

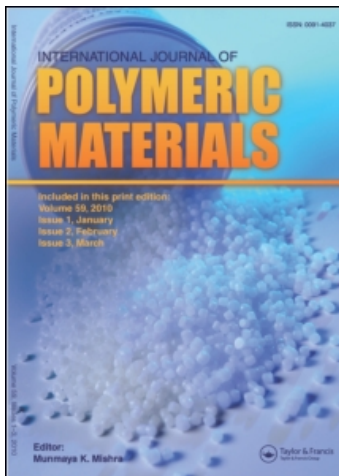
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K. Anver Basha^a; D. S. Franklin^b; R. Balamurugan^a; R. Kannan^a; L. Alegria^c; Angel Leiva^c; Ligia Gargallo^c; Deodato Radić^c

^a P.G. and Research Department of Chemistry, C. Abdul Hakeem College Melvisharam, Tamil Nadu, India ^b Department of Chemistry C. Abdul Hakeem College of Engineering and Technology, Melvisharam, Tamil Nadu, India ^c Departamento de Química Física (502), Facultad de Química, Pontificia Universidad Católica, de Chile, Santiago, Chile

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Comparative Study of Thermal Degradation of N-vinylimidazole/Phenoxy- and Methoxyethylmethacrylate Copolymers

K. Anver Basha,¹ D. S. Franklin,² R. Balamurugan,¹ R. Kannan,¹ L. Alegría,³ Angel Leiva,³ Ligia Gargallo,³ and Deodato Radić³

¹P.G. and Research Department of Chemistry, C. Abdul Hakeem College Melvisharam, Tamil Nadu, India

²Department of Chemistry C. Abdul Hakeem College of Engineering and Technology, Melvisharam, Tamil Nadu, India

³Departamento de Química Física (502), Facultad de Química, Pontificia Universidad Católica, de Chile, Santiago, Chile

Copolymerization reactions involving N-vinylimidazole and its derivatives have stimulated great interest due to the wide possibilities of the preparation of new materials, including the synthetic analogues of biopolymers with imidazole fragments. The role of the imidazole group in polymers is very important, especially due to the high thermal stability at elevated temperatures when it is copolymerized with methacrylates, which contain highly electronegative atoms like oxygen [10,11]. Accordingly, copolymers of N-vinylimidazole with phenoxy- and methoxyethylmethacrylate have been prepared and subjected to thermogravimetric analysis to discover their thermal stability. Copolymers are also characterized by FTIR and ¹H-NMR spectroscopic methods. Results show that the thermal stability is greater for N-vinylimidazole-co-phenoxyethylmethacrylate than for those with N-vinylimidazole-methoxyethylmethacrylate.

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Address correspondence to Deodato Radić, Departamento de Química Física (502), Facultad de Química, Pontificia Universidad Católica, de Chile, Casilla 306, Santiago-22, Chile. E-mail: dradic@puc.cl

Keywords methoxyethylmethacrylate, N-vinylimidazole copolymer characterization, phenoxyethylmethacrylate, thermal stability

INTRODUCTION

In recent years, the synthesis of polymers containing reactive functional groups has been an active field of research in polymer science, because it provides an approach to a subsequent modification of the polymer for the required applications. Phenoxy-based methacrylate has a wide variety of applications in dentistry, optical eye wear, fiber optics holography and microelectronics [1]. Similar copolymers obtained from methoxyethylmethacrylate (MOEMA) possessed controlled molecular weight and composition [2] and are film-forming materials. Its copolymers with zwitterionic monomers are used for medical devices [3]. But it is well-known that poly(methacrylate)s have rather poor thermal stability. Some other properties, such as hardness, softening point, and chemical resistance are not fully satisfactory [4–6]. Thus it is possible to improve these properties by copolymerization with N-vinylimidazole (VIM) particularly thermal properties. Moreover, imidazole-containing macromolecules have a wide range of applications. These materials showed unique properties such as an ion exchange and complexing behaviors, catalytic, biological and physiological activities and heat resistance when N-vinylimidazole (VIM) is copolymerized with styrene [7], N-vinylpyrrolidone [8], acrylonitrile [9] also with methacrylates [11] and phenacrylmethacrylates [12], but not with (methacrylate)s that carry a highly electronegative atom like oxygen. The objective of this study is to synthesize new copolymers of N-vinylimidazole (VIM) with phenoxy- and methoxyethylmethacrylate and to investigate their thermal properties.

The aim of this work is to assess the thermal stability of the copolymers of methoxyethylmethacrylate and phenoxyethylmethacrylate of various compositions. For this thermogravimetric analysis (TGA) is employed. The actual decomposition temperature range depends upon the composition of the constitutional monomeric units in the copolymer. For example, onset of decomposition may be the degradation of side chains with the main polymer chain remaining intact; at some higher temperature, further decomposition could occur, resulting in drastic changes in the properties of materials.

EXPERIMENTAL

Methods and Instrumentation

The FTIR spectra of the copolymer were recorded on a Perkin-Elmer Paragon 1000 Fourier transform IR (FTIR) spectrophotometer using the

potassium bromide pellet technique in the range 500–4000 cm^{-1} . The $^1\text{H-NMR}$ spectra of the copolymer were recorded on a Jeol GSX-400 spectrometer operating at 400 MHz at room temperatures as 15–20% (w/v) solution in CDCl_3 , tetramethylsilane (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. 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 20 K/min under nitrogen atmosphere. Nitrogen flow rate is 70 mL/min.

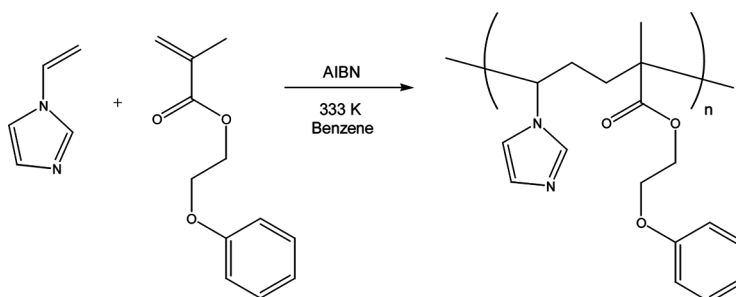
Copolymerization

Copolymerization reactions were carried out in benzene solution (50 mL) in glass vessels with an inlet and outlet. The reactions tube containing the required amount of monomers and initiator (1% total mass of monomer) was dissolved in benzene and was deaerated by flushing with pure, dry nitrogen gas for 30 min prior to immersion in a water bath kept at a temperature of 333 K. The copolymers were precipitated in an excess of hexane. The mass that separated out was dissolved in chloroform and then reprecipitated in hexane to ensure the complete removal of residual monomers.

RESULTS AND DISCUSSION

Scheme 1 show the monomeric constituents of the copolymer and the representation of the copolymerization reaction.

Characterization of the copolymers was performed by FTIR and $^1\text{H-NMR}$. The IR spectrum of random (VIM-co-POEMA) copolymers shows the characteristic band of both monomer units as shown in Figure 1. The ester carbonyl group of the POEMA unit shows a characteristic peak at 1728 cm^{-1} . Peaks at



Scheme 1: Synthesis of copolymer (VIM-co-POEMA).

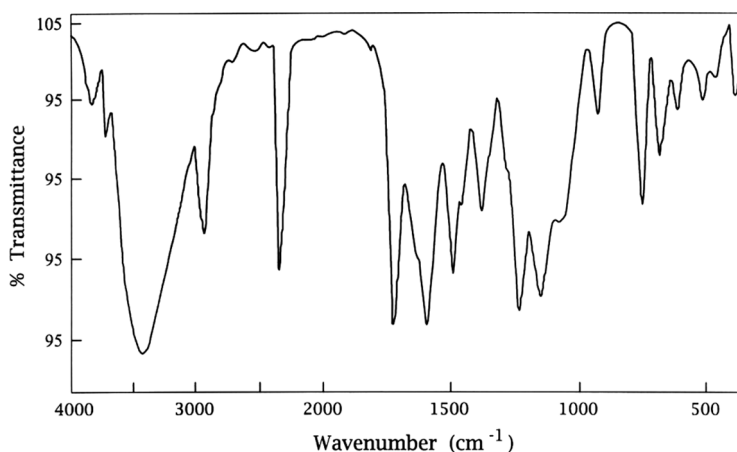


Figure 1: FTIR spectrum of (VIM-co-POEMA) (0.50/0.50).

2938 and 1495 cm^{-1} are due to C-H and CH_2 (main chain) stretching and C-C and C = N (ring) stretching of VIM unit, the peaks at 1385, 1240 and 1153 cm^{-1} are also of VIM unit due to -CH (ring) in plane bending C-N (ring) stretching.

The IR spectrum of poly (VIM-co-MOEMA) is shown in Figure 2. The sharp peak at 1720 cm^{-1} indicates the presence of carbonyl group in MOEMA unit. The broad band at 2886 cm^{-1} and peak at 2348 cm^{-1} corresponds to -CH asymmetric stretching in CH_3 and CH asymmetric stretching in CH_2 , respectively. The other peaks at 1450 cm^{-1} , 1242 cm^{-1} , and 1121 cm^{-1} were due to aromatic C = C stretching and CH_2 stretching.

The $^1\text{H-NMR}$ spectrum of poly (VIM-co-POEMA) is shown in Figure 3. The characteristic signal at 6.7–6.9 ppm corresponds to aromatic protons of POEMA unit. Another sharp signal at 7.2–7.4 ppm is due to 3H and CH groups in free

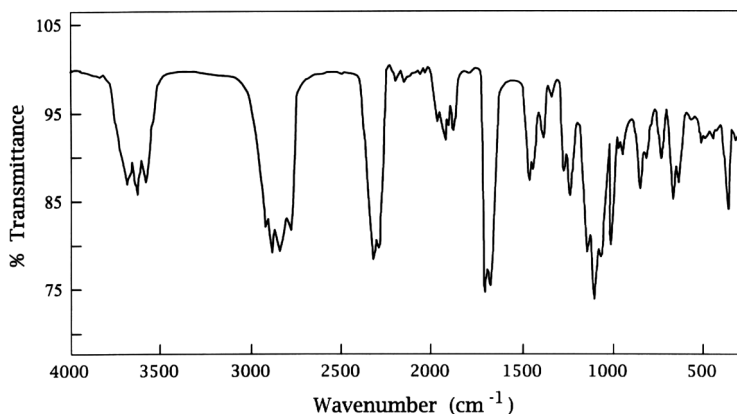


Figure 2: FTIR spectrum of (VIM-co-MOEMA) (0.50/0.50).

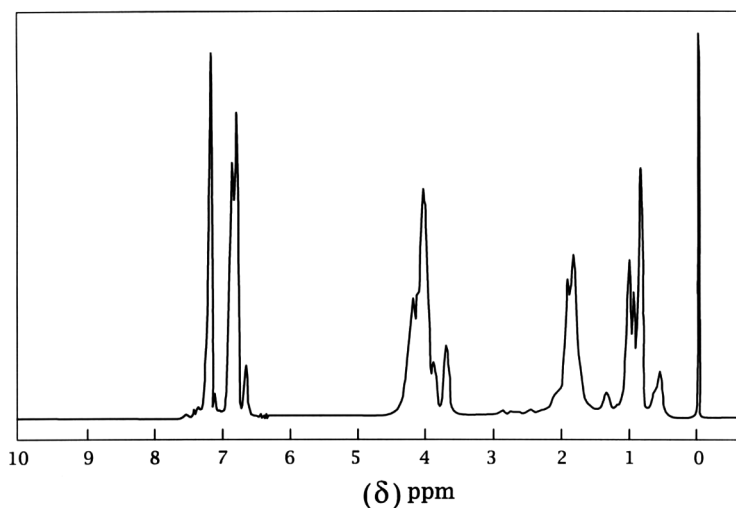


Figure 3: $^1\text{H-NMR}$ spectrum of (VIM-co-POEMA) (0.50/0.50).

imidazole ring. The very broad band at 3.7–4.0 ppm is related to methylene oxy protons of POEMA unit. The well resolved other peaks and multiples correspond to methyl, $-\text{CH}_2$, $-\text{CH}$ backbone protons of both VIM and POEMA unit. Thus participation of two monomeric units in the copolymer is confirmed.

The structure of the synthesized copolymer (VIM-co-MOEMA) is confirmed by $^1\text{H-NMR}$ analysis. Figure 4 shows the significant change in the chemical

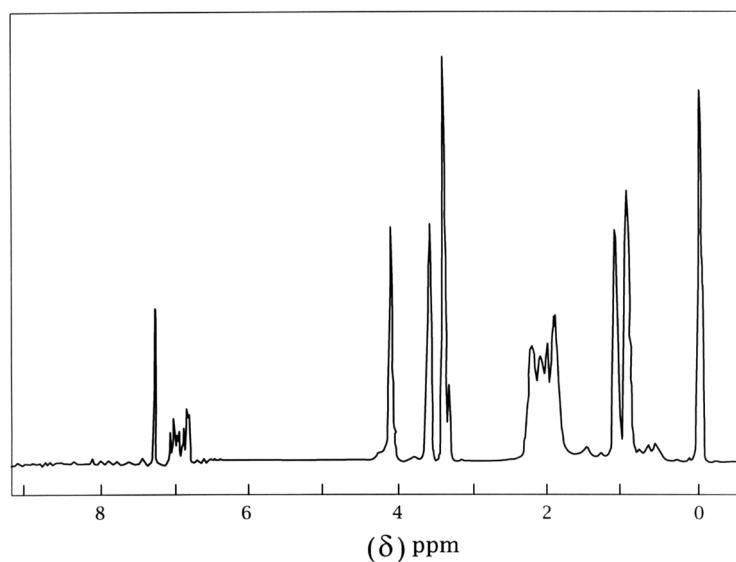


Figure 4: $^1\text{H-NMR}$ spectrum of (VIM-co-MOEMA) (0.50/0.50).

Table 1: TGA data for homopolymer (POEMA).

Polymer	IDT	20%	40%	60%	80%
(POEMA)	243	252	270	288	310

shifts of imidazole rings protons and backbone –CH protons of VIM and MOEMA linkages. The $^1\text{H-NMR}$ shows a characteristic signal at 8.0–7.2 ppm which corresponds to 3H and –CH groups in free imidazole ring. The broad band at 4.8 ppm is due to methylene oxy protons of MOEMA unit. The other peaks and multiples at 3.2, 2.5, 1.6 ppm are due to methylene, methyl and –CH backbone of VIM and MOEMA unit.

In order to know the thermal stability of the copolymers, thermogravimetric analysis was carried out. The results of the thermogravimetric analysis for homopolymer (POEMA), homopolymer (MOEMA), (VIM-co-POEMA), and (VIM-co-MOEMA), copolymers are compiled in Tables 1–4. Their corresponding TGA profiles are shown in Figures 5 and 6. Copolymers show that as the phenoxyethylmethacrylate or methoxyethylmethacrylate decreases the degradation temperature of the copolymers decreases. On the other hand copolymers with high content of phenoxyethyl- and methoxyethylmethacrylate show higher IDT values than the corresponding homopolymer. This result would indicate that the presence of vinylimidazole increases the stiffness of the macromolecule.

In the case of (VIM-co-POEMA) copolymers, except for the copolymer composition 0.20/0.80, the other two copolymer composition, 0.50/0.50 and 0.80/0.20, undergo a two-stage decomposition for the macromolecules containing ester and imidazole fragments (see Figure 5). The intensity and position of these

Table 2: TGA data for homopolymer (MOEMA).

Polymer	IDT	20%	40%	60%	80%
(MOEMA)	209	256	292	330	374

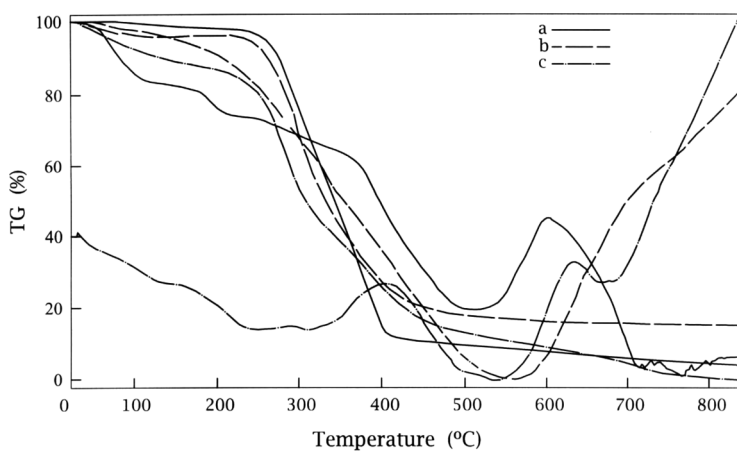
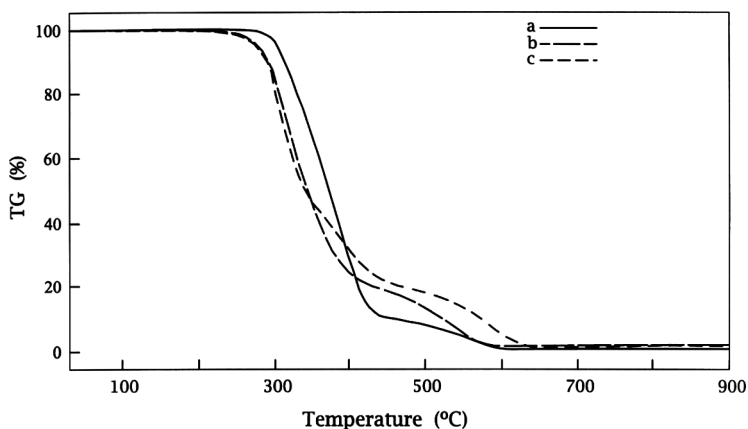
Table 3: TGA data for (VIM-co-POEMA).

Copolymers	Copolymer composition in mole fraction (w/w%)			Temperature (T/°C) of mass loss (%) of copolymers			
	m ₁	m ₂	IDT (T/°C)	20%	40%	60%	80%
(VIM-co-POEMA)	0.20	0.80	269	324	350	375	398
	0.50	0.50	254	304	326	357	392
	0.80	0.20	228	284	298	340	396

IDT – Initial decomposition temperature.

Table 4: TGA data for (VIM-co-MOEMA).

Polymers	Copolymer composition in mole fraction (w/w%)			Temperature (T/°C) of mass loss (%) of copolymers			
	m ₁	m ₂	IDT (T/°C)	20%	40%	60%	80%
(VIM-co-MOEMA)	0.20	0.80	235	297	324	358	392
	0.50	0.50	224	270	294	312	342
	0.80	0.20	180	185	272	314	386

**Figure 5:** TGA profiles of (VIM-co-POEMA) a) 0.20/0.80 b) 0.50/0.50 c) 0.80/0.20.**Figure 6:** TGA profiles of (VIM-co-MOEMA) a) 0.20/0.80 b) 0.50/0.50 c) 0.80/0.20.

peaks depend on the VIM content in the copolymer. The thermal stability increases when POEMA is copolymerized with VIM. (See Tables 1 and 3).

Similarly when MOEMA is copolymerized with VIM, its thermal stability is enhanced. In this case also the two copolymer compositions 0.50/0.50 and 0.80/0.20 undergo double stage decomposition (See Figure 6). The large variation in the initial decomposition temperature with the decreasing on the MOEMA content in the copolymer is significant (see Table 4).

CONCLUSIONS

N-vinylimidazole is copolymerized with methacrylates containing an electronegative atom like oxygen. Thus it is copolymerized with phenoxy- and methoxyethylmethacrylate. The characterization of the copolymers is in agreement with the expected chemical structure. In the case of (VIM-co-POEMA) copolymers, except for the copolymer composition 0.20/0.80, the other two copolymer compositions 0.50/0.50 and 0.80/0.20 undergo a two-stage decomposition for the macromolecules containing ester and imidazole fragments. The intensity and position of these peaks depend on the VIM content in the copolymer. The thermal stability increases when POEMA is copolymerized with VIM. Copolymers with high content of phenoxyethyl- and methoxyethylmethacrylate show higher IDT values than those of the corresponding homopolymers. This result would indicate that the presence of vinylimidazole increases the stiffness of the macromolecule.

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