

# Technology Section

Pakistan J. Sci. Ind. Res., Vol. 30, No. 4, April 1987

## COPOLYMERS FROM $\alpha$ -PINENE Part IV: Cationic Copolymerization of $\alpha$ -Methylstyrene and $\alpha$ -Pinene

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(Received November 5, 1986; revised, March 3, 1987)

The copolymerization of  $\alpha$ -methylstyrene and  $\alpha$ -pinene in benzene has been accomplished at 10-12° using anhydrous  $AlCl_3$  as the initiator. It has been observed that  $\alpha$ -methylstyrene combines with  $\alpha$ -pinene to form copolymer at all monomeric ratios. The physical and chemical parameters of  $\alpha$ -methylstyrene dominate in the product. A copolymer of 1900-4200 molecular weight is obtained. It is a semi solid (at room temperature), highly tacky, yellowish substance that softens at 32-40°. The copolymers have several industrial possibilities.

*Key words:* Intrinsic viscosity, Stretching vibration, Binary mixture.

### INTRODUCTION

Earlier, the cationic copolymerization of styrene and  $\alpha$ -pinene was reported [1]. It was observed that styrene combines with  $\alpha$ -pinene in all monomeric ratios to form copolymers. These copolymers have potential commercial value as plasticizers and tackifying agents in compounding of natural and synthetic elastomers. The addition of the  $\alpha$ -methyl group to the vinyl chain of styrene alters the tendency of chemical reactivity of the monomer ( $\alpha$ -methylstyrene). This is because the double bond of vinyl group becomes more negative and hence slows down the rate of radical and thermal polymerization of the monomers [2]. In spite of increased negative charge on the double bond of the vinyl group  $\alpha$ -methylstyrene polymerizes normally with the Friedel-Crafts type of catalysts at low temperatures and gives a product of low molecular weight in the presence of aromatic solvents [3]. Similarly  $\alpha$ -pinene polymerizes quite readily with these catalysts at low temperatures and gives a product of low molecular weight. The copolymers of  $\alpha$ -pinene and vinyl monomers prepared with the Friedel-Crafts catalysts are becoming familiar to industry. This paper describes the copolymerization of  $\alpha$ -methylstyrene and  $\alpha$ -pinene in aromatic hydrocarbons using anhydrous  $AlCl_3$  as catalyst.

### EXPERIMENTAL

*Materials.*  $\alpha$ -Methylstyrene (BDH) was first washed with sodium hydroxide to remove the inhibitor and then washed with water. Finally, it was dried over anhydrous calcium chloride and distilled. The fraction of the monomer boiling at 165.5° was collected. Commercial grade  $\alpha$ -pinene was dried over metallic sodium and distilled at

156-158°. Laboratory reagent grade benzene, toluene, acetone, ether methyl ethyl ketone, methanol etc. were used. Anhydrous  $AlCl_3$  of E.Merck was used without further purification.

### MATERIALS AND METHOD

The copolymerization of  $\alpha$ -methylstyrene and  $\alpha$ -pinene was carried out in a three-neck round-bottom flask (reactor) with a stirrer, funnel and thermometer and kept in an ice cold bath. Known quantities of monomers in different proportions as shown in Table 1 were transferred in the reactor already containing 100 ml benzene. The contents were stirred for 15 min. To the stirred mixture 5.0 g anhydrous  $AlCl_3$  was added gradually. On the addition of catalyst, the temperature rises which was maintained at 10-12°. The reactants were continuously stirred for 4½ hr. After the required reaction time, the product was transferred to a separating funnel and shaken with distilled water containing HCl (2%) to remove the catalyst. It was finally washed with methanol (five washings each of 25 ml). The bottom layer was collected. The remaining solvents and unreacted monomers were distilled off. A semi-solid substance was obtained which on keeping in ice becomes solid and may be easily powdered. It is observed that if more methanol washings of the product are made, the copolymer in the solid form (not complete) at room temperature is obtained. The colour of the product is different at different monomeric ratios as shown in Table 3. The softening range of the product is 32-40°. The I.R. spectra of the products monomers, poly ( $\alpha$ -methylstyrene) and poly ( $\alpha$ -pinene) indicate that the substance is a copolymer. The viscosity of the dilute solutions of products prepared in benzene was measured at  $25 \pm 0.5^\circ$  using an

Ostwald-type viscometer. The refractive index of these solutions was measured on refractometer No. 122894 of Zeiss Opton, Germany. The other physical parameters of the products like appearance, consistency, density etc. are also presented in Table 3. The product was analysed for C and H.

## RESULTS AND DISCUSSION

The results of the cationic copolymerization of  $\alpha$ -methylstyrene and  $\alpha$ -pinene using  $AlCl_3$  as initiator in the presence of benzene are summarized in Table 1. The copolymer prepared by the cationic copolymerization of a binary mixture of  $\alpha$ -methylstyrene and  $\alpha$ -pinene were characterized by elemental analysis, solubility, density, I.R. spectral studies, etc. The elemental analysis of the product, prepared samples of poly ( $\alpha$ -pinene) and poly ( $\alpha$ -methylstyrene) were carried out. These analyses show

Table 1. Cationic copolymerization of  $\alpha$ -methylstyrene and  $\alpha$ -pinene using 5% anhydrous aluminium chloride as catalyst at 10-12° for 4½ hr.

Sample No.	Monomer in feed		Yield (g)	Elemental analysis	
	$\alpha$ -methylstyrene (g)	$\alpha$ -pinene (g)		(%C)	(%H)
1.	—	100.00	40.8	88.23	11.73
2.	40.00	60.00	39.2	89.54	10.21
3.	50.00	50.00	31.3	89.76	10.08
4.	60.00	40.00	25.8	90.24	9.74
5.	70.00	30.00	23.2	90.72	9.25
6.	80.00	20.00	21.6	90.80	8.97
7.	100.00	—	23.2	91.48	8.28

that five samples of the product contain C and H respectively (89.54-90.8% and 10.21-8.97%). On the other hand, the prepared sample of poly ( $\alpha$ -methylstyrene) contains 91.48% C and 8.28% H, whereas poly ( $\alpha$ -pinene) contains 88.23% and 11.73% C and H respectively. This variation in percentage of C and H suggests that both monomers have participated in the reaction resulting in a new product i.e., a copolymer. This is further supported by the fact that poly ( $\alpha$ -pinene) and poly ( $\alpha$ -methylstyrene) are soluble in ether, while the product is insoluble in ether. The best solvents for copolymers are benzene, toluene, xylene, MEK, ethyl acetate etc. The density of poly ( $\alpha$ -methylstyrene), poly ( $\alpha$ -pinene) and the product was also measured and was found to be 1.09661, 0.97458 and

Table 2. IR. spectra of poly ( $\alpha$ -pinene), poly ( $\alpha$ -methylstyrene) and the copolymer of  $\alpha$ -methylstyrene and  $\alpha$ -pinene

Poly ( $\alpha$ -pinene) $cm^{-1}$ wave number	Poly ( $\alpha$ -methylstyrene) $cm^{-1}$ wave number	Copolymer $cm^{-1}$ wave number
3400 (w)	2900 (s)	3400 (w)
2900 (s)	1720-1940 (w)	2900 (s)
1650 (w)	1600 (m)	2400 (w)
1460 (m)	1440 (m)	1660-2200 (w)
1380 (m)	1380 (w)	1580 (m)
1160 (w)	1230 (w)	1440 (m)
1100 (w)	1080 (w)	1360 (w)
1000 (w)	1020 (w)	1300 (w)
885 (w)	950 (w)	1060 (w)
800 (w)	750 (w)	1020 (w)
675 (w)	880 (w)	750 (m)
	690 (m)	680 (m)

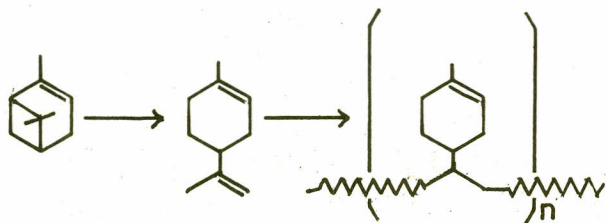
Table 3. Some physical parameters of copolymer samples of  $\alpha$ -methylstyrene and  $\alpha$ -pinene

Sample No.	dl/g	$\bar{M}_n$	Colour	Appearance	Softening range (°C)	Consistency	Density (g/ml)	Refractive index
1.	0.024	—	Brown	Semi soild	32-40	Tacky	0.97458	1.5005
2.	0.028	1905	Yellow	"	32-40	Highly tacky	0.01564	1.5008
3.	0.037	2790	Yellow	"	32-40	"	1.01570	1.5008
4.	0.045	3645	Pale Yellow	"	35-40	"	1.01570	1.5010
5.	0.047	3870	Orange Yellow	"	35-40	"	1.01570	1.5015
6.	0.050	4212	Yellowish Brown	"	32-40	"	1.01572	1.5015
7.	0.029	2940	Yellow	"	32-40	Tacky	1.09661	1.5020

1.01564-1.01572 g/ml, respectively. The difference in density also provides an evidence that the product is a copolymer. I.R. spectral studies of the product, poly ( $\alpha$ -pinene) and poly ( $\alpha$ -methylstyrene) were also recorded and the position of absorption maxima are shown in Table 2. In the spectrum of the product, the absorption band with maxima at about 2900, 1440, 1360, 1300, 1060  $\text{cm}^{-1}$  are characteristics C-C bands, while the absorption band at 1580  $\text{cm}^{-1}$  is the characteristic of C=C stretching vibration. This is further evidence which shows that a copolymer has been formed.

Since the amount of carbon in the copolymer increases with increasing concentration of  $\alpha$ -methylstyrene in the binary mixture of  $\alpha$ -methylstyrene and  $\alpha$ -pinene, (Fig. 1) the physical and as well as chemical parameters of  $\alpha$ -methylstyrene dominate in the product. This is also evident from the density, refractive index and percentage of C and H of the product. The density values of poly ( $\alpha$ -methylstyrene) and poly ( $\alpha$ -pinene) are, respectively, 1.09661 g/ml and 0.97458 g/ml, whereas of the product it is 1.01564-1.01572 g/ml. Similarly the refractive index of the product (1.5008-1.5015) is also in the vicinity of the refractive index of poly ( $\alpha$ -methylstyrene) 1.5020. Furthermore, the percentage of C and H in the copolymer (Table 1) is going in the vicinity of C and H of  $\alpha$ -methylstyrene as the more  $\alpha$ -methylstyrene monomer units link to the growing copolymer chain. All these evidences support to the above assumption. In Fig. 2, the rate of the formation of the copolymer increases with increasing concentration of  $\alpha$ -pinene in the binary mixture (at a slow rate), which shows that both monomers participate in the reaction and form copolymers at all monomeric ratios. Both monomers polymerize quite readily with  $\text{AlCl}_3$  in the presence of aromatic solvents at moderately low temperature.

$\alpha$ -Pinene does not polymerize, although it has an internal double bond. The propagation of  $\alpha$ -pinene is probably impeded by severe steric hindrance. It first isomerizes to its isomer limonene (4-isopropenyl-1-methylcyclohexene) and then limonene isomer begins to polymerize. This is because limonene isomer contains  $=\text{CH}_2$  group which is the prominent site for initiation [7].



Since the terminal end of the growing polymer chain is very reactive, the reactive end of the growing polymer chain of limonene isomer colloid with another radical or growing polymer chain of the same monomer or with reactive radical or growing polymer chain of  $\alpha$ -methylstyrene to terminate the growth resulting a copolymer. In the cationic copolymerization of  $\alpha$ -pinene and styrene [1] both monomers form a copolymer in all monomeric ratios

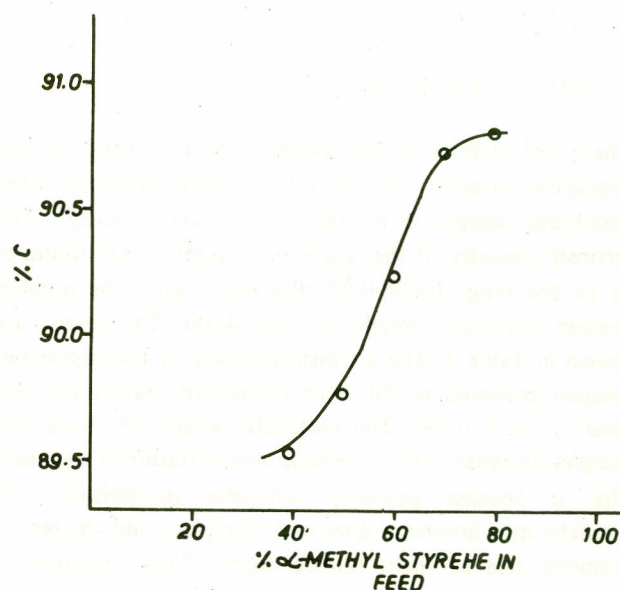


Fig. 1. A plot of percentage carbon (%C) against percentage  $\alpha$ -methylstyrene in feed for the copolymerization of  $\alpha$ -pinene with  $\alpha$ -methylstyrene.

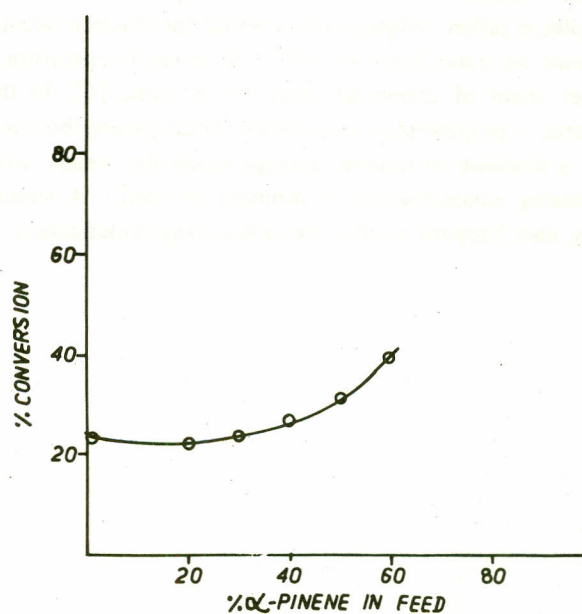


Fig. 2. A plot of percentage conversion against percentage  $\alpha$ -pinene in feed for the copolymerization of  $\alpha$ -pinene with  $\alpha$ -methylstyrene.

and the rate of formation of the copolymer increases with increasing concentration of styrene. In the present case the rate of formation decreases with increasing concentration of  $\alpha$ -methylstyrene. One of the cause is rather the presence of methyl group in place of hydrogen in  $\alpha$ -methylstyrene monomer.

The number average molecular weight ( $\overline{Mn}$ ) of the copolymer samples was determined by viscometry using the following relation ship [4],

$$[\eta] = 1.13 \times 10^{-4} \overline{Mn}^{0.73}$$

where  $[\eta]$  defines as the intrinsic viscosity (dl/g) of the copolymer samples. The viscosity of dilute solutions of the copolymer samples in benzene were measured at 25°. The intrinsic viscosity of the copolymer samples were found to be in the range 0.028-0.05 dl/g which gives the number average molecular weight as 1900-4200. The results are shown in Table 3. The intrinsic viscosity of the copolymer samples prepared at different monomeric ratios are very close to each other. The molecular weight of copolymer samples decreases with increasing concentration of  $\alpha$ -pinene. This is because probably complete isomerization of  $\alpha$ -pinene into limonene does not take place and the rest of  $\alpha$ -pinene acts as chain transfer agent. The formation of copolymer of low molecular weight might be due to partial conversion of  $\alpha$ -methylstyrene into its dimers and trimers at the early stage which acts as chain transfer agent [5]. One of the reasons for low molecular weight of copolymer samples is rather temperature at which the reaction occurs. It must be more lower ( $< 10^\circ$ ). At lower temperature a bigger chain of copolymer may be obtained [6]. In the cationic copolymerization of styrene and  $\alpha$ -pinene there was also a decrease in number average molecular weight with increasing concentration of  $\alpha$ -pinene in feed. A similar thing also happens in the free radical copolymerization of

the monomer pairs AN- $\alpha$ -pinene [7] and MMA- $\alpha$ -pinene [8] where the molecular weight lowers down with the increase in concentration of  $\alpha$ -pinene. These results clearly show that partial isomerization of  $\alpha$ -pinene into limonene occurs and the rest of  $\alpha$ -pinene acts as chain transfer agent.

Some physical parameters are collected in Table 3. The copolymer obtained is semi solid (at room temperature), highly tacky, yellow and yellowish brown. The softening range is 32-40°. The copolymer has many industrial applications. It may be used as plasticizer in hot melt coatings, wax compositions, polishes, calendered products, paper and textile coatings, rubber compositions, adhesives etc. Being highly tacky and having a low softening point and low molecular weight, it may be successfully used in the preparation of all types of tapes including pressure sensitive adhesive tapes.

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