Colloid Polym Sci (2008) 286:761–767
DOI 10.1007/s00396-007-1832-4

ORIGINAL CONTRIBUTION

The linear relations and living feature in cationic ring-opening copolymerization of epoxy/THF system

Qili Wu · Liang Li · Yingfeng Yu · Xiaolin Tang

Received: 19 November 2007 / Revised: 12 December 2007 / Accepted: 17 December 2007 / Published online: 14 January 2008

Abstract The cationic copolymerization of diglycidyl ether of bisphenol-A with tetrahydrofuran (THF) initiated by phosphotungstic acid $H_3PW_{12}O_{40}$ (PW_{12}) was in situ investigated by Fourier transform near infrared spectroscopy. The gelation point of the reaction was determined by rheometrics mechanical spectroscopy. It was found that the conversion of epoxy group at 4,530 and 6,073 cm^{-1} increased linearly with reaction time up to a high conversion (~90%), during which gelation (at ~51%) had no effect. The slope-indicating reaction rate of epoxy group also increased linearly with the content of PW_{12}. In addition, the peak splitting pattern of the overlapping C–H vibration region (5,700–6,200 cm^{-1}) was developed here. The peak-splitting analysis showed that the epoxy behavior agreed with above results, but the reaction rate of THF slowed down gradually with reaction time as the viscosity of the system increased. The results suggest that the kinetic behavior of cationic polymerization shows living feature of the propagating chains in this system and near infrared (NIR) technology could be applied to study such kinetic behavior.

Keywords Polyoxometalate · Cationic polymerization · Epoxy · Near infrared (NIR)

Q. Wu · L. Li · Y. Yu (✉) · X. Tang (✉)
Department of Macromolecular Science and Key
Laboratory of Polymer Engineering Science, Fudan University,
Shanghai 200433, China
e-mail: yfyu@fudan.edu.cn
e-mail: txl@fudan.edu.cn

Introduction

Fourier transform near infrared (FTIR) spectroscopy is a convenient and reliable tool to monitor the kinetics of many reactive systems. There have long been such studies of the epoxy or hardener system [1–7], either in mid infrared (MIR) range or in near infrared (NIR) range. In those studies, the reaction of epoxy group was monitored through the change of epoxy absorption peak at either 915 cm^{-1} in MIR [1] or 4530 cm^{-1} in NIR [2]. Together with changes of other absorption peaks, and sometimes in combination with other methods such as differential scanning calorimetry, the curing behavior and kinetics can be revealed.

The MIR spectroscopy (4,000–400 cm^{-1}) is replete with fundamental absorptions and is richer in information. But sometimes, the sample preparation may be time consuming due to sample thickness requirement; the spectra are very complex due to band overlapping; and, the most important, the epoxy peak at about 915 cm^{-1} is not always reliable as pointed out in previous reports [1, 2], while the NIR (11,000–4,000 cm^{-1}) spectroscopy is much more convenient in sample preparation, simpler, and more reliable on measurement because it only contains overtones and combinations of N–H, C–H, and O–H groups [3]. The epoxy peak at 4,530 cm^{-1} is easy to monitor and proved reliable for quantitative analysis [2]. Thus, in recent years, NIR spectroscopy has emerged as a new tool to study the curing behavior of epoxy systems, such as epoxy or anhydride [3, 4] and epoxy or amine [5–7], in which even the kinetic rate constants can be estimated [7]. However, there are few papers in the literature devoted to monitor the kinetic behavior of cationic polymerization of cyclic ethers by NIR spectroscopy.

Transition metal polyoxometalates (POMs) represent a well-known class of structurally well-defined clusters with an enormous variation in size, metal–oxygen framework topology, composition, and function. Hence, they have promising applications in catalysis [8], optics [9, 10], electronics [11, 12], and energy storage [13]. POMs, such as Keggin-type $H_3PW_{12}O_{40}$ (PW_{12}) and $H_3PMo_{12}O_{40}$ (PMo_{12}), have recently been studied in cationic polymerization [14]. Hongzhi Zhang et al. [15] reported PW_{12}-initiated cationic polymerization of tetrahydrofuran (THF) promoted by a small amount of epoxy monomer.

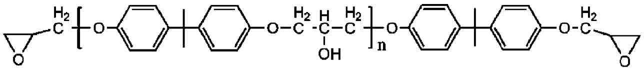
So far, there have been several reports about the cationic polymerizing behavior of cyclic ethers, including epoxy and THF. James Crivello et al. [16–18] reported three typical types of photoinitiated cationic homopolymerizing kinetics of different epoxy monomers. The cationic copolymerizing mechanism of epoxy monomers with expandable cyclic carbonates was investigated by Takeshi Endo et al. [19] and Xavier Ramis et al. [20]. The studies of the cationic polymerization of THF revealed the much higher reactivity of oxonium ion ended with oxirane ring [21] and the S-shape conversion curve of THF [22]. Moreover, the cationic polymerization of THF with different monomers, promoters, and end-capping agents could be used to synthesize PTHF with different topological structures [23, 24]. However, to our best knowledge, there are still no reports about the POMs-initiated cationic homopolymerization or copolymerization of epoxy monomers.

In this work, the copolymerization of epoxy resin with THF in the presence of PW_{12} was in situ investigated by the NIR. Moreover, the peak-splitting pattern assisted by the second derivative peak assignment was developed for the analysis of the complicated C–H vibration region (5,700–6,200 cm^{-1}). Further, the reaction mechanism of this system was discussed. The results suggest that the dual linear relations indicate the living feature of the cationic copolymerization and NIR technology could be a convenient tool to monitor such kinetic behavior.

Experimental

Materials

THF (Shanghai Lingfeng Chemical Reagent Co., China) was purified according to literature [25]. PW_{12} was purchased from Shanghai Chemical Reagent Co. (China) and was used as received. Diglycidyl ether of bisphenol-A (DGEBA; DER 331, Dow Chemical Co. 182–192 g/eq) was used as received (Scheme 1).



Scheme 1 The structure of DGEBA

Sample preparation

First, 2 g epoxy resin was dissolved in 4 g THF; the t_0 spectrum was collected here. Then, just before NIR monitoring, quantitative PW_{12} was added and stirred into homogenous solution. The homogeneous solution was immediately poured into a 2 mm thick polytetrafluoroethylene holder placed between two glass slides. In rhoemetric test, because the viscosity was too low in the beginning, the sample was not poured between two parallel plates (diameter 25 mm) for test until it got an appropriate viscosity. The time was recorded from the preparation of sample until the end of test in order to cover gelation time.

In situ NIR monitoring and determination of gelation point

The near infrared spectrometer used is Nicolet NEXUS 470 FTIR spectrometer. The t_0 spectrum was collected first. Then, the sample just prepared was placed into the compartment and monitored in situ in the near infrared region (11,000–4,000 cm^{-1}) at 25±0.1 °C. The in situ scanning lasted until the reaction became very slow (around 95% epoxy conversion) and the t_∞ spectrum was collected when it reached 100% conversion.

The gelation process was tested on the ARES-9A rheometer. The gelation point was determined by the converging point of the curves under multi-frequency mode, where the 0.5, 1, 5, and 10 Hz were chosen. The gelation time was recorded from the adding of PW_{12} to the occurrence of gelation point, then converted to corresponding conversion.

The different compositions investigated were listed in Table 1.

Table 1 The experimental runs of different compositions

Sample	PW_{12}/ DGEBA /THF (Weight ratio)	Gelation Time (min)	Gelation Conversion[a] (epoxy)
P5	0.05/2/4	77	50.8%
P6	0.06/2/4	66	51.8%
P7	0.07/2/4	54	50.3%
P8	0.08/2/4	49	51.6%
P9	0.09/2/4	42	51.1%

[a] Read from epoxy conversion/time curve calculated from NIR spectra.

Results and discussions

Analysis of epoxy group

All the NIR spectra were collected in the region of 11,000–4,000 cm^{-1}. A consecutive change of absorption intensities of relevant functional groups can be observed. Figure 1 showed a typical spectral evolution of P6 in the region of 6,500–4,450 cm^{-1}.

In Fig. 1, the NIR spectra of P6 represented the typical evolution of relevant functional groups. The consumption of epoxy group was clearly demonstrated by the decrease of the characteristic epoxy peak at 4,530 cm^{-1} together with the one at 6,073 cm^{-1}, which is not quite obvious here. Whereas, the ether related C–H vibration region (5,400–6,200 cm^{-1}) can be divided into two zones: (1) monomer zone (5,735–6,200 cm^{-1}) revealed the decrease of absorption intensity from monomer consumption and (2) polymer zone (5,400–5,735 cm^{-1}) revealed the increase of absorption intensity from polyether formation. It is reasonable that the C–H vibrations of monomers get higher wave number because of their higher ring strain and greater dipole moment than the polymer chain. The change of absorption intensities of epoxy peak and the C–H broad band can be used to monitor the kinetic process of the cationic copolymerization.

Although with different intensities, the two characteristic epoxy peaks (4530 and 6073 cm^{-1}) showed a clear-cut decreasing trend of good resolution. Because the integral intensity of such peak was always used to demonstrate epoxy conversion [3–7], the integration needed to be done carefully. Considering the influences of THF evaporation and sample thickness difference on the spectral intensity, the aromatic peak at 4,680 cm^{-1} was chosen as reference peak [2]. In order to rule out the influence of any small peak contained in the integral peak on the linear baseline correction, the subtraction based on t_∞ spectrum was carried out after normalization. Then, the integration was calculated and converted into epoxy conversion based on the integration of t_0 spectrum. The results were shown in Fig. 2.

As the copolymerization resulted in a cross-linking product, rheometrics mechanical spectroscopy (RMS) was taken to study the influence of gelation on the copolymerizing behavior. Based on the gelation and above analysis, the corresponding gelation conversion could be obtained. The results were contained in Table 1. It can be

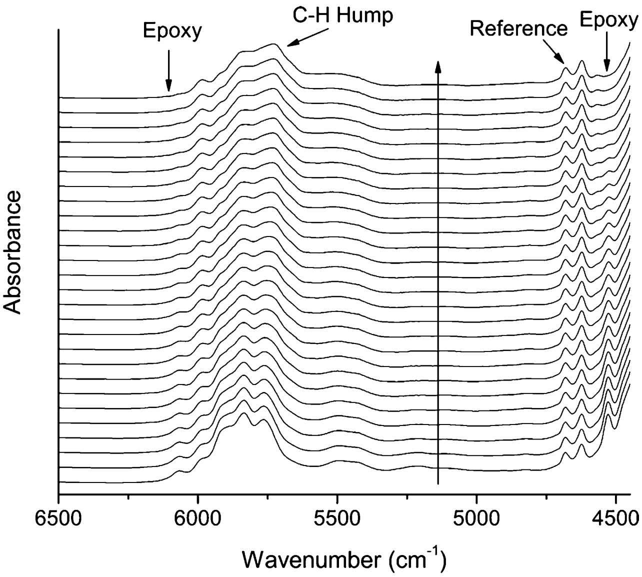


Fig. 1 The evolution of NIR spectra of P6 in the region of 6,500–4,450 cm^{-1}

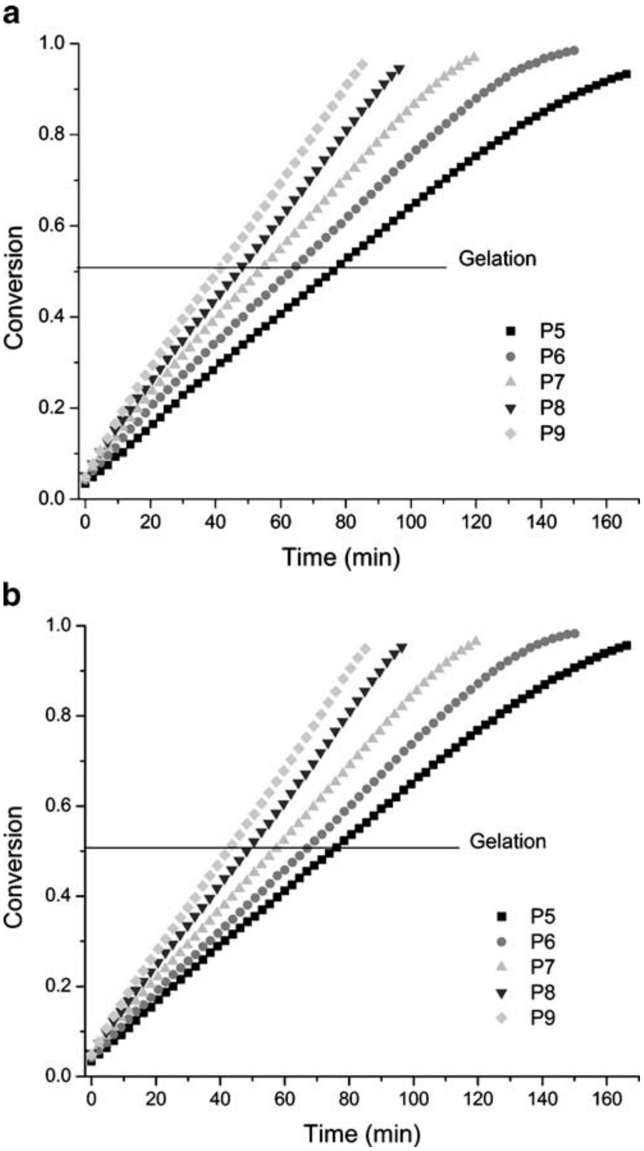


Fig. 2 The variation of epoxy conversion (**a**=4,530 cm^{-1}, **b**=6,073 cm^{-1}) with reaction time of *P5*, *P6*, *P7*, *P8* and *P9*

found that gelation in each composition occurred at the conversion of about 51%; thus, we can draw a gelation line in Fig. 2.

To our surprise, all curves of epoxy conversion with reaction time are well linearly fitted up to epoxy conversion of about 90%, during which gelation seems to have no effect. This extreme linearity aroused our interest because it not only differs from the conventional S-shape conversion or time curve in epoxy or hardener system [1–7] but also differs from the runaway cationic bulk polymerization (photo initiated) [16–18] and solution polymerization (tested in acetone, ester) of epoxy resin which took place in seconds. Furthermore, many other types of epoxy resins (aromatic or aliphatic, monofunctional or multi-functional) applied in our system instead of DGEBA demonstrating similar linearity.

The interesting behavior prompted our two conjectures: (1) there should be living propagating cationic centers associated with the features of PW_{12} to provide a possibility for the linearity and (2) there should be involvement of THF in the polymerization to confine the runaway reaction of epoxy group and realize the linearity after gelation. So, it may just be PW_{12} and THF who distinguished our system.

As a support to our first conjecture, the reaction rates of epoxy group under various contents of PW_{12} were obtained by the linear-fitting slopes of the curves in Fig. 2. The results were listed in Table 2. As expected, the reaction rate increases proportionally with the content of PW_{12}, as shown in Fig. 3. The results indicate the living feature of the propagating species. The reason may lie in the superacidity and weakly coordinating anion of PW_{12} [14]; thus, the active species which are formed from PW_{12} protons and coordinated by PW_{12} anions can maintain their concentration and activity without being terminated or shielded by the anions in normal cases.

So far, it is evident that both the variation of epoxy conversion with reaction time and the variation of epoxy reaction rate with content of PW_{12} display good linearity, and they indicate the living feature of the cationic species due to the unique features of PW_{12}. But why could the conventional runaway ring-opening reaction of epoxy group take on such an unusual behavior? THF may play a key role in such process.

Table 2 The reaction rates of different compositions

Sample	R_p of 4530 cm^{-1} ($\times 10^{-3}$)	R_p of 6073 cm^{-1} ($\times 10^{-3}$)
P5	5.77±0.02	5.87±0.02
P6	6.87±0.02	6.89±0.01
P7	7.89±0.02	7.91±0.01
P8	9.21±0.02	9.35±0.02
P9	10.44±0.03	10.41±0.02

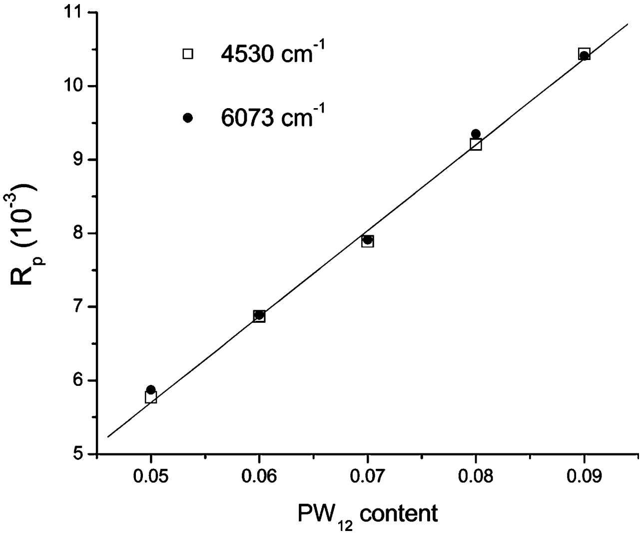


Fig. 3 The variation of reaction rate of epoxy group with the content of PW_{12}

Analysis of CH hump

In order to support our second conjecture, the change of THF contained in the region of 6,200–5,400 cm^{-1} needed to be analyzed. But the changes of the related C–H vibrations in this region are strongly smeared by overlapping; thus, an appropriate peak deconvolution must be carried out.

According to previous study, the multiple peaks overlapped in a hump can be picked out through the second derivative analysis [26]. Here in our system, the second derivative analysis of the monomers was first carried out to locate all the peaks while in the analysis of polymerizing behavior, the subtracted spectra were used again to exclude the influence of any unchanged peak contained in the hump to make the related change clearer and the peak-splitting pattern simpler. The results are presented in Fig. 4.

As an example, the subtracted spectra of sample P6 are presented in Fig. 4a. The subtracted spectra are obtained from the same processing as that of epoxy above (normalization, subtraction based on t_∞). It can be seen that the changes of absorption intensities of both monomer zone and polymer zone are clearly separated.

In Fig. 4b and c, the second derivative spectra did reveal many peaks overlapped in the hump of pure THF and DGEBA while in Fig. 4d of subtracted spectrum, the situation was simpler and the change of the hump in the monomer zone could be ascribed to five separated peaks. Considering the peak assignments reported previously [1, 2], the tentative peak assignments were made in Table 3.

Through the peak assignments, the change of absorption intensities of the characteristic peaks can be well assigned to either DGEBA or THF. What needs to be noticed is that the peak at 5,911 cm^{-1} comes from the

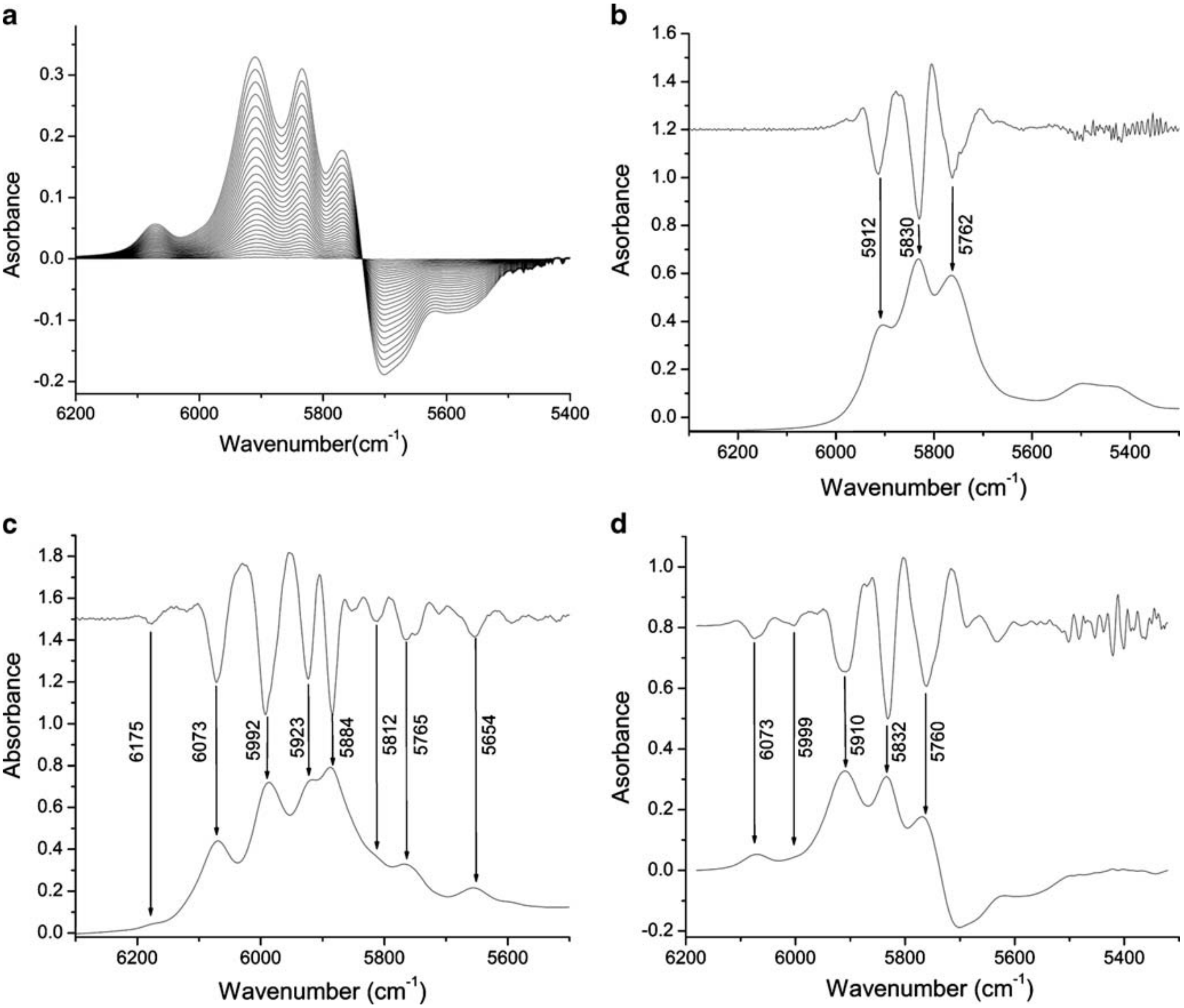


Fig. 4 **a** The subtracted spectra of P6 in 6,200–5,400 cm^{-1}; The second derivative analysis of **b** original spectrum of pure THF, **c** original spectrum of pure DGEBA, and **d** a typical subtracted spectrum of P6

highly overlapping of both decreasing epoxy and THF peaks, while the peak at 5759 cm^{-1} comes from the decreasing THF peak partially overlapped by one increasing polyether peak.

Based on Table 3, the peak-splitting pattern was made for all the subtracted spectra and an example was shown in Fig. 5.

As shown in Fig. 5a, the five separated peaks just fit the subtracted spectrum of monomer zone (6,200–5,735 cm^{-1}).

Table 3 The peak assignments showed by second derivative spectra (cm^{-1})

	Blends (Fig. 4d)	Tentative assignments
Peak position (cm^{-1})	6073	Epoxy CH_2 asymmetric stretching vibration (first overtone)
	5999	Epoxy CH/CH_2 stretching vibrations (first overtone and combination)
	5911	THF CH_2 asymmetric stretching vibration (first overtone), overlapped with combination band of epoxy in-ring CH/CH_2 and out-of-ring CH_2/CH_3 stretching vibrations.
	5832	Combination band of THF CH_2 asymmetric and symmetric vibrations
	5759	THF CH_2 symmetric stretching vibration (first overtone), partially overlapped with CH_2 stretching vibration in polyether chain

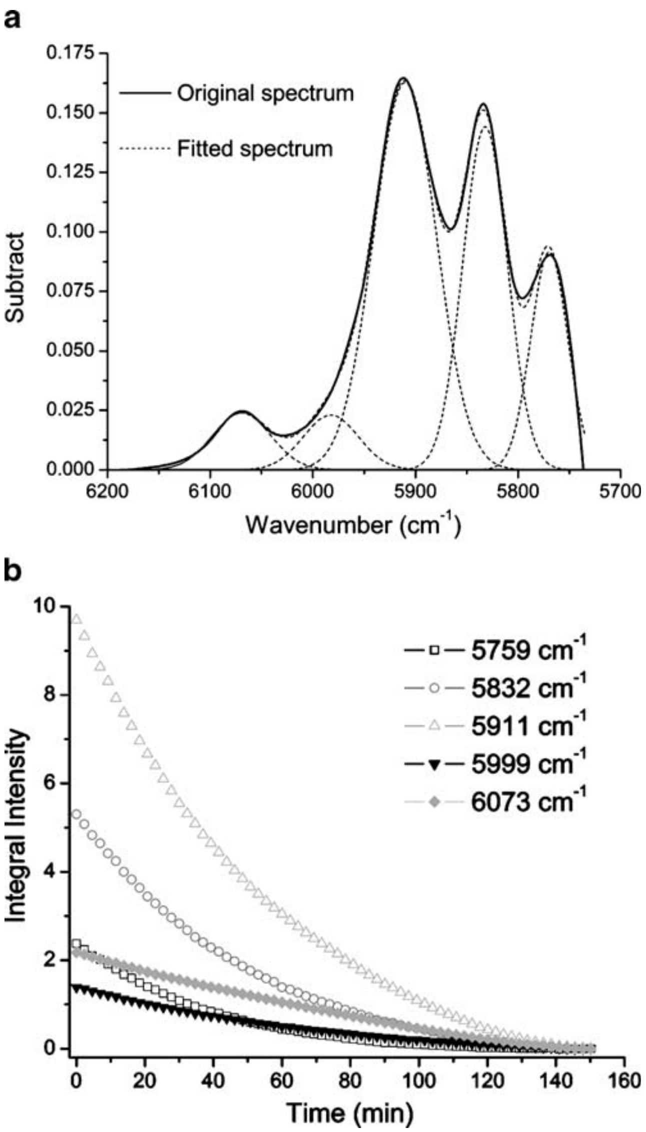


Fig. 5 **a** Peak splitting pattern of the C–H vibration region; **b** the variation of the integral intensity with reaction time from subtracted spectra of P6

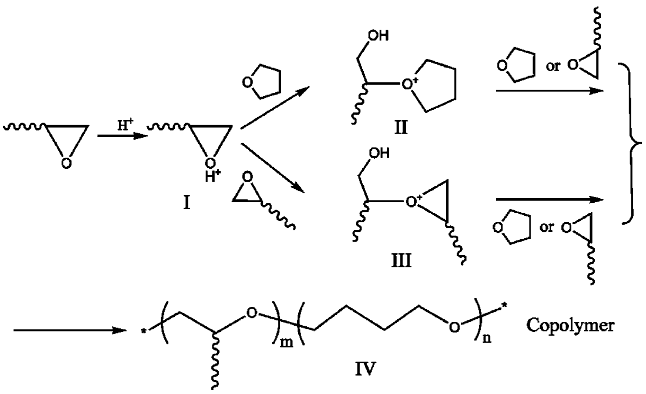
The splitting pattern was figured out by a self-developed MATLAB7.0 subroutine using least square method to give the optimal solution of initial parameters of peak position, peak height, and peak width at half height. As an example, the variation of the integral intensities of the five peaks with reaction time of P6 is presented in Fig. 5b, because all the compositions take on similar diagram. Here again, the linearity of the intensity with time holds true for both the epoxy peaks at 6,073 and 5,999 cm^{-1}, which offers a side evidence to the results obtained above and, on the other hand, convinces the validity of our peak-splitting pattern.

More important is that the consumption of THF can be observed here, which clearly showed that the THF molecules homopolymerized or copolymerized with epoxy resin. It can be seen that, as polymerization goes on, the reaction rate of THF decreases gradually because the increasing viscosity of the system reduces the mobility of THF. The results indicate that the reaction of THF is more affected by the increasing viscosity than of epoxy group and, thus, is a diffusion-controlled kinetic process, while the reaction of epoxy group is a reactivity-controlled thermodynamic process.

Back to our second conjecture, the two roles THF played in the system can be interpreted now. First, THF confined the runaway ring-opening reaction of epoxy group. If copolymerization took place, the epoxy group needed to compete for the propagating cationic centers with the large amount of THF molecules which is more mobile to reach the centers. Considering the similar oxygen nucleophilicities of THF and epoxy group, the reaction chance of epoxy group would be largely reduced. Second, THF provided soft enough segments to realize the linearity of epoxy group after gelation. If the ring-opening reaction of THF is diffusion-controlled and the reaction of epoxy group is reactivity-controlled, due to the higher concentration and mobility of THF molecules, the ring-opening reaction of THF would be more likely to lead the propagating chain to find epoxy groups where they are than the opposite way. Due to the high flexibility of PTHF segments in the network, we could anticipate the diffusion of THF molecules did not change much only with fewer paths. Thus, it might just be the diffusion of THF molecules to realize the linearity after gelation until it is wholly blocked by cross-linking. Indeed, in some cases when other epoxy resins (mono-functional or aliphatic) were applied, the ultimate linearity up to 100% could be observed.

Based on all the analyses above, the schematic copolymerizing process is depicted in Scheme 2.

According to the general accepted mechanism of cationic ring-opening polymerization of cyclic ethers [17], the copolymerizing behavior of this system depicted in



Scheme 2 The schematic copolymerizing process

Scheme 2 might be as follows: after the rapid protonation of epoxy group by reactive proton from PW_{12}, the primary active species (I) were attacked either by THF molecule or by epoxy group, the obtained propagating species (II and III) were attacked repetitively by both monomers, leading to a copolymerization. In the late stage after gelation, the THF molecules played a key role in leading the propagating chain to find the remaining epoxy group and driving the epoxy conversion to 100%. Due to the heat of polymerization of oxiranes (~114.3 kJ/mol) and tetrahydrofuran (~23.6 kJ/mol) [21], the copolymerization is a self-sustainable process.

This is only an initial step into revealing the mechanism of such copolymerization. Further study is being carried out to get a more detailed picture of the copolymerizing process.

Conclusions

NIR spectroscopy was used to monitor the cationic copolymerizing behavior of epoxy resin with THF initiated by phosphotungstic acid $H_3PW_{12}O_{40}$. The epoxy characteristic peaks at 4,530 and 6,073 cm^{-1} were used for quantitative analysis to study the kinetics. The overlapping C–H hump in 6,200–5,400 cm^{-1} was deconvoluted for qualitative analysis to get more support. The results indicate that the reaction rate of epoxy (4,530 and 6,073 cm^{-1}) was a constant up to a high conversion (~90%) under a given content of PW_{12} even when gelation occurred (at ~51%) and the reaction rate increased linearly with the content of PW_{12}. These behaviors suggest the living feature of the propagating species formed from PW_{12} in the system, which is ascribed to the unique properties of PW_{12} while the reaction rate of THF gradually decreased with reaction time, but the diffusion of THF molecules played a really key role in the late stage to realize the epoxy linearity after gelation and drive the epoxy conversion to 100%. So, the reaction of THF is a diffusion-controlled kinetic process, while the reaction of epoxy group is a reactivity-controlled thermodynamic process.

Acknowledgement The Authors gratefully acknowledge the financial support by National Natural Science Foundation of China (NSFC; No. 20704008 and No. 20674014) and the Specialized Research Fund for the Doctoral Program of Higher Education of China (SRFDP; No. 20070246001).

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