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A Bio-Based Tackifier Synthesized by Room-Temperature Cationic Copolymerization of Isobutene and β -Pinene

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Abstract: Whereas the cationic homopolymerization of β -pinene and isobutene (IB) have been extensively studied, their copolymerization is still very scarce, and the conditions under which copolymerization can occur are limited to extremely low temperatures. Moreover, the application of the copolymer has not been reported. Here, a series of room-temperature copolymerizations of β -pinene and IB, using group 13 compounds as catalysts, were conducted. The copolymerizations yielded a low molecular weight ($M_n \sim 10^3$) and a narrow molecular weight distribution ($M_w/M_n < 2.0$) copolymer, with a satisfactory yield at various comonomer feeds, and their glass transition temperature was predictable from the comonomer composition. Furthermore, the tackifying property of the obtained copolymer was investigated using a 180° peel adhesion test. A blend polymer of the copolymer and a styrene-isoprene triblock copolymer showed a high peeling force (0.58 ± 0.14 N/10 mm) and a glass transition temperature low enough for its application as a pressure-sensitive adhesive.

Keywords: statistical cationic polymerization; carbocationic polymerization; aluminum etherate



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1. Introduction

Cationic polymerization allows the polymerization of a wide range of hydrocarbon monomers that generate tertiary cations. Currently, β -pinene has been attracting significant attention, from the standpoint of environmental sustainability, as a plant-derived hydrocarbon monomer for cationic polymerization [1–3]. Its alicyclic structure enables many applications, including optoelectronics, with a high glass transition temperature, or tackifier materials, by blending with a low-glass transition temperature rubber material.

Many catalytic systems for the cationic polymerization of β -pinene have been studied thus far [4–14]. For example, living polymerization was achieved using a titanium system with ammonium chloride additive [4]. Later, a slightly modified titanium system was reported to promote quasi-living polymerization at ambient temperatures [5]. As for group 13 compounds, aluminum catalysts tend to yield high molecular weight poly(β -pinene), especially when a difunctional initiator was applied [6–8]. On the other hand, boron-based catalysts like BCl_3 and $\text{B}(\text{C}_6\text{F}_5)_3$ are known to yield low molecular weight poly(β -pinene) because of frequent β -proton elimination [9–11]. For the low-molecular-weight poly(β -pinene), the adhesive properties of blend polymers with the styrene-isoprene block copolymer or polyethylene are investigated [10,15].

The physical properties of β -pinene-based polymers can be greatly modified by copolymerizing β -pinene with other hydrocarbon monomers. In cationic polymerizations, isobutene (IB) may be the most representative candidate for the comonomer because the cationic polymerization of IB has long been industrialized since its earliest stages [16], and polyisobutene has a much lower glass transition temperature (T_g) than poly(β -pinene). Living homopolymerization of IB was achieved by using BCl_3 or titanium compounds, and their polymerization kinetics and solvent, temperature, and additive effects have been

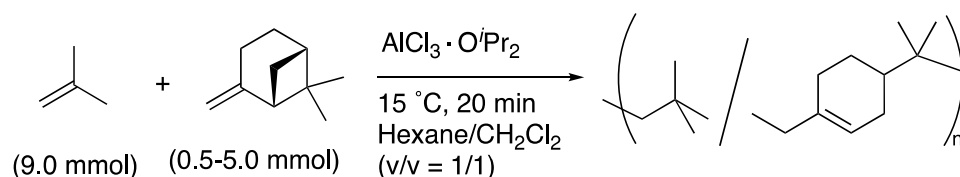
thoroughly investigated [17–21]. Moreover, selectivity in the initiation as well as termination reaction, along with β -proton abstraction in the polymerization using an aluminum halide-based catalyst system, which is widely applied for industrial manufacturing, is vigorously studied [22,23]. The addition of dialkyl ether enabled the yielding of low molecular weight polyisobutene, with vinylidene end groups over 90 mol% [24–30]. The main characteristic of this catalyst system is that the operation temperature is relatively high (-30 – 20 °C). Selective β -proton abstraction was achieved by adding ether as a free base in this system, and the final molecular weight is determined by the amount of ether included. The $B(C_6F_5)_3$ -based initiating system, which yields a low molecular weight polymer in the polymerization of β -pinene, enables the synthesis of high molecular weight polymers at elevated temperatures in the presence of long chain carboxylic acids [31].

While the cationic homopolymerization of these two monomers has been extensively studied, information regarding the copolymerization of β -pinene and IB is still very limited. In the very early stages of the research, Ott claimed that copolymerization occurs by using BF_3 or $AlCl_3$ as a catalyst [32], although the precise structure has not been analyzed. Later, Kennedy and Chou reported the investigation of the monomer reactivity ratio of this cationic copolymerization using various Lewis acids, including $EtAlCl_2$ [33]. A broad range of comonomer compositions have been successfully achieved at very low temperatures, around -100 °C. Here, a copolymer with a broad molecular weight distribution was obtained, and more β -pinene in the feed sharply decreased the molecular weight of the copolymer. On the other hand, the control over the molecular weights and comonomer compositions of the β -pinene/IB copolymers was achieved using a 1-phenylethyl chloride/ $TiCl_n(O^iPr)_{4-n}/nBu_4NCl$ initiating system in CH_2Cl_2 at -40 °C [34]. However, these copolymerizations applied extremely low temperatures to suppress various termination and chain transfer reactions, which require high energy consumption. For the synthesis of a low molecular weight copolymer, operating the process at close to room temperature is adequate and preferable. Moreover, polymerization in hydrocarbon rather than chlorinated solvents is preferred, in view of safety and environmental issues.

Therefore, in this study, we present the room-temperature cationic copolymerization of β -pinene and IB. Various group 13 catalyst systems, including $B(C_6F_5)_3$ and $AlCl_3$ ·dialkyl ether, were investigated, yielding low-molecular-weight copolymers with various compositions at room temperature. Furthermore, the tackifying property of the obtained copolymer was investigated. A blend polymer of the copolymer and styrene-isoprene triblock copolymer showed high peeling force and a very low glass transition temperature.

2. Results and Discussion

First, a series of room-temperature copolymerizations of β -pinene and IB, using $AlCl_3 \cdot O^iPr_2$ with various initial feed ratios, was conducted (Scheme 1, Table 1). This system is known to yield low molecular weight polyisobutene, with high activity. The polymerization is initiated by the proton generated from $AlCl_3$ and adventitious water in solution [35]. All the polymerizations yielded low molecular weight and narrow molecular weight distribution copolymers, with a satisfactory yield. Polymerization with a lower β -pinene feed tended to yield a highly fluid polymer, which is difficult to correct and may cause a lowering of the yield.



Scheme 1. Cationic copolymerization of isobutene (IB) and various β -pinene feeds using $AlCl_3 \cdot O^iPr_2$ catalyst.

Table 1. Properties of IB/ β -pinene copolymer obtained from the $\text{AlCl}_3\cdot\text{O}^i\text{Pr}_2$ catalyst at ambient temperature.

Run	Catalyst (mmol)	Pinene Feed (mmol)	Yield (g)	Yield (wt%)	β -Pinene Incorp. ^a (mol%)	M_n ^b	M_w/M_n ^b	T_g ^c (°C)
1	0.20	0.50	0.23	40	3	1100	1.4	−67
2	0.20	1.0	0.28	44	13	1000	1.4	−39
3 ^d	0.20	1.0	0.29	45	25	1000	1.3	−17
4	0.20	2.0	0.37	48	24	1100	1.5	−13
5	0.20	3.0	0.53	58	37	1400	2.0	10
6	0.10	3.0	0.42	46	42	1400	2.0	13
7	0.05	3.0	0.33	36	43	1200	1.7	7
8 ^e	0.20	3.0	0.44	48	41	1400	2.0	14
9 ^f	0.20	3.0	0.47	52	38	1300	1.9	18
10	0.20	5.0	0.83	70	51	1700	1.7	27
11	0.20	5.0	0.57	84	100	8100	2.1	51

Polymerization condition [IB] = 9.0 mmol, solvent = 20 mL (hexane/ CH_2Cl_2 = 1:1), temperature = 15 °C, time = 20 min. ^a Determined by ^1H NMR. ^b Estimated by GPC, based on polystyrene standards. ^c Determined by DSC. ^d Solvent = hexane. ^e Time = 5 min. ^f Time = 10 min.

A representative ^1H NMR spectrum of the copolymer, which was obtained from Run 4, is shown in Figure 1. According to the previously reported research [33,34], β -pinene generally polymerizes in an isomerization mechanism, exhibiting a cyclohexenyl main chain in the cationic polymerization. Indeed, the spectrum showed typical signals of an olefinic proton in the cyclohexene unit at 5.2–5.5 ppm. Therefore, the amounts of β -pinene in the copolymer were calculated using ^1H NMR, according to the following Equation (1) [34]:

$$\beta\text{-pinene incorp. (mol \%)} = 800 O / (A - 7O) \quad (1)$$

where O is the integral ratio of the olefinic signals at 5.2–5.5 ppm, and A is the integral ratio of the remaining signals assigned to all the other aliphatic protons. The incorporation ratio increased constantly when the initial feed of β -pinene increased (Runs 1, 2, 4, 5, and 10). Here, the comonomer composition of the polymer may change along with the monomer consumption. However, considering that the sole glass transition temperature (T_g) was observed for all the copolymers, and that the value exhibits a linear relationship between β -pinene incorporation, with an intercept value which is the same as that of poly(isobutene) [36] in a broad range (Figure 2), these copolymers have an almost statistical structure, which obeys a Markovian model, similar to the results of the previous example [33]. The gradual increase in the molecular weight (M_n = 1000 to 1700) is probably due to the increase in the β -pinene (M_w = 136) incorporation ratio toward isobutene (M_w = 56). In the previous literature, the chemical shift of the signals assigned to the geminal dimethyl group in the β -pinene unit changes slightly, in accordance with the adjacent comonomer unit in the polymer chain [34], but the evaluation of the average block length of each comonomer from the integral ratio of these signals was not possible because of the severe overlap of signals.

In isobutene polymerization, various termination mechanisms involving β -proton elimination yield various olefinic chain ends. In the obtained copolymers, a couple of singlet signals are observed at 4.85 and 4.63 ppm, which are assigned to the *exo*-olefinic chain end, provided by the direct β -proton elimination of the isobutene chain end (*exo*-IB in Figure 3). An *endo*-olefinic proton at 5.15 ppm, which is another product of the β -proton elimination, was overlapped with the olefinic peak of the β -pinene unit. Additionally, a methylene signal at 2.85 ppm can be assigned to that of the tetra-substituted olefin chain end (tetra-IB, in Figure 3), which is obtained by successive proton and methide rearrangement and chain scission [35]. In the β -pinene rich copolymer (Run 10 and 11, Figures S9 and S10),

a signal at 4.71 ppm is also observed, which is assigned to a vinylidene chain end derived from the β -pinene unit.

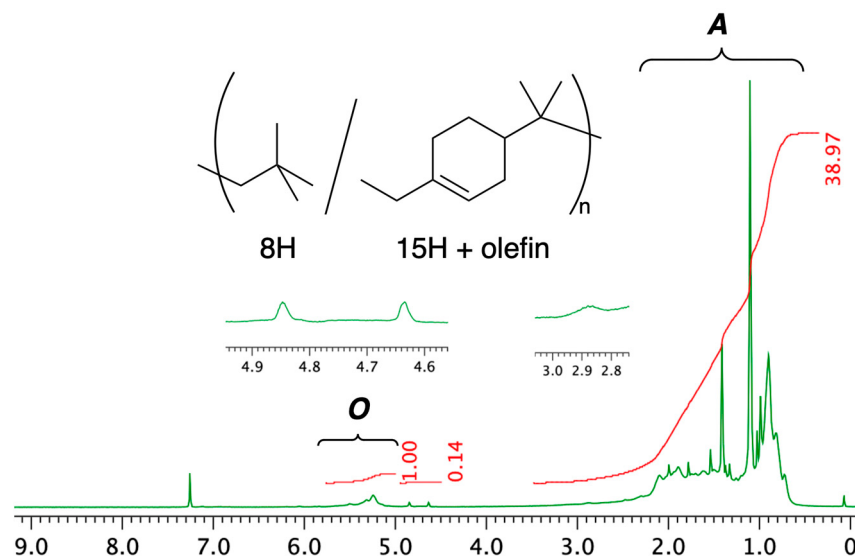


Figure 1. ^1H NMR spectrum of the IB/ β -pinene copolymer obtained with the $\text{AlCl}_3\cdot\text{O}^i\text{Pr}_2$ catalyst (Run 4, in CDCl_3 , 500 MHz).

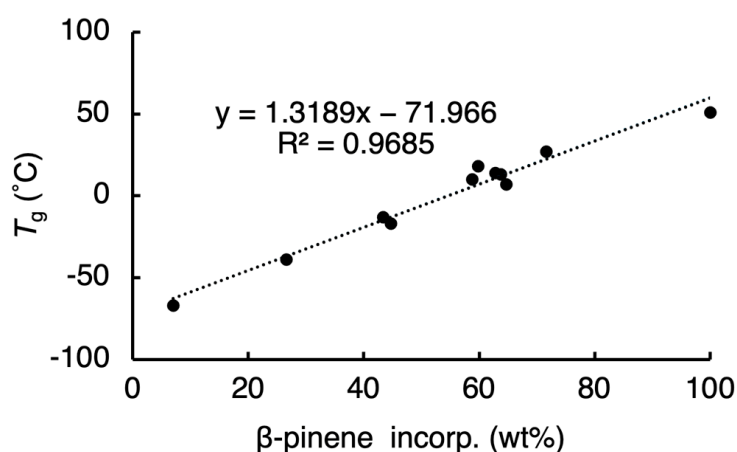


Figure 2. Relationship between β -pinene incorporation and T_g of the copolymer obtained in Table 1.

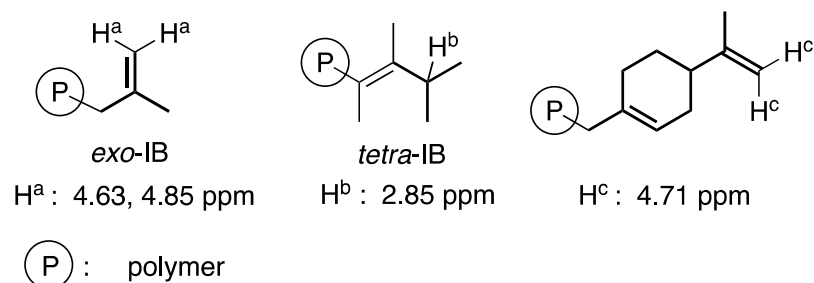


Figure 3. Chain-end structure of the isobutene/ β -pinene copolymer, assigned by ^1H NMR.

The integral ratio of these olefinic chain end peaks toward the main chain signals was much lower than the amount of the chain end estimated from the molecular weight, indicating other types of chain terminations. The other possible end groups, such as *endo*- or trisubstituted olefinic signals, were not observed in ^1H NMR because these signals were overlapped with that of the olefinic peak of β -pinene.

In the ^{13}C NMR spectrum of the copolymer (Figure 4 and Figure S14), a series of signals assigned to the methylene carbons of the isobutene unit was observed at 53–60 ppm ($\text{C}^1\text{--}\text{C}^5$) [37]. These signals show the presence of three and two consecutive isobutene units at the initiating and terminating chain end, respectively, assuming that the polymerization initiated from a proton, which is generated from Lewis acids and residual water in the polymerization system, and terminated with β -proton elimination, yielding *exo*-olefin. In the olefinic region, two characteristic signals at 144 and 114 ppm (C^6 and C^7), which are assigned to the *exo*-olefin chain end, and two broad signals (C^8 and C^9) were observed. C^8 can be assigned as a quaternary centered carbon of the cyclohexenyl structure derived from the β -pinene unit [7,10] as well as a CH-carbon in the *endo*-olefin chain end of the isobutene unit. Therefore, the presence of a DEPT 90 signal in this region shows the presence of an *endo*-olefin chain end. C^9 can be assigned as a CH-carbon of the cyclohexenyl structure of the β -pinene unit, the carbons of the tetrasubstituted olefinic chain end from the β -pinene unit, and the quaternary centered carbon of the *endo*-olefin chain end of the isobutene unit, although the presence of a tetrasubstituted olefin chain end was not fully confirmed. From these NMR analyses, it was shown that frequent β -proton elimination from both isobutene and β -pinene would yield a low molecular weight, narrow molecular weight distribution polymer in the copolymerization using AlCl_3 etherate.

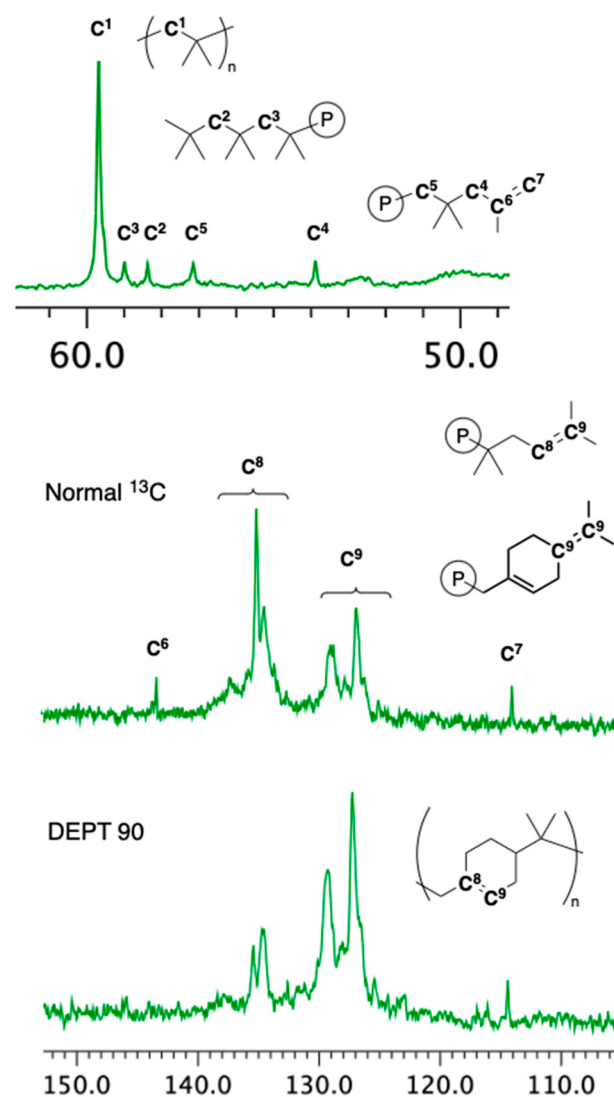


Figure 4. An abstract of the olefinic and methylene region in the ^{13}C NMR spectrum of the IB/ β -pinene copolymer (Run 4, in CDCl_3 , 125 MHz).

An APCI-MS analysis of the obtained polymer showed the presence of several series of polyisobutene sequences, with a different number of poly(β -pinene) sequences (Figure 5). None of the assigned peaks possess chain end groups, which indicates that the polymerization was initiated from the proton generated by a Lewis acid catalyst and the residual water and was terminated by β -proton elimination, as indicated by NMR analysis.

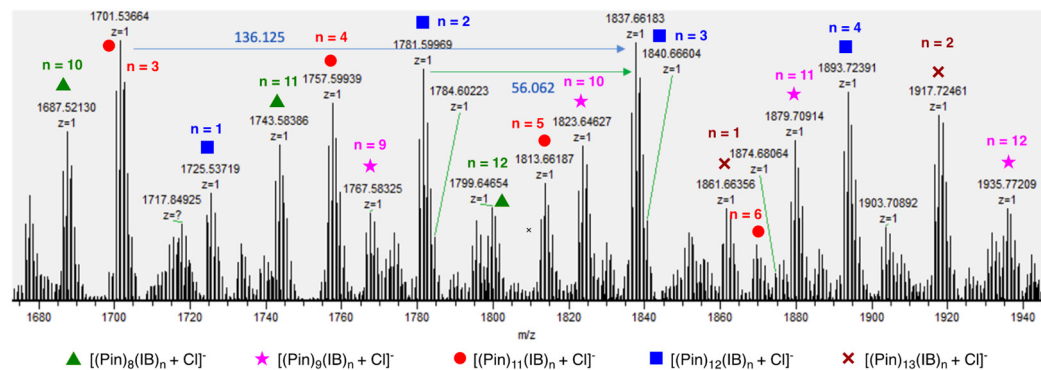


Figure 5. Assignment of peaks in the APCI-MS spectrum of the copolymer (Run 10).

These copolymerizations are mainly conducted in a hexane/ CH_2Cl_2 mixed solvent because the $\text{AlCl}_3 \cdot \text{O}^i\text{Pr}_2$ complex is only soluble in CH_2Cl_2 . The use of 100% hexane (Run 3) instead of mixed solvent (Run 2) slightly increased the incorporation of β -pinene, although the average molecular weights (M_n) remained unchanged. The catalyst loading can be decreased from 200 μmol to 50 μmol , with a slight decrease in the polymer yield, maintaining the M_n and T_g of the copolymer (Runs 5 and 7). We have also attempted to reveal a time-course for the polymerization, but the polymer yield became almost constant within 5 min (Runs 8 and 9).

IB/ β -pinene copolymerization at room temperature, using other Lewis acids, was also attempted (Table 2). In isobutene homopolymerization using AlCl_3 , the effect of ether coordinating with aluminum on the polymerization behavior has been reported, especially regarding the chain-end structure [38]. Moreover, in β -pinene homopolymerization using AlCl_3 , lower electron-donating ether tends to yield a higher molecular weight polymer with high activity, probably because the β -proton abstraction from the propagating chain end is less frequent [7]. Therefore, we tried Bu_2O ($\text{pK}_a = -5.4$) and Et_2O ($\text{pK}_a = -3.6$) as electron donors of AlCl_3 , which possess either weaker or stronger basicity than $i\text{Pr}_2\text{O}$ ($\text{pK}_a = -4.3$), respectively. However, in terms of molecular weight, yield, and β -pinene incorporation, these ethers yielded nearly the same results (Runs 5, 12, 13). $\text{B}(\text{C}_6\text{F}_5)_3$, a catalyst effective for producing low molecular poly(β -pinene) at ambient temperatures, yielded a copolymer with a broader molecular weight distribution ($M_w/M_n = 3.4$) with lower yield, although high β -pinene incorporation was achieved (Run 14). In the ^1H NMR spectrum of the copolymer, no vinylidene chain end signals, which were observed around 4.6–4.8 ppm in the copolymers obtained from AlCl_3 -ether complex catalysts, were observed. This result indicated that the β -proton abstraction from the isobutene chain end takes place with the least frequency. The previous results showed that ultrahigh molecular weight polyisobutene can be obtained using the same catalyst system, supporting this finding [31]. Although we cannot determine the precise chain end structure, β -proton abstraction yielding tetrasubstituted olefin from the β -pinene unit would be the main pathway of the termination reaction in this copolymerization because the same termination is observed in the homopolymerization of β -pinene using the same catalyst system [10]. Surprisingly, $\text{Ti}(\text{O}^i\text{Pr})\text{Cl}_3$, a catalyst promoting the living copolymerization of isobutene and β -pinene, yielded only a tiny amount of copolymer at room temperature, without an initiator (Run 15), although a similar system using $\text{H}_2\text{O}/\text{TiCl}_4/\text{alcohol}$ can promote the cationic polymerization of isobutene at low temperatures [39]. In this reaction, the generation of an oligomer with a very small molecular weight, which cannot be precipitated, is indicated. Therefore, among various conventional Lewis acids effective for cationic

polymerization, the ether adducts of AlCl_3 showed a superior polymerization ability in terms of high operating temperature, good comonomer composition control, and narrowing molecular weight distribution.

Table 2. Catalyst effect on the IB/ β -pinene copolymerization at room temperature.

Run	Catalyst (mmol)	Yield (g)	β -pinene incorp. ^a (mmol)	M_n ^b	M_w/M_n ^b	T_g ^c (°C)
5	$\text{AlCl}_3 \cdot \text{O}^i\text{Pr}_2$	0.53	36	1400	2.0	10
12	$\text{AlCl}_3 \cdot \text{OBu}_2$	0.52	33	1100	1.9	−6
13	$\text{AlCl}_3 \cdot \text{OEt}_2$	0.59	41	1200	1.9	7
14	$\text{B}(\text{C}_6\text{F}_5)_3$	0.12	43	1400	3.4	16
15	$\text{Ti}(\text{O}^i\text{Pr})\text{Cl}_3$	trace	– ^d	– ^d	– ^d	– ^d

Polymerization condition: $[\text{IB}] = 9.0$ mmol, $[\beta\text{-pinene}] = 3.0$ mmol, $[\text{catalyst}] = 0.20$ mmol, solvent = 20 mL (hexane/ $\text{CH}_2\text{Cl}_2 = 1:1$), temperature = 15 °C, time = 20 min. ^a Determined by ^1H NMR. ^b Estimated by GPC, based on polystyrene standards. ^c Determined by DSC. ^d Not determined.

To investigate the possibility of its application, a mixture of styrene-isoprene triblock copolymer (SIS) and the copolymer obtained in Run 10, containing 51 mol% β -pinene, was subjected to the peeling test. A blended polymer prepared by the reprecipitation of a 1:1 mixed polymer solution showed high transparency when coated onto a PET film, showing the high miscibility of two polymers (Figure S18). A sole glass transition temperature (−53 °C, Figure S19) higher than that of SIS alone (−61 °C) observed in DSC analyses supported this observation. The T_g value of the blended polymer was lower than those of the previously reported SIS-based tackifier mixtures (−40~−10 °C) [10,40]. The 180° peel test of the mixture showed a high peeling strength (0.58 ± 0.14 N/10 mm, Figure 6), sufficient for its application to pressure-sensitive adhesives, although this value was comparable to that of the lower end of the previously reported samples (280~1360 gf/25 mm). Considering the low glass transition temperature, the copolymer would be applied to a pressure-sensitive adhesive working in cold weather.

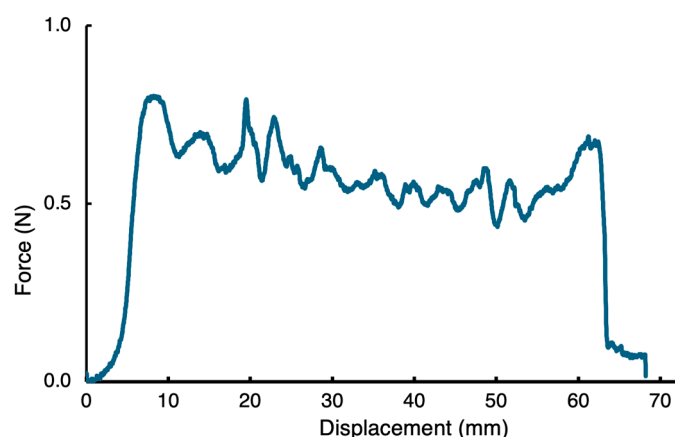


Figure 6. A representative 180° peel test diagram of the SIS/copolymer blend.

3. Experimental Section

3.1. Materials

All operations were performed using the standard Schlenk technique under nitrogen atmosphere. A solution of $\text{B}(\text{C}_6\text{F}_5)_3$ in hexane (0.23 M) was donated from Tosoh-Finechem Co., Ltd. (Shunan, Japan) and was used as received. AlCl_3 dialkyl ether adducts were prepared according to the methods in the literature and stored as 1.0 M stock solutions in CH_2Cl_2 [35]. $\text{Ti}(\text{O}^i\text{Pr})\text{Cl}_3$ was prepared according to the literature procedure [41]. (−)- β -pinene (>94%) was purchased from TCI chemicals and distilled over CaH_2 before use. Dry toluene, hexane, and dichloromethane were purchased from Kanto Chemical Co. Inc. (Tokyo, Japan) and purified after passing through a solvent purification column (Glass

Contour) before use. A hexane solution of isobutene (9 wt%, 1.04 M) was purchased from TCI chemicals and was used as received. Styrene-isoprene-styrene triblock rubber (SIS, $M_n = 157,000$, $M_w/M_n = 1.17$, styrene content = 22 wt%, Sigma-Aldrich Co., St. Louis, MO, USA) was used as purchased.

3.2. Measurements

NMR spectra were measured on a Varian System 500 or a Varian System 400 spectrometer at room temperature. The obtained spectra were referenced to the signal of a residual trace of the partially protonated solvent [^1H : $\delta = 7.26$ ppm (CHCl_3)] or solvent [^{13}C : $\delta = 77.16$ ppm (CDCl_3)]. The molecular weights of the polymers were measured on a TOSOH HLC-8320GPC chromatograph calibrated with polystyrene standards, using THF as the eluent ($T = 40^\circ\text{C}$). The polymer concentration in the injecting solution was ca. 2.0 mg/mL, and the injection volume was 0.20 mL. Atmospheric pressure chemical ionization-mass spectrometry (APCI-MS) of the copolymer was performed on a Thermo Fisher (Waltham, MA, USA) LTQ Orbitrap XL spectrometer. Differential scanning calorimetry (DSC) was performed on a SHIMADZU DSC-60 system, with a temperature elevation rate of $10^\circ\text{C min}^{-1}$.

3.3. Copolymerization of β -Pinene and IB, Using $\text{AlCl}_3\cdot\text{O}^i\text{Pr}_2$ as a Catalyst

A representative procedure for Table 1, Run 1, is described here. In a 50 mL two-neck round-bottomed flask, β -pinene (0.50 mmol, 68 mg, 0.08 mL) in hexane (1.3 mL), isobutene (9% in hexane; 9.0 mmol, 8.7 mL), and CH_2Cl_2 (9.8 mL) were added under an inert N_2 atmosphere. The temperature of the flask was kept at 15°C using a water bath. The copolymerization was started with the injection of $\text{AlCl}_3\cdot\text{O}^i\text{Pr}_2$ in CH_2Cl_2 (0.20 mmol, 1.0 M, 0.20 mL). After 20 min, the polymerization was terminated by adding acidic methanol. The precipitated copolymer was collected by filtration and dried for 6 h at 60°C under vacuum until reaching a constant weight. A 230 mg (40%) of colorless, sticky copolymer was obtained.

3.4. Copolymerization of β -Pinene and IB Using $\text{B}(\text{C}_6\text{F}_5)_3$ as a Catalyst (Table 2, Run 13)

Under an inert N_2 atmosphere, β -pinene (3.0 mmol, 408 mg, 0.47 mL) and isobutene (9% in hexane; 9.0 mmol, 8.7 mL) were charged to a 50 mL two-neck round-bottomed flask and diluted with 10 mL of CH_2Cl_2 . The temperature of the flask was kept at 15°C using a water bath. The copolymerization was started with the injection of a solution of $\text{B}(\text{C}_6\text{F}_5)_3$ in hexane (0.20 mmol, 0.23 M, 0.87 mL). After 20 min, the polymerization was terminated by adding methanol. The precipitated copolymer was collected by filtration and dried for 6 h at 60°C under vacuum until reaching a constant weight. A 121 mg (14%) of colorless solid was obtained.

3.5. Sample Film Preparation for the Peeling Test

A total of 50 mg of SIS and 50 mg of IB/ β -pinene copolymer, obtained in Table 1, Run 10, was mixed and dissolved into 3 mL of THF. The solution was reprecipitated into excess methanol to obtain the blended polymer. The blended polymer was pressed after being coated with a 10 mm wide, 25 μm thick PET film and placed on a steel panel as the adherend. The sample was allowed to stand for around 30 min before testing. The 180° peel test was performed on an A&D RTC-1210A universal testing machine, with a crosshead speed of 50 mm/min. The peeling force was averaged in the range of displacement between 10–60 mm.

4. Conclusions

The cationic copolymerization of isobutene and β -pinene was demonstrated using various Lewis acids at ambient temperatures. In the copolymerization employing AlCl_3 etherate, the frequent elimination of β -protons from both isobutene and the β -pinene propagating chain ends would result in a low molecular weight polymer, with a narrow

molecular weight distribution. $B(C_6F_5)_3$, causing less frequent β -proton elimination from the isobutene chain end, yielded a copolymer with a broader molecular weight distribution and a lower yield. Therefore, the ether adducts of $AlCl_3$ showed a superior polymerization capacity in terms of high operating temperature, good control over the composition of the comonomer, and narrowing molecular weight distribution among other conventional Lewis acids for the cationic copolymerization. Finally, the obtained copolymer showed a high peeling force, sufficient for use as a good tackifying agent, and a very low glass transition temperature, when combined with the styrene-isoprene triblock copolymer, justifying the application of the obtained copolymer.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/catal14070402/s1>, Figures S1–S14: NMR spectra of copolymers; Figure S15 Mass spectrum of the copolymer; Figures S16, S17 and S19: DSC thermograms of copolymers and their samples blended with SIS; Figure S18: A photograph of the peeling test setup.

Author Contributions: Conceptualization, O.A.A. and R.T.; methodology, R.T.; investigation, O.A.A.; resources, T.S.; writing—original draft preparation, O.A.A.; writing—review and editing, R.T. and Y.N.; funding acquisition, R.T. All authors have read and agreed to the published version of the manuscript.

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Data Availability Statement: All the data are included in the article, either in the manuscript or its Supplementary Material.

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Conflicts of Interest: The authors declare no conflicts of interest.

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