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Novel hole-transporting carbazole main chain oligomer and its model glass-forming compound

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Summary

The oligomer containing 9-[2-(9*H*-carbazol-9-yl)cyclobutyl]-9*H*-carbazole moiety in the main chain and its model compound were synthesized by Wittig reaction. Both compounds form glasses with glass transition temperatures of 254°C and 135°C respectively. The optical and photoelectrical properties of the compounds were studied. The hole drift mobilities observed in the film of the oligomer by the time of flight technique were in the range of $2\cdot10^{-6}$ - $7\cdot10^{-6}$ cm^2/(V·s) at an applied electric field ranging from $5.8\cdot10^4$ to $2.7\cdot10^5$ V/cm.

Introduction

9-[2-(9*H*-carbazol-9-yl)cyclobutyl]-9*H*-carbazole (CCBC) which is also known as 1,2-*trans*-bis-(9*H*-carbazol-9-yl)cyclobutane some time ago was widely used as a building block in the design and synthesis of photoconductive polymers [1]. The polymers containing CCBC moieties both in the main chain [2,3] and as pendants [4] were reported. Among CCBC-based main chain polymers polyurethanes [2], polyamides [5], polyimines [3], poly-Schiff bases [6] are known. CCBC being a non-planar moiety does not favour excimer formation and crystallization. For this reason CCBC seems to be very suitable building block for the synthesis of photoconductive molecular glasses. In this paper we report on the synthesis and properties of novel CCBC-based oligomer poly(9-{2-[9-(9*H*-carbazol-3-yl)]-cyclobutyl}-9*H*-carbazol-3-yl-vinylene-*alt*-*p*-phenylene-vinylene) and its low-molar-mass glass-forming model compound.

Experimental

Measurements

^{1}H nuclear magnetic resonance (NMR) spectra were recorded using a Bruker AC 250 (250 MHz) apparatus. All data are given as chemical shifts δ [ppm] downfield from $(CH_3)_4Si$.
Mass spectra (MS) were obtained on a Finnigan MAT 8500 (70 eV) with a MAT 112 S Varian.
Differential scanning calorimetry (DSC) measurements were carried out using a Perkin

Elmer DSC-7 calorimeter.

Thermogravimetric analysis (TGA) was performed on a Perkin Elmer TAS-409.

The molecular weight was determined by a Waters gel permeation chromatography system including a Waters 410 differential refractometer using THF as eluent and polystyrene standards.

The samples for the ionisation potential (I_p) and hole drift mobility measurement were prepared as described previously [7]. The ionisation potentials of the layers of the compounds synthesized were measured by the electron photoemission method in air. The measurement method was, in principle, similar to that described by Miyamoto et al. [8].

The hole drift mobility was measured by time of flight technique in electrophotographic regime [9].

Materials

9*H*-vinylcarbazole (Aldrich) was recrystallized from ethanol before use, trimethylphosphite and *p*-xylenedichloride (Aldrich) were used as received.

1,4-xylene-bis(diethylphosphate) (**1**) was synthesized from trimethylphosphite and *p*-xylenedichloride as described in the literature [10].

9-[2-(9*H*-carbazol-9-yl)cyclobutyl]-9*H*-carbazole (CCBC) was prepared by the photochemical cyclodimerization of 9*H*-vinylcarbazole as described elsewhere [11].

9-[2-(9H-carbazol-9-yl)-cyclobutyl]-9H-carbazole-3-carbaldehyde (**2a**) and *9-[2-(3-formyl-9H-carbazol-9-yl)-cyclobutyl]-9H-carbazole-3-carbaldehyde* (**2b**) were synthesized from CCBC by Vilsmeier reactions as reported elsewhere [12].

Poly(9-{2-[9-(9H-carbazol-3-yl)]-cyclobutyl}-9H-carbazol-3-yl-vinylene-alt-p-phenylene-vinylene) (**3**). 0.885 g (2 mmol) of **2b** and 0.757 g (2 mmol) of **1** were dissolved in dry xylene by heating and stirring under N_2 atmosphere. Then 0.673 g (6 mmol) of the catalyst potassium *tert*-butoxide was added. The reaction mixture was refluxed for 24 h. Then the solvent was removed by distillation. The rest was dissolved in hot THF and filtered. The filtrate was concentrated and poured into cold methanol. The precipitates were filtered and dried. Yield 0.48 g (47%) of **3**. Elemental analysis for $C_{38}H_{28}N_2$: %Calc. C 89.03, H 5.51, N 5.46; %Found C 88.72, H 5.62, N 5.41. IR (in KBr) ν/cm^{-1}: 3020 (ar.C-H), 2956, 2922 (alk.C-H), 1622 (methylidyne C=C), 1598, 1509, 1487 (ar.C=C), 956 (*trans*-vinylene C-H). ^{1}H-NMR (DMSO), δ(ppm): 2.69(s,2H,CH_2 of cyclobutane), 2.93(s,2H,CH_2 of cyclobutane), 6.38(s,2H,CH of cyclobutane), 7.05-7.50(m,8H,ar. of carbazole and CH of methylidyne), 7.61(s,4H,ar. of xylene), 7.65-8.45(m,10H,ar. of carbazole).

9-[2-(9H-carbazol-9-yl)-cyclobutyl]-3-{2-[4-(2-{9-[2-(9H-carbazol-9-yl)-cyclobutyl]-9H-carbazol-3-yl}ethenyl)phenyl]ethenyl}-9H-carbazole (**4**). Compound **4** was prepared by the similar procedure as compound **3**. The molar ratio of the starting compounds **2a** and **1** was 6:1. The crude product was purified by column chromatography (eluent: chloroform-hexane, 2:1). Yield 14% of **4**. Elemental analysis for $C_{66}H_{54}N_4$: %Calc. C 87.77, H 6.03, N 5.46, %Found C 87.71, H 6.07, N 5.41. IR (in KBr) ν/cm^{-1}: 3022 (ar.C-H), 2953, 2924 (alk.C-H), 1622 (methylidyne C=C), 1596, 1509, 1483 (ar.C=C), 1452 (alk.C-H), 956 (*trans*-vinylene C-H). MS (m/z): 502, 399, 387, 323, 219, 193. ^{1}H-NMR (DMSO), δ(ppm): 2.68(d,4H,CH_2 of cyclobutane), 2.93(d,4H,CH_2 of cyclobutane), 6.39(s,4H,CH of cyclobutane), 7.10-

7.25(m,6H,ar. and CH of methylidyne), 7.30(s,2H,CH of methylidyne), 7.40-7.50(m,8H,ar), 7.61(s,4H,ar. of xylene), 7.72(d,2H,ar), 7.80-8.00(m,8H,ar), 8.12(t,6H,ar), 8.40(s,2H,ar).

Results and discussion

Oligomer **3** and the model compound **4** were synthesized by Wittig polycondensation or condensation of the corresponding aldehydes of CCBC (**2a** and **2b**) with 1,4-xylene-bis(diethylphosphate) (**1**) as shown in Figure 1. The condensation reactions were carried out in xylene in the presence of potassium *tert*-butoxide, which forms the reactive ylid intermediate. Oligomer **3** is soluble in tetrahydrofuran, *N*-methylpyrrolidinone. The number average molecular weight (M_n) of **3** is 2230 and the weight average molecular weight (M_w) is 4650. The model compound **4** is soluble in common organic solvents such as chloroform, acetone, tetrahydrofuran.

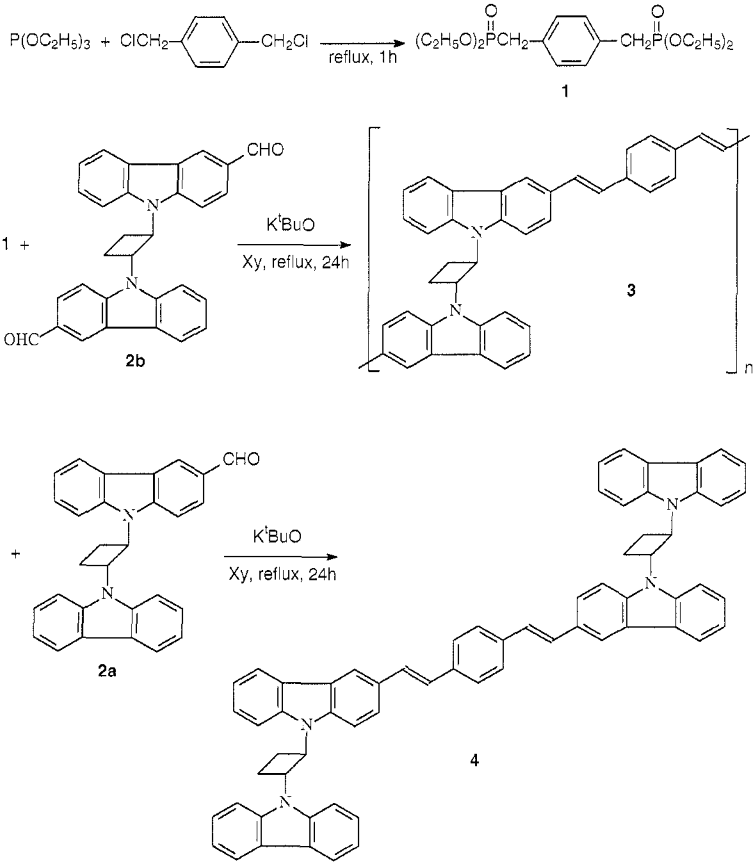

Figure 1. Scheme of synthesis of compounds 3 and 4

The chemical structures of the oligomer and its model compound were confirmed by IR, ^{1}H NMR spectroscopy and elemental analysis. Compound **4** was also characterised by mass spectrometry (see Experimental section).

The characteristic *trans*-vinylene C-H stretch at 956 cm^{-1} appears in the IR spectrum of oligomer **3**. In the spectrum of oligomer **3** there are no clear absorption peaks in the region of 890-900 cm^{-1} due to the *cis*-vinylene C-H bonds. This observation show that vinylene double bonds in the oligomer are mainly of *trans* configuration. The above said also concerns the IR spectrum of the model compound **4**.

The TGA curves of compounds **3** and **4** are shown in Figure 2. The thermal decomposition of these compounds occurs by one step. The 5% weight loss temperature ($T_{dec-5\%}$) of compounds **3** and **4** is 380°C and 350°C respectively. Compounds **3** and **4** were isolated as amorphous materials. Only a glass transition was observed in their DSC curves at 254°C and 135°C respectively. The low-molar-mass compound showed neither melting nor crystallization peaks in the DSC curves of both first and the following heating runs performed after cooling the sample from the temperatures well above its glass transition temperature.

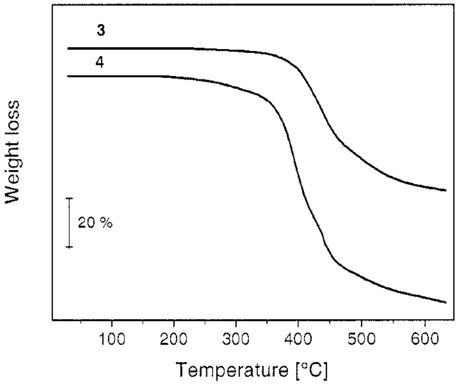

Figure 2. TGA curves of compounds **3** and **4**, recorded at the heating rate of 10°C/min in N_2 atmosphere

Both reported compounds absorb light in the region of 240-450 nm. The UV/vis spectra of the dilute solutions of compounds **3** and **4** are shown in Figure 3. For the comparison UV/vis spectrum of the dilute solution of 9-ethyl-9*H*-carbazole (EK) is also given. The absorption spectra of compounds **3** and **4** are bathochromically shifted with respect of the spectrum of EK. This is the consequence of the increased length of the conjugated double bonds. Obviously, the oligomer **3** and the model compound **4** have very similar absorption bands due to their close structure. The UV spectrum of **4** in the region of 240-300 nm wavelength is more similar to that of EK due to the higher concentration of unsubstituted cyclobutylcarbazole groups.

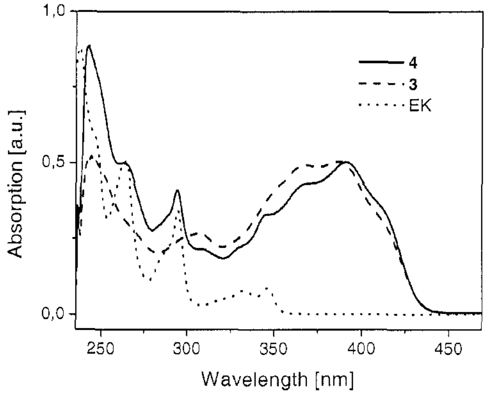

Figure 3. UV/vis spectra of the dilute $CHCl_3$ solutions (10^{-5} M) of compounds **3**, **4** and EK

The compounds containing CCBC units exhibit very intensive fluorescense both in dilute solutions and in bulk due to specific sterically hindered structure of CCBC, which prevents excimer formation [4]. The fluorescense emission spectra of the dilute solutions of compounds **3** and **4** are presented in Figure 4. For the comparison the fluorescence spectra of the CCBC dilute solution is shown. The fluorescense spectra of oligomer **3** and the model compound **4** are strongly shifted to the longer wavelengths with respect of the spectrum of CCBC, which is due to enlarged system of conjugated double bonds. The spectral band shapes of dilute solutions of **3** and **4** are almost identical with that of CCBC showing only monomeric fluorescense.

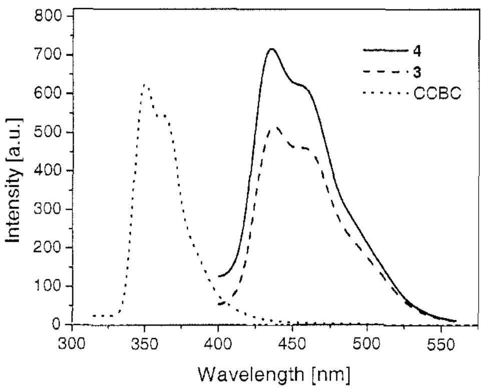

Figure 4. Fluorescense spectra of dilute solutions in 1,2-dichloroethane (10^{-6} M) of compounds **3**, **4** and CCBC, λ_{ex}=295 nm

For the measurements of ionisation potential and charge mobilities the thin amorphous films of oligomer **3** on the substrates were prepared by casting from the solution. The I_p of the film of oligomer **3** was found to be 5.41 eV. This observation shows that oligomer **3** can be useful in electrophotographic photoreceptors as a charge transport material. The ionisation potential values for charge generation materials, widely used in electrophotographic photoreceptors, such as as titanyl phthalocyanines [13,14], perylene pigments [15] and bisazo pigments [16] are in the range of 5.1-5.6 eV. Holes could be easily injected from the layers of these charge generation materials into the charge transport layer of **3.**

The hole drift mobility in the amorphous film of the oligomer was measured by the time of flight technique at 22°C. Figure 5 shows the electric field dependency of the hole drift mobility for oligomer **3**. The linear dependence of the hole drift mobility on the square root of the electric field is observed. Hole mobility ranges from $2 \cdot 10^{-6}$ to $7 \cdot 10^{-6}$ $cm^2/(V \cdot s)$ at an applied electric field ranging from $5.8 \cdot 10^4$ to $2.7 \cdot 10^5$ V/cm.

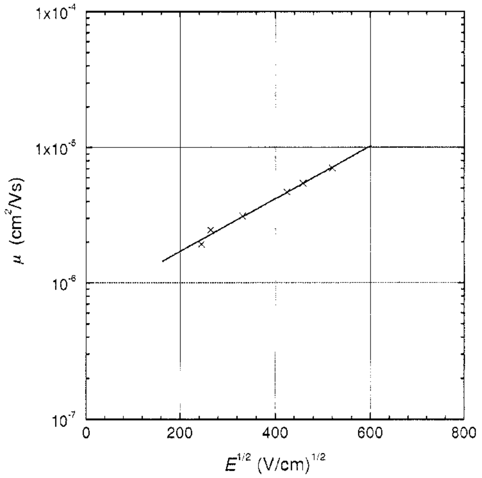

Figure 5. Electric field dependence of the hole drift mobility in the amorphous film of polymer **3** at 22°C

Conclusions

Novel hole-transporting carbazole main chain oligomer and its model compound were synthesized by Wittig reaction. Both compounds form glasses with glass transition temperature of 254°C and 135°C respectively and exhibit intensive fluorescence. The hole drift mobilities observed in the film of the oligomer by the time of flight technique were in the range of $2 \cdot 10^{-6}$ - $7 \cdot 10^{-6}$ $cm^2/(V \cdot s)$ at an applied electric field ranging from $5.8 \cdot 10^4$ to $2.7 \cdot 10^5$ V/cm. Its ionisation potential was found to be 5.41 eV.

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