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Styrene/4-hydroxystyrene random, block and gradient copolymers modified with an organic dye: Synthesis by controlled radical polymerization and characterization of electrorheological properties

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Abstract

Styrene/4-hydroxystyrene block and gradient copolymers containing the organic dye Disperse Red 1 (S/HSDR) were synthesized using nitroxide-mediated controlled radical polymerization, and a random copolymer was made using conventional free radical polymerization. The three types of S/HSDR copolymer, with similar molecular weight and composition but different S/HSDR sequence distributions along each copolymer chain, were used as dispersed particles for a study of electrorheological (ER) suspensions. The characterization of each ER fluid as a function of controlled molecular structure in suspension showed different ER behaviors. In particular, the suspension of the S/HSDR gradient copolymer showed the greatest degree of enhancement in shear viscosity, by as much as a factor of 10, upon application of a 1700 kV/m electric field.

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1. Introduction

Electrorheological (ER) fluids are suspensions of polarizable particles in nonconducting oils. They represent a unique class of electroactive materials that exhibit dramatic changes in rheological and electrical properties (e.g. viscosity, yield stress, viscoelasticity, and dielectric constant) in the presence an electric field. This change originates from particle migration and formation of a chainlike or columnar structure oriented along the electric field direction over the gap between the electrodes [1–12]. Their applications are in dampers, shock absorbers, and as ER valves. As a future potential goal, ER fluids requiring a 0.1 V potential change [4] may be useful in simulating mammalian striated skeletal muscle, which has a response time of 0.015–0.120 s.

The strength of an individual column in an ER fluid increases rapidly with column thickness because of multichain interactions. The complexity of the structures formed makes it difficult to fashion theoretical models for the purpose of matching calculations with actual rheological properties; such theoretical models may hold the key to understanding and improving ER fluids. Because the ER effect is strongly influenced by the dipole moment of particles [13,14] and the geometry of the columnar aggregates of ER particles under applied electric field [15–17], it is important to understand further the effect of particle shape characteristics on ER properties. In the case of copolymers used in ER fluids, the copolymer structure will influence particle shape and thereby should influence ER properties.

Controlled radical polymerization, including nitroxide-mediated controlled radical polymerization (NM-CRP) [18,19], is able to produce not only homopolymers but also

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polymers of more complex architecture, e.g. block and gradient copolymers [20–29]. Gradient copolymers are a new class of materials that possess a gradual change in repeat unit composition along all or a significant fraction of the chain, with molecular structures intermediate to those of block and random copolymers [20–29]. Gradient copolymers cannot be made by conventional free radical polymerization (ConvFRP) but can be made by controlled radical polymerization, due to the latter's pseudo-living nature.

Relatively few studies have addressed how the structure of dispersed phase used in ER fluids influences the ER effect [11,30–32]. Here, we study for the first time the ER properties of gradient copolymers and compare them with those of random and block copolymers. In particular, we prepare heterogeneous, anhydrous ER fluids possessing a substantial dipole moment by employing styrene (S)/4-hydroxystyrene (HS) copolymers that are chemically modified with the organic dye Disperse Red 1. Block and gradient copolymers of S and 4-hydroxystyrene containing the organic dye Disperse Red 1 (HSDR) are synthesized by NM-CRP while random copolymer is made by ConvFRP. Three different types of S/HSDR microspheres are used as ER materials, and we investigate the effect of microstructure of polymers by observing their rheological properties upon an application of the electric field.

2. Experimental

2.1. Materials

Styrene (S) and 4-acetoxystyrene (AS), used to make random, block and gradient copolymer structures were purchased from Aldrich and deinhibited using inhibitor remover (Aldrich) and dried over CaH_2. AIBN (Aldrich) was used as the initiator for bulk, ConvFRP of random copolymer while NM-CRP initiator A-T (*N*-(α-methylbenzyloxy)-di-*tert*-butylamine) was employed for the block and gradient copolymers. (See Ref. [21] for synthesis of A-T). Methanol, tertrahydrofuran (THF), and *N*,*N*-dimethylformamide (DMF) were used as received (Aldrich). Silicone oil (Shinetsu) was thoroughly dried in a vacuum oven for 1–2 days prior to use to eliminate any water traces. The kinematic viscosity of the silicone oil was 10 cS, and its density was 0.955 g/cm^3. Disperse Red 1 (4-[*N*-ethyl-*N*-(2-hydroxyethyl)]amino-4-nitraozobenzene) (Aldrich, dye content, ∼50%), *p*-toluenesulfonyl chloride (Aldrich, ≥99%), hydrazine hydrate (Aldrich), potassium carbonate (Aldrich, 99%) were used as received.

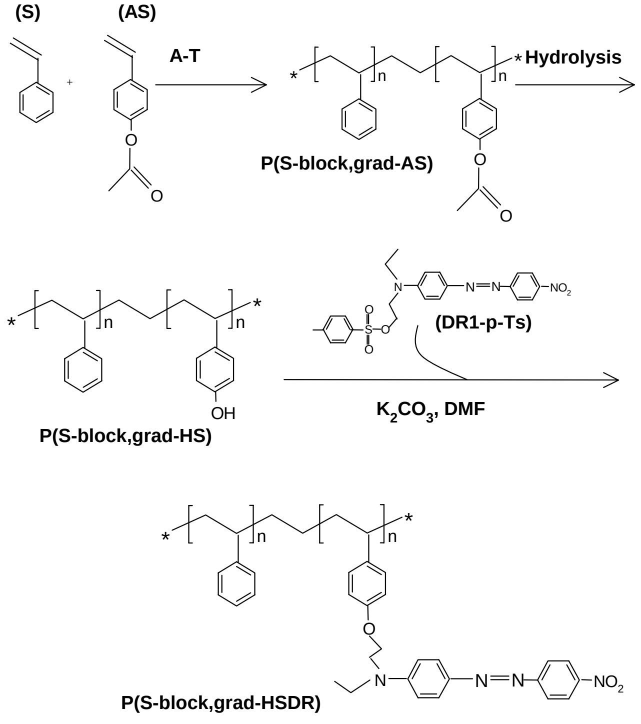
2.2. Synthesis

The S/AS random copolymer was synthesized by a batch, bulk copolymerization. Styrene (13.6 g, 0.131 mol) was combined with AS (14.42 g, 0.089 mol) in a septum-capped test tube, and AIBN (0.056 g, 9.33×10^{-4} mol) was added. The mixture was purged with N_2 for 30 min and then polymerized at 90 °C for 60 min. The resulting copolymer was washed several times via dissolution in THF and precipitation in methanol before being dried under vacuum at 110 °C for several hours, yielding a conversion of 29% as determined gravimetrically.

The S/AS block copolymer was synthesized by two subsequent batches of bulk NM-CRP processes. First, a polystyrene (PS) macroinitiator was synthesized using a mixture of S (9.09 g, 0.087 mol) and A-T (0.009 g, 4.00×10^{-3} mol/l). This mixture was purged with N_2 for 30 min and then reacted at 90 °C for 6 h. GPC: $M_n=35{,}000$ and $M_w/M_n=1.27$. The resulting PS (0.1 g, 3.81×10^{-3} mol/l) was used as a macroinitiator, which was combined with AS (0.800 g, 4.94×10^{-3} mol) and allowed to react further at 90 °C for 1.5 h. The copolymer was washed and dried as described above.

The S/AS 'blocky' gradient copolymer (SgradAS) was synthesized by chain extension of a small M_n PS macroinitiator ($M_n=6500$, $M_w/M_n=1.22$) made by A-T (1.03×10^{-2} mol/l). To a test tube, this PS macroinitiator (0.1 g, 3.81×10^{-3} mol/l) was combined with S (6.36 g, 0.061 mol) and the test tube was placed into an oil bath at 90 °C after being purged with N_2 for 30 min. Semibatch polymerization was performed using a syringe pump to deliver 0.03 ml/min of AS for the first 2 h and then 0.08 ml/min of AS for 4 h to the test tube. During synthesis of the S/AS gradient copolymer, aliquots were removed throughout the reaction to verify the change in overall fractional S content in the copolymer as a function of chain length. The resulting copolymer was washed several times via dissolution in THF and precipitation into methanol, and dried under vacuum at 110 °C for several hours.

In order to transform the S/AS copolymers into S/HS copolymers containing Disperse Red 1 (S/HSDR), hydrolysis of each S/AS copolymer is required. To remove the acetyl



Scheme 1. Schematic for the block and gradient copolymer synthesis pathways.

groups from the AS along the copolymer chain, each S/AS copolymer was added to a flask containing a 9:1 volume ratio of 1,4-dioxane to hydrazine hydrate and stirred in a N_2 atmosphere for 6 h at room temperature [33]. Meanwhile, Disperse Red 1 (DR1) was modified with a toluenesulfonyl group before being tethered to the hydrolyzed copolymers. For this, DR1 was combined with *p*-toluenesulfonyl chloride in a flask, and the mixture was reacted at 45 °C for 48 h, yielding DR1-TS. (See Scheme 1 for the structure of DR1-TS). Finally, to separate flasks were added a DMF solution of potassium carbonate and DR1-TS along with each S/HS copolymer. Each flask was stirred at 45 °C for 6 h after being purged with N_2 for 30 min. The schematic for the reaction pathway is shown in Scheme 1. (It should be noted that Allcock et al. [34] employed a similar procedure to couple the DR1 chromophore to hydroxyl-functionalized polymers, with the hydroxyl units attached to phenyl rings, and achieved 100% coupling efficiency). Excess untethered DR1-TS was extracted by repeated flushing of the copolymer product with methylene chloride during a final filtering process until the methylene chloride being outputted from the filtering apparatus was clear for substantial time.

2.3. Analysis of the copolymers

Gel permeation chromatography (GPC) was used to determine the molecular weights of copolymers and PS macroinitiators relative to PS standards using THF as eluent (Waters Breeze instrument). The styrene mole fraction in each copolymer (F_S) was determined by ^{1}H NMR ($CDCl_3$) spectroscopy using a 500-MHz Varian Inova instrument. (See Ref. [21] for assignment of NMR chemical shift factors used in the determination of the styrene mole fraction of the S/AS copolymers, which is equivalent to the styrene mole fraction in the S/HS and S/HSDR copolymers made by chemically modifying the S/AS copolymers).

2.4. Electrorheological analysis

The DMF solution of each S/HSDR copolymer was precipitated into deionized H_2O, and dried at room temperature for 2 days before being placed in a vacuum oven at 60 °C for 1 day. Prior to preparation of the ER fluid samples, the copolymer was filtered with a 40 μm sieve and further dried in a vacuum oven at a temperature of 40 °C for 12 h. Electrorheological particles and silicone oil were dried in a vacuum oven at 50 °C for 2 days and then stored in a bottle with a molecular sieve to remove any trace of moisture. To prepare the ER fluid for rheological measurements, each copolymer was dispersed in silicone oil. Electrorheological fluids consisting of silicone oil and ER particles were prepared at 20 vol%.

The DC conductivity measurements of each copolymer were done by a four-probe technique using the picoampere-rometer Keithley 237 at room temperature, and graphite glue was used for better contact. A rotational rheometer (Physica MC120) with a couette-type geometry equipped with a high-voltage generator (HV 120) was used to determine the rheological properties of the ER fluids [1]. A concentric, cylinder-type (Z3DIN: the gap between bob and cup is 0.59 mm) measuring system was used. Before each electro-rheological measurement, the suspension in the rheometer was gently stirred using a Teflon rod to ensure that the fluid was uniformly suspended at the outset of the measurement. A slow sedimentation rate was present because the silicon oil had a lower density (0.955 g/cm^3) than the copolymer particles.

3. Results and discussion

Fig. 1 shows the apparent M_n values as a function of polymerization time and the overall styrene mole fraction in the SgradAS sample made via semibatch mode as a function of normalized chain length. There is a steady increase in chain length with polymerization time and a significant reduction in overall fractional styrene content in the gradient copolymers as a function of chain length. The former is proof of the synthesis of 'controlled' polymer; the latter is proof that the product was a gradient copolymer.

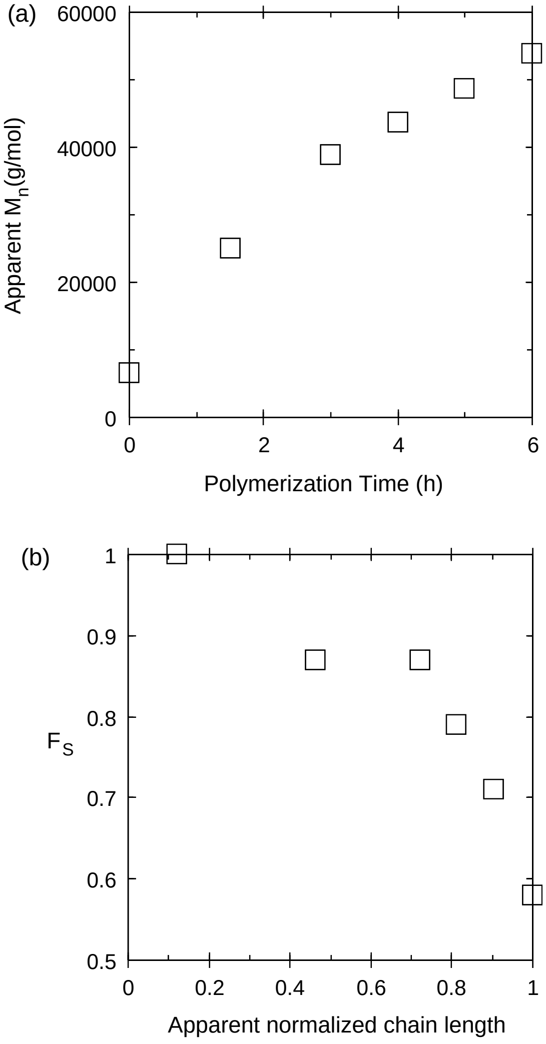


Fig. 1. (a) Apparent number-average molecular weight, M_n, of SgradAS as a function of polymerization time. (b) Cumulative styrene mole fraction (F_S) of SgradAS as a function of apparent normalized chain length.

The resulting S/AS random, block and gradient copolymers were hydrolyzed to S/HS copolymers, and these copolymers were in turn modified to yield S/HSDR random, block and gradient copolymers. Table 1 summarizes the apparent molecular weight average, styrene mole percentage, and conductivity of each S/HSDR copolymer. The S/HSDR random (SranHSDR), block (SblockHSDR) and gradient (SgradHSDR) copolymers have F_S values in a narrow range, 53—58 mol%, and similar values of number average molecular weight, making them good model systems to draw comparisons of ER behavior based on the difference in copolymer structure associated with the sequence distribution of the co-monomers (S and HSDR). The conductivities of the random, block and gradient S/HSDR copolymers were measured to be 4.6×10^{-12}, 9.6×10^{-9}, and 3.1×10^{-10} S/cm, respectively.

Flow curves of shear stress and shear viscosity for SranHSDR, SblockHSDR, and SgradHSDR ER fluids are provided as a function of shear rate in Fig. 2. Data are given both in the absence of an applied field and in the presence of a 1700 kV/m electric field. The flow curves show some common features for each copolymer system. First, there is substantial shear-thinning behavior of all three copolymer ER fluids at low shear rates ($<10^2$ s^{-1}), when hydrodynamic interactions are weaker. Second, at higher shear rates, the curves corresponding to the absence and presence of applied electric field for a given copolymer system tend to merge with increasing shear rate. In other words, above a certain shear rate, the effect of the applied electric field on suspension viscosity is reduced with increasing shear rate. (Related complex ER behavior has been recently noted in ER fluids containing polyaniline-coated poly(methyl methacrylate) particles [35]. This type of shear stress response has been fitted well using a newly introduced constitutive equation [36]).

More importantly, there are noteworthy differences in flow behavior among the copolymer suspensions. In the absence of electric field, the SranHSDR exhibits a shear viscosity of ∼0.02–0.03 Pa s, the SblockHSDR exhibits a shear viscosity of 0.04–0.06 Pa s, and the SgradHSDR exhibits a shear viscosity of 0.11–0.15 Pa s over the shear rate range of 10^2–10^3 s^{-1}. This may be due to differences in the size distribution and the shape of the dispersed aggregates in each S/HSDR copolymer suspension [37–39], which can be influenced by how the polar HSDR units segregate to the particle surface during precipitation. Based on the zero-field shear viscosity values that reflect the macroscopic details associated with dispersed phase of each ER fluid, it is expected that the SgradHSDR system may possess the lowest number of particles that are sufficiently small to be affected by Brownian motion [37,38] as well as the highest fraction of asymmetrically shaped aggregates in the suspension fluid [39].

Table 1
Apparent number-average molecular weight, polydispersity, styrene mole fraction (F_S), and conductivity for S/HSDR copolymers

Sample	$M_{n\ (g/mol)}$ [a]	M_w/M_n [a]	F_S [b]	Conductivity (S/cm)
SranHSDR	66,500	1.64	0.56	4.6×10^{-12}
SblockHSDR	55,000	1.45	0.53	9.6×10^{-9}
SgradHSDR	53,800	1.11	0.58	3.1×10^{-10}

[a] Analysis by GPC on S/AS copolymer precursors.
[b] Analysis by ^{1}H NMR on S/AS copolymer precursors.

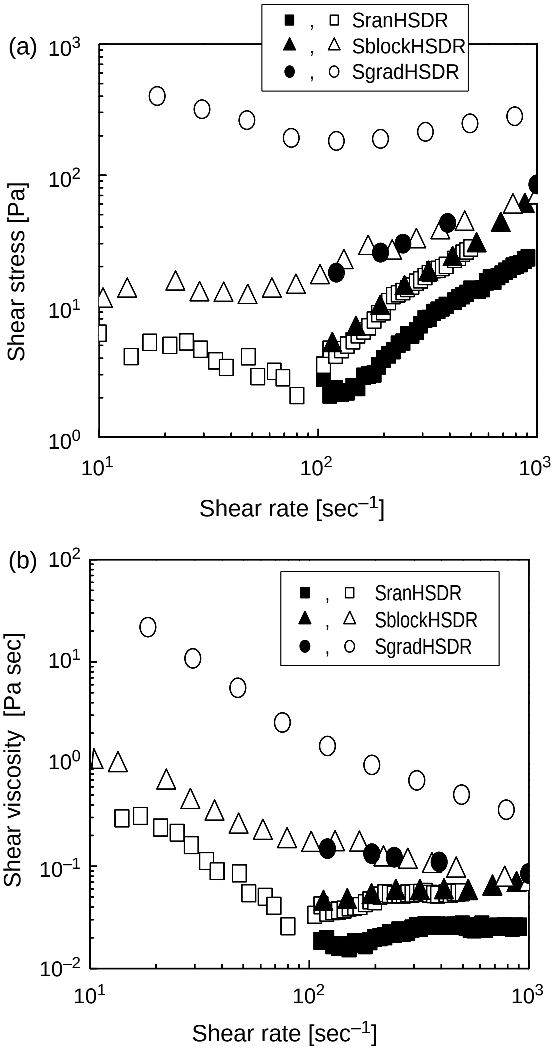


Fig. 2. Flow curves of shear stress (a) and shear viscosity (b) as functions of shear rate for each ER fluid (20 vol % copolymer particles) at 25 °C under 0 and 1700 kV/m electric field. Solid symbols represent the data at 0 kV/m (■, SranHSDR; ▲, SblockHSDR; ●, SgradHSDR), and open symbols represent the data at 1700 kV/m.

Furthermore, upon application of the 1700 kV/m electric field, there is a roughly factor of 2 increase in shear viscosity of SranHSDR, a factor of 1–3 increase in the shear viscosity of the SblockHSDR, and a factor of 3–10 increase in the shear viscosity of the SgradHSDR. Although the SblockHSDR has a substantially higher conductivity (Table 1) than the SgradHSDR as measured in bulk disks, the SgradHSDR ER fluid exhibits a greater electrorheological effect than that of the block copolymer. It is possible that the structure of the SgradHSDR particles may favor an anisotropic shape due to the gradual change in the polarizable HSDR units along the individual copolymer chain. With a greater anisotropic shape, the particles of S/HSDR gradient copolymers would have a greater tendency of fibrillation under the shear flow and external electric field than those of block copolymers.

These results indicate that the details of the copolymer backbone structure can play significant roles in the flow behavior of the copolymer suspensions as well as the response of the copolymer suspensions to an applied electric field. The gradient copolymer system exhibits both the greatest enhancement of the viscosity of the suspension relative to neat silicone oil and the greatest response to the applied electric field, as measured over the shear rate range of 10^2–10^3 s^{-1}. Further investigation is warranted of the detailed mechanism of ER effects associated with the sequence distribution of polarizable units along copolymers and also for developing a better understanding of how particle size and shape distributions impact ER behavior.

4. Conclusions

Styrene/4-hydroxystyrene block and gradient copolymers containing the organic dye Disperse Red 1 (S/HSDR) were synthesized by nitroxide-mediated controlled radical polymerization, and a random copolymer was made by conventional free radical polymerization. Three different types of S/HSDR microspheres were used for a study of electrorheological (ER) behaviors, and each ER fluid system exhibited an enhancement of shear viscosity under application of an electric field, relative to the zero-field viscosity. The ER properties were found to be a function of the type of copolymer used in the ER fluid. In particular, the suspensions of S/HSDR gradient copolymer showed greater enhancement of ER properties than those of random or block copolymer suspensions with similar copolymer MW and overall copolymer composition.

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