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Synthesis and polymerization of 2-(β-N-3'-Halogencarbazolylethyl)-2-oxazolines

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SUMMARY

The synthesis of three novel oxazoline monomers,all of which contain 3-halogen substituted carbazolyl groups [i.e., 2-(β-N-3' chlorocarbazolylethyl) -2-oxazoline ,2-(β-N-3' bromocarbazolylethyl) -2-oxazoline and 2-(β-N-3' iodocarbazolylethyl) - 2 -oxazoline]and their polymerization is described.

INTRODUCTION

In some previous papers,the possibility of spontaneous polymerization and copolymerization of 2-substituted 2-oxazolines,for instance 2-(β -N-carbazolylethyl) - 2 -oxazoline ,with micromolecular acceptors was reported (1-3).Initiation takes place through a charge transfer complex (CTC) intermediate formed between n-type donor oxazoline ring and the π acceptor (i.e. tetracyanoethylene,7.7.8.8-tetracyanoquinodimethane and 2.4.7-trinitrofluorenone) and the polymerization proceeds by ring opening and isomerization of the oxazoline nucleus. By this method intramolecular and intermolecular CTC are obtained.

It is known that by introducing different halogens in 3.6 positions of carbazole ring of polyvinylcarbazole or other type of carbazole containing polymers,the polymer ionization potential is changed (4,5), as well as the electrical properties of the corresponding CTC.For these reasons,in the present paper the synthesis of three new 2-(β -N-carbazolylethyl) - 2 -oxazolines containing 3-halogen carbazolyl groups and preliminary data on their initiated homopolymerization are reported.

EXPERIMENTAL

The elemental analysis results of synthesized compounds are in agreement with theoretical values,therefore they will not be presented. The IR (KBr pellets) and ^{1}H-NMR spectra were recorded using Perkin Elmer 577 and JEOL C60HL (60MHz) spectrophotometers,respectively. Intrinsec viscosities were determined using an Ubbelhode-type viscosimeter and dimethylformamide as solvent ,at 25 ° C.

All the monomers were synthesized according to the reactions presented in Scheme 1. 3-Halogen carbazole derivatives (Ia,Ib and Ic) were obtained from carbazole by halogenation with SO_2Cl_2 in $CHCl_3$ for 3-chlorocarbazole (Ia) synthesis (6),Br_2 in CS_2 for 3-bromocarbazole (Ib) synthesis (7) and with KIO_3-KI in glacial acetic acid for 3-iodocarbazole (Ic) synthesis (8).

<u>2-(N-3'-chlorocarbazolyl) propionitrile (IIa)</u> was synthesized through the cyanoethylation of Ia (20.15 g ,0.1 mole) with acrylonitrile in the presence of 1 ml benzyltrimethyl ammonium hydroxide (Triton B) (40 % methanol solution) as catalyst.The excess acrylonitrile was

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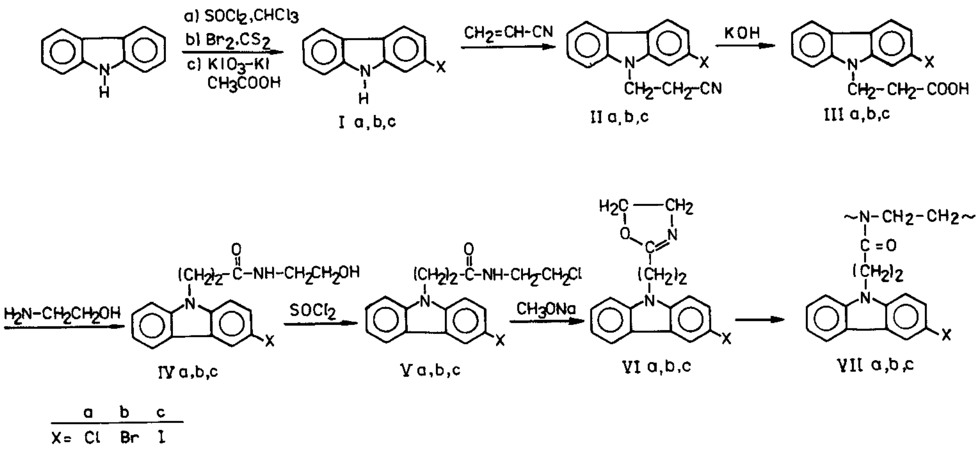

Scheme 1: Synthesis of poly [N-((N-3' halogencarbazolyl)-3-propionyl) ethylenimines]

distilled off under vacuum and a solid product was recrystallized from acetone. Yield = 66.7 % ,m.p. 159-160 °C.
IR (KBr) : 2240 cm^{-1} (νC≡N) ,720 and 745 cm^{-1} (νCH aromatic , 1.2-disubstituted benzene ring) and 800 cm^{-1} (νCH aromatic ,1.2.4-tri substituted benzene ring).
^{1}H-NMR $(CD_3)_2CO$, δ,ppm: 2.82 (2H,t,CH_2CN) , 4.56 (2H,t,-N-CH_2-) , 6.9-7.6 (m,5H ,the 1,2,6,7 and 8 protons in carbazole ring) and 7.8 - 8.1 (m ,2H ,the 4 and 5 protons in carbazole ring).

2-(N-3' chlorocarbazolyl) propionic acid (IIIa)

It was obtained by hydrolysis of IIa. 20 g (0.078 mole) IIa ,300 ml methanol ,40 g KOH and 100 ml water were stirred at reflux temperature until the reaction mixture was dissolved and the heating was continued for 5 hours . The solution was poured in ice-water and acidified with HCl 37 %. The white precipitate was filtered and purified by redissolution in alcaline solution and precipitation with HCl. The solid product was filtered and dried ,yielding 18.5 g (86 %).
IR (KBr): 3020 cm^{-} (νOH) ,1700 cm^{-1} (νC=O) ,720 and 745 cm^{-1} (νCH aromatic ,1.2 -disubstituted benzene ring) and 800 cm^{-1} (νCH aromatic, 1.2.4-trisubstituted benzene ring).
^{1}H-NMR ,$(CD_3)_2CO$, δ ,ppm: 2.72 (2H,t,CH_2CO) ,4.50 (2H,t,NCH_2) , 6.9-7.6 (5H,m,aromatic protons) and 7.85 - 8.10 (2H ,m ,aromatic protons).

N-(2-hydroxyethyl) - 2 - (N-3' chlorocarbazolyl) propionylamide (IVa)

A mixture obtained from 20 g (0.073 mole) IIIa and 300 ml monoethanolamine was refluxed for 6 hours. The excess monoethanolamine was distilled off under vacuum and the remained solid product was recrystallized from $CHCl_3$ yielding 17 g IVa (73.4 %).
IR (KBr): 3180 cm^{-1} (νNH) ,1630 cm^{-1}(amide I) ,1540 cm^{-1}(amide II) , 720 and 745 cm^{-1}(νCH aromatic ,1.2-disubstituted benzene ring) and 800 cm^{-1}(νCH aromatic ,1.2.4-trisubstituted benzene ring).

N-(2-chloroethyl) - 2 -(N-3'chlorocarbazolyl)propionylamide (Va)

To a stirred mixture of 6 g (0.019 mole) IVa and 150 ml CH_2Cl_2 (cooled with ice-water mixture), 1.5 ml $SOCl_2$ were added dropwise during 5 minutes.Then,the resulting solution was stirred and refluxed for 2 hours; solvent was then removed under vacuum. The solid product was passed without other purification to the last step of synthesis.

2-(β-N-3' chlorocarbazolylethyl) - 2 -oxazoline (VIIa)

The solution of Va in 100 ml methanol was added to a refluxing solution of CH_3ONa (obtained from 1.5 g Na and 200 ml absolute methanol) and the reaction mixture was stirred at reflux temperature for 2 hours and at room temperature for 5 hours. The oxazoline monomer was precipitated by addition of water. The precipitate was filtered, dried and recrystallized from methanol. Yield = 3 g (53.6 % based on IVa).

Monomers VIb and VIc and their intermediate compounds were synthesized similarly. Melting temperature and ^{1}H-NMR data of the monomers are given in Table 1.

Poly [N-((N-3' chlorocarbazolyl) -3-propionyl) ethylenimine] (VIIa)

The polymerization of oxazoline monomers was carried out in bulk using ethylene glycol ditosylate initiator (9). Monomer and ethylene glycol ditosylate initiator (1 % mole) were charged into a polymerization ampoule which was placed at 165 °C. After 1.5 hours the polymerization mass was dissolved in dimethylformamide and the polymer was precipitated with ethylic ether. The results of polymerization experiments are given in Table 2.

Table 1: Melting temperatures and chemical shifts of the monomers

Monomer	Yield (%)	Mp (°C)	Chemical shift , δ(ppm)
VIa	53.6	133-134	2.4-2.9 ($-CH_2-C-$),3.5-4.2 ($-N-CH_2-CH_2-O-$),4.3-4.8 ($-CH_2-N-$) ,6.9-7.5 ($H_{1,2,6,7,8}$) ,7.7-8.1 ($H_{4,5}$)
VIb	62.3	135	2.6-3.0 ($-CH_2-C-$) ,3.5 -4.4 ($-N-CH_2-CH_2-O-$),4.5-4.8 ($-CH_2-N-$),7.0-7.8 ($H_{1,2,6,7,8}$) , 7.85-8.5 ($H_{4,5}$)
VIc	58.2	115	2.6-3.5 ($-CH_2-C-$) ,3.6-4.4 ($-N-CH_2-CH_2-O-$),4.5 -5.0 ($-CH_2-N-$) ,7.1-7.8 ($H_{1,2,6,7,8}$) 8.0-8.4 ($H_{4,5}$)

Table 2: Cationic homopolymerization of monomers

Monomer	Conversion (%)	$[\eta i]$
VIa	57.3	0.23
VIb	87.6	0.40
VIc	89.3	0.39

RESULTS AND DISCUSSION

The synthesis and characterization of poly(N-acylethylenimines) containing carbazole or 3.6-disubstituted carbazole (metoxy and hydroxy substituents) as side groups from properly substituted oxazoline monomers has been reported (9-12). For the preparation of 3-halogen carbazole containing oxazolines (VIa,VIb and VIc) a similar route as for 2-(β-N-carbazolylethyl) -2-oxazoline was applied (10) (as outlined in Scheme 1). Their cationic ring opening isomerization polymerization was carried out in bulk,above their melting temperature,using ethylene glycol ditosylate as initiator (Table 2). The polymers are white powders,soluble in polar solvents (DMSO,DMF and THF) and insoluble in ethylic ether,petroleum ether,benzene or methanol. All prepared polymers showed the same characteristic IR absorption bands as the respective monomers except that the oxazoline ring absorptions (νCH oxazoline ring) were absent. ^{1}H-NMR spectra (DMSO-d_6 ,80°C) confirm the poly (N-acylethylenimine) type structure for the polymers. The aromatic protons of the carbazole ring appear as two signals centered at 7.3 ppm (protons from 1.2.6.7 and 8 position) and 8.0 ppm (protons from 4 and 5 position),their integral area ratio being 5:2. This means that electronic interactions between neighboring carbazolyl groups on the chain are lower than those in poly(N-vinylcarbazole). Polymer solubility decreases in the order $H < Cl < Br < I$ and the attempts to accurately estimate the influence of the halogen nature on the ionization potential of the carbazole group failed.

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