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# New 3-Halogencarbazole – Containing Monomers and Polymers

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## SUMMARY

The synthesis of six novel electrono-donor monomers containing 3-halogencarbazole [N-(2-hydroxyethyl)-3-chlorocarbazolyl methacrylate, N-(2-hydroxyethyl)-3-chlorocarbazolyl acrylate, N-(2-hydroxyethyl)-3-bromocarbazolyl methacrylate, N-(2-hydroxyethyl)-3-bromocarbazolyl acrylate, N-(2-hydroxyethyl)-3-iodocarbazolyl methacrylate and N-(2-hydroxyethyl)-3-iodocarbazolyl acrylate], of the corresponding polymers and monomeric models is described. Polymers thermal properties are presented.

## 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 (3-10). In some previous papers we showed that by introducing of different halogenes in 3,6 positions of PVK or other type of carbazole containing polymers, the polymer ionization potential is changed and, as a consequence, the electrical properties of the corresponding CTC (8, 11, 12).

In the same time, the donor-monomer ionization potential value ($I_D$), strongly influence the microstructure of intramolecular CTC copolymer obtained by copolymerization of electrono-donor electrono-acceptor monomer pairs (13, 14). For these reasons, in the present paper will be presented the synthesis of six new 3-halogencarbazole-containing monomers, preliminary data on their polymerization and the synthesis of their monomeric models. The thermal stability of the obtained polymers

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and the relationship between structure and Tg values will be described also.

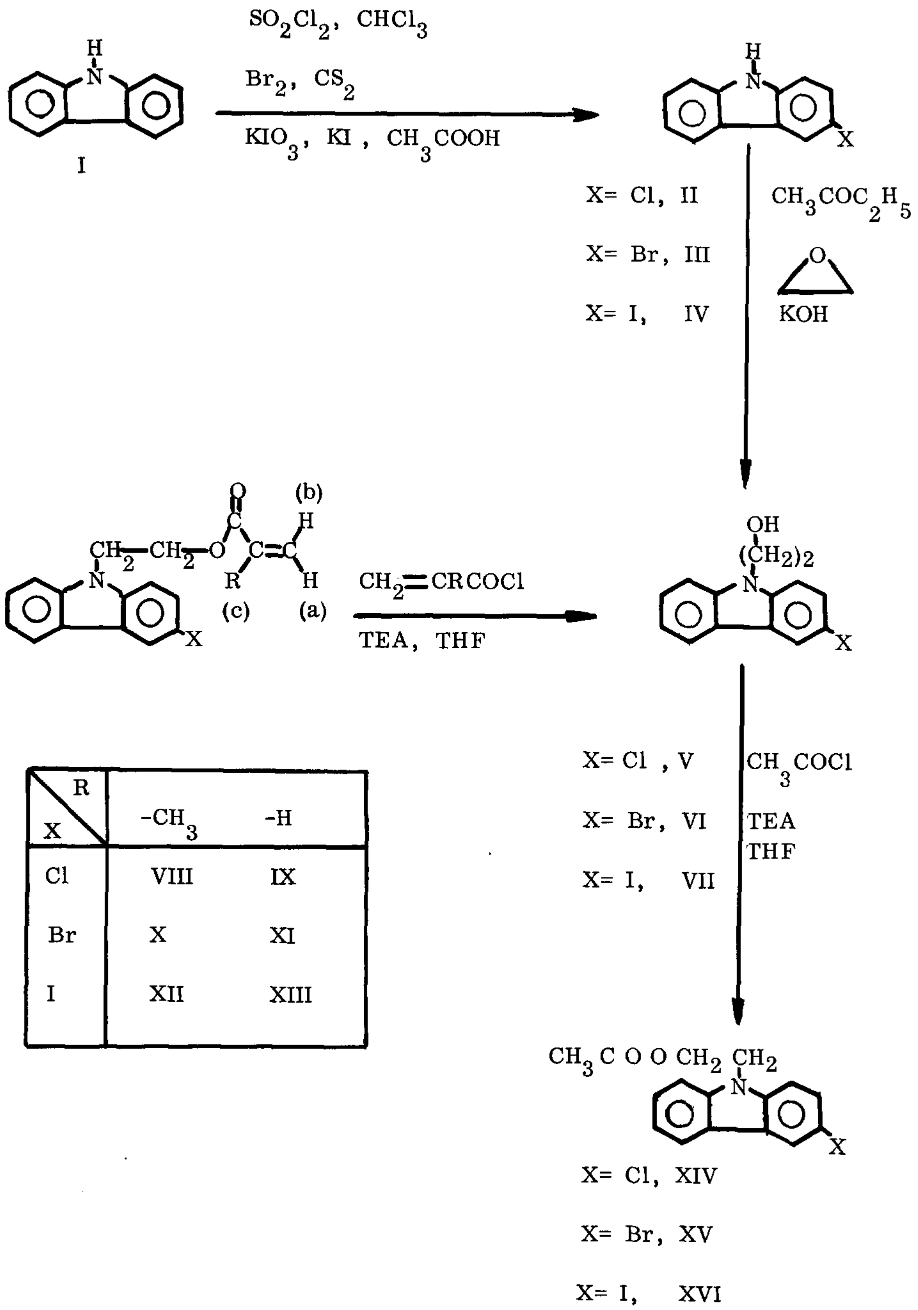
## EXPERIMENTAL

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-chlorocarbazole (II) synthesis m.p. 193-194°C (lit. 15, 192-193°C), $Br_2$ in $CS_2$ for 3-bromocarbazole (III) synthesis m.p. 194-195°C (lit. 16, 194-195°C) and with $KIO_3$ - KI in glacial acetic acid for 3-iodocarbazole (IV) synthesis m.p. 193-194°C (lit. 17, 192-194°C). N-(2-hydroxyethyl)-3-halogencarbazoles were synthesized by ethylene oxide addition to the corresponding 3-halogencarbazole in the presence of KOH and acetone or methyl ethyl cetone solution, as was reported in a previous paper (8) for 3,6-dihalogencarbazole derivatives synthesis. All these compounds were recrystallized from benzene/cyclohexane (1/1, v/v) mixtures. Their NMR spectral data are presented in Table 1. The monomers (VIII-XIII) and the monomeric models (XIV-XVI) were synthesized by reaction of the N-(2-hydroxyethyl)carbazole derivatives with the corresponding acid chloride in tetrahydrofuran (THF) solution in the presence of triethylamine (TEA), as follows.

N-(2-hydroxyethyl)-3-chlorocarbazolyl methacrylate (VIII, ClHECM) A mixture of 1.78 g (0.017 mole) of methacryloyl chloride (MC) and 10 ml of THF was added dropwise (during 10 min.) under vigorous stirring to a solution of 3.5 g (0.0142 mole) of V, 1.4 ml (0.017 mole) of TEA and 50 ml of THF (cooled at 8°C). The mixture was stirred for 1 hr. at 8°C and for 8 hrs. 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 1.8 g (40.2%) of white crystals. m.p. 115-116°C. IR (KBr): 1705 ($\nu$ C=O), 1615 ($\nu$ C=C vinylic), 1588 ($\nu$ C=C aromatic), 889 ($\nu$=CH out of plane), 790 (1,2,4-trisubstituted benzene), 738, 714 $cm^{-1}$ (1,2-disubstituted benzene).

N-(2-hydroxyethyl)-3-chlorocarbazolyl acrylate (IX, ClHECA) It was synthesized by the general method proposed for VIII except that instead of MC, acryloyl chloride (AC) was used. Starting with 3.5 g (0.0142 mole) of V, 2.4 ml (0.017 mole) TEA, 1.54 g (0.017 mole) AC and 50 ml THF, after two recrystallizations from 1,2-dichloroethane/n-octane (1/1, v/v) mixture, 0.7 g (16.2%) of white crystals were obtained. m.p. 100-101°C. IR (KBr): 1715 ($\nu$ C=O), 1610 ($\nu$ C=C vinylic), 1585 ($\nu$ C=C, aromatic), 1400 ($\nu$=CH in plane), 988 ($\nu$=CH out of plane I), 880 ($\nu$=CH out of plane II), 790 (1,2,4-trisubstituted benzene), 738, 714 $cm^{-1}$ (1,2-disubstituted benzene).

N-(2-hydroxyethyl)-3-bromocarbazolyl methacrylate (X, BrHECM) Product X was synthesized by the same method used for product VIII, starting with 3.5 g (0.0121 mole) VI, 1.52 g



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

SCHEME - 1

TABLE 1

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

| Compound, Solvent | | Ethyl Group | | Aromatic Group | | Vinyl Group | | | Other Groups | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | $H_{1,2,6,7,8}$ | $H_{4,5}$ | Ha | Hb | Hc | $-CH_3$ | $-COCH_3$ |
| II | $(CD_3)_2CO$ | - | | 6.9-7.5 | 8.0 | | - | | - | |
| III | $(CD_3)_2CO$ | - | | 7.0-7.6 | 8.08(5)8.22(4) | | - | | - | |
| IV | $(CD_3)_2CO$ | - | | 7.0-7.7 | 7.55(2)8.1(5)8.4(4) | | - | | - | |
| V | $(CD_3)_2CO$ | 3.9 | 4.4 | 6.95-7.6 | 8.0 | | - | | - | |
| VI | $(CD_3)_2CO$ | 3.9 | 4.4 | 6.9-7.55 | 8.05 | | - | | - | |
| VII | $(CD_3)_2CO$ | 3.9 | 4.4 | 6.9-7.6 | 7.95(5)8.28(4) | | - | | - | |
| VIII | $CDCl_3$ | 4.44 | | 6.9-7.4 | 7.8(4,5)5.4 | 5.4 | 5.8 | - | 1.79 | - |
| IX | $CDCl_3$ | 4.46 | | 6.9-7.4 | 7.8(4,5) | | 5.55-6.1 | | - | |
| X | $CDCl_3$ | 4.31 | | 6.9-7.5 | 7.95(4,5)5.35 | 5.35 | 5.75 | - | 1.76 | - |
| XI | $CDCl_3$ | 4.49 | | 7.0-7.7 | 8.05(5)8.19(4) | | 5.6-6.3 | | - | |
| XII | $CDCl_3$ | 4.38 | | 6.9-7.4 | 7.5(2)7.85(5)8.2(4) | 5.35 | 5.75 | - | 1.74 | - |
| XIII | $CDCl_3$ | 4.49 | | 6.9-7.4 | 7.50(2)7.85(5)8.2(4) | | 5.55-6.2 | | - | |
| XIV | $CDCl_3$ | 4.25 | | 6.9-7.3 | 7.75 | | - | | - | 1.81 |
| XV | $CDCl_3$ | 4.38 | | 6.9-7.5 | 7.75(5)7.95(4) | | - | | - | 1.91 |
| XVI | $CDCl_3$ | 4.34 | | 6.9-7.3 | 7.45(2)7.75(5)8.12(4) | | - | | - | 1.90 |

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

(0.0145 mole) MC, 2.02 ml (0.0145 mole) TEA and 60 ml THF. After two recrystallization from 1,2-dichloroethane/n-octane (1/1, v/v) mixture and one from acetone, 1.8 g (41.32%) of white crystals were obtained. m.p. 120-121°C. IR (KBr): 1700 (ν C=O), 1612 (ν C=C vinylic), 982 (ν C=C aromatic), 880 (ν =CH out of plane), 790 (1,2,4-trisubstituted benzene), 740, 715 $cm^{-1}$ (1,2-disubstituted benzene).

N-(2-hydroxyethyl)-3-bromocarbazolyl acrylate (XI, BrHECA) Product XI was prepared by the same method used for product IX using 3.5 g (0.0121 mole) VI, 1.31 g (0.0145 mole) AC, 2.022 ml (0.0145 mole) TEA and 50 ml THF. Two recrystallizations from 1,2-dichloroethane/n-octane (1/1, v/v) mixture afforded 1.12 g (27.3%) of white crystals. m.p. 110-111°C. IR (KBr): 1716 (ν C=O), 1610 (ν C-C vinylic), 1580 (ν C=0 aromatic), 1398 (ν=CH in plane), 985 (ν=CH out of plane I), 880 (ν=CH out of plane II), 790 (1,2,4-trisubstituted benzene), 740, 715 $cm^{-1}$ (1,2-disubstituted benzene).

N-(2-hydroxyethyl)-3-iodocarbazolyl methacrylate (XII, IHECM) By using the same method as for compound VIII synthesis, from 5 g (0.0148 mole) VII, 1.86 g (0.0178 mole) MC, 2.48 ml (0.0178 ml) TEA and 60 ml THF, after two recrystallizations from 1,2-dichloroethane/n-octane (1/1, v/v) mixture, 3.1 g (51.7%) of white crystals were obtained. m.p. 144-145°C. IR (KBr): 1700 (ν C=O), 1614 (ν C=C vinylic), 1583 (ν C=C aromatic), 884 (ν=CH out of plane), 791 (1,2,4-trisubstituted benzene), 740, 718 $cm^{-1}$ (1,2-disubstituted benzene).

N-(2-hydroxyethyl)-3-iodocarbazolyl acrylate (XIII, IHECA) Product XIII was synthesized by the method used for compound XI, starting with 5 g (0.0148 mole) VII, 1.61 g (0.0178 mole) AC, 2.48 ml (0.0178 mole) TEA and 60 ml THF. The product was two times recrystallized from 1,2-dichloroethane/n-octane (1/1, v/v) mixture to provide 1.32 g (23.0%) of white crystals. m.p. 126-127°C. IR (KBr): 1714 (ν C=O), 1610 (ν C=C vinylic), 1580 (ν C=C aromatic), 1398 (ν=CH in plane), 982 (ν=CH out of plane I), 880 (ν=CH out of plane II), 790 (1,2,4-trisubstituted benzene), 740, 715 $cm^{-1}$ (1,2-disubstituted benzene).

N-(2-hydroxyethyl)-3-chlorocarbazolyl acetate (XIV, ClHECAc) To a mixture of 2 g (0.00814 mole) V, 1.37 ml (0.0098 mole) TEA and 40 ml THF maintained at room temperature, 0.7 ml (0.0098 mole) of acetyl chloride solution in 5 ml THF were added (during 10 min.) under vigorous stirring. The mixture was stirred for 8 hrs. at room temperature and then poured into water. The precipitate was filtered, washed with water to neutrality and dried. The product was recrystallized from methanol to afford 1.82 g (77.4%) of white crystals. m.p. 66-67°C. IR (KBr): 1715 (ν C=O), 1585 (ν C=C aromatic), 795 (1,2,4-trisubstituted benzene), 720, 742 $cm^{-1}$ (1,2-disubstituted benzene).

N-(2-hydroxyethyl)-3-bromocarbazolyl acetate (XV, BrHECAc) By using the same method as for synthesis of product XIV, from 2 g (0.0069 mole) VI, 1.16 ml (0.00829 mole) TEA, 0.59 ml (0.00829 mole) acetyl chloride and 40 ml THF, after two recrystallizations from methanol 1.26 g (55.1%) of white crystals were obtained. m.p. 77-78°C. IR (KBr): 1720 (ν C=O), 1582 (ν C=C aromatic), 795 (1,2,4-trisubstituted benzene), 742, 720 $cm^{-1}$ (1,2-disubstituted benzene).

N-(2-hydroxyethyl)-3-iodocarbazolyl acetate (XVI, IHECAc)

Starting with 3 g (0.0089 mole) VII, 1.5 ml (0.0108 mole) TEA, 0.8 ml (0.0108 mole) acetyl chloride and 40 ml THF, 1.95 g (57.86%) of white crystals were obtained using the same procedure as for product XV. m.p. 65-66°C. IR (KBr): 1726 ($\nu$ C=O), 1580 ($\nu$ C=C aromatic), 790 (1,2,4-trisubstituted benzene), 735, 715 $cm^{-1}$ (1,2-disubstituted benzene).

Polymerization of monomers All monomers were subjected to a free radical solution polymerization (solvent THF, monomer concentration 13%), which consists of 1% AIBN, based on the weight of monomer as initiator, a sealed ampoule and air-free conditions. After 19 hrs. of polymerization at 60°C, the polymers were separated by precipitation with methanol, and purified by reprecipitation with methanol from THF solution. Intrinsic viscosities were obtained from THF solutions at 25°C (Table 2).

TABLE 2

Radical Polymerization of Monomers

| Monomer | Conversion (%) | Intrinisic Viscosity ( dl/g ) |
|---|---|---|
| ClHECM | 96.05 | 0.10 |
| ClHECA | 92.24 | 0.09 |
| BrHECM | 97.66 | 0.12 |
| BrHECA | 04.20 | 0.08 |
| IHECM | 95.96 | 0.09 |
| IHECA | 95.10 | 0.04 |

## DISCUSSION

Radical polymerization of monomers produced white polymers of low molecular weight (Table 2). All polymers 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 $CDCl_3$. $^1$H-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 results of air-thermal decomposition of these polymers are presented in Table 3. All of them are stable at least up to 260°C. The thermal decomposition takes place in two steps. Both thermal decomposition temperature range as well as weight losses corresponding to these decomposition domains, are strongly dependent on the polymer structure. A relationship between polymer thermal stability and structure can not be found for the following reasons. First step in thermal decomposition of polymethacrylates is usually the depolymerization reaction. This is not valid for polyacrylates case. In the same time the introduction of the halogen molecule in the carbazoly ring can increase or decrease the polymer thermal stability as a function of halogen nature, not only as a conse-

TABLE 3

| Polymer | First Degradation Step | | Second Degradation Step | | Tg |
|---|---|---|---|---|---|
| | Temp. Range (°C) | Weight Loss (%) | Temp. Range (°C) | Weight Loss (%) | (°C) |
| HECM | 258-438 | 93.43 | 438-552 | 6.57 | 147 |
| HECA | 305-435 | 87.03 | 435-590 | 12.97 | 84 |
| ClHECM | 280-440 | 90.81 | 440-577 | 9.19 | 151 |
| ClHECA | 260-380 | 52.82 | 380-740 | 47.18 | 101 |
| BrHECM | 260-320 | 52.33 | 320-680 | 47.67 | 157 |
| BrHECA | 305-370 | 65.22 | 370-625 | 34.78 | 106 |
| IHECM | 290-363 | 57.45 | 363-660 | 42.55 | 160 |
| IHECA | 275-377 | 48.00 | 377-760 | 52.00 | 106 |

Polymer thermal properties (registered on Mettler thermo-balance and Perkin Elmer 577 DSC instruments, heating rate 10°C/min.)

quence of the difference between the carbon-halogen energy bond, but also due to the different volatility of the products resulted from thermal decomposition (18). In these conditions the only relationship valid for these polymers thermal properties is between the Tg values and the polymer substituent size (Table 3). Indeed by increasing the halogen size the Tg value of the polymer increases, but in all cases these values are lower than PVK Tg value (227°C), because of the increase distance between polymer main chain and pendant group.

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