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CATIONIC TERPOLYMERIZATION OF STYRENE α -METHYL STYRENE AND β -PINENE

A. RASHEED KHAN AND TEHZEEB AKIITAR

PCSIR Laboratories Complex, Off University Road, Karachi-39, Pakistan

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The terpolymerization of styrene, α -methylstyrene and β -pinene has been carried out at 10-12° using anhydrous $AlCl_3$ as initiator and toluene as diluent. It has been observed that the three monomers polymerize simultaneously and form terpolymer in all monomeric ratios. The terpolymer contains molecular units of three monomers incorporated into each terpolymer molecule. The terpolymers of 2800-4800 molecular weight are obtained. It is yellowish brown transparent resinous material soluble in most of organic solvents that softens at 81-82°. The refractive index of terpolymer sample is 1.4940-1.4945. It may be used as tackifying agent in the preparation of adhesives.

Key words: Terpolymerization, Monomers, Resinous material.

Introduction

Terpolymerization allows the synthesis of an almost unlimited number of different products by variations in the nature and relative amounts of more than two monomers units in the polymer product. A prime example of versatility of terpolymerization process is the case of polystyrene. It is a brittle plastic with poor impact strength and poor solvent resistant and as well as limited practical utility. The copolymers of styrene with acrylonitrile leads to increase impact and solvent resistance while copolymerization with butadiene leads to elastomeric properties [1]. Terpolymerization of styrene with both acrylonitrile and butadiene improves all these three properties simultaneously [2]. In our earlier publications carbonium ion catalysed copolymerization of styrene [3], α -methylstyrene [4] and vinyl toluene [5] with terpenic monomers have been reported. These copolymers are highly tacky resins and have potential industrial uses in adhesives whereas copolymers of styrene and α -methylstyrene (by carbonium ion initiation) is soft material. Furthermore, on heating with or without free radical initiator styrene copolymerizes with α -methyl styrene giving a solid product of high softening temperature and found useful as molding plastic [6]: It is observed that the addition of β -pinene to binary mixture of styrene and α -methylstyrene and its copolymerization produces a highly tacky bright yellowish resin. It requires some thorough study. This paper describes carbonium ion initiated terpolymerization of styrene, α -methylstyrene and β -pinene using toluene as diluent.

Experimental

Materials. All monomers were purified before use. Styrene (E. Merck) was shaken with 10% sodium hydroxide to remove the inhibitor and then washed with distilled water. It was finally dried over anhydrous calcium chloride and distilled at 146-150°. Similarly α -methyl styrene was washed and distilled at 165-167°. Laboratory grade β -pinene of Fluka

was dried over metallic sodium and the fraction boiling at 165-166° was collected. Laboratory reagent grade benzene, toluene, methanol, ethanol, methyl ethyl ketone petroleum ether were used. Anhydrous $AlCl_3$ (E. Merck) was used without further purification.

Procedure of terpolymerization. Terpolymerization reactions were carried out in a three neck round bottom flask fitted with a stirrer, thermometer and funnel and kept in an ice cold bath. Known quantity of styrene, α -methylstyrene and β -pinene (Table 1) were transferred in the reaction flask already containing 21.5g (25 ml) toluene. The mixture was stirred for 10 min. and then 1.08g anhydrous $AlCl_3$ (5% based on monomer) was added in steps. Since the reaction is exothermic, the temperature of the contents was maintained at 10-12°. The reactants were continuously stirred for 4 hr. After the required reaction time the product was transferred to a

TABLE 1. CATIONIC TERPOLYMERIZATION OF STYRENE, α -METHYL STYRENE AND β -PINENE IN THE PRESENCE OF TOLUENE USING ANHYDROUS $AlCl_3$ as a Catalyst at 10-12°

Expt. No	Monomers in feed			Yield	Elemental ana.	
	Styrene g	α -methyl styrene (g)	β -Pinene		C%	H(%)
1	9.00	9.00	3.5	98.6	91.63	8.35
2	5.50	11.00	5.00	93.5	91.08	8.90
3	5.30	11.00	5.20	91.3	90.97	9.02
4	7.25	7.25	7.00	90.7	90.90	9.07
5	9.00	4.00	8.50	89.6	90.50	9.43
6	3.80	9.00	8.70	84.1	90.31	9.46
7	5.50	5.50	10.50	65.7	90.32	9.62
8	10.00	10.00	-	82.0	91.85	8.00
9	-	25.00	25.00	76.80	90.74	9.25
10	25.00	-	25.00	80.00	90.24	9.75
11	25.00	-	-	82.00	92.20	7.65
12	-	25.00	-	47.30	91.50	8.45
13	-	-	25.00	60.00	88.20	11.72

separating funnel and shaken with distilled water to remove residual catalyst. Methanol was then added and again shaken. The bottom layer was collected. At the end, the solvent and unreacted monomers were distilled off. A solid yellowish brown bright resinous substance was obtained. It is brittle and may be powdered. The substance was found to be dissolved in most of the organic solvents. The softening range of the product is 81 to 82°. The viscosity of dil solutions of the product samples prepared in toluene was measured at 30° using on Ostwald type viscometer. Refractive index of the same solutions was measured on refractometer No. 122894 of zeiss opton Germany. It was found to be 1.494-1.4945. The product was analysed for C and H.

Results and Discussion

Table 1 summarizes the data collected from the carbonium ion initiated terpolymerization of styrene, α -methylstyrene and β -pinene. The product obtained by carbonium ion initiated terpolymerization of these monomers was characterized by the help of elemental analysis solubility, I.R. spectral studies, intrinsic viscosity, refractive index etc. The elemental estimations show that seven samples of the product contain 90.31-91.63% C and 8.35-9.62% H. The prepared samples of poly (styrene) contains C and H respectively 92.2% and 7.65% whereas the estimation of prepared samples of poly (α -methylstyrene) gives 91.5% C and 8.45% H. The prepared samples of poly (β -pinene) on estimation gives 88.20% C and 11.72% H. Furthermore the samples of styrene co- α -methylstyrene, styrene-co- β -pinene and α -methylstyrene co- β -pinene were also prepared and estimated for C and H with a view to compare with the above estimations of product and polymers. The estimation of the prepared copolymers samples indicates that styrene-co- α -methyl styrene contains 91.85% C and 8.0% H, styrene-co- β -pinene contains 90.24% C and 9.75% H and α -methylstyrene co- β -pinene contains 90.74% C and 9.25% H. This difference in the percentage of C and H suggests that the three monomers participate in the reaction and form a new product. It is also because the three monomers may be readily polymerized with Friedal-Crafts Catalysts like $AlCl_3$ at low temperature (<10°C) and growing polymer chains of these monomers couple to produce a new product (terpolymer). The solubility of these polymers, copolymers and product was also tested in different solvents. It may identify and easure the participation of three monomers in terpolymerization reaction. Poly (styrene) and poly (α -methylstyrene) both swell [7] in acetone (solubility 0.30/100ml) whereas poly (β -pinene) is not soluble in it. The copolymers of styrene, α -methylstyrene and β -pinene as stated in above lines are dissolved in acetone. On the other hand the product is found soluble in acetone. It is noted that

on dissolving the product in acetone a small amount is left behind. It may be because, at the early stage of reaction a part of the growing polymer chain of poly (styrene) and poly (α -methylstyrene) get terminated before going to terpolymerization resulting polymers of styrene and α -methylstyrene. The solubility behaviour supports the results of elemental analysis and identify the product as terpolymer. The best solvents for terpolymer are benzene, toluene, ethyl acetate, butyl acetate, MEK etc. The refractive index of polymers, and product was also measured as shown in Table 3. The refractive index of poly (styrene), poly (α -methylstyrene) and poly (β -pinene) was found to be 1.4960, 1.4965 and 1.5240 respectively whereas it is 1.4948 for styrene-co- α -methylstyrene, 1.4920 for styrene-co- β -pinene and 1.4945 for α -methylstyrene-co- β -pinene. On the other hand, the refractive index of the product was found to be 1.4940-1.4945. This variation in the value of refractive index, though little, provides further evidence that the product is a terpolymer. I.R. spectral studies have also been carried and the I.R. spectrum of product is compared with I.R. spectra of poly (styrene), poly (α -methylstyrene) and poly (β -pinene) as shown in Table 2. These spectra also support the product to be terpolymers. In the spectrum of the product, the absorption maximum bands with maxima at 3040-2620, 1480, 1380, 1160, 1080, 1040 cm^{-1} are characteristic C-C bands. The 1610 cm^{-1} absorption band is a characteristic stretching vibration. Hence all these evidences confirms the addition of

TABLE 2. COMPARATIVE STATEMENT OF I.R. SPECTRA OF POLY (STYRENE), POLY (α -METHYL STYRENE) AND POLY (β -PINENE) AND THE TERPOLYMER OF STYRENE, α -METHYL STYRENE AND β -PINENE.

Poly (styrene) wave No. cm^{-1}	Poly (α -methyl styrene) wave No. cm^{-1}	Poly (β -pinene) wave No. cm^{-1}	product (terpolymer) wave No. cm^{-1}
3000(s)	2900(s)	3000(s)	3440(m)
2900(s)	1940-1720(w)	1670(w)	3040-2620(s)
1940(w)	1600(m)	1480-1450(m)	1950(w)
1875(w)	1440(m)	1400-1380(m)	1880(w)
1800(w)	1380(w)	1160(w)	1720-1680(s)
1740(w)	1230(w)	1040(w)	1610(m)
1600(m)	1020(w)	940(w)	1480(m)
1450(m)	950(w)	725(w)	1380(m)
1350(m)	750(w)		1160(w)
1180(w8w)	880(w)		1080(w)
1075(w)	690(m)	-	1040(w)
1020(m)	-	-	975(w)
900(m)	-	-	920(w)
-	-	-	760(m)
-	-	-	675(m)

TABLE 3. SOME PHYSICAL PARAMETERS OF TERPOLYMERS, COPOLYMERS AND POLYMERS OF STYRENE, α -METHYL STYRENE AND β -PINENE.

Exp. No.	[η]dl/g	$\times 10^3$	\overline{M}_n	Probable number of monomer units in terpolymers (Pn) degree of polymerization			Colour	Appearance	Softening point°C	Refractive Index
				Styrene	α -Methyl styrene	β -Pinene				
1	0.0355	1.1000	3892	15	14	5	Yellowish brown	Solid subst.	82	1.4940
2	0.0415	1.1759	4836	12	21	8	"	"	82	1.4940
3	0.0400	1.0000	4596	11	20	8	"	"	82	1.4940
4	0.028	0.8000	2800	9	8	7	Dark brown	"	81-82	1.4944
5	0.032	1.2550	3372	14	5	10	Yellowish brown	"	81	1.4945
6	0.035	1.1000	3820	8	19	10	Dark brown	"	81	1.4945
7	0.033	0.8000	3518	8	8	13	Yellowish brown	"	81	1.4945
8	0.024	-	2392	-	-	-	Dark brown	Soft subst.	-	1.4948
9	0.028	-	2800	-	-	-	Yellowish brown	Solid subst.	81	1.4945
10	0.038	6.00	3817	-	-	-	"	"	70	1.4920
11	0.033	-	3518	34	-	-	Reddish brown	"	-	1.4960
12	0.026	-	2490	-	21	-	Yellowish brown	Soft subst.	-	1.4965
13	0.045	-	1898	-	-	14	"	"	Solid subst. 68	1.5240

β -pinene monomers units in the copolymers chain of styrene and α -methyl styrene and that the product is certainly terpolymer.

The quantitative treatment of terpolymerization is quite complex since nine propagation reaction, six monomers reactivity ratios and as well as six termination reactions are involved. In earlier paper free radical terpolymerization of methyl methacrylate, acrylic acid and 2, ethyl hexylacrylate, the probable composition of each terpolymer sample had been determined on the basis of elemental analysis and yield [8]. Similarly, the probable composition of the terpolymer samples on the same basis have also been found out and plotted in Fig. 1. These results indicate that the rate of propagation of the growing polymer chain increase with increase concentration of monomer in feed and these three monomers polymerize

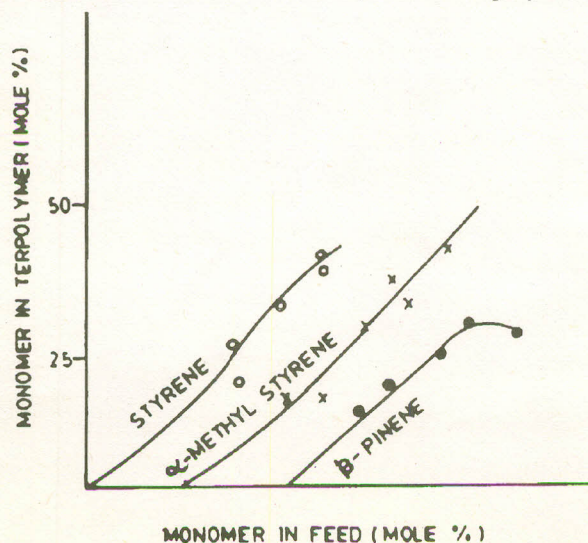


Fig 1. Monomer in Terpolymer (Mole %) and Feed (Mole %)

simultaneously. At the early stage of reaction, the three monomers generate initiating carbonium ion resulting the propagation of growing polymer chain of the monomers. The solvent, unreacted monomers and the carbonium ions of growing polymer chain of each monomer cause the termination of growing polymer chains and hence form terpolymer. This terpolymer contains molecular units of styrene α -methylstyrene and β -pinene incorporated into each terpolymer molecular chain. Some times at the early stage of reaction, the premature termination of growing polymer chain may take place rapidly and some times slowly. It is evident from the insoluble material obtained by dissolving the terpolymer in acetone. This insoluble material is definitely poly (styrene) which swells in acetone.

The number average molecular weight (\overline{M}_n) of terpolymer samples was calculated by using the following equation [9].

$$[\eta] = 0.923 \times 10^{-4} \overline{M}_n^{0.72}$$

where $[\eta]$ is the intrinsic viscosity in dl/g of the terpolymer solution prepared in toluene.

The intercept of the plot η_{sp}/C against C gives the value of $[\eta]$ for each terpolymer sample. All viscosity measurements were made at 30°. The intrinsic viscosities of terpolymer samples were thus determined to be in the range 0.028-0.042 dl/g. Similar results of low intrinsic viscosities were also obtained in the free radical terpolymerization of methyl methacrylate, acrylic acid and 2-ethyl hexylacrylate ($[\eta]=0.053-0.067$ dl/g)[8] and in cationic polymerization of styrene ($[\eta]=0.02-0.07$ dl/g) [11]. The low intrinsic viscosities is certainly due to chain transfer reactions between the monomeric radicals and solvents. The solvent terminates the premature growing polymer chain and form dead polymer. In

this way, the polymers of small molecular chains are obtained. The molecular weight of terpolymer samples were calculated from their intrinsic viscosities which range 2800- 4800. Keeping in view the elemental analysis and probable composition of monomers in terpolymer (Fig. 1), the degree of polymerization of styrene, α -methyl styrene and β -pinene (probable number of monomer units in terpolymer chain, Table 3) have been calculated. These results indicate the major participation of α -methyl styrene monomer units (Pn = 5-21) in the formation of terpolymer in a bigger range as compared with styrene (Pn=8-15) and β -pinene (Pn=5-31). At a feed of 38.17 mole % styrene, 33.64 mole % α -methyl styrene and 28.18 mole % β -pinene an alternating terpolymers of the following type may be prepared.



Some physical parameters like appearance, color, refractive index and softening point have also been studied and shown in Table 3. Terpolymer samples are yellowish brown transparent resinous substances soluble in most of the organic solvents. They are also tacky. The addition of β -pinene molecular units in the copolymer chain of binary mixture of styrene and α -methylstyrene made the product tacky. It softens at 81-82°. The refractive index of the product was found to be 1.494-1.4945. The terpolymer has commercial

value and may be used in adhesives.

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