

Thermoresponsive, Optically Active Films Based On Diels–Alder Chemistry

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Reversible Diels–Alder chemistry was exploited to develop polymer films in which a change in optical clarity can be thermally triggered. SiO₂ nanoparticles of various sizes were functionalized with maleimido moieties. A furyl-terminated poly(ethylene glycol) linker was prepared and tethered to the SiO₂ nanoparticles via a Diels–Alder (DA) linkage. The pegylated SiO₂ nanoparticles were randomly distributed within a poly(methyl methacrylate) (PMMA) matrix, resulting in an optically transparent film. Annealing the film cleaves the DA linkage and effectively renders the SiO₂ particles immiscible within the PMMA matrix creating a driving force for particle aggregation. The large aggregates were able to scatter light and resulted in an optically opaque film.

Introduction

Diels–Alder (DA) chemistry has been studied for an extensive period of time.^{1,2} A number of research groups have exploited the combination of DA chemistry and block copolymers to prepare organic–inorganic polymer hybrids,³ thermoplastic elastomers,^{4,5} polyurethanes, and foams.⁶ For example, DA linkages lead to the formation of a polymer gel by polymers functionalized with a maleimide moiety and in the presence of a multifunctional furan compound. If that gel is damaged or cracked, one need only anneal the sample to recreate the DA linkages and reconstitute the undamaged material. The reversibility of the DA linkages allows polymer cross-links to be removed by heating, returning the polymer chains to a liquid state that flow into the voids created by the damaging process. Upon cooling, DA linkages form, generating new cross-links and resulting in a polymer gel. Figure 1 illustrates the reversible DA reaction between maleimide and furan, where the DA adduct is formed between RT and 60 °C and the adduct is cleaved at temperature greater than 90 °C.^{1,2}

In two prior studies, we utilized DA chemistry and polymer immiscibility to control particle dispersion and migration properties.^{7,8} Core–shell structures were prepared in which the shell and core were tethered together via a DA

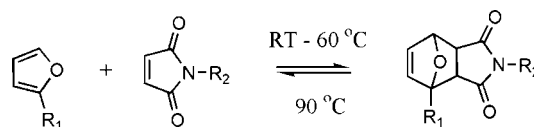


Figure 1. Example of Diels–Alder chemistry, where a furan and maleimide undergo reversible ring formation.

linkage. Depending on the processing conditions, the additive either remained dispersed within the bulk film or migrated to the surface to reduce surface energy. In this work, a similar strategy has been developed to explore the possibility of creating a material that is transparent as prepared but becomes opaque when exposed to specific, elevated temperatures. The concept of manipulating optical properties of films by controlling particle dispersion has been previously demonstrated by Bockstaller et al., in which they found films containing aggregates of Au nanoparticles displayed significantly higher film absorption when compared to films containing a homogeneous dispersion of Au nanoparticles.⁹ Silica particles smaller in size than the wavelength of visible light will be dispersed in a PMMA homopolymer matrix, creating a transparent composite material. A compatibilizing poly(ethylene glycol) (PEG) ligand will be added to the SiO₂ particles to aid dispersion, but the ligand will be attached to the particles via a DA linkage. PEG base ligands were chosen because of their commercial availability and the synthetic accessibility in preparing those ligands. Thus, when the composite is heated above a specific temperature range, the ligands will detach from the particles. The combination of elevated temperature and unfavorable enthalpic and entropic interactions between the SiO₂ particles and the PMMA matrix should lead to the formation of aggregates. If the aggregates are sufficiently large, they will scatter light and render the material opaque. Figure 2 displays a schematic representation of transparent/opaque DA films.

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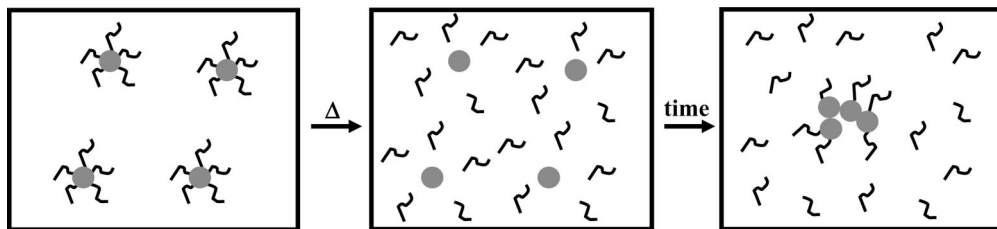
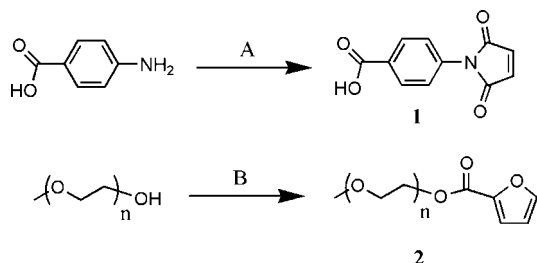


Figure 2. Schematic representation of transparent/opaque DA films. From left to right: SiO₂-DA-PEG additive dispersed within film at RT; thermal treatment results in cleavage of the compatibilizing polymer shell from nanoparticle; aggregation of SiO₂ nanoparticles.

Scheme 1. Synthetic Pathway for Preparation of Maleimido-And Furyl -Functionalized Molecules^a



^a Conditions: (A) maleic anhydride, acetic anhydride, K₂CO₃, DMF, 70 °C, 4 h; (B) 2-furoyl chloride, Et₃N, CH₂Cl₂, 0 °C to RT, 12 h.

Results And Discussion

The synthetic methods utilized will be briefly described (see Schemes 1 and 2). Compound **1** was prepared as previously described.¹⁰ Compound **2** was prepared by treating α -methoxy- ω -hydroxy poly(ethylene glycol) (PEG) (550 g/mol; PDI < 1.05) with 2-furoyl chloride in CH₂Cl₂ in the presence of Et₃N. Poly(methyl methacrylate) (PMMA) matrix was prepared via free-radical polymerization of methyl methacrylate (MMA) utilizing 5 wt % 2,2'-azobis(2-methylpropanitrile) (AIBN) as an initiator, yielding a M_n of approximately 80 000 with a PDI of 1.6. SiO₂ nanoparticles were prepared according to previously published methods,^{11–13} and treated with 3-aminopropyltriethoxysilane to yield SiO₂-NH₂. Next, the carboxylic functionality of compound **1** was activated with *N,N'*-diisopropylcarbodiimide (DIC) in a solution of *N,N*-dimethylformamide (DMF). Subsequently, dimethylamino pyridine (DMAP) was added as a catalyst. The resulting solution was then added to a suspension of SiO₂-NH₂ in DMF and allowed to stir for 24 h. DIC was selected as a coupling agent because the resulting urea byproduct could be removed by centrifugation of the nanoparticles from MeOH. Finally, reacting compound **2** and SiO₂-maleimide together in THF at 60 °C for several days yielded SiO₂-DA-PEG. A stock solution of SiO₂-DA-PEG in THF was prepared. Typically, 50–100 mg of PMMA was dissolved in THF and a portion of the stock solution of SiO₂-DA-PEG was added to prepare films with various weight percentages of additive. After slow evaporation of solvent

(~ 3 days), defect-free films with thicknesses of 150–300 μ m were prepared. PEG and PMMA were selected because they are known to exhibit athermal mixing and form miscible blends over a wide range of temperatures and blend compositions.^{14,15} At room temperature, the value of the Flory–Huggins binary segmental interaction parameter, $\chi_{\text{PMMA/PEG}}$, is -0.005 .¹⁶

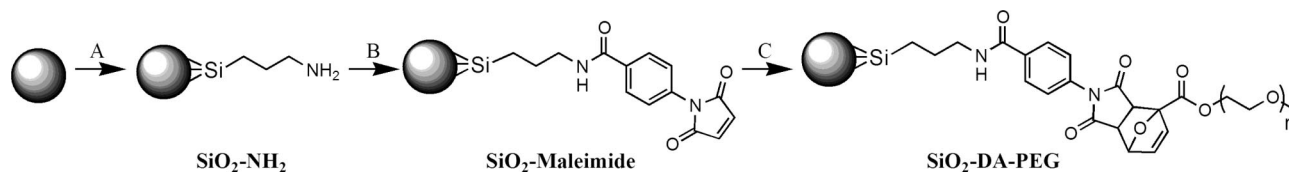
Initial experiments employed 100 nm SiO₂ nanoparticles. A high-quality dispersion of particles this diameter should yield an optically transparent film as determined by Rayleigh scattering intensity, which is proportional to d^6 (where d is particle diameter).¹⁷ After annealing, minimal particle migration would be necessary to yield aggregates with a diameter necessary to affect transparency, i.e., aggregate diameter of ~ 400 nm. Loading 5 and 15 wt % SiO₂-DA-PEG, 100 nm particle diameter, within a PMMA matrix resulted in optically transparent films after room-temperature formation; however, the clarity of films with 30 wt % loading was degraded, indicating the presence of aggregates.

Annealing the 5 and 15% samples resulted in films that were also optically transparent, indicating that significant aggregation did not occur. Figure 3 displays a picture of the film containing 15 wt % additive before and after annealing. Figure 4 displays micrographs from cross-sectional TEM of a film containing 15 wt % 100 nm diameter particles after room-temperature film formation (images A and B) and annealing at 120 °C for 24 h (images C and D). Before annealing, functionalized SiO₂ particles are dispersed within the PMMA matrix at an adequate level, i.e., large areas were present without aggregation. Small aggregates are present, but the overall size and frequency are acceptable. After annealing, no appreciable change in morphology was found, consistent with visual inspection of the samples.

The strength of interparticle interactions in particulate aggregates made the observation of small aggregates in the as prepared materials above undesirable, even though they did not significantly affect the clarity of the samples. To improve the initial dispersion of the 100 nm diameter particles, we subsequently used a longer PEG linker (2,000 g/mol; PDI < 1.05). A longer ligand would improve the solubility of the particles in the PMMA matrix, increasing

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Scheme 2. Synthetic Route for Preparation of SiO₂-DA-PEG Nanoparticles^a

^a Conditions: (A) 3-aminopropyl silane; (B) compound **1**, DIC, DMAP, DMF, RT, 24 h; (C) compound **2**, THF, 60 °C, 3 d.

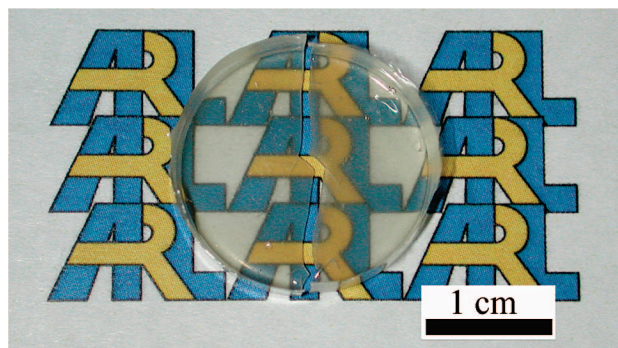


Figure 3. Photograph of 100 nm SiO₂-DA-PEG nanoparticles within a PMMA matrix at a loading of 15 wt % after RT film formation, left, and annealing at 120 °C for 24 h, right.

the favorable interactions between the PEG and PMMA.^{18,19} At room-temperature, however, the behavior of the samples with 2000 g/mol ligands was identical to those with the 630 g/mol ligands. Analysis of the films after annealing at 120 °C for 24 h found a structure similar to that of the nonannealed sample, i.e., a relatively uniform dispersion of individual particles in the presence of small aggregates comprising a few particles only.

Given the miscibility of the ligand and matrix, the minor amount of preliminary aggregation seems unlikely to be a result of enthalpic interactions between these two components. Entropic interactions between the particle and polymer matrix could result in expulsion of the particle from the matrix. The polymer–ligands may not be able to fully wet the matrix resulting in aggregation. The longer PEG linker should have negated this effect by creating more chain entanglements with the ligand and matrix; however, utilizing a longer ligand would also result in fewer polymer–ligands per particle. Because the “grafting onto” approach used here loads the polymer chains onto the particles in a mushroom conformation, increasing the molecular weight of the ligand will also decrease the number of ligands upon the particle, possibly negating the improvement of particle dispersion due to the longer ligand. These conclusions have been previously demonstrated.²⁰ It seems more likely that during the 3 day period required to cast the films, some sedimentation of the particles occurs, resulting in aggregation. If it is the case that aggregation is occurring because of sedimentation, using short ligands such as the 630 g/mol ligands would actually be a good method to address this problem. Smaller ligands

should plasticize the PMMA matrix locally around each nanoparticle, which would improve local particle mobility. A more exact analysis of how the PEG linker affects the PMMA matrix is difficult, because plasticization typically occurs by adding low M_n nonmiscible polymers to a larger M_n matrix. Additionally, recent work by Kumar et al. demonstrated that controlling the interface between the particle and the tethered polymer chain can dramatically alter the T_g of the matrix material.²¹ Therefore, in the case of the 100 nm system, the T_g of the material may have been shifted to above 120 °C, which would also inhibit particle migration. Therefore, after varying the molecular weight of the ligand and observing no improvement upon particle mobility, we propose that the large particles are kinetically trapped once films are formed. Particles of such large diameter exhibit poor mobility and are unable to migrate after solid films are formed.

The Stokes–Einstein relationship shows that the diameter of an object is inversely proportional to the diffusivity of that object through a fluid. Holding all other variables constant, including the viscosity of the fluid and repulsive interactions between the fluid and object, decreasing the diameter of the object increases the diffusivity of that object in the fluid. To improve diffusion within our system, we prepared 40 nm SiO₂ nanoparticles and functionalized them with PEG via the DA linkage following the previously described method. A 40 nm particle should diffuse approximately 2.5 times faster than a 100 nm particle in the same medium and with equivalent repulsive interactions.

Loading the DA-functionalized 40 nm SiO₂ particles into a PMMA matrix at 5 and 15 wt % resulted in optically transparent films after room-temperature film formation. As with the 100 nm diameter particles, 30 wt % loading resulted in opaque films at the end of the solvent evaporation process. Therefore, an empirical upper limit of 15 wt % particle loading was established regardless of the particle diameter. After being annealed at 120 °C for 24 h, films containing 5 wt % SiO₂-DA-PEG, 40 nm particle, were optically transparent, but films containing 15 wt % SiO₂-DA-PEG, 40 nm particle, were optically opaque. Figure 5 displays a photograph of films containing 15 wt % SiO₂-DA-PEG, 40 nm particles, after room-temperature film formation and after annealing at 120 °C for 24 h.

Figure 6 displays micrographs from cross-sectional TEM of a film containing 15 wt % 40 nm diameter particles after room-temperature film formation and annealing at 120 °C for 24 h. The morphological behavior

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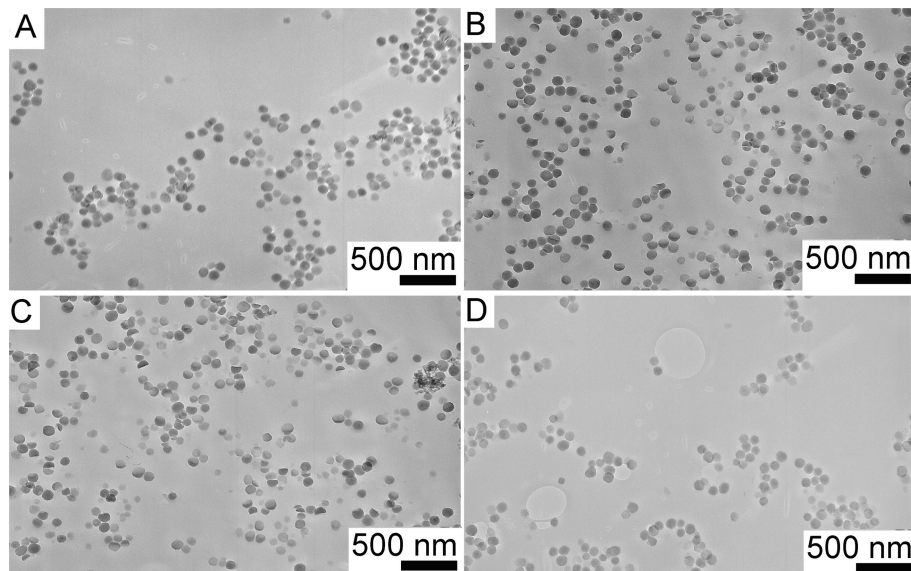


Figure 4. Cross-sectional TEM micrographs of 100 nm SiO₂-DA-PEG nanoparticles within a PMMA matrix at a loading of 15 wt % (A, B) after RT film formation and (C, D) annealing at 120 °C for 24 h.

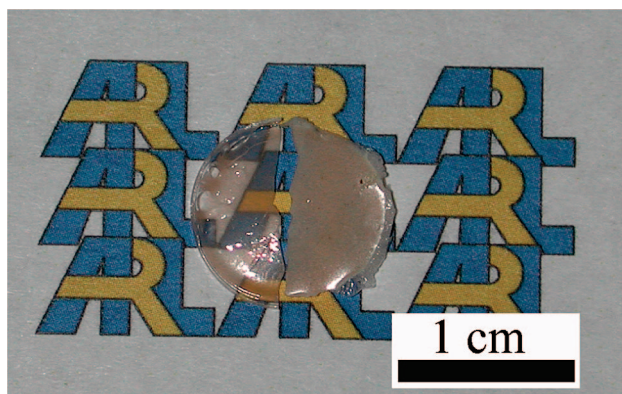


Figure 5. Photograph of 40 nm SiO₂-DA-PEG nanoparticles within a PMMA matrix at a loading of 15 wt % after RT film formation, left, and annealing at 120 °C for 24 h, right.

of these samples is notably different than the comparable samples containing 100 nm particles. Before annealing, small aggregates of the 40 nm particles are visible in the PMMA matrix. A very different film structure is present after the film is annealed at 120 °C for 24 h. Two clear observations can be made. First, the formation of very large and very dense aggregates occurred as the appearance of hexagonal close packed structures are evident. Second, large depletion zones were present. As particles migrate to form aggregates, large areas without particles are created. Attempts to image these depletion zones were unsuccessful because of decomposition of the PMMA matrix with exposure to the TEM electron beam. In general, extended exposure of the sample to the beam resulted in film degradation, which is beginning to occur in Figure 6D. As expected, the mobility of the particles is directly related to the particle diameter.

To better quantify the optical clarity of the films, we measured percent transmission values for the films over the visible spectrum (400–900 nm). Figure 7 displays clarity measurement for films depicted in Figures 3 and 5. Films prepared from solvent evaporation at room temperature (blue

lines) display high percent transmission values indicating high clarity, regardless of the particle size. After annealing at 120 °C for 24 h, the clarity of the film containing 100 nm nanoparticles (red line with circles) remains high, supporting previous results; however, the clarity of the film containing 40 nm nanoparticles (red line with squares) dramatically dropped.

Conclusion

SiO₂ particles, 100 and 40 nm in diameter, were functionalized with PEG via a DA linkage and dispersed in a PMMA matrix. Regardless of particle size, a formulation of additive loading of 30 wt % resulted in opaque films as cast from solution. Lower loadings of 5 and 10 wt % resulted in optically clear films for both particle diameters. Only the sample containing 15 wt % of 40 nm diameter particles resulted in particle aggregation and an optically opaque film. Nanoparticle diameter was critical as large nanoparticles could be dispersed within the matrix, but exhibited poor migration properties. The chemistry involved is simple, straightforward, and amenable to large-scale production.

Experimental Section

Materials. All materials were purchased from Aldrich and used without further purification. Compound **1** was prepared as previously described.¹⁰

Instrumentation. ¹H and ¹³C NMR were conducted on a Bruker-Biospin 600 MHz Ultrashield Avance spectrometer with a standard bore broadband probe (5 mm OD tubes, 32 scans, 5 s d1). Spectra were recorded in CDCl₃, and all resonances were reported as parts per million in reference to the residual solvent peak (δ 7.26 ppm). Bulk films were prepared by slow solvent evaporation of THF solutions of PMMA matrix with various weight percent loading of functionalized SiO₂ nanoparticles. Bulk films were embedded in EpoFix, epoxy-based resin, which cures at room temperature. Specimens for transmission electron microscopy (TEM) were prepared by cutting

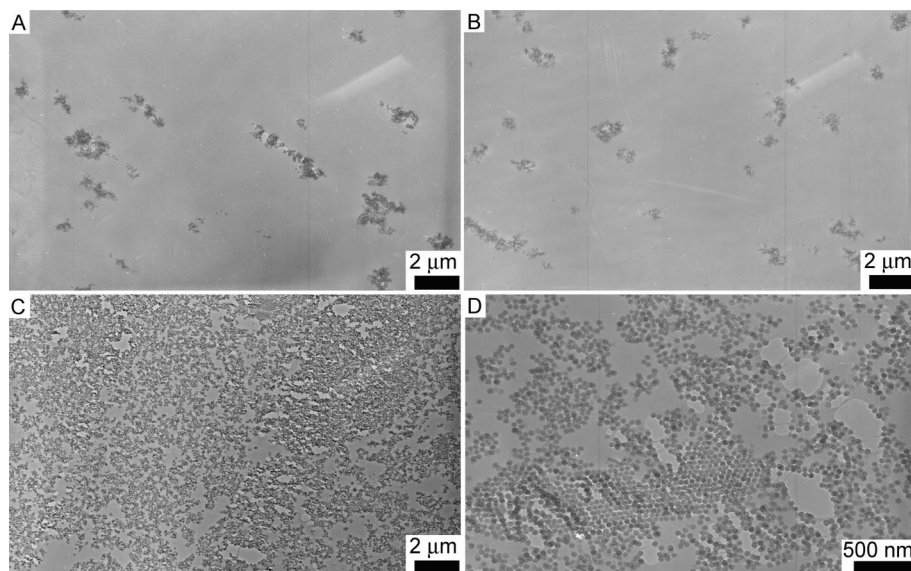


Figure 6. Cross-sectional TEM micrographs of 40 nm SiO₂-DA-PEG nanoparticles within a PMMA matrix at a loading of 15 wt % (A, B) after RT film formation and (C, D) annealing at 120 °C for 24 h.

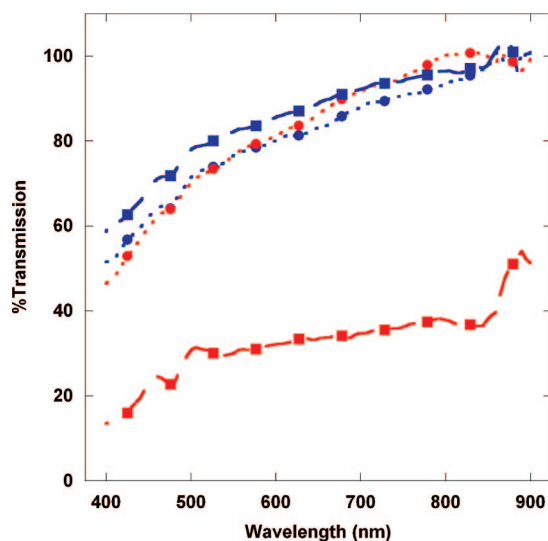


Figure 7. Optical clarity measured as % transmission for samples containing 40 nm (●) and 100 nm (■) functionalized SiO₂ particles at 15 wt % after room-temperature film formation (blue lines) and annealing at 120 °C for 24 h (red lines).

sections approximately 30 nm thick using a Leica Ultracut UCT microtome and a diamond knife utilizing H₂O as a trough liquid. Sections were collected upon Formvar-coated TEM grids. Bright field TEM data were obtained using JEOL 200CX operated at 120 kV accelerating voltage.

Synthesis of α -Methoxy- ω -furfyl Poly(ethylene glycol) (2). Poly(ethylene glycol) ($M_n = 550$ g/mol; PDI < 1.05) (10 g, 18.2 mmol), CH₂Cl₂ (100 mL), Et₃N (3 mL, 22 mmol), and a stir bar were placed into a 250 mL round-bottom flask and cooled to 0 °C. Next, 2-furoyl chloride (2 mL, 20 mmol) was added dropwise over a 15 min period. The flask was warmed to room temperature and stirred for 12 h. The reaction was then washed with H₂O (2 \times , 100 mL), saturated NaHCO₃ (2 \times , 100 mL), and H₂O (2 \times , 100 mL). The solution was dried over anhydrous MgSO₄ and solvent was removed via rotary evaporation to yield **2** (10.3 g, 88%). ¹H NMR: δ 7.58 (1H, d), 7.18 (1H, t), 6.49 (1H, d), 4.42 (2H, t), 3.78 (2H, t), 3.62 (44H, br), 3.52 (2H, t), 3.43 (3H, s).

Preparation of 40 nm Amino-Terminated SiO₂ Nanoparticles (SiO₂-NH₂). Forty nanometer SiO₂ particles were synthesized via a modification of a previously reported method.^{13,22} Igepal CO-520 (40.0 g, 38.4 mL), cyclohexane (100 mL), and a stir bar were placed into a 500 mL round-bottomed flask. The reagents were stirred until a clear microemulsion was present. Next, NH₄OH (8.13 mL, 3.46 M, 28.1 mmol) was added, and the reaction was stirred until clear. Tetraorthosilicate (23.7 mL, 106 mmol) was added, and the reaction was stirred for 16.5 h. Next, aminopropylsilane (1.7 mL, 7.3 mmol) was added and the reaction mixture was stirred for 24 h. Particles were isolated by a series of centrifuge/decant/resuspend cycles with CH₃OH (3 \times) and THF (3 \times) and then stored in THF. A ninhydrin test was positive.

Preparation of 100 nm Amino-Terminated SiO₂ Nanoparticles (SiO₂-NH₂). One hundred nanometer SiO₂ particles were synthesized via a modification of previously reported methods.^{11,12} EtOH (114 mL), NH₄OH (5.7 mL, 28 wt % NH₄OH), and a stir bar were placed into a 250 mL round-bottom flask. Tetraethylorthosilicate (TEOS) (3.8 mL, 25 mmol) was then added and the reaction was stirred at room temperature for 19 h. Next, aminopropylsilane (2.5 mL, 10.7 mmol) was added and the reaction was stirred at room temperature for 24 h. Particles were isolated by a series of centrifuge/decant/resuspend cycles with EtOH (6 \times). A ninhydrin test was positive.

Preparation of Maleimide-Terminated SiO₂ Nanoparticles (SiO₂-maleimide). Compound **1**, DMF and a stir bar were added to a 25 mL round-bottom flask. *N,N'*-Diisopropylcarbodiimide (DIC) was then added and the reaction was stirred at room temperature for 15 min. In a 100 mL round-bottom flask, a suspension of SiO₂-NH₂ particles in DMF was prepared. Next, dimethylamino pyridine (DMAP) was added to the 25 mL round-bottom flask. After being stirred at room temperature for 5 min, the contents of the 25 mL round-bottom flask were transferred to the 100 mL round-bottom flask and stirred at room temperature for 24 h. Particles were isolated by a series of centrifuge/decant/resuspend cycles (5 \times) with CH₃OH/THF (2:1) and dried under a vacuum. A ninhydrin test was negative.

Preparation of Poly(ethylene glycol)-Terminated SiO₂ Nanoparticles (SiO₂-DA-PEG). Compound **2**, SiO₂-maleimide, THF (10 mL) and a stir bar were placed into a 25 mL round-bottom

flask. The suspension was stirred at 60 °C for three days. Particles were isolated by a series of centrifuge/decant/resuspend cycles (5×) with CH₃OH/THF (2:1) and dried under a vacuum.

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