From the Regional Research Laboratory, Hyderabad, India

# Determination of Reactivity Ratios for the Copolymerisation of Vinyl Acetate with Methyl Acrylate by Proton Magnetic Resonance Spectroscopy

By N. G. Kulkarni, N. Krishnamurti, P. C. Chatterjee, and M. A. Sivasamban

SUMMARY:

Reactivity ratios for the copolymerisation of vinyl acetate with methyl acrylate have been determined in bulk at 60 °C for conversions smaller than 1% using proton magnetic resonance spectroscopy. The values ($r_{ma} = 6.3 \pm 0.4$; $r_{va} = 0.031 \pm 0.006$) thus obtained were compared with the values obtained by other workers using different analytical techniques. The present method appears to be extremely simple and accurate.
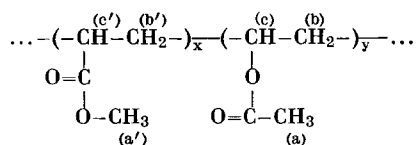
ZUSAMMENFASSUNG:

Die Copolymerisationsparameter des Systems Vinylacetat/Methylacrylat wurden für die Polymerisation in Masse bei 60 °C und Umsätzen unter 1% durch Protonenresonanzspektroskopie zu $r_{ma} = 6{,}3 \pm 0{,}4$ und $r_{va} = 0{,}031 \pm 0{,}006$ bestimmt und mit den Werten anderer Autoren verglichen. Die Methode ist einfach und sehr genau.

Determination of reactivity ratios of monomer pairs in copolymerisation reactions is of considerable importance since the chemical composition of a copolymer depends mainly upon the relative reactivities of the two monomers towards the two radicals. Although vinyl acetate and methyl acrylate are isomeric monomers, they have different reactivities. Mayo et al.[1] were the first to determine the reactivity ratios for this copolymerisation. The procedure employed for the polymer analysis was lengthy and involved hydrolysis of the polymer followed by a determination of the acetic acid thus produced. This together with the rather high conversion to polymer might have been responsible for the large errors involved in this determination. Recently, Garrett and Park[2] redetermined the reactivity ratios using infrared spectroscopy. Advantage was taken of the fact that the vinyl acetate, like other acetate esters, has a band at 1240 cm$^{-1}$ while the acrylate has one at 1160 cm$^{-1}$ similar to the esters of long chain acids. Further, they restricted the conversion to polymer between 2 to 3%. Their values, though lower than those reported by Mayo et al., fall within the range of errors reported by the latter. In both cases the monomers were copolymerised in bulk. Reference

may also be made to the work of Avetisyan, Eliseeva and Larinova[3] who used an interferometer to analyse the copolymer and carried out the copolymerisation in emulsion.

The present work reports the use of proton magnetic resonance (p-NMR) spectroscopy for the analysis of copolymers of methyl acrylate and vinyl acetate. The conversion was kept as low as possible. The method is very fast and the errors are small.

The general structure of the copolymer from methyl acrylate (monomer 1) and vinyl acetate (monomer 2) can be written as

$$\ldots-(-\overset{(c')}{C}H-\overset{(b')}{CH_2}-)_{\overline{x}}-(-\overset{(c)}{C}H-\overset{(b)}{CH_2}-)_{\overline{y}}-\ldots$$
$$O=C \qquad\qquad O$$
$$\underset{(a')}{O-CH_3} \qquad \underset{(a)}{O=C-CH_3}$$

A typical p-NMR spectrum of this system containing three distinct groups of signals is shown in Fig. 1. The following positions and relative areas were found:

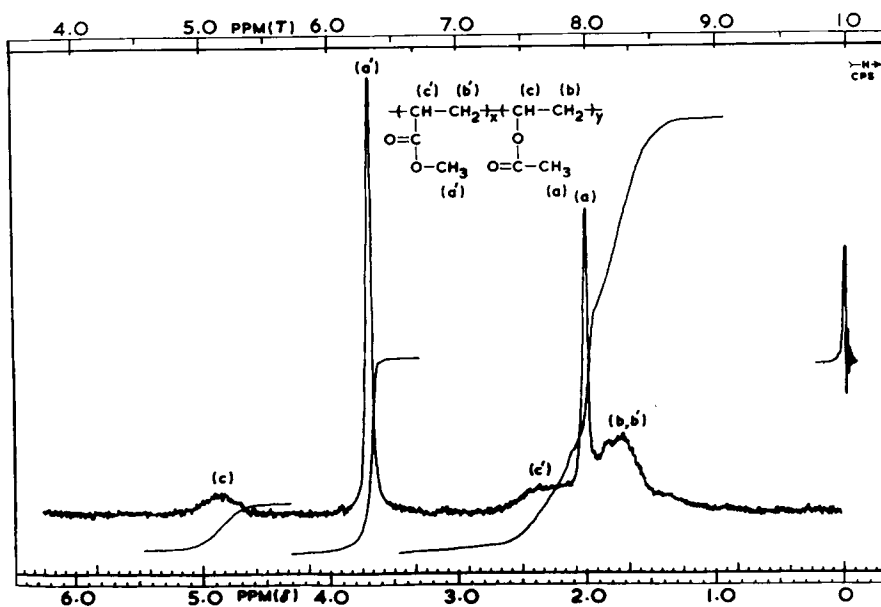| Signal position ($\tau$) | 5.1 | 6.3 | 8.0 |
|---|---|---|---|
| Multiplicity | Multiplet | Singlet | Multiplet |
| Integration (relative areas) | 21 | 92 | 198 |



Fig. 1. p-NMR spectrum of a methyl acrylate and vinyl acetate copolymer

While the signal at $\tau = 6.3$ is characteristic for the methyl protons (a')
of the methyl acrylate moiety in the copolymer, the multiplet at $\tau = 5.1$
is assignable to the proton (c) of the vinyl acetate unit. The multiplet
around $\tau = 8.0$ constitutes a combination of contributions from the
methyl protons (a), methylene protons (b) and (b') and the proton (c').
A confirmation of these assignments is readily available if equation (1) is
satisfied:

$$5\,S_c = S_{abb'c'} - S_{a'} \tag{1}$$

where S is the peak area of the signal, and the subscripts correspond to
the assignments given above. Table 1 shows the agreement obtained in
the experiments studied. The spectra of the homopolymers of vinyl
acetate (Fig. 2) and methyl acrylate (Fig. 3) also confirm the assignments
made. It follows that the $m_1/m_2$ ratio of the copolymer can be calculated
from Eq. (2),

$$\frac{m_1}{m_2} = \frac{5\,S_{a'}}{3\,(S_{abb'c'} - S_{a'})} \tag{2}$$

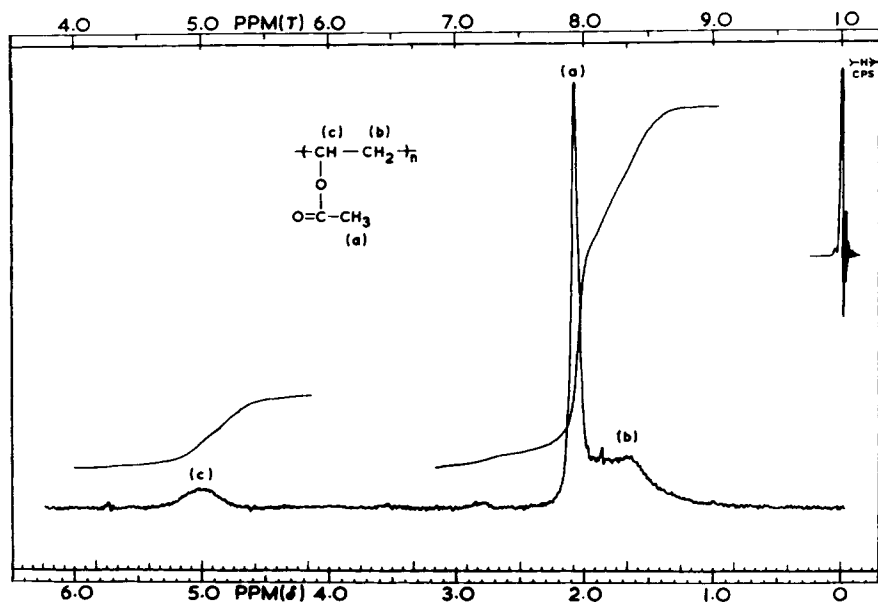which provides a fast and accurate determination of this ratio.



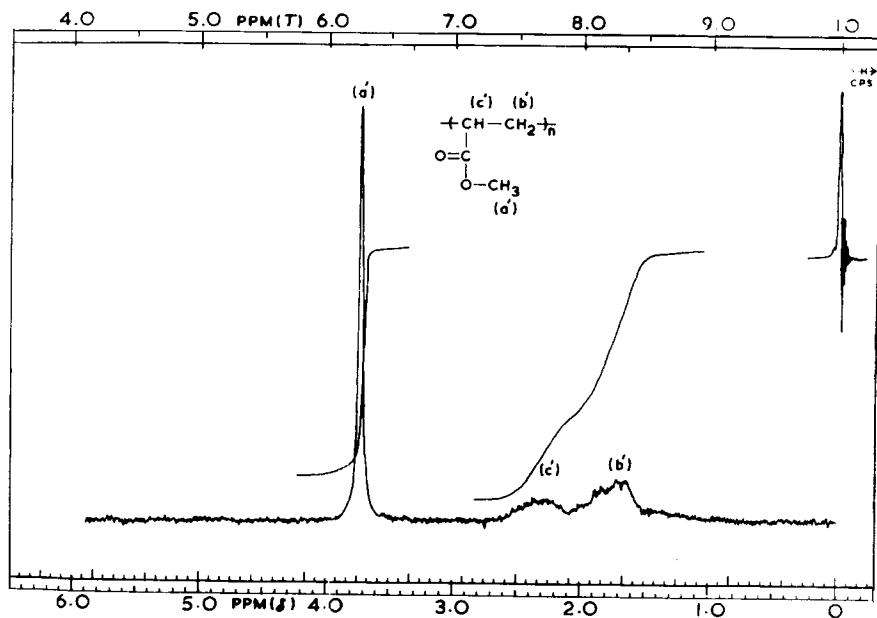Fig. 2. p-NMR spectrum of poly(vinyl acetate)

Fig. 3. p-NMR spectrum of poly(methyl acrylate)

Table 1. Peak areas of proton c

| Experi-<br>ment<br>No. | $M_1 : M_2$<br>ratio<br>(molar) | $S_c$ | |
|---|---|---|---|
| | | Calculated<br>via Eqn. (1) | Determined directly<br>from NMR spectrum |
| 1 | 1:3 | 11.4 | 11 |
| 2 | 1:4 | 12.2 | 12 |
| 3 | 1:6 | 13.4 | 13 |
| 4 | 1:8 | 18.2 | 18 |
| 5 | 1:10 | 23.6 | 23 |
| 6 | 1:15 | 25 | 24 |

At low conversions, the copolymer equation of MAYO and LEWIS[4] can be written as

$$r_2 = \frac{M_1}{M_2} \left[ \frac{m_2}{m_1} \left( 1 + \frac{M_1}{M_2} r_1 \right) - 1 \right]$$

where $M_1$ and $M_2$ are the initial concentrations of the two monomers having reactivity ratios $r_1$ and $r_2$ and $m_2/m_1$ is the ratio of the two mono-mer units in the resulting copolymer.

168

## Experimental

### Materials

Both methyl acrylate (monomer 1) and vinyl acetate (monomer 2) were of Fluka (pure) grade. They were washed with dilute solutions of sodium hydroxide to remove the stabiliser followed by washing with water until the washings were neutral, dried over anhydrous sodium sulfate and finally distilled over copper rosinate. Distilled monomers were stored under nitrogen in the deep-freezer. Dibenzoyl peroxide (May and Baker) contained about 12 to 13 wt.-% of moisture. This material was purified by dissolving the initiator in chloroform at room temperature followed by adding twice its volume of methyl alcohol and keeping it in refrigerator overnight[5]. The chloroform used for taking NMR-spectra was of spectroscopic grade (E. Merck). It was washed free from ethanol (used to stabilise the chloroform), dried, distilled, and used freshly.

### Polymerisation

The two monomers were copolymerised in different molar ratios in bulk at $60 \pm 0.1\,^\circ C$ using 0.05 mole-% dibenzoyl peroxide as initiator. Polymerisation apparatus and technique used were similar to that described earlier[6]. The polymer was isolated by precipitating twice in $n$-hexane and was subsequently heated for several hours $i.vac.$ to remove all traces of monomers and solvents. Only those polymers were subjected to analysis for which the conversions were well below 1%.

### Polymer Analysis

NMR spectra of the copolymers in chloroform solution were recorded in a Varian 60 MC NMR spectrometer using tetramethylsilane as internal standard. The ratio of the molar concentrations of the two monomer units in the copolymers $(m_2/m_1)$ was then calculated from Eq. (2). The reactivity ratios were found by the intersection line method[4].

## Results and Discussion

The values obtained for the reactivity ratios for the methyl acrylate (monomer 1) — vinyl acetate (monomer 2) system are given in Table 2

Table 2. Reactivity ratios for the copolymerisation of methyl acrylate $(r_1)$ with vinyl acetate $(r_2)$

| Source | Temperature (°C) | $r_1$ | $r_2$ |
|---|---|---|---|
| MAYO et al.[1] | 60 (bulk) | $9 \pm 2.5$ | $0.1 \pm 0.1$ |
| GARRETT and PARK[2] | 50 (bulk) | $6.7 \pm 2.2$ | $0.029 \pm 0.011$ |
| AVETISYAN et al.[3] | 60 (emulsion) | $3 \pm 0.3$ | $0.5 \pm 0.06$ |
| Present work | 60 (bulk) | $6.2 \pm 0.4$ | $0.036 \pm 0.006$ |
| Calculated from Q-e scheme[7] | — (bulk) | 9.9 | 0.54 |
| Calculated from $\alpha.\beta$-$\sigma$-parameter[8] | — (bulk) | 3.1 | 0.016 |

169

N. G. Kulkarni, N. Krishnamurti, P. C. Chatterjee, and M. A. Sivasamban

together with those obtained by other workers. The values obtained in the present work are very close to those obtained by Garrett and Park[2]. The errors are however much smaller.

## *Note*

After this manuscript was prepared for publication we have come across an abstract in Chemical Abstracts **72** (1970) 22082y of a publication entitled "Determination of Monomer Reactivity Ratios by NMR-spectroscopy. Monomer Reactivity Ratios of Methyl Acrylate and Vinyl Acetate in Radical Copolymerisation" by M. Ibonai and T. Kuramochi, Kōgyō Kagaku Zasshi **72** (1969) 2161.

[1] F. R. Mayo, C. Walling, F. M. Lewis, and W. F. Hulse, J. Amer. chem. Soc. **70** (1958) 1523.

[2] T. A. Garrett and G. S. Park, J. Polymer Sci. **4**, Part A-1 (1966) 2714.

[3] I. S. Avetisyan, V. I. Eliseeva, and O. G. Larinovo, Vysokomol. Soedin. A **9** (3) (1967) 570.

[4] F. R. Mayo and F. M. Lewis, J. Amer. chem. Soc. **66** (1944) 1594.

[5] A. I. Vogel, Practical Organic Chemistry, 3rd edition, Longmans, Green and Co., London 1957, p. 807.

[6] G. N. Tewari, P. C. Chatterjee, and J. S. Aggarwal, Fette Seifen Anstrichmittel **72** (1970) 470.

[7] L. J. Young, J. Polymer Sci. **54** (1961) 411.

[8] C. H. Bamford and A. D. Jenkins, Trans. Faraday Soc. **59** (1963) 530.