Reactivity Ratios for the Coplymerization of Methyl Methacrylate and Phenyl Methacrylate by Nuclear Magnetic Reasonance Spectroscopy

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Summary: Polymers and copolymers of methyl methacrylate-phenyl methacrylate have been prepared. Reactivity ratios for these copolymer systems have been determined using nuclear magnetic resonance spectroscopy. Results obtained by two different methods are in good agreement with each other.

Introduction

Few values of reactivity ratios for pairs of methacrylates have been reported. This is principally due to the fact that the problem of obtaining reactivity ratios for the copolymerization of pairs of monomers having similar structures usually resolves itself into the problem of accurate analysis. Elemental analysis cannot be made accurate for the purpose[1] and gas liquid chromatographic analysis of pyrolysis products may be of doubtful quantitative validity[1]. Radiometric[2] and isotopic methods[3] are the only ones to be used successfully, but being time consuming and requiring elaborate experimental techniques have only been applied to a few isolated systems.

Nuclear magnetic resonance spectroscopy has been applied to a number of acrylate-methacrylate monomer pairs[4], copolymers[5] of vinyl chloride-vinyl acetate, and to determine the monomer content of vinyl acetate-ethylene copolymers[6].

The present work shows another successful application of n.m.r. spectroscopy, to determine the reactivity ratio for the methyl methacrylate and phenyl methacrylate monomer pairs.

Experimental:

Preparation and Purification of Monomers

Phenyl methacrylate was prepared by refluxing phenol with methacrylyl chloride in the presence of hydroquinone. The monomer was purified by distillation under reduced pressure and characterised by i.r. and n.m.r. spectroscopy.

Methyl methacrylate was freed from inhibitor by washing with alkali, then with water, dried over calcium chloride and finally distilled under vacuum.

Poly (phenyl methacrylate)

PPMA was prepared by bulk polymerisation of the monomer under vacuum at 60°C with 0.05% w/v azodiisobutyronitrile (AIBN) as initiator. The reaction was carried to 5% conversion (2h). The

polymer was precipitated in methanol, purified by reprecipitation by diethyl ether from acetone solution and dried unr vacuum.

Poly (methyl methacrylate)

PPMA was prepared by bulk polymerisation of theer under vacuum to 5% conversion at 60oC with AIBN as initiator. The polymer was isolated and purified as for PPMA.

PMA - MMA Copolymers

The copolymers were prepared by bulk copolymerisation of appropriate mixtures of the monomers at 60°C, with 0.05% w/v AIBN as initiator to less than 5% conversion. They were then precipitated in methanol, reprecipitated by diethyl ether from acetone solution and dried under vacuum at 60°C for 24h. The composition of each copolymer was determined from n.m.r. data.

Copolymer Analysis

NMR spectra were recorded by using a Perkin-Elmer R10 60 MC/S spectrometer. 25 mg of copolymer sample was dissolved in 1 ml of $CDCl_3$ and five integrals were obtained and average result was employed for the calculation of copolymer composition.

Results and Discussion

The methyl methacrylate-phenyl methacrylate system proves especially amenable. The n.m.r. spectrum of a typical methacrylate-phenyl methacrylate copolymer is illustrated in Fig. 1. By comparison with the spectra of poly (methyl methacrylate) and poly(phenyl methacrylate) it can be shown that the peaks are due to respective absorption by the -O-CH_3 protons in MMA (A) and the -O- Ph protons in PMA (B).

The composition of the copolymers were calculated from the relative areas under the two types of proton peaks as measured by the integrator. Results obtained are presented in Table 1. Reactivity ratios were obtained by the two standard methods:-

TABLE-I

Copolymer Composition Data[a]

	Monomer mixture $(M_1)/[M_2]$	Copolymer $d[M_2]/d[M_1]$
1	0.18	4.74
2	0.54	1.7
3	1.62	0.5654
4	4.87	0.20
5	14.58	0.0625

[a] M_1 = MMA. M_2 = PMA

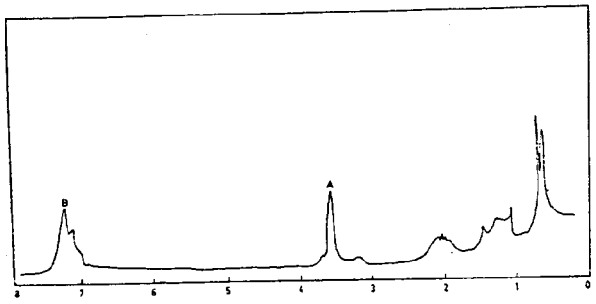

Fig. 1: N.M.R. spectrum of copolymer phenylmethacrylate/methylmethacrylate (copolymer 3 in Table 1).

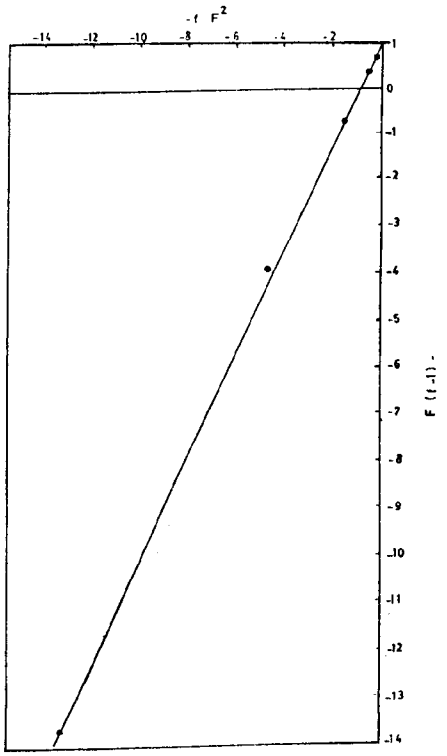

Fig. 2: Fineman-Ross plots for copolymerization of MMA and PMA.

i. Mayo and Lewis method[7], using the equation.

$$r_2 = \frac{[M_1]}{[M_2]} \quad \frac{d[M_2]}{d[M_1]} \quad \left(1 + \frac{[M_1]}{[M_2]}\, r_1\right) - 1$$

the r_1 vs r_2 plot being shown in Fig. 2.

ii. The second method known as Fineman and Ross method and the equation used is

$$F(f-1) = -F^2 f r_1 + r_2$$

where $F = [M_1]/[M_2]$

$$f = d[M_2]/d[M_1]$$

The plot of $F(f-1)$ vs $-F^2f$, shown in Fig. 3 is a straight line, the slope of which is r_1 and the intercept r_2.

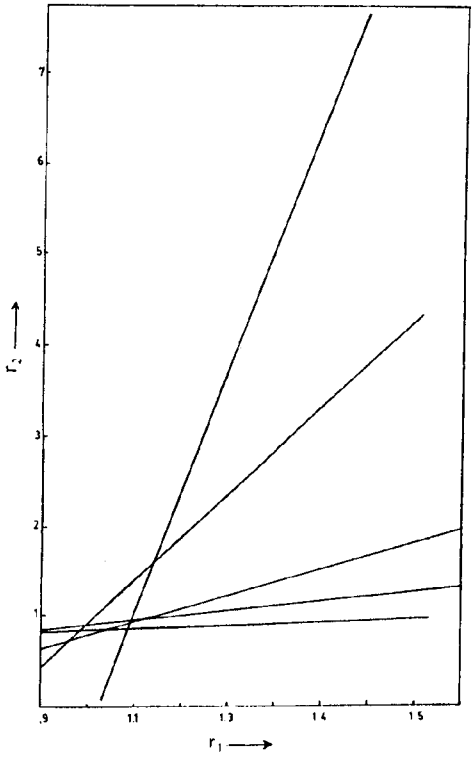

Fig. 3: r_1 vs r_2 diagram for MMA/PMA copolymers.

The results derived from both methods (Figs. 2 and 3), are quoted in Table 2 and are in good agreement with each other. However, these results cannot be compared with those which may be obtained by other analytical methods since reactivity ratio of methyl methacrylate and phenyl methacrylate monomer pairs have not been reported in the literature.

The nuclear magnetic resonance spectroscopy offers a general method of rapid analysis of copolymers from monomer pairs whose similarity in structures make other analytical methods impossible.

TABLE-2

Reactivity Ratios for the copolymerization of Methyl methacrylate (M_1) and phenylmethacrylate (M_2)

r_1	r_2	Temp. °C	
1.065 ± .04	1.0125 ± .18	60	Mayo & Lewis
1.1	0.95	60	Fine & Ross

References

1. G.E. Ham, Copolymerization, High Polymers, Vol.XVIII. Wiley-Interscience, New York, 1964.
2. J.C. Bavington and B.W. Malpass, *European Polymer Journal*, **1**, 19 (1965).
3. M. Shima, S.W. Kotera and J.F. Johnson, *Analyt Chem.*, **35**, 1948 (1963).
4. N. Grassie, B.J.D. Torrance, J.D. Fortune and J.D. Gemmell, *Polymer*, **6**, 653 (1965).
5. N. Grassie, I.C. McNeill and I.F. McLaren, *Polymer Letters*, **3**, 897 (1965).
6. H.Y. Chen, and M.E. Lewis, *Analyt. Chem.*, **36**, 1394 (1964).
7. F.R. Mayo and F.M. Lewis, *J. Amer. Chem. Soc.*, **66**, 1594 (1944).
8. M. Fineman and S.D. Ross, *J. Polym. Sci.*, *5*, 259 (1950).