LITERATURE REVIEWS

Poly(N-octyl-2,7-carbazole) derivatives have been synthesized by Mario Leclerc group in 2001 (Morin and Leclerc, 2001, 2002; Zotti *et al.*, 2002). This synthesis and investigation of new conjugated polymers are essential for improving the electronic and optoelectronic properties of these materials and in turn improvement of the performance of the devices. Due to blue-light-emitting polyfluorenes (PFs) show a tailed emission band at long wavelengths (>500 nm) during device fabrication and operation, leading to both a color instability and reduced efficiency. These were initially assigned to the undesired interchain aggregation and/or excimer formation of the polymer chain, but more recently it has been shown that the emission from PFs arises from emissive fluorenone defects formed by oxidation at the methane bridge. Another serious problem associated with polyfluorene homopolymer is the significant energy barrier for hole or electron injection and transport with the currently available anode and cathode materials.

N-alkyl-2,7-dichlorocarbazoles were prepared in three straightforward steps (see in Figure 10), Suzuki coupling, reductive Cadogan ring closure, and alkylation. Homopolymerizarions were achieved by reductive Yamamoto reaction of N-alkyl-2,7-dihalo-carbazoles in the presence of $P(Ph)_3$, Zn, 2,2'-bipyridine, and $NiCl_2$ catalyst system. Alternating conjugated copolymers were prepared by Suzuki coupling of diboronic functionalized aromatic compounds and N-alkyl-2,7-diiodocarbazole (or dibromo) derivatives. The resulting conjugated polymers are completely solubility in common organic solvents, such as chloroform and THF. In dilute solutions or as thin films poly(N-octyl-2,7-carbazole) exhibits an absorption maximum around 380-390 nm, leading to a pale yellow color and does not exhibit thermochromic or solvatochromic properties, however it has an intense blue emission upon radiative excitation, with a quantum yield of about 80% in chloroform, at room temp. The pale yellow poly(N-octyl-2,7-carbazole-alt-9,9-dioctyl-2,7-fluorene) exhibits solution and solid-state blue emission (without the presence of excimer) with a maximum at 417 and 450 nm, respectively. 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, the fluorescence quantum yield is 30%.

Some chemists accepted the challenge; in attempts to bring more reliable synthetic procedures to the field of electronic materials, a variety of synthetic tools (Grignard, Stille, Yamamoto, Heck, and Suzuki couplings, etc.) (Naarman and Theophilou, 1987; Rehahn *et al.*, 1989; Daoust and Leclerc, 1991; Chen and Rieke, 1992; Heywang and Jonas, 1992; Faid *et al.*, 1993, 1995; Leclerc and Faid, 1997) were utilized that allowed significant advances in this research field. For instance, investigations by Pei and Yang (1996) on nickel-catalyzed Yamamoto couplings of 2,7-dibromo-9,9-disubstituted carbazoles (Figure 10(a)(led to the synthesis of well-defined, highly conjugated, and processable poly[2,7-(9-dialkylcarbazole)]s. This first report on regioregular poly[2,7-(9-dialkylcarbazole)]s was rapidly followed by investigations on the polymerization of well-defined carbazole-containing conjugated polymers using palladium-catalyzed Suzuki coupling reactions between 2,7-dibromocarbazole derivatives and 2,7-diboronylcarbazole derivatives (Figure 10(b)).

Nevertheless, as is usual in polymer chemistry, the preparation of random copolymers and alternating copolymers perturbs short- and long-range organization in the materials (Naarman and Theophilou, 1987; Rehahn *et al.*, 1989; Daoust and Leclerc, 1991; Morin and Leclerc, 2001). A variety of copolymers derived from 2,7-carbazoles were thus recently reported (Figure 11) and tested in different electrooptical devices. Most copolymers were obtained from a Yamamoto (Figure 10(a)), Suzuki (Figure 14(b)), or Stille (Figure 14(c)) coupling reaction. In most cases excimer formation was suppressed and a fairly good correspondence was observed between solution and solid-state fluorescence spectra (usually, a slight red-shift is observed in the solid state that is due to an extended delocalization length), as well as between solid-state fluorescence and electroluminescence spectra.

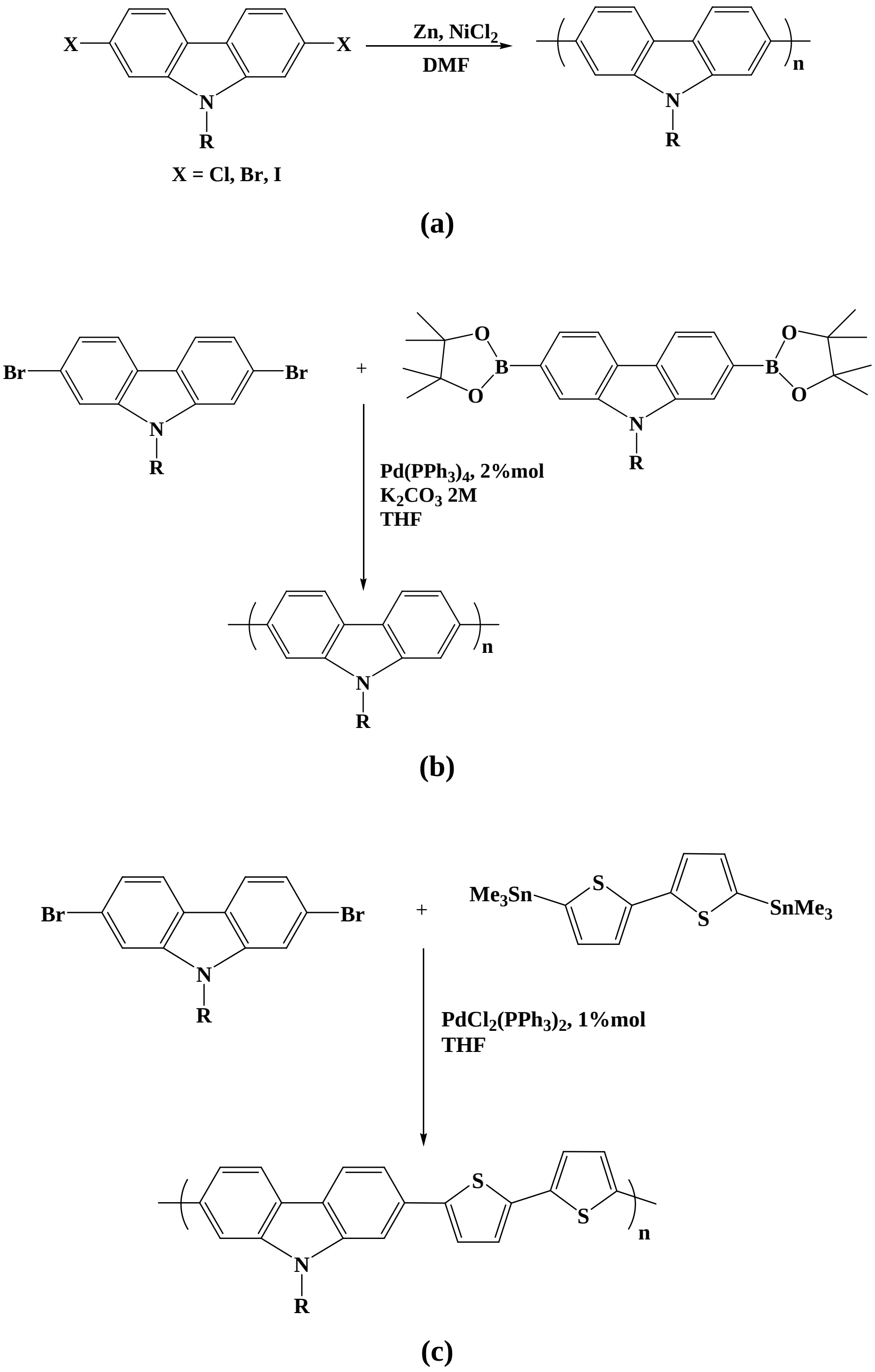

Figure 10 Schematics of the polymerization of carbazoles from (a) Yamamoto, (b) Suzuki, (c) Stille-coupling reactions.

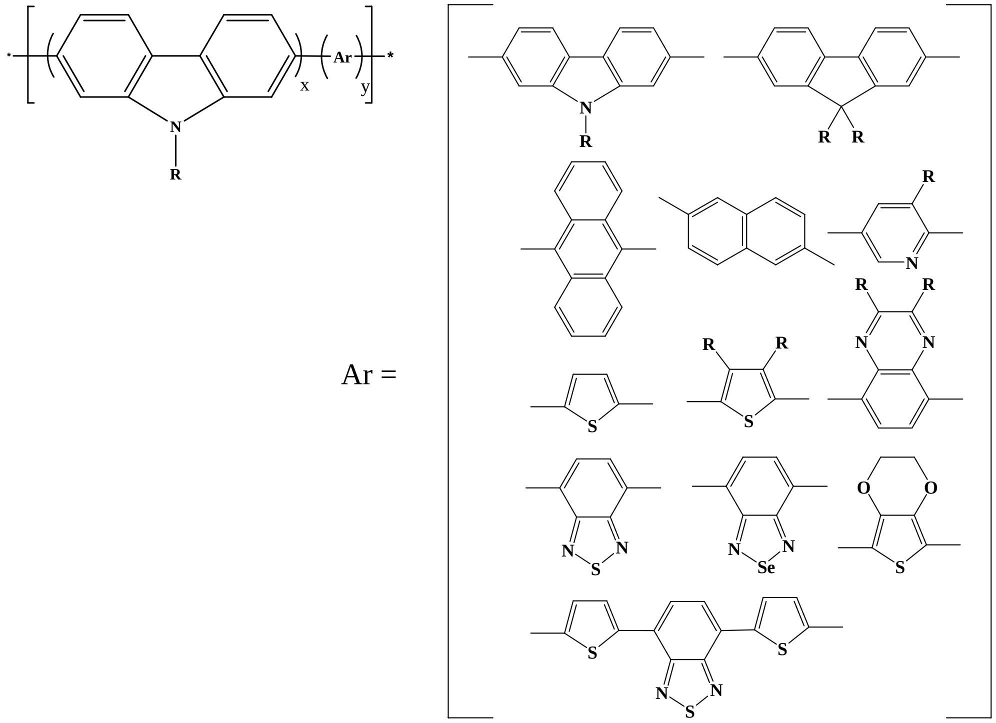

Figure 11 Examples of alternating and random copolymers derived from carbazoles and other aromatic monomers.

In addition, the development of such copolymers permitted the preparation of a variety of carbazole-containing copolymers that emit colors spanning the entire visible range (red, green, blue) (Morin and Leclerc, 2001, 2002; Zotti *et al.*, 2002; Bouchard *et al.*, 2003). In many cases luminance between 100 and 10,000 cd/m^2 was obtained at only few volts. Clearly, poly(N-alkyl-2,7-carbazole)s are seen as one of the most promising classes of electroluminescent polymers. Leclerc *et al.* (Morin and Leclerc, 2001, 2002; Zotti *et al.*, 2002) reported that 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, electrooptical devices, the future development of light-emitting diodes, electrochromic windows, photovoltaic cells, photorefractive materials, etc.. All these physical properties will be carefully investigated in a near future. Structural modifications through the synthesis of alternating copolymers make it feasible to develop tunable light-emitting polymers.

Conjugated polymers have been the subject of considerable academic and industrial research in recent years because of their possible applications in optoelectronic devices such as field-effect transistors (Dimitrakopoulos and Malenfant, 2002), solar cells (Brabec *et al.*, 2001) and light-emitting diodes (LED) (Kraft *et al.*, 1998; Mitschke and Bauerle, 2000). Among these polymers, poly(2,7-carbazole) derivatives show interesting and unique chemical and physical properties because their emission at certain wavelengths spans the entire visible spectrum, they have high fluorescence efficiency, and they possess good thermal stability (Zotti *et al.*, 2002; Bouchard *et al.*, 2003; Inzelt, 2003). It is known that an optimized light-emitting diode requires efficient and balanced charge injection, good and comparable mobilities for both holes and electrons, and a high luminescence quantum yield. Poly(2,7-carbazole) derivatives are a particularly suitable class of materials for applications in light-emitting devices with the advantages of emitting in the blue region of the visible spectrum, chemical and photochemical stability in air, and the high purity. This is because carbazole contains a rigid biphenyl unit (which leads to a large band gap with efficient blue emission) and the facile substitution at the remote N-position provides the possibility of improving the solubility and processability of polymers without significantly increasing the steric interactions in the polymer backbone (Stephan and Vial, 1999; Liu *et al.*, 2001; Xia and Advincula, 2001).

Poly(2,7-carbazole) derivatives (Figure. 11) are a particularly suitable class of materials for applications in light-emitting devices with the advantages of emitting in the blue region of the visible spectrum, chemical and photochemical stability in air, and the high purity (Liu *et al.*, 2001; Huang *et al.*, 2002; Lee *et al.*, 2002; Li *et al.*, 2004). This is because carbazole contains a rigid biphenyl unit (which leads to a large band gap with efficient blue emission) and the facile substitution at the remote N-position provides the possibility of improving the solubility and processability of polymers without significantly increasing the steric interactions in the polymer backbone. Most interestingly, this class of materials is not subject to the formation of ketone defects.

However, theoretical studies on the electronic structures of polymers have made great contributions to the rationalization of the properties of known polymers (Lahti *et al.*, 1887; Sheats *et al.*, 1996; Ma *et al.*, 2002) and the prediction those of yet unknown polymers. For electronic properties, Leclerc *et al.* (Zotti *et al.*, 2002; Belletete *et al.*, 2004; Briere and Cote, 2004; Yang *et al.*, 2006) reported the spectroscopic and photophysical properties of carbazole-based molecules in solution. The absorption and emission energies of these copolymerized derivatives were correlated with their electronic transitions, as computed by ZINDO/S calculations performed on optimized HF/6-31G(d) geometries, and first relaxed excited state as obtained by RCIS/6-31G(d) calculations. The results demonstrated a good agreement between computed electronic transitions and the optical data. Recently, Yang *et al.* (2006) calculated the ground states of the carbazole-based oligomers using the B3LYP/6-31G(d) method, and the low-lying excited states using the time dependent density functional theory (TD-DFT) (Bartolotti *et al.*, 1981, 1982; Bauernschmitt *et al.*, 1996, 1997, 1998; Gies and Gerhardts, 1987; Hirata *et al.*, 1999; Cai *et al.*, 2000; Heinze *et al.*, 2000). A satisfactory linear relationship was found between experimental data and the excitation energy obtained from TD-DFT calculations. Thus, the TD-DFT method can be used to predict the lowest excitation energies for compounds in these systems, and is applicable to the design of new conducting polymers (Adamo and Barone, 2000; Grozema *et al.*, 2001; Hsu *et al.*, 2001, 2002). There is evidence that TD-DFT systematically underestimates the excitation energies by 0.4-0.7eV compared to experimental results. The reason for this is the limitation of the current approximate exchange-correlation function in correctly describing the exchange-correlation potential in the asymptotic region. However, reasonable results can still be expected because HF/DFT hybrid functions such as B3LYP and PBE1PBE can partially overcome the asymptotic problem.

Poolmee *et al.* (2005) it is demonstrated that the molecular conformation affects the electronic spectra of polyfluorene derivatives. It was thus shown that knowledge of the backbone conformation is important. The torsional potential of molecule has attracted much interest as a basic problem of structural chemistry. The potential is also important to understand structures and properties of molecules. The degree of planarity has a direct influence on the effective conjugation length as well as the width of the optical property. The knowledge of the backbone conformation is quite important. Therefore, conformational analysis studies on dimeric species, which serve as model for polymeric systems, are of fundamental importance once it can provide useful information that can enable us to understand the behavior of the real polymer. For more insight into the structure-electronic relationships in these materials, it is believed that the study of optical and photophysical properties, such as vertical electronic transitions of the corresponding carbazole-based oligomers, are important.

The polymers based on the molecules of carbazole and fluorene all possess the sequence of bonded benzene rings characteristic of the geometry of PPP. The similarity in the atomic structure of the polymers and molecules suggests a resemblance in their electronic and optical properties. The conformations of bicarbazole (Briere and Cote, 2004; Belletete *et al.*, 2004) and bifluorene (Blondin *et al.*, 2000; Tirapattur *et al.*, 2003) have been extensively investigated both experimentally (Donat-Bouillud *et al.*, 2000; Huang *et al.*, 2002; Bouchard *et al.*, 2003; Belletete *et al.*, 2004) and theoretically and can be used as a model to obtain information about the structure of polycarbazole and polyfluorene chains. Recently a number of theoretical studies have been reported addressing the torsional potential of bicarbazole and bifluorene. HF and DFT methods have been employed, using, in most of the cases, the split-valence 6-31G* basis sets, which contain polarization function only on the heavy atoms. These features have motivated the investigation performed here. Although several preliminary studies are found in the literature (McLean and Leclerc, 1980; Dunning, 1989; Karpfen, 1991; Woon and Dunning,1993) the question still remains open since torsional potential are largely dependent on the theoretical method chosen. This elusive character clearly deserves systematic application of *ab initio* methods in order to firmly establish a set of benchmark results to be further exploited; cost-effective and widely used density-functional methods are then carefully applied in a second step. Since some weaknesses of this theory have been recently detected for closely related systems (Almenningen *et al.*, 1985), the present study will also analyze the way these functionals describe, not only the torsional barrier heights, but also the entire torsional potential of bicarbazole and bifluorene.

The time-dependent density functional theory (TDDFT) (Bauernschmitt *et al.*, 1996, 1997, 1998; Casida *et al.*, 1998; Wiberg *et al.*, 1998, 2002), a powerful tool for calculating excitation energies, is also employed (Hattig and Weigend, 2000; Gao *et al.*, 2002; Zhang *et al.*, 2002; Suramitr *et al.*, 2005) to extrapolate energy gaps of the polymers from the calculated excitation energies of their oligomers. It is pointed out that TDDFT systematically underestimated the excitation energies by 0.4-0.7 eV comparing to the experimental results (Ma *et al.*, 2002; Suramitr *et al.*, 2005; Keangsak *et al.*, 2006; Yang *et al.*, 2006). The reason for this is due to the limitation of the current approximate exchange-correlation functionals in correctly describing the exchange-correlation potential in the asymptotic region (Casida *et al.*, 1998, Suramitr *et al.*, 2005). However, reasonable results can still be expected here, because the Hartree-Fock (HF)/DFT hybrid functionals such as B3LYP has been used which could partially overcome the asymptotic problem (Casida *et al.*, 1998; Ma *et al.*, 2002). For linear oligoenes, recent studies on the excited energies of the first dipole-allowed 1Bu states also showed that TDDFT calculations with the B3LYP functional can correctly reproduce the general trend of decreasing excitation energy with chain length, with a systematic underestimation of only approximately 0.3-0.5 eV. Therefore, TDDFT with the B3LYP functional is expected to be a relatively reliable tool for evaluating the excitation energies of the low-lying excited states for small- and medium-sized molecules.