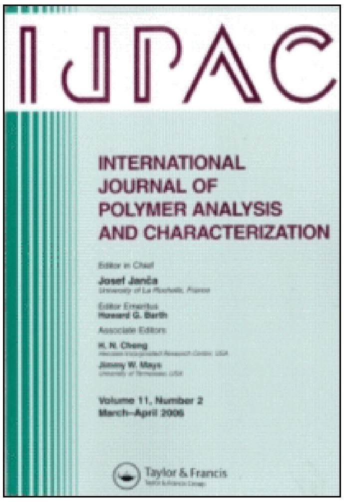

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Copolymers of N-vinylcarbazole with Acrylic Acid, Itaconic Acid, and N-isopropylacrylamide: Synthesis, Determination of Monomer Reactivity Ratios, and Electrochemical Properties

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Abstract: Free radical copolymerizations of N-vinylcarbazole (NVCz) with acrylic acid (AA), itaconic acid (IA), and N-isopropylacrylamide (NIPAAm) at different feed ratios were conducted in 1,4-dioxane at 50°C. The copolymers were characterized by UV and FT-IR spectroscopic techniques, viscosity, and glass transition temperature measurements. The monomer reactivity ratios were determined by application of the extended Kelen-Tüdós method, which is one of the conventional linearization methods, and found to be $r_{NVCz} = 0.29$ and $r_{NIPAAm} = 0.12$, $r_{NVCz} = 0.84$ and $r_{IA} = 0.12$, $r_{NVCz} = 0.86$ and $r_{AA} = 0.31$ by UV, and $r_{NVCz} = 0.32$ and $r_{NIPAAm} = 0.07$ by FT-IR. Polymer-modified electrodes having electroactive, ionic, and hydrophobic properties were prepared by electro-oxidation using PNVCz, NVCz/NIPAAm, and NVCz/IA copolymers and tested as sensor electrodes to dopamine.

Keywords: Cyclic voltammetry; Dopamine; Monomer reactivity ratios; N-vinylcarbazole/itaconic acid copolymer; N-vinylcarbazole/N-isopropylacrylamide copolymer; Poly (N-vinylcarbazole); UV spectroscopy

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INTRODUCTION

Poly(N-vinylcarbazole) (PNVCz) is one of a number of vinyl polymers with aromatic pendant groups that have recently gained academic and industrial interest as potential commercial photoconductor systems because they exhibit unusual electrical and photoelectrical properties and excellent thermal stability.[1–7] However, its extreme brittleness, poor mechanical characteristics, and high processing temperature ($T_g = 486\,K$) limit its commercial applications. These material properties have been modified by preparation of its composites and copolymers.[8–11]

Polymer-modified electrodes (PMEs) have received extensive interest in the detection of analytes because of their selectivities, sensitivities, homogeneities in electrochemical deposition, strong attachment to electrode surface, and high chemical stability in air.[12–18]

Dopamine (DA) is only one of the biochemicals called catecholamines, playing an important role in the functioning of the central nervous, cardiovascular, renal, and hormonal systems.[19] In neurotransmission processes, intermolecular interactions such as hydrophobic interaction, ionic interaction, and hydrogen bonding are important factors affecting selective detection of DA. Carbonyl-containing structures have been shown to promote electron transfer reactions for the redox process of important biomolecules, such as DA.[20] Therefore, PMEs containing –C=O groups in the structures of coated polymers have been widely used in electrochemistry to change the electrical properties of the electrode-solution interface and the electrochemical process through adsorption at interfaces.[21]

In this investigation, we report the synthesis and characterization of PNVCz and its copolymers with acrylic acid (AA), itaconic acid (IA), and N-isopropylacrylamide (NIPAAm) using different feed ratios. The compositions of these copolymers were determined by ultraviolet (UV) and Fourier transform-infrared (FT-IR) spectroscopies. The monomer reactivity ratios were computed by the extended Kelen-Tüdős method at high conversion. The present study is also concerned with the use of Pt electrodes coated with PNVCz, N-vinyl carbazole/itaconic acid (NVCz/IA), and N-vinylcarbazole/N-isopropylacrylamide) (NVCz/NIPAAm) copolymer films as DA sensors. It is expected that DA molecules are confined in these polymer films by electrostatic attraction and hydrophobic interaction, resulting from the molecular structures of monomer (NVCz, hydrophobic) and comonomers (IA, weakly acidic, and NIPAAm, hydrophobic/hydrophilic, depending on the processing temperature).

EXPERIMENTAL SECTION

Reagents

N-vinylcarbazole (NVCz; from Aldrich), acrylic acid (AA; from Fluka), itaconic acid (IA; from Fluka), and N-isopropylacrylamide (NIPAAm; from Aldrich) were used as monomers. Tetrahydrofurane (THF), 1,4-dioxane (copolymerization solvent), potassium persulfate (KPS; initiator), tetrabutylammonium tetrafluoroborate ($TBABF_4$; supporting electrolyte), dichloro metan (CH_2Cl_2), and dopamine (DA) were used as received (from Merck). The initiator, α,α'-azobisisobutyronitrile (AIBN; from Merck) was recrystallized from methanol.

Copolymerization

Copolymers of NVCz with IA, AA (weakly acidic comonomers), and NIPAAm (hydrophobic/hydrophilic comonomer) having different compositions were synthesized by free radical solution polymerization in 1,4-dioxane with AIBN (1.0×10^{-3} mol/L) at 50°C under nitrogen atmosphere. The total monomer concentration of 1.0 mol/L was kept constant, while the feed ratio of the monomers was varied. Further, homopolymers of NVCz, NIPAAm, AA, and IA were synthesized using AIBN (1.0×10^{-3} mol/L) in 1,4-dioxane and potassium KPS in water as initiators under identical experimental conditions. The polymerization mixtures were introduced into large glass tubes of ~30 mm diameter equipped with a rubber cap and a syringe. Solutions were degassed by bubbling nitrogen for about 20 min. Hexane was used to precipitate the polymers. The homopolymers and copolymers were filtered and washed with hexane. The products were dried under vacuum at room temperature to constant weight. The solid samples were reprecipitated by hexane from the solution in THF and finally dried. Tables I–III summarize the feed compositions of NVCz and comonomers (NIPAAm, IA, and AA), experimental conditions, and gravimetric (yield, %) and viscometric results ($[\eta]$, mL/g).

PNVCz, NVCz/IA, and NVCz/NIPAAm copolymers having electroactive, ionic, and hydrophobic properties were deposited by electrooxidation in CH_2Cl_2 containing 0.1 M $TBABF_4$ on Pt wire electrode. Cyclic voltammograms of PMEs were obtained at a scan rate of 100 mV/s between 0 and 1800 mV, by using a Model 2263 Parstat potentiostat. The working electrode (area $= 3.14 \times 10^{-2}$ cm^2) and counter electrode were Pt wires. In all cases, Ag wire was used as a pseudo reference electrode. Electrochemical detection of DA was examined in phosphate buffer at pH 7.0.

Table I. Polymerization conditions of PIA and NVCz/IA copolymers

Sample no.	Feed composition (mole %)	Solvent	Time (h)	Yield (%)	[η] (mL/g)	MW (g/mol)
1	IA(100)/NVCz(0)	Water[a]	48	50.4	6.1	3400
2	IA(100)/NVCz(0)	Dioxane	96	42.9	1.1	770
3	IA(80)/NVCz(20)	Dioxane	96	71.3	9.5	—
4	IA(60)/NVCz(40)	Dioxane	30	70.0	29.5	—
5	IA(40)/NVCz(60)	Dioxane	24	83.9	55.7	—
6	IA(20)/NVCz(80)	Dioxane	12	53.7	69.9	—
7	IA(10)/NVCz(90)	Dioxane	6	52.1	—	—
8	IA(5)/NVCz(95)	Dioxane	6	49.7	—	—
9	IA(0)/NVCz(100)	Dioxane	96	86.7	29.2	122000

[a] KPS was used as initiator.

Table II. Polymerization conditions of PAA and NVCz/AA copolymers

Sample no.	Feed composition (mole %)	Time (h)	Yield (%)	[η] (mL/g)	MW (g/mol)
10	AA(100)/NVCz(0)	96	75.4	7.07	54500
11	AA(80)/NVCz(20)	96	80.0	22.6	—
12	AA(60)/NVCz(40)	21	72.0	26.0	—
13	AA(40)/NVCz(60)	31	63.9	52.7	—
14	AA(20)/NVCz(80)	12	53.7	61.8	—
15	AA(10)/NVCz(90)	24	51.3	—	—
16	AA(5)/NVCz(95)	24	49.7	—	—
9	AA(0)/NVCz(100)	96	86.7	29.2	122000

Table III. Polymerization conditions of PNIPAAm and NVCz/NIPAAm copolymers

Sample no.	Feed composition (mole %)	Time (h)	Yield (%)
17	NIPAAm(100)/NVCz(0)	96	75.0
18	NIPAAm(95)/NVCz(5)	72	80.1
19	NIPAAm(90)/NVCz(10)	72	68.3
20	NIPAAm(80)/NVCz(20)	72	67.9
21	NIPAAm(60)/NVCz(40)	72	75.0
22	NIPAAm(45)/NVCz(55)	72	77.4
23	NIPAAm(30)/NVCz(70)	96	78.0
24	NIPAAm(20)/NVCz(80)	96	64.0
25	NIPAAm(10)/NVCz(90)	96	80.3
9	NIPAAm(0)/NVCz(100)	96	86.7

Copolymer Characterization

FT-IR spectra of the samples were recorded on Mattson 3000 and Perkin Elmer Spectrum One (FTIR-reflectance, Universal ATR with diamond and ZnSe) spectrophotometers using KBr pellets and the samples in powder form (Figures 1 and 2), respectively. Viscosity measurements were performed by an Ubbelohde viscometer. The intrinsic viscosities of the homopolymers and copolymers were determined by using the

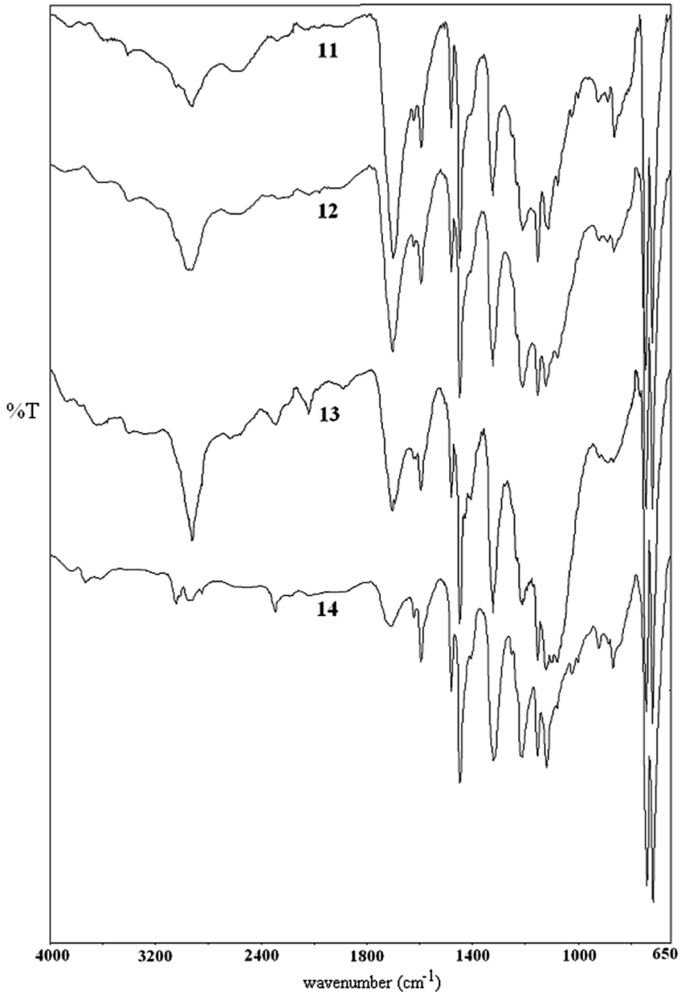


Figure 1. FT-IR spectra of NVCz/AA copolymers, which are given in Table II.

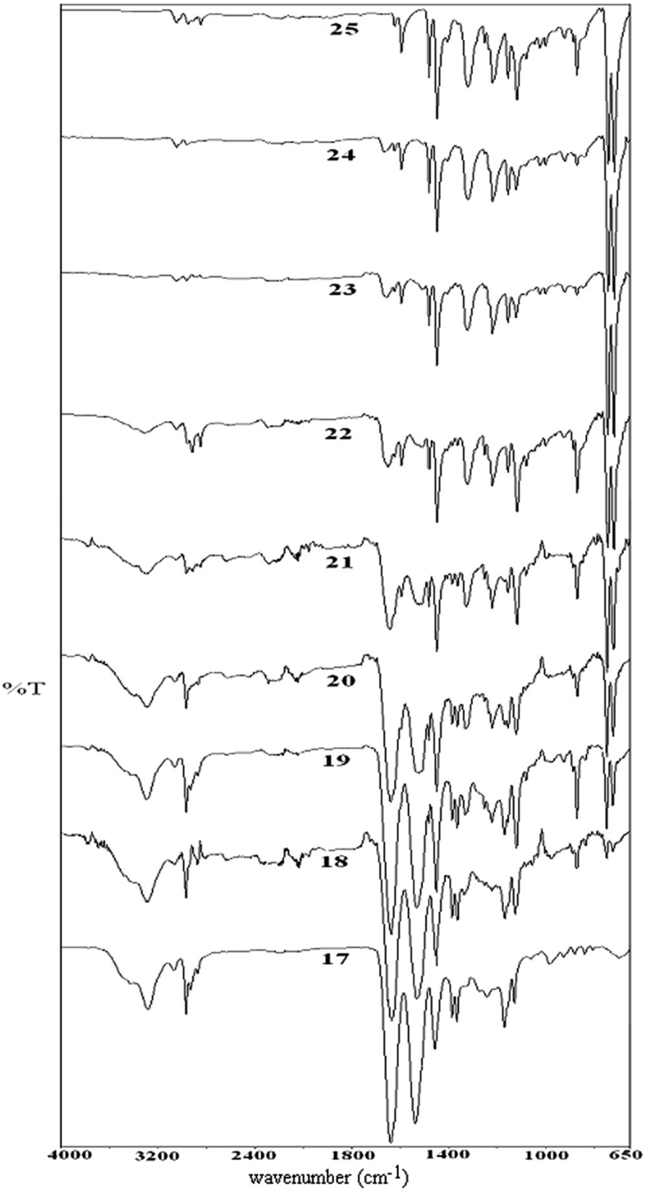


Figure 2. FT-IR spectra of NVCz/NIPAAm copolymers, which are given in Table III.

single-point method (c = 0.5% w/v). They were converted to molecular weight by using the following relations for PIA, PAA, and PNVCz:[22–24]

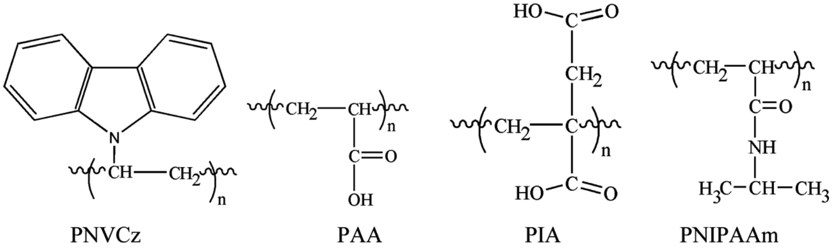
$$[\eta] = 15.47 \times 10^{-3}\,M^{0,90}(25°C;\ 1\,M\ \text{NaCl for PIA and PAA}) \qquad (1)$$

$$[\eta] = 14.40 \times 10^{-3}\,M^{0,65}(25°C,\ \text{THF for PNVCz}) \qquad (2)$$

The compositions of copolymers were determined using a Shimadzu UV-visible 160 A double beam spectrophotometer, equipped with a temperature-controlled cell. UV spectra of the copolymers and the blends of PAA/PNVCz, PIA/PNVCz, and PNIPAAm/PNVCz, which were used to draw the calibration curves, were measured in the range of 200–400 nm. The glass transition temperatures (T_gs) of the samples were determined using a Perkin Elmer differential scanning calorimeter (Model DSC 6). All thermograms were taken between 25° and 250°C in nitrogen atmosphere at a heating rate of 10°C/min.

RESULTS AND DISCUSSION

The chemical structures of PNVCz, PAA, PIA, and PNIPAAm are shown in Scheme 1. The free radical polymerization of NVCz gave a white product, p-type semiconductive with photoconductive and insulating character. In addition, NVCz can be polymerized by chemical and electrochemical oxidation of the ring to produce a conductive polymer.[1,5,6] Copolymers of NVCz with IA, AA, and NIPAAm were prepared at high yields and were characterized by measurements of the intrinsic viscosity and the glass transition temperature. In the case of IA, chain transfer to the monomer, because of the presence of allylic hydrogens in the molecular structure, results in the production of PIA chains with low molecular weight, while its copolymers with the vinyl monomers producing more stable radicals have higher molecular weights. The viscosity results of NVCz/IA and NVCz/AA copolymers show that



Scheme 1. Chemical structures of homopolymers.

the molecular weights of copolymers increased on increasing the mole fraction of NVCz in the feed (Tables I and II).

FT-IR and UV spectroscopic techniques were employed to determine the copolymer compositions and to calculate the reactivity ratios of monomer pairs. C=O stretching ($1730\,\text{cm}^{-1}$) and −OH dimerization (3500–$2500\,\text{cm}^{-1}$) bands in the FT-IR spectra of PAA and its copolymers indicate the presence of AA units in the chains, while the bands at 1600–$1450\,\text{cm}^{-1}$ for aromatic stretching and aromatic −CH in plane bending and $750\,\text{cm}^{-1}$ for aromatic −CH out-of-plane bending are characteristic for PNVCz (Figure 1). Further, the bands due to −C=O stretching and NH- bending for secondary amides at 1660 and $1540\,\text{cm}^{-1}$ and a double band for isopropyl group at 1385 and $1370\,\text{cm}^{-1}$ are characteristic absorptions of PNIPAAm (Figure 2).

The comparison of the ratios of the absorption intensities of −C=O stretching at $1730\,\text{cm}^{-1}$ to those of C=C aromatic stretching at $1600\,\text{cm}^{-1}$, which are the characteristic bands of the polyelectrolytes (PAA and PIA) and PNVCz, respectively, would give qualitative information about the reactivities of IA and AA units in the copolymeric structures. The ratios of the absorption intensities of the C=O and C=C peaks and the variation of the T_gs of copolymers with the mole fraction of IA and AA units in the copolymers are given in Table IV. All the copolymers showed a single T_g, indicating the absence of formation of a mixture of homopolymers or the formation of a block copolymer. According to the results obtained from the C=O/C=C ratios, AA and IA have nearly the same reactivities for the same feed compositions and their T_gs decrease with increasing AA and IA contents. The T_g values

Table IV. FT-IR and DSC results of the samples in Tables I and II

Sample no.	C=O/C=C	T_g^a	T_g
2	—	—	141
4	4.339	158.4	158
5	2.268	166.4	164
6	1.212	173.9	170
7	0.469	—	—
9	—	—	181
10	—		
12	1.893		
13	1.618		140
14	1.239		144
15	0.555		
9	—		181

[a] Calculated from the Fox equation.

of copolymers can be described by using the Fox equation ($1/T_g = (w_1/T_{g1}) + (w_2/T_{g2})$), where w_1 and w_2 are the weight fractions of monomer (NVCz) and comonomers (IA, AA, and NIPAAm) in the copolymers, respectively. The T_g of PIA (T_{g2}) was measured as 141°C and that of PNVCz (T_{g1}) was 181°C. The T_g values calculated by the Fox equation were slightly higher than the values obtained from differential scanning calorimetry (DSC) thermograms for NVCz/IA copolymers (Table IV). Figure 3 shows the relationship between $1/T_g$ and w_{IA}. It can be seen that good linear relationship can be obtained. This implies that the structure of NVCz/IA copolymers is random in nature.

In addition, the quantitative composition of copolymers for a wide range of monomer feed can be determined by FT-IR spectroscopy through recorded analytical absorption bands for comonomers.[25–27] For compositional analysis of NVCz/NIPAAm copolymers, characteristic absorption bands of 747 cm^{-1} (for NVCz units) and 1635 cm^{-1} (for NIPAAm units) were chosen as analytical bands. The least changing absorption band of 1447 cm^{-1} was used as a standard band ($A = \log I_o/I$, $\Delta A^C = A^C/A^{1447}$) to calculate the copolymer composition. The ratios of mole fractions of comonomer units (F_1 and F_2) in NVCz (1)/NIPAAm (2) copolymers were calculated using the following relation:

$$F_1/F_2 = [\Delta A^{747}/M_1]/[\Delta A^{1635}/M_2] \tag{3}$$

The mole fractions (in mole %) of NIPAAm (2) and NVCz (1) in the copolymers of various compositions calculated by using FT-IR analysis data are given in Table V.

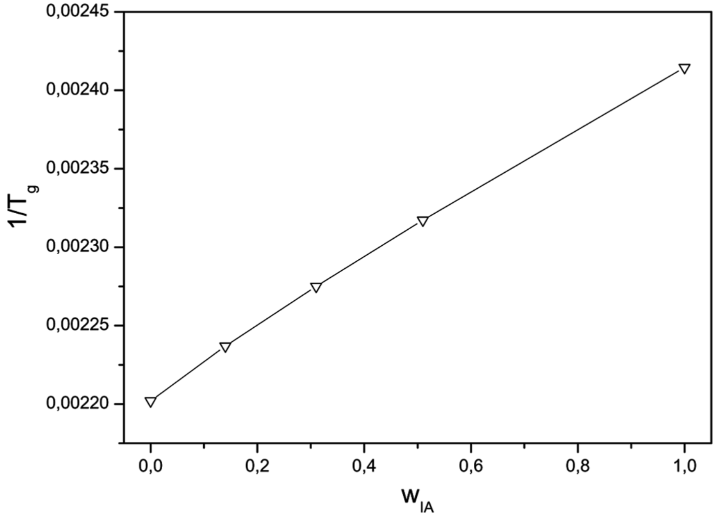


Figure 3. Relationship between $1/T_g$ and w_{IA}.

Table V. Copolymerization composition data for reactivity ratio calculation of copolymers of NVCz (1) and NIPAAm (2)

Sample no.	$^{a}_{1}$	f_2^a	ΔA^{747} (by FT-IR)	ΔA^{1635} (by FT-IR)	F_1^b	F_2^b	F_1^b (by UV-vis)	F_2
20	20	80	1.5143	0.8571	29.25	70.75	29.14	70.86
21	40	60	1.0781	1.4468	50.85	49.15	45.51	54.49
22	55	45	—	—	—	—	56.72	43.28
23	70	30	1.3733	0.4533	71.66	28.34	70.48	29.52
24	80	20	1.6171	0.1943	82.98	17.02	82.35	17.65

[a] f_1 and f_2 are the mol fractions of NVCz and NIPAAm in the feed.
[b] F_1 and F_2 are the mol fractions NVCz and NIPAAm in the copolymer.

The copolymer compositions were also determined quantitatively by means of UV spectroscopy.[28–30] UV spectra of homopolymer blends, i.e., the physical mixtures of PNVCz/PNIPAAm, PNVCz/PIA, and PNVCz/PAA prepared in THF were used to draw the calibration curves. It is known that four absorption bands observed at 345, 295, 262, and 237 nm are attributed to $\pi \rightarrow \pi^*$ electronic transitions of PNVCz homopolymer.[31] Calibration curves for NVCz/NIPAAm, NVCz/AA, and NVCz/IA copolymers were obtained by choosing only one of these characteristic transitions of PNVCz. The maximum absorbances at 295 nm were plotted against mole percent of PNVCz in the physical mixtures (Figure 4). All the graphs showed linear dependence of the absorbance on the composition and regression coefficients, which were in the range of 0.991–0.997. From these calibration curves, the composition of the copolymers was determined by using the maximum absorbance values at 295 nm of the copolymer solutions in THF (Figure 5). The results, which are summarized in Tables V and VI, indicate that IA and AA have almost the same reactivities, which are smaller than that of NVCz.

The extended Kelen-Tüdős method considers the drifts of copolymer composition with the conversion.[32] Therefore, it is suitable for our high conversion data. The extended Kelen-Tüdős copolymer composition equation is

$$\eta = [(r_1 + r_2)/\alpha]\zeta - r_2/\alpha \tag{4}$$

where $\eta = G/(\alpha + H)$; $\zeta = H/(\alpha + H)$; $X = f_1/f_2$; $Y = F_1/F_2$; $G = (Y - 1)/z$; $H = Y/z^2$, and $\alpha = (H_{min}.H_{max})^{1/2}$.

H_{min} and H_{max} are the lowest and the highest values of H. The effect of conversion is given by partial molar conversion:

$$\xi_2 = w(\mu + X)/(\mu + Y) \tag{5}$$

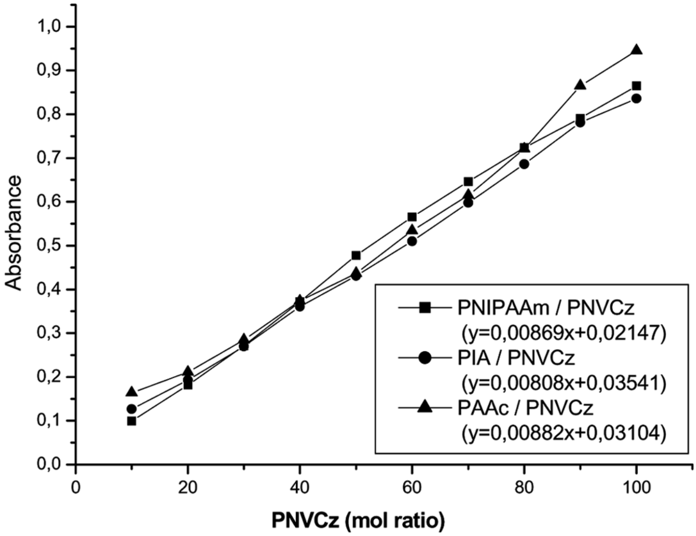


Figure 4. Calibration curves for NVCz/AA, NVCz/IA, and NVCz/NIPAAm copolymers.

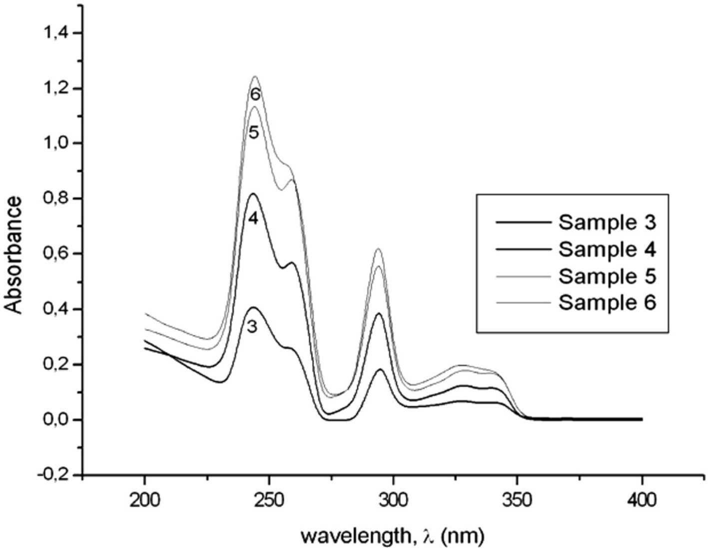


Figure 5. UV spectra of NVCz/IA copolymers ($\lambda_{max} = 295\,nm$), which are given in Table I.

where w is the weight conversion of polymerization and μ is the ratio of molecular weight of IA, AA, or NIPAAm (2) to that of NVCz (1). The partial molar conversion of NVCz is

$$\xi_1 = \xi_2\ Y/X \tag{6}$$

Then,

$$z = \log(1 - \xi_1)/\log(1 - \xi_2) \tag{7}$$

The extended Kelen-Tüdős (EKT) parameters were calculated from the above equations using experimental data in Tables I–III, V, and VI. They are summarized in Tables VII and VIII. The plots of η versus ζ of NVCz/NIPAAm and NVCz/IA copolymers are shown in Figures 6–8. In all cases, the plots were linear, indicating that the reactivity of a polymer radical is determined only by the terminal monomer unit. The reactivity ratios of monomer pairs (r_1 and r_2) were evaluated, using the data in Tables I–III and V–VIII from η versus ζ plots for the NIPAAm (2)-NVCz (1), IA (2)-NVCz (1), and AA (2)-NVCz (1) pairs. The results are summarized in Table IX. The fact that $r_1 > r_2$ indicates that NVCz is the more active comonomer in the copolymerizations with IA, AA, and NIPAAm. For all the copolymers $r_1 < 1$ and $r_2 < 1$ with $r_2 < r_1$, showing that the homopolymerization of the two monomers is not favored. The probability for the incorporation of IA and AA units is greater than for the incorporation of NIPAAm units.

It is known that the product of the monomer reactivity ratios (r_1r_2) for a given binary copolymerization is often used to indicate the sequencing in the resultant copolymer composition, i.e., random, alternating, and ideal. Further, it depends only on the difference in the polarity for the two monomers, and it is generally believed that $r_1r_2 = 1$ represents the upper limit for proper copolymerization. As evidenced from the values of monomer reactivity ratios, which are given in Table IX, random copolymerization is realized in AA-NVCz and IA-NVCz systems ($r_1r_2 \approx 0.20$), while the product of r_1r_2 is nearly zero ($r_1r_2 \approx 0.020$), which

Table VI. UV spectroscopy data for determining of composition of IA (2)/NVCz (1) and AA (2)/NVCz (1) copolymers synthesized from various initial monomer mixtures

Sample no.	f_{IA} (mol %)	Abs. $\lambda_{max} = 295\,nm$	F_{IA}	Sample no.	f_{AA} (mol %)	Abs. $\lambda_{max} = 295\,nm$	F_{AA}
6	20	0.759	10.45	14	20	0.797	13.16
5	40	0.661	22.58	13	40	0.607	34.70
4	60	0.483	44.61	12	60	0.512	45.47
3	80	0.277	70.10	11	80	0.225	78.01

Table VII. Extended Kelen-Tüdös parameters for NIPAAm (2) and NVCz (1) using FT-IR analysis data

Sample no.	X	Y	ξ_2	ξ_1	z	G	H	ζ	H
20	0.25	0.41	0.57	0.94	3.33	−0.176	0.037	0.044	−0.211
21	0.67	1.03	0.58	0.90	2.65	0.013	0.147	0.156	0.014
23	2.33	2.53	0.73	0.79	1.19	1.278	1.768	0.689	0.498
24	4.00	4.87	0.53	0.64	1.37	2.825	2.591	0.764	0.833

indicates that the NIPAAm-NVCz system follows an alternative distribution of monomeric units.

The preliminary information about the electrochemical behaviors and biological applications of PNVCz and NVCz/NIPAAm and NVCz/IA copolymers containing 10 mole% of comonomers in the feed was obtained by using a simple, rapid, and sensitive electrochemical procedure.

Figures 9 and 10 show the cyclic voltammograms (CVs) of DA obtained on the PNVCz, NVCz/NIPAAm, and NVCz/IA polymer-modified electrodes (PMEs) in phosphate buffer solution (pH = 7.0) at two different scan rates (50 and 500 mV/s).

The cyclic voltammetric curves of DA on these modified electrodes showed an anodic peak that corresponds to two-electron oxidation of DA to dopaquinone, which then undergoes deprotonation to produce an imine as suggested in the literature, whereas the CVs of PMEs did not show any signals in the absence of DA.[33–35]

The peak potentials and currents at two different scan rates (50 and 500 mV/s) for the PMEs prepared by electrochemical deposition of PNVCz and its copolymers on Pt wire electrode were collected in Tables X and XI. From these tables, it is seen that the electrochemical behavior of DA at these electrode surfaces is a quasi-reversible process in all cases, because the electrode potential differences is about 200 mV and I_{pc}/I_{pa} is close to 1. Dopaquinone is an electron-deficient species, and it reacts with nucleophiles in the medium to produce leucochrome

Table VIII. Extended Kelen-Tüdös parameters for IA (2) and NVCz (1) using UV-vis spectroscopy data

Sample no.	X	Y	ξ_2	ξ_1	z	G	H	ζ	H
3	0.25	0.4265	0.418	0.713	2.307	−0.248	0.080	0.091	−0.283
4	0.67	1.2417	0.376	0.700	2.554	0.095	0.190	0.193	0.096
5	1.50	3.4287	0.367	0.839	3.993	1.608	0.215	0.212	0.600
6	4.00	8.5694	0.251	0.537	2.668	2.837	1.203	0.601	1.417

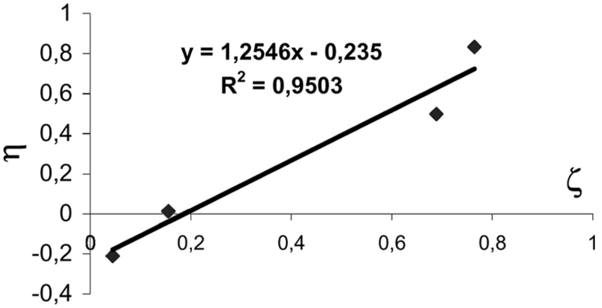


Figure 6. EKT method for determining monomer reactivity ratios in the copolymerization of NVCz (1) and NIPAAm (2) by using FT-IR spectroscopy data ($\alpha = 0.3104$).

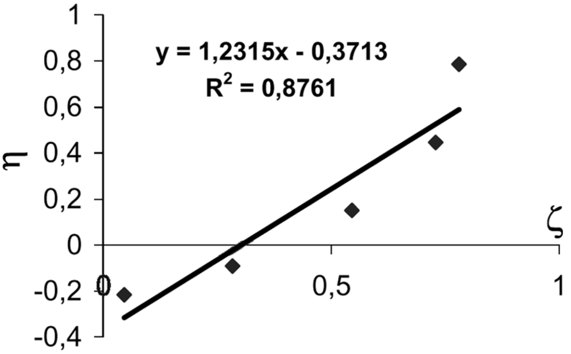


Figure 7. EKT method for determining monomer reactivity ratios in the copolymerization of NVCz (1) and NIPAAm (2) by using UV spectroscopy data ($\alpha = 0.3299$).

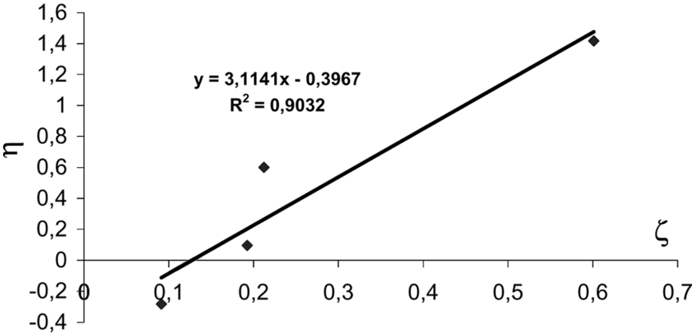


Figure 8. EKT method for determining monomer reactivity ratios in the copolymerization of NVCz (1) and IA (2) by using UV spectroscopy data ($\alpha = 0.3106$).

Table IX. Monomer reactivity ratios for the copolymerization of NVCz (monomer 1) with NIPAAm, IA, and AA (monomer 2) using FT-IR and UV spectroscopy techniques

Method	NIPAAm/NVCz (r_2)/(r_1)	IA/NVCz (r_2)/(r_1)	AA/NVCz (r_2)/(r_1)
UV-vis	0.12/0.29	0.12/0.84	0.31/0.86
FT-IR	0.07/0.32	—	—

by a cyclization process that can be easily oxidized to dopaminechrome.[36] This reaction is responsible for the quasi-reversibility.

ΔE values decreased from 267 mV on PNVCz electrode to 190 mV and 185 mV on the NVCz/IA- and NVCz/NIPAAm-coated electrodes, respectively. The oxidations observed at lower potentials for NVCz/NIPAAm copolymer, which indicate the ease of electron transfer reaction, demonstrate its superiority to PNVCz and NVCz/IA copolymer electrodes. Further, the highest currents were observed in the case of the NVCz/NIPAAm-coated electrode. This means that the presence of hydrophobic isopropyl group in the structures of electrode-coating materials provides better electrochemical reactivity than that of the hydrophilic carboxyl groups of IA.

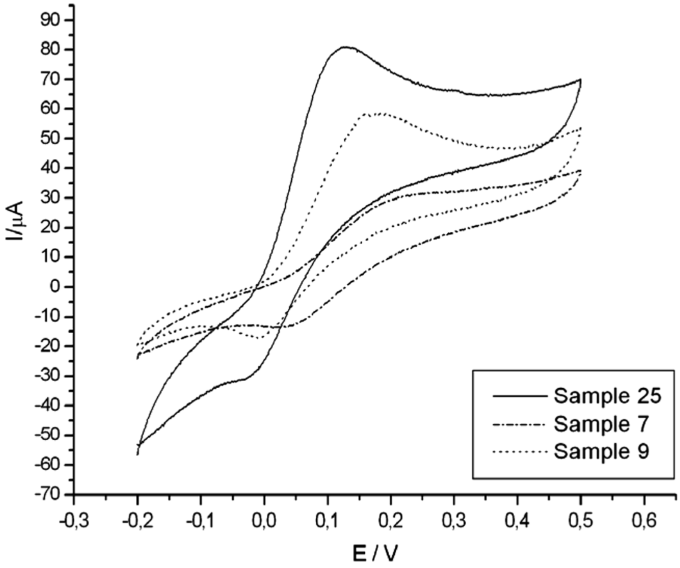


Figure 9. CVs of 9.0×10^{-4} mol/L of DA on the PNVCz-, NVCz/NIPAAm-, and NVCz/IA-modified electrodes in phosphate buffer solution (pH 7.0) at 50 mV/s scan rate.

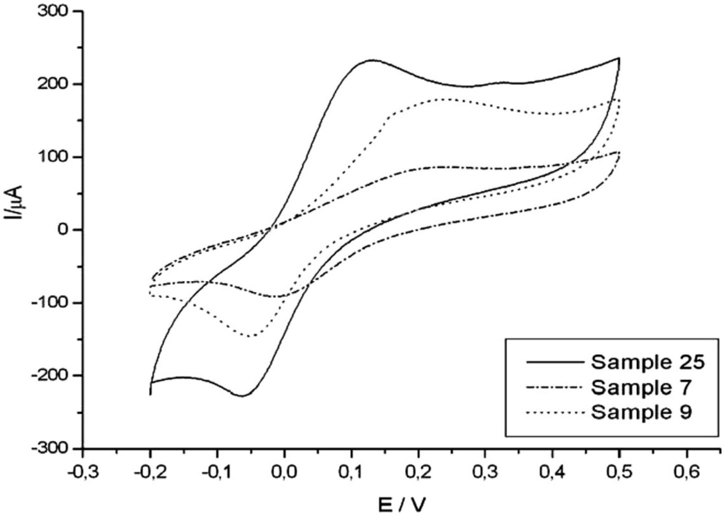


Figure 10. CVs of 9.0×10^{-4} mol/L of DA on the PNVCz-, NVCz/NIPAAm-, and NVCz/IA-modified electrodes in phosphate buffer solution (pH 7.0) at 500 mV/s scan rate.

Table X. Changes of peak potentials and currents of DA for three different PMEs at 500 mV/s scan rate

Polymer	E_a (mV)	E_c (mV)	ΔE (mV)	I_{pa} (μA)	I_{pc} (μA)
NVCz/IA (90/10)	188	−2	190	84	−90
NVCz/NIPAAm (90/10)	125	−60	185	233	−227
PNVCz	218	−49	267	178	−146

Table XI. Changes of peak potentials and currents of dopamine for three different PMEs at 50 mV s^{-1} scan rate

Polymer	E_a (mV)	E_c (mV)	ΔE (mV)	I_{pa} (μA)	I_{pc} (μA)
NVCz-co-IA (90/10)	201	49	152	29.3	−12.7
NVCz/NIPAAm (90/10)	127	−25	152	80.9	−30.8
PNVCz	165	−8	173	58.7	−16.9

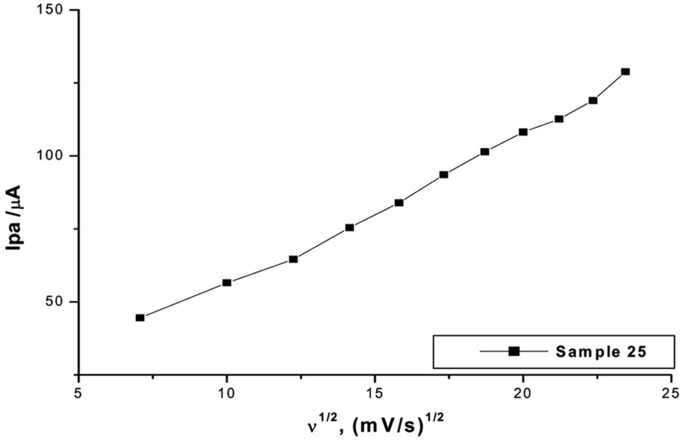


Figure 11. Scan rate dependence of DA response on NVCz/NIPAAm-coated electrode.

The electrochemical oxidation of DA was also examined as a function of scan rates (Figure 11). Current intensities and reversibility increased as the scan rate increased, owing to a decreased extent of internal cyclization, as expected. The oxidation peak currents varied linearly with the square root of scan rate in the range of 50–500 mV/s ($r > 0.9967$), indicating semi-infinite linear diffusion of the reactant to the interface.

CONCLUSIONS

PNVCz, PIA, PAA, and PNIPAAm homopolymers and NVCz/IA, NVCz/AA, and NVCz/NIPAAm copolymers having different compositions were synthesized by free radical polymerization in solution, using AIBN as initiator. These homopolymers and copolymers were characterized by calorimetric (DSC) and spectroscopic (FT-IR and UV) methods. Analysis of the data by the extended Kelen-Tüdős method (for high conversion) yields $r_1 = 0.29$ and $r_2 = 0.12$, $r_1 = 0.84$ and $r_2 = 0.12$, $r_1 = 0.86$ and $r_2 = 0.31$ by UV (for NVCz/NIPAAm, NVCz/IA, and NVCz/AA copolymers, respectively), and $r_1 = 0.32$ and $r_2 = 0.07$ by FT-IR (for NVCz/NIPAAm copolymers). From these results, it was observed that in the case of NVCz-IA and NVCz-AA systems there is a tendency to obtain random copolymers, while the NIPAAm-NVCz system follows an alternative distribution of monomeric units. In addition, the relationship between T_g^{-1} (obtained from DSC thermograms and the Fox equation) and w_{IA} supported the conclusion that NVCz/IA copolymer chains have a random distribution of monomeric units.

Electrochemical behavior of NVCz/IA- and NVCz/NIPAAm-coated electrodes was studied by CV measurements and found dependent on the type of comonomer. The present work provides useful data for biological application of new DA-sensitive materials based on copolymers of NVCz with IA and NIPAAm.

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