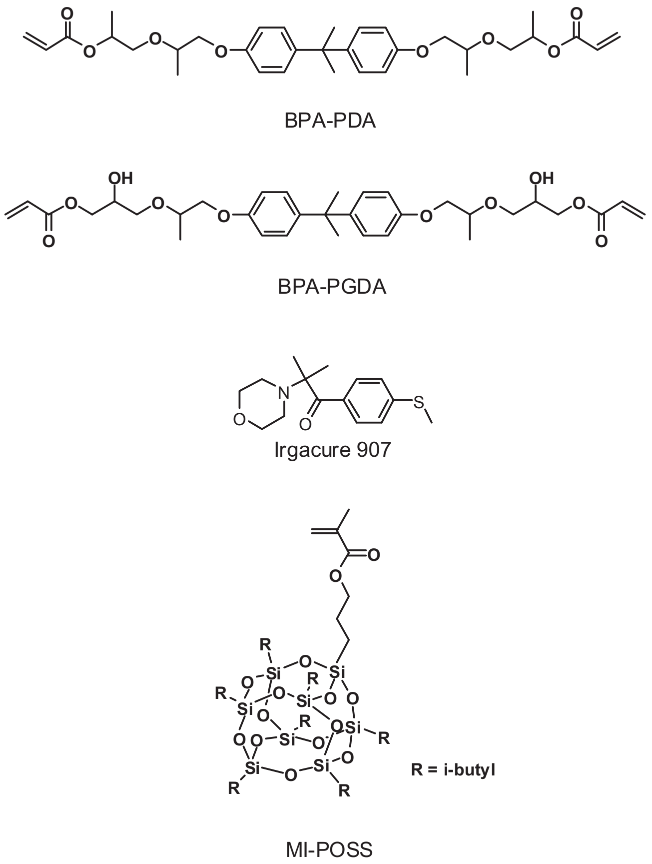
Two series of photocurable resins, BPA-PDA/MI-POSS/Irgacure 907 and BPA-PGDA/MI-POSS/Irgacure 907, were prepared with weight ratios $(100 - X)/X/10$ (where $X = 0$, 5, 10, 20, 30, and 40, respectively) by dissolving in a proper amount of THF. Approximately 2 mg of photocurable resin was placed in the aluminum DSC pan after removing THF at 80 °C for 30 min. The photo-polymerization exotherm was detected by a photo-DSC [Perkin-Elmer DSC 7 with Perkin-Elmer DPA 7 Photocalorimeter, a 100 W mercury lamp (wavelength from 250 to 600 nm) was used] under a nitrogen flow at 30 °C. Morphologies of the cross sections of cured resin films were observed by a Hitachi S-4200 scanning electron microscope.

3. Results and discussion

The chemical structures of monomers are illustrated in Scheme 1. BPA-PDA and BPA-PGDA are structurally similar, both monomers contain bisphenol A in the molecular center and two acryloyl group ends. However, the BPA-PGDA has two hydroxyl groups while BPA-PDA contains no hydroxyl groups. MI-POSS has a methacrylate group attached on the POSS cage as illustrated in Scheme 1.

Basic properties of these three monomers are listed in Table 1. The BPA-PGDA possesses significantly higher viscosity (59,900 cP) than the BPA-PDA (2100 cP) due to the presence of hydrogen bonding interaction even their molecular weight and chemical structure are fairly comparable. In addition, the inhibitor content employed in BPA-PGDA (1000 ppm) is higher than BPA-PDA (300 ppm). Cook indicated that the curing behaviors of monomers are nearly identical whether the monomer is purified or not [31]. Thus, all monomers employed in this study were directly used without further purification. The MI-POSS exhibits significantly lower theoretical heat of polymerization (58.1 J g^{-1}) than BPA-PDA (303.1 J g^{-1}) and BPA-PGDA (287.0 J g^{-1}) due to the relatively higher molecular weight with only one methacryloyl group.

Fig. 1 displays the FT-IR spectra in the 1250–1000 cm^{-1} region for various compositions of MI-POSS/BPA-PDA and MI-POSS/BPA-PGDA blends. The absorption at 1107 cm^{-1} is assigned to the free Si–O–Si stretch vibration of MI-POSS/diacrylate blends [27]. In both Fig. 1(a) and (b), the intensity of Si–O–Si absorption peak dramatically decreases with the increase in the diacrylate concentration. Furthermore, a shoulder centered at 1070 cm^{-1} occurred in the spectrum of MI-POSS/BPA-PGDA blend (Fig. 1(b) and (c)), indicating the presence of the hydrogen bonding interaction between MI-POSS siloxane and BPA-PGDA hydroxyl [27].



Scheme 1. Chemical structures of monomers.

Fig. 2 shows the FT-IR spectra in the 1780–1660 cm^{-1} region for various compositions of these MI-POSS/BPA-PDA and MI-POSS/BPA-PGDA blends. Pure MI-POSS possesses a weak absorption peak at 1724 cm^{-1} corresponding to the C=O stretch vibration. This absorption peak intensity progressively increases with the increase of the diacrylate content. As compared with MI-POSS/BPA-PDA blends, the C=O absorption peak of MI-POSS/BPA-PGDA blends is wider and shifts toward lower wavenumber. These results reveal that the hydrogen bonding interaction is formed between MI-POSS carbonyl and BPA-PGDA hydroxyl.

Fig. 3 shows SEM micrographs of cured BPA-PDA series and BPA-PGDA series resins with MI-POSS contents of $X = 5$ and $X = 40$ (SEM micrographs of samples with $X = 10$, 20, and 30 are shown in Supporting information). The cured resin does not contain MI-POSS showing smooth sections. Single or/and aggregated particles are dispersed in the cured resins containing MI-POSS. The size of the aggregated particles increases with increasing MI-POSS content. The size of the aggregated particles of the cured BPA-PDA series resins is larger than that of the cured BPA-PGDA series resins. The methacryloyl group of MI-POSS is able to react with BPA-PDA or PBA-PGDA and the organic–inorganic compatibility is improved by the i-butyl substitutents of MI-POSS. In this organic–inorganic photocurable resin, MI-POSS molecules tend to form their own single or aggregated particle domains [32].

Fig. 4 depicts photo-DSC exothermal curves and plots of C=C bond conversion versus time for the photo-polymerization of these POSS free photocurable resins. DSC heat flux is directly related to the rate and extent of photo-polymerization [12]. The reaction heat, ΔH, is derived from integrating the exothermal curve. The

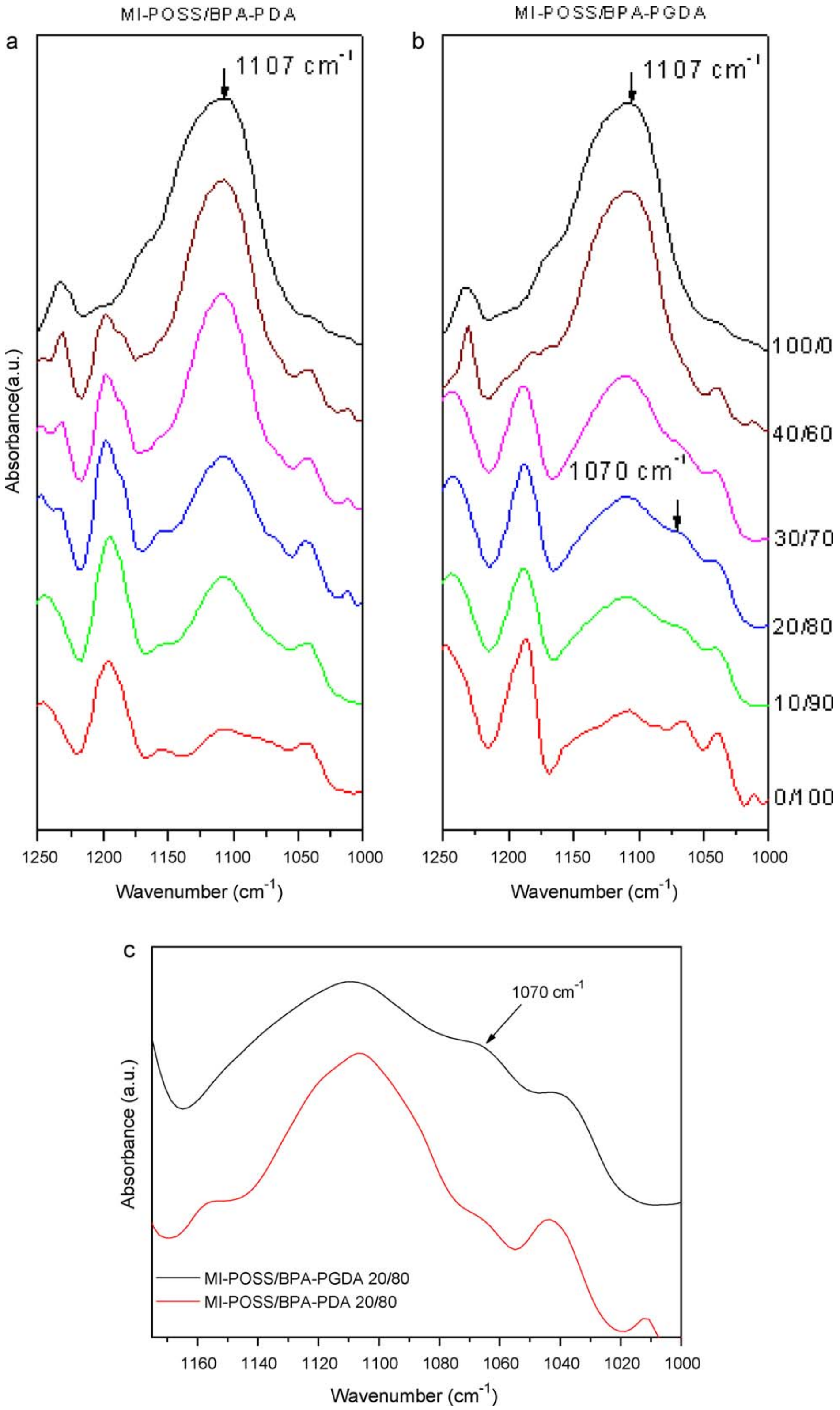


Fig. 1. FT-IR spectra in the 1250–1000 cm^{-1} region for various compositions of (a) MI-POSS/BPA-PDA blends, (b) MI-POSS/BPA-PGDA blends, and (c) MI-POSS/BPA-PDA 20/80 and MI-POSS/BPA-PGDA 20/80 blends.

ΔH divided by theoretical reaction heat, ΔH_{theor}, gives C=C bond reaction conversion.

$$\text{C=C bond reaction conversion}\,(\%) = \frac{\Delta H}{\Delta H_{\text{theor}}} \qquad (1)$$

According to these photo-DSC results, the BPA-PDA photocurable resin exhibits faster photo-polymerization, larger exothermal heat, and higher conversion than the BPA-PGDA photocurable resin. These properties, including chemical structure, the presence of hydrogen bonding interaction, and viscosity of monomer

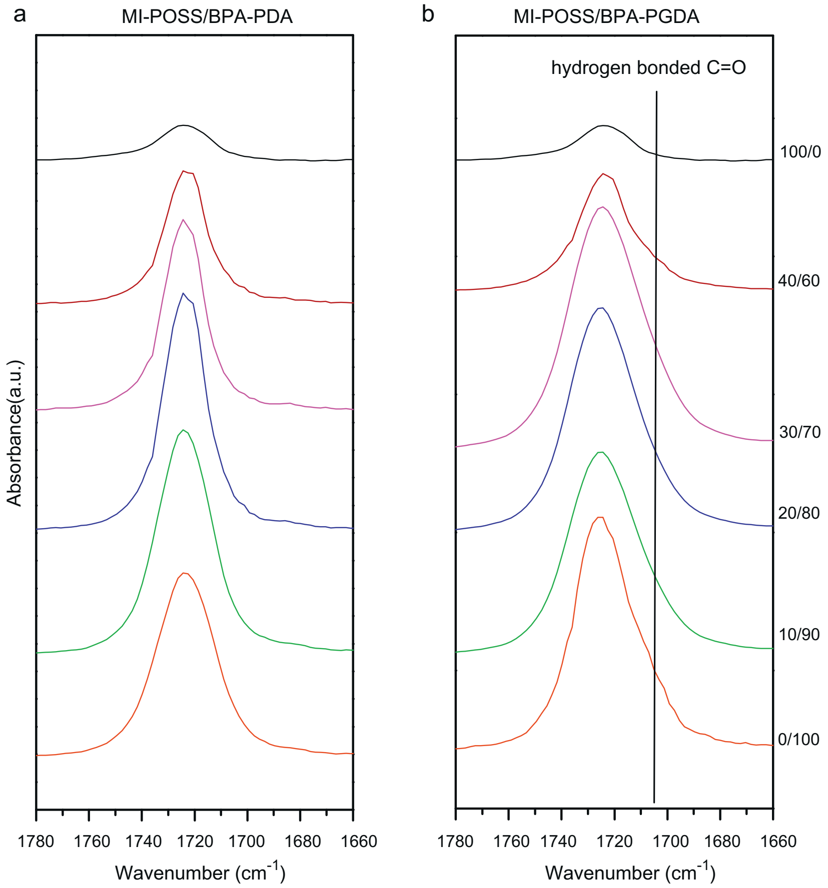


Fig. 2. FT-IR spectra in the 1780–1660 cm^{-1} region for various compositions of (a) MI-POSS/BPA-PDA and (b) MI-POSS/BPA-PGDA blends.

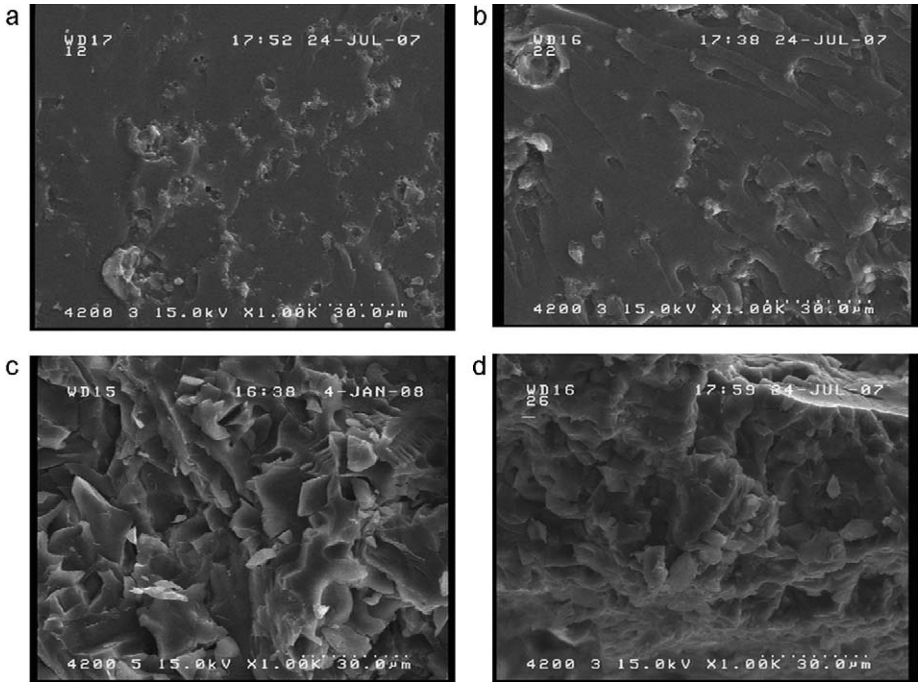


Fig. 3. SEM micrographs of (a) BPA-PDA/MI-POSS/Irgacure 907 = 95/5/10, (b) BPA-PDGA/MI-POSS/Irgacure 907 = 95/5/10 (c) BPA-PDA/MI-POSS/Irgacure 907 = 60/40/10, and (d) BPA-PGDA/MI-POSS/Irgacure 907 = 60/40/10.

Table 1
Properties of monomers studied.

Monomer	Molecular weight (g mol^{-1})	Inhibitor[a] content (ppm)	Viscosity (cP)	n_{D}^{20}[d]	Theoretical heat of polymerization[e] (J g^{-1})
BPA-PDA	568.71	300	2100[b]	1.521	303.1
BPA-PGDA	600.70	1000	59,900[c]	1.476	287.0
MI-POSS	943.64	–	White powder	–	58.1

[a] Hydroquinone monomethyl ether.

[b] Observed with Brookfield DV-II + Pro viscometer, spindle No. 63, 20 rpm at 25 °C.

[c] Observed with Brookfield DV-II + Pro viscometer, spindle No. 64, 2 rpm at 25 °C.

[d] Refractive index for the sodium D line (589.3 nm) at 20 °C.

[e] Heat of polymerization for methacrylates = 54.8 kJ mol^{-1} (13.1 kcal mol^{-1}).
Heat of polymerization for acrylates = 86.2 kJ mol^{-1} (20.6 kcal mol^{-1}) [12].

dramatically influence the photo-polymerization and conversion [33]. The presence of hydrogen bonding interaction between BPA-PGDA monomers results in relatively higher viscosity, lower photo-polymerization rate, and lower conversion. Though hydrogen bonding is able to accelerate photo-polymerization rate of small monomer with monofunctional group [10–13]. In this study, we obtained different results because the BPA-PGDA molecular structure is larger and contains two acryloyl groups to form hydrogen bonding and thus retards its mobility.

Fig. 5 illustrates the exothermal curves of photo-polymerizations for these two series of MI-POSS containing photocurable resins. For these MI-POSS/BPA-PDA photocurable resins, the peak height of heat flux decreases with increasing MI-POSS content due to dilution effect and results in C═C double bond concentration decrease. For MI-POSS/BPA-PGDA series photocurable resins, the peak height of heat flux increases and then decreases ($X > 20$) as the MI-POSS content is increased. Conversion–time curves for the photo-polymerization of these photocurable resins based on Eq. (1) are shown in Fig. 6. The initial conversions of MI-POSS/BPA-PGDA series photocurable resins are obviously raised by adding MI-POSS while the MI-POSS/BPA-PDA photocurable resins remain nearly unchanged. It is reasonable to interpret that increase in photo-polymerization rate and conversion of these MI-POSS/BPA-PGDA photocurable resins are come from the hydroxyl–siloxane hydrogen bonding

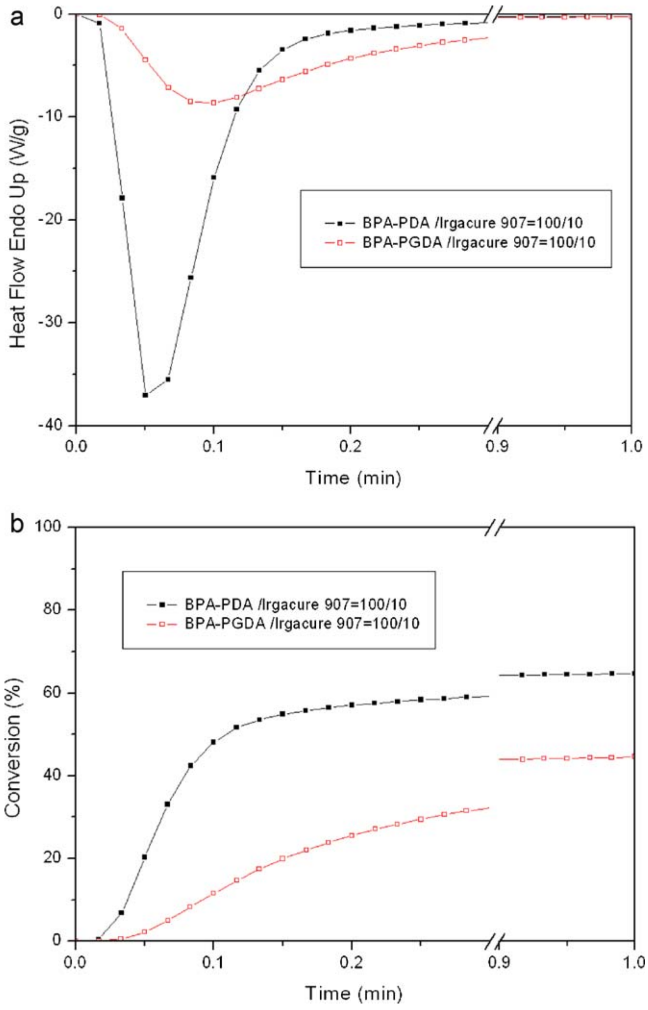


Fig. 4. (a) Photo-DSC exothermal curves and (b) C═C bond conversion versus time curves for the photo-polymerization of POSS free photocurable resins.

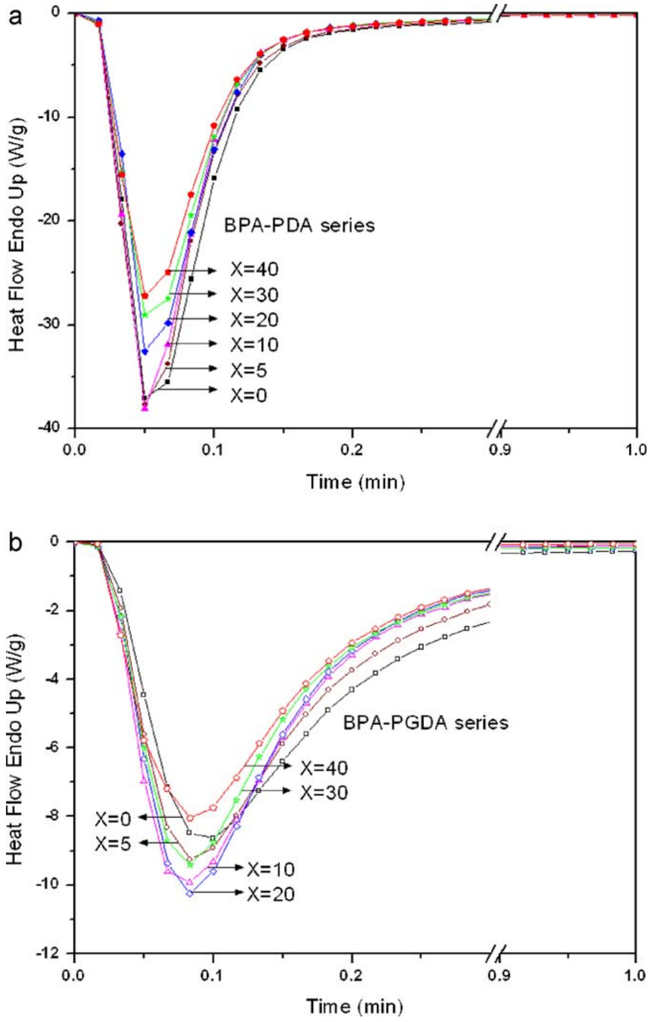
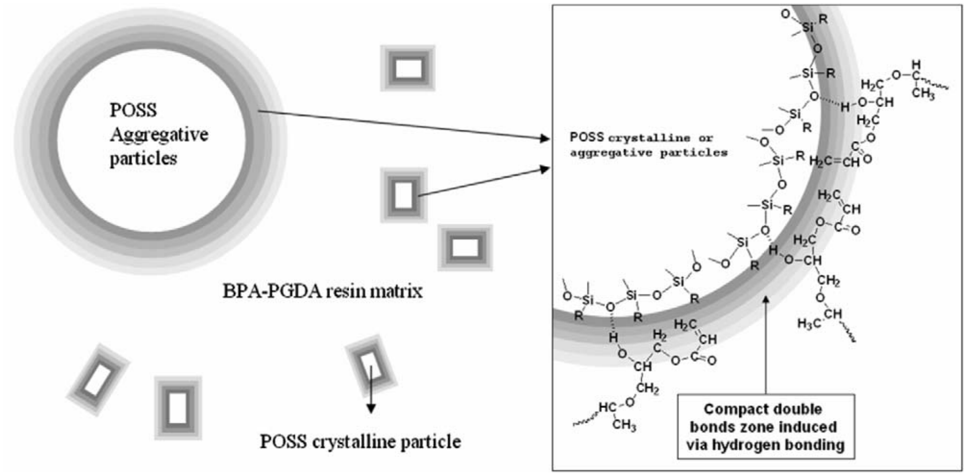


Fig. 5. Photo-DSC exothermal curves for the photo-polymerization of photocurable resins [(a) BPA-PDA/MI-POSS/Irgacure 907 or (b) BPA-PGDA/MI-POSS/Irgacure 907 = (100 − X)/X/10 (weight ratio)].



Scheme 2. The proposed microstructure via hydrogen bonding interaction between MI-POSS and BPA-PGDA molecules.

interaction between the POSS siloxane and hydroxyl group in the double bond side chain of the BPA-PGDA monomer. The hydrogen bonding interaction tends to dense these acrylate double bonds near the vicinity of POSS particles and results in higher local concentration of these acrylate double bonds around POSS particles and thus enhances the rate of photo-polymerization. The proposed schematic microstructure via hydrogen bonding interaction between POSS particles and hydroxyl groups resulting in higher concentration of double bonds side chain surrounding

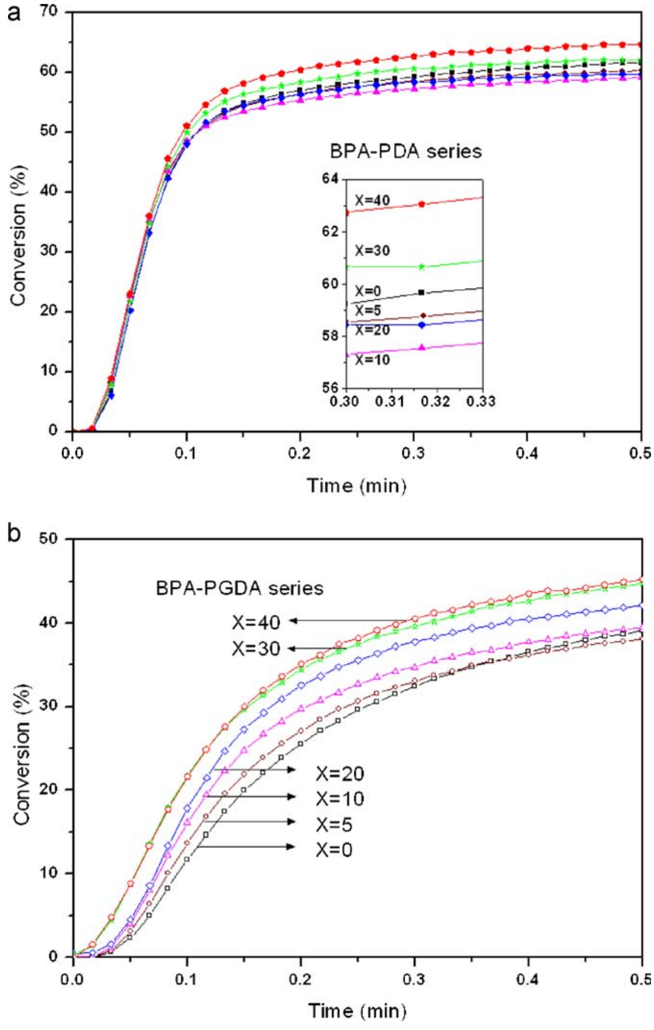


Fig. 6. Conversion–time curves for the photo-polymerization of photocurable resins [(a) BPA-PDA/MI-POSS/Irgacure 907 or (b) BPA-PGDA/MI-POSS/Irgacure 907 = (100 − X)/X/10 (weight ratio)].

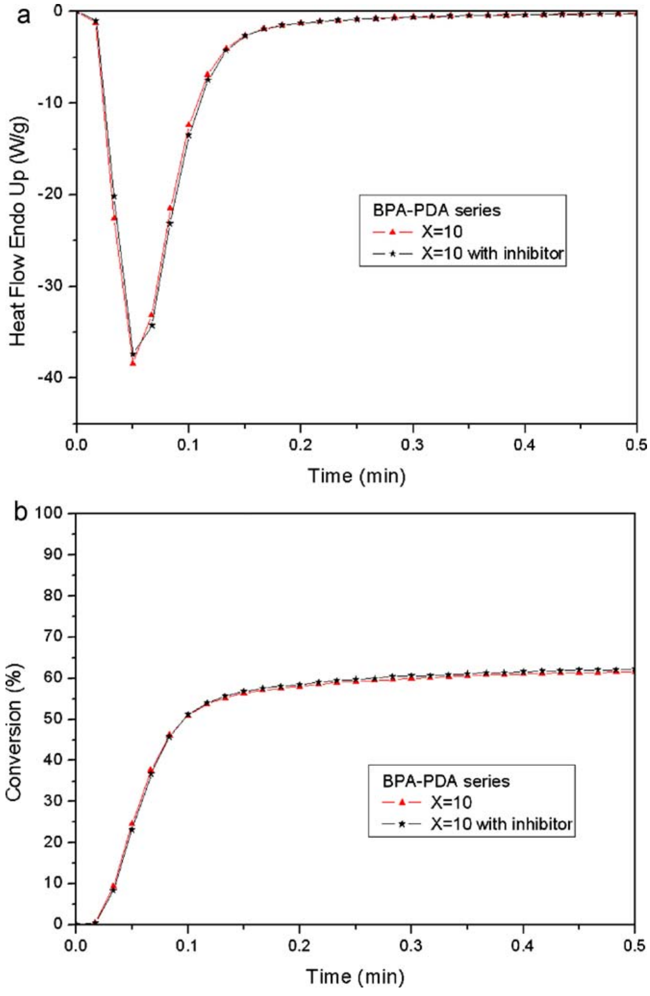


Fig. 7. (a) Photo-DSC exothermal curves and (b) conversion–time curves for the photo-polymerization of BPA-PDA series resin (X = 10) and BPA-PDA series resin (X = 10) with 900 ppm HQME as inhibitor.

POSS particles is shown in Scheme 2. POSS molecules tend to aggregate and form particles [34–37]. We also suspect that the photo-polymerization can be more efficient by using small particles through scattering light. However, the photo-polymerization rate of BPA-PDA series photocurable resins is not increased by the increase in the MI-POSS content. The light scattering assumption is not tenable.

For further confirming the effect of the inhibitor on photo-polymerization, more amount of inhibitor was added to the photocurable resin. Fig. 7 shows the photo-DSC exothermal curves and conversion–time curves for the photo-polymerization of MI-POSS/BPA-PDA ($X = 10$) and MI-POSS/BPA-PDA resins ($X = 10$) with 900 ppm HQME as inhibitor. Essentially no difference was observed between these two resins, implying that the presence of several hundred ppm (general adding amount) variation of inhibitor does not alter the photo-polymerization rate and conversion.

4. Conclusions

This study investigated the rate and conversion of photo-polymerizations of two series of photocurable resins comprising acrylate monomer, BPA-PDA or BPA-PGDA, MI-POSS macromer, and photoinitiator. Hydrogen bonding interaction within BPA-PGDA monomer causes higher viscosity dramatically, and thus limits its molecular chain motion and reduces its photo-polymerization rate. Photo-polymerization rate and conversion of MI-POSS/BPA-PGDA photocurable resins are increased by the addition of MI-POSS because the siloxane of MI-POSS tends to attract the hydroxyl of BPA-PGDA by hydrogen bonding interaction and thus concentrates acrylate double bonds around MI-POSS moieties to enhance the photo-polymerization rate and conversion. Similar phenomenon does not occur for these MI-POSS/BPA-PDA photocurable resins due to absence of hydroxyl group.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.matchemphys.2011.09.061.

References

[1] M. Podgórski, Dent. Mater. 26 (2010) e188.
[2] S.M. Gasper, D.N. Schissel, L.S. Baker, D.L. Smith, R.E. Youngman, L.M. Wu, S.M. Sonner, R.R. Hancock, C.L. Hogue, S.R. Givens, Macromolecules 39 (2006) 2126.
[3] J. Taniguchi, Y. Kamiya, T. Ohsaki, N. Sakai, Microelectron. Eng. 87 (2010) 859.
[4] R.A. Ortiz, A.E.G. Valdéz, M.G.M. Aguilar, M.L.B. Duarte, Carbohyd. Polym. 78 (2009) 282.
[5] K. Kim, S.Y. Cho, D.M. Yeu, S.Y. Shin, Chem. Mater. 17 (2005) 962.
[6] R.M.K. Ramanan, P. Chellamuthu, L. Tang, K.T. Nguyen, Biotechnol. Prog. 22 (2006) 118.
[7] D.P. Dworak, M.D. Soucek, Macromolecules 37 (2004) 9402.
[8] P. Granat, M. Pudas, O. Hormi, J. Hagberg, S. Leppävuori, Carbohyd. Polym. 57 (2006) 225.
[9] E.R. Beckel, J.W. Stansbury, C.N. Bowman, Macromolecules 38 (2005) 3093.
[10] M. Schott, S. Spagnoli, G. Weiser, Chem. Phys. 333 (2007) 246.
[11] T.Y. Lee, T.M. Roper, E.S. Jönsson, C.A. Guymon, C.E. Hoyle, Macromolecules 37 (2004) 3659.
[12] L.J. Mathias, B.S. Shemper, M. Alirol, J.F. Morizur, Macromolecules 37 (2004) 3231.
[13] D. Avci, L.F. Mathias, Polymer 45 (2004) 1763.
[14] J.F.G.A. Jansen, A.A. Dias, M. Dorschu, B. Coussens, Macromolecules 36 (2003) 3861.
[15] E.R. Beckel, J.W. Stansbury, C.N. Bowman, Macromolecules 38 (2005) 9474.
[16] Y. Ni, S. Zheng, K. Nie, Polymer 45 (2004) 5557.
[17] J.C. Huang, C.B. He, Y. Xiao, K.Y. Mya, J. Dai, Y.P. Siow, Polymer 44 (2003) 4491.
[18] M.J. Abad, L. Barral, D.P. Fasce, R.J.J. Williams, Macromolecules 36 (2003) 3128.
[19] W.Y. Chen, Y.Z. Wang, S.W. Kuo, C.F. Huang, P.H. Tung, F.C. Chang, Polymer 45 (2004) 6897.
[20] Y.J. Lee, J.M. Huang, S.W. Kuo, J.S. Lu, F.C. Chang, Polymer 45 (2005) 173.
[21] A. Sellinger, R.M. Laine, Chem. Mater. 8 (1996) 1592.
[22] Y. Ni, S. Zheng, Chem. Mater. 16 (2004) 5141.
[23] B.K. Lee, N.G. Cha, L.Y. Hong, D.P. Kim, H. Tanaka, H.Y. Lee, Y. Kawai, Langmuir 26 (2010) 14915.
[24] M. Fujiwara, K. Shiokawa, N. Kawasaki, Y. Tanaka, Adv. Funct. Mater. 13 (2003) 371.
[25] B. Pan, T. Clark, C.E. Hoyle, J.D. Lichtenhan, Polym. Prepr. 45 (2004) 170.
[26] Y.J. Lee, S.W. Kuo, W.J. Huang, H.Y. Lee, F.C. Chang, J. Polym. Sci. Polym. Phys. 42 (2004) 1127.
[27] X. Xu, S.W. Kuo, J.S. Lee, F.C. Chang, Polymer 43 (2005) 5117.
[28] C.F. Huang, S.W. Kuo, F.J. Lin, W.J. Huang, C.F. Wang, W.Y. Chen, F.C. Chang, Macromolecules 39 (2006) 300.
[29] H.C. Lin, S.W. Kuo, C.F. Huang, F.C. Chang, Macromol. Rapid Commun. 27 (2006) 537.
[30] (a) H.M. Lin, S.Y. Wu, P.Y. Huang, C.F. Huang, S.W. Kuo, F.C. Chang, Macromol. Rapid Commun. 27 (2006) 1550;
(b) K. Studer, C. Decker, E. Beck, R. Schwalm, Prog. Org. Coat. 48 (2003) 101.
[31] W.D. Cook, J. Polym. Sci. Polym. Chem. 31 (1993) 1053.
[32] Y. Zhang, S. Lee, M. Yoonessi, K. Liang, C.U. Pittman, Polymer 47 (2005) 2984.
[33] S.H. Dickens, J.W. Stansbury, K.M. Choi, C.J.E. Floyd, Macromolecules 36 (2003) 6043.
[34] E. Tegou, V. Bellas, E. Gogolides, P. Argitis, D. Eon, G. Cartry, C. Cardinaud, Chem. Mater. 16 (2004) 2567.
[35] A.J. Waddon, L. Zheng, R.J. Farris, E.B. Coughlin, Nano Lett. 2 (2002) 1149.
[36] L. Zheng, A.J. Waddon, R.J. Farris, E.B. Coughlin, Macromolecules 35 (2002) 2375.
[37] Y.J. Lee, S.W. Kuo, Y.C. Su, J.K. Chen, C.W. Tu, F.C. Chang, Polymer 45 (2004) 6321.