Preparation and Properties of Novel Low Dielectric Constant Benzoxazole-Based Polybenzoxazine

Kan Zhang, Qixin Zhuang, Yunchao Zhou, Xiaoyun Liu, Guang Yang, Zhewen Han

Key Laboratory for Specially Functional Polymeric Materials and Related Technology of the Ministry of Education, East China University of Science and Technology, Shanghai 200237, China Correspondence to: X. Liu (E-mail: liuxiaoyun@ecust.edu.cn)

Received 28 April 2012; accepted 12 August 2012; published online DOI: 10.1002/pola.26344

ABSTRACT: A novel benzoxazine monomer containing a benzoxazole group was synthesized using a nonsolvent method and then named DAROH-a. The structure of DAROH-a was confirmed by FTIR, ¹H NMR, elemental analysis, and mass spectrometry. The curing reaction activation energy was calculated at 140 kJ/mol. Its corresponding crosslinked polybenzoxazines, poly(DAROH-a), displayed a higher glass transition temperature at 402 °C, a 9% weight loss at the said temperature, and a high char yield of 42 wt % (800 °C, in nitrogen). Moreover, the dielectric constants of poly(DAROH-a) were low and changed only slightly at different temperatures. Furthermore, the dielectric constants and dielectric loss of poly(DAROH-a) at the same

INTRODUCTION Phenolic resin is widely used because of its good heat resistance, flame resistance, mechanical strength, corrosion resistance, and electrical insulation. However, strong acid catalyst is often required and reaction byproducts are released in the curing process, thereby limiting its application. Benzoxazine is a newly developed thermosetting phenolic resin that can be synthesized via Mannich condensation from phenol, amine, and formaldehyde.^{1,2} The molecular structural design of benzoxazine is very flexible. Various phenols and amines offer enormous flexibility, and many benzoxazines with different structures have been synthesized for various applications. The benzoxazine monomer can be polymerized by thermal-activated ring-opening polymerization reaction to form a spatial network structure. During the self-crosslinking polymerization reaction, no reaction byproducts are released and no catalyst is required.³⁻⁵ Benzoxazine resin has good mechanical properties and thermal properties, low water absorption, high carbon residue, and low surface energy, $^{6\mbox{-}14}$ which make benzoxazine a promising matrix for composite materials, especially for use in microelectronics, aerospace, and packaging industries.^{8,15}

Many reports on benzoxazine have been published in recent years. The majority of studies reported have focused on synthesis methods,⁵ polymerization,^{15,16} blending and com-

frequency barely changed from room temperature to 150 °C. The photophysical properties of poly(DAROH-a) film were also investigated. Poly(DAROH-a) showed an absorption peak at 280 nm. The photoluminescent emission spectrum of poly(DAROH-a) film displayed predominant emission peaks at 521 nm. It might have potential application as high-performance materials because of its excellent dielectric constants stability and thermal stability under high temperature. © 2012 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 000: 000–000, 2012

KEYWORDS: benzoxazine; benzoxazole; dielectric properties; highperformance polymers; thermal properties

posites,^{17–19} properties,^{20,21} and reaction mechanisms^{22,23} of benzoxazine monomers and the resultant polymers. Many chemical groups have been incorporated in benzoxazine monomers to improve the properties of benzoxazines and polybenzoxazines. For example, a benzoxazine compound possessing a fluorene group and two terminal furan groups has been reported. The photoluminescent intensity of this benzoxazine reaches sixfold of the intensity recorded with 4,4'-(9-fluorenylidene) diphenol, which is the phenol for benzoxazine.²⁴ Poly(siloxane) segments increase the toughness or decrease the dielectric constants of the resulting benzoxazine-based polymers.^{25–27} Polymers and oligomers containing benzoxazine in the main chains have also caught the attention of numerous researchers.^{28,29}

Polybenzoxazole is a class of high-performance liquid crystal polymers.^{30,31} Among these benzoxazole polymers, poly(benzobisoxazole) (PBO) exhibits high tensile strength, high modulus, and excellent thermal and environmental stability. PBO has been used in protection and insulation layers for very large-scale integration circuits and multichip modules for computers owing to their high thermal stability and excellent mechanical property.³² Moreover, PBO are considered relatively lower dielectric materials because of the absence of carbonyl groups in their structure.³³ Lower dielectric

^{© 2012} Wiley Periodicals, Inc.



WWW.MATERIALSVIEWS.COM

1

constants are required to increase the circuit speed, so many studies have been focused on lowering the dielectric constant of PBO.

The above features inspired the idea to incorporate benzoxazine and benzoxazole groups into one compound. In this study, a novel benzoxazole-based benzoxazine monomer named DAROH-a was synthesized and characterized. The ring-opening polymerization of the DAROH-a monomer was investigated with differential scanning calorimetry (DSC) in dynamic conditions. The polymerization behavior, network structure, and thermal properties of the monomers and the polybenzoxazines were investigated. Moreover, the liquid crystalline structure was studied by polarized optical microscopy (POM). Finally, the dielectric and photophysical properties of polybenzoxazine were investigated.

EXPERIMENTAL

Materials

The polymerization medium, poly(phosphoric acid) (PPA) with a phosphorus pentoxide (P_2O_5) content of 80.8%, was freshly prepared using phosphoric acid and P_2O_5 (Shanghai 1st Chemical), which was used as received.

Other reagents and solvents, including *p*-hydroxybenzoic acid, paraformaldehyde, 4,6-diaminobenzene-1,3-diol dihydrochloride (DAR), and aniline, were obtained from Aldrich and used as received.

Measurements

FTIR spectra were obtained with a Nicolet 5700 FTIR Spectrometer at a resolution of 4 cm^{-1} . All samples were finely ground with KBr powder and pressed into disk. ¹H NMR spectra were recorded with ArANCEIII (400 MHz) using dimethylsulfoxide (DMSO- d_6) as solvent and tetramethylsilane as an internal standard. Mass spectra were recorded with an IonSpec HIResMALDI high-resolution mass spectrometer with matrix-assisted laser desorption ionization. The matrix 2,5-dihydroxybenzoic acid was dissolved in DMSO (10 mg/mL) and mixed with the sample solution (1 mg/mL) in 1:1 v/v ratio. Samples were spotted onto the target and dried in air. DSC measurements were conducted with a DSC Q2000 V24.9 Build 121 using N₂ as a purge gas (100 mL/min) at scanning rate of 10 °C/min. Samples of 3-5 mg were placed in aluminum pans with pierced lids. In the dynamic analyses, the samples were scanned at different heating rates of 5, 7.5, 10, 12.5, and 15 °C/min, respectively. Thermogravimetry analysis (TGA) was undertaken using a NETZSCH STA 409 PC/PG thermogravimetric analyzer. Experiments were carried out on \sim 7 mg samples heated in flowing nitrogen or air (20 mL/min) at a heating rate of 10 °C/min. Elemental analyses were run in a VARIO ELIII analyzer with 4-nitroaniline as a standard. UV-vis absorption spectra were recorded with a Shimadzu UV-2550 spectroscopy. Photoluminescent (PL) emission spectra were measured on a Jobin Yvon Fluorolog-3-p spectrofluorometer. Dielectric constant measurement was carried out using a Concept 40 broadband dielectric spectrometer (Novocontrol Technologies GmbH & Co., KG, Germany). The films were



SCHEME 1 Chemical reaction of DAROH-a monomer synthesis.

dried at 120 °C under vacuum for 8 h before measurements. A sample of 20 mm in diameter and 1 mm in thickness was placed between the two copper electrodes; thus, a parallel plate capacitor was formed. The dependence of the dielectric constant and dielectric loss on the frequency of the applied field was studied in the temperature range of 25–200 °C and within the frequency range of 10 Hz–5 MHz. Optical observations were made with a POM (model WETZLAR).

Synthesis of DAROH

The synthesis reaction route of DAROH is shown in Scheme 1. Five grams of DAR, 6.48 g of *p*-hydroxybenzoic acid, and 75 g of PPA were mixed together in a glass reactor vessel. The dehydrochlorination was performed at 90–110 °C for 12 h. The reaction temperature was raised to 130 °C for 12 h, then to 150 °C for 12 h, and finally to 180 °C, which was maintained for 8 h. The highly viscous light-yellow dope was placed in water. The solution was washed several times with water to remove the PPA completely. At last, the solution was dried at 60 °C in a vacuum oven for 12 h, and a brown powder was obtained.

The chemical structure of DAROH was confirmed with 1 H NMR, FTIR, and elemental analysis.

Figure 1 shows the ¹H NMR spectrum of DAROH. The peaks at 6.98 to -7.00 ppm, 7.40–7.42 ppm, and 8.04–8.26 ppm are assigned to the aromatic protons. Resonance appearing at 10.4 ppm is assigned to the hydroxybenzene protons.

The FTIR spectrum of DAROH is shown in Figure 2. The bands at 1608 and 989 cm⁻¹ are related to the absorption of C=N and C-0 in the benzoxazole ring, respectively. The band at 3448 cm⁻¹ is attributed to the hydroxyl of hydroxybenzene.

Elemental analysis of DAROH shows that the experimental results (C, 68.67%; H, 3.22%; N, 7.65%) are in reasonable



FIGURE 1¹H NMR spectrum of DAROH.

agreement with the calculated value (C, 69.77%; H, 3.51%; N, 8.13%).

Synthesis of DAROH-a

DAROH-a was synthesized according to Scheme 1. Paraformaldehyde (1.39 g) and aniline (2.16 g) were mixed in a 100-mL three-necked round-bottom flask equipped with a mechanical stirrer, a thermometer, and a reflux condenser. The mixture was stirred for 15 min before adding DAROH (4 g). The temperature was then gradually raised to 110 °C. Subsequently, the yellow product was washed several times with 1 mol/L sodium hydroxide aqueous solution and deionized water, respectively. During the purification process, the product was precipitated and filtered out in a separatory funnel. Thereafter, it was dried at 60 °C in a vacuum oven for 12 h, and a yellow powder was obtained.

The chemical structure of DAROH-a was confirmed with ¹H NMR, FTIR, elemental analysis, and mass spectrometry.

The ¹H NMR spectrum of DAROH-a is shown in Figure 3. The peaks at 6.60–8.42 ppm are assigned to the aromatic protons. The benzoxazine rings of DAROH-a are character-







FIGURE 3 ¹H NMR spectrum of DAROH-a.

ized with the resonance peaks at 4.58 (Ar-CH₂—N) and 5.75 ppm (O—CH₂—N), and the intensity ratio of these two peaks is 1:1.02. The intensity ratio results and no other major peaks in the ¹H NMR spectrum, indicating that DAROH-a has high purity. The resonance peaks at 4.58 (Ar-CH₂—N) and 5.75 ppm (O—CH₂—N) separate more than 1 ppm. No other benzoxazines have been reported to show this phenomenon. The possible reason is that the π inductive effect by benzoxazole groups, which have stronger deshielding effect to O—CH₂—N than Ar-CH₂—N.

The FTIR spectrum of DAROH-a is shown in Figure 4. The benzoxazine ring of DAROH-a displays characteristic absorption at 1234 cm⁻¹ (asymmetric stretching of C—O—C), 1007 cm⁻¹ (symmetric stretching of C—O—C), and 1351 cm⁻¹ (CH₂ wagging). The disubstituted benzene groups of DAROH-a exhibit an absorption peak at 1514 cm⁻¹. The absorption bands at 938 cm⁻¹ corresponding to the out-of-plane bending vibration of C—H are due to the characteristic mode of benzene with an attached oxazine ring.²⁴ The band at 1611



FIGURE 4 FTIR spectrum of DAROH-a.



FIGURE 5 Mass spectrometry of DAROH-a.

 $\rm cm^{-1}$ is related to the absorption of C=N in the benzoxazole ring.

Figure 5 shows the mass spectrum of DAROH-a. A peak at 578.3 is observed, which is in accord with the empirical formula of DAROH-a. This result is in good agreement with the structural data obtained from 1 H NMR and FTIR spectroscopy.

Elemental analysis of DAROH-a shows that the experimental results (C, 73.06%; H, 4.39%; N, 9.89%) are in reasonable agreement with the calculated values (C, 74.73%; H, 4.53%; N, 9.68%).

RESULTS AND DISCUSSION

Polymerization Behavior of DAROH-a Monomer

The polymerization behavior of DAROH-a was studied by DSC and FTIR. The corresponding *in situ* FTIR spectra are shown in Figure 6. The peak at 938 cm⁻¹ corresponds to the out-of-plane bending vibration of C—H.²⁴ The new band at 3417 cm⁻¹ is assigned to the stretching of OH group.¹⁶ The disappearance of 938 cm⁻¹ and the appearance of 3417 cm⁻¹ indicate the occurrence of ring-opening polymerization of DAROH-a (Scheme 2).

The curing behavior of the monomer DAROH-a was monitored by DSC. Figure 7 shows the DSC plots for DAROH-a recorded at a heating rate of 10 °C/min. The endothermal peak with an onset at 145 °C and a maximum at 175 °C is believed as the melting phase of DAROH-a. The exothermal peak in the range of 192–223 °C is assigned to the curing reaction of DAROH-a. The curing temperature observed is slightly lower compared with other benzoxazines, which generally exhibit exothermic ring-opening reaction at \sim 220–260 °C.



FIGURE 6 FTIR spectra during the ring-opening reaction of DAROH-a at 190 °C (0–120 min).

JOURNAL OF POLYMER SCIENCE Chemistry



SCHEME 2 Ring-opening polymerization of DAROH-a.

In the second scan (Fig. 8), poly(DAROH-a), the corresponding crosslinked polymer from DAROH-a, did not show any exothermic peaks in the DSC thermogram. The curing reaction of the DAROH-a benzoxazine groups was carried out, and the degree of conversion was found to be high. Poly(DAROH-a) showing a high glass transition temperature of about 400 °C, higher than common polybenzoxazine, was a notable finding. The possible reasons include the formation of additional physical crosslinks via hydrogen bonds and the existence of a rigid benzobisoxazole group.



FIGURE 7 DSC thermograms of the DAROH-a monomer.



FIGURE 8 DSC thermograms of the cured polybenzoxazine.

Figures 9 and 10 show the DSC plots of DAROH-a and the conversion versus temperature at different heating rates. Figure 9 also shows the initial curing temperature (T_i) and peak temperature (T_p) at different heating rates. The figures indicate that the exothermic peak shifts to a higher temperature with the increase of heating rate. The data are summarized in Table 1.

The curing reaction activation energy was investigated using the well-known Kissinger and Ozawa methods.^{33,34}

According to the Kissinger method, the activation energy can be calculated by eq 1 as follows:

$$\ln\left(\frac{\beta}{T_{\rm p}^2}\right) = \ln\left(\frac{AR}{E}\right) - \frac{E}{RT_{\rm p}},\tag{1}$$

where β is the heating rate, *A* is the frequency factor, $T_{\rm p}$ is the temperature of the exothermic peak, $E_{\rm a}$ is the activation energy, and *R* is the gas constant. If the plot of $\ln(\beta/T_{\rm p}^2)$



FIGURE 9 DSC curves of DAROH-a at different heating rates.

5



FIGURE 10 Conversion versus temperature for DAROH-a cured at different heating rates.

against $1/T_p$ is linear, E_a can be obtained from the slope of the corresponding straight line.

Another theoretical treatment, namely, the Ozawa method, can also be applied to the thermal data using eq 2 as follows:

$$\ln\beta = -1.052\frac{E}{RT_{\rm p}} + C,\tag{2}$$

where C is a constant.

Figure 11 shows the plot of $\ln(\beta/T_p^2)$ and $\ln(\beta)$ against $1/T_p$ for the DAROH-A according to Kissinger and Ozawa methods. The E_a value is estimated to be ~140 kJ/mol and is listed in Table 1.

In addition, comparing the kinetic results of DAROH-a with that of bisphenol-A-based benzoxazine (BA-a) reported by Ishida and Rodriguez,³⁵ it can be found that the activation energy values of DAROH-a are higher than that of BA-a. In the dynamic polymerization mode, the activation energy values of DAROH-a are 140.6 kJ/mol by Kissinger's method and 142.6 kJ/mol by Ozawa's method, whereas those of BA-a are 116 kJ/mol by Kissinger's method and 107 kJ/mol by Ozawa's method. This may be ascribed to the structural difference between DAROH-a and BA-a monomers. The benzoxazole groups in DAROH-a are flexible.

-					
Heating Rate (°C/min)	<i>T</i> i (°C)	<i>Τ</i> _p (°C)	<i>T</i> _f (°C)	Kissinger <i>E</i> (kJ/mol)	Flynn-Wall- Ozawa <i>E</i> (kJ/mol)
5	184.0	196.2	212.7		
7.5	190.0	200.1	218.2		
10	192.6	205.5	223.4	140.6	142.6
12.5	192.9	207.9	226.0		
15	195.5	209.1	241.2		



FIGURE 11 Representations of Kissinger and Ozawa methods for the calculation of activation energy from nonisothermal data for the benzoxazine monomer.

Liquid Crystalline Property of Crosslinked Poly(DAROH-a)

The POM photos in Figure 12 demonstrate the ordered texture of the polymer poly(DAROH-a). At room temperature, the appearance of a fine birefringence pattern suggests the liquid crystalline structure of poly(DAROH-a), which means that the poly(DAROH-a) is in the lyotropic liquid crystal phase at room temperature.

Thermal Stability of Crosslinked Poly(DAROH-a)

TGA was carried out under nitrogen atmospheres to determine the thermal stability and the decomposition behavior. Figure 13 shows the TGA curves and the first derivative curves, and Table 2 summarizes the TGA data.

Two weight-loss stages in the TGA curve of poly(DAROH-a) were observed in Figure 13. The first weight-loss stage that occurred at 260 °C and ended at 430 °C is probably attributed to the weight loss of alkyl. The second stage that occurred at 603 °C is believed to be the thermal



FIGURE 12 Polarized optical micrographs for poly(DAROH-a) at room temperature.



FIGURE 13 TGA thermograms of the crosslinked polybenzoxazines poly(DAROH-a).

decomposition of benzobisoxazole. The weight loss of the first stage is about 8% and the char yield at 800 °C is 42%. TGA results indicated that the thermal stability of poly-(DAROH-a) was a little lower than that of PBO, which is very stable below 600 °C under air.³⁶ However, this thermal decomposition temperature is higher than most other polybenzoxazines.

Dielectric Property Analysis of Crosslinked Poly(DAROH-a)

The dependence of dielectric constant and dielectric loss on the frequency of the applied field was studied in the temperature range of 25-200 °C and within the frequency range of 10 Hz-5 MHz. The variation of the dielectric constant with the frequency of the applied field is shown in Figure 14. The dielectric constant was observed to vary from 2.1 to 2.3 at room temperature within the frequency range of 10 Hz-5 MHz. The dielectric constants of poly(DAROH-a) are fairly low, especially in the high-frequency range, which suggests its potential application as microelectronic packaging material. The dielectric constant has a higher value within the lower frequency region, after which it decreases with increase in frequency and remains practically constant. At a slightly higher temperature (i.e., 200 °C), the value of the dielectric constant decreases from a maximum value of 3.9 at 10 Hz to a value of 2.4 at 10 MHz and remains almost constant beyond 100 kHz. These data imply that the poly-(DAROH-a) crystal exhibits normal dielectric behavior. In normal dielectric behavior, the dielectric constant decreases with the increase in frequency and reaches a constant value beyond a certain frequency on the electric field. The dipole does not follow the alternating field. Figure 14 also suggests that unlike the dielectric constant of common polybenzoxa-

TABLE 2 Thermal Properties of Crosslinked Polybenzoxazines

 Poly(DAROH-a)

Sample	T5%	T10%	Y _c (%)
poly(DAROH-a)	375	416	42





FIGURE 14 Dielectric constant versus frequency of poly-(DAROH-a) at different temperatures.

zine, which strongly depends on temperature,³⁷ the dielectric constants of poly(DAROH-a) at the same frequency barely change under low temperatures up to 150 °C.

The dependence curve of dielectric loss on frequency at different temperatures is shown in Figure 15. These curves suggest that the dielectric loss also depends on the frequency of the applied field and barely changes under low temperatures up to 150 °C at the same frequency, which is similar to the phenomenon with the dielectric constant of poly(DAROH-a) (Fig. 14). The dielectric loss decreases from 0.015 to 0.01 at 25 °C, whereas it decreases from 0.17 to 0.02 at high temperature (200 °C) as the frequency of the applied AC field is increased from 10 Hz to 5 MHz. Dielectric loss decreases very little with the increase in frequency at lower temperature and appears to achieve saturation at the higher frequency range of 1 kHz and above at temperatures ranging from 25 to 150 °C.



FIGURE 15 Dielectric loss versus frequency of poly(DAROH-a) at different temperatures.

7



FIGURE 16 Dielectric constant of poly(DAROH-a) versus temperature.

Figures 16 and 17 show the dependence curves of the dielectric constant and dielectric loss on temperature for the frequency range of 1 MHz. The curves show that the effect of temperature on the dielectric properties of poly(DAROH-a) is weak until 150 °C. A low, steady dielectric loss at high frequency for a broad range of temperatures mainly characterizes poly(DAROH-a).

Photophysical Properties of Crosslinked Poly(DAROH-a)

Figure 18 shows the absorbance spectra of the poly(DAROHa) films. The spectrum of poly(DAROH-a) film shows a absorption peak at 280 nm. The absorption band of benzobisoxazole chromophore appears in a lower energy range with the maxima at 402 and 426 nm,³⁸ so the absorption of poly-(DAROH-a) shows blue shift. The PL emission spectrum of the poly(DAROH-a) film is exhibited in Figure 19. The excitation wavelength is 353 nm. The poly(DAROH-a) film displays a strong PL emission peak at 521 nm, which has a slight red shift compared with the emission of benzobisoxazole chro-



FIGURE 17 Dielectric loss of poly(DAROH-a) versus temperature.



FIGURE 18 Normalized absorbance spectra of poly(DAROH-a) film.

mophore units.³⁷ The possible reason for this red shift is the incorporation of benzoxazine rings to benzobisoxazole, which might hinder the aggregation of benzobisoxazole groups. The application potential of the poly(DAROH-a) film in PL and EL fields is worthy of further studies.

CONCLUSIONS

A novel benzoxazine containing a benzoxazole group, DAROH-a, was synthesized. DSC indicates that the curing reaction occurred at 205 °C. The curing reaction activation energy was 140 kJ/mol. POM photos of corresponding cross-linked polybenzoxazines from DAROH-a showed an ordered texture, suggesting the existence of liquid crystal.

Poly(DAROH-a) behaved at a higher glass transition temperature of 402 °C after 9% weight loss, which was ascribed to the highly crosslinked polybenzoxazine networks and the existence of the benzoxazole structure. Poly(DAROH-a) also showed good thermal stability. The 10% weight-loss



FIGURE 19 PL spectra of poly(DAROH-a) film at excitation wavelength of 353 nm.

temperature obtained was 416 °C and the char yield at 800 °C was 42%. The dielectric constants of poly(DAROH-a) at different temperatures were low. Meanwhile, the dielectric constants and dielectric loss of poly(DAROH-a) at the same frequency barely changed from room temperature to 150 °C. Furthermore, poly(DAROH-a) film showed an absorption peak at 280 nm. The PL emission spectrum of the poly-(DAROH-a) film showed predominant emission peaks at 521 nm. It might have potential application as high-performance materials because of its excellent dielectric constants stability and thermal stability under high temperature.

ACKNOWLEDGMENTS

The authors express their gratitude to the National Natural Science Foundation of China (NSFC) for their financial support (contract grant numbers 50703010 and 50973028). This project is also supported by Innovation Program of Shanghai Municipal Education Commission (12ZZ049) and the Fundamental Research Funds for the Central Universities.

REFERENCES AND NOTES

 Holly, F.; Cope, A. C. J. Am. Chem. Soc. 1994, 66, 1875–1979.
 Ning, X.; Ishida, H. J. Polym. Sci. Part A: Polym. Chem. 1994, 32, 1121–1129.

3 Ishida, H.; Ohba, S. Polymer 2005, 46, 5588-5595.

4 Velez, H. P.; Doyama, K.; Abe, H.; Ishida, H. *Macromolecules* 2008, *41*, 9704–9714.

5 Agag, T.; Takeichi, T. Macromolecules 2003, 36, 6010-6017.

6 Endo, T.; Sudo, A. J. Polym. Sci. Part A: Polym. Chem. 2009, 47, 2847–2858.

7 Nagai, A.; Kamei, Y.; Wang, X. S.; Omura, M.; Sudo, A.; Nushida, H.; Kawamoto, E.; Endo, T. *J. Polym. Sci. Part A: Polym. Chem.* **2009**, *46*, 2316–2325.

8 Kiskan, B.; Aydogan, B.; Yagci, Y. J. Polym. Sci. Part A: Polym. Chem. 2009, 47, 804–811.

9 Herreta, P. V.; Ishida, H. *J. Polym. Sci. Part A: Polym. Chem.* **2009**, *47*, 5871–5881.

10 Yagci, Y.; Kiskan, B.; Ghosh, N. N. J. Polym. Sci. Part A: Polym. Chem. **2008**, 47, 5565–5576.

11 Spontón, M.; Larrechi, M. S.; Ronda, J. C.; Galià, M.; Cádiz, V. *J. Polym. Sci. Part A: Polym. Chem.* **2008**, *46*, 7162–7172.

12 Kiskan, B.; Demirel, A. L.; Kamer, O.; Yagci, Y. J. Polym. Sci. Part A: Polym. Chem. **2008**, 46, 6780–6788.

13 Chou, C. I.; Liu, Y. L. J. Polym. Sci. Part A: Polym. Chem. 2008, 46, 6509–6517.

14 Andreu, R.; Reina, J. A.; Ronda, J. C. J. Polym. Sci. Part A: Polym. Chem. 2008, 46, 6091–6101.

15 Jin, L.; Agag, T.; Ishida, H. Eur. Polym. J. 2010, 46, 354-363.

16 Liu, Y. F.; Yue, Z. Q.; Gao, J. G. *Polymer* **2010**, *51*, 3722–3729.

17 Kubra, D. D.; Mehmet, A. T.; Tamer, U.; Awei, W. K.; Atsushi, S.; Takeshi, E.; Yusuf, Y. *J. Polym. Sci. Part A: Polym. Chem.* **2011**, *49*, 4213–4220.

18 Zuniga, C.; Larrechi, M. S.; Lligadas, G.; Ronda, J. C.; Galia, M.; Cadiz, V. *J. Polym. Sci. Part A: Polym. Chem.* **2011**, *49*, 1219–1227.

19 Baris, K.; Narendra, N. G.; Yusuf, Y. *Polym. Int.* **2011**, *60*, 167–177.

20 Hwang, H. J.; Lin, C. Y.; Wang, C. S. J. Appl. Polym. Sci. 2008, 220, 2413–2423.

21 Qu, L.; Xin, Z. Langmuir 2011, 27, 8365-8370.

22 Chutayothin, P.; Ishida, H. *Macromolecules* **2010**, *43*, 4562–4572.

23 Liu, C.; Shen, D. M; Sebastian, R. M.; Marquet, J.; Schonfeld, R. *Macromolecules* **2011**, *44*, 4616–4622.

24 Liu, Y. L.; Chang, C. Y.; Hsu, C. Y.; Tseng, M. C.; Chou, C. I. *J. Polym. Sci. Part A: Polym. Chem.* **2010**, *48*, 4020–4026.

25 Takeichi, T.; Aaga, T.; Zeidam, R. *J. Polym. Sci. Part A: Polym. Chem.* **2001**, *39*, 2633–2641.

26 Liu, Y. L.; Hsu, C. W.; Chou, C. I. J. Polym. Sci. Part A: Polym. Chem. 2007, 45, 1007–1015.

27 Liu, H. C.; Su, W. C.; Liu, Y. L. *J. Mater. Chem.* **2011**, *21*, 7182–7187.

28 Kiskan, B.; Yagci, Y.; Ishida, H. *J. Polym. Sci. Part A: Polym. Chem.* **2008**, *46*, 414–420.

29 L, J.; Agag, T.; Ishida, H. Polymer 2010, 51, 5688-5694.

30 Wolfe, J. F.; Arnold, F. E. *Macromolecules* **1981**, *14*, 909–915.

31 Wolfe, J. F; Loo, B. H.; Arnold, F. E. *Macromolecules* **1981**, *14*, 915–920.

32 Maiyer, G. Prog. Polym. Sci. 2001, 26, 3-65.

- 33 Kissinger, H. E. Anal. Chem. 1957, 29, 1702-1706.
- **34** Ozawa, T. *Therm. Anal.* **1970**, *2*, 301–324.

35 Ishida, H.; Rodriguez, Y. Polymer 1995, 36, 3151-3158.

36 Krause, S. J.; Haddock, T. B.; Vezie, D. L. *Polymer* **1998**, *3*, 338–345.

37 Hwang, H. J.; Lin, C. Y.; Wang, C. S. *J. Appl. Polym. Sci.* **2008**, *110*, 2413–2423.

38 Xu, X.; Zhang, H.; Liu, X.; Zhuang, Q.; Han, Zh. *Eur. Polym. J.* **2010**, *46*, 528–534.

