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COPOLYMERS FROM α -PINENE

Part III. Free Radical Copolymerization of Acrylonitrile with α -Pinene

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The homopolymerization of α -pinene and copolymerization of α -pinene with acrylonitrile (AN) has been carried out at 70° and 100° using a free radical initiator. α -pinene homopolymerizes with very low degree of polymerization. The rate of copolymer formation decreases with increased concentration of α -pinene. At higher concentration of catalyst, good yields of copolymer is obtained. The monomer reactivity ratios of AN (r_1) and α -pinene (r_2) were determined to be 13.5 ± 0.1 and 0.07 ± 0.01 respectively. With increasing concentration of α -pinene in the binary mixture, copolymers with decreasing molecular weight (2300-4910) were obtained and α -pinene also acts as a chain transfer agent. The copolymer obtained were yellowish powdery substances soluble in many organic solvents. It decomposes around 120-135°.

Key words: Homopolymerisation; Tackifying agents; Isomerisation.

INTRODUCTION

α -Pinene is a natural product of outstanding properties. It is widely used as a commercial intermediate for the synthesis of synthetic pine oil, terpinhydrate, terpineol, terpene esters and others, camphene, camphor, terpene - phenol resins and reaction products with phosphorous sulfide for use as oil additive. Besides these uses of α -pinene, it is also extensively used in the preparation of polymers and copolymers with other terpenic monomers and vinyl monomers of commercial values. Earlier, the cationic copolymerization of α -pinene and styrene using $AlCl_3$ as catalyst was reported [1]. It was found that α -pinene and styrene forms copolymers at all monomeric ratios and these copolymers may be used as plasticizer and tackifying agents in the compounding natural and synthetic elastomers for ply adhesion, coatings and adhesives. We have been trying to prepare some useful copolymers of α -pinene and vinyl monomers [2] by free radical mechanism. This paper describes the free radical copolymerization of acrylonitrile and α -pinene using benzoyl peroxide as a catalyst.

EXPERIMENTAL

Material. Commercial grade α -pinene was first dried over metallic sodium and then distilled off at 157-158°. Acrylonitrile (BDH) was dried over sodium sulphate, distilled at 76.5° and stored in a dark container. Benzoyl peroxide was recrystallized in chloroform. Solvents like

methanol, petroleum ether, dioxane, DMF, Methyl ethyl ketone, dimethyl sulfoxide etc were distilled before use.

Copolymerization Procedure. All copolymerization reactions were carried out in sealed pyrex tubes. The required amount of acrylonitrile, α -pinene and benzoyl peroxide (1%) was transferred to reaction tubes, cooled and then were sealed at constriction. These tubes were then heated at desired temperature for known time in a thermostatic controlled water bath. After heating for a desired reaction time, the tubes were cooled and broken open. The product was separated with petroleum ether and dried. The product, thus, obtained is light yellow in colour and becomes more yellowish if the content of α -pinene in the product increases. The substance is found soluble in dimethyl formamide, dimethyl sulfoxide, partially in hot α -pinene, chlorobenzene and swelled in tetrahydrofuran and dioxane. It is also soluble in hot aqueous solution of sodium hydroxide. It begins to decompose at 120° and turns into yellowish brown at 135° and dark above 160°. Ultimately at 220° an insoluble black material is left behind.

I.R. spectra were recorded by a Jasco IRA-1 spectrophotometer in KBr discs. These spectra showed that the product is a copolymer.

Viscosity of copolymer solutions prepared in dimethyl formamide was measured at 25° using ostwald's type viscometer. The accuracy of our determination is ± 0.0004 CP. Melting point of copolymer samples was determined on Gallenkamp melting point apparatus.

RESULTS AND DISCUSSION

All the results of copolymerization of acrylonitrile and α -pinene are summarized in Tables 1, 2, & 3. The copolymers prepared by copolymerizing the binary mixtures of acrylonitrile and α -pinene were characterised by elementary analysis, solubility, melting point, I.R. spectral studies and molecular weight. The elementary analysis of the product gave 18.5 – 25.29 % nitrogen whereas prepared sample of poly (acrylonitrile) contains 26.32 % nitrogen. Furthermore the product prepared by copolymerizing

acrylonitrile (4g) and α -pinene (1g) was estimated also for carbon and hydrogen. It contains 68.32 % C, 5.8 % H and 25.29 % nitrogen whereas polyacrylonitrile contains 67.9 % C, 5.58 % H and 26.32 % N. All these differences in percentage of H, C and N clearly indicate that α -pinene has entered in the growing polymer chain of acrylonitrile and hence form copolymer. When powdered poly-(acrylonitrile) was heated with hot conc. aqueous solution of NaOH, the colour of polyacrylonitrile primarily becomes yellow which gradually turns into orange and then brilliant red due to hydrolyzing -CN groups to COONa group of poly

Table 1. Copolymerization of acrylonitrile and α -pinene at 100° for 30 minutes using 1 % benzoyl peroxides as initiator

Expt No	Monomer in feed		Yield g	Analysis % N	Rate of polymerization Rp x 10 ⁵ moles/l/sec.		[η] dl/g	Mn
	acrylonitrile g	α -pinene g			acrylonitrile	α -pinene		
1.	1.0	4.0	0.303	18.500	37.9137	6.3215	0.13	2300
2.	1.5	3.5	0.695	22.360	104.3680	7.3764	0.15	2780
3.	2.0	3.0	0.743	23.190	114.9060	6.2278	0.18	3540
4.	2.5	2.5	0.820	24.178	131.3030	4.7350	0.23	4910
5.	4.0	1.0	1.728	25.29	283.5820	4.9168	0.38	9594

(C68.32 %, H5.8 %)

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Table 2. Effect of benzoyl peroxide on copolymerization of acrylonitrile (2g) and α -pinene (3g) at 70° for an hour

Expt No.	Weight of benzoyl peroxide g	Yield g	Analysis % N	Rate of polymerization Rp x 10 ⁵ moles/l/sec.		[η] dl/g	Mn
				acrylonitrile	α -pinene		
1.	0.050	0.490	23.85	38.8863	1.6650	0.18	3540
2.	0.062	0.640	24.16	51.5583	1.8755	0.19	3810
3.	0.075	0.686	24.23	55.4247	1.9477	0.18	3540
4.	0.087	0.769	24.30	62.3098	2.2495	0.17	3280
5.	0.100	0.823	24.31	66.7127	2.2512	0.17	3280

Table 3. Effect of time on the copolymerization of acrylonitrile (2.0 g) and α -pinene (3.0 g) at 100° using 1 % benzoyl peroxide as initiator

Expt No	Reaction time minutes	Analysis		Rate of polymerization Rp x 10 ⁵ moles/l/sec.		[η] dl/g	Mn
		Yield g	% N	acrylonitrile	α -pinene		
1.	30	0.7430	23.19	114.9060	6.2278	0.22	6430
2.	60	0.8205	23.54	64.4036	3.0651	0.18	3540
3.	90	0.9130	23.37	47.4308	2.4085	0.18	3540
4.	120	0.956	23.31	37.1528	1.9287	0.17	3280

(AN). Finally a colourless viscous solution is obtained. While the product first changes into orange colour and then brilliant red. The product is dissolved partially and finally a solution of yellow colour is obtained. This, perhaps, may be due to the attachment of α -pinene monomer unit in the growing chain of poly (AN) and loss of HCN under alkaline catalytic influence on copolymer. The product was also treated with conc. H_2SO_4 giving light yellow solution with no charring. On the other hand, poly (AN) is dissolved in conc. H_2SO_4 without charring giving a clear solution. This is further supported by the fact that the product was found soluble in partially or completely in DMF, DSO, chlorbenzene, α -pinene etc. and swells in dioxane, tetrahydrofuran. The solubility or swelling of the product in the above mentioned solvent is due to the fact that the product contains a major portion of AN which is clearly evident from nitrogen contents present in each sample as given in Tables 1, 2, & 3.

All the copolymer samples shown in Tables, 1, 2 & 3 are yellowish substances. Polyacrylonitrile prepared from

Table 4. I.R. Spectra of poly (α -pinene), poly (AN) and copolymer of acrylonitrile and α -pinene. s = strong, m = medium and w = weak.

Poly (α -pinene) cm ⁻¹ wave number	Poly (AN) cm ⁻¹ wave number	Copolymer cm ⁻¹ wave number
2900 (s)	2940 (s)	3400 (m)
1650 (w)	2240 (s)	2900 (s)
1460 (m)	1590 (w)	2220 (s)
1380 (m)	1450 (s)	1700-1600 (w)
1160 (w)	1350 (w)	1430 (m)
1100 (w)	1240 (w)	1340 (w)
1000 (w)	1060 (w)	1240 (w)
885 (w)	850 (w)	1050 (w)
800 (w)		740 (w)
675 (w)		675 (w)

its monomer is white powdery substance decomposes around 160-165° into brown substance insoluble in DMF, DSO etc. The product decomposes around 120-135° into yellowish brown. Above 150°, it becomes first brown and then an insoluble black material is left behind when temperature reaches to 220°. The colouration of polymer at or above 150° in the presence of air is likely to formation of long chain conjugated double bonds by the loss of HCN and insolubility in the solvents as a result of crosslinking. These observations further show that AN & α -pinene colloid to form copolymers. I.R. spectral studies of the product and polymers were also carried out. It is generally believed that the spectra of polymer much simpler than the spectra of monomer. This is due to the fact that the degree of freedom of vibration is restricted in the polymer and copolymer. The spectra of the product, poly (α -pinene) and poly (AN) are tabulated in Table 4. On comparison these spectra support the assumption that the product is a copolymer. The I.R. spectrum of the copolymer indicate nitrile absorption band at 2200 cm⁻¹ wave number whereas the C-C bands appear at 2900, 1430, and 1240 cm⁻¹ wave number.

Since the amount of nitrogen in the copolymer is 70-95.75% of total nitrogen in polyacrylonitrile (26.32) the nitrogen content increases with an increasing concentration of acrylonitrile in the feed as shown in Table 1, the copolymerization of binary mixture of AN and α -pinene gives an initial product which is virtually pure polyacrylonitrile. After propagation of polymer chain of acrylonitrile, α -pinene monomer units colloid with the growing polymer chain of poly (AN). It shows that polymerization of acrylonitrile is rapid while the entrance of α -pinene in the copolymer chain is very slow. Table 2 shows the effects of catalyst on the rate of copolymerization of acrylonitrile and α -pinene. In Fig. 1. rate of copolymerization ($R_p \times 10^5$ moles/l/sec) is plotted against the concentration of benzoyl peroxide, it shows that the increasing concentration of benzoyl peroxide enhances the rate of polymerization of both monomers and the formation of copolymer

Table 5. Homopolymerization of α -pinene at 100° using 1 % benzoyl peroxide as initiator

Expt No	Time of heating hr	Colour before heating	Colour after heating	Viscosity before heating stokes	Viscosity after heating stokes
1.	—	Colour less	—	1.88134	—
2.	20	Colourless	Colourless	1.88134	1.88938
3.	30	Colourless	Light yellow	1.88134	1.91940
4.	40	Colourless	Pale yellow	1.88134	1.95940

may be increased by increase concentration of catalyst. From the results summarized in Table 3, it is evident that rate of formation of copolymer may be effected by the change of reaction time. In Table 5, the results of homopolymerization of α -pinene but free radical mechanism using benzoyl peroxide, as catalyst are depicted. On heating, α -pinene in the presence of 1% benzoyl peroxide for 40 hours at 100° does not give any solid material. The difference in viscosity of the contents and colour before and after heating shows that some polymer is indeed formed although the degree of polymerization appeared to be

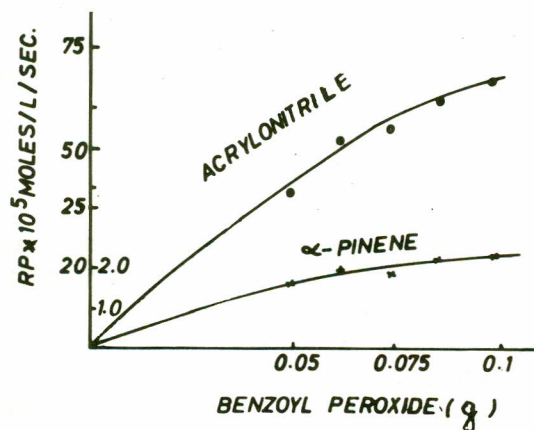
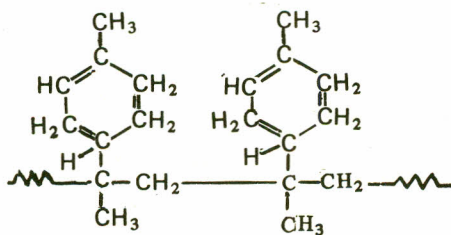


Fig. 1. Mayo and Lesis plot of r_2 vs r_1 for copolymerization of acrylonitrile and α -pinene at 100°C .

very low. The increase in viscosity of α -pinene after heating 20 hours is not appreciable while after heating 30 hours ($\eta = 1.9194$ stokes) and 40 hours ($\eta = 1.9594$ stokes), the changes is quite considerable. Further-more the colour of contents first changes into light yellow and then becomes darker. On distillation of unreacted α -pinene a brown viscous material of very low molecular weight is left behind. These evidences are quite enough and supporting that α -pinene may be homopolymerized by free radical mechanism with low rate of polymerization. α -pinene first isomerizes into limonene (4-isopropenyl-1-methyl cyclohexene) before going to polymerization and these limonene isomer begins to polymerize. Limonene isomer contains $=\text{CH}_2$ group which is the prominent site for the activation. The growing polymer chain of limonene isomer propagates its chain and couple with growing polymer chain of poly (AN) to form a copolymer.



The monomer reactivity ratios of AN (r_1) and α -pinene (r_2) were determined by using the integrated form of the copolymerization composition equation of Mayo and Lewis [3], In Fig 2, r_2 values are plotted against r_1 values. The number marked on each curve shows the experiment summarized in Table 1, The values of r_1 and r_2 obtained from these plots are 13.5 ± 0.1 and 0.07 ± 0.0 respectively.

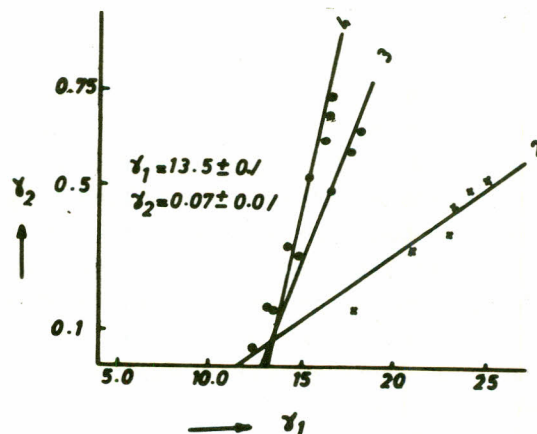


Fig. 2. Plot showing the effect of benzoyl peroxide on the rate of polymerization of acrylonitrile and α -pinene. For α -pinene Y-axis starts from 1×10^5 moles/l/Sec and for a acrylonitrile Y-axis starts from 20×10^5 moles/l/Sec.

Since one reactivity is greater than unity ($r_1 \pm 13.5$) and the other is less than unity ($r_2 = 0.07$), the present system is nonazeotropic. As both r_1 and r_2 are greater than unity, both radicals prefer the same monomer i.e., acrylonitrile. Here acrylonitrile is about 193 times more reactive than α -pinene. At the initial stages homopolymerization of acrylonitrile takes place and than α -pinene (partial isomerization of α -pinene into limonene) radicals begin to enter in the growing polymer chain of polyacrylonitrile resulting copolymer, which has already been discussed in above lines. Survey of the literature provides evidence that those monomer which do not polymerize easily may be copolymerized readily with easily polymerizeable monomers. Tetrachloroethylene [4] allyl alcohol [5], trichloroethylene [6], diethyl maleat [7], diphenyl acetylene [7], are some examples of the monomers which do not homopolymerize easily but forms copolymers with acrylonitrile very easily. In those copolymerization of methylmethacrylate and α -pinene [2], the reactivity ratios of these monomers are respectively 10 and 0.08. It indicates that 125 MMA monomer units combine with one α -pinene monomer unit hence AN is more reactive towards α -pinene than methylmethacrylate.

The number average molecular weight of copolymers samples were determined by using the following relation-

ship of intrinsic viscosity and number average molecular weight M_n [8].

$$[\eta] = 3.92 \times 10^{-4} M_n^{0.75}$$

Where $[\eta]$ is the intrinsic viscosity in dl/g which is the intercept of the plot η_{sp}/C and C is the concentration of solution prepared in dimethyl formamide. The viscosities were measured at 25°. The intrinsic viscosity of the prepared sample of poly (AN) was measured as 2.75 dl/g, which gives number average molecular weight as 134296. The intrinsic viscosity of the copolymer samples was found in the range 0.13-0.23 dl/g giving number an average molecular weight as 2300-4910. The molecular weight of copolymer has been decreased with increasing concentration of α -pinene. The molecular weight of polyacrylonitrile is very high and can be compared with the molecular weight of prepared sample of poly (AN). Similar thing happens in the copolymerization of α -pinene with methyl methacrylate [2] and styrene [1], where the molecular weight lowers down with the increase in concentration of α -pinene. The decrease in molecular weight with the increased concentration of α -pinene in feed may be due to partial isomerization of α -pinene into limonene, which then copolymerize with AN and also help in terminating the growth of polymers chain. So, α -pinene not only copolymerizes with AN but also acts as a chain transfer agent.

The copolymer obtained is light yellowish amorphous powder. A small sheet of it (0.2 cm thick) was cast at 60-100° under a pressure of 400 lb without using any plasticizer or solvent. The sheet so formed may be easily broken on bending. Similarly unplasticized poly (AN) films free from solvent are considerably more brittle. The

sheet of copolymer so cast is soluble in hot DMF showing that during casting cross linking of AN- α -pinene copolymer does not take place at 60-100°.

When a solution of copolymer prepared in DMF is treated with toluene-2,4-diisocyanate for an hour, a solid white substance insoluble in DMF is obtained. Diisocyanates contain highly reactive unsaturated -N=C=O groups which are extremely reactive with the compounds containing active hydrogen. The insolubility of the product in DMF may be due to cross linking of copolymer chain with diisocyanate and this crosslinking might take place by the abstraction of hydrogen from copolymer chain and cross linking with toluene-2,4-diisocyanate. The product is tough may be grinded and does not show any sharp melting point and become dark brown at 220°

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