CATIONIC TERPOLYMERIZATION OF STYRENE, α- METHYLSTYRENE AND α- PINENE

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A study of cationic terpolymerization of styrene, α-methylstyrene and α-pinene in toluene has been carried out at 10-12° using anhydrous $AlCl_3$ as catalyst. It has been observed that these three monomers form terpolymer in all monomeric ratios. A terpolymers of 42963- 61850 molecular weight are obtained. The terpolymer samples are yellowish brown tacky substances soluble in most of the organic solvents. It is soft at room temperature. The refractive index of terpolymer samples ranges 1.494-1.495. The terpolymer may be used as tackifying agent in the preparation of all type of adhesives.

Key words: Terpolymerization, Tackifying agent, Binary mixture.

Introduction

In our earlier communication, the cationic polymerization of a binary mixture of styrene and α-methylstyrene and α-pinene has been reported [1]. It was observed that the three monomers polymerize simultaneously and form terpolymers in all monomeric ratios. These terpolymers are tacky and soften at 82°. Furthermore, the copylymerization of β-pinene with styrene or an alkyl or alkenyl styrene using $AlCl_3$ in toluene gives a tacky resinous product of softening point 87° [2]. But the addition of α-pinene in place of β-pinene lowers the softening point of the product (e.g., 80, 70, 32-40°) which makes it more tacky [2-3]. That is why for getting the terpolymer of lower softening point and more tacky appearance and working, the terpolymerization of styrene, α-methylstyrene and α-pinene using $AlCl_3$ as catalyst in toluene has been undertaken and the physical parameters studied.

Material and Methods

All monomers were purified before use. Commercial grade α-pinene was dried over metallic sodium and the fraction boiling at 150° was collected. Styrene (BDH) and α-methylstyrene (Merck) were purified each by washing with 10% NaOH to remove the added inhibitor and then washed with distilled water many times. The monomers were finally dried over $CaCl_2$ and distilled. Anhydrous $AlCl_3$ (E. Merck) was used without further purification. Laboratory reagent grade benzene, toluene, acetone MEK, Pet. ether were used.

Terpolymerization. All terpolymerization reactios were carried out in a three neck round bottom flask fitted with a stirrer, thermometer and funnel and kept in an ice cold bath. The required amount of monomers shown in Table 1 was added in the reaction flask already containing toluene (21.5 g; 25 ml). The mixture was stirred for 15-20 mins and thus anhydrous $AlCl_3$ (1.075g) was gradually added. During the addition of $AlCl_3$, the temperature was maintained at 10-12°. The reactants were stirred for 4 hrs. After required reaction time the product was shaken with 1% aquous solution of HCl three times to remove residual $AlCl_3$. It was then washed with methanol thrice. The bottom layer was collected.

The solvent and unreacted monomers were distilled off under reduced pressure. A highly tacky semisolid material was obtained. It is soft at room temperature. The colour of the product is pale or yellowish brown depending upon the monomeric ratios of the feed and also on the gradual addition of $AlCl_3$ during the reaction. The product was found to be soluble in most of the organic solvents. The IR spectrum of the product was recorded to ensure the terpolymer formation, 3000(s), 2920(s), 1960(w), 1875(w), 1740(w), 1620(m), 1460(m), 1350(m), 1150(w), 1040(w), 900(w), 820(w), 780(m), 680(m) cm^{-1}. Here s, m and w indicates strong, medium and weak bands respectively. The viscosity of dilute solutions of the products prepared in toluene was measured at $30° \pm 0.5°$ using an Ostweld type viscometer. The refractive index of the same solutions was also determined on Refractomer No. 122894 of Zeiss Opton Germany. The terpolymer samples were estimated for C and H on Perkin Elmer analyser.

Results and Discussion

The data collected from aluminium chloride initiated terpolymerization of styrene, α-methylstyrene and α-pinene have been shown in Table 1. Elemental analysis, solubility, IR spectral studies refractive index, viscosity of dilute solutions, softening point etc. are some significant physical parameters which help in the characterization of polymeric products. The product samples were estimated for C and H. These analysis show that six samples of the resinous product (Table 1) contain 90.3- 91.48% C and 8.5-9.68% H, whereas the prepared samples of poly (styrene) contains carbon and hydrogen respectively 90.28% and 7.66%. The estimation of prepared samples of poly (α- methylstyrene) gives 91.5% C and 8.45% H while prepared sample of poly (α-pinene) on analysis gives 88.2% C and 11.76% H. The variation found in elemental analysis suggests that these three monomers participate in the reaction and form a new product. Solubility is another impor-

tant parameter which is being used in the identification of the polymer. Polystyrene and poly (α- methylstyrene) both swell [3] in acetone. The solubility of these polymer samples is not more than 0.3 g/100 ml in acetone whereas poly (α-pinene) is insoluble in acetone. On the other hand the product samples get dissolved in acetone. The solubility behaviour of these polymer products towards acetone supports the results of elemental analysis and provide further evidence a new product is definitely formed. The best solvents for terpolymer are benzene toluene, xylene, acetone, ethyl acetate, methyl acetate. The IR spectra of the product was recorded as given in procedure. The absorption bands with maxima at about 3000, 2910, 1460, 1350, 1160, 1040 cm^{-1} are characteristic C-C bands. The 1630 cm^{-1} band is characteristic of the C=C stretching vibration. Further the absorption in the 900-820 cm^1 region indicates the association of α-pinene molecules in the product [6]. Furthermore the refractive indexes of poly (styrene) poly (α-methylstyrene) and poly (α-pinene) was measured respectively as 1.4960, 1.4965 and 1.5005 whereas it is 1.4940-1.4950 for product samples. This variation in refractive index provides further evidence that the product is a terpolymer.

It has already been mentioned in our earlier publications [1,5] that the quantitative treatment of terpolymerization is quite difficult. It is because there are nine propagation reactions, six monomer reactivity ratios and six termination reactions are involved in the process of terpolymerization. The probable composition of each terpolymer sample has been estimated on the basis of elemental analysis and yield and plotted in Fig. 1. These results show that the rate of propagation of growing polymer chain increases with increase in concentration of monomers in the feed and these three monomers are polymerized simultaneously. From the slopes of these plots (Fig. 1) it is also evident that the rate of propagation of these monomer are not uniform. Styrene is polymerized more rapidly than α-methylstyrene and α-pinene. The order of polymerization may be like.

Styrene > α-methylstyrene > α-pinene.

The high rate of polymerization of styrene is due to its negligible induction period [6]. It polymerizes quite readily with AlCl$_3$ in the presence of aromatic solvents at low temperature. On the other hand α-pinene and α-methylstyrene on polymerization with Friedel Crafts catalysts in the presence of aromatic solvents show notable induction periods. In the case of α-pinene, it does not readily polymerize. It first isomerizes into limonene before polymerization and thus the limonene isomers begin to polymerize. For further clarification of the role of α-pinene in the terpolymerization reactions, the effects of additions of α-pinene in the aluminium chloride initiated copolymerization of binary mixture of styrene and α-methylstyrene was also undertaken as shown in Fig. 2. The addition of α-pinene first lowers the rate of copolymerization and then the rate of copolymerization increases with increasing concentration of α-pinene. At the early stages it passes through the

process of isomerization forming limonene and then limonene begins to polymerize and hence participate in the formation of terpolymer. Similarly α-methylstyrene also shows an induction period. It is due to the addition of α-methyl group of the vinyl side chain of styrene (increase of negative charge) which alters its chemical activity [2,9]. The rate of polymerization is affected. Hence in the beginning of the reaction heomopolym-

TABLE 1. Aluminium Chloride (5%) Initiated Terpolymerization of Styrene, α-Methylstyrene and α-Pinene in the Presence of Toluene at 10-12° for 4 Hours.

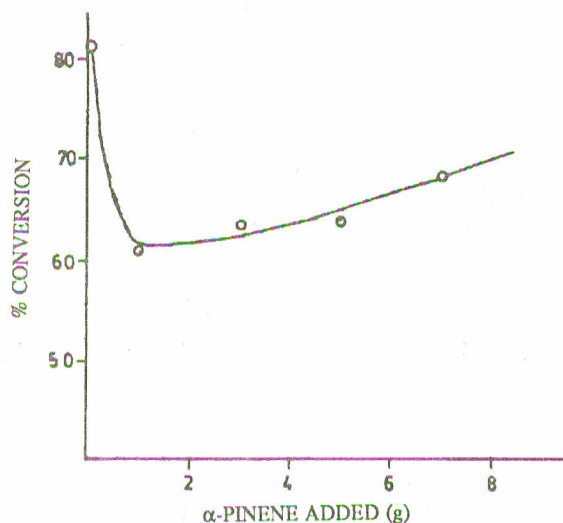| Expt. No.	Monomers in feed			Yield	Elemental analysis	
	Styrene (g)	α-Methyl styrene (g)	α-Pinene (g)		C (%)	H (%)
1.	9.00	9.00	3.50	87.4	91.48	8.50
2.	3.50	11.00	5.20	69.3	90.88	9.10
3.	7.25	7.25	7.00	66.8	90.47	9.47
4.	9.00	4.00	8.50	66.0	90.42	9.50
5.	4.00	9.00	8.50	61.2	90.32	9.67
6.	5.50	5.50	10.50	59.8	90.30	9.68

Fig. 1. A plot of conversion (g) against monomer (g) in feed for cationic terpolymerization of styrene, α-methyl styrene and α- pinene. Each plot starts from O-axis, 1 division = 10 mole %.
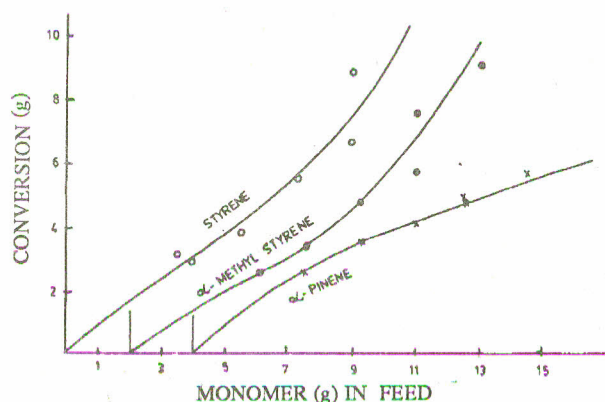

Fig. 2. Effect of addition of α-pinene on conversion in the AlCl$_3$ initiated copolymerization of styrene and α-methyl styrene.

TABLE 2. PHYSICAL PARAMETERS OF TERPOLYMER OF STYRENE, α-METHYLSTYRENE AND α-PINENE.

Expt. No.	[η] dl/g	$\overline{Mn}$	Probable number of monomer units in terpolymer Pn (α-methyl			Colour	Appearance	Consistancy	Soft-ening point	Refracion index
			Styrene	Styrene	α-Pinene					
1.	0.22	49045	200	173	57	Yellowish brown	Soft	Hihgly tacky	25-30	1.4942
2.	0.24	55345	93	260	110	Pale yellow	Soft		25-30	1.4940
3.	0.26	61850	198	174	151	Pale yellow	Soft	"	25-30	1.4950
4.	0.23	52167	208	81	154	Yellowish brown	Soft	"	25-30	1.4942
5.	0.25	58572	103	208	171	Pale yellow	Soft	"	25-30	1.4940
5.	0.20	42963	105	92	155	Pale yellow	Soft	"	25-30	1.4940

erization of styrene occurs and then the growing polymer chains of three monomers are developed. The coupling of these growing polymer chains and results in the formation of terpolymer.

Solution viscosity methods offered for the quickest and simple diagnostic tool for the measuring of the flow times through a capillary viscometer of a terpolymer solution and of the pure solvent at specified conditions of temperature and concentration. The intercept of the plot η sp/C against C determines the value of intrinsic viscosity [η]. The units of [η] are expressed in dl/g. The number average molecular weight Mn of the terpolymer samples may be determined from their values of intrinsic viscosities by the following relationship [8].

$$[\eta] = 0.923 \times 10^{-4} \overline{Mn}$$

The values of [η] obtained for five terpolymer samples range 0.2 to 0.26 dl/g. From these values the average molecular weight was found to be 42963-61850. Keeping in view the elemental analysis and probable composition of monomers in the terpolymer (Fig.1), the degree of polymerization of styrene, α-methylstyrene and α-pinene (probable number of monomers units in terpolymer chain, Pn in Table 2) have been calculated. These results find the major participation of styrene monomer units (Pn = 93-200) and α- methylstyrenemonomer units (Pn=81-260) in the formation of terpolymer as compared with α-pinene (Pn=57-155). At a feed of 38.3 mole % styrene, 33.8 mole % α-methylstyrene and 27.9 mole % α-pinene and alternating terpolymer of the following type may be prepared.

$(Styrene)_{198} \text{——} (\alpha\text{-methylstyrene})_{174} \text{——} (\alpha\text{-pinene})_{151}$

The terpolymer samples are pale yellowish, brown (depending upon the addition of catalyst during reaction) tacky substances soluble in most organic solvents. All samples were soft at room temperature (25-30°). The refractive index of terpolymer sample was found to be 1.4940 - 1.4950. The terpolymer have commercial applications particularly in adhesives.

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