

Ring-Opening Polymerization of Cyclohexene Oxide by Recyclable Scandium Triflate in Room Temperature Ionic Liquid

Jun Ling, Lixin You, Yifei Wang, Zhiquan Shen

MOE Key Laboratory of Macromolecular Synthesis and Functionalization, Department of Polymer Science and Engineering, Zhejiang University, Hangzhou 310027, China

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ABSTRACT: In this article, we provide a concept of a two-phase polymerization system consisting of immiscible monomer and room temperature ionic liquid (IL). The catalyst is immobilized in the IL phase where polymerization takes place. The produced polymer is extracted by the monomer, and the remaining IL phase is catalytically active for more polymerizations. Thus, common volatile organic solvents are no longer needed. Ring-opening polymerization of cyclohexene oxide (CHO) in 1-*n*-butyl-3-methylimidazolium tetrafluoroborate IL ([bmim][BF₄]) using scandium triflate [Sc(OTf)₃] catalyst serves as a real-

istic example of such concept. The yield of polyCHO in [bmim][BF₄] is higher than that in bulk. IL containing Sc(OTf)₃ can be used for at least three times. A circulatory polymerization process is carried out with added catalyst to keep a relatively high yield in following circulation processes. The assignments of proton signals of polyCHO in ¹H NMR are discussed in detail. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 124: 2537–2540, 2012

Key words: room temperature ionic liquid; ring-opening polymerization; scandium triflate; catalysts; polyethers

INTRODUCTION

Room temperature ionic liquids (ILs), molten salts at or below room temperature, have attracted extensive interest because of their advantages including extremely low vapor pressure, nonflammability, low toxicity, high chemical and thermal stability, high solubility of certain chemicals (especially organometallic compounds), and adjustability of solubility by changing the structures of cations and anions.^{1–4} It is promising to use IL as recoverable green media in polymerizations to replace common volatile organic solvents,^{4–6} which decreases not only the pollution of environment but also the cost of manufactory by reusing ILs and recovering catalysts, as long as feasible and efficient reacting and recycling processes are applied. Moreover, contributing to the high polarity, ILs are able to increase the catalytic activities in certain cases such as free-radical polymerizations and cationic polymerizations.¹

To our best knowledge, the state-of-the-art recycling processes of polymerization need additional organic solvent, toluene for instance, to extract either polymer or catalyst.^{7–9} In this article, we provide both a concept and an example to perform polymerization in IL and extract polymers by monomer itself. All of the monomer, IL and catalyst can be reused, and no organic solvent is needed. The ring-opening polymerization (ROP) of cyclohexene oxide (CHO) catalyzed by scandium triflate [Sc(OTf)₃] in IL is selected as a model experimental system to realize such concept. Some catalysts for ROP of CHO have been reported.^{10–17} So far, there is no report concerning the CHO polymerization by Sc(OTf)₃.

EXPERIMENTAL

N-Methyl imidazole and CHO were purified by distillation under reduced pressure after stirring over CaH₂ for 24 h. The IL of [bmim][BF₄] was prepared by anionic exchange reaction of [bmim][Cl] precursor,¹⁸ and stored in argon after that volatile chemicals were completely removed in high vacuum at 60°C.

Polymerizations are carried out in air- and moisture-free ampoules equipped with magnetic stir bars using Schlenk techniques. In argon atmosphere, Sc(OTf)₃ was dissolved in [bmim][BF₄] at 60°C and preserved at polymerization temperature. CHO was then added to start the polymerization under

Correspondence to: J. Ling (lingjun@zju.edu.cn).

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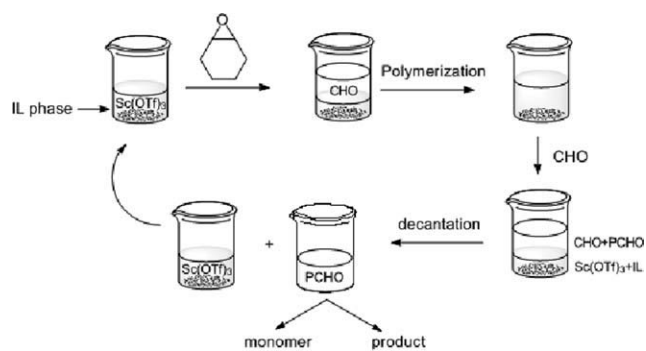


Figure 1 A schematic process of CHO polymerization catalyzed by reusable $\text{Sc}(\text{OTf})_3$ in a room temperature ionic liquid (IL) $[\text{bmim}][\text{BF}_4]$ without common volatile organic solvents.

vigorous stirring. After predetermined time, the polymer was extracted by an additional proportion of CHO if polymer precipitated. The CHO (upper) layer was separated and the polyCHO was recovered after distillation of CHO under reduced pressure. This amount of CHO was collected and used again. Another run of polymerization was started when fresh CHO monomer was introduced into the remaining $[\text{bmim}][\text{BF}_4]$ layer.

Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker Avance III 500 (^1H : 500 MHz and ^{13}C : 125 MHz) spectrometer in CDCl_3 with tetramethylsilane as the internal reference. Molecular weights and polydispersity indexes (PDIs) were measured on a Waters 1515 apparatus with two PL mixed-C columns at 40°C , with tetrahydrofuran as the eluent (1.0 mL/min). Commercial polystyrene samples with narrow distributions were used as standards for calibration.

RESULTS AND DISCUSSION

1-*n*-Butyl-3-methylimidazolium tetrafluoroborate ($[\text{bmim}][\text{BF}_4]$), a generally available and inexpensive IL, is a good solvent of $[\text{Sc}(\text{OTf})_3]$ while it is immiscible with CHO, the monomer, generating a two-phase system. ROP of CHO performs in vigorous stirring. Because the produced polyCHO is soluble in CHO but not in $[\text{bmim}][\text{BF}_4]$, it precipitates at high conversion of CHO. We either control the polymerization time to keep the CHO conversion low or add another fraction of CHO as solvent for polyCHO. This differs from the report of the ROP of ϵ -caprolactone using toluene to extract the products.⁷ After standing for 2 min, the CHO phase, the upper layer, is easy to be separated. The proportion of polymerization is negligible in such a short period without being stirred. The polymer is recovered after the removal of CHO. New monomer can be added into the lower layer of IL to continue another runs

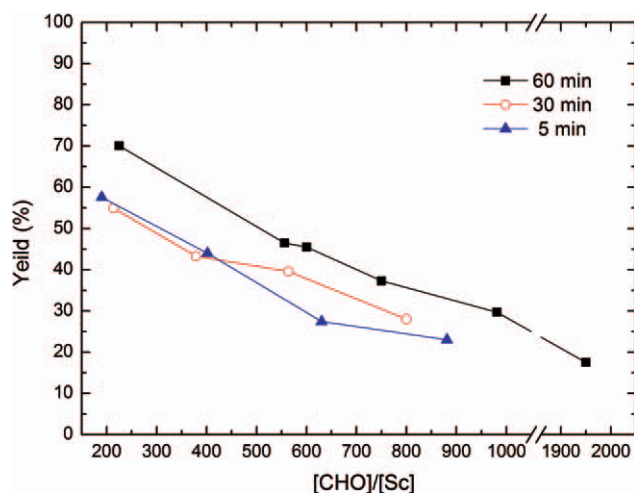


Figure 2 Effects of the molar ratios of CHO and $\text{Sc}(\text{OTf})_3$ and reaction time on the yields of polymerizations. Conditions: $[\text{Sc}(\text{OTf})_3] = 0.03$ mol/L in $[\text{bmim}][\text{BF}_4]$ at 15°C . [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://www.interscience.wiley.com).]

of ROP. The whole recycling process is illustrated in Figure 1.

$\text{Sc}(\text{OTf})_3$ is found for the first time as an efficient catalyst for ROP of CHO at room temperature. Polymerization conditions, such as the molar ratio of monomer and catalyst ($[\text{CHO}]/[\text{Sc}]$), polymerization time and reaction temperature, control the yield of polyCHO. In Figure 2, the yield increases when increasing reaction time or/and decreasing the ratio of $[\text{CHO}]/[\text{Sc}]$, i.e., increasing the amount of $\text{Sc}(\text{OTf})_3$ catalyst, which is common phenomena in most polymerization systems. It is worthy of mentioning that the yield of polyCHO by ROP in $[\text{bmim}][\text{BF}_4]$ is higher than that in bulk. In the same

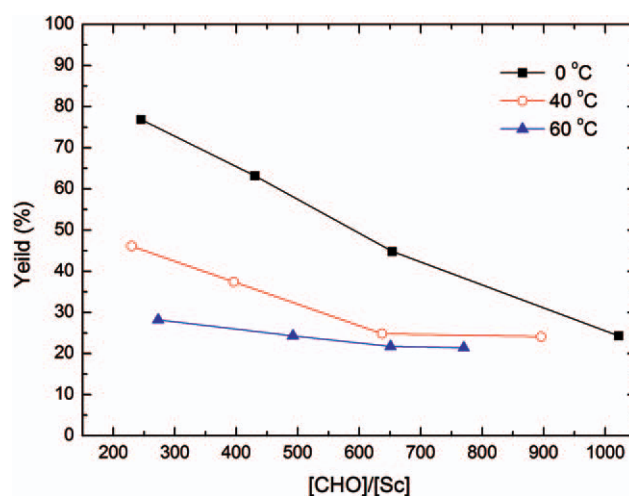


Figure 3 Effects of the molar ratios of CHO and $\text{Sc}(\text{OTf})_3$ and reaction temperatures on the yields of polymerizations. Conditions: $[\text{Sc}(\text{OTf})_3] = 0.03$ mol/L in $[\text{bmim}][\text{BF}_4]$, 60 min. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://www.interscience.wiley.com).]

TABLE I
Polymerization of CHO Catalyzed by Sc(OTf)₃
(0.03 mol/L) in 1 mL [bmim][BF₄]

Run	[CHO]/[Sc] ^a	<i>t</i> (min)	<i>T</i> (°C)	Yield (%)	<i>M</i> _n (kg/mol) ^b	PDI ^b
1	200	5	15	57.6	1.3	1.6
2	200	30	15	54.9	1.3	1.6
3	600	30	15	39.6	1.6	1.6
4	250	30	0	76.9	1.5	1.7
5	270	30	60	28.2	0.8	1.5
6 ^c	290	60	15	46.0	25.3	1.6

^a Molar ratio.

^b by SEC measurements.

^c Bulk polymerization of CHO without [bmim][BF₄].

condition of [CHO]/[Sc] = 200 and 60-min polymerization at 15°C, the yield of polyCHO in [bmim][BF₄] is more than 70% while it is only 40% in bulk polymerization of CHO. It can be expected that the polymerization active species are stabilized by IL with high polarity, indicating ionic intermediates of growing chain ends. According to the polymerization temperature-dependent yield plots shown in Figure 3, higher temperature leads to slower polymerization and lower polyCHO yield, which is an evidence for negative activation energy of the polymerization.

Table I compares the number-average molecular weights (*M*_ns) and PDIs of the products. The *M*_ns of polyCHO obtained from IL are all in the range of 1.3 to 1.6 kg/mol except for the case of polymerization at 60°C. It is well known that the chain transfer reaction becomes intense at high temperature. In addition, the *M*_n of the polyCHO obtained from IL is much smaller than that from bulk polymerization (run 6 in Table I). It is due to the much lower monomer concentration and faster chain transfer reaction in IL phase than those in CHO bulk. It is also reported that chain transfer reactions were accelerated in IL media in some other cationic polymerizations.¹ The PCHOs with low *M*_ns (below 3 kg/mol) may have applications differing from those with high *M*_ns (over 10 kg/mol).

Based on the experimental phenomena discussed above, ROP of CHO catalyzed by Sc(OTf)₃ in IL is

TABLE II
Polymerization of CHO Using Recycled [bmim][BF₄] and Sc(OTf)₃^a

Cycles	Sc(OTf) ₃ (mg)	CHO (g)	<i>t</i> (min)	Yield (%)
1	26	1.24	60	61.5
2	– ^b	1.24	60	40.6
3	– ^b	1.24	90	11.7
4	– ^b	1.24	15 h	0

^a Polymerization conditions: [bmim][BF₄] = 1.6 mL, [Sc] = 0.03 mol/L, [CHO]/[Sc] = 250 (molar ratio), 15°C.

^b No more Sc(OTf)₃ was added.

TABLE III
Polymerization of CHO by Additional Sc(OTf)₃ in Recycled [bmim][BF₄]^a

Cycles	Sc(OTf) ₃ (mg)	CHO (g)	<i>t</i> (min)	Yield (%)
1	11.2	0.56	60	75.2
2	– ^b	0.56	60	40.7
3	12.0	0.56	60	>99
4	– ^b	0.56	60	39.6

^a Polymerization conditions: [Sc] = 0.02 mol/L, [CHO]/[Sc] = 250 (molar ratio), [bmim][BF₄] = 1.0 mL, 25°C.

^b No more Sc(OTf)₃ was added.

speculated to take a cationic mechanism.^{10,15,19} Sc(OTf)₃ activates CHO monomer and generates oxonium ion, which propagates via CHO ring cleavage at CH–O bond to produce polyCHO.

After polyCHO being removed together with CHO layer, new ROP runs are carried out by more proportions of CHO monomers added into the Sc(OTf)₃-containing [bmim][BF₄] layer. PolyCHO of 11.7% yield is obtained in the third cycle of polymerization (Table II), though the catalytic activity decreases. It is due to the loss of Sc(OTf)₃ catalyst during the separation of polyCHO. A semiquantitative titration of scandium in IL layer indicates that the amount of Sc(OTf)₃ decreases after every polymer removal procedure. As shown in Table III, when another fraction of Sc(OTf)₃ catalyst is added into the IL layer after two polymerizations, the catalytic activity is recovered and gives another two polymerization cycles with high catalytic activities. For instance, the yield of polyCHO of run 4 is the same as run 2 in Table III. The method to decrease the catalyst lost by fixing the scandium catalyst in IL is still under investigation. It is worthy of mentioning that no detectable loss of [bmim][BF₄] has been found in experiments.

The ¹H NMR and ¹H-¹³C HMQC spectra are shown in Figures 4 and 5. The methine proton (OCH) signals of backbone locate in the range of 3.2

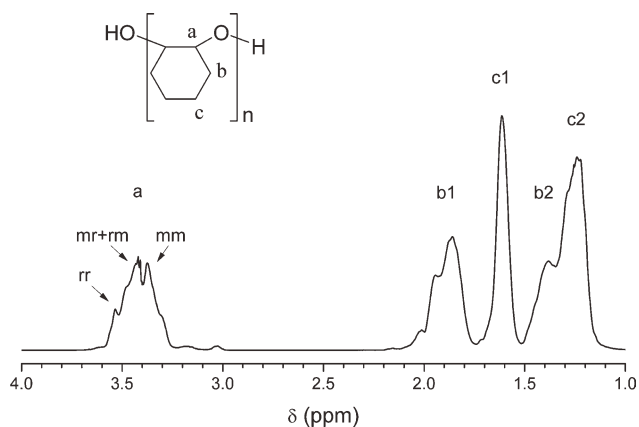


Figure 4 ¹H NMR spectrum of polyCHO.

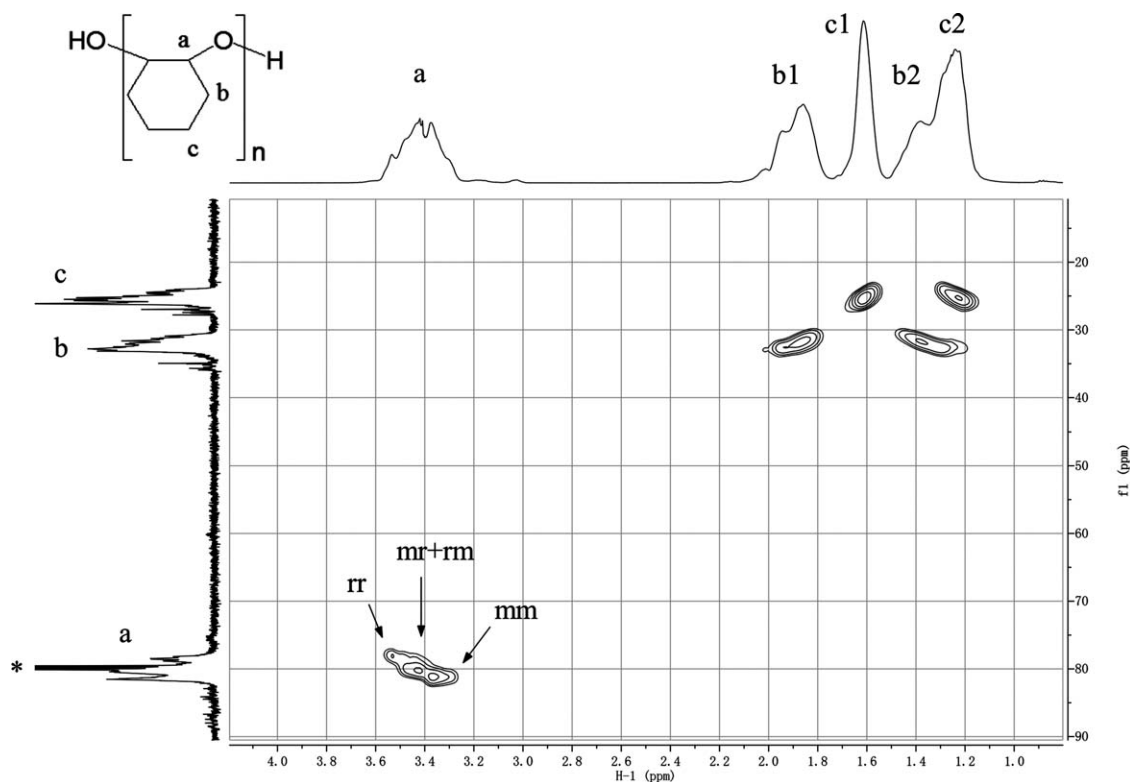


Figure 5 ^1H - ^{13}C HMQC spectrum of polyCHO. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

and 3.6 ppm. Triads of rr, mr + rm, and mm in separated peaks (Figs. 4 and 5) indicate that the produced polyCHO is atactic.^{11,12,17} It is interesting that two kinds of methylene protons (H-b and H-c) exhibit roughly three groups of signals and most references do not distinguish them. Based on ^1H - ^{13}C HMQC and ^1H - ^1H COSY analyses, they actually consist of four groups with the assignments as shown in Figure 5. The coupling signals of C-b with H-b1 and H-b2, as well as those of C-c with H-c1 and H-c2, clearly prove that both of H-b and H-c split into two groups of peaks. Moreover, the H-b protons are next to the chiral center of C-a and thus show more complicated peaks than H-c signals do. The assignments differ from previous reports.^{12,20}

CONCLUSIONS

ROP of CHO can be catalyzed by $\text{Sc}(\text{OTf})_3$ either in [bmim][BF_4] IL or in bulk. The two-phase CHO polymerization in IL provides a recyclable organic solvent-free process. Both the IL and catalyst can be reused at least three times. The catalytic activity decreases along the recycle batches of polymerization because of the loss of $\text{Sc}(\text{OTf})_3$ during the extraction process of polymers, and it can be recovered by the addition of another proportion of catalyst.

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