

Review Article

Novel Complex Polymers with Carbazole Functionality by Controlled Radical Polymerization

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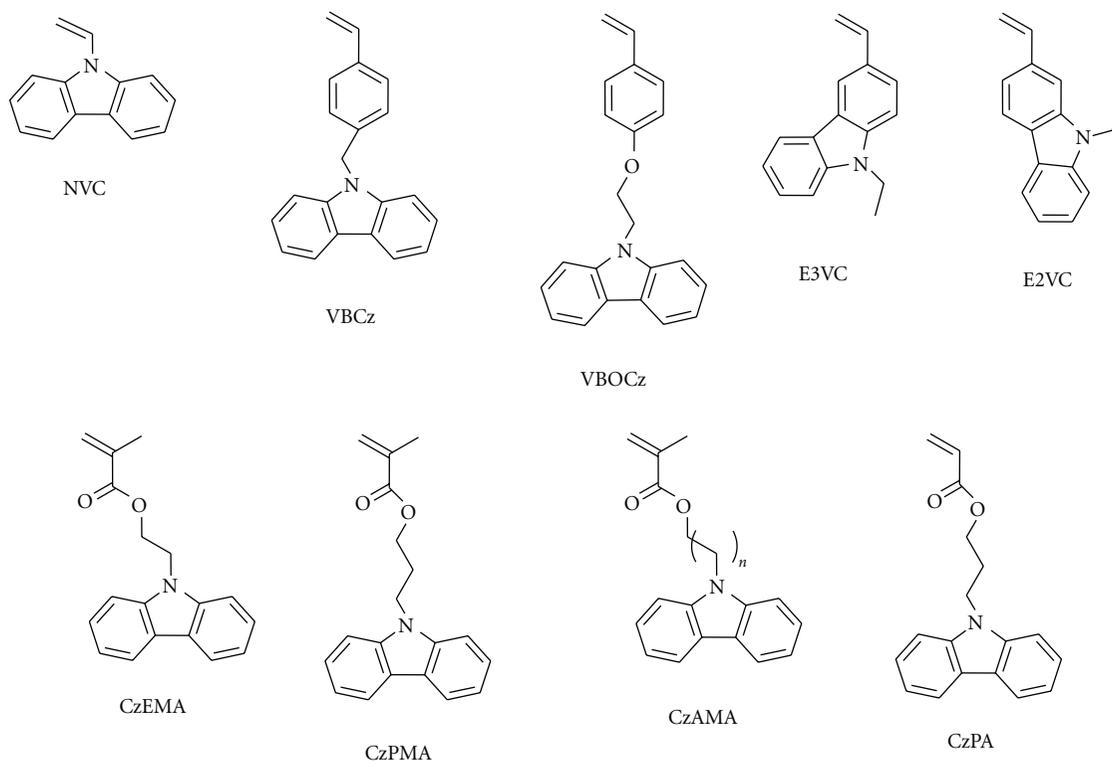
This review summarizes recent advances in the design and synthesis of novel complex polymers with carbazole moieties using controlled radical polymerization techniques. We focus on the polymeric architectures of block copolymers, star polymers, including star block copolymers and miktoarm star copolymers, comb-shaped copolymers, and hybrids. Controlled radical polymerization of *N*-vinylcarbazole (NVC) and styrene and (meth)acrylate derivatives having carbazole moieties is well advanced, leading to the well-controlled synthesis of complex macromolecules. Characteristic optoelectronic properties, assembled structures, and three-dimensional architectures are briefly introduced.

1. Introduction

Polymers with carbazole groups are of considerable scientific and industrial interest because of their attractive features, such as their hole-transporting, high charge-carrier, and electroluminescent properties [1]. The hole-transporting ability of carbazole-containing polymers makes them especially useful for applications in organic electronics. Numerous studies have been devoted to carbazole-containing polymers as a result of the success of poly(*N*-vinylcarbazole), poly(NVC), in electrophotographic applications [1]. Recent developments in this field are mostly connected to applications in polymeric light-emitting diodes, organic photorefractive materials, and photovoltaic devices. For example, conjugated poly(3,6-carbazole) and poly(2,7-carbazole) derivatives having carbazole moieties in the main chain have been employed for applications in solar cells and white-light-emitting diodes [2–4]. Carbazole-containing polymers can be divided into two general groups: polymers containing carbazole moieties in the main chain, or those containing carbazole moieties in the side chains. Poly(NVC) belongs to the group of polymers having carbazolyl groups in the side chains. A variety of polymers with pendant carbazolyl groups has been reported, including polyacrylate [5, 6],

polymethacrylate [7–10], and polystyrene [11, 12] derivatives. Many factors play crucial roles in the manipulation of their properties and practical applications, such as their chemical structures, polymer architectures, conformation, location, and stacking of carbazole units. However, it was difficult to control their molecular weights and architectures, because most of these polymers with pendant carbazolyl groups have been traditionally synthesized by conventional radical polymerization. To manipulate their unique electronic and photonic functions, it is desirable to establish precise synthetic methods of controlling molecular weight, polydispersity, topology, composition, and functions. This can be achieved by using controlled polymerization systems.

In the past few decades, considerable attention has been given to the self-assembly of block copolymers, because of the feasibility of using them to generate nanostructured materials and their numerous potential applications in separation technology, controlled drug delivery and release, and smart catalyst separation technology [13–17]. Traditional amphiphilic block copolymers containing chemically connected hydrophilic and hydrophobic segments provide a great variety of morphologies in selective solvents, for example, water, in which micellar aggregates occur as a result of the association of the insoluble blocks. Block copolymers



SCHEME 1: Representative examples of carbazole-containing vinyl monomers used for controlled radical polymerizations.

incorporating semiconducting segments and characteristic optoelectronic functions have attracted significant research interest [18–23]. Block copolymers are emerging as a promising class of materials for optoelectronic applications, such as organic light-emitting devices, photovoltaics, and organic field-effect transistors, because of their ability to form a variety of ordered structures via self-assembly processes. Depending on the chemical nature of the functional segments and their composition, block copolymers provide a great opportunity to tune their chemical, physical, and optoelectronic properties and assembled structures.

Controlled radical polymerization (aka controlled/“living” radical polymerization or reversible deactivation radical polymerization) combines the benefits of the robust nature of conventional radical polymerization with the capability to prepare well-defined macromolecular architectures common to living polymerization techniques. This method has facilitated the synthesis of various functional polymers with predetermined molecular weights, narrow molecular weight distribution, and controlled architectures, such as star and branched polymers, block and graft copolymers, using a facile approach. The synthesis of functional polymers with controlled molecular weights, low polydispersity, and complex architectures has been possible because of recent significant progress in controlled radical polymerization techniques, such as nitroxide-mediated polymerization (NMP) [24, 25], atom transfer radical polymerization (ATRP) [26, 27], reversible addition-fragmentation chain transfer (RAFT) polymerization [28–41], single

electron transfer-living radical polymerization (SET-LRP) [42], organoheteroatom-mediated living radical polymerization [43], and organometallic-mediated radical polymerization [44]. All these systems are based on establishing a rapid dynamic equilibration between a minute amount of growing free radicals and a large majority of dormant species and are more tolerant of functional groups and impurities. Such controlled radical polymerization methods have become key tools for polymer synthesis, especially for synthesizing complex polymers with well-defined structures.

This review highlights recent developments in the design and synthesis of novel complex polymers with carbazole moieties using controlled radical polymerization techniques of carbazole-containing monomers, as shown in Scheme 1. We mainly focus on three classes of carbazole-containing polymers, as follows:

- (i) self-assembled block copolymers including amphiphilic block copolymers, block copolymers composed of “more activated” and “less activated” monomers, rod-coil-type block copolymers, and block copolymers possessing a metal ligating functionality
- (ii) branched polymers, such as star block copolymers, miktoarm star copolymers, star polymers having a metalcore, and comb-shaped copolymers;
- (iii) hybrids obtained by controlled radical polymerization of carbazole-containing monomers.

2. Carbazole-Containing Block Copolymers

Block copolymers incorporating carbazole functionality have attracted significant research interest, mainly as a result of the feasibility of using them to create highly ordered structures and their potential applications in the optoelectronic fields. Depending on the ordered structures and stacking of the carbazole moiety, the three-dimensional hierarchical structures formed by self-organization of the carbazole-containing block copolymers may lead to unique electronic and photonic functions. There has been much research for the synthesis of carbazole-containing block copolymers using controlled radical polymerization of NVC. Styrene and (meth)acrylate derivatives having carbazole moieties have also been used for the controlled synthesis of carbazole-containing block copolymers.

2.1. Controlled Radical Polymerization of *N*-Vinylcarbazole.

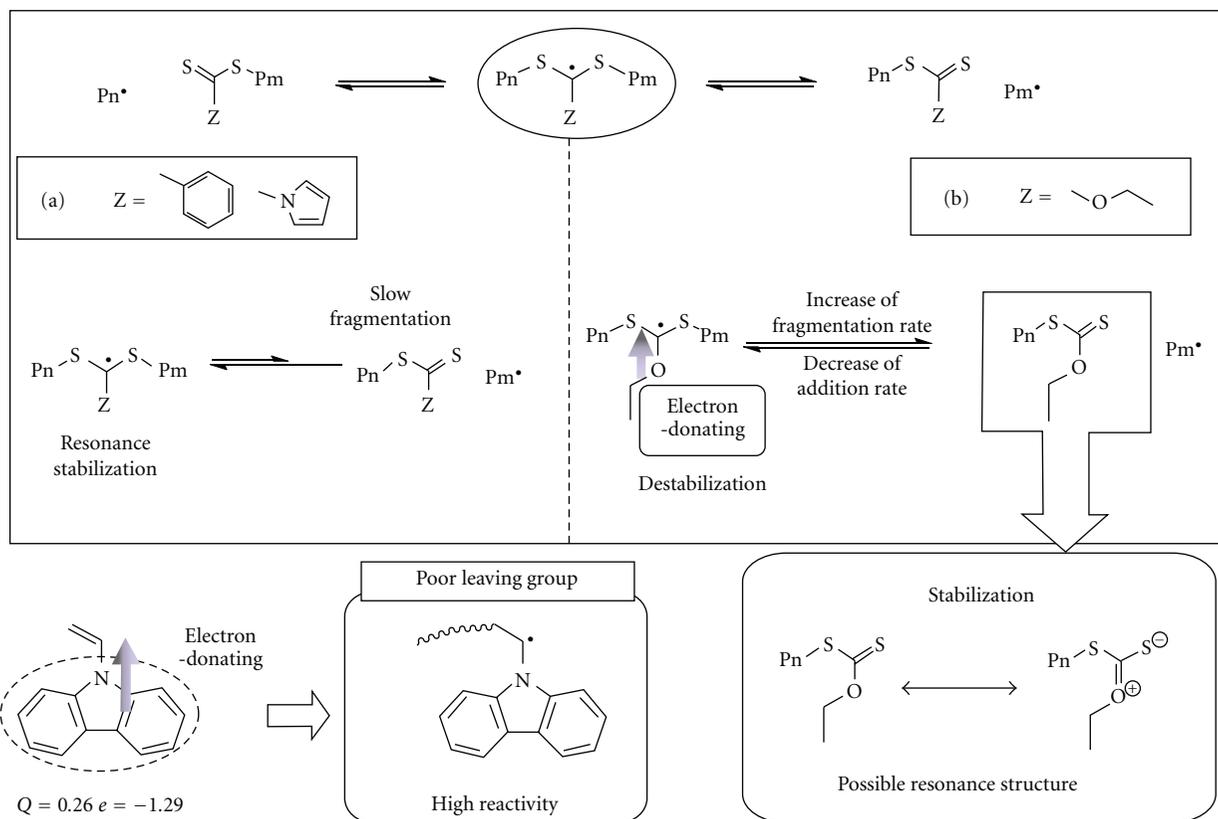
Poly(NVC) was the first and most widely studied polymeric photoconductor. NVC, a strong basic monomer, undergoes facile cationic polymerization with almost all cationic initiators to give poly(NVC). The living cationic polymerization of NVC with hydrogen iodine has also been reported [45]. Free radical initiators, such as azo compounds and peroxides, readily polymerize NVC, and radical polymerization was used in manufacturing the polymer [1]. Several attempts to synthesize poly(NVC) using controlled radical polymerization systems have been reported in the literature. For example, Fukuda et al. demonstrated that the control of NVC homopolymerization could not be achieved by a typical NMP, whereas the copolymerization with styrene under the same conditions proceeded in a living fashion [46]. Baethge et al. also reported the controlled NMP of styrene and NVC, while they demonstrated that the synthesis of the homopolymer, poly(NVC), with controlled molecular weights and a narrow polydispersity, was still problematic [47, 48]. Nowakowska et al. reported that the synthesis of poly(sodium styrenesulfonate-*b*-NVC) by NMP was possible only when the polymerization of NVC was conducted in the presence of acetic anhydride as an accelerator [49]. ATRP ($C_{60}Cl_n/CuCl/2,2'$ -bipyridine) was also used for the synthesis of poly(NVC) having a narrow polydispersity ($M_w/M_n = 1.33$). However, the actual structure of the product was a star-like architecture with a C_{60} core because of multiple chlorine atoms in one initiator molecule, $C_{60}Cl_n$, and there was no information on each poly(NVC) and its detachments from the surface of C_{60} [50]. They also demonstrated that the attempt to synthesize the block copolymer, poly(NVC-*b*-styrene), using the ATRP system provided products with bimodal molecular weight distributions [51]. These previous studies failed to provide convincing proof of the controlled character of the homopolymerization of NVC, such as a kinetic investigation, evaluation of the end groups, and a chain extension experiment. The difficulties in adapting controlled radical polymerization to NVC may also be based on the fact that the NVC propagating radical is relatively unstable and thus highly reactive, mainly because of the electron-donating carbazolyl pendant ($Q = 0.26$, $e = -1.29$) [52], leading to a tendency to undergo chain transfer and

chain termination reactions. In other words, systems suitable for inducing a fast interconversion between the dormant and the reactive radical species having a high electron density at the radical center derived from NVC were difficult to find.

However, recent advances in the field of controlled radical polymerization have resulted in successful controlled polymerization of NVC. Mori et al. recently synthesized poly(NVC) with predetermined molecular weights (M_n in the range of 3000–48000) and low polydispersities (M_w/M_n in the range of 1.15–1.20) by xanthate-mediated controlled radical polymerization [53]. The RAFT process is generally accomplished by performing a radical polymerization in the presence of a thiocarbonylthio compound, such as a dithioester, dithiocarbamate, trithiocarbonate, or xanthate, all of which act as reversible chain transfer agents (CTAs). When xanthates are employed, the terminology MADIX (macromolecular design via the interchange of xanthates) is frequently used to describe the process [54–56]. In general, the controlled radical polymerization of the *N*-vinyl and *O*-vinyl monomers was considered difficult, since the generated radical species are highly reactive due to their nonconjugated nature and strong electron-donating pendant groups. However, dithiocarbonates (xanthates) were recently reported to be useful for controlling the radical polymerization of highly reactive *O*-vinyl and *N*-vinyl monomers, such as vinyl acetate [57–60], *N*-vinylpyrrolidone [61–63], *N*-vinylcarbazole (NVC) [53], *N*-vinylindole derivatives [64], *N*-vinylphthalimide [65–67], *N*-vinylphthalimide [66], and *N*-vinylimidazolium salts [68].

Both the MADIX and RAFT processes are based on the generally accepted reversible addition-fragmentation chain transfer mechanism between an active and a dormant species. To achieve control of the radical polymerization via the RAFT/MADIX process, a delicate balance of the forward and reverse rates of addition (k_{add} and k_{-add}) and fragmentation (k_{β} and $k_{-\beta}$), together with the rates of reinitiation (k_i) and propagation (k_p), is required. Because the NVC propagating radical is a poor homolytic leaving group, the fragmentation of the RAFT-adduct radical (intermediate radical) is thought to be very slow when dithioesters are used, resulting in insufficient control of the polymerization. In contrast, the xanthate-type CTA is useful for achieving controlled radical polymerization of NVC, because it increases electron density at the radical center, which may lead to the destabilization of the RAFT-adduct radicals relative to the normal dithioester-type CTA and an increase in the fragmentation rate. The electron-donating *O*-alkyl substituents may lead to stabilization of the thiocarbonyl product of fragmentation through their conjugation with the C=S double bond, as shown in Scheme 2. This lowers the rate of addition of the propagating radicals to the sulfur atom, and consequently the overall rate of chain transfer [30, 57, 69–71]; whereas the introduction of electron-withdrawing groups in the Z moiety leads to an increase in the rate of addition [70].

The blocking order is crucial for the synthesis of well-defined block copolymers by the RAFT process. The first dithioester-terminated polymer, S=C(Z)S-A, in which the A block corresponds to the first polymer and Z is the stabilizing



SCHEME 2: Proposed mechanism of xanthate-mediated controlled radical polymerization of NVC.

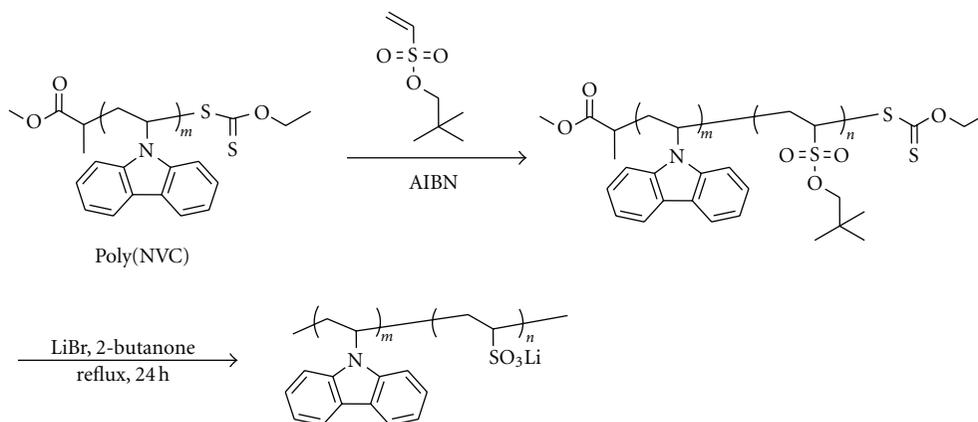
group, should have a high transfer constant in the subsequent polymerization of the second monomers to give the B block [72, 73]. The rapid conversion of macro-CTA to a block copolymer is also required to achieve a block copolymer with low polydispersity, which allows all the second blocks to be initiated at approximately the same time [74, 75].

The xanthate-mediated controlled radical polymerization of NVC was also applied for the synthesis of well-defined block copolymers involving a poly(NVC) segment. For example, a well-defined block copolymer involving a poly(lithium vinyl sulfonate) segment was synthesized by RAFT polymerization of a vinyl sulfonate ester, neopentyl ethenesulfonate, using xanthate-terminated poly(NVC) macro-CTA, followed by deprotection (Scheme 3) [76]. The resulting product can be regarded as an amphiphilic block copolymer, comprising poly(lithium vinyl sulfonate) as a strong anionic polyelectrolyte and poly(NVC) as a hydrophobic segment. Amphiphilic block copolymers, poly(NVC)-*b*-poly(*N*-vinylpyrrolidone), were prepared by xanthate-mediated RAFT polymerization (Scheme 4) [77]. The amphiphilic block copolymers dissolved in several organic solvents; however, depending on their composition, formed either micelles or large aggregates in methanol. The presence of globular aggregates was confirmed by tapping mode atomic force microscopy. The xanthate-mediated RAFT polymerization of NVC was applied for the synthesis of three types of block copolymers, poly(ethylene

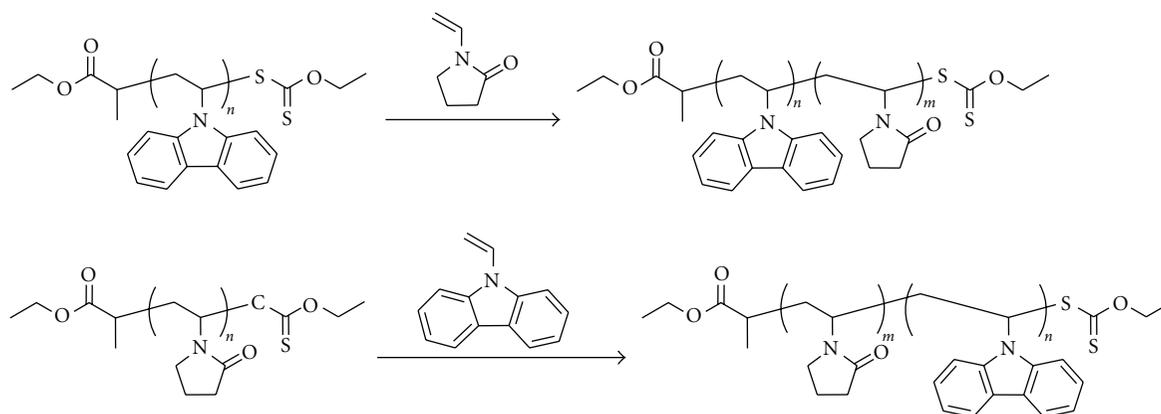
glycol)-*b*-poly(NVC), poly(NVC)-*b*-poly(vinyl acetate), and poly(NVC)-*b*-poly(vinyl alcohol), as shown in Scheme 5 [78].

Well-defined pH- and thermomultiresponsive fluorescent micelles based on the self-assembly of diblock copolymers, poly(*N*-isopropylacrylamide-*co*-NVC)-*b*-poly[2-(dimethylamino)ethyl acrylate], were obtained by RAFT copolymerization of *N*-isopropylacrylamide and NVC followed by chain extension in the presence of 2-(dimethylamino)ethyl acrylate [79]. The micelles were formed in aqueous solutions in a wide range of temperatures, and their sizes increased from 40 to 65 nm when the pH was varied from basic to acidic. Cross-linking of the poly[2-(dimethylamino)ethyl acrylate]-containing shell with 1,2-bis(2-iodoethoxy)ethane results in spherical soft nanoparticles. The presence of NVC in concentrations as low as 4% in the core of the micelles was reported to allow the nanoparticles to be tagged by fluorescence, making them well suited to therapeutic applications.

The synthesis of poly(NVC)-based block copolymers functionalized with rhenium diimine complexes or pendant terpyridine ligands was reported [80]. The copolymers were synthesized by RAFT polymerization, and they exhibited interesting morphological properties as a result of the phase separation between different blocks. It was demonstrated that the rhenium complex polymer block could function as a photosensitizer, while the terpyridine-containing polymer



SCHEME 3: Synthesis of poly(NVC)-*b*-poly(lithium vinyl sulfonate) by RAFT polymerization of neopentyl ethanesulfonate using poly(NVC) as macro-CTA and subsequent deprotection.



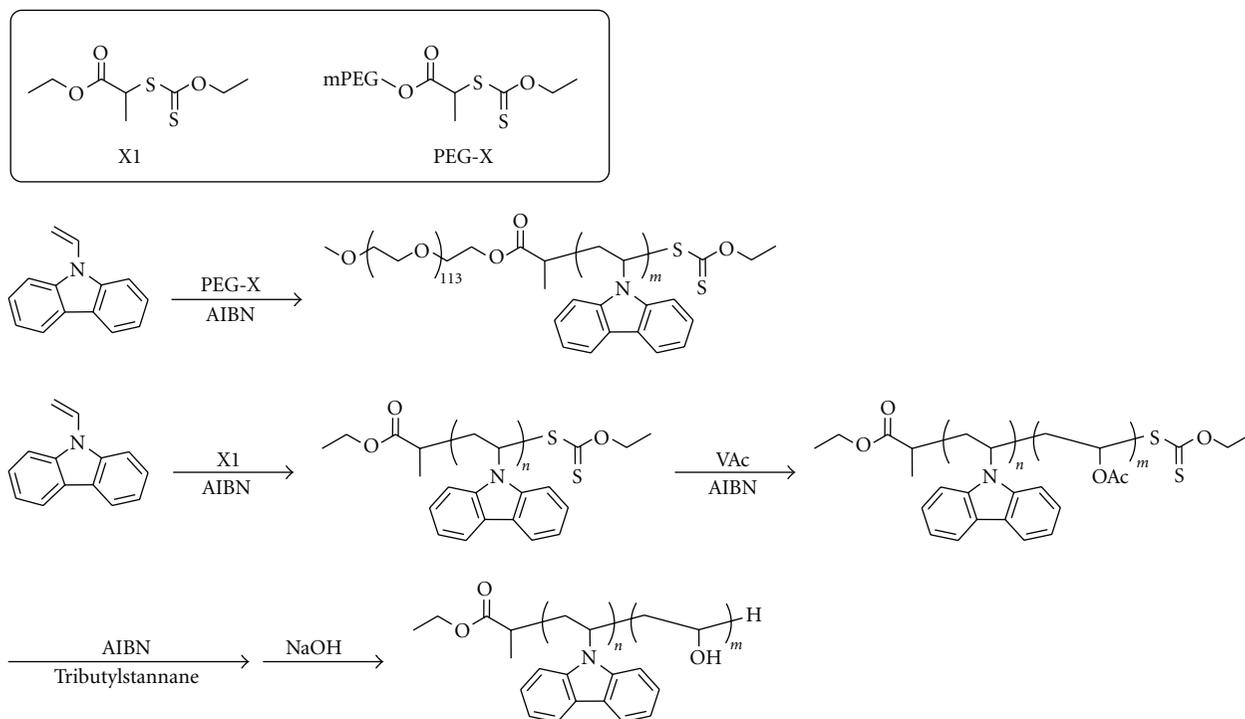
SCHEME 4: Synthesis of poly(NVC)-*b*-poly(*N*-vinylpyrrolidone) by xanthate-mediated RAFT polymerization.

block can be used as a template for nanofabrication by selective deposition of zinc complexes.

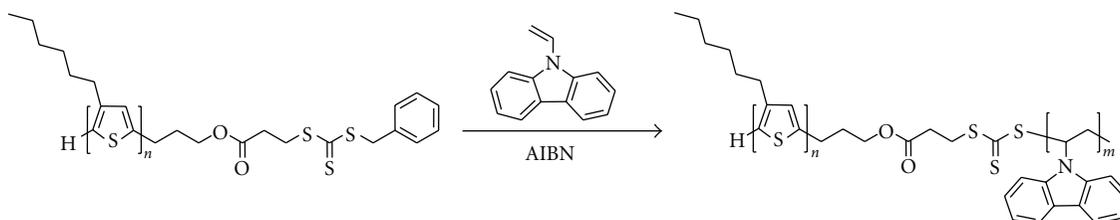
Generally, the selection of the RAFT agent is dictated by the types of monomer being polymerized. The RAFT agents (dithioesters, trithiocarbonates) suitable for controlling polymerization of “more activated” monomers (e.g., styrene, acrylates, and methacrylates) tend to inhibit polymerization of “less activated” monomers (e.g., NVC, vinyl acetate, and *N*-vinylpyrrolidone). Similarly, RAFT agents suitable for polymerizations of “less activated” monomers tend to give little or poor control over polymerizations of “more activated” monomers. Hence, the synthesis of block copolymers composed of “less activated” and “more activated” monomers was difficult. Recently, switchable RAFT polymerization using *N*-(4-pyridinyl)-*N*-methylthiocarbamates was found to provide excellent control over polymerization of “less activated” monomers and, after addition of 1 equivalent of a protic or Lewis acid, become effective in controlling polymerization of “more activated” monomers [81]. Switchable RAFT polymerization allowed the synthesis of poly(methyl acrylate)-*b*-poly(NVC) with narrow molecular weight distributions. The preparation of unimodal low dispersity block copolymers of poly(*N*,

N-dimethylacrylamide) with NVC was also conducted by switchable RAFT polymerization [82]. The controlled radical polymerizations of “less activated” monomers, NVC, vinyl acetate, and *N*-vinylpyrrolidone, were successfully achieved in the presence of a disulfide, isopropylxanthic disulfide, using AIBN as the initiator [83]. The use of RAFT polymerization for the synthesis of optoelectronic polymers was recently reviewed by Moad et al [22]. The polymerization proceeded via MADIX process, where xanthate was formed *in situ* from the reaction of AIBN and isopropylxanthic disulfide. Organoheteroatom-mediated living radical polymerization using organotellurium, organostibine, and organobismuthine chain transfer agents were also useful methods for achieving the controlled character of polymerization of conjugated and nonconjugated monomers [43].

A rod-coil block copolymer consisting of poly(3-hexylthiophene) and poly(NVC) was synthesized by RAFT polymerization of NVC using trithiocarbonate-terminated poly(3-hexylthiophene) as a macro-CTA (Scheme 6) [84]. The rod-coil block copolymer was employed for a white organic electroluminescence device. It is possible to suppress energy transfer from poly(NVC) as wide bandgap units to poly(3-hexylthiophene) as low bandgap blocks by obtaining



SCHEME 5: Synthesis of poly(ethylene glycol)-*b*-poly(NVC), poly(NVC)-*b*-poly(vinyl acetate), and poly(NVC)-*b*-poly(vinyl alcohol) by xanthate-mediated RAFT polymerization.



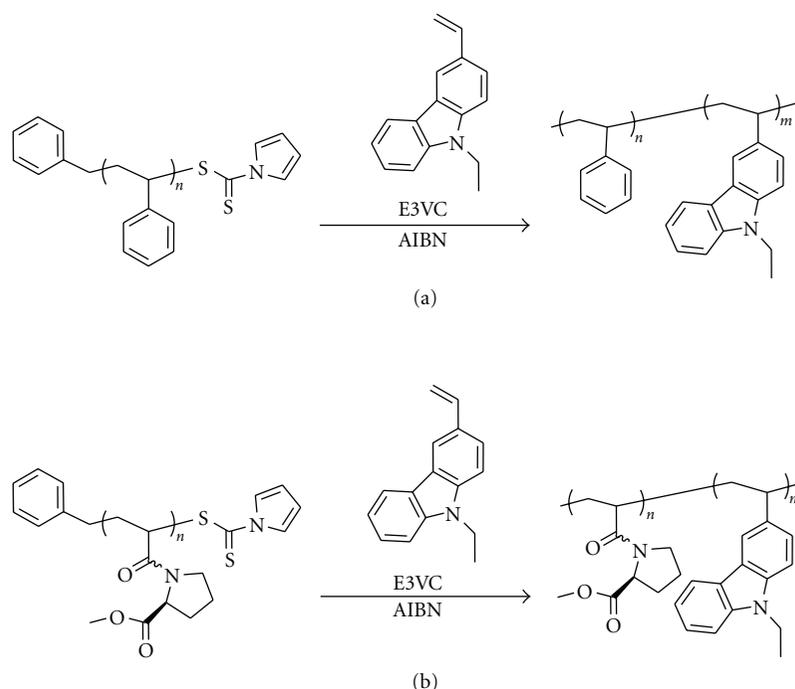
SCHEME 6: Synthesis of poly(3-hexylthiophene)-*b*-poly(NVC) by RAFT polymerization.

the phase-separated domains from thin films of the resulting block copolymer, yielding dual emissions for white electroluminescence with a CIE coordination of (0.34, 0.33).

The homopolymerization of NVC was performed with ATRP with Cu(I)/Cu(II)/2,2'-bipyridine as the catalyst system at 90°C in toluene [85]. *N*-2-Bromoethyl carbazole was used as the initiator, and the optimized ratio of Cu(I) to Cu(II) was found to be 1/0.3. The resulting poly(NVC) was used as a macroinitiator for the ATRP of methyl methacrylate, and this resulted in the formation of a block copolymer. The order of blocking is considered to be also crucial for ATRP or NMP as RAFT process. The polymerization of NVC and 3-(9H-carbazole-9-yl)propyl methacrylate (CzPMA) was carried out using various controlled radical polymerization methods, such as ATRP, single electron transfer-living radical polymerization (SET-LRP), and single electron transfer initiation followed by RAFT (SET-RAFT) [86]. In the case of NVC, well-controlled polymerization with narrow molecular weight distribution

was achieved by high-temperature ATRP, while SET-RAFT polymerization was relatively slow and controlled at ambient temperature. In the case of CzPMA, SET-RAFT was more suitable for ambient temperature polymerization. The synthesis of diblock copolymers was achieved from poly(NVC) and poly(CzPMA) macroinitiators using a flavanone-based methacrylate as the second monomer. The emission spectra of these block copolymers showed higher intensities compared with homopolymers.

2.2. Controlled Radical Polymerization of Styrene Derivatives Having Carbazole Moieties. The functional polymer containing carbazole units was successfully prepared via nitroxide-mediated radical polymerization of 9-(4-vinylbenzyl)-9H-carbazole (VBCz) [87]. New nonconjugated random copolymers containing pendant electron-donating poly(VBCz) and electron-accepting 2-(4-vinylbiphenyl)-5-(4-phenyl)-1,3,4-oxadiazole or 2-(4-vinylbiphenyl)-5-(4-phenyl)-1,3,4-oxadiazole were successfully synthesized by



SCHEME 7: Synthesis of block copolymers by RAFT polymerization of E3VC.

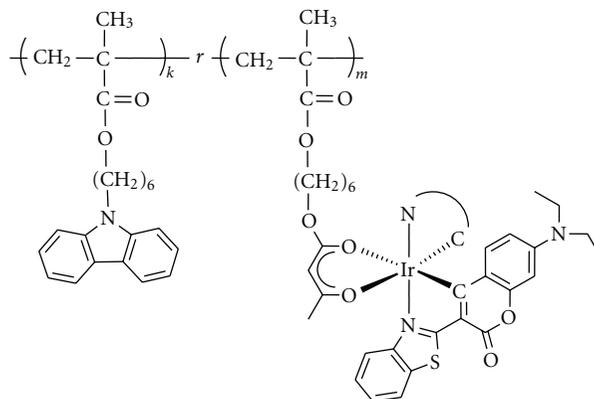
the NMP method [88]. The electrical switching behavior, based on the ITO/ polymer/Al device configuration, could be tuned through the donor/acceptor ratio or acceptor trapping ability. The controlled nitroxide-mediated homopolymerization of VBCz and the copolymerization of methyl methacrylate with varying amounts of VBCz were accomplished by using 10 mol % nitroxide relative to 2-((tert-butyl[1-(diethoxyphosphoryl)-2,2-dimethylpropyl]amino)oxy)-2-methylpropionic acid [89]. VBCz was found to be an effective controlling comonomer for NMP of methyl methacrylate, and such low levels of VBCz comonomer ensured transparency in the final copolymer. Well-defined cyclic polymers, cyclic poly(VBCz), with differing molecular weights were efficiently prepared by successive ATRP and a click reaction [90].

N-ethyl-3-vinylcarbazole (E3VC) was also employed as a carbazole-containing monomer, which can be regarded as a styrene derivative. The controlled RAFT polymerization of E3VC was performed using benzyl 1-pyrrolicarbothioate as a suitable CTA to afford well-defined poly(E3VC) in which the carbazole unit is directly bound to the polymer main chain [91]. Well-defined block copolymers with poly(E3VC) segments have been synthesized using dithiocarbamate-terminated polystyrene as a macro-CTA (Scheme 7(a)). Amino-acid-containing amphiphilic block copolymers composed of poly(E3VC) as a hydrophobic segment and poly(*N*-acryloyl-*L*-proline methyl ester) [92, 93] as a hydrophilic segment were prepared by RAFT polymerization (Scheme 7(b)) [94]. Formation of micelles consisting of a hydrophobic core of poly(E3VC) and a hydrophilic shell of poly(*N*-acryloyl-*L*-proline methyl

ester) segment. The chiroptical properties were affected by the assembled structure induced by the selective solvent and were evaluated by fluorescence and circular dichroism spectra.

N-Ethyl-2-vinylcarbazole (E2VC) is a monomer structurally similar to the styrenes, which are known to polymerize well by NMP [95]. Polymerization of E2VC from a unimolecular alkoxyamine was reported to show a molecular weight that increases steadily with time, whereas termination or decomposition of the “living” radical ends was clearly evident. Nevertheless, a sufficient fraction of the chains remained living that poly(E2VC)-*b*-polystyrene could be formed by chain extension of the poly(E2VC) macroinitiator with styrene.

2.3. Controlled Radical Polymerization of (Meth)Acrylate Derivatives Having Carbazole Moieties. Photorefractive active block copolymers were successfully synthesized via ATRP of acrylate containing liquid crystalline moieties and hole transporting carbazole moieties [96]. The photorefractive characteristics of the copolymers indicated a higher diffraction efficiency and larger coupling gain for the block copolymer, compared to the corresponding statistical random copolymer. The controlled radical polymerization of 2-(*N*-carbazolyl)ethyl methacrylate (CzEMA) and 4-(5-(4-*tert*-butylphenyl-1,3,4-oxadiazol-2-yl)phenyl) methacrylate via the RAFT process has been studied for the synthesis of functional polymers with hole- or electron-transfer ability [97]. RAFT polymerization of these monomers using cumyl dithiobenzoate as a suitable CTA and AIBN as an initiator afforded well-defined polymethacrylates having hole- and electron-transporting groups. Monomers containing a



SCHEME 8: Methacrylate copolymers containing phosphorescent Ir(III)-complex and carbazole moiety.

chromophore group, that is, 9-anthrylmethyl methacrylate and CzEMA, were copolymerized with methyl methacrylate using ATRP, resulting in two series of copolymers with various amounts of included chromophore units [98]. Luminescence comparison demonstrated more intense light emission by polymethacrylates with carbazolyl groups than by copolymers with anthryl groups. The wavelength of emitted light also differed in the range of blue-violet and blue-green fluorescence for carbazolyl and anthryl copolymers, respectively.

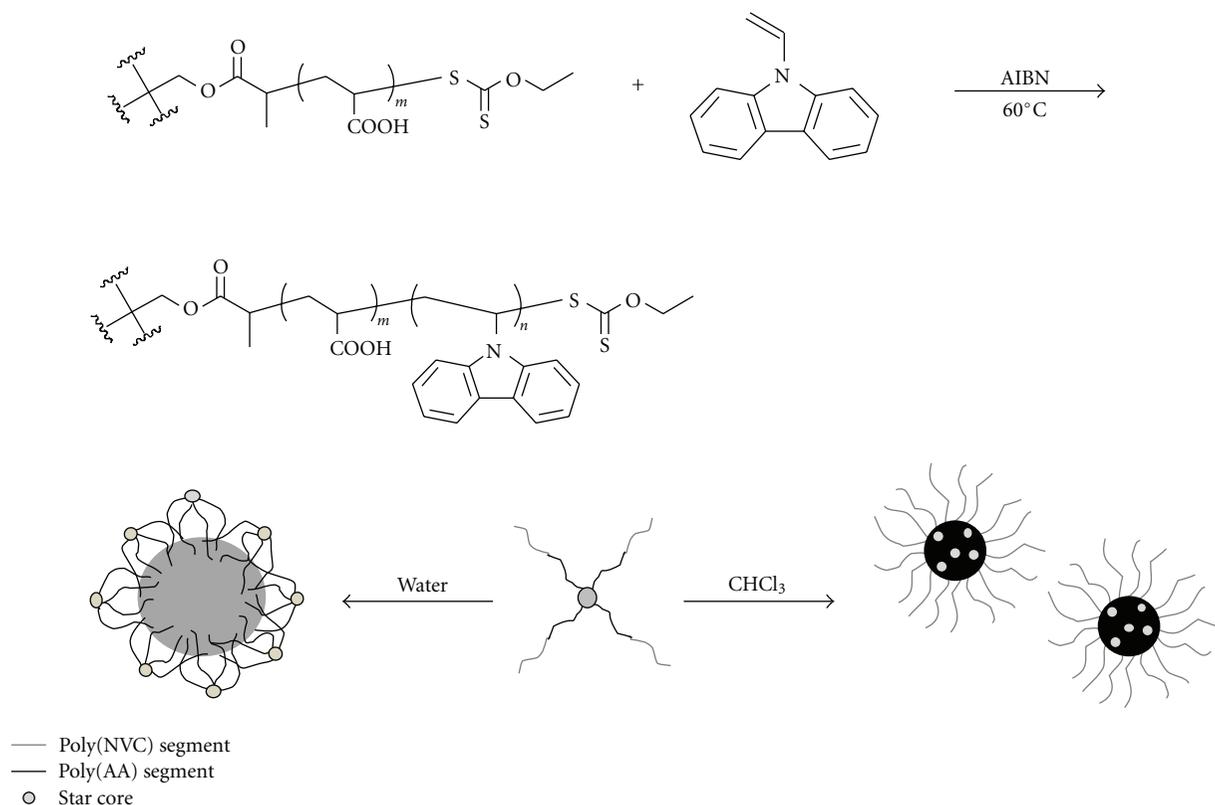
A methacrylate-functionalized phosphorescent Ir(III)-complex was copolymerized with a methacrylate-functionalized carbazole-derivative using ATRP (Scheme 8), with the aim of applying this type of host-guest-system to organic light-emitting devices [99]. In the system, the emission originated almost exclusively from the complex, suggesting efficient intrachain energy transfer.

3. Carbazole-Containing Branched Polymers

3.1. Star Polymer/Star Block Copolymer/Miktoarm Star Copolymer. There are two basic routes for synthesizing star polymers [100]: the “core first” method (polymerization from multifunctional initiators or microgels), and the “arm first” method, in which growing polymer chain ends are reacted with a multifunctional terminating agent or a divinyl compound. The use of multifunctional initiators or terminators leads to stars with a well-known (though often, low) number of arms; while the use of microgels or divinyl compounds leads to a rather broad arm number distribution, with a high average arm number. The design and synthesis of novel star copolymers having characteristic architectures, such as star block copolymers and heteroarm or miktoarm (mixed) star polymers, are attracting significant attention because of their interesting structures and properties [17, 101–106]. Amphiphilic star block copolymers and miktoarm star polymers can form a variety of superstructures as a result of self-organization, and the resulting assembled structures should be governed by the branched architecture, as well as the chemical nature of the components, their composition, and molecular weight.

The xanthate-mediated RAFT polymerization of NVC was also applied for the synthesis of star polymers [107]. RAFT polymerization was employed for the purpose, using three different xanthate-type tetrafunctional CTAs: two Z-designed CTAs having different *R* (leaving) groups in which the Z (stabilizing) groups are linked to the core, and one *R*-designed CTA. The *R*-group approach was found to be the most efficient for the controlled synthesis of four-arm poly(NVC) stars having low polydispersities and controlled molecular weights. Amphiphilic star block copolymers were synthesized by the polymerization of NVC using the poly(acrylic acid) star, which was prepared from the *R*-designed tetrafunctional CTA (Scheme 9) [108]. DLS measurements of the amphiphilic stars in THF solution, which is a good solvent for both components, suggested the existence of unimolecular star micelles. In contrast, the formations of the micelles and inverse micelles were observed in water, which is a good solvent only for the poly(acrylic acid) segment, and in CHCl_3 , which is a good solvent only for poly(NVC) segment. The absorbance and fluorescence spectra indicated that specific conformations of amphiphilic stars, like micelles and inverse micelles, affected the characteristic optoelectronic properties.

Star polymers containing chemically different arms are designated heteroarm or miktoarm (mixed arm) star polymers when they comprise two or more different kinds of arms, respectively. Their unique architectures cause them to reveal interesting properties in the solid state and in solution [109]. A novel amphiphilic A_3B miktoarm star copolymer, poly(*N*-isopropylacrylamide)₃-poly(NVC), was successfully synthesized by a combination of single-electron transfer living radical polymerization and RAFT polymerization (Scheme 10) [110]. First, the well-defined three-armed poly(*N*-isopropylacrylamide) was prepared via SET-LRP of *N*-isopropylacrylamide using a tetrafunctional bromoxanthate iniferter (Xanthate- Br_3) as the initiator and $\text{Cu}(0)/\text{PMDETA}$ as a catalyst system. Secondly, the target amphiphilic A_3B miktoarm star copolymer was prepared via RAFT polymerization of NVC employing three-armed poly(*N*-isopropylacrylamide) having a xanthate moiety as the macro-CTA. The amphiphilic A_3B miktoarm star



SCHEME 9: Synthesis and assembled structures of amphiphilic star block copolymers.

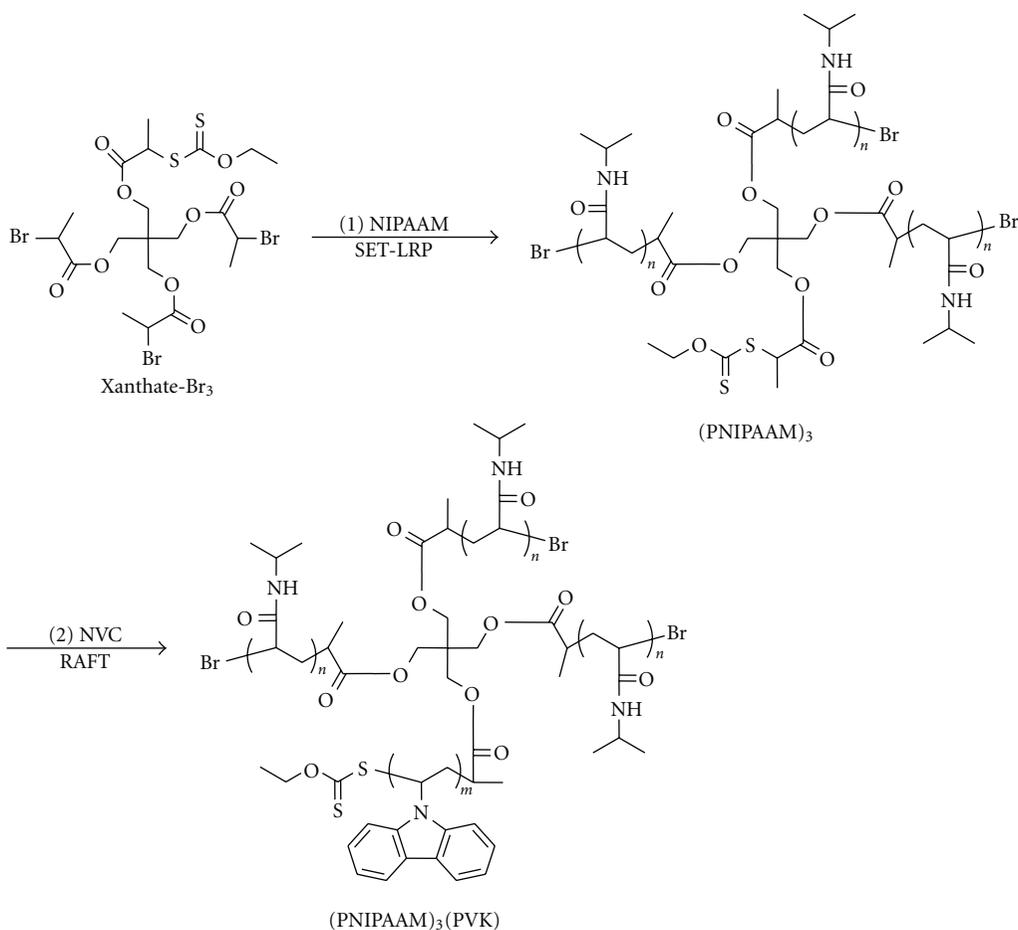
copolymer showed an increase in the fluorescence intensity of micelle with temperature and had good temperature reversibility.

Styrene-type monomer, VBCz, and methacrylate-type monomer, 2-(9H-carbazole-9-yl)ethyl methacrylate (CzEMA), were polymerized to star polymers via ATRP using zinc 5,10,15,20-tetrakis(4-(2-methyl-2-bromopropoxy) phenyl) porphyrin as an initiator (Scheme 11) [111]. The emission spectra of the two star polymers, poly(VBCz) and poly(CzEMA) stars, displayed red light emission in the solid state, while those of the two monomers showed blue light emission, suggesting the effective energy transfer from the carbazole to the Zn porphyrin core. It was demonstrated that the flexible arms of star polymers can effectively hinder π - π interaction of the porphyrin cores and prevent aggregation, which would lead to fluorescent self-quenching in the solid state.

A derivative Ru(II) complex with radical initiating sites was employed in the ATRP of functional *N*-(ω' -alkylcarbazoly) methacrylates to provide linear metallopolymers with the metal chromophores at one terminus of the polymer chain [112]. Similar Ru(II) complexes with one and three initiating sites were also employed as metalloinitiators for ATRP of *N*-(ω' -alkylcarbazoly) methacrylates with $\text{NiBr}_2(\text{PPh}_3)_2$ as a catalyst (Scheme 12) [113]. Star-like three-armed polymers could be obtained from the metalloinitiators with three initiating sites.

3.2. Comb-Shaped Copolymers. There have been very few reports of the synthesis of comb-shaped copolymers with carbazole-containing segments. These comb-shaped copolymers can be regarded as cylindrical polymer brushes having the same number of side chains as the degree of polymerization of the main chain. These cylindrical polymer brushes with carbazole-containing segments are architecturally interesting for both experimental and theoretical chemists because of the possibility of forming extended chain conformations, based on the intramolecular excluded-volume interactions between side chains densely grafted to the backbone. The homopolymerization of macromonomers, "grafting onto" and "grafting from" can be used in much the same way as conventional graft copolymers and comb-shaped copolymers. The "grafting from" method was mainly employed for the synthesis of comb-shaped copolymers with carbazole-containing segments.

The comb-shaped copolymer having poly(VBCz) side chains was prepared via NMP of VBCz using a macro-TEMPO agent, which was synthesized by anion ring-opening polymerization of 4-glycidyloxy-2,2,6,6-tetramethylpiperidine1oxyl (Scheme 13) [114]. The fluorescence, ultraviolet intensities, and cyclic voltammeteries of the comb-shaped copolymers with different molecular weights showed a regular order. It was reported that the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energy levels accompanied by bandgaps



SCHEME 10: Synthesis of A₃B miktoarm star copolymer, poly(*N*-isopropylacrylamide)₃-poly(NVC).

were adjustable via molecular weights of the polymers, which should be favorable to the application of these polymers in electronic devices.

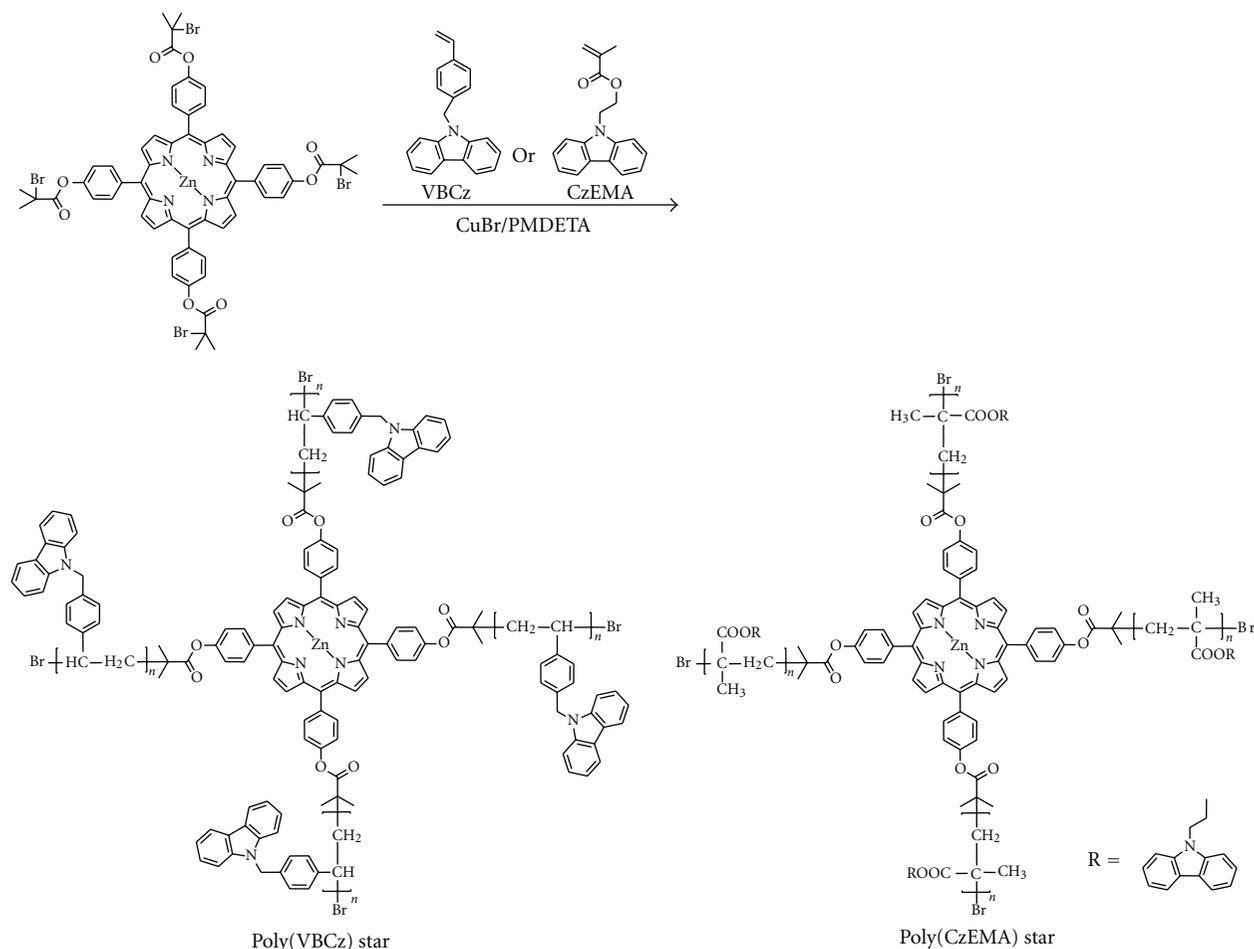
A new light-emitting and hole transporting comb-shaped copolymer was prepared via ATRP of an acrylate monomer, 3-(*N*-carbazolyl)propyl acrylate (CzPA), initiated by a macroinitiator with ATRP initiating sites distributed along a polythiophene backbone (Scheme 14). This polymer can be regarded as a rod-coil-type comb-shaped copolymer, in which the polythiophene rod is located in the backbone and the poly(CzPA) coil is located in the side chain. The energy transfer process from the poly(CzPA) side chains to the polythiophene backbone was evidenced in both the solution and film states. Electroluminescence devices fabricated from the copolymer demonstrated that the copolymer could act as both a light emissive and hole-transporting material [115].

4. Carbazole-Containing Hybrids

Carbazole-containing polymer chains attached to planar and spherical surfaces have recently attracted much interest as candidates for various optoelectronic industrial applications. Electroactive substrates, such as carbon nanotubes, fullerene,

graphene, and quantum dots, were mainly employed. The so-called “grafting onto,” and “grafting from” methods can be used for the synthesis of carbazole-containing hybrids. In the “grafting from” process, the side chains of the brush are formed via controlled radical polymerizations involving ATRP and NMP initiated by the pendant initiating groups on the surface. When RAFT polymerization was employed, the CTA moiety was attached to the surface. Well-defined polymer brushes with high grafting density and rather narrow distributions can be obtained using this method. The “grafting onto” technique was frequently used for the synthesis of the hybrids, in which the carbazole-containing polymers were attached to the substrates by adsorption or chemical reaction of end-functionalized polymers or block copolymers onto the surfaces.

The poly(NVC)-grafted multiwalled carbon nanotubes hybrid materials were synthesized by RAFT polymerization of NVC in the presence of a trithiocarbonate-type CTA functionalized covalently onto multiwalled carbon nanotubes (Scheme 15) [116]. Incorporation of poly(NVC) onto the surfaces of the multiwalled carbon nanotubes can considerably improve their solubility and processability. Hybrid materials that are suitable candidates for viable optical limiting devices exhibit significant nonlinear optical



SCHEME 11: Synthesis of star polymers via ATRP using zinc porphyrin as a tetrafunctional initiator.

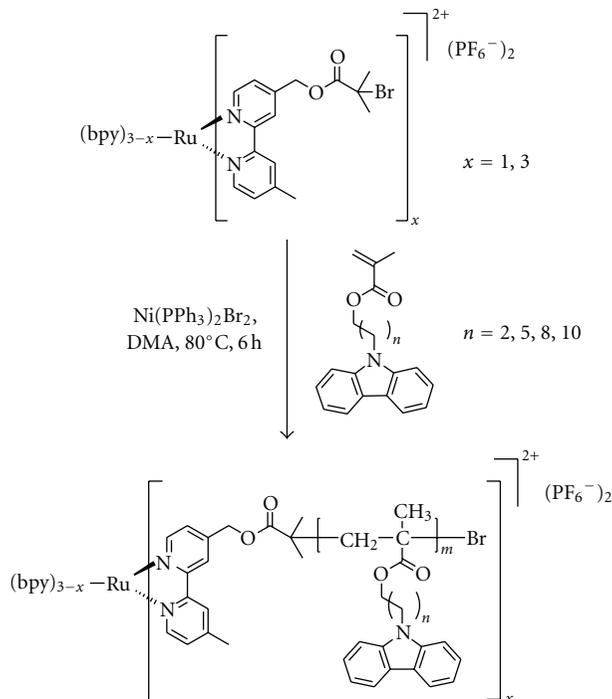
responses. Poly(NVC) chemically modified graphene oxide was obtained by RAFT polymerization of a trithiocarbonate type-CTA functionalized on graphene oxide [117, 118]. The resulting hybrid material showed good solubility in organic solvents and a significant energy bandgap in the vicinity of 2.49 eV [118]. The poly(NVC)-C₆₀ composites were synthesized by ATRP (C₆₀Cl_n/CuCl/2,2'-bipyridine) of NVC [50, 119, 120]. The photoconducting properties of poly(NVC)-C₆₀ composites were also investigated.

The CdSe-polymer composite was prepared via ATRP of NVC on functionalized CdSe quantum dots (Scheme 16) [121, 122]. It was revealed that grafting poly(NVC) onto the surface of CdSe nanocrystals would reduce the bandgap of poly(NVC) and cause a red shift in the emission peak. The nanocrystal-polymer nanocomposite was employed as the electron acceptor in polymer bulk heterojunction solar cells. Ultrasound-assisted bulk synthesis of CdS-poly(NVC) nanocomposites was reported via RAFT polymerization [123]. Poly(methyl methacrylate)/zinc oxide (ZnO) or carbazole-containing polymers, poly(CzEMA)/ZnO nanocomposites, which are composed of high molecular weight polymers with narrow molecular weight distributions and ZnO quantum dots, were prepared

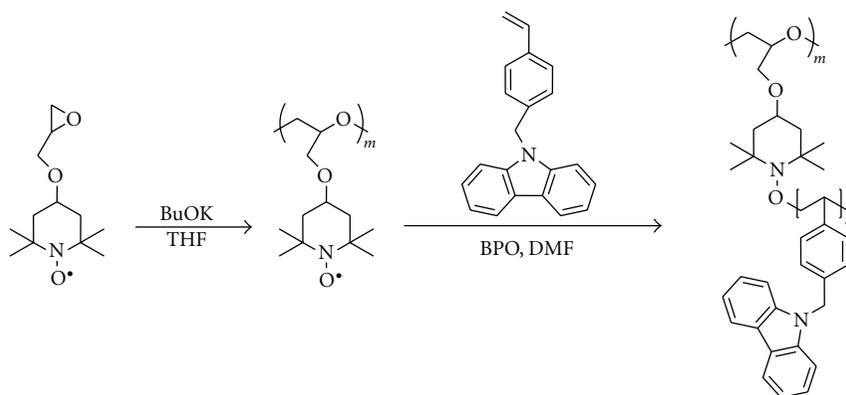
by ATRP [124]. 2-Bromo-2-methylpropionyl group was introduced onto the ZnO nanoparticle surfaces, which was employed for the surface-initiated ATRP.

The styrene derivative having a carbazole moiety (VBCz) was employed for the synthesis of bifunctional nanoparticles with fluorescence and magnetism by surface-initiated iron(III)-mediated ATRP with activators generated by electron transfer (AGET ATRP) [125]. VBCz was grafted from magnetic nanoparticles (ferroferic oxide) via AGET ATRP, using FeCl₃·6H₂O as the catalyst, tris(3,6-dioxahexyl)amine as the ligand, and ascorbic acid as the reducing agent. Another interesting system involves the synthesis of multistimuli-response hybrid nanoparticles with magnetic cores and thermoresponsive fluorescence-labeled shells by surface-initiated RAFT polymerization using carbazole-containing CTA-functionalized magnetic silica nanoparticles [126].

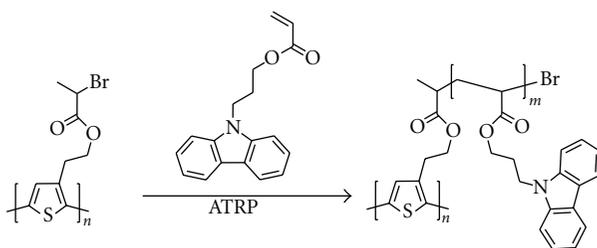
Polymer brushes refer to an assembly of polymer chains, which are tethered by one end to a surface or an interface. Surface-initiated polymerization has the advantage of allowing easy modification of surface properties by varying the composition of the polymer brush, grafting density, and the degree of polymerization. Electrochemically



SCHEME 12: Synthesis of three-armed polymer by ATRP of the carbazole-containing methacrylates with a metalloinitiator.



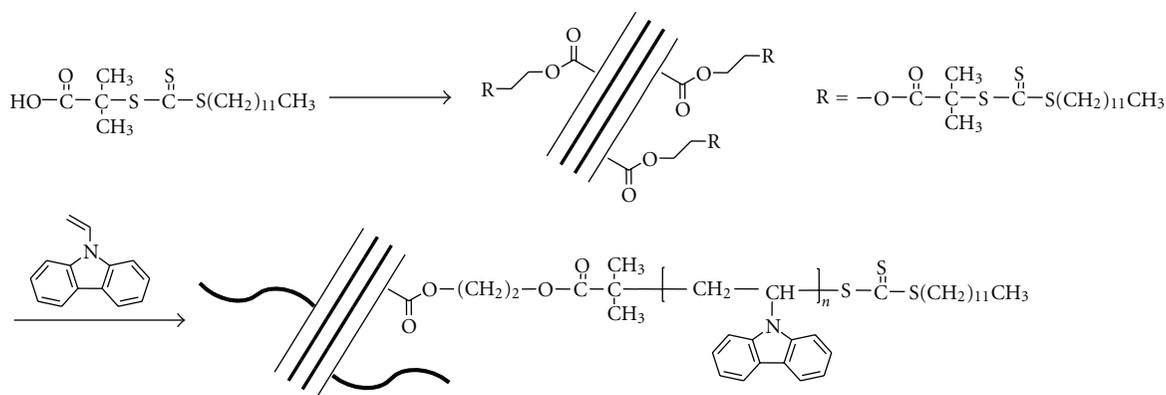
SCHEME 13: Synthesis of a comb-shaped copolymer having poly(VBCz) side chains.



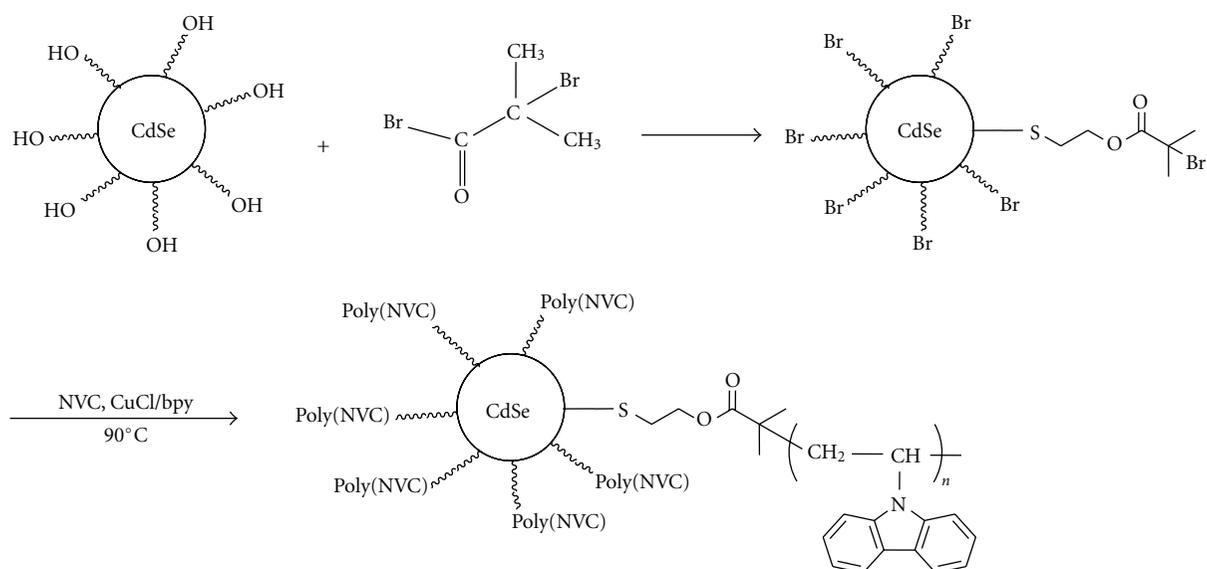
SCHEME 14: Synthesis of a comb-shaped copolymer by ATRP of CzPA from a polythiophene backbone.

crosslinked surface-grafted poly(NVC) brushes have been demonstrated as hole transport layers on a photovoltaic device using surface-initiated polymerization [127, 128]. The pendant carbazole group made the poly(NVC) an electrochemically cross-linkable precursor, capable of forming

conjugated polymer network films. The covalent linkage of the poly(NVC) brush allowed for direct electroluminescent device preparation on modified ITO, giving the advantage of strong adhesion to ITO with possible long-term stability against acid dopants and oxygen. Surface-initiated ATRP of



SCHEME 15: Synthesis of poly(NVC)-grafted multiwalled carbon nanotubes by RAFT polymerization of NVC.



SCHEME 16: Synthesis of CdSe-polymer composite by ATRP of NVC.

9-(2-(4-vinyl(benzyloxy)ethyl)-9H-carbazole (VBOCz) was also employed for the synthesis of carbazole-based polymer brushes on silicon surfaces [129]. Conductance switching at a voltage of about 2.1 V was observed in the memory device based on the brushes.

5. Conclusion

This review has summarized the approaches to synthesis of a variety of tailor-made polymers containing carbazole functionality. The combination of different polymerization mechanisms, self-organization of block copolymers, and surface-initiated polymerization have allowed great advances in the design and synthesis of various nano- and mesoscale polymeric materials with sophisticated structures, in addition to recent progress in controlled radical polymerization techniques. The synthetic methodologies for novel architectures, characteristic bulk, and solution properties related to the self-organization process, and a wide range of applications of block copolymers containing poly(NVC)

segments have been extensively investigated in the last decade. Controlled radical polymerization of NVC, styrene, and (meth)acrylate derivatives having the carbazole moiety were well advanced, leading to the well-controlled synthesis of complex macromolecules, such as star polymers, star block copolymers, and polymer brushes with the carbazole functionality. The carbazole-containing complex macromolecules can be combined with a broad range of functional groups, such as fluorophores, electroactive groups, dyes, and other biorelated materials. These carbazole-containing polymers with well-defined architectures can provide viable tailored materials with unique electronic and photonic properties for a wide range of applications, including polymeric light-emitting materials, and organic photorefractive materials.

References

- [1] J. V. Grazulevicius, P. Strohriegel, J. Pielichowski, and K. Pielichowski, "Carbazole-containing polymers: synthesis,

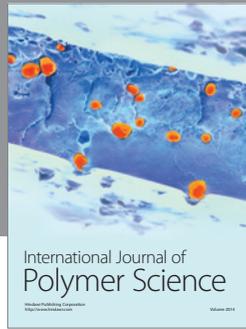
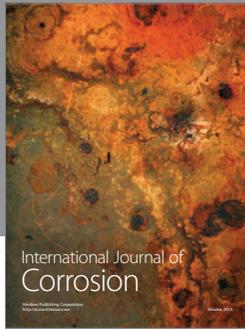
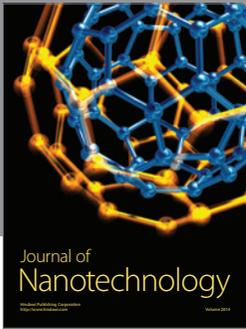
- properties and applications," *Progress in Polymer Science*, vol. 28, no. 9, pp. 1297–1353, 2003.
- [2] P. L. T. Boudreault, S. Beaupré, and M. Leclerc, "Polycarbazoles for plastic electronics," *Polymer Chemistry*, vol. 1, no. 2, pp. 127–136, 2010.
 - [3] S. Beaupré, P. L. T. Boudreault, and M. Leclerc, "Solar-energy production and energy-efficient lighting: photovoltaic devices and white-light-emitting diodes using poly(2,7-fluorene), poly(2,7-carbazole), and poly(2,7-dibenzosilole) derivatives," *Advanced Materials*, vol. 22, no. 8, pp. E6–E27, 2010.
 - [4] J. Li and A. C. Grimsdale, "Carbazole-based polymers for organic photovoltaic devices," *Chemical Society Reviews*, vol. 39, no. 7, pp. 2399–2410, 2010.
 - [5] T. Uryu, H. Ohkawa, and R. Oshima, "Synthesis and High Hole Mobility of Isotactic Poly(2-*N*-carbazolethyl acrylate)," *Macromolecules*, vol. 20, p. 705, 1987.
 - [6] C. J. Hu, R. Oshima, S. Sato, and M. Seno, "Synthesis and photoinduced discharge characteristics of polyacrylates with pendant carbazole group," *Journal of Polymer Science Part C*, vol. 26, no. 10, pp. 441–446, 1988.
 - [7] M. Keyanpour-Rad, A. Ledwith, A. Hallam et al., "Some photophysical properties of five new carbazole-containing methacrylate polymers," *Macromolecules*, vol. 11, no. 6, pp. 1114–1118, 1978.
 - [8] F. S. Du, Z. C. Li, W. Hong, Q. Y. Cao, and F. M. Li, "Vinyl monomers bearing chromophore moieties and their polymers. XI. Synthesis and photochemical behavior of carbazole-containing methacrylic monomers and their polymers," *Journal of Polymer Science Part A*, vol. 38, no. 4, pp. 679–688, 2000.
 - [9] A. Ledwith, N. J. Rowley, and S. M. Walker, "Fluorescence emission from poly[2-(9-ethyl)carbazolyl-methylmethacrylate]," *Polymer*, vol. 22, no. 4, pp. 435–436, 1981.
 - [10] S. Barik and S. Valiyaveetil, "Synthesis and self-assembly of copolymers with pendant electroactive units," *Macromolecules*, vol. 41, no. 17, pp. 6376–6386, 2008.
 - [11] T. Kanbara, Y. Yokokawa, and K. Hasegawa, "Palladium-catalyzed modification of poly(*p*-bromostyrene) with carbazole and related heteroarenes containing an N-H bond and their properties," *Journal of Polymer Science Part A*, vol. 38, no. 1, pp. 28–34, 2000.
 - [12] Y. S. Cho, S. W. Kim, C. S. Ihn, and J. S. Lee, "Anionic polymerization of 4-(9-carbazolyl)methylstyrene," *Polymer*, vol. 42, no. 18, pp. 7611–7616, 2001.
 - [13] S. Förster and T. Plantenberg, "From self-organizing polymers to nanohybrid and biomaterials," *Angewandte Chemie International Edition*, vol. 41, no. 5, pp. 688–714, 2002.
 - [14] T. Liu, C. Burger, and B. Chu, "Nanofabrication in polymer matrices," *Progress in Polymer Science*, vol. 28, no. 1, pp. 5–26, 2003.
 - [15] D. E. Discher and A. Eisenberg, "Polymer vesicles," *Science*, vol. 297, no. 5583, pp. 967–973, 2002.
 - [16] M. Sauer and W. Meier, "Polymer nanocontainers with controlled permeability," *Australian Journal of Chemistry*, vol. 54, no. 3, pp. 149–151, 2001.
 - [17] G. Riess, "Micellization of block copolymers," *Progress in Polymer Science*, vol. 28, no. 7, pp. 1107–1170, 2003.
 - [18] F. J. M. Hoeben, P. Jonkheijm, E. W. Meijer, and A. P. H. J. Schenning, "About supramolecular assemblies of π -conjugated systems," *Chemical Reviews*, vol. 105, no. 4, pp. 1491–1546, 2005.
 - [19] J. Liu, E. Sheina, T. Kowalewski, and R. D. McCullough, "Tuning the electrical conductivity and self-assembly of regioregular polythiophene by block copolymerization: nanowire morphologies in new di- and triblock copolymers," *Angewandte Chemie International Edition*, vol. 41, no. 2, pp. 329–332, 2002.
 - [20] R. A. Segalman, B. McCulloch, S. Kirmayer, and J. J. Urban, "Block copolymers for organic optoelectronics," *Macromolecules*, vol. 42, no. 23, pp. 9205–9216, 2009.
 - [21] I. Botiz and S. B. Darling, "Optoelectronics using block copolymers," *Materials Today*, vol. 13, no. 5, pp. 42–51, 2010.
 - [22] G. Moad, M. Chen, M. Häussler, A. Postma, E. Rizzardo, and S. H. Thang, "Functional polymers for optoelectronic applications by RAFT polymerization," *Polymer Chemistry*, vol. 2, no. 3, pp. 492–519, 2011.
 - [23] A. de Cuendias, R. C. Hiorns, E. Cloutet, L. Vignau, and H. Cramail, "Conjugated rod-coil block copolymers and optoelectronic applications," *Polymer International*, vol. 59, no. 11, pp. 1452–1476, 2010.
 - [24] C. J. Hawker, A. W. Bosman, and E. Harth, "New polymer synthesis by nitroxide mediated living radical polymerizations," *Chemical Reviews*, vol. 101, no. 12, pp. 3661–3688, 2001.
 - [25] R. B. Grubbs, "Nitroxide-mediated radical polymerization: limitations and versatility," *Polymer Reviews*, vol. 51, no. 2, pp. 104–137, 2011.
 - [26] K. Matyjaszewski and J. Xia, "Atom transfer radical polymerization," *Chemical Reviews*, vol. 101, no. 9, pp. 2921–2990, 2001.
 - [27] M. Kamigaito, T. Ando, and M. Sawamoto, "Metal-catalyzed living radical polymerization," *Chemical Reviews*, vol. 101, no. 12, pp. 3689–3745, 2001.
 - [28] J. Chiefari, Y. K. Chong, F. Ercole et al., "Living free-radical polymerization by reversible addition—fragmentation chain transfer: the RAFT process," *Macromolecules*, vol. 31, no. 16, pp. 5559–5562, 1998.
 - [29] C. Barner-Kowollik, T. P. Davis, J. P. A. Heuts, M. H. Stenzel, P. Vana, and M. Whittaker, "RAFTing down under: tales of missing radicals, fancy architectures, and mysterious holes," *Journal of Polymer Science Part A*, vol. 41, no. 3, pp. 365–375, 2003.
 - [30] G. Moad, E. Rizzardo, and S. H. Thang, "Living radical polymerization by the RAFT process," *Australian Journal of Chemistry*, vol. 58, no. 6, pp. 379–410, 2005.
 - [31] C. L. McCormick and A. B. Lowe, "Aqueous RAFT polymerization: recent developments in synthesis of functional water-soluble (Co)polymers with controlled structures," *Accounts of Chemical Research*, vol. 37, no. 5, pp. 312–325, 2004.
 - [32] S. Perrier and P. Takolpuckdee, "Macromolecular design via reversible addition-fragmentation chain transfer (RAFT)/xanthates (MADIX) polymerization," *Journal of Polymer Science Part A*, vol. 43, no. 22, pp. 5347–5393, 2005.
 - [33] A. Favier and M. T. Charreyre, "Experimental requirements for an efficient control of free-radical polymerizations via the reversible addition-fragmentation chain transfer (RAFT) process," *Macromolecular Rapid Communications*, vol. 27, no. 9, pp. 653–692, 2006.
 - [34] G. Moad, E. Rizzardo, and S. H. Thang, "Living radical polymerization by the RAFT process—a first update," *Australian Journal of Chemistry*, vol. 59, no. 10, pp. 669–692, 2006.
 - [35] A. B. Lowe and C. L. McCormick, "Reversible addition-fragmentation chain transfer (RAFT) radical polymerization and the synthesis of water-soluble (co)polymers under homogeneous conditions in organic and aqueous media," *Progress in Polymer Science*, vol. 32, no. 3, pp. 283–351, 2007.

- [36] C. Barner-Kowollik, M. Buback, B. Charleux et al., "Mechanism and kinetics of dithiobenzoate-mediated RAFT polymerization. I. The current situation," *Journal of Polymer Science Part A*, vol. 44, no. 20, pp. 5809–5831, 2006.
- [37] M. L. Coote, E. H. Krenske, and E. I. Izgorodina, "Computational studies of RAFT polymerization-mechanistic insights and practical applications," *Macromolecular Rapid Communications*, vol. 27, no. 7, pp. 473–497, 2006.
- [38] L. Barner, T. P. Davis, M. H. Stenzel, and C. Barner-Kowollik, "Complex macromolecular architectures by reversible addition fragmentation chain transfer chemistry: theory and practice," *Macromolecular Rapid Communications*, vol. 28, no. 5, pp. 539–559, 2007.
- [39] A. Goto and T. Fukuda, "Kinetics of living radical polymerization," *Progress in Polymer Science*, vol. 29, no. 4, pp. 329–385, 2004.
- [40] G. Moad, E. Rizzardo, and S. H. Thang, "Radical addition-fragmentation chemistry in polymer synthesis," *Polymer*, vol. 49, no. 5, pp. 1079–1131, 2008.
- [41] C. Barner-Kowollik, *Handbook of RAFT Polymerization*, Wiley-VCH, Weinheim, Germany, 2007.
- [42] B. M. Rosen and V. Percec, "Single-electron transfer and single-electron transfer degenerative chain transfer living radical polymerization," *Chemical Reviews*, vol. 109, no. 11, pp. 5069–5119, 2009.
- [43] S. Yamago, "Precision polymer synthesis by degenerative transfer controlled/living radical polymerization using organotellurium, organostibine, and organobismuthine chain-transfer agents," *Chemical Reviews*, vol. 109, no. 11, pp. 5051–5068, 2009.
- [44] M. Hurtgen, C. Detrembleur, C. Jerome, and A. Debuigne, "Insight into organometallic-mediated radical polymerization," *Polymer Reviews*, vol. 51, no. 2, pp. 188–213, 2011.
- [45] M. Sawamoto, J. Fujimori, and T. Higashimura, "Living cationic polymerization of N-vinylcarbazole initiated by hydrogen iodide," *Macromolecules*, vol. 20, no. 5, pp. 916–920, 1987.
- [46] T. Fukuda, T. Terauchi, A. Goto, Y. Tsujii, T. Miyamoto, and Y. Shimizu, "Well-defined block copolymers comprising styrene-acrylonitrile random copolymer sequences synthesized by "living" radical polymerization," *Macromolecules*, vol. 29, no. 8, pp. 3050–3052, 1996.
- [47] H. Baethge, S. Butz, C. H. Han, and G. Schmidt-Naake, "Rate enhancement of the N-oxyl-controlled free radical copolymerization of styrene with N-vinylcarbazole," *Die Angewandte Makromolekulare Chemie*, vol. 267, pp. 52–56, 1999.
- [48] H. Baethge, S. Butz, and G. Schmidt-Naake, "'Living' free radical copolymerization of styrene and N-vinylcarbazole," *Macromolecular Rapid Communications*, vol. 18, no. 10, pp. 911–916, 1997.
- [49] M. Nowakowska, S. Zapotoczny, and A. Karczmarczyk, "Polymeric photosensitizers. Part 4. Synthesis of poly(sodium styrenesulfonate-block-N-vinylcarbazole) by nitroxide-mediated free radical polymerization," *Polymer*, vol. 42, no. 5, pp. 1817–1823, 2001.
- [50] J. Hua, D. B. Chen, Y. L. Yu et al., "Preparation of C60 bonded poly(N-vinylcarbazole) with C60Cl_n/CuCl/Bpy catalyst system," *Polymer Bulletin*, vol. 48, no. 2, pp. 135–141, 2002.
- [51] J. Hua, D. Chen, X. Jing, L. Xu, Y. Yu, and Y. Zhang, "Preparation and photoconducting property of C60Cl_n-m-bonded poly(N-vinylcarbazole) with C60Cl_n/CuCl/Bpy catalyst system," *Journal of Applied Polymer Science*, vol. 87, no. 4, pp. 606–609, 2003.
- [52] J. Brandrup and E. H. Immergut, *Polymer Handbook*, John Wiley & Sons, New York, NY, USA, 3rd edition, 1991.
- [53] H. Mori, H. Ookuma, S. Nakano, and T. Endo, "Xanthate-mediated controlled radical polymerization of N-vinylcarbazole," *Macromolecular Chemistry and Physics*, vol. 207, no. 12, pp. 1005–1017, 2006.
- [54] D. Charmot, P. Corpart, H. Adam, S. Z. Zard, T. Biadatti, and G. Bouhadir, "Controlled radical polymerization in dispersed media," *Macromolecular Symposia*, vol. 150, pp. 23–32, 2000.
- [55] D. Taton, A. Z. Wilczewska, and M. Destarac, "Direct synthesis of double hydrophilic statistical di- and triblock copolymers comprised of acrylamide and acrylic acid units via the MADIX process," *Macromolecular Rapid Communications*, vol. 22, no. 18, pp. 1497–1503, 2001.
- [56] M. Destarac, D. Taton, S. Z. Zard, T. Saleh, and Y. Six, "On the importance of xanthate substituents in the MADIX process," in *Advances in Controlled/Living Radical Polymerization*, K. Matyjaszewski, Ed., vol. 854 of *ACS Symposium Series*, chapter 37, pp. 536–550, American Chemical Society, Washington, DC, USA, 2003.
- [57] M. H. Stenzel, L. Cummins, G. E. Roberts, T. P. Davis, P. Vana, and C. Barner-Kowollik, "Xanthate mediated living polymerization of vinyl acetate: a systematic variation in MADIX/RAFT agent structure," *Macromolecular Chemistry and Physics*, vol. 204, no. 9, pp. 1160–1168, 2003.
- [58] M. L. Coote and L. Radom, "Substituent effects in xanthate-mediated polymerization of vinyl acetate: Ab initio evidence for an alternative fragmentation pathway," *Macromolecules*, vol. 37, no. 2, pp. 590–596, 2004.
- [59] M. H. Stenzel, T. P. Davis, and C. Barner-Kowollik, "Poly(vinyl alcohol) star polymers prepared via MADIX/RAFT polymerisation," *Chemical Communications*, vol. 10, no. 13, pp. 1546–1547, 2004.
- [60] M. Destarac, D. Charmot, X. Franck, and S. Z. Zard, "Dithiocarbamates as universal reversible addition-fragmentation chain transfer agents," *Macromolecular Rapid Communications*, vol. 21, no. 15, pp. 1035–1039, 2000.
- [61] T. L. U. Nguyen, K. Eagles, T. P. Davis, C. Barner-Kowollik, and M. H. Stenzel, "Investigation of the influence of the architectures of poly(vinyl pyrrolidone) polymers made via the reversible addition-fragmentation chain transfer/macromolecular design via the interchange of xanthates mechanism on the stabilization of suspension polymerizations," *Journal of Polymer Science Part A*, vol. 44, no. 15, pp. 4372–4383, 2006.
- [62] D. Wan, K. Satoh, M. Kamigaito, and Y. Okamoto, "Xanthate-mediated radical polymerization of N-vinylpyrrolidone in fluoroalcohols for simultaneous control of molecular weight and tacticity," *Macromolecules*, vol. 38, no. 25, pp. 10397–10405, 2005.
- [63] R. Devasia, R. L. Bindu, R. Borsali, N. Mougin, and Y. Gnanou, "Controlled radical polymerization of N-vinylpyrrolidone by reversible addition-fragmentation chain transfer process," *Macromolecular Symposia*, vol. 229, pp. 8–17, 2005.
- [64] Y. Maki, H. Mori, and T. Endo, "Xanthate-mediated controlled radical polymerization of N-vinylindole derivatives," *Macromolecules*, vol. 40, no. 17, pp. 6119–6130, 2007.
- [65] Y. Maki, H. Mori, and T. Endo, "Controlled RAFT polymerization of N-vinylphthalimide and its hydrazinolysis to poly(vinyl amine)," *Macromolecular Chemistry and Physics*, vol. 208, no. 24, pp. 2589–2599, 2007.
- [66] Y. Maki, H. Mori, and T. Endo, "Synthesis of well-defined alternating copolymers by RAFT copolymerization of

- N-vinylnaphthalimide," *Macromolecules*, vol. 41, no. 22, pp. 8397–8404, 2008.
- [67] Y. Maki, H. Mori, and T. Endo, "Synthesis of amphiphilic and double-hydrophilic block copolymers containing polyvinyl amine segments by RAFT polymerization of N-vinylphthalimide," *Macromolecular Chemistry and Physics*, vol. 211, no. 1, pp. 45–56, 2010.
- [68] H. Mori, M. Yanagi, and T. Endo, "RAFT polymerization of N-vinylimidazolium salts and synthesis of thermoresponsive ionic liquid block copolymers," *Macromolecules*, vol. 42, no. 21, pp. 8082–8092, 2009.
- [69] G. Moad, J. Chiefari, Y. K. Chong et al., "Living free radical polymerization with reversible addition—fragmentation chain transfer (the life of RAFT)," *Polymer International*, vol. 49, no. 9, pp. 993–1001, 2000.
- [70] M. Destarac, W. Bzducha, D. Taton, I. Gauthier-Gillaizeau, and S. Z. Zard, "Xanthates as chain-transfer agents in controlled radical polymerization (MADIX): structural effect of the O-alkyl group," *Macromolecular Rapid Communications*, vol. 23, no. 17, pp. 1049–1054, 2002.
- [71] A. Favier, C. Barner-Kowollik, T. P. Davis, and M. H. Stenzel, "A detailed on-line FT/NIR and ¹H NMR spectroscopic investigation into factors causing inhibition in xanthate-mediated vinyl acetate polymerization," *Macromolecular Chemistry and Physics*, vol. 205, no. 7, pp. 925–936, 2004.
- [72] B. Y. K. Chong, T. P. T. Le, G. Moad, E. Rizzardo, and S. H. Thang, "More versatile route to block copolymers and other polymers of complex architecture by living radical polymerization: the RAFT process," *Macromolecules*, vol. 32, no. 6, pp. 2071–2074, 1999.
- [73] R. T. A. Mayadunne, E. Rizzardo, J. Chiefari et al., "Living polymers by the use of trithiocarbonates as reversible addition-fragmentation chain transfer (RAFT) agents: ABA triblock copolymers by radical polymerization in two steps," *Macromolecules*, vol. 33, no. 2, pp. 243–245, 2000.
- [74] Y. A. Vasilieva, D. B. Thomas, C. W. Scales, and C. L. McCormick, "Direct controlled polymerization of a cationic methacrylamido monomer in aqueous media via the RAFT process," *Macromolecules*, vol. 37, no. 8, pp. 2728–2737, 2004.
- [75] P. Vana, T. P. Davis, and C. Barner-Kowollik, "Kinetic analysis of reversible addition fragmentation chain transfer (RAFT) polymerizations: conditions for inhibition, retardation, and optimum living polymerization," *Macromolecular Theory and Simulations*, vol. 11, no. 8, pp. 823–835, 2002.
- [76] H. Mori, E. Kudo, Y. Saito, A. Onuma, and M. Morishima, "RAFT polymerization of vinyl sulfonate esters for the controlled synthesis of poly(lithium vinyl sulfonate) and sulfonated block copolymers," *Macromolecules*, vol. 43, no. 17, pp. 7021–7032, 2010.
- [77] C. F. Huang, J. A. Yoon, and K. Matyjaszewski, "Synthesis of N-vinylcarbazole-N-vinylpyrrolidone amphiphilic block copolymers by xanthate-mediated controlled radical polymerization," *Canadian Journal of Chemistry*, vol. 88, no. 3, pp. 228–235, 2010.
- [78] N. Hu, W. X. Ji, Y. Y. Tong, Z. C. Li, and E. Q. Chen, "Synthesis of diblock copolymers containing poly(N-vinylcarbazole) by reversible addition-fragmentation chain transfer polymerization," *Journal of Polymer Science Part A*, vol. 48, no. 20, pp. 4621–4626, 2010.
- [79] N. Suchao-in, S. Chirachanchai, and S. Perrier, "pH- and thermo-multi-responsive fluorescent micelles from block copolymers via reversible addition fragmentation chain transfer (RAFT) polymerization," *Polymer*, vol. 50, no. 17, pp. 4151–4158, 2009.
- [80] W. Y. Tam, C. S. K. Mak, A. M. C. Ng, A. B. Djurišič, and W. K. Chan, "Multifunctional poly(N-vinylcarbazole)-based block copolymers and their nanofabrication and photosensitizing properties," *Macromolecular Rapid Communications*, vol. 30, no. 8, pp. 622–626, 2009.
- [81] M. Benaglia, J. Chiefari, Y. K. Chong, G. Moad, E. Rizzardo, and S. H. Thang, "Universal (Switchable) RAFT agents," *Journal of the American Chemical Society*, vol. 131, no. 20, pp. 6914–6915, 2009.
- [82] D. J. Keddie, C. Guerrero-Sanchez, G. Moad, E. Rizzardo, and S. H. Thang, "Switchable reversible addition-fragmentation chain transfer (raft) polymerization in aqueous solution, n, n -dimethylacrylamide," *Macromolecules*, vol. 44, no. 17, pp. 6738–6745, 2011.
- [83] Y. Yan, W. Zhang, Y. Qiu et al., "Universal xanthate-mediated controlled free radical polymerizations of the "less activated" vinyl monomers," *Journal of Polymer Science Part A*, vol. 48, no. 22, pp. 5206–5214, 2010.
- [84] M. Heo, J. Kim, J. Y. Kim, and C. Yang, "A first approach to white organic electroluminescence device from a single rod-coil poly[thiophene-block-(N-vinylcarbazole)] diblock copolymer," *Macromolecular Rapid Communications*, vol. 31, no. 23, pp. 2047–2052, 2010.
- [85] A. S. Brar and S. Kaur, "Atom transfer radical polymerization of N-vinyl carbazole: optimization to characterization," *Journal of Polymer Science Part A*, vol. 44, no. 5, pp. 1745–1757, 2006.
- [86] N. Haridharan and R. Dhamodharan, "Controlled polymerization of carbazole-based vinyl and methacrylate monomers at ambient temperature: a comparative study through ATRP, SET, and SET-RAFT polymerizations," *Journal of Polymer Science Part A*, vol. 49, no. 4, pp. 1021–1032, 2011.
- [87] W. Zhang, Y. Yan, N. Zhou et al., "Controlled synthesis and fluorescent properties of poly(9-(4-vinylbenzyl)-9H-carbazole) via nitroxide-mediated living free-radical polymerization," *European Polymer Journal*, vol. 44, no. 10, pp. 3300–3305, 2008.
- [88] Y. K. Fang, C. L. Liu, and W. C. Chen, "New random copolymers with pendant carbazole donor and 1,3,4-oxadiazole acceptor for high performance memory device applications," *Journal of Materials Chemistry*, vol. 21, no. 13, pp. 4778–4786, 2011.
- [89] B. Lessard, E. J. Y. Ling, M. S. T. Morin, and M. Marić, "Nitroxide-mediated radical copolymerization of methyl methacrylate controlled with a minimal amount of 9-(4-vinylbenzyl)-9H-carbazole," *Journal of Polymer Science Part A*, vol. 49, no. 4, pp. 1033–1045, 2011.
- [90] X. Zhu, N. Zhou, Z. Zhang et al., "Cyclic polymers with pendent carbazole units: enhanced fluorescence and redox behavior," *Angewandte Chemie International Edition*, vol. 50, no. 29, pp. 6615–6618, 2011.
- [91] H. Mori, S. Nakano, and T. Endo, "Controlled synthesis of poly(N-ethyl-3-vinylcarbazole) and block copolymers via RAFT polymerization," *Macromolecules*, vol. 38, no. 20, pp. 8192–8201, 2005.
- [92] H. Mori, H. Iwaya, and T. Endo, "Structures and chiroptical properties of thermoresponsive block copolymers containing L-proline moieties," *Macromolecular Chemistry and Physics*, vol. 208, no. 17, pp. 1908–1918, 2007.
- [93] H. Mori, H. Iwaya, and T. Endo, "Controlled synthesis of thermoresponsive polymer via RAFT polymerization of an acrylamide containing l-proline moiety," *Reactive and Functional Polymers*, vol. 67, no. 10, pp. 916–927, 2007.

- [94] H. Mori and S. Okabayashi, "Synthesis, assembled structure, and chiroptical properties of amino acid-based amphiphilic block copolymers containing carbazole moiety," *Reactive and Functional Polymers*, vol. 69, no. 7, pp. 441–449, 2009.
- [95] J. D. Quinn and R. A. Register, "Nitroxide-mediated radical polymerization of N-ethyl-2-vinylcarbazole," *Polymers for Advanced Technologies*, vol. 19, no. 6, pp. 556–559, 2008.
- [96] K. Ogino, T. Goma, D. Kageyama, H. Sato, and N. Yonezawa, "Multifunctional block copolymers for organic photorefractive materials," *Journal of Photopolymer Science and Technology*, vol. 19, no. 3, pp. 419–424, 2006.
- [97] P. Zhao, Q. D. Ling, W. Z. Wang, J. Ru, S. B. Li, and W. Huang, "Reversible addition-fragmentation chain transfer polymerization of methacrylates containing hole-or electron-transporting groups," *Journal of Polymer Science Part A*, vol. 45, no. 2, pp. 242–252, 2007.
- [98] D. Neugebauer, D. Charasim, A. Swinarew et al., "Polymethacrylates with anthryl and carbazolyl groups prepared by atom transfer radical polymerization," *Polymer Journal*, vol. 43, no. 5, pp. 448–454, 2011.
- [99] C. Ulbricht, C. R. Becer, A. Winter, D. Veldman, and U. S. Schubert, "Copolymers containing phosphorescent iridium(III) complexes obtained by free and controlled radical polymerization techniques," *Macromolecular Rapid Communications*, vol. 29, no. 24, pp. 1919–1925, 2008.
- [100] N. Hadjichristidis, M. Pitsikalis, S. Pispas, and H. Iatrou, "Polymers with complex architecture by living anionic polymerization," *Chemical Reviews*, vol. 101, no. 12, pp. 3747–3792, 2001.
- [101] A. Hirao, M. Hayashi, S. Loykulnant et al., "Precise syntheses of chain-multi-functionalized polymers, star-branched polymers, star-linear block polymers, densely branched polymers, and dendritic branched polymers based on iterative approach using functionalized 1,1-diphenylethylene derivatives," *Progress in Polymer Science*, vol. 30, no. 2, pp. 111–182, 2005.
- [102] H. Mori and A. H. E. Müller, "New polymeric architectures with (meth)acrylic acid segments," *Progress in Polymer Science*, vol. 28, p. 1403, 2003.
- [103] N. Hadjichristidis, H. Iatrou, M. Pitsikalis, S. Pispas, and A. Avgeropoulos, "Linear and non-linear triblock terpolymers. Synthesis, self-assembly in selective solvents and in bulk," *Progress in Polymer Science*, vol. 30, no. 7, pp. 725–782, 2005.
- [104] K. V. Bernaerts and F. E. du Prez, "Dual/heterofunctional initiators for the combination of mechanistically distinct polymerization techniques," *Progress in Polymer Science*, vol. 31, no. 8, pp. 671–722, 2006.
- [105] Y. Yagci and M. A. Tasdelen, "Mechanistic transformations involving living and controlled/living polymerization methods," *Progress in Polymer Science*, vol. 31, no. 12, pp. 1133–1170, 2006.
- [106] D. Taton, Y. Gnanou, R. Matmour et al., "Controlled polymerizations as tools for the design of star-like and dendrimer-like polymers," *Polymer International*, vol. 55, no. 10, pp. 1138–1145, 2006.
- [107] H. Mori, H. Ookuma, and T. Endo, "Synthesis of star polymers based on xanthate-mediated controlled radical polymerization of N-vinylcarbazole," *Macromolecular Symposia*, vol. 249–250, pp. 406–411, 2007.
- [108] H. Mori, H. Ookuma, and T. Endo, "Poly(N-vinylcarbazole) star polymers and amphiphilic star block copolymers by xanthate-mediated controlled radical polymerization," *Macromolecules*, vol. 41, no. 19, pp. 6925–6934, 2008.
- [109] N. Hadjichristidis, S. Pispas, M. Pitsikalis, H. Iatrou, and C. Vlahos, "Asymmetric star polymers: synthesis and properties," *Advances in Polymer Science*, vol. 142, pp. 71–127, 1999.
- [110] W. Zhang, W. Zhaing, Z. Zhang et al., "Thermo-responsive fluorescent micelles from amphiphilic A3B miktoarm star copolymers prepared via a combination of SET-LRP and RAFT polymerization," *Journal of Polymer Science Part A*, vol. 48, no. 19, pp. 4268–4278, 2010.
- [111] Y. Tao, Q. Xu, N. Li, J. Lu, L. Wang, and X. Xia, "Synthesis and photoluminescent property of star polymers with carbazole pendent and a zinc porphyrin core by ATRP," *Polymer*, vol. 52, no. 19, pp. 4261–4267, 2011.
- [112] A. A. Farah and W. J. Pietro, "Atom transfer radical polymerization of N-(ω' -alkylcarbazolyl) methacrylates via the use of novel heteroleptic Ru(II) polypyridyl initiator," *Inorganica Chimica Acta*, vol. 357, no. 13, pp. 3813–3824, 2004.
- [113] A. A. Farah and W. J. Pietro, "Synthesis and characterization of multifunctional polymers via atom transfer radical polymerization of N-(ω' -alkylcarbazolyl) methacrylates initiated by Ru(II) polypyridyl chromophores," *Journal of Polymer Science Part A*, vol. 43, no. 23, pp. 6057–6072, 2005.
- [114] C. Chang, J. Zhu, Z. Zhang, N. Zhou, Z. Cheng, and X. Zhu, "Synthesizing and characterization of comb-shaped carbazole containing copolymer via combination of ring opening polymerization and nitroxide-mediated polymerization," *Polymer*, vol. 51, no. 9, pp. 1947–1953, 2010.
- [115] J. Shen, H. Masaoka, K. Tsuchiya, and K. Ogino, "Synthesis and properties of a novel brush-type copolymers bearing thiophene backbone and 3-(N-carbazolyl)propyl acrylate side chains for light-emitting applications," *Polymer Journal*, vol. 40, no. 5, pp. 421–427, 2008.
- [116] B. Zhang, J. Wang, Y. U. Chen et al., "Multiwalled carbon nanotubes covalently functionalized with poly(N-vinylcarbazole) via RAFT polymerization: synthesis and imonliner optical properties," *Journal of Polymer Science Part A*, vol. 48, no. 14, pp. 3161–3168, 2010.
- [117] B. Zhang, Y. U. Chen, X. Zhuang et al., "Poly(N-vinylcarbazole) chemically modified graphene oxide," *Journal of Polymer Science Part A*, vol. 48, no. 12, pp. 2642–2649, 2010.
- [118] B. Zhang, Y. Chen, L. Xu et al., "Growing poly(N-vinylcarbazole) from the surface of graphene oxide via RAFT polymerization," *Journal of Polymer Science Part A*, vol. 49, no. 9, pp. 2043–2050, 2011.
- [119] J. Hua, D. Chen, X. Jing, L. Xu, Y. Yu, and Y. Zhang, "Preparation and Photoconducting Property of $C_{60}Cl_n$ -Bonded Poly(N-vinylcarbazole) with $C_{60}Cl_n$ /CuCl/Bpy Catalyst System," *Journal of Applied Polymer Science*, vol. 84, 2003.
- [120] J. Hua, W. Yang, and Y. Zhu, "Optical-limiting effect of C_{60} bonded poly(N-vinylcarbazole) initiated with $C_{60}Cl_n$ /CuCl/Bpy catalyst system," *Materials Letters*, vol. 59, p. 644, 2005.
- [121] T.-L. Wang, C.-H. Yang, Y.-T. Shieh, A.-C. Yeh, L.-W. Juan, and H. C. Zeng, "Synthesis of new nanocrystal-polymer nanocomposite as the electron acceptor in polymer bulk heterojunction solar cells," *European Polymer Journal*, vol. 46, p. 634, 2009.
- [122] T. L. Wang, C. H. Yang, Y. T. Shieh, and A. C. Yeh, "Synthesis of CdSe-Poly(N-vinylcarbazole) nanocomposite by atom transfer radical polymerization for potential optoelectronic applications," *Macromolecular Rapid Communications*, vol. 30, no. 19, pp. 1679–1683, 2009.
- [123] M. Feng, Y. Chen, N. He et al., "Ultrasound-assisted bulk synthesis of CdS-PVK nanocomposites via RAFT

- polymerization,” *Journal of Polymer Science Part A*, vol. 46, no. 16, pp. 5702–5707, 2008.
- [124] M. Sato, A. Kawata, S. Morito, Y. Sato, and I. Yamaguchi, “Preparation and properties of polymer/zinc oxide nanocomposites using functionalized zinc oxide quantum dots,” *European Polymer Journal*, vol. 44, no. 11, pp. 3430–3438, 2008.
- [125] J. Liu, W. He, L. Zhang et al., “Bifunctional Nanoparticles with Fluorescence and Magnetism via Surface-Initiated AGET ATRP Mediated by an Iron Catalyst,” *Langmuir*, vol. 27, pp. 12684–12692, 2011.
- [126] Q. Li, L. Zhang, L. Bai et al., “Multistimuli-responsive hybrid nanoparticles with magnetic core and thermoresponsive fluorescence-labeled shell via surface-initiated RAFT polymerization,” *Soft Matter*, vol. 7, no. 15, pp. 6958–6966, 2011.
- [127] T. M. Fulghum, P. Taranekar, and R. C. Advincula, “Grafting hole-transport precursor polymer brushes on ITO electrodes: surface-initiated polymerization and conjugated polymer network formation of PVK,” *Macromolecules*, vol. 41, no. 15, pp. 5681–5687, 2008.
- [128] M. C. Tria, K. S. Liao, N. Alley, S. Curran, and R. Advincula, “Electrochemically crosslinked surface-grafted PVK polymer brushes as a hole transport layer for organic photovoltaics,” *Journal of Materials Chemistry*, vol. 21, no. 28, pp. 10261–10264, 2011.
- [129] Y. Wei, D. Gao, L. Li, and S. Shang, “Memory effect in polymer brushes containing pendant carbazole groups,” *Polymer*, vol. 52, no. 6, pp. 1385–1390, 2011.



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