

Synthesis and characterization of *N*-vinylimidazole–ethyl methacrylate copolymers and determination of monomer reactivity ratios

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Abstract

Radical-initiated copolymerization of *N*-vinylimidazole (VIM) and ethyl methacrylate (EMA) was carried out with 2,2'-azobisisobutyronitrile (AIBN) as an initiator in benzene at 70°C in nitrogen atmosphere. Structure and composition of copolymers for a wide range of monomer feed were determined by elemental analysis (content of *N* for VIM-units) and by Fourier transform infrared spectroscopy through recorded analytical absorption bands for VIM (667 cm⁻¹ for C–N of imidazole ring) and EMA (1729 cm⁻¹ for C=O of ester group) units, respectively. Monomer reactivity ratios for VIM (M₁)–EMA (M₂) pair were determined by Fineman–Ross and Kelen–Tüdös (KT) methods. They are $r_1 = 0.35 \pm 0.02$ and $r_2 = 3.47 \pm 0.2$ as determined by KT method. Parameters of $Q_1 = 0.14$ and $e_1 = -0.61$ for VIM monomer were calculated by using the Alfrey–Price scheme. Observed relatively high activity of EMA growing radical was explained by effect of complex formation between carbonyl group and imidazole fragments in chain growth reactions. Thermal behaviors of copolymers with various compositions were investigated by differential scanning calorimetry and thermogravimetric analysis. It was observed that glass transition temperature and thermal stability of copolymers increased with increasing of VIM content in copolymers. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: *N*-vinylimidazole; Ethyl methacrylate; Radical copolymerization; Complex formation; Reactivity ratios; Thermal behaviors

1. Introduction

Imidazole-containing macromolecules have been suggested as carrying an active moiety of several electrolytic enzymes [1–3]. The imidazole ring is present in most proteins (i.e., histamine, histidine, etc.) and is partly responsible for their catalytic activity. Consequently, extensive studies of the catalytic behaviors of monomeric [4] and polymeric [5] imidazole have been reported. Thus, Sebille and coworkers [6,7] have developed a new coating technology for protein separations using poly(vinylimidazole) and/or poly(vinylimidazole)–

poly(*N*-vinylpyrrolidone) block copolymers. Jilde et al. [8] applied this technology to synthesis of non-porous silica-based strong anion exchangers containing vinyl-imidazole–*N*-vinylpyrrolidone copolymers. The conditions for protein separations were optimized by varying the copolymer composition and the amount adsorbed on the non-porous silica supports.

N-vinylimidazole–4-aminostyrene copolymer as a new tailor-made steric stabilizer for polyaniline colloids was synthesized by free-radical precipitation copolymerization of monomers in benzene at 70°C using 2,2'-azobisisobutyronitrile (AIBN) as an initiator [9].

Silane (γ -methacryloxypropyltrimethoxysilane) – modified poly(*N*-vinylimidazole) copolymer coatings has been shown to have good corrosion protection and adhesion promotion capabilities for copper substrate in severe environments [10,11].

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It has been reported that the polymerization of 1-vinylimidazole at high monomer concentration is accompanied by degradative addition of a growing radical to the 2-position of the imidazole ring of the monomer [12]. The template radical polymerization of *N*-vinylimidazole (VIM) along poly(methacrylic acid) in water at 50°C was studied by Grampel et al. [13]. It was shown that degradative addition is impeded in the case of template-associated radicals due to propagation with adsorbed monomers.

Spontaneous polymerization of maleic anhydride (MA) in the presence of various derivatives of imidazole such as methyl-, ethyl-, phenyl-, methylethyl-, and methyl vinylimidazole at 50–60°C in chloroform and at 25°C in benzene in nitrogen atmosphere was observed [14]. It was shown that the reaction is accompanied by partial decarboxylation. Maximum absorption of the UV-spectra observed at equimolar ratio of MA–imidazole (1:1) suggest that the polymerization proceeds through charge transfer complex formation in the acceptor–donor system studied. The equilibrium constant for the MA ··· methylvinylimidazole complex was found to be 1.5 l/mol. In the case of the addition of 10 mol% of methylvinylimidazole to molten MA at 100°C in the absence of solvent, explosive decarboxylation and instantaneous completion of reaction were observed [14]. It has been also reported that VIM and MA spontaneously copolymerize in *p*-dioxane in the range from 20 to 80 mol% imidazole monomer in the feed. Constants of charge transfer complex formation and copolymerization were determined as $K_c = 0.8 \text{ mol}^{-1}$ (UV-method) and $r_1 = -0.153 \pm 0.045$ and $r_2 = 1.33 \pm 0.18$ (by Kelen–Tüdös (KT) method) [15].

It is well known that physical properties and sequence length distribution are important characteristics of copolymers. The most fundamental quantity characterizing a copolymer is its compositions on a molar basis which eventually is used for determination of the relevant monomer reactivity ratios. Spectroscopic methods, preferably ^1H NMR, ^{13}C NMR [16–21], IR and Fourier transform IR (FTIR) [22,23] and UV [24–27] spectroscopy are probably the most widely used methods for analysis of copolymers, and determination of r_1 and r_2 . In general, IR method has never been regarded as the foremost technique for determining copolymer composition and has been favoured mainly more as a “qualitative” technique [28]. However, FTIR spectroscopy can provide not only qualitative but also very good quantitative analysis.

In the present work, the results of radical copolymerization of VIM with ethyl methacrylate (EMA), determination of monomer reactivity ratios using different method including FTIR spectroscopy and the effects of imidazole units in copolymer composition–thermal behaviour relationships are presented and discussed.

2. Experimental section

2.1. Materials

VIM monomer (Aldrich) was distilled under vacuum before use: b.p. 78.5°C/13 mm, d_4^{20} 1.0388, n_D^{20} 1.5290. EMA monomer (Darmstadt, Germany) was purified by filtration through alumina column to remove hydroquinone inhibitor and distilled: b.p. 118.5°C, d_4^{20} 0.9178, n_D^{20} 1.4132.

AIBN initiator was twice recrystallized from methanol.

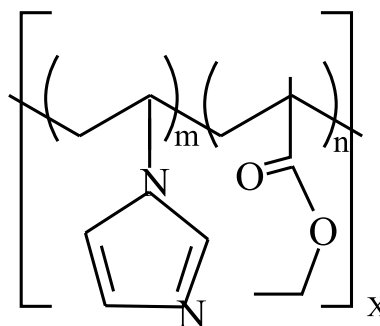
Benzene as a solvent and *n*-hexane as a precipitant were dried under metallic sodium chips and distilled before use.

2.2. Synthesis of copolymers

The synthesis of VIM–EMA copolymers using various monomer feed ratios was carried out in benzene solution at 70°C with AIBN as initiator at constant total concentration of monomers in nitrogen atmosphere. Reaction conditions: $[M]_{\text{total}} = 2.5 \text{ mol/l}$, $[AIBN] = 5 \times 10^{-3} \text{ mol/l}$ and monomer ratios of $[VIM]/[EMA] = 0.25 - 0.20$, conversion $\leq 10\%$. Appropriate quantities of monomers, solvent and initiator were placed in a standard glass tube, and the mixture was cooled by liquid nitrogen and flushed with dried nitrogen gas for at least 2 min, then soldered and placed in a thermostated silicon oil bath at $70 \pm 0.1^\circ\text{C}$. The VIM–EMA copolymers were isolated from reacted mixture by precipitation in *n*-hexane, then washed with several portions of methanol and dried under vacuum at 40°C. The copolymer compositions were determined by elemental analysis (N content for VIM units and O content for EMA units) and FTIR spectroscopy using 667 cm^{-1} (C–N bond for VIM unit) and 1729 cm^{-1} (C=O bond for EMA unit) as absorption bands for quantitative analysis.

In similar conditions, poly(VIM) and poly(EMA) were synthesized. Copolymer prepared from equimolar ratio of initial monomers and homopolymers of VIM and EMA have the following average characteristics:

VIM–EMA copolymer:



where $m = 0.06$ – 0.21 and $n = 0.79$ – 0.94 . Content of N 3.27%, monomer unit ratio of $m_1/m_2 = 0.142$, $[\eta]_{\text{in}}$ in benzene at 25°C 0.28 dl/g, T_g 83.7°C.

FTIR spectra (KBr pellet), cm^{-1} : 3121 ($\nu_{\text{C}=\text{N}}$), 1643 ($\nu_{\text{C}=\text{C}}$), 815 and 667 (C–N) for VIM unit and 1729 ($\nu_{\text{C}=\text{O}}$), 1179–1027 (C–O and C–O–C) and 971 ($\delta_{\text{C}=\text{O}}$) for EMA unit; 2987 ($\nu_{\text{a C-H}}$ in CH_3), 2943 ($\nu_{\text{a C-H}}$ in CH_2), 2910 ($\nu_{\text{s C-H}}$ in CH_2 and CH_3), 1450 ($\delta_{\text{a CH}_2}$), 1372 ($\delta_{\text{a CH}_3}$), 1272 ($\delta_{\text{s CH}_2}$) and 1235 ($\delta_{\text{s CH}_3}$).

Poly(VIM) – content of N 29.5%, $[\eta]_{\text{in}}$ in benzene at 25°C 0.34 dl/g, T_g 175.1°C.

Poly(EMA) $[\eta]_{\text{in}}$ in benzene at 25°C 0.91 dl/g, $M_v \sim 180000$, T_g 78.2°C.

2.3. Measurements

FTIR spectra of homo- and copolymers were recorded with FTIR Nicolet 520 spectrometer on KBr pellets in 4000–400 cm^{-1} range, where 10 scans were taken at 4 cm^{-1} resolution. For the composition analysis of copolymers, specifically contents of VIM and EMA units, characteristic absorption bands of 667 cm^{-1} (for VIM unit), 1729 cm^{-1} (for EMA units) were used as analytical bands. The least changing absorption band of 1040 cm^{-1} was used as a standard band ($A = \log(I_0/I)$, $\Delta A^i = A^i/A^{1040}$) to calculate the copolymer compositions.

Contents of nitrogen in copolymers were determined using a CHN-800 model elemental analyzer.

Intrinsic viscosities of homo- and copolymers were determined in benzene at $25 \pm 0.1^\circ\text{C}$ in the concentration range of 0.1–1.0 g/dl using an Ubbelohde viscometer.

Differential scanning calorimetric (DSC) and thermogravimetric analyses (TGA) of homo- and copolymers were carried out with a DuPont 910 and DuPont TA 951 thermogravimetric analyzer, respectively, in nitrogen atmosphere at a heating rate of 10°C/min.

3. Results and discussion

3.1. Copolymerization

The monomer pair studied differs by nature of the conjugation between double bond and functional group VIM is an electron-donor monomer with $\pi(\text{C}=\text{C})$ vinyl) \leftarrow p(N) \leftarrow $\pi'(\text{N}=\text{C})$ imidazole ring-conjugated system and EMA is an electron-acceptor comonomer with $\pi(\text{C}=\text{C})$ acrylic \rightarrow $\pi'(\text{C}=\text{O})$ ester-conjugated system. These distinctive structural peculiarities allow to predict that the monomers may show sufficient activity in radical-initiated copolymerization.

Copolymerizations were carried out in low conversion conditions ($\leq 10\%$) in order to determine monomer reactivity ratios in the stationary kinetic stage by using

known terminal models of the Fineman–Ross (FR) [29] and KT [30] equations, respectively:

$$F(f-1)/f = r_1(F^2/f) - r_2 \quad (1)$$

$$\eta = (r_1 + r_2/\alpha)\xi - r_2/\alpha \quad (2)$$

where $F = [\text{VIM}]/[\text{EMA}]$ and $f = m_1/m_2$; $\eta = (F^2/f)/(F^2/f + \alpha)$; $\xi = [F(f-1)/f]/(F^2/f + \alpha)$; α (arbitrary constant) $= \sqrt{(F^2/f)_{\text{min}}(F^2/f)_{\text{max}}} = 3.776$.

Molar fractions (in mol%) of comonomer units (m_1 and m_2) in VIM(M_1)–EMA(M_2) copolymers using FTIR analysis data are calculated according to the following equations:

$$m_1 = \frac{\Delta A^{667}/M_1}{\Delta A^{667}/M_1 + \Delta A^{1729}/M_2} 100 \quad (3)$$

$$m_2 = \frac{\Delta A^{1729}/M_2}{\Delta A^{667}/M_1 + \Delta A^{1729}/M_2} 100 \quad (4)$$

where $m_1/m_2 = [\Delta A^{667}/M_1]/[\Delta A^{1729}/M_2]$, $\Delta A = A^i/A^{1040}$ (standard band), M_1 and M_2 are molecular weights (g/mol) of VIM and EMA monomer units, respectively.

Results of FTIR analyses of VIM–EMA copolymers for various initial monomer ratios, and poly(VIM) and poly(EMA) as model systems synthesized are illustrated in Fig. 1 and Table 1, respectively. Copolymer compositions calculated using elemental analysis data (content of N) were in very good agreement with those obtained from FTIR analysis (Table 1). On the basis of FTIR analysis data (Fig. 1) the values of absorption bands for the comonomer units are calculated and then used for the determination of copolymer compositions according to Eqs. (3) and (4). The results are presented in Table 1. As evidenced from these data, increase of VIM concentration in monomer feed dominantly leads to the formation of random copolymers enriched with m_2 monomer units.

Fig. 2 shows the plot of $(\Delta A^{1729}/\Delta A^{667})$ vs. (m_1/m_2) for the copolymers, which can be considered as a curve of calibration; it satisfactorily agrees to with those for various [poly(VIM)]/[poly(EMA)] mixtures and copolymers synthesized.

Copolymerization constants (r_1 and r_2) were evaluated using experimental data (Tables 1 and 2) from KT plots of η vs. ξ (Fig. 3a) and FR plots of (F^2/f) vs. $[F(f-1)/f]$ (Fig. 3b) for the VIM (M_1) and EMA (M_2) pair as $r_1 = 0.32 \pm 0.02$ and $r_2 = 3.60 \pm 0.2$ (by FR method) and $r_1 = 0.35 \pm 0.02$ and $r_2 = 3.47 \pm 0.2$ (by KT method). As evidenced from the values of monomer reactivity ratios, random radical copolymerization is realized in the VIM–EMA system.

The parameters of specific activity (Q_1) and polarity (e_1) for VIM monomer were calculated using the Q – e scheme of Alfrey and Price [31]. According to Jenkins and Jenkins [32], this scheme is still virtually the only

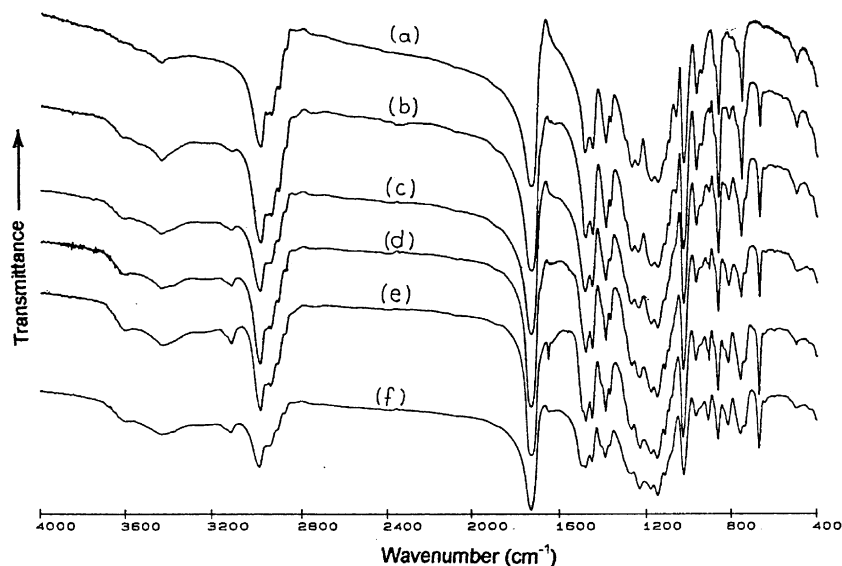


Fig. 1. FTIR spectra of: (a) poly(EMA) and VIM-EMA copolymers with different compositions (mol% of VIM-unit); (b) 6.0, (c) 10.6, (d) 12.4, (e) 13.3 and (f) 25.5.

Table 1

FTIR analysis data for determining the composition of VIM-EMA copolymers synthesized from various initial monomer mixtures

Monomer feed (mol%)		^a ΔA^{667} (VIM unit)	ΔA^{1729} (EMA unit)	N(%)	Copolymer composition (mol%)			
[VIM]	[EMA]				By FTIR analysis		By nitrogen analysis	
					m_1	m_2	m_1	m_2
20	80	0.089	1.697	1.50	5.98	94.02	6.05	93.95
40	60	0.142	1.452	2.42	10.60	89.40	9.68	90.32
50	50	0.247	2.108	3.27	12.44	87.56	13.01	86.99
60	40	0.153	1.206	3.77	13.33	86.67	15.06	84.94
66.5	33.5	0.158	0.560	5.42	25.49	74.51	21.26	78.74

Analytical absorption bands: 667 cm^{-1} ($\nu_{\text{C-N}}$ in imidazole ring) and 1729 cm^{-1} ($\nu_{\text{C=O}}$ in EMA-unit).

^a ΔA^{667} (or ΔA^{1729}) = A^{667} (or A^{1729})/ A^{1040} ; where A^{1040} is an absorption of least changing band.

method used for the analysis of copolymerization data, even though it is expected to give way soon to a fundamentally more sound procedure. Alfrey and Price [31] postulated that the parameters e of the monomer and the corresponding radical are equal, i.e., $e = e^*$. As a result simple equations were obtained linking the relative activities of the monomers to the parameters of the reactivity

$$r_1 = (Q_1/Q_2) \exp[-e_1(e_1 - e_2)] \quad (5)$$

$$r_2 = (Q_2/Q_1) \exp[-e_2(e_2 - e_1)] \quad (6)$$

Using obtained values of r_1 and r_2 and Eqs. (5) and (6), as well as known $Q_2 = 0.56$ and $e_2 = 0.17$ values for

the EMA monomer [33] the values of $Q_1 = 0.14$ and $e_1 = -0.61$ for VIM monomer were calculated, which correlates the energy of localization, order and π -electron density of VIM double bond.

The values of copolymerization constants (r_1 and r_2) and parameter of Q_1 and e_1 obtained using FR and KT equations and both methods for FTIR and elemental analysis of copolymer compositions are presented in Table 3. As seen from these values, EMA is the more active comonomer in copolymerization with VIM. Therefore, chain growth reactions proceed primarily by addition of free EMA and VIM monomers to growing macroradical of $\sim\text{EMA}^*$. The known values of Q_1 and e_1 for VIM are $Q_1 = 0.11$ and $e_1 = -0.68$ [34] which differ from those obtained for VIM in VIM-EMA system.

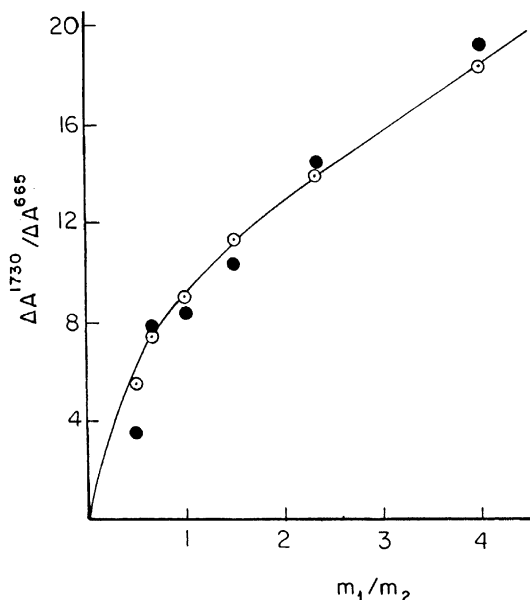


Fig. 2. Plot of $(\Delta A^{1730}/\Delta A^{667})$ vs. (m_1/m_2) for the $(-\circ-)$ copolymers and $(-\bullet-)$ [poly(VIM)]/[poly(EMA)] mixtures.

Formation of charge transfer complex between imidazole ring and EMA carbonyl group in the monomer feed (essential shift of $\text{C}=\text{O}$ band) and in polymer mixtures (visible shift of $\text{C}=\text{O}$ band), where benzene is used as a solvent-reaction medium, was confirmed by using FTIR analysis (Fig. 4). It was proposed that this complex could play an important role in chain growth. This proposal can be confirmed by observed changes of Q_1 and e_1 values for VIM from 0.11 and -0.68 to 0.14 and -0.61 , for known and found values, respectively. In the copolymerization reactions, activity of complexed $\sim\text{EMA}^{\bullet}$ growing radical increases, and therefore more easily adds to EMA monomer than that to VIM monomer. On the other hand, the character of double bond conjugation in VIM molecule also changed and electron-donor property of VIM monomer is decreased.

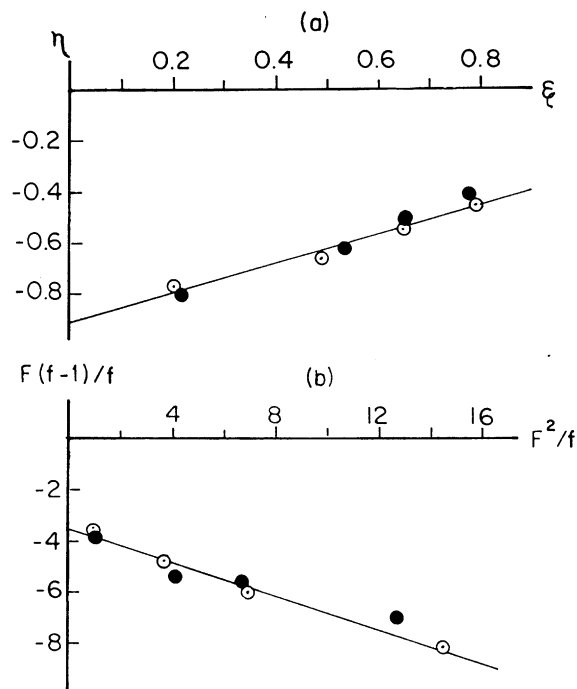


Fig. 3. KT (a) and FR (b) methods for determining monomer reactivity ratios in copolymerization of VIM (M_1) and EMA (M_2) data of FTIR $(-\circ-)$ and elemental $(-\bullet-)$ analyses: (a) – intercept is r_2/α and $\text{tg}\alpha = r_1 + r_2/\alpha$ and (b) – intercept is r_2 and $\text{tg}\alpha = r_1$.

Probably, homopolymerization rate of EMA in the presence of VIM is dramatically increased. It is known that polymerization of other carbonyl-containing monomers such as MA proceeds spontaneously in the presence of imidazole and its derivatives [14].

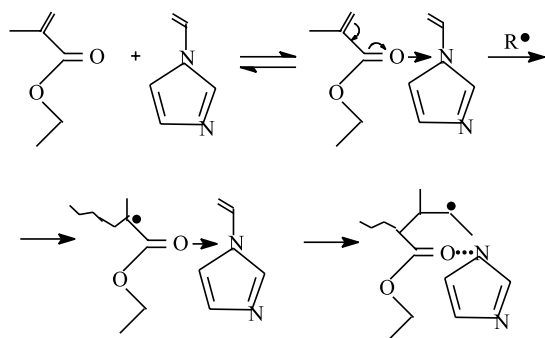
Observed relatively high activity of complexed growing radical $\sim\text{EMA}^{\bullet} \cdots \text{VIM}$ was explained by the effect of complex formation between carbonyl group and imidazole fragments in the initial monomer mixture and chain growth reactions as described below:

Table 2
Radical-initiated copolymerization of VIM (M_1) with EMA (M_2)

Monomer ratio $F = [M_1]/[M_2]$	M-unit ratio in copolymer $f = m_1/m_2$	Parameters of FR-Eq.		Parameters of KT-Eq.		
		F^2/f	$F(f-1)/f$	$F^2/f + \alpha^a$	η	ξ
0.250	0.064	0.976	−3.656	4.753	−0.769	0.206
0.667	0.119	3.739	−4.938	7.515	−0.657	0.497
1.000	0.142	7.042	−6.042	10.818	−0.558	0.651
1.500	0.154	14.610	−8.240	18.386	−0.448	0.795
1.985	0.342	11.521	−3.819	15.297	−0.250	0.753

Reaction conditions: Solvent (S) – benzene, $[M]_{\text{total}} = 2.5 \text{ mol/l}$, $[\text{AIBN}] = 5 \times 10^{-3} \text{ mol/l}$, 70°C , conversion $\leq 10\%$.

^a α (arbitrary constant) = $\sqrt{(F^2/f)_{\min}(F^2/f)_{\max}} = 3.776$.



Probably, this effect also impedes the degradative addition of growing radical to the imidazole ring and allows chain growth by the usual random copolymerization mechanism.

The formation of EMA···VIM complex is confirmed by FTIR spectral analysis (Fig. 4) of free monomers and EMA/VIM mixtures in benzene solution having yellowish colour. FTIR analysis of free monomers and their mixture (spectra a), as well as homopolymers of VIM and EMA and their mixture (spectra b) indicated that the characteristic band of ester group ($\text{C}=\text{O}$) is shifted from 1740 to 1713 cm^{-1} (for the monomer mixtures) and from 1729 to 1725 cm^{-1} (for the polymer mixtures), respectively. Relatively weak shift of $\text{C}=\text{O}$ band in the polymer mixtures can be explained by the disappearance of the conjugation effect between double bond corresponding functional groups ($\text{C}=\text{O}$ and imidazole ring) during chain propagation reaction.

Similar weak band shifts are observed in the spectra of VIM–EMA copolymers (Fig. 1), while the characteristic band of imidazole ($\text{C}-\text{N}$) visibly shifted from 656 to 680 cm^{-1} . This observed fact can be explained by the formation of inter- or intramolecular complex between

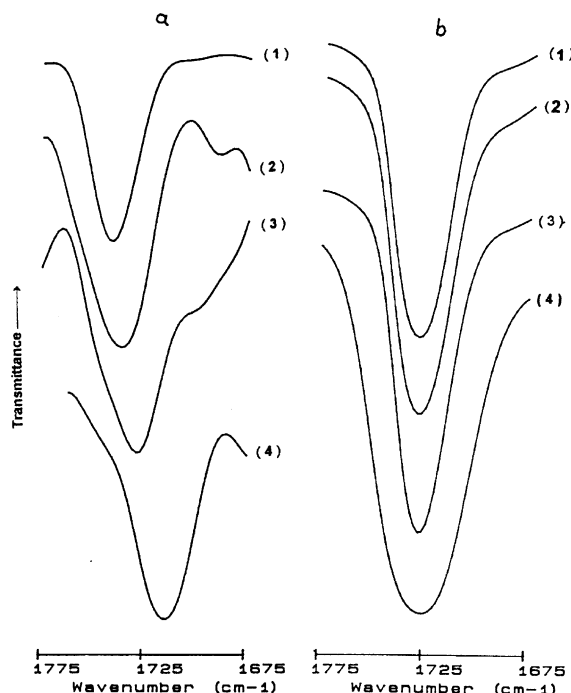


Fig. 4. Fragments of FTIR spectra of (a): EMA (1) and monomer mixtures at monomer molar ratios of EMA:VIM = 1:10 (2), 1:5 (3) and 1:1 (4); (b): poly(EMA) (1) and poly(EMA)/poly(VIM) mixtures (2–4) with molar ratios as in monomer feed. (1) Solvent – benzene, [EMA] = constant = 0.1 mol/l.

monomer units through (ester group) $-\text{C}=\text{O} \cdots \text{N}-$ (imidazole ring) bond. Thus, increase of VIM unit content in copolymers has caused the shift of carbonyl group to the lower field of spectra, while $\text{C}-\text{N}$ band of imidazole ring shifted to relatively high field of spectra (Fig. 1). It is also a known fact that interpolymer complex is formed through a donor–acceptor interaction between the imidazole units and the carboxylate anions in the poly-(VIM)/poly(acrylic acid) system [35].

Table 3

The values of copolymerization constants (r_1 and r_2) and specific activity (Q_1) and polarity (e_1) for VIM (M_1) and EMA (M_2) monomer pair determining by KT and FR methods using FTIR and elemental analysis techniques

Methods	r_1	r_2	Q_1	e_1
KT (FTIR analysis)	0.35 ± 0.02 (0.36) ^a	3.47 ± 0.2 (3.38)	0.14	−0.61
KT (elemental analysis)	0.26 ± 0.01 (0.33)	3.35 ± 0.2 (3.51)	0.15	−0.54
FR (FTIR analysis)	0.32 ± 0.02 (0.33)	3.60 ± 0.2 (3.56)	0.14	−0.55
FR (elemental analysis)	0.31 ± 0.01 (0.26)	3.75 ± 0.2 (3.89)	0.13	−0.56

^a These values are calculated by linear square analysis.

3.2. Copolymer composition–thermal behaviors relationships

DSC and TGA methods were used in studying thermal properties and copolymer composition–thermal behavior relationships of VIM–EMA copolymers containing various molar fraction of imidazole units. Results of these studies are illustrated in Figs. 5 and 6.

As can be seen from Fig. 5, DSC thermograms are different because before thermodecomposition process, endo-effects appear at 78.2°C for poly(EMA) and 175°C for poly(VIM), and at 80.6–94.1°C for the VIM–EMA copolymers. These endo-effects on the DSC curves are

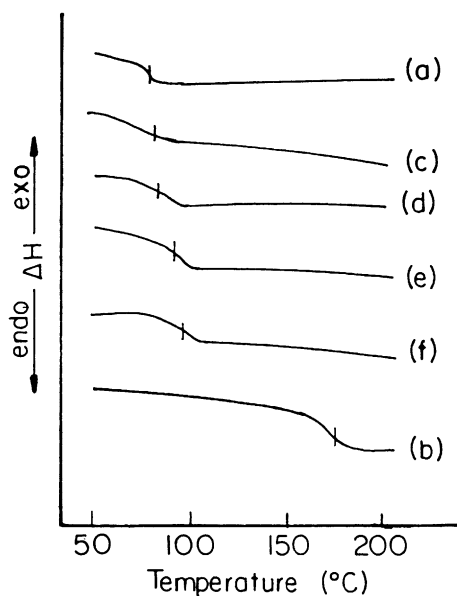


Fig. 5. DSC thermograms of: (a) poly(EMA), (b) poly(VIM) and (c)–(f) VIM–EMA copolymers (mol% of VIM-unit as in Fig. 1).

related to glass-transition temperatures (T_g) of polymers and copolymers studied. It is shown that increase of VIM unit content in copolymers has provided a visible increase in T_g .

TGA and respective derivative curves are presented in Fig. 6. Evidence from the character of TGA curves shows that the thermal stability of copolymers increases with increasing imidazole fragment in copolymers in comparison with those for poly(EMA), and on the contrary, thermal stability of copolymers decreases in comparison with those for poly(VIM). This observed additive change of thermal behaviors can be explained by an effect of VIM units in copolymers.

As can be seen from Fig. 6, differential TGA (DTA) curves of VIM–EMA copolymers different from those for poly(VIM) and have two peaks relating to two-steps of thermal decomposition process for the macromolecules containing ester and imidazole fragments, respectively. Intensity and position of these peaks depend on VIM unit content in copolymers, and higher temperature degradation peak grows at the expense of lower temperature shoulder of poly(EMA). Similar character of decomposition with two exo-peaks was previously observed for pure poly(EMA) [36].

From the data of Figs. 5 and 6, the characterization of VIM–EMA copolymers are determined and are summarized in Table 4. It is observed that the copolymers showed distinct glass transitions and thermal decomposition behaviors quite different from the corresponding homopolymers. The glass transition tem-

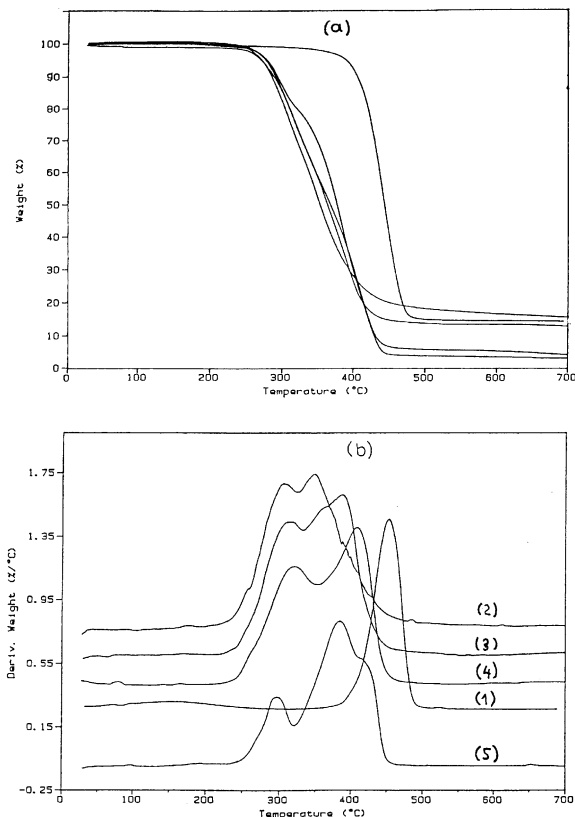


Fig. 6. (a) TGA and (b) DTA curves of (1) poly(VIM), (2–4) VIM–EMA copolymers (mol% of VIM-unit as in Fig. 1(b)–(d)) and (5) poly(EMA).

perature of the resulting copolymers increased with increasing VIM molar fraction in the copolymer. However, insignificant change of the temperatures of thermal decomposition (from 319°C to 301°C for T_{d1} values and from 407°C to 393°C for T_{d2} values) is observed. This fact can be explained by specific macromolecular interaction through carbonyl and imidazole fragments in the glass-transition and melting-decomposition stages.

4. Conclusion

The VIM and EMA pair has been selected to investigate free-radical copolymerization behavior and thermal properties of resulting copolymers. By applying FR and KT methodologies to the copolymerization data obtained from elemental analysis and FTIR analysis of copolymers obtained at low conversions the reactivity ratios of VIM(1) and EMA(2) were found to be $r_1 = 0.35 \pm 0.02$ and $r_2 = 3.47 \pm 0.20$. The differences in reactivity ratios are explained on the basis of differences in electron-donating and receiving properties of these monomers. Relatively high activity of EMA growing

Table 4

Effect of vinylimidazole fragment on the thermal behaviours of VIM–EMA copolymers

Content of VIM-units (mol%)	DSC analysis		DTGA analysis		TGA analysis, weight loss (%) at		
	T_g (°C)	ΔH (J/g)	T_{d1} (°C)	T_{d2} (°C)	250°C	300°C	350°C
100 (PVIM)	175.1	349	–	438	1.3	2.0	2.7
25.5	94.1	266	301	393	2.7	17.6	45.6
13.3	92.0	286	305	347	2.0	21.3	51.3
12.4	83.7	358	319	363	2.2	15.6	42.8
10.6	82.0	490	314	389	2.0	16.7	44.7
6.0	80.6	630	319	407	2.1	14.9	42.1
0.0 (PEMA)	78.2	690	298	383	1.3	14.0	32.0

radical was explained by effect of complex formation between carbonyl group and imidazole fragments in chain growth reactions. The formation of random copolymers was further substantiated by the thermal characterization of copolymers. DSC study revealed the existence of single T_g value between the T_g s of individual homopolymers. Thermal stability of copolymers were shown to be improved by incorporation of VIM moieties into dominating EMA units.

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