Reactivity ratios of the 3-methoxy-4-(2-hydroxy-3-methacryloloxypropoxy)benzaldehyde and methyl methacrylate system from ^{1}H n.m.r.

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3-Methoxy-4-(2-hydroxy-3-methacryloloxypropoxy)benzaldehyde (MHMPB) was prepared by reacting vanilline with glycidyl methacrylate in the presence of tetrabutylammonium bromide. Copolymers of MHMPB and methyl methacrylate (MMA) were prepared in dimethylformamide using azobisisobutyronitrile as the initiator. The compositions of the copolymers were determined by ^{1}H n.m.r. analysis and reactivity ratios were calculated using the Kelen–Tüdös linear differential equation.

(Keywords: copolymer; n.m.r. analysis; reactivity ratio)

INTRODUCTION

The combination of durability and versatility and the ability to tailor molecules relatively easily have made acrylic and methacrylic esters prime candidates for diverse applications. The uses of acrylics in textile finishing[1–4] and acrylic ester emulsions in leather finishing[5] are well documented. Estimation of the copolymer composition and determination of the reactivity ratios of its constituents assume importance in evaluating end applications of copolymers. N.m.r. spectroscopy is well established as a convenient method for determining the compositions of constituent monomer units in a copolymer[6,7]. The monomer 3-methoxy-4-(2-hydroxy-3-methacryloxypropoxy)benzaldehyde (MHMPB) was prepared in order to make copolymers of different compositions with methyl methacrylate (MMA). This communication reports the determination of the reactivity ratios for the MHMPB–MMA system by n.m.r. spectroscopy.

EXPERIMENTAL

Materials

Vanillin (Fluka), glycidyl methacrylate (Merck), tetrabutylammonium bromide (Fluka) and dimethylformamide (Glaxo) were used as received. Azobisisobutyronitrile (AIBN) was recrystallized from methanol. Methyl methacrylate (Fluka) was distilled under reduced pressure.

3-Methoxy-4-(2-hydroxy-3-methacryloloxypropoxy)benzaldehyde was prepared by the method reported in the literature (m.p. 96°C; reported m.p. 95–98°C)[8].

Copolymerization

Appropriate quantities of MHMPB and MMA with dimethylformamide and AIBN (2% based on the total weight of monomers) were placed in a standard reaction tube (100 ml capacity) and the mixture was flushed with oxygen-free nitrogen for at least 10 min. The tube was tightly sealed and immersed in a thermostatted bath at 70°C. Copolymerization was allowed to proceed to about 10% conversion. The copolymer was precipitated in an excess of methanol–water, filtered off, and purified by dissolving in acetone and reprecipitating in methanol–water. It was finally dried in a vacuum oven at 50°C for 24 h. All copolymers with different compositions of MHMPB and MMA were prepared in the same way (*Table 1*).

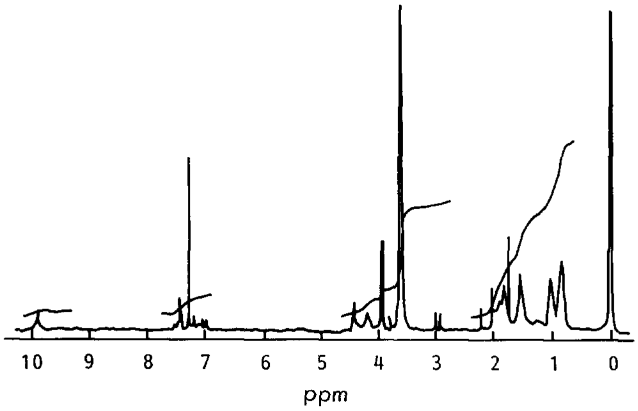

Figure 1 ^{1}H n.m.r. spectrum of MHMPB–MMA prepared from a 0.1:0.9 feed ratio

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Table 1

Feed composition (molar fractions)		Intensity of aromatic protons	Intensity of aliphatic protons	Copolymer composition (molar fractions)	
MHMPB (M_1)	MMA (M_2)	(I_A)	(I_a)	MHMPB (m_1)	MMA (m_2)
0.1	0.9	0.8	13.2	0.188	0.812
0.2	0.8	1.2	14.2	0.271	0.729
0.3	0.7	2.8	23.4	0.442	0.558
0.4	0.6	2.1	14.4	0.589	0.411
0.5	0.5	2.5	15.4	0.690	0.310
0.6	0.4	2.5	14.8	0.743	0.257

Table 2

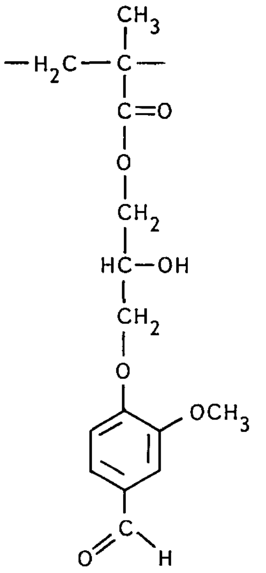
	Feed composition		Copolymer composition							
Sample number	MHMPB (M_1)	MMA (M_2)	MHMPB (m_1)	MMA (m_2)	F	f	G	H^a	η	ε
1	0.1	0.9	0.188	0.812	0.111	0.231	−0.370	0.053	−1.438	0.206
2	0.2	0.8	0.271	0.729	0.250	0.371	−0.424	0.169	−1.137	0.453
3	0.3	0.7	0.442	0.558	0.428	0.792	−0.112	0.231	−0.257	0.531
4	0.4	0.6	0.589	0.411	0.666	1.433	0.201	0.310	0.391	0.603
5	0.5	0.5	0.690	0.310	1.000	2.250	0.556	0.444	0.858	0.730
6	0.6	0.4	0.743	0.257	1.500	2.890	0.981	0.779	0.998	0.792

[a] $\alpha = \sqrt{H_{max} H_{min}} = 0.204$

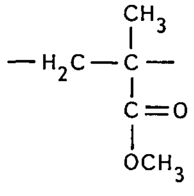
^1H n.m.r. spectra for all the copolymer samples were recorded in $CDCl_3$ with tetramethylsilane as the internal standard.

RESULTS AND DISCUSSION

The constituent monomeric units of the copolymer can be represented as



MHMPB



MMA

The CH_2 and CH_3 protons present in MHMPB and MMA are almost indistinguishable. Hence, in the present study the peaks for the aromatic protons (7–7.26 ppm), which are distinct, were chosen for the estimation of the MHMPB composition in the copolymer (see *Figure 1*). Since the peak intensity corresponds to the total number of protons in a particular group, the molar fraction of the copolymer can be calculated from

$$\frac{\text{intensity of aromatic protons } (I_A)}{\text{intensity of aliphatic protons } (I_a)} = \frac{3m_1}{15m_1 + 8m_2} \quad (1)$$

where m_1 is the molar fraction of MHMPB and m_2 is that of MMA. Equation (1) is based on the fact that MHMPB contains 18 protons, of which three are aromatic, and MMA contains eight protons. Since $m_2 = (1 - m_1)$, we get

$$m_1 = 8I_A/(3I_a - 7I_A) \quad (2)$$

The mole fractions of MHMPB were calculated from equation (2) using the intensities of the peaks for the aromatic and total aliphatic protons in the spectra of the copolymer samples. *Table 1* lists the fractions of the MHMPB and MMA monomeric units in the corresponding copolymers.

The reactivity ratios were determined using the Kelen–Tüdös method[9,10]. A linear equation proposed in the method that can be evaluated graphically is

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

where

$$\eta = G/(\alpha + H) \qquad \varepsilon = H/(\alpha + H)$$

and

$$G = F(f-1)/f \qquad H = F^2/f$$

and

$$F = M_1/M_2 \qquad f = m_1/m_2$$

$r_1 = 2.0$ (intercept where $\varepsilon = 1$)

$-\frac{r_2}{\alpha}$ = intercept on $-y$ axis where $\varepsilon = 0$

$$-\frac{r_2}{0.204} = -2.44$$

$$r_2 = 0.204 \times 2.44 = 0.498$$

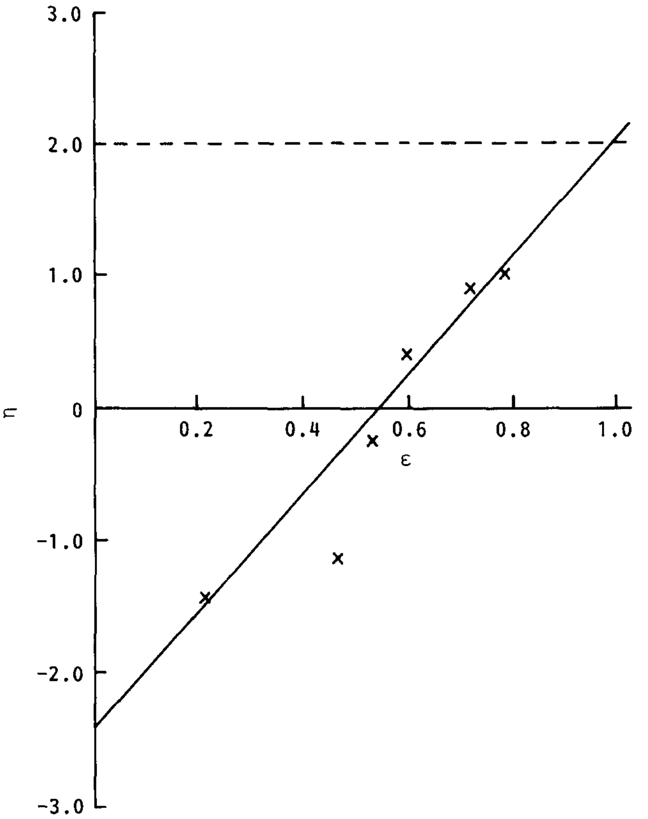


Figure 2 Kelen–Tüdös plot

M_1 and M_2 are the initial feed compositions and m_1 and m_2 are the copolymer compositions of MHMPB and MMA, respectively. The parameter α is an arbitrary constant ($\alpha > 0$) calculated from

$$\alpha = \sqrt{H_{\max} H_{\min}}$$

where $H_{\max}$ and $H_{\min}$ are the highest and lowest values of H. From the data in *Table 2*, a Kelen–Tüdös plot was drawn between η and ε (*Figure 2*). The values r_1 and r_2/α are obtained from the intercepts at $\varepsilon = 1$ and $\varepsilon = 0$, respectively. The reactivity ratios $r_1 = 2.0$ and $r_2 = 0.498$ were obtained with a correlation coefficient $r = 0.9522$ from the best linear fitting.

Since the present system is being reported for the first time, its reactivity ratio values could not be compared with literature values.

CONCLUSION

The product $r_1 r_2 \approx 1$ indicates the tendency of the system towards random copolymerization (with slight alternating behaviour). The higher fraction of MHMPB in the copolymer indicates that the probability of MHMPB entry into the chain is greater than that of MMA entry. Thus the copolymer formed is richer in MHMPB.

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