

This article was downloaded by:

On: 24 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



## Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597274>

### Copolymers from $\alpha$ -Pinene. 2. Cationic Copolymerization of Styrene and $\alpha$ -Pinene

A. Rashed Khan<sup>a</sup>; A. H. K. Yousufzai<sup>a</sup>; H. A. Jeelani<sup>a</sup>; Tehzeeb Akhter<sup>a</sup>

<sup>a</sup> Pakistan Council of Scientific and Industrial Research Laboratories, Karachi, Pakistan

**To cite this Article** Khan, A. Rashed , Yousufzai, A. H. K. , Jeelani, H. A. and Akhter, Tehzeeb(1985) 'Copolymers from  $\alpha$ -Pinene. 2. Cationic Copolymerization of Styrene and  $\alpha$ -Pinene', *Journal of Macromolecular Science, Part A*, 22: 12, 1673 – 1678

**To link to this Article:** DOI: 10.1080/00222338508063364

**URL:** <http://dx.doi.org/10.1080/00222338508063364>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

## Copolymers from $\alpha$ -Pinene. 2. Cationic Copolymerization of Styrene and $\alpha$ -Pinene

A. RASHEED KHAN, A. H. K. YOUSUFZAI, H. A. JEELANI, and TEHZEEB AKHTER

Pakistan Council of Scientific and Industrial Research Laboratories  
Karachi 39, Pakistan

### ABSTRACT

A study of the copolymerization of  $\alpha$ -pinene and styrene has been carried out at 10°C using anhydrous  $AlCl_3$  as the initiator. It is found that styrene forms copolymer with  $\alpha$ -pinene at all monomeric ratios. A copolymer of 2320-3080 molecular weight is obtained. The softening range of the copolymer is 82 to 85°C. The copolymers are of commercial value.

### INTRODUCTION

The free-radical-type copolymerization of  $\alpha$ -pinene and methyl methacrylate has been reported [1]. It was observed that not only does  $\alpha$ -pinene copolymerize with methyl methacrylate, but it also acts as a chain transfer agent, resulting in a copolymer of low molecular weight. The polymerization of terpene monomers with  $AlCl_3$  at moderately low temperatures has been of industrial importance,  $\beta$ -Pinene, which contains the  $=CH_2$  group, polymerizes readily with Friedel-Crafts catalysts at low temperature to give polymers with longer chains and melting above 100°C.  $\alpha$ -Pinene and limonene polymerize less readily under similar conditions and give a product

of low molecular weight [2]. Terpene monomers also copolymerize with vinyl monomers with  $\text{AlCl}_3$  as the catalyst in suitable aliphatic or aromatic solvents. Terpene polymers [3, 4] and copolymers [5-7] are resins of low molecular weight which are now generally used in pressure-sensitive adhesive coatings, sizings, rubber compounding, concrete curing, floor waxes, polishes, etc. Efforts are being made to prepare copolymers of higher molecular weight by copolymerizing  $\alpha$ -pinene with some vinyl monomers.

This paper deals with the copolymerization of  $\alpha$ -pinene with styrene in the presence of benzene using  $\text{AlCl}_3$  as the catalyst.

## EXPERIMENTAL

### Materials

Styrene (BDH) was washed with 10% NaOH to remove the inhibitor and then washed with water many times. It was finally dried over  $\text{CaCl}_2$  and distilled. Commercial grade  $\alpha$ -pinene was dried over metallic sodium, and the fraction boiling at 157-158°C was collected. Laboratory reagent-grade acetone, petroleum ether, methyl ethyl ketone, methanol, and benzene (BDH) were used. Anhydrous aluminum chloride (BDH) was used without further purification.

### Procedure of Copolymerization

A three-neck round-bottom flask was fitted with a stirrer, funnel, and thermometer, and kept in an ice-cold bath. Known quantities of monomers in different proportions (given in Table 1) were transferred to the reaction flask already containing 100 mL benzene. The mixture was stirred for 15 min, and 5.0 g anhydrous  $\text{AlCl}_3$  (5% based on monomers) was gradually added. During the addition of  $\text{AlCl}_3$ , the temperature was maintained at 10°C. The reactants were continuously stirred for 3 h. After the required reaction time the product was transferred to a separating funnel and shaken with distilled water to remove the catalyst. Methanol was then added. The bottom layer was collected. The solvent and unreacted monomers were distilled off. A solid pale yellow substance was obtained; it may be powdered. The substance was found to be soluble in most organic solvents. The softening range of product is 82 to 85°C. The IR spectra of the product and of the monomers indicate that the substance is a copolymer. The viscosity of dilute solutions of products prepared in benzene was measured at 30 ± 0.5°C using an Ostwald-type viscometer. The refractive index of the same solution was measured on Refractometer No. 122 894 of Zeiss Opton, Germany. The product was analyzed for carbon and hydrogen.

## RESULTS AND DISCUSSION

The data collected from the cationic copolymerization of styrene and  $\alpha$ -pinene using  $AlCl_3$  as initiator in the presence of benzene are summarized in Table 1. The elementary analysis of the resulting product, prepared samples of poly(styrene) and poly( $\alpha$ -pinene), were carried out for H and C. The five samples of the product contain 89.97-90.81% carbon and 9.13-9.88% hydrogen. The prepared sample of poly(styrene) contains 92.24 and 7.68% C and H, respectively, whereas poly( $\alpha$ -pinene) contains 88.20 and 11.75% C and H, respectively. This shows that both monomers have participated in the reaction and a new product has been formed. It is also because styrene and  $\alpha$ -pinene may both be polymerized cationically by  $AlCl_3$ , and growing polymer chains of poly(styrene) and poly( $\alpha$ -pinene) couple to produce a new product. Further, poly(styrene) swells [8] in acetone (solubility of 0.3 g/100 mL) whereas poly( $\alpha$ -pinene) is insoluble in acetone. On the other hand, the product is highly soluble in acetone. The solubility behavior also supports the results of the analysis for carbon and hydrogen and shows that the product is obviously a copolymer. IR spectral studies also favor the assumption that the product is a copolymer. The IR spectra of poly(styrene), poly( $\alpha$ -pinene), and the product are recorded and the positions of the absorption maxima are listed for comparison in Table 2. In the spectrum of the product, the bands with maxima at about 2900, 1450, 1380, and 1160  $cm^{-1}$  are characteristic C-C bands. The 1600  $cm^{-1}$  band is characteristic of the C=C stretching vibration.

It is evident from the results shown in Table 1 that the rate of formation of copolymer increases with an increase in the monomeric ratio of styrene in the binary mixture of the monomers (Fig. 1). The conversion is maximum at a high feed value of styrene. The yield and chemical analysis of the copolymer samples indicate that both styrene and  $\alpha$ -pinene form a copolymer at all monomeric ratios. Both  $\alpha$ -pinene and styrene may be polymerized quite readily with  $AlCl_3$  in the presence of aromatic solvents at low temperature. In the case of  $\alpha$ -pinene, it first isomerizes to limonene before polymerizing and then the limonene isomer begins to polymerize. The growing polymer chain of the limonene isomer propagate the chain and couple with growing polymer chain of poly(styrene) and hence form a copolymer.

The viscosity of the copolymer solutions in benzene was measured at 30°C. The number-average molecular weight  $\bar{M}_n$  of the copolymer samples was determined by using the following relationship of intrinsic viscosity and number-average molecular weight [9]:

$$[\eta] = 0.97 \times 10^{-4} \bar{M}_n^{0.74}$$

TABLE 1. Cationic Copolymerization of Styrene and  $\alpha$ -Pinene Using 5% Anhydrous Aluminum Chloride as the Catalyst at 10°C for 3 h

Sample	Monomer in feed		Yield, g	Analysis	
	Styrene, g	$\alpha$ -Pinene, g		C, %	H, %
1	-	100.00	28.9	88.20	11.75
2	30.0	70.00	65.0	89.97	9.88
3	40.00	60.00	70.8	90.20	9.59
4	50.00	50.00	75.1	90.61	9.23
5	60.00	40.00	80.8	90.69	9.22
6	80.00	20.00	90.7	90.81	9.13

TABLE 2. IR Spectra of Poly( $\alpha$ -Pinene), Poly(Styrene) and the Copolymer of Styrene and  $\alpha$ -Pinene<sup>a</sup>

Poly( $\alpha$ -pinene), cm <sup>-1</sup> wavenumber	Poly(styrene), cm <sup>-1</sup> wavenumber	Copolymer, cm <sup>-1</sup> wavenumber
3400 (w)	3000 (s)	3400 (w)
2900 (s)	2900 (s)	2900 (s)
1650 (w)	1940 (w)	1940 (w)
1460 (m)	1875 (w)	1875 (w)
1380 (m)	1800 (w)	1800 (w)
1160 (w)	1740 (w)	1750 (w)
1100 (w)	1600 (m)	1600 (m)
1000 (w)	1450 (m)	1450 (m)
885 (w)	1350 (m)	1380 (m)
800 (w)	1180 (w)	1160 (w)
675 (w)	1075 (w)	1030 (m)
	1020 (m)	900 (w)
	900 (m)	840 (w)
	850 (w)	750 (m)
	725 (m)	680 (m)
	680 (m)	

<sup>a</sup>s = strong, m = medium, w = weak.

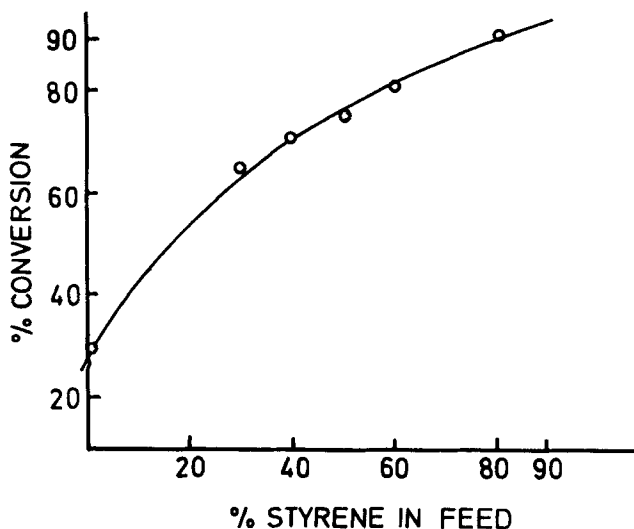


FIG. 1. A plot of percentage conversion against percentage styrene in feed for the copolymerization of  $\alpha$ -pinene with styrene.

The intrinsic viscosity of the prepared sample of poly( $\alpha$ -pinene) was measured at 0.024 dL/g (Table 3). The intrinsic viscosities of the copolymer samples were found to range from 0.03-0.037 dL/g, giving number-average molecular weights of 2320 to 3080. The entrance of styrene monomer into the growing polymer chain of poly( $\alpha$ -pinene) increases the intrinsic viscosity, and the molecular weight of the copolymer increases with the high feed value of styrene. Hence, the molecular weight of the copolymer depends upon how many styrene molecules are attached to the growing polymer chain of poly( $\alpha$ -pinene). The number-average molecular weights of poly( $\alpha$ -pinene) are reported [2] in the literature as being 650, 690, and 708 with refractive indexes of 1.5334, 1.5275, and 1.5300, respectively. The refractive index of the prepared sample of poly( $\alpha$ -pinene) was found to be 1.5005 at 30°C whereas those of the copolymers were 1.5095 to 1.5100. Further, there was a decrease in molecular weight with an increase in the concentration of  $\alpha$ -pinene (Table 1) in the feed, which indicates that the terpene monomer acts as a chain transfer agent. The same thing happens in the copolymerization of methyl methacrylate and  $\alpha$ -pinene where the molecular weight decreases with an increase of the concentration of  $\alpha$ -pinene in the feed [1].

The copolymers have potential commercial value as plasticizers and tackifying agents in the compounding of natural and synthetic elastomers for ply adhesion, coatings, and adhesives. This copolymer

TABLE 3. Intrinsic Viscosity  $[\eta]$  Number-Average Molecular Weight  $\bar{M}_n$  and Refractive Indices of Copolymer Samples of Styrene and  $\alpha$ -Pinene

Sample	$[\eta]$ , dL/g	$\bar{M}_n$	Refractive index
1	0.024	-	1.5005
2	0.030	2320	1.5095
3	0.031	2424	1.5095
4	0.033	2638	1.5098
5	0.035	2856	1.5098
6	0.037	3080	1.5100

may also be useful in the preparation of pressure-sensitive tapes by blending with rubber antioxidants, etc. The softening range of the copolymer is 82-85°C.

#### ACKNOWLEDGMENT

The authors are grateful to Professor Otsu of Osaka City University for providing analytical facilities.

#### REFERENCES

- [1] A. H. K. Yousufzai, A. Rasheed Khan, and T. Akhter, Pak. J. Sci. Ind. Res., In Press.
- [2] W. J. Roberts and A. R. Day, J. Am. Chem. Soc., **72**, 1226 (1950).
- [3] B. Golding, Polymers and Rosins, Van Nostrand, Princeton, New Jersey, 1959, p. 536.
- [4] M. Modena, R. B. Bates, and C. S. Marvel, J. Polym. Sci., **A3**(3), 949 (1965).
- [5] H. Sheffer, G. Greco, and G. Paik, J. Appl. Polymer Sci., **28**(5), 170 (1983).
- [6] H. Sheffer, A. Sivola, and J. Savelainen, Finn. Chem. Lett., **2-3**, 122 (1978).
- [7] C. Snyder, W. Molver, and H. Sheffer, J. Appl. Polym. Sci., **21**(1), 131 (1977).
- [8] K. W. Suh and D. H. Clarke, J. Polym. Sci., Part A-1, **5**, 1671 (1967).
- [9] A. H. K. Yousufzai and A. Rasheed Khan, J. Macromol. Sci.-Chem., **A18**(6), 949 (1982).

Accepted by editor July 27, 1984

Received for publication August 13, 1984