Reactivity Ratios for the Copolymerization of Acrylates and Methacrylates by Nuclear Magnetic Resonance Spectroscopy

N. Grassie, B. J. D. Torrance, J. D. Fortune and J. D. Gemmell

Nuclear magnetic resonance spectroscopy has been applied to the analysis of copolymers of methyl methacrylate with ethyl acrylate, propyl acrylate, butyl acrylate, ethyl methacrylate and methyl acrylate and the reactivity ratios calculated. In the first four of these systems accurate analyses were possible by comparing the —O—CH$_2$— *and* —O—CH$_3$ *absorption bands which are sufficiently resolved. A lower order of accuracy was achieved for the methyl methacrylate–methyl acrylate system as neither incorporates* —O—CH$_2$— *structures, and recourse had to be made in this case to measurement of the total absorption for analytical purposes. Even this method cannot be used, however, when both monomer molecules contain the same number of protons, as for example ethyl methacrylate and propyl acrylate.*

FEW values of reactivity ratios for pairs of acrylate and methacrylate monomers have been reported. This is principally due to the fact that the similarities of the structures of the components make analysis of the copolymers difficult. Elemental analysis cannot be made accurate enough for the purpose[1] and the application of i.r. or u.v. spectroscopic methods would require the two monomers to have absorbing structures which are significantly different.

The gas–liquid chromatographic analysis of pyrolysis products has been applied but may be of doubtful quantitative validity[1]. Radiometric[2] and isotopic[3] methods are the only ones to have been used successfully but, being time consuming and requiring elaborate experimental technique, have only been applied to a few isolated systems.

This paper shows how nuclear magnetic resonance spectroscopy can be successfully used for such monomer pairs, although this method also has its limitations. It has previously been used to determine the monomer content of vinyl acetate–ethylene copolymers[4,5] but reactivity ratios were not calculated. The method is clearly widely applicable to copolymer analysis and is particularly valuable for its rapidity and simplicity.

EXPERIMENTAL

Monomer purification

Methyl methacrylate (MMA) (I.C.I. Ltd), methyl acrylate (MA) (B.D.H. Ltd), butyl acrylate (BuA) (Koch Laboratories), ethyl acrylate (EA) (Light and Co.), ethyl methacrylate (EMA) (I.C.I. Ltd) and propyl acrylate (PrA)

(prepared by alcoholysis of methyl acrylate[6]) were washed with caustic soda solution to remove inhibitor, subsequently with distilled water, and dried over calcium chloride. The monomers were vacuum distilled and stored at $-18°C$.

Polymerization

Copolymers of MMA with MA, EA, PrA, BuA and EMA were studied.

After degassing and distillation in vacuum, monomer mixtures of known composition were polymerized in bulk under vacuum to about five per cent conversion. The pair MMA–MA was polymerized at 65°C with 0·075 per cent w/v azoisobutyronitrile as catalyst. All other pairs were polymerized at 60°C with 0·18 per cent w/v catalyst.

The copolymers were precipitated three times from chloroform solution by methanol and dried in a vacuum oven for 24 hours at 50°C.

Copolymer analysis

N.m.r. spectra were obtained using a Perkin–Elmer R10 60 Mc/s spectrometer with integrator using 20 mg copolymer samples dissolved in 1 ml of $CDCl_3$. Ten integrals were obtained for each sample and the average used for the calculation of copolymer composition.
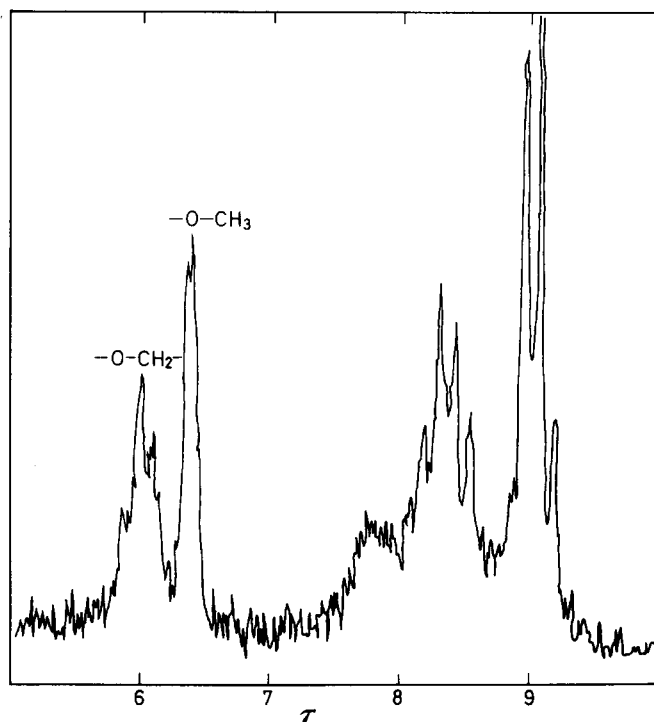

Figure 1—Nuclear magnetic resonance spectrum of 1–4, MMA–PrA copolymer

654

RESULTS AND DISCUSSION

In the n.m.r. spectra of the copolymers MMA–EA, MMA–PrA, MMA–BuA and MMA–EMA the peak due to the —O—CH$_3$ protons (in MMA) was resolved from those due to the —O—CH$_2$— protons (in the second monomer) as shown for a representative example in *Figure 1*. The monomer compositions of the copolymers were calculated from the ratios of the areas under those peaks, as measured by the integral curves, the areas being proportional to the number of protons contributing to the peaks. Thus

$$I_{-OCH_2-} \propto 2 \text{ (number of second monomer units in chain)}$$

$$I_{-OCH_3} \propto 3 \text{ (number of MMA units in chain)}$$

in which I_{-OCH_2-} and I_{-OCH_3} are the integrals of the —OCH$_2$— and —OCH$_3$ peaks respectively.

If X is molar ratio MMA/second monomer in copolymer, then

$$I_{-OCH_2-}/I_{-OCH_3} = 2/3X$$

No characteristic peaks could be distinguished for MMA–MA copolymers, MA and MMA both contain —O—CH$_3$ groups and the absorptions
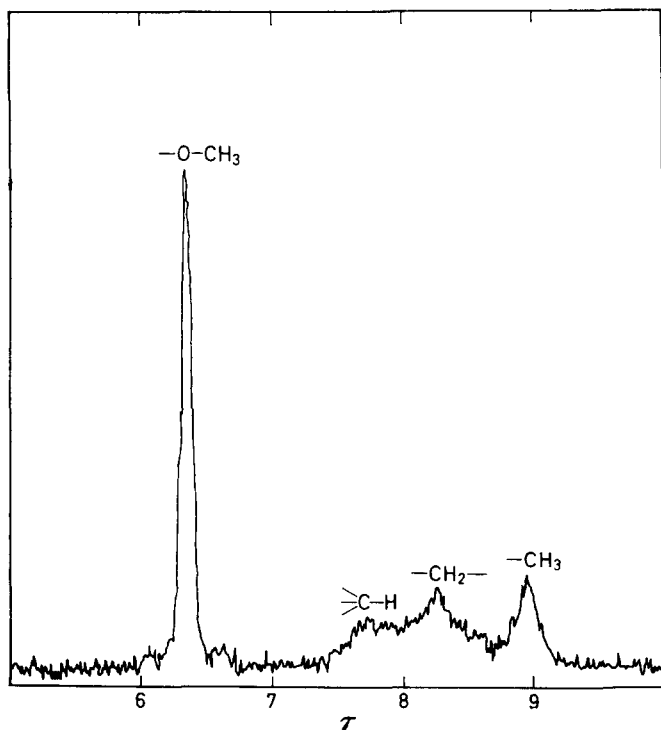

Figure 2—Nuclear magnetic resonance spectrum of 1–5, MMA–MA copolymer

due to the tertiary protons in MA and the methylene protons overlap as illustrated in *Figure 2*. Thus the total proton difference (8 from MMA, 6 from MA) between the two monomers had to be used here to calculate copolymer composition. Thus, if $X =$ molar ratio MMA/MA in copolymer, then

$$I_{total}/I-\text{o}-\text{CH}_3 = Y = (8X + 6)/(X + 1) 3$$

Therefore

$$X = (3Y - 6)/(8 - 3Y)$$

The ratios obtained by averaging ten determinations of the appropriate integrals when applied to the appropriate equations above gave the values for copolymer compositions shown in *Table 1(a)* and (*b*).

Table 1. Nuclear magnetic resonance spectral analyses

(*a*)

Monomer pair M₁	M₂	Molar ratio in monomer mixture (M₁/M₂)	$\dfrac{I-\text{OCH}_2-}{I-\text{OCH}_3}$	Molar ratio in copolymer (X)
MMA	EA	4·05	0·08	8·76
		2·02	0·15	4·45
		1·01	0·23	2·78
		0·52	0·47	1·39
		0·25	0·67	0·78
MMA	PrA	4	0·09	7·41
		2	0·20	3·33
		1	0·32	2·0
		0·5	0·63	1·06
		0·25	0·97	0·69
MMA	BuA	4	0·09	7·41
		2	0·17	3·92
		1·2	0·26	2·56
		1	0·34	1·96
		0·25	1·01	0·66
		0·125	2·86	0·23
MMA	EMA	4	0·15	4·44
		2	0·29	2·39
		1	0·67	1·0
		0·5	1·27	0·53
		0·25	2·53	0·26

(*b*)

Monomer pair M₁	M₂	Molar ratio in monomer mixture (M₁/M₂)	$\dfrac{3I_{total}}{I-\text{o}-\text{CH}_3}$	Molar ratio in copolymer (X)
MMA	MA	5·2	7·77	7·7
		1·0	7·32	1·94
		0·85	7·33	2·0
		0·38	6·86	0·76
		0·20	6·78	0·64

From the values of M_1/M_2 and X shown in *Tables 1(a)* and (*b*), reactivity ratios were calculated by the method of Mayo and Lewis[7], using the equation

$$r_2 = (M_1/M_2)\{(1/X)[1 + (M_1/M_2) r_1] - 1\}$$

r_1 versus r_2 plots for the systems under investigation are illustrated in *Figure 3*. In estimating r_1 and r_2 values from the data the intersections of adjacent lines were discounted, and the reactivity ratios obtained are shown
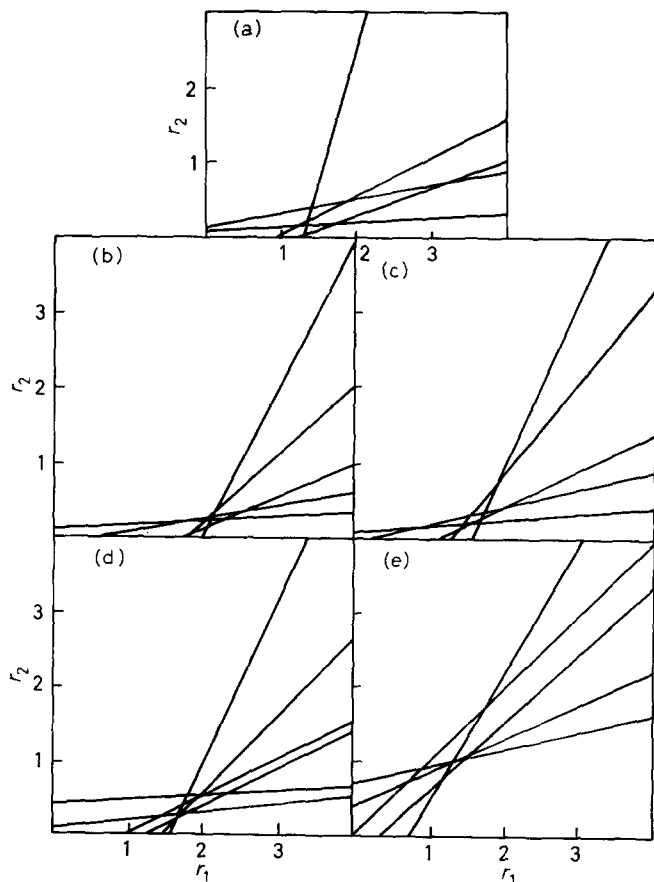

Figure 3—r_1 versus r_2 plots for (a) MMA–MA; (b) MMA–EA; (c) MMA–PrA; (d) MMA–BuA; (e) MMA–EMA

in *Table 2*. These values are seen to be in good agreement with those calculated from Q and e data for these monomers[9,10] with the exception of the MMA–EA system.

The last column in *Table 2* shows the only other results obtained directly for the radical copolymerization of these systems. The values for MMA–MA were obtained by the use of deuterated monomer[3] (polymerization temperature 130°C) while the MMA–EMA system was studied by the use of radioactive tracers[2], and both are in reasonable agreement with the present results.

Thus nuclear magnetic resonance spectroscopy offers a general method

Table 2. Reactivity ratios

Polymerization temperature, °C	Monomer pair		Experimental		Q–e values		Other experimental values
	M_1	M_2	r_1	r_2	r_1	r_2	r_2
65	MMA	MA	$1·8 \pm 0·4$	$0·35 \pm 0·1$	1·9	0·5	$2·3 \pm 0·5$ $0·47 \pm 0·1$ (at 130°C)
60	MMA	EA	$2·03 \pm 0·12$	$0·24 \pm 0·12$	1·43	0·73	—
60	MMA	PrA	$1·61 \pm 0·1$	$0·29 \pm 0·1$	—	—	—
60	MMA	BuA	$1·8 \pm 0·1$	$0·37 \pm 0·1$	1·86	0·37	—
60	MMA	EMA	$1·09 \pm 0·1$	$0·98 \pm 0·1$	1·08	0·96	0·92 1·08

of analysis of copolymers with an accuracy comparable with that achieved by other analytical methods. It has the additional advantages that it is rapid and can cope with monomer pairs whose similarity in structure makes other analytical methods inapplicable. It is clearly of maximum use among the acrylates and methacrylates where one of the monomers does not incorporate the —O—CH_2— structure. It is still useful, although less accurate when this is not so, provided the constituent monomers have different numbers of protons as in the MMA–MA system. It cannot be readily applied, however, when both monomers incorporate —O—CH_2— groups and the same number of protons, as for example, the system ethyl methacrylate–propyl acrylate.

Chemistry Department,
University of Glasgow,
Glasgow, W.2.

REFERENCES

[1] HAM, G. E. *Copolymerization, High Polymers,* Vol. XVIII. Interscience: New York, 1964.
[2] BEVINGTON, J. C. and MALPASS, B. W. *European Polymer Journal,* 1965, **1,** 19
[3] SHIMA, M. and KOTERA, A. *Polymer Sci. A,* 1963, **1,** 1115
[4] PORTER, R. S., NISKSIC, S. W. and JOHNSON, J. F. *Analyt. Chem.* 1963, **35,** 1948
[5] CHEN, H. Y. and LEWIS, M. E. *Analyt. Chem.* 1964, **36,** 1394
[6] REHBERG, C. E. and FISHER, C. H. *J. Amer. chem. Soc.* 1944, **66,** 1203
[7] MAYO, F. R. and LEWIS, F. M. *J. Amer. chem. Soc.* 1944, **66,** 1594
[8] ALFREY, T. and PRICE, C. C. *J. Polym. Sci.* 1947, **2,** 101
[9] YOUNG, L. J. *J. Polym. Sci.* 1961, **54,** 411
[10] OTSU, T., ITO, T. and IMOTO, M. *J. Polym. Sci. B.* 1963, **3,** 113