XPS and ESR Studies of Electrochemically Synthesized Polycarbazole Post-Doped with Iodine

J. C. BERNEDE,¹ H. TAOUDI,¹ A. BONNET,¹ P. MOLINIE,² M. MORSLI,¹ M. A. DE VALLE,² F. DIAZ³

¹ EPSE, Groupe Couches Minces et Matériaux Nouveaux, FSTN, 2 rue de la Houssinière, BP 92008, 44322 Nantes Cedex 3, France

² IMN, 2 rue de la Houssinière, BP 92008, 44322 Nantes Cedex 3, France

³ Laboratorio de Polimèros Facultad de Quimica PUC, Chile

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ABSTRACT: Polycarbazole powders obtained by electrochemical oxidation of carbazole thin films or of carbazole in solution in the electrolyte have been post-doped with iodine and characterized by room temperature electrical conductivity, X-ray photoelectron spectroscopy (XPS), and electron spin resonance (ESR). Similar results are obtained with polymers saturated with iodine at room temperature after 6 weeks and with polymers doped at 383 K for 24 h. The polymers obtained from carbazole thin films have a higher electrical conductivity ($\sigma \sim 10^{-4} \ \Omega^{-1} \ \text{cm}^{-1}$) and a higher spin density (9.9 10^{21} spins $mol^{-1} g^{-1}$), which corresponds to 71 atom % of ionic iodine. The polymer radicals are located on the nitrogen, and the percentage of N^+ is 40 atom %. The electrical conductivity of the polymers obtained from carbazole in solution in the electrolyte is two order of magnitude smaller. The percentage of N⁺ is only 25 atom % with an ionic iodine percentage of 13 atom %. So, the most important parameter is not the iodine percentage introduced after doping into the polymers but the percentage of ionic iodine present in the polymers. The differences that are put in evidence can be explained by a better polymerization efficiency of the carbazole when it is deposited on thin film form by vacuum evaporation before electrochemical oxydation. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 71: 115-124, 1999

Key words: polyarbazole; photoelectron spectroscopy; electron spin resonance; iodine doping

INTRODUCTION

Polymers based on heterocyclic units can be used as semiconducting or conducting materials. Usually, to obtain conductive polymers, the dopant is provided by a chemical or electrochemical process. However, these doped polymers are often instable in air. Polymers having noncarbon elements in the chain have been found to provide more stable properties.¹ Polyaniline,² polythiophene,³ and polypyrrole⁴ have been extensively studied, but only few works have been devoted to polycarbazole.^{5–11}

The electrical conductivity of polycarbazole has been yet found quite smaller than that obtained with the more classical conductive polymers.¹¹ Therefore, in the present work, the properties of polycarbazole obtained by electrochemistry and post-doped by iodine have been studied in order to improve its conductivity. Experimental results of

Correspondence to: M. Morsli.

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		Conductiv	ity (Ω^{-1} cm ⁻¹)	
Sample	Before Iodine Doping	After 2 Weeks of Iodine Doping	After 2 Months of Iodine Doping	After Annealing for 24 h at 383 K of Iodine Doping
Sample obtained from carbazole diluted in the electrolyte	$2.5 10^{-12}$	$2.5 10^{-9}$	$4.5 \ 10^{-6}$	$5 \ 10^{-6}$
Sample obtained from carbazole thin films	$2 \ 10^{-11}$	$2 \; 10^{-7}$	$1.5 10^{-4}$	$1.5 \ 10^{-4}$

Table I Evolution of the Room Temperature Conductivity with Iodine Doping Time

the electrical conductivity measurements are interpreted with the help of X-ray photoelectron spectroscopy (XPS) and electron spin resonance (ESR) studies.

EXPERIMENTAL

The following 2 kinds of samples have been studied: polycarbazole obtained by electrochemical oxidation of carbazole monomers in solution in the electrolyte [referenced as PCZS(I) in the following text]; polycarbazole obtained by electrochemical oxidation of carbazole deposited by evaporation on the SnO₂ electrode [referenced as PCZS(II)].

The carbazole monomer was provided by Aldrich with a purity of 99%. For PCZS(II) samples, the thin films of carbazole were obtained by classical thermal evaporation of powder from a molybdenum boat under a vacuum better than 10^{-4} Pa. The evaporation boat has a special configuration with 2 superposed multiholed covers in order to avoid the powder calefaction. The evaporation rate (3 nm s⁻¹) and the film thicknesses were measured *in situ* by the vibrating quartz method. Thickness was also checked by a mechanical stylus profilometer.

For electrochemical oxidation, a 3-electrode, 1-compartment cell has been used. The 3 electrodes were a SnO_2 -coated glass, a platinum counter-electrode, and a saturated calomel electrode (SCE) with respect to which all the potentials were measured. The electrolytes used were similar in each case.

It must be noticed that the second technique needs only a very small quantity of monomer, and the contamination of the electrolyte solution during polymerization by the oligomers is quite small. The solution used for the electrochemical polymerization of the thin evaporated films was acetonitrile and water, in the volume ratio 1/2, containing 0.1M tetraethylammonium perchlorate as electrolyte. The oxidation of the films on the SnO₂-coated substrate was carried out by applying a constant dc voltage of 2.5 V between the SnO₂ electrode and the reference electrode.

The charge density was monitored with a potentiostat PGP20. PCZS(I) polycarbazole films were obtained from the same solution than above but containing 0.1M of carbazole.

After polymerization, the films were first washed with distilled water, dried for 24 h at room temperature, and then scratched from the substrate and grinded before post-doping.

The polycarbazole was post-doped with iodine according to the method of Gutierrez et al..¹² The polymer was placed at room temperature under vacuum with iodine in a separate glass cup.

Periodically, samples were removed, weighed, and returned to the bell until no more iodure was taken up. Moreover, some powder was sometimes taken out to check the evolution of the electrical conductivity. It has been shown that the conductivity stabilizes only after 2 months (Table I), when no more iodine was taken up.

In order to reduce this time, some samples have been heated during doping. For annealing treatment, the powder was introduced with a small amount of iodine ($\sim 1 \text{ mg}$) in a vacuum-sealed Pyrex tube, and the powders were annealed in an oven for 24 h. The optimum temperature has been found to be 383 K; for higher temperatures, there is partial decomposition of

the polymer, as shown by infrared (IR) absorption measurements.

PCZS(I) and PCZS(II) polymers have been characterized by XPS, ESR, conductivity measurements, and also, as previously said, checked by IR absorption measurements.

Infrared spectra were obtained by the KBr disk method (pressed pelled of KBr mixed with a small amount of polymer) using a Fourier transform infrared (FTIR) spectrometer. Band positions are expressed in wave numbers (cm^{-1}).

XPS measurements were carried out with a Leybold LHS.12 apparatus (University of Nantes, CNRS) using a magnesium source radiation (1253.6 eV) operating at 10 KV and 10 mA, and the pass energy was set at 50 eV. High-resolution scans with a good signal ratio were obtained in the C1s, N1s, Fe2p, Cl2p, and I3d regions of the spectrum. The quantitative analysis was based on the determination of the C1s, N1s, Cl2p, and I3d peak areas with 0.2, 0.36, 0.58, and 6.4 as sensitivity factors, respectively (the sensitivity factors of the spectrometer are given by the manufacturer). The vacuum in the analysis chamber was about 10^{-6} Pa. All the spectra were recorded under identical conditions.

To check the evolution of the composition in the bulk (more particularly, the iodine content), successive XPS spectra were recorded after argon etching for short periods. Sputtering was performed at pressures lower than 5×10^{-4} Pa, with a 10-mA emission current and a 3-KV beam energy using an ion gun. The Ar ion beam could be rastered over the whole sample surface. Before sputtering the pressure was below 5 10^{-7} Pa.

Electron spin resonance (ESR) experiments were performed at ambient temperature on a Bruker ER 200D spectrometer operating at the X band. Spin density Ns was estimated using an ESR comparison technique. The minimal sensitivity of the detector is about 10^{15} spins cm⁻³ mol⁻¹.

Conductivity measurements were performed on pressed polymer pellets with the help of an electrometer.

EXPERIMENTAL RESULTS

It can be seen in Table I that the highest electrical conductivity values of the samples doped at room temperature can be obtained more rapidly by using annealing during iodine doping. Similar results are also obtained for other measurements (XPS, ESR, and IR absorption), which means that the satura-

Table II XPS Quantitative Analysis

			Atomic %	, 2	
Sample	С	Ν	Cl	Ι	0
After electro	ochemical	l synthes	is:		
PCZS(I)	82	5	5		8
PCZS(II)	88	5	2		5
After iodine	doping (2 months	at 300 K	():	
PCZS(I)	80	3		3	14
PCZS(II)	77	3	3	7	10
After iodine	doping (24 h at 3	83 K):		
PCZS(I)	78	2.5		5.5	14
PCZS(II)	75	4	1.5	6.5	13

tion of the iodine doping is achieved. Some attempts to improve the doping efficiency by increasing the doping temperature ($T \ge 120^{\circ}$ C) and the iodine pressure have failed; the IR spectra, which are very different from those of polycarbazole, show that the polymers were destroyed.

XPS Measurements

Results of the quantitative analysis are reported in Table II. The evolution of the relative concentrations C, N, Cl, I, and O atoms has been studied as a function of the doping process. All the peaks have been decomposed, and the results are reported Table II and Figures 1 to 5.

First, it can be seen that there is some contamination of the polymer with oxygen just after the electrochemical synthesis. The chlorine concentration is higher in the samples obtained from carbazole diluted in the electrolyte. After iodine doping, there is some increase of the surface contamination, and chlorine cannot be detected any more in PCZS(I) samples.

The N1s signal is slightly attenuated by the surface contamination. The post-doping process appears to be quite efficient since at the end of the reaction there is about 3 to 7 atom % of iodine. The atomic percentage of iodine is the same before and after a surface etching of 1 min.

Qualitatively, it can be seen in Figure 1 that if the iodine quantity present in the polymer is nearly the same in PCZS(I) and (II), the localization of the iodine doublets is quite different, which shows that the iodines are not chemically equivalent in the 2 kinds of samples.



Figure 1 XPS iodine spectra: (a) PCZS(I); (b) PC-ZS(II).

Before iodine doping, the C1s signal can be modelized with the help of 3 components. The first one is attributed to the hydrocarbon bonds with a binding energy of 285 eV. The second one with a binding energy of about 286 eV can be assigned to C—N bonds. However, its relative atomic percentage is highest than the theoretical value (7.7 atom %), and the experimental value may correspond to C—O—H bonds due to surface contamination. The binding energy of the third component is about 288 eV. This binding energy domain may correspond to —C—O bonds.

Whereas the N1s peak of the carbazole monomer is symmetrical, the N1s peak of polycarbazole located at about 400 eV becomes asymmetric on its high binding energy side, and it is decomposed in 2 contributions. The high binding energy component is due to positively charged nitrogen atoms $N^{\delta+}$, and the second one corresponds to the C—N bond of the carbazol units.

At the end of the iodine doping process, the $N^{\delta+}$ contribution has reached values of 40% in the case of polycarbazole obtained from carbazole thin films and only 25% in the case of PCZS(I) samples. The high-energy shoulder is presented in Fig. 2(a) and (b).

During the iodine doping, there is not only a broadening of the high-energy tail of the C1s peak, but the shape of the envelope is also modified, especially in the case of polycarbazole obtained from monomers diluted in the electrolyte. The decomposition of this peak is reported Figure 3 and Table III.

It can be seen that 4 contributions are necessary to obtain a theoretical curve well fitted with the experimental one. Three peaks correspond to the contributions previously described (C—C, C—N, C—O—H, and C=O). Because of the bond tail broadening, it is necessary to introduce a fourth component with a binding energy of about 289.5 eV. This binding energy domain may correspond to COOR functions.

The second contribution (C—N bond), which has strongly increased after doping, can also correspond to C—I bonds. It can be seen that it is the main contribution in PCZS(I), while it stays smaller than the C—C component in the case of polymers synthezized from carbazol thin films.

Additional information concerning the oxidation process can be obtained from the O1s peak [Fig. 4(a) and (b)]. This peak can be systematically decomposed into 2 components, as follows: the first one at 532 eV is attributed to C=O but also to ClO_4^- , and the higher energy peak at about 533.5 eV corresponds to C-O-H groups. While before iodine doping, the main contribution (60 atom %) corresponds to the former component, after iodine doping, the relative intensity of the 2 peaks depends on the electrochemical process. When carbazole thin films are oxidized, the main



Figure 2 XPS spectra: N1s on (a) PCZS(I) and (b) PCZS(II) after iodine doping.



Figure 3 XPS spectra: C1s on (a) PCZS(I) and (b) PCZS(II) after iodine doping.

contribution still corresponds to the C= O/ClO_4^- component, while, in the other case, there is nearly 70 atom % of C-O-H bonds.

Before iodine doping, the decomposition of the Cl2p peak is not easy in the case of PCZS(I) because its signal is very small. The decomposition of the Cl2p peak of the other polymer shows that, as expected, the main part (70 atom %) of the chlorine is in the ClO_4^- anion. However, 2 other Cl2p doublets are also present. The one located at 200 eV corresponds to neutral chlorine, while that located at 198 eV could be assigned to Cl^- .¹³ After doping, the highest contamination of the surface induces a decrease of the Cl2p signal, but the same decomposition can be proposed.

As described before, the binding energy and the shape of the envelope of the doublet of the iodine dopant depends on the polymer (Fig. 5). In the case of the polycarbazole obtained from thin films, the binding energy is around 620 eV, and the peak is skewed towards the high energy side. In the other case, the binding energy of the I3d peak is around 622 eV, and it is skewed towards the small energies.

The decomposition of these peaks in 2 components shows that there is 1 contribution located at about 620 eV, which corresponds to I^- anions, while the other contribution located at 621.5 eV can be assigned to neutral iodine. The main information is that 70 atom % of iodine are ionic in the case of the polymer obtained from thin films, while 85% of iodine are neutral in the case of the other polymer.

ESR Measurements

No ESR signal was observed on the carbazole powder. After polymerization, a well-resolved ESR signal is systematically observed.

The ESR spectra of doped samples are shown in Figures 6(b) and 7(b). Before iodine doping, the spectra are quite different for PCZS(I) and PC-ZS(II) [Fig. 6(a) and 7(a)]. The g factor has been fitted by using the poles method integration.¹⁴ The theoretical ESR signal was computed using a Gaussian or a Lorentzian or a mixture shape. The polymer obtained from carbazole thin films corresponds to 1 isotropic g with $g_x = g_y = g_z = 1.9998$ and Hpp = 2.8 G (Table IV). The radicals can be attributed to the nitrogen of the carbazol units or to a carbon.

The shape of the signal obtained with PCZS(I) is more complex. A good accordance between experimental and theoretical curves can be obtained only by using 2 isotropic g (Table IV and Fig. 8), as follows: $g_1 = 1.9990$, Δ Hpp = 3; and $g_2 = 2.000$ Δ Hpp = 8.

After iodine doping, only 1 isotropic g is necessary to obtain a good accordance between experimental and theoretical curves. Whatever the technique of polymerization used, g is slightly higher than 2 (g = 2.003), but *Hpp* is far higher in the case of polymer obtained from carbazole in solution ($\Delta Hpp \ge 13$) than in the case of the other polymer ($\Delta Hpp = 3$). It can be seen in Figure 8 that, systematically, the intensity of the signal increases after iodine doping.

DISCUSSION

The aim of this work was to compare the properties of polymers obtained electrochemically either from monomers diluted in the electrolyte or from carbazole thin films. When anhydric electrolyte and/or low oxidation voltage ($V \le 1.5$ V) were used, no polymer deposition occurs on the Sno₂ electrode. At a higher and constant voltage, thick

		C1s			N	ls				Cl2p		01s	
Sample	C C	c—N c—0—H c—I	C=0	COOR	$^+$ N	C—N	Ι		C104—	CI	CI–	C0H	C=0
After electro	s provincial s	yntheses:											
$PCZS(I)^{a}$	285°	286.5	288.2		402	400.3			208.1	200.4	198.3	533.3	532
	80	13	7		15	85			48	34	18	40	60
PCZS(II) ^b	285°	286.1	288.5		402	400			208.1	200.2	197.8	533.3	532
	79	16	Ð		15	85			72	16	12	40	60
After iodine	doping (24	¦ h at 384 K):											
PCZS(I)	285°	286.1	288	290.5	402.6	401	621.5	619.4				533.7	531.8
	33	50	13	4	25	75	87	13				66	34
PCZS(II)	285°	286	287.4	289.1	401.2	400.2	621.6	620	209.0	201		534.4	532.8
	57	32	80	က	40	60	29	71	70	30		20	80
The first I	ine in the ta	ble corresponds	to the bind	ing energy of	f the bond,	and the seco	and line to t	the relative	atomic percer	ntage.			

Table III Qualitative Analysis

^a PCZS(I) was obtained from carbazole diluted in the electrolyte. ^b PCZS(II) was obtained from carbazol thin films. ^c The binding energy of the C1s hydrocarbon bond has been taken in Beam and Briggs.¹³



Figure 4 XPS spectra: O1s on (a) PCZS(I) and (b) PCZS(II) after iodine doping.

deposition on the active electrode of polycarbazole films can be obtained. It has been already shown⁸ that polycarbazole polymers complexed with ClO_4^- ions were obtained after electrodeposition.

Although the 2 electrosynthesis techniques described above allow growth of polymers insoluble in chlorobenzene, there are some differences between the properties of the synthetized polymers, which are summarized in Table V. It can be seen that the quality of the polymers obtained from evapored thin films appears to be higher than that obtained in the same experimental conditions but from carbazole diluted in the electrolyte. However, the electrical conductivity of all the samples is quite poor just after the electrochemical synthesis. This small value may be attributed to the electrochemical oxydation conditions. Therefore, a post-doping by iodine has been carried out. The doping efficiency and the evolution of the electrical conductivity with the doping time have been regularly checked.

It can be seen in Table I that a saturation effect of the iodine doping process occurs after 8 weeks.



Figure 5 XPS spectra: I3d on (a) PCZS(I) and (b) PCZS(II).

In the last column, results correspond to samples doped only during 24 h, but at a temperature of 383 K. It can be seen that the electrical conductivity value is similar to that obtained after saturation of the doping at room temperature. In fact, whatever the measurement technique used



Figure 6 ESR spectra on PCZS(I): (a) before iodine doping; (b) after iodine doping.



Figure 7 ESR spectra on PCZS(II): (a) before iodine doping; (b) after iodine doping.

was, the same results have been systematically obtained after saturation of the iodine doping process at room temperature or after doping at 383 K for 24 h. This result is in good accordance with the work of Jenekhe et al.,¹⁵ who have shown that doping polycarbazole in liquid iodine is a very efficient way to optimize the polymer properties. An improvement of the doping efficacity has been tested by using a higher doping temperature, but there was polymer degradation with iodine attack of the polymer as shown by IR spectroscopy.

Much information about the properties of the polymers can be deduced from the evolution of the XPS spectra after iodine doping.

The more striking difference between the 2 families of polymers concerns the chemical state

Table IV ESR Resu

Sample	g	ΔHpp (G)	Ns (spins mol ⁻¹ g ⁻¹)		
After electro	chemical sy	nthesis:			
PCZS(I) ^a	1.9990	3	$2.7 10^{20}$		
	2.0000	8	$2.9 10^{20}$		
PCZS(1I) ^b	1.9998	2.8	7.2. 10^{20}		
After iodine	doping (2 n	nonths at 3	300K):		
PCZS(I)	2.0030	13	$3.4 10^{21}$		
PCZS(1I)	2.0020	11	$8.4 10^{21}$		
After iodine doping (24 h at 838 K):					
PCZS(I)	2.0070	15.7	$1.6 \ 10^{21}$		
PCZS(1I)	2.0030	3	$9.7 10^{21}$		

 $^{\rm a}$ PCZS(I) was obtained from carbazole diluted in the electrolyte.

 $\overset{\,\,{}_{\mathbf{b}}}{\mathbf{PCZS}}(\mathbf{II})$ was obtained from carbazole thin films.



Figure 8 ESR spectra on PCZS(I): experimental and theoretical curves before iodine doping.

of the iodine dopant. If the same atomic percentage of iodine is present in all the polymers, 70 atom % is active as dopant in the polymers obtained from carbazole thin films, while only 13 atom % is active is the other polymers. This is in good accordance with the N1s peak decomposition.

As there is only a C—N contribution in carbazole, the N+ present after polymerization is attributed to radical formation, with the g value measured by ESR being in good agreement with this hypothesis.

After electrochemical synthesis, the N⁺ percentage is nearly the same (about 15 atom %), which is in good agreement with the spin density. It should be noted that in the case of the polymer obtained from carbazole in solution in the electrolyte, there are 2 contributions to the spin density. As the sum of these contributions is not very different from the spin density present in the other polymer, the extension of 1 contribution is quite large. This corresponds to more localized carriers, which justify the smaller conductivity of these polymers (Table V). After iodine doping, the N^+ atomic percentage is 40 in polymers, with 71 atom % of ionic iodine, while it is only 25 atom % in the other case. This puts in evidence a correlation between the N^+ concentration and the I^{-3} percentage. It can be seen in Table IV that the spin density follows the same evolution.

The efficiency of the iodine doping is correlated with the C1s peak decomposition. It has been shown that the energy domain of the C—I bonds is around 286-286.5 eV.¹³ The second contribu-

Measurement	Sample Obtained from Carbazole Monomere Diluted in the Electrolyte	Sample Obtained from Carbazole Deposited by Evaporation on the ${\rm SnO_2}$ Electrode
Thermal gravimetric Analysis		
weight loss at 573 K (%)	20%	15%
XPS: Chlorine relative		
percentage	5%	2%
Spin density obtained by ESR		
$(\text{spins mol}^{-1} \text{ g}^{-1})$	2.710^{20}	$7.2 10^{20}$
Room Temperature		
Conductivity $(\Omega^{-1} \text{ cm}^{-1})$	2.510^{-12}	$2 \ 10^{-11}$

Table V Main Differences Between the Properties of Electrochemically Polymerized Polycarbazole

tion of the C1s peak can be attributed not only to C—N and C—O—H bonds but also to C—I. This is in good agreement with the large increase of this contribution in the case of the polymers in which about 85% of iodine is covalent. In the other case, in which only 29 atom % of iodine is covalent, the increase of the contribution is not so large. It has already shown¹⁶ that during doping polymer with iodine, not only the donor–acceptor action between polymer and iodine is important, but also the linking with iodine in polymer chains in the disordered regions of the polymer. This corroborates the higher density of C—I bonds in PCZS(I), which are the most disordered polymers.

It should be noted that, as shown by quantitative analysis, the atomic percentage of oxygen has increased after doping and, probably, the C—O—H contribution has also increased. This is corroborated by the O1s peak decomposition. In the case of the polymer obtained from carbazole diluted in the electrolyte, the main contribution of the O1s peak corresponds to the C—O—H bonds. Therefore, the increase of this contribution with doping and the new C—I bonds justify that the second component of the C1s peak becomes the main contribution in these polymers. In the case of the other polymers, the main component of the O1s peak should be attributed to the other contribution. However, since absolute intensity of the C=O and COOR components are not very different in the 2 polymers, the main part of this contribution should be attributed to adsorbed oxygen, the polymers being kept in room atmosphere.

Electrical conductivity, ESR, and XPS measurements lead to the following comments. First, the iodine doping efficiency is better in the case of the polymer obtained from carbazole thin films. This result is a confirmation of an earlier study (Table V),¹¹ in which it has been shown that the polymerization efficiency of these polymers was better than that of the other polymer obtained from carbazole in solution in the electrolyte. The better polymerization induces longer chain formation, which facilitates the formation of the complex salt iodine-polymer. In the case of the polymers obtained from carbazole in solution, the chain length domain is very broad with a large concentration of small chain lengths where carriers are localized. Therefore, not only the radical concentration will be smaller, but the chain ends concentration is quite large, which facilitates the C-I, the C-O-H, and, also, the C=O chain, terminating group formation.¹³ The presence of only 1 g after doping of the polymers obtained from carbazole diluted in the solution should correspond to the reaction of quite localized radicals with iodine, which induces C-I bonds formation.

CONCLUSION

It has been shown that iodine doping of electrochemically synthetized polycarbazoles increases the electrical conductivity. There is a correlation between conductivity, ESR, and XPS results. The main parameter to increase the conductivity is not the percentage of iodine present in the polymer after doping but the percentage of ionic iodine.

It is shown that iodine ionic percentage is far higher in the case of the polymer synthesized from carbazole thin films. This fact is explained by the longer chains of this polymer. All the results confirm that the efficiency of polymerization is higher when the polymer is obtained from carbazole thin films than when it is obtained from carbazole in solution in the electrolyte.

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