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PHENACYL METHACRYLATE AND N-VINYL-2-PYRROLIDONE COPOLYMERS: SYNTHESIS, CHARACTERIZATION, AND REACTIVITY RATIOS

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NOTE

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Key Words: Phenacyl Methacrylate, N-Vinyl-2-pyrrolidone, Copolymers, Characterization, Reactivity Ratios, Elemental Analysis, Thermogravimetric Analysis

ABSTRACT

The free radical copolymerization of phenacyl methacrylate (PAMA) and N-Vinyl-2-pyrrolidone (N-Vp) was carried out

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using 2,2'-azobisisobutyronitrile (AIBN), in 1,4-dioxane solution at 70°C. The polymers were characterized by FT-IR, ^{1}H- and ^{13}C-NMR spectroscopic methods. Solubility parameters, inherent viscosities, average molecular weight and densities of polymers were determined. Thermal properties of the homo- and copoly-mers were also studied by thermogravimetric analysis and differantial scanning calorimetry. The percentage composition of the copolymers were established by microelemental analysis. The copolymerization reactivity ratios were computed using the Fineman-Ross and Kelen-Tudos methods. The experimental data indicate random comonomer incorporation with a slightly alternating tendency.

INTRODUCTION

Functional polymers are employed as polymer supports and polymeric reagents for a wide range of chemical and biochemical applications, including chromatography peptide synthesis and biochemical and chemical catalysis [1].

Functional polymers are produced either by chemical modification of preformed nonfunctional polymers, or by direct (Co) polymerization of the desired functional monomers with suitably chosen structural and crosslinking monomers [2-4].

Ketone polymers are used as photodegradable packaging materials [5, 6] and photoresists for microlithography [7]. N-Vinyl-2-pyrrolidone (N-Vp) polymer has good properties such as biocompatability, low toxicity, and film-forming and adhesive characteristics [8-10].

In the classic terminal model of copolymerization, it has been suggested that, for a given pair of monomers, the instantaneous copolymer composition is a function of instantaneous feed only [11]. Monomer reactivity ratios are important quantitative values to predict the copolymer composition for any starting feed and to understand the kinetic and mechanistic aspects of copolymerization. It is known that monomer reactivity ratios are generally determined at low conversions (under 5%) [12-16].

The technique of thermogravimetric analysis (TGA) has been widely used in polymer characterization in thermal stability studies [17].

Previously [18], we reported the synthesis, characterization and polymerization of the new functional phenacyl methacrylate monomer.

The present paper deals mainly with the synthesis and characterization of six PAMA-N-Vp copolymers of different composition by free radical polymerization and the reactivity ratios determined by the Fineman-Ross (F-R) method [19] and Kelen-Tudos (K-T) method [20].

EXPERIMENTAL

Materials

Phenacyl methacrylate was prepared by the method reported in previous work [18]. N-Vinyl-2-pyrrolidone (Fluka) was distilled under reduced pressure before use. 2,2'-Azobisisobutyronitrile was recrystallized from a chloroform and petroleum ether mixture and dried in a vacuum oven for 24 hours. Chloroform, formic acid, n-heptane and 1,4-dioxane (Aldrich) were used as received. Methanol and ethanol were purified by distillation before use.

Copolymerization

Known mixtures of PAMA (2), N-Vp (1), 1% (total weight of monomers) AIBN and 1,4-dioxane (monomer/solvent:1/3, w/v) were placed in a standard reaction tube, and the mixture was flushed with oxygen-free argon for 10 minutes. The tube was then tightly sealed and immersed in a thermostatic water both at 70°C. The reaction time was selected to give conversions < 10%, in order to satisfy the differential copolymerization equation. The conversions were controlled and determined by the gravimetric measurements. The copolymers were precipitated in an excess of ethanol and filtered off. They were dissolved in 1,4-dioxane and precipitated in the same nonsolvent to ensure the complete removal of residual monomers. It was then dried in a vacuum oven at 40°C for 24 hours. The copolymers were soluble in chloroform, tetrahydrofuran and 1,4-dioxane, but insoluble in nonpolar and hydroxy-group containing solvent (benzene, n-hexane, methanol, and ethanol).

Measurements

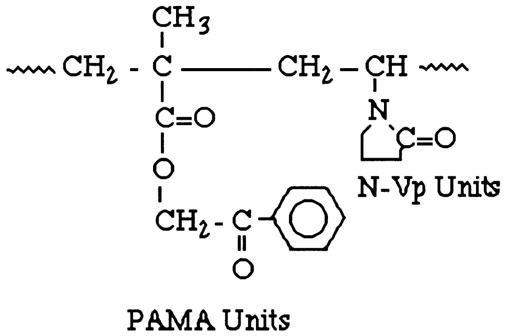
The FT-IR spectra of the copolymers were recorded with a Mattson 1000 FT-IR spectrometer. ^{1}H- and ^{13}C-NMR spectra of the copolymers were recorded in $CDCl_3$ with tetramethylsilane as the internal standard using a Jeol FX-90 Q NMR spectrometer. Microelemental analyses were carried out by a LECO-932 microanalyzer. Molecular mass [59% (by mol) PAMA] was obtained by gel permeation chromatography and the thermal properties were studied using Shimadzu DSC-50 instrument and TGA-50 thermobalance.

RESULTS AND DISCUSSION

Six copolymers of PAMA-N-Vp having different copolymer compositions, were prepared according to the experimental details given in Table 1, using AIBN as initiator in 1,4-dioxane solution under argon atmosphere.

Characterization of Poly(PAMA-co-N-Vp)

The constituent monomeric units of the copolymer are as follows:



The FT-IR spectra show the most characteristic absorption bands: Absorption at 1735 cm^{-1} was due to the ester groups of PAMA units. The peak

TABLE 1. Copolymerization of PAMA-N-Vp, Copolymer Composition of Poly(PAMA-co-N-Vp) by Elemental Analysis

	Feed Composition in Mole Fraction			Elemental Analysis			Copolymer Composition in Mole Fraction	
Sample	N-Vp (M_1)	PAMA (M_2)	Conversion (%)	C %	H %	N %	N-Vp (m_1)	PAMA (m_2)
1	0.10	0.90	7.95	71.85	5.88	0.59	0.08	0.92
2	0.25	0.75	8.35	70.44	5.31	1.15	0.16	0.84
3	0.40	0.60	8.67	71.11	5.75	2.16	0.28	0.72
4	0.50	0.50	7.80	68.46	5.39	3.37	0.41	0.59
5	0.60	0.40	8.27	70.61	5.54	4.74	0.53	0.47
6	0.75	0.25	8.91	68.69	5.53	5.72	0.61	0.39

Temperature : 70± 1°C; Solvent:1,4-Dioxane; Initiator : 2,2'-azobisisobutyronitrile 1 % (total weight of monomers). Nonsolvent for precipitation : Ethanol.

at 1690 cm^{-1} corresponds to the carbonyl group of N-Vp and PAMA units. The bands at 770 cm^{-1} and 710 cm^{-1} correspond to the bonding vibrations of C-H and C…C, respectively which also explains the monosubstituted aromatic nature of PAMA unit.

The ^{13}C-NMR spectrum of a copolymer is shown in Figure 1. The ^{13}C-NMR spectra of the copolymers have the characteristic peaks of the monomeric units. The ester and keto carbonyl of PAMA unit gave lines at 175.5 and 192.2 ppm. Quaternary carbon of the phenyl ring gave a less intense peak at 135.1 ppm and ortho, meta and para carbons of the phenyl ring gave more intense peaks at 127.0, 128.8, and 133.7 ppm, respectively. The keto carbonyl of N-Vp appeared with the keto carbonyl of PAMA unit at 177.4 ppm. A distinct peak appears at 66.05 ppm for the $-OCH_2$ carbon peak corresponding to the PAMA unit. Another distinct peak appears at 45.7-46.2 ppm for the -CH-(methine) carbon peak corresponding to the N-Vp unit. The less intense peak at 18.0 ppm is caused by $-CH_3$ group of PAMA unit. The chemical shift differences of backbone methy-lenes of PAMA and N-Vp unit result in a broad peak around 51.1-53.2 ppm.

The disappearance of 128.0 and 132.0 ppm peaks (Vinylic carbons) also explains the polymerization of both monomeric units.

The ^{1}H-NMR spectrum of a copolymer is shown in Figure 2. ^{1}H-NMR spectra of copolymers show resonances at 7.1-7.6 ppm for meta and para protons, and 7.6-8.0 ppm for ortho protons to phenyl ring of PAMA units. 5.0-5.7 ppm for methylene protons of phenacyl group. The methylene protons of the

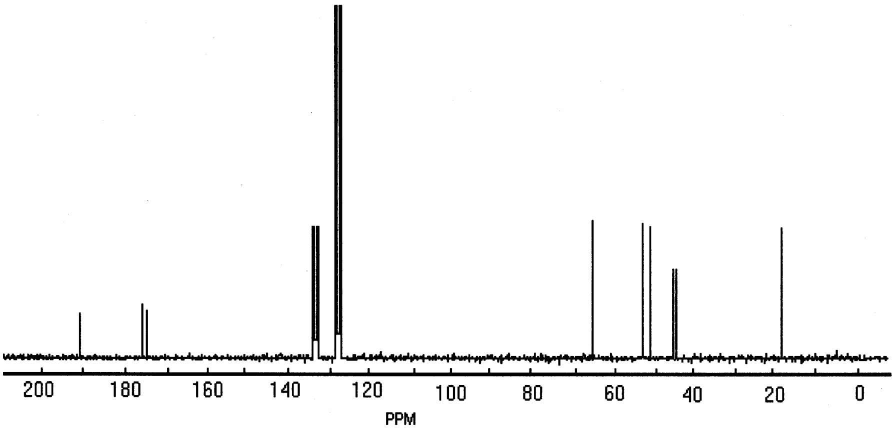


Figure 1. ^{13}C-NMR spectrum of Poly(PAMA-co-N-Vp) 59% (by mol) PAMA unit.

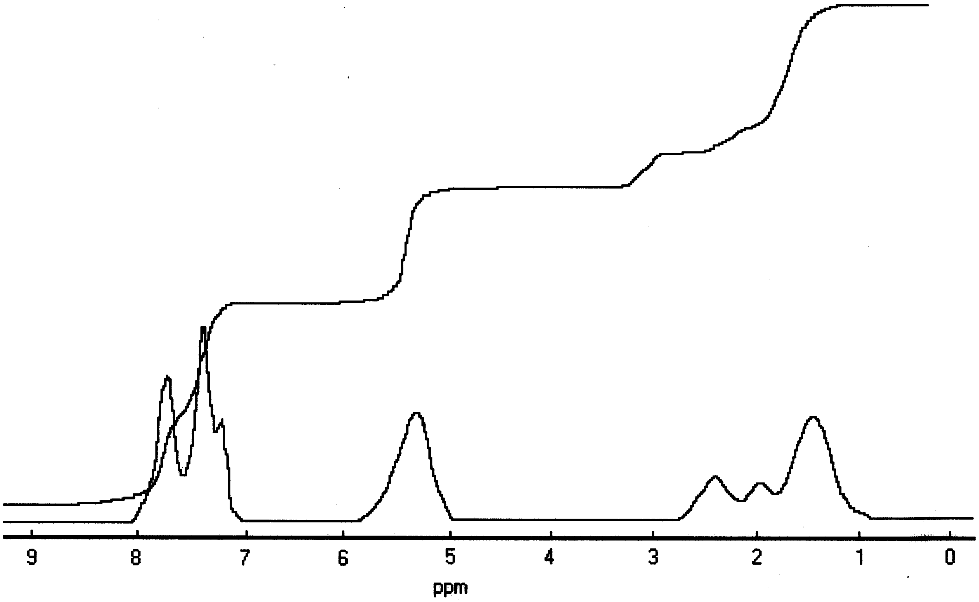


Figure 2. ^{1}H-NMR spectrum of Poly(PAMA-co-N-Vp) 59% (by mol) PAMA unit.

polymer backbone appear at 1.8-2.2 ppm. The methine protons of the polymer backbone appear at 2.2-2.7 ppm, respectively. The signals at 1.1-1.8 ppm are due to a methyl group of PAMA.

The GPC system calibrated with polystyrene in tetrahydrofuran (THF) showed that the weight-average molecular mass of the PAMA-co-N-Vp (59% PAMA) was 24640 (Polydispersity index, PDI : 1.96).

The Polydispersity index of the PAMA-co-N-Vp (59% PAMA) are close to 2.0. The theoretical values of PDI for polymers produced via radical combination and disproportionation are 1.5 and 2.0, respectively [21, 22]. The value of PDI in copolymerization is also known to depend on chain termination in the same way as in homopolymerization [23, 24]. The value of PDI is 1.96 for the copolymer, suggests that there is a strong tendency for radical recom-bination to terminate the polymeric chains.

Physical Parameters

Some physical parameters like densities (d), solubility parameters (δ) and inherent viscosity (η_{inh}) of polymers were determined in the study. The density of the polymers were determined experimentally by the floatation method

TABLE 2. Some Physical Parameters of Polymers

Copolymer	d (g/cm^3)	η_{inh} (d/g)	δ (cal/cm^3)$^{1/2}$
1	1.30	-	10.20
2	1.29	0.26	10.33
3	1.27	-	10.54
4	1.24	0.23	10.66
5	1.20	-	10.70
6	1.19	0.21	10.96
Poly (PAMA)	1.35	-	9.90
Poly (N-Vp)	1.15	-	11.34

[25] at 25°C using mixtures of methanol and formic acid as the floating agent, and lots of glass beads of known densities. The solubility parameter of the polymers were determined by using titration method [25] at 25°C from solubility test using 1,4-dioxane as solvent, n-heptane and ethanol as non-solvent. The inherent viscosity of 1% (w/v) solution of the polymers in 1,4-dioxane were determined at 30°C using an Ubbelohde viscometer. These values are shown in Table 2.

While the mole fraction of N-Vp in the copolymer increased, density values decreased. This result showed that PAMA units increased chain stiffness and better packing of polymer segments more than N-Vp units. This may be due to two polar groups such as ester and keton containing of PAMA. Increasing of PAMA fraction in the copolymer increased η_{inh} values of the copolymer are found. This is probable, since molecular mass increased with increasing of PAMA fraction and/or PAMA fraction increased flow resistance of the copolymer. However solubilty parameter values of the copolymers are increasing with increasing N-Vp fraction in the copolymer. Similar results have been reported in the literature [26].

Thermal Analysis

Differential Scanning Calorimetry (DSC) was performed at a heating rate of 20°C/min under nitrogen atmosphere. A plot of copolymer composition versus glass transition temperature of the copolymer is shown in Figure 3.

Tg values of poly (PAMA) and poly (N-Vp) obtained under the same conditions as the copolymers were found at 105 and 85°C, respectively. Tg val-

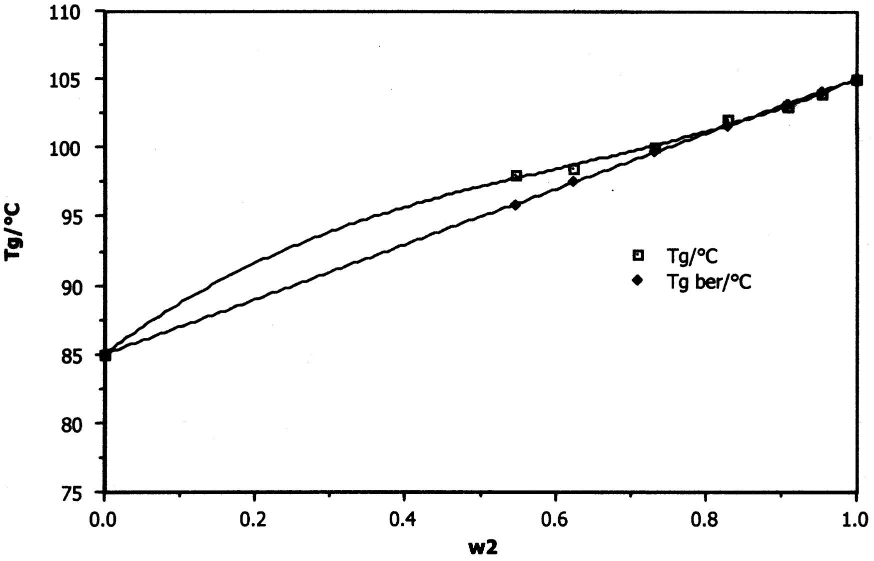


Figure 3. Plot of glass transition temperature vs. copolymer composition: w_2 = weight fraction of PAMA in copolymer.

ues of all the copolymers are between those of the homopolymers of the same monomers. When the mol fraction of PAMA in the copolymer changed from 0.92 to 0.39, Tg values changed from 104 to 98°C. Chain flexibility of Poly (N-Vp) is higher than that of Poly (PAMA). This means that the free volume in Poly (N-Vp) is higher than that in Poly (PAMA). Therefore, an increase of Tg as a function of the number of PAMA units in the copolymer is an expected result.

The thermal stability of the homopolymers and copolymers were studied by programmed thermogravimetric analysis over a temperature range from 10 at 500°C under nitrogen atmosphere. The TGA curves of poly(PAMA), poly(N-Vp) and copolymer (1, 3, 4) are shown in Figure 4. In poly(PAMA), first degradation occurs at 207-300°C and weight loss was about 67% in this region. The second degradation occurs 300-410°C with weight loss of 31.5%. In poly (N-Vp), the first and major degradation starts around 250°C, and complete degradation takes place around 475°C. Copoly (PAMA-N-Vp)s, show a similar thermal behavior like that of the homopolymers.

Determination of the Monomer Reactivity Ratios

Monomer reactivity ratio values for the copolymerization of N-Vp and PAMA were determined from the monomer feed ratios and the copolymer com-

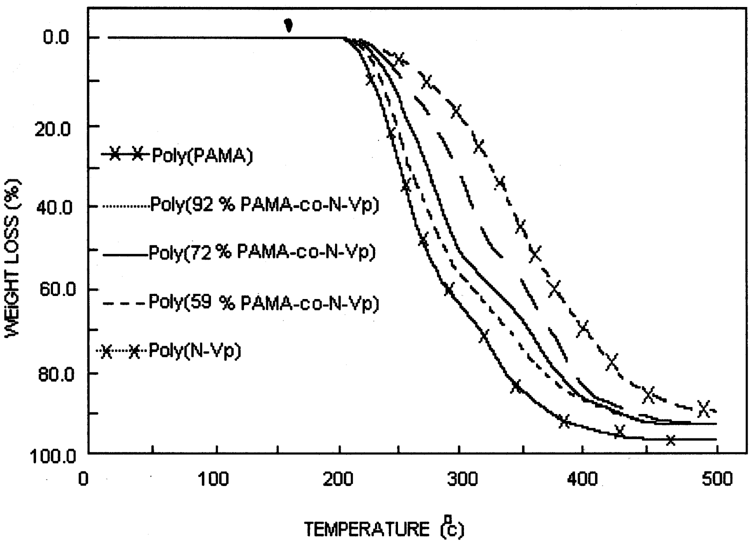


Figure 4. TGA curves for poly(PAMA), poly (N-Vp) and copoly(PAMA-N-Vp)s at 10°C/min.

position. The Finemann-Ross (F-R) and Kelen-Tudos (K-T) methods were used to determine the monomer reactivity ratios. F-R and K-T parameters are summarized in Table 3.

The plot of the mol fraction of PAMA in feed vs. that of PAMA in copolymer is shown in Figure 5. There is no azeotropic composition and the incorporation of PAMA is always higher than N-Vp in all the copolymers

Copolymerization reactivity ratios of N-Vp and PAMA were determined using the data given in Table 3. by the F-R and K-T methods. The equations used are:

$G = r_1F - r_2$ (F-R equation)

$\eta = r_1\varepsilon - r_2/\alpha\ (1-\varepsilon)$ (K-T equation)

r_1 and r_2 are the reactivity ratios relating to the monomers N-Vp (monomer 1) and PAMA (monomer 2), respectively. G and F are F-R parameters, η, ε and α are K-T parameters. The plot of G vs. F will give a straight line with r_1 as the slope and $-r_2$ as the intercept (Figure 6).

η, ε, and α are mathematical functions of G and F as defined and entered in Table 3. for K-T method, respectively. The plot of η vs. ε also shown in Figure

TABLE 3. Copolymerization Reactivity Ratios of Poly(PAMA-co-N-Vp), by the Fineman-Ross and Kelen-Tudos Methods

Sample	$x = \frac{M_1}{M_2}$	$y = \frac{m_1}{m_2}$	$G = \frac{x(y-1)}{y}$	$F = \frac{x^2}{y}$	$\eta = \frac{G}{\alpha + F}$	$\varepsilon = \frac{F}{\alpha + F}$
1	0.111	0.090	-1.125	0.137	-1.188	0.145
2	0.333	0.185	-1.473	0.602	-1.044	0.427
3	0.667	0.380	-1.086	1.168	-0.459	0.591
4	1.000	0.671	-0.490	1.490	-0.277	0.648
5	1.500	1.108	0.147	2.030	0.052	0.715
6	3.000	1.526	1.034	5.897	0.154	0.879

$\alpha = \sqrt{F_{min.} F_{max.}} = 0.810$

M_1 = Mole Fraction of N-Vp in Feed

M_2 = Mole Fraction of PAMA in Feed

m_1 = Mole Fraction of N-Vp in Copolymer

m_2 = Mole Fraction of PAMA in Copolymer

7. In the K-T plots, r_1 will be obtained as the intercept at $\varepsilon = 1$ and $-r_2/\alpha$ will be obtained as the intercept at $\varepsilon = 0$.

The Fineman-Ross method yielded reactivity ratios for N-Vp and PAMA of $r_{N\text{-}Vp} = 0.42 \pm 0.030$ and $r_{PAMA} = 1.29 \pm 0.046$, respectively; $r_{N\text{-}Vp}$ x r_{PAMA} =

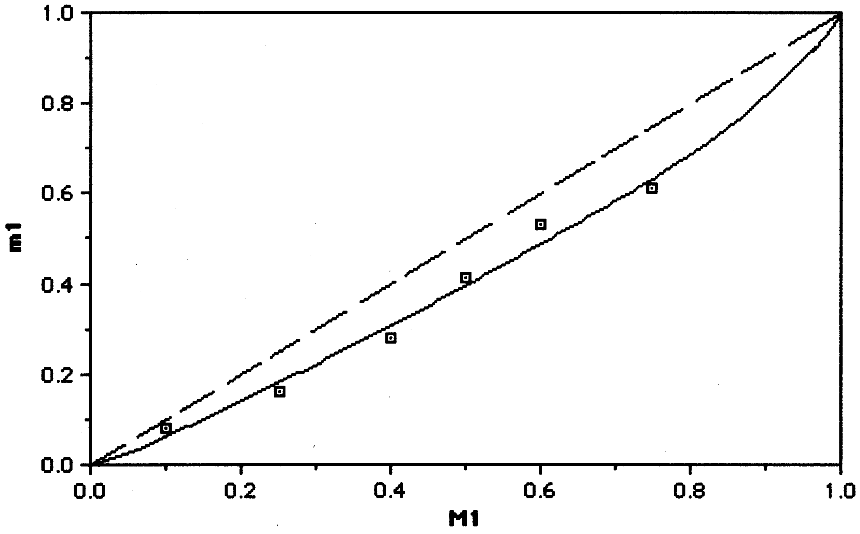


Figure 5. Plot of mole fraction of N-Vp in copolymer (m_1) by elemental analysis vs. mole fraction of N-Vp in feed (M_1).

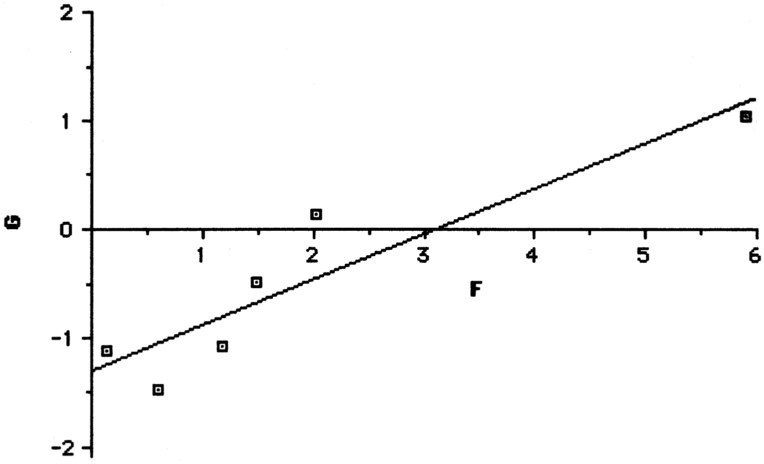


Figure 6. Fineman-Ross plot.

0.542. The Kelen-T¸dˆs method gave reactivity ratios of $r_{N\text{-}Vp} = 0.42 \pm 0.060$ and $r_{PAMA} = 1.33 \pm 0.015$, respectively; $r_{N\text{-}Vp} \times r_{PAMA} = 0.559$.

The higher r_2 value of PAMA confirms the higher reactivity of PAMA than of N-Vp, and the copolymer sequence will be of random nature with more PAMA units. This may be because the PAMA monomer is more reactive towards the growing chain regardless of whether the radical end was derived from PAMA or N-Vp.

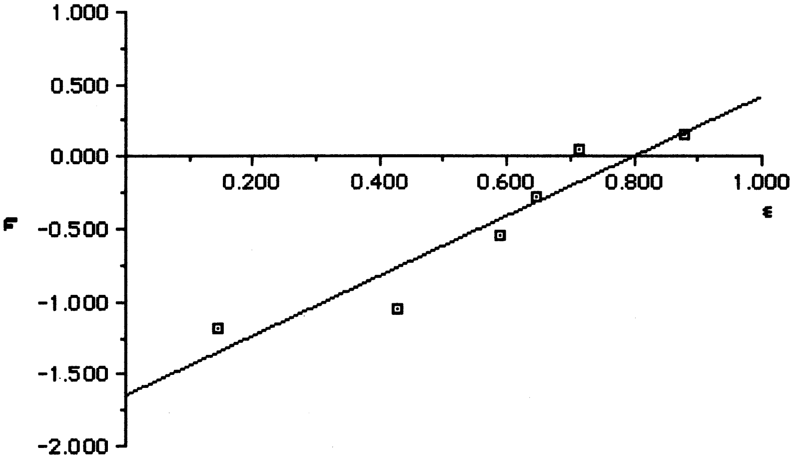


Figure 7. Kelen-Tudos plot.

The correlation coefficients for F-R and K-T plots are 0.92 and 0.94 for elemental analysis data, respectively.

CONCLUSION

Six copolymers of N-Vp-PAMA were prepared using AIBN as catalyst in 1,4-dioxane solution at 70°C. IR, ^{1}H- and ^{13}C-NMR spectroscopy reveals the presence of both monomeric constituents in the copolymer structure. The copolymer compositions were determined by the elemental analyses. The reactivity ratios obtained by the F-R and K-T methods agree well with each other $r_{N\text{-}Vp} = 0.42$ and $r_{PAMA} = 1.31$ indicates that PAMA is more reactive in the polymerization and the copolymer structure will be of random nature. The feed vs. copolymer composition curve also confirm $r_{N\text{-}Vp} < 1$ and $r_{PAMA} > 1$. Thermal stability of the polymer are also good.

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