Spectroscopic Methods for the Determination of Monomer Reactivity Ratios in Glycidyl Methacrylate-StyreneCopolymerization

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ABSTRACT

The copolymerization of glycidyl methacrylate with styrene was carried out in bulk by free-radical initiation. The composition of the copolymers were determined by ^{1}H-NMR, IR, and chemical analysis. The monomer reactivity ratios were calculated by the YBR method from the copolymer composition data. The values obtained for different techniques were compared.

INTRODUCTION

The accurate estimation of the composition of copolymers and the precise determination of monomer reactivity ratios from them is of paramount importance for tailor making copolymers with the required physicomechanical properties. Though chemical methods

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have been employed for quite some time, physical techniques for co-polymer composition analysis have been gaining importance in recent years because of their inherent sensitivity and rapidity [1]. In fact, quantitative IR and NMR spectroscopic techniques are well established as convenient methods for determining the composition ratio of the constituent monomer units in copolymers [2-7].

The present paper describes the use of IR and ^{1}H-NMR techniques for the estimation of composition of glycidyl methacrylate (GMA)-styrene(sty) copolymer and compares them with the values obtained by chemical analysis. Copolymers based on glycidyl methacrylate have wide applications in biology for the binding of drugs and bio-molecules [8, 9] and in electronic industries as negative electron-beam resists [10]. Since the performance properties of these co-polymers are influenced by the relative amounts of GMA and the co-monomer present in the copolymer, it was thought important to find convenient and rapid methods for the determination of copolymer com-position and the calculation of monomer reactivity ratios.

EXPERIMENTAL

Copolymerization

Styrene (SiSCO Laboratories) was washed successively with 5% sodium hydroxide and distilled water, dried over anhydrous sodium sul-fate, and subsequently distilled under reduced pressure. Glycidyl methacrylate (Fluka AG) was purified by vacuum distillation. 2,2'-Azobisisobutyronitrile (AIBN), obtained from Fluka AG, was purified by recrystallization from chloroform.

Copolymerization reactions for different monomer feed ratios were carried out in bulk at 60°C with free-radical initiator. Since the dif-ferential form of the copolymer equation was used to calculate the monomer reactivity ratio, the conversion of the monomers was in all cases restricted to 10%. Detailed procedures dealing with copolym-erization and purification have been given elsewhere [11].

Copolymer Composition Analysis

The compositions of the copolymers were determined by chemical analysis, ^{1}H-NMR, and IR techniques.

The chemical method involves the estimation of the epoxy group by the hydrochloric acid-dioxane reagent method [12].

^{1}H-NMR spectra of the copolymers were recorded on a Bruker WP80 FTNMR spectrometer with CCl_4 as the solvent ($\approx$ 10% w/v) and TMS as the internal reference. Copolymer compositions were deter-mined from the relative peak areas of the characteristic peaks.

Infrared spectra were generated from solutions of the copolymers in chloroform (0.5% solution w/v). The spectra were recorded over the 4000 to 600 cm^{-1} range with a Perkin-Elmer Model 637 Spectrophotometer. The instrument was calibrated with a polystyrene marker, and the quoted frequencies are accurate to within ±0.5 cm^{-1}.

RESULTS AND DISCUSSION

The composition of the copolymers estimated by all three methods mentioned earlier are summarized in Table 1. The monomer reactivity ratios were calculated from the composition data by the YBR method [13], which is one of the most reliable methods available at the present time for the precise determination of monomer reactivity ratios [14]. The reactivity ratio data calculated are presented in Table 2.

In ^{1}H-NMR spectra, the distinct peaks due to the methyl group ($\approx$ 0.9 ppm) of GMA unit and phenyl group ($\approx$ 7 ppm) of the styrene unit (Fig. 1) are considered for the composition analysis. Since the peak area corresponds to the total number of protons of a particular group, the composition of the copolymer was calculated by

$$\% \text{ GMA} = \frac{^1\text{H-methyl}/3}{^1\text{H-methyl}/3 + {}^1\text{H-phenyl}/5} \, .$$

The equation is based on the fact that the methyl group corresponds to three protons and the phenyl group to five protons. Integrated peak intensities and peak area measurements were employed for this calculation.

TABLE 1. Composition of Glycidyl Methacrylate-Styrene Copolymers

Mole fraction of GMA in the feed	Mole fraction of GMA in the copolymers		
	Chemical analysis	IR	^{1}H-NMR
0.2	0.34	0.36	0.36
0.4	0.52	0.51	0.50
0.6	0.65	0.62	0.63
0.8	0.78	0.80	0.79

TABLE 2. Monomer Reactivity Ratio for GMA (m_1)-Styrene (m_2)
Copolymerization Based on Various Composition Data

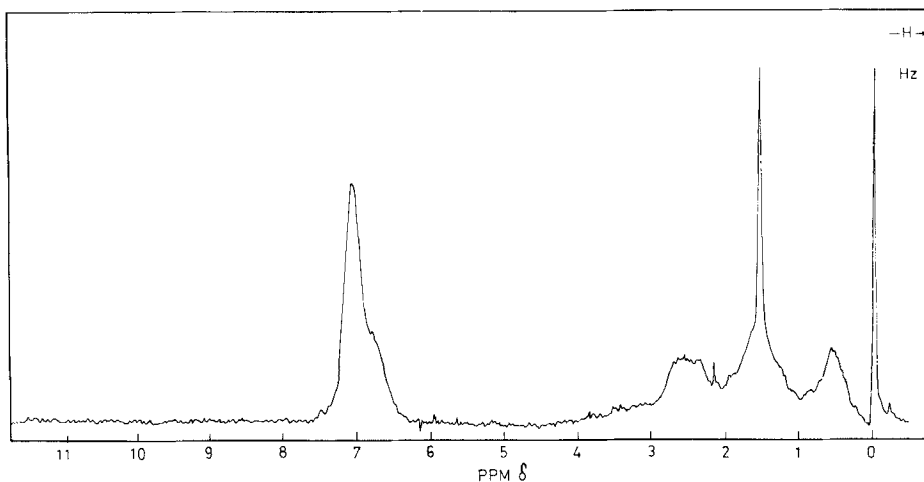|	Chemical analysis	IR	¹H-NMR	Reported value [15]
r_1	0.65	0.78	0.74	0.63
r_2	0.36	0.29	0.30	0.34

FIG. 1. Typical ¹H-NMR (80 MHz) spectrum of GMA-styrene co-
polymer (36:64).

     In the IR spectra, the constituent monomers show distinct charac-
teristic peaks: for GMA, carbonyl absorption is at 1735 cm^{-1}; for
styrene, aromatic ring absorption is at 1600 cm^{-1} (Fig. 2). This sug-
gests that an IR spectroscopic method based on absorption band in-
tensity ratios could be developed to estimate the composition of this
copolymer. It was assumed that absorptivity of key functional groups
is not significantly different in homopolymers compared to copoly-
mers. The baseline tangent points of the characteristic carbonyl
peak and phenyl peak were corrected, and the peak areas, determined
planimetrically, were used for the determination of relative compo-
sition. To determine the composition accurately from IR spectral
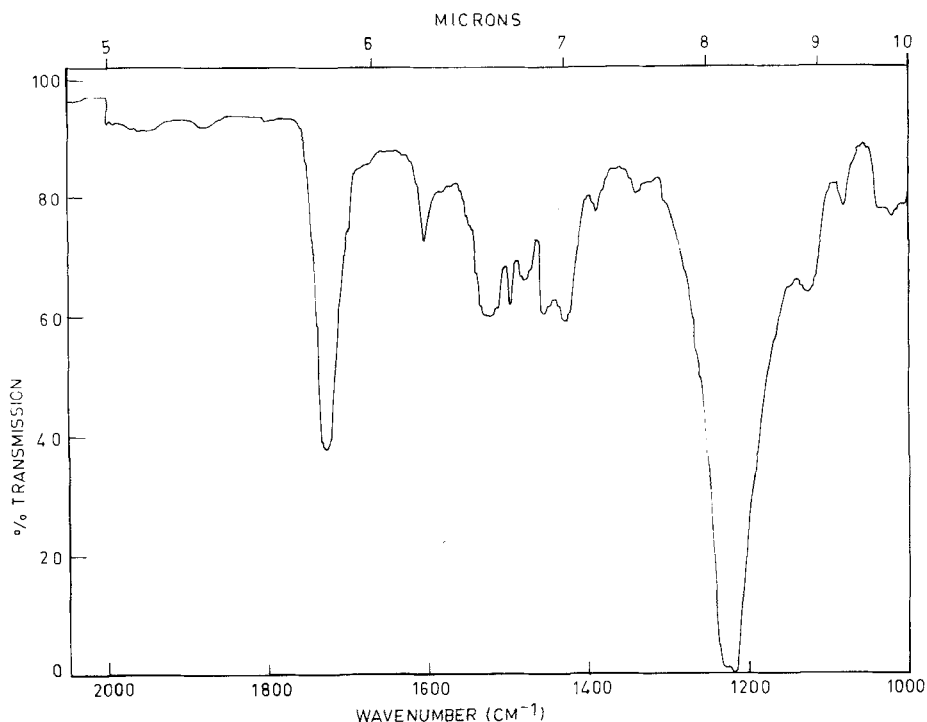data, a calibration plot of wt% GMA vs I_{1735}/I_{1600} (Fig. 3) was pre-

FIG. 2. Typical IR spectrum of GMA-styrene copolymer (63:37).

pared from blends of polyGMA and polystyrene homopolymers in five different proportions. The percentage of GMA could be determined conveniently from this plot when the band area ratio was known.

   The data obtained by all three methods (Tables 1 and 2) were in close agreement with each other, indicating the accuracy of analysis by physical techniques. The reactivity ratios obtained from the different sources of composition data match each other as well as the results reported earlier [15]. Inspection of the reactivity ratios indicates that this copolymerization process is of the almost random type and that GMA monomer prefers self-propagation.

CONCLUSIONS

   Spectroscopic techniques like NMR and IR can be conveniently used for accurate and rapid estimation of the composition of certain copolymers, thus avoiding the difficulties associated with chemical methods.
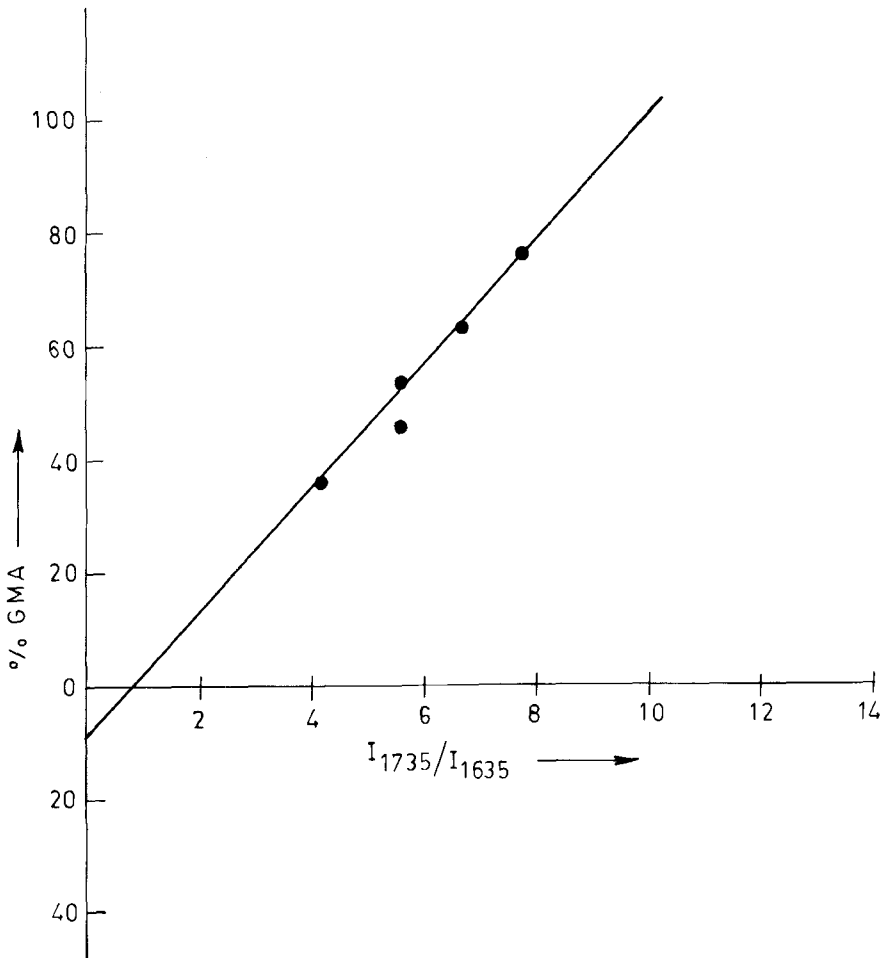
FIG. 3. Weight percentage of GMA vs I_{1735}/I_{1635} of GMA-styrene blends.

ACKNOWLEDGMENTS

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