

The Characterization of Styrene- β -Pinene Polymers

HOWARD SHEFFER, * GARY GRECO, and GEORGE PAIK, *Union College, Schenectady, New York 12308*

Synopsis

Styrene was polymerized with β -pinene at 30°C and -50°C in methylene dichloride and in *m*-xylene solvents. The styrene-to-terpene ratio on pyrolysis suggests that the polymers made at 30°C are copolymers, whereas most of the polymers made at -50°C are not copolymers. On the other hand, ethylene, ethane, and propylene analysis suggests that more of the polymers made at -50°C are copolymers.

INTRODUCTION

The purpose of this work was to use polymer pyrolysis as a method of determining whether styrene and β -pinene copolymerize in two different solvents at two different temperatures.

Bimodal peaks were obtained by GPC analysis of polymers prepared from a mixture of styrene and β -pinene with Lewis acid catalyst in methylene dichloride solvent¹ and were interpreted as evidence for lack of copolymerization. In a later study² samples of the bimodal peaks obtained by GPC were analyzed by NMR and shown to contain both monomers in amounts close to the feed ratio. Solubility studies confirmed that these polymers were copolymers. Solvent extraction and GPC were used in another study³ to prove that styrene and β -pinene copolymerize in *m*-xylene solvent. Polymers of styrene and β -pinene were shown to be mostly copolymers by solvent extraction.⁴ Curie-point pyrolysis confirmed that those polymers made in Finland at 30°C were copolymers, but those made at -50°C may not have been. Pyrolysis⁵ has been used to distinguish copolymers from mixtures of homopolymers in the styrene-acrylonitrile system. Pyrolysis-gas chromatography has been used to determine the sequence distribution in vinyl copolymers.⁶

EXPERIMENTAL

β -Pinene was purified by vacuum distillation (α -pinene 0.07%, myrcene 0.35%, and dipentene 0.38%). The styrene- β -pinene polymers were prepared by adding aluminum chloride in multiple portions over a period of 1 h and continuing the polymerization for 5 h. After quenching with methanol and washing with dilute acid, the polymers were precipitated from solution by methanol. The polymers were prepared at 30°C and -50°C in either methylene dichloride or *m*-xylene, using 5 mol % catalyst. The yields of polymer were in the 60-100% range, mostly about 95%. Yields over 100% were sometimes observed in *m*-xylene due to chain

* Permanent address: Chemistry Department, Union College, Schenectady, New York 12308.

transfer to solvent. The molecular weights were in the neighborhood of 1000 in methylene dichloride and lower in *m*-xylene.

Because of the fact that the pyrolysis studies reported in Table I were performed on high-conversion polymers, one must be concerned with the possibility that in the later stages of copolymerization the copolymer formed could be quite rich in one of the two monomer units. A recent determination of the monomer reactivity ratios in methylene dichloride at 30°C for low conversions gave $r_1 = 0.85$ and $r_2 = 1.40$ ($M_1 = \text{styrene}$, $M_2 = \beta\text{-pinene}$). Since the r values are close to 1, there should not be large amounts of copolymer rich in one or the other monomer units.

Another set of pyrolysis studies performed over the temperature range shown in Table I on low-conversion polymers confirmed that these polymers are copolymers since the styrene-to-terpenes ratio after pyrolysis in the 1:1 copolymer divided by the same ratio in a mixture of homopolymers was 5.5 at 500°C and 5.0 at 450°C for low conversion polymers made at 30°C in methylene dichloride.

The composition of polymers was determined with a Jeol JNM-PM \times 60 NMR Spectrometer. Pyrolysis was performed with a Hewlett-Packard Unit 80 using a pyrolysis time of 10 s. Vapor phase chromatography of the product was conducted at 130°C on a silicon column using a Gow-Mac Series 500 Vapor Phase Chromatograph with a thermal conductivity detector. The pyrolysis products were identified by retention times. The identity of pyrolysis products was confirmed with a Hewlett-Packard 5990A Gas Chromatograph/Mass Spectrometer.

The chief product of thermal decomposition of polystyrene was styrene, whereas terpenes were the main products of thermal decomposition of poly(β -pinene). In pyrolysis studies of copolymers and mixtures of homopolymers particular attention was paid to the styrene-to-terpene ratio.

TABLE I
Styrene- β -Pinene Copolymer Made at 30°C in CH_2Cl_2 with 1:1 Mole Ratio

Pyrolysis temp. (°C)	Ratio of styrene to terpenes on pyrolysis		Styrene-to-terpenes ratio after pyrolysis for copolymer divided by the same ratio for mixture
	Copolymer	1:1 mixture of homopolymers	
400	1.18	0.095	12.5
450	1.40	0.16	9.2
	0.91	0.15	6.5
	0.91	0.19	4.9
500	1.72	0.32	5.4
	1.23	0.32	4.0
	1.18	0.20	5.8
525	1.79	0.25	7.5
550	1.87	2.46	0.74
	1.91	1.27	1.5
600	4.80	2.97	1.6
	3.56	3.56	1.0
800	6.27	5.02	1.3

The ratio of the area under the curve for styrene to the area under the curve for terpenes was converted to mole ratio of styrene to terpenes using phellandrene as the reference terpene.

In calculating the molar ratio of gas to terpene, an average value of the response factor for the three gases (ethylene, ethane, and propylene) was used, with phellandrene being the reference for terpenes.

DISCUSSION

Pyrolysis was conducted at eight different temperatures in the 400–800°C range in order to determine the optimum temperature for distinguishing a copolymer from a mixture of homopolymers. The lower temperatures gave larger values to the key factor: namely, the styrene-to-terpene ratio after pyrolysis of a 1:1 copolymer divided by the same ratio for a 1:1 mixture of homopolymers (Table I).

Polystyrene is more thermally stable than poly(β -pinene). However, at higher temperatures both polystyrene and poly(β -pinene) decompose, resulting in little distinction between a copolymer and mixtures of homopolymers. At lower temperatures a higher concentration of styrene appears on pyrolysis of copolymer than in a mixture of homopolymers because the terpene portions of the copolymer, which crack readily, expose styrene radicals which then unzip.

Pyrolysis of styrene- β -pinene polymers (1:1 and 4:1) prepared at 30°C and -50°C in *m*-xylene or methylene dichloride was conducted at both 450°C and 500°C (Table II). When the styrene-to-terpene ratio after pyrolysis of the polymer prepared from styrene and β -pinene, divided by the same ratio for the mixture of homopolymers, is much greater than unity, then the polymer is assumed to be a true copolymer.

Polymers made from styrene and β -pinene in either methylene dichloride or in *m*-xylene at 30°C appear to be copolymers regardless of the styrene-to- β -pinene feed ratio (1:1 or 4:1).

Polymers made in methylene dichloride or *m*-xylene at -50°C are not copolymers except for those made at the 4:1 feed ratio in *m*-xylene.

A study of monomer reactivity ratios at 30°C in methylene dichloride shows that the carbonium ions prefer β -pinene monomers slightly over styrene monomers. At -50°C this preference is accentuated, leading essentially to a mixture of homopolymers or at least a block copolymer. Apparently the 4:1 feed ratio and change of solvent to *m*-xylene enhance the ability of styrene to compete with β -pinene for carbonium ions at -50°C.

The pyrolysis of polystyrene gives small amounts of gases identified as ethylene and ethane. The pyrolysis of poly(β -pinene) gives larger quantities of gases identified as ethylene, ethane, and propylene.

Poly(β -pinene) and a 1:1 polymer of styrene and β -pinene made in methylene chloride at 30°C were pyrolyzed at temperatures ranging from 250°C to 800°C. At all temperatures poly(β -pinene) gave a higher gas-to-terpenes ratio than the copolymer. For poly(β -pinene) the ratio increases with decreasing temperature. For the copolymer the ratio decreases with decreasing temperature except for an increase at 350°C.

TABLE II
Pyrolysis of Polymers

Polymerization temp (°C)	Solvent	Mole ratio of styrene to β -pinene in feed	Pyrolysis temp (°C)	Ratio of styrene to terpenes on pyrolysis		Styrene-to-terpenes ratio on pyrolysis for copolymer divided by the same ratio for mixture
				Copolymer	Homopolymer mixture	
30	CH ₂ Cl ₂	1:1	500	1.35	0.28	4.7
		4:1		3.08	1.14 ^a	2.7
-50	CH ₂ Cl ₂	1:1	500	0.56	0.91	0.61
		4:1		2.05	3.64 ^a	0.56
30	<i>m</i> -Xylene	1:1	500	0.99	0.10	9.6
		4:1		14.0	0.40 ^a	34
-50	<i>m</i> -Xylene	1:1	500	0.14	0.25	0.56
		4:1		2.62	1.00 ^a	2.62
30	CH ₂ Cl ₂	1:1	450	1.16	0.16	7.3
		4:1		2.28	0.64 ^a	3.6
-50	CH ₂ Cl ₂	1:1	450	0.29	0.23	1.3
		4:1		1.07	0.92 ^a	1.2
30	<i>m</i> -Xylene	1:1	450	0.46	0.05	10
		4:1		5.13	0.20 ^a	39
-50	<i>m</i> -Xylene	1:1	450	0.13	0.07	1.8
		4:1		1.67	0.28 ^a	6.0

^a Calculated.

The different gas-to-terpenes ratio for poly(β -pinene) and the 1:1 polymer of styrene and β -pinene made in methylene chloride at 30°C is further evidence that this is a copolymer.

The fact that the gas-to-terpenes ratio increases with decreasing temperature for poly(β -pinene) and the ratio decreases for the copolymer of styrene and β -pinene suggests that the terpene units present in the copolymer differ from the terpene units in poly(β -pinene) homopolymer.

A calculation based on the molecular weight of the polymer and the amount of *m*-xylene obtained on pyrolysis of the polymer at 800°C gives an estimate of the proportion of the chains terminated by chain transfer to the solvent, *m*-xylene. At 30°C about one third of the chains are terminated by *m*-xylene, while at -50°C about one fifth are terminated.

Analyses of gases from the pyrolysis at 800°C of polymers of styrene and β -pinene and of homopolymers were compared. Polymers of styrene and β -pinene made in methylene dichloride at 30°C and -50°C gave both more propylene than ethylene and ethane. Mixtures of homopolymers, on the other hand, gave less propylene than ethylene and ethane. This would suggest that even the -50°C polymers of styrene and β -pinene may be copolymers in contradiction to the styrene-to-terpene ratio study mentioned earlier.

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