Xiaoqian Zhang*, Wenli Guo, Yibo Wu*, Yuwei Shang, Shuxin Li and Weihao Xiong

Synthesis of random copolymer of isobutylene with *p*-methylstyrene by cationic polymerization in ionic liquids

<https://doi.org/10.1515/epoly-2018-0017>

Received January 25, 2018; accepted April 24, 2018; previously published online June 20, 2018

Abstract: Poly(isobutylene-*co-p*-methylstyrene) (IB/*p*-MeSt) random copolymer is a new generation of polyisobutylene-based elastomer. The cationic copolymerization of IB with *p*-MeSt was thoroughly examined by using various initiating systems in [Hmim][NTf₂] at −30°C. The effects of initiating systems and monomer feed ratio on the monomer conversion, molecular weight and copolymer composition are discussed. The polymers were characterized by ¹H-nuclear magnetic resonance (NMR), Fourier transform infrared (FTIR) spectroscopy and matrix-assisted laser desorption/ionization-time-of-flight-mass spectroscopy (MALDI-TOF-MS) to determine their chemical composition and molecular structure. The results show that high polarity, high viscosity and ionic environment of ionic liquids (ILs) influenced the copolymerization. The corresponding mechanism of cationic copolymerization in ILs is also proposed.

Keywords: cationic copolymerization; ionic liquids; isobutylene; mechanism; *p*-methylstyrene.

1 Introduction

Polyisobutylene (PIB) is widely applied in various industrial areas because of its attractive properties, namely,

extremely low permeability, excellent oxidative stability and chemical resistance (1–4). *p*-Methylstyrene (*p*-MeSt) is an inexpensive and attractive monomer that provides rigid polymers of pendant methyl repeating units with attractive thermal, mechanical, high glass-transition temperatures and low dielectric constants. Poly(isobutylene-*co-p*-methylstyrene) (IB/*p*-MeSt) random copolymer is a new generation of PIB-based elastomer that contains several percentages of “reactive” *p*-MeSt. IB/*p*-MeSt random copolymer also has many properties, which are superior to the traditional butyl rubber (5, 6). IB/*p*-MeSt random copolymer can only be synthesized by cationic polymerization. However, the traditional cationic polymerizations usually occur in chlorinated solvents, which are toxic, volatile and corrosive. In addition, in cationic polymerization, the disposal of the conventional Lewis acid catalysts (e.g. SnCl₄, TiCl₄, AlCl₃, AlCl₃OBU₂ and BF₃OEt₂) (7–11) remains an issue. Thus, cationic polymerization in environmentally friendly green solvents is an important development direction for the present PIB industry.

Ionic liquids (ILs), which are composed solely of anions and cations, are a class of chemicals that have recently emerged as alternatives to environmentally damaging volatile organic compounds. ILs are regarded as polar but non-coordinating solvents with high charge density because of their ionic nature (12, 13). Thus, ILs are not simple solvents for cationic polymerizations. As a new style of green solvent, ILs possess numerous peculiar properties, such as non-flammability, negligible vapor pressure, low melting point, high thermal stability and chemical inertia (14–18); they can be widely used in several synthesis fields (19–27).

However, to date, studies on the application of ILs in ionic polymerization, especially in cationic copolymerization, are limited. It has been reported that ILs could also be used as efficient catalysts of cationic polymerizations (28). In addition, several water- and air-stable ILs, such as *N*-butyl-*N*-methyl pyrrolidinium bis(trifluoromethanesulfonyl) amide ([C₄mpyr][NTf₂]) (29), trihexyltetradecylphosphonium bis(trifluoromethanesulfonyl)amide ([P_{6,6,6,14}][NTf₂]) (30), 1-butyl-3-methylimidazolium hexafluorophosphate ([Bmim][PF₆]) (31, 32), 1-octyl-3-methylimidazolium tetrafluoroborate ([Omim][BF₄]) (33), 1-octyl-3-methylimidazo-

***Corresponding authors: Xiaoqian Zhang**, College of Environmental Engineering, North China Institute of Science and Technology, Yanjiao, Beijing 101601, P.R. China; and College of Materials Science and Engineering, Beijing University of Chemical Technology, Beijing 100029, P.R. China, e-mail: zxqphd@163.com; and **Yibo Wu**, Beijing Key Lab of Special Elastomer Composite Materials, Beijing Institute of Petrochemical Technology, Beijing 102617, P.R. China; and College of Materials Science and Engineering, Beijing University of Chemical Technology, Beijing 100029, P.R. China, e-mail: wuyibo@bupt.edu.cn

Wenli Guo, Yuwei Shang, Shuxin Li and Weihao Xiong: Beijing Key Lab of Special Elastomer Composite Materials, Beijing Institute of Petrochemical Technology, Beijing 102617, P.R. China; and College of Materials Science and Engineering, Beijing University of Chemical Technology, Beijing 100029, P.R. China

lium bis(trifluoromethanesulfonyl)amide ([Omim][NTf₂]), 1-octyl-3-methylimidazolium bromide ([Omim][Br]), and 1-octyl-3-methylimidazolium hexafluorophosphate ([Omim][PF₆]) (34), have been successfully applied as cationic polymerization solvents. To date, cationic copolymerization in IL solvents has not been reported yet, and the mechanism is still vague.

In this study, first we report the application of IL as a solvent in the cationic copolymerization of IB with *p*-MeSt, initiated by various initiating systems. The effects of monomer feed ratios on monomer conversion, molecular weight and copolymer composition were investigated. In addition, the copolymerization mechanism of IB/*p*-MeSt in ILs is proposed based on the results. This study expands the application of ILs and enriches and develops the theory of cationic polymerization.

2 Experimental section

2.1 Materials

1-Butyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide ([Bmim][NTf₂]) and 1-hexyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide ([Hmim][NTf₂]) were purchased from Sigma Aldrich (USA), and the purities were more than 99.0%. The ILs were dried and degassed at 70°C for a few days. When the H₂O content of IL was reduced to less than 30 ppm, it can be used (35). *p*-Methylstyrene (*p*-MeSt, TCI Shanghai, China, purity >98%) was dried by introduction of CaH₂ before use. Isobutylene (IB, Beijing Yansan Petroleum Chemical Corp., Beijing, China, purity >99.9%) was cooled in the cold bath of a glovebox before use. Dichloromethane (CH₂Cl₂, Beijing Chemical Co., Beijing, China, 99.9%) and *n*-hexane (Hex, Beijing Chemical Co., Beijing, China, >98%) were distilled twice over CaH₂ under reduced pressure before use. Commercially available titanium tetrachloride (TiCl₄, Aldrich, USA, 99.9%), boron trifluoride etherate complex (BF₃OEt₂, Aldrich, USA, purity >98%) and anhydrous methanol (Beijing Chemical Co., Beijing, China, purity >99.9%) were used as received. Cumyl chloride (CumCl, J&K Scientific Ltd., Shanghai, China, purity >97.0%) was also used with further purification by double distillation from CaH₂ under reduced pressure. The 2-chloro-2,4,4-trimethylpentane (abbreviated as TMPCl) was synthesized according to the literature (36). The clean and quantitative formation of TMPCl adduct was confirmed by ¹H nuclear magnetic resonance (NMR) spectroscopy.

2.2 Polymerization copolymer of IB with *p*-MeSt

The procedures and cationic polymerizations were carried out under a dry nitrogen atmosphere ([H₂O] < 0.5 ppm; [O₂] < 10 ppm) in the MBraun 150-M glovebox. Fifty milliliter screw-cap vials with an IKA-MS3 vortex stirrer were used as polymerization reactors. A representative procedure is described as follows: Into a 50 ml screw-cap vial 4.85 ml of [Hmim][NTf₂], 1.94 ml of *p*-MeSt and 0.34 ml of CumCl stock solution in dichloromethane (0.4 mol/l) were added and mixed thoroughly, and then the mixture were cooled to -30°C. Then 1.29 ml of IB was added to the cold mixture. IB should be added into the system after the addition of *p*-MeSt resulting from its limited solubility in IL. The polymerization was started by the addition of 0.31 ml of BF₃OEt₂ at -30°C. The polymer precipitated over the course of the polymerization. After a predetermined time, the polymerization was terminated by the induction of excess prechilled methanol. ILs and initiator could be dissolved in methanol, and the mixture was handled under decompress filter with 0.25 μm ultra-filtration membrane. After that the products were washed several times with fresh methanol and then dried in a vacuum oven at 40°C to a constant weight in a few days. The IL was reused according to our previous report (37). Monomer conversions were determined by gravimetric analysis.

2.3 Measurements

The number-average molecular weight (*M_n*) and molecular weight distribution (MWD; i.e. *M_w*/*M_n*) of the polymers were detected by gel permeation chromatography (GPC, waters GPC, USA) using tetrahydrofuran (THF) as an eluent at a flow rate of 1.0 ml/min at room temperature. The GPC system was equipped with four Waters styragel columns connected in the following series: 500, 103, 104 and 105 at 30°C. The columns were calibrated against standard polystyrene samples.

NMR spectroscopy (Siemens, Germany) of the polymers was performed on a Bruker AV600 MHz spectrometer using CDCl₃ as a solvent at 25°C. ¹H-NMR spectra of solutions in CDCl₃ were calibrated to tetramethylsilane as an internal standard (δ^H = 0.00).

Matrix-assisted laser desorption ionization time-of-flight mass spectrometry (MALDI-TOF-MS) analyses were performed on a Ultraflex (AB Sciex, USA) TOF-MS, equipped with a 337 nm, 50 Hz N₂ laser, a reflector and a delayed extraction. The apparatus was operated at an

accelerating potential of 20 kV in the reflected mode. The matrix solution [DHB (2,5-dihydroxybenzoic acid), 10 μl of 20 g l^{-1} in THF] was mixed with 1 μl of polymer solution (10 g l^{-1} in THF). The spectra were recorded in the reflector mode in the absence of any cationizing agent. The final solution (1 μl) was deposited onto the target and dried in air at room temperature before irradiation. The mass spectra represent averages over 250 consecutive laser shots. External calibrations were performed with peptide calibration standard (Bruker Daltonic, Bremen, Germany).

The functional groups of poly(*p*-MeSt) and [Bmim][NTf₂] were investigated using a Fourier transform infrared spectrometer (FTIR, Nicolet-Nexus 670, China).

The glass transition temperature (T_g) was recorded by TA DSC Q2000 (differential scanning calorimetry, USA) and the instrument was calibrated using indium as a standard (sample size 6–10 mg, heating rate 10°C min^{-1} , nitrogen atmosphere).

3 Results and discussion

3.1 Copolymerization of IB with *p*-MeSt using various initiating systems

ILs are regarded as polar but non-coordinating solvents with high charge density; thus, they do not behave as simple solvents for ionic polymerizations. We comprehensively compared the cationic copolymerization in IL with those in organic solvents by employing a series of

initiating systems to understand the ionic environment and its effect on cationic polymerizations.

As shown in Table 1, the cationic copolymerization of IB with *p*-MeSt was conducted in [Hmim][NTf₂] at -30°C using various initiating systems. Cationic copolymerization in the traditional molecular solvent *n*-Hex/ CH_2Cl_2 was also compared, as shown in Table 1. Generally, initiator/Lewis acid combinations, called initiating systems, play an important role in cationic copolymerization (38). The selected initiators include (a) H_2O ; (b) TMPCl, selected as a model of PIB living end; and (c) CumCl, selected as a similar model of poly(*p*-MeSt) living end. Lewis acids, which include TiCl_4 and BF_3OEt_2 , are commonly used in cationic polymerizations. From Table 1, the oligomers were obtained in the copolymerization of an equimolar mixture of IB and *p*-MeSt in [Hmim][NTf₂]. In comparison with the products obtained from *n*-Hex/ CH_2Cl_2 solvent, those obtained from [Hmim][NTf₂] exhibited lower M_n and M_w/M_n , whereas the IB content in the product polymer changed. Notably, the product obtained from IL using BF_3OEt_2 Lewis acid resulted in a higher yield, regardless of the initiator used. Here, we selected the CumCl/ BF_3OEt_2 initiating system to study the cationic copolymerization of IB with *p*-MeSt further.

3.2 Effects of comonomer feed ratios

The effects of monomer ratios in the feed on the copolymer composition was studied. The IB monomer is almost insoluble in pure [Hmim][NTf₂], whereas it can be dissolved in the mixture of [Hmim][NTf₂] and *p*-MeSt. The feed ratio of $[\text{IB}]_0$ to $[\text{p-MeSt}]_0$ was changed from 0:100 (mol:mol) to 60:40

Table 1: Results for the cationic copolymerization of IB with *p*-MeSt using various initiating systems.^a

Run	Initiating system	Solvent	M_n (GPC)	M_w/M_n	Yield % ^b	IB content (%) ^c
1	TMPCl/ TiCl_4	[Hmim][NTf ₂]	1311	1.20	7.1	—
2	CumCl/ TiCl_4		1227	1.19	13.6	—
3	$\text{H}_2\text{O}/\text{TiCl}_4$		1935	1.98	7.9	—
4	TMPCl/ BF_3OEt_2	<i>V</i> (Hex)/ <i>V</i> (CH_2Cl_2) = 50:50	1146	1.21	82.6	36.3
5	CumCl/ BF_3OEt_2		1172	1.21	86.2	36.1
6	$\text{H}_2\text{O}/\text{BF}_3\text{OEt}_2$		1102	1.25	61.6	33.1
7	TMPCl/ TiCl_4		2588	2.41	93.8	—
8	CumCl/ TiCl_4		3112	2.25	95.0	—
9	$\text{H}_2\text{O}/\text{TiCl}_4$		2504	2.62	92.3	—
10	TMPCl/ BF_3OEt_2		5275	1.99	60.0	33.6
11	CumCl/ BF_3OEt_2		5128	2.14	67.7	32.0
12	$\text{H}_2\text{O}/\text{BF}_3\text{OEt}_2$		4435	2.16	68.3	36.1

^aConditions: $[\text{p-MeSt}]_0 = [\text{IB}]_0 = 1.768 \text{ mol l}^{-1}$; $[\text{TMPCl}]_0 = [\text{CumCl}]_0 = [\text{H}_2\text{O}]_0 = 6.162 \text{ mmol l}^{-1}$; $[\text{BF}_3\text{OEt}_2]_0 = [\text{TiCl}_4]_0 = 0.111 \text{ mol l}^{-1}$; M_n (theor) = 50,000 g mol^{-1} ; at -30°C for 60 min.

^bTotal monomer conversion.

^cIB content in product polymer; Determined by $^1\text{H-NMR}$; “—” stands for no test because of their low yield.

Table 2: Effect of the initial feed ratios.^a

Run	[IB] ₀ : <i>p</i> -MeSt] ₀	IB content (%) ^b	<i>M_n</i> (calcd.)	<i>M_n</i> (GPC)	<i>M_w</i> / <i>M_n</i>	Yield % ^c
1	0:100	0	12,580	5148	2.10	62.9
2	10:90	13.0	17,540	2085	1.57	87.7
3	20:80	20.6	18,170	1898	1.46	90.7
4	30:70	25.7	18,920	1416	1.39	94.6
5	40:60	31.3	17,940	1157	1.29	89.7
6	50:50	33.1	17,180	1057	1.25	85.9
7	60:40	38.7	8200	950	1.21	41.0

^aConditions: [CumCl]₀ = 15.405 mol l⁻¹; [BF₃OEt₂]₀ = 0.277 mol l⁻¹; *M_n* (theor) = 20,000 g mol⁻¹; at -30°C for 60 min.

^bIB content (mol %) in product polymer; determined by ¹H-NMR.

^cTotal monomer conversion.

Figure 1: GPC curves of copolymers and refractive index (I) and UV (256 nm) GPC traces of IB/*p*-MeSt copolymer are shown in Figure 1B. (A) GPC traces of the synthesized copolymers; (B) the UV/RI ratio, RI and UV traces of IB/*p*-MeSt copolymer obtained in [Hmim][NTf₂] (monomer feed ratio of: *p*-MeSt-IB = 1:1).

(mol:mol). When the feed ratio was larger than 60:40, IB was insoluble in the polymerization system. The effect of the comonomer composition on the copolymerization is shown in Table 2. From the table, the comonomer composition significantly influenced *M_n*, *M_w*/*M_n*, and the yield. Under identical reaction conditions, a high concentration of IB in the comonomers resulted in narrow *M_w*/*M_n* and low *M_n* due to the rapid cross-transfer relative to propagation. Moreover, yield had a maximum value as the concentration of IB increases under the same reaction time. In addition, the polymerizations that generated oligomers only indicated that chain transfer occurred in [Hmim][NTf₂].

The GPC curves of copolymers with different compositions are shown in Figure 1A. The curves were unimodal, which suggested the successful formation of the corresponding copolymer. In addition, a clear lateral shift of maxima toward a high molecular weight region was observed as IB:*p*-MeSt ratios decreased. Therefore, the *M_n* of the product evidently increased with the IB monomer

content increasing in the initial feed ratios (Figure 1). IB could easily participate in the polymerization when dissolved, although dissolving IB in the polymerization

Figure 2: DSC curves of the synthesized copolymers.

Figure 3: FTIR spectra of the synthesized copolymers IB/*p*-MeSt copolymer (A); PIB (B); poly(*p*-MeSt) (C).

system was difficult. This indicated that IB was more “active” in the chain transfer reaction.

The refractive index (RI) and UV (256 nm) GPC traces of IB/*p*-MeSt copolymer are shown in Figure 1B. The RI signal was proportional to the total mass of the polymer chain. The UV signal was only proportional to the number of aromatic monomer units incorporated into the chain because the UV absorption of the IB unit was negligible at 256 nm. The RI and UV traces of the IB/*p*-MeSt random copolymers obtained in [Hmim][NTf₂] were close to perfect overlapping. Thus, the IB units were introduced into the copolymer homogeneously, and the product was the random copolymer. The UV/RI ratio was proportional to the *p*-MeSt content of the given molecular weight fraction and was constant over the entire molecular weight range. The *T_g* of IB/*p*-MeSt copolymer was strongly dependent on its microstructure. Figure 2 shows the DSC curves for copolymers with different IB:*p*-MeSt ratios. All samples provided only one *T_g* value, which was only

Figure 4: Representative ¹H NMR spectrum of the synthesized IB/*p*-MeSt copolymer (A); PIB (B); poly(*p*-MeSt) (C).

between that of IB (-66.7°C) and *p*-MeSt (110°C). The T_g value decreased and moved to that of IB with the increase in IB:*p*-MeSt ratios. This result indicated that the copolymer without phase separation was a random copolymer.

3.3 Microstructure of the copolymer

The structure of the copolymer in a feed ratio of 50:50 was characterized by IR, ^1H -NMR, and MALDI-TOF-MS. Figure 3 shows the FTIR spectra of the obtained polymers. In Figure 3A, the band at 3018 cm^{-1} was attributed to the C-H in the phenyl ring, and the band at 812 cm^{-1} was the out-of-plane CH bending of two adjacent aromatic hydrogens of *p*-MeSt. However, the band at 1363 cm^{-1} could only be caused by the twisted vibration absorption peak of tertiary butyl of IB. Figure 4 shows the ^1H -NMR spectrum of the polymers with the signal assignment to the possible structures. Figure 4A shows the aromatic ring protons at δ 6.3–7.3 ppm and the methyl protons of IB at δ 1.0 ppm (37, 38). The IR and ^1H -NMR data suggested that the copolymer was successfully obtained. Figure 4A also shows three possible end groups of the copolymers, which include the methoxy terminal group ($-\text{OCH}_3$, 3.1 ppm) that resulted from the quenching of the polymerization with methanol (i) and indanyl rings (ii) and (iii) formed by the Friedel-Crafts reactions. The characteristic resonance at 4.0 ppm was assigned to the indanyl ring (ii), and that at 1.68 ppm was assigned to the indanyl ring (iii) (39, 40). Therefore, the main chain transfer reaction was a Friedel-Crafts reaction.

The copolymer was also analyzed via MALDI-TOF-MS. Figure 5A shows the spectra of the copolymer, revealing two series of periodic groups of peaks. Each series of groups was separated by 56 m/z , which corresponded to the addition of an isobutyl group; whereas each isotopic distribution in the cluster was separated by 6 m/z . This result could be accounted for by the mass difference between one *p*-MeSt unit (118 u) and two isobutyl units ($2 \times 56 = 112\text{ u}$) (41). Thus, when moving from left to right in an oligomer group, a gain of 6 m/z corresponded to one more *p*-MeSt monomer and two less isobutyl monomers. When moving from one grouping of oligomers to another, one isobutyl group was gained or lost. In addition, a series of peaks could be attributed to the copolymer chains that bear a methoxy terminal group (structure a) at the ω -end caused by the quenching of the polymerization with methanol ($M_n = 926.6$, 932.6 , and 939.5 g mol^{-1} ; Figure 5B). The other peak was 22 Da above the previous value ($M_n = 939.5\text{ g mol}^{-1}$) and could be attributed to the copolymer with indanyl ring structures (structures b, $M_n = 961.2\text{ g mol}^{-1}$), which were the results of Friedel-Crafts alkylations. These

Figure 5: Spectra of the copolymer.

(A) MALDI-TOF-MS for cationic copolymerization (in IL) of *p*-MeSt and IB (feed ratio of IB: *p*-MeSt-IB = 1:1); (B) expanded view of spectrum in Figure 5A.

results suggested that the IB/*p*-MeSt random copolymer could be obtained in $[\text{Hmim}][\text{NTf}_2]$ via cationic copolymerization. In addition, the chain transfer reaction resulted in a lower M_n relative to the theoretical value.

3.4 Effects of solvents on copolymerization

Although NTf_2^- can stabilize the propagating carbocationic species through the moderation or delocalization of the positive charges in homopolymerization of *p*-MeSt (37), the factors for copolymerization are highly complex. In $[\text{Hmim}][\text{NTf}_2]$, the copolymerization only generated oligomers. Thus, we attempted to identify the reason for this low molecular weight. We investigated the different polarity of solvents, including ILs and the traditional solvents for cationic polymerizations. Table 3 shows the results of the different polarities of solvents on copolymerization. The results show that a

Table 3: Effects of different type of solvents and their polarity on copolymerization of IB with *p*-MeSt.^a

Run	Solvent	Polarity	M_n (GPC)	M_w/M_n	Yield % ^b
1	V(n-Hex)/V(CH ₂ Cl ₂) = 60:40	↓	3364	2.75	85.6
2	CH ₂ Cl ₂		2650	2.30	92.4
3	[Bmim][NTf ₂]		1247	1.25	80.8
4	[Hmim][NTf ₂]		1057	1.25	85.9

^aConditions: $[p\text{-MeSt}]_0 = [\text{IB}]_0 = 1.768 \text{ mol}\cdot\text{l}^{-1}$;
 $[\text{CumCl}]_0 = 15.405 \text{ mmol}\cdot\text{l}^{-1}$, $[\text{BF}_3\text{OEt}_2]_0 = 0.277 \text{ mol}\cdot\text{l}^{-1}$;
 $M_n(\text{theor}) = 20,000 \text{ g/mol}$; at -30°C .

^bTotal monomer conversion.

high polarity of solvents yielded low M_n and narrow M_w/M_n . Therefore, the high polarity of ILs resulted in the low M_n and narrow M_w/M_n , although they could stabilize carbocation (36). In addition, the high viscosity of ILs that resulted in the low releasing rate of reaction heat possibly caused the low molecular weight (32).

3.5 Copolymerization mechanism in ILs

From the aforementioned results, we proposed the corresponding mechanism of cationic copolymerization

Main reactions

Side reactions

Where $R_1 = \text{H}$ and $R_2 = p\text{-MeAr}$, or $R_1 = R_2 = \text{Me}$.

Scheme 1: The mechanism of cationic copolymerization of IB with *p*-MeSt in ILs.

of IB with *p*-MeSt in ILs system, as shown in Scheme 1. BF_3OEt_2 activated the C-Cl bond of the cumyl chloride to form the initiating cationic species. The copolymerization in ILs occurred by chain breaking via the predominant Friedel-Crafts alkylations, which created a new polymer chain via protic reinitiation and resulted in a lower M_n relative to the theoretical value. The high polarity, high viscosity, and ionic environment of ILs influenced the copolymerization, although ILs did not participate in the initiation or termination reactions in the entire polymerization process.

4 Conclusions

The IB/*p*-MeSt random copolymer with high conversion, average molecular weight (M_n) ranging from 800 to 2100, and narrow molecular weight distribution (M_w/M_n ca. 1.1–1.5) could be prepared via cationic copolymerization in an IL medium. The different compositions of IB from 13 mol% to 39 mol% in IB/*p*-MeSt random copolymers could be mediated by changing the monomer ratio in the feed. The GPC curves were unimodal throughout the copolymerization. The polymerizations that generated oligomers only indicated that chain transfer occurred in ILs. The high polarity, high viscosity, and ionic environment of ILs were the possible reasons for the chain transfer of copolymerization.

Acknowledgments: This work was supported by the Hebei Province Science Foundation for Youths (E2018508091), the Fundamental Research Funds for the Central Universities (3142017097), the Langfang Technology Support Project (2017011040), the National Natural Science Foundation of China (No. 51373026, No. 51573020, and No. 51503019), and Beijing Natural Science Foundation (No. 2172022 and No. 2162014).

References

- Kang J, Erdodi G, Kennedy JP. Polyisobutylene-based polyurethanes with unprecedented properties and how they came about. *J Polym Sci Part A Polym Chem*. 2011;49:3891–904.
- Alvarez Albarran A. Modular surface functionalization of polyisobutylene-based biomaterials. *Diss Theses Gradworks*. 2014;50(12):273–90.
- Pratap G, Mustafa S, Hollis W, Heller J. Living carbocationic polymerization of isobutylene by tert-amyl alcohol/ BCl_3 /1-methyl-2-pyrrolidinone initiating system. *J Appl Polym Sci*. 1992;44(6):1069–74.
- Ren P, Wu YB, Guo WJ, Li SX, Mao J, Xiao F, Li K. Synthesis, characterization and haemocompatibility of poly(styrene-*b*-isobutylene-*b*-styrene) triblock copolymers. *Polym Korea*. 2011;35:40–6.
- Xie Y, Chang JJ, Wu YB, Yang D, Wang H, Zhang T, Li SX, Guo WL. Synthesis and properties of bromide-functionalized poly(isobutylene-co-*p*-methylstyrene) random copolymer. *Polym Int*. 2016;66:468–76.
- Tsou AH, Favis BD, Hara Y, Bhadane PA, Kirino Y. Reactive compatibilization in brominated poly(isobutylene-co-*p*-methylstyrene) and polyamide blends. *Macromol Chem Phys*. 2009;210(5):340–8.
- Vasilenko IV, Shiman DI, Kostjuk SV. Highly reactive polyisobutylenes via $\text{AlCl}_3\text{OEt}_2$ -coinitiated cationic polymerization of isobutylene: effect of solvent polarity, temperature, and initiator. *J Polym Sci Part A Polym Chem*. 2012;50(4):750–8.
- De P, Faust R. Determination of the absolute rate constant of propagation for ion pairs in the cationic polymerization of *p*-methylstyrene. *Macromolecules* 2005;38(13):5498–505.
- Jun A, Hidehiro Y, Motomasa Y, Shokyoku K, Sadahito A. Living cationic polymerization of styrene derivatives using $\text{S}_n\text{Cl}_4/\text{EtAlCl}_2$ in the presence of a Lewis base. *Polym Preprints*. 2009;50(1):156.
- Satoh K, Nakashima J, Kamigaito M, Sawamoto M. Novel $\text{BF}_3\text{OEt}_2/\text{R-OH}$ initiating system for controlled cationic polymerization of styrene in the presence of water. *Macromolecules* 2001;34(3):396–401.
- Kostjuk SV, Dubovik AY, Vasilenko IV, Mardiykin VP, Gaponik LV, Kaputsky FN, Antipin LM. Novel initiating system based on AlCl_3 etherate for quasiliving cationic polymerization of styrene. *Polym Bull*. 2004;52(3):227–34.
- Reichardt C. Polarity of ionic liquids determined empirically by means of solvatochromic pyridinium *N*-phenolate betaine dyes. *Green Chem*. 2005;7(5):339–51.
- Earle MJ, Engel BS, Seddon KR. Keto–Enol tautomerism as a polarity indicator in ionic liquids. *Aust J Chem*. 2004;57(2):149–50.
- Kowsari MH, Fakhraee M. Influence of butyl side chain elimination, tail amine functional addition, and C2 methylation on the dynamics and transport properties of imidazolium-based $[\text{Tf}_2\text{N}]^-$ ionic liquids from molecular dynamics simulations. *J Chem Eng Data*. 2015;60(3):551–60.
- Figoli A, Marino T, Simone S, Di Nicolo E, Li XM, He T, Tornaghi S, Drioli E. Towards non-toxic solvents for membrane preparation: a review. *Green Chem*. 2014;16(9):4034–59.
- Cevasco G, Chiappe C. Are ionic liquids a proper solution to current environmental challenges? *Green Chem*. 2014;16(5):2375–85.
- LoSETTY V. Recent advances and thermophysical properties of acetate-based protic ionic liquids. *Chem Sci*. 2016;7(2):1–7.
- Patel R, Kumari M. Interaction between pyrrolidinium based ionic liquid and bovine serum albumin: a spectroscopic and molecular docking insight. *Biochem. & B Anal. Biochem*. 2016;5(2). DOI: 10.4172/2161-1009.1000265.
- Lozinskaya EI, Shaplov AS, Vygodskii YS. Direct polycondensation in ionic liquids. *Eur Polym J*. 2004;40(9):2065–75.
- Zhang S, Dias Goncalves L, Lefebvre H, Tessier M, Rousseau B, Fradet A. Direct poly(β -alanine) synthesis via polycondensation in ionic liquids. *ACS Macro Lett*. 2012;1(8):1079–82.
- Vygodskii YS, Lozinskaya EI, Shaplov AS. Ionic liquids as novel reaction media for the synthesis of condensation polymers. *Macromol Rapid Commun*. 2002;23(12):676–80.

22. Brusseau SGN, Boyron O, Schikaneder C, Santini CC, Charleux B. Nitroxide-mediated controlled/living radical copolymerization of methyl methacrylate with a low amount of styrene in ionic liquid. *Macromolecules* 2011;44(2):215–20.
23. Jeličić A, Beuermann S, García N. Influence of ionic liquid structure on the propagation kinetics of methyl methacrylate. *Macromolecules* 2009;42(14):5062–72.
24. Muginova SV, Galimova AZ, Polyakov AE, Shekhovtsova TN. Ionic liquids in enzymatic catalysis and biochemical methods of analysis: capabilities and prospects. *J Anal Chem.* 2010;65(4):331–51.
25. Li Y, Qiang Q, Zheng X, Wang Z. Controllable electrochemical synthesis of Ag nanoparticles in ionic liquid microemulsions. *Electrochem Commun.* 2015;58:41–5.
26. Biedroń T, Kubisa P. Atom-transfer radical polymerization of acrylates in an ionic liquid. *Macromol Rapid Commun.* 2001;22(15):1237–42.
27. Zhang H, Zhang Y, Liu W, Wang H. Kinetic study of atom transfer radical polymerization of methyl methacrylate in ionic liquids. *J Appl Polym Sci.* 2008;110(1):244–52.
28. Vasilenko IV, Bereziianko IA, Shiman DI, Kostjuk SV. New catalysts for the synthesis of highly reactive polyisobutylene: chloroaluminate imidazole-based ionic liquids in the presence of diisopropyl ether. *Polym Chem.* 2016;7(36):5615–9.
29. Vijayaraghavan R, MacFarlane DR. Organoborate acids as initiators for cationic polymerization of styrene in an ionic liquid medium. *Macromolecules* 2007;40(18):6515–20.
30. Vijayaraghavan R, MacFarlane DR. Novel acid initiators for the rapid cationic polymerization of styrene in room temperature ionic liquids. *Sci China Chem.* 2012;55(8):1671–76.
31. Biedro T, Kubisa P. Cationic polymerization of styrene in a neutral ionic liquid. *J Appl Polym Sci.* 2004;42(13):3230–5.
32. Han L, Wu YB, Dan Y, Wang H, Zhang XQ, Wei XL, Guo WL, Li SX. Characteristics and mechanism of styrene cationic polymerization in 1-butyl-3-methylimidazolium hexafluorophosphate ionic liquid. *RSC Adv.* 2016;6(107):105322–30.
33. Wu Y, Han L, Zhang X, Mao J, Gong L, Guo W, Gu K, Li S. Cationic polymerization of isobutyl vinyl ether in an imidazole-based ionic liquid: characteristics and mechanism. *Polym Chem.* 2015;6(13):2560–8.
34. Yoshimitsu H, Kanazawa A, Kanaoka S, Aoshima S. Cationic polymerization of vinyl ethers with alkyl or ionic side groups in ionic liquids. *J Polym Sci Part A Polym Chem.* 2016;54(12):1774–84.
35. Huddleston JG, Visser AE, Reichert WM, Willauer HD, Broker GA, Rogers RD. Characterization and comparison of hydrophilic and hydrophobic room temperature ionic liquids incorporating the imidazolium cation. *Green Chem.* 2001;3(4):156–64.
36. Hadjikyriacou S, Acar M, Faust R. Living and controlled polymerization of isobutylene with alkylaluminum halides as coinitiators. *Macromolecules* 2004;37(20):7543–7.
37. Zhang X, Guo W, Wu Y, Gong L, Li W, Li X, Li S, Shang Y, Yang D, Wang H. Cationic polymerization of p-methylstyrene in selected ionic liquids and polymerization mechanism. *Polym Chem.* 2016;7(32):5099–112.
38. De P, Faust R. Living carbocationic polymerization of p-methoxystyrene using p-methoxystyrene hydrochloride/SnBr₄ initiating system: determination of the absolute rate constant of propagation for ion pairs. *Macromolecules* 2004;37(21):7930–7.
39. Ashbaugh JR, Ruff CR, Shaffer TD. Characterization of signals in the solution ¹H NMR spectrum of poly(isobutylene-co-p-methylstyrene) and their utility. *J Polym Sci Part A Polym Chem.* 2000;38(9):1680–6.
40. Lubnin AV, Országh I, Kennedy JP. The microstructure of poly(isobutylene-co-p-methylstyrene) by NMR spectroscopy. *J Macromol Sci. Part A Pure Appl Chem.* 1995;32(11):1809–30.
41. Cox FJ, Johnston MV, Qian K, Peiffer DG. Compositional analysis of isobutylene/p-methylstyrene copolymers by matrix-assisted laser desorption/ionization mass spectrometry. *J Am Soc Mass Spectrom.* 2004;15(5):681–8.