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A Soluble Green-Light-Emitting Alternating Copolymer with Acceptor-Substituted Bicarbazyl Units

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Introduction. Since the first report on electroluminescence in poly(*p*-phenylenevinylene)[1] (PPV), a wide variety of conjugated polymers used as emissive layers in light-emitting diodes (LEDs) have been studied. Over the past few years, progress in LED research has been made concerning the control of color, efficiency, long-term emission stability, brightness, processability, and the adjustment of the electrode work function.[2a−d] Recently, poly(*N*-vinylcarbazole) (PVK) has attracted attention in utilization as a hole-transporting matrix of polymer blends composed of a PPV derivative as the electron-transporting layer. LEDs in which the emitting layer is constituted by such PVK blends have shown remarkable increase of the luminescence efficiency as compared to those PVK-free.[3,4] We previously reported on multilayer organic diodes based on either poly(*N*-alkyl-3,6-carbazolylene)[5] (PCZ), a polymer with an all-carbazole skeleton, or derivatives of the PCZ constituting dyads, i.e., bicarbazyl.[6,7] These LEDs display a bright blue light. Recently, we studied the possibility to ally advantages of the transporting features of both the PPV and the PCZ into a sole polymeric structure. In such a way, we synthesized by Knoevenagel condensation a new alternating copolymer, i.e., poly[bicarbazolylene-*alt*-phenylenebis(cyanovinylene)][8] (PCPV). Unfortunately, the obtained materials were mostly insoluble in organic solvents and were not sufficiently processable to be incorporated as a thin layer in LED. Insolubility of these materials was attributed to the rigidity of the macromolecular chains and the relatively high molecular weights obtained (corresponding to $\mathrm{DP_n} \geq 40$) together with a slight cross-linking arising from Michael or Thorpe additions onto the vinylene or the cyano groups, respectively. In the conditions used only a small amount of oligomers ($\mathrm{DP_n} \approx 6$) was obtained.

We report herein on the synthesis conditions in which Knoevenagel condensation between the aldehyde monomer and the appropriate diacetonitrile can be controlled. In such a way, a readily soluble well-defined polymer with $\mathrm{DP_n} \approx 17$ was obtained. Furthermore, the electroluminescence feature of LEDs based on PCPV as an emissive layer are described and compared with those of bicarbazyl taken as a model compound. In particular, it was found that this copolymer exhibits an internal charge transfer between the electron-donor carbazole subunits and the electron-acceptor cyanovinylene moieties which allows to shift the luminescence from blue (emission color of bicarbazyl) to green (emission color of PCPV).

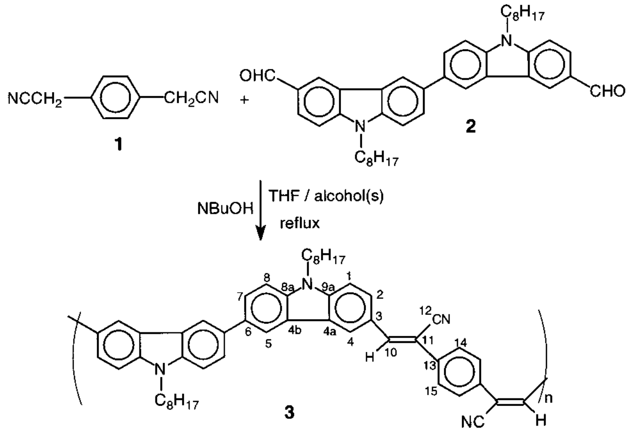


Figure 1. Reaction scheme for polymer synthesis.

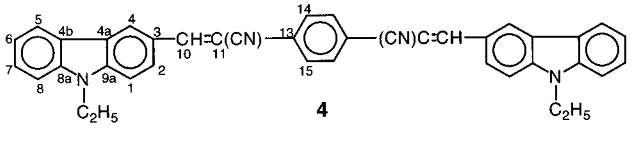
Results and Discussion. The alternating copolymer **3** (PCPV) was synthesized by using the Knoevenagel condensation between the *N*,*N*′-dioctyl-3,3′-bicarbazyl-6,6′-dialdehyde **2** and cyanoterephthalylidene **1** (benzene-1,4-diacetonitrile) as the active methylene component (Figure 1). Carbonylmethylene condensation has been shown to proceed through three reaction steps[9] shown in eqs 1−3.

$$\mathrm{R_1R_2CH_2} \overset{K_1}{\rightleftharpoons} \mathrm{R_1R_2CH^-} + \mathrm{H^+} \qquad (1)$$

$$\mathrm{R_1R_2CH^-} + \mathrm{ArCHO} \xrightarrow{k_2} \mathrm{R_1R_2CHCH(Ar)O^-} \qquad (2)$$

$$\mathrm{R_1R_2CHCH(Ar)O^-} \xrightarrow{k_3} \mathrm{R_1R_2C{=}CHAr} + \mathrm{OH^-} \qquad (3)$$

According to this scheme, the equilibrium (1) may be displaced by mass-law action, and the reaction is retarded or even completely inhibited by added protonic acids and is accelerated by more or less strong bases (such as piperidine, sodium or quaternary ammonium hydroxides) or by the solvent effect. Knoevenagel condensation has been found kinetically controlled by reaction 1 and/or 2, reaction 3 being the faster of the sequence.[10] In the case of condensation between *N*-ethylcarbazole-3-carbaldehyde and cyanoterephthalylidene that we took as a reaction model of the polymerization between **1** and **2**, kinetics between first and second order were found[11] for the formation of the arylvinylene compound 1,4-phenylenebis[(1-cyanovinylene)-3-(*N*-ethyl)carbazole] **4**. Moreover, by varing the dielectric constant (ε) of the reaction media from various THF/alcohol mixtures, the reaction rate was found to vary, and the logarithm of the apparent rate constant of the condensation reaction showed a linear dependence with 1/ε according to the Born and Kirkwood laws[12,13] (Figure 2). In such a way, we were able to control the polycon-



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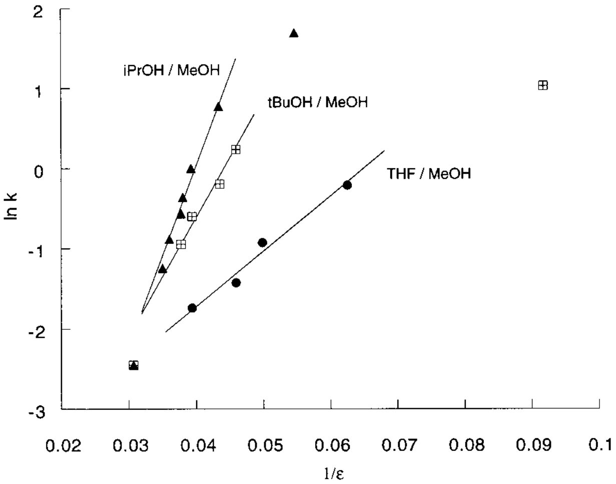

Figure 2. Dependence of the apparent rate constant k with dielectric constant ϵ of THF/MeOH, tBuOH/MeOH, and ^{i}PrOH/MeOH mixtures, in the case of condensation between N-ethylcarbazole-3-carbaldehyde and cyanoterephthalylidene. (See Experimental Section for reaction conditions and calculation of dielectric constant of the medium.)

densation yield and thus, in the case of polycondensation, the molecular weight of the polymer.[11] In low-permittivity media (2-propanol or *tert*-butyl alcohol; $\epsilon_{25} = 18.3$ and ~11, respectively), the concentration of carbanions formed in reaction 1 has been found to reach equilibrium practically instantaneously.[10] Addition of methanol, owing to its higher dielectric constant ($\epsilon_{25} = 32.6$), stabilizes the carbanions, effectively depressing both their recombination rate with protons and their nucleophilicity. Furthermore, we observed that by performing polycondensation at reflux and at $[-CH_2CN]/[NBu_4OH] = 1$ cross-linking of the polymer due to the Thorpe−Ziegler and/or Michael[14] side reactions of carbanions onto the cyano or vinylene groups can be overcome. Indeed, PCPV is readily soluble in organic media (THF, $CHCl_3$, nitrobenzene, etc.) up to $DP_n \approx 17$,[15] and any signal corresponding to abnormal cross-linking structure was detected neither in NMR nor in FT-IR spectra. SEC measurement of a typical sample of PCPV shows a monomodal chromatogram with a molecular weight $M_w = 12\,000$ and a polymolecularity of 2.4. NMR and DSC analysis of PCPV are not different from these we previously published for lower molar weight material.[8]

Comparison of the UV spectra of the copolymer and that of the bicarbazyl (Figure 3) shows that the substitution of the latter by two electron-acceptor groups such as the cyanovinylenephenylene moieties provokes the appearance of a charge-transfer (CT) band in the visible region ($\lambda_{max} = 420$ nm). Such an internal CT between the donor carbazole subunits and acceptor cyanovinylenephenylene moieties leads to an important lowering of the band gap, since the PCPV E_g value measured at the onset of absorption threshold of the spectrum is close to 2.5 eV as compared with that of bicarbazyl, which is $E_g = 3.05$ eV.[6] Moreover, since the absorption band of PCPV in the visible region overlaps the emission peak of bicarbazyl ($\lambda_{max} = 413$ nm), an energy transfer occurs in the electroluminescence (EL) of the polymer (Figure 3). Hence, a green-light emission is observed for PCPV ($\lambda_{max} = 558$ nm) instead of a blue one for the bicarbazyl. A similar green-light emission has recently been observed by Tao et al.[16] and by Maruyama et al.[17] for a cyclic oligomer and hyperbranched polymers, respectively. These materials are based on monocarbazole units 3,6-disubstituted by vinylene cyanoester groups. Nevertheless, authors observed a more or less shifted and broadened electroluminescence spectrum relative to the photoluminescence one. These phenomena have been attributed to structural defects of hyperbranched polymer[17] or by exciplex formation in the cyclic oligomer.[16] The resulting effects should show up in the quality of the color observed. In our case, the excellent coincidence of photoluminescence and EL spectra (see Figure 3) leads to a well-defined bright-green emission from PCPV layer and indicates a classical mechanism of photon emission from recombination of excitons, involving the whole thickness of the PCPV emissive layer.[18] EL measurements were carried out by applying a dc voltage to the LED, positive polarity being at the ITO electrode. Charge injection in this device was achieved at fields above 2×10^8 V/m. Intensity of the EL was found to be proportional to the applied current. A brightness of about 1 μW at a current density of 50 mA/cm^2 and an external efficiency of 3.3×10^{-3}% were observed for this LED. Finally, such CTs could be a novel means of tuning the emission color within a conjugated macromolecular chain by an internal guest−host effect. Synthesis and luminescence of other charge-transfer-type materials in which bicarbazyl plays the role of emitter and the CT moieties the role of guest dopant will be published elsewhere.[19]

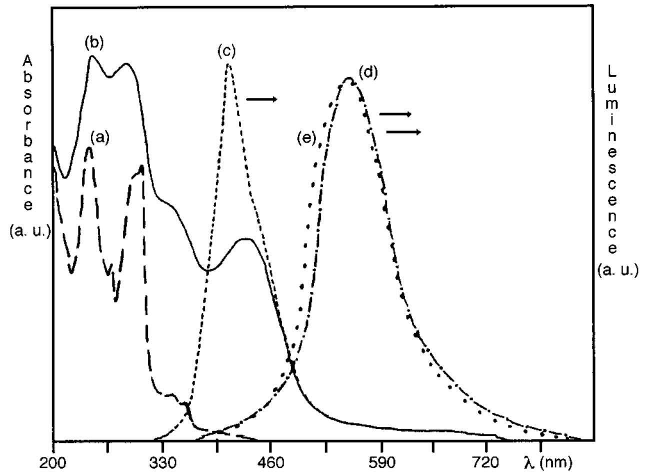

Figure 3. Absorption spectra of (a) bicarbazyl and (b) PCPV; emission spectra of (c) bicarbazyl; electroluminescence (d) and photoluminescence (e) spectra of PCPV.

Experimental Section. Tetrahydrofuran (THF), 2-propanol (^{i}PrOH), *tert*-butyl alcohol (tBuOH), and methanol (MeOH) were distilled prior to utilization. Tetrabutylammonium hydroxide in solution in methanol and cyanoterephthalylidene **1** (ACROS Organics) were used as received. All reactions were performed under nitrogen. Synthesis of the dialdehyde **2** was previously described.[8] Synthesis of the polymer is shown in Figure 1. In a typical experiment a stoichiometric amount of the carbazole compounds, i.e., N-ethylcarbazole-3-carbaldehyde, or monomer **2** and the cyanoterephthalylidene **1** was dissolved in mixtures of THF/alcohol or alcohols as mentioned in Figure 2. The resulting dielectric constant of the alcohol mixture is calculated according to the following equation: $\epsilon_{25}^{mixture} = \epsilon_{25}^{MeOH}\Phi_{MeOH} + \epsilon_{25}^{tBuOH}\Phi_{tBuOH}$, with Φ_{MeOH} the volumic fraction of MeOH in the alcohol mixture. An equimolar quantity of tetrabutylammonium hydroxide is added at reflux. After refluxing for 1 h reaction was stopped by cooling the reaction medium at 0 °C for 5 min. The resulting solid obtained was then filtered off and purified by Soxhlet extraction with methanol. Orange-colored powders were obtained. **3**: ^{1}H NMR ($CDCl_3$, ppm): 0.9−1.9 ($-C_7H_{15}$) and 4.2 (α-CH_2); 7.4 (1,8); 7.6 (10,14,15); 7.7 (2); 6.1 (7); 8.4 (4); and 8.6 (5). **4**: ^{1}H NMR ($C_2D_2Cl_4$, ppm): 1.4 (CH_3) and 4.3 (CH_2); 7.3 (8); 7.4 (1,7,8); 7.66 (2); 7.72 (14,15); 8.1 (5,10); and 8.6 (4). ^{13}C NMR ($C_2D_2Cl_4$, ppm): 13.7 (CH_3) and 37.9 (CH_2); 107.1 (11); 109.1 (1,8); 118.6 (CN); 120.0 (4); 120.7 (7); 122.5 (8); 123.1 (5); 123.7 (6); 125.0 (3); 126.3 (2,14,15); 126.6 (4b); 127.4 (4a); 135.6 (13); 140.7 (8a); 141.5 (10); and 143.6 (9a). NMR and UV−vis spectra were recorded on a Bruker AC200 spectrometer (200 and 50 MHz for ^{1}H and ^{13}C) and on a Varian DMS 100, respectively. FT-IR spectra were recorded on a Perking-Elmer 1600. SEC measurements were performed in THF with Ultrastyragel columns (100, 500, and 10^3 Å) equipped with a differential refractometer (Waters). Polystyrene standards (Aldrich) were used for calibration. LED was fabricated from a solution of the copolymer **3** in $CHCl_3$ that was spin-cast onto indium−tin oxide (ITO)-covered glass substrates. This technique yielded uniform films with nominal thickness of about 1000 Å. Magnesium electrode was deposited under vacuum of 10^{-6} Torr at a rate less than 1 Å s^{-1}. Photoluminescence of the polymer film was obtained by excitation of the latter by the $\lambda_{exc} = 352$ nm line of an argon ion laser.

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