ORIGINAL ARTICLE

New initiating systems for cationic polymerization of plant-derived monomers: GaCl₃/alkylbenzene-induced controlled cationic polymerization of β -pinene

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An initiating system composed of GaCl₃ and an alkylbenzene was demonstrated to be highly effective for the controlled cationic polymerization of a plant-derived monomer, β -pinene. Alkylbenzenes such as pentamethylbenzene and hexamethylbenzene were shown to function as suitable additives for the polymerization of β -pinene, an alkene monomer with low reactivity, although the alkylbenzenes are much less basic than conventional additives such as esters and ethers for base-assisting living cationic polymerization. For example, when two equivalents of hexamethylbenzene were added to GaCl₃ in conjunction with 2-chloro-2,4,4-trimethylpentane as an initiator, cationic polymerization of β -pinene successfully proceeded in a living manner at -78°C . Successful control over the reaction, i.e., control of an active–dormant equilibrium, was attributed to the formation of a complex between GaCl₃ and the alkylbenzene, as confirmed by UV–vis and ⁷¹Ga NMR analyses.

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INTRODUCTION

A variety of potential monomers for cationic polymerization are widely available in plants as well as in petroleum. For example, β -pinene, a terpene that occurs in pine resin, is a typical monomer that undergoes cationic polymerization.^{1,2} Precision polymer syntheses that use such plant-derived monomers are appealing because of their low environmental load.³ However, most of those monomers belong to a family of alkene and aliphatic hydrocarbon monomers, which are known to be difficult to polymerize efficiently and in a controlled manner. This is in sharp contrast to vinyl ethers and styrene derivatives, for which various new systems for living cationic polymerization have been developed as recently as in the last decade.^{4–12}

The difficulty of performing cationic polymerizations of alkenes and similar aliphatic monomers is considered to be primarily due to their low reactivity, which results from the low electron density on their double bond. Moreover, this low electron density can lead to a less stable carbocation, in contrast to the cases of alkyl vinyl ethers and styrene derivatives that have electron-donating substituents. Thus, the low electron density and the less efficient stabilization of the carbocation result in frequent side reactions, such as β -proton elimination reactions. This persistent and adverse situation is evidenced by several examples of living/controlled polymerization, including reactions of the alkene monomers isobutene¹³ or β -pinene,¹⁴ despite a long history of cationic polymerization and a large number of alkene monomers that can react via a cationic mechanism.¹⁵

To realize controlled cationic polymerizations of monomers with low reactivity, the Lewis acid catalyst utilized must have a fairly high reactivity; however, it must simultaneously be able to induce an appropriate dormant–active equilibrium.^{4–12} To this end, the use of an initiating system for which the catalytic activity can be fine-tuned would be advantageous. A base-assisted initiating system that consists of a Lewis acid and a weak Lewis base is a good candidate system for altering catalytic activity during living cationic polymerization.^{11,12} For example, living cationic polymerizations of a variety of alkyl vinyl ethers and styrene derivatives have been achieved with suitable combinations of various metal halides and an ester or an ether. In addition, unprecedented, highly active living polymerizations that can be completed in seconds have become possible with initiating systems that involve Lewis bases with weak basicity, such as the SnCl₄/ethyl chloroacetate and the FeCl₃/1,3-dioxolane systems. However, the identification of a suitable additive for adjusting the catalytic activity of a metal halide to achieve the controlled polymerization of an alkene monomer remains a challenge.

Because of the low reactivity of alkene monomers, a Lewis base that is much weaker than an ester or an ether should be used as an additive because such a base may interact weakly with a metal halide catalyst such that its catalytic activity is not significantly reduced. Alkylbenzenes are suitable candidates because they exhibit very weak basicity^{16–18} and form complexes with metal halides. In fact, alkylbenzenes have been reported to form π -complexes with conventional Lewis acidic metal halides, such as GaCl₃, TiCl₄, and AlBr₃.^{19–24} This complexation behavior is expected to function efficiently in generating a uniform active catalytic species for cationic polymerization.

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Scheme 1 Cationic polymerization of β -pinene.Table 1 Cationic polymerization of β -pinene using various Lewis acids^a

Entry	Catalyst	Time	Conv. (%)	$M_n \times 10^{-3}$	M_w/M_n
1	GaCl ₃	4.3 min	100	7.6	1.74
2	TiCl ₄	24 h	100	4.8	1.94
3	SnCl ₄	24 h	21	1.5	3.87

^a[β -pinene]₀ = 0.63 M, [TMPCl]₀ = 4.0 mM, [catalyst]₀ = 1.0 mM in CH₂Cl₂/methylcyclohexane (1/1 v/v) at -78 °C.

Against this background, we became interested in developing an initiating system that consists of a metal halide and an aromatic hydrocarbon, which would be suitable for cationic polymerization of alkenes and related monomers that are known to have low reactivity. In this study, the cationic polymerization of β -pinene was examined with an initiating system that consisted of an alkylbenzene as a weak Lewis base (Scheme 1). We used β -pinene because past studies have demonstrated its good cationic polymerizability and the living nature of the polymerization, which are attributable to the ring strain release and the formation of the isomerized tertiary carbocation.^{2,14,25,26} In the current study, we describe the controlled cationic polymerization of β -pinene using a metal chloride/alkylbenzene initiating system. An alkylbenzene with suitable basicity was indispensable for the controlled polymerization. In addition, the interactions between the metal chlorides and the alkylbenzenes were examined by spectrometric methods to reveal the effect of the complexation on polymerization control.

EXPERIMENTAL PROCEDURE

Materials

β -Pinene [(−)- β -pinene; Sigma-Aldrich, St Louis, MO, USA; 99%] and anisole (Sigma-Aldrich; 99.7%) were distilled twice over CaH₂ under reduced pressure. A stock solution of GaCl₃ in hexane was prepared from anhydrous GaCl₃ (Sigma-Aldrich; >99.999%). Commercially available TiCl₄ (Sigma-Aldrich; 1.0 M solution in dichloromethane) and SnCl₄ (Sigma-Aldrich; 1.0 M solution in heptane) were used without further purification. 2-Chloro-2,4,4-trimethylpentane (TMPCl) was prepared by the addition reaction of 2,4,4-trimethyl-1-pentene (TCI, Tokyo, Japan; ≥98.0%) with HCl according to the method described in the literature.²⁷ Hexamethylbenzene (TCI; >99.5%) and pentamethylbenzene (TCI; >99.0%) were crushed with a mortar, dried under reduced pressure for at least 3 h, and dissolved in dichloromethane, successively. Mesitylene (Nacalai Tesque, Kyoto, Japan; 98%) was distilled over CaH₂ under reduced pressure. Toluene (Wako, Osaka, Japan; 99.5%) and dichloromethane (Wako; 99.0%) were purified by being passed through solvent purification columns (Glass Contour; PPT, Nashua, NH, USA). Stock solutions of mesitylene and toluene were prepared by dissolution of the purified compounds in dichloromethane. Ethyl acetate (Nacalai Tesque; 99.5%) and methylcyclohexane (Nacalai Tesque; 98%) were distilled twice over CaH₂. 1,4-Dioxane (Wako; >99.5%) was distilled over CaH₂ and over LiAlH₄, successively. All reagents except for dichloromethane were stored in brown ampules under dry nitrogen.

Table 2 Cationic polymerization of β -pinene with GaCl₃ in the presence of additives^a

Entry	Additive (ΔH / kJ mol ⁻¹ b; DN ^c)	Time	Conv. (%)	$M_n \times 10^{-3}$	M_w/M_n
1	None	4.3 min	100	7.6	1.74
2	Toluene (7.9; 0.1)	1 min	100	8.0	1.65
3	Mesitylene (8.8; —)	9 min	100	9.7	1.80
4	C ₆ HMe ₅ (10.3; —)	10 min	56	4.7	1.38
5		27 min	100	11.2	1.58
6	C ₆ Me ₆ (10.8; —)	40 min	34	3.8	1.20
7		2 h	100	11.7	1.42
8	Anisole (—; 7.9 ^d)	7 min	50	4.9	2.14
9		13 min	100	8.4	1.66
10	1,4-Dioxane (20.1; 14.8)	24 h	12	2.4	2.81
11	Ethyl acetate (20.8; 17.1)	24 h	8	1.7	3.43

^a[β -pinene]₀ = 0.63 M, [TMPCl]₀ = 4.0 mM, [GaCl₃]₀ = 1.0 mM, [additive]₀ = 0 (entry 1), 10 (entries 10 and 11), or 20 (entries 2–9) mM, in CH₂Cl₂/methylcyclohexane (1/1 v/v) at -78 °C. ^bEnthalpy of interaction with 4-fluorophenol as basicity scale.¹⁸

^cDonor number.²⁸

^dThe donor number of anisole is shown in reference 29, although the book cited as the source does not appear to include the value. On the other hand, the donor number estimated from other methods was reported to be 9 for anisole in reference 30.

Polymerization procedure

Polymerization was conducted under dry nitrogen in a glass tube equipped with a three-way stopcock and dried using a heat gun (Ishizaki, Tokyo, Japan; PJ-206A; the blow temperature was ~450 °C). Dichloromethane, methylcyclohexane, β -pinene, and a TMPCl solution in dichloromethane were added successively into the tube using dry syringes. In another tube, GaCl₃ and an alkylbenzene were mixed in dichloromethane at 0 °C and aged for 1 h. The polymerization was initiated by the addition of the catalyst mixture to the monomer solution, which had been cooled to -78 °C. After a predetermined time, the reaction was terminated by the addition of prechilled methanol that contained a small amount of aqueous ammonia solution (0.1%). The quenched mixture was washed with dilute hydrochloric acid, an aqueous NaOH solution and then water to remove the initiator residues. The volatiles were removed under reduced pressure at 50 °C, and the residue was vacuum dried for more than 3 h at 60 °C to yield a white, rigid polymer. The monomer conversion was determined by gravimetry.

Characterization

The molecular weight distribution (MWD) of the polymers was measured by gel permeation chromatography (GPC) in chloroform at 40 °C with three polystyrene gel columns [Tosoh, Tokyo, Japan; TSKgel G-4000H_{XL}, G-3000H_{XL}, and G-2000H_{XL} (exclusion limit molecular weight = 4 × 10⁵, 6 × 10⁴, and 1 × 10⁴, respectively; bead size = 5 μ m; column size = 7.8 mm I.D. × 300 mm) or TSKgel MultiporeH_{XL}-M × 3 (exclusion limit molecular weight = 2 × 10⁶; bead size = 5 μ m; column size = 7.8 mm I.D. × 300 mm); flow rate = 1.0 mL/min] connected to a Tosoh DP-8020 pump, a CO-8020 column oven, a UV-8020 ultraviolet detector (wavelength: 254 nm), and an RI-8020 refractive index detector. The number-average molecular weight (M_n) and polydispersity ratio [weight-average molecular weight/number-average molecular weight (M_w/M_n)] were calculated from the chromatographs with respect to 16 polystyrene standards (Tosoh; M_n = 577–1.09 × 10⁶, M_w/M_n ≤ 1.1). NMR spectra were recorded using a JEOL JNM-ECA 500 spectrometer (JEOL, Tokyo,

Figure 1 (a) M_n and M_w/M_n for polymerization of β -pinene and (b) molecular weight distribution (MWD) curves for the poly(β -pinene)s obtained using GaCl_3 alone or $\text{GaCl}_3/\text{C}_6\text{Me}_6$: $[\beta\text{-pinene}]_0 = 0.63 \text{ M}$, $[\text{TMPCl}]_0 = 4.0 \text{ mM}$, $[\text{GaCl}_3]_0 = 10 \text{ mM}$, $[\text{C}_6\text{Me}_6] = 0$ or 20 mM in CH_2Cl_2 /methylcyclohexane (1/1 v/v) at -78°C .

Figure 2 ^1H NMR spectrum of the poly(β -pinene) obtained using $\text{GaCl}_3/\text{C}_6\text{Me}_6$ (sample: entry 6 in Table 2; in CDCl_3 at 30°C ; * TMS, grease, and CHCl_3).

Japan; 500 MHz for ^1H and 152 MHz for ^{71}Ga). UV-vis spectra were recorded on a JASCO V-550 UV-vis spectrometer (JASCO, Tokyo, Japan) equipped with an ETC-505 Peltier-type thermostatic cell holder. A quartz cell with an optical path length of 1.0 cm was used.

RESULTS AND DISCUSSION

Cationic polymerization of β -pinene using various Lewis acids

The cationic polymerization of β -pinene was conducted using GaCl_3 , TiCl_4 , and SnCl_4 as the Lewis acid catalyst in conjunction with 2-chloro-2,4,4-trimethylpentane (TMPCl) as the initiator in a solvent mixture of dichloromethane and methyl cyclohexane at -78°C (Table 1). The polymerization was successful with all of the catalysts used, yielding polymers with broad MWDs. The catalytic activity decreased in the order $\text{GaCl}_3 > \text{TiCl}_4 > \text{SnCl}_4$. The molecular weights of the obtained polymers also differed among the catalysts and the highest molecular weights were obtained with GaCl_3 . The lower molecular weights and the broader MWDs of the polymers obtained with TiCl_4 and SnCl_4 compared to those obtained with GaCl_3 were possibly due to more frequent side reactions. On the basis of these results, GaCl_3 was determined to be superior to the other two

chlorides in terms of both activity and controllability. Therefore, the polymerization of β -pinene was subsequently examined using GaCl_3 combined with a variety of alkylbenzenes as additives.

Controlled cationic polymerization of β -pinene with the GaCl_3 /alkylbenzene initiating systems

Toluene, mesitylene, pentamethylbenzene (C_6HMe_5), and hexamethylbenzene (C_6Me_6) increase in basicity in this order; however, they are much less basic than either esters or ethers. These alkylbenzenes were mixed with $GaCl_3$ in dichloromethane at $0^\circ C$ prior to polymerization. The mixture solutions became a yellow to orange color, depending on the compounds used. After aging for 1 h, the mixtures were added to the solutions that contained solvents, a monomer, and a cationogen to initiate polymerization.

When two equivalents of alkylbenzenes were used per GaCl_3 formula unit, the polymerization reactions of β -pinene proceeded smoothly to quantitative conversion (Table 2). The polymerization rates decreased with increasing basicity of the additives. Among the alkylbenzenes used, hexamethylbenzene, a compound with greater basicity than other alkylbenzenes, allowed the most controlled polymerization and produced polymers with narrow MWDs (entries 6 and 7; Figure 1). Pentamethylbenzene, a compound that is slightly less basic than hexamethylbenzene, also induced controlled polymerization to yield polymers with similar molecular weights but with slightly broader MWDs (entries 4 and 5) compared to those obtained with hexamethylbenzene. The controllability was inferior with the less basic compounds toluene (entry 2) and mesitylene (entry 3); however, the molecular weights of the products were slightly greater than those obtained without the use of any additives (entry 1; Figure 1). The reactions were also examined with one equivalent of 1,4-dioxane or ethyl acetate per GaCl_3 formula unit; however, the additives with greater basicity strongly suppressed the polymerization activity, which resulted in very low conversions and ill-defined products (entries 10 and 11). Anisole was not effective (entries 8 and 9) in controlling the reaction, although the phenyl ring has high electron density due to the electron-donating effect induced by the methoxy group. This finding suggests that anisole functioned not as an aromatic compound but rather as an ether. The fast and quantitative reaction, in contrast to the reactions with 1,4-dioxane and ethyl acetate, is attributed to a basicity lower than that of these Lewis bases.

Among the weak Lewis bases examined, hexamethylbenzene was the most appropriate additive for the controlled polymerization of

β -pinene. The M_n -conversion plot (Figure 1a) further indicates that the polymerization was a living reaction when the GaCl₃/hexamethylbenzene initiating system was used. The M_n values increased linearly with increasing monomer conversion, indicating that side reactions such as chain transfer did not occur. In addition, the MWD curves of the obtained polymers were unimodal and shifted to the higher-molecular-weight region, in sharp contrast to the curves of the polymers obtained without the use of any additives (Figure 1b). ¹H NMR analysis also supports the fact that the polymerization proceeded without side reactions and yielded a polymer with a main chain structure resulting from the isomerization mechanism (Figure 2).

To confirm the living nature of the polymerization, a monomer addition experiment was performed with the GaCl₃/hexamethylbenzene initiating system (Figure 3). A fresh feedstock of β -pinene was added when ~80% of the first feedstock was consumed in the

polymerization. The polymerization proceeded smoothly after the β -pinene addition to reach quantitative conversion. The MWD curves of the products shifted toward the higher-molecular-weight region after the addition while retaining their unimodal and narrow shapes (Figure 3b). In addition, the M_n value increased along a straight line (Figure 3a). These results suggest that the polymerization of β -pinene proceeds in a living manner.

Interaction between GaCl₃ and hexamethylbenzene and postulated polymerization mechanisms

In the controlled cationic polymerization of β -pinene using the initiating system with a GaCl₃/hexamethylbenzene combination, the interaction between GaCl₃ and hexamethylbenzene is likely to be responsible for the alteration of the Lewis acidity of GaCl₃. In fact, benzene and mesitylene have been reported to form π -complexes with GaCl₃.¹⁹ In the current study, the solution of GaCl₃ and hexamethylbenzene became orange after being mixed. This orange color resulted from the interaction of the two components, as evidenced by the fact that both GaCl₃ and hexamethylbenzene are colorless.

To examine the interaction in detail, we performed UV-vis spectrometric analyses of solutions containing GaCl₃ and hexamethylbenzene. Figure 4a shows the spectra obtained with different ratios of GaCl₃ and hexamethylbenzene. Absorption peaks appeared at ~270,

Figure 3 Monomer-addition experiments performed in the polymerization of β -pinene: (a) M_n and M_w/M_n for polymerization of β -pinene, and (b) molecular weight distribution (MWD) curves for the poly(β -pinene)s: [β -pinene]₀ = [β -pinene]_{add} = 0.32 M, [TMPCl]₀ = 4.0 mM, [GaCl₃]₀ = 10 mM, [C₆Me₆] = 20 mM in CH₂Cl₂/methylcyclohexane (1/1 v/v) at -78 °C.

Figure 5 ⁷¹Ga NMR spectra of mixtures of GaCl₃ and C₆Me₆: [GaCl₃]₀ = 50 mM, [C₆Me₆] = 0–100 mM in CD₂Cl₂/hexane (3/1 v/v) at 25 °C.

Figure 4 (a) UV-vis absorption spectra and (b) absorbance at 404 nm of mixtures of GaCl₃ and C₆Me₆: [GaCl₃]₀ = 0.25 mM, [C₆Me₆] = 0.13–0.75 mM in CH₂Cl₂/methylcyclohexane (1/1 v/v) at 0 °C.

Scheme 2 Postulated complex formation and polymerization mechanisms with the GaCl₃/C₆Me₆ initiating system (other complexes such as Ga₂Cl₆–hexamethylbenzene may have also formed).

~290, and ~404 nm, and the intensities of these peaks increased with increasing [C₆Me₆]/[GaCl₃] ratios. The plot of the absorbance at 404 nm showed a nonlinear change (Figure 4b), indicating that the interaction between GaCl₃ and hexamethylbenzene was in an equilibrium state. In addition, the absorption saturated when the [C₆Me₆]/[GaCl₃] ratio was greater than ~2, which may indicate that all of the GaCl₃ present formed complexes with C₆Me₆ at ratios greater than ~2.

⁷¹Ga NMR analyses^{19,20} also revealed the nature of the interaction between GaCl₃ and hexamethylbenzene (Figure 5). In CD₂Cl₂/hexane (3/1 v/v), GaCl₃ alone yielded a broad peak at ~220 ppm, indicating that, in the absence of any additives, Ga atoms existed in various forms, such as a monomer, a dimer, a trimer, etc. After being mixed with hexamethylbenzene, the broad peak of GaCl₃ clearly sharpened and shifted downfield. With two equivalents of hexamethylbenzene per GaCl₃ formula unit, a very sharp peak was observed at ~260 ppm, suggesting that the two components interacted and formed a relatively stable, nearly single species.

On the basis of the polymerization behaviors and the UV–vis and ⁷¹Ga NMR analyses, we proposed the polymerization mechanism for GaCl₃/alkylbenzene-initiated reactions shown in Scheme 2. In this mechanism, we propose that, when an alkylbenzene has the appropriate basicity (e.g., hexamethylbenzene), a dimer or a larger cluster of GaCl₃ can dissociate to form a π -complex such as C₆Me₆–GaCl₃ (Scheme 2a). The formation of this complex might also occur between one hexamethylbenzene molecule and a dimer, Ga₂Cl₆. The Lewis acidity of GaCl₃ was moderated by the formation of a complex, which resulted in a suitable dormant–active equilibrium (Scheme 2b). Another possibility is that the alkylbenzene may interact with the propagating carbocation to suppress side reactions, such as β -proton elimination, as suggested by the relative lack of side reactions exhibited by the GaCl₃/alkylbenzene initiator systems.

CONCLUSION

In conclusion, a GaCl₃/alkylbenzene initiating system was demonstrated to successfully induce the controlled cationic polymerization of β -pinene. An alkylbenzene with an appropriate basicity, such as hexamethylbenzene or pentamethylbenzene, was effective in producing well-defined polymers. The complex formation between GaCl₃ and the alkylbenzene, which was confirmed by UV–vis and ⁷¹Ga NMR

analyses, was most likely to be responsible for the controlled polymerization. Because alkylbenzenes have much lower basicities than either esters or ethers (which are additives that are suitable for the living cationic polymerization of more reactive monomers such as vinyl ethers), the present initiating system is promising for increasing the level of control that is possible for cationic polymerization reactions of less reactive monomers such as alkenes.

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