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Synthesis and Nonlinear Optical Analysis of Triblock Copolymers Containing Discrete Polyenes

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ABSTRACT: Ring-opening metathesis polymerization of methyltetracyclododecene with Mo(CHCMe$_3$)(NAr)(OCMe$_3$)$_2$ (Ar = 2,6-diisopropylphenyl) followed by termination with an excess of conjugated dialdehyde yielded end-functionalized homopolymers with low polydispersities. Subsequent linking of the homopolymers with either a conjugated, difunctional molybdenum alkylidene complex or a bisphosphonate ester resulted in triblock copolymers containing a discrete 9-, 10-, 11-, or 12-ene. The hyperpolarizabilities of the polyenes were measured with electronic field induced second harmonic generation and corresponded well with polyene hyperpolarizabilities found in a previous study of triblock copolymers containing a distribution of polyenes.

Introduction

Research on the nonlinear optical (NLO) properties or organic molecules and polymers has been driven both by interest in their use in NLO devices and by the desire to understand the molecular and electronic processes that cause their NLO behavior. Organic NLO materials have several advantages over their crystalline inorganic counterparts. They have a sub-picosecond response time and would be relatively inexpensive and easy to fabricate.[1–3] The NLO behavior of a vast array of organic molecules and polymers has been examined.[4] In all of these molecules the magnitude of the first and second hyperpolarizabilities, β and γ, respectively, depends on the extent of π electron conjugation. Thus, a firm knowledge of the relationship between the molecular hyperpolarizability and the conjugation length is necessary for the development of new NLO organic materials, the study of existing organic NLO materials, and the enhanced understanding of the electronic origin of NLO behavior.

In previous research,[5] we experimentally characterized the exponential relationship between second hyperpolarizability and conjugation length in a series of triblock copolymers containing unsubstituted, all-trans polyenes. The triblock copolymers increased the solubility of the model polyenes by 3 orders of magnitude, permitting the NLO properties of the polyenes to be characterized in solution by electronic field induced second harmonic generation (EFISH). Although the copolymer system had the advantage of increased solubility without destroying the model nature of the polyenes studied, it was complicated by the presence of a distribution of polyene lengths in each copolymer. Because of the polyene distribution, the UV/vis spectrum of each copolymer had to be deconvoluted to determine the mole fraction of each polyene in the copolymer. Then the polyene mole fractions were used in a model of the EFISH data to determine the contribution of each polyene to the effective hyperpolarizability of the copolymer.[5]

In this article, we present a method for the synthesis of a series of triblock copolymers, each of which contains only one specific polyene. The synthesis of copolymers containing discrete polyenes eliminated the need to deconvolute the UV/vis spectra and to extract NLO behavior indirectly using a model of the EFISH data as was done with the previously studied copolymers that contained a distribution of polyene lengths. Triblock copolymers containing a discrete 9-, 10-, 11-, or 12-ene were synthesized. The synthesis was a two-step procedure, first using ring-opening metathesis polymerization (ROMP) with a molybdenum neopentylidene initiator,[6] methyltetracyclododecene monomer (MTD), and an excess of one of two conjugated dialdehydes to form an aldehyde end-functionalized homopolymer of MTD. The end-functionalized homopolymers then were linked together with either a conjugated, difunctional molybdenum alkylidene complex[7] or a bisphosphonate ester,[8] resulting in an A–B–A triblock copolymer in which the discrete polyene was the center block. The resulting series of triblock copolymers was subsequently examined with UV/vis spectroscopy and EFISH. The hyperpolarizabilities of the discrete polyenes were compared with the exponential fit that we obtained in our previous work.[5]

Copolymer Synthesis

General Procedures. All syntheses were performed under a nitrogen atmosphere in a Vacuum Atmospheres drybox or by using standard Schlenk/vacuum line techniques. Tetrahydrofuran (THF) was degassed, stirred over sodium/potassium alloy (Na/K) until the solvent turned blue, and then vacuum transferred immediately before use. Toluene for polymerizations was distilled over sodium and then stored over Na/K under nitrogen and filtered and degassed prior to use. Pivaldehyde was distilled twice from calcium hydride, degassed, and stored under nitrogen at −40 °C. Lithium *tert*-butoxide was prepared from *n*-butyllithium and *tert*-butyl alcohol. MTD (**2**) was purified by vacuum distillation over sodium. Mo(CHCMe$_3$)(NAr)(OCMe$_3$)$_2$ (Ar = 2,6-diisopropylphenyl) (**1**),[9] hexa-2,4-diene-1,6-dial (**3a**),[10] octa-2,4,6-triene-1,8-dial (**4a**),[11,12] (*E*)-tetraethyl but-2-ene-1,4-diphosphonate (**3b**),[13,14] and (THF)(R$_{F6}$O)$_2$(ArN)Mo(CH)$_6$Mo(NAr)(OR$_{F6}$)$_2$(THF) (**4b**)[7] were synthesized according to literature procedures. The numbers **3a**, **3b**, **4a**, and **4b** correspond to the number of double bonds each molecule adds to the polyene in the synthesis.

Synthetic Method. All polymers were synthesized by ROMP using initiator **1**. This initiator yields homopoly-

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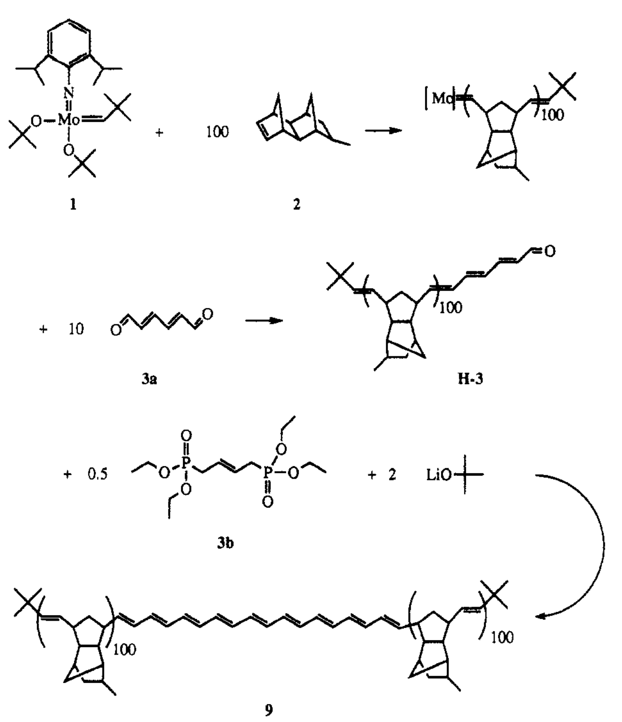

Figure 1. Example of linking copolymerization route to triblock copolymer **9**.

mers of norbornene that have a very narrow molecular weight distribution.[6] Unlike its tungsten alkylidene analogs, **1** reacts with an aldehyde to form only the trans olefin.[15,16] **2** was used to form the solubilizing blocks because its polymer precipitates more readily than polynorbornene.

All of the copolymers studied here have the same basic structure: $[2]_{100}$–polyene–$[2]_{100}$. The subscripts refer to the number of equivalents added during the polymerization; the actual block lengths may vary. The copolymer numbers **9–12** used below refer to the conjugation length of the discrete polyene in the copolymer.

The linking copolymerization of **9**, diagrammed in Figure 1, is presented as an example of the polymerization technique. A solution of **1** (51.4 mg, 0.105 mmol) in 2 mL of toluene was injected into a solution of **2** (1.84 g, 10.5 mmol) in 25 mL of toluene at room temperature, and the mixture was stirred. After 5 min this mixture was added to a solution of **3a** (116 mg, 1.05 mmol) in 30 mL of toluene to terminate the polymerization, yielding the end-functionalized homopolymer **H-3**. Initiator residue and excess dialdehyde were removed by precipitating **H-3** by dropwise addition of the polymerization solution to cold methanol. The polymer was collected on a glass frit, washed with cold methanol, and dried under vacuum. Part of the polymer was set aside for analysis. The remaining polymer (1.60 g, 0.09 mmol) was redissolved in 40 mL of THF. Solutions of **3b** (14.6 mg, 0.044 mmol) in 1.5 mL of THF and lithium *tert*-butoxide (14.2 mg, 0.178 mmol) in 1.2 mL of THF were added to the polymer solution. The solution was stirred for 1 h. Then the solvent was removed in vacuo to drive the linking reaction to completion.

The polymer was redissolved in 6 mL of toluene. An excess of pivaldehyde was added to the solution to deactivate any extant linking agent. After the solution was stirred for 30 min, the polymer was fractionated by dropwise addition of approximately 12 mL of pentane to the polymer solution at room temperature. The addition of pentane was stopped when the mixture appeared slightly cloudy. It was stirred for 1 h and then placed in a −40 °C refrigerator overnight, during which time the solution separated into two phases. The top phase contained all of the unlinked homopolymer, and the bottom phase contained the pure triblock copolymer. The bottom phase was isolated, the solvent was removed in vacuo, and the polymer was analyzed by gel permeation chromatography (GPC) and UV/vis spectroscopy.

A few aspects of the general synthetic route deserve special attention. Use of **4a** instead of **3a** synthesized the end-functionalized homopolymer **H-4**, which has one more conjugated double bond than **H-3**. **H-3** linked with **3b** or **4b** yielded copolymer **9** or **11**, respectively. Similarly, **H-4** linked with **3b** or **4b** yielded copolymer **10** or **12**, respectively. **3b** and **4b** react with aldehydes to form trans olefins,[15,17] such that the final polyene is all-trans. As before,[5] use of 0.5 equiv of **3a** terminated the polymerization and yielded copolymer **4**, which had a discrete 4-ene as its middle block. Due to a lack of **4a**, the analogous copolymer **5** was not synthesized. In all cases, no photoisomerization was necessary, unlike the polyenes in our previous research.[5]

Experimental Section

The polymers were characterized by GPC, UV/vis spectroscopy, and EFISH as in our previous research.[5] GPC was used primarily to determine the quality of the end-functionalized homopolymer of MTD. The purity of the final triblock copolymer was analyzed with UV/vis spectroscopy. The effective molecular weight M_P of each copolymer was calculated from the UV/vis spectra and the extinction coefficients found in the literature.[18] and used in our previous study.[5] M_P is the mass of copolymer per mole of polyene.

The hyperpolarizability $\gamma_P^{2\omega}$ of each copolymer was determined from EFISH at a fundamental wavelength of $\omega = 1.34\ \mu$m. All measurements of $\gamma_P^{2\omega}$ were performed with the copolymer dissolved in THF. Absorption studies showed that less than 0.5% of the fundamental beam is absorbed by the solvent THF in the EFISH cell. $\gamma_{MTD}^{2\omega}$ of $[MTD]_{200}$ homopolymer was 250 $\times 10^{-36}$ esu. The hyperpolarizability of each discrete N-ene moiety $\gamma_N^{2\omega}$ was calculated directly from

$$\gamma_N^{2\omega} = \gamma_P^{2\omega} - \frac{M_P}{M_H}\gamma_{MTD}^{2\omega} \qquad (1)$$

where M_H is the mass of $[MTD]_{200}$ homopolymer. The factor M_P/M_H accounts for variations in effective copolymer molecular weight from sample to sample. The sign of $\gamma_P^{2\omega}$ was determined directly from the EFISH measurements of copolymer in THF and similar relative EFISH measurements of THF in acetone. The macroscopic nonlinear coefficient of THF was referenced to acetone and chloroform, which in turn were referenced to quartz.[19]

Results

Copolymer Synthesis. Polymerization of homopolymers of **2** with the ROMP initiator **1** has been reported previously.[20] It was necessary to use a large excess of the difunctional terminating agents **3a** or **4a** to avoid linking two homopolymers and forming a double molecular weight polymer. Termination with a 10-fold excess of **3a** or **4a** prevented the formation of a significant amount of double molecular weight material, as determined by GPC. The GPC scans of the end-functionalized homopolymers consisted of a single, narrow peak, with polydispersities in the range 1.04–1.07. Both **H-3** and **H-4** were white in color.

The linking of the end-functionalized homopolymers with **3b** or **4b** yielded a material that primarily consisted of the linked triblock copolymer. However, a nonnegligible amount of unlinked homopolymer was apparent in both the GPC scan and the UV/vis spectrum for each sample. Repeated fractionation effectively isolated the triblock

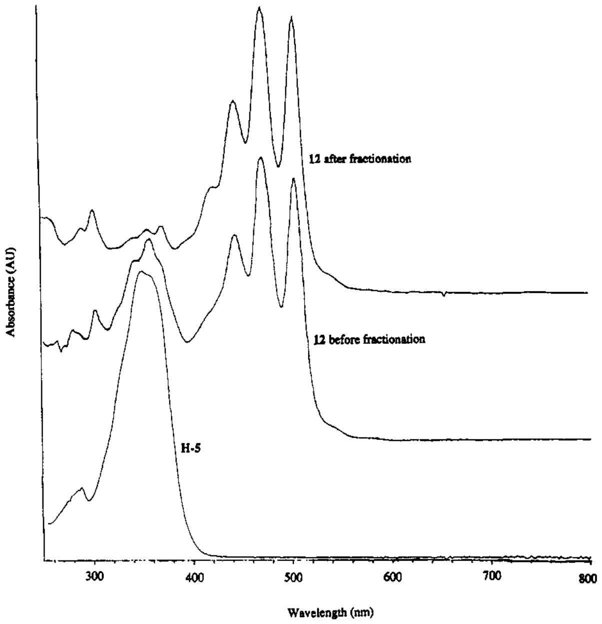

Figure 2. Comparison of UV/vis spectrum of homopolymer **H-5** and copolymer **12** before and after fractionation.

copolymer. The triblock copolymers **9–12** ranged in color from orange to red.

UV/Vis Spectroscopy. The UV/vis spectra of the end-functionalized homopolymers **H-3** and **H-4** in THF consisted of a single broad peak with a λ_{max} at 322 or 352, respectively. This peak corresponded to the absorbance of the conjugated aldehyde of **H-3** and **H-4**. The conjugated aldehyde absorbance had no distinct features such as the vibronic fingers seen in the polyene spectra. After the linking reaction, there were two dominant features in the spectra, as shown in Figure 2. The peak corresponding to the conjugated aldehyde was still present. The other dominant feature was the polyene $\pi\pi^*$ absorption band consisting of a series of vibronic fingers as seen before.[5,18] In the case of samples **9** and **11**, which were linked with the bisphosphonate, the absorbance corresponding to the polyene was much larger than that of the conjugated aldehyde. For samples **10** and **12**, which were linked with the difunctional molybdenum complex, the absorbance corresponding to the conjugated aldehyde was approximately equal to that of the polyene.

After isolation of the copolymers by fractionation, their spectra did not have the absorbance corresponding to the conjugated aldehyde of **H-3** and **H-4**, as shown in Figure 2. The spectra of the isolated copolymers were virtually identical to the spectra of isolated *tert*-butyl-capped polyenes,[18] except for a small (~8 nm) red shift in the wavelength of absorption. Small absorbances corresponding to the $3^1A_g \leftarrow 1^1A_g$ and the $2^1B_u \leftarrow 1^1A_g$ transitions were observed at wavelengths shorter than those corresponding $\pi\pi^*$ transition.

Electronic Field Induced Second Harmonic Generation. The hyperpolarizability of the poly(MTD) homopolymer (approximately 200 equiv) was 250×10^{-36} esu. The hyperpolarizabilities of the discrete polyenes in the triblock copolymers were positive and are presented in Figure 3. The straight line in the log–log graph displays the previously determined[5] exponential dependence of polyene hyperpolarizability on conjugation length.

Discussion

Triblock copolymers containing polyenes were synthesized previously[5] by ROMP with **1** and a polyacetylene precursor monomer,[21] followed by linking termination with **3a** or **4a**. The use of the polyacetylene precursor monomer resulted in a distribution of conjugation lengths within each block copolymer. The synthetic route presented here was more arduous but resulted in a polymer containing only one particular polyene. This technique also had the advantage that the synthesis yielded all-trans polyenes; the photoisomerization used in our earlier study was not required here. As before,[5] the poly(MTD) chains solubilized the polyene, allowing its NLO behavior to be studied in solution with EFISH.

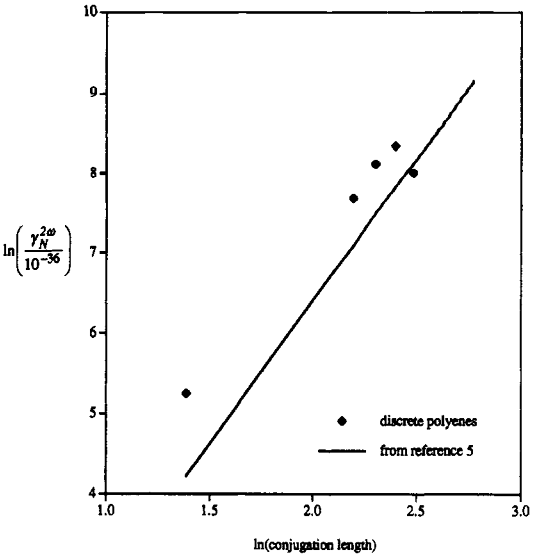

Figure 3. Comparison of the $\gamma_N^{2\omega}$ of the discrete, polyenes and the exponential dependence determined from a set of copolymers that contained a distribution of polyenes.[5]

The UV/vis spectra of **9–12** were different from those in our previous study[5] in that the $\pi\pi^*$ transition for only one particular polyene was apparent and the λ_{max} of the vibronic fingers of the discrete polyenes were red shifted by 4–6 nm from the corresponding previously determined λ_{max} values.[5] The red shift in the absorbance of the polyenes was caused by the presence of the long poly(MTD) chains, as compared to the short polynorbornene chains of our previous study, and, to a lesser extent, by the greater trans character of the discrete polyenes. In the previous study, the polyenes were only ~95% all-trans, whereas in this study they are 100% all-trans.

The hyperpolarizabilities determined here were positive, as predicted by theory,[22] and corresponded well in form and magnitude with the fit determined in our previous study, as shown in Figure 3. The least-square fit on the exponential law $\gamma_N^{2\omega} = \gamma_1^{2\omega}/N^{\alpha}$ performed on $N = 9$, 10, and 11, gives the same value of α ($\alpha = 3.6$) as found in our previous study.[5] In addition, it must be pointed out that, owing to the large contribution of the poly(MTD) blocks to $\gamma_P^{2\omega}$, the augmentation in γ obtained upon going from the poly(MTD) homopolymer to the polyene-containing block copolymers is not as large as in our previous study. As an example, $\gamma_{N=9}^{2\omega} = 4.5\gamma_{MTD}^{2\omega}$ whereas the corresponding coefficient in our previous study was 9.2.[5] We also note the disconcerting fact that the measured value of $\gamma_{12}^{2\omega}$ is less than $\gamma_{11}^{2\omega}$. This result could be due to sample degradation; of all the samples, **12** was the most susceptible to degradation because it contained the longest polyene. The larger values of $\gamma_9^{2\omega}$, $\gamma_{10}^{2\omega}$, and $\gamma_{11}^{2\omega}$ compared to the previous study might be due to the greater trans isomer content of the discrete polyenes.

Conclusion

Similar to previous work, ROMP of MTD with a molybdenum neopentylidene initiator yielded homopolymers with very low polydispersities. These homopolymers could be end-functionalized and subsequently linked with either a bisphosphonate ester or a conjugated, difunctional molybdenum alkylidene complex to yield triblock copolymers containing discrete 9-, 10-, 11-, or 12-enes. After separation from unlinked diblock copolymer by fractionation, these polyenes were shown to be pure and discrete by UV/vis spectroscopy.

The poly(MTD) chains solubilized the otherwise isoluble polyenes, thereby permitting examination of their hyperpolarizabilities, which corresponded well with the values determined in our previous study. Although there were some inconsistencies between the hyperpolarizabilities determined in this study, we do not wish to place any undue significance on what could be simply scatter in the data. We are satisfied that the hyperpolarizabilities have approximately the same magnitude and follow the same exponential relationship that we have previously observed.

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