Block Copolymers of *N*-Vinyl Carbazole and α,ω-Dihydroxy Polydimethylsiloxane

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ABSTRACT: The redox system of ceric ammonium nitrate (Ce^{4+}) and α,ω-dihydroxy polydimethylsiloxane (DH.PDMS) was used to polymerize N-vinyl carbazole (NVCz) to produce poly(N-vinylcarbazole)-*b*-α,ω-dihydroxy polydimethylsiloxane(PNVCz-*b*-DH.PDMS). The ratio of NVCz/ceric salt/DH.PDMS has an important effect on the properties of formed copolymers. White insulating PNVCz-*b*-PDMS copolymers with high fluorescence intensity are produced if the ratio of ceric salt/NVCz is below 0.2. Green conductive PNVCz-*b*-PDMS copolymers are produced if this ratio is well above 0.2. The concentration and the type of DH.PDMS affected the polymerization yield. PNVCz-*b*-DH.PDMS copolymers were also prepared by electroinduced polymerization in the presence of catalytic amount of Ce^{4+} in a divided electrochemical cell where Ce^{3+} is readily oxidized to Ce^{4+} at the anode. White insulating PNVCz-*b*-DH.PDMS copolymers show higher contact angle value and lower Tg values than of white poly(*N*-vinyl carbazole) (PNVCz). © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 106: 3694–3702, 2007

Key words: block copolymers; conducting polymers; fluorescence; polylsiloxanes and radical polymerization

INTRODUCTION

Block copolymers of polydimethylsiloxane (PDMS) posses rather interesting properties due to their siloxane blocks. These are higher elasticity, higher solubility and higher contact angle values than their homopolymers.[1]

A few synthetic methods for production of the copolymers containing poly(N-vinyl carbazole) (PNVCz) and siloxane units were described so far (Scheme 1). These methods have a number of steps and some limitation of experimental procedure. Dihydroxy derivatives of carbazole and phenyl methyl dichlorosiloxane are condensed to give copolymers of carbazole and siloxane.[2] PDMS with pendant carbazole have been synthesized by the reaction of poly(hydrogen methyl siloxane) with various ω-alkenyl carbazoles.[3] Also the preparations of PDMS with carbazole and sulfonyl-indole based chromophore groups as side chains were described.[4]

Recently, we have started to use the redox system of Ce^{4+} and hydroxyl containing compounds such as α,ω-dihydroxy polydimethylsiloxane (DH.PDMS), α,ω-diamino polydimethylsiloxane (DA.PDMS) and ketonic resins to polymerize *N*-vinyl carbazole (NVCz), styrene (ST), acrylonitrile (AN), and pyrrole (Py). The resulting products were the copolymers of polystyrene-*b*-α,ω-dihydroxy polydimethylsiloxane (PS-*b*-DH.PDMS),[5] polyacrylonitrile-*b*-α,ω-dihydroxy polydimethylsiloxane (PAN-*b*-DH.PDMS),[5] polypyrrole-*b*-α,ω-dihydroxy polydimethylsiloxane (PPy-*b*-DH.PDMS),[6] high conductive polypyrrole-*b*-α,ω-diamino polydimethylsiloxane (DA.PDMS),[7] and PNVCz-ketonic resins[8] respectively. These copolymers have better solubility,[6] higher conductivity,[6,7] and higher contact angle values.[5,6] Besides, the electroinduced oxidative copolymerization of NVCz with methyl ethyl ketone-formaldehyde resin was studied and the copolymerization yield was found to be almost 10 times higher than the yield obtained by the redox polymerization method for the same Ce^{4+} concentration.[8] Electrolysis of NVCz solution usually coats the electrode surface with a green conducting PNVCz.[9] However, in the case of electroinduced oxidative polymerization method, the addition of a catalytic amount of Ce^{4+} to the system prevents the formation of dark green PNVCz and the copolymer of PNVCz does not precipitates on the electrode surface.[10] The concentration of Ce^{4+} remained constant during the polymerization due to its electro-regeneration at the anode from Ce^{3+}. The same system was first used to obtain polyacrylamide[11,12] and polyacrylonitrile.[13]

The aim of this work was to use the redox system of DH.PDMS and Ce^{4+} for the polymerization of NVCz to produce PNVCz-*b*-DH.PDMS copolymers in one step at room temperature.

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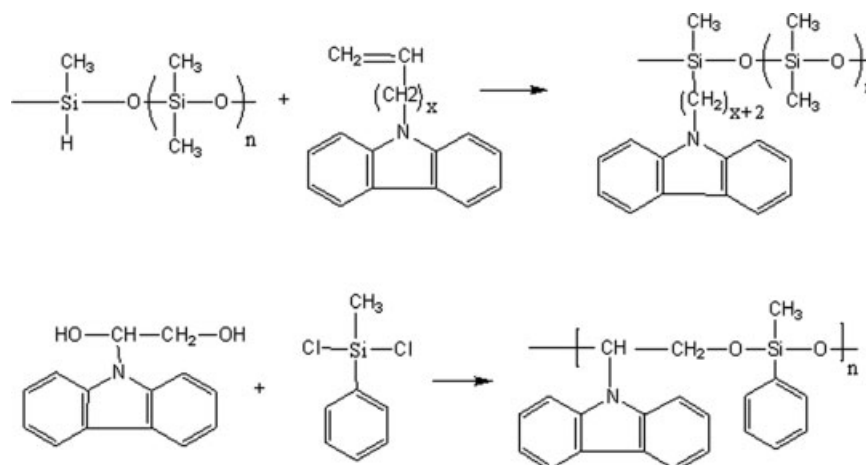
Scheme 1 The synthesis of copolymers of PDMS and NVCz.

EXPERIMENTAL

Materials

Ceric ammonium nitrate (BDH, England) was oven dried at 105° for 1 h and stored in a desiccator. A calculated amount was dissolved in $1M$ HNO_3 solution to prepare $0.2M$ stock solution that was stored in a refrigerator. Tegomers: α,ω-dihydroxy polydimethylsiloxane [polydimethylsiloxane, bis(4-hydroxy-butyl) terminated)] (DH.PDMS) were the products of Goldschmidt Chemical Corporation (Germany). Molecular weight of tegomer H-Si 2111 and tegomer H-Si 2311 are 950 ± 80 and 2500 ± 250 respectively. NVCz (Aldrich), dimethylformamide(DMF), acetone, toluene, dimethylsulphoxide (DMSO), acetonitrile (HPLC grade), and dichloromethane (Fluka A.G., Buchs, Switzerland) were used without further purification. $NaClO_4$ was dried under vacuum at room temperature. All solutions were freshly prepared before each run.

Analyses

Infrared (IR) spectra were recorded on a JASCO FTIR 5300 Fourier Transform Infrared Spectrometer.

^{1}H-NMR spectra of the polymers were obtained from their DMSO-d_6 solutions without TMS and from their $CDCl_3$ solutions by using a Bruker AC 250 MHz instrument.

Glass transition temperatures (T_g) of copolymers were determined with DSC-6 under nitrogen atmosphere. Heating rate was $10°C/min$.

Molecular weights were determined by GPC equipped with Waters styragel columns (HR series 2, 3, 5E) with THF as the eluent at a flow rate of 0.3 mL/min a Waters 410 differential refractometer detector. Molecular weights were calculated by PL GPC software using polystyrene standards.

Fluorescence spectra of the polymer solutions in DMF were recorded on Perkin-Elmer LS 50 luminescence spectrophotometer. The excitation wavelength is 292 nm. I_f of DMF is zero at 292 nm.

A Kernco model GIII contact angle instrument was used for the contact angle measurements.

Conductivity measurement

In order to measure the electrical conductivity, the polymers were pressed with 10 tons of weight to obtain thin pellets. Typical sample dimensions were 13 mm diameter and 0.8 mm thickness. Conductivity measurements were performed by four probe technique and calculated from the following equation.

$$\sigma = V^{-1}I\ln\left(\frac{2}{\pi d_n}\right)$$

where V is the potential in volts, I is current in ampere and d_n is the thickness in centimeters. The distance among probes is 1 mm.

Polymerization procedures

Oxidative copolymerization

First NVCz, DH.PDMS, and Ce^{4+} were dissolved in acetonitrile separately. Then the solution of Ce^{4+} was added dropwise into the mixture of NVCz and DH.PDMS solution while stirring. The total volume is 60 mL in all experiments. According to $Ce^{4+}/$ NVCz molar ratio, green or white copolymer precipitated as powder almost instantaneously. After 1 h of the polymerization time at $25°C$, the polymer powder was filtered, washed with acetonitrile. For further purification, the product was washed with hexane and dried at room temperature.

| Voltage (V)	Electrolyte concentration (mol/L)	Conversion (%)
3	0.1	20.0
3	0.5	17.0
2.5	0.1	20.0
1.6	0.1	5.7

[a] $Ce^{4+} = 1 \times 10^{-4}$ M, [NVCz] = 0.12 M. [DH.PDMS] = 0.012 M.

Electroinduced copolymerization

The electroinduced copolymerization of NVCz has been studied in acetonitrile in the presence of catalytic amount of Ce^{4+}. Polymerization was carried out in a cell divided into two compartments by means of a sintered disc of porosity 264.

Platinum Gauss electrodes of 5×4 cm^2 and 4×10 cm^2 area were used as anode and cathode respectively. The cell assembly was connected to a thermostat, and the reaction mixture contains required amounts of NVCz and DH.PDMS dissolved in acetonitrile and Ce^{4+} salt in the acetonitrile solution of $NaClO_4$. Anolyte contains the acetonitrile solution of $NaClO_4$. The total volume is 80 mL in all experiments. The reaction mixture was stirred continuously during 1 h reaction period in the anode compartment and the cell was placed in a thermostatic bath at constant temperature of 25°C. A potential of 3 V was applied to the reaction mixture during polymerization. At the end of the polymerization, the precipitated copolymer (PNVCz-b-DH.PDMS) was washed with acetonitrile then with hexane in order to remove monomer and electrolyte contaminations and dried at room temperature.

Conditions for electroinduced polymerization: First the effect of voltage and the electrolyte concentration on
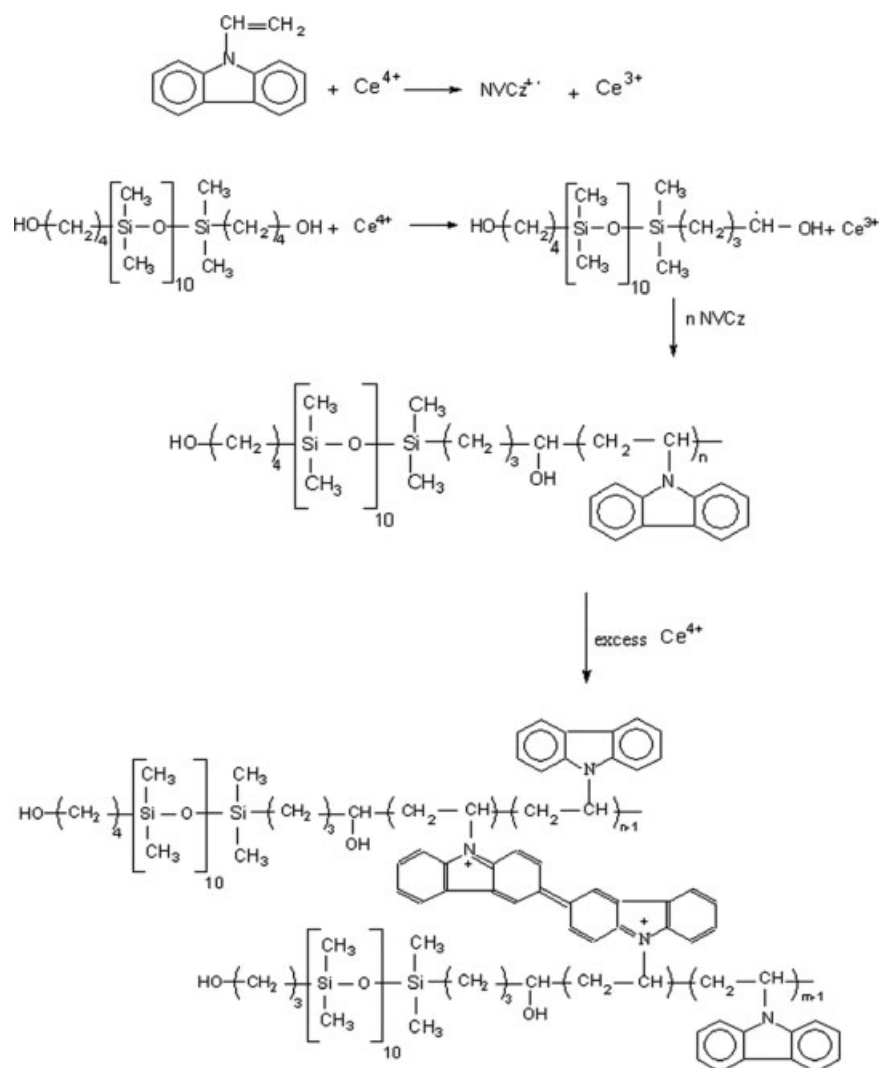
Scheme 2 The formation mechanism of PNVCz-b-DH.PDMS copolymers.

TABLE II
Effect of Concentration of NVCz, DH.PDMS, and Ce^{4+} on the Yield and Solubility of White PNVCz and PNVCz-*b*-DH.PDMS Obtained by Chemical and Electroinduced Oxidative Polymerization Methods

Type	Cop. no	NVCz (mmol/L)	DH.PDMS (tegomer 2111) (mmol/L)	Ce^{4+} (mmol/L)	Mole ratio of Ce^{4+}/NVCz	Conversion (%)	Yield per mmol Ce^{4+}
C	C1	52	1.8	4	0.08	42	10.5
C	C2	52	1.8	8	0.15	34	4.2
C	C3	52	20	8	0.15	0.6	0.08
C	C4	52	34.4	8	0.15	0.0	0
C	C5	52	34.4	12	0.2	0.0	0
C	C6	52	1.8	12	0.23	37.3	3.1
C	C7	52	34.4	30	0.57	0.0	0
C	C8	52	1.8^a	8	0.15	49.3	6.1
C	B1	52	–	4	0.08	36	9
E	E1	33	12	0.1	0.003	0	0
E	E2	60	12	0.1	0.0017	8.5	85
E	E3	120	6	0.1	0.0007	24	24
E	E4	120	12	0.1	0.0007	22.7	22
E	E5	120	47	0.1	0.0007	28.6	28
E	EB	120	–	0.1	0.0007	30	30

^{a} Tegomer 2311.
C, chemical; E, electroinduced; B1 and EB, blank experiments.

the copolymerization yield was studied (Table I). 0.1M electrolyte concentration is enough and 2.5 or 3 V is suitable for high electroinduced copolymerization yield under the experimental conditions described in this work. Thus, the voltage was chosen as 3 V in all electroinduced polymerization experiments. Then, by keeping the electrolyte concentration 0.1M and the voltage at about 3 V, the effect of Ce^{4+} concentrations on the polymerization yield was studied and the highest yield was obtained at 10^{-4} M

Ce^{4+} concentration while keeping NVCz and DA.PDMS concentrations constant.

RESULTS AND DISCUSSION

We produced PNVCz-*b*-DH.PDMS copolymers in one step at room temperature in 1 h by the polymerization of NVCz monomer with the redox initiation system of Ce^{4+} and DH.PDMS. The polymerization
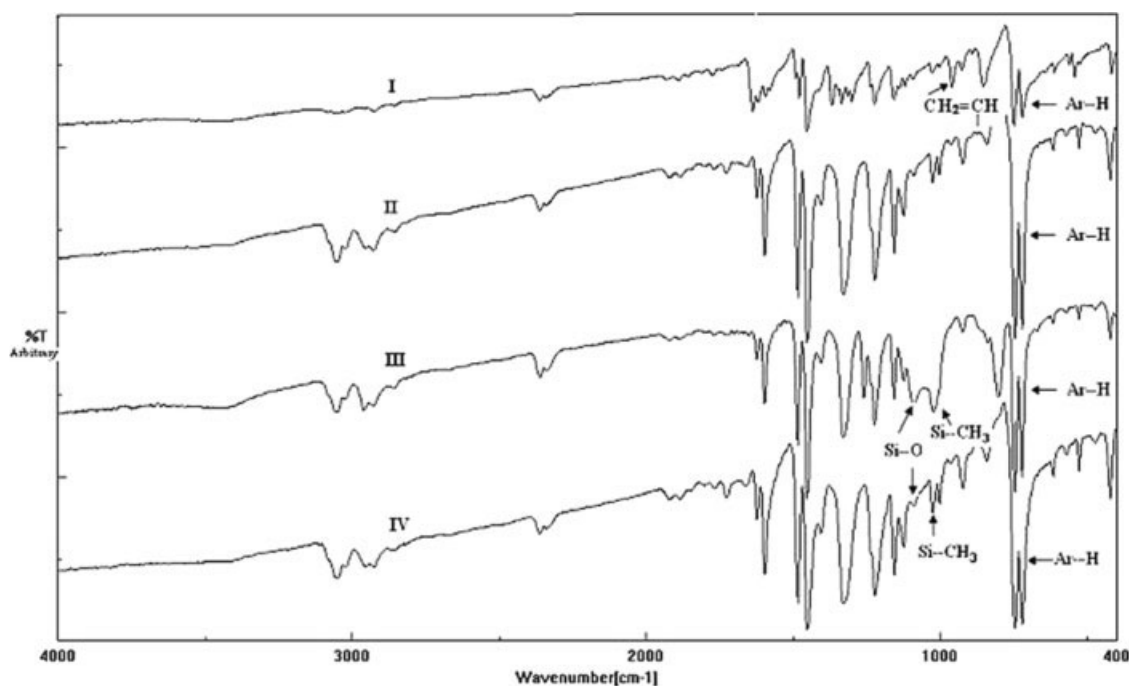

Figure 1 FTIR spectra of (I) NVCz, (II) PNVCz (B1), (III)PNVCz-*b*-DH.PDMS (C2), (IV) PNVCz-*b*-DH.PDMS (C8).
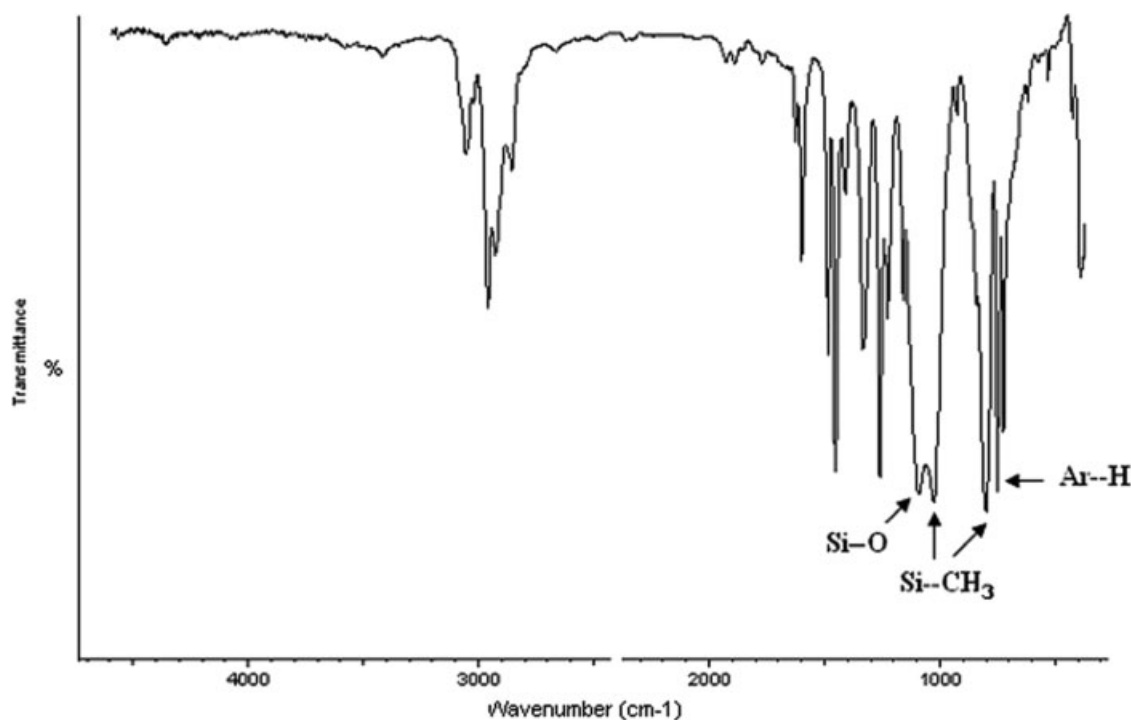
Figure 2 FT-IR spectrum of PNVCz-b-DH.PDMS (E4) produced with electroinduced oxidative polymerization.

probably proceeds with a mechanism similar to the redox systems of Ce^{4+}/DH.PDMS and Ce^{4+}/polyethylene glycol as proposed earlier.[5,14] The redox reaction between Ce^{4+} and the hydroxyl group of DH.PDMS produces a radical that initiates the polymerization of NVCz (Scheme 2) to form PNVCz-b-DH.PDMS copolymers.

The polymerization may proceed from other hydroxyl chain end of DH.PDMS to give triblock copolymers if the ratio of Ce^{4+}/DH.PDMS is well above 2. The reaction between NVCz and Ce^{4+} may produce $NVCz^+$ which may initiate radical homopolymerization of NVCz. Growing PNVCz chains may be terminated by either with DH.PDMS or copolymer radicals. These termination reactions also produce copolymer chains. Thus homopolymer formation is less probable. DSC termograms of the copolymer products did not show any T_g value at about 168°C and 209°C due to homopolymer. In the case of electroinduced polymerization, the polymerization mechanism is probably similar to the oxidative polymerization mechanism including electrogeneration of Ce^{4+} from Ce^{3+} at the anode and the concentration of Ce^{4+} was almost kept at the initial value.

Ce^{4+} was alone used to polymerize NVCz before.[9] It was found that the structure of the formed PNVCz was depending on the ratio of Ce^{4+}/NVCz. If this ratio is below 0.2, the polymerization occurs via double bond. When the ratio is well above 0.2, both vinyl polymerization and the oxidative coupling via benzene rings of NVCz occur. White insulating or

green conductive PNVCz-b-DH.PDMS copolymers were produced in this work depending on the mol ratio of Ce^{4+}/NVCz keeping DH.PDMS concentration constant.

White insulating PNVCz-b-DH.PDMS copolymer

These copolymers were produced by using Ce^{4+}/NVCz molar ratio 0.2 or below. In this case, the polymerization occurs only via vinyl group of NVCz monomer. The produced PVCz-b-DH.PDMS copoly-
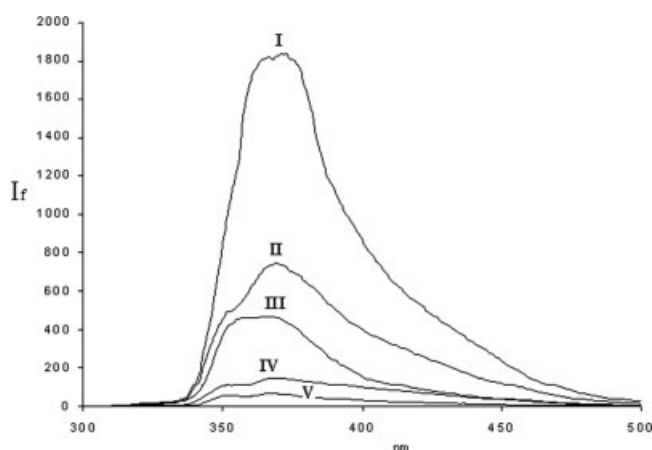

Figure 3 Fluorescence spectra of the PNVCz-b-DH.PDMS copolymers in DMF (I) C2, (II) C1, (III) NVCz monomer, (IV) B1, (V) E4.

TABLE III
Quantum Yield of Polymers and NVCz Monomer

Sample	Quantum yield	I_f
NVCz	0.47	210
C2	2.49	700
E4	0.4	60
B1	0.138	60
C1	–	–

mers are soluble and nonconductive ($<10^{-7}$ S/cm) (Table II).

Using excess DH.PDMS caused no copolymer to precipitate even if the ratio of Ce^{4+}/NVCz was as high as 0.6 (C4, C5, and C7). This showed that Ce^{4+} reacts preferably with hydroxyl end groups of DH.PDMS rather than NVCz since Ce^{4+} with similar concentration could homopolymerize NVCz monomer as described earlier.[15] Initial concentration of Ce^{4+}, DH.PDMS, and NVCz and their ratios are important for obtaining a precipitated copolymer product during polymerization experiment.

In case of the electroinduced polymerization, the initial mole ratio of Ce^{4+}/DH.PDMS is in the range of 0.07–0.002 and the mole ratio of Ce^{4+}/NVCz is in the range of 0.003–0.0007. This means that only one of hydroxyl chain ends of DH.PDMS reacts initially with Ce^{4+} to form an AB type block copolymer. Homopolymer or copolymer was not obtained from the oxidative polymerization of NVCz by these low concentrations of Ce^{4+} under the experimental conditions described in this work. In the electroinduced polymerization system, Ce^{4+} was regenerated from Ce^{3+} at the anode and initiated the redox polymerization. Thus, the polymer yield per mol of Ce^{4+} used is much higher than the chemical polymerization. Besides, this regeneration prevented occurrence of polymer film on the anode surface.

The FTIR spectra of PNVCz-b-DH.PDMS copolymers produced with both oxidative and electroinduced polymerization systems are shown in Figures 1 and 2. The vinyl bands of the monomer at 860 and 960 cm^{-1} are not present in the spectrum of the colorless form of PNVCz-b-DH.PDMS copolymer indicating that NVCz monomer polymerized via its vinyl group. The FTIR spectrum of PNVCz is characteristic of isolated noninteracting carbazole groups.[15] As well as typical peaks due to PNVCz blocks, the presence of characteristic peaks of PDMS blocks of the PNVCz-b-DH.PDMS copolymers at 1030, 1010, and 800 cm^{-1} appear intensely in the spectrum of copolymer produced with electroinduced system. Besides, the aliphatic C—H peak at about 2950 cm^{-1} was more intense in the PNVCz-b-DH.PDMS copolymers compare to the PNVCz (Fig. 2).

White form of PNVCz has been known to exhibit excimer fluorescence in the solution and in the solid state.[16] Fluorescence spectra of PNVCz-b-DH.PDMS and nonconducting PNVCz produced with both oxidative and electroinduced polymerizations are given in Figure 3. Their spectra were recorded in DMF at 292 nm wavelength. The fluorescence peak intensities of PNVCz-b-DH.PDMS copolymers are higher than of PNVCz produced under the similar polymerization conditions. Also quantum yields were calculated by using their fluorescence and UV spectrum. The results were as in Table III. As expected, the results were in good agreement with Figure 3. PNVCz-b-DH.PDMS copolymers have higher quantum yield values. This is due to dilution effect of DA.PDMS blocks on PNVCz chains preventing the quenching of fluorescence groups.

Green conductive PNVCz-b-DH.PDMS copolymers

These copolymers were produced in chemical oxidative polymerization system using Ce^{4+}/NVCz molar ratio well above 0.2. In this case, both vinyl polymerization and the oxidative coupling reactions (Scheme 2) are possible.

The solubility and conductivity of green PNVCz-b-DH.PDMS copolymers are better than of PNVCz produced under similar conditions. The polymerization

TABLE IV
Effect of Concentration of NVCz, DH.PDMS, and Ce^{4+} on the Yield, Conductivity, and Solubility of Green PNVCz, and PNVCz-b-DH.PDMS Copolymers Obtained by Chemical Oxidative Polymerization Method

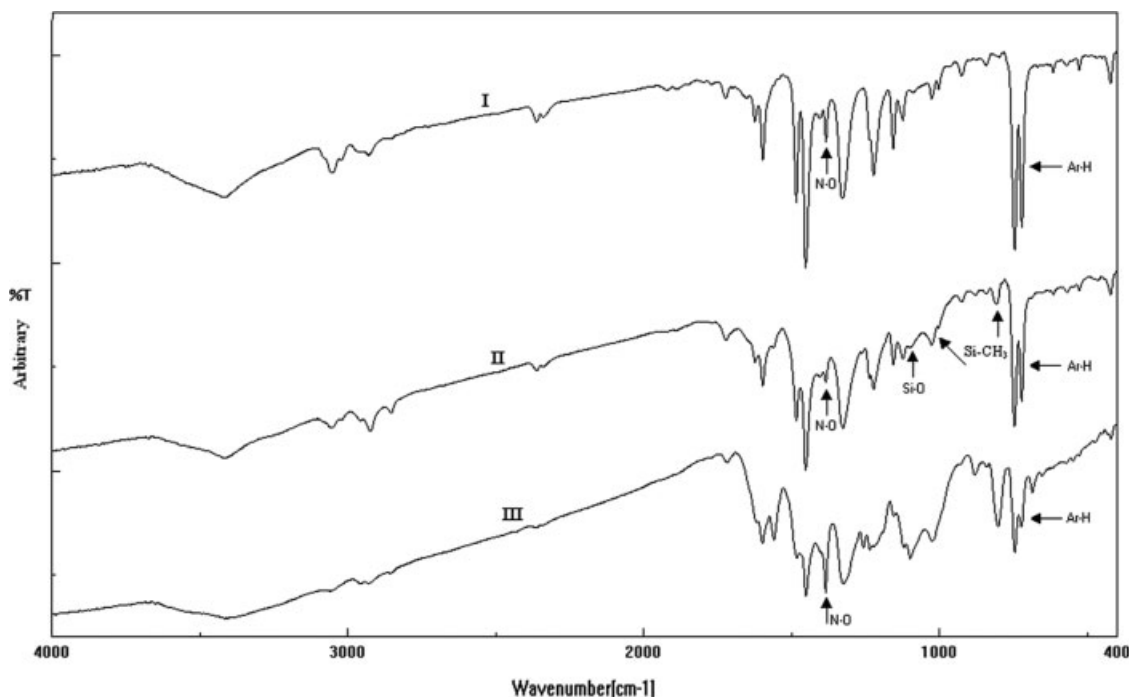| Cop. No	NVCz (mmol/L)	DH.PDMS (mmol/L)	Ce^{4+} (mmol/L)	Ce^{4+}/NVCz mol ratio	Conductivity (S/cm)	Conversion (%)
C9	150	1.8	50	0.33	$(7 \pm 1) \times 10^{-6}$	90
C10	100	1.8	50	0.50	$(4 \pm 1) \times 10^{-6}$	66.3
C11	75	1.8	50	0.67	$(3 \pm 1) \times 10^{-6}$	73.7
C12	52	1.8	50	0.96	$(1 \pm 1) \times 10^{-6}$	85
C13	52	3.5	50	0.96	$(2 \pm 1) \times 10^{-7}$	44.4
C14	52	1.8	75	1.44	$(3 \pm 1) \times 10^{-6}$	169
C15	52	1.8	100	1.90	$(5 \pm 1) \times 10^{-6}$	169
C16	52	1.8	200	3.84	$(7 \pm 1) \times 10^{-6}$	400
B2	75	–	50	0.67	$(5 \pm 1) \times 10^{-5}$	70

B2, blank experiment.

Figure 4 FTIR spectra of (I) PNVCz (B2), (II) PNVCz-*b*-DH.PDMS (C11), (III) PNVCz-*b*-DH.PDMS (C8).

yield and the conductivity of these copolymers increased with increasing Ce^{4+} (Table IV). Increasing the ratio of Ce^{4+}/NVCz results an increase in the oxidative coupling reaction between NVCz molecules.

FTIR spectra (Fig. 4) of conductive green PNVCz and PNVCz-*b*-DH.PDMS copolymers are similar to the spectra of nonconductive white PNVCz and PNVCz-*b*-DH.PDMS copolymer counterparts if the ratio of Ce^{4+}/NVCz is about 0.5. However, a small peak at 1380 cm^{-1} due to NO_3 anion appears and its intensity increases with increasing the initial ratio of Ce^{4+}/NVCz. The appearance of NO_3^- peak at 1380 cm^{-1} is the evidence of doped polaron or bipolaron structure that occurred by over oxidation of coupled carbazole rings.

NMR studies

The ^{1}H-NMR spectrum of both white and green PNVCz-*b*-DH.PDMS copolymers in DMSO without TMS are similar as shown in Figure 5. The peak at about 0.04 ppm is due to the —CH_3 protons of PDMS blocks and the peaks between 6.6 and 8 ppm are due to the aromatic C—H protons of carbazole rings. Aromatic region of the ^{1}H-NMR spectra of white and green PNVCz-*b*-DH.PDMS copolymers in $CDCl_3$ were examined in details as shown in Figure 6. Peaks at about 7.7, 7.0, and 6.5 ppm are due to *a*, *b/c*, and *d* aromatic protons of carbazole rings respectively. Aromatic protons of green copolymers at 6.5 ppm decreases while the intensity of the small peak at about 7.4 ppm increases with increasing initial Ce^{4+}/NVCz ratio. These changes are due to oxidative coupling reaction between carbazole rings.

Molecular weight and contact angle

Molecular weight values PNVCz and PNVCz-*b*-DH.PDMS produced with the redox initiation system of Ce^{4+}/DH.PDMS are shown in the Table V. As expected the mole ratio of Ce^{4+}/NVCz has an effect on the molecular weight of the polymers. However, M_n of the copolymers is in the range of 2000–3000 and dispersity is about 1.1–1.9. If the ratio of Ce^{4+}/NVCz is much higher than 0.2, the solubility of the copolymer in THF is limited and molecular weight of only soluble part could be determined. The M_n of the copolymer of PNVCz-*b*-DH.PDMS was about 1000 g/mol higher than the PNVCz produced with electroinduced polymerization method.
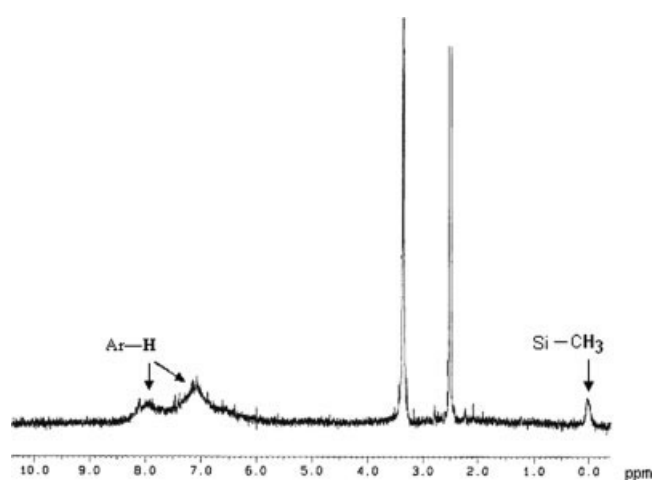

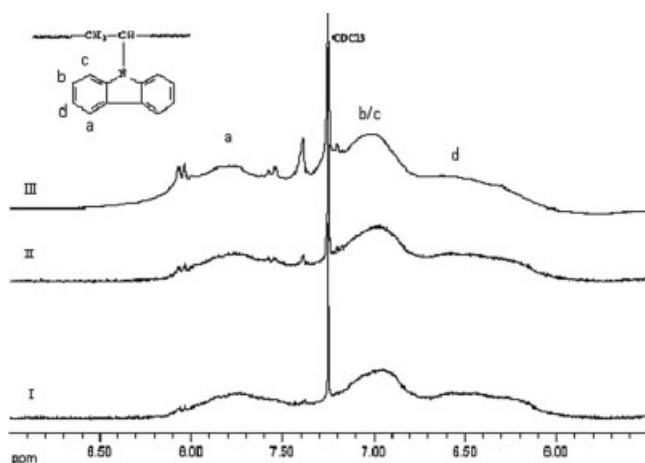**Figure 5** ^{1}H-NMR spectrum of the PNVCz-*b*-DH.PDMS copolymer no: C16 in DMSO-D_6.

Figure 6 ^{1}H-NMR spectrum of PNVCz-*b*-DH.PDMS copolymers in CDCl$_3$ (I) the copolymer no. C1, (II) the copolymer no. C8, (III) the copolymer no. C9.

TABLE VI
T_g Values of the Polymers Determined by DSC with Heating Rate of 10°C/min

No.	Polymer type	Appearance	T_g (°C)
B1	PNVCz	White	168.6 and 209.2
B2	PNVCz	Green	161 and 215
C1	PNVCz-*b*-DH.PDMS	White (light yellow)	153
C2	PNVCz-*b*-DH.PDMS	White (light yellow)	142.7
C3	PNVCz-*b*-DH.PDMS	White (light yellow)	130
C6	PNVCz-*b*-DH.PDMS	White (light yellow)	125
C12	PNVCz-*b*-DH.PDMS	Light green	–
EB	PNVCz	White	165
E4	PNVCz-*b*-DH.PDMS	White (light brown)	160–210

The contact angle measurements were performed on pellets of the polymers with a thickness of about 1 mm. The contact angle values of PNVCz (EB) and the PNVCz-*b*-DH.PDMS (E4) are 90° and 104° respectively. Higher contact angle value of the copolymer is due to PDMS blocks.

DSC studies

Tg values of produced PNVCz and copolymers (PNVCz-*b*-DH.PDMS) are shown in Table VI. Two T_g values of the white PNVCz (B1) was obtained, one was at about 168.6°C and the other at about 209.2°C (Fig. 7). T_g of white PNVCz-*b*-DH.PDMS copolymers were much lower than of PNVCz (see C2 in Fig. 7 and Table VI). This is expected since the copolymer is probably a triblock type and the PDMS

blocks affect T_g considerably. On the other hand, T_g of PNVCz(EB) was about 165°C and of the copolymer (E4) obtained by electroinduced copolymerization method was not very clear and was between 160–220°C. Two T_g values of green PNVCz (B2) was observed at about 161°C and 210°C. This is expected since it was reported earlier that the overoxidized PNVCz contains both white and green PNVCz.[15] However, T_g of green PNVCz-*b*-DH.PDMS copolymers could not be determined as the general behavior of conductive PNVCz.[9]

CONCLUSION

PNVCz-*b*-DH.PDMS copolymers were produced by using the redox system of Ce^{4+} and DH.PDMS in

TABLE V
M_n, M_w, and dispersity of PNVCz and PNVCz-*b*-DH.PDMS Copolymer Solutions in THF Calculated from GPC Measurements

| No.	The color of the polymer	Ce^{4+}/NVCz ratio	M_n	M_w	M_w/M_n
C1	White	0.08	3100	5120	1.65
C3	White	0.15	2940	4920	1.67
C6	White	0.23	3170	5670	1.78
C8	White	0.15	2930	5010	1.70
C9	Green	0.33	2420	3900	1.61
C10	Green	0.5	2700	4680	1.73
C11	Green	0.67	2640	4660	1.76
C12[a]	Green	0.96	2340	3470	1.48
C13	Green	0.96	2660	5310	1.99
C14[a]	Green	1.44	1800, 7900	2000, 9990	1.11, 1.26
C15[a]	Green	1.90	1680	1910	1.13
C16[a]	Green	3.84	1490	1530	1.02
EB	White	–	926	1127	1.21
E4	White	–	1919	2505	1.30

[a] Only THF soluble part used for measurements.
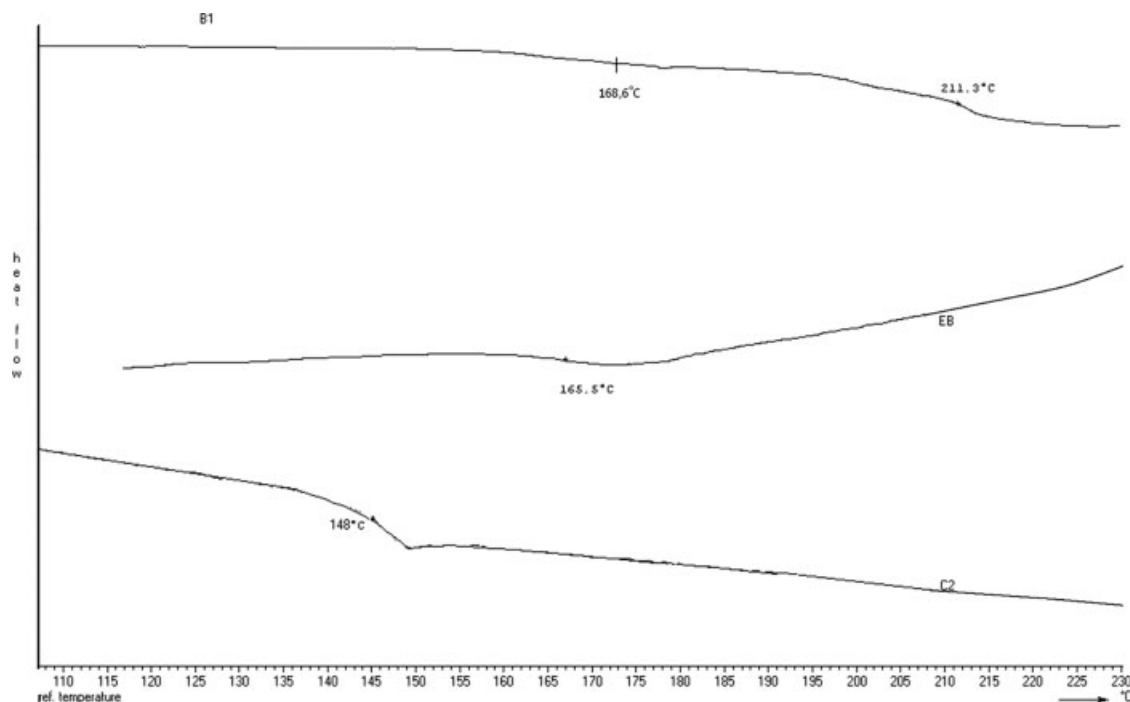
Figure 7 DSC thermogram of white PNVCz (B1), PNVCz-*b*-DH.PDMS copolymer (C2), PNVCz produced with electro-induced polymerization (EB).

acetonitrile in one step. The physical properties of the copolymers are regulated by Ce^{4+}/NVCz/ DH.PDMS ratios. When the ratio of Ce^{4+}/NVCz is lower than 0.2, white insulating PNVCz-*b*-DH.PDMS copolymers are produced while this ratio is much higher than 0.2, the green conductive PNVCz-*b*-DH.PDMS copolymers are formed. The advantage of this method is that the commercial monomers and chemicals are been used to prepare the copolymers in one step at ambient temperature. Besides, the requirements such as exclusion of air, high vacuum, and high-pressure techniques are not necessary during the polymerization process.

White PNVCz-*b*-DH.PDMS copolymers have higher fluorescence intensity and quantum yield, higher molecular weight and higher contact angle values than white PNVCz produced under similar conditions. PNVCz-*b*-DH.PDMS copolymers were also produced by the electroinduced polymerization method in the presence of catalytic amount of ceric salt at the anode compartment. Electrochemical oxidation of Ce^{3+} to Ce^{4+} at anode prevents the formation of the polymer on the anode surface and the polymer is precipitated at the anode compartment. The yield per mole of Ce^{4+} in the electroinduced polymerization system was much higher than of the chemical polymerization. These copolymerization methods allow us to regulate the conductivity, fluorescence properties, contact angle values and molecular weights of the formed PNVCz-*b*-DH.PDMS copolymers. These block copolymers may increase

the application areas of PVCz, where lower T_g, higher fluorescence quantum yield, higher contact angle are desired.

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