

FREE RADICAL TERPOLYMERIZATION OF METHYL METHACRYLATE 2-ETHYLHEXYL ACRYLATE AND ACRYLIC ACID

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The terpolymerization of methyl methacrylate, 2-ethylhexyl acrylate and acrylic acid in ethyl acetate has been accomplished at 100° using benzoyl peroxide as initiator. It has been observed that these three monomers form terpolymer in all monomeric/ratios. A terpolymers of 11300-20400 molecular weight is obtained. It is white solid substance soluble in most of the organic solvents that softens at 69-70°. The refractive index of terpolymer samples is 1.337-1.338. The terpolymer may be used as plasticizer in the preparation of nail varnishes.

Key words: Simultaneous polymerization, Degradation, Intrinsic viscosity.

INTRODUCTION

The versatility of the multicomponent copolymerization is now well known. It helps in synthesising an unlimited different products of varying properties. In recent years the copolymers and terpolymers with of certain molecular weight (10^4 - 10^5) have been used in the preparation of different cosmetic products like nail varnishes, shampoos, lotions, hair colourants etc. Researchers have been trying their best to replace cellulose nitrate and low molecular weight sulphonamide or formaldehyde resin used to plasticize the nitrocellulose by these polymers [1]. Survey of the literature provides reference that terpolymers based on unsaturated polar and methacrylate monomers are becoming familiar to cosmetic products [2, 3]. Attempts have been made to prepare some useful multicomponent copolymers of vinyl monomers. This paper deals with the benzoyl peroxide-initiated terpolymerization of acrylic acid, methyl methacrylate and 2-ethylhexyl acrylate using ethyl acetate as diluent.

MATERIAL AND METHODS

Methyl methacrylate (E. Merck) and 2-ethylhexyl acrylate (E. Merck) were washed with sodium hydroxide to remove inhibitor and dried over calcium chloride. These monomers were then distilled. Acrylic acid (Sealze Hannover) was distilled and the fraction boiling at 141.5° was collected. Solvents like ethyl acetate, acetone, ethyl alcohol, methyl ethyl ketone (E. Merck) were used. Benzoyl peroxide (BPO) was recrystallized in chloroform twice.

Procedure of terpolymerization. All copolymerization reactions were carried out in sealed pyrex tubes. The required amount of methyl-acrylate (MMA), 2-ethylhexyl acrylate (EHA), acrylic acid (AA) and benzoyl peroxide (1%) was transferred in the reaction ampules already containing 5 ml ethyl acetate. The ampules were then cooled and sealed at constriction. The contents of tubes were

heated at 100° for 4 hours. After the required reaction time, the tubes were broken open. The product so obtained was first dissolved in ethyl acetate and then precipitated with distilled water or petroleum ether. Finally it was dried under reduced pressure to a constant weight. In place of precipitating with distilled water, it may be recommended to distilled off the solvent and the unreacted monomers for getting water free final product. The product thus obtained was found soluble in most of the organic solvents. It is white solid substance that softens at 69-70°. The IR spectra of the product, poly (MMA) poly (EHA) and poly (AA) were recorded (Table 2) for comparison and to ensure terpolymer formation. The viscosity of the solutions of terpolymer samples prepared in acetone was measured by Ostwald's viscometer at 30°, by following the procedure given else where [4]. The refractive index was measured on refractometer No. 122894 of Zeis Opton (Germany). The terpolymer samples were estimated for C and H.

RESULTS AND DISCUSSION

The detailed results of the free terpolymerization MMA, AA and EHA are summarized in Table 1.

Table 1. Benzoyl peroxide (1%) initiated terpolymerization of MMA, AA and EHA using ethyl acetate as a diluent for 4 hours (expt No. 7 with diluent for 2½ hours).

Expt. No.	Monomer MMA mole (%)	feed in AA mole (%)	EHA mole (%)	Yield (g)	Elemental analysis (%)		
					C	H	O
1.	63.12	16.90	19.97	4.80	61.81	8.42	29.77
2.	33.73	26.79	17.47	4.93	61.89	8.54	29.57
3.	51.38	23.80	24.82	4.87	62.20	8.52	29.28
4.	49.10	22.64	28.25	4.78	62.25	8.65	29.10
5.	48.34	20.14	31.52	4.25	62.29	8.69	29.02
6.	24.88	34.56	40.55	4.8	64.73	9.19	26.08
7.	55.73	26.79	17.47	4.92	61.24	8.31	38.45

The terpolymers are characterized by the elemental analysis, solubility, IR spectral studies, refractive index and number average molecular weight (\bar{M}_n). The elemental estimations indicate that seven samples of the product contain C and H, respectively, as 61.24-64.73% and 8.31-9.9%. On the other hand the estimation of prepared samples of poly (MMA) gives 60% C and 7.95% H, whereas poly (AA) contains 50% and 5.45% C and H, respectively. In the prepared samples of poly (EHA), the percentage of C and H are found as 71.70 and 10.85, respectively. Further the percentage of oxygen in the product samples ranges from 26.08-30.45 which is less than the percentage of oxygen found in poly (AA) (44.44%) and poly (MMA) (32%) and higher percentage of oxygen is found in the sample of poly (EHA) (17.39%). This variation in percentage of C, H and O suggests that both acrylates (MMA and EHA) and AA participate in the reaction to form terpolymer. The acrylates (MMA and EHA) when free of cross linking are soluble in acetone, chloroform, ethyl acetate, toluene, acetic acid and related solvents, whereas poly (AA) gets dissolved in dioxane, water, aqueous solution of NaCl, aqueous solution of NaOH, DMF, alcohol etc and insoluble in acetone, ethyl ether, benzene. Beside this, the product is soluble in most of the organic solvents, whereas petroleum ether and water

Table 2. I.R. spectra of poly (MMA), poly (AA), poly (EHA) and terpolymer.

Poly wave number (cm ⁻¹)	wave number (cm ⁻¹)	wave number (cm ⁻¹)	Terpolymer wave number (cm ⁻¹)
2960 (s)	2820-3500 (s)	2900 (s)	3200 (w)
2400 (w)	1900 (w)	1720 (s)	2950 (s)
1960 (w)	1720 (s)	1620 (w)	1725 (s)
1700 (s)	1440 (w)	1440 (w)	1450 (m)
1440 (m)	1380 (w)	1400 (m)	1380 (w)
1380 (w)	1250 (w)	1240 (w)	1240 (w)
1120-1240 (m)	1100 (m)	1180 (m)	1170-1150 (w)
1060 (w)	1020 (w)	1050 (m)	980 (w)
960 (m)	800 (w)	980 (m)	820-850 (w)
825 (w)	860 (m)	800 (m)	750 (m)
740 (s)		720 (w)	

(s = strong, m = medium, w = weak)

are suitable precipitant for this product. The solubility behaviour supports the results of elemental analysis and ensures that the product is a terpolymer. IR spectral studies have also been carried out which support that the product is a terpolymer. It is observed that the spectra of the polymer is much simpler than monomer itself. This is due to the fact that the degree of freedom of vibration is restricted in the polymer. However, the general pattern of the spectra of polymers and monomers remain the same. The spectra of copolymer of terpolymer as a rule should show the addition on commutative behaviour of its monomers. In the present case, the IR spectra of terpolymer of MMA, AA and EHA are compared with the spectra of poly (MMA), poly (AA), and poly (EHA). In the spectrum of the product, the absorption bands with maxima at 2950, 1450, 1380, 1240, 1150, cm⁻¹ are characteristic C-C bands. The 1725 cm⁻¹ absorption band is a characteristic stretching vibration.

Due to experimental problems involved in the determination of functional groups (-OCH₃, -OCH₂CH(C₂H₅)-(CH₂)₃CH₃-COOH) of the monomers, the quantitative treatment of terpolymer composition equation [5-7] is difficult. It involves nine propagation reactions, six monomers reactivity ratios and six termination reactions. However with the help of elemental analysis (C, H, O) an effort has been made to know the probable composition of terpolymer samples. The results have been plotted as monomers in terpolymer (mole%) vs monomers in feed (mole %) as shown in Fig. 1.

From these results, it may be concluded that the rate of propagation of the growing polymer chain of MMA, AA and EHA increase with increase concentration of the three monomers in feed and these monomers get polymerized simultaneously. Survey of the literature and our observations evidence that these three monomers may be readily homopolymerized by free radical mechanism and at the early stage of the reaction each monomer forms initiating free radicals resulting the propagation of growing polymer chains of the monomers. Ultimately the growing polymer chain of the monomers couple and form terpolymer. Further the growing polymer chains of the either monomers or

Table 3. Physical parameters of terpolymer of MMA, AA and EHA.

Expt. No.	Intrinsic viscosity [η] dl/g	Probable number of monomer units in terpolymer (\bar{M}_n)	Probable number of monomer units in terpolymer (Pn)			Colour	Appearance	Softening point °C	Refractive index
			MMA	AA	EHA				
1.	0.067	15830	100	37	17	White	Solid	70	1.380
2.	0.076	18950	106	70	18	"	"	70	1.380
3.	0.056	12250	63	40	17	"	"	69	1.387
4.	0.080	20390	100	64	31	"	"	70	1.380
5.	0.053	11325	55	32	19	"	"	69	1.388
6.	0.61	13842	34	66	31	"	"	69	1.387
7.	0.114*	33820	190	123	32	"	"	70	1.373

*without diluent

unreacted monomers help in the termination of the polymer chains. It results these growing polymer chain result both polymers and terpolymer. The physical parameters support that the product containing major portion of terpolymer.

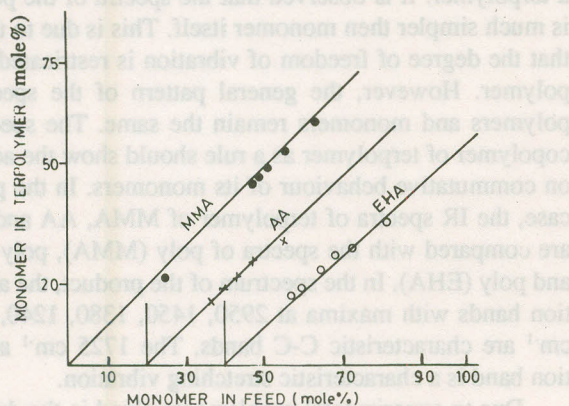
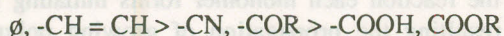


Fig. 1. A plot of monomers in terpolymer (mole %) against monomers in feed (mole %) for free radical terpolymerization of MMA, AA, and EHA MMA, AA and EHA. Each plot starts from o-axis, 1 division = 10 mole %.

This terpolymer contains units of three monomers incorporated into each terpolymer molecule. A terpolymer sample was also prepared by bulk polymerization of MMA (55.73 mole%), AA (26.79 mole%) and EHA (17.47%). It was observed that complete polymerization of the monomers took place in about 2-1/2 hours whereas these monomers in the presence of ethyl acetate, (as diluent) polymerize completely in 4 hours. It might be due to the spontaneous formation of initiating species which results increase in heat of reaction. The propagation of growing polymer chain takes place rapidly. It is difficult to control bulk polymerization of these monomers. The rate of polymerization of different monomers depending upon their functional groups have been reported [8] else where as,



Keeping the reactivity of functional groups and the results of the estimation of C, H, O in view this may be concluded that MMA enter in the growing polymer chain more rapidly than AA and EHA and EHA. The order of reactivity of the monomers may be rather in the following order,

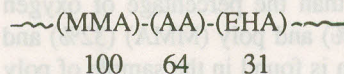


The intrinsic viscosity $[\eta]$ of the dilute solutions of terpolymer samples prepared in acetone was measured at $30 \pm 0.5^\circ$ using an Ostwald type viscometer. By using following intrinsic viscosity-molecular weight relationship [9], the number average molecular weight (\bar{M}_n) of terpolymer samples was determined from these intrinsic viscosities.

$$[\eta] = 7.7 \times 10^{-5} \bar{M}_n^{0.7}$$

The intrinsic viscosities of terpolymer samples prepared in the presence of diluent (ethyl acetate) was found to

be in the range 0.053-0.08 dl/g which gives the molecular weight as 11300-20400. Keeping in view the elemental analysis and probable composition of monomers in terpolymer (Fig. 1), the degree of polymerization of chain, Table 3 have been calculated. The results indicate the major participation of MMA monomer units ($\bar{P}_n=34-190$) in the formation of terpolymer as compared with EHA ($\bar{P}_n=17-32$) and AA ($\bar{P}_n=37-123$). At a feed of 49.1 mole % MMA, 22.64 mole % AA and 28.25 mole % EHA, and alternating terpolymer of the following type may be proposed.



This is also supported by the fact that all terpolymer samples first soften at $69-70^\circ$ and then converts into liquid which disappears at 150° leaving behind an insoluble brownish black material. The conversion of terpolymer on heating into liquid and its disappearance indicates the degradation of terpolymer into acrylate dimers, trimers etc. The insoluble black material left out may be due to AA. Further the molecular weight of terpolymer samples prepared in the presence of ethyl acetate was determined as 19000 whereas the terpolymer sample prepared in the absence of any diluent was found to be 33800. This shows that ethyl acetate not only facilitates the polymerization reaction but also acts as chain transfer agent [10].

Some physical parameters like molecular weight, color, appearance, softening range and refractive index have been studied and depicted in Table 3. The terpolymers are white plastic substances soluble in most of the organic solvents. It softens at $69-70^\circ$. The refractive index of terpolymers was found to be 1.373-1.388. The terpolymers may have commercial application as plasticizer in nail varnishes. It helps in making the nail varnishes stable and produces thin films with excellent adhesion and good gloss to the nail keratin.

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