

## Cationic Polymerization of $\beta$ -Pinene and Styrene

CHARLES SNYDER,\* WILLIAM McIVER,<sup>†</sup> and HOWARD SHEFFER,  
*Polymer Chemistry Laboratory, Union College, Schenectady, New York*  
12308

### Synopsis

The yield, composition, and molecular weight of homopolymers and copolymers of  $\beta$ -pinene and styrene are described as a function of the feed, temperature, and solvent. Fractionation, gel permeation chromatography, and nuclear magnetic resonance spectroscopy of GPC fractions are used as analytical tools to present evidence for copolymerization in methylene dichloride. Additional support for copolymerization is obtained from the relation of polymer composition to per cent conversion. The reduction of molecular weights of homopolymers by aromatic solvents was investigated.

### INTRODUCTION

The polymerization of  $\beta$ -pinene and styrene in *m*-xylene with aluminum chloride at 30°C gives a copolymer.<sup>1</sup> For this solvent, gel permeation chromatography was not conclusive in proving copolymerization, but fractionation supported it. In methylene dichloride at temperatures from -50° to +30°C,  $\beta$ -pinene and styrene give only homopolymers with aluminum chloride.<sup>2</sup> Analysis in this case was based on fractionation followed by IR spectroscopy. At -30°C in methylene dichloride,  $\beta$ -pinene and styrene do not copolymerize with 0.05 molar titanium chloride.<sup>3</sup> However, with 0.5 molar titanium chloride at mole fractions of  $\beta$ -pinene less than 0.5, copolymerization occurs, becoming complete at mole fraction 0.2. This study with titanium tetrachloride also suggests that the double bond in poly- $\beta$ -pinene may be involved in grafting styrene to form poly( $\beta$ -pinene-*g*-styrene).

### EXPERIMENTAL

#### Yield, Composition, and Molecular Weight Versus Conditions of Polymerization

$\beta$ -Pinene and styrene were polymerized at 30° and -78°C in methylene dichloride and at -78° in *m*-xylene using a molar ratio of solvent to monomer of three to one. Anhydrous aluminum chloride was the catalyst. No cocatalyst was used other than traces of impurities present in the reagent. The reactants

\*Present address: 85 Wesleyan Avenue, Amsterdam, New York 12010.

<sup>†</sup> Present address: W. H. Wright Research Laboratories, Schenectady Chemical Co., Schenectady, New York 12309.

were used as received without further purification. The  $\beta$ -pinene was Catalog no. 11,208-9 from Aldrich Chemical Company. In order to prevent more than a one-degree exotherm, catalyst was added over a period of 1 to 2 hr in multiple portions of from five to 20 portions. After 5 hr, the polymerizations were quenched with methanol and water. Benzene was added and part of it distilled off with water. The residue was added to methanol slowly with rapid stirring and the precipitated polymer dried in a vacuum oven. The results of these experiments are reported in Tables I and II.

Molecular weights were determined by vapor-phase osmometry with a Hitachi Perkin-Elmer 115 molecular weight apparatus with polystyrene samples as a reference.<sup>4</sup> When benzil was used as a reference, the molecular weights were approximately 20% higher. The composition of the copolymer was determined by nuclear magnetic resonance (NMR) spectroscopy. Molecular weights and their distribution were determined also with a Waters GPC/ALC 301 with five Styragel columns (one 10,000 Å, one 250 Å, and three 60 Å) using polystyrene standards as the reference. The Waters instrument was equipped with a differential refractometer. A flow rate of 1 ml/min of toluene and a short 6-sec sample injection time were used. Weight and number-average molecular weights were calculated according to Billmeyer.<sup>5</sup> Gel permeation chromatography (GPC) was carried out also with 80-mg samples of polymer in a 2.5 cm by 100 cm column packed with Sephadex LH-20 in chloroform. Samples were collected automatically and weighed. These samples proved large enough for NMR analysis.

### Composition of Copolymer, Molecular Weight, and Conversion Versus Time

Two batches were prepared in methylene dichloride at 30°C with different mole ratios of  $\beta$ -pinene to styrene. Samples were collected often to follow conversion to polymer with time. Samples were withdrawn every 6 min as each of ten portions of catalyst was added. Each successive portion of catalyst was reduced to compensate for the samples already withdrawn. A few other samples were taken until 5 hr had elapsed when the batch was quenched with methanol and water and worked up as usual. These results are shown in Table III.

### The Effect of Solvent Type on Homopolymerization

Homopolymers of  $\beta$ -pinene and styrenes were prepared at 30°C from 20 g monomer, 13.3 g solvent (40% of total weight of batch), and 0.6 g (3%) anhydrous aluminum chloride. The number-average molecular weights were determined by vapor-phase osmometry with a Perkin-Elmer Model 115 instrument. Table IV shows the effect of the solvent on the molecular weight of the homopolymers.

## RESULTS AND DISCUSSION

### Yield and Composition of Polymers

The polymerizations summarized in Tables I and II were carried out in methylene dichloride and in *m*-xylene at 30° and -78°C. The *m*-xylene at 30°C results are taken from a previous paper<sup>1</sup> where the weight per cent solvent was 40%.

TABLE I  
Yield and Composition Versus Feed

Batch no.	Feed P/S, mole ratio	Catalyst, mole-%	Yield, wt-%	Insoluble in acetone, wt-%	Styrene in acetone insoluble portion, mole-%	Insoluble in hexane, wt-%	Styrene in hexane insoluble portion, mole-%	Styrene in polymer, mole-%	Styrene in polymer calcd. from yield, mole-%
A. Methylene Dichloride at 30° C									
6	s	1	100						
9	p	1	62						
3	1:1	0.5	66	100	31	0	—	35	16
4	1:1	1	82	84	46	1	—	32	40
7a	1:1	5	92	69	48	2	—	37	44
10	1:4	1	85	68	75	83	79	67	76
B. Methylene Dichloride at -78° C									
17	s	5	100						
16	p	5	22						
19	p	5	33						
13	1:1	5	93	99	50	2	—	45	49
18	1:4	1	94	100	73	100	61	—	—
15	1:4	5	100	98	79	98	60	72	80
C. <i>m</i> -Xylene at 30° C									
105	s	2.6	82						
106	p	2.6	20						
104	1:1.33	2.6	50	15				65	0
D. <i>m</i> -Xylene at -78° C									
26	s	5	79						
25	p	5	84						
24	1:1	5	71	0	—	0	—	27	24
23	1:4	5	59	0	—	0	—	58	65
28	1:1	1	low	3	—	7	—	37	—
27	1:4	1	low	31	—	66	—	83	—
33	1:4	5	—	31	—		—		

TABLE II  
 Molecular Weight Versus Feed

Batch no.	Feed P/S, mole ratio	Catalyst, mole-%	Polymer				Acetone insoluble			
			$\bar{M}_n$ VPO	$\bar{M}_n$ GPC	$\bar{M}_w$ GPC	$\bar{M}_w/\bar{M}_n$ VPO	$\bar{M}_n$ VPO	$\bar{M}_n$ GPC	$\bar{M}_w$ GPC	$\bar{M}_w/\bar{M}_n$ VPO
A. Methylene Dichloride at 30° C										
6	s	1	3500	4600	12,000	3.4				
9	p	1	3200	2900	3,600	1.1				
3	1:1	0.5	3100	7500	11,000	3.7	3000	8700	32,000	3.7 <sup>a</sup>
4	1:1	1	3700	4500	7,800	2.1	3700	5700	8,500	2.3
7a	1:1	5	1900	3600	4,300	2.3	3500	4800	6,600	1.9
10	1:4	1	3600	6700	11,000	3.1	6000	10,000	12,000	2.1
B. Methylene Dichloride at -78° C										
17	s	5	18,000	31,000	93,000	5.2				
16	p	5	1,800	2,400	2,600	1.4				
19	p	5	2,800	5,800	8,400	3.0				
13	1:1	5	6,500	7,600	14,000	2.2	6,400	7,400	14,000	2.1
18	1:4	1	16,000	15,000	28,000	1.8	13,000	13,000	31,000	2.6
15	1:4	5	8,600	15,000	37,000	4.3	8,200	12,000	29,000	3.5
C. <i>m</i> -Xylene at 30° C										
105	s	2.6	845	840	1450	1.7				
106	p	2.6	1,890	930	1220	1.3a				
104	1:1.33	2.6	1,100	1000	1380	1.3				
D. <i>m</i> -Xylene at -78° C										
26	s	5	370	530	700	1.9				
25	p	5	3,900	5,900	8,500	2.2				
24	1:1	5	700	920	800	1.1				
23	1:4	5	500	1,240	1,780	1.4a				
28	1:1	1	450	3,700	5,000	1.4a				
27	1:4	1	2,600	20,000	43,000	2.2a				
33	1:4	5	10,000	5,000	12,000	1.2				

<sup>a</sup>  $\bar{M}_w/\bar{M}_n$  GPC.

In general, the yield of polymer increases with catalyst concentration. This is consistent with the well-known requirement of having to add catalyst continually in cationic polymerization. The yield is higher for styrene than for  $\beta$ -pinene and increases as the styrene content of the feed increases at both temperatures in methylene dichloride and at 30°C in *m*-xylene. At -78°C in *m*-xylene  $\beta$ -pinene seems to give the higher yield.

Two attempts to polymerize a 1:1 mole ratio of  $\beta$ -pinene to styrene at -78°C in methylene dichloride with 1% catalyst gave no polymer. One per cent catalyst was sufficient for the 1:4 ratio, batch 18. Low yields were obtained at -78°C in *m*-xylene at both mole ratios using 1% catalyst, batches 27 and 28.

In spite of the increasing yield with styrene content of feed, an analysis of the polymers shows less styrene than is expected from the feed composition. A calculation was made of the mole-% styrene predicted in the polymer based on the feed composition, the yield, and the assumption of complete conversion of  $\beta$ -pinene and incomplete conversion of styrene. These values are given in Table I as mole-% styrene in polymer calculated from the yield. There is fair agreement between observed and calculated values.

### Molecular Weights

In general, low temperature and low catalyst concentration favor high molecular weight. For styrene homopolymers, molecular weights are lower in *m*-

TABLE III  
Per Cent Conversion, Molecular Weight, and Polymer Composition Versus Time

Time, min	% Converted	$\bar{M}_n$ VPO	Styrene in polymer, mole-%
A. $\beta$ -Pinene-to-Styrene Ratio 1:1, Batch 29			
12	7		
18	11		
24	15		
30	24		
36	28	6300	36
42	28		
48	31		
60	36	2100	36
90	49		
150	50		
300	50	1900	40
B. $\beta$ -Pinene-to-Styrene Ratio 1:4, Batch 30			
6	5		
12	7	4300	73
24	20		
30	21	3000	73
36	30		
42	36		
48	53		
54	64	2500	73
60	66		
90	74		
150	79		
300	84	2500	75

xylene than in methylene dichloride. Insufficient data prevent drawing correlations with  $\beta$ -pinene homopolymers or copolymers.

The molecular weight distribution was calculated as the ratio of weight-average molecular weight by GPC to number-average molecular weight by vapor phase osmometry (VPO). The molecular weight distributions follow the pattern of copolymer distribution falling between homopolymer values. Polystyrene appears to have a broader molecular weight distribution than poly- $\beta$ -pinene. However, this latter conclusion is dependent on the calibration of both instruments with polystyrene standards and neither instrument with poly- $\beta$ -pinene standards.

### Evidence for Copolymerization in Methylene Dichloride

In batch 3, the combination of 66 wt-% yield and 100% insolubility in acetone is incompatible with the synthesis of a mixture of homopolymers. For a mixture of homopolymers with a 66% yield, the maximum possible per cent insoluble in acetone would be 85%. For batch 3, the composition of acetone-insoluble portion of 31 mole-% suggests that a copolymer was formed which is insoluble in acetone because of a preponderance of  $\beta$ -pinene. The same argument applies to batches 4, 7a, and 13. This solubility behavior is based on the known fact that poly- $\beta$ -pinene is insoluble in acetone and polystyrene is soluble.

Batches 10, 15, and 18 had considerable polymer insoluble in both acetone and hexane. Obviously, these copolymers have solubility parameters too far from the solubility parameters of either acetone or hexane to dissolve in these solvents.

The molecular weight of the acetone-insoluble portion of batches prepared in methylene dichloride was almost always higher than the molecular weight of the corresponding crude polymer. If there had been much high molecular weight polystyrene homopolymer in the crude polymer, then extraction with acetone should have lowered the molecular weight. The mole-% styrene usually increased after extraction of the crude polymer with acetone, most likely because the more soluble low molecular weight portion of crude polymer was richer in  $\beta$ -pinene. It dissolved because of its low molecular weight.

The evidence from GPC with Waters instrument is inconclusive. Batch 16

TABLE IV  
Molecular Weight Versus Solvent Type

Solvent	$\bar{M}_n$ VPO	
	Styrene	$\beta$ -Pinene
Heptane	1500	1400
Benzene	2100	2000
Toluene	650	2200
<i>o</i> -Xylene	490	1400
<i>m</i> -Xylene	550	1200
<i>p</i> -Xylene	830	1200
Mesitylene	800	2000
Durene	720	—
Anisole	300	890
Phenyl acetate	1700	510
Acetophenone	2100	340
Nitrobenzene	920	710

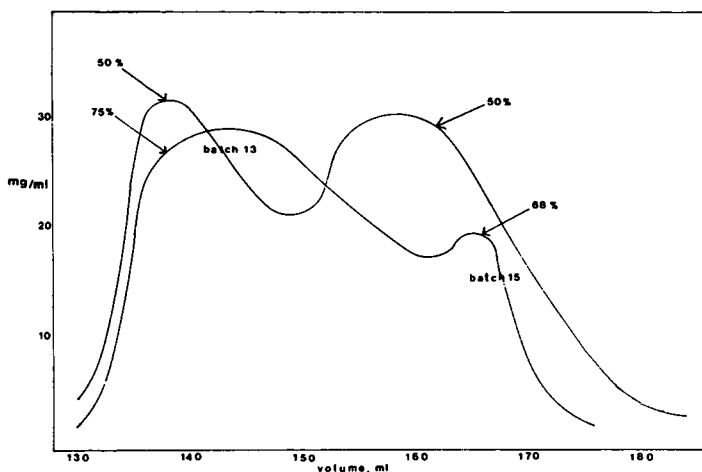


Fig. 1. GPC of batches 13 and 15 and mole-% styrene in selected fractions.

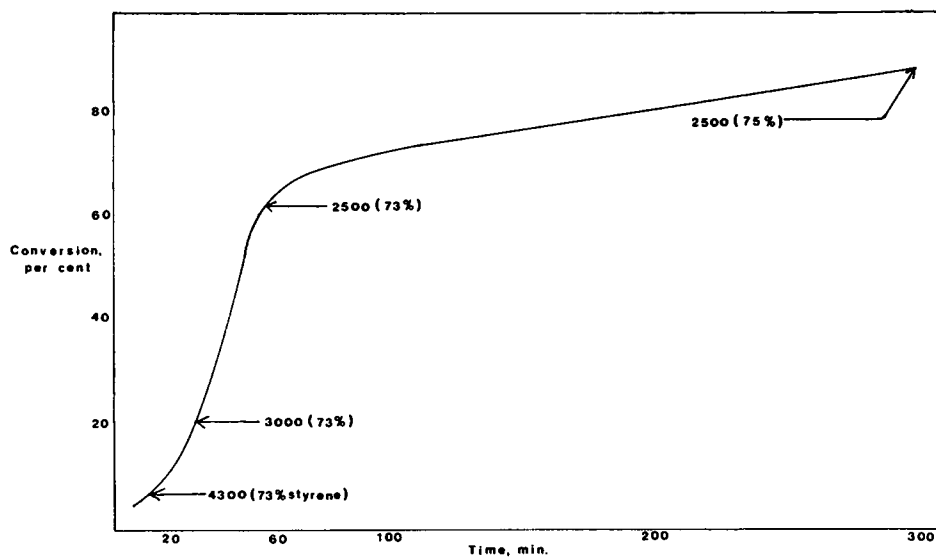


Fig. 2. Conversion, molecular weight, and composition (mole-% styrene) vs. time.

had a flat neck because the difference in refractive index of toluene and poly- $\beta$ -pinene is small. Batch 17 was bimodal even though a homopolymer. A mixture of 16 and 17 homopolymers gave the bimodal polystyrene trace followed by a tail due to the lower molecular weight poly- $\beta$ -pinene. Copolymer 13 had a small low molecular weight tail; copolymer 15 is a monomodal trace.

When Sephadex LH-20 was used, a bimodal trace was obtained with a mixture of batches 17 and 19. However, the copolymer batch 13 also gave a bimodal trace and the copolymer batch 15 gave a peak with a shoulder (Fig. 1). Analysis by NMR of the styrene content of fractions taken from the peaks or shoulder for two separate GPC runs with Sephadex LH-20 or batches 13 and 15 follow: GPC run 1, batch 13: 53 and 58 mole-% styrene; GPC run 2 batch 13: 50 and 50

mole-% styrene; GPC run 1, batch 15: 78 and 73 mole-% styrene; GPC run 2, batch 15: 75 and 68 mole-% styrene.

Since the peaks of batch 13 and the peak and shoulder of batch 15 have similar compositions, these batches appear to be copolymers. The bimodal traces of batches 13 and 15 may be caused by two different molecular weight ranges of copolymers. This bimodal distribution has been observed for homopolymers<sup>6</sup> and claimed to be caused by the presence of two types of initiators. Another possible explanation in our case for bimodal traces is the changing catalyst to monomer ratio during polymerization.

The data presented in Table III for batches 29 and 30 (Fig. 2) demonstrate that the composition of copolymer changes very little with per cent conversion. This result seems highly unlikely for two simultaneous homopolymerizations and possible for copolymerization only if the monomer reactivity ratios were close.

It is difficult to account for the difference between Sivola and Harva's homopolymerization of  $\beta$ -pinene and styrene in methylene dichloride and the copolymerization results of this paper. They used high-purity  $\beta$ -pinene. The presence of other terpenes in our sample should not have affected our results since they claim that none of these terpenes copolymerizes with styrene either.<sup>2</sup>

### Molecular Weight Versus Conversion

During the study of per cent conversion versus time, samples were taken to determine the composition of the copolymer, batches 29 and 30 in Table III. These same samples were shown to vary in molecular weight with per cent conversion. The molecular weights decrease during copolymerization from an initial value of 8000 to 1900 for batch 29 and from 4300 to 2500 for batch 30 (Fig. 2). This is probably due to the catalyst-to-monomer ratio increasing during polymerization.

Using this same technique, homopolymers of styrene were found to decrease in molecular weight when using 0.5% aluminum chloride in methylene dichloride from 3100 to 2500. When 1% aluminum chloride was used in *m*-xylene, the decrease was from 630 to 490.

### Solvent Effects on Molecular Weight

The molecular weight of polystyrene is decreased more than the molecular weight of poly- $\beta$ -pinene by chain transfer with aromatic solvents. Anisole is a very effective chain transfer agent for styrene and acetophenone for  $\beta$ -pinene. In the styrene polymerizations, the effectiveness of methyl-substituted benzene for chain transfer reaches a maximum with dimethylbenzene. Neither monomer polymerized in furan.

### References

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