Supramolecular Polymer Network-Mediated Self-Assembly of Semicrystalline Polymers with Excellent Crystalline Performance

Chih-Chia Cheng,* Wei-Tsung Chuang, Duu-Jong Lee, Zhong Xin, Chih-Wei Chiu

A novel application of supramolecular interactions within semicrystalline polymers, capable of self-assembling into supramolecular polymer networks via self-complementary multiple hydrogen-bonded complexes, is demonstrated for efficient construction of highly controlled self-organizing hierarchical structures to offer a direct, efficient nucleation pathway resulting in superior crystallization performance. Herein, a novel functionalized poly(ε-caprolactone) containing self-complementary sextuple hydrogen-bonded uracil-diamidopyridine (U-DPy) moieties is successfully developed and demonstrated excellent thermal and viscoelastic properties as well as high dynamic structural stability in the bulk state due to physical cross-linking created by reversible sextuple hydrogen bonding between U-DPy units. Due to the ability to vary the extent of the reversible network by tuning the U-DPy content, this newly developed material can be readily adjusted to obtain the desired crystalline products with specific characteristics. Importantly, incorporating only 0.1% U-DPy resulted in a polymer with a high crystallization rate constant, short crystallization half-time, and much more rapid crystallization kinetics than pristine PCL, indicating a low content of U-DPy moieties provides highly efficient nucleation sites that manipulate the nucleation and growth processes of polymer crystals to promote crystallization and chain alignment in bulk. This new system is suggested as a potential new route to substantially improve the performance of polymer crystallization.

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1. Introduction

Growing environmental awareness in recent years has shifted attention from fully synthetic plastics to the development of more sustainable and environmentally friendly biopolymers for a wide range of applications, including the biomedical and packaging industries. Poly(ε-caprolactone) (PCL) is commonly employed as a commercial biopolymer due to its unique combination of biocompatibility, predictable degradation kinetics, ease of fabrication, and regulatory approval as a biomedical material by the United States Food and Drug Administration; hence PCL represents a potentially appealing alternative to conventional nondegradable polymers.[1–5] Nevertheless, poor crystallization kinetics and inherent brittleness restrict the ability of PCL to undergo plastic deformation below its melting temperature (T_m = 60 °C), resulting in poor mechanical properties and limiting its use in further applications.[6–8] To address these issues, a number of recent studies have aimed to improve the crystallization behavior and mechanical properties of PCL. Incorporation of nucleating agents such as layered silicate clays, polyhedral oligomeric silsesquioxanes, cyclodextrins, carbon nanotubes, and graphene[9–14] is regarded as a promising approach. Nanosized nucleating agents, as nanofillers, provide an incomparably high density of nucleation sites due to their large specific surface area; the density of nucleation sites is one of the most vital factors affecting the crystallization of PCL.[15] However, there is great concern that nanodimensional nanofillers tend to aggregate into new individual discrete crystals and form a immiscible phase morphology within the PCL matrix, even at low nanofiller loadings (<5 wt%).[16–19] This dilemma inspired us to pursue a new nucleation technology that integrates efficient crystallization with acceleration of overall crystallization kinetics.

Multiple hydrogen bonding (MHB) interactions are a particularly effective method of joining polymer chains to form supramolecular polymer networks (SPNs). SPNs have recently been confirmed to undergo spontaneous self-assembly processes that efficiently promote polymer crystallization, and the transient dynamic behavior of SPNs can be easily manipulated to adjust polymer conformation and obtain a variety of multifunctional supramolecular polymers.[8,20–25] These properties can be attributed to the presence of MHB interactions and the formation of an orderly hierarchical structure, which allows the hydrogen bonding moieties to serve as connectors between the polymer chains. However, the introduction of MHB units into the polymer bulk, even at a MHB content as low as 5 wt%, induces a plasticized effect and significantly reduces the crystallization rate, eventually resulting in low crystallinity polymers with discontinuous physical properties.[8,23,26–28] Although this method provides a convenient approach to manipulate the crystallization behavior of a polymer, defining the optimal SPN content for supramolecular polymers to obtain highly enhanced crystallization and mechanical performance remains a great challenge. Therefore, based the progress described above, we boldly assume that the introduction of an extremely low content of MHB groups into the polymer backbone may profoundly alter the mechanism of crystallization and enable the formation of a more orderly hierarchical microstructure to generate polymer films with a well-defined crystal arrangement, due to the low cross-linking density of SPNs that act as efficient nucleating sites. Exploitation of dynamically cross-linked supramolecular semicrystalline polymers may provide a significant breakthrough in the development of next-generation crystallization processes with improved performance predictability and controllability.

Recent studies in our laboratory have demonstrated that various self-assembled supramolecular polymers can efficiently self-assemble into robust SPN structures with unique physical and mechanical properties due to the presence of (self-)complementary MHB interactions.[29,30] These materials were directly employed to generate functional electronic devices with excellent performance.[31,32] More recently, we reported a novel hydrogen bonding derivative of uracil-diamidopyridine (U-DPy) that is able to form highly stable and reversible dimers via self-complementary sextuple hydrogen bonds with association constants over 10^6 M^{-1}.[33,34] We found that the incorporation of U-DPy into the polymer chain plays a crucial role in the self-assembly process and enables U-DPy-functionalized polymers to directly self-assemble into a stable supramolecular micelle and single-chain polymer nanoparticles in aqueous solution with excellent drug delivery characteristics.[35–37] Based on these previous findings, we further propose that introducing U-DPy into semicrystalline polymer systems within an SPN with a low extent of crosslinking may significantly enhance the nucleating ability of the polymer to create well-defined polymer crystals with excellent crystalline performance; this strategy may represent a promising route to improve the physical properties of semicrystalline polymers (Scheme 1). To the best of our knowledge, the use of SPN-functionalized semicrystalline polymers based on MHB interactions with the aim of tuning mechanical properties and achieving high crystallization ability has not yet been thoroughly explored for crystallization engineering purposes. Herein, we successfully developed a novel series of semicrystalline PCL polymers with varying contents of pendant U-DPy groups (PCL-U-DPy), ranging from 0.1 to 1.5 mol%. These materials demonstrated excellent thermal properties as well as easily tunable viscoelastic characteristics due to the varied extents of U-DPy-induced physical cross-linking. In addition, scattering analysis and isothermal crystallization kinetic studies indicated

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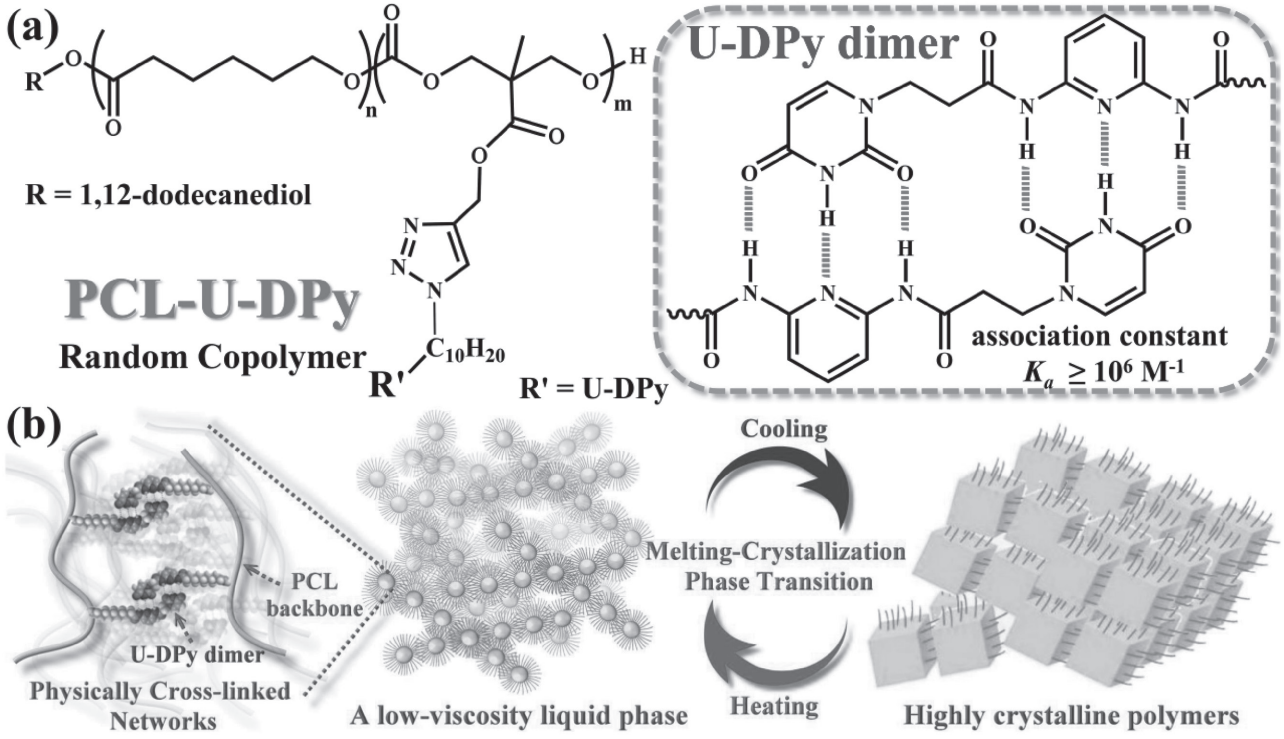

Scheme 1. a) Structural representation of PCL-U-DPy and U-DPy dimer cross-links. b) Suggested processes by which polymer crystallization can be effectively manipulated by the self-complementary sextuple hydrogen-bonded motifs of PCL-U-DPy polymers.

that the incorporation of a low content of U-DPy moieties results in formation of well-ordered hierarchical microstructure and strongly enhances the crystallization properties of PCL. More importantly, when the isothermal crystallization process was examined at 20 °C, the polymer with a U-DPy content of only 0.1% exhibited a high crystallization rate constant (k = 1.6) and short crystallization half-time ($t_{1/2}$ = 0.43 min), whereas original PCL had a k value of 0.503 and a $t_{1/2}$ of 1.27 min. These data suggest an extremely low cross-linking level of 0.1% U-DPy within the polymer introduces sufficient nanosized nucleation sites to provide a high surface area and rapid pathway for crystal growth, leading to improved crystalline performance and simultaneously enhancing the solid-state properties of PCL. Thus, this evidence indicates that this newly devised approach provides a clear and efficient pathway toward the fabrication of highly crystalline cross-linked polymeric materials based on supramolecular interactions.

2. Results and Discussion

Here, we present a facile and efficient synthetic route for the preparation of supramolecular PCL with varying contents of pendant U-DPy units, as shown in Scheme 1a and Scheme S1 (see the Supporting Information for details). First, controlled ring-opening copolymerization of ε-caprolactone and alkyne-functionalized carbonate was examined using tin(II) 2-ethylhexanoate as a catalyst and 1,12-dodecanediol as the initiator at 110 °C. Pendant propargyl-functionalized PCL (PCL-yne) was obtained, and the resulting polymer exhibited a high yield (85%) and narrow polydispersity index (PDI = 1.23) with approximately 1.5% of the propargyl units contained within the polymer backbone, as determined by size-exclusion chromatography (Figure S1, Supporting Information) and proton nuclear magnetic resonance spectroscopy (^{1}H NMR; Figure S2, Supporting Information). Subsequently, PCL-yne was further reacted with different molar amounts of azide-labeled U-DPy via a copper-catalyzed azide–alkyne cycloaddition reaction to obtain a nearly 100% yield of PCL-U-DPy polymer, the chemical structure of which is presented in Scheme 1a. The different contents of U-DPy in PCL-U-DPy were determined to be around 0.1%, 0.4%, 0.8%, and 1.5%, respectively (Figures S3 and S4, Supporting Information). Hereafter, these samples will be referred to as 0.1% U-DPy, 0.4% U-DPy, 0.8% U-DPy, and 1.5% U-DPy, respectively. To evaluate the effect of the intermolecular hydrogen-bonded SPN on thermal properties and phase transition, thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) measurements were performed and the results are shown in Figure S5 (Supporting Information) and Figure 1. The TGA curves revealed a significant

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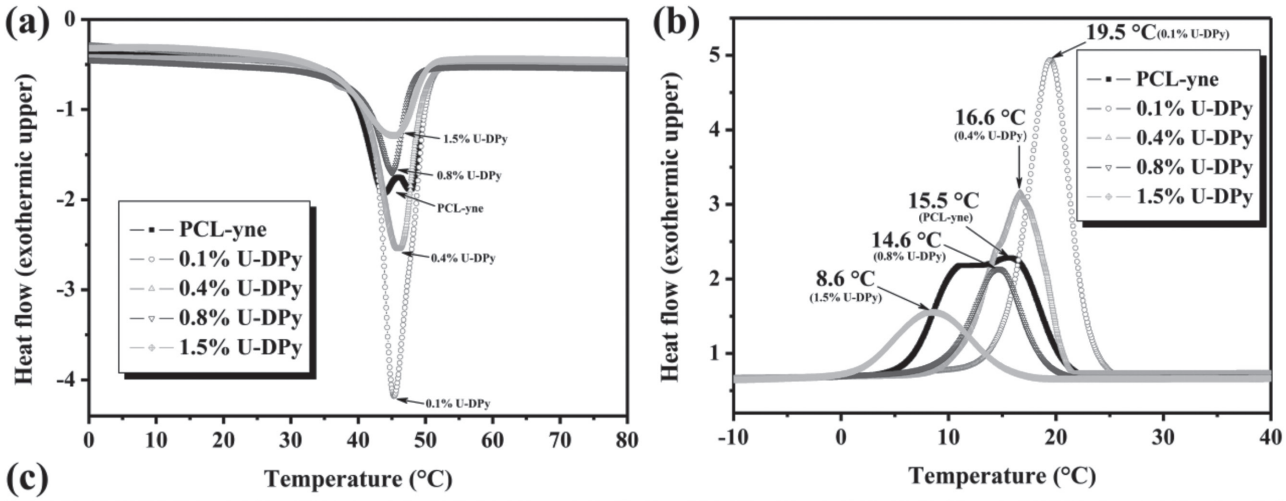

(c)

Samples	Temperature (°C)	n	k	$t_{1/2}$ (min)
PCL-yne	20	1.318	0.503	1.27
0.1% U-DPy	20	1.098	1.598	0.43
0.4% U-DPy	20	1.182	0.842	1.05
0.8% U-DPy	20	1.427	0.238	2.88
1.5% U-DPy	20	1.744	0.061	3.37

Figure 1. DSC second a) heating and b) cooling traces obtained at 10 °C min^{-1} and c) kinetic analysis of the PCL and PCL-U-DPy samples.

increase in the thermal decomposition temperature for all PCL-U-DPy samples (T_d; 5% weight loss) compared to pristine PCL-yne (T_d = 298 °C), especially the T_d of 0.1% U-DPy, which increased to 322 °C. These observations suggest the presence of the strong self-complementary hydrogen bonds between the U-DPy groups in the polymer matrix promotes the formation of stable physically crosslinked networks, which restrict relaxation of the polymer backbone and significantly increase the thermal stability of PCL.

Figure 1 displays the DSC thermograms for the PCL-U-DPy samples. Pristine PCL-yne displayed two distinct melting points (T_m) at 43.7 and 47.7 °C and a heat of fusion (ΔH) of 21.8 J g^{-1}. The double melting point of PCL-yne can be attributed to initial melting of the crystals followed by recrystallization and final melting of the crystals during the heating scan.[8] The DSC curves of all PCL-U-DPy samples had similar melting points at around 45 °C, indicating that the introduction of a low content of U-DPy moieties did not significantly affect the phase transition properties of PCL. Surprisingly, the ΔH value of 0.1% U-DPy was 40.1 J g^{-1}, which was nearly two times higher than that of pristine PCL-yne (ΔH = 21.8 J g^{-1}; Table S1, Supporting Information). Further increasing the U-DPy content to 0.4% resulted in a ΔH value of 27.9 J g^{-1}, implying that an extremely low U-DPy content significantly improves the degree of crystallinity of PCL. These enhanced ΔH values can possibly be attributed to achieving an optimized state of nucleation conditions and the reinforcing effect of crystallization within the PCL matrix. However, the ΔH values of the PCL-U-DPy samples gradually decreased as the U-DPy content increased above 0.8%. The ΔH values of the 0.8% and 1.5% U-DPy samples were 9.8 and 11.6 J g^{-1}, respectively, implying that the formation of a large SPN domain significantly inhibited crystallization of PCL and promoted transformation of the crystalline phase to an amorphous phase. The optimal operating temperature for kinetic experiments (20 °C) was selected based on the DSC cooling scans depicted in Figure 1b. DSC data recorded in isothermal crystallization were further fitted using the Avrami equation to obtain kinetic parameters,[38,39] and the results are summarized in Figure 1c and Figure S6 (Supporting Information). Correlations between the content of U-DPy (ranging from 0.1% to 1.5%) and the overall rate constant (k), half-crystallization time ($t_{1/2}$), and dimensions and directions of crystal growth of PCL were observed. Interestingly, at the extremely low U-DPy content of 0.1%, PCL-U-DPy exhibited a high k value of 1.598 with a short $t_{1/2}$ of 0.43 min; reflective of much more rapid crystallization kinetics compared to PCL-yne (k = 0.503 and $t_{1/2}$ = 1.27) under the same conditions. Similar results were also observed for the sample with a U-DPy

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content of 0.4% (k = 0.842 and $t_{1/2}$ = 1.05). In addition, the Avrami exponents (n) of the 0.1% and 0.4% U-DPy samples were ≈1.1, lower than that of PCL-yne (n = 1.3). These results suggest that the MHB interactions between the U-DPy units within the polymer structure of PCL promote spontaneous nucleation and linear crystal growth while the presence of slightly crosslinked SPNs enhances the crystallization process.[38,39] However, further increasing the U-DPy content above 0.8% significantly decreased the crystallization rate due to extension of the dynamic network, which eventually constrains the mobility of the polymer chains. Moreover, when the experimental temperature was reduced to 10 °C, the PCL-U-DPy samples exhibited similar crystallization behaviors as at 20 °C (Figure S7, Supporting Information). Thus, these data indicate that the presence of a semicrystalline polymer with a low physical cross-linking density is a key property that controls the nucleation process, which strongly enhances the viscoelastic transition and crystallization of polymers. To date, there have been no reported examples of dynamic cross-linked polymeric systems in which the crystallization process can be manipulated to produce well-defined, stable, and uniform growth of polymer crystals in a similar manner.

To further confirm the DSC and crystallization kinetics analyses, polarizing optical microscopy (POM) and synchrotron small- and wide-angle X-ray scattering (SAXS and WAXS) experiments were performed at 20 °C to observe the microstructural evolution of these materials. After annealing at 120 °C and full crystallization at 20 °C for 24 h, spherulite images of pristine PCL-yne and PCL-U-DPy samples were generated by POM (Figure S8, Supporting Information). PCL-yne showed distinct crystalline spherulites with a diameter of more than 100 μm. For 0.1% U-DPy, the spherulites were slightly smaller and denser than PCL-yne, indicating the presence of an extremely low content of U-DPy moieties promoted the nucleation process of PCL and markedly increased the spherulite density. In contrast, the spherulites of 1.5% U-DPy appeared very small due to the higher physical cross-linking density; thus, crystallization proceeded very slowly within the limited space resulting in small spherulites, substantially inhibiting the overall crystallization rate. Furthermore, the characteristic grain microstructures of the PCL-yne and PCL-U-DPy samples were examined by SAXS and WAXS. As shown in Figure 2a, the SAXS profiles of pristine PCL-yne exhibited a single scattering peak at q = 0.36 nm^{-1}, corresponding to a spacing of d = 17.4 nm that can be ascribed to the closely packed structure of the PCL chains, which eventually determines the crystal lamellar thickness.[40,41] For all PCL-U-DPy samples, crystal lamellar thicknesses gradually decreased from 17.0 to 13.9 nm as the U-DPy content increased. Characteristic U-DPy dimer peaks at q = 4.01 nm^{-1} were observed in each sample, corresponding to a d spacing of 1.57 nm, reflecting formation of the self-complementary MHB complex on the d-spacing of PCL-U-DPy that kinetically traps the polymer chains in an entangled structure,[33,34] thereby permitting different extents of physical cross-linking within the polymer matrix. In the higher q region of the WAXS profiles (Figure 2b), multiple-scattering peaks were located at q = 15.0, 15.4, and 16.6 nm^{-1}, corresponding to the (110), (111), and (200) directions of PCL.[42] The WAXS patterns of the 0.1% and 0.4% U-DPy samples displayed higher scattering intensity than PCL-yne, indicating the production of high-performance polymer crystals at an extremely low U-DPy content. Conversely, further increasing the U-DPy content to 0.8% and 1.5% shifted the characteristic peaks to slightly higher q values compared to PCL-yne, and the peak intensities reduced significantly as the U-DPy content increased. This obser-

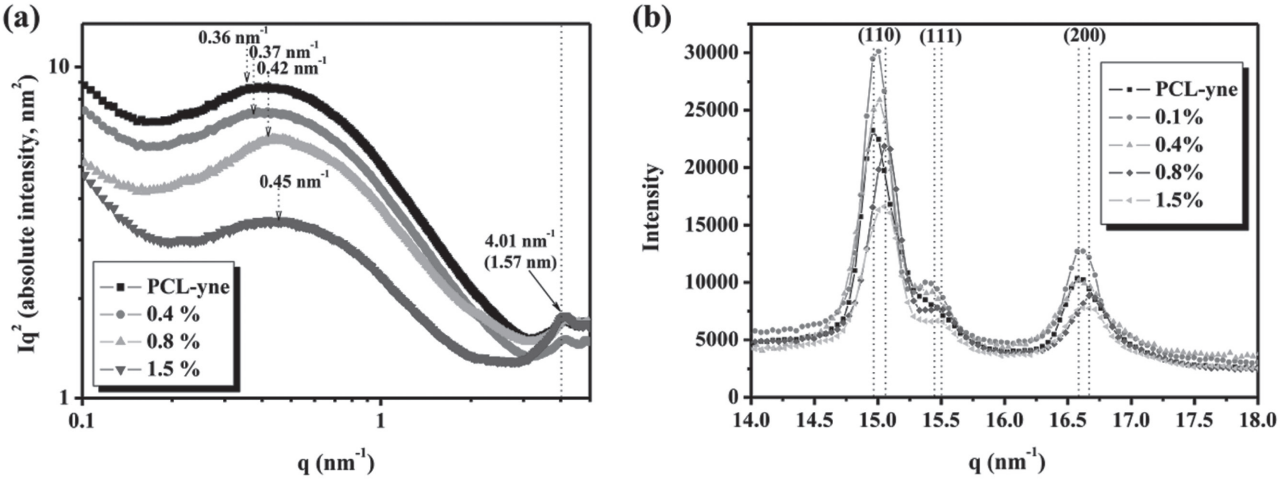

Figure 2. a) SAXS and b) WAXS profiles for PCL-yne and PCL-U-DPy samples with various U-DPy contents (%) recorded at 20 °C.

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vation indicates a high physical crosslinking density functions as a compatibilizer to destroy the crystal structure of PCL and promote the formation of a small extent of an amorphous phase in the crystalline matrix of PCL. Compared to pristine PCL-yne, introduction of an ultralow content of U-DPy dimers in PCL could possibly be used as method of providing powerful nucleating sites to promote strong coupling between neighboring polymer chains, resulting in the formation of highly crystalline structures in the bulk state. This intriguing result led us to further explore the crystallization mechanism of these materials in more detail.

As the crystallization performance of polymers is mainly dependent on the viscoelastic nature of the material matrix, we investigated the dynamic viscoelastic properties of U-DPy-functionalized semicrystalline polymers via rheological measurements. To avoid the effects of crystallization, all samples were melted above the T_m of PCL-yne and rheological measurements were carried out between 60 and 160 °C. Dynamic storage modulus (G'), loss modulus (G'') and complex viscosity were plotted against temperature in a logarithmic format, as shown in Figure 3a and Figure S9 (Supporting Information). Over the entire temperature range, the rheological responses of PCL-yne and 0.1% U-DPy demonstrated a fluid-like behavior ($G'' > G'$) with low G' (≈10^2 Pa) and viscosity (<10^2 Pa s), indicating that attachment of 0.1% U-DPy units did not affect the rheological properties of the PCL backbone. Interestingly, 0.4% U-DPy displayed a clear phase transition at 65 °C from an elastic-like solid ($G' > G''$) to a fluid-like state ($G'' > G'$). This observation implies that a temperature-dependent association occurs between the hydrogen bonding U-DPy moieties, in which the U-DPy dimers can reversibly rebind, even though only a small amount of U-DPy is present. In agreement, the viscosity of 0.4% U-DPy dropped rapidly from 425 Pa s at 60 °C to 270 Pa s at 65 °C. This suggestion was further supported by the evidence that dissociated hydrogen-bond complexes formed as the temperature increased, indicating a significant conformational change in the polymer network. Further increasing the U-DPy content above 0.8% led to a fully elastic state ($G' > G''$) with strong rubber-like properties, reflecting the fact that a high number of physical "cross-linking points" were still present within the polymer matrix. Surprisingly, the viscosity of the 0.8% and 1.5% U-DPy samples did not significantly change over a wide temperature range. Even at temperatures over 160 °C, these samples maintained a high viscosity above 5200 Pa s, suggesting the robust physically cross-linked SPN was not appreciably destroyed during the heating process and conferred excellent thermal stability and mechanical properties.[33,34] These observations also indicate that the formation of reversible cross-linking networks depends linearly on the content of U-DPy dimers in PCL, as the 0.1% and 0.4% U-DPy moieties could rapidly and reversibly induce new rebinding sites to enhance the crystallization ability of PCL.

To further interpret the viscoelastic behavior of these samples, especially at extremely low U-DPy contents, the activation energy (E_a) of dissociation for these SPNs was estimated using the Arrhenius equation. Subsequently, the temperature dependence of the shift factors (a_T) was used to establish modulus master curves.[43] A plot of a_T (ordinate) versus inverse temperature (abscissa) generated linear relationships for the PCL-yne and PCL-U-DPy samples (Figure S10, Supporting Information), indicating these materials follow the Arrhenius behavior over the wide temperature range from 80 to 160 °C and the extent of E_a within the PCL-U-DPy matrix could be evaluated

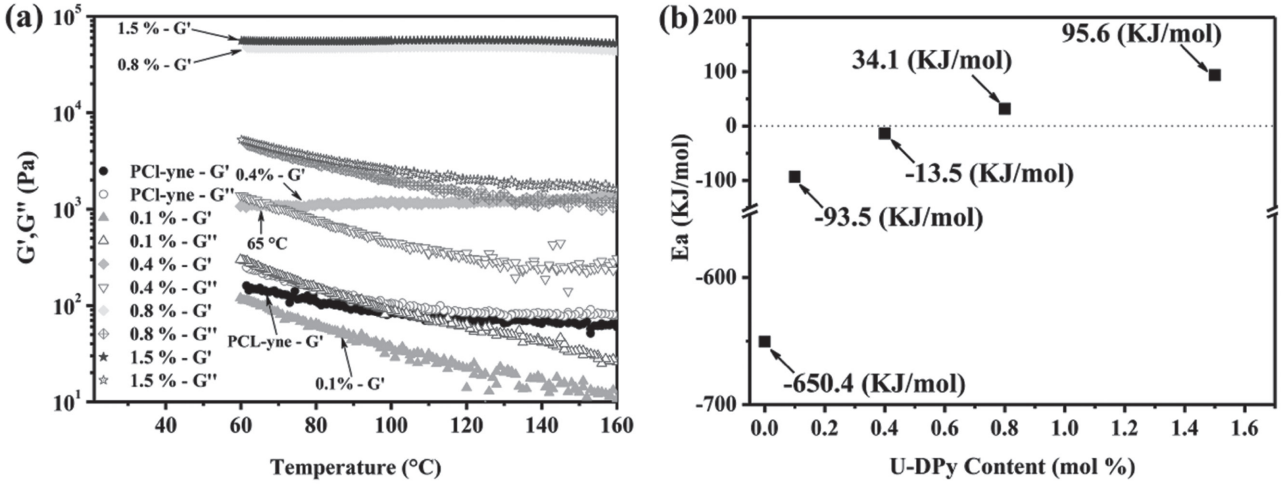

Figure 3. a) Dynamic rheology analysis for PCL-yne and PCL-U-DPy samples with various U-DPy contents (%): temperature stability sweep of storage modulus (G') and loss modulus (G') from 60 to 160 °C. b) Activation energy (E_a) as a function of U-DPy content in the PCL matrix. The E_a values were calculated from the temperature dependence of the shift factors (a_T).

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from the gradient of the line. As shown in Figure 3b, all PCL-U-DPy samples had substantially increased E_a values compared with PCL-yne (–650.4 kJ mol^{-1}). The E_a values of the 0.1% and 0.4% U-DPy samples were –93.5 and –13.5 kJ mol^{-1}, respectively, which were lower than the 0.8% (34.1 kJ mol^{-1}) and 1.5% (95.6 kJ mol^{-1}) U-DPy samples. These data indicate that the elevation in E_a induced by increasing the U-DPy content of PCL can be attributed to the phase transition from an orderly semicrystalline structure to a partly cross-linked structure, which decreases the rate of crystallization and crystal size due to the kinetic equilibrium of molecular recognition between higher numbers of U-DPy units. Notably, the 0.1% and 0.4% U-DPy samples possessed a negative E_a close to zero, which permits crystallization to proceed spontaneously, implying that an extremely low content of U-DPy moieties provides sufficient nucleating sites and strongly affects the alignment, self-assembly, and crystallization behavior of the PCL chains. In other words, at temperatures above the melting temperature of PCL, the relaxation processes in polymer networks seem to be a crucial factor to maintain a homogeneous liquid phase with negative activation energy due to the destruction of hydrogen-bonding interactions between lower numbers of U-DPy units. Thus, an extremely low content of U-DPy moieties will reform dimers and small clusters during the cooling crystallization process of PCL-U-DPy, which may provide nucleation sites for facilitating crystal growth and reducing the crystallization half time. In addition, the enhanced overall crystallization performance can also be attributed to improved balance in polymer chain mobility within a dynamic SPN and achievement of a moderate degree of viscoelasticity within the polymer, due to the increased numbers of effective collisions between pendant U-DPy groups. Collectively, this study indicates that these PCL-U-DPy materials represent a highly efficient SPN system that could be employed to substantially improve the performance of polymer crystallization.

3. Conclusion

In conclusion, we have successfully developed a new breakthrough strategy for fabricating a high-performance semicrystalline polymer, PCL-U-DPy, based on the presence of self-complementary hydrogen-bonded U-DPy moieties and functionalized PCL. In contrast to previous studies of conventional PCL materials,[9–14] physically cross-linked PCL-U-DPy can spontaneously self-assemble into a stable SPN structure in the bulk state that exhibits several unique properties, including excellent thermal and viscoelastic properties, as well as high dynamic structural stability. Due to the ability to vary the extent of the reversible network by tuning the U-DPy content, these materials can be easily tailored to obtain the desired crystallization properties, a feature which is an extremely rare and highly desirable within polymer-based crystalline materials. Excitingly, incorporating only 0.1% U-DPy resulted in a polymer with a high crystallization rate constant and short crystallization half-time, as well as more rapid crystallization kinetics, compared to pristine PCL-yne. Therefore, introduction of an extremely low content of U-DPy moieties into the PCL matrix provides an efficient method of introducing nucleation sites in order to manipulate the nucleation and growth process of the polymer crystals to promote crystallization and chain alignment in bulk. While the main objective of this study was to create a dynamic SPN strategy for development of hydrogen-bonded semicrystalline polymers with tunable crystalline integrity, we envision that this newly developed strategy could have more widespread potential for range of practical applications, especially for fully biodegradable synthetic polymers. These avenues of research are currently being pursued in our laboratory, including further exploration of the mechanical properties and degradation ability of these materials with respect to biomedical applications.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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