Technology Section

COPYLMERS FROM α-PINENE
Part I. Free Radical Copolymerization of Methyl Methacrylate with α-Pinene

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A study of the copolymerization of α-pinene with methyl methacrylate has been made at 80° using benzoyl peroxide as a catalyst. The rate of copolymer formation is found to decrease with increased concentration of α-pinene. At a higher concentration of the catalyst, good yields of the copolymer is obtained. The monomer reactivity ratios of MMA (r_1) and α-pinene (r_2) are determined as $r_1 \mp 10.0$ and $r_2 \mp 0.08$. With an increasing concentration of α-pinene in the binary mixture, copolymers with decreasing molecular weight are obtained and α-pinene also acts as a chain transfer agent. The copolymers are white powdery substances and soluble in many organic solvents. The softening range of the copolymer is $120-125^\circ$ and it decomposes at $155 - 160^\circ$

INTRODUCTION

The preparation of polymers by heating terpene hydrocarbons with metallic halide catalysts like aluminium chloride at moderately low temperatures is of industrial importance [1-3]. These polymers are used in conjunction with other materials in the formulation of a wide variety of end products including adhesives, adhesive tapes, rubber goods and coating compositions. The copolymers of terpene with monomers other than terpense have been developed and used successfully in the tackification and compounding of rubber. It is observed [4] that those monomers which do not homopolymerize easily can be copolymerized readily with easily polymerizable monomers. Tetrachloroethylene for example does not homopolymerize but copolymerizes easily at all ratios with acrylonitrile. Efforts have been made to copolymerize α-pinene with some easily polymerizable vinyl monomers like MMA, MA, styrene and acrylonitrile by the free radical process.

This paper deals with copolymerization of MMA with α-pinene in the presence of benzoyl peroxide as catalyst.

EXPERIMENTAL

Material

1. Methyl methacrylate (BDH) was washed with sodium hydroxide to remove the inhibitor and dried over $CaCl_2$. It was then distilled.
2. Commercial grade α-pinene was dried over metallic sodium and the fraction distilled at $156-159^\circ$ was collected.
3. Laboratory grade petroleum ether, acetone, chloroform, toluene, dioxane, and ethyl acetate were purified according to known methods.
4. Benzoyl peroxide of reagent grade was twice recrystallized in chloroform.

Copolymerization Procedure

All copolymerization reactions were carried out at $80 \pm 0.5^\circ$ in Pyrex glass sealed tubes according to the procedure stated elsewhere [5]. After the desired heating time syrupy material was obtained. The resulting product was separated by using chloroform-petroleum ether as a solvent-precipitant system. The product thus obtained was found soluble in toluene, benzene, dioxane, DMF, DMS, and tetrahydrofouran. it is a white powdery substance. It decomposes at $155^\circ - 60^\circ$ and turns brown at 170°. The softening range is $120-25^\circ$. I.R. spectra of MMA, α-pinene and the product showed that the substance is a copolymer. The viscosity of dilute solutions of copolymer prepared in acetone was measured at $30 \mp 0.5^\circ$ using an Ostwald type viscometer. The copolymer was analysed by estimating the methoxyl ($-OCH_3$) group.

Determination of the methoxyl group

The methoxyl group was estimated in the form of an ester by treating the copolymer sample with boiling hydroiodic acid using modified Clark's apparatus [6]. By this treatment the methoxyl group in the copolymer chain was split off and converted into methyl iodide. Methyl iodide so formed was determined iodometrically. For this purpose,

a modification of the method of Vieboch and Breacher [7] was used, methyl iodide being oxidized with bromine to iodic acid. This is treated with an excess of potassium iodide in an acid solution yielding iodine which is determined by titrating with thiosulphate. The method was standardized by the analysis of poly (methyl methacrylate). The experimental error was of the order of $\mp$ 0.3 %.

RESULTS AND DISCUSSION

Detailed results for the copolymerization of binary mixture of MMA and α-pinene using benzoyl peroxide as initiator at 80° are summarized in (Table 1 and 2).

Estimation of prepared samples of poly (MMA) gives 30.5% $-OCH_3$ group whereas the resulting product contains 24.22-27.17% $-OCH_3$ group. This difference may be due to the attachment of α-pinene in the growing polymer chain of poly (MMA). This suggests that the product prepared is a copolymer. Further, poly (MMA) when free of cross linking is soluble in acetone, chloroform, ethyl acetate, toluene acetic acid, formic acid and related solvents whereas the product is found soluble in acetone, chloroform methyl

acetate, dioxane, toluene, benzene ethyl methyl ketone, dimethyl suphoxide, tetrahydrofuran, DMF etc. The solubility of this product in the solvents of wide range supports the result of estimation of $-OCH_3$ group.

I.R. spectral studies are also in the favour of the assumption that the product is a copolymer. The spectra of poly (MMA) poly (α-pinene) and copolymer are recorded and position of the absorption maxima are depicted for comparison in Table 3. The spectra of the product (copolymer) shows carbonyl band at 1720 cm^{-1} wave number and C–C bands at 2960, 1450, 1380, 1140 cm^{-1} wave number.

From the results given in Table 1, the rate of polymerization of MMA ($R_p \times 10^{-4}$ moles/1/sec) has been plotted against the concentration of MMA moles/1 (Fig. 1). It shows that rate of polymerization of MMA increases with an increased concentration of MMA. On the other hand, the rate of polymerization of α-pinene decreases with the increased concentration of α-pinene. It shows that a certain amount of α-pinene may be copolymerized with MMA and the rest of it acts as solvent and that is why each system appears to behave like a solution polymerization (8). Table 2

Table 1. Copolymerization of methyl methacrylate with α-pinene at 80° ± 0.5° for an hr. using 0.1 % benzoyl peroxide as catalyst

Expt. No.	Monomer in feed		Weight of copolymer g	Analysis $-OCH_3$%	Rate of polymerization $R_p \times 10$ moles/1/sec.		η dl/g	$\overline{Mn}$
	MMA g	α-pinene g			MMA	α-Pinene		
1.	0.25	4.75	0.030	25.51	0.1191	0.0188	–	
2.	0.50	4.50	0.045	25.83	0.1817	0.0268	0.365	178298
3.	1.00	4.00	0.145	26.39	0.6037	0.0777	0.400	203215
4.	1.50	3.50	0.380	26.78	1.6168	0.1883	0.435	229085
5.	2.00	3.00	0.495	27.17	2.1635	0.2244	0.440	23856

Table 2. Effects of benzoyl peroxide on copolymerization of MMA with α-pinene at 80° $\mp$.5° for 85 min.

Expt.	Monomer in feed		Benzyl peroxide g	Weight of copolymer	Analysis $-OCH_3$%	Rate of polymerization $R_p 10^{-4}$ moles/1/Sec.		$[\eta]$ dl/g	$\overline{Mn}$
	MMA g	α-pinene g				MMA	α-Pinene		
6.	2.50	2.50	0.05	2.2371	26.59	6.6500	0.9185	0.34	161111
7.	2.50	2.50	0.04	2.1250	25.82	6.2529	0.9223	0.35	167923
8.	2.50	2.50	0.03	1.7944	24.85	5.0818	0.9247	0.36	174818
9.	2.50	2.50	0.02	1.3835	24.22	3.8921	0.7862	0.365	178297

shows the effect of benzoyl peroxide on the copolymerization of MMA and α-pinene. The results indicate that the rate of the entrant α-pinene to the growing polymer chain of MMA increases slightly with increase in the concentration of benzoyl peroxide. It also supports the results shown in Table 1 regarding the use of α-pinene in copolymerization. α-Pinene probably isomerizes to limonene before polymerization [9] and then the limonene isomer reacts with growing polymer chain of poly (MMA) to yield a copolymer [10-11].

The monomer reactivity ratios of MMA (r_1) and α-pinene (r_2) were determined by following rate equation due to Fineman and Ross,[12] :

$$\frac{F(f-1)}{f} = r_1 \frac{f_2}{f} - r_2$$

where f is $d(M_1)/d(M_2)$, F is the monomer ratio $\frac{(M_1)}{(M_2)}$, and M_1 and M_2 are respectively the concentrations of MMA and α-pinene. A plot of $\frac{F(f-1)}{f}$ vs $\frac{f_2}{f}$ gives a straight line whose slope is r_1 and the intercept is r_2. The values of r_1 and r_2 so determined are 10 and 0.08 respectively. Since the monomer reactivity ratio of MMA is 125 times more
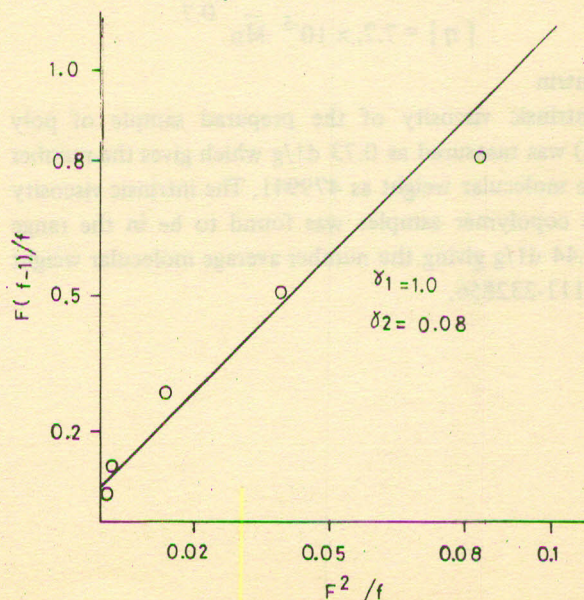
than that of α-pinene, the polymerization of the binary mixture gives an initial product which is virtually pure poly (MMA). This copolymeization system is nonazeotropic, since $r_1 > 1$ and $r_2 < 1$. Furthermore, as both r_1 and are greater than unity, both monomer. radicals in this system prefer the same monomer methyl methacrylate.
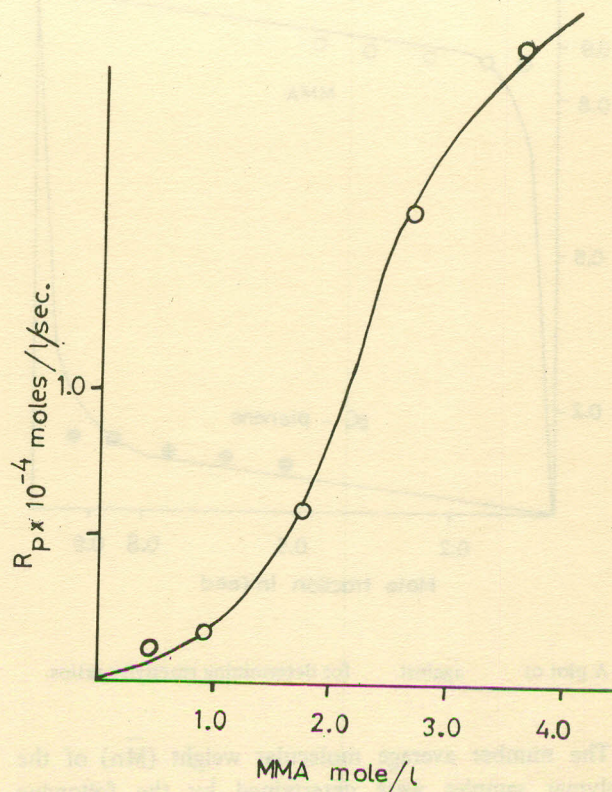

1. A plot of $R_p \times 10^{-4}$ moles/l/sec. vs MMA moles/l.

2. A plot of mole fraction in copolymer (fl) vs mole fraction in feed (F_1).

Table 3. I. R. Spectra of poly (α-pinene) poly (MMA) and copolymer of MMA and α-pinene.
s=strong, m=medium and w=weak

Poly (α-pinene) cm^{-1} Wave number	Poly (MMA) cm^{-1} Wave number	Copolymer cm^{-1} Wave number
2900 (s)	2960 (s)	2960 (s)
1650 (s)	2400 (w)	2400 (w)
1460 (m)	1960 (w)	1940 (w)
1380 (m)	1700 (s)	1720 (s)
1160 (w)	1440 (m)	1600 (w)
1100 (w)	1380 (w)	1450 (m)
1000 (w)	1120-1240 (m)	1380 (w)
885 (w)	1960 (w)	1240 (w)
800 (w)	960 (m)	1140 (m)
675 (w)	825 (w)	1060 (w)
	740 (m)	960 (m)
		840 (w)
		720 (m)
		680 (w)

The copolymer composition curve is shown in Fig. 3. It is quite obvious from these results that the mole fraction of MMA in the copolymer is consistent with the comonomer feed which also indicates greater reacting of MMA in this system.
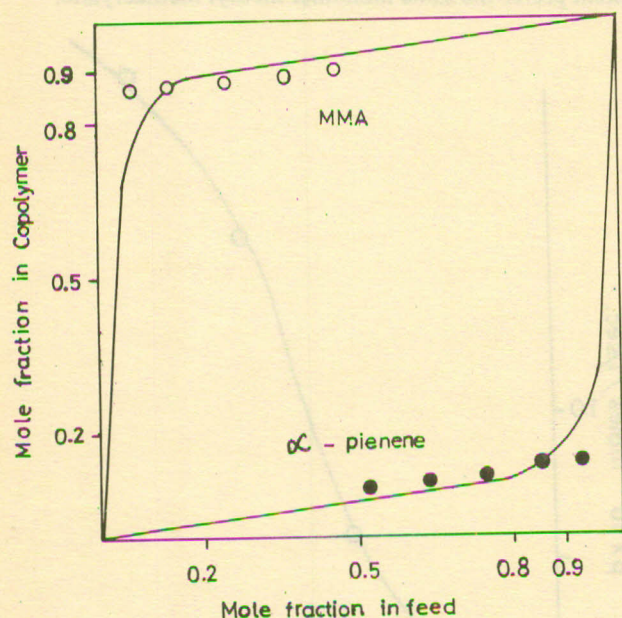
3. A plot of   against   for determining reactivity ratios.

The number average molecular weight $(\overline{Mn})$ of the copolymer samples were determined by the following intrinsic viscosity $[\eta]$-molecular weight relationship.

$$[\eta] = 7.7. \times 10^{-5} \; \overline{Mn}^{0.7}$$

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The intrinsic viscosity of the prepared sample of poly (MMA) was measured as 0.73 dl/g which gives the number average molecular weight as 479941. The intrinsic viscosity of the copolymer samples was found to be in the range 0.34-0.44 dl/g giving the number average molecular weight as 161111-232856.

The molecular weight of the copolymer has been found to decrease with the increasing concentration of α-pinen. It shows that not only does α-pinene copolymerize with MMA but it also acts as a chain transfer agent resulting in a copolymer of lower molecular weight. Some amount of α-pinene is used up in copolymerizing with MMA and the rest of it acts as a solvent to lower down the molecular weight of the copolymer.

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