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Monomer Reactivity Ratios of Some Methyl Aryloxymethacrylates

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Summary

The monomer reactivity ratios of methyl phenoxymethacrylate (MPMA), methyl p-cresoxymethacrylate (MCMA) and methyl p-nitrophenoxymethacrylate (MNMA) were evaluated both by Fineman-Ross and Kelen-Tüdös methods. The tendency to form alternating copolymers of these monomers is discussed.

Introduction

The syntheses of these monomers have been recently reported[1]. Subsequently LENZ et al.[2] published their study on the stereospecific polymerization of methyl phenoxymethacrylate and ethyl phenoxymethacrylate. In order to assess the advantages and also to examine whether in these monomers (MPMA, MCMA and MNMA) the radical copolymerization occurs through the conventional copolymerization mechanism, KELEN-TÜDÖS method[3] (KT method) has been employed besides the FINEMAN-ROSS method[4] (FR method).

Experimental

A series of comonomer feed ratios with 0.15 to 0.90 mole fractions for each of these freshly prepared methyl aryloxymethacrylates and the required quantity of the suitable monomer (AN or MMA) for each system was prepared and to each of this mixture 40 ml of pure and dry DMF was added. Azobisisobutyronitrile (AIBN) was added to each mixture in the ratio 1:50. The contents in a reaction vessel were deaerated by passing with pure dry nitrogen. The vessel was sealed off from atmosphere and it was thermostated at 80°C. The reac-

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tion was restricted to 2h so that the conversion was less than 5% and that the compositions of the comonomers in the various mixtures remain almost the same as the initial values. The copolymers precipitated out from water were separated, reprecipitated, dried and weighed. ^{1}H-NMR spectra (90 MHz, Perkin Elmer R-32) and elemental analysis of the copolymers of various compositions were obtained for the computation of copolymer composition in various mixtures. Signals corresponding to the phenyl protons and →CH or >CH_2 respectively in the NMR spectra of MPMA/MCMA and AN copolymers and signals of phenyl and methyl protons in MNMA-MMA were considered for evaluating the compositions in mole fractions of these copolymers. The compositions calculated by both the methods agree well within experimental error (Table 1).

TABLE 1

Copolymerization of MPMA and MCMA with AN and MNMA with MMA

Monomer	Copolymer sample	Initial monomer ratio in mole	Polymer composition in mole		Conversion (%)
			Elemental analysis	NMR	
MPMA	1	0.15	0.167	0.16	2.5
	2	0.30	0.298	0.28	2.0
	3	0.45	0.371	0.40	1.5
MCMA	1	0.15	0.057	0.08	1
	2	0.30	0.096	0.13	<1
	3	0.45	0.331	0.31	<1
	4	0.60	0.315	0.32	<1
MNMA	1	0.30	0.065	0.11	3.5
	2	0.45	0.088	0.11	4.0
	3	0.60	0.095	0.12	4.0
	4	0.75	0.108	0.17	4.5

However, for the evaluation of r_1 and r_2, mole fraction ratios obtained from elemental analyses only were used.

In the FR method the comonomer feed mole ratios (G) were plotted against the corresponding copolymer mole fraction ratios (F) so that, for the straight line drawn through these points by the method of least squares, the slope and the intercept are equal to r_1 and $-r_2$ respectively in the linearized equation:

$$G = r_1 F - r_2$$

The term α in the Kelen-Tüdös equation:

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

affords maximum distribution of the data which enables the experimental values to be located symmetrically along the interval (0,1) with respect to ε. The values of the monomer reactivity ratios are obtained from the values of the intercepts for the values of $\varepsilon = 0$ and $\varepsilon = 1$ of the extrapolated line drawn by the method of least squares. r_1 and r_2 values do not change in this method when the values are reindexed.

Results and Discussion

MPMA-Co-AN system forms copolymers of mole fraction ratios from 0.15 to 0.45 with respect to MPMA, MCMA-Co-AN system from 0.15 to 0.60 with respect to MCMA and MNMA-Co-MMA from 0.30 to 0.75 with respect to MNMA. This may be attributed to the low ceiling temperatures of these monomers[5], and may indicate that either complexity is involved in copolymerization or the little copolymer formed is soluble in the monomer so that its separation could not be effected.

It can be seen from the values of the reactivity ratios (Table 2) that MPMA has copolymerized well with AN and the values of r_1 and r_2 evaluated both by the FR and KT methods are in good agreement. A good linearity in the KT plot (Fig. 1) also indicates that MPMA-Co-AN system adequately explains the mechanism of copolymerization based on two parameter model and the system conforms to Symbol I of copolymers classified by Kennedy et al.[6]. Scattering of points both in the KT and FR methods (Fig. 2) for the MCMA-Co-AN system would show that this system belongs to the Symbol II of Kennedy's classification and that the mechanism of copolymerization has changed. Whereas a positive reactivity ratio, which is more reliable, for MCMA is obtained in the KT method, the FR method gives an absolutely meaningless and physically insignificant negative reactivity ratio for MCMA. Again a negative reactivity ratio for MNMA is obtained for the MNMA-Co-MMA system by the FR method and the KT method gives a curve, from which the calculation of the reactivity ratios of the monomers is not possible without the knowledge of the improved forms of the Kelen and Tüdös equation[6]. Thus it is clear that this system also belongs to Symbol II of Kennedy's

TABLE 2

Reactivity ratios of MPMA, MCMA and MNMA

Present systems			Reported systems[8]	
Monomer	Values of reactivity ratio		Monomer	Values of reactivity ratio
	FR method	KT method		
AN (r_1)	0.77	0.76	AN (r_1)	0.70
MPMA (r_2)	0.36	0.31	D-Glucitol triallylene (r_2)	0.26
AN (r_1)	2.83	2.57	AN (r_1)	2.70
MCMA (r_2)	-1.52	0.22	2-Me Butene (r_2)	0.27
MMA (r_1)	5.02	-	MMA (r_1)	5.00
MNMA (r_2)	-0.31	-	Methacrylonitrile (r_2)	0.05

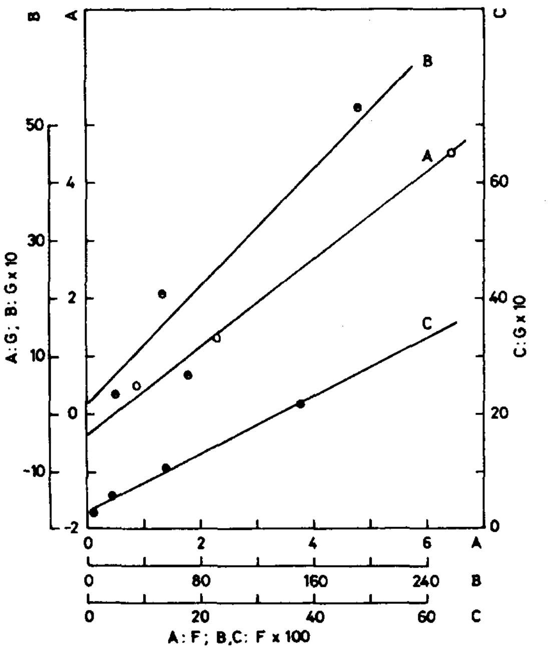

Fig. 1. Plots A-C: Fineman-Ross plots. A: MPMA-AN; B: MCMA-AN; C: MNMA-MMA systems

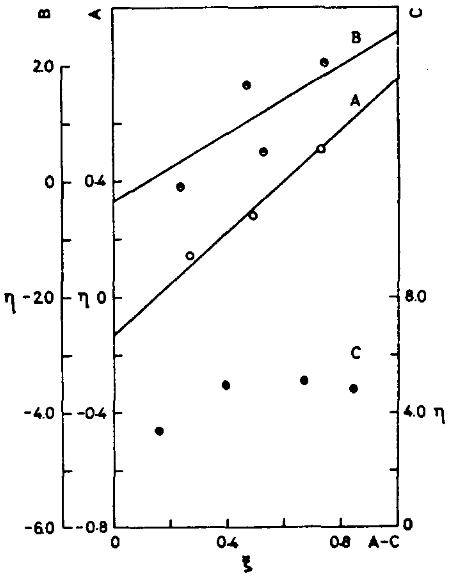

Fig. 2. Plots A-C: Kelen-Tüdős plots A: MPMA-AN; B: MCMA-AN; C: MNMA-MMA systems

classification and the mechanism of copolymerization cannot be explained with the conventional two parameter model. Therefore the reactivity ratios for the MNMA-Co-MMA system calculated by the FR method only are reported.

The tendency for alternation in copolymers is given by the products of the reactivity ratios $r_1 \cdot r_2$ and the alternating tendency increases as $r_1 \cdot r_2 \rightarrow 0$. In MPMA-Co-AN and MCMA-Co-AN this value is less than one and in the former the value is very small indicating that the tendency for more regular alternation in copolymerization.

The reactivities i.e. the reciprocal of reactivity ratios, of MPMA and MCMA (with AN) are comparable to those of MMA (4.0), methyl vinyl ketone (5.5) and 2,5-dichlorostyrene (5.0) also with AN radical[7]. The radicals formed these methyl aryloxymethacrylate monomers may be expected to be reactive as they are incapable of any conjugation with the carbon double bond.

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