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Junction-Controlled Topological Polymerization

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Abstract: Methodology that enables controlled synthesis of linear and branched polymers from an identical monomer will present a novel pathway for polymer synthesis and processing. In this paper, firstly, controllable one or both of C(3)-C(3') and C(6)-C(6') coupling reactions of carbazolyl are described. In the second approach, an identical monomer containing two carbazolyls is polymerized using chemical and electrochemical oxidizers, leading to topologically controllable growth of linear in weak oxidizer or cross-linked polymer chain in strong oxidizer, with satisfactory long chain propagation of step growth polymerization ($M_n = 6.0\times10^4$ g mol^{-1}, $M_w/M_n = 2.3$). This very simple polymerization with cheap reagents and low levels of waste has provided a flexible pathway for synthesis and processing of polymers.

The topology of macromolecules is an essential parameter to govern their properties and functions.[1] Driven by the need of novel polymeric materials with sophisticated properties and performances, tremendous efforts on the design and synthesis of well-defined polymers with controllable architectures and topologies have been a central theme in the research area of polymer science in the past three decedes.[2] For step growth polymerization, a linear polymer is prepared from monomers with two reactive sites, and a branched polymer is prepared from monomers with more than two reactive sites. Methodology that enables controlled synthesis of linear and branched topological polymers from an identical monomer will offer a flexible pathway for polymer synthesis and processing. However, starting an identical monomer strategy, for controlling polymeric topology by simple reaction conditions to afford linear and cross-linked polymeric materials with controllable molecular weight, has been an enduring ongoing synthetic challenge in polymer science and technology. In this paper, by marrying the controllable radical C-C coupling reactions (Figure 1A), starting from an identical monomer, both chemical and electrochemical radical initiated step growth polymerization is developed. This polymerization can prepare the polymers with different primary structures with linear or cross-linked backbone via one or both of C(3)-C(3') and C(6)-C(6') coupling reactions of carbazolyl in presence of weak or strong chemical or electrochemical oxidizer (Figure 1B).

C-C Coupling Control of Carbazolyl

We firstly demonstrate that the sole formation of 9,9'-dihexyl-3,3'-dicarbazolyls can be considered to be the only product if its oxidative reaction is carefully carried out in weak oxidizer medium ($FeCl_3$) or at low oxidative potential (c.a. 1.0 V vs. Ag/Ag$^+$) (Figure S1-3), probably due to trapping of 9,9'-dihexyl-3,3'-bicarbazolyls radicals could appear in *N-C-C-N* delocalization region that effectively disable coupling at the 6,6'-positions because it could be most stable among other resonance structures (Figure S4). Multiple oligomers and polymers appeared in strong oxidizer medium ($(NH_4)_2S_2O_8$) or at high oxidative potential (c.a. > 1.2 V vs. Ag/Ag$^+$) (Figure S2-3). Though oxidative products of carbazolyls have been studied before,[3] structural definition has been remaining difficult because their polymers are generally insoluble with inadequate characterizations[3g,h] and unknown dependence of electrochemical potential.[3i,j,k,4] Herein, we have first provided the effect of oxidative strength on N-alkylcarbazolyl reactions.

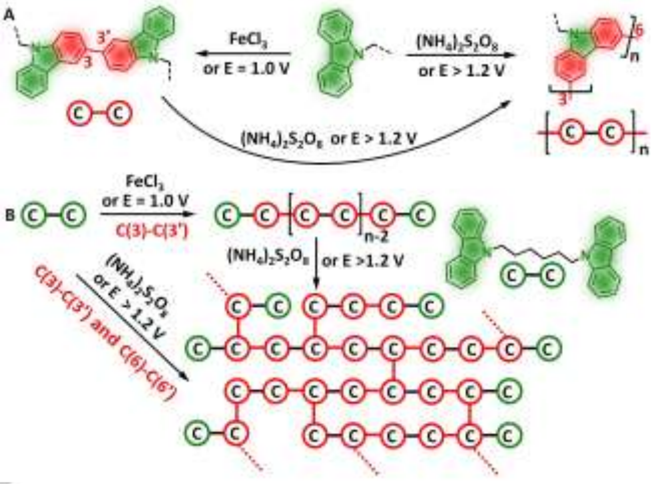

Figure 1. (A) C-C coupling mechanism of carbazolyl; (B) radical initiated topological polymerizations of monomer containing two carbazolyl.

Topologically Controlled Polymerizations

The reaction conditions for general step growth polymerization can be drastic (high temperatures and without oxygen and water), which could affect the properties of desirable functional building blocks. To marry mild radical C-C coupling reactions of carbazolyls with chain propagation of step growth polymerization will be interesting for synthesis of polymers. Based on sole C(3)-C(3') coupling reaction, α,ω-bis(N-carbazolyl)hexane (Figure 2a) has two carbazolyls, whose radicals can react with other carbazolyls of monomers and any size oligomers, and form 3,3'-bicarbazolyl inter-connected polymers (Figure 2b). Via chemical radical initiated step growth polymerization in $FeCl_3/CHCl_3$ medium, rapid loss of monomer α,ω-bis(N-carbazolyl)hexane early in the reaction can be confirmed by absorption peak intensity of 295 nm in reaction system (Figure S5), which is one of typical features of step growth polymerization. In the reaction system of $FeCl_3$/MeCN, only insoluble dimer of α,ω-bis(N-carbazolyl)hexane (Figure 2c) can be found as precipitated phase, most probably due to difficult coupling dynamics of carbazolyl in solid state.

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Interestingly, this dimer in $FeCl_3/CHCl_3$ with good solubility can further react via C(3)-C(3') coupling reactions of solitary carbazolyls at both ends of dimer and produce precipitate poly(α,ω-bis(N-carbazolyl)hexane) as well as polymerization of α,ω-bis(N-carbazolyl)hexane in $FeCl_3/CHCl_3$. Via electrochemical radical initiated step growth polymerization of α,ω-bis(N-carbazolyl)hexane and its dimer at low oxidative potential of 1.0 V, poly(α,ω-bis(N-carbazolyl)hexane) film as product can be formed on indium tin oxide (ITO) (Figure S6). In principle, dimer or other any size oligomer of α,ω-bis(N-carbazolyl)hexane has two unreactive carbazolyls at ends of chain with further coupling possibility.

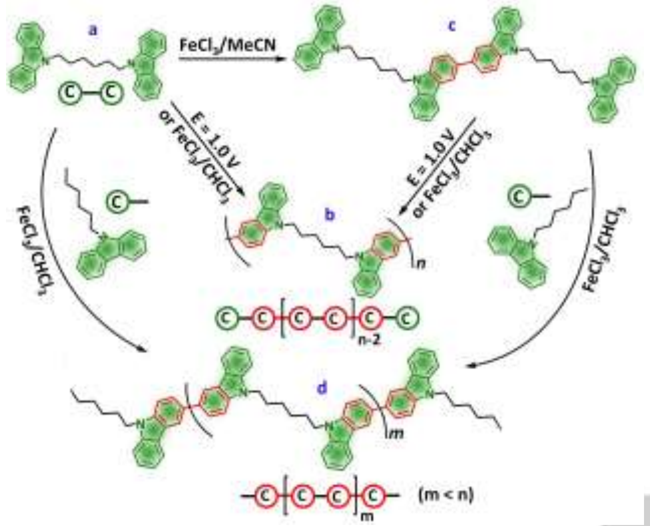

Figure 2. Chemical and electrochemical initiated radical step growth polymerizations of α,ω-bis(N-carbazolyl)hexane via C(3)-C(3') coupling of carbazolyl.

In order to synthesize the soluble polymer and define the structures of polymers, two solutions were taken into account:

(1) *N*-hexylcarbazolyl as end-terminating reagent was added into reaction in order to terminate the long term polymerization and reduce the molecular weight (m<n, Figure 2d). This synthesis of soluble polymer can also imply that C(3)-C(3') coupling of carbazolyl should be only reaction, otherwise, no soluble polymer could be obtained.

(2) Long alkyl chain was introduced into monomer (Figure 3A). As reaction time lasting, rapid loss of monomer early in the reaction can be observed (Figure 3A-a), and linear molecular weight (M_n, measured by GPC) slowly increases and reaches 54700 g mol^{-1} after 40 h and 59800 g mol^{-1} after 1752 h (73 days), respectively (Figure 3A-b), with dispersity (*Đ*) of 2.1 ~ 2.3. There is relatively sharp increase in molecular weight at 3 ~ 5 h, probably due to rapid consumption of short polymers, and the slow increase in molecular weight after 5 h probably because of lack presence of short polymers. For more reactive time, the molecular weight of polymer slowly increases, and more precipitated phase can be observed, demonstrating that the molecular weight of polymer has reached the limitation of solubility. In the presence of $(NH_4)_2S_2O_8$, the polymerization via both C(3)-C(3') and C(6)-C(6') couplings show more rapid loss of the monomer and rapid increase of molecular weight within 2 h (Figure 3A-c,d). This reaction does not run for long time because of solubility limitation. In this paper, all polymerizations did run in non-purified $CHCl_3$ and they are indeed insensitive to oxygen and water.[5] Though *Đ* of 2.1~2.3 was obtained from soluble polymers, *Đ* of polymers in precipitated phase is suggested to be narrow with the assistance of solubility limitation of polymers.

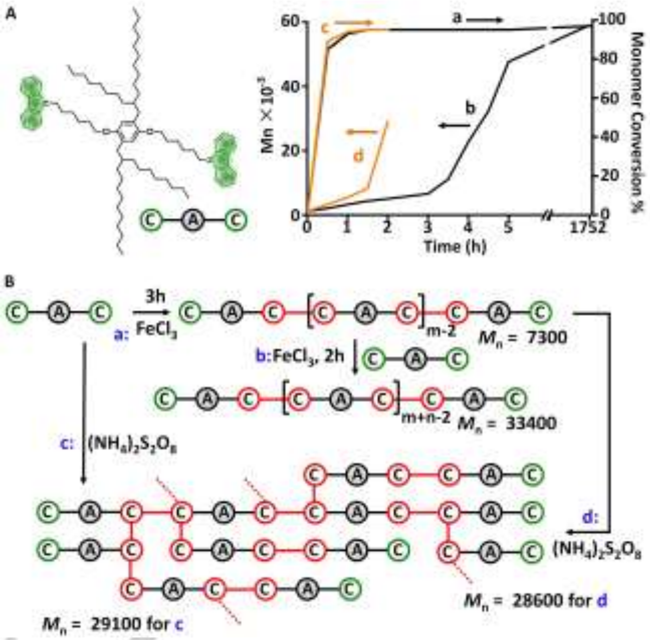

Figure 3. (A) Structure of monomer, and percent conversions of monomer and molecular weight of polymers measured by GPC as a function of reaction time via one (a,b) or both (c,d) of C(3)-C(3') and C(6)-C(6') couplings of carbazolyls; (B) Topological controllable synthesis: short linear polymer (a) and its further polymerization with additional monomer, cross-linked polymerizations from initial monomer (c) and short linear polymer (d).

As for reaction shown in Figure 3B-a,b, the linear polymerization was terminated after molecular weight reached M_n = 7300 g mol^{-1}. This polymer purified can further react with monomer again and provide the polymer with high molecular weight (M_n = 33400 g mol^{-1}), indicating that this polymerization of polymer can be further activated. In strong oxidizer medium (c.a. $(NH_4)_2S_2O_8$ and >1.2 V), the identical monomer can have four reactive sites on C(3) and C(6) positions of two carbazolyls. Thus, there is no surprising that the cross-linked polymer can be obtained from identical monomer or linear polymer (Figure 3B-c,d). Similarly, the linear polymers synthesized via chemical C(3)-C(3') coupling can react with each other via electrochemical C(6)-C(6') coupling on surface of ITO electrode at 1.5 V. After washing any unreactive linear polymer with $CHCl_3$ solvent, the insoluble (cross-linked) polymeric film can be observed in AFM images on ITO substrate (Figure 4A-C) and TEM images as a presence of free-standing film (Figure 4D,E), which could have a great potential for surface active film applications.

Synthesis and Process of Electrochromic Polymers

3,3'-bicarbazolyl unit is better transparent in the visible and infrared regions (Figure S7), and does not impair the optical properties of additional functional building blocks. Thus, N-alkylcarbazolyl could be a universal reactive site to incorporate various building blocks with good oxidative stability into polymers. As shown in Figure 5, linear PDI containing polymer has similar absorption to monomer in solution, and the absorption of dipped polymer film show a broad absorption peak due to strong π-π* interaction of PDI in solid state.[6] Similarly to experiment in Figure 4, the cross-linked polymer film can be prepared via electrochemical C(6)-C(6') coupling of spin-coated linear polymers on surface of ITO electrode at 1.5 V. The cross-linked polymer as 2D free-standing film can be observed in TEM images (Figure 5C). Electrochromic function can be demonstrated by in situ spectroelectrochemistry, that the absorption of linear and cross-linked polymers can be enhanced through negatively charged state of PDI. Though there is clear absorption shoulder peak at 350 nm (Figure 5E) owning to polycarbazole species after electrochemical C(6)-C(6') coupling, the electrochromic behavior at visible absorption region remains. Beyond the one-step synthesis of functional polymers, this polymerization can also take place at nanoscale and enable to preprogram the dimension of 1D gold nanorods (Figure S8).

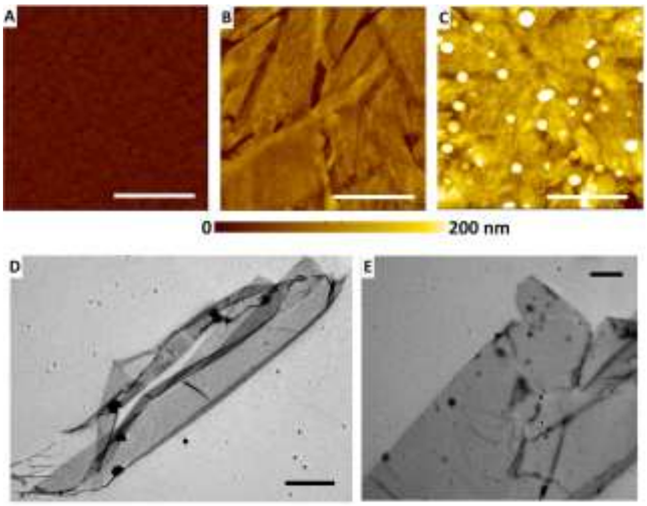

Figure 4. AFM images of ITO electrode (A), spin-coated linear polymer film of 150 nm (B), and cross-linked film (C) after further electrochemical oxidation at 1.5 V and $CHCl_3$ rinsing; TEM images of cross-linked polymer nanofilms (D,E). Scale bar: 2 µm.

In conclusion, this paper has showed a junction controlled topological polymerization via both chemically and electrochemically initiated C(3)-C(3') and C(6)-C(6') couplings of carbazolyls. Taking advantages of versatile modification at N-position of carbazole, this very simple and general polymerization with cheap reagents and low levels of waste as novel conceptual methodology has produced a revival of interest in oxidative C-C coupling reaction, and also offered a novel pathway for synthesis and processing of functional polymers.

Acknowledgements

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Keywords: topological control, step polymerization, C-C coupling, C-H bond activation, radical coupling

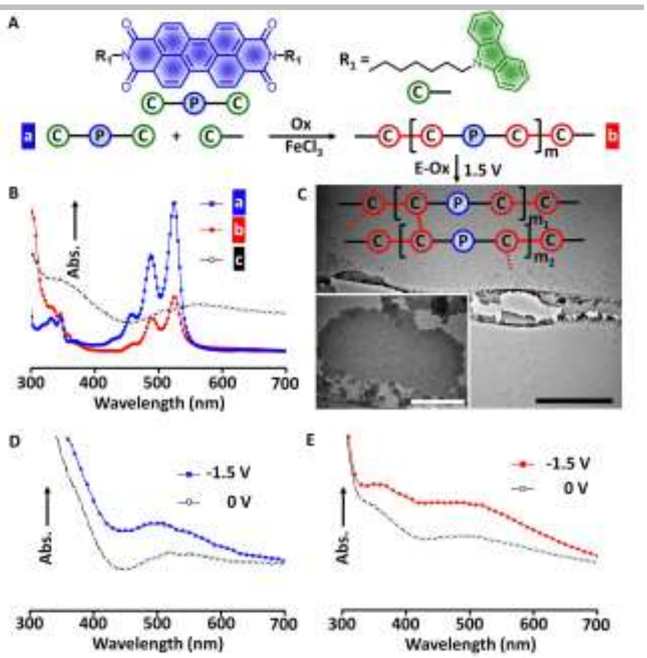

Figure 5. (A) Synthesis of linear PDI containing polymer and its cross-linked polymer; (B) Absorption spectra of monomer (a, 4 mM) and linear polymer (b, 2 mM) in solution, and dipped linear polymer film (c); (C) TEM images of cross-linked polymer film (scale bar: 0.5 µm (left) and 5 µm (right)); In situ spectroelectrochemistry of dipped linear polymer before (D) and after (E) electrochemical C(6)-C(6') coupling on ITO in 0.1 M $TBAPF_6$ acetonitrile.

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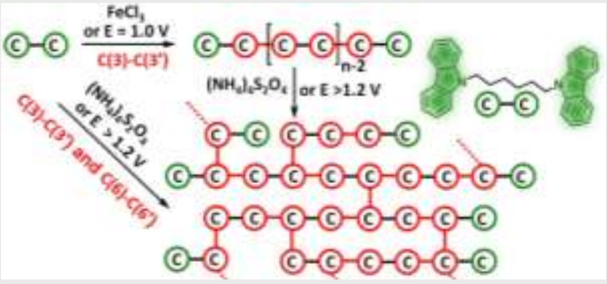

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By marrying radical C-C coupling reactions of carbazoles, junction-controlled topological polymerization was developed. This very simple and general polymerization with cheap reagents and low levels of waste has produced a novel pathway for synthesis and processing of polymers.