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### Studies on the Cationic Copolymerization of $\alpha$ -Pinene and Styrene with Complex $SbCl_3/AlCl_3$ Catalyst Systems. I. Effects of the Polymerization Conditions on the Copolymerization Products

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# STUDIES ON THE CATIONIC COPOLYMERIZATION OF $\alpha$ -PINENE AND STYRENE WITH COMPLEX $\text{SbCl}_3/\text{AlCl}_3$ CATALYST SYSTEMS. I. EFFECTS OF THE POLYMERIZATION CONDITIONS ON THE COPOLYMERIZATION PRODUCTS

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## ABSTRACT

The copolymerization products of  $\alpha$ -pinene and styrene were prepared with the compound catalyst system  $\text{SbCl}_3/\text{AlCl}_3$  by changing the Sb/Al ratio, feeding monomer ratio, solvent, and polymerization temperature. The compositions of the copolymerization products were quantitatively characterized by the method of the combination of micro-ozonization and thin-layer chromatography in terms of the contents of the homopolymers and the copolymers containing high or low mole fractions of  $\alpha$ -pinene, the yields of pure copolymer, and the monomer unit ratios ( $F_1$ ) of copolymers. The results show that it was easier to obtain the higher yield (up to 80%) of the pure copolymer with the complex catalyst system than with  $\text{AlCl}_3$  alone. The  $F_1$  values could be controlled between 30 and 56% under the following polymerization

conditions:  $\text{Sb/Al} \geq 1/2$ ,  $\alpha$ -pinene/styrene  $\leq 70\%$ , and the conversion of styrene  $\leq 90\%$ .

## INTRODUCTION

$\alpha$ -Pinene is a main component separated from terpentine, a natural forest product. Compared with  $\beta$ -pinene, another component from terpentine,  $\alpha$ -pinene has a lower market price and a higher output in the world. Therefore it is important to develop other products by using  $\alpha$ -pinene as a starting material. In addition to its use for the manufacture of a variety of other terpenic hydrocarbons and as a solvent,  $\alpha$ -pinene can be polymerized or copolymerized to produce terpene resins which are widely used in adhesive formulations and rubber processing [1, 2]. The studies showed that as a monomer,  $\alpha$ -pinene has a low polymerization reacting rate and the homopolymer of  $\alpha$ -pinene has low molecular weight, which limits its applications.  $\alpha$ -Pinene cationic copolymerization with styrene had been investigated by several authors [3, 4]. The results showed that the polymerization reaction rate of  $\alpha$ -pinene is much lower than that of styrene. In general, the copolymerization of  $\alpha$ -pinene with styrene is accompanied by the homopolymerizations of  $\alpha$ -pinene and styrene. Therefore, the copolymerization products are a mixture of poly( $\alpha$ -pinene), polystyrene, and copoly( $\alpha$ -pinene-styrene). Also, the average molecular weights of the copolymerization polymers are lower than those of the terpene resins manufactured from  $\beta$ -pinene.

Based on a series of studies of the  $\alpha$ -pinene cationic polymerizations, a new complex catalyst  $\text{SbCl}_3/\text{AlCl}_3$  was successfully prepared by our group [5, 6]. As an electron-donor catalyst system,  $\text{SbCl}_3/\text{AlCl}_3$  has been effectively used for the cationic copolymerizations of  $\alpha$ -pinene with styrene. Our studies showed that the difference of the polymerization reactivities between  $\alpha$ -pinene and styrene became smaller by using  $\text{SbCl}_3/\text{AlCl}_3$  complex catalyst in  $\alpha$ -pinene/styrene copolymerization, and the melting point of the copolymerization products obviously increased [7]. This paper describes the effect of different reaction conditions on  $\alpha$ -pinene/styrene copolymerizations by using  $\text{SbCl}_3/\text{AlCl}_3$  complex catalyst. A method with the combination of micro-ozonization and thin-layer chromatography (TLC) was introduced in this study for the separation of the copolymerization products which include the homopolymers and copolymers of both monomers. This paper also presents the reaction conditions in which only  $\alpha$ -pinene/styrene copolymers were formed.

## EXPERIMENTAL

### Reagents

$\alpha$ -Pinene, purity  $\geq 98\%$ , was dried over calcium hydride and distilled under reduce pressure. Styrene, a guaranteed reagent grade, was washed with aqueous alkali to remove inhibitors and dried over calcium hydride, then distilled at vacuum. Powder aluminum chloride ( $\text{AlCl}_3$ ) and antimony chloride ( $\text{SbCl}_3$ ) have 99.9% purity. Toluene, methylene chloride, and heptane were distilled over calcium hydride before use.

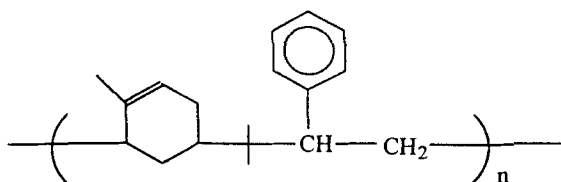


FIG. 1. Chain structure of copoly( $\alpha$ -pinene-styrene).

### Preparations of Complex Catalyst $\text{SbCl}_3/\text{AlCl}_3$ Solution

Based on the predetermined Sb/Al ratio,  $\text{AlCl}_3$  and  $\text{SbCl}_3$  were charged into a flask under dried nitrogen protection. The mixture was melted at  $110\text{--}120^\circ\text{C}$ . After cooling, a certain amount of the  $\text{SbCl}_3/\text{AlCl}_3$  mixture was weighed and dissolved in toluene to prepare a determined concentration of catalyst solution.

### Copolymerizations of $\alpha$ -Pinene/Styrene and Treatments of Copolymerization Products

The copolymerization procedures and the copolymerization products treatments have been described in the literature [4, 6].

### Separations and Measurements of Copolymerization Products

It is quite difficult to separate the  $\alpha$ -pinene/styrene copolymers from their homopolymers due to the complex compositions of the products, the broad distributions of their molecular weights, and the similar solubilities of the copolymers and homopolymers in solvents. The experiments showed that quantitative separation of the copolymerization products cannot be achieved by either solvent abstraction or TLC alone. It is known that the chain structures of poly( $\alpha$ -pinene-styrene) (Fig. 1), poly( $\alpha$ -pinene) (Fig. 2), and polystyrene (Fig. 3) differ in their double-bond contents. For every chain unit, poly( $\alpha$ -pinene) has the highest double-bond content while polystyrene has no double bonds. The double-bond content in  $\alpha$ -pinene/styrene copolymer is lower than that of poly( $\alpha$ -pinene) and increases with an increase in the chain unit ratio of  $\alpha$ -pinene to styrene in one copolymer chain unit. Our experiments showed that when the copolymerization products were subjected to ozonization, their polarities changed differently [7, 8]. That is, poly( $\alpha$ -pinene) becomes the most polar and polystyrene stays at the lowest polarity (because it has no double bonds to be oxidized by ozone), while  $\alpha$ -pinene/styrene copolymers

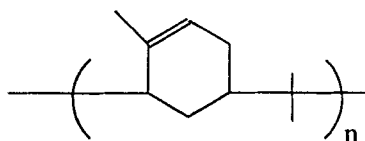


FIG. 2. Chain structure of poly( $\alpha$ -pinene).

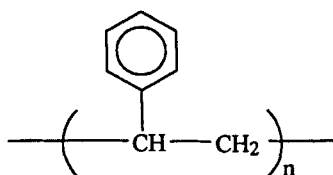


FIG. 3. Chain structure of polystyrene.

have moderate polarities according to their double-bond contents. In this paper the compositions of the  $\alpha$ -pinene/styrene copolymerization products were separated and measured by a combination of the methods of micro-ozonization and TLC. The product separation procedures are shown in Scheme 1. Four products were obtained quantitatively by this method: poly( $\alpha$ -pinene) (PP); copoly( $\alpha$ -pinene-styrene) (CoPs), which has a higher content of  $\alpha$ -pinene units and is soluble in methanol; copoly( $\alpha$ -pinene-styrene) (CoPi), which has a lower  $\alpha$ -pinene unit content and is insoluble in methanol; and polystyrene (PS).

The  $^1\text{H-NMR}$  spectrum of the poly( $\alpha$ -pinene-styrene) was obtained by Jeol GSX-270 (270 MHz) spectroscopy.

### Calculation of $F_1$ , the Ratio of $\alpha$ -Pinene Units ( $M_1$ ) to Copolymer $\alpha$ -Pinene/Styrene Units ( $M_1 + M_2$ )

$F_1$  is defined as the molar ratio of  $\alpha$ -pinene units ( $M_1$ ) to copolymer  $\alpha$ -pinene/styrene units ( $M_1 + M_2$ ) in the copolymer chains:  $F_1 = M_1/(M_1 + M_2)$ . The  $F_1$  values were calculated from the monomer conversions of  $\alpha$ -pinene and styrene, and the yields of products:

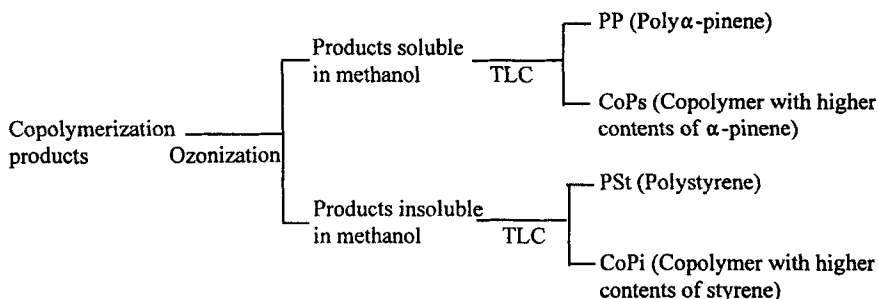
$$F_1 = \frac{M_1}{M_1 + M_2} = \frac{f_{10}m_1 - m_{10}}{(f_{10}m_1 - m_{10}) + [(1 - f_{10})m_2 - m_{20}]}$$

- where
- $M_1$  =  $\alpha$ -pinene chain units (mol) in the copolymer
  - $M_2$  = styrene chain units (mol) in the copolymer
  - $m_1$  =  $\alpha$ -pinene conversion (mol%)
  - $m_2$  = styrene conversion (mol%)
  - $m_{10}$  = homopoly( $\alpha$ -pinene) yield (mol%)
  - $m_{20}$  = homopolystyrene yield (mol%)
  - $f_{10}$  =  $\alpha$ -pinene feeding ratio (mol%)

## RESULTS AND DISCUSSION

### Comparison of the Copolymerization Products

The cationic copolymerizations of  $\alpha$ -pinene and styrene were carried out with  $\text{SbCl}_3/\text{AlCl}_3$  catalyst at different Sb/Al ratios (0/1, 1/4, 1/2, and 1/1 mol). The copolymerization products separated by TLC combined with micro-ozonization can be classified into four groups: poly( $\alpha$ -pinene) (PP), polystyrene (PS), copoly( $\alpha$ -pinene-styrene) with higher portions of  $\alpha$ -pinene chain units (CoPs), and copoly( $\alpha$ -pinene-styrene) with lower portions of  $\alpha$ -pinene chain units (CoPi). The representa-

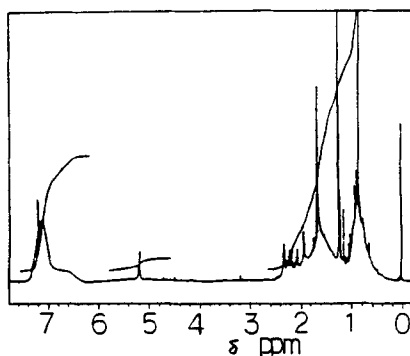
SCHEME 1. Separation procedures of  $\alpha$ -pinene/styrene copolymerization products.

tive experimental data are given in Table 1. The data show that  $\alpha$ -pinene/styrene copolymerization products prepared by using catalyst  $\text{AlCl}_3$  alone were quite different from those prepared by using  $\text{SbCl}_3/\text{AlCl}_3$  complex catalysts. In the case of using only  $\text{AlCl}_3$  in the catalyst system, 13.6% (wt) polystyrene homopolymer was formed in the copolymerization products, 86.2% (wt) poly( $\alpha$ -pinene/styrene), which had higher styrene chain unit contents (CoPi), was obtained, and only 0.2% (wt) copolymer, which had a higher content of  $\alpha$ -pinene chain units (CoPs), was present in the products even when the  $\alpha$ -pinene feeding ratio was 50% (mol). However, polystyrene in the copolymerization products was reduced to 6.5% (wt) when the Sb/Al ratio in  $\text{SbCl}_3/\text{AlCl}_3$  complex catalyst was 1/4. Furthermore, no styrene homopolymerization occurs in higher Sb/Al ratio catalyst systems (Sb/Al = 1/2 and 1/1), and all the products were composed of 100% copolymers (CoPs and CoPi). With an increase of the Sb/Al ratio from 0 to 1/4 to 1/2 to 1/1, the CoPs (copolymer with a higher content of  $\alpha$ -pinene units) increased from 0.2 to 2.1 to 5.6 to 11.4% (wt), respectively. The  $F_1$  value was 23.6% (mol) without  $\text{SbCl}_3$  in the catalyst system, while in the  $\text{SbCl}_3/\text{AlCl}_3$  complex catalyst systems the  $F_1$  values

TABLE 1. Effect of  $\text{SbCl}_3/\text{AlCl}_3$  Catalyst Systems in the  $\alpha$ -Pinene/Styrene Copolymerizations<sup>a</sup>

Sample	Sb/Al ratio, mol	Compositions of copolymerization products, wt%				Copolymer yields, %	$F_1$
		PP	PSt	CoPs	CoPi		
1	0	0	13.6	0.2	86.2	42.9	23.6
2	1/4	0	6.5	2.1	91.4	71.9	39.1
3	1/2	0	0	5.6	94.4	68.6	36.7
4	1/1	0	0	11.4	88.6	73.2	36.3

<sup>a</sup>Copolymerization conditions.  $\alpha$ -Pinene feeding ratio:  $f_{10} = 50\%$ ;  $[m_1 + m_2] = 3.16 \text{ mol} \cdot \text{L}^{-1}$ ;  $m_1 = \text{pinene}$ ;  $m_2 = \text{styrene}$ ;  $[\text{AlCl}_3] = 80 \text{ mmol} \cdot \text{L}^{-1}$ ; temperature =  $-15^\circ\text{C}$ ; solvent = toluene; styrene conversion  $\leq 93\%$ .

FIG. 4.  $^1\text{H-NMR}$  spectrum of copoly( $\alpha$ -pinene-styrene).TABLE 2. Effect of Monomer Feeding Ratios on the  $\alpha$ -Pinene/Styrene Copolymerizations<sup>a</sup>

Feeding ratios $f_{10}$ , mol%	Sb/Al, mol	Monomer conversions, mol%		Compositions of copolymerization products, wt%				Copolymer yields, %	$F_1$
		$m_1$	$m_2$	PP	PSt	CoPs	CoPi		
90	0	7.6	62.9	0	0	3.6	96.4	13.1	52.1
70	0	18.6	86.0	0	4.6	1.0	94.4	38.8	35.3
50	0	20.4	79.8	0	13.6	0.2	86.2	42.9	23.6
90	1/4	51.6	98.6	5.6	0	12.1	82.3	52.3	81.2
70	1/4	43.4	90.3	0	3.7	7.0	89.3	55.0	55.2
50	1/4	56.2	98.8	0	6.5	2.1	91.4	71.9	39.1
30	1/4	57.2	96.7	0	11.4	0.4	88.2	74.6	23.0
90	1/2	34.6	72.4	3.3	0	12.9	83.8	37.1	80.6
70	1/2	42.4	75.8	0	0	9.3	90.7	52.4	56.6
50	1/2	50.3	86.9	0	0	5.6	94.4	68.6	36.7
85	1/1	31.0	80.4	0	0	21.3	78.7	38.4	68.6
75	1/1	32.4	77.8	0	0	14.6	85.2	46.0	49.3
50	1/1	53.2	93.2	0	0	11.4	88.6	73.2	36.3

<sup>a</sup>Copolymerization conditions.  $[m_1 + m_2] = 3.16 \cdot \text{mol} \cdot \text{L}^{-1}$ ;  $[\text{AlCl}_3] = 80 \text{ mmol} \cdot \text{L}^{-1}$ ; solvent = toluene; temperature =  $-15^\circ\text{C}$ ;  $m_1 = \alpha$ -pinene;  $m_2 = \text{styrene}$ .

TABLE 3. Solvent Effect on the  $\alpha$ -Pinene/Styrene Copolymerizations<sup>a</sup>

Solvent	Feeding ratios $f_{10}$ , mol%	Monomer conversions, mol%		Compositions of copolymerization products, wt%				Copolymer yields, mol%	
		$m_1$	$m_2$	PP	PSt	CoPs	CoPi		$F_1$
CH <sub>2</sub> Cl <sub>2</sub>	85	56.4	94.5	0	0	19.0	81.0	62.1	77.2
Toluene	85	34.6	72.4	3.3	0	12.9	83.8	40.3	72.2
Heptane	85	10.6	85.4	0	0	4.6	95.4	21.8	41.3
CH <sub>2</sub> Cl <sub>2</sub>	70	50.1	92.4	0	0	12.6	87.4	62.8	55.9
Toluene	70	42.4	75.8	0	0	9.3	90.7	52.4	56.6
Heptane	70	22.4	80.6	0	0	8.2	91.8	39.9	39.3
CH <sub>2</sub> Cl <sub>2</sub>	50	68.3	93.6	0	0	6.1	93.9	80.9	42.2
Toluene	50	50.3	86.9	0	0	5.6	94.4	68.6	36.7
Heptane	50	36.2	83.2	0	0	6.9	93.1	59.7	30.3

<sup>a</sup>Copolymerization conditions.  $[m_1 + m_2] = 3.16 \text{ mol} \cdot \text{L}^{-1}$ ;  $\alpha$ -pinene feeding ratio  $f_{10} = 50\%$ ;  $[\text{AlCl}_3] = 80 \text{ mol} \cdot \text{L}^{-1}$ ; temperature =  $-15^\circ\text{C}$ ;  $\text{Sb}/\text{Al} = 1/2$ ;  $m_1 = \alpha$ -pinene;  $m_2 = \text{styrene}$ .

were 36.3–39.1% (mol). This indicates more  $\alpha$ -pinene chain units had been added to the copolymer chain units when the complex catalysts were used. The fact that without  $\text{SbCl}_3$  in the catalyst system the reactivity of styrene is much higher than that of  $\alpha$ -pinene shows  $\text{SbCl}_3$  reduces the reactivity of styrene and increases the reactivity of  $\alpha$ -pinene. The reaction centers and their balance with the anion groups in  $\text{AlCl}_3$  and  $\text{SbCl}_3/\text{AlCl}_3$  are different and may affect the chain propagating reactivities of  $\alpha$ -pinene and styrene.

Table 1 also shows that no poly( $\alpha$ -pinene) homopolymer was found in the copolymerization products for all  $\text{Sb}/\text{Al}$  ratios in catalyst systems when the  $\alpha$ -pinene/styrene feeding ratio was 50% (mol) and the styrene conversion was controlled below 93%. Therefore, it can be concluded that styrene used in these cationic copolymerization conditions was not only a comonomer but also acted as a cocatalyst. This assumption is discussed in Ref. 4.

After removing of homopolymers (PP and PSt) from the copolymerization products, the copolymers (CoPs and CoPi) were analyzed by <sup>1</sup>H NMR. One spectrum of the copolymers is shown in Fig. 4. There are three characteristic hydrogen absorption peaks in the <sup>1</sup>H-NMR spectrum of the  $\alpha$ -pinene/styrene copolymer. The peak locations are 6.6–7.1 ppm for phenyl, 0.84–0.91 ppm for methylene, and 5.0–5.5 ppm for cyclic olefinic bonds. The styrene chain units give both phenyl and methylene peaks, and the  $\alpha$ -pinene chain units give both methylene and cyclic olefinic bond peaks. Therefore, the spectrum clearly indicates the chain unit structures of copoly( $\alpha$ -pinene–styrene) as shown in Fig. 1.



TABLE 4. Effect of Temperature on the  $\alpha$ -Pinene/Styrene Copolymerizations<sup>a</sup>

Temperature, °C	Feeding ratios $f_{10}$ , mol%	Monomer conversions, mol%		Compositions of copolymerization products, wt%				Copolymer yields, mol%	$F_1$
		$m_1$	$m_2$	PP	PSt	CoPs	CoPi		
-30	85	25.2	95.8	0	0	9.1	90.9	35.8	59.9
-15	85	31.0	80.4	0	0	21.3	78.7	38.4	68.6
0	85	40.2	80.8	0	0	15.6	84.4	46.3	73.8
15	85	34.4	66.8	0	0	15.4	84.6	39.3	74.5
-30	70	36.0	88.4	0	0	5.2	94.8	51.7	48.7
-15	70	32.4	77.8	0	0	14.6	85.2	46.0	49.3
0	70	47.7	86.2	0	0	9.8	90.2	59.3	56.4
15	70	35.0	63.2	0	0	10.3	89.7	43.5	56.4
-30	50	31.4	90.6	0	0	3.1	96.9	61.0	25.7
-15	50	53.2	93.2	0	0	11.4	88.6	73.2	36.3
0	50	52.3	84.3	0	0	7.8	92.2	68.3	38.3
15	50	48.8	78.3	0	0	8.6	91.4	63.6	38.4

<sup>a</sup>Copolymerization conditions.  $[m_1 + m_2] = 3.16 \text{ mol} \cdot \text{L}^{-1}$ ;  $[\text{AlCl}_3] = 80 \text{ mmol} \cdot \text{L}^{-1}$ ; Sb/Al = 1/1; solvent = toluene;  $m_1 = \alpha$ -pinene;  $m_2 =$  styrene. The reactions carried out at 15°C were terminated at lower conversions of styrene.

### Effect of the Feeding Ratios ( $f_{10}$ ) on the Copolymerization Products

Table 2 shows the compositions of the  $\alpha$ -pinene/styrene copolymerization products and the conversions with different monomer feeding ratios at different Sb/Al ratios. The results indicate the compositions of the copolymerization products can be controlled by changing the  $\alpha$ -pinene feeding ratios and the Sb to Al ratios. With Sb/Al ratios at 0 and 1/4, homopolymers (PP or PSt) were formed in the products. However, in most of the cases, 100% copolymers (CoPs and CoPi) were obtained with Sb/Al ratios at 1/2 and 1/1. By increasing the  $\alpha$ -pinene feeding ratio at the same Sb/Al ratio, the  $F_1$  values obviously increase. For example, increasing the  $\alpha$ -pinene feeding ratio from 50 to 70 to 90% (mol) at Sb/Al = 1/2, the  $F_1$  values increased from 36.7 to 56.6 to 80.6%, respectively. At Sb/Al = 1/1, increasing the feeding ratio gave the same  $F_1$  changing trend as at Sb/Al = 1/2.

### Effect of Solvents on the Copolymerization Products

Toluene, methylene chloride, and heptane, which offer different polarities, were used as solvents in  $\alpha$ -pinene/styrene copolymerizations at -15°C and Sb/Al = 1/2 with different  $\alpha$ -pinene feeding ratios. The experimental results are shown in Table 3. Methylene chloride, the highest polarity solvent, gave the highest copolymer production yields and the highest  $F_1$  values compared with toluene and heptane at the same feeding ratios and the same Sb/Al ratios. Under the copolymerization

conditions showed in Table 3, no polystyrene was formed. With the exception of one experiment with a feeding ratio of 85% in toluene, no homopolymer of  $\alpha$ -pinene was formed for all other copolymerizations. In general, with methylene chloride or toluene as solvent at higher feeding ratios (85 or 70%), the  $F_1$  values of the copolymers (CoPs and CoPi) can be more than 55% (mol).

### Effect of Temperature on the $\alpha$ -Pinene/Styrene Copolymerizations

The  $\alpha$ -pinene/styrene copolymerizations were carried out at  $-30$ ,  $-15$ ,  $0$ , and  $15^\circ\text{C}$  with the same feeding ratios, the same Sb/Al ratios (1/1), and the same solvent (toluene). The temperature effect on the copolymerization products is given in the Table 4. By increasing temperature from  $-30$  to  $15^\circ\text{C}$  at the same feeding ratio, the product yields did not change very much. However, the  $F_1$  values became higher when the polymerization temperature was increased. At the lower temperature range ( $-30$  to  $-15^\circ\text{C}$ ), the  $F_1$  values are lower than those at the highest temperature range ( $0$  to  $15^\circ\text{C}$ ). For example, with a feeding ratio of 85%, the  $F_1$  values were 59.9% at  $-30^\circ\text{C}$  and 68.6% at  $-15^\circ\text{C}$ , while the  $F_1$  values were 73.8% at  $0^\circ\text{C}$  and 74.5% at  $15^\circ\text{C}$ . This indicates that  $\alpha$ -pinene molecules become more active than styrene molecules at higher temperatures.

### CONCLUSIONS

1.  $\text{SbCl}_3/\text{AlCl}_3$  is an effective complex catalyst system for  $\alpha$ -pinene/styrene cationic copolymerizations.  $\text{SbCl}_3$  plays an important role in the catalyst system which can reduce the difference of monomer reactivities between  $\alpha$ -pinene and styrene and suppress the formation of homopolymers.
2. The  $F_1$  values of copoly( $\alpha$ -pinene-styrene) can be controlled by changing the monomer feeding ratios at the same Sb/Al ratios.
3. A higher polarity solvent, such as methylene chloride, is favorable for the production of higher  $F_1$  value copolymers.
4. Temperature has little effect on copolymer productivity, but increasing the temperature increases the  $\alpha$ -pinene chain units in the copolymer chains.
5. The combination of TLC with micro-ozonization is an effective method for the separation of  $\alpha$ -pinene/styrene copolymerization products. The copolymers and homopolymers can be quantitatively separated by using this method.

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