

DILUENT EFFECTS OF BENZENE AND TOLUENE ON THE CATIONIC COPOLYMERIZATION OF STYRENE AND β -PINENE

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AlCl_3 initiated copolymerization of styrene and β -pinene in benzene and toluene has been carried out at 10° using anhydrous AlCl_3 as a catalyst. Both monomers combine in all monomeric ratios to form copolymer. The rate of copolymerization of the binary mixture of styrene and β -pinene is higher in toluene than in benzene. Furthermore the copolymer obtained at different monomeric ratios in toluene possess higher molecular weight than the copolymer prepared in benzene at the same monomeric ratios. Toluene and benzene not only serve as diluent in the cationic copolymerization but also response as chain transfer agent. The value of K' obtained in these solvents is $5.5 - 6.4 \times 10^{-3}$ showing the product is highly tacky and contain more flexible molecules.

Key words: Dielectric constant, Flexible molecules, Premature growing polymer chain.

Introduction

The copolymers of electron donating vinyl monomers like vinyl toluene [1], α -methylstyrene [2] and styrene [3] with β -pinene have been reported earlier. These copolymers have potential commercial values as plasticizers and tackifying agents in the compounding of natural and synthetic elastomers for ply adhesion, coatings and adhesives [4]. β -pinene is another important terpenic monomer which contains $=\text{CH}_2$ group. It polymerizes quite readily with Friedel crafts catalysts at low temperature resulting resin melting above 100° [5]. These resins may be modified by copolymerizing β -pinene with vinyl monomers in the presence of different aromatic diluents. It has already been communicated earlier that not only the diluents facilitate the initiation of cationic polymerization of styrene [6], α -methylstyrene [7] and β -pinene [8], but also partially serve as a chain transfer agents. It means that with the help of diluents, some physical parameters of the resins may be controlled. This paper deals with the copolymerization of styrene and β -pinene in the presence of benzene and toluene at low temperature (10°) using anhydrous AlCl_3 as catalyst.

Experimental

Material. β -pinene [6,6-dimethyl-2-methylenebicyclo (3.1.1) heptane] of Fluka and styrene (BDH) were purified before use. Laboratory reagent grade ethanol, toluene, benzene were distilled before use. Anhydrous AlCl_3 (E.Merck) was used without further purification.

Procedure of copolymerization. Reactions were carried out in a three neck round bottom flask fitted with a stirrer, thermometer and separating funnel. β -pinene and styrene in different ratios as given in Tables 1 and 2 were transferred to the reaction flask already containing and equal volume of diluent (benzene or toluene). Anhydrous AlCl_3 (50% with

respect to monomers) was added in steps. The reaction was conducted for 4 hr at 10° in ice bath since the reaction is exothermic. After required reaction time, an aqueous solution of ethyl alcohol (20 %) was added to the reactants to stop the reaction. Then the product was transferred to a separating funnel and washed many times with alcohol to remove unreacted monomers and solvents. The bottom layer of the separating funnel was collected in a ground neck flask. At the end, the unreacted monomers solvents were distilled off. A yellowish brown transparent brittle resin was obtained. It was observed that the yield of the product does not repeat but the order remain the same at all monomeric ratios. The product is soluble in most of the organic solvents and softens at $69-70^\circ$. The I.R. spectrum of the product of poly (styrene) and poly (β -pinene) was recorded which is given below. They are expressed in cm^{-1} wavenumber, 3000 (s), 2900 (s), 1940 (w), 1875 (w), 1750 (w), 1620 (m), 1450 (m), 1380 (m), 1180 (w), 1020 (m), 920 (m), 840 (w), 750 (m), 680 (m). This spectrum shows the product to be a copolymer. The viscosity of dilute solutions of copolymers prepared in toluene was measured at 30° using an Ostwald type viscometer. The composition of the copolymer was determined by analysing copolymer samples for C and H. Refractive index of copolymer samples was measured on Refractometer No. 122894 of Zeissopton, Germany.

Results and Discussion

Tables 1 and 2 summarize the data collected from diluent effects of aromatic solvents on cationic copolymerization of β -pinene and styrene. The copolymer was characterized by means of elemental analysis, solubility, infrared spectra and intrinsic viscosity. The copolymer samples were estimated for C and H. The prepared sample of poly (styrene) contains 92.25% carbon and 7.66% hydrogen whereas prepared sample

of poly (β -pinene) contains 88.21 - 88.22% C and 11.74 - 11.76% H. On the other hand the ten samples of the product prepared in toluene and benzene contain 89.45 - 91.08% C and 8.9 - 10.5% H. This variation in the percentage of carbon and hydrogen suggests the attachment of styrene molecules in the growing polymer chain of β -pinene or vice versa. It is because styrene and β -pinene both may be easily homopolymerized by Friedel crafts catalysts like anhydrous $AlCl_3$. The growing polymer chains of both monomers couple and result a new product. Solubility is an other important criteria for ensuring the attachment of growing polymer chains of these monomers. It is observed that poly (styrene) swells [9] in acetone (solubility of 0.3g/100 ml) whereas poly (β -pinene) does not show any solubility in acetone. On the other hand, the product is highly soluble in acetone. The solubility behaviour of homopolymers and product towards acetone supports the elemental analysis for C and H and show that the product is a copolymer. The best solvents for the copolymer are acetone, toluene, benzene, xylene methylene chloride, ethyl acetate, chloroform etc. Infra red spectral studies also provides the evidences in the support of elemental analysis and solubility. The I.R. spectra of the product has been recorded which is given in procedure. In the spectrum of the product the absorption bands with maxima at about 2900 (s), 1450 (m), 1380 (m), 1180 (w), 1020 (m) cm^{-1} are characteristics C-C bands. The 1620 cm^{-1} band is characteristic of the C=C stretching vibration.

The plot shown in Fig. 1 indicates that rate of formation of copolymers increases with an increase in the monomeric ratio of styrene in the binary mixture of the monomers. The conversion is maximum at a high feed value of styrene. Both monomers form copolymer at all monomeric ratios. The similar results have been observed in the copolymerization of α -pinene with vinyl toluene, α -methyl styrene and styrene [1-3]. Both styrene and α -pinene may be polymerized quite readily with anhydrous $AlCl_3$ in the presence of toluene and benzene at low temperature ($\leq 12^\circ$) and result a highly tacky solid resinous material of low molecular weight. It is also evident from this plot that rate of copolymerization of the binary mixture of styrene and β -pinene is higher in toluene than in benzene. It is because the propagating species produced in toluene during copolymerization is more efficient than the propagating species produced in benzene. This efficiency of propagating species may be due to the dielectric constant which is higher of toluene (2.3661) than of benzene (2.2628). Increase in dielectric constants enhances the efficiency of propagating species. This is also observed in the polymerization of β -pinene using benzene and toluene as diluents [8].

The measurement of the viscosity of dilute solutions is the most commonly used method for determining the molecular weight M_n of macromolecules. The number of average

molecular weight \overline{M}_n of resins were calculated from the following intrinsic viscosity $[\eta]$ molecular weight relationship [10].

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

The intrinsic viscosity may be obtained from the plot η_{sp}/C against C. Here η_{sp} is the specific viscosity and C is the concentration of dilute solutions of resins prepared in toluene. The intrinsic viscosity of copolymers samples was found to be in the range .029- .052 dl/g which determines the molecular

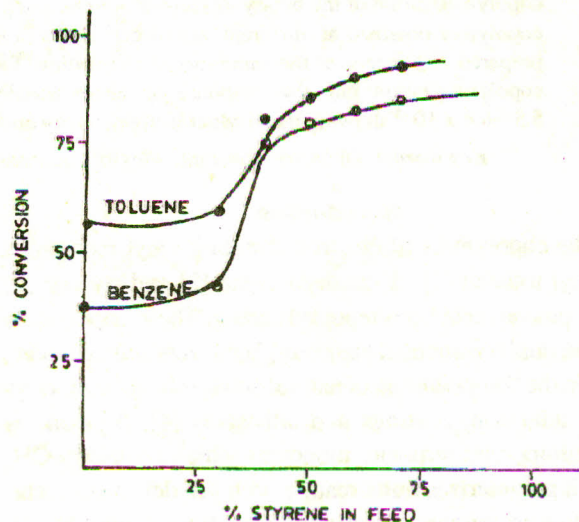


Fig. 1. Plot showing the rate of cationic copolymerization of styrene and β -pinene in the presence of benzene and toluene using anhydrous $AlCl_3$ as initiator.

TABLE 1. CATIONIC COPOLYMERIZATION OF STYRENE AND β -PINENE IN BENZENE USING ANHYDROUS $AlCl_3$ AS INITIATOR AT 10° .

S. No.	Monomers in feed		Yield %	Elemental analysis	
	Styrene mole ratio	β -Pinene mole ratio		C%	H%
1.	0.754	0.246	42.5	91.08	8.90
2.	0.662	0.338	41.5	90.67	9.31
3.	0.566	0.434	40.0	90.24	9.75
4.	0.465	0.535	38.0	89.87	10.13
5.	0.395	0.641	21.0	89.45	10.51
6.	—	0.184	23.5	88.22	11.76

TABLE 2. CATIONIC COPOLYMERIZATION OF STYRENE AND β -PINENE IN TOLUENE USING ANHYDROUS $AlCl_3$ AS INITIATOR AT 100° .

S. No.	Monomers in feed		Yield %	Elemental analysis	
	Styrene mole ratio	β -Pinene mole ratio		C%	H%
1.	0.754	0.246	46.5	90.87	9.10
2.	0.662	0.338	45.0	90.49	9.32
3.	0.566	0.434	42.5	90.09	9.82
4.	0.465	0.535	40.5	89.86	10.04
5.	0.395	0.641	29.5	89.64	10.23
6.	—	0.184	28.0	88.21	11.74

weight as 2900 - 6600. The intrinsic viscosity of poly (β -pinene) prepared in toluene and benzene was determined as 0.043 and 0.037 respectively. From these values, the molecular weight of poly (β -pinene) prepared in toluene was calculated as 1800 whereas it is prepared in benzene was determined as 1557. It is obvious from these results depicted in Tables 3 and 4 that the molecular weight of resins depends upon how many styrene molecules could be entered in the growing polymer chain of β -pinene. Furthermore, the copolymer samples prepared in toluene or benzene at various monomeric ratios are obtained of different molecular weight. It is due to the fact that toluene and benzene both act as chain transfer agents. The copolymer obtained at different monomeric ratios in toluene possess higher molecular weight than copolymer prepared in benzene at the same monomeric ratio. It is perhaps due to the dielectric constant of the solvents used. These solvents not only facilitate the carbonium ion initiated polymerization but also terminate the premature propagating growing polymer chain resulting the copolymers of lower molecular weight. Similar results have been obtained in carbonium ion initiated polymerization of styrene [6] and β -pinene [8]. It was concluded that size of the chain may be controlled by using specific solvent of specific dielectric constant as reaction medium. These solvents not only produce solvations effect but also response as chain transfer agent. The chain transfer constant for toluene and benzene in the cationic

polymerization of β -pinene were reported respectively as 12.5×10^{-3} and 16.5×10^{-3} . In the cationic polymerization of styrene using benzene and toluene as reaction medium, the chain transfer constant for toluene and benzene are 8×10^{-3} and 14×10^{-3} respectively. The behaviour of aromatic solvents towards styrene and β -pinene polymerization as reaction medium is nearly the same. It is also observed that η_{sp}/C wholly depends upon C . The increase of η_{sp}/C with C is attributed to changes in chain shape, the interaction of polymer solvent and other factors which determine K' in the following empirical relation [11].

$$\eta_{sp}/C = [\eta] + K' [\eta]^2 C$$

Here K' is a constant depending upon rigidity and flexibility of the molecules of the product. The values of K' are higher (0.7) for rigid molecules whereas lower (0.4 - .02) for flexible molecules. For more flexible polymer molecules the value of K' will go on lower side. In the present case the value of K' are near about same for toluene and benzene and ranges from 5.5×10^{-3} - 6.4×10^{-3} showing that copolymer of styrene and β -pinene is highly tacky and contain more flexible molecules.

The copolymers are yellow or yellowish brown solid material which exhibit high degree of tackiness. The softening range is 69-70°. The refractive index of copolymer was found to be 1.492-1.494 whereas that of prepared samples of poly (β -pinene) was 1.5220. The product may be used in the preparation of adhesives.

In brief the addition of aromatic solvents in the cationic copolymerizations of terpenic monomers and electron donating vinyl monomers, facilitate the reaction and help in controlling the molecular weight of product. The product depends upon the nature of solvent added.

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TABLE 3. SOME PHYSICAL PARAMETERS OF COPOLYMER SAMPLES OF STYRENE AND β -PINENE PREPARED IN BENZENE.

S.No.	$[\eta]$ dl/g	\bar{M}_n	$K' \times 10^3$	Softening point	Refractive index
1.	0.045	5400	6.0	69.7	1.4920
2.	0.039	4400	6.0	70.0	1.4920
3.	0.035	3800	6.0	69.5	1.4920
4.	0.031	3200	5.5	69.5	1.4920
5.	0.029	2900	5.0	69.0	1.4920
6.	0.037	1557	—	68.5	1.5200

TABLE 4. SOME PHYSICAL PARAMETERS OF COPOLYMER SAMPLES OF STYRENE AND β -PINENE PREPARED IN TOLUENE.

S.No.	$[\eta]$ dl/g	\bar{M}_n	$K' \times 10^3$	Softening range °C	Refractive index at 22°C
1.	0.052	6600	6.0	70.0	1.4920
2.	0.050	6300	5.5	70.0	1.4920
3.	0.038	4300	6.4	70.0	1.4920
4.	0.035	3800	6.0	69.5	1.4920
5.	0.035	3800	6.0	69.0	1.4920
6.	0.043	1800	—	68.5	1.5200