

## FREE RADICAL TERPOLYMERIZATION OF METHYL METH ACRYLATE N-BUTYL ACRYLATE AND 2-ETHYL HEXYLACRYLATE

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Free radical terpolymerization of methylmeth acrylate (MMA), n-butyl acrylate (BA) and 2-ethyl hexyl acrylate using methyl ethyl ketone as solvent was accomplished at 60 °C. It was observed that all the monomers participated in the reaction simultaneously and formed terpolymer in all monomeric ratios. The product, apart terpolymer also contained small quantity of homopolymers of the monomers used in the reaction. Terpolymers of 175000 - 590000 were obtained which were found to be viscous, highly tacky, soft at room temperature and soluble in most of the organic solvents. The refractive index of terpolymer samples was found to be 1.4945 - 1.4946. This terpolymer may be used in the modification of chlorinated rubber as the film forming agent on leather.

**Key words:** Free radical, Terpolymerization, Homopolymers

### Introduction

In our earlier publications terpolymerization of different combinations of vinyl monomers has been reported (Rasheed and Yousufzai 1989; Rasheed and Tehzeeb 1990; Rasheed *et al* 1993; 1994; 1998;). This method allows the synthesis of different products by varying the nature and relative amounts of more than two units. This paper describes the terpolymerization of MMA, butyl acrylate and 2-ethyl and hexyl acrylate using benzoyl peroxide as catalyst and MEK as solvent.

### Experimental

**Materials.** Methyl methacrylate (E. Merck), n-butyl acrylate (Fluka), and 2-ethyl hexyl acrylate (E. Merck) were purified before use. These monomers were washed with sodium hydroxide to remove inhibitor, dried over calcium chloride then distilled and middle fractions were collected. Solvents like MEK, toluene, xylene were used after distillation. Benzoyl peroxide (BPO) AR grade was recrystallised twice in chloroform.

**Procedure of polymerization.** All polymerization reactions were carried out in a flange flask fitted with stirrer, thermometer, condenser, nitrogen inlet and funnel and kept at 60°C for 5h. The required amount of monomers shown in Table 1 was transferred to the reaction flask already containing MEK (50 ml) and BPO (1%). The contents were stirred with uniform speed. After required reaction time 5h, aqueous methanol 50%

was added to stop the reaction. The product was precipitated washed to remove unreactive monomers with water methanol mixture and dried to constant weight. A highly tacky transparent material was obtained. The material was soluble in most of the organic solvents like acetone, xylene, benzene toluene etc but insoluble in MEK. The IR spectra (Table 1) of the product and individual polymers were recorded to verify the participation of each monomer in the reaction. The refractive index was measured on Refractometer No. 122894 Opton (Germany). The products were also analysed for C and H.

**Measurement of tensile properties:** Tensile properties like tensile strength and elongation at break were measured on Instron Universal Testing Machine Model No. 4031 as per (ASTM 1965; Rasheed *et al* 1998).

**Measurement of hardness:** Hardness of films prepared from the blends of terpolymer & chlorinated rubber (CR) were measured on Rubber Tester Model 1951.

### Results and discussion

Tables 2 and 3 describe the terpolymerization of MMA, n-BA and EHA using MEK as solvent at 60°C.

Tables 1 illustrates comparison of IR spectra of poly (MMA), poly (n-BA) and poly (EHA) with the product.

The product obtained by terpolymerization of MMA, n-BA & EHA was identified with the help of elemental analysis, solubility, IR spectral studies, intrinsic viscosities, refractive index etc. The five samples of the product contain 66.5 - 67.7% car-

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bon, 8.9- 9.7% H and 22.8 - 24. 3% oxygen (by difference) whereas the prepared samples of poly (MMA) contain 59. 9% and 7. 98% C and H respectively. Similarly the prepared samples of poly (n-BA) contain 65.5% & 9.28% C & H respectively whereas poly (EHA) 71.6% C and 10.82% H. The variation in elemental analysis suggests that all the three monomers participated in the reaction to form a new product. Solubility is another tool which is being used in the characterisation and ensuring the participation of three monomers in the reaction. The acrylates when free of crosslinking are soluble in chloroform, ethyl acetate, toluene, acetic acid and related solvents whereas poly (MMA) and other acrylates slowly dissolve in acetone. The product is soluble in most of the organic solvents like carbon tetrachloride, DMSO, benzene, DMF, acetone, ethyl acetate, methylene dichloride, benzene, toluene, xylene, chloroform whereas it does not dissolve in ethyl alcohol and acetic acid. These findings show that the product is a terpolymer. The spectrum of the product is compared with IR spectra of poly (MMA), poly (n-BA) and poly (EHA) as depicted in Table 1. These spectra also ensure that the product is a terpolymers. In the spectrum of the product, the absorption bands with maxima at 2960 (s), 1440 (m), 1380 (w), 1220 (w), 1160 (m)  $\text{cm}^{-1}$  are characteristics of C- C bands. The 1720  $\text{cm}^{-1}$  absorption band is a characteristic stretching vibration. The above evidences are sufficient to confirm the coupling of the growing polymer chains of poly (EHA), poly (nBA) & poly (MMA) to form terpolymer. Some experimental problems are involved in the determination of functional groups of these monomers (Walling and Briggs 1945; Ham 1964). Terpolymer involves nine propagation reactions, six monomers reactivity ratios and as well as six terminations reactions. In earlier papers the probable composition of terpolymers samples has been calculated on the basis of elemental analysis and yield (Rasheed and Yousufzai 1989; Rasheed and Tehzeeb 1990). Similarly the probable compositions of terpolymer samples are determined and summarized in Table 3. The plots of conversion vs monomer (Fig 1) indicate that the rate of propagation of growing polymer chains increase with increasing concentration of monomer in the feed and these three monomers polymerize simultaneously. At the early stage of the reaction, the three monomers generate initiating free radicals resulting in the propagation of growing polymer chains of the monomers. Depending upon the reactivity of different monomers and their initial feed ratio, a range of composition of terpolymers and mixture of homopolymers is obtained. Similarly for termination, along with all the free radicals present in the system solvent, molecules also compete and take part in chain transfer reactions.

It is evident from the plots (Fig 1) that the rates of propagation of these monomers are not uniform. In this system n-BA polymerizes more rapidly than MMA and EHA. The order of polymerization may be



The viscosity of dilute solutions of the product samples prepared in acetone was determined at 30°C using Ostwald's type viscometer. The number average molecular weight  $\bar{M}_n$  of terpolymer samples was calculated by using the following intrinsic viscosity  $[\eta]$  and molecular weight  $\bar{M}_n$  relationship.

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

The intrinsic viscosity of dilute solutions of polymer samples prepared in acetone was determined by plotting  $\text{ns}_p/\text{C}$  versus C where  $\text{ns}_p$  is the specific viscosity and C is the concentration of dilute solution expressed in percentage. Viscosity was measured at 30°C. The intrinsic viscosity of terpolymer samples was found to be in the range 0.36 - 0.84  $\text{dl g}^{-1}$  and the molecular weight was calculated to be 175,000 - 590,000.

Terpolymer samples which are highly tacky transparent soft material. Start melting at 132°C and the whole mass is distilled off upto 220°C leaving behind black spot. It shows that during 132-220°C degradation of terpolymer takes place. Furthermore it burns with candle like flame. The refractive index of terpolymer samples was found to be 1.4945 - 1.4946. It may be exploited commercially in the form of adhesive. Polyacrylates are used in the finishing of leather. But they are highly tacky. This disadvantage may be easily overcome by blending with chlorinated rubber. Blends of chlorinated rubber and terpolymers in xylene were prepared at 60°C according to the ratios shown in the Table 4. Films (10 x 15  $\text{cm}^2$ ) of these blends were casted at room temperature,

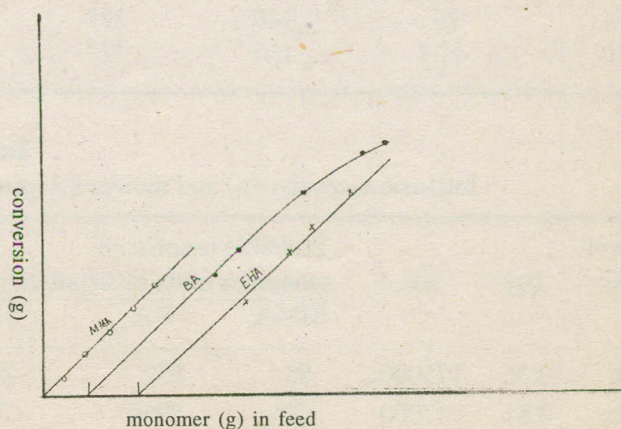


Fig 1. Plot of conversion (g) against monomer (g) in feed for free radical terpolymerization of MMA, n-BA & EHA. Each plot starts from o-axis 4 small division = 0.1g.

**Table 1**

Benzoyl peroxide (1%) initiated terpolymerization of MMA, EHA and n-BA using methyl ethyl ketone (MEK) as solvent for 5h at 60°C

Poly (MMA) wave number cm <sup>-1</sup>	Poly (EHA) wave number cm <sup>-1</sup>	Poly (BA) wave number cm <sup>-1</sup>	Terpolymer wave number cm <sup>-1</sup>
2960 (s)	2900(s)	2940 (s)	2960(s)
2400(w)	1720(s)	2325(w)	1940(w)
1960(w)	1440(m)	1725(w)	1850(w)
1700(s)	1380(w)	1450(m)	1720(s)
1440(m)	1250 (w)	1380(w)	1600(m)
1380(w)	1160(m)	1250-1149(m)	1440(m)
1240-1120 (m)	1030(w)	1065(w)	1380(w)
960(w)	770(w)	960-940 (w)	1220(w)
825(w)	730(w)	840 (w)	1160(m)
740(m)		700(w)	1030(w)
			830(w)
			720(s)
			690(w)

solvent was evaporated slowly over a period of 2 days and then the films were dried in vacuum desiccator. Tensile strength and elongation at break were measured on Instron Universal Testing Machine (Table 4). Hardness of these film were determined on rubber Tester modal 1951. Tensile strength of the films prepared from 100% CR was measured as 7.5 MPa whereas elongation at break was found as 0.5%. The addition of chlorinated paraffin (CP) lowered the tensile strength upto 6.1 MPa whereas it enhanced the elongation at break upto 1.3%. The results (Table 4) further indicate that addition of terpolymer in chlorinated rubber enhanced the tensile strength and elongation at break. This enhancement might be due to intermolecular or intermolecular rearrangements or linkages of terpolymer molecules with CR units and an increase in the crosslink density of the system (Rasheed *et al* 1998) This rearrangement of molecules increased the elongation. Terpolymer monomer units also affect the tensile properties as indicated by the tensile properties of blends prepared with terpolymer samples of different monomeric ratios prepared from different composition (Table 4). The addition of plasticizer and terpolymers affect the shore A hardness of the films prepared with Cr, it decreases from 75 to 25. It shows that the addition of plasticizer and terpolymer makes the films soft and flexible. The

**Table 2**

Terpolymerization of methyl methacrylate (MMA), n-butyl acrylate (n-BA) and 2-ethyl hexylacrylate (EHA) in the presence of methyl ethyl ketone (MEK) using benzoyl peroxide (1%) as catalyst for 5h at 60°C

Expt No.	MMA (g)	n-BA (g)	EHA (g)	Yield (g)	Elemental analysis		
					C	H	O
1.	2.3	30.6	11.0	37.2	66.8	8.9	24.3
2.	4.7	28.4	11.0	39.1	66.5	9.6	23.3
3.	7.0	22.0	15.5	42.3	67.0	9.7	23.3
4.	9.4	13.0	22.0	42.8	67.7	9.5	22.8
5.	11.7	15.3	17.7	43.9	66.6	9.6	23.8

**Table 3**

Intrinsic viscosity  $[\eta]$  and molecular weight ( $\bar{M}_n$ ) of terpolymer (MMA-n-BA-EHA)

Expt No	$[\eta]$	$\bar{M}_n$	Probable number of monomer units in terpolymer ( $\bar{P}_n$ )			Colour appearance	Consistency	R I
			MMA	BA	EHA			
1.	0.36	175000	91	252	238	White transparent	Soft tacky	1.4945
2.	0.84	587000	625	2950	795	"	"	1.4946
3.	0.57	340000	530	1301	638	"	"	1.4950
4.	0.45	240500	509	550	647	"	"	1.4946

Table 4

Tensile properties of binary blends of terpolymer samples and chlorinated rubber (CR) in the presence/absence of plasticizer (chlorinated paraffin)

Terpolymer No.	Terpolymer %	CR %	Plasticizer chlorinated paraffin (g)	Tensile strength MPa	Elongation at break %	Shore A hardness
1.	40	60	-----	31.5	505	35
	40	60	0.3	36.9	541	30
2.	40	60	-----	14.7	665	45
	40	60	0.1	35.3	670	38
3.	40	60	-----	67.0	6.2	35
	40	60	0.1	52.5	4.0	25
4.	-	100	-----	7.5	0.5	75
	-	100	0.1	6.1	1.3	60

tensile properties and hardness show that particularly the blends of CR and terpolymer along with plasticizer may be used in leather finishing which will be free from tackiness. These blends will make soft and flexible films on the surface of leather.

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