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Syntheses of Conjugated Polymers Derived from *N*-Alkyl-2,7-carbazoles

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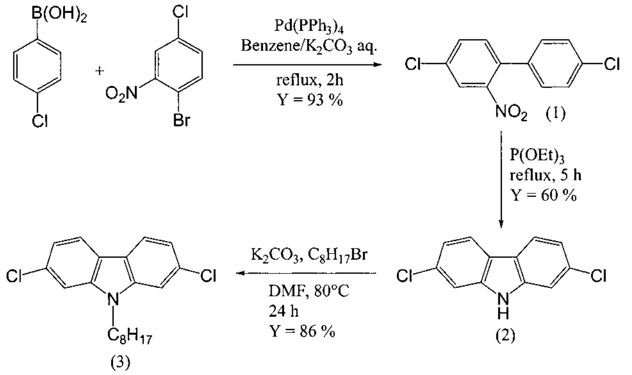
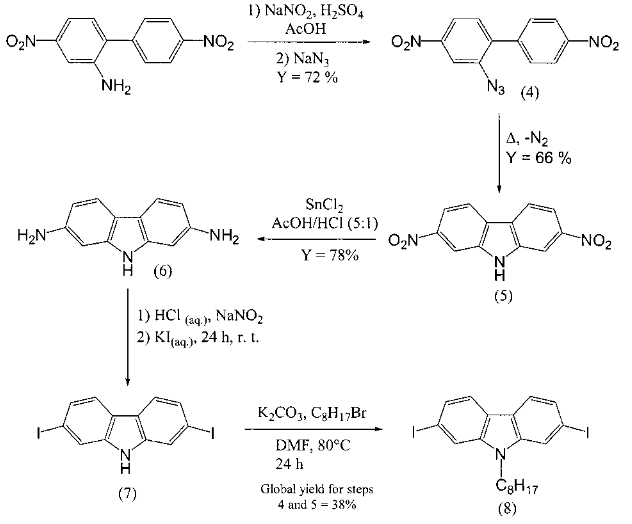
Introduction. Conjugated polymers are now considered as a very important class of electroactive and photoactive materials by both academic and industrial laboratories.[1] This development over the last 20 years has been sustained by the clever utilization of a variety of synthetic tools (Kumada, Stille, Yamamoto, Suzuki couplings, etc.) to prepare highly pure polymers with optimized physical properties. For instance, the synthesis of well-defined polyacetylene,[2] polythiophenes,[3] polyphenylenes,[4] polyfluorenes,[5] ladder-conjugated polymers,[6] and other aromatic polymers[7] have led to a significant improvement in the performance of these polymeric materials and to a better understanding of their structure−property relationships. However, one important class of conjugated polymers was still missing in the inventory of chemist's toolbox, and it was easy access to well-defined poly(*N*-alkyl-2,7-carbazole)s and related conjugated polymeric derivatives. Indeed, up to now, only poorly conjugated poly(*N*-alkyl-3,6-carbazole) derivatives were available.[8] We report here the first syntheses of homopolymers and copolymers derived from *N*-alkyl-2,7-carbazoles and some preliminary studies of their physical properties. These new polymeric materials are particularly promising for the future development of light-emitting diodes, electrochromic windows, photovoltaic cells, photorefractive materials, etc.

Scheme 1



Scheme 2



Results and Discussion. As shown in Scheme 1, *N*-alkyl-2,7-dichlorocarbazoles have been easily prepared in three straightforward steps. First, this synthetic scheme involves a Suzuki coupling between 4-chlorophenylboronic acid (Aldrich Co.) and 1-bromo-4-chloronitrobenzene (Aldrich Co.) in the presence of Pd($(PPh_3)_4$ in a mixture of benzene and aqueous K_2CO_3 solution to give 1-chloro-4-(4′-chlorobenzene)-2-nitrobenzene in a 93% yield. This compound undergoes then a reductive Cadogan ring closure[9] using $P(OEt)_3$. Finally, the alkylation of the nitrogen atom of the resulting 2,7-dichlorocarbazole in DMF and K_2CO_3 using, for instance, 2-ethylhexyl bromide leads to *N*-(2-ethylhexyl)-2,7-dichlorocarbazole in a 86% yield. Alternatively, for Suzuki or Stille coupling, it could be useful to prepare the more reactive 2,7-diiodocarbazole (or 2,7-dibromocarbazole) derivatives. As previously reported,[1,4−7] Suzuki or Stille couplings can lead to a large number of alternating conjugated copolymers. For these purposes, *N*-alkyl-2,7-diiodocarbazoles have been obtained in five steps, starting from 4,4′-dinitro-2-biphenylamine (Aldrich Co.) (see Scheme 2). Following the procedure developed by Smith and Brown,[10] 4,4′-dinitro-2-biphenylamine was treated with $NaNO_2$ and NaN_3 to give the corresponding azide via the transformation of the amino group into a diazonium salt. A ring closure reaction, assured by a nitrene intermediate, was carried out to give 2,7-dinitrocarbazole[11] in a 66% yield. Following procedures similar to those utilized in the preparation of 3,6-diaminocarbazoles,[12] this compound was then reduced using $SnCl_2$ in a mixture of acetic acid/HCl (5:1) to give 2,7-diaminocarbazole in a 78% yield. Then, the amino groups of the resulting product were transformed into iodine atoms.[13] This reaction was carried out in a 3 M HCl aqueous solution using $NaNO_2$ and KI. If needed, 2,7-dibromocarbazole can be obtained from 2,7-diaminocarbazole through a similar Sandmeyer reaction using CuBr, HBr, and $NaNO_2$, but purification steps are more difficult. Finally, *N*-octyl-2,7-diiodocarbazole was prepared from 2,7-diiodocarbazole upon reaction with K_2CO_3 and 1-bromooctane in anhydrous DMF at 80 °C. All these compounds have been characterized by NMR spectroscopies and mass spectrometry (see Supporting Information).

Homopolymerizations were achieved by a reductive Yamamoto reaction[14] using *N*-alkyl-2,7-dihalogenocarbazoles as starting materials in the presence of triphenylphosphine, zinc, 2,2′-bipyridine, and $NiCl_2$ (Scheme 3A). Alternating conjugated copolymers can be prepared from a Suzuki coupling reaction[4,5b] between diboronic functionalized aromatic units and *N*-alkyl-2,7-diiodocarbazole (or dibromo) derivatives. For instance, poly(*N*-octyl-2,7-carbazole-*alt*-9,9-dioctyl-2,7-fluorene) was pre-

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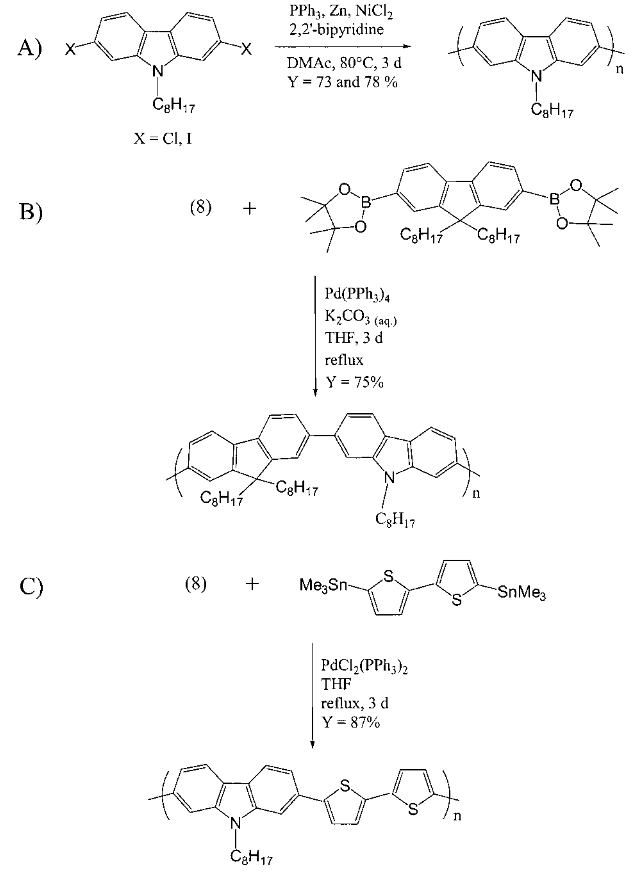
Scheme 3



pared from a reaction between 2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-dioctylfluorene[5b] and *N*-octyl-2,7-diiodocarbazole using $(PPh_3)_4Pd(0)$ as catalyst in a mixture of THF and 2 M K_2CO_3 aqueous solution (Scheme 3B). Moreover, Stille couplings[7a] between distannyl aromatic derivatives and *N*-alkyl-2,7-diiodocarbazole derivatives are possible. As an example, poly(*N*-(2-ethylhexyl)-2,7-carbazole-*alt*-5,5′-(2,2′-bithiophene)) has been obtained in a good yield from *N*-(2-ethylhexyl)-2,7-diiodocarbazole and 5,5′-bis(trimethylstannyl)-2,2′-bithiophene,[15] in the presence of $Cl_2(PPh_3)_2Pd(0)$ in THF (Scheme 3C). All these polymerization reactions show a yield between 73 and 87%.

The resulting conjugated poly(*N*-octyl-2,7-carbazole-*alt*-9,9-dioctyl-2,7-fluorene)s are completely soluble in common organic solvents, such as chloroform and tetrahydrofuran. However, poly(*N*-octyl-2,7-carbazole) and poly(*N*-(2-ethylhexyl)-2,7-carbazole) are only partially soluble (ca. 50% fraction) and an even smaller fraction (ca. 10%) of the resulting poly(*N*-(2-ethylhexyl)-2,7-carbazole-*alt*-5,5′-(2,2′-bithiophene)) is soluble in these solvents. These properties can be partly related to the degree of substitution of each polymer; flexible substituents being necessary to obtain soluble conjugated polymers.[1,3−7] The number-average molecular weight (measured by size exclusion chromatography against monodisperse polystyrene standards) of the soluble part (presumably of lower molecular weight) of these polymers is about 5 kDa with a polydispersity of around 1.5. Nevertheless, all these polymers can be processed by spin coating or by simple casting to yield thin polymer films with good mechanical properties.

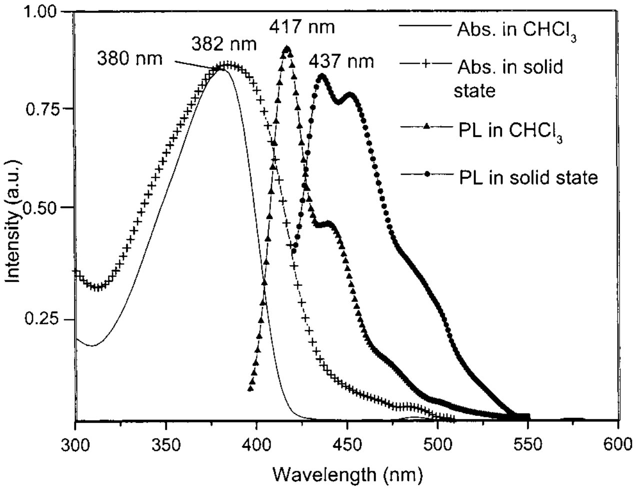


Figure 1. Absorption (Abs.) and emission (PL) spectra of poly(*N*-octyl-2,7-carbazole) in chloroform and in the solid state.

As reported in Figure 1, the solution and solid-state optical properties of poly(*N*-octyl-2,7-carbazole) have been investigated in more detail. In dilute solutions or as thin films, this polymer exhibits an absorption maximum around 380−390 nm, leading to a pale yellow color in both forms. Accordingly, this polymer does not exhibit any significant thermochromic or solvatochromic properties. This absorption maximum is significantly red-shifted compared to that previously reported for poly(*N*-alkyl-3,6-carbazole)s (i.e., 300−320 nm)[8] and can be related to a more conjugated structure. Moreover, poly(*N*-octyl-2,7-carbazole) exhibits an intense blue emission upon radiative excitation, with a quantum yield of about 80% in chloroform, at room temperature. In solution, poly(*N*-octyl-2,7-carbazole) shows a maximum of emission at 417 nm followed by two vibronic sidebands at 439 and 474 nm whereas in the solid state, the polymer exhibits an emission maximum at 437 nm followed by two other maxima at 453 and 492 nm (Figure 1). It is worth noting that, in contrast to semicrystalline poly(9,9-dialkyl-2,7-fluorene)s,[5a,16] the emission spectrum of poly(*N*-octyl-2,7-carbazole) does not give any evidence of excimer formation. This behavior could possibly be explained by the amorphous structure of poly(*N*-octyl-2,7-carbazole).

Interestingly, the pale yellow poly(*N*-octyl-2,7-carbazole-*alt*-9,9-dioctyl-2,7-fluorene) exhibits also solution and solid-state blue emission (without the presence of excimer) with a maximum at 417 and 450 nm, respectively. The solution fluorescence quantum yield is 43% in chloroform. Moreover, in chloroform solution, poly(*N*-(2-ethylhexyl)-2,7-carbazole-*alt*-5,5′-(2,2′-bithiophene)) emits a green radiation with a maximum of emission at 504 nm. In this case, the fluorescence quantum yield is 30%. With these possibilities of structural modifications through the synthesis of various alternating copolymers, it could then be possible to develop tunable light-emitting polymers.[17]

Conclusion. These syntheses of highly conjugated polymers based on *N*-alkyl-2,7-carbazole derivatives give an easy access to a completely new class of interesting conjugated polymers which could find applications in diverse electrical, electrochemical, optical, and electrooptical devices. All these physical properties will be carefully investigated in a near future.

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Supporting Information Available: Text giving details of all synthetic and purification steps and NMR and mass spectrometry data and figures showing 300 MHz ^{1}H and 75 MHz ^{13}C spectra of all new compounds (compounds **1**−**8**). This material is available free of charge via the Internet at http://pubs.acs.org.

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