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Synthesis of poly(β-pinene)-*b*-polytetrahydrofuran from β-pinene-based macroinitiator

Jiang Lu*, Hui Liang, Rongfu Zhang, Baoeng Li

Department of Polymer and Materials Science, Zhongshan University, Guangzhou 510275, People's Republic of China

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Abstract

The living cationic polymerization of β-pinene was carried out with 1-phenylethyl chloride/Ti(O*i*Pr)$_4$/TiCl$_4$ (Ti(O*i*Pr)$_4$/TiCl$_4$ mole ratio 1:3) in the presence of *n*Bu$_4$NCl in CH$_2$Cl$_2$ at −40°C. Styrene was added to cap the living poly(β-pinene) just before β-pinene had been consumed almost completely (conversion ~98%) and then the reaction was stopped at low conversion of styrene to give β-pinene macroinitiator with benzyl chloride terminal. ^{1}H NMR analysis of the obtained polymer showed that one macroinitiator possessed almost one benzyl chloride end group. The macroinitiator in conjunction with silver salt, AgClO$_4$ or AgSbF$_6$, could readily initiate the ring-opening polymerization of THF in the presence of small amounts of propylene oxide. The macroinitiator/AgSbF$_6$ system gave an almost pure block copolymer of β-pinene/THF (weight content: 45% for β-pinene segments and 55% for THF segments) with a relatively narrow molecular weight distribution. In contrast, homopolyTHF and unblocked macroinitiator formed along with the block copolymer with the macroinitiator/AgClO$_4$ system owing to the competing side reactions. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: β-Pinene-based macroinitiator; Poly(β-pinene)-*block*-polytetrahydrofuran

1. Introduction

Living polymerization techniques offer the best way to produce well-defined polymers with controlled molecular weights, polydispersities, and terminal functionalities [1–3]. β-Pinene, one of the main constituents of natural turpentine, can polymerize cationically under a ring-opening isomerization mechanism to produce polymers with unique repeating units that consist of an alternating sequence of isobutene and cyclohexene [4–6]. Despite this complexity of the polymerization mechanism, the living cationic polymerization of β-pinene has been achieved using an initiating system that consists of an HCl-adduct of 2-chloroethyl vinyl ether and isopropoxytitanium chloride [TiCl$_3$(O*i*Pr)] in the presence of *n*Bu$_4$NCl [7]. The achievement of the living polymerization of β-pinene has made the design and preparation of β-pinene-based precise polymers possible. These polymers include random, block and graft copolymers with styrene [8,9], acetoxy or methacryloxy-capped polymers [10].

This paper deals with the synthesis of another β-pinene-based polymer, block copolymer with tetrahydrofuran (THF). This block copolymer is expected to exhibit special characters owing to the differing properties of the two blocking segments: poly(β-pinene) is hydrophobic, rigid and amorphous whereas polyTHF is hydrophilic, flexible, and semicrystalline.

Unlike the previously prepared block copolymer of β-pinene with styrene, the block copolymer with THF cannot be synthesized by the sequential living cationic polymerizations, because it is difficult to find an initiating system suitable for both β-pinene and THF. Thus, the benzyl-chloride-capped poly(β-pinene) was synthesized on the base of the developed living system for β-pinene polymerization, and then was used as a macroinitiator to initiate the ring-opening polymerization of THF in the presence of silver salt, such as AgClO$_4$ and AgSbF$_6$, to give the desired block copolymer.

2. Experimental

2.1. Materials

(-)-β-Pinene (Wako Chemicals; purity >97%) was distilled twice under reduced pressure over CaH$_2$ before use. 1-Phenylethyl chloride (Wako Chemicals; purity >97%) was distilled twice under reduced pressure. TiCl$_4$, tetraisopropoxytitanium [Ti(O*i*Pr)$_4$], AgSbF$_6$ (all Aldrich;

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* Corresponding author.
E-mail address: cedc10@zsu.edu.cn (J. Lu).

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purity >99.99%), and $n\text{Bu}_4\text{NCl}$ (Tokyo Kasei; puity >98%) were used as received. AgClO_4 was obtained by drying $\text{AgClO}_4{\cdot}\text{H}_2\text{O}$ (Aldrich; purity >99.99%) in vacuum. THF was refluxed and distilled over Na metal and benzophenone mixture after producing a purple color just before use. Propylene oxide was distilled twice under reduced pressure before use. CH_2Cl_2 was doubly distilled over P_2O_5 and then over CaH_2 before use.

2.2. Synthesis of benzyl-chloride-capped poly(β-pinene)

In a baked glass tube equipped with a three-way stopcock under dry nitrogen, the polymerization of β-pinene was initiated by sequentially adding, via dry syringes, a solution of 1-phenylethyl chloride (in CH_2Cl_2, 0.50 ml) and a mixture of TiCl_4, $\text{Ti(O}i\text{Pr)}_4$ and $n\text{Bu}_4\text{NCl}$ (in CHCl_2, 1.0 ml) into a solution (in CH_2Cl_2, 3.5 ml) of β-pinene (0.39 ml) at −40°C. β-Pinene conversion reached 98% after the reaction was run for 25 min. Then, styrene (0.29 ml) was added to the preformed living poly(β-pinene) solution, and the reaction was quenched with prechilled methanol (2 ml) at low conversion of styrene (~15%). The quenched reaction mixture was diluted with toluene, washed sequentially with 2% hydrochloric acid, aqueous 1% NaOH solution, and water to remove Ti-containing residues. The organic layer was evaporated to dryness under reduced pressure, and dried in vacuum at 40°C for 10 h to give benzyl-chloride-capped poly(β-pinene).

2.3. Synthesis of block copolymer of β-pinene/THF

Block polymerization was carried out in a baked glass tube equipped with a three-way stopcock and a magnetic stirring bar. The glass tubes were charged with 4.0 ml of THF and 0.20 g of benzyl-chloride-capped poly(β-pinene) macroinitiator. A solution of the silver salt (0.104 g of AgClO_4 or 0.172 g of AgSbF_6) in 1.0 ml of THF was added into the charge and the reaction was allowed to proceed for predetermined time with constant stirring under dry nitrogen at 20°C. A white milky precipitate (AgCl) was observed instantaneously. The polymerization was stopped by adding 0.5 ml of methanol. The precipitates were removed by a centrifugal separator and the solvents (including unreacted THF) were evaporated. The resulting polymers were vacuum dried at room temperature overnight and the yield was determined by gravimetry.

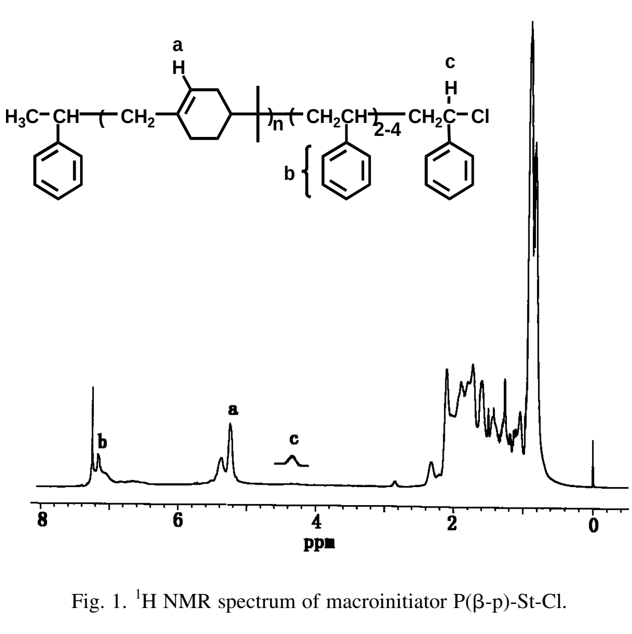


Fig. 1. ^{1}H NMR spectrum of macroinitiator P(β-p)-St-Cl.

2.4. Characterization

The molecular weight distributions were measured by Waters 208 LC-GPC in CHCl_3 at room temperature on polystyrene gel columns (A-803) connected with a refractive index detector (RI-401). ^{1}H NMR spectra were recorded in CDCl_3 at room temperature on a Varian Unity INOVA 500 spectrometer.

3. Results and discussion

3.1. Synthesis of benzyl-chloride-capped poly(β-pinene)

Previously, the β-pinene/styrene block copolymer has been prepared by the sequential living cationic polymerization initiated with 1-phenylethyl chloride (PEC, initiator) and $\text{TiCl}_3\text{(O}i\text{Pr)}$ (activator) in the presence of $n\text{Bu}_4\text{NCl}$ [8]. This block copolymer carries a chloride group adjacent to the polystyrene segment end. If the block copolymerization is stopped at low conversion of the second monomer styrene, benzyl-chloride-capped poly(β-pinene) may be obtained. Thus, the living cationic polymerization of β-pinene (0.50 M) was carried out with 1-phenylethlenyl chloride/$\text{Ti(O}i\text{Pr)}_4$/TiCl_4/$n\text{Bu}_4\text{NCl}$ (20 mM/25 mM/10 mM) initiating system in CH_2Cl_2 at −40°C. Herein $\text{TiCl}_3\text{(O}i\text{Pr)}$ activator was generated in situ by the reaction of $\text{Ti(O}i\text{Pr)}_4$ and TiCl_4 at 1:3 mole ratio rather than by synthesizing and using it directly, because the synthesis of $\text{TiCl}_3\text{(O}i\text{Pr)}$ involves a complicated procedure and it must be stored at low temperature for its instability. After 25 min of the reaction (β-pinene conversion ~98%), the living poly(β-pinene) was capped with styrene (0.5 M) and the polymerization was stopped at about 15% of styrene conversion.

The structure of the obtained polymer was then analyzed by ^{1}H NMR spectroscopy. As shown in Fig. 1, there appeared the absorption of the benzenyl chloride terminal (c) at $\delta \sim 4.5$ ppm, besides the characteristic signals of the endo-olefin (a) in the isomerized β-pinene units and the phenyl group (b) in the styrene units. The number of capping styrene units can be obtained from the peak intensity ratio of $(b/5a) \times 25$, where 25 is the degree of polymerization of β-pinene determined from the initial feed ratio of monomer to initiator in the living polymerization. The value, minus 1 for one phenyl group derived from the initiator fragment, was 3.6, which was in good agreement with the calculated value ($[\text{styrene}]_0/[\text{PEC}]_0 \times \text{conversion} = 3.7$).

More importantly, the number of benzyl chloride terminals per polymer chain, obtained from the peak intensity ratio of $c/a \times 25$, was 1.1, close to unity. GPC analysis showed that the molecular weight distribution of the product was relatively narrow ($M_w/M_n \sim 1.30$, see below). These results demonstrate that the benzyl-chloride-capped poly(β-pinene) [P(β-p)-St-Cl] ($M_n \sim 4000$, measured by ^{1}H NMR) was synthesized by capping living poly(β-pinene) with a few units of styrene (Scheme 1). P(β-p)-St-Cl, reacting with silver salt, can be used as a macroinitiator to initiate the ring-opening polymerization of THF to form the block copolymer. In fact, *tert*-alkyl-chlorine-capped poly(β-pinene) has been prepared by the living cationic polymerization of β-pinene per se [8] and by the so-called "inifer" technique [11]. As a macroinitiator, however, P(β-p)-St-Cl is more suitable because of the higher reactivity of benzyl chloride.

3.2. Synthesis of block copolymer of β-pinene and THF

3.2.1. Block polymerization of THF with P(β-p)-St-Cl in conjunction of $AgClO_4$ or $AgSbF_6$

The ring-opening polymerization of THF was initiated with macroinitiator P(β-p)-St-Cl in conjunction with $AgClO_4$ and $AgSbF_6$, respectively, at 20°C in THF. The polymerizations of THF were extremely slow although the macro-cation initiating species had resulted via the reaction of P(β-p)-St-Cl with the silver salt, as evidenced by the rapid formation of AgCl precipitation. For example, conversions in 40 h for $AgClO_4$ and $AgSbF_6$ were 0.2 and 0.7%, respectively (Fig. 2A, filled square and triangle). The slow polymerizations were due to the difficult initiating reaction of unreactive THF. As well known, active cyclic ethers, such as epoxide, are usually used as co-catalysts (or promoters) to initiate the polymerization of unreactive cyclic ethers such as THF [12,13]. Therefore, propylene oxide was added to increase the polymerization rate of THF. The addition of small amounts of propylene oxide (2.7% macroinitiator by weight) dramatically accelerated the polymerizations. Moreover the reaction rate for $AgSbF_6$ (Fig. 2B) increased much more obviously than that for $AgClO_4$ (Fig. 2A, open square) under the same conditions. For example, the polymerization reached 13.6% in only 18 min with $AgSbF_6$, whereas it reached 9.0% in as long as 5 h with $AgClO_4$. The big difference in rate between the two silver salt systems arises from their different counterions, SbF_6^- and ClO_4^-. The association of ClO_4^- to the propagation chain end is closer than that of SbF_6^- and thereby leads to a much slower polymerization.

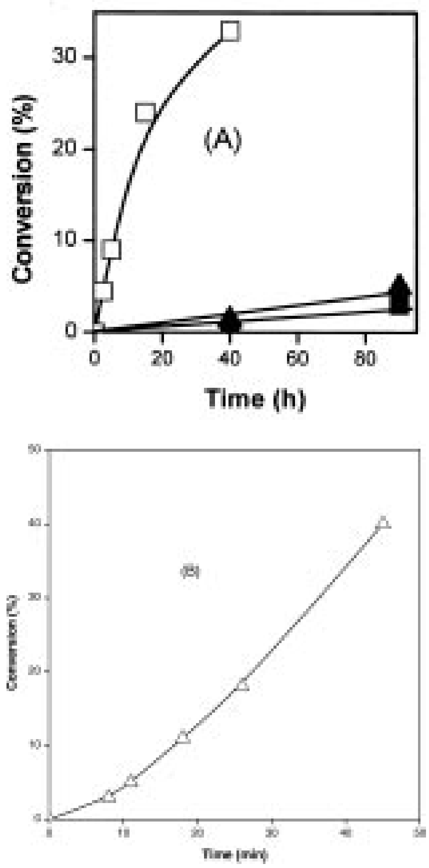
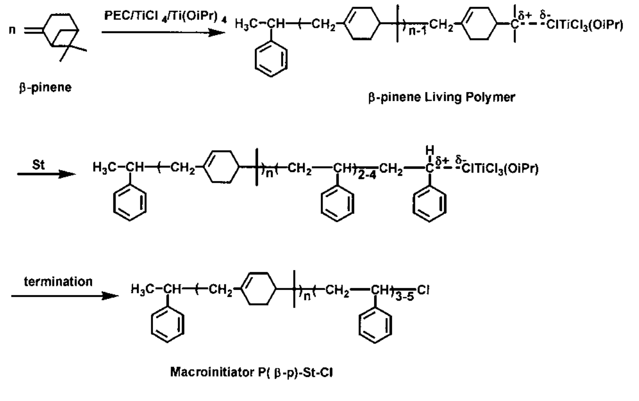


Fig. 2. Time–conversion curves for the ring-opening polymerization of THF with P(β-p)-St-Cl/silver salt in the absence or presence of propylene oxide in THF at 20°C: $[P(\beta\text{-p})\text{-St-Cl}]_0 = 10$ mM; $[\text{silver salt}]_0 = 0.10$ M; silver salt: $AgClO_4$ (■,□), $AgSbF_6$ (▲,△); $[\text{propylene oxide}]_0 = 0$ (■,▲), 20 mM (□,△).



Scheme 1.

3.2.2. Characterization of the block copolymers

To investigate whether block copolymers resulted, the products of the block polymerization of THF obtained with P(β-p)-St-Cl/silver salt in the presence of propylene oxide were then characterized by GPC and ^{1}H NMR. The samples obtained at ~5% of THF conversion were chosen to be analyzed, because the corresponding block copolymers, if formed, would contain polyTHF segments with a comparable weight content to that of poly(β-pinene) segments (52% for THF segments and 43% for β-pinene segments).

Figs. 3 and 4 illustrate the molecular weight distribution

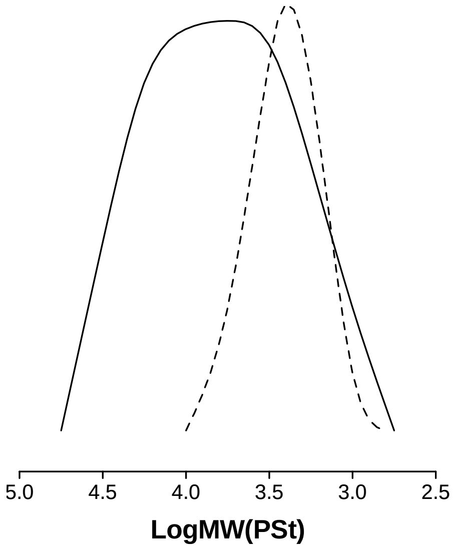


Fig. 3. MWD curves of P(β-p)-St-Cl (broken line, M_n(GPC) = 2200, M_w/M_n = 1.33) and the product (solid line, M_n(GPC) = 3830, M_w/M_n = 2.55) obtained in the ring-opening polymerization of THF with P(β-p)-St-Cl/$AgClO_4$/propylene oxide (10 mM/100 mM/20 mM) in THF at 20°C. Conversion of THF ~5%.

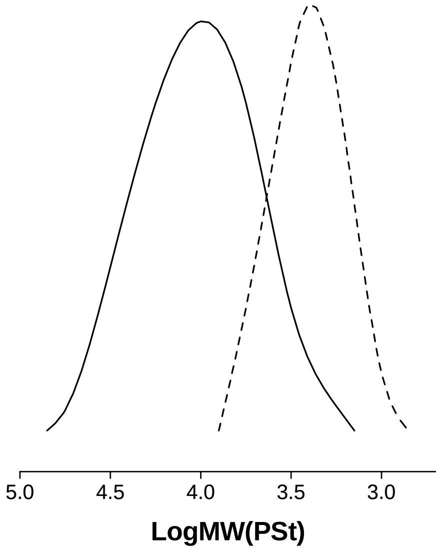


Fig. 4. MWD curves of P(β-p)-St-Cl (broken line, M_n(GPC) = 2200, M_w/M_n = 1.33) and the product (solid line, M_n(GPC) = 4500, M_w/M_n = 1.61) obtained in the ring-opening polymerization of THF with P(β-p)-St-Cl/$AgSbF_6$/propylene oxide (10 mM/100 mM/20 mM) in THF at 20°C. Conversion of THF ~5%.

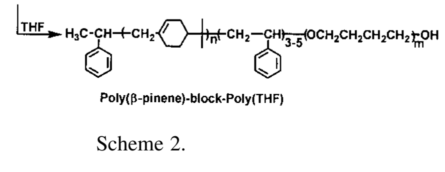
(MWD) curves of the products obtained with $AgClO_4$ and $AgSbF_6$, respectively. The $AgClO_4$ system gave polymers with very broad MWD (M_w/M_n ~ 2.55), which seem to consist of higher molecular weight block copolymers of β-pinene/THF and lower molecular weight homopolymers, probably polyTHF and unblocked macroinitiator. Pure block copolymers could not be prepared with the $AgClO_4$ system. In contrast, the MWD of the polymers obtained with $AgSbF_6$ was relatively narrow (M_w/M_n ~ 1.6), and the GPC profiles shifted toward higher molecular weight. More importantly, the GPC trace was symmetric and there was an absence of skewing or shoulder toward low molecular weights, indicating the absence of significant amounts of unblocked macroinitiator. The polymer was also extracted with *n*-hexane [solvent for poly(β-pinene) but nonsolvent for polyTHF]. No residues were observed, suggesting the absence of THF homopolymers. These results demonstrated that almost pure block copolymers of β-pinene/THF were synthesized with P(β-p)-St-Cl in conjunction with $AgSbF_6$ (Scheme 2).

In the block polymerization of THF initiated with P(β-p)-St-Cl in conjunction with silver salt, some side reactions, competing with the propagation of THF, may occur [14]. These reactions include β-proton elimination of the macroinitiator initiating species and chain transfer to monomer (THF), which generated unblocked macroinitiator and homopolyTHF. As discussed above, the $AgClO_4$ system induced a much slower polymerization than the $AgSbF_6$ system. Correspondingly, the probability of occurrence of the competing side reactions in the $AgClO_4$ system was higher and thus led to the formation of homopolymers.

Fig. 5 shows the ^{1}H NMR spectrum of the product obtained with the $AgSbF_6$ system (the same sample for GPC analysis). In addition to the absorptions of endo-olefin (a) and phenyl (b) from the P(β-p)-St-Cl, there appeared the characteristic absorption of oxymethylene protons (c) at δ 3.4 ppm of the polyTHF segments. Moreover, the absorption at $\delta \sim 4.5$ ppm of benzyl chloride terminal inherent in the P(β-p)-St-Cl disappeared. Furthermore the number-average degree of polymerization of THF segments determined from the peak area ratio of the endo-olefin to the oxymethylene protons ($c/4a \times 25$) was 59, close to the calculated value ($[\mathrm{THF}]_0/[\mathrm{Macroinitiator}]_0 \times$ conversion = 61). ^{1}H NMR results further confirmed the formation of the block copolymer of β-pinene/THF.

4. Conclusions

The macroinitiator, poly(β-pinene) carrying an active benzyl chloride terminal, can be synthesized by capping the living poly(β-pinene), which is obtained with 1-phenylethyl chloride/Ti(O*i*Pr)$_4$/$TiCl_4$/*n*Bu_4NCl initiating system in CH_2Cl_2 at −40°C, with a few units of styrene. The macroinitiator in conjunction with $AgSbF_6$ can readily initiate the ring-opening polymerization of THF in the presence of propylene oxide at 20°C to give a new block copolymer of β-pinene and THF where poly(β-pinene) is nonpolar, rigid,



Scheme 2.

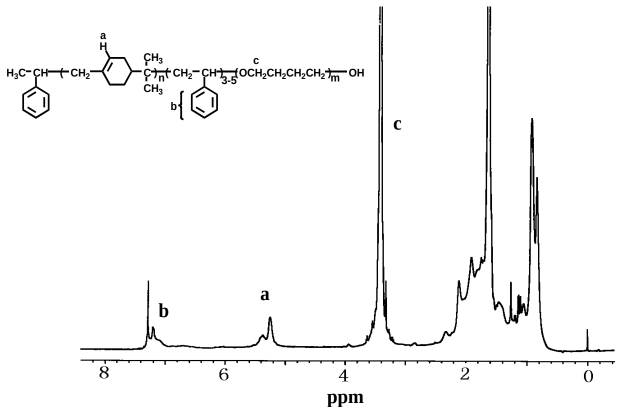


Fig. 5. ^{1}H NMR spectrum of poly(β-pinene)-*block*-poly(THF) obtained in the same experiment as for Fig. 4.

and amorphous and polyTHF is polar, soft, and semicrystalline.

Acknowledgements

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