

Block Copolymers of Acrylonitrile and Poly(dimethylsiloxane)s

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ABSTRACT: The chemical redox system of ceric ammonium nitrate(Ce^{4+}) and poly(dimethylsiloxane)s (PDMS) with monohydroxy (MH), dihydroxy (DH), and diamine(DA) chain ends was used to polymerize acrylonitrile (AN) to produce monohydroxy poly(dimethylsiloxane)s-*b*-polyacrylonitrile (MH.PDMS-*b*-PAN), dihydroxy poly(dimethylsiloxane)s-*b*-polyacrylonitrile (DH.PDMS-*b*-PAN), and α , ω -diamine poly(dimethylsiloxane)s-*b*-polyacrylonitrile (DA.PDMS-*b*-PAN) block copolymers. The concentration, reaction time, and the type of poly(dimethylsiloxane) affect the yield and the molecular weight of the copolymers. The ratio of AN/ceric salt/PDMS has remarkably affects the properties of formed copolymers. DH.PDMS-*b*-PAN 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 into Ce^{4+} at the anode. The products were characterized by Fourier transform infrared spectroscopy, 1H -NMR spectroscopy, DSC, and their surface properties were investigated through contact-angle measurements. © 2012 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 000: 000–000, 2012

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INTRODUCTION

Polydimethyl siloxane (PDMS) copolymers have been recently studied for their potential technological importance as thermoplastic elastomers and for their unusual properties.¹ Di, tri, and multiblock siloxane containing copolymers have been prepared by different synthetic methods which have higher elasticity, higher solubility, and higher contact angle values than their homopolymers.²

Sequential anionic polymerization of styrene with hexamethyl cyclotrisiloxane (D_3) using an alkyl lithium initiator has been described before.³ In general, anionic polymerization has certain limitations and the reaction conditions require strict exclusion of impurities such as moisture, O_2 and CO_2 and the use of highly purified solvents and monomers. Alternative methods such as nitroxide-mediated radical polymerization (NMRP),⁴ polyaddition of α , ω -dihydroxy terminated polysiloxane to α , ω -divinyl terminated polymers,⁵ and cationic polymerization system⁶ have been used to produce block copolymers of PDMS.

We have previously studied the polymerization of vinyl monomers with the redox initiation system of ceric salt and various reducing agents. The reducing agents were ketonic resins,⁷ cellulose derivatives,⁸ amino methylene phosphonic acids,⁹ ethoxylated nonylphenols,¹⁰ polyethylene glycol,¹¹ and α , ω -dihydroxy

terminated polysiloxane.^{12,13} The resulting polymers have chain ends of reducing agent moieties that impart the physical properties of the polymers. For example, polyacrylonitriles with ethoxylated nonyl phenol chain ends have significantly better water absorption than polyacrylonitrile.¹¹

The redox reaction between ceric salt and the reducing agent produces a radical center that initiates the polymerization of vinyl monomer. Water is the preferred media for this redox polymerization system and the strict purification of the monomers and the exclusion of impurities are not favorable. The method has also been used to produce soluble conductive copolymers of ketonic resin-polypyrrole^{14,15} and poly(dimethylsiloxane)-*b*-polypyrrole copolymers.^{16,17}

The electroinduced polymerization of acrylonitrile (AN) has been reported in the presence of catalytic amounts of a ceric salt and oxidant during the electrochemical cell.¹⁸

The aim of this study was to use the redox initiation system of Ce^{4+} salt and a differently terminated type of the tegomer such as α , ω -diamine poly(dimethylsiloxane)s (DA.PDMS), α , ω -dihydroxy poly (dimethylsiloxane)s (DH.PDMS), and monohydroxy-terminated poly(dimethylsiloxane)s (MH.PDMS) for the polymerization of acrylonitrile to produce monohydroxy poly (dimethylsiloxane)s-*b*-polyacrylonitrile

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Table I. Synthesis of MH.PDMS-*b*-PAN Copolymers with Redox System of MH.PDMS/Ce⁴⁺/AN ([AN] = 0.7 mol/L), at 20°C for 4 h

Copolymer no.	[Ce ⁴⁺] (mmol/L)	[PDMS] (mmol/L)	Mol ratio of Ce ⁴⁺ /DHPDMS	(Mol wt) M _v	Yield (%)	Contact angle (°)	T _g (°C)
1	5.3	0.14	37.8	355,000	30	73	-
2	5.3	0.31	17.0	601,000	34	75	-
3	5.3	0.50	10.6	423,000	53	76	60
4	5.3	1.01	5.2	415,000	60	95	72
5	5.3	1.09	4.8	382,000	65	92	62
6	5.3	2.02	2.6	279,000	59	93	65
7	5.3	3.03	1.7	230,000	56	97	57
8	5.3	4.04	1.3	168,000	45	98	59
9	5.2	1.72	3.0	128,000	25	100	57
10	5.2	2.66	1.9	439,000	51	93	83
11	5.2	6.6	0.8	100,000	51	102	48
12	4.5	2.66	1.6	308,000	38	104	73
13	6	2.66	2.2	62,000	25	103	55

to 140°C, and then cooled back to 30°C. This cycle was repeated three times and T_g was determined from the last cycle.

Contact angle measurements of the copolymer films were carried out on a KSV CAM-200 optical video contact angle system at room temperature using distilled water. The measurements were made immediately in the beginning firstly, then after 10 s and finally after 3 min for water droplets on the films prepared by casting from 2% (w/v) polymer solution in DMF for PDMS-*b*-PAN copolymers.

All polymers were analyzed by scanning electron microscopy (SEM) using a Jeol JSM-5410 SEM. The samples were coated with gold for SEM.

Determination of Molecular Weight

The solution viscosities of PDMS-*b*-PAN copolymers in DMF at 25°C were measured using a Cannon-Fenske capillary viscometer and their molecular weights were calculated from single-point values using the following equations.^{19,20}

$$[\eta] = (\eta_{sp}/c)/(1 + 0.28 \times \eta_{sp})$$

$$[\eta] = 2.43 \times 10^{-4} \times M_v^{0.75} \quad (\text{for PDMS-}b\text{-PAN})$$

The viscosity average molecular weights of these copolymers are obviously approximate values because the proceeding relations were given for pure PAN.

Polymerization Procedures

Preparation of PDMS-*b*-PAN. Poly(dimethylsiloxane)s and acrylonitrile were added into water and the stirred. The reaction solution was bubbled by nitrogen to remove dissolved gases by rigorous stirring. The ceric ammonium nitrate stock solution was then added drop by drop to the reaction mixture in about 20 min while stirring under nitrogen atmosphere at 20°C. Water insoluble copolymer was precipitated during the polymerization. Approximately 4 h later, the powdery product was filtered, washed several times with water, then with methanol and was finally dried under vacuum at 60°C. The copolymer was freed

from any residual poly(dimethylsiloxane) by extracting with 2-butanone in a Soxhlet extractor.

Electroinduced Copolymerization of DH.PDMS-*b*-PAN. The electroinduced copolymerization of DH.PDMS-*b*-PAN was carried out in a cell divided into two compartments by means of a sintered disk of porosity 264.

Platinum Gauss electrodes with an area of 2.6 cm² were used as anode and cathode. The cell assembly was connected to a thermostat, and the reaction mixture containing required amounts of AN and DH.PDMS dissolved in acetonitrile and Ce⁴⁺ salt in the acetonitrile solution of NaClO₄. Anolyte contained the acetonitrile solution of NaClO₄. The total volume was 80 mL in all

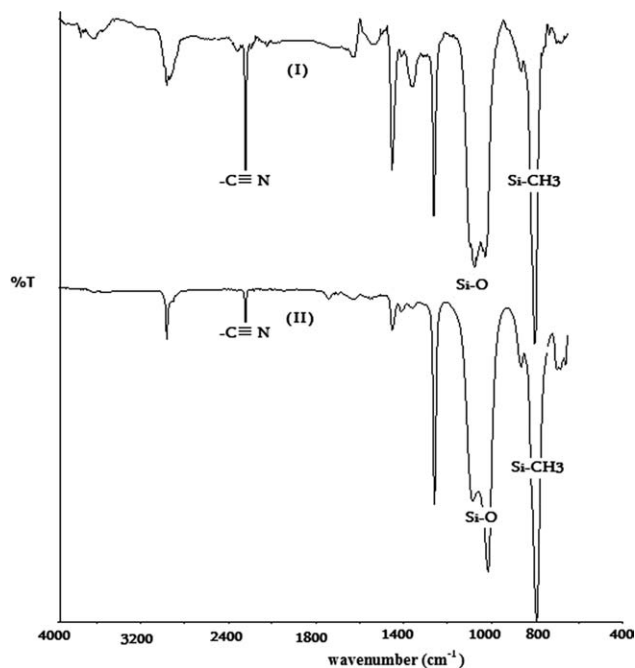


Figure 1. FTIR spectra of MH.PDMS-*b*-PAN (I) Cop. no: 1 and (II) Cop. no: 7

Table II. Effect of Concentration of DH.PDMS, and Ce^{4+} on the Yield and Molecular Weight of PAN-*b*-DH.PDMS Obtained by Chemical Oxidative Polymerization Methods at 20°C

Copolymer no.	[Ce^{4+}] (mmol/L)	[AN] (mol/L)	Water (mL)	[DH.PDMS] (mmol/L)	Molar ratio of Ce^{4+} /DHPDMS	M_v	Yield (%)	Reaction time (h)
15	5.2	0.7	200	4.53	1.14	323,000	33	4
16	5.2	0.7	200	6.6	0.78	142,000	62	4
17 ^a	9.8	1.3	100	3.29	2.98	80,000	10	4
17	9.8	1.3	100	3.29	2.98	300,000	70	4
18	16.9	2.2	50	7.61	2.22	271,000	42	4

^a Without degassed nitrogen.

experiments. The reaction mixture was stirred continuously during 90 min reaction period in the anode compartment and the cell was placed in a thermostatic bath at constant temperature of 25°C. Electrolysis was carried out using a constant potential of 3.0 V by using a Thurlby Thander PL 320 DC source. The precipitated copolymer was formed in the cathodic compartment, and the reduced initiator was reoxidized in the anode. At the end of the polymerization, the precipitated copolymer (PAN-*b*-DH.PDMS) was washed with hot water, and then with hot methanol to remove monomer and electrolyte contaminations, and was finally dried at 40°C under vacuum.

The Blank Experiments

In the absence of DH.PDMS, MH.PDMS, and DA.PDMS polymer was formed in 4 h at 20°C through, similar experiments under comparable conditions using the vinyl monomers and ceric salt.

RESULTS AND DISCUSSION

We produced MH.PDMS-*b*-PAN (diblock), PAN-*b*-DH.PDMS-*b*-PAN, and PAN-*b*-DA.PDMS-*b*-PAN (triblock) copolymers at one step at room temperature in 4 h through polymerization of AN monomer with the redox initiation system of Ce^{4+} and PDMS. The polymerization probably proceeds with a mechanism similar to the redox systems of Ce/DH.PDMS and Ce^{4+} /DA.PDMS as proposed earlier.^{1,16}

The redox reaction between Ce^{4+} and the hydroxyl group of MH.PDMS produces a radical that initiates the polymerization of AN to form MH.PDMS-*b*-PAN diblock copolymers (Scheme 1). The polymerization may proceed from other amine chain end of DA.PDMS to give triblock copolymers if the ratio of Ce^{4+} /DA.PDMS is well above 2 (Scheme 2). The reaction between AN and Ce^{4+} may produce PAN, which may initiate radical homopolymerization of PAN. Growing PAN chains may be terminated with either DA.PDMS/MH.PDMS or copolymer radicals. These termination reactions also produce copolymer chains. Thus, homopolymer formation is less probable.

MH.PDMS with a molecular weight of about 4670 was used as reducing agent and polymerization yield, viscosity average molecular weights of MH.PDMS-*b*-PAN, T_g and contact angle value were given in Table I. Polysiloxanes, particularly PDMS, have an extremely low T_g (about-130°C)^{2,21} and the other main chains of PAN are tightly packed so that the intermolecular

spaces in the amorphous regions are reduced and the triple bond of the cyano group restricts free rotation leading to molecular stiffness hence a high T_g for PAN.²⁴ The T_g of the MH.PDMS-*b*-PAN diblock copolymers were lower than the T_g value of PAN (Table I). By comparison of copolymers, it is concluded that with increasing MH.PDMS concentration up to the value of the Ce^{4+} salt concentration, both the yield and contact angle value increased, while the molecular weight decreased (Table I). Contact angle measurements were made on the films of the MH.PDMS-*b*-PAN copolymers prepared by casting from DMF solutions on the glass slides. Higher contact angle value of the copolymer is due to PDMS blocks. The high contact angle values of the copolymers with rather low silicone content is explained by the fact that PDMS segments migrate to the air-polymer surface, probably because of the high surface energy and low solubility parameter of PDMS during the process of their solutions on the glass slides. By comparison of copolymer 12 with 13, linear chain termination by Ce^{4+} became dominant at high initial Ce^{4+} concentrations, short PAN chains formed, and a copolymer with low-molecular weight and low yield was produced.

FTIR spectra of MH.PDMS-*b*-PAN copolymers showed a characteristic PAN spectrum including a peak at 800 cm^{-1} due to Si-CH₃, and 1020 and 1080 cm^{-1} due to Si-O bonds of

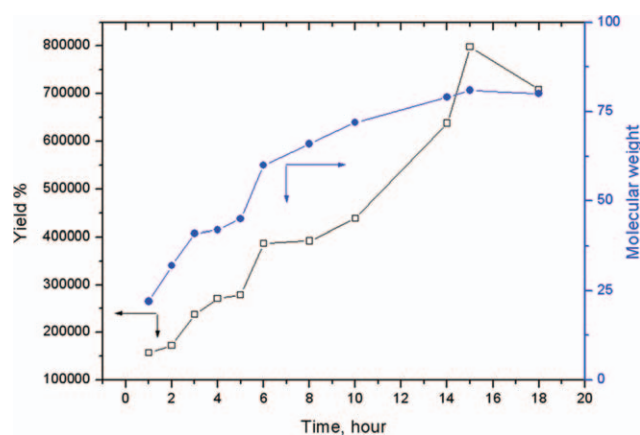
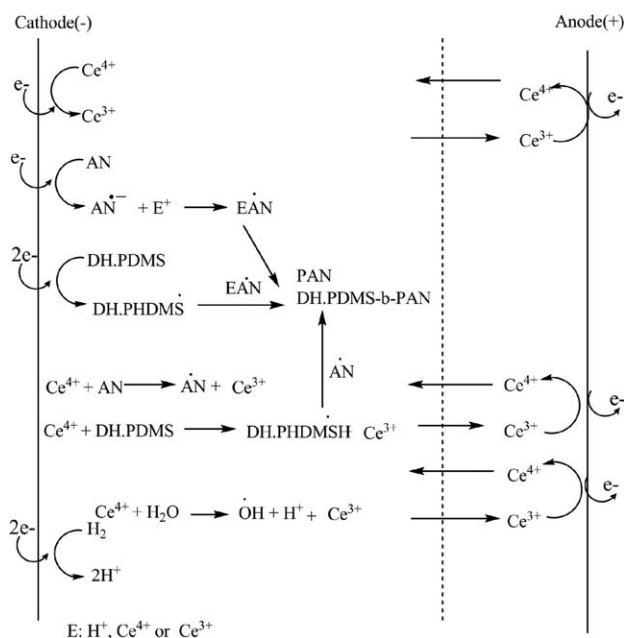


Figure 2. The relation of molecular weight and yield of copolymers with reaction time. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]



Scheme 3. Formation of DH.PDMS-*b*-PAN by electroinduced copolymerization method.

PDMS blocks (Figure 1). The spectra of cop. 1 (line I) and cop. 7 (line II) were similar. Peaks appeared at about 2243 cm^{-1} due to $\text{—C}\equiv\text{N}$, 1450 cm^{-1} due to C—N and at 1620 cm^{-1} due to N—H bonds of PAN blocks, and its intensity was increased when the initial ratio of AN/MH.PDMS was higher.

DH.PDMS with molecular weights of about 2500 was used as reducing agent and polymerization yield, and the viscosity average molecular weights of DH.PDMS-*b*-PAN, are, given in Table II. Next experiment was done by changing reaction time from 1 to 18 h, and comparison of yield and molecular weight of copolymers is given in Figure 2. Both molecular weight and yield were increased in time at constant concentration of Ce^{4+} salt, AN, and DH.PDMS (Figure 2). The Cop. 17 has a higher molecular weight and higher yield than the Cop. 17* produced under the same concentration and reaction time that was produced under the nitrogen atmosphere. Cop. no. 17 and no. 17* were produced in the presence and absence of N_2 , respectively.

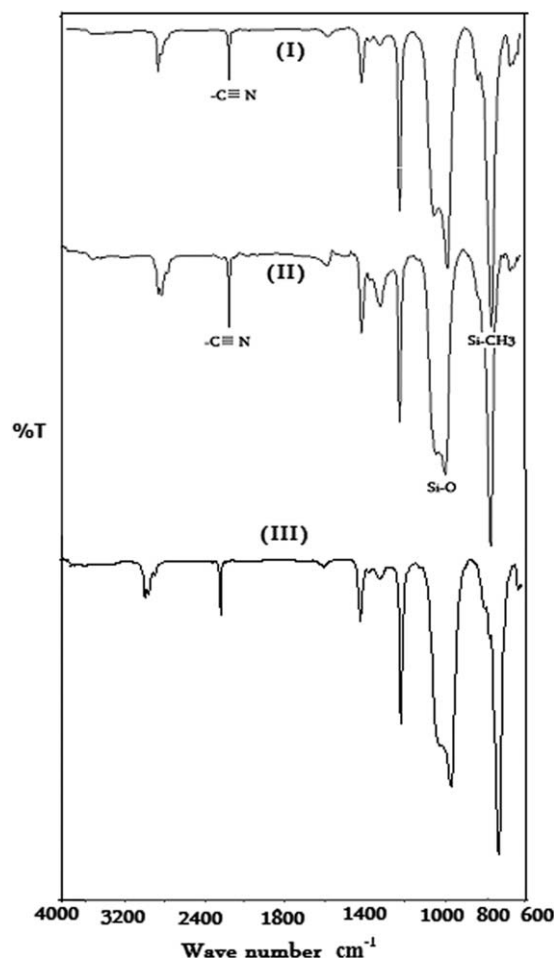


Figure 3. FTIR spectra of DH.PDMS-*b*-PAN (I) Cop. no: 16, (II) Cop. no: 18, (III) Cop. no: EI 6.

Seven times higher yield and three times higher molecular weight of Cop 17 than the latter one might be due to this difference and all experiments were done at N_2 atmosphere.

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

Table III. Effect of Concentration of DH.PDMS, and Ce^{4+} on the Yield and Molecular Weight of PAN-*b*-DH.PDMS Obtained by Electroinduced Oxidative Polymerization Methods ($[\text{AN}] = 0.7\text{ mol/L}$), at 20°C for 1.5 h

Copolymer no.	$[\text{Ce}^{4+}]$ (mmol/L)	[DH.PDMS] (mmol/L)	Mol ratio of $\text{Ce}^{4+}/\text{DHPDMS}$	Mol ratio of AN/DHPDMS	M_0	Yield (%)
EI 1	10^{-3}	5.2	2×10^{-4}	134	—	3.3
EI 2	10^{-3}	10.4	1×10^{-4}	67	543,000	9.5
EI 3	10^{-3}	15.6	6×10^{-5}	44	493,000	8.7
EI 4	10^{-3}	18.2	5×10^{-5}	38	27,400	3.7
EI 5	10^{-3}	20.8	5×10^{-5}	33	219,000	6.1
EI 6	2.10^{-3}	10.4	2×10^{-4}	67	99,000	7.9
EI 7	5.10^{-4}	10.4	5×10^{-5}	67	—	0

Table IV. Effect of Concentration of DA.PDMS, and Ce^{4+} on the Yield and Molecular Weight of PAN-*b*-DA.PDMS Obtained by Chemical Oxidative Polymerization Methods at 20°C ([AN] = 0.7 mol/L, Amount of Water = 200 mL), Reaction Time: 4 h

CopolymerNo	[Ce^{4+}] (mmol/L)	[PDMS] (mmol/L)	Molar ratio of Ce^{4+} /DHPDMS	M_n	Yield (%)	T_g (°C)	Contact angle (°)
19	4.5	4.43	1.02	219,000	17	-	74.9
20	5.3	0.56	9.4	206,000	25	64	76.5
21	5.3	1.10	4.8	501,000	49	42	88.2
22	5.3	2.20	2.4	287,000	33	-	78.8
23	5.3	4.43	1.2	206,000	23	53	84.7
24	5.3	6.00	0.8	247,000	9	47.6	86.3
25	6	4.43	1.4	360,000	25	-	70.4

initial value. Ce^{4+} was alone used to polymerize AN before.¹⁸ The copolymerization of DH.PDMS-*b*-PAN in the presence of Ce^{4+} in aqueous nitric acid shows characteristics of the resulting heterogeneous polymerization product, as the copolymer is insoluble in the aqueous solution. Possible reaction mechanisms are also given in Scheme 3.

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 the occurrence of polymer on the anode surface. The initial mole ratio of Ce^{4+} /DH.PDMS is in the range of 0.0002–0.00004 (Table III), which means that only one of hydroxyl chain ends of DH.PDMS reacts initially with Ce^{4+} to form an AB type block copolymer. DH.PDMS-*b*-PAN copolymer was not obtained with 5×10^{-4} M Ce^{4+} under the same 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 significantly higher than the chemical polymerization. Besides, this regeneration prevented the occurrence of polymer film on the anode surface.

The FTIR spectra of PAN-*b*-DH.PDMS copolymers produced with both oxidative (line I and II) and electroinduced polymerization systems (line III) are given in Figure 3. As well as typical peaks due to PAN blocks, the presence of characteristic peaks of PDMS blocks of the PAN-*b*-DH.PDMS copolymers at 1030 cm^{-1} , 1010 cm^{-1} , and 800 cm^{-1} appear intensely in the spectrum of copolymer produced with electroinduced system.

DA.PDMS with molecular weight of about 1000 was used as reducing agent and similar polymerization yield, contact-angle value, and viscosity average molecular weights of DA.PDMS-*b*-PAN were given in Table IV. The average molecular weights of the copolymers obtained from DA.PDMS increased with the $Ce(IV)$ concentration to increased 0.0053M. Moreover, a larger amount of silicone tegomer in the redox reaction gave a copolymer with a lower yield molecular weight when the initial $Ce(IV)$ concentration was high. The contact-angle measurements were performed on pellets of the copolymer with a thickness of about 1 mm. The glass transition temperatures of the copolymers were measured with DSC-6 Instrument with the heating rate of 10°C/min in a nitrogen atmosphere starting

from the room temperature. T_g of DA.PDMS-*b*-PAN copolymers were approximately 40–60°C lower than their corresponding PAN homopolymers even if the size of PDMS segment was remarkably smaller than the size of vinyl polymer segments

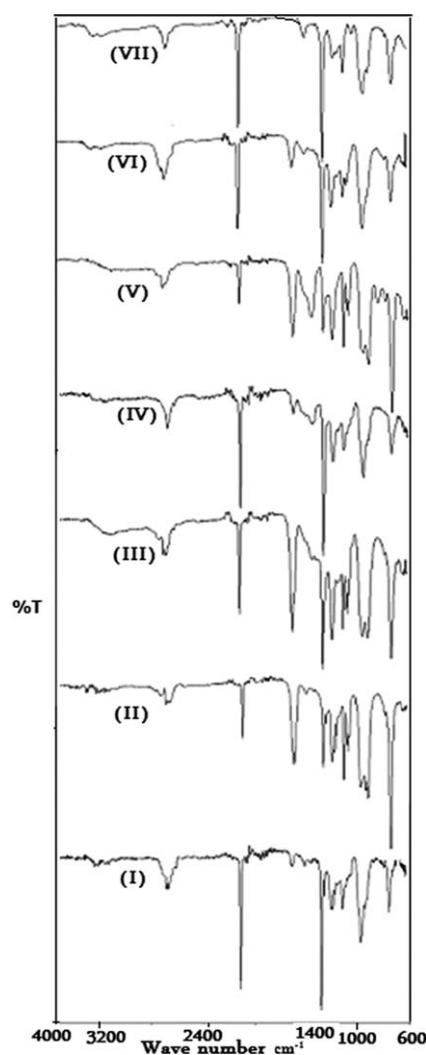


Figure 4. FTIR spectra of DA.PDMS-*b*-PAN (I) Cop. no: 19, (II) Cop. no: 20, (III) Cop. no: 21, (IV) Cop. no: 22, (V) Cop. no: 224, (VI) Cop. no: 23, and (VII) Cop. no: 25.

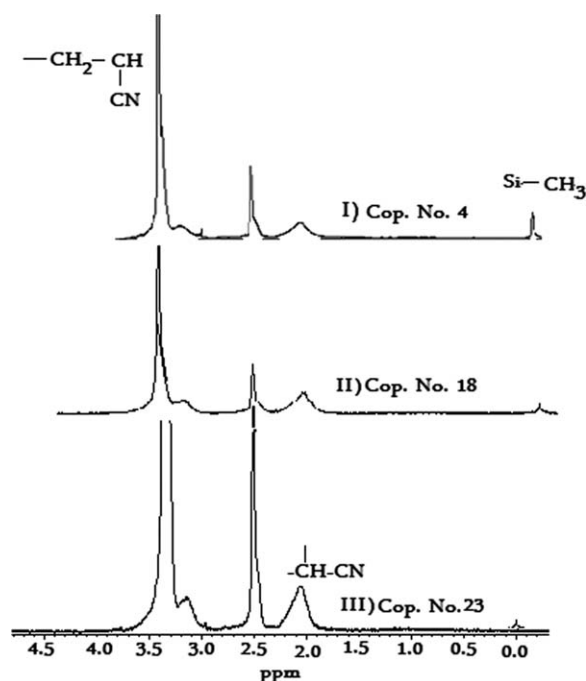


Figure 5. $^1\text{H-NMR}$ spectra of MH.PDMS-*b*-PAN (I) Cop. no. 4, DH.PDMS-*b*-PAN, (II) Cop. no. 18, DA.PDMS-*b*-PAN, and (III) Cop. no. 21.

(Table IV). Only one T_g of DA.PDMS-*b*-PAN copolymer was observed at about 42°C . This single T_g value was in good agreement with the single T_g value of triblock PDMS-*b*-PAN copolymer reported earlier.¹

In the spectra of the DA.PDMS-*b*-PAN copolymers (Figure 4), the bands that appear at about 1250 cm^{-1} , 1100 cm^{-1} , 1030 cm^{-1} , and 800 cm^{-1} are due to Si-O and Si-CH₃ groups of polydimethylsiloxane blocks. A sharp peak appeared at about 2243 cm^{-1} due to $\text{—C}\equiv\text{N}$, bonds of PAN blocks, and its intensity goes up with increasing the initial ratio of AN/DA.PDMS (lines I, II and lines V, VI). These results are similar to the FTIR spectrum of the PAN-*b*-DH.PDMS copolymers.

NMR Studies

The $^1\text{H-NMR}$ spectrum of MH.PDMS-*b*-PAN (diblock), PAN-*b*-DH.PDMS-*b*-PAN, and PAN-*b*-DA.PDMS-*b*-PAN copolymers in DMSO without TMS are similar as shown in Figure 5 $^1\text{H-NMR}$ spectrum of the PDMS-*b*-PAN demonstrated a small signal at about 0.08 ppm due to Si-CH₃ groups of the PDMS segment, and signals at 2.06 ppm and 3.14 ppm due to —CH— and —CH_2 protons of polyacrylonitrile blocks.

SEM Results

As can be seen from the SEM micrographs, PDMS-*b*-PAN has a very rough surface while the DH.PDMS-*b*-PAN (Cop. no. 16) has a smoother surface copolymer, indicating that there is an amount of DA.PDMS in comparison to the PAN chain. It can clearly be seen in the SEM micrograph of the copolymers in Figure 6.

CONCLUSIONS

MH.PDMS-*b*-PAN (diblock), PAN-*b*-DH.PDMS-*b*-PAN, and PAN-*b*-DA.PDMS-*b*-PAN copolymers were easily produced in one step with the redox system of MH.PDMS, DA.PDMS, and α , ω -dihydroxy poly(dimethylsiloxane)/Ceric ammonium nitrate at ambient temperature in water. The molecular weight and yield of the copolymers could be regulated by the concentration ratios of PDMS/ monomer/ceric salt. The copolymer products have significantly higher contact angle values than the corresponding homopolymers although their silicone content is as low. DH.PDMS-*b*-PAN copolymers were also produced by the electroinduced polymerization method in the presence of catalytic amount of ceric salt at the anode compartment.

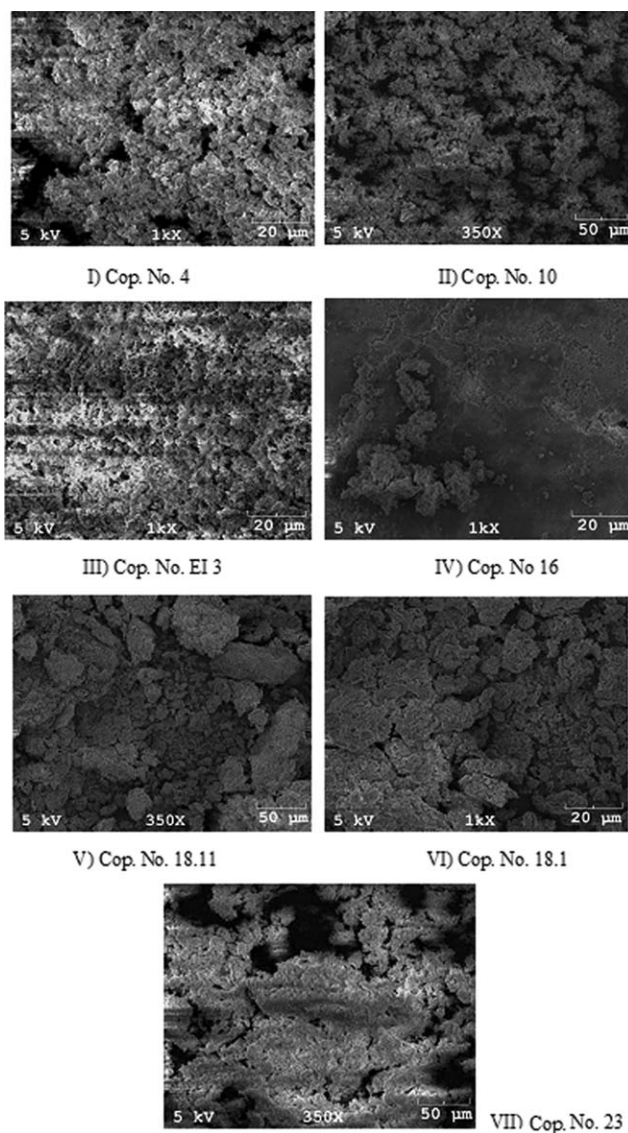


Figure 6. SEM micrographs of MH.PDMS-*b*-PAN (I) Cop. no. 4, (II) Cop. no. 10, DH.PDMS-*b*-PAN with produced electroinduced method, (III) Cop. no. EI.3, DH.PDMS-*b*-PAN with tegomer H-Si 2311, (IV) Cop. no. 16, (V) Cop. no. 18 (Reaction time:1 h), and (VI) Cop. no. 18 (Reaction time:18 h), DA.PDMS-*b*-PAN.

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 cathode compartment.

The yield per mole of Ce^{4+} in the electroinduced polymerization system was remarkably higher than of the chemical polymerization. These copolymerization methods allow us to regulate the contact angle values and molecular weights of the formed DH.PDMS-*b*-PAN copolymers. This method may be useful to produce the PDMS-*b*-vinyl polymers with higher contact angle values. Besides, these block copolymers may act as compatibilizer in the blending application of vinyl polymers with polysiloxanes as well as in existing application of the block copolymers of PDMS and vinyl polymers where lower T_g and, higher contact angle are desired.

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REFERENCES

1. Öz, N.; Akar, A. *J. Appl. Polym. Sci.* **2006**, *102*, 2112.
2. Yilgör, I.; Grath, M. J. E. *Adv. Polym. Sci.* **1988**, *86*, 1.
3. Saam, J. C.; Gordon, D. J.; Lindsey, S. *Macromolecules* **1970**, *3*, 1.
4. Morgan, A. M.; Pollack, S. K.; Beshah, K. *Macromolecules* **2002**, *35*, 4238.
5. Busfield, W. K.; Cowie J. M. G. *Polym. Bull.* **1980**, *2*, 619.
6. Rosati, D.; Perrin, M.; Navard, P.; Harabagiu, V.; Pinteala, M.; Simionescu, B. C. *Macromolecules* **2002**, *35*, 4238.
7. Akar, A.; Galioglu, O.; Göçmen, A.; Saraç, A. S. *J. Appl. Polym. Sci.* **1990**, *39*, 1657.
8. Galioglu, O.; Akar, A.; Saraç, A. S.; Soydan, B. D. *Angew. Makromol. Chem.* **1993**, *19*, 214.
9. Öz, N.; Akar, A. *Eur. Polym. J.* **2000**, *36*, 193.
10. Öz, N.; Akar, A.; Yilmaz, N. *J. Appl. Polym. Sci.* **2001**, *82*, 310.
11. Atıcı, O. G.; Akar, A.; Ayar, Y.; Mecit, O.J. *Appl. Polym. Sci.* **1999**, *71*, 1385.
12. Akar, A.; Kızılcan, N.; Ustamehmetoglu, B.; Colak, D.; Sarac, A. S.; Colak, C. J. *Appl. Polym. Sci.* **2007**, *106*, 3694.
13. Ustamehmetoğlu, B.; Kızılcan, N.; Saraç, A. S.; Akar, A. J. *Appl. Polym. Sci.* **2001**, *82*, 1098.
14. Kızılcan, N.; Ustamehmetoğlu, B. *J. Appl. Polym. Sci.* **2005**, *96*, 618.
15. Kızılcan, N.; Ustamehmetoğlu, B.; Öz, N.; Saraç, A. S.; Akar, A. *J. Appl. Polym. Sci.* **2003**, *89*, 2896.
16. Kızılcan, N.; Öz, K. N.; Ustamehmetoğlu, B.; Akar, A. *Eur. Polym. J.* **2006**, *42*, 2361.
17. Saraç, S. A.; Özkara, S.; Ustamehmetoğlu, B.; Özgür, G. *J Polym. Sci. Part A: Polym. Chem.* **1999**, *37*, 2319.
18. Braun, D.; Cherdon, H.; Kern, W. *Practical Macromolecular Organic Chemistry*; Harwood Academic Publishers: London, **1980**; p 80.
19. Cleland, R. J.; Stockmayer, W. H. *J. Polym. Sci.* **1955**, *17*, 473.
20. Chaumont, P.; Beinert, G.; Prud' Homme, C.; Herz, J. *Angew. Macromol. Chem.* **1984**, *20*, 43.
21. Kızılcan, N.; Mecit, O.; Uyanık, N.; Akar, A. *J. Appl. Polym. Sci.* **1998**, *67*, 643.