

Synthesis of Poly(β -pinene)-*g*-Polystyrene from Allylic Brominated Poly(β -pinene)

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ABSTRACT: Poly(β -pinene) was brominated by *N*-bromosuccinimide on the allylic carbons. Then the brominated product was activated by AlEt_2Cl to initiate the polymerization of styrene to give a β -pinene/styrene graft copolymer. AlEt_2Cl was selected because it alone could not initiate the polymerization of styrene. The obtained graft copolymer was characterized by GPC, $^1\text{H-NMR}$, and DSC measurements, respectively. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 75: 599–603, 2000

Key words: β -pinene; styrene; graft copolymer; bromination

INTRODUCTION

Block and graft copolymers can combine widely different properties in a single molecule and thereby provide a means of introducing special properties that are not inherent in the parent backbone. That usually makes them have unique properties in solution and in a solid state as a consequence of the immiscibility of the constitutive sequence. Block and graft copolymers are also useful as additives in the control of morphology and overall properties of the main types of multiphase systems. Therefore, the synthesis of block and graft copolymers has significant academic and commercial interest.

Recently, based on the achievement of living cationic polymerization of β -pinene (β -P),^{1,2} a main component of natural turpentine, poly(β -P)-*b*-polystyrene and poly(methyl methacrylate) (PMMA)-*g*-poly(β -P) were synthesized.^{2,3} In this study we investigated the synthesis of a graft

copolymer of β -pinene and styrene from allylic brominated poly(β -P). Such a graft copolymer is expected to function as a compatibilizer for the blends of polyolefins and polystyrenes due to the compatibility of poly(β -P) and polyolefins.

Poly(β -P) chains contain allylic hydrogen atoms, which can be replaced by allylic halogenation with a Wohl–Ziegler reaction to give reactive allylic halide on three sites (marked with 1, 2, 3 in Scheme 1). The resulting brominated poly(β -P) can be activated by Lewis acids such as AlEt_2Cl to initiate the polymerization of styrene and generate poly(β -P)-*g*-polystyrene. AlEt_2Cl was selected as the Lewis acid activator because it alone cannot induce the polymerization of styrene.

EXPERIMENTAL

Materials

The β -P (purity > 97%) was distilled twice under reduced pressure over calcium hydride (CaH_2) before use. Styrene (purity > 99%) was washed with 10% aqueous sodium hydroxide and water, dried overnight with anhydrous calcium chloride, and distilled twice under reduced pressure over CaH_2 before use. AIBN (purity > 99%) and *N*-bromosuccinamide (NBS, purity > 99.5%) were recryst-

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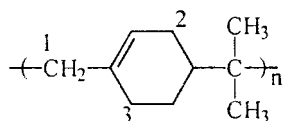
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Scheme 1 Poly(β -pinene) chains.

tallized from methanol and water, respectively. AlEt_2Cl (1.05M in hexane) and AlCl_3 (purity > 99.99%) were used as received. Carbon tetrachloride (CCl_4) was refluxed under phosphorus pentoxide over 2 h and distilled before use. CH_2Cl_2 and toluene were washed with 10% aqueous sodium hydroxide and then water, dried overnight with anhydrous calcium chloride, and distilled twice over CaH_2 before use.

Preparation of Poly(β -P)

Fine β -P was polymerized with AlCl_3 in toluene at -30°C . The initial concentration of β -P and AlCl_3 was 3.6 and 10 mmol/L, respectively. The reaction was quenched by methanol. Then the reaction mixture was washed sequentially with 5% hydrochloric acid and water to remove catalyst residue. The organic layer was precipitated into methanol. The precipitated β -P polymer was filtered and dried in a vacuum under phosphorus pentoxide.

Bromination of Poly(β -P)

The bromination reaction was carried out in a baked glass flask equipped with a condenser pipe and a magnetic stirring bar. A typical example is 0.8 g of poly(β -P), 1.0 g of NBS (mole ratio to β -P unit = 1), and 0.068 g of AIBN (7% mol NBS) were added to 16 mL of dry CCl_4 . The mixture was heated carefully to boiling and cooled when the reaction was too vigorous. The mixture was refluxed for a further 10 min after all of the precipitated NBS was converted to the suspended succinimide. Then the succinimide was filtered hot and washed with CCl_4 (2×10 mL). The filtrate was precipitated into 200 mL of methanol. The precipitated polymer was purified by repeating the dissolution and precipitation with CCl_4 and methanol, dried in a vacuum at room temperature, kept away from light, and stored at low temperature. The content of bromine by gravimetry was in good agreement with that by titration after the combustion in a Schoenigen apparatus.⁴ The brominated poly(β -P) was dried overnight under P_2O_5 in a vacuum before use.

Graft Polymerization

The graft 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 the solution of AlEt_2Cl via dry syringes into the solution of brominated poly(β -P) and styrene in CH_2Cl_2 at 0°C . The polymerization was quenched by methanol. Conversion of styrene was determined from its residual concentration measured by gas chromatography with benzene as an internal standard. The quenched reaction mixture was washed sequentially with 10% hydrochloric acid and water. The product in the organic layer was precipitated by methanol then filtered and dried in a vacuum.

Measurement

The molecular weight distribution and number average molecular weight of the polymers were measured by size-exclusion chromatography in chloroform at room temperature on a Jasco Triritar-V chromatograph equipped with three polystyrene columns (Shodex K-802, K-803, and K-804). The $^1\text{H-NMR}$ spectra of the polymers were recorded in CDCl_3 at room temperature on a Jeol JNM GSX-270 spectrometer. DSC thermograms of the polymers were measured on a Perkin-Elmer DSC-7 at a scan rate of $10^\circ\text{C}/\text{min}$.

RESULTS AND DISCUSSION

Bromination of Poly(β -P)

Poly(β -P) was brominated by NBS with AIBN as the initiator in CCl_4 . Figure 1 shows the theoretical and experimental values of the bromine content of the brominated products (mole ratio of Br to β -P unit: $\text{Br}/\beta\text{-P}$) under various NBS feed ratios (mole ratio of NBS to β -P unit: $\text{NBS}/\beta\text{-P}$). When $\text{NBS}/\beta\text{-P}$ was ≤ 1 , the bromine content increased in direct proportion to the NBS feed ratio and was in good agreement with the theoretical values, suggesting that the bromination reaction was quantitative. When $\text{NBS}/\beta\text{-P}$ was > 1 , the bromine contents, although increased with increasing NBS feed ratio, were lower than the theoretical values; thus, the bromination efficiency was < 1 .

In the bromination reaction, the bromination reagent was the Br_2 molecule that was generated from NBS. When $\text{NBS}/\beta\text{-P}$ was ≤ 1 , the concentration of Br_2 was relatively low; furthermore, the bromination reaction occurred dominantly on the *exo*-allylic carbon atoms (carbon 1 in Scheme 1)

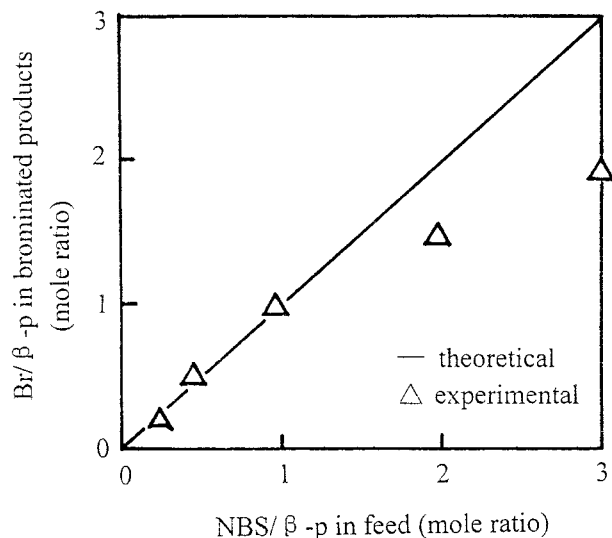


Figure 1 Content of bromine in the brominated poly(β -pinene) (β -P) under various NBS/ β -P in the feed.

whose steric hindrance was slight; thus, the displacement reaction occurred smoothly and quantitatively. When NBS/ β -P was > 1 , the bromination reaction could occur on the *endo*-allylic carbons (carbon 2 or 3 in Scheme 1) rather than the *exo*-allylic carbon atoms; the former reaction was difficult because of the heavy steric hindrance. Furthermore, the Br_2 concentration yield was higher, and the reaction was vigorous to induce side reactions. Thus, the bromination efficiency decreased.

Figure 2 shows the $^1\text{H-NMR}$ spectra of brominated poly(β -P) obtained under NBS/ β -P of 1 and 1.5 for curves a and b, respectively. The spectrum of the brominated product obtained under an NBS/ β -P of 1 (Fig. 2, curve a) exhibits new absorption peaks of $-\text{C}=\text{C}-\text{CHBr}-$ at 3.2–3.4 ppm and remains the characteristic absorption of the *endo*-olefin inherent in the parent poly(β -P) at 5.1–5.5 ppm.¹ This suggested that the bromination indeed occurred on the allylic carbons. On the other hand, no obvious absorption at 5.1–5.5 ppm was observed in the spectrum of the brominated product obtained under an NBS/ β -P of 1.5 (Fig. 2 curve b), indicating the disappearance of the *endo*-olefin double bond. Furthermore, new absorptions at 3.0–4.0 ppm due to the H adjacent to the C—Br were observed. These suggested that a side addition reaction of Br to *endo*-olefin occurred under the vigorous reaction because of the high concentration of Br_2 generated under the high NBS feed ratio.

The GPC results showed that no obvious degradation occurred during the bromination reaction under the NBS/ β -P ratios investigated.

Graft Polymerization of Styrene

Activated by AlEt_2Cl , the brominated poly(β -P) initiated the polymerization of styrene in CH_2Cl_2 at 0°C . As shown in Figure 3, the polymerization of styrene proceeded smoothly (95% conversion in 20 min) with the brominated poly(β -P) obtained under an NBS/ β -P of 1. But the polymerization was much slower with the brominated poly(β -P) obtained under an NBS/ β -P of 1.5 or 0.5.

As discussed above, the *endo*-olefin double bonds almost disappeared during the bromination under an NBS/ β -P of 1.5 because of the side addition reaction. Namely, the bromine introduced onto the poly(β -P) chains was not allylic bromine; thus, the Br—C bond was difficult to activate by a Lewis acid to initiate the polymerization of styrene. On the other hand, the amount of the bromine atoms on the brominated poly(β -P) obtained under an NBS/ β -P of 0.5 was smaller than that under an NBS/ β -P of 1; correspondingly, the concentration of the initiating species generated from the Br—C was lower and thereby led to a slower polymerization of styrene.

Figure 4 shows the GPC curves and molecular weights of the graft polymerization products with

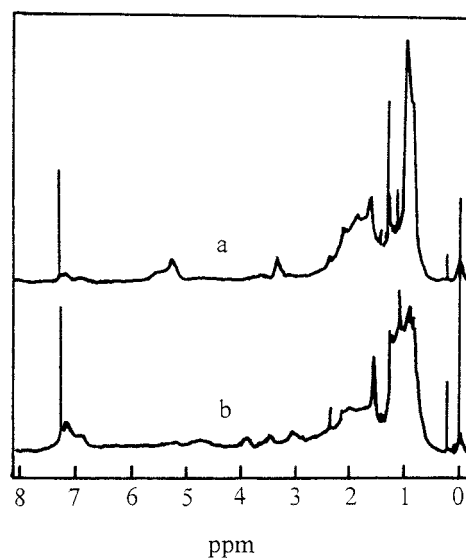


Figure 2 $^1\text{H-NMR}$ spectra of the brominated poly(β -P) under various NBS/ β -P: curve a, brominated under NBS/ β -P = 1 and curve b, brominated under NBS/ β -P = 1.5.

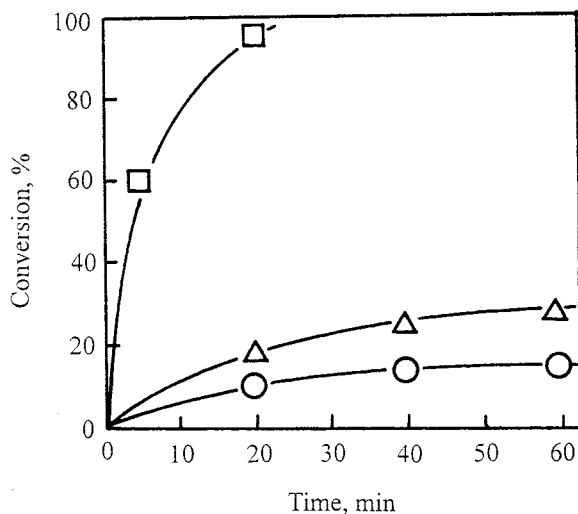


Figure 3 Conversion-time curves of styrene polymerization with brominated poly(β -P) under different NBS/ β -P: $W_{\text{poly}(\beta\text{-P})} = 0.5 \text{ g}$, $W_{\text{styrene}} = 0.5 \text{ g}$, $[\text{AlEt}_2\text{Cl}] = 31.5 \text{ mmol/L}$; CH_2Cl_2 ; 0°C ; NBS/ β -P (mole ratio): (\square) 1, (Δ) 0.5, and (\circ) 1.5.

various feed ratios of styrene to the brominated poly(β -P) obtained under an NBS/ β -P of 1. Compared to that of the parent poly(β -P), the GPC curves of the graft polymerization products shifted toward a higher molecular weight and the molecular weight increased with increasing styrene feed ratio. These results suggest the forma-

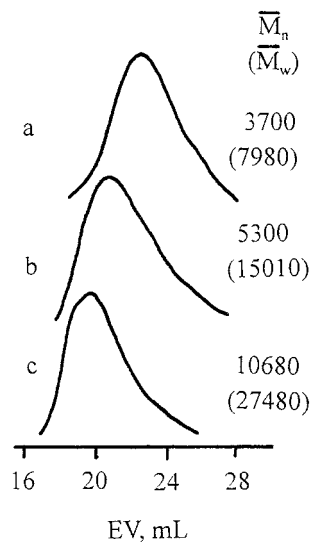


Figure 4 GPC curves of the graft products under various styrene/brominated poly(β -pinene) (w/w): curve a, brominated poly(β -pinene); curve b, 1.1; curve c, 3.6. The other conditions are the same as Figure 3, curve \square .

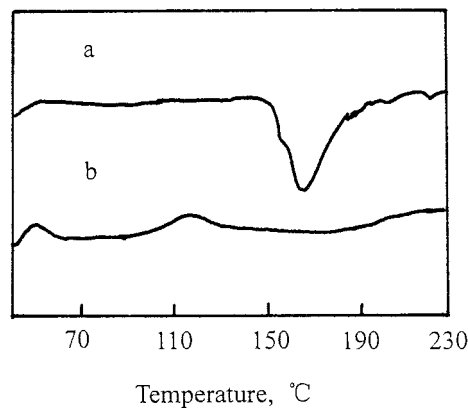


Figure 5 DSC thermograms of brominated poly(β -pinene) and graft product: curve a, brominated poly(β -pinene) and curve b, graft product.

tion of graft copolymers. Furthermore, the GPC curves of the products were unimodal, regardless of the feed ratio of styrene, which means almost no homopolymer of styrene was produced in the course of the graft polymerization.

Characterization of Graft Polymers

Figure 5 shows the DSC thermograms of the brominated poly(β -P) and graft polymerization product. The thermogram of the brominated poly(β -P) showed a strong absorption between 144.1 and 211.8°C, which was due to the elimination of HBr from the heated brominated products; whereas this absorption disappeared on the thermogram of the graft product, and a glass transition absorption of polystyrene appeared at 83.3–134.7°C. These results indicate that the bromine atoms on

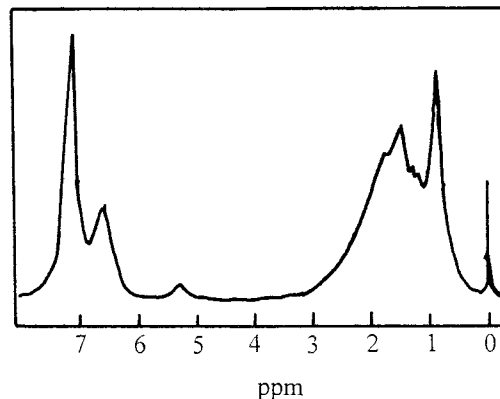
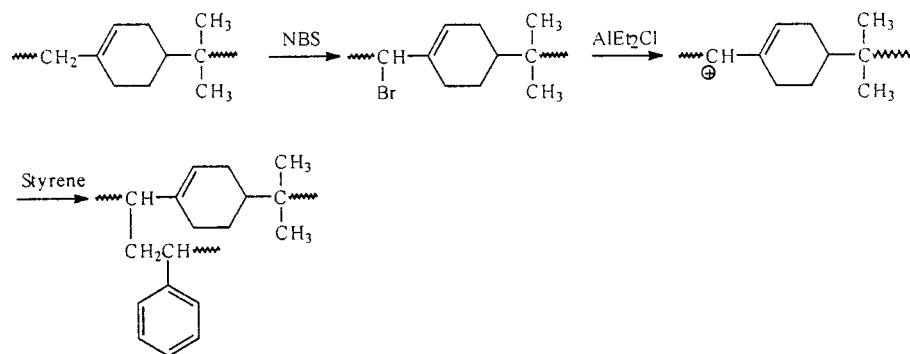


Figure 6 $^1\text{H-NMR}$ spectrum of the graft product under the conditions in Figure 3, curve \square .



Scheme 2 Bromination of poly(β -pinene) with NBS.

the brominated poly(β -P) had been replaced by the branches of polystyrene.

Figure 6 shows the $^1\text{H-NMR}$ spectrum of the graft copolymer. Besides the absorption of the *endo*-olefin of the β -P units, the characteristic phenyl absorption of the styrene units appeared. The absorption at 3.2–3.4 ppm of $-\text{C}=\text{C}-\text{CHBr}-$ disappeared. The $^1\text{H-NMR}$ results confirmed the formation of graft copolymer.

In conclusion, Scheme 2 shows that poly(β -P) can be brominated with NBS by the Wohl–Ziegler reaction. Then brominated poly(β -P) was activated by AlEt_2Cl to initiate the polymerization of

styrene, and a new graft copolymer with a poly(β -P) backbone chain and polystyrene graft chains resulted.

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