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DETERMINATION OF CHAIN TRANSFER CONSTANT FOR SOME AROMATIC HYDROCARBON IN THE CATIONIC POLYMERIZATION OF β -PINENE

A. RASHEED KHAN

PCSIR Laboratories Complex, Karachi, Pakistan

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Cationic polymerization of β -pinene in benzene and toluene has been accomplished at 10-12° using anhydrous AlCl_3 as initiator. The solvating power of reaction medium increased the rate and degree of polymerization. The values of chain transfer constants measured for benzene and toluene were respectively 16.5×10^{-3} and 12.5×10^{-3} whereas the value of chain transfer constant to monomer (C_m) obtained was as 60×10^{-3} .

Key words: Propagating species, Carbonium ion, Chain Transfer constant.

Introduction

The preparation of polymers by treating terpene hydrocarbons with anhydrous AlCl_3 at low temperature has been of industrial importance. β -pinene which contains $=\text{CH}_2$ group, a prominent site for initiation, polymerizes quite readily with Friedel Crafts catalysts (like BF_3 , AlCl_3 , SnCl_4) at low temperature to give moderately high polymers melting above 100° [3]. Polyterpene of low molecular weight and low melting point (<100°) may be prepared by using diluents particularly of low dielectric constant. These diluents not only facilitate the cationic polymerization but also behave as transfer agent [1,2]. Keeping this view in mind, the cationic polymerization of β -pinene in the presence of anhydrous AlCl_3 as catalyst has been carried out at 10-12° using benzene or toluene as diluents. Some physical parameters of the products are also studied.

Experimental

Material. β -pinene (6,6-dimethyl, 2-methylene-bicyclo-3,7-heptane) of Fluka was purified before use. Laboratory reagent grade toluene, benzene, ethyl alcohol, methanol, acetone were used. Anhydrous AlCl_3 (E.Merck) was used without further purification.

Procedure of polymerization. β -pinene was polymerized in a three neck round bottom flask fitted with a stirrer, funnel and a thermometer and kept in an ice cold bath. The required quantity of the monomer and diluent were transferred in the reaction flask. The mixture was stirred for half an hour. To the stirred mixture 5% anhydrous AlCl_3 based on β -pinene was added in steps. The temperature of the contents was maintained strictly at 10-12°. The duration of the reaction was 4 hr. After the required reaction time, an aqueous solution of ethyl alcohol (20%) was added to the reactants. This was then transferred to a separating funnel and shaken to remove the catalyst residue. It was further washed with ethyl alcohol (or methanol). The bottom layer was collected in a ground neck round bottom flask. The unreacted monomer and solvents were distilled off. A solid pale orange colour resins was

obtained, it may be powdered. The resin so obtained was found soluble in most of the organic solvent. It softens at 68°. It was also noted that the conversion of the monomer into polymer does not repeat but order remains more or less the same. The light colour of polymer may be maintained by adding catalyst in steps and maintaining the temperature constant. The I.R. spectra of poly (β -pinene) was also recorded in wave number (Cm^{-1}) as 3000 (s), 1670(w), 1480-1450 (m), 1400(m), 1160 (w), 1030 (w), 920 (w) and 725 (w). Here S, m, w stands for strong, medium and weak absorption respectively. The I.R. spectra show that poly (β -pinene) is free from diluents. The viscosities of dilute solutions of poly (β -pinene) prepared in toluene was measured at 25° using an Ostwald type viscometer. The refractive index of the same solutions was measured as 1.5210. On refractometer NO. 122894 of Leiss Opton Germany.

Results and Discussion

The data obtained from the carbonium ion initiated polymerization of β -pinene in benzene and toluene are described in Tables 1 and 2. In Fig. 1, the rate of polymerization ($R_p \times 10^5$ moles/l) of β -pinene is plotted against the concentration β -pinene moles/l. It indicates that the rate of polymerization of β -pinene increases with increase concentration of the monomer. Further solvating power of toluene is greater than that of benzene. It might be due to the fact that the propagating species (solvent separated ion pair and free ions) produced by the polymerization of β -pinene in toluene are more efficient than produced in benzene. It is almost due to the dielectric constant of benzene (2.2628) and toluene (2.3661). Increase in dielectric constant enhances the efficiency of propagating species. This is further proved by polymerizing β -pinene in the absence of any solvent. A less viscous polymer of less yield is obtained. It is evident that solvents are advantageous for obtaining maximum yield and uniform polymers in place of dimers and trimers etc.

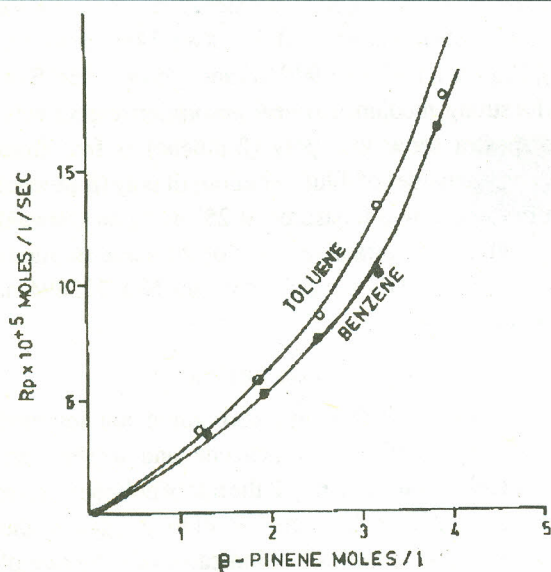
The number average molecular weight (M_n) of the resin samples was calculated by using the following relationship.

TABLE 1. CATIONIC POLYMERIZATION OF β -PINENE IN BENZENE USING 5% ANHYDROUS $AlCl_3$ AS THE CATALYST AT 10-12°C FOR 4 HRS.

Exp. No.	β -Pinene [M] moles/l	Benzene [S] moles/l	Yield (g)	$[\eta]$ dl/g	Number average molecular weight \bar{M}_n	Degree of polymerization $\bar{DP} \times 10^2$
1.	3.8540	4.4799	18.80	0.039	1642	1207
2.	3.2149	5.5056	11.75	0.037	1557	1145
3.	2.5746	6.7337	8.10	0.029	1218	895
4.	1.9330	7.8640	5.90	0.025	1048	770
5.	1.2900	8.9968	3.80	0.024	1006	740

TABLE 2. CATIONIC POLYMERIZATION OF β -PINENE IN TOLUENE USING 5% ANHYDROUS $AlCl_3$ AS THE CATALYST AT 10-12°C FOR 4 HRS.

Exp. No.	β -Pinene [M] moles/l	Toluene [S] moles/l	Yield (g)	$[\eta]$ dl/g	Number average molecular weight \bar{M}_n	Degree of Polymerization $\bar{DP} \times 10^2$
1.	3.8329	3.7774	20.5	0.045	1898	1395
2.	3.1930	4.7201	15.0	0.043	1812	1332
3.	2.5535	5.6621	9.6	0.034	1644	1208
4.	1.9145	6.6036	6.5	0.027	1133	833
5.	1.2759	7.5443	4.0	0.023	963	708

Fig. 1. Rate of Carbonium ion initiated polymerization of β -pinene in different aromatic solvents.

$$[\eta] = 2.55707 \times 10^{-5} \bar{M}_n^{0.99}$$

where $[\eta]$ is the intrinsic viscosity in dl/g of the polymer solutions prepared in toluene. The values of 'a' (2.55707×10^{-5}) and α (0.99) for above relation have been determined from the intrinsic viscosity value (0.056 dl/g) of a polyterpene fraction and average molecular weight (2190 by cryoscopic method) of the same sample [5]. The intrinsic viscosity was determined by the following relationship of intrinsic viscosity and specific viscosity (η_{sp}).

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

The intercept of the plot η_{sp}/C VS/ C gives the value of $[\eta]$ for each sample. Here C is the concentration of the resin

solution prepared in toluene. The increase or decrease of η_{sp}/C with C is attributed to changes in chain shape. The intrinsic viscosity of poly(β -pinene) prepared in benzene and toluene were determined respectively in the range 0.024-0.039 dl/g and 0.023-0.045 dl/g. The number average molecular weight calculated from these values was found for benzene as 1006-1642 whereas for toluene it was 963-1998. These results indicate that both solvents (diluent) behave also as chain transfer agent in the cationic polymerization of β -pinene using Friedel Crafts Catalyst. It is because of the facility of Friedel Crafts alkylation reactions on benzene and toluene [2]. There is no an appreciable difference in molecular weight of poly (β -pinene) prepared in benzene and toluene. It may be because the dielectric constant of both solvents are in the vicinity of each other. The molecular weight of poly (β -pinene) may be regulated by using aromatic solvent as diluent. The results shown in Table 1 and 2 indicate that the degree of polymerization (DP) of β -pinene enhances with dilution of monomer. It varies solvent to solvent. The results also indicate that the value of DP is higher in the solvent possessing the higher dielectric constant. The rate of polymerization of terpenic resin, its number of average molecular weight and degree of polymerization conclude that not only benzene or toluene behave as reaction medium but also provides the facility in the transfer and premature termination of growing polymer chain of β -pinene. This premature termination results in the formation of low molecular weight tacky resinous product of small chain ($DP = 740 - 1395 \times 10^2$) and low softening point.

When the polymerization is carried out in the presence of a solvent, the growing polymer carbonium ion will transfer its activity to solvent molecule. In such cases the degree of polymerization \overline{DP} which is the rate of chain growth divided by the total rate of termination will depend upon the nature of the solvent. If $[M]$, $[S]$ and $[I]$ are the concentration of monomer, solvent initiator respectively, then according to Mayo [6]

$$\frac{1}{\overline{DP}} = \frac{(K_1 K_3)^{1/2} [I]^{1/2}}{K_2 [M]^{1/2}} + \frac{K_4}{K_2} + \frac{K_5}{K_2} \times \frac{[S]}{[M]}$$

where K_1 , K_2 , K_3 , K_4 and K_5 are the rate constants for initiation, propagation, termination, monomer transfer and

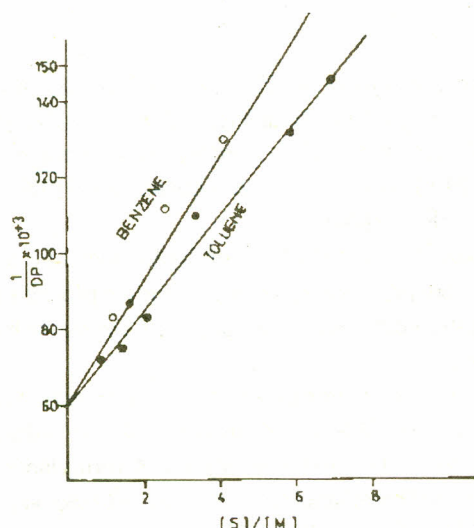


Fig. 2. Chain transfer constant of toluene (●) and benzene (o) in carbonium ion initiated polymerization of β -pinene using $AlCl_3$ as initiator at 10-12°.

solvent transfer respectively and $K_4/K_2 = C_m$ (Chain transfer constant), and $K_5/K_2 = C_s$ (monomer transfer constant).

$$\frac{1}{\overline{DP}} = \frac{(K_1 K_3)^{1/2}}{K_2} \times \frac{[I]^{1/2}}{[M]^{1/2}} + C_m + C_s \frac{[S]}{[M]}$$

Since a fixed concentration of $AlCl_3$ has been taken in each experiment, the first term of above equation may be neglected. The slope of the plot $\frac{1}{\overline{DP}} \text{ vs } \frac{[S]}{[M]}$ in Fig. 2 then determines the value of chain transfer constant whereas the intercept of the plot is the measure of C_m . Thus the chain transfer constant obtained from these plots for benzene is 16.5×10^{-3} whereas for toluene it is 12.5×10^{-3} . From these results it is evident that degree of polymerization, chain transfer constant and C_m obtained from the intercept is 60×10^{-3} . Further the value of C_m depend upon the solvents used as reaction medium. Not only the solvents serve as reaction medium but also act as chain transfer agent. The higher the value of chain transfer constant, the lower the molecular weight of the polymer formed in the presence of a given amount of a chain transfer agent.

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