

Complex-radical copolymerization of *N*-vinyl pyrrolidone with isostructural analogs of maleic anhydride

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Abstract

Radical copolymerizations of *N*-vinyl-2-pyrrolidone (VP) with isostructural analogs of maleic anhydride (MA), such as citraconic anhydride (CA) and *N*-substituted maleimides [maleimide (MI), *N*-ethylmaleimide (EMI) and *N*-phenylmaleimide (PhMI)] were studied. Compositions of copolymers synthesized in a wide range of monomer feed ratios were determined by alkali titration (for anhydride copolymers), FTIR and ¹H NMR spectroscopy using 1495 and 630 cm⁻¹ (for VP–MI), 1289 and 1225 cm⁻¹ (for VP–EMI) and 1050 and 3067 cm⁻¹ (for VP–PhMI) analytical bands and integral areas of CH₂ (pyrrolidone ring) and CH (MI), CH₃ (EMI) and CH= (benzene ring in PhMI) groups, respectively. Electron-donor VP monomer was found to have substantially different reactivities in the radical copolymerization with MA, CA and *N*-substituted (H, C₂H₅ and phenyl) maleimides as electron-acceptor comonomers. Effects of H-bonding and N→O=C coordination on the monomer reactivity ratios were evaluated. Tendency to alternation of the monomer pairs increases in the order of VP–MA > VP–CA > VP–MI > VP–PhMI > VP–EMI. Structure-thermal property-relationship for the synthesized copolymers was also studied.

Keywords

copolymerization; *N*-vinyl-2-pyrrolidone; maleic and citraconic anhydrides; maleimides; monomer reactivity ratios; thermal behavior

Introduction

Homo- and copolymers of *N*-vinyl-2-pyrrolidone (VP) are of considerable academic and industrial interest due to their unique properties allowing to use of these polymeric systems in lithography as light sensitive thin coatings for printing plates, for preparation of separating membranes for ultrafiltration, biocompatible polymers with low toxicity and carriers of biologically active compounds, sorbents, coagulants and flocculants.^{1,2} VP (M₁) has been copolymerized with a considerable variety of functional comonomers (M₂), such as styrene,³ vinyl acetate,⁴ 2-vinyl- and 4-vinylpyridines,⁵ vinylcyclohexane,⁶ maleic anhydride,^{7,8} hydroxypropyl maleimide⁹ and *N*-isopropylacrylamide.¹⁰ VP as a electron donor monomer shows an increase in

its propagation rate constant in polar solvent, due to solvation of VP monomer and growing macroradicals in the radical polymerization conditions.¹¹ Radical copolymerization/crosslinking method was used for preparation of VP-containing biodegradable, thermoresponsive and biocompatible hydrogels for drug delivery.^{12,13} Effect of H-bonding interactions on the miscibility and thermal behavior in poly(VP) and poly(ethylene-*co*-acrylic acid) mixtures was studied by DSC, DMTA and IR spectroscopy.¹⁴

On the other hand, *N*-substituted maleimides as electron-acceptor monomers have been reported to copolymerize alternatively with a variety of functional comonomers¹⁵⁻²² by a free-radical and/or complex-radical mechanism. These alternating copolymers have some unique properties such as high and superior thermal stabilities,^{16,23,24} fire resistances,²⁵ photo-, X-ray and E-beam sensitivities^{18,23,26,27} as well as catalytic and chiroptical activities.^{28,29}

Alternating copolymers of *N*-vinylpyrrolidone (VP) with maleic anhydride (MA) were synthesized by solution homogeneous or heterogeneous radical copolymerization using various solvents such as benzene,^{8,30} tetrahydrofuran³¹ and 1,4-dioxane.³² Obtained copolymers predominantly used for the covalent immobilization of protein in aqueous buffers,^{8,31} specially for the conjugation of bovine serum albumin.³² Radical copolymerization of *N*-phenyl maleimide with 2-hydroxyethyl(ethyl) methacrylates, determination monomer reactivity ratios and evaluation of H-bonding effect on the formation of complexed macromolecular structure were also an subject of our recent publications.^{10,33}

In this paper we report the synthesis and characterization of copolymers VP with *R-N*-substituted (*R* = H, ethyl and phenyl) maleimides, determination of monomer reactivity ratios using quantitative FTIR and ¹H NMR analysis methods, evaluation of structural peculiarities and effect of H-bonding and $-N \rightarrow O=C-$ coordination on the monomer reactivity ratios, as well as composition-structure-thermal behavior relationship of synthesized copolymers.

Experimental

Materials

N-Vinyl-2-pyrrolidone (VP) (Fluka) was purified before use by distillation under moderate vacuum. Maleic anhydride (MA) (Aldrich) was purified by recrystallization from anhydrous benzene and sublimation in vacuum. Citraconic anhydride (CA) (Aldrich) was distilled under vacuum before use. MI (Aldrich) and EMI (Fluka) were purified before use by distillation under vacuum: mp 93.0°C, PhMI (Aldrich) was purified by recrystallizing twice from anhydrous solution in ethanol and then by distillation under vacuum.

2,2'-Azobisisobutyronitrile (AIBN) radical initiator (Aldrich) was recrystallized just before use from chloroform solution with diethyl ether. The procedure was repeated twice: mp 102°C.

Copolymerization

The donor-acceptor type of radical copolymerizations of the three monomer pairs (VP-MA, VP-CA, VP-MI, VP-EMI and VP-PMI) were carried out in similar conditions: in 1,4-dioxane as solvent at 65°C with AIBN as the initiator in glass tube

type of microreactors. The appropriate amount of comonomers in various mol percentages were mixed with solvent and initiator and placed into the tubes. The reaction mixture was cooled by liquid nitrogen and flushed with nitrogen gas for 2 min, then thawed. The tubes were sealed and placed in a thermostated silicon oil bath at 65°C. The time of copolymerization was about 48 hours. All copolymers were isolated from reaction mixture and purified by two precipitation procedures from 1,4-dioxane to diethyl ether, and washing with benzene. Then, all of them were dissolved in dimethyl formamide and reprecipitated in diethyl ether. After last extraction by diethyl ether, the copolymers were then isolated by centrifugation and dried at 40°C and under moderated vacuum to constant weight. The copolymer compositions were determined by both ¹H-NMR (400 MHz) and FTIR spectroscopy, thermal behavior of the copolymers were determined by DSC and TGA analysis.

The copolymers synthesized from equimolar ratio of monomer feed had the following average characteristics:

Poly(VP-co-MA): $[\eta]_{in}$ in 1,4-dioxane at 25 ± 0.1°C 0.79 dl g⁻¹; T_g 31.8°C; ΔH 14.76 J g⁻¹ (by DSC). ¹H NMR spectra (in CHCl₃-*d*₁ at 27°C), δ (ppm): 1.30-1.83 ¹CH₂, 1.84-2.33 ⁴CH₂, 2.95-3.54 ^{3,5}CH₂, 3.56-3.95 ²CH, 4.08-4.45 ^{6,7}CH.

Poly(VP-co-CA): $[\eta]_{in}$ in 1,4-dioxane at 25 ± 0.1°C 0.68 dl g⁻¹; T_g 37.6°C; ΔH 0.63 J g⁻¹ (by DSC). ¹H NMR spectra (in CHCl₃-*d*₁ at 27°C), δ (ppm): 0.85-1.58 ⁷CH₃, 1.60-1.96 ¹CH₂, 1.98-2.62 ⁴CH₂, 2.63-3.92 ^{2,3,5}CH₂, 4.02-4.95 ⁶CH.

Poly(VP-co-MI): $[\eta]_{in}$ in DMF at 25 ± 0.1°C 0.12 dl g⁻¹; T_g 31.8°C; ΔH 14.76 J g⁻¹ (by DSC); ¹H NMR spectra (in CHCl₃-*d*₁ at 27°C), δ (ppm): 1.25-1.59 ³⁻⁵, ¹CH₂, 2.08 ²CH, 3.12-3.58 ^{6,7}CH, 10.86-11.38 ⁸NH.

Poly(VP-co-EM): $[\eta]_{in}$ in 1,4-dioxane at 25 ± 0.1°C 0.08 dl g⁻¹; T_g 37.6°C; ΔH 0.63 J g⁻¹ (by DSC); ¹H NMR spectra (in CHCl₃-*d*₁ at 27°C), δ (ppm): 1.05 ⁹CH₃, 1.18-1.73 ¹CH₂, 1.75-2.03 ⁴CH₂, 2.05-2.51 ⁵CH₂, 2.95-3.15 ³CH₂, 3.16-3.49 ⁸CH₂, 3.50-3.75 ²CH, ^{6,7}CH.

Poly(VP-co-PhMI): $[\eta]_{in}$ in 1,4-dioxane at 25 ± 0.1°C 0.13 dl g⁻¹; T_g 59.2°C; ΔH 3.09 J g⁻¹ (by DSC); ¹H NMR spectra (in CHCl₃-*d*₁ at 27°C), δ (ppm): 1.15-1.70 ¹CH₂, 1.72-2.00 ⁴CH₂, 2.03-2.82 ⁵CH₂, 2.91-3.42 ^{2,3}CH, 4.05-4.72 ^{6,7}CH, 2.91-3.42 ⁸⁻¹²CH=(Ph).

Characterization

Fourier transform infrared (FTIR) spectra of the copolymers (KBr pellet) were recorded by FTIR Nicolet 510 spectrometer in the 4500-400 cm⁻¹ range, where 30 scans were taken at 4 cm⁻¹ resolution. Proton NMR spectra were recorded on a JEOL 6X-400 (400 MHz) spectrometer with CHCl₃-*d*₁ as a solvent at 27°C. For the composition analysis of copolymers, specifically contents of VP and maleimide units, well-known FTIR³⁴ and ¹H NMR³⁵ analysis methods were used. In these procedures, the absorption bands of characteristic functional groups in FTIR spectra and integral area for the proton signals from different functional groups in NMR spectra were used as analytical bands and signals, respectively. Use of the elemental analysis method (by nitrogen contents) for the composition analysis of these copolymers is not possible because both monomer units in the VP-Maleimide systems contain nitrogen atoms.

The compositions of the copolymers, specifically molar fraction ratios of the comonomer units (m_1/m_2), synthesized using various monomer feed ratios were determined using to following equations:

$$m_1/m_2 = (\Delta A_{m_1} / \Delta A_{m_2}) \times (M_2/M_1) \text{ (by FTIR analysis)} \quad (1)$$

where $Am_i = \log(I_0/I)$, $\Delta Am_i = Am_i / A^s$ (A^s is least changing absorption band as a standard peak); M_1 and M_2 are molecular weights of VP and imide comonomer units, respectively.

$$m_1/m_2 = n_2 Am_1 / n_1 Am_2 \quad (\text{by } ^1\text{H NMR analysis}) \quad (2)$$

where Am_1 and Am_2 are the normalized areas per H from the corresponding functional groups of the monomer unit regions in $^1\text{H NMR}$ spectra; n_1 and n_2 are the integers of proton(s) in the functional group of the monomers.

Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) of copolymers were performed on a DuPont TA 2000 calorimeter and Setaram Labsys TG-TGA 12 Thermal Analyzer, respectively, under nitrogen atmosphere at a heating rate of $10^\circ\text{C min}^{-1}$.

Crystallization behavior of copolymers was determined by Phillips manual spectrogonimeter employing CuK_α ($\lambda = 1.54184\text{\AA}$) radiation over the range $S^\circ \leq 2\theta \leq 50^\circ$.

Acid Numbers (AN) of the water-soluble anhydride-containing copolymers were determined by a standard alkali titration method with a Consort P901 pH-meter.

Intrinsic viscosities of the copolymers with different compositions were determined in 1,4-dioxane at $25 \pm 0.1^\circ\text{C}$ in the concentration range of $0.1\text{-}1.0 \text{ g dl}^{-1}$ by using an Ubbelohde viscometer.

Results and Discussion

The Monomer Reactivity Ratios

Taking into consideration of the character of double bond-functional group conjugation, the monomer pairs studied can be classified as donor (VP)-acceptor (anhydrides) monomer systems with $\pi(\text{C}=\text{C})\leftarrow\rho(\text{N})\leftarrow\pi^*(\text{C}=\text{O})$ (VP) and $\pi(\text{C}=\text{C})\rightarrow\pi^*(\text{C}=\text{O})$ (MA or CA), and, therefore, they will have a tendency toward alternation in radical copolymerization. The synthesized copolymers were characterized by elemental analysis (content of N for VP unit), alkali titration (acid numbers for anhydride units), FTIR and $^1\text{H NMR}$ spectroscopy for the determination of VP and MA (or CA) unit contents. The following absorption bands and chemical shifts of proton signals were used for the quantitative analysis of the copolymers with different compositions: 1665 , 1775 and 1126 cm^{-1} analytical bands and proton integral areas of CH-N (VP unit), CH (MA unit), and CH_3 (CA unit) groups, respectively. FTIR spectra of poly(VP), poly(VP-co-MA) and poly(VP-co-CA), which were synthesized in the similar conditions, are illustrated in Fig 1. Observed partial shift of C=O band from 1650 (for VP homopolymer) to 1665 cm^{-1} (for copolymer), appear of 1735 cm^{-1} and shift of CH_2 band (in $\text{CH}_2\text{-C}=\text{O}$ of pyrrolidone ring) from 1425 (for VP homopolymer) to 1440 cm^{-1} (for copolymer) are indicated the presence of complexed $\text{-C}=\text{O}\dots\text{N-}$ fragments in structure of copolymers.

Similar changes are observed in $^1\text{H NMR}$ spectra of copolymers, which are presented in Fig. 2.

Copolymerizations of VP with MA and CA were carried out under relatively lower conversion conditions (around 5-7.5 %), i.e., in the steady-state, in order to essentially reduce the effect of copolymer composition drift and to determine constants of copolymerization (r_1 and r_2) by using known terminal models of Kelen-Tüdös (KT)^[36]

equations. For comparison, non-linear regression (NLR) procedure using a micro-computer program^[37] has also been applied to calculate monomer reactivity ratios.

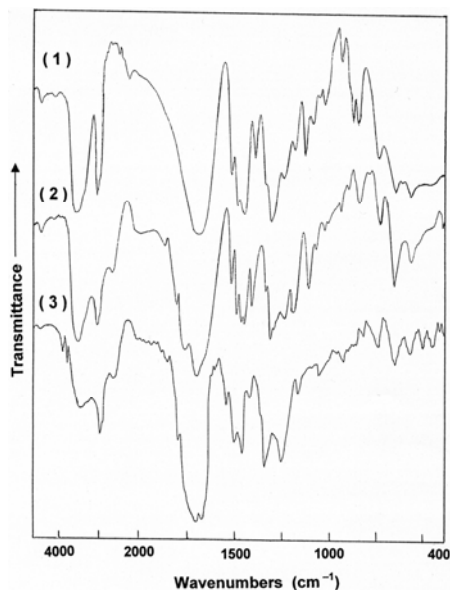


Figure 1. FTIR spectra of (1) Poly(VP), (2) poly(VP-*alt*-MA) and (3) poly(VP-*alt*-CA).

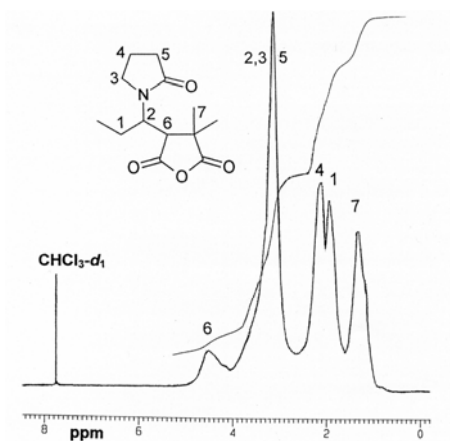
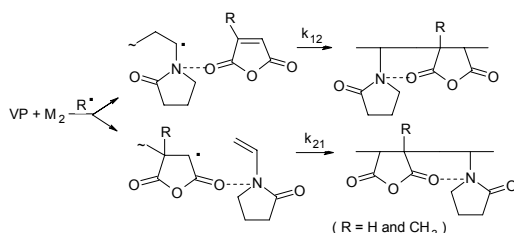


Figure 2. ¹H NMR spectra of (a) poly(VP-*alt*-MA) and (b) poly(VP-*alt*-CA).

Results of radical copolymerizations at various monomer feed ratios and monomer-copolymer composition relationships are summarized in Table 1 and 2. Copolymer compositions calculated by using elemental analysis data (N, %) (Table 1) were in a reasonable agreement with those obtained from FTIR and ¹H NMR analysis using Eqs. (1) and (2), respectively (Table 2). Monomer reactivity ratios (r_1 and r_2) for the

studied two monomer pairs were obtained from experimental data and calculated by parameters of FR and KT equations, presented in Table 1, as well as NLR analysis. As seen from these values (Table 3) nature of anhydride comonomers exerts a visible influence on the reactivity ratios of monomers, and, therefore on the regularity of chain growth reactions, i.e., tendency of the monomer units to alternation. Relatively lower degree of alternation of the monomer units ($r_1.r_2 \rightarrow 0$) observed in the VP-CA system can be explained by effect of α -CH₃ group on the reactivity of CA monomer, which is decreased the acceptor properties of double bond. Observed tendency to alternation in the both monomer systems can be explained complexing effect, realizing between monomer/comonomer molecules and monomers/growing macroradicals, on the chain growth, which are responsible for the formation of copolymers with primary alternating structure as shown in the following Scheme 1:



Scheme 1. Chain growth in radical copolymerization of VP with MA or CA.

The monomer unit composition of anhydride-containing copolymers was assessed by potentiometric titration with 0.1 N aqueous KOH in aqueous solution and confirmed by FTIR and ¹H NMR spectra.

Effect of H-bonding and N→O=C coordination on the monomer reactivity ratios

Taking into consideration the character of double bond-functional group conjugation, the monomer pairs studied can be classified as donor (VP)-acceptor (imides) monomer systems, and therefore, they will have a tendency toward alternation in radical copolymerization. This tendency will certainly be dependent on the nature of *N*-substituent in the imide comonomers.

Copolymerizations of VP with *R-N*-substituted maleimides (R = H, C₂H₅ and C₆H₅) were carried out under relatively lower conversion conditions (around 5-7.5 %).

The synthesized copolymers were characterized by FTIR and ¹H NMR spectroscopy for the determination of VP and maleimide unit contents. The following absorption bands and chemical shifts of proton signals were used for the quantitative analysis of the copolymers with different compositions: 1495 and 630 cm⁻¹ (for VP-MI), 1289 and 1225 cm⁻¹ (for VP-EMI) and 1050 and 3067 cm⁻¹ (for VP-PhMI) analytical bands and integral areas of CH₂ (pyrrolidone ring) and CH (MI), CH₃ (EMI) and CH= (benzene ring in PhMI) groups, respectively.

FTIR and ¹H NMR results of poly(VP) and poly(VP-co-imide) radical copolymerizations of various monomer feed ratios and monomer-copolymer composition relationships are summarized in Table 1. Copolymer compositions calculated using FTIR spectroscopy method and Eqn. (1) were in a reasonable agreement with those obtained from ¹H NMR analysis using Eqn. (2) (Table 2).

Table 1. Radical copolymerization of VP (M_1) with *N*-substituted ($R = H, C_2H_5$ and C_6H_5) maleimides (M_2)^a

Monomer feed (mol %)		FTIR analysis		Copolymer composition (mol %)		Parameters of KT-eq.				
[M_1]	[M_2]	ΔAm_1	ΔAm_2	m_1	m_2	F^2/f	$F(f-1)/f$	$(F^2/f + \alpha^b)$	ξ	η
VP – MI		(1495)	(630)							
20	80	1.602	0.605	46.82	53.18	0.07	-0.034	0.97	0.072	-0.035
33.4	66.6	1.354	0.790	48.89	51.11	0.29	-0.024	1.19	0.244	-0.020
50	50	0.626	0.824	52.16	47.84	0.92	0.083	1.82	0.505	0.046
66.6	33.4	1.057	0.984	53.88	46.12	3.21	0.278	4.11	0.781	0.068
80	20	0.883	0.987	58.01	41.99	11.59	1.104	12.49	0.928	0.088
VP – EMI		(1289)	(1225)							
20	80	0.340	0.322	54.34	45.66	0.05	0.04	1.39	0.128	0.103
33.4	66.6	0.377	0.244	63.50	36.50	0.14	0.21	0.48	0.292	0.437
50	50	0.346	0.172	69.33	30.67	0.44	0.56	0.78	0.564	0.718
66.6	33.4	0.458	0.112	82.14	17.86	0.87	1.56	1.21	0.777	1.393
80	20	0.485	0.080	87.21	12.79	2.37	3.41	2.69	0.912	1.268
VP – PhMI		(1050)	(3067)							
20	80	0.030	0.006	33.33	66.37	0.13	-0.25	0.86	0.146	-0.292
33.4	66.6	0.046	0.050	47.92	52.08	0.27	-0.04	1.00	0.271	-0.043
50	50	0.067	0.043	60.94	39.06	0.64	0.36	1.37	0.464	0.262
66.6	33.4	0.093	0.038	71.02	28.98	1.63	1.18	2.36	0.691	0.501
80	20	0.120	0.032	78.95	21.05	4.27	2.93	5.00	0.854	0.587

^a Reaction conditions: solvent, 1,4-dioxane; $65 \pm 0.1^\circ\text{C}$; initiator, $[\text{AIBN}] = 3.04 \times 10^{-3} \text{ mol/L}$; $[\text{M}]_{\text{total}} = 2.5 \text{ mol/L}$; conversion $\leq 10\%$ (around 7.6 – 9.2 %).

^b α (arbitrary parameter) = 0.90 (for VP–MI), 0.34 (for VP–EMI) and 0.73 (for VP–PhMI).

Table 2. Copolymer compositions determined by ¹NMR and FTIR analysis^a

Copolymer	Analytical groups in monomer units		Integral area (Absorbance)		Copolymer composition (mol %)			
	VP	Imide	Am_1	Am_2	by ¹ NMR		by FTIR	
					m_1	m_2	m_1	m_2
Poly(VP-co-MI)	(² CH ₂)	(^{6,7} CH)	0.147	0.113	53.28	46.72	52.16	47.84
Poly(VP-co-EtMI)	(³ CH ₂)	(⁹ CH ₃)	0.236	0.148	70.55	29.45	69.33	30.67
Poly(VP-co-PhMI)	(⁴ CH ₂)	(⁸⁻¹² Ph)	0.399	0.601	62.43	37.57	60.94	39.06

^a All copolymers were synthesized using equimolar monomer mixture (1:1).

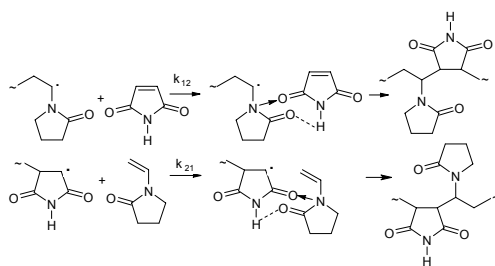
Monomer reactivity ratios (r_1 and r_2) for the studied three monomer pairs were obtained using experimental data and calculated parameters of KT equation, presented in Table 1, as well as by NLR analysis. Obtained the monomer reactivity ratios were presented in Table 3.

As seen from these values, nature of *N*-substituent in maleimide comonomers exerts a significant influence on the reactivity ratios of monomers, and, therefore on the regularity of chain growth reactions. Monomer reactivity ratios determined by

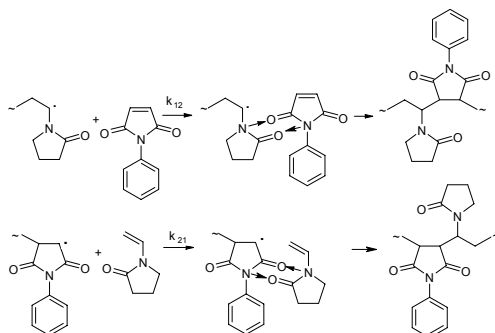
Table 3. The monomer reactivity ratios for the VP-maleimides monomer pairs.

Monomer pair	Method	r_1	r_2	$r_1 \cdot r_2$
VP-MI	KT	0.11	0.04	$4.4 \cdot 10^{-3}$
	NLR	0.098	0.03	$2.9 \cdot 10^{-3}$
VP-EMI	KT	1.58	0.04	0.063
	NLR	1.53	0.02	0.031
VP-PhMI	KT	0.79	0.21	0.166
	NLR	0.77	0.22	0.169

various methods have almost similar values, indicating reasonable agreement between these methods. It was shown that the alternating copolymerizations are realized in the VP-MI and VP-PhMI monomer systems, while copolymerization of VP with EMI is predominantly proceeding by random copolymerization mechanism. Alternation tendency of the monomer units increases in the order of VP-MI > VP-PhMI > VP-EMI. Relatively higher degree of alternation of the monomers units ($r_1 \cdot r_2 \rightarrow 0$) observed in the VP-MI system can be explained by H-bonding and $N \rightarrow C=O$ coordination effects on the chain growth, which are responsible for the formation of copolymers with primary alternating structure as shown in the following Scheme 2:

**Scheme 2.** Chain growth in radical copolymerization of VP with imide comonomers

Observed relatively low tendency to alternation of monomer units in VP-PhMI system can be explained only by effect of $N \rightarrow O=C$ coordination which is less than H-bonding effect as shown in the following Scheme 3.

**Scheme 3.** Coordination of VP with MI and PhMI.

Obtained high value of r_1 (>1), and, therefore a low tendency to alternation between VP and EMI monomers in radical copolymerization allows to assume that ethyl group as an electrophilic substituent essentially reduces coordination force of $N \rightarrow O=C$ bond in chain growth reactions.

In general, these results indicate that chain growth reactions proceed predominantly by the addition of VP monomer to maleimide macroradicals through intermediate coordination and H-bonding between carbonyl and imide groups of monomers.

Copolymer composition-thermal behavior relationship

The possibility of the formation of specific molecular side-chain fragments through various complexing agents (coordinating, H-bonding, charge transfer complexing, etc.) in most of alternating copolymers containing free carboxylic and other functional groups can allowed us to use these polymers for the fabrication of stable mesophases of side chain polymers, compatible polymeric systems, stable hydro- and sol-gel, stable organized molecular films with non-linear optical properties, liquid crystalline polymers with flexible backbones, biomolecular complexes and other specific polymer materials. It is known that one of the important intra- and intermolecular structural characteristics of polyfunctional polymers is structural regularity and bond flexibility of their macromolecules^[38]. When the polar polymers possess H-bonding capability, the most energetically favored crystal structures will tend to capitalize on these features. Clark et al.^[39] used thermal analysis and IR spectroscopy to study the interactions between poly(VP) and 3,5-dihydroxybenzoic acid as a hydrogen bonding active aromatic compounds. A remarkable strong interaction was observed in this system, which is consistent with the crosslinking of the poly(VP) by acid dimers. This polymer/acid interaction can be served as a model system for the copolymers containing VP unit and acidic anhydride linkage in this system.

Synthesized copolymers display different thermal properties, including melting and glass-transition behavior, depending on content of hydrogen-bonding fragment. The VP-MA and VP-CA alternating copolymers (Fig.3) with their characteristic glass-transition endotherms (T_g) in the field of 195 and 186.5°C, respectively.

TGA thermograph of hydrolyzed terpolymer differs from thermograph of initial copolymer and has multi-step character of decomposition process. A first step of decomposition is related to dehydration reaction, i.e., transferred acid units to anhydride forms in side-chain of macromolecules. Thermal behavior of the synthesized copolymers with different compositions, as well as the homopolymer of VP, which is prepared in the similar conditions, were studied by DSC and TGA-DTG methods. DSC scans of homo- and copolymers are also recorded at relatively lower temperature condition and summarized in Table 4 and poly(VP-co-MI)s show almost similar endo-effects around 31.6-59.2°C which are almost not changed in increasing the amount of MI-unit in the copolymers. The second endo-effects observed on the DSC curves around 175-225°C would be related to glass-transition temperature (T_g). This fact indicated that the copolymers have semi-crystalline structure due to formation complex fragments through $-NH \dots O=C-H$ -bonding in the side-chain macromolecules. The first endo-peaks (broad peaks for the MI copolymers and relatively narrow peaks for the EMI and PhMI copolymers) appeared on the DSC curves can be related to the points of thermal sensitivity (T_s) of the copolymers in the solid state. Both poly(VP-co-EMI) and poly(VP-co-PhMI) samples show a single glass transition at the temperature range from T_g (for the homopolymer of VP) to T_g

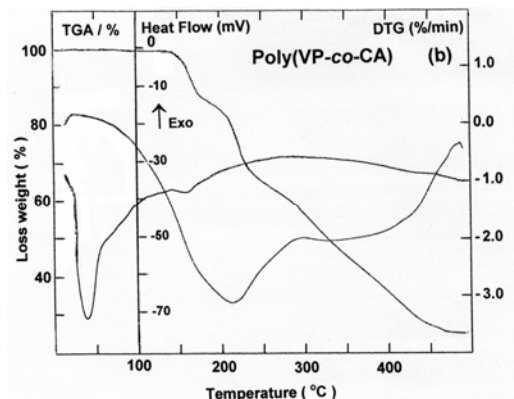


Figure 3. TGA–DTG–DSC curves of (a) poly(VP-*alt*-MA) and (b) poly(VP-*alt*-CA).

Table 4. Effect of imide unit on the thermal behavior and crystallinity of the copolymers.

Content of imide units (mol %)	DSC analysis			XRD analysis
	T_s^a (°C)	T_g (°C)	ΔH (Jg ⁻¹)	Crystallinity, χ_c (%)
VP – MI				
Poly(VP)	40.9	154.5	1.68	21.07
42.0	37.5	92.5	2.08	13.06
46.1	45.8	95.8	2.44	14.11
47.8	50.2	98.2	2.67	14.66
51.1	66.7	95.9	3.12	16.23
53.2	70.8	96.7	3.26	18.90
VP – EMI				
12.8	74.4	159.9	1.09	19.07
17.9	69.8	165.9	1.16	17.56
30.7	68.3	170.0	1.22	16.07
36.5	67.4	184.8	1.29	14.81
45.7	58.1	188.1	1.31	13.08
VP – PhMI				
21.1	61.4	170.4	1.40	18.96
29.0	63.6	175.5	1.35	17.21
39.1	61.0	181.8	1.33	14.92
52.1	64.9	188.6	1.37	14.12
66.4	67.8	193.2	2.24	12.76

^a T_s is temperature sensitiveness which is equivalent to low critical solution temperature in solid state.

(for the copolymer with the maximum content of imide unit). This fact can be explained by the impossibility of microphase separation in bulk state, i.e., in the conditions of DSC analysis.

Thermal stabilities of the copolymers were measured by the onset decomposition temperature, T_a , which is calculated from TGA curves. Unlike one-step degradation of

poly(VP), poly(VP-*co*-imide)s degraded according to three-step decomposition mechanism.

Conclusion

Radical copolymerization of VP as electron donor monomer with acceptor type of anhydride and maleimide comonomers has been studied. It was shown that nature of N-substituent in maleimide comonomers exerts a significant influence on the monomer reactivity ratios of monomers, and, therefore on the regularity of chain growth reactions. Alternation tendency of the monomer units increases in the order of VP-MA>VP-CA>VP-MI>VP-PhMI>VP-EMI. Observed relatively higher degree of alternation of the monomers units ($r_1.r_2 \rightarrow 0$) in the VP-MI and VP-PhMI systems was explained by H-bonding and N \rightarrow C=O coordination effects on the chain growth, which are responsible for the formation of copolymers with predominantly alternating structure. Obtained results from copolymer composition-structure (crystallinity)-thermal behavior relationship studies, which are significantly depended on the nature of imide comonomer, are also confirmed the formation of H-bonding and/or N \rightarrow C=O coordinated macromolecular complexes.

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