

# Reactivity Ratios of Ethyl Acrylate, *n*-Butyl Methacrylate Copolymer System by $^1\text{H}$ -NMR

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## Synopsis

Ethyl acrylate (EA) and *n*-butyl methacrylate (*n*-BMA) copolymers were prepared in solution and the composition of the copolymer samples was estimated by  $^1\text{H}$ -NMR spectroscopic techniques. Because the characteristic signals, which vary with the composition of the copolymer, were absent, the ratio of intensities of down-field protons to that of the total protons was used for the estimation of copolymer composition. Reactivity ratios were calculated from these values by using the Kelen-Tudos differential linear equation.

## INTRODUCTION

Acrylic copolymers have achieved prime importance in various avenues of industrial applications.<sup>1-5</sup> A knowledge of copolymer composition is an important step in the evaluation of their utility. The estimation of the composition of copolymer containing acrylate and methacrylate monomers was difficult by ordinary analytical techniques because of the similarity in the structural units of the monomer units. Use of ultraviolet (UV) and infrared (IR) spectroscopic methods required the constituent monomer units to have structurally different absorbancies. Although gas liquid chromatography, radiometric,<sup>6</sup> and isotropic<sup>7</sup> methods are useful,  $^1\text{H}$ -NMR spectroscopic technique was used in the present case because of its simplicity and rapidity.<sup>8-10</sup>

Copolymer composition and its distribution are dependent on the reactivity ratios of the system concerned, hitherto not reported in the literature. Hence an attempt was made to evaluate the reactivity ratios of the system.

## EXPERIMENTAL

Ethyl acrylate (Mitsubishi Chemicals, Japan) and *n*-butyl methacrylate (Riedel, LR) were washed successively with 5% sodium hydroxide and distilled water, dried over anhydrous sodium sulfate, and distilled under vacuum. The middle fraction of the monomers was used for the copolymerization. Methyl ethyl ketone (MEK) was purified and distilled by standard procedures.<sup>11</sup> Benzoyl peroxide (BPO), recrystallized from a chloroform methanol system, was used as the initiator.

A mixture of EA, *n*BMA, and BPO in calculated quantities (Table I) was added to a fixed volume of MEK in glass ampoules and a slow stream of purified nitrogen was passed in. The ampoules were sealed and the polymerization was carried out at  $60 \pm 0.5^\circ\text{C}$ . The copolymerization was terminated at a conversion of less than 10% by precipitation into the water-methanol mixture. The copolymers were redissolved in acetone, reprecipitated as above, and dried over vacuum for constant weight.

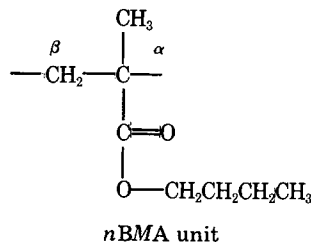
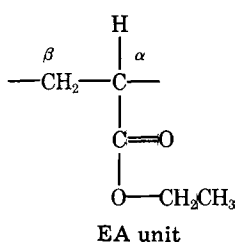
TABLE I  
Copolymerization of Ethyl Acrylate and *n*-Butyl Methacrylate  
[BPO] =  $2.65 \times 10^{-2}M$       Temperature =  $60^\circ C$

Serial No.	Feed composition in mole fraction		Conver- sion (%)	Downfield protons	Composition in copolymer in mole fraction	
	EA	<i>n</i> -BMA		Total	EA	<i>n</i> -BMA
	$M_1$	$M_2$		protons <i>C</i>	$m_1$	$m_2$
(1)	0.2621	0.7379	9.2	0.155	0.114	0.886
(2)	0.4860	0.5140	10.1	0.1712	0.265	0.735
(3)	0.5869	0.4131	8.7	0.1791	0.338	0.662
(4)	0.6805	0.3195	9.4	0.193	0.468	0.532
(5)	0.8503	0.1497	11.5	0.2075	0.603	0.397

$^1H$ -NMR spectra for all the copolymer samples (Fig. 1) were run with a 270-MHz spectrometer,  $CDCl_3$  was used as the solvent at a temperature of  $55^\circ C$ , and TMS was the internal standard. The spectra were run three times, and the average value of integrals was used in the estimation of copolymer composition.

## RESULTS AND DISCUSSION

The main chain of carbon atoms of EA and *n*-BMA (named as  $\alpha$  and  $\beta$  carbon atoms, respectively) is represented in the following structural units:



The distribution of protons in the two units is an important means of distinguishing these monomers in the copolymer chain. Because the monomers are esters of the same acrylic family, the characteristic chemical environment of the given proton is almost identical even though the nature of alkyl group differs in both ester linkages. Hence the proton resonance in the two structural units is identical and indistinguishable.

The identifiable difference corresponds to the methyl group in *n*-BMA and a single proton in EA on the  $\alpha$  carbon of the main chain. The methyl and methylene proton signals appear at high field. The carbon methyl proton signals of *n*-BMA have almost merged with the other alkyl  $\text{---CH}_3$  proton signals. The methine proton signal alone does not offer any help in the estimation of copolymer composition. The  $\text{---OCH}_2$  proton signals appear at low field for both units and the signals are indistinguishable. Therefore the evaluation of the monomer unit content in the copolymer based on a characteristic NMR signal is ruled out. Hence a different approach was followed to achieve the estimation of copolymer composition for the present system.

The combined  $\text{---OCH}_2$  proton signals appear distinctly at 3.98–4.1  $\delta$ , whereas

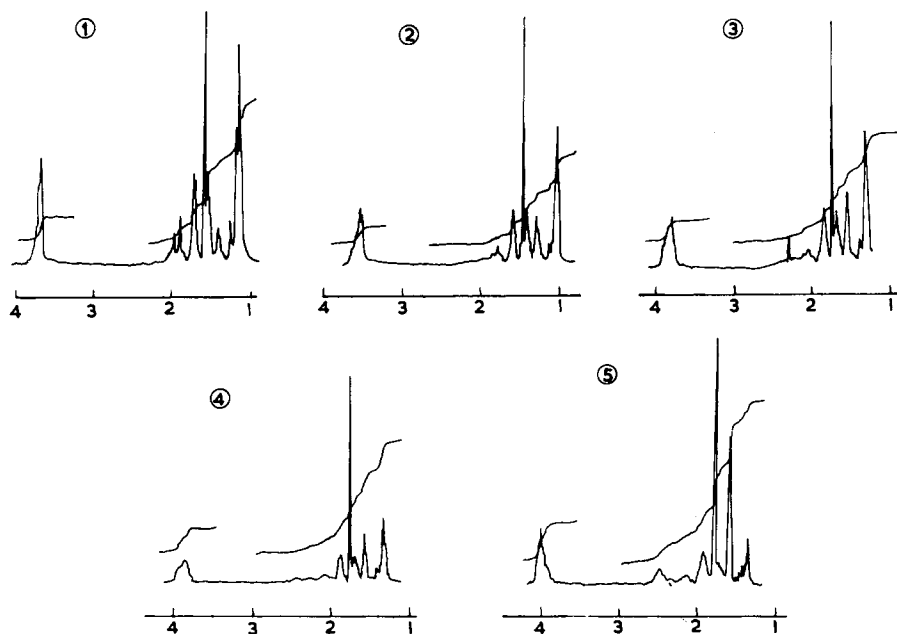


Fig. 1. The  $^1\text{H}$  NMR spectra (Copolymer ①, ②, ③, ④ and ⑤)

other proton resonance occurs at high field. Grassie et al.<sup>12</sup> made use of the total proton difference for the evaluation of the molar ratio of MMA to MA in the MMA-MA copolymer; in this case the composition of the copolymer was estimated by taking the ratio of intensities of down-field protons to that of the total protons.

The following expression was derived from copolymers consisting of both monomer units:

Let  $m_1$  be the mole fraction of ethyl acrylate and  $(1 - m_1)$  that of *n*-butyl methacrylate. The total proton in each monomeric unit is in the ratio of 4:7. Therefore it is evident from the structure

$$\frac{m_1}{4} + \frac{1 - m_1}{7} = \frac{\text{intensities of down-field protons}}{\text{intensities of total protons}} = C \quad (1)$$

that on simplification

$$m_1 = \frac{28C - 4}{3} \quad (2)$$

Based on eq. (2), the ratio of intensities of the down-field protons to that of the total protons was calculated from the spectra of all copolymer samples. Table I lists the values (i.e.,  $C$ ) and corresponding mole fractions of the monomeric units in the copolymer.

To ascertain normal copolymer kinetic behavior a plot of  $m_1$  versus  $M_1$  was drawn, in which  $m_1$  is the mole fraction of EA in the copolymer and  $M_1$  is that of the feed (Fig. 2). The concave shape of the curve indicates that the distribution of monomeric units is random and in no case is a homopolymer formation

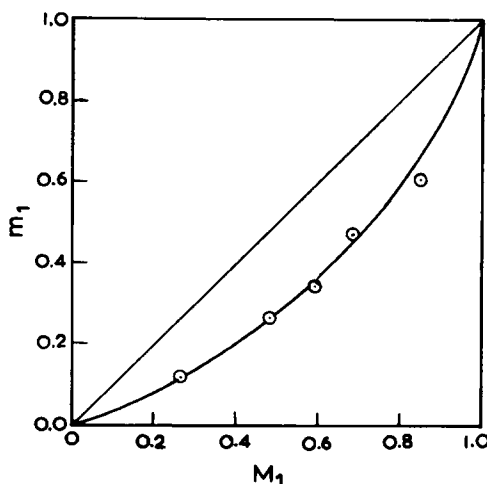


Fig. 2. Molefraction of EA in the copolymers vs molefraction in the feed composition.

expected. To evaluate the reactivity ratio the Kelen-Tudos<sup>13</sup> method was followed. A graphically evaluable linear equation proposed by these authors is

$$\frac{G}{\alpha + F} = \left( r_1 + \frac{r_2}{\alpha} \right) \frac{F}{\alpha + F} - \frac{r_2}{\alpha} \quad (3)$$

where  $G$  and  $F$  represent

$$G = \frac{x(y-1)}{y}$$

$$F = \frac{x^2}{y}$$

$x$  and  $y$  denote the ratios of mole fractions of the monomer feed composition and in the copolymers formed, respectively;  $\alpha$  is an arbitrary constant ( $\alpha > 0$ ) given by

$$\alpha = \sqrt{F_m F_M}$$

where  $F_m$  and  $F_M$  represent the lowest and highest value calculated from the series of measurements in the copolymerization. By introducing

$$\eta = \frac{G}{\alpha + F} \quad \text{and} \quad \xi = \frac{F}{\alpha + F}$$

TABLE II  
Kelen-Tudos Method

Sl. No.	$x$	$y$	$\eta$	$\xi$
(1)	0.3552	0.1287	-0.4338	0.1769
(2)	0.9455	0.3605	-0.2381	0.3521
(3)	1.4207	0.5106	-0.1548	0.4642
(4)	2.1299	0.8797	-0.0299	0.5305
(5)	5.68	1.5189	+0.0752	0.8232

$$\alpha = 4.5634$$

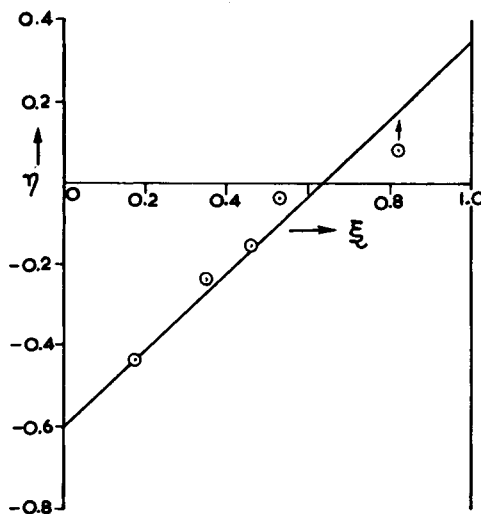


Fig. 3. K-T Method

eq. (3) can be written as

$$\eta = \left( r_1 + \frac{r_2}{\alpha} \right) \xi - \frac{r_2}{\alpha} \quad (4)$$

The variable cannot be given any possible value but it does have values in the interval (0,1). A plot of  $\eta$  versus  $\xi$  from the experimental shows a straight line, the extrapolation of which to  $\xi = 0$  and  $\xi = 1$  gives  $-r_2/\alpha$  and  $r_1$  (both as intercepts).

From the data in Table II a *K-T* plot was drawn between  $\eta$  and  $\xi$  and  $r_1$  and  $r_2/\alpha$  were obtained from the intercepts at  $\xi = 1$  and  $\xi = 0$ , respectively. The plot is shown in Figure 3. The  $r_1$  and  $r_2$  values obtained were  $r_1 = 0.35$  and  $r_2 = 2.69$ . The value of  $r_2$  is more than 1, whereas  $r_1$  is less than 1. The product of  $r_1$  and  $r_2$  (0.9415), however, remains less than 1, thus indicating that the system follows random distribution of the monomeric units. The  $r_2$  value, which is more than 1, indicates that the sequence of *n*-BMA units appears as long blocks. The values (i.e.,  $r_1$  and  $r_2$ ) are of the same order as those of similar copolymer systems that contain acrylic and methacrylic esters.<sup>14</sup>

The authors wish to acknowledge the help of Dr. (Mrs.) V. Kalpagam, Assistant Professor, Department of Inorganic and Physical Chemistry, Indian Institute of Science, Bangalore, in taking  $^1\text{H}$ -NMR spectra and to express their thanks to Mr. V. V. Krishnamoorthy of Kent State University, Ohio, for his helpful suggestions. The authors are also grateful to Dr. K. Thomas Joseph, Head of Polymer Division, Central Leather Research Institute, for his keen interest in this work. The junior author (SP) thanks the CSIR for awarding him a research fellowship.

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Received June 2, 1980

Accepted August 3, 1981