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## Studies on Synthesis and Characterization of Charge Transfer Polymerization of Styrene and Alkyl Methacrylates

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### ABSTRACT

Copolymers involving styrene and homologues of alkyl methacrylates (viz., methyl, ethyl, and butyl methacrylates) were synthesized at 60°C by employing a mixture of *n*-butylamine and carbontetrachloride as charge transfer (CT) initiators in dimethyl sulphoxide medium. The CT complex was characterized by UV spectroscopy while the respective copolymers were characterized by employing infrared (IR) and <sup>1</sup>H NMR spectroscopy. The copolymer compositions were determined by using <sup>1</sup>H NMR spectroscopy and the reactivity ratios were computed by Fineman–Ross (F–R) and Kelen–Tudos (K–T) methods. The reactivity ratios of Sty-MMA and Sty-EMA copolymers indicate that higher level of styrene is incorporated in the copolymer. On the other hand the Sty-BMA system exhibits different behavior. The higher value of  $r_2$  is obtained denoting that BMA is more active than styrene and hence, more BMA is present in the copolymer chain. In Sty-MMA and Sty-BMA systems, the product of  $r_1$  and  $r_2$  is greater than 1, representing the formation of high degree of random copolymers. However, in the case of Sty-EMA, the product of  $r_1$  and  $r_2$  is less than 1 indicating the formation of alternating copolymer.

*Key Words:* CT polymerization; Copolymer; Reactivity ratios; Styrene-MMA.

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## INTRODUCTION

In many instances, the composition of a copolymer are found to be different to that of the copolymer feed from which it is produced. In other words, different monomers exhibit different tendencies towards copolymerization. Some monomers are more reactive in copolymerization than indicated by their rate of homopolymerization.<sup>[1]</sup> For example, monomers like the maleic anhydride/stilbene pair, undergo copolymerization readily although they have little tendency to homopolymerize. Thus, the composition of a copolymer cannot be determined from the knowledge of homopolymerization rates of the two monomers. Several workers<sup>[2-4]</sup> determined copolymer composition by assuming the chemical reactivity of the propagating chain (which may be a free radical or ion) in a copolymerization to be dependent only on the monomer unit at the growing end and independent of the chain composition preceding the last monomer unit. Mayo et al. proposed that composition formed at any instant is dependent not only on the concentration of monomer species present in the system but also on the reactivity ratios.

The reactivity ratios indicate whether a growing chain, carrying an active center on a particular monomer unit, would prefer to add its own monomer or a co-monomer unit. The reactivity ratios of monomers 1 and 2 are dependent on the type of monomer and polymerization temperature. The reactivity ratios will throw light on copolymerization behavior and also on the type of copolymer obtained (viz., random, ideal or alternating). Although several techniques have been reported<sup>[5,6]</sup> for the determination of copolymer composition for estimating reactivity ratios, <sup>1</sup>H NMR spectroscopy<sup>[7,8]</sup> has been preferred in this work because of its simplicity and rapidity.

In recent years there has been increasing interest for synthesizing low molecular weight polymers by employing charge transfer (CT) techniques.<sup>[9-11]</sup> The copolymers so obtained are different from those prepared by conventional free radical polymerization techniques and are reported<sup>[12,13]</sup> elsewhere. The copolymer behavior of styrene and alkyl methacrylate has been presented in this article with an aim to understand the behavior of monomers and their reactivities in the copolymer chain.

## EXPERIMENTAL

### Materials and Methods

MMA, EMA, BMA (Aldrich), Styrene (Fluka), DMSO (Merck), CCl<sub>4</sub> (SD Fine), and *n*BA (SISCO) were purified as per standard procedures.<sup>[14,15]</sup> Monomers of different feed compositions of Styrene-MMA, Styrene-EMA, and Styrene-BMA were prepared and copolymers were synthesized using *n*BA-CCl<sub>4</sub> as CT initiators in DMSO medium at 60°C. The polymerization was restricted to a 15% level conversion for computing reactivity ratios by Fineman-Ross (F-R)<sup>[16]</sup> and Kelen-Tudos (K-T)<sup>[17]</sup> methods.

### UV Spectrophotometric Studies

A Shimadzu-260 UV spectrophotometer was used for studying the formation of a CT complex. The UV absorption characteristics of the initiators (*n*BA, CCl<sub>4</sub>) dissolved in hexane solvent and the CT complex of *n*BA and CCl<sub>4</sub> were studied.





### Infrared Spectroscopy

The Fourier Transformer (F-T) IR spectrophotometer was used for characterizing the polymer or copolymer samples. KBr pellets are prepared with the polymer samples and the spectra were recorded on a Nicolet 20 DXB machine.

### <sup>1</sup>H NMR Spectroscopy

<sup>1</sup>H NMR spectra of copolymer samples were recorded using a Bruker 300 MHz FT-NMR instrument with CDCl<sub>3</sub> as solvent and TMS as internal standard.

## RESULTS AND DISCUSSION

### Characterization of Charge Transfer Complex

UV spectroscopy is used for characterizing the formation of a CT complex for the *n*BA-CCl<sub>4</sub> initiating pair. Predetermined concentrations of *n*BA and CCl<sub>4</sub> dissolved in hexane are used for the UV spectral studies. The individual components gave UV bands at 273 and 272.8 nm respectively (Fig. 1). The CT complex formation is noticed by observing the change in absorbance values.

### FT-IR Spectroscopy

#### Sty-MMA Copolymer

FT-IR spectrum of the copolymer (50:50 feed composition) is shown in Fig. 2. The C—H stretching vibrations of the aromatic ring in the styrene unit and backbone methylene and  $\alpha$ -methyl units of MMA are seen at 3030 and 2980 cm<sup>-1</sup>, respectively. The characteristic ester carbonyl of MMA co-unit appeared as a sharp signal at 1730 cm<sup>-1</sup>. The C—H bending vibrations of the  $\alpha$ -methyl group on MMA is seen at 1453 cm<sup>-1</sup>, whereas the sharp signal at 1620 cm<sup>-1</sup> is attributed to C=C stretching vibrations of the aromatic ring in the styrene unit. The characteristic C—H bending vibrations for the phenyl ring are registered at 700 and 780 cm<sup>-1</sup>.

#### Sty-EMA Copolymer

The IR spectrum of the Sty-EMA copolymer (50:50 feed composition) is shown in Fig. 3. The characteristic absorption bands are observed at 3058–2854 cm<sup>-1</sup> as a series of signals. They are due to C—H stretching of aromatic and methylene, methane, and methyl groups. The ester carbonyl of the EMA unit gave a very strong band at 1724 cm<sup>-1</sup>. The other characteristic absorption frequencies typical for co-monomeric units are 1453, 1180–1156, and 759,700 cm<sup>-1</sup>. The presence of these signals in the spectrum supports the formation of a copolymer.



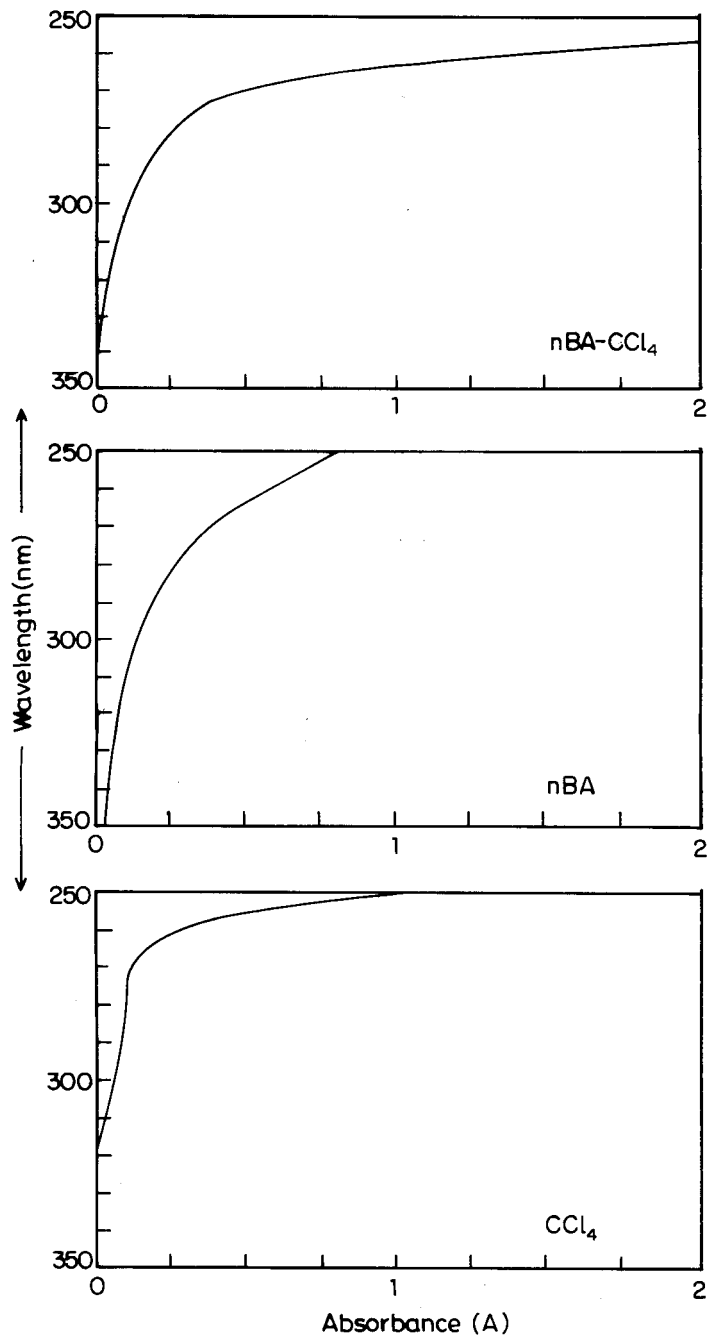


Figure 1. Characterization of CT complex.

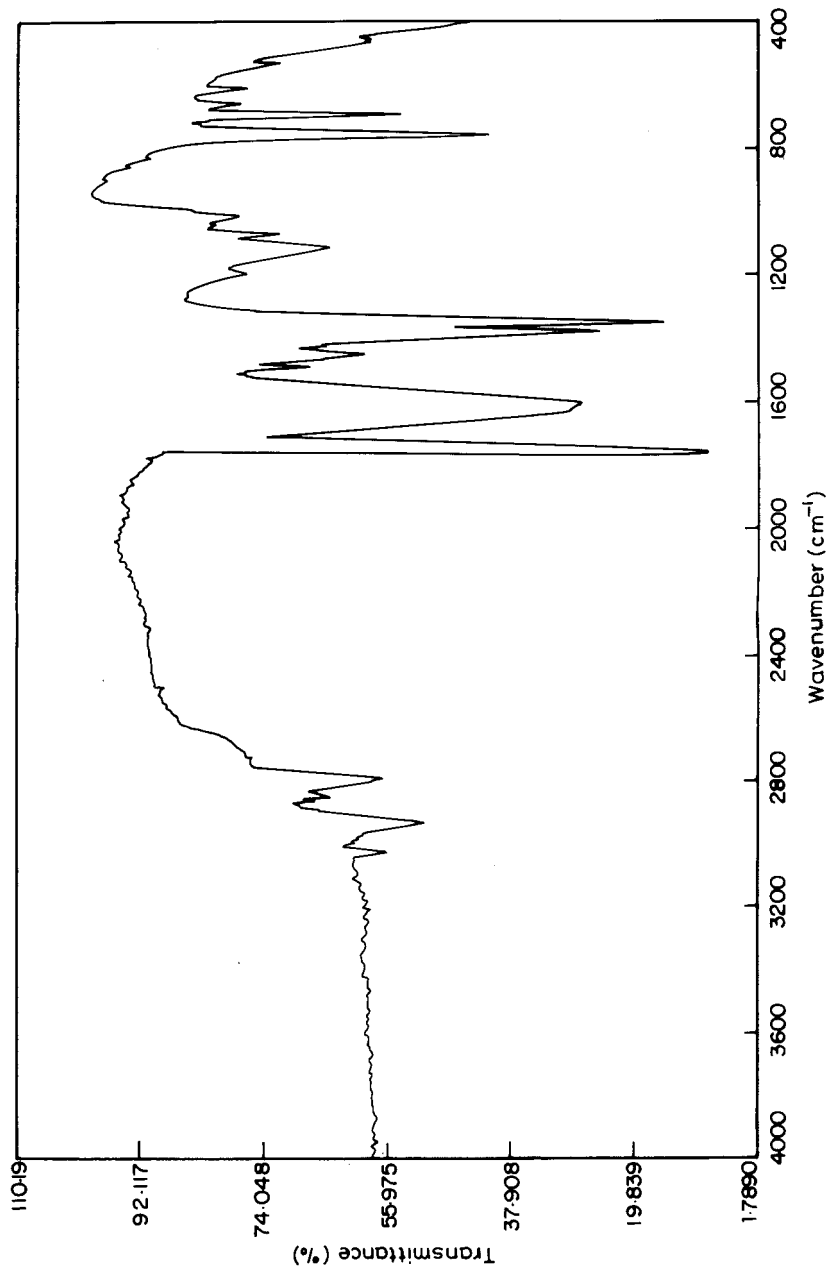


Figure 2. FT-IR spectrum of copolymer of Sty-MMA (50:50 feed composition).



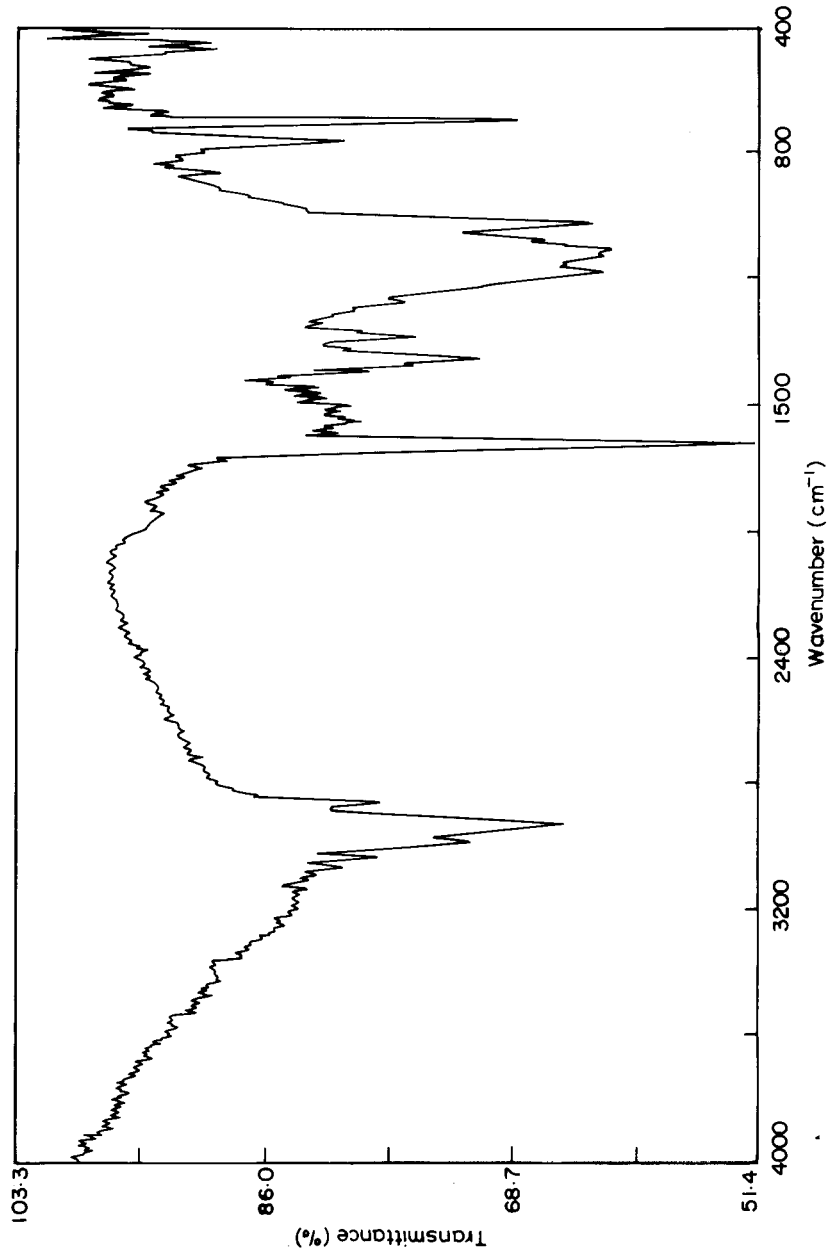


Figure 3. FT-IR spectrum of copolymer of Sty-EMA (50:50 feed composition).





## Sty-BMA Copolymer

The FT-IR spectrum of the Sty-BMA (feed composition 50 : 50), as shown in Fig. 4, indicates the presence of C—H stretching for the phenyl ring at 3058 and 3030  $\text{cm}^{-1}$ . The same aliphatic saturated units (C—H,  $\text{CH}_2$ ,  $\text{CH}_3$ ) signals are noticed at 2959, 2931, and 2868  $\text{cm}^{-1}$ . The intensity of the latter signals is very high due to the butyl side chain on the BMA unit. The ester carbonyl also gave a very sharp and intense signal at 1755  $\text{cm}^{-1}$ . The presence of aromatic ring is observed by noticing two sharp signals at 759 and 700  $\text{cm}^{-1}$ , typical for a styrene unit. They are due to C—H deformations. FT-IR studies of these copolymers reveal the absence of vinyl-acrylic double bonds.

 $^1\text{H}$  NMR Spectroscopy

## Sty-MMA Copolymers

$^1\text{H}$  NMR spectra of all the synthesized copolymers were examined. The  $^1\text{H}$  NMR spectra is not only used for identifying individual monomeric units in the copolymer but also employed for determining the copolymer composition. Since the monomers used in this system structurally differ with each other viz., aromatic and aliphatic, the respective signal intensities are compared for obtaining copolymer composition. For instance, the aromatic protons of the styrene phenyl ring and the  $\alpha$ -methyl protons of MMA are selected for determining the copolymer composition using the following equation:

$$m_1 = \frac{I_A/5}{I_A/5 + I_M/3}$$

Where  $m_1$  is the mole fraction of styrene in the copolymer. This equation is based on the fact that styrene is endowed with five aromatic protons while  $\alpha$ -methyl contributes three protons. Here,  $I_A$  denotes the intensity of aromatic protons and  $I_M$  represents the intensity of methyl protons. The  $^1\text{H}$  NMR spectra of copolymer samples of Sty-MMA are shown in Fig. 5. It can be seen (Table 1) that the feed composition of styrene and MMA varies with the copolymer composition.

## Sty-EMA Copolymers

Since EMA is a homologue of the alkyl methacrylate series, the consideration of aliphatic and aromatic protons (phenyl ring) for the calculation of copolymer composition is justified. The  $^1\text{H}$  NMR spectra of the Sty-EMA copolymers at various feed composition are given in Fig. 6. The intensities of the aromatic (styrene) and the aliphatic protons are compared and the following correlation is employed for computing copolymer composition of Sty-EMA and Sty-BMA copolymers.

$$m_1 = \frac{KA_1}{LA_1 + MA_2}$$

where  $m_1$  is the mole fraction of styrene in the copolymer;  $A_1$  is the number of aromatic protons of styrene unit;  $A_2$  is the number of aliphatic protons of EMA unit.





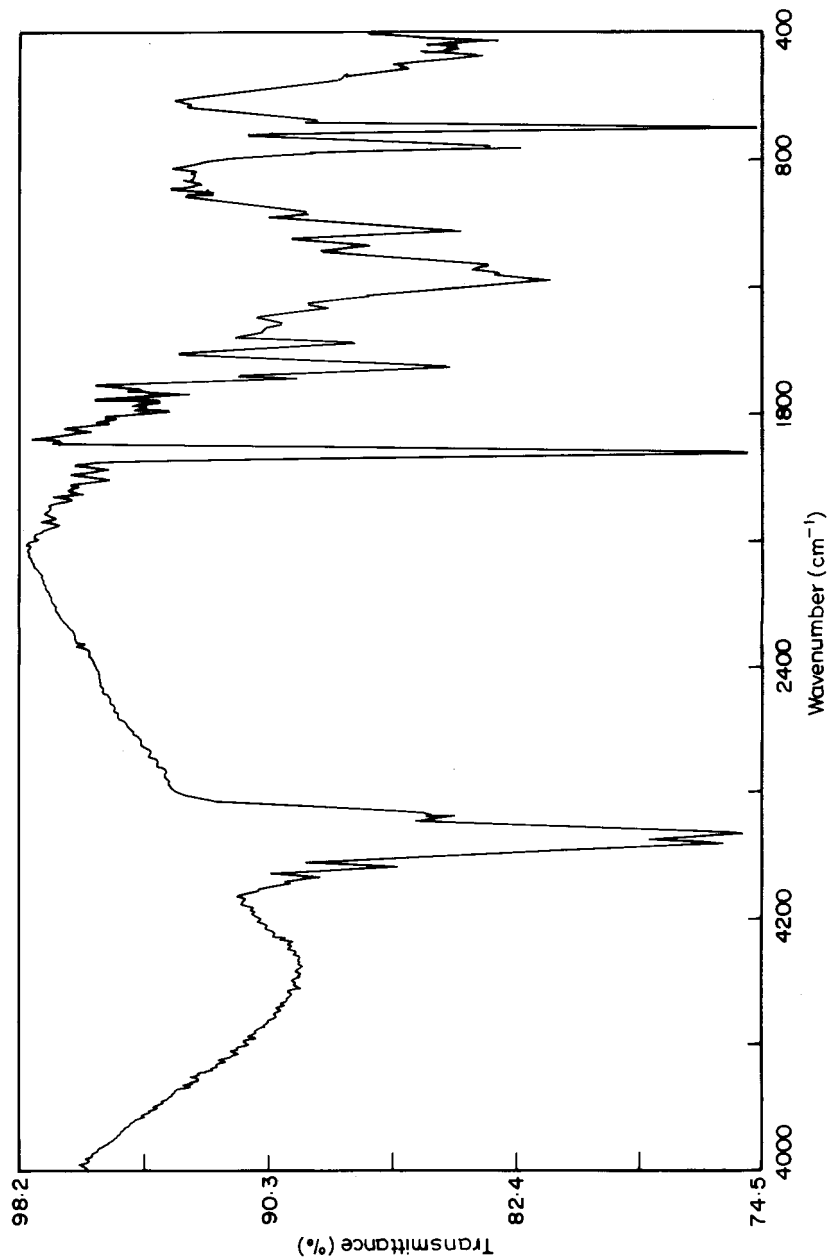


Figure 4. FT-IR spectrum of copolymer of Sty-BMA (50:50 feed composition).



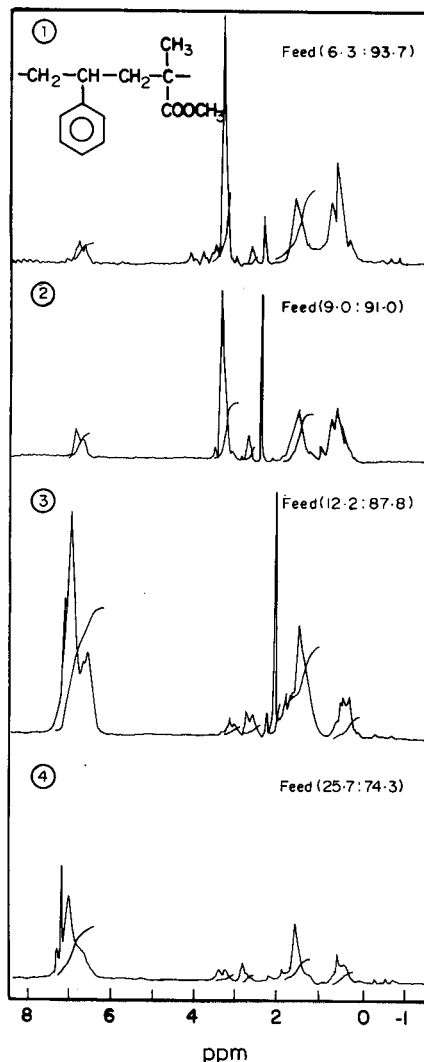


Figure 5.  $^1\text{H}$  NMR spectra of copolymer of Sty-MMA with different feed composition.

When  $K = 10$ ,  $L = 7$ , and  $M = 5$ , the above equation represents Sty-EMA system. The corresponding values for Sty-BMA system are 12, 9, and 5, respectively. The copolymer compositions for Sty-EMA are given in the Table 2. They are used for determining the reactivity ratios.

#### Sty-BMA Copolymers

The  $^1\text{H}$  NMR spectra at various feed compositions of Sty-BMA, are shown in Fig. 7. The intensities of aliphatic and aromatic protons are compared at each feed composition of



**Table 1.** Copolymer composition of styrene and methylmethacrylate system.

S. no.	Feed composition		Copolymer wt (g)	Conversion (%)	Copolymer composition	
	Mole fraction of Sty ( $M_1$ )	Mole fraction of MMA ( $M_2$ )			Mole fraction of Sty ( $m_1$ )	Mole fraction of MMA ( $m_2$ )
1	0.0628	0.9372	0.3592	11.22	0.1231	0.8769
2	0.0902	0.9098	0.4223	12.79	0.1928	0.7182
3	0.1218	0.8782	0.4542	13.35	0.2955	0.7145
4	0.2574	0.7226	0.4823	10.35	0.4022	0.5978
5	0.5098	0.4902	0.3347	8.35	0.7579	0.2421
6	0.6094	0.3906	0.3162	7.89	0.8557	0.1443
7	0.7573	0.2427	0.2125	5.14	0.9255	0.0745

Note: Reaction temperature =  $60^\circ\text{C} \pm 0.1^\circ\text{C}$ .

the Sty-BMA copolymers. The styrene and BMA contents in the copolymers, as given in Table 3, have been used for estimating the reactivity ratios. In all the cases  $m_1$  represents the mole fraction of styrene and  $m_2$  [equivalent to  $(1 - m_1)$ ] is the mole fraction of alkyl methacrylates in the copolymer.

### Computation of Reactivity Ratios

The copolymerization reactivity ratios can be computed by any of the following three reported methods viz.,

1. Fineman–Ross (F–R)
2. Kelen–Tudos (K–T)
3. Extended Kelen–Tudos (Ex K–T)

They are all governed by the fundamental equation:

$$\frac{m_1}{m_2} = \frac{M_1 r_1 M_1 + M_2}{M_2 r_2 M_2 + M_1}$$

where  $M_1, M_2$  = Mole fractions of monomers 1 and 2, respectively in feed;  $m_1, m_2$  = Mole fraction of monomers 1 and 2, respectively in copolymer.

#### Sty-MMA Copolymers

##### *Fineman–Ross Method*

Calculation is based on the equation  $G = r_1 F - r_2$  wherein  $G = x(y - 1)/y$  and  $F = x^2/y$ , where in  $x = M_1/M_2$  and  $y = m_1/m_2$ .

The  $G$  and  $F$  parameters are calculated by employing copolymer composition from  $^1\text{H}$  NMR data as presented in Table 4. By plotting  $G$  vs.  $F$ , the reactivity ratios of styrene



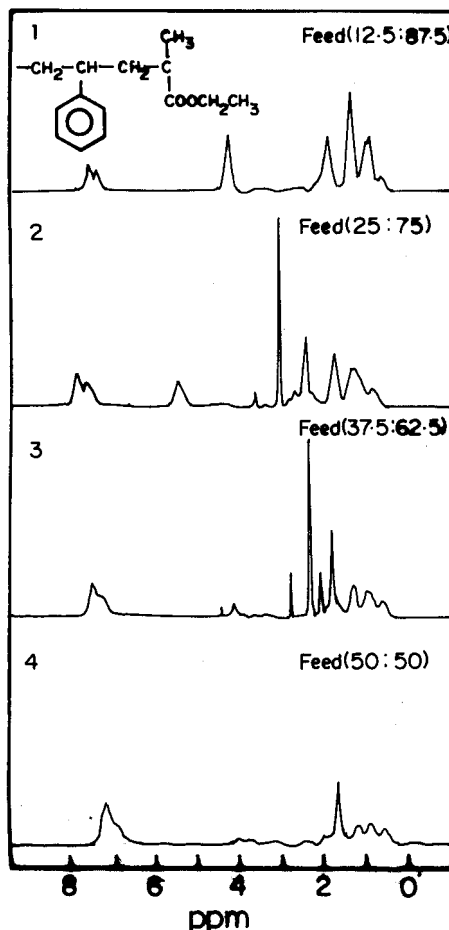


Figure 6.  $^1\text{H}$  NMR spectra of copolymer of Sty-EMA with different feed composition.

and MMA from the slope ( $r_1$ ) and intercept ( $-r_2$ ) are obtained. The F-R plot is given in Figs. 8 and 9 shows the plot of feed vs. copolymer composition ( $F_1$  vs.  $f_1$ ).

*Kelen-Tudos Method*

The K-T method<sup>[17]</sup> incorporates an additional factor viz.  $\alpha = (F_{\min} \times F_{\max})^{1/2}$  into the following equation:

$$\eta = \frac{r_1 \xi - r_2}{\alpha(1 - \xi)}$$

where  $\eta = G/(\alpha + F)$  and  $\xi = F/(\alpha + F)$ .

The K-T parameters  $\eta$ ,  $\xi$ , and  $\alpha$  for Sty-MMA copolymer system are given in Table 4. The composition of copolymer is an important factor to calculate K-T parameters. The



**Table 2.** Copolymer composition of styrene and ethyl methacrylate system.

S. no.	Feed composition			Conversion (%)	Copolymer composition	
	Mole fraction Sty ( $M_1$ )	Mole fraction EMA ( $M_2$ )	Copolymer weight (g)		Mole fraction ( $m_1$ )	Mole fraction ( $m_2$ )
1	0.1250	0.8750	0.2025	4.48	0.2410	0.7590
2	0.2500	0.7500	0.2166	4.89	0.3737	0.6263
3	0.3750	0.6250	0.2179	4.82	0.4757	0.5243
4	0.5000	0.5000	0.1828	4.04	0.6526	0.3474
5	0.6250	0.3750	0.1499	3.32	0.6407	0.3693
6	0.7500	0.2500	0.1429	3.14	0.7701	0.2299
7	0.8750	0.1250	0.1476	3.26	0.8540	0.1460

Note: Reaction temperature =  $60^\circ\text{C} \pm 0.1^\circ\text{C}$ .

plot of  $\eta$  vs.  $\xi$  is shown in Fig. 10. It is a straight line with  $r_1$  and  $-r_2/\alpha$  as intercepts at  $\xi = 1$  and  $\xi = 0$ , respectively.

#### Extended Kelen-Tudos Method

As the copolymerization proceeds, the monomer composition undergoes continuous change with time and the differential equation<sup>[17]</sup> is valid only at low conversions. The compositional drift leads to erroneous result in specific cases. However, in the Ex K-T equation, (Kelen et al. 1977 and Tudos et al. 1981), a conversion factor is introduced to consider an average feed composition  $\mathbf{x}$  instead of the initial feed composition ( $x$ ) as employed in other equations. The reported correlations for Ex K-T method are highlighted below:

$$\delta_2 = \frac{w(\mu + x)}{(\mu + y)/w_0}$$

$$\delta_1 = \frac{v_2 y}{x}$$

$$Z = \frac{\log(1 - \delta_1)}{\log(1 - \delta_2)}$$

$$\mathbf{x} = \frac{y}{Z}$$

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

$$G = \frac{y - 1}{Z}$$

$$\alpha = (F_{\min} \times F_{\max})^{1/2}$$



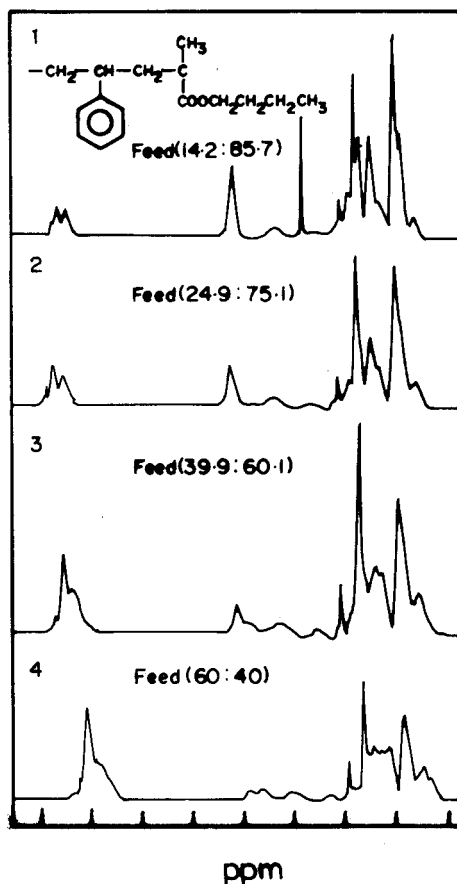


Figure 7.  $^1\text{H}$  NMR spectra of copolymer of Sty-BMA with different feed composition.

$$\eta = \frac{G}{\alpha + F}$$

$$\xi = \frac{F}{\alpha + F}$$

where  $w$  = wt.% conversion;  $\mu$  = molecular weight of monomer 2/molecular weight of monomer 1;  $x = M_1/M_2$ ;  $y = m_1/m_2$  (copolymer compositions of monomer 1 and 2);  $\delta_1$  and  $\delta_2$  = partial molar conversion of monomer 1 and 2;  $x$  = average feed molar ratio;  $G$  and  $F$  are F-R parameters and  $\eta$ ,  $\xi$ , and  $\alpha$  are K-T parameters.

As in the K-T method, the plot of  $\eta$  vs.  $\xi$  will result in a straight line with  $r_1$  as intercept at  $\xi = 1$  and  $-r_2/\alpha$  at  $\xi = 0$ . The Ex K-T parameters of Sty-MMA are given in Table 5. The Ex K-T plots are shown in Fig. 11.

The results of Sty-MMA indicate that individual  $r_1$  and  $r_2$  values and their product are less than 1. They show that copolymerization has the tendency to alternate and the



**Table 3.** Copolymer composition of styrene and butylmethacrylate system.

S. no.	Feed composition		Copolymer Wt (g)	Conversion (%)	Copolymer composition	
	Mole fraction Sty ( $M_1$ )	Mole fraction BMA ( $M_2$ )			Mole fraction ( $m_1$ )	Mole fraction ( $m_2$ )
1	0.1423	0.8577	0.5823	16.63	0.1715	0.8285
2	0.2491	0.7509	0.4265	12.15	0.2691	0.7309
3	0.3999	0.6001	0.3430	8.30	0.4024	0.5976
4	0.6003	0.3997	0.6268	12.53	0.5581	0.4419
5	0.7505	0.2495	0.4056	10.14	0.6731	0.3269
6	0.8006	0.1994	0.2717	8.36	0.8058	0.1942
7	0.9229	0.0771	0.3314	8.83	0.9031	0.0969

Note: Reaction temperature =  $60^\circ\text{C} \pm 0.1^\circ\text{C}$ .

presence of higher styrene content in the copolymers. The numerical values of the inverse of  $r_1$  and  $r_2$  indicate that both monomer radicals have the cross propagation tendency.

#### Sty-EMA Copolymers

Copolymer samples prepared at various feed compositions by using CT initiators are analyzed by  $^1\text{H}$  NMR for determining reactivity ratios  $r_1$  and  $r_2$ .

#### Fineman–Ross Method

The values of  $G$  and  $F$  parameters are calculated from the earlier described F–R equation for which the data has been reported in Table 6. A plot of  $G$  vs.  $F$  (Fig. 12) was employed to calculate  $r_1$  and  $r_2$ . Figure 13 provides a plot of feed composition vs. copolymer composition.

**Table 4.** Fineman–Ross and K–T parameters for styrene and methyl methacrylate copolymers.

S. no.	$x = M_1/M_2$	$y = m_1/m_2$	$G = x(y-1)/y$	$F = x^2/y$	$\zeta = F/(\alpha + F)$	$\eta = G/(\alpha + F)$
1	0.0670	0.1404	-0.3842	0.028	0.1665	-2.2809
2	0.0991	0.2389	-0.2915	0.035	0.1996	-1.6614
3	0.1387	0.4194	-0.1727	0.0371	0.2091	-0.9728
4	0.3466	0.6728	-0.1608	0.1625	0.5365	-0.5309
5	1.0400	3.3105	0.6664	0.3063	0.6857	1.4918
6	1.5602	5.9300	1.2190	0.3626	0.7208	2.4237
7	3.1203	12.4228	2.7173	0.7030	0.8335	3.2219

Note:  $\alpha = (F_{\min} \times F_{\max})^{1/2} = 0.1404$ .



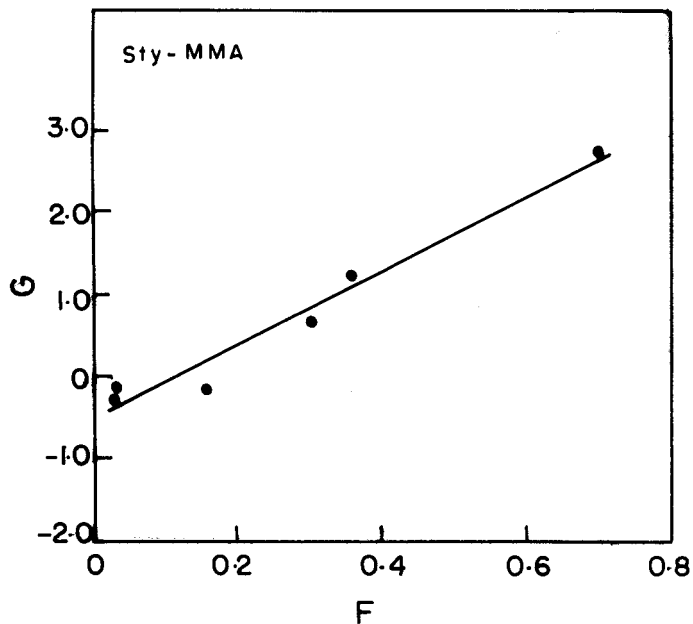


Figure 8. Fineman-Ross plot of Sty-MMA.

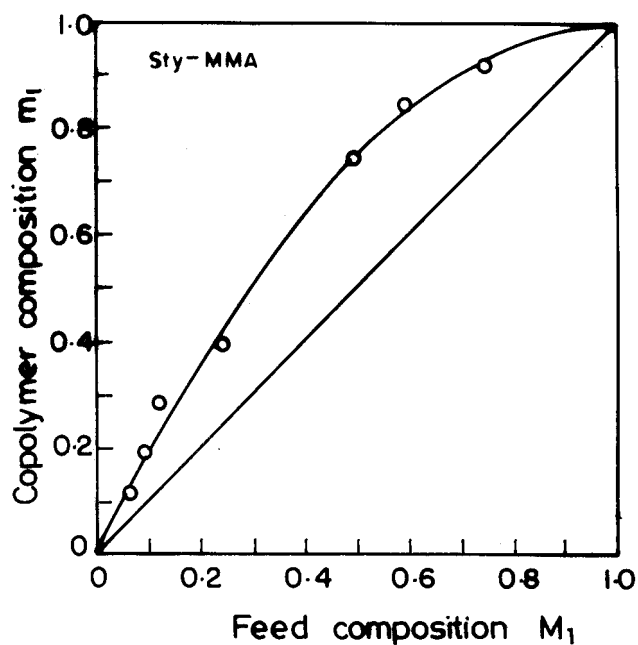


Figure 9. Plot of feed vs. copolymer composition of Sty-MMA.





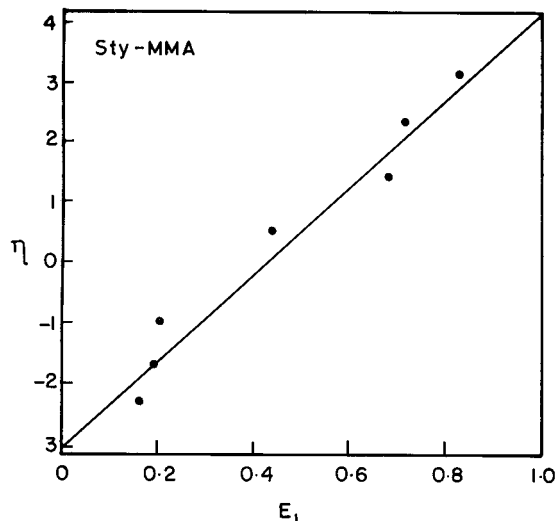


Figure 10. Kelen-Tudos plot of Sty-MMA.

*Kelen-Tudos Method*

Kelen-Tudos parameters and plot ( $\eta$  vs.  $\xi$ ) are given in Table 6 and Fig. 14, respectively. The K-T equations reported earlier were used to calculate the K-T parameters. From the intercept at  $\xi = 1$  and  $\alpha$  values,  $r_1$  and  $r_2$  are calculated.

*Extended Kelen-Tudos Method*

The Ex K-T method equations reported earlier were used to calculate Ex K-T parameters (Table 7). The plot of  $\eta$  vs.  $\xi$  is shown in Fig. 15. From the intercept and  $\alpha$  values,  $r_1$  and  $r_2$  are calculated. The magnitude of reactivity ratios of Sty-EMA copolymer points towards a higher level of styrene incorporation in the copolymer. Their inverse values clearly show that styrene radical has less cross propagation tendency as compared to EMA. The magnitude of their product is indicative of the copolymer tendency towards alternating.

Table 5. Extended Kelen-Tudos T parameters for Sty-MMA copolymers.

S.no.	$\delta_2$	$\delta_1$	$Z$	$x$	$F$	$G$	$\eta$	$\xi$
1	0.1681	0.2194	2.2390	0.0627	0.0280	-0.3889	-2.2394	0.1633
2	0.2063	0.2723	2.6502	0.0901	0.0340	-0.2872	-1.6185	0.1917
3	0.2246	0.2325	3.3080	0.1268	0.0383	-0.1775	-0.9655	0.2109
4	0.5300	0.1383	2.0137	0.3341	0.1659	-0.1625	-0.5252	0.5363
5	0.6857	0.1234	3.1464	0.9950	0.3162	0.6771	1.4731	0.6879
6	0.7216	0.1088	3.9660	1.4952	0.3770	1.2431	2.3885	0.7244
7	0.8319	0.0824	4.1118	3.0212	0.7348	2.7780	3.1633	0.8367

Note:  $\alpha = 0.1434$ .



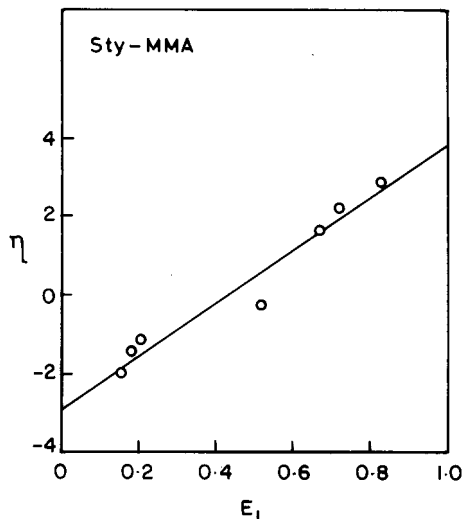


Figure 11. Extended Kelen-Tudos plot of Sty-MMA.

Sty-BMA Copolymers

Fineman-Ross Method

The  $G$  and  $F$  parameters are calculated from the equation reported earlier and are given in Table 8. The plot of  $G$  vs.  $F$  is shown in Fig. 16 and from the slope and intercept values,  $r_1$  and  $r_2$  are calculated. The plot of feed vs. copolymer composition is shown in Fig. 17.

Kelen-Tudos Method

The  $r_1$  and  $r_2$  are calculated from the K-T plot which is given in Fig. 18. The K-T method equations reported earlier were used to calculate K-T parameters (Table 8). From the intercept and  $\alpha$  values,  $r_1$  and  $r_2$  are calculated.

Table 6. Fineman-Ross and K-T parameters for styrene and ethyl methacrylate copolymers.

S. no.	$x = M_1/M_2$	$y = m_1/m_2$	$G = x(y - 1)/y$	$F = x^2/y$	$\xi = F / (\alpha + F)$	$\eta = G / (\alpha + F)$
1	0.1429	0.3175	-0.2867	0.0560	0.0748	-0.3826
2	0.3333	0.5967	-0.2161	0.1713	0.1982	-0.2500
3	0.6000	0.9073	-0.0597	0.3761	0.3517	-0.0558
4	1.667	1.7832	0.7290	1.5450	0.6903	0.3257
5	3.000	3.3497	2.0906	2.6518	0.7928	0.6250
6	7.000	5.8493	5.8723	8.5775	0.9252	0.6334

Note:  $\alpha = (F_{\min} \times F_{\max})^{1/2} = 0.6932$ .



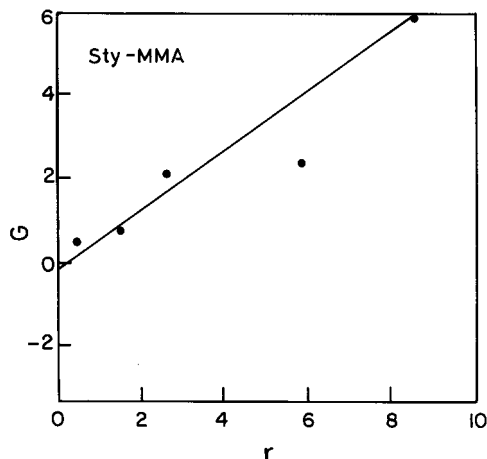


Figure 12. Fineman-Ross plot of Sty-EMA.

*Extended Kelen-Tudos Method*

In a similar manner, the Ex K-T method parameters are calculated and given in Table 9. From Ex K-T parameters, the plot of ( $\eta$  vs.  $\zeta$ ) is made (Fig. 19). Table 10 shows the  $r_1$  and  $r_2$  values calculated by different methods for styrene-alkyl methacrylates.

The magnitude of reactivity ratios of Sty-BMA copolymer and their product is indicative of the copolymer's favorable tendency to alternate. The  $r_1$  value which is close to unity somewhat explains the equal affinity of styrene radicals towards styrene and BMA monomers. However, the BMA radical has more affinity towards a styrene radical rather than its own monomer as indicated by the magnitude of  $r_2$ . The higher  $r_1$  value of styrene

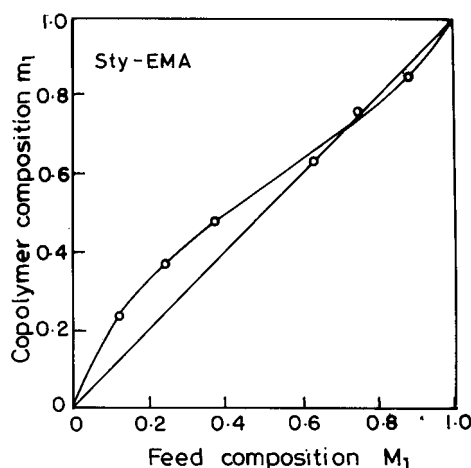


Figure 13. Plot of feed vs. copolymer composition of Sty-EMA.

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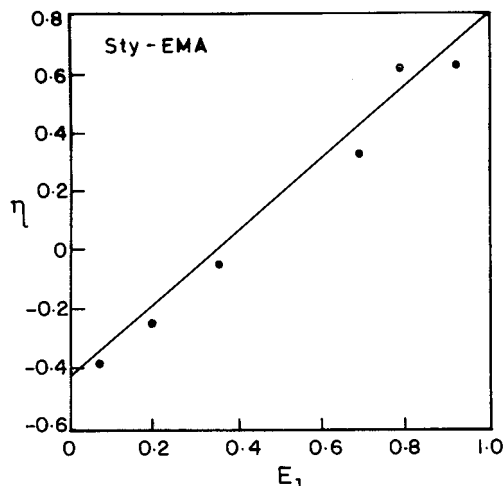


Figure 14. Kelen–Tudos plot of Sty-EMA.

compared to BMA explains more incorporation of styrene in the copolymer. The comparison of  $r_1$  and  $r_2$  values of styrene and alkyl methacrylates in the presence of HQ unambiguously reveals that styrene is more reactive than alkyl methacrylates. Table 11 shows  $r_1$ ,  $r_2$ , and their product along with propagation constants of styrene and alkyl methacrylates.

CONCLUSION

Copolymers involving styrene and homologues of alkyl methacrylates (viz., methyl, ethyl, and butyl methacrylates) were synthesized at 60°C by employing a mixture of *n*-butylamine and carbon tetrachloride as CT initiators in dimethyl sulphoxide medium. The CT complex was characterized by UV spectroscopy while the respective copolymers were characterized by employing IR and <sup>1</sup>H NMR spectroscopy. The copolymer compositions

Table 7. Extended Kelen–Tudos parameters for Sty-EMA copolymers.

S. no.	$\delta_2$	$\delta_1$	$Z$	$x$	$F$	$G$	$\eta$	$\xi$
1	0.0799	0.1044	2.2919	0.1385	0.0604	-0.2978	-0.3812	0.0774
2	0.2011	0.0689	1.8188	0.3281	0.1804	-0.2218	-0.2461	0.2002
3	0.3491	0.0515	1.5259	0.5946	0.3897	-0.0607	-0.0547	0.3009
4	0.6752	0.0433	1.0859	1.6638	1.5322	0.7428	0.3297	0.6801
5	0.7841	0.0356	1.1187	2.9943	2.6765	2.1004	0.6183	0.7879
6	0.9201	0.0422	0.8185	7.0332	8.5928	5.8815	0.6240	0.9226

Note:  $\alpha = 0.7207$ .



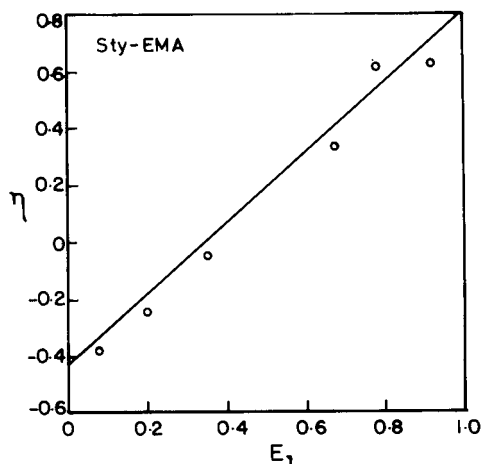


Figure 15. Extended Kelen-Tudos plot of Sty-EMA.

Table 8. Fineman-Ross and K-T parameters for styrene and butylmethacrylate copolymers.

S. no.	$x = M_1/M_2$	$y = m_1/m_2$	$G = x(y - 1)/y$	$F = x^2/y$	$\xi = F/(\alpha + F)$	$\eta = G/(\alpha + F)$
1	0.1659	0.2070	-0.6262	0.1291	0.1544	-0.7492
2	0.3317	0.3682	-0.5655	0.2950	0.2945	-0.5646
3	0.6664	0.6734	-0.3231	0.6586	0.4824	-0.2366
4	1.5019	1.2630	0.3160	1.8244	0.7208	0.1249
5	3.0080	2.0590	1.5831	4.6186	0.8456	0.2978
6	4.0150	4.1493	2.4413	3.8696	0.8673	0.5646

Note:  $\alpha = (F_{\min} \times F_{\max})^{1/2} = 0.7067$ .

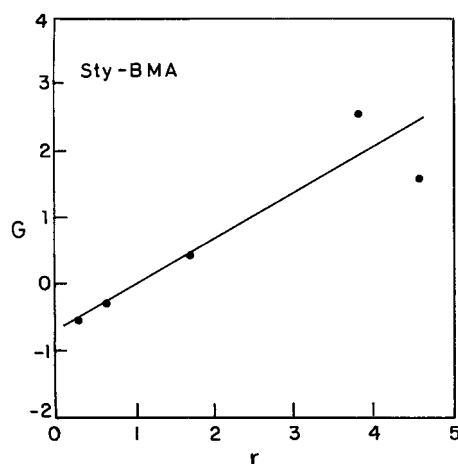


Figure 16. Fineman-Ross plot of Sty-BMA.



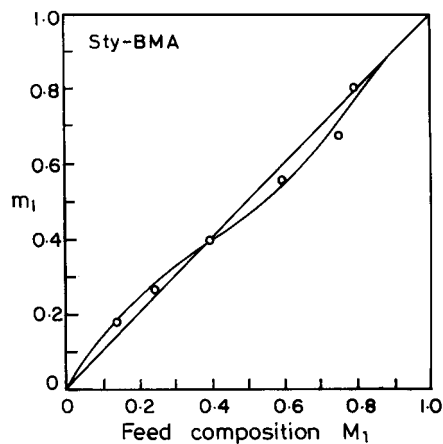


Figure 17. Plot of feed vs. copolymer composition of Sty-BMA.

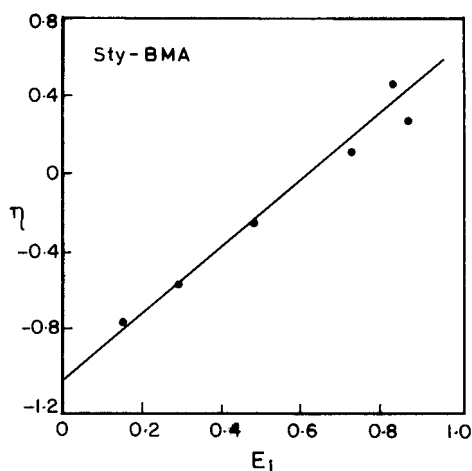


Figure 18. Kelen-Tudos plot of Sty-BMA.

Table 9. Extended Kelen-Tudos parameters for Sty-BMA copolymers.

S. no.	$\delta_2$	$\delta_1$	$Z$	$x$	$F$	$G$	$\eta$	$\xi$
1	0.1561	0.2021	1.2776	0.1620	0.1268	-0.6207	-0.7500	0.1532
2	0.2937	0.0940	1.1154	0.3301	0.2959	-0.5664	-0.5683	0.2969
3	0.4785	0.0691	1.0108	0.6661	0.6590	-0.3231	-0.2376	0.4846
4	0.7130	0.1149	0.8308	1.5202	1.8300	0.3165	0.1201	0.7231
5	0.8439	0.0886	0.6693	3.0764	4.5965	1.5823	0.2987	0.8477
6	0.8594	0.0887	1.0352	4.0083	3.8720	3.0423	0.6653	0.8688

Note:  $\alpha = 0.7007$ .



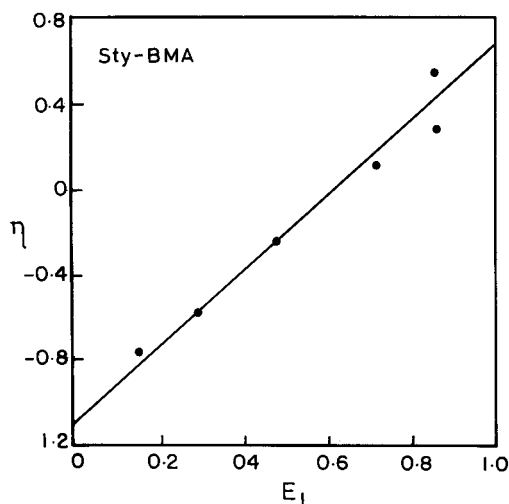


Figure 19. Extended Kelen-Tudos plot of Sty-BMA.

Table 10. Reactivity ratios of styrene and alkyl methacrylates by different methods.

	Methods		
	Fineman-Ross	Kelen-Tudos	Extended Kelen-Tudos
Reactivity ratios of copolymers			
Sty-MMA			
$r_1$	4.02	$3.99 \pm 0.46$	$3.90 \pm 0.32$
$r_2$	0.54	$0.45 \pm 0.08$	$0.47 \pm 0.05$
Sty-EMA			
$r_1$	0.71	$0.80 \pm 0.09$	$0.81 \pm 0.08$
$r_2$	0.25	$0.29 \pm 0.05$	$0.30 \pm 0.07$
Sty-BMA			
$r_1$	0.68	$0.69 \pm 0.08$	$0.68 \pm 0.06$
$r_2$	0.84	$0.74 \pm 0.07$	$0.73 \pm 0.05$

Table 11. Reactivity ratios and propagation constants for styrene and alkyl methacrylates prepared in the absence of HQ.

System	$r_1$	$r_2$	$1/r_1 = k_{12}/k_{11}$	$1/r_2 = k_{21}/k_{22}$	$r_1 r_2$
Sty-MMA	0.66	0.43	1.51	2.32	0.28
Sty-EMA	1.20	0.40	0.83	2.50	0.48
Sty-BMA	1.09	0.48	0.91	2.08	0.52





were determined by using  $^1\text{H}$  NMR spectroscopy and the reactivity ratios were computed by F-R and K-T methods. The reactivity ratios of Sty-MMA and Sty-EMA copolymers indicate that higher level of styrene is incorporated in the copolymer. On the other hand the Sty-BMA system exhibits a different behavior. The higher value of  $r_2$  is obtained denoting that BMA is more active than styrene and hence, more BMA is present in the copolymer chain. In Sty-MMA and Sty-BMA systems, the product of  $r_1$  and  $r_2$  is greater than 1, representing the formation of high degree of random copolymers while in the case of Sty-EMA, the product of  $r_1$  and  $r_2$  is less than 1 indicating the formation of alternating copolymer.

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