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Stretched Exponential Stress Relaxation in a Thermally Reversible, Physically Associating Block Copolymer Solution

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ABSTRACT

The shear stress relaxation of a thermally reversible, physically associating solution formed from a triblock copolymer in solvent selective for the mid-block was found to be well described over a broad temperature range by a stretched exponential function with a temperature independent 'stretching exponent', $\beta \approx 1/3$. This same exponent value has been suggested to have particular significance in describing structural relaxation in a wide range of disordered viscoelastic materials ranging from associating polymer materials ('gels') to glass-forming liquids. We quantify the temperature dependence of the high frequency, or short time, shear modulus as function of temperature and find that this property also follows a variation often observed in gels and glass-forming materials.

INTRODUCTION

Stretched exponential functions are frequently utilized to describe the relaxation dynamics of complex fluids and other strongly interacting materials. [1] In particular, this functional form has been employed to describe the relaxation of polymer networks and gels, including transient telechelic networks in water [2] and symmetric triblock copolymer melts. [3] More recently, the relaxation of triblock copolymer physically associating solutions has been found to display stretched exponential relaxation having the specific form [4]:

$$G(t,\gamma_0) = G(0,\gamma_0)\exp\left[-\left(\frac{t}{\tau}\right)^{\beta}\right], \qquad 0 < \beta < 1 \tag{1}$$

where $G(0, \gamma_0)$ is the relaxation shear modulus extrapolated to zero time, τ is the apparent viscoelastic relaxation time in the small-strain linear regime, and the 'stretching exponent' β describes the width of the relaxation time distribution ($\beta = 1$ indicates a single relaxation time [1]). As illustrated in the present work, the thermo-reversibility of the triblock copolymer solution allows for the deduction of a relaxation master curve that can be well described by a stretched exponential function with $\beta = 1/3$ over a broad temperature range. The potential significance of this finding is briefly discussed.

EXPERIMENT

Materials

The physically associating solution is composed of a volume fraction of 5 % acrylic triblock copolymer dissolved in a midblock-selective solvent. The triblock copolymer molecule is comprised of two 8 900 g/mol, poly(methyl methacrylate) (PMMA) end-blocks separated by a 53 000 g/mol, poly(n-butyl acrylate) (PnBA) mid-block (Kuraray, Inc.‡). The polydispersity of the copolymer chain is 1.26. The solvent is 2-ethyl-1-hexanol, used as received (Sigma-Aldrich).

Rheometry

The mechanical properties of the physically associating solutions were studied in their self-assembled viscoelastic state over a range of temperatures. A rotational rheometer (MCR 300, Anton-Paar) was employed to probe the strength and relaxation behavior of the solutions. Both the linear (small strain) and non-linear (large strain, > 5 % strain) regimes were investigated in step-strain experiments, during which a fixed value of shear strain, γ_0, is applied and the resulting shear stress response is measured. Samples were contained in a single-gap Couette shear cell (1.1 mm gap) with Peltier temperature control. The uncertainty associated with the relaxation times determined from our fits to the stress relaxation data was approximately 5 %, determined from repeated measurements and fitting attempts.

Because of the thermo-reversibility of the triblock copolymer solution and the temperature controls of the rheometer, one sample could be used for multiple step-strain experiments. After each experiment, the sample was heated to temperatures above 50 °C and allowed to rest in a low-viscosity fluid state for at least 5 min. After cooling and equilibrating at the temperature of interest, a new experiment could be performed, yielding nearly identical results (within an experimental uncertainty of ≈ 5 % due to slight variation in copolymer concentration in the solutions). Our experimental results were entirely reproducible and in agreement for one sample deformed multiple times, for different samples from the same batch of material, and for samples taken from different batches.

RESULTS & ANALYSIS

Self-assembly of the triblock copolymer solution is driven by the temperature dependence of the enthalpic interaction parameter between the solvent and the end-blocks of the copolymer chain (see Figure 1a, details provided elsewhere [4,5]). For the PMMA/alcohol system, this temperature dependence is unusually strong within the experimentally accessible temperature window. Thus, at high temperatures (> 50 °C), the triblock copolymer is fully dissolved in the solvent, forming a free-flowing, low-viscosity solution with a near zero storage modulus (see Figure 1b). At reduced temperatures (< 35 °C), G' becomes larger than G'' as the PMMA end-blocks self-assemble into spherical aggregates in order to minimize their interaction with the solvent. These end-block aggregates act as physical cross-links, interconnected by flexible PnBA mid-block bridges. Scattering techniques and self-consistent mean field theory simulations have been performed previously to validate the self-assembled transient network structure. [5,6] From small angle x-ray scattering, the end-block aggregates were found to be approximately 5 nm in radius. The mesh size depended on the molecular weight of the mid-block and the overall copolymer concentration and was typically tens of nanometers via elastic scaling estimates. [7]

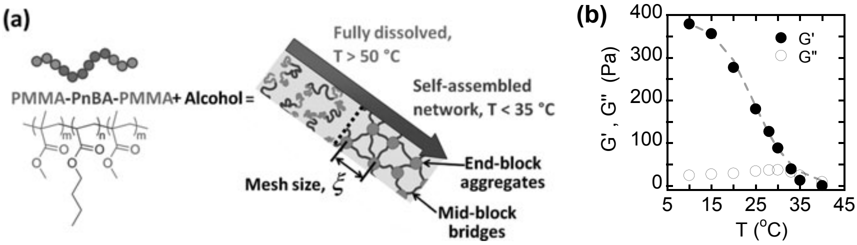

Figure 1. (a) Cartoon depicting the thermo-reversible self-assembly of physically associating solutions composed of triblock copolymer molecules dissolved in a mid-block-selective solvent. (b) Temperature dependence of the storage (*G'*) and loss (*G''*) shear moduli of the triblock copolymer solution from high frequency oscillatory measurements ($\omega = 100$ rad s^{-1}) in the linear regime ($\gamma_0 < 10$ %). Dashed line is fit from Eq. 3.

Linear and non-linear stress relaxation responses of the triblock copolymer physically associating solutions are displayed in Figure 2a and b. As seen in Figure 2a, stress relaxation occurred more quickly as the temperature of the system was increased; the variation of *G*(t) is very slow at low T so that the solution at low temperatures can be considered a 'gel' with a finite shear modulus $G(0, \gamma_0)$ from a practical rheological measurement standpoint.

Past work has shown that stress relaxation occurs by reorganization of the physically associating structure into more energetically favorable arrangements. [8] At lower temperatures (such as 10 °C), the end-block segments become 'frozen' or kinetically trapped in the aggregates, [6] preventing chain pull-out and forming an elastic-like network with extremely slow relaxation as evident from Figure 2a. At elevated temperatures, the exchange of end-block segments between neighboring aggregates should occur more rapidly, accounting for the increasing rate of stress relaxation.

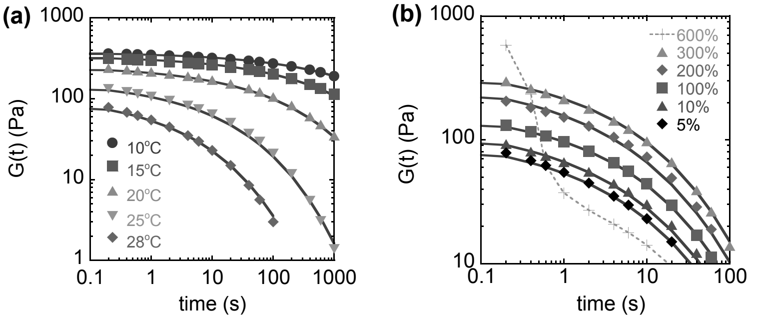

Figure 2. Shear modulus measurements with time during step-strain experiments of triblock copolymer solutions deformed to fixed values of applied strain. (a) Linear relaxation over a range of temperatures with $\gamma_0 = 5$ %. (b) Non-linear relaxation at 28 °C for a range of γ_0, 10 % to 600 % (5 % data included from (a) for comparison). Lines in (a) and (b) are stretched exponential fits from Eq. 1; parameters reported in Table I.

Figure 2b shows that a similar relaxation behavior is observed for solutions deformed at increasing values of applied strain, 10 % to 300 % (at a constant temperature of 28 °C). The vertical shift of the data was due to elastic strain stiffening, a phenomenon often observed in self-assembled materials having a biological origin. [4,9] Beyond a 300 % applied strain, a two-step response is observed, indicative of localized failure taking place in the network for the highest values of applied strain. [2,4]

To determine the characteristic relaxation times at each temperature and applied strain of the physically associating solutions, a stretched exponential functional form (Eq. 1) was fit to the stress relaxation data for all T and γ_0; τ and β were adjusted to achieve a best fit to the data. These fits were initially achieved for the data in Figure 2a with $\beta = 0.330 \pm 0.017$. For all the data reported here, stretched exponential fits were obtained with β fixed at 1/3 (see lines in Figure 2a and b); the remaining fitting parameters are reported in Table I. For the linear viscoelastic regime relaxation data ($\gamma_0 = 5$ %), the zero-time shear modulus, $G(0)$, was also independently determined by small-amplitude oscillatory measurements of $G'(\gamma_0 = 5\ \%, \omega = 100$ rad s^{-1}) at each temperature of interest.

Table I. Parameters used in Eq. 1 to describe the stress relaxation behavior. Uncertainty affiliated with τ is approximately 5 %.

T , γ_0	$G(0)$ (Pa)	τ (s)
10 °C, 5 %	373	3300
15 °C, 5 %	338	700
20 °C, 5 %	264	120
25 °C, 5 %	167	10
28 °C, 5 %	113	2.4
28 °C, 10 %	127	3.7
28 °C, 100 %	180	3.7
28 °C, 200 %	290	3.7
28 °C, 300 %	400	3.7
10 °C, 100 %	490	2600
10 °C, 200 %	670	2600
20 °C, 100 %	320	150
20 °C, 200 %	470	150

The general finding of a stretched exponential form of all the stress relaxation data reported here allowed for the construction of a relaxation master curve (see Figure 3). This master curve illustrates that for all values of temperature and applied strain, the stress relaxation behavior of the physically associating solutions investigated here was accurately described by a stretched exponential function with β equal to a constant value of 1/3.

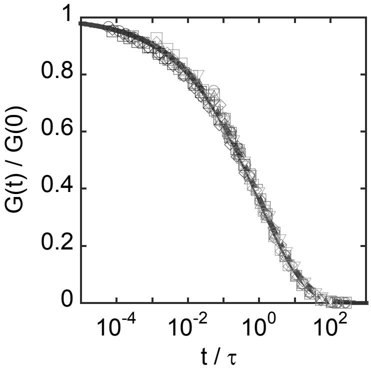

Figure 3. Relaxation master curve, illustrating the reduction of all stress relaxation data (for temperatures of 10 °C to 28 °C and γ_0 of 5 % to 300 %; colors correspond to data in Figure 2a) to a single exponential curve with a stretching exponent of $\beta = 1/3$ (solid line in background).

A value of β that is much less than unity is usually interpreted to indicate the existence of a broad spectrum of relaxation times, reflecting some kind of heterogeneity in the system. [1] For example, a broadening of this kind might arise from a polydispersity of the polymer chains that comprise the self-assembled network, as short, highly stretched chains would be expected to relax much more quickly than longer chains. [2,10] Indeed, a stretching exponent of 1/3 resulted from simulations of polydisperse polymer networks with Rouse-like relaxation dynamics. [11]

For sphere-forming block copolymer materials, the dynamics of stress relaxation by chain pull-out and rearrangement can be quantified by a 'hindered' diffusion coefficient, the magnitude of which reflects the enthalpic penalty associated with pulling one block of the chain through the region populated by the other block. [12] Prior work has shown that the enthalpic penalty, and thus the overall relaxation response, is affected by the polydispersity of the block segments as well as by the overall degree of domain segregation in the system. [12,13] Indeed, stretched exponential relaxation was experimentally observed in materials composed of micelle-forming block copolymers with increasing levels of polydispersity. [12] The polydispersity of our triblock copolymer is modest and may influence the relaxation dynamics, although additional experiments are needed to directly investigate the effect of polydispersity and degree of segregation on the relaxation response of these gels. Here, alternative causes of the stretched exponential stress relaxation are explored, and specifically, we consider the effect of other sources of heterogeneity on the stress relaxation dynamics that might be *intrinsic* to the self-assembly process.

DISCUSSION

Both theory and experimental studies have indicated that a stretching exponent β near 1/3 has particular significance in both self-assembling and glass-forming materials. Stukalin, *et al.* [14] analytically considered stress relaxation in solutions of dynamically associating polymers that form through self-assembly where the resulting dynamic polymer structures are naturally polydisperse due to their formation under equilibrium conditions. Such 'equilibrium polymers' grow in extent either by lowering the temperature or by increasing the concentration of the associating species so that the mass of these polymers is *tunable* with thermodynamic conditions. Under conditions where these dynamic polymer structures are persistent, Stukalin, *et al.* [14] find stretched exponential stress relaxation where β varies from 1 at high temperatures (where the fluid is uniform due to absence of self-assembly) to a constant β near 1/3 over an extended low temperature range where the self-assembly process is fully developed. The exponent is found to be 1/3 both for persistent self-assembled polymers exhibiting reptation dynamics and fiber-like assembled polymeric structures. Additionally, β is found to be near 0.3 even for flexible self-assembled polymer structures exhibiting Rouse dynamics, appropriate to unentangled polymers at high polymer concentrations where a small change in β arises from averaging the stress relaxation response over the internal modes of the self-assembled flexible polymer chains.

These calculations, which amplify on the conclusions of an earlier work by Douglas and Hubbard [15], indicate that a value of β near 1/3 should be characteristic of structural relaxation in diverse self-assembled polymer materials. Douglas and Hubbard [15] further proposed that this same stress relaxation model of equilibrium polymers applies to a wide class of glass-forming liquids where the dynamic polymeric structures arise from packing fluctuations in these complex liquids. Supporting evidence for this type of stretched exponential structural relaxation with β approaching a value near 1/3 under low temperature or high concentration conditions has been observed in persistent worm-like micelles solutions [16], concentrated microgel particle suspensions [17] and diverse glass-forming polymer materials [18] so there is indeed some evidence for universality of a limiting value of the stretching exponent β.

At very low temperatures, the decay of $G(t)$ in diverse amorphous materials becomes very slow and relaxation in both gels and glasses is often modeled as a power law in time. This common observation is not inconsistent with the present work and provides a further opportunity to check into the universality of β. When τ is very long, we can simply expand Eq.(1) in a Taylor series to obtain an approximate power-law relaxation form over extremely long timescales, and indeed Douglas and Hubbard [15] have previously observed that this type of expansion leads directly to the ubiquitous Andrade power-law creep phenomenon with a creep exponent equal to 1/3, the characteristic exponent of Andrade creep. [19] This power-law scaling is observed in an astoundingly large class of disordered solid materials, and we take this as further evidence of a high regularity in the magnitude of β.

An additional similarity exists between the temperature-dependent viscoelastic responses of our triblock copolymer solutions with other network and glass-forming materials. The softening of amorphous materials upon heating, as measured by the shear modulus at short times $G(t\to0^+)$ or high frequencies, typically varies sigmoidally with temperature over a broad temperature range rather than dropping nearly discontinuously as in the melting of crystals and other highly ordered materials. The temperature dependence of $G(t\to0^+) \equiv G_0$ exhibits some significant regularity between materials; we also consider this property in our thermo-reversible solutions and briefly compare to observations of other disordered gel and glass-forming materials.

As described by Lin, *et al.* [20], an effective medium treatment of rigidity percolation theory motivates taking the shear modulus of a self-assembled system to be proportional to the fraction, Φ, of associating species in the self-assembled state:

$$G_0 / G_0^* \approx \Phi , \qquad (2)$$

where G_0^* is the limiting value of the shear modulus in the fully self-assembled state, *i.e.*, normally this means low temperatures but some materials can assemble upon heating. The temperature dependence of self-assembly upon cooling can be approximated by a simplified two-state model for the order parameter for the extent of self-assembly, Φ [20,21]:

$$\Phi \approx \frac{G_0}{G_0^*} = \frac{1}{1+\exp\left(\frac{\Delta h - T\Delta s}{RT}\right)}, \tag{3}$$

where Δh and Δs are the enthalpies and entropies of the assembly process and RT represents the thermal energy. As seen in Figure 1b, the temperature dependence of the shear modulus is well captured by Eq. 3 with $G_0^* = 430$ Pa, $\Delta h = -\ 140\ 000$ J mol^{-1}, and $\Delta s = -\ 475$ J mol^{-1} K^{-1}. As discussed by Lin, *et al.* [20], this sigmoidal temperature dependence of G_0 has been observed in a variety of amorphous solid materials [22–24], including both glass and gel materials. Evidently, this relation is a phenomenological counterpart for material stiffness to the Vogel-Fulcher-Tammann relation describing the temperature dependence of the viscosity and structural relaxation time found in both glass-forming and self-assembled gel materials (*e.g.*, see Kumar and Douglas [25]).

The essential physical requirement for the stretching exponent β near 1/3 in the work of Stukalin, *et al.* [14] and Douglas and Hubbard [15] is the self-assembly of persistent and polydisperse polymer structures that dominate the stress relaxation process, a phenomenon that should be extremely common in disordered materials. At present, we cannot identify exactly what structures might be responsible for this type of stress relaxation in our block copolymer solution, which exhibits a rather complex multi-scale organization. However, idealized model calculations of stress relaxation in self-assembling solutions provide clues about what to look for in future scattering and microscopy experiments.

CONCLUSIONS

Thermally reversible, physically associating solutions composed of triblock copolymer molecules in a mid-block-selective solvent undergo stress relaxation when deformed to small (linear) and large (non-linear) values of strain. The relaxation behavior at all temperatures and values of applied strain was fully described by a stretched exponential relationship with the stretching exponent β equal to 1/3, a value observed in simulations of self-assembling networks and other complex fluids. We also find that the temperature dependence of the high frequency shear modulus exhibits a broad sigmoidal variation with temperature that is striking similar between diverse gel and glass-forming materials.

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‡ Certain commercial materials and equipment are identified in this paper in order to adequately specify the experimental procedure. In no case does such identification imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that these are necessarily the best available for the purpose.

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Oxygen-Generating Gel Systems Induced by Visible Light and Application to Artificial Photosynthesis

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ABSTRACT

Toward complete artificial photosynthesis systems to generate hydrogen and oxygen using visible light and water, we firstly design and fabricate oxygen-generating gel systems using the electrostatic interactions of ionic functional groups and steric effects of a polymer network. By using a graft polymer chain with $Ru(bpy)_3^{2+}$ units as sensitizers to closely arrange RuO_2 nanoparticles as catalyst, the functional groups transmit multiple electrons cooperatively to generate oxygen. In this study, a novel strategy is shown to design a hierarchical network structure using colloidal nanoparticles and macromonomers.

INTRODUCTION

Electronic transmission circuits to generate oxygen induced by visible light have been designed by several strategies using supramolecules.[1-6] The circuit is composed of the O_2-generating catalyst, the sensitizer, and the oxidant. But the higher-order structures are necessary for the complete artificial photosynthesis. Here, we firstly constructed oxygen generating gel systems that contained RuO_2 as a catalyst, and $Ru(bpy)_3^{2+}$ units as a sensitizer (Fig. 1). The gel is an open material system capable of the transformation or transmission of energy or information. By utilizing such a material, we could arrange the functional groups to cooperate with each other. In fact, many kinds of functional gels have been developed by devising the inner network structure to respond to the chemical and physical signals from the exterior.[7, 8] The photo-excited reaction needs four electrons simultaneously to generate one O_2 molecule;

$$2H_2O \xrightarrow{h\nu} O_2 + 4H^+ + 4e^- \qquad (1).$$

Therefore, it is necessary for RuO_2 and $Ru(bpy)_3^{3+}$ to interact smoothly. To accomplish the reaction, the gel systems were constructed by using the electrostatic interactions of ionic molecules and steric effects. Firstly, for the RuO_2 nanoparticles (NPs) and $Ru(bpy)_3^{2+}$ units to coexist in the gel, the RuO_2 NPs dispersed by the anionic surfactant sodium dodecyl sulfate (SDS-RuO_2 NPs) were mixed with poly(NIPAAm-*co*-$Ru(bpy)_3$). The SDS-RuO_2 NPs and cationic $Ru(bpy)_3^{2+}$ units are arranged closely by electrostatic interactions. Simultaneously, the polymer chain physically restricts the aggregation among the same functional groups; each RuO_2 NP and each $Ru(bpy)_3^{2+}$ unit. Secondly, by grafting poly(NIPAAm-*co*-$Ru(bpy)_3$) to a crosslinked PNIPAAm network, a gel that contained RuO_2 NPs and the

$Ru(bpy)_3^{2+}$ units was fabricated. This hierarchical arrangement of a polymer network allows the different functional groups (RuO_2 NPs and $Ru(bpy)_3^{2+}$) to coexist closely by electrostatic interactions and the same functional groups to exist separately by physical restriction. Thus, by introducing the functional groups hierarchically, oxygen-generating gel systems were achieved to operate the multi-electronic transmitting circuit smoothly.

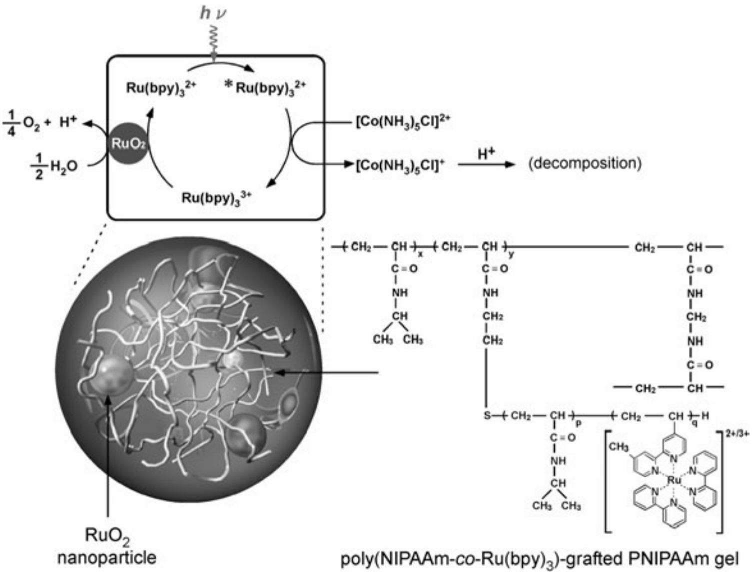

Figure 1 Oxygen-generating system formed by using a poly(NIPAAm-*co*-$Ru(bpy)_3$)-grafted PNIPAAm gel that contains RuO_2 nanoparticles.