

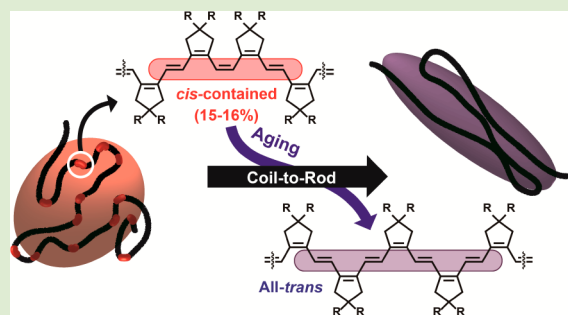
Coil-to-Rod Transition of Conjugated Polymers Prepared by Cyclopolymerization of 1,6-Heptadiynes

Eun-Hye Kang and Tae-Lim Choi*

Department of Chemistry, Seoul National University, Seoul 151-747, Korea

Supporting Information

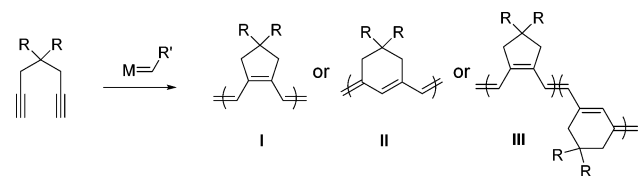
ABSTRACT: We report the conformational change resulting from the coil-to-rod transition in conjugated polymers prepared by the cyclopolymerization of 1,6-heptadiyne derivatives (poly(cyclopentenylene-vinylene), PCPV). By aging a PCPV solution under various conditions, we observed dramatic changes in their absorption spectra (appearance of a 0–0 vibronic peak) and an increase in the Mark–Houwink–Sakurada shape parameter, thereby confirming the coil-to-rod transition of the polymer. Further studies using NMR spectroscopy and various control experiments demonstrated that the coil-to-rod transformation resulted from the *cis*-to-*trans* isomerization of the conjugated olefins by a radical mechanism.



The conformational behavior of conjugated polymers (CPs) is understood to differ from the classic random-coil model, because of their longer persistence lengths derived from π -electron delocalization.¹ These studies of CPs have been of great interest to many physicists and chemists because the optical and electronic properties of CPs are affected by both the conformation of the single chains and the interaction between individual chains.² Many spectroscopic investigations have been carried out on well-known CPs such as poly(3-alkylthiophenes) (PATs)³ and poly(phenylenevinyls) (PPVs) to elucidate structure–property relationships with respect to the electronic transitions and energy transfer of the CPs.⁴

The cyclopolymerization of 1,6-heptadiyne derivatives via olefin metathesis reaction is one of the most powerful methods for synthesizing soluble polyacetylenes with either cyclopentenylene-vinylene alternating repeat units (I), methylidene-cyclohexene repeat units (II), or a random mixture of the two units (III) (Scheme 1).⁵ During the past two decades,

Scheme 1. Cyclopolymerization of 1,6-Heptadiynes by Various Olefin Metathesis Catalysts



many efforts have been made to avoid the random structure seen in III by developing a regioselective polymerization to expand the scope of this polymerization.⁶ We recently reported an efficient living cyclopolymerization using a third-generation Grubbs catalyst to afford polyenes containing either regioregular five- or six-membered rings.⁷ This powerful catalysis

provided access to several interesting polymer architectures such as block copolymers,⁷ molecular brushes,⁸ and core–shell nanostructures.⁹ However, the macromolecular conformation and optical properties of these poly(cyclopentenylene-vinylene)s (PCPVs, I) are still little understood; only a few studies on II or III, prepared from the cyclopolymerization of diethyl dipropargylmalonate (DEDPM), have been reported.¹⁰ On the other hand, I exhibits an interesting absorption spectrum showing clear vibronic bands, which are absent in the spectra of II and III,^{7a,11} and these bands provide information on the conformational order of the more coplanar polymer backbone.⁸ Unfortunately, little attention has been paid to investigating the conformational-spectroscopic correlation for PCPV systems.¹²

Recently, we reported the synthesis of brush polymers containing a PCPV backbone and observed a unique change in the absorption spectrum by simple “aging”. From the absorption spectrum, the Huang–Rhys factor (S), a measure of the degree of how CP adopts a 1-D-like conformation, as predicted by quantum mechanical calculations, was extracted. The decrease in S suggested that the brush polymers underwent a coil-to-rod conformational change.⁸ This conformational transformation was further confirmed by the increase in the Mark–Houwink–Sakurada shape parameter, α . This analysis was quite meaningful because for the first time, a theoretical prediction obtained from spectroscopy was confirmed by a chemical method using viscosity measurements. Here, we address the origins of these coil-to-rod conformational changes by investigating PCPV as a model. Using NMR analysis, UV–vis spectroscopy, and viscosity measurements, we confirmed that simple aging under light caused *cis*-to-*trans* isomerization

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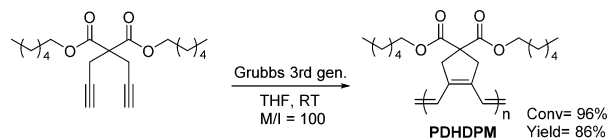
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of the olefins of the polyenes. This isomerization to the more stretched *E*-olefins in turn led to the coil-to-rod transition.

To check the generality of the previously observed conformational change, we chose to examine poly-(dihexyldipropargylmalonate) (PDHDPM, $M_n = 44.3$ kDa, PDI = 2.1, yield = 86%) as a model polymer and measured the absorption spectra at various aging times in THF (Scheme 2).¹³

Scheme 2. Synthesis and Chemical Structure of PDHDPM



The Huang–Rhys factor, S , is a theoretical prediction of the configurational displacement of the potential energy curve upon electronic excitation, so that S reflects the conformational disorder of CPs.¹⁴ In other words, a lower S value as a result of an increased intensity of the 0–0 vibronic peak in the absorption spectra corresponds to a more extended conformation for CPs. Similar to the brush polymer, when a dilute solution of PDHDPM was aged, λ_{\max} of the 0–0 band was red-shifted (approximately 13 nm), and a gradual increase in the vibronic signal was observed with the aging time. From these spectral changes, S was easily calculated from the relative intensities of the 0–1 and 0–0 vibronic peaks in the absorption spectrum (eq 1 and Figure 1a).

$$I_{1\leftarrow 0}/I_{0\leftarrow 0} = S \quad (1)$$

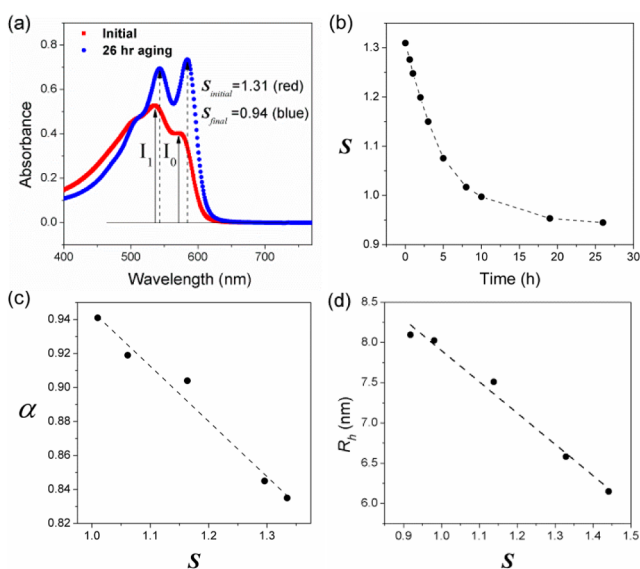


Figure 1. (a) Change in the absorption spectrum of PDHDPM in THF (0.2 g/L); (b) Time-dependent changes in the Huang–Rhys factor S ; (c) Linear correlation between S – α and (d) S – R_h during the aging process in THF (2 g/L for (c) and 1 g/L for (d)).¹⁵

As shown in Figure 1b, S decreased from 1.31 to 0.94 over a period of 1 day in THF, demonstrating that the change to a more extended conformation was not limited to brush polymers. As another proof for the coil-to-rod transition, the shape parameter α , obtained by SEC-viscometry analysis, gradually increased from 0.83 to 0.94 (Figure 1c). Moreover, the increase in hydrodynamic radius (R_h) of the polymer

measured by dynamic light scattering (DLS) with the decrease in S and the shift of SEC trace to the left after the aging further supported the conformation transition (Figure 1d and see Supporting Information, Figure S1). With an excellent correlation between S and α for PDHDPM and other substituted PCPVs (Figure S2), we concluded that this coil-to-rod transformation was a general phenomenon for cyclo-polymerized products containing five-membered rings.

To obtain a better understanding of this coil-to-rod transition, we investigated how the transformation rate was affected by various changes in the aging conditions such as solvent, concentration, and light source. (i) *Solvent*: Among the many organic solvents tested, chloroform and dichloromethane (DCM) induced the fastest transition, which was completed in only a few minutes (monitored by UV–vis analysis), while other solvents (chlorobenzene, THF, etc.) showed much slower changes on the time scale of hours (Figure S3). This explains why the transition has not been observed by others; the changes are too rapid in chloroform and DCM, which are the most commonly used solvents to prepare and study these polyenes. This extreme solvent dependence implied a transformation based on chemical reactions rather than physical folding or aggregation, because all the tested solvents were good solvent to fully dissolve PDHDPM. (ii) *Concentration*: A lower concentration induced a faster conformational change (Figure S4). Consequently, the transition to the extended conformation was not caused by intermolecular aggregation of the polymers. (iii) *Light source*: The presence of light and the nature of the light source significantly affected the transition rate. The transition in dark was much slower than that when the polymer solution was exposed to an ordinary fluorescent lamp (Figure S5). To compare the effect of light in detail, polymer solution in THF was exposed to blue and green LED with narrow wavelength ranges for aging. Irradiation by the blue LED provoked a faster change than did irradiation by the green LED, even though the absorption λ_{\max} of PDHDPM matched well with the wavelength of the green LED (Figure S6). These results suggest that changes in the chemical structure of the conjugated backbone are responsible for the transition rather than changes in the electronic structure.

Based on all the factors that influenced the transition, we hypothesized that the conformational change was caused by *cis*-to-*trans* isomerization of the vinyl group in the conjugated backbone through a radical process, as the transition was accelerated in chlorinated solvents¹⁶ and by exposure to light. If the transformation depended on the stereochemistry of the conjugated olefin, NMR spectroscopy would be a definitive tool for a precise analysis. Unfortunately, the signals for the olefinic protons in the previously studied brush polymers were too weak in ^1H NMR spectra because of overwhelming signals from the polymeric side chains. Conversely, the ^1H NMR spectrum of PDHDPM showed clear signals for the conjugated olefinic protons. To suppress the transformation, we chose THF- d_8 as the optimal solvent for NMR analysis. Before aging, three different olefinic signals were initially observed (Figure 2), labeled as A (6.86 ppm), B (6.52 ppm), and C (6.33 ppm). Interestingly, other groups observed only a single olefinic signal at 6.8 ppm in CDCl_3 .¹⁷

To fully characterize these peaks, we conducted two-dimensional (2-D) NMR analysis, homonuclear correlation spectroscopy (COSY), and Nuclear Overhauser effect spectroscopy (NOESY; Figures S7 and S8). First, singlet A was unambiguously assigned as the *E*-olefin proton.¹⁷ Definitive

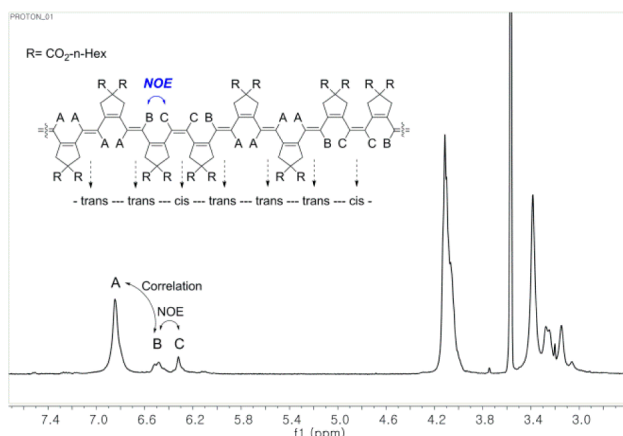


Figure 2. ^1H NMR spectrum of PDHDPM in $\text{THF-}d_8$ with the protons assigned by 2-D NMR.

cross peak coupling between the A and B protons was observed in the COSY spectrum, confirming that B was also an *E*-olefin proton but located in a different environment than A. NOESY revealed a strong interaction between B and C, but no through-bond interaction was shown by COSY. Therefore, we assigned the C proton as belonging to the *Z*-olefins and B as the *E*-proton next to the *Z*-olefin, which brings B and C very close to each other in space (Figure 2). The integration values for B and C were nearly equal, supporting the assignment of a *trans*–*cis*–*trans* structure. From these results, the initial *E*:*Z* ratio was calculated as 5.4:1 (16% *cis*-olefin).

To understand the origin of the coil-to-rod transition, we monitored the changes in the *E*:*Z* ratio of the polymer with aging time. Indeed, as the aging proceeded, a gradual decrease in the signals for B and C was evident, and the initial *E*:*Z* ratio of 5.4 increased to 11.7 after 5 h. The signals from B and C disappeared completely after 8 h (Figure 3a). Moreover, the real-time changes in the *S* values correlated well with the integration changes in the NMR spectra when the polymer

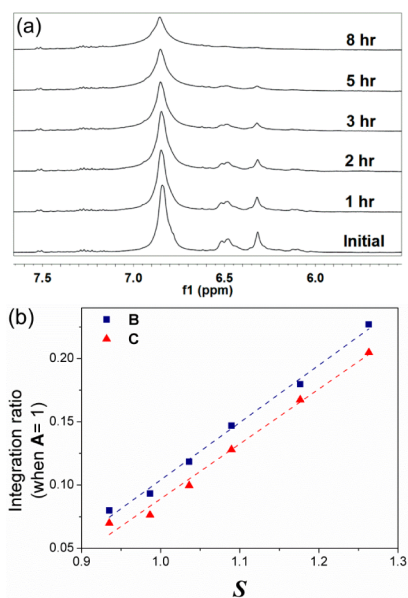


Figure 3. (a) Change in the ^1H NMR spectrum for a PDHDPM solution in $\text{THF-}d_8$ aged by blue LED light and (b) a plot of *S* and the corresponding integration ratios of B and C from ^1H NMR.

solution was aged by blue LED light (Figure 3b). For example, the initial *E*:*Z* ratio in Figure 3a was 5.4:1 when *S* was 1.26, and after 5 h of aging, the *E*:*Z* ratio increased to 11.7:1 with a concomitant decrease of *S* to 0.99, confirming that the *cis*-to-*trans* isomerization caused the coil-to-rod transition. This isomerization extended the polymer conformation because the *cis*-geometry of the olefin imposes kinks in the polymer (more steric hindrance), resulting in a twist in the conjugated backbone and a lower coplanarity, while the *trans*-olefin experiences no such hindrance, thereby increasing the conjugation length and stretching the polymer chain. In short, the conformational transformation by aging was caused by a change in the molecular structure, *cis*-to-*trans* isomerization, which led to a macroscopic change.

To provide further support for the *cis*-to-*trans* isomerization and to understand the mechanism, we designed two more experiments. (i) *I*₂ addition: Iodine is a well-known reagent that isomerizes olefins including polyacetylene.¹⁸ We prepared a PDHDPM film and exposed it to iodine vapors. The excess iodine was removed by vacuum, and subsequent absorption spectrum analysis and shape parameter analysis in THF revealed that the coil-to-rod transition occurred rapidly within 30 min (Figure 4a). Addition of iodine to the polymer solution induced the same rapid isomerization and transformation to the rod-like structure. (ii) Addition of a radical scavenger: Based on the observation that the isomerization was facilitated by light, a radical generator, we proposed that the isomerization proceeded through a radical mechanism. To test this idea, a radical scavenger, butylated hydroxytoluene (BHT), was added to the polymer solution in chloroform to monitor the effect. Indeed, the solution exposed to 0.001 M BHT underwent a much slower transition compared to the control experiment without BHT. Furthermore, adding more BHT (0.01 M) retarded the transition even further (Figure 4b). TEMPO, another radical scavenger, worked in a similar fashion to reduce the rate of isomerization by the same mechanism (Figure S9). All the data supported the coil-to-rod transition due to *cis*-to-*trans* isomerization via a radical mechanism.

Even though the initial *cis*-vinylene content was relatively low (16%), the *cis*-component could behave as a “defect” to shorten the effective conjugation length, resulting in a more coil-like conformation. Therefore, the irreversible isomerization to *trans*-vinylene resulted in a dramatic spectral change. We can perceive this phenomenon as an extension of short polyene systems such as carotenoids, which show a similar behavior. For example, a similar change in the vibronic peaks was observed in the absorption spectra for the mono-*cis* and all-*trans* isomers of β -carotene.¹⁹ However, in the case of the polymer, the changes are more drastic, as they involved more than just a local molecular change, but a macroscopic conformational change in the nanostructure, as confirmed by the Mark–Houwink–Sakurada parameter.

Our conclusion can explain many observations in the literature. First, others could not notice this transition because DCM and chloroform were used, both of which promote rapid isomerization, and thus, only *E*-olefins were obtained. Second, a clean transformation to a rod-like structure was observed for the brush polymer, as confirmed by the viscosity and AFM analysis.⁸ This also explains why the isomerization for the brush polymer was much slower than that for PDHDPM, because the bulky polymeric side chains retarded the radical isomerization. We were fortunate to observe this transformation for the brush

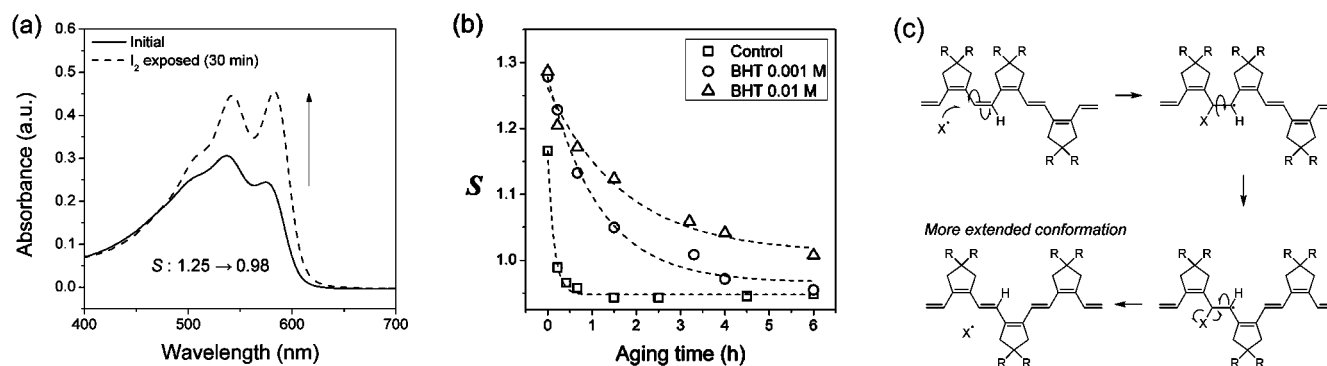


Figure 4. Change in the UV-vis spectra by (a) I_2 vapor and (b) BHT addition in chloroform. (c) Isomerization by radical mechanism.

polymers even in isomerization-promoting solvents such as DCM and chloroform.

The observation of well-resolved vibronic bands in solution even at room temperature is a unique characteristic of PCPV, which distinguishes it from many other CPs whose absorption spectra usually exhibit ill-defined and broadened electronic transitions. With numerous debates on the origins and contributions of the inhomogeneous line broadening of the optical spectra of PPVs,²⁰ the intense 0–0 vibronic transition of PCPVs containing only *E*-olefins may provide an interesting insight into the structure–property relationships of CPs¹⁰ as well as their energy relaxation dynamics.²¹

In summary, we demonstrated that PCPV, a product of cyclopolymerization, underwent *cis*-to-*trans* isomerization leading to a coil-to-rod conformational transition. From our detailed 1H NMR observations, we confirmed that the initial polymer containing 16% *cis*-olefin was isomerized to the final structure of all-*trans*-vinylene. This *cis*-to-*trans* isomerization resulted in a decrease in *S* and an increase in the shape factor α , confirming the chain extension of PCPV leading to the coil-to-rod transition. A radical mechanism was proposed for the isomerization based on several control experiments (solvent, light, and the addition of iodine and radical scavengers). The linear relationships among *S*, the *E*:*Z* ratio, and α showed a unique correlation of chemical, optical, and physical properties, supporting the changes in macroscopic structure. It is very important to emphasize that all the transitions were slow enough in THF so that the analyses could be reliably conducted, whereas the transition in DCM or chloroform was too rapid to be detected.

■ ASSOCIATED CONTENT

Supporting Information

Detailed experimental procedures, isomerization results of other polymers, control experiments data in various conditions, and NMR analysis. This material is available free of charge via the Internet at <http://pubs.acs.org>.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: tlc@snu.ac.kr.

Notes

The authors declare no competing financial interest.

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stabilizer, the decomposition of the CPs occurred at faster rate, presumably due to peroxide radical generated from THF.

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