

## Reactivity Ratios for the Copolymerization of Styrene and Glycidyl Methacrylate by Nuclear Magnetic Resonance Spectroscopy

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**Summary:** Polymers and copolymers of styrene and glycidyl methacrylate have been prepared. Reactivity ratios for the copolymer system have been determined by using nuclear magnetic resonance spectroscopy. Results obtained by two different methods are in good agreement with each other.

### Introduction

The determination of monomer reactivity ratios in copolymerization is entirely dependent on the accuracy of analysis of the copolymers. Elemental analysis cannot be made accurate for the purpose [1] and the gas liquid chromatographic analysis of pyrolysis products may be of doubtful quantitative validity. Radiometric [2] and isotopic [3] methods are the only ones to be used successfully but, being time consuming and requiring elaborate experimental technique, 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 of vinyl chloride-vinyl acetate [5] and to determine the monomer content of vinylacetate-ethylene copolymers [6], Dhal *et al.* [7,8] investigated glycidylmethacrylate-*n*-butyl acrylate, - isobutyl acrylate and -tert butyl acrylate copolymers by means of <sup>13</sup>C-NMR spectroscopy and determined the respective reactivity ratios. S. Zulfiqar *et al.* [9] determined the reactivity ratios for the copolymerization of methyl methacrylate and phenyl methacrylate by <sup>1</sup>H-NMR spectroscopy. The present work shows another successful application of <sup>1</sup>H-NMR spectroscopy, to determine the reactivity ratios for the styrene and glycidyl methacrylate monomer pair.

The method is widely applicable to copolymer analysis and is particularly valuable for its rapidity and simplicity.

### Results and Discussion

The nmr spectrum of a typical glycidyl methacrylate-styrene copolymer is illustrated in Fig. 1. By comparison with the spectra of

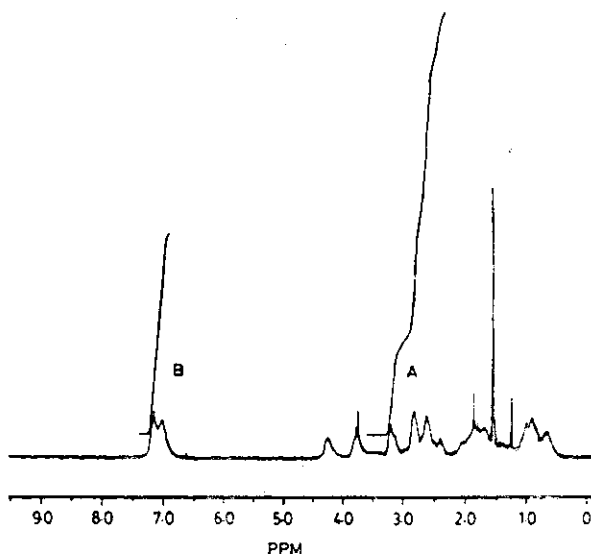


Fig. 1: NMR spectrum of copolymer ST/GMA (copolymer 2 in Table 1).

poly(glycidylmethacrylate) and polystyrene it can be shown that the peaks are due to respective absorption by the epoxy protons in GMA (A) and -Ph (Phenyl) protons in styrene (B).

The compositions of the copolymers were calculated from the relative areas under the two types of proton peaks as measured by the integral curves, the areas being proportional to the number of protons contributing to the peaks. Results obtained are presented in Table 1. Reactivity ratios were calculated by the two standard methods:

(i) Mayo and Lewis method [10] using the equation

$$r_1 = [m_1 M_2^2 / m_2 M_1^2] r_2 + [M_2 / M_1] [m_1 / m_2 - 1]$$

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

(ii) The second method known as Fineman and Ross method [11] and the equation used is:

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

$$\text{where } F = [M_1/M_2]$$

$$f = [m_2/m_1]$$

Table 1: Copolymer composition data

	Monomer mixture [M <sub>1</sub> ]/[M <sub>2</sub> ]	Copolymer [m <sub>2</sub> ]/[m <sub>1</sub> ]
1.	0.0765	6.358
2.	0.2762	3.5045
3.	1	1.6267
4.	1.8531	1.0220
5.	6.72	0.3064
6.	24	0.1098

\* M<sub>1</sub>= ST; M<sub>2</sub>= GMA

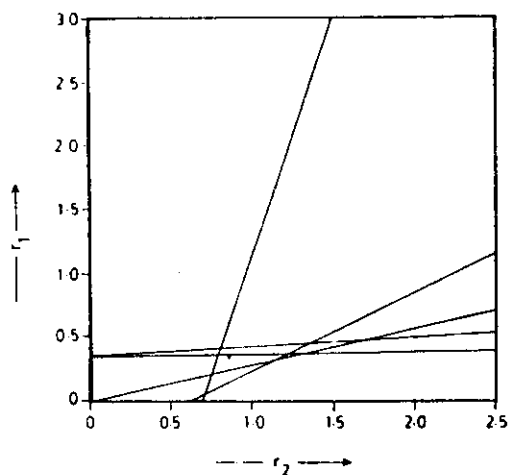


Fig. 2:  $r_1$  vs  $r_2$  diagram for ST/GMA copolymers.

Table 2: Comparison of conditions and reactivity ratios determined by different investigators.

Conditions	Sorokin <i>et al</i>	Investigator J.A. Simms	M.Zulfiqar <i>et al</i> (This paper)
Temperature	65°C	60°C	60°C
Initiator	0.5 mol % AIBN	0.1% BZ <sub>2</sub> O <sub>2</sub>	0.05% AIBN
Conversion %	6.5 - 8.0	5 - 10	up to 5
Analysis of Polymer	Analysis for glycidyl group and for C	Analysis for Oxygen content	By <sup>1</sup> H-NMR
Reactivity ratios	$r_1 = 0.441 \pm 0.007$ (By least squares) $r_2 = 0.544 \pm 0.004$	$r_1 = 0.34 \pm 0.03$ (Mayo and Lewis) $r_2 = 0.63 \pm 0.1$	$r_1 = 0.33 \pm 0.02$ $r_2 = 0.85 \pm 0.03$ Mayo & Lewis $r_1 = 0.3553 \pm 0.014$ $r_2 = 0.8015 \pm 0.014$ Fineman & Ross

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  $r_2$ . The results derived from both methods are quoted in Table 2 and are in good agreement with each other. However, these results cannot be compared with those obtained by Sorokin and Kochnov [12] who determined the copolymer composition by the analysis for glycidyl groups and for carbon. The reactivity ratios were calculated by least squares. Simms [13] evaluated the copolymer composition by analysing the copolymers (ST-GMA) for their oxygen content and the reactivity ratios were determined by Mayo and Lewis method. The discrepancies in the results are probably due to differences in experimental conditions and method of copolymer analysis. Typical experimental conditions and results by different investigators are given in Table 2. The nuclear magnetic resonance spectroscopy offers an accurate and a rapid method of copolymer analysis.

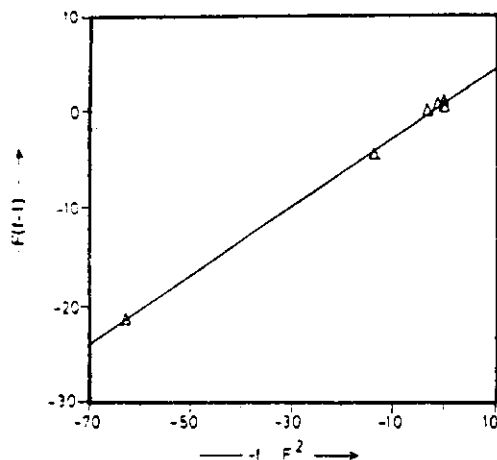


Fig. 3: Fineman - Ross plot for copolymerization of ST and GMA.

## Experimental

### Monomer purification

Styrene (ST) (Aldrich) was freed from inhibitor by washing with 5% aqueous sodium hydroxide, dried over calcium chloride and calcium hydride, in turn, and finally distilled under reduced pressure.

Glycidyl methacrylate (GMA) (E. Merck) was purified by drying with calcium chloride and calcium hydride for 24 h each, followed by distillation under vacuum.

### Polymerization

Polystyrene (PS) was prepared by bulk polymerization of the monomer under vacuum at 60°C with 0.05% w/v azobisisobutyronitriles (AIBN) as initiator. The polymer was precipitated in methanol, purified by reprecipitation in methanol from tetrahydrofurane (THF) solution, dried in vacuum oven at 50°C for 24 h.

Poly(glycidyl methacrylate) (PGMA) was prepared by bulk polymerization of GMA under vacuum at 60°C using 0.05% w/v AIBN as initiator. The polymer was isolated and purified as for PS. Copolymer of GMA and ST with six different compositions were prepared by bulk polymerization of appropriate mixture 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, purified by reprecipitation by methanol from THF solution and dried under vacuum at 50°C for 24 h. The composition of each copolymer was determined from nmr data.

### Copolymer analysis

The nmr spectra were recorded by using a Bruker NMR spectrometer, operating at 300 MHz. 25 mg of each copolymer sample was dissolved in 1 ml of CDCl<sub>3</sub> and five integrals were obtained and

average result was employed for the calculation of copolymer composition.

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