

## Real-time Monitoring of Living Cationic Ring-opening Polymerization of THF and Direct Prediction of Equilibrium Molecular Weight of PolyTHF\*

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**Abstract** A convenient real-time monitoring of monomer concentration during living cationic ring-opening polymerizations of tetrahydrofuran (THF) initiated with methyl triflate (MeOTf) has been developed for kinetic investigation and determination of equilibrium monomer concentration ( $[M]_e$ ) via *in situ* FTIR spectroscopy in combination with a diamond tipped attenuated total reflectance (ATR) immersion probe. The polymerization rate was first order with respect to monomer concentration and initiator concentration from the linear slope of  $\ln([M]_0 - [M]_e)/([M] - [M]_e)$  versus polymerization time at different temperatures in various solvents.  $[M]_e$  decreased linearly with initial monomer concentration while increased exponentially with increasing polymerization temperature. The equilibrium also strongly depends on solvent polarity and its interaction with monomer. The equilibrium polymerization time ( $t_e$ ) decreased with increasing solvent polarity and decreased linearly with increasing  $[M]_0$  in three solvents with different slopes to the same point of bulk polymerization in the absence of solvent. Equation of  $M_{n,e} = 72.1/(0.14 - 0.04[M]_e)$  has been established to provide a simple and effective approach for the prediction for the number-average molecular weight of polyTHFs at equilibrium state ( $M_{n,e}$ ) in the equilibrium living cationic ring-opening polymerization of THF at 0 °C.

**Keywords:** Cationic ring-opening polymerization; Living polymerization; Tetrahydrofuran; Equilibrium; Kinetics.

### INTRODUCTION

The living cationic ring-opening polymerization of tetrahydrofuran (THF) initiated by triflate esters offered a promising route to obtain end-group functionalized polytetrahydrofuran (polyTHF or PTHF) by simple end-capping reaction and polyTHF-containing block copolymers by sequential monomer addition<sup>[1–11]</sup>. The cationic polymerization of THF is well-known as a typical equilibrium polymerization among several cyclic ethers<sup>[12–15]</sup>. The polymerization proceeded by the attack of a monomer molecule on the endo cyclic carbon atom in the growing polytetrahydrofuranium ion with a rate constant for propagation ( $k_p$ ) but the reversible depropagation reaction proceeded with a rate constant ( $k_d$ ) due to the small strain in the five-member ring and this phenomenon existed in solution polymerizations for many cyclic ethers<sup>[13–15]</sup>. The equilibrium between propagation ( $k_p$ ) and depropagation ( $k_d$ ) of THF polymerization was expressed in Scheme 1<sup>[14, 15]</sup>.

The monomer did not completely converse to polymer due to the above equilibrium and the equilibrium concentration of monomer ( $[M]_e$ ) was defined as the concentration of monomer when equilibrium between propagation and depropagation reached. The equilibrium between propagation and depropagation was related to the polymerization conditions, such as solvent, polymerization temperature and initial monomer

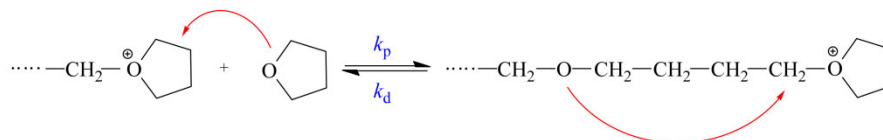
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concentration<sup>[16–21]</sup>. The reciprocal of  $[M]_e$  has been found to be equal to the ratio of the above two rate constants ( $k_p/k_d$ ), i.e.  $k_p/k_d = 1/[M]_e$ <sup>[15, 22]</sup>.



**Scheme 1** Equilibrium between propagation and depropagation in cationic ring-opening polymerization of THF

Kinetic study on the equilibrium cationic ring-opening polymerization of THF is very important for understanding the polymerization mechanism. The cationic ring-opening polymerization of THF in  $\text{CH}_3\text{NO}_2$  was the first order with respect to both THF and initiator by using 1,3-dioxolan-2-ylum cations with  $\text{AsF}_6^-$  and  $\text{SbF}_6^-$  anions or esters of  $\text{FSO}_3\text{H}$  or  $\text{CF}_3\text{SO}_3\text{H}$  as initiators<sup>[20–23]</sup>. An UV spectroscopic method was described for the determination of the concentration of propagating species ( $[p^*]$ ) and the rate constant of propagation ( $k_p$ ) was determined from the time- $[p^*]$  curve and the time-conversion data, in the ring-opening polymerization of THF catalyzed by binary systems consisting of a Lewis acid and epichlorohydrin<sup>[24, 25]</sup>.

*In situ* monitoring via attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR) is an efficient and convenient technique to obtain instantaneous monomer concentration, kinetic information and monomer reactivity ratio for free-radical, anionic or cationic polymerizations<sup>[26–47]</sup>. The kinetic study on the cationic polymerizations of isobutylene and styrene was conducted by using real-time ATR-FTIR monitoring<sup>[26–42]</sup>. An approach utilizing *in situ* FTIR data to determine the reactivity ratios of monomers in the cationic copolymerization of isobutylene and isoprene from a single experiment has also been developed by *in situ* ATR-FTIR spectroscopy<sup>[30]</sup>. However, there was no report on kinetic investigation or determination of equilibrium monomer concentration ( $[M]_e$ ) or observation of the shortest time ( $t_e$ ) for reaching at equilibrium in the cationic ring-opening polymerizations via *in situ* ATR-FTIR spectroscopy.

In this present work, a convenient real-time method of monitoring THF consumption during polymerization by *in situ* ATR-FTIR spectroscopy has been developed for investigating polymerization kinetics in the equilibrium living cationic ring-opening polymerization of THF initiated with methyl triflate (MeOTf) by immersing the probe directly in the reaction vessel for the first time. The livingness of cationic ring-opening polymerization of THF initiated with MeOTf was inspected under various initial initiator concentrations ( $[I]_0$ ) in different solvents. The effect of initial monomer concentration ( $[M]_0$ ), polymerization temperature ( $T_p$ ) and solvent polarity on equilibrium monomer concentration ( $[M]_e$ ), shortest time ( $t_e$ ) for getting equilibrium monomer conversion ( $c_e$ ), apparent rate constant of propagation ( $k_p^A$ ) and kinetic order was systematically investigated. Furthermore, a simple and effective approach was proposed for the prediction for the number-average molecular weight of polyTHFs at equilibrium state ( $M_{n,e}$ ) in the equilibrium living cationic ring-opening polymerization of THF at 0 °C.

## EXPERIMENTAL

### Materials

Dichloromethane ( $\text{CH}_2\text{Cl}_2$ , A.R. Beijing Yili Fine Chemicals), toluene (A.R. Beijing Yili Fine Chemicals), acetonitrile ( $\text{CH}_3\text{CN}$ , A.R. Beijing Yili Fine Chemicals) and *n*-hexane (*n*-Hex, A.R. Beijing Yili Fine Chemicals) were dried before use by distillation from calcium hydride. Tetrahydrofuran (THF, A.R. Beijing Chemical Company) was dried on sodium wire under reflux in the presence of traces of benzophenone until a blue color persisted and was directly used after distillation. Methyl triflate (MeOTf, Acros, 98%) was purified by distillation under dry nitrogen. Methanol (MeOH, A.R. Beijing Yili Fine Chemicals) was used as received.

### Procedures

All the manipulation, reactions and cationic ring-opening polymerizations were carried out under a dry nitrogen atmosphere. General procedures of reagents were as described in our previous work<sup>[38–42]</sup>. The monomer solution was introduced into a glass reactor and the attenuated total reflection (ATR) probe was immersed into the monomer solution. The initiator MeOTf was added through a syringe to start the polymerization at a definite temperature and the polymerization process was monitored by the ATR probe simultaneously. The FTIR spectra were recorded by a Nicolet 6700 spectrophotometer with a diamond tipped ATR immersion probe (Axiom DMD-270X-LT). Experimental set-up for the *in situ* monitoring of THF concentration during polymerization has been built as shown in our previous publications<sup>[38–42]</sup>. FTIR data collection and processing were performed with a Nicolet's OMNIC Series software. The FTIR spectrum of solvent was chosen as the background for spectrum record. Each spectrum was collected every 32 s by accumulating 32 scans with an instrument resolution of 4 cm<sup>-1</sup> over the spectral range of 600–1800 cm<sup>-1</sup>. For parallel gravimetric analysis of conversion and structural characterization, about 10 mL of polymer solution was taken out from the polymerization system at different specified time and then terminated by adding methanol. After evaporation of the volatiles, the polymer was rewashed with methanol and *n*-Hex for 3 times. The polymer products were dried in a vacuum oven at 45 °C to a constant weight overnight. The polymer yield was determined gravimetrically.

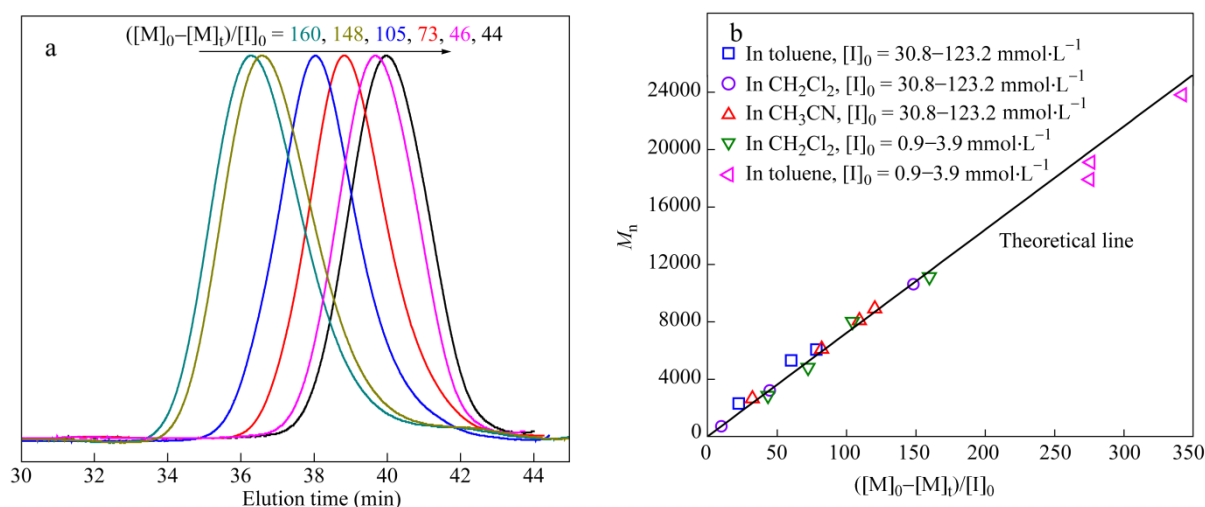
### Characterization

The number average molecular weight ( $M_n$ ), weight average molecular weight ( $M_w$ ) and molecular weight distribution (MWD,  $M_w/M_n$ ) of polytetrahydrofuran (polyTHF or PTHF) were measured by gel permeation chromatography (GPC) using a Waters 1515 isocratic HPLC pump connected to four Waters Styragel HT3, HT4, HT5 and HT6 columns and a Waters 2414 Refractive Index Detector at 30 °C. THF served as solvent of polyTHF with the concentration of 20 mg of polyTHF/10 mL of THF and the mobile phase at a flow rate of 1.0 mL·min<sup>-1</sup>. The columns were calibrated against twenty-five standard polystyrene samples with peak molecular weights from 162 to 8500000 g·mol<sup>-1</sup>. The calibration of molecular weight was based on polystyrene standards ( $K = 0.000128$  and  $\alpha = 0.712$ ).

## RESULTS AND DISCUSSION

### *Livingness of Cationic Ring-opening Polymerization of THF Initiated by MeOTf in Different Solvents*

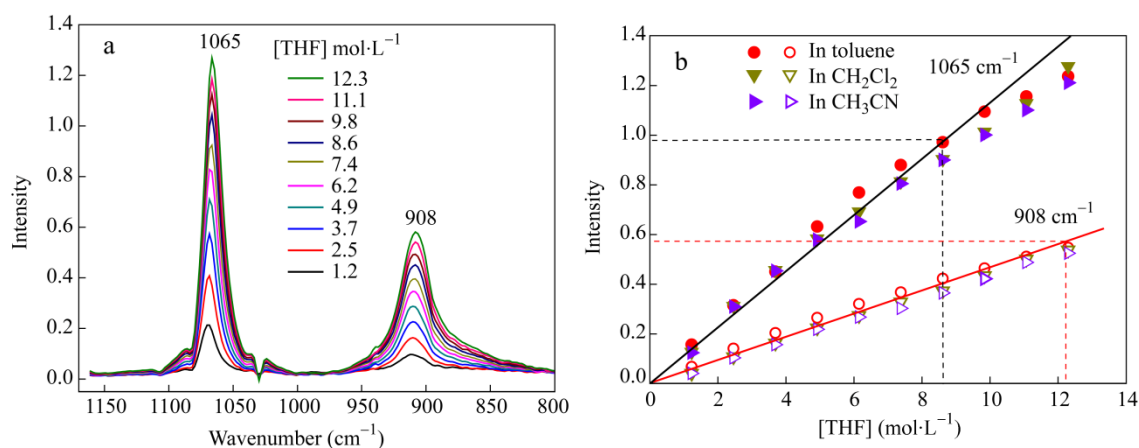
The cationic ring-opening polymerizations of tetrahydrofuran (THF) initiated with methyl triflate (MeOTf) were carried out at 0 °C at  $[THF]_0 = 6.16 \text{ mol}\cdot\text{L}^{-1}$  in toluene, CH<sub>2</sub>Cl<sub>2</sub> and CH<sub>3</sub>CN respectively. The representative GPC traces of polyTHFs obtained at different molar ratios of  $([M]_0 - [M]_t)/[I]_0$  from 44 to 160 in CH<sub>2</sub>Cl<sub>2</sub> are shown in Fig. 1(a). It can be clearly observed from Fig. 1(a) that all the GPC traces of polyTHFs obtained at various  $([M]_0 - [M]_t)/[I]_0$  ratios exhibit unimodal narrow molecular weight distributions. The relationship between  $M_n$  of polyTHF and  $([M]_0 - [M]_t)/[I]_0$  is given in Fig. 1(b).  $M_n$  of the resulting polyTHF in three different solvents increased theoretically with increasing  $([M]_0 - [M]_t)/[I]_0$ . Based on the above observation in Fig. 1, the living cationic ring-opening polymerization of THF initiated by MeOTf could be achieved and the polymers with theoretical molecular weight and narrow molecular weight distribution could be obtained in large scale of  $[I]_0$  from 0.9 mmol·L<sup>-1</sup> to 123.2 mmol·L<sup>-1</sup> at 0 °C in toluene, CH<sub>2</sub>Cl<sub>2</sub> and CH<sub>3</sub>CN before the polymerization reached equilibrium. It can be also concluded from these experimental results that the initiator efficiency almost reached 100% in these polymerization systems, and the concentration of polymer chain ([P]) equals to  $[I]_0$  in every polymerization system, which is similar to the report on the high reactivity of MeOTf for initiating THF polymerization in a fast and quantitative way<sup>[48]</sup>.



**Fig. 1** (a) Representative GPC traces of PolyTHFs obtained at different  $([M]_0 - [M]_t)/[I]_0$  in  $\text{CH}_2\text{Cl}_2$ ; (b) Relationship between  $M_n$  and  $([M]_0 - [M]_t)/[I]_0$  in toluene,  $\text{CH}_2\text{Cl}_2$  and  $\text{CH}_3\text{CN}$  at various initial initiator concentrations. The theoretical line was plotted by setting  $M_n = 72.1([M]_0 - [M]_t)/[I]_0$ .  $[\text{THF}]_0 = 6.16 \text{ mol}\cdot\text{L}^{-1}$ ,  $T_p = 0^\circ\text{C}$ ,  $t < t_e$ . Toluene:  $t_p = 50 \text{ min}$  at  $[I]_0 = 0.9\text{--}3.9 \text{ mmol}\cdot\text{L}^{-1}$ ;  $t_p = 60 \text{ min}$  at  $[I]_0 = 30.8\text{--}123.2 \text{ mmol}\cdot\text{L}^{-1}$ .  $\text{CH}_2\text{Cl}_2$ :  $t_p = 5\text{--}15 \text{ min}$  ( $[I]_0 = 3.9 \text{ mmol}\cdot\text{L}^{-1}$ );  $t_p = 20 \text{ min}$  ( $[I]_0 = 30.8\text{--}123.2 \text{ mmol}\cdot\text{L}^{-1}$ ).  $\text{CH}_3\text{CN}$ :  $t_p = 10\text{--}30 \text{ min}$  ( $[I]_0 = 30.8\text{--}123.2 \text{ mmol}\cdot\text{L}^{-1}$ ).

#### Kinetic Study of Equilibrium Living Cationic Ring-opening Polymerization of THF at Various $[I]_0$ by In situ ATR-FTIR

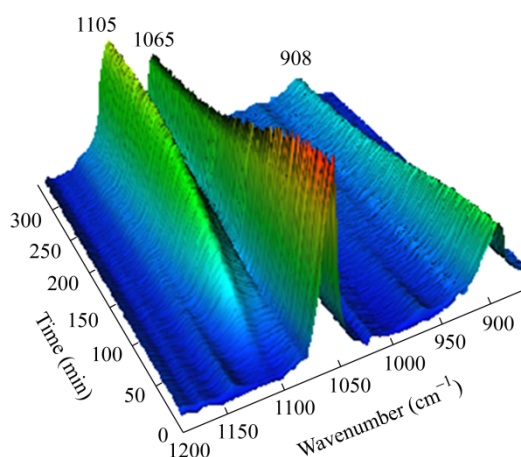
The real-time monitoring of monomer concentration during polymerization process by ATR-FTIR has been developed for kinetic study in the equilibrium living cationic ring-opening polymerization of THF and the calibration curve should be established in advance. The FTIR spectra of THF solution at various THF concentrations ranging from  $1.2 \text{ mol}\cdot\text{L}^{-1}$  to  $12.3 \text{ mol}\cdot\text{L}^{-1}$  in different solvents (toluene,  $\text{CH}_2\text{Cl}_2$  and  $\text{CH}_3\text{CN}$ ) were collected by ATR probe. The representative FTIR spectra of THF solution in toluene at different concentrations by an ATR probe are given in Fig. 2(a). The signal bands at  $1065 \text{ cm}^{-1}$  and  $908 \text{ cm}^{-1}$  are assigned to the asymmetric stretching vibration and symmetric stretching vibration of C—O bonds in THF molecules respectively. Both the signal intensity at  $1065 \text{ cm}^{-1}$  or at  $908 \text{ cm}^{-1}$  enhanced with increasing THF concentration.



**Fig. 2** (a) In situ FTIR spectra obtained at various concentrations of THF in toluene and (b) the plots of signal intensity with monomer concentration in toluene,  $\text{CH}_2\text{Cl}_2$  and  $\text{CH}_3\text{CN}$  (The spectra were constructed from 32 scans at  $0^\circ\text{C}$ .)

The relationship between signal intensity at  $1065\text{ cm}^{-1}$  or at  $908\text{ cm}^{-1}$  and THF concentration is shown in Fig. 2(b). It can be observed from Fig. 2(b) that the linear plots of the signal intensity versus THF concentration in different solvents could be obtained for characteristic absorbance at  $1065\text{ cm}^{-1}$  when THF concentration was below  $8.7\text{ mol}\cdot\text{L}^{-1}$  and for characteristic absorbance at  $908\text{ cm}^{-1}$  when THF concentration was below  $12.3\text{ mol}\cdot\text{L}^{-1}$  respectively. The determination range of THF concentration in solution was established according to the linear plots for selecting the characteristic bands at  $1065\text{ cm}^{-1}$  and  $908\text{ cm}^{-1}$  respectively. It can be induced from the linearity that the characteristic signal bands of THF could reflect its concentration in the corresponding THF range in the polymerization system.

*In situ* monitoring of the living cationic ring-opening polymerization of THF with MeOTf as an initiator *via* ATR-FTIR spectroscopy was performed at various initial initiator concentrations ( $[I]_0$ ) in toluene or  $\text{CH}_2\text{Cl}_2$  at  $0\text{ }^\circ\text{C}$  at initial monomer conversion ( $[M]_0$ ) of  $6.16\text{ mol}\cdot\text{L}^{-1}$  by taking FTIR spectrum of the corresponding solvent as background. The representative waterfall plots of FTIR spectra of THF and PTHF during the living cationic ring-opening polymerization of THF at  $[I]_0 = 2.9\text{ mmol}\cdot\text{L}^{-1}$  are given in Fig. 3. It can be seen from Fig. 3 that the intensity of the corresponding signals at  $1065\text{ cm}^{-1}$  and  $908\text{ cm}^{-1}$  of THF gradually decreased with prolonging polymerization time during the cationic ring-opening polymerization of THF initiated by MeOTf at  $0\text{ }^\circ\text{C}$ . Meanwhile, the signal at  $1105\text{ cm}^{-1}$  for the antisymmetric stretching vibration of C—O bond in polyTHF increased gradually with polymerization time, indicating that polymer gradually formed during polymerization.



**Fig. 3** Waterfall plots of FTIR spectra of THF and PTHF during living cationic ring-opening polymerization of THF in toluene  
FTIR spectrum of toluene was taken as the background.  $[\text{THF}]_0 = 6.16\text{ mol}\cdot\text{L}^{-1}$ ,  $[I]_0 = 2.9\text{ mmol}\cdot\text{L}^{-1}$ ,  $T_p = 0\text{ }^\circ\text{C}$ .

Both the signal bands at  $1065\text{ cm}^{-1}$  and  $908\text{ cm}^{-1}$  could be chosen for *in situ* monitoring THF conversion during the polymerization. It has been checked that THF conversion during polymerization determined on the basis of the signal intensity at  $908\text{ cm}^{-1}$  agreed very well with that by using the signal intensity at  $1065\text{ cm}^{-1}$ . Herein, the single band at  $908\text{ cm}^{-1}$  was selected for determination of THF concentration and its conversion during polymerization. The concentration of THF ( $[M]_t$ ) at a given time ( $t$ ), equilibrium monomer concentration ( $[M]_e$ ) and monomer conversion during polymerization could be determined according to the equations (1), (2) and (3) respectively.

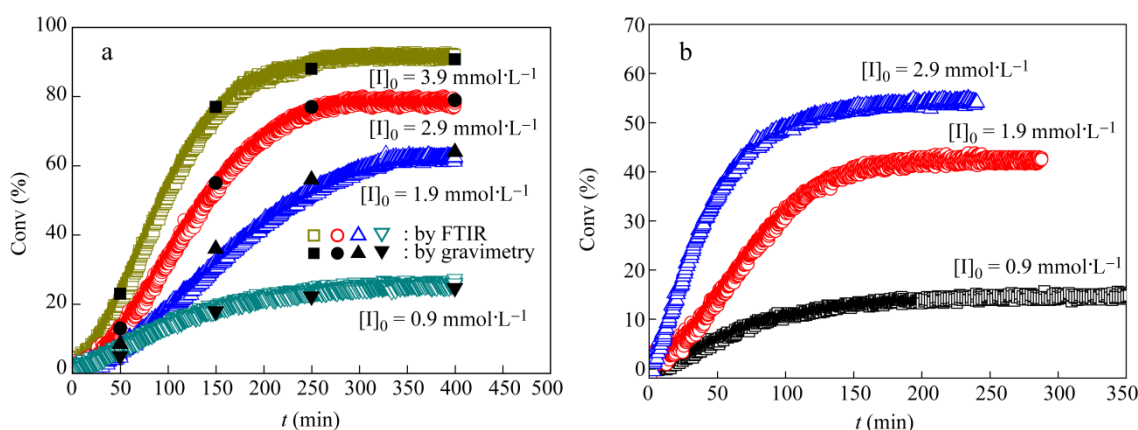
$$[M]_t = \frac{A_{908,t}}{A_{908,0}} \times [M]_0 \quad (1)$$

$$\text{Conv}\% = \frac{[M]_0 - [M]_t}{[M]_0} \times 100 \quad (2)$$

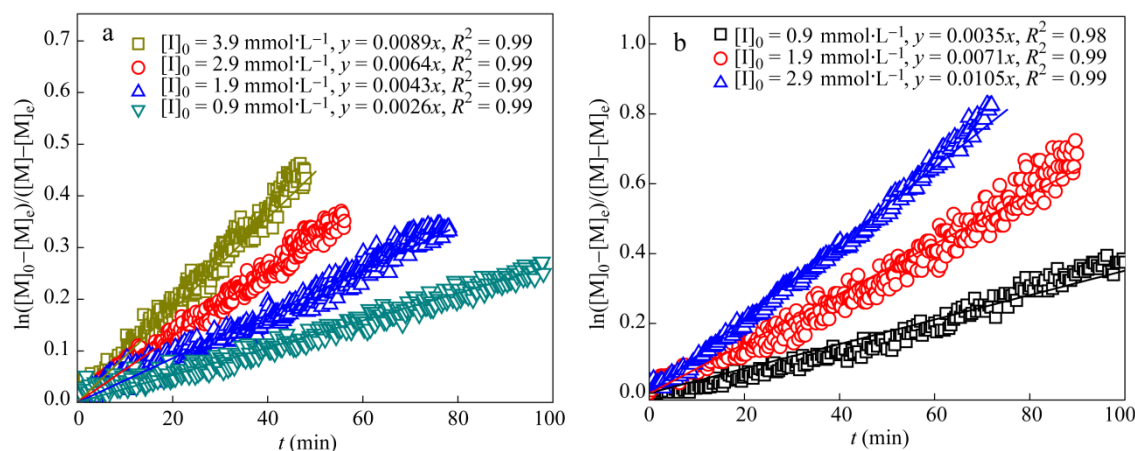
$$[M]_e = \frac{A_{908,e}}{A_{908,0}} \times [M]_0 \quad (3)$$

where, the subscripts 0, t and e denote the corresponding value obtained at the beginning, polymerization time t and at equilibrium state respectively;  $A_{908}$  is the intensity of bands at  $908 \text{ cm}^{-1}$ .

Figure 4 presents the conversion-time curves in living cationic ring-opening polymerization of THF in toluene (4a) and in  $\text{CH}_2\text{Cl}_2$  (4b) at various initial initiator concentrations ( $[I]_0$ ) from  $0.9 \text{ mmol}\cdot\text{L}^{-1}$  to  $3.9 \text{ mmol}\cdot\text{L}^{-1}$ . It can be seen from Fig. 4 that monomer conversion increased gradually with polymerization time at every set of  $[I]_0$  and then reached to an equilibrium state of  $[M]_e$  at a certain polymerization time, *i.e.*, equilibrium polymerization time ( $t_e$ ). It can be observed from Figure 4(a) the data obtained from real-time monitoring by ATR-FTIR matched with those by conventional gravimetry measurements. Moreover, the first-order kinetics was measured for living cationic ring-opening polymerization of THF in toluene and in  $\text{CH}_2\text{Cl}_2$  at  $0^\circ\text{C}$  at different  $[I]_0$  by plotting  $\ln([M]_0 - [M]_e)/([M] - [M]_e)$  versus polymerization time while keeping other conditions constant. As shown in Fig. 5, all the first-order plots of  $\ln([M]_0 - [M]_e)/([M] - [M]_e)$  with time were

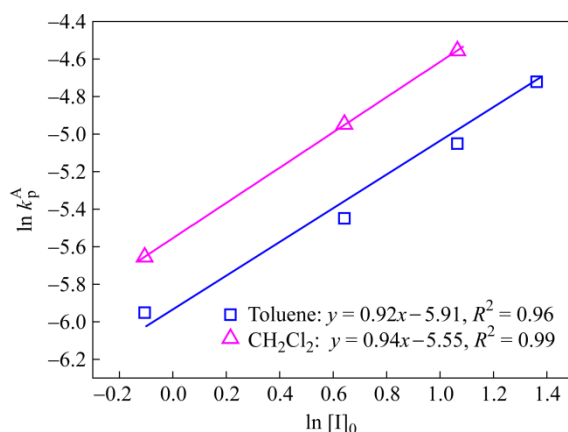


**Fig. 4** Conversion-time curves of THF polymerization with different  $[I]_0$  on the basis of FTIR spectra and gravimetry data in toluene (a) and in  $\text{CH}_2\text{Cl}_2$  (b) ( $[\text{THF}]_0 = 6.16 \text{ mol}\cdot\text{L}^{-1}$ ,  $T_p = 0^\circ\text{C}$ , initiator: MeOTf)



**Fig. 5** First-order plots for THF polymerization in toluene with different starting initiator concentrations ( $[I]_0$ ) in toluene (a) and  $\text{CH}_2\text{Cl}_2$  (b)

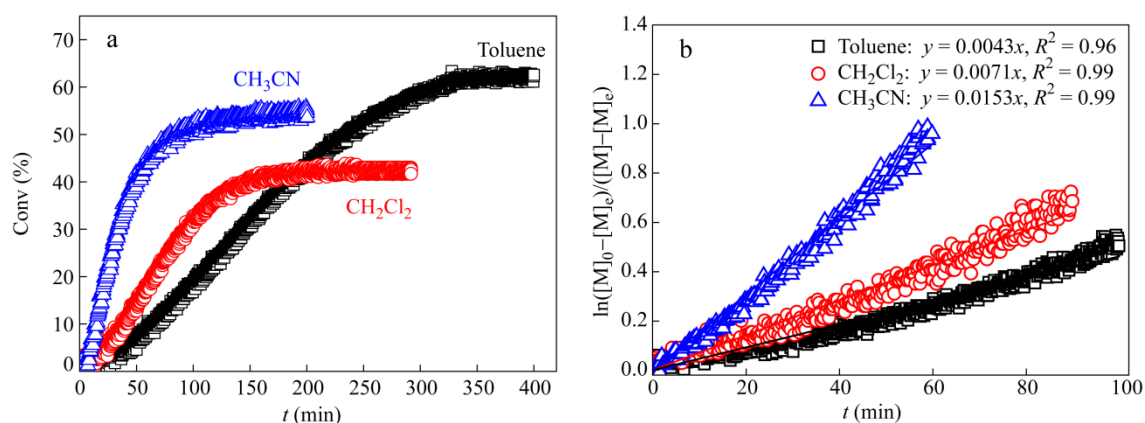
linear and passed through the origin at four  $[I]_0$  of 0.9, 1.9, 2.9 and 3.9  $\text{mmol}\cdot\text{L}^{-1}$  respectively. The apparent rate constant for propagation ( $k_p^A$ ) could be determined from the slopes of the linearity in Fig. 5.  $k_p^A$  increased with increasing initial initiator concentration and the kinetic reaction order of the polymerization with respect to  $[I]_0$  was further determined by plotting  $\ln(k_p^A)$  versus  $\ln([I]_0)$ . The linear relationship of  $\ln(k_p^A)$  versus  $\ln([I]_0)$  is given in Fig. 6, and the kinetic orders were determined to be 0.92 and 0.94 from the linear slope of  $\ln(k_p^A)$  versus  $\ln([I]_0)$  in toluene and in  $\text{CH}_2\text{Cl}_2$  respectively. It is clear that the polymerization rate was nearly in the first order for initiator concentration, which is in agreement with that in THF polymerization by using allyl triflate or methyl triflate as an initiator reported by Goethals *et al*<sup>[48]</sup>.



**Fig. 6** Relationship between  $\ln k_p^A$  and  $\ln[I]_0$  for equilibrium living cationic ring-opening polymerization of THF in toluene and in  $\text{CH}_2\text{Cl}_2$

#### ***Kinetic Study of Equilibrium Living Cationic Ring-opening Polymerization of THF at Various Initial Monomer Concentrations in Different Solvents***

Solvent polarity is a critical factor for the equilibrium living cationic ring-opening polymerization of THF and its kinetics. The effect of solvent polarity on  $[M]_e$  and  $t_e$  of THF polymerization using MeOTf as an initiator at 0 °C was further investigated in toluene,  $\text{CH}_2\text{Cl}_2$  and  $\text{CH}_3\text{CN}$  by setting  $[M]_0 = 6.16 \text{ mol}\cdot\text{L}^{-1}$  and holding all other components constant. The dielectric constant order of the above three solvents is that  $\text{CH}_3\text{CN}$  ( $\epsilon = 36$ ) >  $\text{CH}_2\text{Cl}_2$  ( $\epsilon = 8.9$ ) > toluene ( $\epsilon = 2.3$ ). The monomer conversion and semilogarithmic kinetic plots of  $\ln([M]_0 - [M]_e)/([M] - [M]_e)$  versus polymerization time in different solvents are shown in Fig. 7. It can be seen from Fig. 7(a)



**Fig. 7** The plots of conversion with polymerization time (a) and first-order plots for THF polymerization (b) in toluene,  $\text{CH}_2\text{Cl}_2$  and  $\text{CH}_3\text{CN}$  ( $[\text{THF}]_0 = 6.16 \text{ mol}\cdot\text{L}^{-1}$ ,  $T_p = 0 \text{ }^\circ\text{C}$ ,  $[I]_0 = 1.9 \text{ mmol}\cdot\text{L}^{-1}$ ).

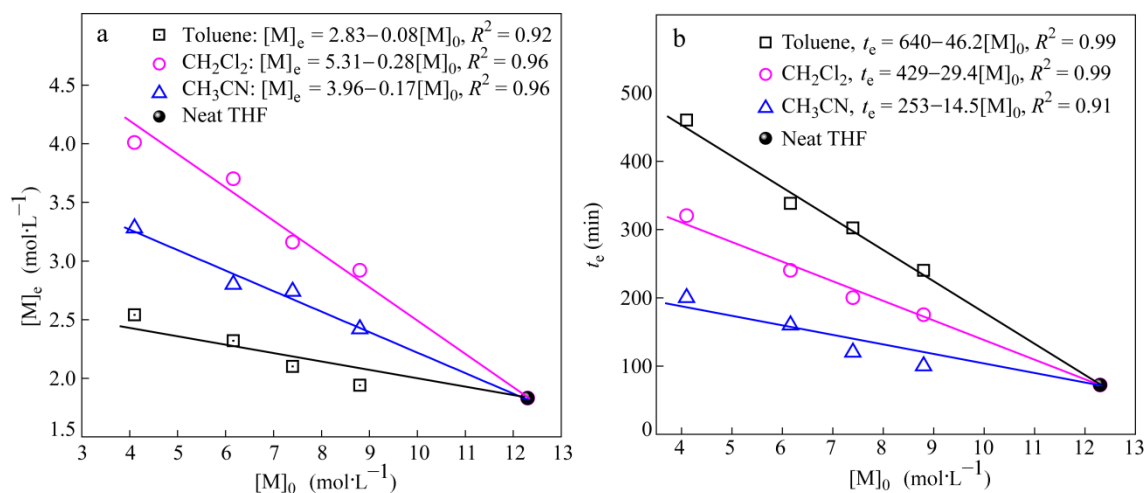
that the equilibrium monomer concentration ( $[M]_e$ ) depended on the sort of solvents and the equilibrium polymerization time ( $t_e$ ) for getting the equilibrium monomer conversion ( $c_e$ ) could be shortened by increasing solvent polarity, and  $c_e$  in the above three solvents could be expressed by  $c_{e,\text{toluene}} > c_{e,\text{CH}_3\text{CN}} > c_{e,\text{CH}_2\text{Cl}_2}$ . The highest monomer conversion of THF polymerization could be obtained in toluene while it is needed to take longer polymerization time. On the other hand, it can be also seen from Fig. 7(b) that all the three resulting first-order plots were linear and passed through the origin, indicating that the polymerization rate was the first order with respect to monomer concentration for the three polymerization systems. The apparent rate constants for propagation ( $k_p^A$ ) were determined to be  $0.0043 \text{ min}^{-1}$ ,  $0.0071 \text{ min}^{-1}$  and  $0.0153 \text{ min}^{-1}$  for the equilibrium living cationic ring-opening polymerizations of THF in toluene,  $\text{CH}_2\text{Cl}_2$  and  $\text{CH}_3\text{CN}$  respectively.

In order to investigate deeply the effect of solvent polarity on the equilibrium monomer concentration ( $[M]_e$ ) and equilibrium polymerization time ( $t_e$ ), the polymerizations of THF were conducted at  $0^\circ\text{C}$  by setting different initial monomer concentrations ( $[M]_0$ ) in various solvents of toluene,  $\text{CH}_2\text{Cl}_2$  and  $\text{CH}_3\text{CN}$  to the bulk polymerization system. The kinetic data for every set of experiment could be collected as shown in Fig. 8. Figure 8 illustrates the dependence of equilibrium monomer concentration ( $[M]_e$ ) and equilibrium polymerization time ( $t_e$ ) on initial monomer concentration ( $[M]_0$ ). It can be seen from Fig. 8(a) that  $[M]_e$  decreased linearly with increasing  $[M]_0$  in the above three solvents and  $[M]_e$  in bulk polymerization was  $1.83 \text{ mol}\cdot\text{L}^{-1}$ , which is similar to the reports that  $[M]_e$  decreased linearly with increasing  $[M]_0$  in various solvents<sup>[19–21]</sup>. On the basis of the three linear plots in Fig. 8(a), the relationship between  $[M]_e$  and  $[M]_0$  ( $4.10 \text{ mol}\cdot\text{L}^{-1}$ – $12.3 \text{ mol}\cdot\text{L}^{-1}$ ) could be expressed for the three polymerization systems as follows:

$$[M]_{e,\text{CH}_2\text{Cl}_2} = 5.31 - 0.28[M]_0$$

$$[M]_{e,\text{CH}_3\text{CN}} = 3.96 - 0.17[M]_0$$

$$[M]_{e,\text{toluene}} = 2.83 - 0.08[M]_0$$



**Fig. 8** Initial monomer concentration dependence of  $[M]_e$  (a) and  $t_e$  (b) at  $0^\circ\text{C}$  in toluene,  $\text{CH}_2\text{Cl}_2$  and  $\text{CH}_3\text{CN}$  respectively ( $[I]_0 = 1.9 \text{ mmol}\cdot\text{L}^{-1}$ )

As shown in Fig. 8(a), the equilibrium position depends strongly on the polarity of the reaction medium but to the same point of bulk polymerization in the absence of solvent.  $[M]_e$  in the above three solvents could be expressed by  $[M]_{e,\text{CH}_2\text{Cl}_2} > [M]_{e,\text{CH}_3\text{CN}} > [M]_{e,\text{toluene}}$  when  $[M]_0$  was in the range of  $4.10$ – $12.3 \text{ mol}\cdot\text{L}^{-1}$ .  $[M]_e$  in  $\text{CH}_2\text{Cl}_2$  was even higher than that in  $\text{CH}_3\text{CN}$ , which might be attributed to the stronger interaction, *e.g.* hydrogen bonding, of  $\text{CH}_2\text{Cl}_2$  with nucleophilic THF for a given  $[M]_0$ . The results are similar to the report that equilibrium



monomer concentration  $[M]_e$  of THF in  $\text{CH}_2\text{Cl}_2$  was higher than that in  $\text{CCl}_4$  at  $25\text{ }^\circ\text{C}$  at the same  $[\text{THF}]_0$ <sup>[7]</sup>. It can be also seen from Fig. 8(b) that the equilibrium polymerization time ( $t_e$ ) decreased with increasing solvent polarity and decreased linearly with increasing  $[M]_0$  in three solvents with different slopes to the same point of bulk polymerization in the absence of solvent. Therefore, according to the three linear plots in Fig. 8(b), equilibrium polymerization time ( $t_e$ ) for getting the equilibrium monomer conversion ( $C_e$ ) could be predicted quantitatively from  $[M]_0$  according to the equations as follows.

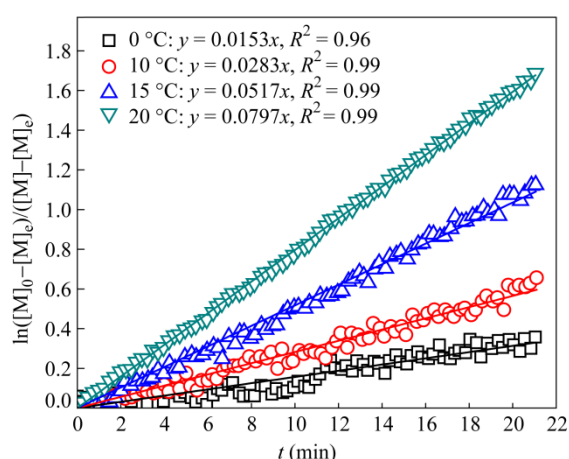
$$t_{e,\text{toluene}} = 640 - 64.2[M]_0$$

$$t_{e,\text{CH}_2\text{Cl}_2} = 429 - 29.4[M]_0$$

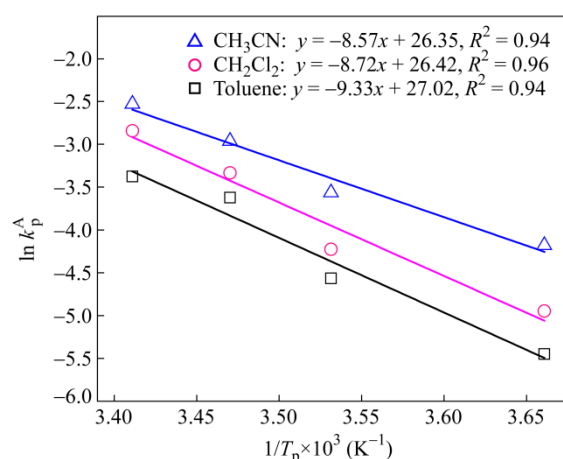
$$t_{e,\text{CH}_3\text{CN}} = 235 - 14.5[M]_0$$

### Kinetic Study of Equilibrium Living Cationic Ring-opening Polymerization of THF at Various Polymerization Temperatures in Different Solvents

Polymerization temperature ( $T_p$ ) and solvent polarity are also the important factors for the elementary reactions in the cationic ring-opening polymerization of THF, which is responsible for the reversible propagation, side reactions and termination. To examine the effect of polymerization temperature, the cationic ring-opening polymerizations of THF initiated by MeOTf were conducted at various temperatures ranging from  $0\text{ }^\circ\text{C}$  to  $20\text{ }^\circ\text{C}$  in toluene,  $\text{CH}_2\text{Cl}_2$  and  $\text{CH}_3\text{CN}$  respectively. The representative semilogarithmic kinetic plots of  $\ln([M]_0 - [M]_e)/([M] - [M]_e)$  versus time for THF polymerization in  $\text{CH}_3\text{CN}$  at various temperatures are shown in Fig. 9. It can be observed from Fig. 9 that all the plots passed linearly through the origin at different polymerization temperatures, indicating that the polymerization rate was the first order with respect to monomer concentration at different temperatures. The apparent rate constant of propagation ( $k_p^A$ ) for THF polymerization was obtained from the slope of linear plots for the every experimental set at different polymerization temperatures. It can be seen that  $k_p^A$  increased from  $1.53 \times 10^{-2}$  to  $7.97 \times 10^{-2}\text{ min}^{-1}$  with increasing temperature from  $0\text{ }^\circ\text{C}$  to  $20\text{ }^\circ\text{C}$ . The effect of  $T_p$  on  $k_p^A$  has been further quantitatively expressed by Arrhenius equation, *i.e.*  $\ln k_p^A = -E_a/RT_p$ , in which  $R = 8.314\text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ . The Arrhenius plot of  $\ln k_p^A$  versus the reciprocal of absolute temperature ( $1/T_p$ ) is linear, as shown in Fig. 10, the apparent activation energy for THF polymerization in toluene ( $E_{a,\text{Tol}}$ ),  $\text{CH}_2\text{Cl}_2$  ( $E_{a,\text{CH}_2\text{Cl}_2}$ ) and  $\text{CH}_3\text{CN}$  ( $E_{a,\text{CH}_3\text{CN}}$ ) could be determined to be  $77.6\text{ kJ}\cdot\text{mol}^{-1}$ ,  $72.5\text{ kJ}\cdot\text{mol}^{-1}$  and  $71.3\text{ kJ}\cdot\text{mol}^{-1}$  respectively. The effect of temperature on polymerization rate was similar in the three solvent systems.



**Fig. 9** First-order plots for THF at various polymerization temperatures in  $\text{CH}_3\text{CN}$  ( $[\text{THF}]_0 = 6.16\text{ mol}\cdot\text{L}^{-1}$ ,  $T_p = 0\text{ }^\circ\text{C}$ ,  $[\text{I}]_0 = 1.9\text{ mmol}\cdot\text{L}^{-1}$ )



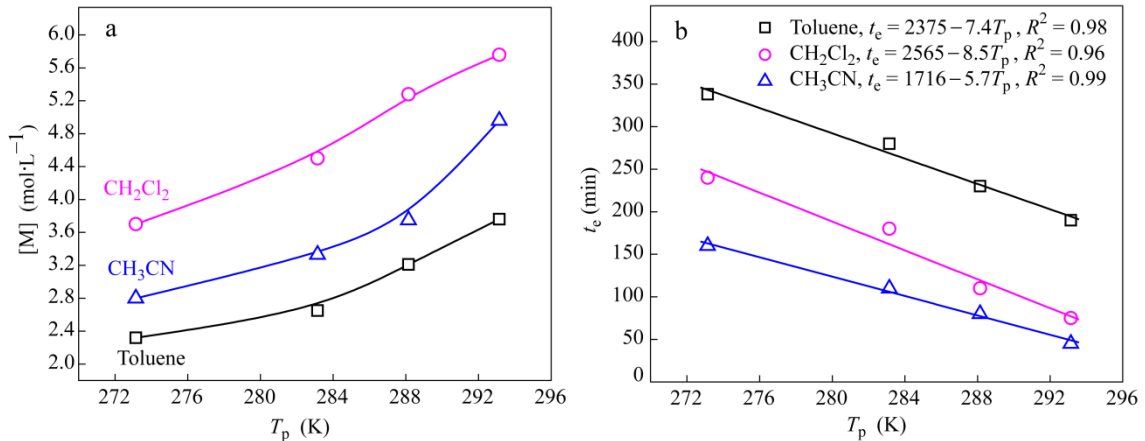
**Fig. 10** The relationship between  $\ln k_p^A$  and  $1/T_p$  for THF polymerization in toluene,  $\text{CH}_2\text{Cl}_2$  and  $\text{CH}_3\text{CN}$

On the other hand, the depropagation rate ( $k_d$ ) or termination could also be increased at an elevated temperature. Thus, polymerization temperature would influence  $k_p$ ,  $k_d$  and  $k_d/k_p$ . Figure 11 presents  $[M]_e$  or  $k_d/k_p$  and  $t_e$  for equilibrium living cationic ring-opening polymerization of THF at various polymerization temperatures in toluene,  $\text{CH}_2\text{Cl}_2$  and  $\text{CH}_3\text{CN}$ . As shown in Fig. 11(a), the equilibrium position strongly depends on the polarity of reaction medium and  $[M]_{e,\text{CH}_2\text{Cl}_2} > [M]_{e,\text{CH}_3\text{CN}} > [M]_{e,\text{toluene}}$  when polymerization temperatures were in the range from 0 °C to 20 °C. Moreover,  $[M]_e$  increased with increasing polymerization temperature in the three kinds of solvents, leading to lower equilibrium monomer conversion ( $c_e$ ) at higher polymerization temperatures. It suggests that the reversible depropagation reaction rate constant  $k_d$  increased with increasing polymerization temperature in the equilibrium cationic ring-opening polymerization of THF. It can be also seen from Fig. 11(b) that equilibrium polymerization time ( $t_e$ ) decreased with increasing solvent polarity and decreased linearly with increasing polymerization temperature. Therefore, the equilibrium polymerization time ( $t_e$ ) for getting the equilibrium monomer conversion ( $c_e$ ) could be predicted quantitatively from  $T_p$  according to the following equations shown in Fig. 11.

$$t_{e,\text{toluene}} = 2375 - 7.4T_p$$

$$t_{e,\text{CH}_2\text{Cl}_2} = 2565 - 8.5T_p$$

$$t_{e,\text{CH}_3\text{CN}} = 1716 - 5.7T_p$$

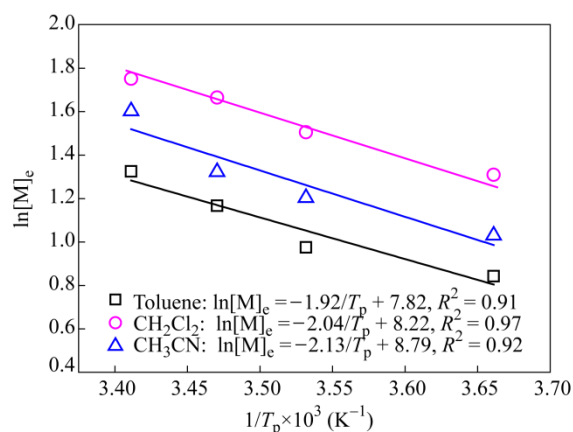


**Fig. 11** Variation of  $[M]_e$  (a) and  $t_e$  (b) with polymerization temperature ( $T_p$ ) for the polymerization of tetrahydrofuran in toluene,  $\text{CH}_2\text{Cl}_2$  and  $\text{CH}_3\text{CN}$  ( $[\text{THF}]_0 = 6.16 \text{ mol}\cdot\text{L}^{-1}$ ,  $[\text{I}]_0 = 1.9 \text{ mmol}\cdot\text{L}^{-1}$ )

According to Dainton-Ivin equation (4), the quantitative relationship between  $[M]_e$  and polymerization temperature ( $T_p$ ) was further investigated<sup>[49]</sup>.

$$\ln[M]_e = \frac{\Delta H_p}{RT_p} - \frac{\Delta S_p}{R} \quad (4)$$

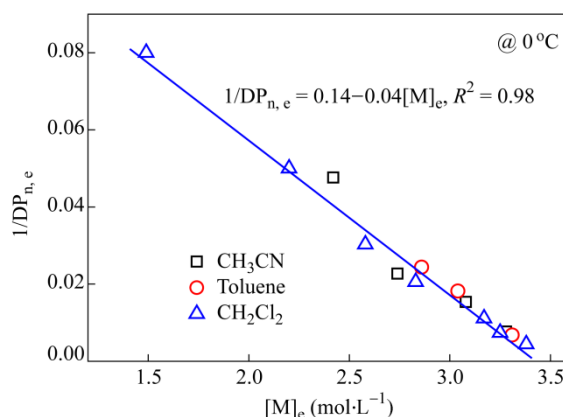
where,  $\Delta H_p$  and  $\Delta S_p$  are the enthalpy and entropy respectively,  $R = 8.314 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ ,  $T_p$  is the absolute temperature (K). The dependence of  $\ln[M]_e$  on  $1/T_p$  for the polymerizations of THF in toluene,  $\text{CH}_2\text{Cl}_2$  and  $\text{CH}_3\text{CN}$  is shown in Fig. 12. It can be observed that  $\ln[M]_e$  decreased linearly with  $1/T_p$  in the above three solvent systems and the equations are given in Fig. 12. According to the three linear plots in Fig. 12, the corresponding activation parameter  $\Delta H_p$  was determined to be  $-15.9$ ,  $-17.0$  and  $-17.7 \text{ kJ}\cdot\text{mol}^{-1}$ , and  $\Delta S_p$  was determined to be  $-65.0$ ,  $-68.4$  and  $-72.3 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$  for toluene,  $\text{CH}_2\text{Cl}_2$  and  $\text{CH}_3\text{CN}$  respectively. Both  $\Delta H_p$  and  $\Delta S_p$  decreased slightly with increasing solvent polarity. Thermodynamic properties of these three polymerization systems are some different, as indicated by differences in enthalpy and entropy. This difference was reflected in their equilibrium monomer concentrations ( $[M]_e$ ).



**Fig. 12** Relationship between  $\ln[M]_e$  and  $1/T_p$  for polymerization of THF in toluene,  $\text{CH}_2\text{Cl}_2$  and  $\text{CH}_3\text{CN}$  ( $[I]_0 = 1.9 \text{ mmol}\cdot\text{L}^{-1}$ ,  $[M]_0 = 6.16 \text{ mol}\cdot\text{L}^{-1}$ )

### Prediction of Number-average Molecular Weight of polyTHFs at Equilibrium State ( $M_{n,e}$ ) in Living Cationic Ring-opening Polymerization of THF at 0 °C

Dependence of equilibrium polymerization degree ( $\text{DP}_{n,e}$ ) or number-average molecular weight of polyTHFs at equilibrium state on equilibrium monomer concentration ( $[M]_e$ ) was further investigated by plotting  $1/\text{DP}_n$  versus  $[M]_e$  for the equilibrium living cationic ring-opening polymerization of THF at 0 °C in toluene,  $\text{CH}_2\text{Cl}_2$  and  $\text{CH}_3\text{CN}$ . As shown in Fig. 13,  $1/\text{DP}_n$  decreases linearly with increasing  $[M]_e$  and the relationship could be quantitatively expressed as  $1/\text{DP}_n = 0.14 - 0.04[M]_e$ , *i.e.*  $M_{n,e} = 72.1/(0.14 - 0.04[M]_e)$ , which provides a simple and effective approach for the prediction for number-average molecular weight of polyTHFs at equilibrium state ( $M_{n,e}$ , calibration on PS standards) in the equilibrium living cationic ring-opening polymerization of THF at 0 °C.



**Fig. 13** Linear plot of  $1/\text{DP}_{n,e}$  versus  $[M]_e$  for the equilibrium living cationic ring-opening polymerization of THF ( $12 < \text{DP}_{n,e} < 227$ ,  $M_{n,e}$  was determined by calibration on PS standards.)

## CONCLUSIONS

The equilibrium living cationic ring-opening polymerization of THF initiated with MeOTf has been achieved at various initial initiator concentrations from  $0.9 \text{ mmol}\cdot\text{L}^{-1}$  to  $123.2 \text{ mmol}\cdot\text{L}^{-1}$  at 0 °C in  $\text{CH}_2\text{Cl}_2$ , toluene and  $\text{CH}_3\text{CN}$ . An effective real-time monitoring of monomer consumption during THF polymerization *via* ATR-FTIR spectroscopy has been successfully developed for kinetic investigation and determination of equilibrium monomer concentration ( $[M]_e$ ), equilibrium polymerization time ( $t_e$ ), equilibrium monomer conversion ( $c_e$ ). The polymerization rate was the first order with respect to monomer concentration and to initiator concentration at

different temperatures in various solvents. The apparent activation energy for THF polymerization in toluene,  $\text{CH}_2\text{Cl}_2$  and  $\text{CH}_3\text{CN}$  could be determined from Arrhenius plots of  $\ln k_p^A$  versus  $1/T_p$  to be 77.6, 72.5 and 71.3  $\text{kJ}\cdot\text{mol}^{-1}$  respectively.  $[\text{M}]_e$  decreased while  $c_e$  increased with increasing initial initiator concentrations ( $[\text{I}]_0$ ) or initial monomer concentration ( $[\text{M}]_0$ ). Different quantitative linear relationships of  $[\text{M}]_e$ ,  $c_e$  or  $t_e$  with  $[\text{I}]_0$  or  $[\text{M}]_0$  have been established for these equilibrium living cationic ring-opening polymerizations of THF. On the other hand,  $[\text{M}]_e$  increased while  $c_e$  decreased with increasing polymerization temperature from 0 °C to 20 °C due to the increase in depropagation at elevated temperatures. The thermodynamic properties of enthalpy ( $\Delta H_p \sim -17 \text{ kJ}\cdot\text{mol}^{-1}$ ) and entropy ( $\Delta S_p \sim -70 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ ) for the equilibrium living cationic ring-opening polymerizations of THF reflect that  $\ln[\text{M}]_e$  decreases linearly with  $1/T_p$ . On the basis of the quantitative relationships, the equilibrium living cationic ring-opening polymerizations of THF could be predicted and controlled by mediating the polymerization conditions, such as  $[\text{M}]_0$ , solvent polarity and temperature. Furthermore, number-average molecular weight of polyTHFs at equilibrium state ( $M_{n,e}$ ) in the equilibrium living cationic ring-opening polymerization of THF at 0 °C could also be predicted according to  $M_{n,e} = 72.1/(0.14 - 0.04[\text{M}]_e)$ .

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