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Electrical conductivity of homopolymer and copolymers of *N*-vinylcarbazole

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Abstract Poly(*N*-vinylcarbazole) (PVCz) is well known as an electroactive material due to its good photoconductivity, charge-transfer complexes, photoluminescence and electroluminescence properties. The block copolymers of *N*-vinylcarbazole were prepared and the effects of the relative composition, molar masses, architecture and doping on its electrical behavior were investigated. Controlled free radical polymerization has been carried out using nitroxide-mediated process in order to prepare a series of block copolymers of *N*-vinylcarbazole. 2,2,6,6-Tetramethyl-1-piperidinyloxy radical (TEMPO) was used to end-cap ''living'' homopolymer of *p*-bromostyrene, which was further used as a macroinitiator to polymerize *N*-vinylcarbazole and styrene. The copolymers have been doped at room temperature with $LiClO_4$ and the electrical conductivities were measured by two-probe method, which have shown to depend on copolymer's relative composition and molar masses.

Introduction

Poly(*N*-vinylcarbazole) (PVCz) is a remarkable material due to its photoconductivity properties [1,2] and photo- and electroluminescence characteristics [3]. It has been used as high-temperature electric insulator, active layer in polymeric light emitting diodes and photoconductor in photocopies and electro-photographic printing plates [2]. However, the controlled preparation of poly(*N*-vinylcarbazole) in order to reach pre-established and/or high molar mass polymers [4], along with the block copolymers of *N*-vinylcarbazole still present scientific challenge. The ''living'' free radical polymerization has recently attracted considerable attention as a convenient method for synthesis of macromolecules characterized by low polydispersity, accurate control of molar mass and architecture [5–7]. In recent times, some researchers have attempted to prepare PVCz by a ''living'' process initiated by $C_{60}Cln/CuCl/2,2'$-Bpy, via an atom transfer radical polymerization (ATRP) [8]. However, it has been reported that *N*-vinylcarbazole could not be homopolymerized by benzoyl peroxide (BPO)/TEMPO systems, via ''living'' process [9] and only *N*-vinylcarbazole copolymerization with another monomer (for example sodium styrenesulfonate and styrene) has been reported to present ''living'' character and yield polymers with high molar masses [9,10].

Additionally, block copolymers of *N*-vinylcarbazole seem to be a very promising new class of polymeric material, which might preserve PVCz optical and electrical properties and additionally incorporate the unusual characteristics of block copolymers, like ability to form nanostructured materials itself and to contribute to stabilize nanosize dispersed phases in polymer

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blends, acting as fine tuning dispersants or compatibilizers.

We have prepared block copolymers containing substituted styrene [11], due to their very unique photochemical and photophysical properties [12,13]. We anticipate the possibility of preparing block copolymers bearing carbazole groups along with another high photoluminescent chromophore, in an on-going study that will be reported in a future communication.

In this work, we report the synthesis of homopolymers of VCz (Fig. 1) using BPO and TEMPO as initiators by a free radical polymerization process and the synthesis of block copolymer of *N*-vinylcarbazole and styrene (Fig. 3) from nitroxide-terminated poly(*p*-bromostyrene) (PBS-*b*-PVCz/PS) (Fig. 2).These copolymers have been doped with $LiClO_4$ and the conductivity data have been obtained.

Experimental

Materials

N-vinylcarbazole (Aldrich, 99%) was purified by recrystallization from methanol. BPO (Aldrich, 75%) was recrystallized in ethanol. Styrene (BASF) and *p*-bromostyrene (Acros, 96%) were purified by inhibitor elimination using a basic alumina column prior to polymerization reaction. TEMPO (Aldrich, 98%), methanol and chloroform were used without further purification.

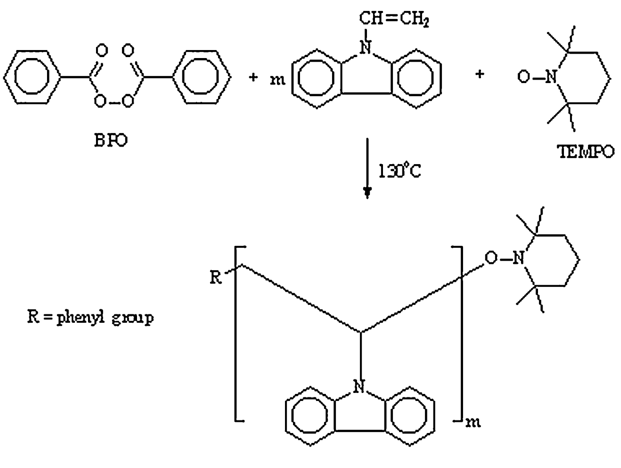

Fig. 1 Scheme of synthesis of *N*-vinylcarbazole homopolymer (PVCz)

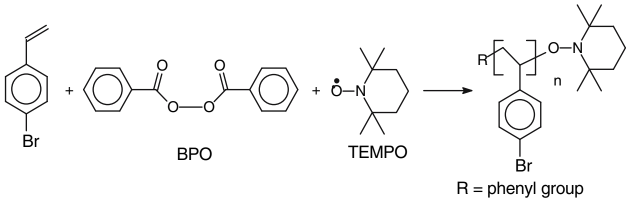

Fig. 2 Scheme of synthesis of *p*-bromostyrene homopolymer (PBS)

Synthesis of homopolymers of VCz

The homopolymers of *N*-vinylcarbazole (PVCz) (Fig. 1) were synthesized by bulk polymerization of *N*-vinylcarbazole in the presence of the pre-established TEMPO:BPO molar ratio of 1:1.3. The polymerization mixture was heated to 130 °C and allowed to polymerize for 141 h. After polymerization, the formed polymer was purified by precipitation in methanol (twice). The homopolymers were characterized by gel permeation chromatography, infrared spectroscopy and ^{1}HNMR spectrometry.

Synthesis of homopolymer of *p*-bromostyrene (PBS)

The homopolymer of *p*-bromostyrene (PBS) (Fig. 2) was synthesized by bulk polymerization of *p*-bromostyrene in the presence of the pre-established TEMPO:BPO molar ratio of 1:1.3. The polymerization mixture was heated to 130 °C and allowed to polymerize for 48 h. After polymerization, the formed polymer was purified by precipitation in methanol (twice). The yield was 75%. The homopolymer was characterized by infrared spectroscopy and ^{1}HNMR spectrometry.

Synthesis of PBS-*b*-PVCz/PS

The block copolymers PBS-*b*-PVCz/PS (Fig. 3) were synthesized by bulk copolymerization of *N*-vinylcarbazole and styrene in the presence of 0.1 g (0.05 mmol) of TEMPO-terminated poly(*p*-bromostyrene) (except for Cop9, with 0.05 g of PBS). The polymerization mixture was heated to 130 °C and allowed to polymerize for 48 h. After polymerization, the formed polymer was diluted in chloroform and precipitated in methanol (twice) and, finally, dried in vacuum oven for 24 h. The copolymer (Scheme 1) was characterized by infrared spectroscopy and ^{1}HNMR spectrometry. Table 1 shows the monomers molar ratios in the feed and the polymerization yields.

Characterization

The IR spectra were obtained using a Vector 22 Bruker Spectrometer and the ^{1}HNMR spectra were

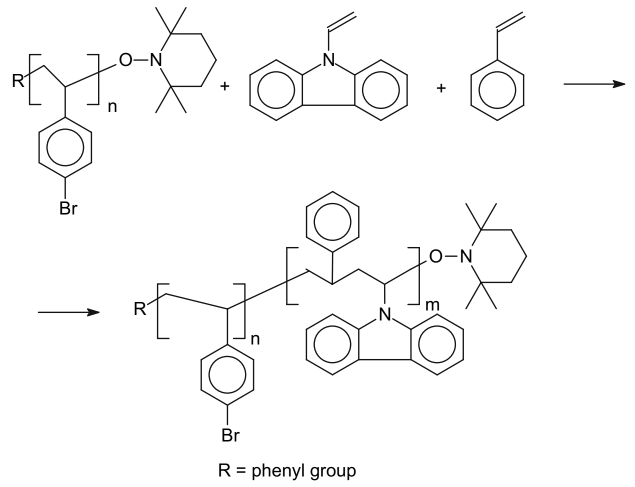

Fig. 3 Scheme of synthesis of block copolymer (PBS-*b*-PVCz/PS)

Table 1 Block copolymers characteristics

Sample	Monomer feed molar ratio		Polymerization yield (%)
	VCz	Styrene	
Cop1	1	9	76.7
Cop3	3	7	61.3
Cop5	5	5	70.4
Cop7	7	3	45.2
Cop9[a]	9	1	45.2

[a] The block copolymers PBS-*b*-PVCz/PS were synthesized by bulk copolymerization of *N*-vinylcarbazole and styrene in the presence of 0.1 g (0.05 mmol) of TEMPO-terminated poly(*p*-bromostyrene) (PBS) (except Cop9, with 0.025 mmol of PBS)

obtained using a Bruker DPX 300. Chemical shifts were taken against internal tetramethylsilane (TMS) as standard. Molar masses and polydispersity were determined by gel permeation chromatography (GPC) using a Waters HPLC equipped with two columns in series, PLgel mixed-B and PLgel mixed-C. GPC measurements were carried out in tetrahydrofuran using polystyrene samples as standards. The copolymer compositions were determined by UV spectroscopy.

Electrical conductivity

The conductivity data have been obtained from copolymers doped at room temperature with $LiClO_4$. To a 5% copolymer solution in chloroform, 1% of $LiClO_4$ was added. Solid films were prepared by casting and spin coating onto glass plates, followed by evaporation to dryness. Electrical contacts (0.5 mm diameter) on polymer films were accomplished by aluminum vapor deposition using a metal screen as mask. Current versus voltage ($I \times V$) curves were obtained from two-probe method measurements in a ‘‘clean room’’ (40–50% of relative humidity at 20 °C) using an HP4145 Semiconductor Parameter Analyzer. Films thickness were measured using an Alpha Step 500 profilometer in order to calculate electrical resistivities ρ (Ω cm).

Results and discussion

Characterization of PVCz and PBS

The infrared spectra of the polymer synthesized by bimolecular system shows the following characteristic absorption bands: (PVCz) 747 and 722 cm^{-1} (arom. C–H, out of plan bend.); (PBS) 3079, 3060 and 3024 cm^{-1} (arom. C–H, stretch.); 2926 cm^{-1} (assym. CH_2, stretch.); 2851 cm^{-1} (sym. C–H, stretch.); 754 cm^{-1} (arom. C–H, out of plan bend.); and 1079 cm^{-1} [C–X (X = Cl or Br), stretch.].

The analysis of the molar masses of homopolymers and copolymers of VCz, prepared under various experimental conditions, allowed the observation of the influence of reaction parameters on the molar mass evolution. Figure 4 shows the correlation between calculated and experimental molar mass of PVCz, prepared in the presence of different relative amounts of BPO/TEMPO. The observed linear behavior indicates ‘‘living’’ character up to a molar mass of 50,000 g/mol. Under these experimental conditions it was not possible to reach higher molar masses, however the homopolymers having molar masses lower than

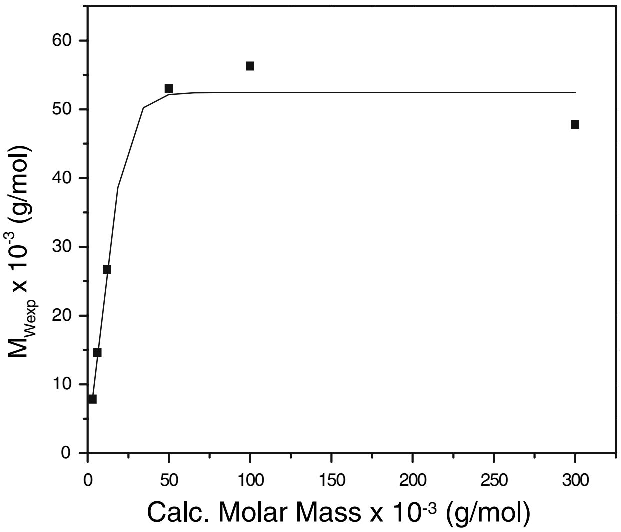

Fig. 4 Correlation between calculated and experimental molar mass of PVCz

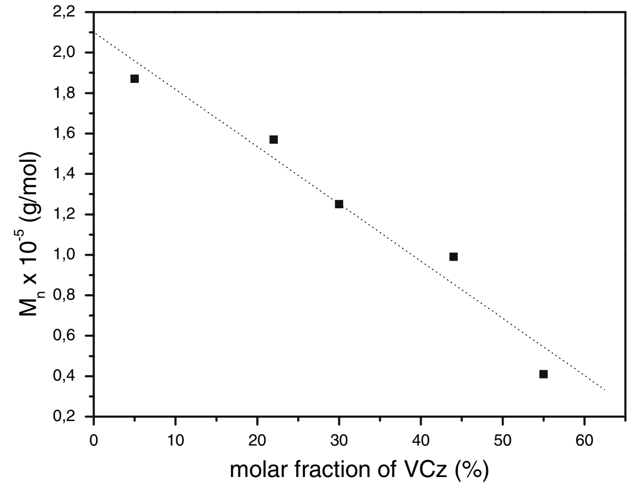

Fig. 5 Molar mass of PBS-*b*-PVCz/PS as a function of molar fraction of VCz in PVCz/PS segment

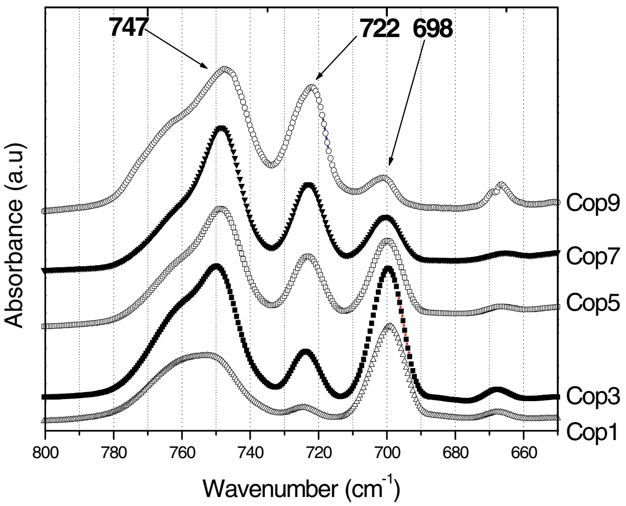

Fig. 6 Infrared spectra of the PBS-*b*-PNVC/PS copolymers

50,000 g/mol were submitted to an additional reaction with styrene and block copolymers were obtained.

The copolymerization behavior is shown in the Fig. 5. A linear correlation between molar fraction of VCz in the copolymer and its molar mass was observed. Although all reaction mixtures presented a constant amount of the initiation system (BPO/TEMPO = 1.3), the increase of molar fraction of VCz in the monomers feed provoked a reduction in the molar mass of the correspondent copolymer. We believe that the bulk polymerization reaction of VCz is characterized by radical deactivation due to resonance effects by stacking of carbazole rings, which also hinders the monomer approximation.

Characterization of PBS-b-PNVC/PS

The infrared spectra of the copolymers synthesized by the bimolecular system BPO/TEMPO were determined and the infrared region 800–650 cm^{-1}, correspondent to aromatic CH, out of plane bending, is detailed in Fig. 6. Characteristic absorption bands are at 698 cm^{-1} for polystyrene (PS), at 747 cm^{-1} and 722 cm^{-1} for PVCz; and at 747 cm^{-1}, 722 cm^{-1} and 698 cm^{-1} for the block copolymer. The PVCz and PS bands presented relative intensity variations, which are due to differences in the copolymers composition, indicating the block copolymer formation. All the ^{1}HNMR spectra of homopolymers and copolymers are in accordance with those previously reported [14,15].

The electrical conductivities of homopolymer and copolymers of VCz were measured after doping with $LiClO_4$ (Tables 2, 3) and are compared to those found in literature [16,17]. In this work, PVCz doped with $LiClO_4$ presented higher conductivity values than those reported for PVCz doped with bromine or chlorine. Furthermore, even the copolymer (VCz5) having 30 mol% of VCz presented higher conductivity, which indicates the effectiveness of the $LiClO_4$ doping. It deserves to mention that the conductivity in copolymers was also observed to be strongly dependent on the molar mass and the VCz relative amount. Therefore, higher conductivity was observed in copolymer with higher molar mass and higher VCz content, which is consistent with the VCz unit contribution as well as

Table 2 Conductivity data of PVCz homopolymers

Homopolymers	σ (Ω cm)$^{-1}$
PVCz	$\leq 10^{-10}$; 10^{-14}–10^{-17} [16]
PVCz doped with $LiClO_4^a$	1.34×10^{-7}
PVCz doped with Iodine	10^{-6} [17]
PVCz doped with Bromine	10^{-9} [16]
PVCz doped with Chlorine	$\leq 10^{-10}$ [17]

[a] Present work

Table 3 Conductivity data of PBS-*b*-PVCz/PS copolymers

Copolymers	PBS block (wt.%)[a]	Molar fraction of VCz in PVCz/PS block[b]	σ (Ω cm)$^{-1}$
VCz1	2.21	5	Insulator
VCz3	2.63	22	Insulator
VCz5	3.30	30	1.62×10^{-8}
VCz7	4.19	44	8.21×10^{-9}
VCz9	10.1	55	2.30×10^{-7}

[a] Percentage of *p*-bromostyrene block in copolymer

[b] Determined by UV spectroscopy

the polymer chain extension for the charge carriers' mobility.

The electrical conduction in polymers depends on many factors, among which the dopant nature, reactivity and concentration as well as the doping mechanism involved should be emphasized. Most of semiconducting polymers behaves as *p* charge carriers, through oxidative doping, like PVCz. Itoh et al. [18] reported on the effect of the ionic charges on the electrical conductivity in PVCz LEDs and concluded that the accumulation of ionic space charges at the electrode/polymer interface contributes to the enhancement of charges injections and electrical conductivity, however in those devices the observed electrical current was due to the electronic charge carriers. Recently, Syed Abthagir and Saraswathi [19] reported on the charge transport properties of PVCz prepared by electrochemical deposition, however non-conclusion was established regarding the nature of the charge carrier in $LiClO_4$ doped PVCz, although the loss in conductivity was associated to the dopant elimination. Further investigations are necessary to clarify the nature of the charge carriers involved in the $LiClO_4$ doped PVCz films.

Conclusions

Homopolymers of *N*-vinylcarbazole with molar mass up to M_w = 50,000 g/mol were synthesized by ''living'' free-radical polymerization. Poly(*N*-vinylcarbazole)s were doped with $LiClO_4$ and exhibited higher conductivity values than those reported previously.

Block copolymers of *p*-bromostyrene with styrene and vinylcarbazole were synthesized with various compositions. After doping with $LiClO_4$, the block copolymers have shown improved electrical conductivities, which increased with the molar mass and the VCz content.

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