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Copolymers of Phenoxyethyl Methacrylate with N-Vinyl-2-pyrrolidone: Synthesis, Characterization and Reactivity Ratios

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Copolymers of Phenoxyethyl Methacrylate with N-Vinyl-2-pyrrolidone: Synthesis, Characterization and Reactivity Ratios

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The free radical copolymerization of phenoxyethyl methacrylate (POEMA) and N-vinyl-2-pyrrolidone (Vp) was carried out using α,α' -azobisisobutyronitrile (AIBN) in 2-butanone solution at $333\text{ K} \pm 1$. The copolymers were characterized by FTIR, ¹H-NMR and ¹³C-NMR spectroscopic methods. Thermal properties of the copolymers were also studied by thermogravimetric analysis (TGA). The composition of the copolymers was established by ¹H-NMR analysis. The monomer reactivity ratios were computed using the Fineman–Ross (F-R) and Kelen–Tüdös (K-T) methods. These parameters were also estimated using a non-linear computational fitting procedure, known as reactivity ratios error in variable model (RREVM). The mean sequence lengths determination indicates that the copolymer was random in nature.

Keywords: phenoxyethylmethacrylate; N-vinyl-2pyrrolidone; copolymers; characterization; monomer reactivity ratios; thermogravimetric analysis

1 Introduction

The study of structure-property relationship exhibited by vinyl monomers in their radical copolymerization is very important (1). Functional polymers are employed as polymer supports and polymeric reagents for a wide range of chemical and biochemical applications (2). They are produced either by chemical modification of preformed nonfunctional polymers or by direct copolymerization of the functional monomers with desired physico mechanical properties (3).

Polymers are an excellent replacement for glass due to their inherent properties of being lightweight, has optical clarity and impact resistance. Acrylates and methacrylates of phenoxy polymers are used coating materials for optical fiber and UV curable adhesive film (4). They are also used as optical data storage materials (5). Copolymerization of such methacrylates with N-vinyl-2-pyrrolidone which has good properties such as low toxicity, film forming and

adhesive characteristics (6–8) provide a simple route for preparation of optical materials that possess good mechanical properties.

The copolymerizability of vinyl monomers with a bulky substituent that also carries a highly electronegative atom like oxygen is not discussed as yet. The possible effect of such a pendant group as the backbone with respect to reactivity is significant. Due to the presence of electronegative atom, the higher reactivity of POEMA is expected when compared to Vp.

The present paper deals mainly with the synthesis and characterization of copolymers of phenoxyethyl methacrylate (POEMA) with N-vinyl-2-pyrrolidone (Vp) of different compositions by free radical polymerization and the monomer reactivity ratios were determined by the Fineman–Ross (F-R) (9), Kelen–Tüdös (K-T) (10) and using an algorithm known as reactivity ratios error in variable model (RREVM) methods (11, 12).

2 Experimental

2.1 Materials

Phenoxyethyl methacrylate (ALDRICH) and N-vinyl-2-pyrrolidone (Fluka) were purified by vacuum distillation.

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α,α' -azobisisobutyronitrile (AIBN) was recrystallized twice from methanol, 2-butanone, methanol and chloroform were purified by standard procedures.

2.2 Copolymerization

Copolymerization reactions were carried out in 2-butanone solutions (50 ml) in glass vessels with a inlet and outlet. The reaction tube containing the required amount of monomers (total concentration of the comonomer was 1.5 mol L^{-1}) and initiator (1% total mass of monomer) dissolved in 2-butanone was deaerated by flushing with pure, dry nitrogen gas for 30 min prior to immersion in a waterbath kept at a temp of 333 K. The comonomer mixtures in ratios ranging from POEMA/Vp = 20/80 to 80/20 were prepared. The reaction was carried out for 3–5 h to give conversion <10% in order to satisfy the differential copolymerization equation. The copolymers were precipitated in an excess of cold methanol. The pure white powdery mass which separated out was dissolved in chloroform and then reprecipitated in methanol to ensure the complete removal of residual monomers. It was then dried in vacuum oven at 313 K for 24 h.

2.3 Measurements

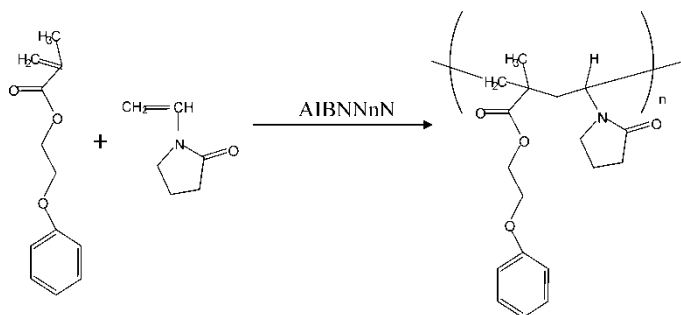
The FT-IR spectra of the copolymers were recorded on a Perkin–Elmer paragon 1000 Fourier Transform IR (FTIR) spectrophotometer using the potassium bromide pellet technique in the range $500\text{--}4000 \text{ cm}^{-1}$. The $^1\text{H-NMR}$ spectra of the copolymers were recorded on a Jeol GS X–400 spectrometer operating at 400 MHz at room temperature as 15–20% (W/V) solution in CDCl_3 . Tetramethyl silane (TMS) was the internal standard. $^1\text{H-NMR}$ spectra were obtained using a spectral width of 5000 Hz, an acquisition time of 2 sec and pulse delay of 3.3 sec. Spectra were generally obtained after accumulating 32 scans. The proton noise decoupled $^{13}\text{C-NMR}$ spectra of the copolymers were also recorded using a Jeol GSX–400 spectrometer operating at 100 MHz. The protons were decoupled by broad-band irradiation. Thermogravimetric analysis (TGA) was performed using a Mettler TA 3000 thermal analyzer. Thermograms were recorded with 5–10 mg of samples at a heating rate of 293 K/min under nitrogen atmosphere. Nitrogen flow rate 70 ml/min .

3 Results and Discussion

3.1 Characterization of (POEMA-co-Vp) Copolymer

Scheme 1 shows the monomeric constituent of the copolymer.

The FT-IR spectra in Figure 1 shows the most characteristic absorption at 1728 cm^{-1} due to the ester group of POEMA unit. The peak at 1688 cm^{-1} corresponds to the carbonyl group of the Vp unit. The bands at 752 cm^{-1} and 688 cm^{-1} correspond to the bending vibrations of C-H and



Sch. 1. Monomeric constituent of the copolymer.

C-C, respectively. The peaks at 3450 and 2932 cm^{-1} are due to aromatic and aliphatic C-H stretching, respectively. The aromatic skeletal vibrations (C=C) are observed between $1490 \text{ cm}^{-1}\text{--}1600 \text{ cm}^{-1}$. The band at 1147 cm^{-1} may be assigned to ester C-O-C stretching. The IR spectrum of carbonyl band was more sensitive to copolymer composition, position and shape of the carbonyl band in the IR spectra vary with the copolymer composition (13).

The $^{13}\text{C-NMR}$ spectrum of the copolymer is shown in Figure 2. The spectrum shows the characteristic peaks of the two monomeric units. The ester carbonyl of POEMA unit gave the lines at 176.4 and 177.4 ppm. Ortho, meta and para carbons of phenyl ring gave more intense peaks at 129.4, 120.9 and 114.4 ppm, respectively. The keto carbonyl of Vp appeared with the keto carbonyl of POEMA unit at 158.3 ppm. A distinct peak appears at 67.1 ppm for -OCH₂ carbon peak corresponding to the POEMA unit. Another distinct peak appears at 65.1 ppm for the -CH (methane) carbon peak corresponding to the Vp unit.

The $^1\text{H-NMR}$ spectrum of the copolymer is shown in Figure 3. The resonance signals between 7.4–7.8 ppm are due to aromatic protons and the signals at 4.2 and 4.4 ppm are due to methyleneoxy protons. The γ -methylene and methane protons of Vp unit shows signals at 2.8–3.4 ppm. While the signals at 0.8–1.4 ppm and the multiple between 1.6–2.4 ppm are due to methylene and backbone protons of POEMA and Vp. The phenyl group in $^1\text{H-NMR}$ spectrum of poly(POEMA-co-Vp) is very sensitive with the variation of copolymer composition.

3.2 Determination of the Monomer Reactivity Ratios (MRR)

Monomer reactivity ratios were determined by the least squares method according to Fineman and Ross (8) or Kelen–Tudös (9). It is necessary to take into account that these linear methods do not consider the implicit error in the variables involved for the determination of MRR. Nevertheless, this kind of method is a powerful tool as a first approximation, to obtain MRR. For this reason, these days non-linear methods are most commonly used. These methods are based on the statistically valid error-in-variable

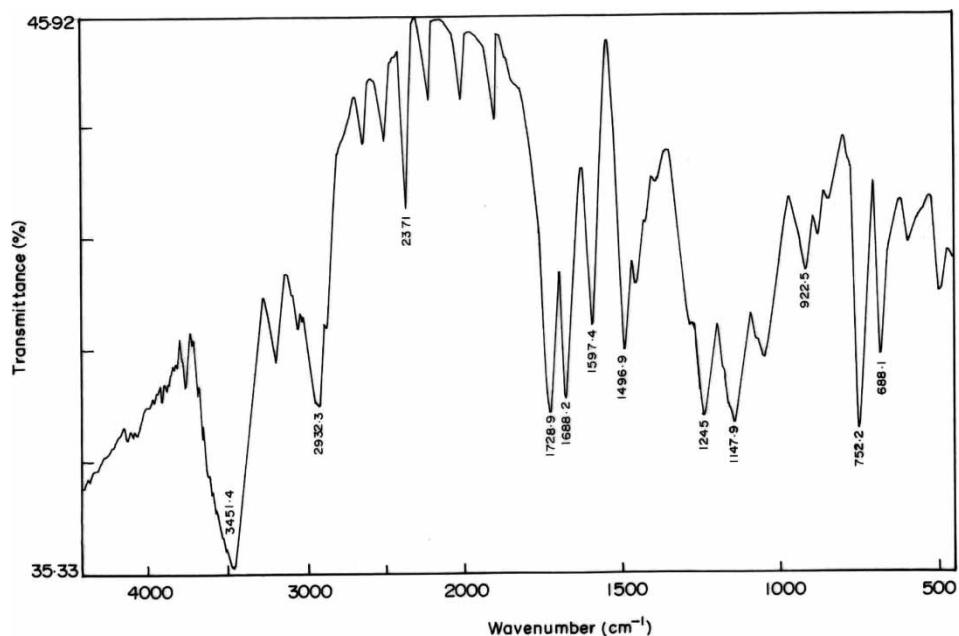


Fig. 1. FT-IR of (POEMA-co-Vp) copolymer (0.35 : 0.65).

model (EVM) (12, 14, 15). These methods allow us to take accurately into account all the sources of experimental error. Likewise, the non-linear computational methods needs, as starting values, good initial monomer reactivity ratios, although these values come from straight line

intersection methods such as those of Fineman and Ross (8) and Kelen-Tudös (9) which could be considered as statistically invalid (12, 14, 16).

The composition of the copolymers was determined from the corresponding $^1\text{H-NMR}$ spectra. The mole fraction of

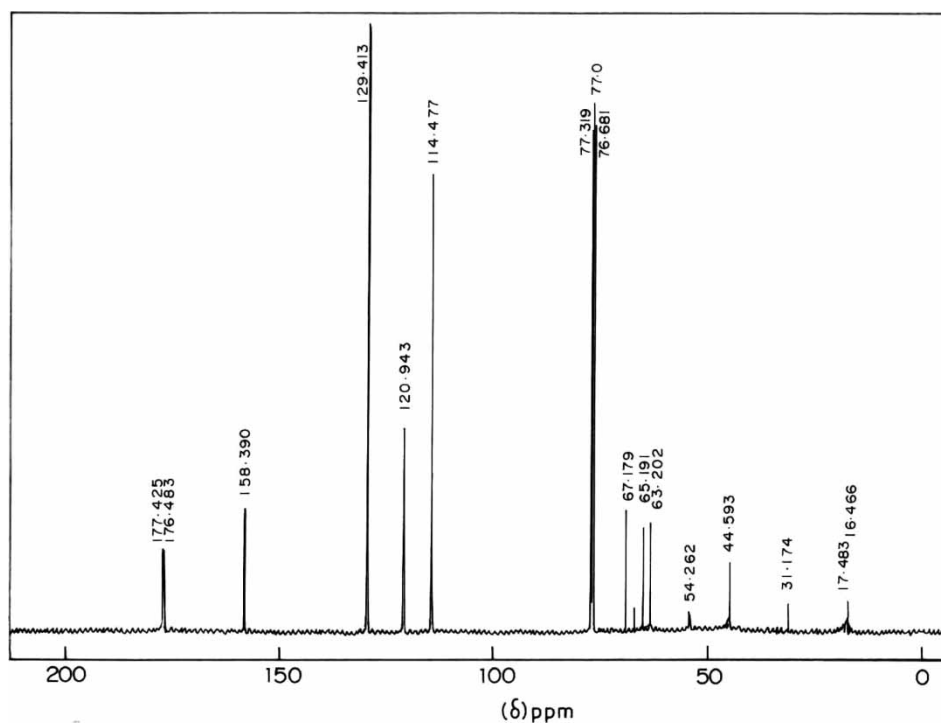


Fig. 2. $^{13}\text{C-NMR}$ spectrum of (POEMA-co-Vp) copolymer (0.50 : 0.50).

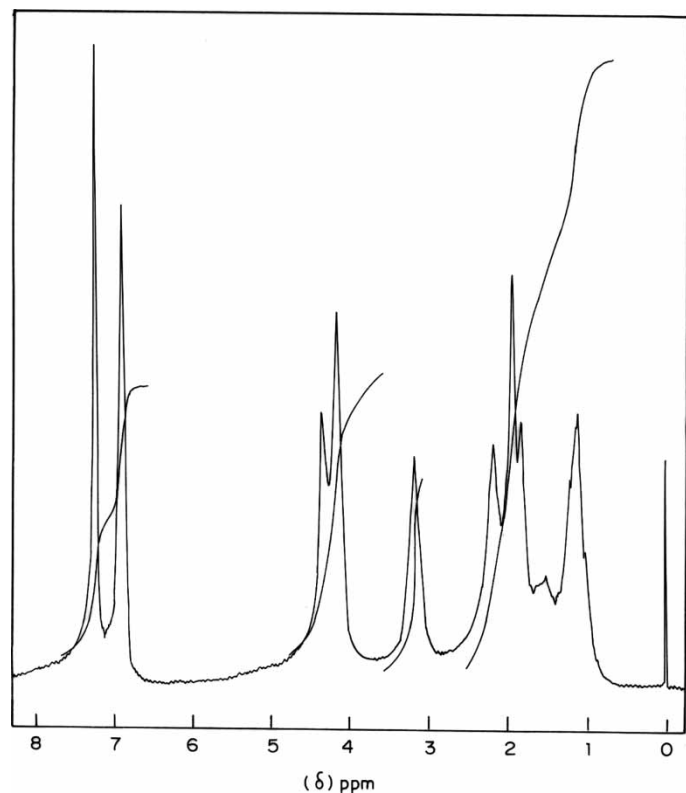


Fig. 3. $^1\text{H-NMR}$ spectrum of (POEMA-co-Vp) copolymer (0.50 : 0.50).

POEMA in the copolymer chain was determined from the ratio of the integrated intensities of the aromatic protons. Protons of POEMA to those of the total aliphatic protons of POEMA and Vp units.

$$C = \frac{\text{Intensities of aromatic protons of POEMA } (I_A)}{\text{Intensities of total aliphatic protons } (I_a)} \quad (1)$$

$$C = \frac{5m_1}{9m_1 + 9(1 - m_1)} \quad (2)$$

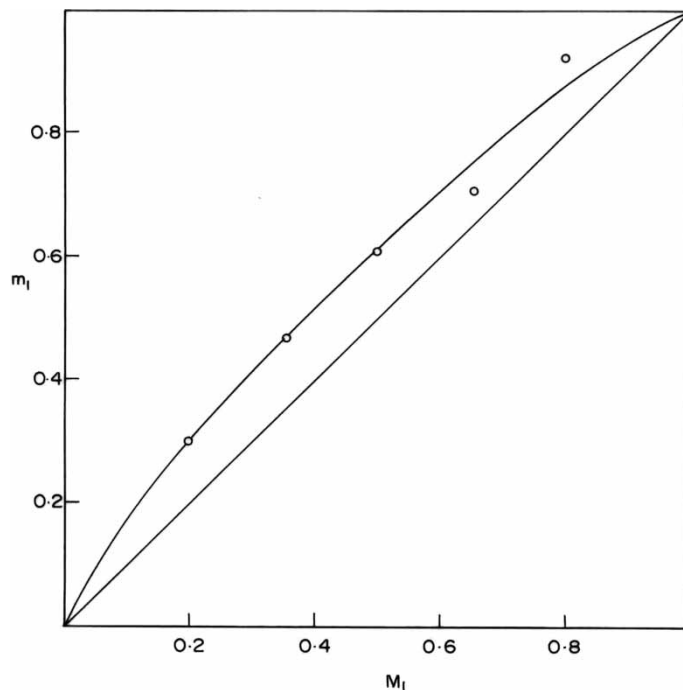


Fig. 4. Composition curves of (POEMA-co-Vp) copolymer.

On simplification,

$$m_1 = \frac{9C}{5}$$

Based on the above equation, the mole fraction of POEMA in the copolymer system was determined. The value of 'C' and the corresponding mole fractions of POEMA in the copolymer are presented in Table 1. A plot of mole fraction of POEMA in feed (m_1) against the composition in the copolymer (M_1) is shown in Figure 4. There is no azeotropic copolymer composition.

From the monomer feed ratios and copolymer composition, the reactivity ratios of POEMA and Vp were determined by F-R, K-T and RREVM (Figures 5 (a, b and c) and they are presented in Table 2. Traditionally a number of linearization

Table 1. Low conversion copolymerization data of (POEMA-co-Vp)

S. no.	Feed composition in mole fraction		Percentage of conversion	Intensity of aromatic protons I_A	Intensity of aliphatic protons I_a	$C = I_A/I_a$	Copolymer composition in mole fraction	
	M_1	M_2					dM_1	dM_2
1	0.20	0.80	8.2	0.210	1.312	0.162	0.292	0.708
2	0.35	0.65	3.3	0.327	1.262	0.259	0.466	0.534
3	0.50	0.50	6.4	0.499	1.479	0.337	0.607	0.393
4	0.65	0.35	3.8	0.666	1.707	0.390	0.702	0.298
5	0.80	0.20	8.7	1.634	3.194	0.512	0.921	0.079

Solvent: 2-butanone, temperature $333 \text{ K} \pm 1$.
Initiator: AIBN (1% mass of the monomers).

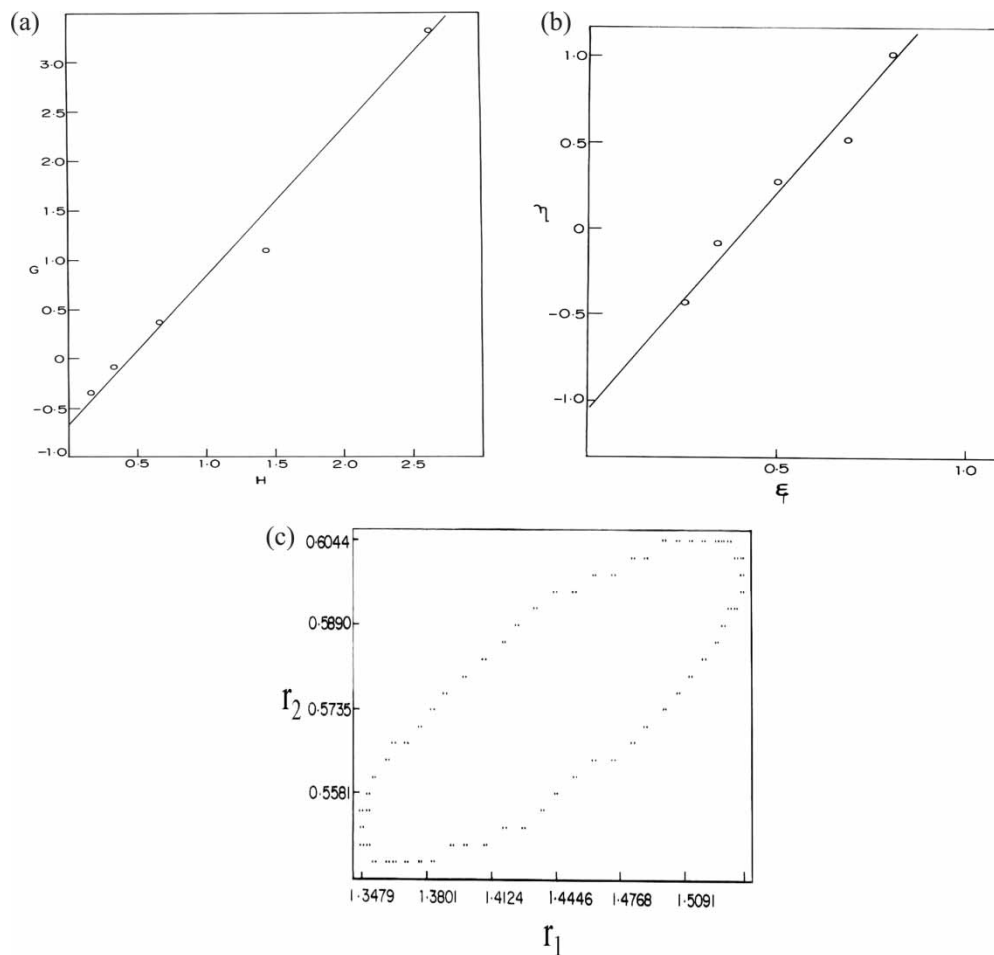


Fig. 5. (a) F-R plot for the POEMA-co-Vp copolymer system; (b) K-T Plot for POEMA-co-Vp copolymer system; (c) RREVM plot for POEMA-co-Vp copolymer system.

Table 2. F-R and K-T parameters of (POEMA-co-Vp) copolymer

S. no.	$X = M_1/M_2$	$y = dm_1/dm_2$	$G = X(y - 1)/y$	$F = X^2/y$	$\eta = G/\alpha + F$	$\xi = F/\alpha + F$
1	0.2500	0.4130	-0.3553	0.1513	-0.4530	0.1929
2	0.5385	0.8719	-0.0791	0.3325	-0.0819	0.3444
3	1.0000	1.5464	0.3533	0.6466	0.2761	0.5053
4	1.8571	2.3534	1.0679	1.4654	0.5089	0.6983
5	4.0000	6.0422	3.3790	2.6480	1.0173	0.8070

Fineman-Ross equation: $G = Fr_1 - r_2$. Kelen-Tudós: $\eta = (r_1 + (r_2/\alpha))\xi - r_2/\alpha$, $\alpha = (F_1/F_h)$ where F_1 and F_h are the lowest and highest values of F , respectively.

methods have been employed for the determination of monomer reactivity ratios. The values obtained by these methods are not accurate. To obtain correct values of monomer reactivity ratios, currently, non-linear methods are employed. Notable among them is the non-linear error-invariable model (EVM) method. The values of r_1 and r_2 by various methods are shown in Table 3, the higher r_1 value

Table 3. Comparison of reactivity ratios by various method for (POEMA-co-Vp) copolymer

Methods	r_1	r_2	$1/r_1$	$1/r_2$	$r_1 \cdot r_2$
F-R	1.4	0.66	0.71	1.51	0.924
K-T	1.52	0.67	0.66	1.49	1.018
RREVM	1.44	0.57	0.69	1.75	0.820

Table 4. Mean sequence lengths in (POEMA-co-Vp) copolymerization

Mole percentage of V _P in feed, M ₂	\bar{l}_1	\bar{l}_2	$\bar{l}_1 : \bar{l}_2$	Distribution
100				VP
80	1.34	3.6	1:3	PVpVpVpP
65	1.73	2.22	1:1	PVpP
50	2.37	1.6	2:1	PPVpPP
35	3.54	1.35	3:1	PPPVpPPP
20	6.48	1.16	6:1	PPPPPVpPPPPP
0				P

of POEMA confirms the higher reactivity of POEMA than of Vp.

The copolymer sequence will be of random nature with more POEMA units. Depending on the composition of the

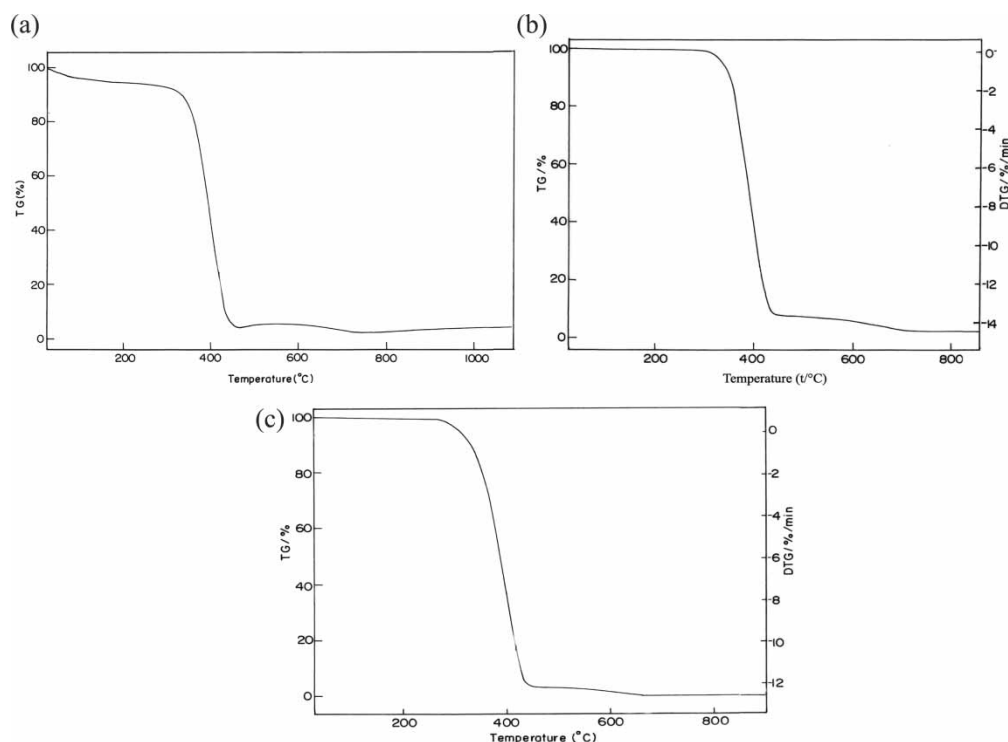
copolymer, some tendency to give small blocks is observed. In fact, based on the higher feed composition of POEMA in the feed, with the help of reactivity ratios, small block formation tendency is observed. This may be because the POEMA monomer is more reactive towards the growing chain regardless of whether the radical was derived from POEMA or Vp. The mean sequence length determination is shown in Table 4. This behavior is similar to other copolymers containing Vp (17, 18).

3.3 Thermogravimetric Analysis

The TGA data of the copolymer of POEMA with Vp is presented in Table 5. The thermal stability of the copolymer was found to increase with the increasing of Vp content in the copolymer chain which is shown in Figure 6. For the (POEMA-co-Vp) copolymer samples of (0.20:0.80) and

Table 5. TGA data for POEMA-co-Vp copolymers

Polymer	Copolymer composition		IDT	Temperature (°C) of weight loss (%) of copolymers			
	m ₁	m ₂		20%	40%	60%	80%
(POEMA-co-Vp)	0.20	0.80	338	372	396	413	452
	0.50	0.50	326	366	388	400	424
	0.80	0.20	307	354	382	410	418

**Fig. 6.** TGA curves of (POEMA-co-Vp) copolymers, (a) 0.20–0.80; (b) 0.50:0.50; (c) 0.80:0.20.

(0.50:0.50); above 80°C at mass does not change with the increase of temperature. Whereas for the (POEMA-co-Vp) copolymer sample (0.80:0.20), the same trend is obtained after a lesser temperature i.e., above 620°C.

4 Conclusions

Five copolymers of POEMA-co-Vp were prepared using AIBN as initiator in 2-butanone solution at 333 K. FT-IR, ¹H- and ¹³C-NMR spectroscopy reveals the presence of both monomeric constituents in the copolymer structure. The copolymer composition was determined by ¹H-NMR spectroscopy. The reactivity ratios obtained by the F-R, K-T and RREVM methods agree well with each other. The reactivity ratios value indicates that POEMA is more reactive than Vp and the copolymer structure will be of random nature with some tendency to form small blocks. The antimicrobial activity of this copolymer is in progress.

5 Acknowledgements

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