

Synthesis of styrene and tetrahydrofuran block copolymers by *in situ* transformation*

LIU Yanfei (刘燕飞), WAN Xiaolong (万小龙) and YING Shengkang (应圣康)**

(Laboratory of Living Polymerization, East China University of Science and Technology, Shanghai 200237, China)

Received March 1, 1999; revised June 14, 1999

Abstract In order to transfer the halogen terminus of polymers for block copolymer synthesis, the *in situ* transformation of living free radical polymerization of styrene into living cationic ring-opening polymerization of tetrahydrofuran was successfully performed. Three different initiator/catalyst systems of styrene were employed, i. e. (a) PhCH₂Cl/Bpy/CuCl, (b) 1-PEBr/Bpy/CuCl and (c) CCl₄/BDE/CuCl system. With these monofunctional initiator or difunctional initiator, both AB and ABA type block copolymers of styrene and tetrahydrofuran were obtained using a silver salt with strong acid (AgClO₄) as the transformation agent in the transformation of polymerization type. Characterization of these copolymers by nuclear magnetic resonance hydrogen spectra (¹H-NMR), gel permeation chromatography (GPC) and differential scanning calorimetry (DSC) indicated this method is simple and feasible.

Keywords: living free radical polymerization, ring-opening polymerization, synthesis, poly (styrene-*b*-tetrahydrofuran), block copolymer.

Since Szwarc's concept of living polymerization was accepted for its significant scientific and commercial interest^[1,2], the preparation of novel structural macromolecules with unique properties has become one of the hottest fields in polymer science. Various approaches have been developed to synthesize the block copolymers including (i) sequential addition of monomer, (ii) ion coupling reaction and (iii) transformation between two different types of polymerization.

Although sequential adding of monomer can be used for synthesis of block copolymers, it is limited by a single propagating mechanism so the type of monomer to be copolymerized is restricted. Ion coupling method is based on the coupling reactions^[3-5], but it is limited by restricted reaction conditions, the unavoidable inactivation of the living prepolymer species by impurities and the difficulty in ion coupling between the high molecular weight prepolymers. Compared to these two methods, the transformation of polymerization method involves the interconversion of the three main propagating mechanisms, i. e. anionic, cationic and free radical polymerization, which has been studied extensively in block copolymer synthesis^[6-15]. This method starts with the polymerization of the first monomer, then the living chain propagation species is end-capped by a functional group, which is suitable for initiating the second monomer polymerizing in a different way. The key process in this method is the end group functionalization. In spite of all the reported transformation approaches were not *in situ* transformations that the needed complicated multi-step path is a great disadvantage,

* Project supported by the National Natural Science Foundation of China (Granted No. 29630410-2).

** Corresponding author.

this method is more useful for synthesis of copolymers, e. g. poly (styrene-*b*-tetrahydrofuran) (poly (S-*b*-THF)) block copolymer. There were many reports on the synthesis of poly (S-*b*-THF) by transforming living cationic polymerization of THF into living polymerization of styrene, or vice versa. Most of these studies were focused on the transformation from anionic polymerization of styrene into cationic polymerization of tetrahydrofuran (THF)^[9–13], or on the transformation from cationic polymerization of THF into anionic or free radical polymerization of styrene^[14–15].

Recently developed transitional metal catalyzed living free radical polymerization has attracted a lot of attention in free radical polymerization studies^[16–18]. Using alkyl halides as initiator, it is ascertained that the chain end of the obtained polymers is end-capped with halogen atom. Since the bond dissociation energies of C-X (X = Br, Cl) are low, the halogen terminus may be used as a useful initiating site in the synthesis of block copolymers. Based on this assumption, we studied the transformation of living free radical polymerization of styrene into living cationic ring-opening polymerization of THF and found that the *in situ* transformation of polymerization can be performed successfully.

1 Experimental

1.1 Materials

Styrene (CP) was distilled over CaH₂ twice in vacuum just before used. THF (AR) was dried with Na, then distilled under Ar. CCl₄ was distilled twice. Commercial products of Bis(2-dimethylaminoethyl) ether (BDE) and Benzyl chloride (PhCH₂Cl) (AR) were distilled in vacuum. 97% 1-Bromoethylene benzene (1-PEBr) (Acros) and 2,2'-Bipyridine (Bpy) (AR) were used without purification. CuCl and CuBr (CP) were purified according to ref. [19]. AgClO₄ was synthesized in our laboratory. All the solvents were dried and distilled under Ar.

1.2 Synthesis of block copolymer of styrene and THF by *in situ* transformation

CCl₄/BDE/CuCl or PhX/Bpy/CuX initiating living free radical polymerization of styrene was proceeded as the first step in a sealed three-neck flask at 130 °C. During the process, 1.0 mL sample was taken out from the flask every 30 min for gel permeation chromatography (GPC) detection, then the polymerization system was cooled and THF was added into it, the polymer was dissolved in THF. Then AgClO₄/THF solution prepared before was added directly into the flask under Ar. The solution of polystyrene turned off-white quickly, and the ash-like precipitate was observed. The flask was immersed into an ice-water bath at 10 °C for about 24 h, and 1.0 mL sample was taken out from the system every 6 h for GPC detection. The resulted mixture was filtrated. The filtrate was poured into water, a yellowish oil phase floated above water, which was separated by a funnel, then dried in vacuum at 50 °C, an opalescent solid was obtained.

In the transformation, for CCl₄/BDE/CuCl/St system, [CCl₄]:[BDE]:[CuCl]:[AgClO₄] = 1:2:1:8; for PhX/Bpy/CuX/St system, [PhX]:[Bpy]:[CuX]:[AgClO₄] = 1:3:1:4.

1.3 Characterization

Molecular weight (Mn) and molecular weight distribution (Mw/Mn) of polymers were deter-

mined by a Waters 150 GPC/ALC instrument equipped with Waters HT2 and HT4 polystyrene gel columns at 25 °C. Calibration was based on monodispersed molecular weight polystyrene standards. Nuclear magnetic resonance hydrogen spectra ($^1\text{H-NMR}$) were recorded on Bruker DRX 500 MHz spectrometers at 25 °C, with TMS as the internal standard and CDCl_3 as the solvent. The melting point ($T_m/^\circ\text{C}$) and the glass temperature ($T_g/^\circ\text{C}$) of copolymers were determined by Dupond instrument DSC 2910 differential scanning calorimetry (DSC) with rising temperature of 20 °C per min from -100 °C to 200 °C.

2 Results and discussion

Three initiator/catalyst (I/C) systems were employed in the *in situ* transformation of living free radical polymerization of styrene into living cationic polymerization of THF, i. e. (a) $\text{PhCH}_2\text{Cl}/\text{CuCl}/\text{Bpy}$, (b) $1\text{-PEBr}/\text{CuBr}/\text{Bpy}$ and (c) $\text{CCl}_4/\text{CuCl}/\text{BDE}$ system.

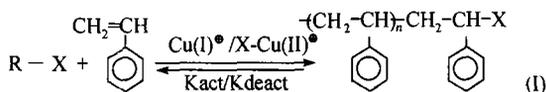
It is known that the C-Cl bond dissociation energies ($E_{\text{b.d.e.}}$) in CCl_4 ^[20] are: $\text{CCl}_3\text{-Cl}$, 298 $\text{kJ}\cdot\text{mol}^{-1}$; $\text{Cl}_2\text{-Cl}$, 281 $\text{kJ}\cdot\text{mol}^{-1}$, CCl-Cl , 386 $\text{kJ}\cdot\text{mol}^{-1}$; C-Cl , 331 $\text{kJ}\cdot\text{mol}^{-1}$, so CCl_2 -group can be easily formed in proper conditions. In our previous study, characterizations of GPC and $^1\text{H-NMR}$ demonstrated that CCl_4 is a two functional initiator in the living radical polymerization of methyl methacrylate, i. e. the degree of polymerization (DP_n) of the obtained polymer detected by GPC is double of that detected by $^1\text{H-NMR}$ ¹. And also CCl_4 was used as a chain transfer agent in the telomerization of vinyl acrylate, the formed poly (vinyl acetate) was terminated by - CCl_3 group, which could initiate styrene to living radical polymerization². These experimental results were in accord with the $E_{\text{b.d.e.}}$ values presented in ref. [20], which confirm that CCl_4 is a difunctional initiator in living free radical polymerization. So a propagating species with two halogen terminals: $\text{Cl-P-C(Cl)}_2\text{-P-Cl}$ could be formed with CCl_4 used as the initiator in polymerization of styrene. So it is possible to synthesize AB or ABA type styrene-tetrahydrofuran block copolymers through the monofunctional initiator system (a) and (b) or difunctional initiator system (c), respectively.

In this study, while adding $\text{AgClO}_4/\text{THF}$ solution directly into the styrene polymerizing system, the irreversibly precipitating reaction between AgClO_4 and Cu(II)X or Cu(I)X ran perfectly well. At the same time, the precipitating reaction between AgClO_4 and organic halide also occurred with a little lower reaction rate at room temperature. So the first living free radical polymerization of styrene was ended at low temperature by the two precipitating reactions, forming a new cationic species with ClO_4^- as the counterion. The nucleophilicity of ClO_4^- and the stability of newly formed oxonium living species made the cationic ring-opening polymerization of THF possible^[21], so the first living polymerizing stage transformed into cationic ring-opening polymerization of THF (Scheme 1). Since CCl_4 is a difunctional initiator, the new cationic species is a difunctional propagating species, so THF monomer could polymerize from both living sides, then forming ABA type Poly (THF-b-S-b-THF) block copolymer.

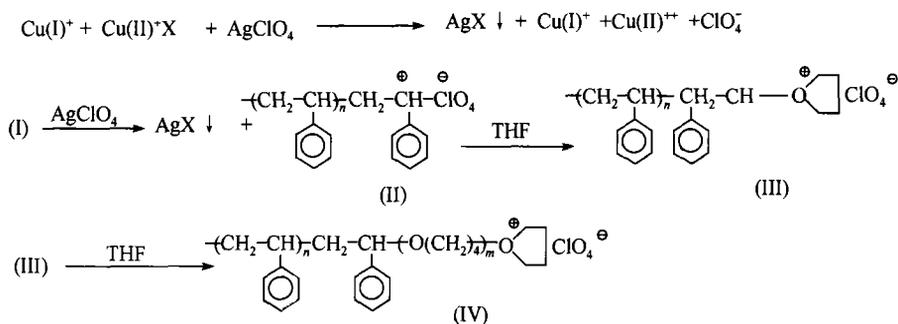
1) Cheng, G.L., Study on the atom transfer radical polymerization(ATRP) induced by a novel catalyst-initiator system, Ph. D Thesis, East China University of Science and Technology, 1998.

2) Zhang Y.M., Study on the Atom Transfer Radical Polymerization (ATRP) of vinyl monomers initiated by the macroinitiators with chlorine functional groups, Ph. D. Thesis, East China University of Science and Technology, Shanghai, P.R. China, 1998.

The first stage (living free radical polymerization):



The second stage (transfer to living cationic ring-opening polymerization):



Scheme 1

All the characterizations of the obtained copolymers are summarized in table 1. As it shows, the increasing rate of Mn in I/C system (c) is faster than that in system (a) or (b) at the first stage. This difference can also be observed in fig. 1. Because P1 and P2 were synthesized with monofunctional initiator systems, they are AB type Poly(S-b-THF) block copolymers. P3, P4 and P5 were produced by difunctional initiator system, they are ABA type Poly(THF-b-S-b-THF) block copolymers.

Table 1 Characterizations of AB or ABA type styrene-THF block copolymers obtained from the *in situ* transformation

Entry	Polymerization of styrene ^{b)}					Block copolymer				T _g /°C	T _m /°C
	I/C system ^{a)}	T/h	Conv% of St	Mn	Mw/Mn	Mn	Mw/Mn	x of chain			
								PS %	P(THF) %		
P1	a	2.5	67.9	3226	1.55	4084	1.46	72.3	27.7	24.24	38.93
P2	b	2.5	30.0	3865	1.52	6576	1.18	49.6	50.4	1.62	73.03
P3	c	0.5	65.1	7919	1.44	10021	1.34	73.1	26.9	80.09	
P4	c	1.0	30.7	5002	1.36	7160	1.29	62.1	37.9	77.42	
P5	c	2.0	42.5	13271	1.50	15221	1.44	82.5	17.5		

a) The I/C system is (a) PhCH₂Cl/CuCl/Bpy, (b) 1-PEBr/CuBr/Bpy and (c) CCl₄/CuCl/BDE. b) All these items are in accord with the values at the inflexion point in fig. 1.

The corresponding values at the inflexion points (I, II, III) on each Mn ~ t plot shown in fig. 1 were listed in table 1. As shown in the plot, the time adding AgClO₄/THF into the living free radical polymerization system is in accord with these inflexion points which divided the two polymerizing stages clearly. The change of the slop in each stage means the transformation indeed occurred.

GPC trace also shows a living peak in the course of whole polymerization although there exists a slight difference between the two stages (fig. 2). Take P2 as an example, in the first stage, a single

peak was observed, showing the living polymerization of styrene (curve 1). After adding $\text{AgClO}_4/\text{THF}$ into the system, along with the single peak representing the living copolymerization (curve 2 a), a shoulder peak appears at low molecular weight region (curve 2 b), this new peak vanishes after purification (curve 3). The observation of the shoulder peak should be ascribed to the homo-polymerization of THF. It might be the initiator RX was not consumed up during the first stage, then the remained alkyl halide reacted with AgClO_4 and formed R-ClO_4 , which could initiate THF to homopolymerization. Undoubtedly, the side reaction could be avoided if the alkyl halide was consumed up in the first stage.

The purified copolymers P1, P3 and P4 were analyzed by 500 MHz $^1\text{H-NMR}$ (fig. 3).

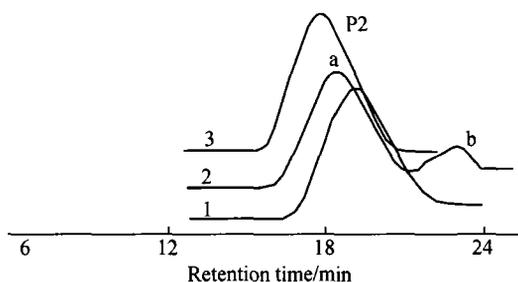


Fig. 2. GPC trace of P2 obtained from different polymerization stages. Curve 1 obtained from the first stage; curve 2 obtained from the second stage; curve 3 is the GPC trace of purified copolymer. 1, 2.5 h, $M_n = 3865$; $M_w/M_n = 1.52$; 2a, 10.0 h, 6104, 1.22; 2b, 10.0, 429, 1.31; 3, 22.0, 6576, 1.18.

Moreover, the copolymers were thermally analyzed by DSC (fig. 4). The results were in agreement with the other characterizations summarized in table 1. In poly (S-b-THF) block copolymer, the hard segment is \sim poly(styrene) segment, the soft segment is \sim poly(THF). It is well known that T_g of polystyrene is about 100°C , T_g of poly(THF) is lower than 0°C . Moreover, because poly(THF) is a crystalline polymer, T_m also can be observed in its DSC curve. In fig. 4, only one T_m and/or one T_g , which is between that of poly(THF) and polystyrene, is observed in each curve, it means \sim poly(styrene) and \sim poly(THF) segments in the obtained copolymer are compatible. Due to the high content of \sim poly(THF) in block copolymer, T_g of AB type block copolymers P1 and P2 are

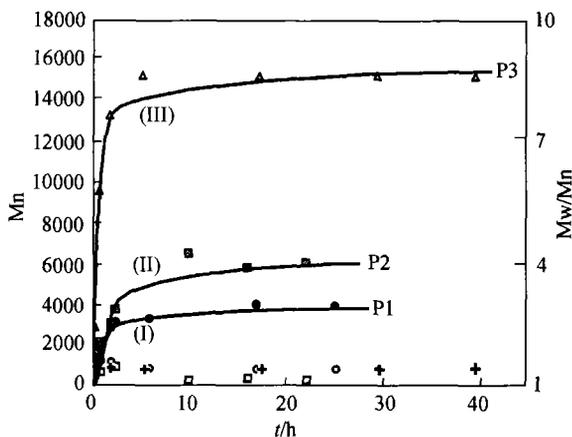


Fig. 1. M_n and M_w/M_n of polymers vs. polymerization time in the *in situ* transformation system. The point before the inflexion is the first living free radical polymerization stage at 130°C of styrene, after that is the living cationic ring-opening polymerization stage at 10°C of THF. \bullet , M_n of P1; \blacksquare , M_n of P2; \blacktriangle , M_n of P3; \circ , M_w/M_n of P1; \square , M_w/M_n of P2; $+$, M_w/M_n of P3.

The proton signals of \sim poly (styrene) segment and \sim poly (THF) segment are separated clearly. The signals at 6.2—7.5 (peaks a and b) and 1.2—2.5 (peaks c and d) are assigned to the aromatic ring, the methylene and methine in \sim poly (styrene) segment respectively. While peak c' (~ 3.4) and peak b' (~ 1.6) are assigned to the methylene proton in the \sim poly(THF) segment. Especially, due to the high resolution of 500 MHz $^1\text{H-NMR}$, the attached methylene fragment between \sim poly (styrene) and \sim poly (THF) segments is also observed clearly. The signal of the attached atoms is shown at about 3.7 or 4.5 (peak a') which neighboring peak c'.

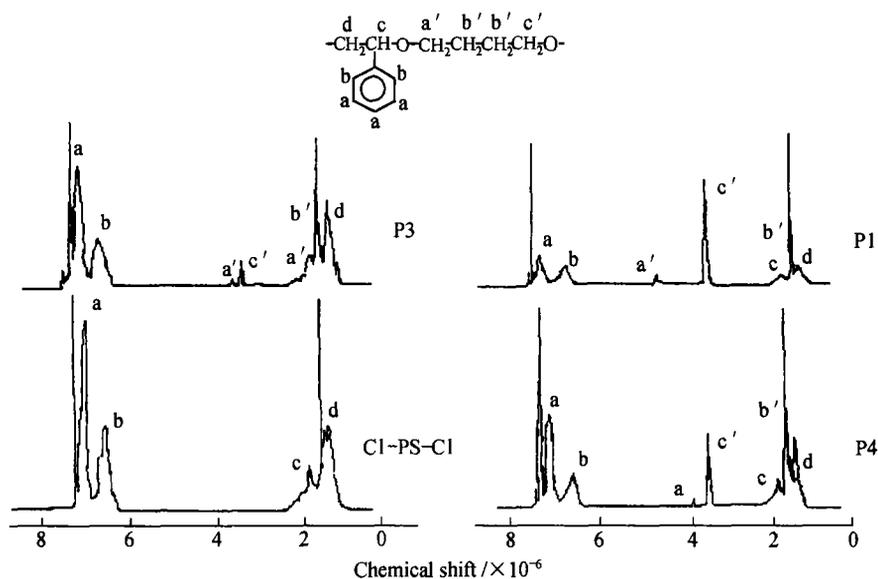


Fig. 3. $^1\text{H-NMR}$ spectra of AB and ABA type styrene-THF block copolymers. Cl-PS-Cl was obtained with L/C system (c). P1, P3 and P4 refer to table 1.

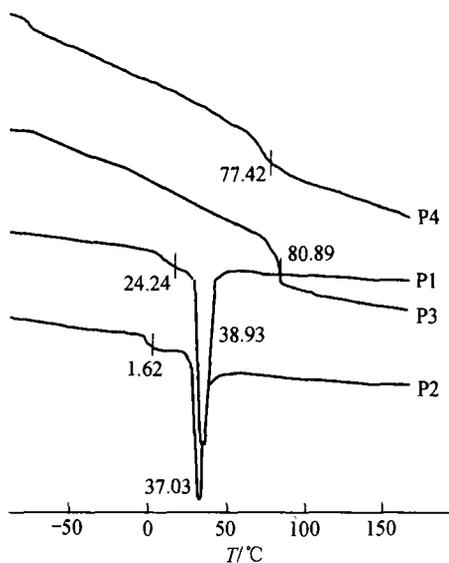


Fig. 4. DSC curves of AB and ABA type styrene-THF block copolymers. P1, $T_m = 38.93^\circ\text{C}$; $T_g = 24.24^\circ\text{C}$; P2, $T_m = 1.62^\circ\text{C}$, $T_g = 37.03^\circ\text{C}$; P3, $T_m = 80.09^\circ\text{C}$; P4, $T_m = 77.42^\circ\text{C}$.

near to that of poly(THF) (24.24°C for P1, 1.62°C for P2), and a sharp melting peak of this \sim poly(THF) crystalline segment is also shown clearly (38.93°C for P1, 37.03°C for P2). While in the ABA type block copolymers P3 and P4, the chain length of \sim polystyrene segment is longer, T_g of the copolymers are near to that of PS (80.09°C for P3 and 77.42°C for P4, respectively), and no T_m is observed.

In conclusion, all the characterizations confirm that the resulted polymers were all block copolymers. The result demonstrates that the *in situ* transformation provides an efficient and simplified way to synthesize AB or ABA type styrene-THF block copolymers using monofunctional initiator or difunctional initiator.

References

- 1 Szwarc, M., Levy, M., Milkovich, R., Polymerization initiated by electron transfer to monomer, *J. Am. Chem. Soc.*, 1956, 78: 2656.
- 2 Szwarc, M., *Carbanions Living Polymers and Transfer Processes*, New York: Wiley, 1968.
- 3 Berger, G., Levy, M., Vofsi, D., The preparation and chemistry of dicationically active polymers of tetrahydrofuran, *J. Polym. Sci.*, 1966, Part B(4): 183.
- 4 Smith, S., Hubin A. J., Mutual termination of anionic and cationic "living" polymers, *J. Macromol. Sci. Chem.*, 1973, A7(7): 1399.
- 5 Yamashita, Y., Hirotsu, M. A., Nakamura, Y. et al., Block copolymerization I. Ion coupling of polytetrahydrofuran dication and polystyrene dianion, *J. Polym. Sci.*, Part B, 1970, 8: 483.
- 6 Nomura, R., Narita, M., Endo, T., Polarity inversion of cationic growing centers into anionic ones by samarium iodide, synthesis of poly (tert-butyl-methacrylate-*b*-tetrahydrofuran-*b*-tert-butyl-methacrylate), *Macromolecular*, 1995, 28: 86.
- 7 Nomura, R., Narita, M., Endo, T., Novel transformation reaction of a cationic propagating end into an anionic one via electron transfer induced by samarium iodide, *Macromolecular*, 1994, 27: 7012.
- 8 Richard, D.H., Cohen, P., Abadie, M., Block copolymers synthesis via anionic to Ziegler-Natta transformation, *Polymer*, 1981, 22: 1316.
- 9 Burgess, F.J., Cunliffe, A.V., Richard, D.H. et al., Reaction to effect the transformation of anionic polymerization into cationic polymerization: I. Synthesis and reactivities of anionically generated bromine terminated polymers, *Polymer*, 1977, 18: 719.
- 10 Burgess, F.J., Cunliffe, A.V., Richard, D.H. et al., Reaction to effect the transformation of anionic polymerization into cationic polymerization: II. Synthesis and reactivities of anionically generated xylene bromine-terminated polymers, *Polymer*, 1977, 18: 726.
- 11 Richards, D.H., Thompson, D., Initiation of cationic polymerization using p-methyl benzyl bromide, *Polymer*, 1979, 20: 1399.
- 12 Haese, D.F., Eric, J.G., Synthesis and reactions of macromolecular polytetrahydrofuran azoinitiators, *Macromol. Chem., Rapid. Commun.*, 1986, 7: 165.
- 13 Cakmak, I., Aysa, A., Synthesis of tetrahydrofuran-styrene and tetrahydrofuranmethyl methacrylate block copolymers via poly (tetrahydrofuran) with azo groups, *Ang. Macromol. Chem.*, 1996, 238: 55.
- 14 Eastmond, G., Woo, C.J., Synthesis of block copolymers: IV. Poly (tetrahydrofuran) as a macroinitiator for free radical polymerization, *Polymer*, 1990, 31: 358.
- 15 Yoshida, E., Sugita, A., Synthesis of poly(tetrahydrofuran) with a nitroxyl radical at the china end and its application to living radical polymerization, *Macromolecular*, 1996, 29: 6422.
- 16 Wang, J.S., Matyjaszewski, K., Controlled/"living" radical polymerization, atom transfer radical polymerization in the presence of transition-metal complex, *J. Am. Chem. Soc.*, 1995, 117: 5614.
- 17 Wan, X.L., Ying, S.K., Controlled radical polymerization catalyzed by Cu/BDE complex in water medium I. Polymerization of styrene and synthesis of poly(St-*b*-MMA), *J. App. Polym. Sci.*, 1999, accepted
- 18 Colombani, D., China-growth control in free radical polymerization, *Prog. Polym. Sci.*, 1997, 22: 1649.
- 19 Keller, R.N., Wycoff, H.D., The synthesis and purified of copper halide, *Inorg. Synth.*, 1946, 2: 1.
- 20 Robin, W., Bond dissociation energy values in silicon-containing compounds and some of their implications, *Acc. Chem. Res.*, 1981, 14: 246.
- 21 Inoue, S., Okada, T., Cyclic Ethers, *Ring-Opening Polymerization V(I)* (ed. Ivin, K. J., Saegusa, T.), New York: Elsevier Applied Science Publishers, 1984.