SHORT COMMUNICATIONS

Reactivity ratios of ethyl acrylate, n-butylmethacrylate copolymers by ^{13}C NMR.

It has earlier been reported[1] that the proton NMR was extremely useful in estimation of copolymer composition of ethylacrylate, n-butylmethacrylate copolymers thereby facilitating the determination of reactivity ratios. Besides this, the application of carbon-13 NMR in the quantitative analysis of the above copolymer system was also described in our earlier article.[2] In this present communication, determination of reactivity ratios of these copolymers using Finemann-Ross and Kelen-Tudos methods are described.

Both the monomers, ethylacrylate and n-butylmethacrylate, were purified by washing with caustic soda and then distilling under vacuum. For different monomer feed ratios, copolymerizations were carried out in ethylmethylketone using benzoylperoxide as initiator at 60°C. The conversion to polymers were restricted to less than 10 per cent to avoid hetrogeneity in composition. The compositions were estimated by running ^{13}C NMR spectrum for all the copolymers as described in our earlier paper.[2]

Reactivity ratios can be evaluated using Finemann-Ross method[3] and also by a graphically evaluable linear equation proposed by Kelen-Tudos.[4] The first method is effective in general for most of the systems. However, it gives over estimation of reactivity ratios for the system in which one of the components of the copolymer is relatively small. The latter method is effective for all the type of systems in general.

Finemann and Ross linearesed the Lewis-Mayo equation[4] as follows :

$$G = r_1 F - r_2 \qquad \ldots(1)$$

$$\text{and } G/F = -\frac{F}{r_2} + r_1 \qquad \ldots(2)$$

$$\text{where } G = \frac{x(y-1)}{y} \text{ and } F = \frac{x^2}{y}$$

x and y represent the ratios of mole fractions of the monomer units in the monomer feed and in the copolymer respectively. From the data obtained by ^{13}C NMR analysis of copolymers, G and F values are calculated and recorded in Table I. A plot is drawn between G and F for eq. 1 (Fig. 1). From the intercept of the plot, r_2 value is obtained and from the slope, r_1 value is calculated. The values thus obtained are $r_1 = 0.45$ and $r_2 = 2.02$.

TABLE I

Finemann-ross method (for ^{13}C NMR data)

Sl. No.	x	y	F (x^2/y)	G $(x(y-1)/y)$
1.	0.3552	0.1655	0.7625	-1.7909
2.	0.9455	0.4609	1.9397	-1.1059
3.	1.4207	0.7007	2.8805	-0.6068
4.	2.1299	0.9048	5.0138	-0.4595

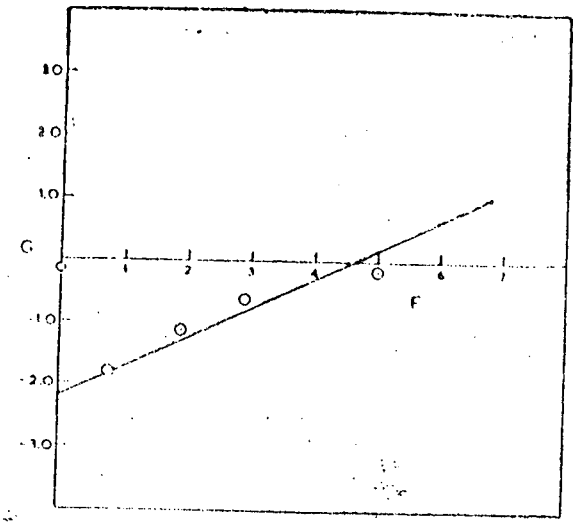

FIG 1 Emmann Ross Plot (for ^{13}C NMR data)

The graphically evaluable linear equation proposed by Kelen-Tudos, is given by

$$\frac{G}{\alpha+1} = (r_1+r_2/\alpha)\frac{F}{\alpha+F} - \frac{r_1}{\alpha} \quad (3)$$

Where G and F is same as described above, α is an arbitrary constant ($\alpha > 0$) which is given by

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

Where F_m and F_M stand for the lowest and highest value calculated from the series of measurements in the copolymerization. By introducing

$$\eta = \frac{G}{\alpha+1} \quad \text{and} \quad \xi = \frac{F}{\alpha+F}$$

The equation (1) can be written as

$$\eta = (r_1+r_2/\alpha)\xi - r_2/\alpha \quad \ldots \quad (4)$$

The variation of ξ can take any positive value only in the interval (0,1). A plot of η Vs ξ from the experimental data gives a straight line, the extrapolation of which $\xi = 0$ and $\xi = 1$ gives r_2/α and r_1 (both as intercepts). Thus the method provides the determination of r_1 and r_2 and the above equation is invariant to the inversion of data.

TABLE 2

Kelen-Tudos method (for ^{13}C NMR data)

Sl. No.	x	y	$\eta = x(y-1)/(\alpha+x^2)$	$\xi = x^2/(\alpha+x^2)$
1	0.3552	0.1455	-0.6591	0.2806
2	0.9455	0.4609	-0.2840	0.4981
3	1.4207	0.7047	-0.1255	0.5957
4	2.1299	0.9048	-0.0066	0.7195

$\alpha = 1.9548$

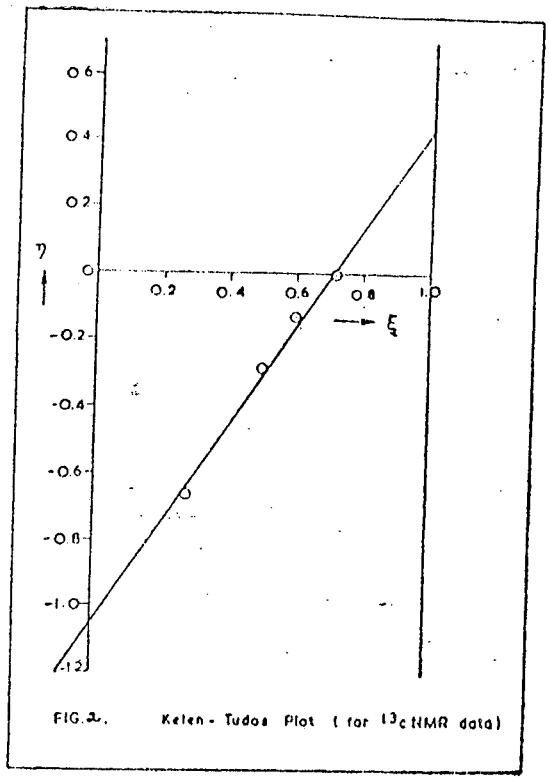

FIG. 2. Kelen - Tudos Plot (for ^{13}C NMR data)

The treatment of ^{13}NMR data by Kelen-Tudos (K-T) method is represented in Table 2. Fig. 2 represents K-T plot between η and ξ and r_1 and r_2/α were obtained from

the intercept at $\xi = 1$ and $\xi = 0$. The r_1 and r_2 values obtained are $r_1 = 0.43$ and $r_2 = 2.03$.

TABLE 3

Reactivity ratios of EA and nBMA

Monomer	*Finemann Ross method*	*Kelen-Tudos method*
EA (r_1)	0.43	0.43
nBMA(r_2)	2.02	2.03

The r_1 and r_2 values obtained by both the methods are recorded in Table 3. It can be seen that the values of r_1 and r_2 are almost the same in the two methods. The product of r_1 and r_2 thus evaluated remains less than 1 indicating that the system follows random distribution of the monomeric units. But the r_2 value, which is more than 1, indicates that the sequence of n-BMA units appear as long blocks. The determination of r_1 and r_2 of the system thus clearly indicates that copolymerization is absolutely favoured ruling out the homopolymer formation. This is in accordance with our earlier studies[6] of determination of cross termination rate constant of the copolymer system which is greater than 1, at all the feed compositions studied. This confirms that the copolymerisation is most favoured thus ruling out the homopolymerization.

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