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New 3,6-Dihalogencarbazole-Containing Monomers and Polymers

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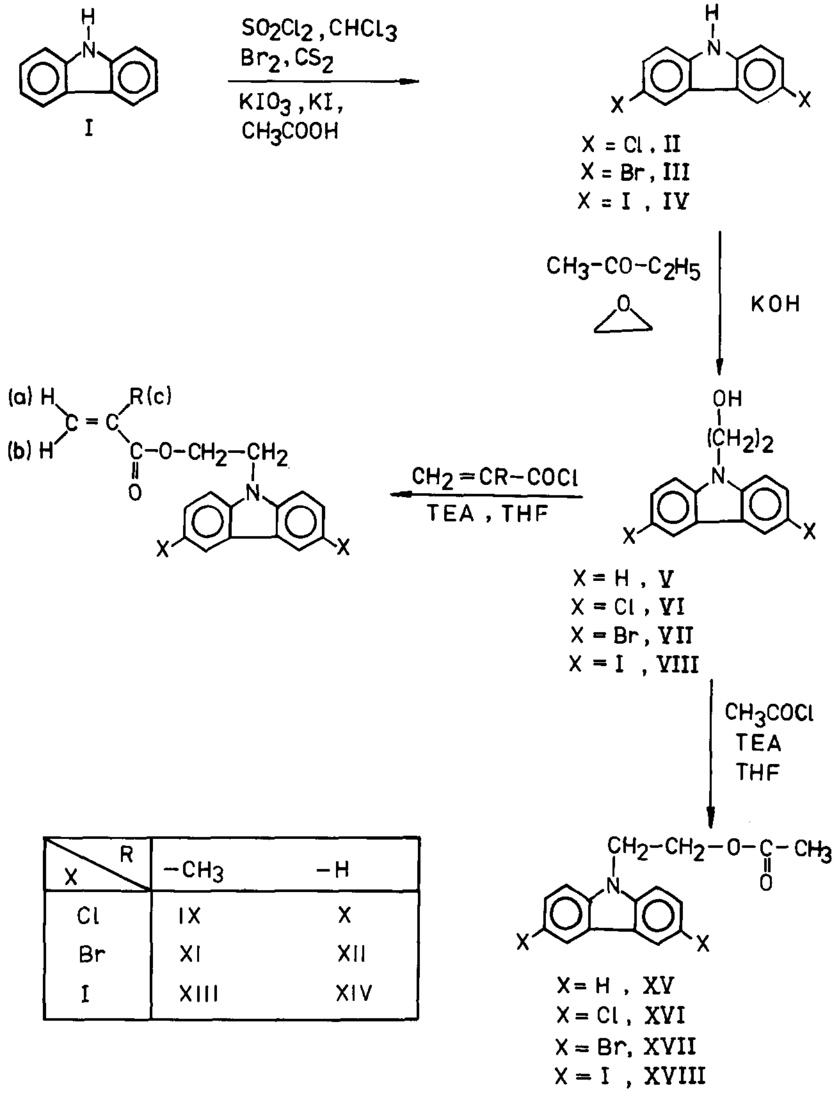
Summary

The synthesis of six novel electrono-donor monomers containing 3,6-dihalogencarbazole [N-(2-hydroxyethyl)-3,6-dichlorocarbazolyl methacrylate, N-(2-hydroxyethyl)-3,6-dichlorocarbazolyl acrylate, N-(2-hydroxyethyl)-3,6-dibromocarbazolyl methacrylate, N-(2-hydroxyethyl)-3,6-dibromocarbazolyl acrylate, N-(2-hydroxyethyl)-3,6-diiodocarbazolyl methacrylate and N-(2-hydroxyethyl)-3,6-diiodocarbazolyl acrylate], of the corresponding polymers and of the monomeric models is described. The ionization potentials values of the monomeric models were determined.

Introduction

In the last time a great attention has been given to carbazole-containing polymers, due to their electrical and photoelectrical properties. The constantly increasing interest in this polymer class started particularly when the charge transfer complex (CTC) poly(N-vinylcarbazole) (PVK) - 2,4,7-trinitro-9-fluorenone was used as a photoconductor in electrophotography (1). A review on the most recent literature data on synthesis and properties of PVK and of other vinylcarbazole polymers was recently published (2). The most important drawbacks of PVK are the high glass-transition temperature value (227°C) and the brittleness. The decrease of both glass-transition temperature and brittleness of carbazole-containing polymers can be realized by the increase of the distance between the pendant carbazolyl group and the polymer main chain. These are the reasons, in the last time an important number of new carbazole-containing monomers and polymers were published (3-7).

In two previous papers we showed that by introducing of different halogenes in 3,6 positions of PVK, the polymer ionization potential is changed (8) and, as a consequence, the electrical properties of the corresponding CTC (9). In the same time, the donor-monomer ionization potential value (I_D), strongly influences the intramolecular CTC copolymers microstruc-



X \ R	$-CH_3$	$-H$
Cl	IX	X
Br	XI	XII
I	XIII	XIV

Scheme 1.

ture which are obtained by copolymerization of electrono-donor electrono-acceptor monomer pairs (6,7,10, 11). For these reasons, in the present paper we will present the synthesis of six new 3,6-dihalogencarbazole-containing monomers, preliminary data on their polymerization and on their ionization potentials, and the synthesis of their monomeric models [N-(2-hydroxyethyl)-carbazolyl acetate and N-(2-hydroxyethyl) -3,6-dihalogencarbazolyl acetates] . The synthesis, polymerization and copolymerization of N-(2-hydroxyethyl) carbazolyl methacrylate and of N-(2-hydroxyethyl) carbazolyl acrylate were already reported (6, 7,11).

Experimental

The elemental analysis results of synthesized compounds are in agreement with theoretical values, therefore they will not be presented. The ^{1}H-NMR spectral data are given in Table-1. All the monomers and monomeric models were synthesized according to the reactions presented in Scheme-1. Some literature methods were checked for carbazole halogenation. Between them the most suitable were found to be with SO_2Cl_2 in $CHCl_3$ for 3,6-dichlorocarbazole (II) synthesis m.p. 205-206°C (lit. 12, 204-205°C), Br_2 in CS_2 for 3,6-dibromocarbazole (III) synthesis m.p. 212-213°C (lit. 13, 211-213°C) and with KIO_3-KI in glacial CH_3COOH for 3,6-diiodocarbazole (IV) synthesis m.p. 215-216°C (lit. 14, 202-204°C). The synthesis of N-(2-hydroxyethyl) carbazole (V) was already presented (6). N-(2-hydroxyethyl)-3,6-dihalogencarbazoles were synthesized by ethylene oxide addition to the corresponding 3,6-dihalogencarbazole in the presence of KOH and acetone or methyl ethyl cetone solution, according to a published method (12). A typical example is given below.

<u>N-(2-hydroxyethyl)-3,6-diiodocarbazole (VIII)</u>
To a mixture of 36g (0.086 mole) of IV, 200 ml of methyl ethyl cetone and 4.8g of KOH maintained at 0°C, 5 ml of ethylene oxide was added. The solution was stirred for 1 hr at 45-50°C and then poured slowly into an ice-water mixture. After the mixture's pH was changed to neutrality (with HCl), the precipitate was filtered, washed with water and dried. Recrystallization from acetone/methanol (1/2,V/V) produced 29.8g (75%) of white crystals. m.p. 180-181°C.
<u>N-(2-hydroxyethyl)-3,6-dichlorocarbazole (VI)</u>, m.p. 162-164°C and <u>N-(2-hydroxyethyl)-3,6-dibromocarbazole (VII)</u>, m.p. 170-171°C were recrystallized from cyclohexane/benzene (1/1,V/V) and acetone/methanol (1/2,V/V) respectively.
The monomers (IX-XIV) and the monomeric models (XV-XVIII) were synthesized by reaction of the N-(2-hydroxyethyl) carbazole derivatives with the corresponding acid chloride in tetrahydrofuran (THF) solution

Table 1

Chemical shifts (δ, ppm) and coupling constants (J, Hz)* of carbazole derivatives

Compound	Solvent	Ethyl group	Aromatic group $H_{1,8}$	$H_{2,7}$	$H_{4,5}$	Vinyl group H_a	H_b	H_c	Other groups - CH_3	$-COCH_3$
II	$(CD_3)_2CO$	-		7.58	8.30		-			-
III	"	-		7.58	8.38		-			-
IV	"	-	7.32	7.54	8.43		-			-
VI	"	3.97 4.50	7.71	7.49	8.24		-			-
VII	"	3.97 4.50		7.59	8.35		-			-
VIII	"	3.97 4.50	7.49	7.78	8.53		-			-
IX	$CDCl_3$	4.42		7.25	7.88	5.40	5.81	-	1.82	-
X	"	4.42		7.25	7.88		5.7 - 6.5			-
XI	"	4.42	7.30	7.60	7.95	5.51	5.91	-	1.82	-
XII	"	4.42	7.30	7.60	7.95		5.5 - 6.1			-
XIII	"	4.42	7.10	7.56	8.10	5.41	5.80	-	1.78	-
XIV	"	4.42	7.10	7.56	8.10		5.6-6.2			-
XV	"	4.34	7.0-7.6		8.02		-		-	1.83
XVI	"	4.40	7.18-7.50		7.89		-		-	1.93
XVII	"	4.30	7.17	7.50	7.97		-		-	1.90
XVIII	"	4.30	7.05	7.64	8.15		-		-	1.87

(*) $J_{-CH_2CH_2-} = 6$; $J_{orto} = 8$; $J_{meta} = 2.5$.

in the presence of triethylamine (TEA), as follows.

N-(2-hydroxyethyl)-3,6-dichlorocarbazolyl methacrylate (IX)

A mixture of 14.21g (0.136 mole) of methacryloyl chloride (MC) and 20 ml of THF was added dropwise (during 20 min) under vigorous stirring to a solution of 25g (0.089 mole) of VI, 19 ml (0.136 mole) of TEA and 150 ml of THF (cooled at 8°C). The mixture was stirred for 1 hr at 8°C and for 8 hr at room temperature, and then poured into water. The precipitate was filtered, washed with water to neutrality and dried. The product was two times recrystallized from 1,2-dichloroethane/n-octane (1/1,V/V) mixture to provide 18.9g (61%) of white crystals. m.p. 154-156°C. IR (KBr): 1700 (ν C=O), 1610 (C=C), 889 (ν=CH out of plane), 790 cm^{-1} (1,2,4-trisubstituted benzene).

N-(2-hydroxyethyl)-3,6-dichlorocarbazolyl acrylate (X)

It was synthesized by the general method proposed for IX, except that instead of MC, acryloyl chloride (AC) was used. Starting with 30g (0.107 mole) of VI, 25.2 ml (0.180 mole) TEA, 16.2g (0.180 mole) AC and 150 ml THF, after two recrystallization from 1,2-dichloroethane/n-octane (1/1,V/V) mixture, 24g (43.4%) of white crystals were obtained. m.p. 130-131°C. IR(KBr):1710 (ν C=O), 1620 (ν C=C), 1400 (ν =CH in plane), 976 (ν =CH out of plane I), 880 (ν =CH out of plane II), 790 cm^{-1} (1,2,4-trisubstituted benzene).

N-(2-hydroxyethyl)-3,6-dibromocarbazolyl methacrylate (XI)

Product XI was synthesized by the same method used for product IX, starting with 43.2g (0.117 mole) VII, 18.81g (0.18 mole) MC, 25.11 ml (0.18 mole) TEA and 150 ml THF. After two recrystallization from 1,2-dichloroethane/n-octane (1/1,V/V) mixture, 42g (82.0%) of white crystals were obtained. m.p. 165-167°C. IR (KBr): 1700 (ν C=O), 1610 (ν C=C), 885 (ν =CH out of plane), 790 cm^{-1}(1,2,4-trisubstituted benzene).

N-(2-hydroxyethyl)-3,6-dibromocarbazolyl acrylate (XII)

Product XII was prepared by the same method used for product X using 45g (0.138 mole) VII, 16.6g (0.183 mole) AC, 25.25 ml (0.183 mole) TEA and 150 ml THF. Two recrystallizations from 1,2-dichloroethane/n-octane (1/1,V/V) mixture afforded 40.9g (70%) of white crystals. m.p. 146-147°C. IR(KBr): 1710 (ν C=O), 1615 (ν C=C), 1400 (ν =CH in plane), 978 (ν =CH out of plane I), 905 (ν =CH out of plane II), 790 cm^{-1}(1,2,4-trisubstituted benzene).

N-(2-hydroxyethyl)3,6-diiodocarbazolyl methacrylate (XIII)

By using the same method as for compound IX synthesis, from 14.5g (0.0313 mole) VIII, 4.9g (0.047 mole) MC, 6.6 ml (0.047 mole) TEA and 100 ml THF, after two recrystallizations from 1,2- dichloroethane/n-octane (1/1,V/V) mixture, 9.5g (57.5%) of white crystals were obtained. m.p. 183-184°C. IR(KBr): 1700 (ν C=O), 1619 (ν C=C), 888 (ν =CH out of plane), 800 cm^{-1} (1,2,4-trisubstituted benzene).

N-(2-hydroxyethyl)-3,6-diiodocarbazolyl acrylate (XIV)

Product XIV was synthesized by the method used for compound XII, starting with 29g (0.063 mole) VIII, 8.5g (0.0'% mole) AC, 13.2 ml (0.094 mole) TEA and 150 ml THF. The product was two times recrystallized from 1,2-dichloroethane/n-octane (1/1,V/V) mixture to provide 15.2 g (46.03%) of white crystals. m.p. 156-157°C. IR(KBr): 1700 (ν C=O), 1605 (ν C=C), 1400 (ν =CH in plane), 976 (ν =CH out of plane I), 880 (ν =CH out of plane II), 790 cm^{-1} (1,2,4-trisubstituted benzene).

N-(2-hydroxyethyl) carbazolyl acetate (XV)

To a mixture of 7.5g (0.0355 mole) V, 6.5 ml (0.047 mole) of TEA and 75 ml of THF maintained at room temperature, 3.4 ml (0.047 mole) of acetyl chloride solution in 20 ml of THF were added (during 10 min) under vigorous stirring. The mixture was stirred for 8 hr at room temperature and then poured into water. The precipitate was filtered, washed with water to neutrality and dried. The product was recrystallized from ethanol to afford 5g (55.6%) of white crystals. m.p. 44-45°C. IR(KBr): 1715 (ν C=O), 748 and 720 cm^{-1} (carbazolyl group).

N-(2-hydroxyethyl)-3,6-dichlorocarbazolyl acetate (XVI)

By using the same method as for synthesis of product XV, from 3.5g (0.0125 mole) VI, 2.61 ml (0.019 mole) TEA, 1.33 ml (0.019 mole) acetyl chloride and 50 ml THF, after one recrystallization from 1,2-dichloroethane/n-octane (1/1,V/V) mixture and one from ethanol 2.4g (60%) of white crystals were obtained. m.p. 124-125°C. IR(KBr): 1725 (ν C=O), 795 cm^{-1}(1,2,4-trisubstituted benzene).

N-(2-hydroxyethyl)-3,6-dibromocarbazolyl acetate (XVII)

Starting with 6g (0.0163 mole) VII, 3.4 ml (0.0244 mole) TEA, 1.8 ml (0.0244 mole) acetyl chloride and 50 ml THF, 5.04g (75.5%) of white crystals were obtained using the same procedure as for product XVI. m.p. 136-139°C. IR(KBr): 1725 (ν C=O), 800 cm^{-1}(1,2,4-trisubstituted benzene).

N-(2-hydroxyethyl)-3,6-diiodocarbazolyl acetate (XVIII)

It was synthesized in the same manner as product XV. 7.79g (50.0%) of white crystals were obtained from 14.5g(0.0313 mole) VIII, 6.55 ml (0.047 mole) TEA, 3.4 ml (0.047 mole) acryloyl chloride and 100 ml THF. m.p. 153-154°C. IR(KBr): 1720 (ν C=O), 800 cm^{-1}(1,2,4-trisubstituted benzene).

Polymerization of monomers

All monomers synthesized were subjected to a free radical solution polymerization (solvent THF, monomer concentration 5%), which consists of 1% AIBN, based on the weight of monomer as initiator, a sealed ampoule and air-free conditions. After 26 hr of polymerization at 60°C, the polymers were separated by precipitation with acetone (polymethacrylates) or with methanol (polyacrylates). Intrinsic viscosities were obtained from THF solutions at 25°C (Table 2).

Table 2
Radical Polymerization of Monomers

monomer	conversion (%)	[η] (dl/g)
IX	89.2	0.08
X	84.5	0.06
XI	90.0	0.09
XII	85.3	0.07
XIII	85.4	0.05
XIV	65.7	0.03

Ionization potential values of the model compounds

The ionization potential values (I_p) of model compounds (XV-XVIII) were calculated from the absorption maxima of the CTC with TCNQ (solution in $CHCl_3$), by using the following equation:

$$h\nu_{CT} = (I_p - C_1) + C_2/(I_p - C_1)$$

where C_1 and C_2 are constants for a given acceptor. Their values for TCNQ (15) are as follows: C_1=6.10 ± 0.09 and C_2=0.25 ± 0.09. The donor concentrations were in all cases 0.5×10^{-1}mole/l and of TCNQ was 3.0×10^{-2}mole/l. The values of the first (I_{p1}) and the second (I_{p2}) ionization potentials corresponding to the transition from the highest and the second highest occupied molecular orbitals of the donor to the lowest empty molecular orbital of the acceptor, are presented in Table-3.

Table 3
The absorption maxima of the CTC with TCNQ, and the ionization potentials of the donors

Donor	λ_1	λ_2	$h\nu_1$	$h\nu_2$	I_{p1}	I_{p2}
	(nm)		(eV)		(eV)	
VI	710	550	1.75	2.26	7.69	8.24
VII	712	552	1.74	2.25	7.68	8.23
VIII	745	572	1.67	2.17	7.61	8.15
V	760	602	1.63	2.06	7.56	8.03

Discussions

Radical polymerization of monomers produced white polymers of low molecular weight (Table 2). All polymers prepared showed the same characteristic IR absorption bands as the respective monomers, except that the vinyl absorptions were absent. All polymers were soluble in THF, DMF, DMSO. The polyacrylates are also soluble in $CHCl_3$. ^1H-NMR spectra of these polymers do not present shielding effects for the aromatic protons of the carbazolyl groups, as in the cases of

PVK, poly(N-ethyl-2-vinylcarbazole) and poly(N-ethyl-3-vinylcarbazole) (2), which means that electronic interactions between neighboring carbazolyl groups on the chain are lower than in the vinylcarbazole polymers. The ionization potential values of model compounds are in the same succession as in the case of the PVK, its 3,6-dihalogen derivatives and of their monomeric models, i.e., $I_{pV} < I_{pVIII} < I_{pVII} < I_{pVI}$. As was already shown by us and by other authors (8,16,17) in the cases of macromolecular CTC the dominant factor of the "polymer effect" is the steric hindrance (which affects the equilibrium constants of the CTC and the CTC configuration) but not the electron-donating character of the polymer i.e., the ionization potential of the polymer. As a consequence, we believe that the ionization potential values of the polymers must be the same with that of the monomeric models. Detailed results on the polymerization of these monomers, on the polymeric CTC and on the physical properties of the polymers will be published in the near future.

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