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C. I. Simionescu[a]; V. Bulacovschi[a]; Maria Grovu-ivanoiu[a]; M. Darnga[a]
[a] Department of Macromolecular Chemistry Polytechnic, Institute of Jassy Bvd., Jassy, Romania

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ELECTROINITIATED POLYMERIZATION OF 3,3-BIS(*N*-CARBAZOLYLMETHYL)OXETANE

C. I. SIMIONESCU,* V. BULACOVSCHI, MARIA GROVU-IVANOIU,
and M. DARÂNGA

Department of Macromolecular Chemistry
Polytechnic Institute of Jassy
Bvd. Copou 11A, 6600 Jassy, Romania

ABSTRACT

3,3-Bis(*N*-carbazolylmethyl)oxetane, a cyclic compound with carbazolyl substituents closely linked to the oxetane ring, was polymerized by electrochemical initiation in aprotic polar solvents using a quaternary ammonium salt as electrolyte. Colored polymers were obtained as thin films deposited on the anode and were characterized by IR, ^{1}H NMR, and thermogravimetry. The data obtained refute the classical cationic polymerization of oxetanes.

INTRODUCTION

A tremendous amount of work has been reported on the polymerization of *N*-vinylcarbazole and its derivatives as a result of the valuable electrophysical properties of the polymers [1–8]. Recent investigations showed that electrochemical oxidation of some heterocycles (pyrrole, thiophene, furane, carbazole) results in the formation of adherent films on electrode surfaces which may undergo cyclic transformation from an oxidized state (conductor) to a neutral one (insulator) when current polarity is changed [9].

Such observations prompted us to investigate the electropolymerization of 3,3-bis(*N*-carbazolylmethyl)oxetane (BCMO), a less studied monomer, whose products might exhibit interesting electrophysical properties.

EXPERIMENTAL

BCMO was prepared by the reaction of 3,3-bis(chloromethyl)oxetane with potassium carbazole in dimethylacetamide (DMAA) solution. Typically, into a round-bottomed four-necked flask equipped with an efficient stirrer, nitrogen inlet tube, thermometer, and a water collector with an upright condenser were charged 100 mL DMAA, 100 mL toluene, 15.5 g (0.1 mol) 3,3-bis(chloromethyl)oxetane, and 33.4 g (0.2 mol) carbazole. The mixture was heated to 100–110°C, 30 g K_2CO_3 was added, and the mixture was boiled with stirring for an additional 4 h. Finally, the contents were cooled down and filtered. The filtrate was poured into MeOH, neutralized, and the solid product filtered off and dried.

The crude BCMO, after crystallization from dioxane, weighed 36.7 g (88.2% yield), mp 184°C.

Analysis. Calculated for $C_{29}H_{24}ON_2$ (MW = 416): C, 83.65%; H, 5.77%; O, 3.85%; N, 6.73%. Found: C, 84.03%; H, 5.51%; N, 6.77%. UV absorptions (in THF): 252, 261, 296, 330, and 342 nm (carbazolyl ring) (Fig. 1). IR bands (Fig. 3, Curve 1): 930 and 1030 cm^{-1} (oxetane ring); 720, 750, and 760 cm^{-1} (carbazolyl group). ^1H NMR (in $CDCl_3$, Fig. 4, Curve 1): δ 7.85–8.2 ppm (carbazolyl protons) and δ 4.6 ppm (S, 8H, CH_2, oxetane ring).

The solvents were purified and dried before use. The support electrolyte, $(C_4H_9)_4NClO_4$, was synthesized and purified according to Ref. 10.

The apparatus and polymerization method have been described elsewhere [11]. The electropolymerization was carried out at 10°C, with BCMO placed only in the anodic compartment.

Two fractions were isolated: an insoluble dark-brown deposit on the anode surface and a soluble fraction extracted from the anodic compartment.

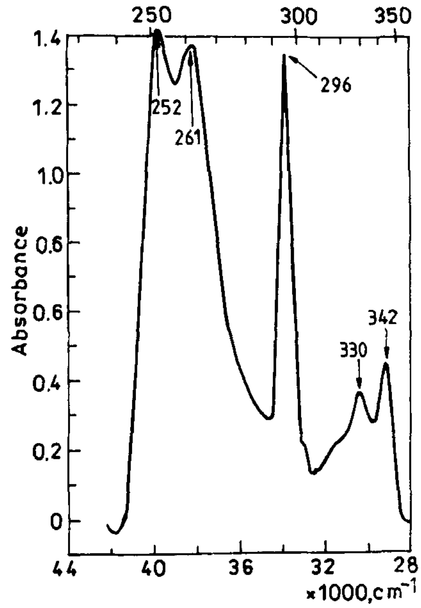


FIG. 1. UV spectrum of BCMO.

TABLE 1. Electroinitiated Polymerization of BCMO (T = 10°C; time = 2 h; [BCMO] = [TBAP] = 0.1 M; I = 10 mA)[a]

		Conversion		Fraction		Polymerization efficiency, mol monomer/F
Exp.	Solvent	g	%	I, g	II, g	
1	$(CH_2Cl)_2$	0.163	15.67	0.135	0.028	0.53
2	CH_2Cl_2	0.156	15.0	0.104	0.052	0.50
3	CH_3CN	0.059	5.67	0.059	–	0.19

[a] I = insoluble fraction; II = soluble fraction.

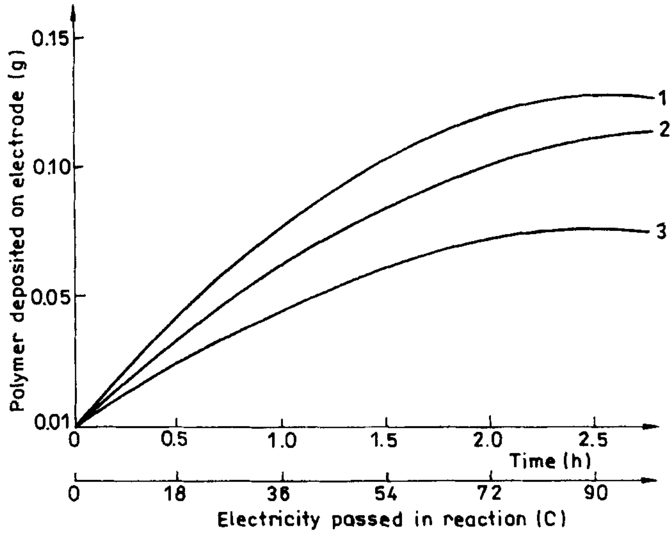
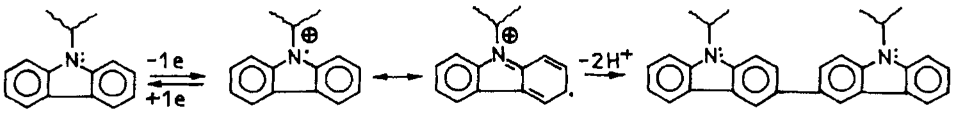
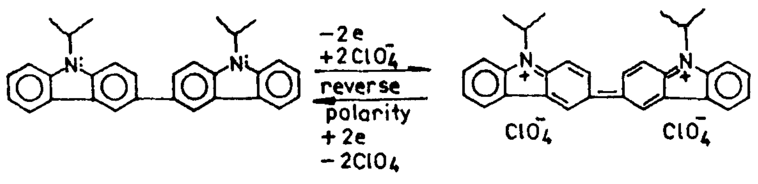


FIG. 2. Conversion of insoluble fraction vs time and current passed in experiment: (1) dichloroethane, (2) methylene chloride, (3) acetonitrile.



SCHEME 1.



SCHEME 2.

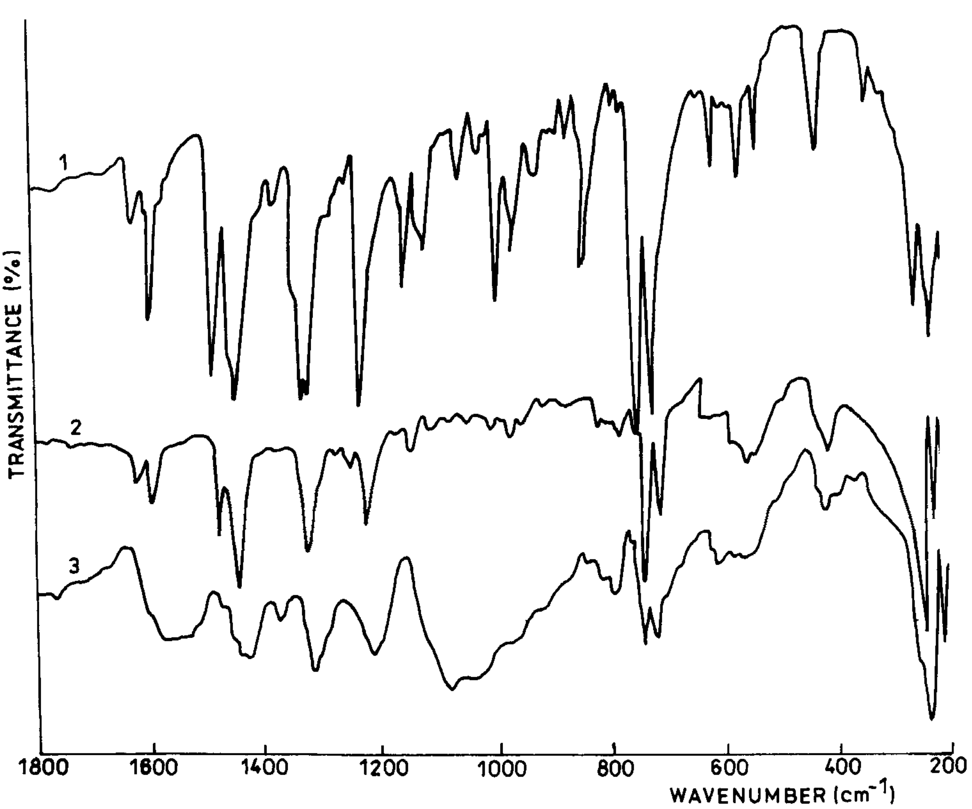


FIG. 3. IR spectra of BCMO (1), poly-BCMO soluble fraction (2), and poly-BCMO insoluble fraction (3).

The polymers were characterized by UV (Unicam SP-800 apparatus), IR (KBr pellets, Perkin-Elmer spectrometer), and ^{1}H NMR (Jeol 60 MHz).

RESULTS AND DISCUSSION

Electrochemical polymerization of BCMO was carried out in different aprotic solvents by using tetrabutylammoniumperchlorate (TBAP) as the support electrolyte (1:1 monomer/electrolyte molar ratio); the most efficient in this reaction. Some results are presented in Table 1 and Fig. 2.

Polymerization occurs in the anodic compartment (which turns green) on the anode surface, and it is favored by low density current (10 mA/cm^2). A polymer film is formed, and its adherence to the electrode surface depends on the reaction time. At higher current densities, higher reaction rates are reached, but the quality of the film is worse (nonuniform).

Since polymerization occurs on the electrode surface, the conversion to polymer is limited by diffusion of the monomer to the surface. Therefore, the nature of the solvent should play an important role in the reaction through its ability to swell the polymer film. This explains the differences in the results obtained in various

FIG. 4. ^{1}H-NMR spectra of BCMO (*1*) and poly-BCMO soluble fraction (*2*).

liquids. The film peeled from the electrode surface is colored. It is green at the beginning of the reaction and turns brown as the process proceeds.

The ring-opening polymerization of oxetanes usually results in a white, spongy, solid polymer, insoluble in common organic solvents [12]. The electroinitiated polymerization of BCMO most likely occurs through oxidation of carbazole rings to cation-radical species which are unstable and recombine in Position 3,

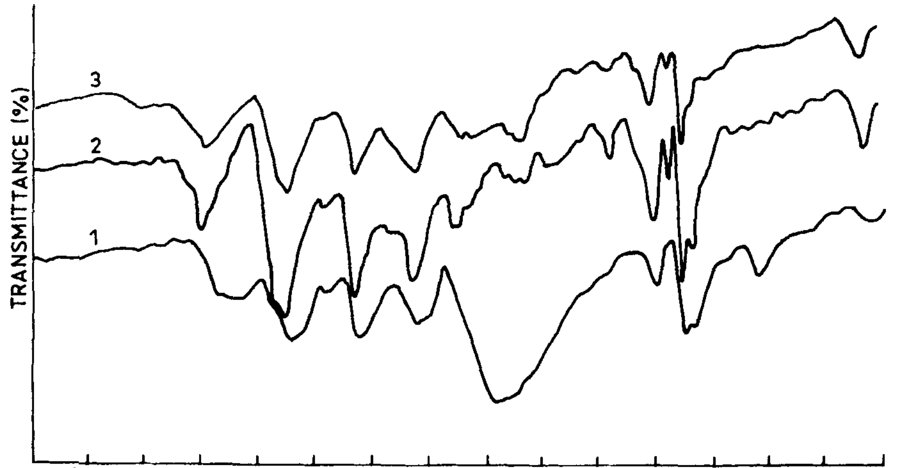


FIG. 5. IR spectra of poly-BCMO: (1) initial insoluble fraction, (2) electrochemically decomplexed fraction, (3) electrochemically decomplexed and extracted insoluble fraction.

TABLE 2. Thermal Characteristics of Poly-BCMO Fractions Obtained by Electropolymerization

No.	Sample	Weight losses at 300°C, %	Softening range, °C
1	Soluble fraction	3	220...240
2	Insoluble fraction	26	—
3	Decomplexed film extracted in THF	8	—
4	Insoluble film extracted in THF	8	—

releasing two protons (Scheme 1). Subsequently, the process proceeds by oxidation of the formed products [8, 14] (Scheme 2).

The starting green color in the anodic compartment can be attributed to the complex between the cation-radical species and perchlorate ions. Upon changing the polarity, the film formed on the anode surface decomplexes and remains as a transparent, nonadherent pellicle. Meanwhile, a new colored film is deposited on the cathode.

The electrochemical complexation and decomplexation in such conditions most likely occurs through the reversible transformation of the benzenoidal structure into the quinoidal one. Upon reversing the polarity, the doped film is reduced

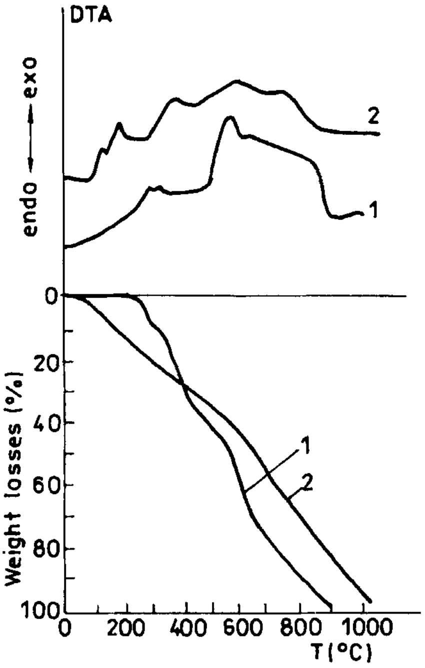


FIG. 6. DTA and TGA curves of poly-BCMO: (1) soluble fraction, (2) insoluble fraction.

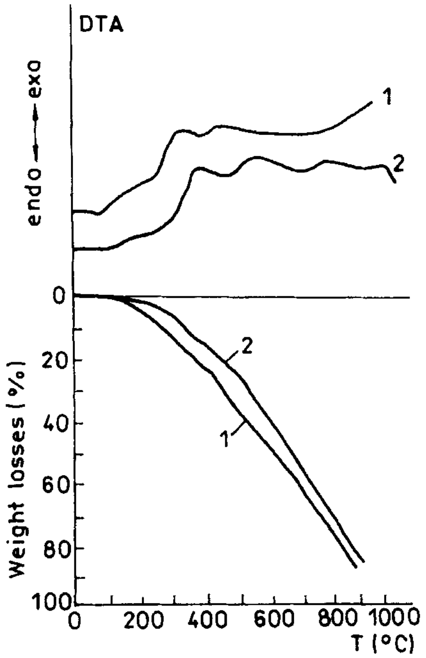


FIG. 7. DTA and TGA curves of poly-BCMO: (1) extracted insoluble fraction, (2) decomplexed and extracted fraction.

and perchlorate ions are released (Scheme 2). In fact, the reversal of electrode polarity during electropolymerization may represent a valuable synthetic route for obtaining membranes complexed with various doping agents coming from the ground electrolyte.

Spectral analysis of the prepared products (Fig. 3) indicates that structural modifications occur during electroplymerization. According to literature data, the IR spectrum of BCMO shows two characteristic absorptions at 960 and 930 cm^{-1} [13]. They are very weak in the spectrum of the soluble fraction and nearly disappear in the spectrum of the insoluble product. Large absorptions are seen in the 850–1170 cm^{-1} region, and two maxima at 720 and 750 cm^{-1} are assigned to δ_{C-H} in 1,2-disubstituted benzene rings. Unlike the monomer, the IR spectra of the polymers reveal the 800 cm^{-1} band attributed to a 3-substituted carbazole ring. The 1080 cm^{-1} absorption (large and intense for the insoluble fraction) was assigned to ClO_4^- ions complexed with oxidized carbazole rings and is supported by the curves in Fig. 5.

The ^{1}H-NMR spectrum of the soluble fraction (Fig. 4, Curve 2) reveals a complex signal in the 6.5–8.3 ppm region which denotes some structural modifications in the carbazole unit. Unlike the monomer, this fraction shows some changes in the 3–4.5 ppm region also. Based on these data, it is assumed that the 3-substituted carbazole rings constitute the macromolecular chain. Some work is in progress to define this structure more accurately.

Samples of decomplexed polymer were extracted in THF to remove all interstitially retained monomer and soluble products. Spectral analysis of the decomplexed and extracted film offers supplementary information on complexation in the electrochemical process (Fig. 5). Thus, the absorptions assigned to the ClO_4^- ion (625 and 1100 cm^{-1}, Fig. 5, Curve 1) in the spectrum of the complexed polymer are markedly diminished in the decomplexed and extracted films (Fig. 5, Spectra 2 and 3) without any evident differences except for these absorptions. The registrations correspond to a product in which carbazole rings are 3-substituted.

The above data suggest that the electrochemical transformation of BCMO predominantly involves only the carbazole units which oxidize to 3,3-dicarbazolyls and which, by "ring to ring" recombination, give more complex structures [14, 15].

Soluble fractions of poly-BCMO showed a reduced viscosity (0.074 dL/g in DMF, 30°C, $c = 1$ g/100 mL) which denotes oligomers.

Thermal properties were investigated on both extracted and unextracted soluble and insoluble fractions. Some results are summarized in Table 2. The weight losses of 26% for the unextracted insoluble fraction can be attributed to ClO_4^- which accelerates the decomposition of the polymer (Fig. 6).

The likeness of the DTA and TGA curves for the extracted fractions proves the similarity of the thermooxidative processes (Fig. 7).

CONCLUSIONS

The electroinitiated polymerization of BCMO occurs by anodic oxidation of the monomer on the electrode surface but not in the anolyte. Since the carbazole ring has a strong tendency for oxidation at positive potentials, polymerization is accompanied by crosslinking of the product and involves Position 3 of the aromatic ring. In this case the process is more pronounced, which accounts for each monomer molecule containing two carbazole units.

The anion of the electrolyte complexes the partially oxidized oligomers which decomplex electrochemically when the polarity is changed.

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