Chapter 19

Gradient Sequence \(\pi\)-Conjugated Copolymers

Edmund F. Palermo and Anne J. McNeil*

Department of Chemistry and Macromolecular Science and Engineering Program, University of Michigan, 930 North University Avenue, Ann Arbor, Michigan 48109-1055

*E-mail: ajmcneil@umich.edu

Gradient sequence copolymers exhibit a gradual change in comonomer composition along the polymer chain. These novel materials are interesting because they exhibit unique properties compared to their random, alternating and block copolymer counterparts. We describe herein the synthesis and characterization of the first \(\pi\)-conjugated gradient sequence copolymers, which have only recently been accessible via a controlled, chain-growth synthetic method. We demonstrate that the gradient sequence copolymers exhibit unique thermal, optical and morphological properties compared to the analogous block and random copolymers. In addition, we show that gradient sequence copolymers can act as additives to modulate the thin film morphologies and phase separation behavior of polymer/polymer and polymer/fullerene blends. The impact of gradient sequence copolymer-based additives in stabilizing bulk heterojunction organic solar cells is also described.

Introduction

Naturally-occurring biopolymers perform sophisticated functions due to their precisely defined chemical structure, which dictates their folding and assembly into complex molecular machinery. Inspired by nature, the precise control of synthetic polymer structures represents a challenging goal for modern polymer science (1–5). Precise control over copolymer sequence can be obtained through iterative, step-wise approaches that are labor-intensive, expensive and impractical on the large scale. Alternatively, living polymerization methods (6–9) provide
some level of sequence control with substantially less effort and can be quite scalable.

In 2004, Yokozawa (10, 11) and McCullough (12) independently reported Ni-catalyzed polymerizations of thiophene-based monomers that proceed in a pseudo-living, chain-growth fashion to give regioregular poly(3-hexylthiophene) (P3HT) with low dispersities ($D \geq 1.15$). This synthetic method, now known as catalyst transfer polycondensation (CTP) (13–19), paved the way for synthesizing all-conjugated diblock copolymers (20–27), star polymers (28, 29) and surface-grafted polymers (30–32). CTP also provides access to all-conjugated gradient sequence copolymers (33–36). These studies have demonstrated that the copolymer sequence and architecture can dramatically influence the optical, electronic, thermal, and mechanical properties of the material. Nevertheless, the monomer scope remains quite narrow, ultimately limiting the diversity of new materials that can be made (13).

Gradient copolymers are characterized by a compositional drift – a gradual change in the copolymer composition along the polymer chain length. This microstructure differs from block copolymers, which exhibit a sharp compositional discontinuity, and random or alternating copolymers, which exhibit a uniform composition (Scheme 1).

To date, most gradient sequence copolymers have been synthesized from vinyl-containing monomers (37–40). These reports have demonstrated that the gradient sequence materials exhibit unique properties compared to their block, random and alternating counterparts. For example, Torkelson and co-workers showed that macrophase separated polymer/polymer blends can be rendered thermally stable by including a gradient copolymer as an additive (41–44). This effect has been attributed to the gradient copolymer localizing at the interface, lowering the interfacial tension, and as a result, suppressing the phase separation process. These studies motivated us to pursue $\pi$-conjugated gradient copolymers and examine their impact on phase separation in polymer/polymer and polymer/fullerene blends. The latter goal is aimed at understanding the impact of phase separation on the performance of bulk heterojunction solar cells. This chapter reviews our work in this area over the past five years, where we have focused on identifying pairs of comonomers that can undergo controlled CTP.
synthesizing gradient sequence copolymers with a linear change in copolymer composition, and understanding the impact of these sequences on their properties and ultimately, their performance in various applications (33–36).

Synthesis and Characterization of Gradient Copolymers

The first example of an intentionally synthesized π-conjugated gradient copolymer was reported in 2010 (36). This copolymer was composed of thiophene-based repeating units with different side chain identities (i.e., poly(3-hexylthiophene-grad-3-((hexyloxy)methyl)thiophene)). This proof-of-concept paper laid the foundation for our future studies by establishing a protocol for the semi-batch synthesis of these novel materials. In 2012, we reported the second example of a π-conjugated gradient sequence copolymer, this time with varying heteroatoms in the backbone (i.e., poly(3-hexylthiophene-grad-3-hexylselenophene) (35)). These gradient copolymers exhibited sequence-dependent physical properties; for example, their extent of microphase separation was between that of the analogous random and block copolymers. These early papers demonstrated that π-conjugated gradient sequence copolymers can be prepared using CTP and that their sequence plays a role in the solid-state properties.

![Diagram of gradient copolymers](image_url)


We next turned our focus to synthesizing gradient copolymers that can be used to determine the impact of phase separation in polymer/polymer and polymer/fullerene blends. To overcome some synthetic limitations of the CTP method, we targeted gradient copolymers that could be further modified in a post-polymerization step. Specifically, the copolymerization of monomers 1 and 2 were pursued (34). Although monomer 1 was known to homopolymerize under CTP conditions (10, 12), monomer 2 was largely untested (45, 46). Thus, the synthesis of poly(3-(6-bromohexyl)thiophene) (P3BrHT) was attempted via CTP. The resulting homopolymers exhibited number-average molecular weights ($M_n$) consistent with the [monomer]/[catalyst] ratios, low D, and high regioregularities. Importantly, the alkyl bromide side chains were inert to the CTP reaction conditions. Based on these promising results, the synthesis of gradient, random and block copolymers containing monomers 1 and 2 were pursued (Scheme 2). The sequence was controlled by the method of comonomer addition: To obtain a random copolymer, monomers 1 and 2 were first added, followed by precatalyst 3 (a “batch” process). To obtain a block copolymer, 1 was first polymerized to high conversion with precatalyst 3, and then monomer 2 was injected (a “sequential addition” process). To obtain a gradient copolymer, a stock solution of monomer 2 was gradually added to the reaction mixture containing monomer 1 and precatalyst 3 using a syringe pump (a “semibatch” process).
Scheme 2. Synthesis of random, block, and gradient copolymers via CTP.

The copolymer sequences were elucidated by plotting the copolymer composition (as determined by 1H NMR spectroscopy) as a function of the normalized chain length (as determined by gel permeation chromatography (GPC)) using aliquots withdrawn throughout the polymerization. The three copolymers were shown to possess similar molecular weights and dispersities (Figure 1B), as well as high regioregularities (>99%). Hence, the only salient structural difference between the three copolymers was their sequence, rendering these polymers suitable for identifying sequence-dependent properties in π-conjugated polymers. As evident in Figure 1C, the melting temperatures vary from the random copolymer ($T_m = 198 \, ^\circ C$) to the gradient copolymer ($T_m = 206 \, ^\circ C$) to the block copolymer ($T_m = 235 \, ^\circ C$). These results suggest that the sequence with the large bromine atoms distributed uniformly (in the random copolymer) forms the least stable crystallites. In contrast, when all the bromine atoms are concentrated on one chain end (in the block copolymer), it forms the most stable crystallites. Intermediate between these extremes resides the gradient copolymer. The impact of these copolymers on phase-separated P3HT/P3BrHT blend morphologies will be discussed in a later section.

Figure 1. Characterization data for the random (red), gradient (green) and block (blue) copolymers containing monomers 1 and 2. (A) Plot of the copolymer composition as a function of the normalized chain length, (B) GPC data, and (C) DSC data. (see color insert)
We next pursued post-polymerization functionalization of these copolymers to incorporate an electron-acceptor fullerene derivative (33). Although there have been examples of random and block copolymers bearing pendant fullerenes (47–52), there were no examples of gradient sequence copolymers with such functionality. To access such copolymers, the side chain bromines in the gradient copolymer were quantitatively converted to azides. A subsequent copper-catalyzed azide-alkyne cycloaddition (CuAAC) reaction was used to covalently attach a fullerene derivative (Scheme 3) (33). Using an excess of the fullerene, maintaining strictly oxygen-free conditions, and rigorously purifying the PMDETA ligand were all required to avoid deleterious side-reactions. We also found that elongating the linker between the polymer and fullerene (from a C1 to a C9 linkage) reduced the extent of intra- and interpolymer crosslinking. A gradient copolymer with approximately 10 mol% of the side chains bearing a fullerene group was prepared with this method. It is worth noting that a higher percentage fullerene loading could not be achieved due to increased crosslinking. With these materials, the impact of gradient copolymers on phase separation in polymer/fullerene blends was examined.


Impact of Gradient Copolymers on Polymer/Polymer Phase Separation

The motivation for synthesizing the gradient copolymer of monomers 1 and 2 was to assess its impact on the morphology of phase separated blends composed of the two homopolymers (P3HT and P3BrHT). Without any copolymer additive, the physical blend of P3HT and P3BrHT undergoes micron-scale phase separation during the spin-coating process as evidenced by scanning transmission electron microscopy with high angle annular dark field detection (STEM/HAADF, Figure 2A). Strong contrast can be observed between isolated domains dispersed in...
a continuous matrix. Energy dispersive spectroscopy (EDS) was performed on selected areas, which revealed the presence of bromine atoms in the bright regions (P3BrHT-rich domains) and their absence in the dark regions (P3HT-rich domains).

![Figure 2. STEM/HAADF images of the as-cast blend of P3HT and P3BrHT with (A) 0 wt% and (B) 20 wt% gradient copolymer additive.](image)

Next, physical blends of the homopolymers in a 1:1 volume ratio (which is based on the solvent excluded molecular volume of the corresponding repeat unit structures) were prepared with the gradient copolymer as an additive, ranging from 0–20 wt%. Spin-casting these solutions gave rise to thin films that were analyzed by STEM/HAADF to determine the domain sizes. As evident in Figure 2B, the domain sizes decreased when gradient copolymer additive was included in the blend. Measurements of domain size from randomly selected regions revealed that the average domain size decreased from 0.9 ± 0.3 μm to 0.27 ± 0.08 μm when the gradient copolymer concentration was increased from 0 to 20 wt%. Further studies revealed that the gradient copolymer out-performed the random and block copolymer analogues with smaller domain sizes and distributions. Overall, these studies revealed that semicrystalline π-conjugated gradient copolymers can influence the morphology of polymer/polymer blends, and that the effect is sequence-dependent.

It is important to note that the influence of the semicrystalline gradient copolymer described herein is different than what was reported for amorphous gradient copolymers. Specifically, Torkelson and co-workers showed that the amorphous copolymer additives suppressed a thermodynamically-driven phase separation process during thermal annealing, and suggested the mechanism involved the gradient copolymer localizing at the domain interface and lowering the interfacial tension (44). In contrast, the semicrystalline gradient copolymers described herein modulate the blend morphology during a kinetically-driven spin-coating process. Though the mechanism is unclear at this time, one rationale is that the gradient copolymer localizes at the interface and mediates the aggregation/crystallization process.

The role of thermal annealing in the P3HT/P3BrHT blends was complicated by the fact that thin films of P3BrHT undergo crosslinking with annealing above its melting temperature ($T_m = 168$ °C). Nevertheless, annealing the thin films for
1 h at 150 °C avoids the crosslinking. Processing films in this manner revealed an intriguing and novel morphology (Figure 3). Fibrils of crystalline P3BrHT were observed in the continuous matrix and appear to align parallel to the P3HT/P3BrHT interface. Interestingly, this morphology appears regardless of whether any copolymer additive is used. The similarity of this morphology to the stars depicted in van Gogh’s famous painting have led us to name it the “Starry Night morphology”. That the nanofibrils appear to be preferentially oriented around the P3HT domains suggests that P3BrHT fibril growth process is influenced by the interface. Evaluating this new morphology in the context of bulk heterojunction devices represents an exciting avenue for future exploration.

**Figure 3.** STEM/HAADF image of the P3HT/P3BrHT blend with 10 wt% block copolymer additive after annealing at 150 °C for 1 h.

### Impact of Gradient Copolymers on Polymer/Fullerene Phase Separation

Thin films of P3HT/[6,6]-phenyl-C61-butyric acid methyl ester (PCBM) undergo crystallization-induced phase separation when thermally annealed for 1 h at 150 °C, as evidenced by the micron-sized needle-shaped domains of PCBM observed under an optical microscope (Figure 4A). This process is known to be detrimental to photovoltaic device performance as the donor/acceptor domains need to be on the nanometer length scale to enable efficient exciton dissociation (53). Motivated by the fact that π-conjugated gradient copolymers suppress phase separation in polymer/polymer blends, we next examined their impact on P3HT/PCBM blends. When the gradient copolymer (at 10 wt%) is added to the blend, this undesirable process is completely suppressed (Figure 4B). Thus, the gradient copolymer bearing side-chain fullerenes acts as a phase compatibilizer for this polymer/fullerene blend.
Photoluminescence measurements were used to further support the conclusion that this novel gradient copolymer is suppressing micron-scale phase separation in the P3HT/PCBM physical blend (Figure 5). With spin-cast films, PCBM efficiently quenches the P3HT emission due to the efficient charge transfer from donor to acceptor in the film. On thermal annealing, the P3HT-based emission is typically recovered because the micron-scale domains minimize the chances of the exciton finding a PCBM molecule within its diffusion length. Excitingly, when a gradient copolymer additive was included in the blend, the P3HT emission remained quenched regardless of annealing time. These results are consistent with the notion that the donor/acceptor domains maintain intimate contact at the nanometer length scale when gradient copolymer is present.

The ultimate test of the gradient copolymer additive involved fabricating and testing solar cells based on the traditional P3HT/PCBM bulk heterojunction. In the control device, annealing for 10 min at 150 °C improves the short-circuit current ($J_{sc}$) and leads to a higher overall power conversion efficiency (PCE, Figure 6). Annealing for longer times reduces the $J_{sc}$, leading to a decrease in PCE, presumably due to the micron-scale phase separation. When 10 wt% gradient copolymer is included in the blend, an S-shaped curve was observed in the current density versus voltage plot (Figure 6A). As a result, the fill factor (FF) is reduced, leading to a lower overall PCE (Figure 6B). Related S-shaped distortions have been previously observed and attributed to an imbalance of electron/hole charge transport rates (53–58). We speculate that the gradient copolymer may be inhibiting growth of P3HT fibrils within the blend, which would restrict hole transport and increase the likelihood of non-geminate recombination (59–61). Indeed, when the gradient copolymer was added, the P3HT/PCBM blend exhibited some modest changes in the solid-state organization as evident in the powder X-ray diffraction and differential scanning calorimetry. When the gradient copolymer additive was reduced to just 1 wt%, the S-shaped distortion was minimized, leading to an improved PCE (compared to 10 wt%), albeit still with sub-optimal FF.

![Figure 4. Optical microscope images of P3HT/PCBM (60:40 wt ratio) blends after annealing at 150 °C for 1 h (A) without and (B) with gradient copolymer additive (10 wt%).](image-url)
Figure 5. Contour maps of PL intensity as a function of the emission and excitation wavelengths for (A and B) P3HT/PCBM and (C and D) P3HT/PCBM + 10 wt% gradient copolymer. Each film was annealed at 150 °C for either 10 min (A and C) or 60 min (B and D). The color represents the relative PL intensity with red as the maximum. (see color insert)

Figure 6. (A) Plot of the short-circuit current density ($J_{sc}$) versus voltage ($V$) for blends of P3HT/PCBM after 60 min of annealing at 150 °C. (B) Plot of the power conversion efficiency (PCE) versus annealing time (min) for blends of P3HT/PCBM. (0 wt% gradient copolymer (red solid line), 1 wt% gradient copolymer (black dot-dash line), and 10 wt% gradient copolymer (blue dashed line)). (see color insert)

The main advantage of a gradient copolymer additive is evident at longer annealing times. While the conventional device (no additive) undergoes phase separation, which results in lower PCEs, the devices containing gradient copolymer additive showed virtually no change in PCE even after annealing at 150 °C for 60 min (Figure 6B). Because the overall PCE in the gradient-containing devices was lower than the conventional device, we plan to synthesize a library of
gradient copolymers with systematically tuned structural parameters (e.g., mole fraction fullerene loading, gradient sequence distribution and molecular weight) to identify a gradient structure that achieves high PCE while maintaining the thermal stability.

**Conclusions and Future Outlook**

With just a few structurally similar monomers, a broad range of sequence-dependent properties have been observed. For example, copolymer sequence has been shown to influence both the physical and optical properties of random, block and gradient π-conjugated copolymers. Excitingly, gradient copolymers were shown to modulate and suppress phase separation in polymer/polymer and polymer/fullerene blends. The impact of these novel copolymers as additives in photovoltaic devices was shown to improve long-term thermal stability, albeit at the expense of reducing the fill factor. Future efforts will focus on modifying the gradient structure to obtain both high power conversion efficiencies and long term stabilities.

To date, we have been limited to thiophene- and selenophene-based monomers due to limitations of the CTP method. As a consequence, we have barely scratched the surface of what may be achievable with gradient sequence π-conjugated copolymers. As new catalysts are discovered and the monomer scope is broadened, we anticipate that additional unique, sequence-dependent properties will emerge from the synthesis and characterization of gradient π-conjugated copolymers. The utility of these gradient copolymers should also be expanded to include a more diverse range of applications, such as chemical/biological sensors and biomaterials (62–66). With much excitement in a rapidly growing field, there are many potential applications for these new sequence-controlled macromolecules.

**References**


45. Although the homopolymerization of monomer 2 was reported under similar conditions, there was no evidence supporting (or refuting) a living, chain-growth mechanism. For reference, see: Zhai, L.; Pilston, R. L.; Zaiger, K. L.; Stokes, K. K.; McCullough, R. D. Macromolecules 2003, 36, 61–64.