Light-Induced Shape Changes in Azobenzene Functionalized Polymers Prepared by Ring-Opening Metathesis Polymerization

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ABSTRACT: A method for producing well-defined azobenzene functionalized polymers via ring-opening metathesis polymerization (ROMP) is described. ROMP of an isomerically pure *exo*-norbornene ester tethered to an azobenzene unit in the presence of the third generation Grubbs' catalyst was investigated in detail. The polymerization was determined to be living on the basis of a linear relationship between M_n and [M]/[I] and the ability to quantitatively produce chain extended homopolymers. The polymer's physical response to plane-polarized light was studied in thin films and latex particles. A relief grating was inscribed on the surface of a thin film by irradiation with an interference pattern of linearly polarized light. The same material was used to prepare isotropic colloidal particles of the polymer. These latex particles were transformed to ellipsoids in response to irradiation by linearly polarized light perpendicular to the sample surface.

Introduction

Polymers containing azobenzene units in the main chain or as pendant groups along the backbone (azopolymers) have been studied in great detail in recent years due to their rich potential in a variety of applications.[1,2] An assortment of possible photonic applications have been identified, including, but not limited to, reversible optical information storage, chiroptical switches, channel waveguides, and photonic band-gap materials.[3−5] The key process involved is a repeated *trans*−*cis* photoisomerization of the azobenzene units in the presence of polarized light, which ultimately results in the reorientation of the chromophores perpendicular to the plane of polarization.[6] One of the most interesting phenomena associated with the photoisomerization process is massive macroscopic motions of the polymer chains leading to physical deformation of the material.[2] This deformation process has been used to create surface relief gratings (SRGs) in polymer films and to transform isotropic colloidal spheres to ellipsoidal-shaped colloids.[7−9] A number of mechanisms have been proposed to describe the driving force behind the mass transport process, but none can fully account for all the experimental observations put forth.[4]

The majority of side-chain azobenzene polymers reported have the pendant unit tethered to either an epoxy- or acrylic-based backbone.[5] For both cases, the azobenzene unit can be attached to the backbone directly during the polymerization process[10,11] or via a postpolymerization modification.[12−15] The epoxy-based azo polymers are typically formed via a polycondensation between diglycidyl ether of bisphenol A and a functionalized aniline moiety. The acrylic-based polymers are usually prepared using an uncontrolled free-radical polymerization, resulting in a poorly defined and often low molecular weight polymer. These procedures are not amenable for creating more complex systems, such as block copolymers. Recently, well-defined amphiphilic diblock azo copolymers have been prepared via atom transfer radical polymerization.[16,17] However, in those reports, the azo chromophore was substituted with either a methoxy group or an alkyl group *para* to the azo group. In many cases, the desired azo chromophore is substituted with a nitro group at the *para* position, but azopolymers with this substitution have not been synthesized to date in a controlled fashion. Since nitrobenzene groups are known to retard free-radical polymerizations,[18−20] it would be difficult to use any controlled free-radical process to prepare an azopolymer containing a nitro group in the azo chromophore.

Ring-opening metathesis polymerization (ROMP) is an attractive alternative to controlled free-radical polymerizations because well-defined polymers can be obtained with good functional group tolerance.[21,22] Of the various catalyst systems surveyed, Grubbs' first (**1**) and third (**2**) (Figure 1) generation ruthenium complexes have been shown to be effective for preparing highly functional, well-defined, polymers.[23,24] ROMP has previously been shown to be compatible with azobenzenes in the production of cationic organoiron polynorbornenes functionalized with azobenzene chromophores.[25,26]

Herein, we report a detailed study of the polymerization of a pure *exo*-norbornene ester functionalized with an azobeneze chromorphore containing a nitro group in the presence of catalyst **2**. It is shown that the polymerization of the monomer is indeed living and that well-defined polymers can be readily prepared. To study the physical response of the polymer to plane-polarized light, the polymer was cast as a thin film and exposed to a periodic interference pattern. Colloids of the polymer were also prepared by gradual hydrophobic aggregation. Shape transformation of these latex particles was observed upon irradiation with plane-polarized light.

Experimental Section

Materials. Unless otherwise noted, all materials were used as received. CH_2Cl_2 was dried over CaH_2 and distilled prior to use. Deionized water (resistivity = 18.1 MΩ) was obtained from a Millipore water purification system. Complex **2**[27,28] and *exo*-bicyclo-[2.2.1]hept-5-ene-2-carboxylic acid (**3**)[29] were synthesized as previously described.

Bicyclo[2.2.1]hept-5-ene-2-carboxylic Acid 2-{[4-(2-Chloro-4-nitrophenylazo)phenyl]ethylamino}ethyl Ester (4). Disperse Red 13 (DR13) (11.12 g, 31.88 mmol), **3** (4.0 g, 28.95 mmol), and DMAP (0.039 g, 0.32 mmol) were dissolved in CH_2Cl_2 (160 mL). DCC (6.56 g, 31.8 mmol) was dissolved in CH_2Cl_2 (20 mL) and

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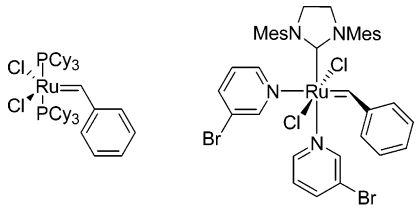


1 **2**

Figure 1. First generation (**1**) and third generation (**2**) Grubbs' catalysts.

added to the above solution dropwise via addition funnel. After stirring overnight, the mixture was cooled over an ice bath prior to vacuum filtration. The filtrate was concentrated, and the remaining crude material was purified by column chromatography (SiO_2; 50:50 petroleum ether:ethyl acetate). The collected fractions were concentrated, and the remaining solid was recrystallized from EtOH to yield 9.64 g (71%) of a deep red solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.27 (t, J = 7.1, 1H), 1.39−1.34 (m, 2H), 1.49 (d, J = 8.9, 1H), 1.89 (td, J = 3.9 11.8, 1H), 2.22 (dd, J = 4.5, 10.06, 1H), 2.92 (s, 1H), 3.00 (s, 1H), 3.55 (q, J = 7.10, 1H), 3.70 (t, J = 6.34, 1H), 4.31 (t, J = 6.3, 2H), 6.11 (ddd, J = 25.31, 5.64, 3.02, 1H), 6.81 (d, J = 9.2, 2H), 7.76 (d, J = 8.9, 1H), 7.93 (d, J = 9.1, 2H), 8.13 (dd, J = 2.4, 8.9 1H), 8.36 (d, J = 2.4, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 12.23, 30.37, 41.55, 43.00, 45.69, 46.32, 46.50, 48.83, 61.16, 111.52, 117.97, 122.56, 125.96, 126.90, 133.96, 135.58, 138.12, 144.40, 147.11, 151.71, 153.02, 176.20. IR cm^{-1} (thin film): 3054, 2987, 1601, 1421, 1340, 1265, 1140, 896, 740, 705. Anal. Calcd for $C_{24}H_{25}ClN_4O_4$: C, 61.47; H, 5.37; N, 11.95. Found: C, 61.26; H, 5.32; N, 11.84. Mp 93−96 °C.

Polymerization Studies. A stock solution of monomer **4** was prepared in dry, degassed CH_2Cl_2 such that the concentration was 0.01 M. A 2 mL portion of the stock solution was transferred to a septa-sealed vial under a N_2 atmosphere. A stock solution of complex **2** (1.0 M) was prepared in degassed CH_2Cl_2, and the desired amount was rapidly added via syringe to the vigorously stirred monomer solution. After 5 min, a large excess of ethyl vinyl ether was injected to stop the polymerization. The samples were allowed to air-dry and dissolved directly in THF for analysis by GPC. For the chain extension experiment, a 1 mL aliquot was removed 5 min after injection of catalyst followed by addition of a second 1 mL portion of monomer. After an additional 5 min, the polymerization was quenched with a large excess of ethyl vinyl ether and allowed to air-dry. TLC analysis was performed for each polymerization which indicated that no residual monomer was present.

Large-Scale Polymerization of 4. A solution of **2** (0.0664 g, 0.075 mmol) in CH_2Cl_2 (10 mL) was rapidly injected via syringe to a vigorously stirred solution of **4** (3.0 g, 6.40 mmol) in CH_2Cl_2 (54 mL) under a N_2 atmosphere at room temperature. After 10 min, a large excess of ethyl vinyl ether was added to quench the reaction. The reaction mixture was poured into stirred methanol, and the resulting precipitate was collected by vacuum filtration and dried under high vacuum to yield 2.98 g of red solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.92−1.26 (bm, 5H), 1.42−1.68 (bm, 1H), 1.72−2.12 (bd, 2H), 2.30−2.75 (bm, 2H), 2.80−3.16 (bd, 1H), 3.32−3.68 (bm, 4H), 4.21 (bs, 2H), 4.99−5.38 (bm, 2H), 6.70 (bs, 2H), 7.66 (bs, 1H), 7.81 (bs, 2H), 8.02 (bs, 1H), 8.25 (bs, 1H). GPC (89% THF, 10% MeOH, 1% TEA): M_n = 35 kDa, PDI = 1.11. DSC (25−200 °C, 10 °C/min, 3 cycles): T_g = 90 °C; UV/vis (0.01 M in CH_2Cl_2): λ_{max} = 490 nm.

Characterization. All ^{1}H and ^{13}C NMR spectra were obtained on a Varian Unity 500 MHz spectrometer in the VOICE NMR laboratory, School of Chemical Sciences (SCS), University of Illinois. Chemical shifts are reported in parts per million (δ) using residual solvent protons as internal standards. Coupling constants (J) are expressed in hertz (Hz), and splitting patterns are expressed as s (singlet), d (doublet), t (triplet), q (quartet), or m (multiplet). The molecular weight and polydispersity of the polymers were estimated in a mixture of THF (89%), methanol (10%), and triethylamine (1%) at 30 °C with a Waters 515 HPLC pump, a Viscotek TDA model 300 triple detector, and a series of three ViskoGEL HR high-resolution columns (1 × G3000 HR, 2 × GMHHR-H mixed bed) at a flow rate of 1.0 mL/min. Molecular weight data are reported as polystyrene equivalents. Scanning electron microscopy (SEM) images were captured on a Phillips XL30 ESEM-FEG operating at an accelerating voltage of 5 kV. Samples were coated with a thin layer of gold/palladium. Atomic force microscopy (AFM) images were obtained on a Digital Instruments Multimode Nanoscope IIIa operating in tapping mode.

Thin Film and Latex Particle Preparation. Thin films were prepared by spin-coating from a filtered THF solution onto glass slides treated with 5:1 H_2SO_4:30% H_2O_2. To prepare colloidal suspensions, the polymer was initially dissolved in *N*-methylpyrrolidone (NMP) (1.25 mg/mL) followed by addition of a suitable amount of water (30 wt % in NMP) via syringe pump at a rate of 5 mL/h. The resulting suspension was dialyzed against deionized water for 3 days to remove NMP. Samples for irradiation were prepared by placing several drops of the water suspension on a glass slide and were dried under ambient conditions.

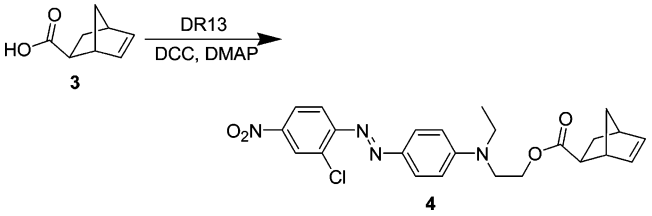
Irradiation Geometry. SRGs were inscribed in the films prepared using a setup similar to those reported previously.[7,8] A linearly polarized beam at 488 nm from an argon laser was passed through a spatial filter, expanded, and collimated. The beam was split by a mirror and reflected onto the sample to create an interference pattern. The angle between the beam propagation axis and the mirror was set at 15°. The power of the laser was measured to be 150 mW/cm^2. For the colloidal spheres, the sample was placed perpendicular to the beam propagation axis.

Results and Discussion

Monomer Synthesis. The proper choice of monomer is crucial for preparing polymers with predefined chain lengths and physical properties. When choosing the appropriate monomer, one has to consider the polymerizable group, the isomeric purity of the polymerizable group, the anchor group, the spacer, and the functional group. The different parts of the monomer structure can influence the kinetics of the polymerization and/or the physical properties of the resulting polymer. For the preparation of highly functional polymers, norbornene-based monomers are typically employed because useful functionalities can be readily incorporated via the [4 + 2] cycloaddition of cyclopentadiene and an electron-deficient olefin.[22] The resulting norborbene is typically a mixture of *endo* and *exo* isomers. It has previously been shown that the *exo* isomer reacts much faster then the *endo* isomer.[30] Our own lab has demonstrated that the difference in rates of polymerization between *endo*- and *exo*-dicyclopentadiene is primarily due to steric interactions between the growing polymer chain and the incoming monomer.[31] The influence of the stereochemical purity of the monomer has also been studied in detail. Weck and co-workers showed that k_p is greatly dependent on the stereochemical purity of the monomer.[32] They showed that a pure *exo* monomer propagated 15 times faster then an 80/20 *endo*/*exo* mixture in presence of complex **1**. Thus, we chose to use a pure *exo* monomer to maintain a high rate of polymerization. The anchor group was chosen to be a carboxylic acid due to the ease of functionalization, and the spacer was chosen to be a short alkyl chain to maintain a high-T_g polymer.

In the case of the azobenzene chromophore, there are many structural factors that affect the macroscopic motion of the polymer in response to plane-polarized light. One such factor with significant influence is the bulkiness of the azo group. The size of the azo group affects the free volume requirements of the chromophore as well as the efficiency of the repeated *trans*−*cis* photoisomerization process. In a study conducted by Rochon et al.,[33] polymers bearing the bulky azo dye DR13 showed a significantly higher diffraction efficiency during SRG

Scheme 1. Synthesis of Azobenzene Functionalized Norbornene Monomer 4 from Pure *exo*-Acid 3



formation then less bulky azo dyes of similar structure. Thus, we chose to incorporate DR13 in the polymer backbone to maximize the physical response of the polymer to plane-polarized light. The synthesis of the monomer involves the DCC/DMAP coupling of pure *exo*-norbornene acid (**3**) prepared according to the method reported Kiesssling et al.[29] with DR13 (Scheme 1).

Polymerization Study. As mentioned previously, complexes **1** and **2** are generally used when polymers of well-defined molecular weight are desired. While **1** is sufficient in many cases, it suffers from low metathesis activity and some functional group intolerance. Complex **2** has been shown to provide high metathesis activity,[24] rapid and complete initiation,[34] and excellent functional group tolerance, making it arguably the most versatile ROMP catalyst. Since we are interested in using ROMP to provide a variety of functional, well-defined polymers, the polymerization of **4** in the presence of **2** was studied in detail. To explore the living nature of the polymerization, the relationship between M_n and [M]:[I] (Figure 2) was examined. As expected, a linear relationship between M_n and [M]:[I] was observed, indicating a living polymerization. To further test the living character of the polymerization, a reinitiation of polymerization was performed by sequential monomer addition to provide a chain extended homopolymer. Monomer **4** was polymerized in the presence of complex **2** for 5 min at room temperature with a target M_n of 25 kDa. An aliquot was removed for analysis followed by injection of a second portion of monomer. During our initial attempts at preparing a chain extended homopolymer, we observed premature termination of the active chain end and were unable to quantitatively reinitiate polymerization. The reaction temperature was subsequently lowered to 0 °C, and early termination was effectively suppressed, allowing for quantitative formation of an elongated homopolymer (Figure 3). While well-defined homopolymers can be obtained with this initiator and monomer combination at room temperature, quantitative chain extension required lowering the reaction temperature to 0 °C.

Polymer Synthesis and Characterization. In order to study the physical properties of the polymer, monomer **4** was

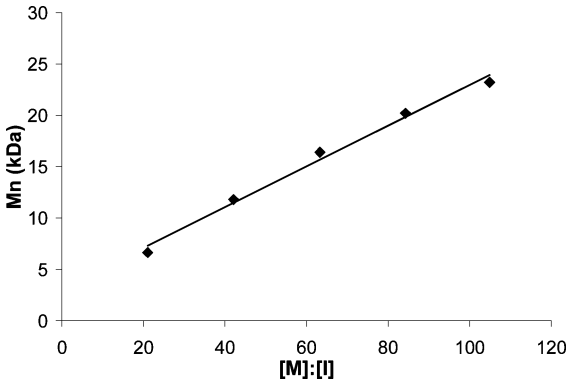


Figure 2. Plot of M_n vs monomer-to-catalyst ratio for the polymerization of monomer **4** in the presence of complex **2**.

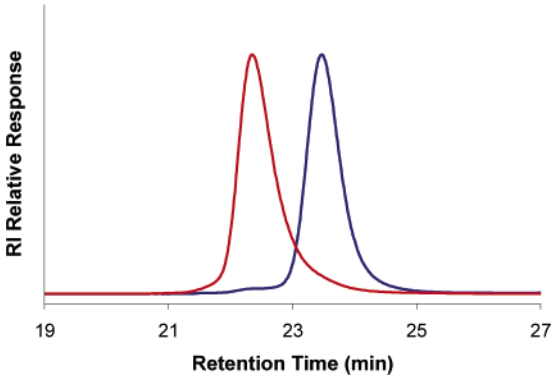


Figure 3. GPC traces of chain-extended homopolymer (red) prepared by sequential addition of monomer **4** to homopolymer (blue) prepared by polymerization of monomer **4** in the presence of initiator **2** at 0 °C for 5 min.

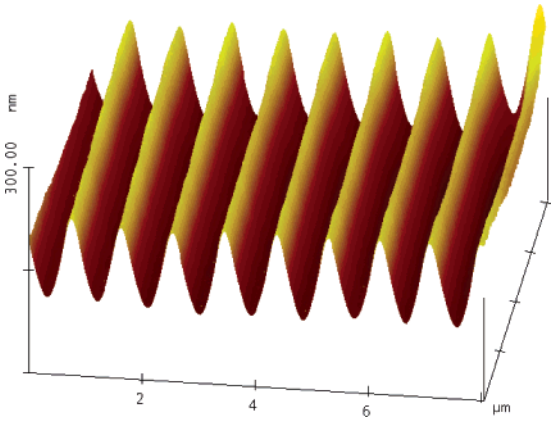


Figure 4. 3-D AFM surface profile of an SRG optically inscribed in a thin film of the polymer by irradiation with an interference pattern of linearly polarized light from an argon laser at 488 nm for 30 min.

polymerized in the presence of complex **2** on a multigram scale. The monomer to catalyst ratio was set such that the target M_n was 40 kDa. The polymer was analyzed by GPC and a well-defined structure was obtained, as evidenced by a low PDI (1.11). Thermal characterization of the polymer by DSC estimated the T_g to be 90 °C, which is similar to methacrylate-based azo polymers.[35] The λ_{max} of the polymer was determined to be 490 nm by UV/vis, indicating that the maximum response to plane-polarized light could be achieved at 488 nm.

Shape Deformation Studies. One of the most interesting uses of azopolymers is in the formation of SRGs from homogeneous thin films. When thin films of azopolymers are exposed to a periodic interference pattern of polarized light, a sinusoidal diffraction grating is formed in the polymer. To study this effect in the polymers prepared by ROMP, thin films of the polymer were prepared by spin-coating from a filtered THF solution. The films were then exposed to an interference pattern of linearly polarized light from an argon laser at 488 nm for 20 min. The resulting surface modulation was characterized by AFM (Figure 4). A regularly spaced sinusoidal pattern was inscribed in a 780 nm thin film with a depth from peak to trough of about 125 nm. The observed depth is comparable to other azobenzene polymers irradiated under similar conditions.[8,33]

Recently, Wang et al. have taken advantage of the macroscopic motions associated with the repeated *trans*−*cis* isomerization process to transform isotropic colloidal spheres to ellipsoids.[9,36] This process allows one to systematically vary the shape asymmetry of the colloid simply by varying the exposure time. We are interested in preparing shape-anisotropic

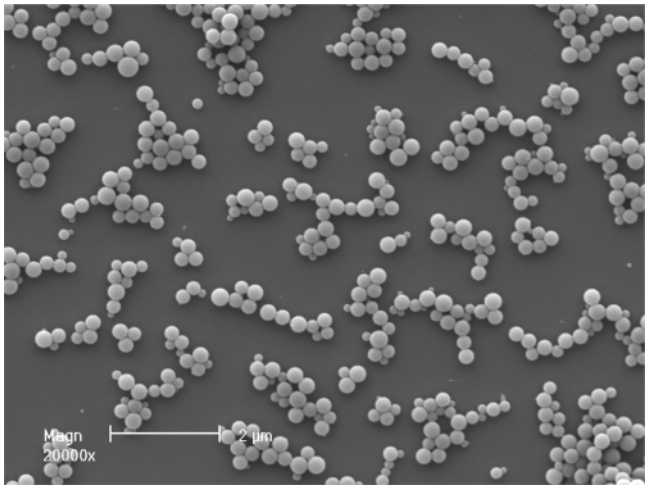


Figure 5. SEM image of colloidal particles formed by controlled addition of water to an NMP solution of the polymer. Average particle diameter is 300 nm.

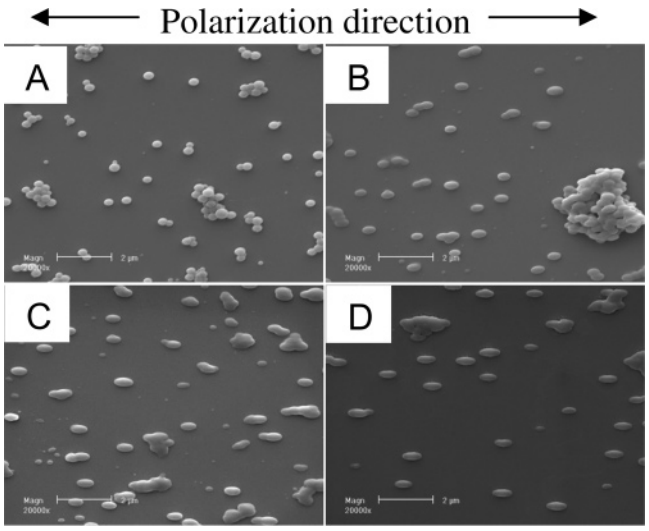


Figure 6. SEM images of colloidal particles photodeformed by irradiation with linearly polarized light for different lengths of time: (A) 5, (B) 10, (C) 15, and (D) 20 min.

colloidal particles to study their self-assembly into well-defined macroscopic structures.

Colloidal spheres were prepared in a manner similar to methods used to prepare polymer colloids from amphiphilic random and block copolymers.[37,38] The polymer was initially dissolved in NMP (1.25 mg/mL), a good solvent for the polymer. Deionized water was added in a controlled manner via syringe pump (5 mL/h) to the vigorously stirred NMP solution, during which the solution became turbid. After addition of water, NMP was removed by dialysis. The formed particles were imaged by SEM (Figure 5), which showed the particles to be moderately polydisperse with an average size of 300 nm. We are currently working toward an optimization of the procedure to produce monodisperse particles.

The colloids were deposited on a glass slide and exposed to a beam of linearly polarized light incident perpendicular to the sample surface. The irradiated particles were imaged by SEM (Figure 6). The particles were observed to elongate in the direction of polarization with time. In some cases, the elongated particles began to "melt" together forming larger, undefined particles. The gradient electric force mechanism described by Kumar et al.[39] could explain why the particles stretch in the direction of polarization since the optically induced gradient

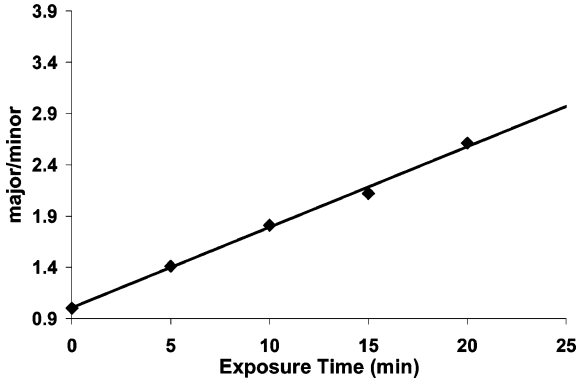


Figure 7. Plot of the ratio of the major axis to the minor axis of the elongated particles vs time.

force is proposed to be in the same direction as the polarization. The elongation process can be quantified by plotting the ratio of the major axis to the minor axis of the stretched particles vs time (Figure 7). The particles elongated in a linear fashion for the time range studied, demonstrating that the anisotropy of the particles can be easily varied by adjusting the exposure time.

Conclusion

We have reported a method for preparing well-defined azopolymers using ROMP. The polymerization of monomer **4** in the presence of complex **2** was studied in detail and was confirmed to be living. This procedure provides a method to readily polymerize monomers functionalized with azobenzene units which contain a nitro group that otherwise could cause retardation in free-radical-based methods. The ability to readily prepare well-defined azobenzene polymers in a living fashion allows for the construction of more complex polymer architectures such as random or block copolymers, which could potentially further expand the scope of azopolymers. Monomer **4** was polymerized on a multigram scale, and the resulting polymer's physical response to linearly polarized light was studied. When the polymer was cast as a thin film, SRG's were inscribed in the film surface when exposed to an interference pattern of linearly polarized light. Moderately polydisperse latex particles were also prepared from the polymer by gradual hydrophobic aggregation. When irradiated with linearly polarized light, the particles stretched in the direction of polarization to form ellipsoids. The degree of stretching was proportional to the irradiation time, allowing for the fine-tuning of the anisotropy induced in the latex particles. We are currently employing ROMP to synthesize a wide variety of azopolymers and other highly functional polymers for the preparation of anisotropically shaped and functionalized colloids.

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Supporting Information Available: Figure S1, DSC curve for third heating cycle of azopolymer; Figure S2, UV/vis spectrum of azopolymer (0.01 M in CH_2Cl_2). This material is free of charge via the Internet at http://pubs.acs.org.

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