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

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 \([\text{Hmim}]\text{[NTf}_2\text{]}\) at \(-30^\circ\text{C}\). 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 \(^1\text{H}-\text{nuclear magnetic resonance}\) (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. \( \text{SnCl}_4\), \( \text{TiCl}_4\), \( \text{AlCl}_3\), \( \text{BF}_3\text{OEt}_2\)) 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 cationic 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 \textit{water-and-air-stable ILs, such as \( \text{N}_4\text{-butyl-N-methyl pyrrolidinium bis(trifluoromethanesulfon})\) amide ([C\(_{\text{mpyr}}\)\text{[NTf}_2\text{]}]) (29), trihexyltetradecylphosphonium bis(trifluoromethanesulfonfyl)amid ([P\(_{\text{6,6,6,14}}\text{[NTf}_2\text{]}]) (30), 1-butyl-3-methylimidazolium hexafluorophosphate ([Bmim]\text{[PF}_6\text{]}]) (31, 32), 1-octyl-3-methylimidazolium tetrafluoroborate ([Omim]\text{[BF}_4\text{]}]) (33), 1-octyl-3-methylimidazo-...
Combining bis(trifluoromethanesulfonyl)amide ([Omin][NTf$_2$]), 1-octyl-3-methylimidazolium bromide ([Omin][Br]), and 1-octyl-3-methylimidazolium hexafluorophosphate ([Omin][PF$_6$]) (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][NTf$_2$]) and 1-hexyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide ([Hmim][NTf$_2$]) 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 H$_2$O 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 CaH$_2$ before use. Isobutylene (IB, Beijing Yansan Petroleum Chemical Corp., Beijing, China, purity >99.9%) was cooled in the cold bath of a glovebox ([H$_2$O] < 0.5 ppm; [O$_2$] < 10 ppm) in the MBraun 150-M glovebox. Fifty milliliter screw-cap vials with an IKAMS3 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][NTf$_2$], 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 was 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 BF$_3$OEt$_2$ 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.

2.2 Polymerization copolymer of IB with p-MeSt

The procedures and cationic polymerizations were carried out under a dry nitrogen atmosphere ([H$_2$O] < 0.5 ppm; [O$_2$] < 10 ppm) in the MBraun 150-M glovebox. Fifty milliliter screw-cap vials with an IKAMS3 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][NTf$_2$], 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 was 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 BF$_3$OEt$_2$ 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. $M_n/M_M$) 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 CDCl$_3$ as a solvent at 25°C. $^1$H-NMR spectra of solutions in CDCl$_3$ were calibrated to tetramethylsilane as an internal standard ($δ^1H = 0.00$).

Matrix-assisted laser desorption ionization time-of-flight mass spectrometry (MALDI-TOF-MS) analyses were performed on an Ultraflex (AB Sciex, USA) TOF-MS, equipped with a 373 nm, 50 Hz N$_2$ 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, Brenem, 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/CH₂Cl₂ 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) H₂O; (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 TiCl₄ and BF₃OEt₂, 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/CH₂Cl₂ 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 BF₃OEt₂ Lewis acid resulted in a higher yield, regardless of the initiator used. Here, we selected the CumCl/BF₃OEt₂ 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 [IB]₀ to [p-MeSt]₀ was changed from 0:100 (mol:mol) to 60:40

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*Total monomer conversion.

*IB content in product polymer; Determined by ¹H-NMR; “−” stands for no test because of their low yield.
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][NTf$_2$].

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...
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 Tₘ 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 Tₘ value, which was only

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

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

Where R₁ = H and R₂ = p-MeAr, or R₁ = R₂ = Me.
between that of IB (−66.7°C) and p-MeSt (110°C). The $T_s$ 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, $^1$H-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 $^1$H-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 $^1$H-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 (-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 (2×56 = 112 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 ($M_n = 939.5$ g mol$^{-1}$) and could be attributed to the copolymer with indanyl ring structures (structures b, $M_n = 961.2$ g mol$^{-1}$), which were the results of Friedel-Crafts alkylations. These results suggested that the IB/p-MeSt random copolymer could be obtained in [Hmim][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 [Hmim][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...
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.
of IB with p-MeSt in ILs system, as shown in Scheme 1. BF₃OEt, 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 alkylation, 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 ($M_w$) 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.

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