Cationic Polymerization of β-Pinene with the AlCl₃/SbCl₃ Binary Catalyst: Comparison with α-Pinene Polymerization

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SYNOPSIS

The polymerization of β-pinene with the AlCl₃/SbCl₃ binary catalyst was investigated in toluene at −40°C and was compared with that of α-pinene. The polymerization of β-pinene with AlCl₃ alone was very rapid and retarded on addition of SbCl₃, in sharp contrast to that of α-pinene where added SbCl₃ remarkably accelerated it to give relatively high molecular weight oligomers. Attempted copolymerization of the two isomers with the binary catalyst, in turn, induced their parallel homopolymerizations, indicating that the copolymerization was difficult due to the large difference in reactivity. The homopolymerizations with AlCl₃/SbCl₃ were not seriously affected by a sterically hindered base, 2,6-di-tert-butyl-4-methylpyridine (DTBMP); the initiating species, therefore, would be different in nature from a proton. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

α- and β-Pinenes are the main constituents of natural turpentine oil, and their polymers are commercially available as hydrocarbon resins.[1-3] When treated with Lewis acids such as AlCl₃, β-pinene is readily polymerized to relatively high molecular weight polymers ($\bar{M}_n \sim 2000$) via isomerization of the growing cationic species (Eq. 1).[4] On the other hand, the polymerization of α-pinene is extremely slow and results in only lower oligomers. The low reactivity of α-pinene is due to the lack of the highly reactive exo-methylene double bond that exists in the β-isomer.[1]
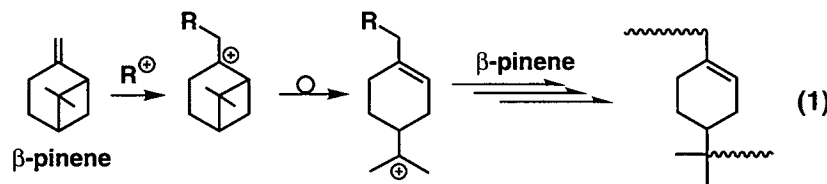
We have recently found that the addition of SbCl₃ to aluminum halide catalysts like AlCl₃ and AlBr₃ accelerates the polymerization of α-pinene to give relatively high molecular weight polymers ($\bar{M}_n \sim 1500$).[5-8] This polymerization may involve two types of the isomerized growing-ends (Eq. 2): one via the opening of one of the monomer's fused and strained cyclobutane ring and the other via a Meerwein-type isomerization. The main chain of the poly(α-pinene) thus obtained consists of two

repeat units: one of which is similar to that of poly(β-pinene), and the other is a norbornane-like structure. It has been revealed that the former repeat unit is more favored in the poly(α-pinene) obtained with the $AlCl_3/SbCl_3$ system than with

$AlCl_3$ alone.[7] Such effects of $SbCl_3$ have been considered due to the formation of new initiating and/or propagating species generated from $AlCl_3$ and $SbCl_3$, but the nature has not been clarified yet.

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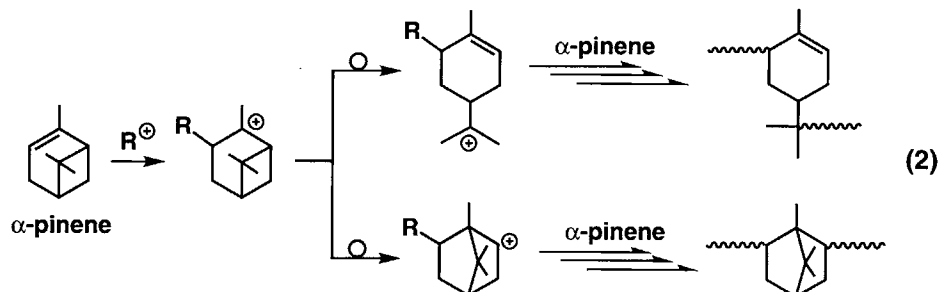
In this study, the cationic polymerization of β-pinene with the $AlCl_3/SbCl_3$ binary catalyst was investigated and compared with that of α-pinene in terms of the effects of $SbCl_3$ on the polymerization rate, the products' molecular weights, and molecular weight distributions (MWDs). Furthermore, the efficient polymerization of α-pinene with $AlCl_3/SbCl_3$ led us to examine the possibility of copolymerization of α- and β-pinenes with the binary catalyst. The copolymerization has been considered difficult because of the absence of reactive catalysts toward α-pinene polymerizations and the large difference in the reactivity of the double bonds in the two pinenes. Finally, to elucidate the initiating species in the binary catalyst-mediated polymerization, we have investigated the polymerizations of α- and β-pinenes in the presence of a sterically hindered base, 2,6-di-tert-butyl-4-methylpyridine, which interacts with protons preferentially in organic reactions[9,10] and cationic polymerizations.[11]

RESULTS AND DISCUSSION

Homopolymerization of β-Pinene with $AlCl_3$/$SbCl_3$: Comparison with the α-Pinene Polymerization

As reported in our previous papers,[5–8] a mixture of $AlCl_3$ and $SbCl_3$ leads to an efficient polymerization of α-pinene in toluene at $-15°C$. We then employed this binary catalyst for polymerization of β-pinene in toluene at $-40°C$. Because β-pinene is cationically much more reactive than α-pinene,[4] the polymerization was attempted at the lower temperature, at

the $AlCl_3$ and $SbCl_3$ concentrations optimal for the polymerization of α-pinene at $-15°C$ ([$AlCl_3]_0$ = 42.5 mM, [$SbCl_3]_0$ = 21.3 mM; Sb/Al = 0.50).[6]

As shown in Figure 1, the polymerization of β-pinene with $AlCl_3$ alone was very rapid and almost instantaneous both in the absence and presence of $SbCl_3$. Under the same conditions, in contrast, the polymerization of α-pinene with $AlCl_3$ alone at $-15°C$ was extremely slow, whereas the $AlCl_3/SbCl_3$ binary catalyst led to an efficient polymerization. These polymerizations were, however, still slower than that of β-pinene even in the presence of $SbCl_3$.

Figure 2 compares the molecular weights and MWDs of the polymers obtained from the two isomers. α-Pinene gave low oligomers with $AlCl_3$ [Fig. 2(A)] and higher oligomers with $AlCl_3/SbCl_3$ [Fig. 2(B)]. On the other hand, for β-pinene, there were
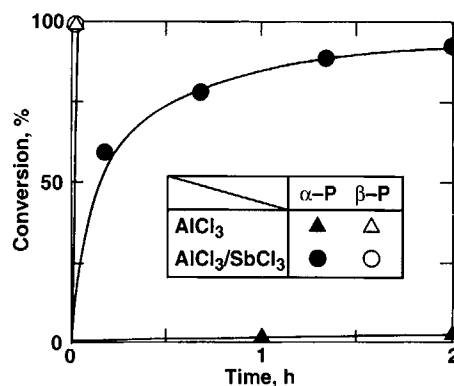
Figure 1 Time-conversion curves for the homopolymerization of α-pinene (▲, ●) and β-pinene (△, ○) with $AlCl_3$ and $AlCl_3/SbCl_3$ in toluene at $-40°C$: [M]$_0$ = 1.8M; [$AlCl_3]_0$ = 42.5 mM; [$SbCl_3]_0$ = 21.3 mM.
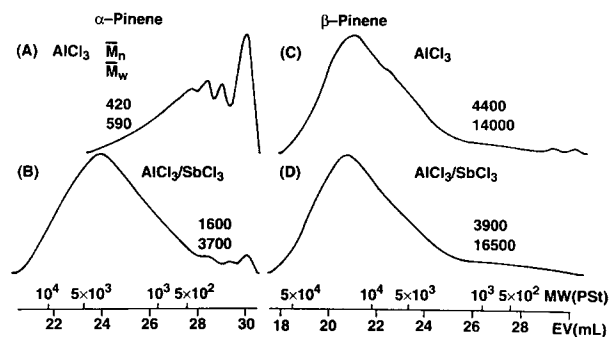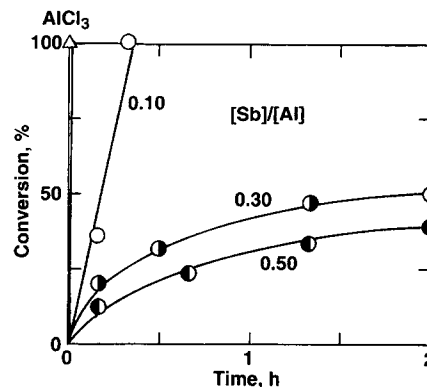
Figure 2 $\bar{M}_n$, $\bar{M}_w$, and MWD curves of the polymers obtained in the same experiments as for Figure 1: poly(α-pinene) with (A) $AlCl_3$ and (B) $AlCl_3/SbCl_3$; poly(β-pinene) with (C) $AlCl_3$ and (D) $AlCl_3/SbCl_3$.

Figure 3 Time-conversion curves for the polymerization of β-pinene with $AlCl_3/SbCl_3$ in toluene at $-40°C$: $[M]_0 = 1.8M$; $[AlCl_3]_0 = 10.0$ mM. Sb/Al: ($\triangle$) 0; ($\bigcirc$) 0.10; ($\ominus$) 0.30; ($\oplus$) 0.50.

no such remarkable differences in molecular weight and MWD between the products with $AlCl_3$ and $AlCl_3/SbCl_3$ systems, where the $\bar{M}_n$ values were both around 4000 [Figs. 2(C) and (D)].

Under these conditions, the $AlCl_3$-mediated polymerizations of β-pinene were too fast, which might mask effects of $SbCl_3$. Thus, the concentration of $AlCl_3$ was decreased to 10.0 mM, where effects of the $SbCl_3$ concentration were investigated (Fig. 3; Sb/Al = 0-0.5 mol ratio). The polymerization with $AlCl_3$ alone was still very fast; but, interestingly, the additional use of $SbCl_3$ decreased the polymerization rate, in contrast to the acceleration for α-pinene.[6] The higher the Sb/Al ratio, the slower the polymerization.

Figure 4 shows the molecular weights and MWDs of the polymers obtained at varying Sb/Al ratios (the same experiments as for Fig. 3). The molecular weights with $AlCl_3/SbCl_3$ [Figs. 4(B)-(D)] were lower than that with $AlCl_3$ alone [Fig. 4(A)].

The different effects of the $SbCl_3$ concentrations for β-pinene and α-pinene suggest that the initiating and/or propagating species generated with the $AlCl_3/SbCl_3$ binary catalyst is different from that with $AlCl_3$ alone. $AlCl_3$ induces conventional cationic polymerizations of β-pinene, as well as usual vinyl monomers,[1-4] and it is retarded by the presence of $SbCl_3$. This is probably due to the suppression of the $AlCl_3$-induced polymerization by $SbCl_3$, which may generate other growing species by the interaction with $AlCl_3$. The active species generated from the $AlCl_3/SbCl_3$ binary catalyst is less reactive than that from $AlCl_3$. In contrast, for α-pinene, $AlCl_3$, for example, gives oligomers only in low yield and is much less reactive than the $AlCl_3/SbCl_3$ binary catalyst.

Copolymerization of α- and β-Pinenes with $AlCl_3/SbCl_3$

These results suggest the possibility of copolymerization of α- and β-pinenes with $AlCl_3/SbCl_3$ because $SbCl_3$ retards the very fast polymerization of β-pinene with $AlCl_3$, whereas it accelerates the extremely slow polymerization of α-pinene. The copolymeri-
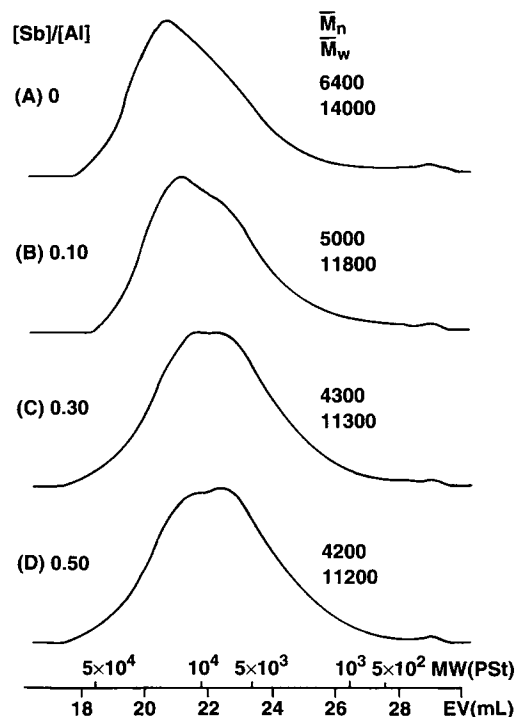
Figure 4 $\bar{M}_n$, $\bar{M}_w$, and MWD curves of the poly(β-pinene) obtained in the same experiments as for Figure 1. Sb/Al: (A) 0; (B) 0.10; (C) 0.30; (D) 0.50.

zation of the two pinenes has been considered difficult because of the great difference in their reactivity toward conventional cationic catalysts.[1]

Thus, an equimolar mixture of α- and β-pinenes was polymerized with $AlCl_3/SbCl_3$ under varying conditions (Figs. 5 and 6). The Sb/Al ratio was fixed at 0.50 because, at this ratio, the homopolymerization was the slowest for β-pinene but the fastest for α-pinene.[6]

With the conditions shown in Figure 5 (open symbols; [α-pinene]$_0$ = [β-pinene]$_0$ = 1.8M; [AlCl$_3$] = 21.3 mM; in toluene at −40°C), the polymerization of β-pinene occurred smoothly and reached 60% in 2 h, but α-pinene polymerization was hardly observed. The MWD of the products [Fig. 6(A)] was similar to that of the homopolymers of β-pinene with $AlCl_3/SbCl_3$ (cf. Fig. 4).

At a higher temperature (−15°C), both α- and β-pinenes consumed simultaneously at very high rates (Figure 5; filled symbols). However, the obtained polymers showed very broad MWDs, which seem to consist of two populations with different molecular weights [MW(peak) ∼ 10,000 and ∼ 4000] [Fig. 6(B)]. These two fractions apparently correspond to the products in the $AlCl_3/SbCl_3$-catalyzed homopolymerizations of β-pinene [cf. Fig. 4(D)] and α-pinene [cf. Fig. 2(B)], respectively. Namely, the products most likely consist of the two homopolymers.

Polymerizations with a lower catalyst concentration ([AlCl$_3$]$_0$ = 10.6 mM) were also attempted. While the polymerization of β-pinene was slightly retarded, α-pinene was hardly polymerized; and homopolymers of β-pinene alone were obtained.
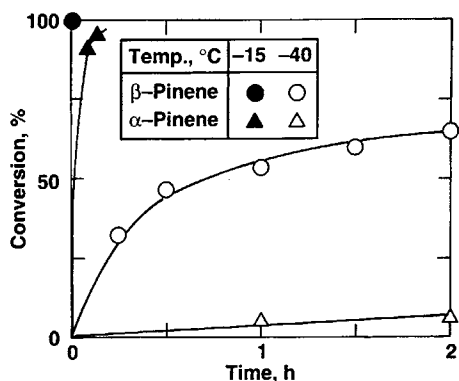
Figure 5 Time-conversion curves for the copolymerization of α-pinene (△, ▲) and β-pinene (○, ●) with AlCl$_3$/SbCl$_3$ in toluene at −40 and −15°C: [α-pinene]$_0$ = [β-pinene]$_0$ = 1.8M (−40°C), 0.90M (−15°C); [AlCl$_3$]$_0$ = 21.3 mM; [SbCl$_3$]$_0$ = 10.6 mM.
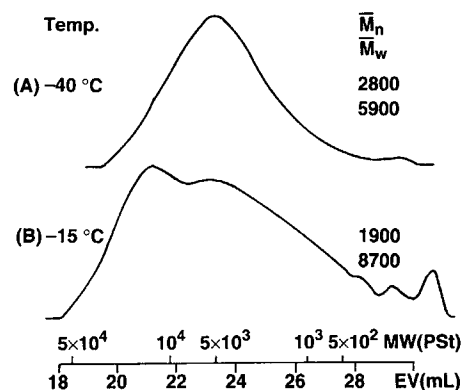
Figure 6 $\bar{M}_n$, $\bar{M}_w$, and MWD curves of the polymers obtained in the same experiments as for Figure 5: (A) −40°C; (B) −15°C.

These results indicate that the $AlCl_3/SbCl_3$ binary catalyst induced polymerizations of both α- and β-pinenes but that β-pinene is still more reactive toward the binary catalyst than α-pinene. Thus, the copolymerization of the two monomers is difficult even with $AlCl_3/SbCl_3$.

Polymerization in the Presence of 2,6-Di-*tert*-butyl-4-methylpyridine: Initiating Species in the AlCl₃/SbCl₃-Mediated Polymerization

In general, cationic polymerizations with Friedel-Crafts acids like AlCl$_3$ are initiated by the proton generated from adventitious water and the Lewis acids.[1-3] To discuss the nature of initiating species generated from AlCl$_3$ and AlCl$_3$/SbCl$_3$, the polymerizations of α- and β-pinenes were carried out in the presence of a sterically hindered base, 2,6-di-*tert*-butyl-4-methylpyridine (DTBMP), which is considered to interact with proton preferentially and thereby suppresses its initiation.[9-11]

Polymerization of α-Pinene

Figure 7(A) shows the polymerization of α-pinene with AlCl$_3$/SbCl$_3$ at varying concentrations of DTBMP ([DTBMP]$_0$ = 0–10.0 mM) in toluene at −40°C. In the presence of 5.0 mM of DTBMP (half-filled circles), the reaction proceeded almost at the same rate as in its absence (open circles). Although a higher concentration of DTBMP (10.0 mM; filled circles) decelerated the polymerization, almost quantitative polymerizations occurred. The $\bar{M}_n$ and MWDs of the obtained polymers were almost independent of the concentrations of DTBMP.

Therefore, the effects of DTBMP were very small in the polymerization of α-pinene with AlCl$_3$/SbCl$_3$.
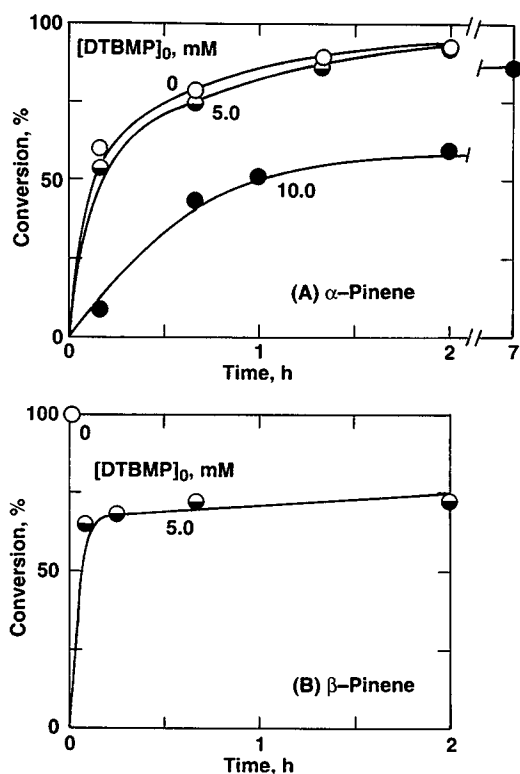
Figure 7 Effects of DTBMP on the homopolymerization of (A) α-pinene and (B) β-pinene with $AlCl_3/SbCl_3$ in toluene at $-40°C$: $[M]_0$ = $1.8M$; $[AlCl_3]_0$ = 42.5 mM (α-pinene), 10.0 mM (β-pinene); $[SbCl_3]_0$ = 21.3 mM (α-pinene), 10.0 mM (β-pinene); $[DTBMP]_0$ = (○) 0, (◓) 5.0, (●) 10.0 mM.

These results suggest that the initiating species is not a proton but another cationic species that cannot be trapped by DTBMP. This is consistent with the fact that the polymerization is not accelerated by the addition of protonic acids.[7]

Polymerization of β-Pinene

Figure 7(B) shows effects of DTBMP on the polymerization of β-pinene with $AlCl_3/SbCl_3$ in toluene at $-40°C$. For β-pinene, the initial rate was still very high, even in the presence DTBMP (Fig. 10; open circles), although the reaction seemed to stop around 70% conversion. These data indicate that the initiating species in the β-pinene polymerization is not exclusively a proton, as with those from α-pinene.

In conclusion, this study has shown that the $AlCl_3/SbCl_3$ binary catalyst effectively induces the cationic polymerizations of not only α-pinene but also β-pinene. However, the addition of $SbCl_3$ retarded the polymerization of β-pinene, which is in sharp contrast to the fact that the same additive

accelerates the α-pinene polymerization. Copolymerization of α- and β-pinenes was difficult even with the binary catalyst, although the catalyst is effective in polymerizations of both isomers. The initiating species in the $AlCl_3/SbCl_3$-mediated polymerizations of both pinenes was suggested to differ in nature from a proton.

EXPERIMENTAL

Materials

(−)-α-pinene (Tokyo Kasei; purity > 98%) and (−)-β-pinene (Wako Chemicals; purity > 97%) were distilled under reduced pressure over calcium hydride before use. $AlCl_3$, $SbCl_3$ (both Aldrich; purity > 99.99%), and 2,6-di-*tert*-butyl-4-methylpyridine (Aldrich; purity > 98%) were used as received. Toluene (solvent) and benzene (an internal standard for gas chromatography) were washed with 30% sulfuric acid, 10% aqueous sodium hydroxide, and then water, dried overnight over calcium chloride, and distilled twice over calcium hydride before use.

Polymerization Procedures

Polymerization was carried out under dry nitrogen in a baked glass flask equipped with a three-way stopcock and a magnetic stirring bar. The reaction was initiated by adding, via dry syringes, solutions of monomer and $SbCl_3$ in toluene sequentially in this order into $AlCl_3$ dispersed in toluene under vigorous magnetic stirring. The polymerization was quenched with precooled methanol. Monomer conversion was determined from its residual concentration measured by gas chromatography with benzene as an internal standard.

Measurement

The MWD of polymers was measured by gel-permeation chromatography (GPC) in chloroform at room temperature on a Jasco Trirotar-V chromatograph equipped with three polystyrene gel columns (columns: Shodex K-802, K-803, and K-804). The $\bar{M}_n$ and $\bar{M}_w$ of the polymers were calculated from GPC eluograms on the basis of a polystyrene calibration.

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