Poly(*N*-glycidyl carbazole): A New Crosslinkable Conjugated Polymer

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ABSTRACT: A poly(*N*-glycidyl carbazole) was synthesized by electropolymerization of 3,6-dibromo-*N*-glycidyl carbazole. Characterization of both products by different chemical and electrochemical techniques is then discussed. The polymer that showed electronic conductive properties when doped was crosslinked by *cis*-cyclohexane 1,2 dicarboxylic anhydride. The crosslinking reaction was followed by Fourier-transform infrared spectroscopy (FT-IR). An optimization of the crosslinking conditions was first performed on the monomer and subsequently applied to the polymer. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 73: 1483–1492, 1999

Key words: functionalized monomer; poly(*N*-glycidyl) carbazole; electronic conductivity; FT-IR; crosslinking

INTRODUCTION

The conductive adhesives commonly used in electronics are most often crosslinkable resins loaded with conductive inorganic powders such as silver, carbon, and nickel.¹⁻⁴ The amount of conductive powder can range from 60 to 90% (w/w) to reach optimal conductivity.⁵ These compounds have many drawbacks: resin degradation due to metal particles, thermal oxidation, bad resistance in aqueous solutions, and metal particles corrosion.⁶⁻⁸ Many studies have been performed to substitute the metal particles used in conductive adhesives by conductive polymers such as polyaniline.^{9,10} In this case, however, resulting properties, especially the electronic conductivity (approximately 10^{-3} S.cm⁻¹) remained insufficient to replace metallic loaded adhesives. One alternative could be synthesizing conjugated polymers containing crosslinkable functions. After doping and crosslinking, these compounds could combine conductivity and adhesion.

This article presents one example of conjugated crosslinkable polymer, poly(N-glycidyl carbazole) (PNGCz). The polymer was synthesized by electrochemical means, from 3,6-dibromo-*N*glycidyl carbazole (DBNGCz) by aromatic coupling of C-Br links in the presence of zero-valent nickel Ni(0), according to a widely used method.¹¹

Whereas epoxy ring opening polymerization of DBNGCz was already studied¹² and led to materials with interesting photoconductive properties, the epoxy functions remain untouched in the synthesis described herein. Thus, crosslinking of the epoxy function can be subsequently performed in a controlled way.

Crosslinking studies were performed on a nondoped polymer. More often, epoxy resins are reacted with a hardener to form a thermoset material. In this work, amine or acid anhydride were used as a crosslinking agent. The most interesting results were obtained with *cis*-cyclohexane 1,2-dicarboxylic anhydride (CDA). An optimization of the crosslinking conditions was performed

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	Electrolyte	DBNGCz	NiBr ₂ bipy/ x bipy	Applied Potential (V/ECS)	Released Br ⁻ (%)	Weight of Crude Product (g)	Yield (%)
PNGCz 1 PNGCz 2	${ m LiBF_4}\ { m LiBF_4}$	${2\ 10^{-3}\ 2\ 10^{-3}}$	$10^{-3}/2 \ 10^{-3}$ $10^{-3}/0$	$-1.3 \\ -1.3$	94 100	$\begin{array}{c} 0.4\\ 0.436\end{array}$	90.5 98.6

Table I Experimental Conditions and Results of Electrosynthesis of PNGCz

PNGCz, poly(N-glycidyl carbazole); DBNGCz, 3,6-dibromo-N-glycidyl.

on the monomer. These optimal conditions were then applied to the polymer.

EXPERIMENTAL

Chemicals

Epichlorohydrin and 3,6-dibromocarbazole (Aldrich Chemical Co.) were used without purification. NiBr₂ 2,2'-bipyridine [NiBr₂(bipy)] was prepared according to the method described previously.¹³ N,N Dimethyl acetamide (DMA) (SDS), which is used as a solvent for the polymer electrosynthesis, was distilled on calcium hydride under inert atmosphere and at reduced pressure (10 mm Hg). The salts (LiBF₄, LiClO₄) (Fluka) were dried under vacuum at 100°C for 24 h. All other reagents, such as CDA and solvents, were used as received.

Synthesis of 3,6-Dibromo-N-glycidylcarbazole

Five grams of 3,6-dibromocarbazole (0.015 mol) and 17 ml of epichlorohydrin (0.15 mol) were mixed at 40°C for 15 min. Then 2.52 g of potassium hydroxide KOH (0.045 mol) and 0.5 g of sodium carbonate Na₂CO₃ were added. The reaction takes place at ambient temperature under inert atmosphere (N_2) and constant stirring for 24 h. A solid yellow precipitate is obtained. After washing with water and ethanol, this compound was then recrystallized (in ethanol) and finally dried under vacuum (10 mm Hg): Yield 56%; mp 141–142°C (lit.^{14,15} mp 141°C). ¹H NMR (270 MHz); solvent CDCl₃: (ppm: 8.48 (2H, dd); 7.67(4H, m); 4.95 (1H, dd); 4.52 (1H, dd); 3.47 (1H, m); 2.88 (2H, m). Elemental analysis (C₁₅H₁₁ ONBr₂): Calculated values, 47.24 C%, 3.67 N%, 41.99 Br%; experimental values, 47.52 C%, 3.76 N%, 41.87 Br%.

Synthesis of Poly(*N*-glycidylcarbazole)

The PNGCz was obtained by electropolymerization of the DBNGCz according to the method already described 13,16 for the synthesis of the *N*-substituted polycarbazoles.

The electrolysis was achieved by using a Radiometer apparatus (PRT40-1X potentiostat, IG5-N coulometer) connected with an X-Y Plotter (Sefram TGM 101). A cell with two compartments divided by a fritted disc was used. A mercury pool under permanent stirring was used as a cathode, whereas saturated calomel electrode (SCE) was used as reference and a magnesium rod as auxiliary electrode.

Two types of electrosynthesis were performed: 1. 4 mmol of monomer, 2 mmol of NiBr₂(bipy) and 2 mmol (of) bipyridine were introduced under argon atmosphere with 100 ml of DMA containing 0.01 mol of LiBF₄; and 2. there was no excess of bipyridine.

In both cases, electrosynthesis was performed in a potentiostatic mode, a constant potential was applied, and fitted with the catalytic precursor reduction potential. After electrolysis, the mercury was removed and the polymer (a grey powder) was obtained. After washing with water and ether, the powder was then dried under vacuum at 100°C for 24 h. The quantity of released Br⁻ was then measured by an argentimetric titration. All experimental conditions are listed in Table I.

Physicochemical Characterization

Infrared spectra were performed with a Nicolet Fourier transform infrared spectrophotometer (impact 400). The nuclear magnetic resonance (NMR) spectrum were recorded on a JEOL 270 spectrometer, using CDCl₃ or deuterated dimethylsulfoxide (DMSO) as solvents. Molecular weights were determined by size exclusion chromatography (SEC) with a Waters apparatus (Waters R 410 differential refractometric detector and Waters 486 UV-visible detector), using a set of three columns (Waters: HR1, HR2, 10^3 A). The mobile phase was tetrahydrofuran, with a 0.9 ml/mn eluent flow rate. Chromatograms were treated with Millenium 2.0 software. Polystyrene samples were used as standards. Thermal analy-



Scheme 1

ses were performed on DSC 7 a Perkin-Elmer apparatus and melting point were determined with a Buchi 510 device.

Reaction Between CDA and DBNGCz Monomer

Triethylamine was chosen as the nucleophilic initiator required in the reaction of epoxy functions and CDA. Triethylamine was introduced in catalytic amounts in the CDA + monomer mixture, which was then heated at 110°C after homogenization. Small amounts of the mixture were withdrawn for the infrared analysis at regular time intervals to follow the reaction between CDA and monomer. In a first series of experiments, the impact of DBNGCz/CDA stoichiometric ratio on reaction was studied. Different ratios were experimented with: 0.5; 0.66; 1; 1.3; and 2. In a second type of experiment, the reaction was studied in the presence of the solvent (acetone or THF). DBNGCz and CDA were mixed with triethylamine and 1 ml of solvent. The mixture was put in an oven at 110°C and the reaction was followed.

Method of the Kinetic Following Reaction by Fourier-transform infrared Spectroscopy

Each sample was inserted between two KBr windows and then analyzed by Fourier-transform infrared (FT-IR) between 4000 and 400 cm⁻¹. The C=O bond of the CDA showed characteristic absorption bands at 1856 cm⁻¹ and 1776 cm⁻¹. The decrease and the subsequent disappearance of these bands during the reaction on one hand, and the appearance of one band at 1700–1730 cm⁻¹ (C=O of ester functions) on the other hand, allows the determination of the rate of CDA conversion. The crosslinking quantification was made vs a reference band (cyclohexyl ring of CDA: 1478 cm⁻¹), using the Beer-Lambert law.

Unfortunately, it was not possible to simultaneously follow this technique, the opening of the epoxy ring during the reaction, because the CDA presents a characteristic absorption band at the same wavelength as an epoxy characteristic band (910 cm^{-1}) . This brought us to proceed to an NMR study.

Reaction Between CDA and Polymer

We have postulated that the optimal conditions determined with the monomer were applicable to the polymer. Thus, the crosslinking reaction between polymer and CDA was followed by FT-IR according to the same protocol as used previously for the monomer.

RESULTS AND DISCUSSION

Part 1: Synthesis and Characterization of PNGCz

Synthesis and characterization of the monomer

The DBNGCz was synthesized according to nucleophilic substitution reaction in basic conditions¹⁴ (see Scheme 1).

The monomer was characterized by ¹H and ¹³C NMR and FT-IR. The identification of all the protons and carbons confirmed the molecular structure of DBNGCz. Figure 1 shows the monomer infrared spectrum, which displays carbazole absorption bands;^{13,16} 802 cm⁻¹: C=H deformation outside of the plane of the isolated hydrogen (4,5); 878 cm⁻¹: deformation of two adjacent hydrogen (2,7–1,8); 1223 cm⁻¹: (valence vibration of the N=CH₂ bond), and that of the epoxy (epoxy C=O stretching: 1249 cm⁻¹, epoxy vibration out of the cycle plane: 910 cm⁻¹).

Electrosynthesis and Polymer Characterization

As for other N-substituted polycarbazolylenes,¹³ PNGCz electrosynthesis was achieved in potentiostatic mode by applying at the cathode a potential fitting with the catalytic precursor reduction potential (-1.3V/ECS). As observed previously,¹⁶ at the beginning of the electrolysis, the solution turns green, which denotes the formation of zero-valent nickel by electrochemical reduction. This color rapidly changes from red



Figure 1 FT-IR spectrum of DBNGCz.

to brown, denoting the Ni(0) oxidant insertion reaction in the C-Br link of the monomer. At the end of the electrolysis, a brown precipitate was obtained. After treatment, the product was characterized by ¹H- and ¹³C-NMR, IR spectroscopy, and SEC.

The electrosynthesis results (Table I) show that the yield of the reaction realized without excess of bipy (98.6 %) was higher than the yield obtained with an excess of 2 mol of bipy (90.5%). This result is in agreement with bromine argentimetric titration after electrolysis, since 100% of bromines are released in the first case, against 94% in the second case.

The very weak solubility of PNGCz in deuterated solvents such as tetrahydrofuran (THF) or DMSO impedes a good NMR spectroscopy characterization of this polymer. Furthermore, the bad resolution of the ¹³C- NMR spectrum does not allow an exact identification. Nevertheless, the ¹H- NMR spectrum presents a slightly better resolution, with broad peaks corresponding to the same chemical shifts as observed with the monomer.



Figure 2 SEC chromatogram of DBNGCz.



Figure 3 FT-IR spectrum of PNGCz.

On the other hand, the solubility of the PNGCz in THF is sufficient to allow the molecular weight determination by SEC. The chromatogram (Fig. 2) shows that the soluble fraction is essentially composed of polydispersed oligomers (I = 2.2, Mn = 2000, DPn = 9-10).

The IR polymer spectrum (Fig. 3) displays two new absorption bands at 3424 cm^{-1} and 1382 cm^{-1} compared with the monomer spectrum. Drying

the polymer at 100°C under vacuum during several days seemed to exclude residual water presence. These new bands could correspond to —OH resulting from the opening of epoxy rings. The quantity of epoxy groups transformed to alcohol was thus assessed using the Beer-Lambert law,



Figure 4 Cyclic voltamograms of evaporated PNGCz thin layer on glassy carbon in $CH_3CN/LiClO_4$ medium as a function of sweep rate: (a) 0.2; (b) 0.3; (c) 0.4; (d) 0.5; (e) 0.6; (f) 0.7 V.s⁻¹.



Figure 5 Doping kinetic of PNGCz under saturated I_2 atmosphere.

considering the following absorption bands: 910 cm^{-1} (corresponding to the epoxy ring band) and reference 802 cm^{-1} (carbazolic C—H stretching). Comparing the ratio of absorbance of these two bands in the polymer and in the monomer, leads to the following (*A*, absorbance).

appears on the thermogram at about 120° C, corresponding to PNGCz glass transition. Neither melting nor other thermal phenomenon is observed in a temperature range of -10 to 230° C.

$(A_{\rm epx}/A_{\rm ref})_{\rm polv} = 0.59 (A_{\rm epx}/A_{\rm ref})_{\rm mono}$

This allows an estimation of 59% opened epoxy rings in the polymer. A weak endothermic peak

DNCCa was denosited on a glassy earbon a

Electrochemical Characterization of PNGCz

PNGCz was deposited on a glassy carbon electrode by evaporating the solvent from a THF solution. Electrochemical characterization was per-



Figure 6 FT-IR spectrum showing the reaction between DBNGCz and CDA: (a) initial spectrum; (b) final spectrum (after 35 min).

formed in acetonitrile/LiClO₄ solution from 0.0 to 1.5 V. The resulting voltamograms are shown in Figure 4. Electrochemical behavior of PNGCz seems similar to that described previously for different poly(*N*-alkylcarbazoles).¹⁷ The PNGCz seems oxidizable in two bad-defined steps occurring at about 1.10 V and 1.40 V for a sweet rate of 0.3 V.s⁻¹. On the reverse scan from 1.50 V, there are two well-defined reduction peaks at 1.05 V and 0.65 V corresponding to the cathodic ones. According to Ambrose et al.,¹⁸ the first process may correspond to the electronic transfer leading to radical cation of bicarbazolylene unit formation, whereas the second process may be attributed to the dication formation.

On the other hand, the cathodic and anodic peak variation vs the square root of scanning rate is linear. This means that the observed electrochemical phenomenon is controlled by ion diffusion into the material as reported for poly(N-al-kylcarbazoles).¹⁷

Doping Kinetics and Conductivity Measurement

PNGCz doping was achieved with iodine in a desiccator under primary static vacuum. The evolution of mass and conductivity was followed as a function of time (Fig. 5). The highest conductivity level corresponding to 4.10^{-4} S.cm⁻¹ is reached when the mass intake is the highest.



Figure 7 DBNGCz/CDA ratio effect on the crosslinked reaction.



Part 2: Study and Optimization of Polymer Crosslinking Conditions

Determination of the Optimal Conditions of the CDA Reaction with the Monomer IR Analysis

Figure 6 shows the IR spectra of a stoichiometric molar ratio DBNGCz/CDA mixture at t = 0 and after 35 min reaction, respectively. As indicated previously, the CDA is characterized by a double band absorption at 1778 cm⁻¹ and 1854 cm⁻¹ corresponding to the two carbonyl group vibrations.¹⁹ The higher frequency is attributed to the symmetrical vibration, whereas the lower is due to the asymmetrical vibration. The opening of the CDA causes the disappearance of these bands and the appearance of one band at



Scheme 2

 1722 cm^{-1} , attributed to the ester formation. Simultaneously, we can note the appearance of an OH vibration absorption band at about 3410 cm⁻¹, probably due to the reaction with ambient water vapor.

The influence of the DBNGCz/CDA stoichiometric ratio on the final conversion rate was investigated with FT-IR spectroscopy, matching the number of anhydride sites of CDA opened during reaction. Figure 7 shows that the maximum rate of anhydride opening is obtained with the DBNGCz/CDA stoichiometric molar ratio.

NMR analysis. The ¹³C NMR spectrum of DBNGCz crosslinked by CDA (Fig. 8) shows the appearance of two new peaks at 70 ppm and 64 ppm compared with the spectrum of the monomer. These two peaks respectively correspond to the $C_{\beta'}$ and $C_{\gamma'}$ carbons of the epoxy ring after the crosslinking reaction, those carbons appearing at 51.0 ppm and 45.6 ppm, respectively, in the unmodified epoxy as shown by the carbon DEPT sequence.

The two C_{β} and $C\gamma$ carbons at 51 and 45.6 ppm also appear in the crosslinked product spectrum, but their integration vs that of the opened ring carbons, only corresponds to about 5% of the initial corresponding rings.

Solvent effect on the reaction. The crosslinking experiment (same DBNGCz/CDA ratio, same conditions) was performed with or without solvent (acetone, THF). The solvent does not participate directly at the reaction but promotes the homogenization of the mixture. Thus, the percentage of anhydride conversion is higher (98%) with acetone or THF than in the bulk (91%). The use of solvent seems therefore to be more beneficial.

Polymer Crosslinking Reaction with CDA

The crosslinking mechanism reaction between the PNGCZ and CDA can be seen in Scheme 2. It has been noted previously that 59% of the epoxy functions open during polymerization. This modification of the PNGCz functionality does not represent a handicap for crosslinking because acid anhydrides are also reactive toward alcohol functions. Moreover, this represents an advantage since their presence will cause another initiation of the crosslinking reaction. The optimal experimental conditions determined for the monomer (T° cross-linking = 110°C, molar stoichiometric ratio: epoxy functions/CDA = 1) were then applied to the polymer. Two FT-IR spectra were performed, one at the beginning, and the other at the end of the reaction (see Fig. 9). As in the case of the monomer, the FT-IR spectrum showed the total disappearance of the C=O characteristic vibration bands of the anhydride (1853 cm^{-1} , 1778 cm^{-1}) and the appearance of the 1701 cm⁻¹ band characteristic of the C=O ester bond. Hence, the anhydrides had been fully consumed. Nevertheless, the reaction time was longer (3 h vs 2 h for the monomer). This could be attributed to the bad homogeneity of the reaction mixture from the beginning, and probably to the steric hindrance around the active sites, which is not the case for the monomer.



Figure 9 FT-IR spectrum of the crosslinking reaction between PNGCz and CDA.

Electrical Properties of PNGCz after Reticulation: Doping Kinetics and Conductivity Measurement

The same doping method used in the case of the noncrosslinked polymer was applied to the crosslinked product. The maximum conductivity was about 10 times below that obtained with the noncrosslinked PNGCz. This was probably due to the effect of the dilution generated by the presence of CDA as well as the rigidifying process of the structure of the material after crosslinking, which makes the diffusion of the doping agent (I₂) in the polymer matrix more difficult.

CONCLUSION

The results reported in this study show that the functionalization of monomers like 3,6-dibromocarbazole bearing an epoxy group allows conducting and crosslinked material to be obtained. The FT-IR analysis seems to be a good technique for the study of the crosslinking reaction for the monomer and corresponding polymer. In this way, we determined the optimal conditions for the elaboration of our material.

This study seems to be a good way to investigate a new generation of conductive adhesives. Also, other investigations with other functionalized conjugated polymers like thiophen derivatives will be explored in future studies.

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