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Synthesis, Characterization, and Reactivity Ratios of Phenyl Methacrylate-*N*-vinyl-2-pyrrolidone Copolymers

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SYNTHESIS, CHARACTERIZATION, AND REACTIVITY RATIOS OF PHENYL METHACRYLATE-*N*-VINYL-2-PYRROLIDONE COPOLYMERS

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ABSTRACT

Free radical solution copolymerization of phenyl methacrylate and *N*-vinyl-2-pyrrolidone was carried out using benzoyl peroxide in 2-butanone solution at 70°C. The composition of the copolymer was determined using ¹H-NMR spectra by comparing the intensities of aromatic protons to that of total protons. The results were used to calculate the copolymerization reactivity ratios by both the Fineman-Ross (F-R) and Kelen-Tüdös (K-T) methods. The reactivity ratios are $r_1 = 4.49 \pm 1.27$ and $r_2 = 0.05 \pm 0.09$ as determined by the K-T method. These values are in good agreement with those determined by the F-R method. The FT-infrared and ¹³C-NMR spectra of the copolymer are discussed.

INTRODUCTION

Acrylic copolymers have achieved prime importance in various avenues of industrial applications [1]. Accurate estimation of the composition of copolymers and precise determination of monomer reactivity ratios from them are important for polymer applications. Due to inherent sensitivity and rapidity, NMR spectroscopic techniques are well es-

established as convenient methods for determining the reactivity ratios of the constituent monomer units in the copolymer [2-6].

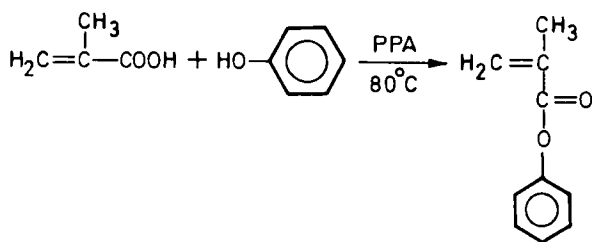
Yokota et al. [7] studied the copolymerization behavior of phenyl methacrylate (PhMA) with styrene in the presence of diethyl aluminum chloride. Photoluminescent behavior was observed in copolymers of PhMA with methyl methacrylate [8]. Stereoregular polymers of PhMA possess surface wettability [9]. Recently, Tadatomi and Saita [10] investigated thermocrosslinking reactions of copolymers of PhMA and polyfunctional epoxy compounds. The present paper reports the synthesis and characterization of phenyl methacrylate/*N*-vinyl-2-pyrrolidone (VPD) copolymers consisting of components which differ markedly in their selective solubility.

EXPERIMENTAL

Materials

Anhydrous phosphorus pentoxide (E. Merck), methacrylic acid (Sisco-chem), phosphoric acid, phenol, 2-butanone, and methanol were of BDH grades and used as received. Benzoyl peroxide (Fluka) was recrystallized from chloroform/methanol. *N*-Vinyl-2-pyrrolidone (Fluka) was distilled under reduced pressure before use.

Polyphosphoric acid was prepared by mixing equimolar quantities of phosphoric acid and anhydrous phosphorus pentoxide. Phenyl methacrylate was prepared by reacting 0.1 mol methacrylic acid with 0.2 mol phenol in the presence of 100 g polyphosphoric acid at 80°C using a thermostated water bath (Scheme 1); the reaction was continued for 24 h. The unreacted methacrylic acid, phenol, and polyphosphoric acid



SCHEME 1. Synthesis of phenyl methacrylate.

were removed by extracting the reaction mixture dissolved in toluene with saturated sodium bicarbonate, sodium hydroxide solution, and water sequentially. The solvent was removed by means of a rotary evaporator, and the resulting liquid was distilled under vacuum at 105–110°C/12 mm [11].

The formation of PhMA was confirmed by IR and NMR spectroscopy.

IR (cm⁻¹): 3030, 2920, 1726, 1635, 1590, 1290, 700.

¹H-NMR (δ ppm): 7.35–7.26 (2H), 7.20–7.03 (3H), 6.29 (1H), 5.66 (1H), 2.03 (3H).

¹³C-NMR (δ ppm): 135.68 (=C), 126.69 (=CH₂), 150.79 (¹C), 129.06 (³C and ⁵C), 125.36 (⁴C), 121.34 (²C and ⁶C), 175.19 (—C=O), 16.00 (CH₃).

Measurements

¹H-NMR spectra of all the copolymer samples (Fig. 1) were run on a Bruker 90 MHz FT-NMR spectrometer at room temperature using CDCl₃ as solvent and TMS as internal standard. Proton decoupled ¹³C-NMR spectra of the copolymer were run on a Bruker FT-NMR, operating at 22.63 MHz and using the above conditions. The FT-IR spectra of the samples were recorded on a Nicolet 20 DXB using KBr pellet.

Copolymerization

Appropriate quantities of PhMA and VPD with 2-butanone and benzoyl peroxide were placed in a standard reaction tube (100 mL), and the mixture was flushed with oxygen-free nitrogen for at least 10 min. The tube was tightly sealed and immersed in a thermostated water bath at 70 ± 1°C. Copolymerization was allowed to proceed to ~10% conversion. All the copolymers were precipitated in excess methanol, filtered off, purified by reprecipitation from chloroform solution by methanol, and finally dried in a vacuum oven at 50°C for 24 h.

RESULTS AND DISCUSSION

Copolymers were synthesized in 2-butanone at 70°C using benzoyl peroxide as radical initiator. Copolymerization was allowed to proceed to <10% conversion in order to obtain polymer samples having homo-

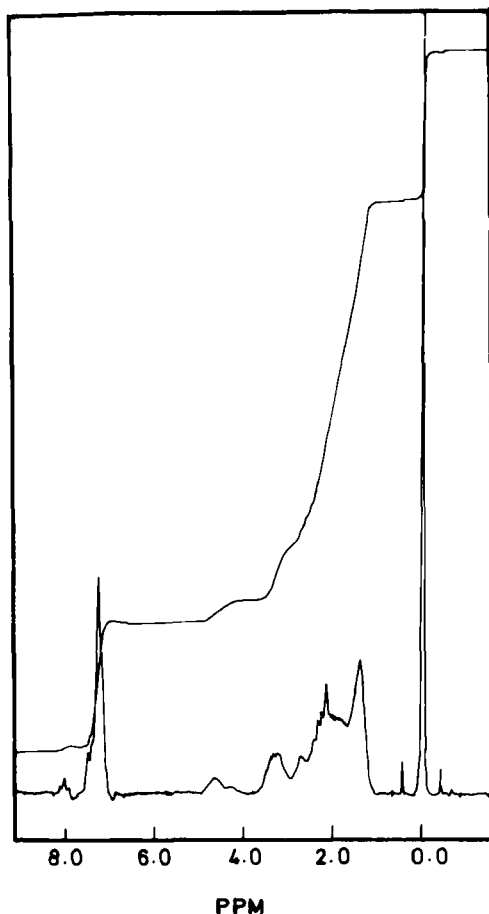


FIG. 1. ¹H-NMR spectra of phenyl methacrylate and *N*-vinyl-2-pyrrolidone copolymer ($m_1/m_2 = 42:58$).

geneous composition as far as possible (Table 1). The copolymers were characterized by IR, ¹³C, and ¹H-NMR spectroscopic methods.

IR Spectroscopy

The FT-IR spectra of the copolymer are shown in Fig. 2. The IR spectra show the same characteristic absorption bands as the homopolymer mixtures. The absorption bands due to PhMA unit were observed

TABLE 1. Copolymerization of Phenyl Methacrylate and *N*-Vinyl-2-pyrrolidone^a

Feed composition in mole fraction		Conversion, %	Intensity of aromatic protons (I_A)	Intensity of total protons (I_T)	Copolymer composition in mole fraction	
PhMA (M_1)	VPD (M_2)				PhMA (m_1)	VPD (m_2)
0.0898	0.9102	8.56	4.00	17.75	0.4247	0.5753
0.1982	0.8018	9.49	2.95	8.65	0.6588	0.3412
0.2933	0.7067	8.33	4.20	10.80	0.7529	0.2471
0.4021	0.5979	7.31	4.80	11.80	0.7970	0.2030
0.4982	0.5018	6.37	6.10	14.55	0.8237	0.1763
0.6000	0.4000	8.63	6.90	15.50	0.8796	0.1204

^aTemperature = 70 ± 1 °C; solvent = ethyl methyl ketone; benzoyl peroxide = 0.2 g; nonsolvent: methanol.

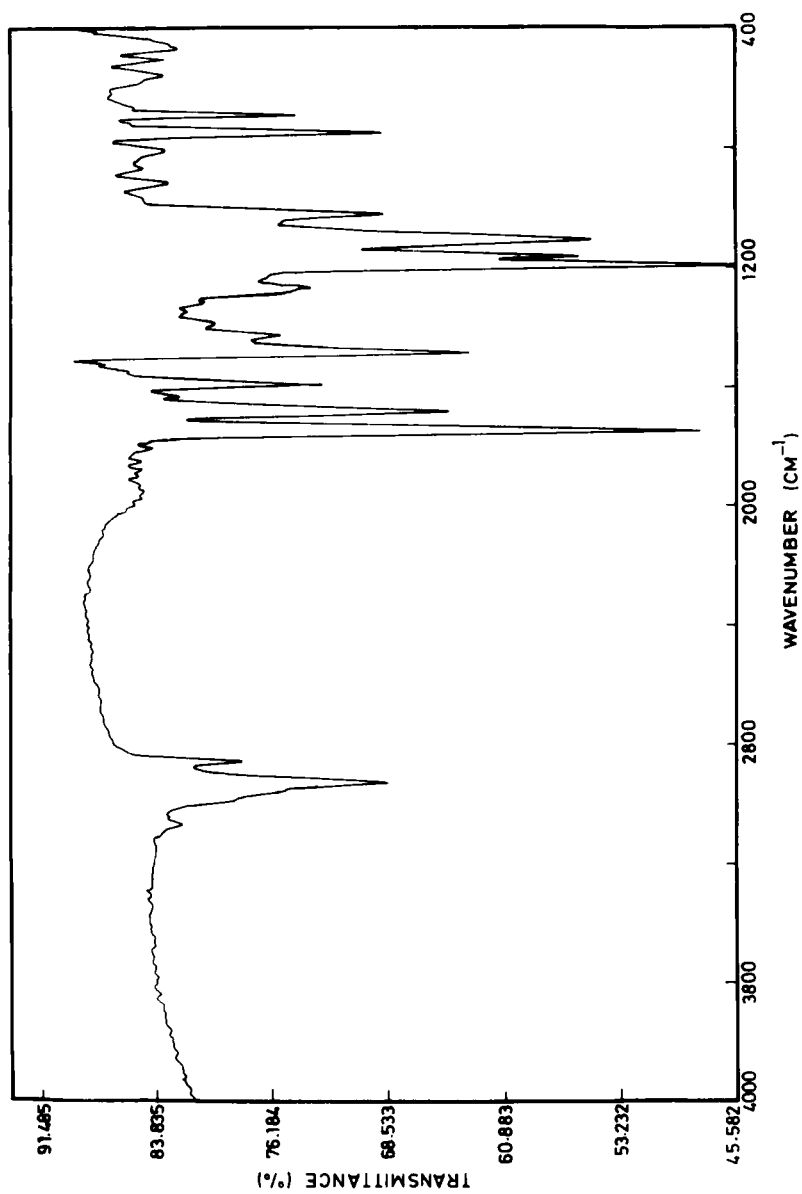


FIG. 2. FT-IR spectra of phenyl methacrylate and *N*-vinyl-2-pyrrolidone copolymer ($m_1/m_2 = 82:18$).

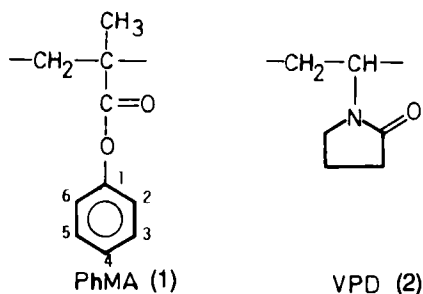
at 3025, 2976, 1746, 1591, 747, and 689 cm^{-1} . The ester carbonyl group of the PhMA unit is seen at 1746 cm^{-1} as a strong band. The sharp band at 1591 cm^{-1} is due to the aromatic ring and the absorptions at 747 and 689 cm^{-1} seem to have been due to the monosubstituted pattern of the PhMA. In the case of VPD, the characteristic pyrrolidone ring carbonyl gives a sharp absorption band at 1683 cm^{-1} . The band at 2880 cm^{-1} is due to the stretching vibrations of chain and ring methylenes, and the $-\text{C}-\text{O}$ band from the ester of PhMA is present at 1190 cm^{-1} . The appearance of 1683 cm^{-1} absorption not only explains the incorporation of the VPD unit in the copolymer, but also indicates the stability of the pyrrolidone ring in the polymerization process.

^{13}C -NMR Spectroscopy

The copolymer was also characterized with decoupled ^{13}C -NMR spectroscopy. The aromatic carbon nuclei of the phenyl ring appeared as four lines. The peak of 150.72 ppm is the $\text{O}-^{13}\text{C}$ of the phenyl ring of the PhMA unit. The peak at 129.41 ppm is due to ^3C and ^5C . ^4C gave a peak at 125.79 ppm. This follows the sharp line at 121.03 due to ^2C and ^6C atoms. The ester carbonyl group of PhMA appears at 175.60 ppm as a small peak. The α -methyl group of PhMA unit split into three broad lines around 16.39 ppm due to tacticity. The backbone carbons of PhMA unit appear at 45.8 and 53.5 ppm, respectively. In the case of VPD, the ring carbonyl gives a small peak at 175.41 ppm. The ring methylene carbon which is adjacent to carbonyl group appears at 19.29 ppm and the backbone methine at 31.49 ppm. The group of lines seen around 44.0–46.0 ppm is due to the remaining methylene carbon atoms (Fig. 3).

Copolymer Composition and Reactivity Ratios

The constituent monomeric units (phenyl methacrylate and *N*-vinyl-2-pyrrolidone) of the copolymer are as follows:



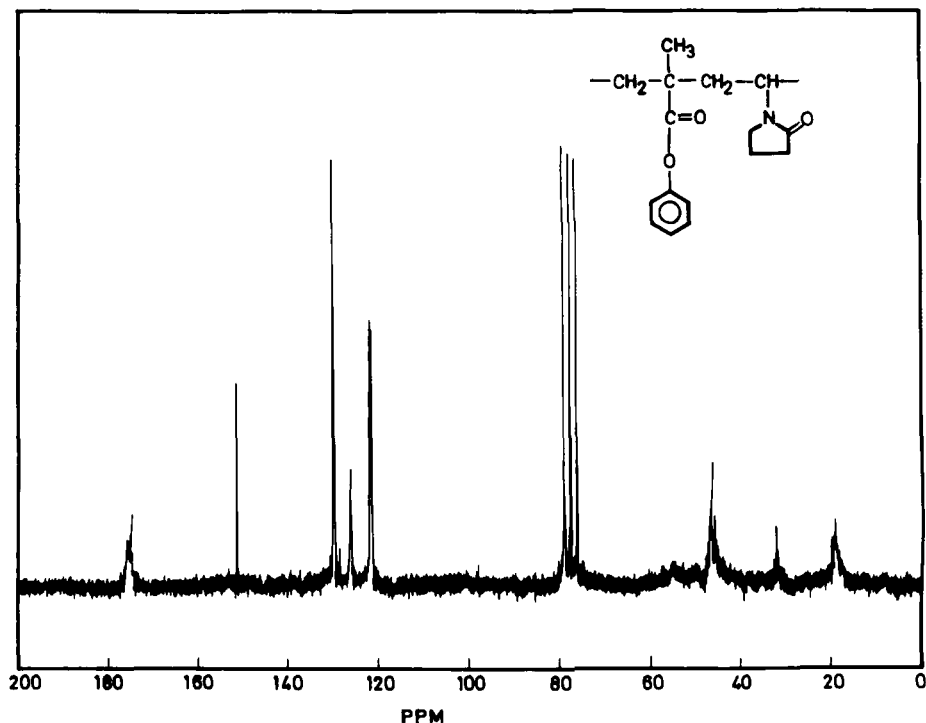


FIG. 3. $\{^1\text{H}\}$ - ^{13}C -NMR spectra of phenyl methacrylate and *N*-vinyl-2-pyrrolidone copolymer ($m_1/m_2 = 82:18$).

The distribution of protons in the two units is an important means of distinguishing monomers in the copolymer chain. The $-\text{CH}_2$ and $-\text{CH}_3$ group protons of PhMA and the $-\text{CH}_2$ and $-\text{CH}$ group protons of VPD are almost undistinguishable. Hence, in the present study the distinct peaks of aromatic protons are chosen for the estimation of PhMA composition in the copolymer. Since the peak intensity corresponds to the number of protons of a particular group, the mole fraction of the copolymer was calculated by

$$\frac{\text{Intensity of aromatic protons } (I_A)}{\text{Intensity of total protons } (I_T)} = \frac{5m_1}{10m_1 + 9m_2} \quad (1)$$

Equation (1) is based on the fact that there are 10 protons in a PhMA unit and 9 protons in a VPD unit, and only PhMA contains 5 aromatic

protons, which are well separated from the rest of the protons. By substituting $m_2 = 1 - m_1$, the following equation was derived:

$$m_1 = 9I_A/5I_T - I_A \quad (2)$$

Integrated peak intensities were employed for this calculation. Here m_1 is the mole fraction of PhMA and $(1 - m_1)$ is that of VPD.

Based on Eq. (2), the mole fraction of PhMA was calculated by measuring the intensities of aromatic protons and the total protons from the spectra of all copolymer samples. Table 1 lists the values and the corresponding mole fractions of the monomeric units in the copolymer.

To ascertain copolymer kinetic behavior, a plot of the mole fraction of PhMA in the copolymer (m_1) versus that of the feed (M_1) was drawn. The curve (Fig. 4) indicates that the distribution of monomeric units is random.

To determine the copolymerization behavior, the reactivity ratios were calculated by the graphical methods of Fineman-Ross and Kelen-Tüdös.

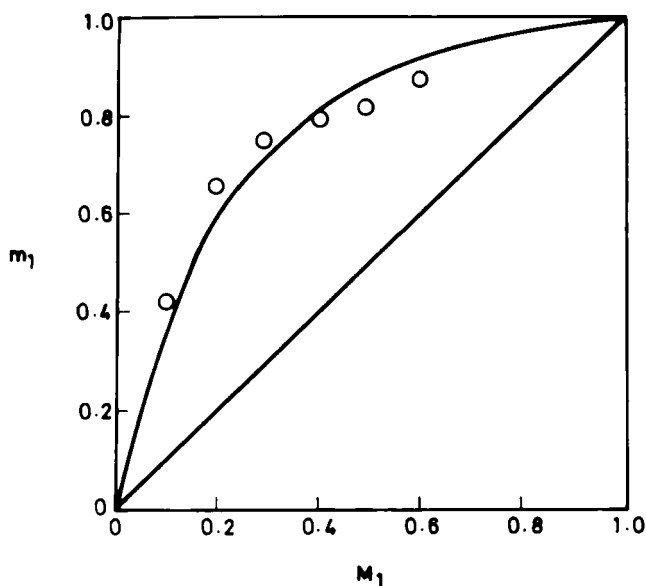


FIG. 4. Feed vs copolymer composition curve of phenyl methacrylate and *N*-vinyl-2-pyrrolidone.

Fineman and Ross linearized the Mayo–Lewis equation [13] as

$$G = r_1 F - r_2$$

where $G = X(Y - 1)/Y$ and $F = X^2/Y$. X and Y represent the mole ratios of monomers in the feed and the mole ratios of monomers in the copolymer, respectively. From the data of Table 1, the F-R plot (Fig. 5) was drawn between G and F . The ordinate intercept is $-r_2$ and the slope of the line is r_1 . The r_1 and r_2 values obtained were 4.19 ± 0.22 and 0.02 ± 0.11 , respectively. Kelen and Tüdös proposed a simple graphically linear evaluation method for the determination of reactivity ratios. The K-T equation is [14]

$$\eta = [r_1 + r_2/\alpha]\xi - r_2/\alpha$$

where $\eta = G/\alpha + F$ and $\xi = F/\alpha + F$. α is an arbitrary constant ($\alpha > 0$) which is calculated by

$$\alpha = F_m^{1/2} F_n^{1/2}$$

where F_m and F_n are the lowest and highest values of F , respectively. From the data in Table 2, the K-T plot was drawn by using η and ξ data; the r_1 and r_2/α values were obtained from the intercepts at $\xi = 1$ and $\xi = 0$, respectively. The r_1 and r_2 values obtained were 4.49 ± 1.27 and 0.05 ± 0.09 , respectively. The 95% confidence intervals were calculated according to the standard procedure given by Kelen–Tüdös [15] (Fig. 6).

The value of $1/r_1$ explains that the PhMA radical has a tendency to attack its own monomer rather than the VPD monomer, whereas the VPD radical prefers the PhMA monomer to the VPD monomer (i.e., the value of $1/r_2$ is higher than 1). This type of behavior is observed in styrene, methyl methacrylate [16], 2-carboxyphenyl acrylate [17], and glycidyl methacrylate [18] with VPD. The product of r_1 and r_2 remains less than 1, thus indicating that the system follows a random distribution of monomeric units. The high values of r_1 indicate that the probability of PhMA entering the copolymer chain is much higher than that of VPD, and the copolymer formed is therefore richer in PhMA units.

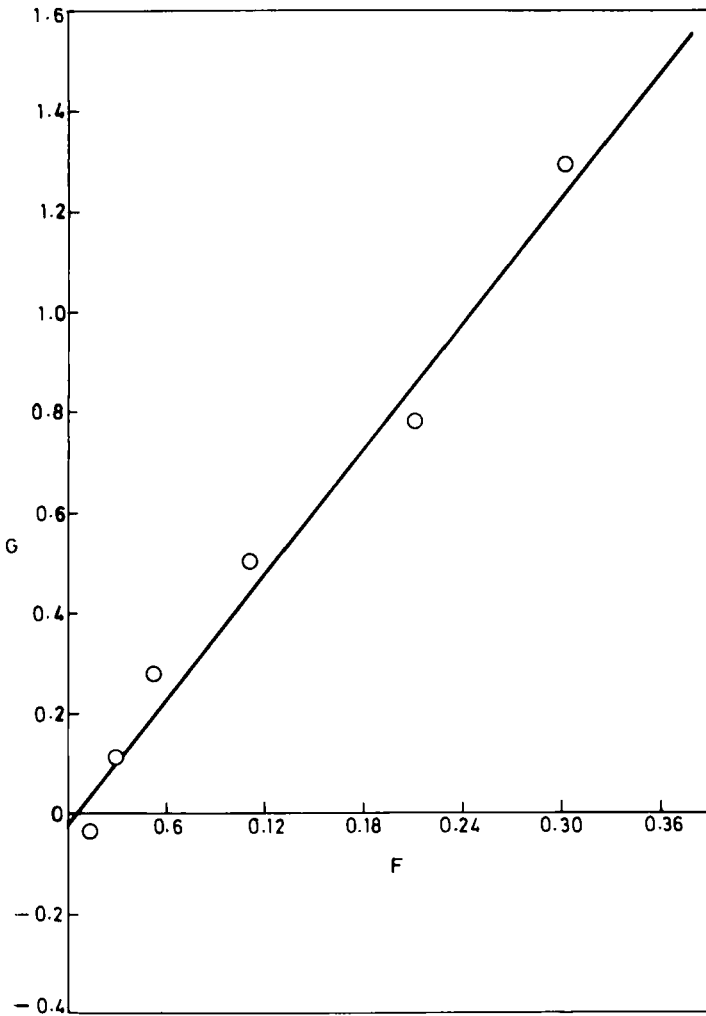


FIG. 5. Fineman-Ross plot.

TABLE 2. Fineman-Ross and Kelen-Tüdös Parameters^a

X	Y	G	F	ξ	η
0.0987	0.7382	-0.0350	0.0132	0.1714	-0.4549
0.2472	1.9308	0.1192	0.0316	0.3318	1.2495
0.4150	3.0469	0.2788	0.0565	0.4701	2.3185
0.6725	3.9261	0.5012	0.1152	0.6438	2.8013
0.9928	4.6722	0.7803	0.2110	0.7680	2.8407
1.5000	7.3056	1.2947	0.3080	0.8286	3.4831

^a $\alpha = 0.0631$.

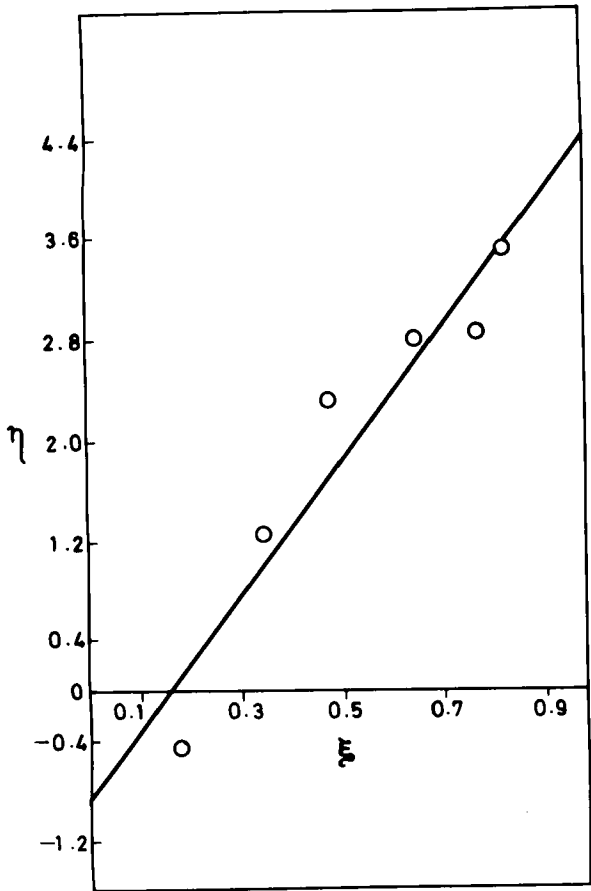


FIG. 6. Kelen-Tüdös plot.

CONCLUSION

Copolymers of phenyl methacrylate and *N*-vinyl-2-pyrrolidone were synthesized in solution by free radical polymerization. The identification of monomeric units in the copolymer was performed with FT-IR and proton decoupled ^{13}C -NMR spectroscopy. ^1H -NMR spectra were utilized to determine the copolymer composition. The reactivity ratios were calculated by both F-R and K-T methods, and the values obtained are in good agreement. The reactivity ratio values show that the copolymerization of phenyl methacrylate with *N*-vinyl-2-pyrrolidone yields random copolymers. The higher value of r_1 explains the tendency of the PhMA radical to react with its own monomer rather than the VPD monomer.

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