Polymer Compression in Shear Flow

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ABSTRACT Polymers in flow deform elastically as a result of reduced entropy stored in the distorted chain. Elastic stretching of the chains in flow is assumed; however, measurement of the deformation of individual chains in concentrated solution in flow has largely eluded experiment. Several recent simulations have shown that the chains may compress in flow to elastically deform. Here, we show that polymer chains compress in simple shear flow, using time-resolved fluorescence to measure changes in fluorescence resonance energy transfer of a tagged polymer molecule. Time resolved measurements allow quantitative determination of changes in polymer chain dimensions, and are free from potential artifacts that could affect steady-state fluorescence. Flow-induced chain compression is reconciled with the observed rheological behavior of polymers, namely, shear thinning and elasticity. The ability to understand the flow behavior and model these complex systems will evolve through this important finding. The implications for reptation are profound, as the observed compressive behavior suggests that entanglements are not statistically significant at the concentrations measured.

SECTION Macromolecules, Soft Matter
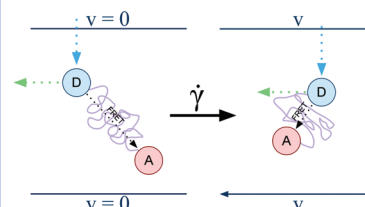
Polymer solutions are complex fluids that show both Newtonian and Hookean, so-called viscoelastic, responses in deformation.[1] When external stresses are applied to polymer solutions, such as those in simple shear (Couette) and extensional flows, the polymer molecules deform elastically.[2,3] The dumbbell model of the hydrodynamic forces on chains in flow was first introduced by Kuhn.[3] Flory first utilized statistical mechanics,[4] later generalized in scaling concepts by de Gennes,[2] to yield a universal physical description of polymer size. While traditional models of polymer physics have assumed that the elasticity arises from extension of the polymer molecules,[2,3] a number of experiments have presented results that do not support these assumptions.[5–8] Namely, compression and tumbling of the molecules is observed rather than the assumed extension in flow.

Polymer molecules have been modeled using Kuhn's bead–spring dumbbell model to deform under applied hydrodynamic forces as a function of the shear rate and the angle of the molecule with respect to the shear direction.[3] The precession of the chains in Jeffrey orbits makes the angle a time-dependent function,[9] resulting in hydrodynamic forces that alternate from extensive to compressive as the molecules rotate.[3] The bead–spring model describes an elastic "spring constant" or an overall restorative force that resists deformation of the molecule, as developed by de Gennes.[2] When the polymers are at steady state in the flow, the hydrodynamic and elastic forces are equal. Both the equations describing the dumbbell and the hydrodynamic forces are linear functions of the polymer end-to-end distance. Finite extensibility has been introduced in order to limit the extension of the chains to more closely resemble the true physics of the chains in traction.[2,10] The assumption that the chains have finite extensibility is consistent with the physics at high concentration, where the chains are restricted by the presence of their neighbors.[11–13]

DNA molecules are often used as model polymers in shear flow studies, and extensive literature exists for these systems.[5–8] DNA molecules are semiflexible worm-like structures, where molecules of sufficiently large contour length can have behavior similar to that of flexible polymer molecules.[8] DNA molecules have been studied in steady shear flow using video fluorescence microscopy and show elongation and rotation of the molecules, resulting in fluctuation of the molecules between extended states and tumbling compressed states.[5,7] While ensemble averages suggest an overall orientation of molecules relative to the flow direction, molecules perpendicular to flow were also often observed in a manner counter to expectation for the classical models of polymer physics.[2,5,14]

The chromophoric polymer, diacetylene 4-butoxycarbonyl-methylurethane (4BCMU), has been studied in an extended dichroism measurement of the polymer segment orientation and deformation in Couette flow.[15,16] The polymer molecules were found to align parallel to the shear direction at shear rates below 500 s^{-1}, but aligned perpendicular to the shear direction at higher shear rates. The conjugated
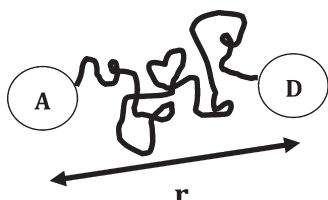
Figure 1. Schematic of the FRET tagged polymer. Here the acceptor group is the dithiobenzoyl group, and the donor is the anthryl group.

segment lengths decreased with increasing shear rate as a result of the compression of the initially random coil polymer molecules.[15,16]

Several recent simulations have shown that the chains may compress in flow to elastically deform.[11−13] In order to further investigate these intriguing and counterintuitive results, we have undertaken time-resolved fluorescence measurements on fluorescently tagged poly(methyl methacrylate) (PMMA) to investigate the effect of Couette shear flow on the deformation of the polymer molecules. PMMA is a synthetic polymer that is widely used in industry and its properties are well-known.[17] Time-resolved measurements are substantially more robust than equivalent steady-state measurements reported previously, being able to more accurately quantify distances and eliminate potential artifacts such as light scattering, phase separation, or temperature.

Reversible-addition fragmentation chain transfer (RAFT) polymerization allows the synthesis of monodisperse PMMA with the donor and acceptor fluorophores attached singularly to alternate ends of the polymer chain. The resulting polymers are of the type shown schematically in Figure 1. Fluorescence resonance energy transfer (FRET) between the FRET donor and acceptor bound to the ends of the polymer chains allows direct calculation of the average end-to-end distance of the polymers.[18−20]

The intensity of the fluorescence emission of an optically excited donor fluorophore is quenched due to resonance energy transfer to the acceptor chromophore. The fluorescence emission efficiency is then a function of the distance between the donor and the acceptor, which is equivalent to the end-to-end distance of the polymer molecule investigated.

The energy transfer efficiency, ϕ_T, of a FRET-tagged molecule is described by eq 1.[20,21]

$$\phi_T = 1 - \frac{\tau_{DA}}{\tau_D} = 1 - \frac{F_{DA}}{F_D} \qquad (1)$$

where τ_D is the fluorescence lifetime of the donor tag (in the absence of energy transfer), τ_{DA} is the fluorescence lifetime of the donor in the presence of the acceptor, and F_D and F_{DA} are the fluorescence intensities of the donor and the donor in the presence of the acceptor, respectively. FRET measurements may be performed by either steady-state or time-resolved fluorescence techniques.[20] Under the conditions used here, where the polymer is tagged at both ends, the end-to-end distance of the tags is related to the fluorescence intensity by eq 2.[20,21]

$$r = \left(\frac{1}{\phi_T} - 1 \right)^{1/6} R_0 \qquad (2)$$

where r is the separation distance of the donor−acceptor pair and R_0 the Förster critical radius.[20,21] The Förster critical
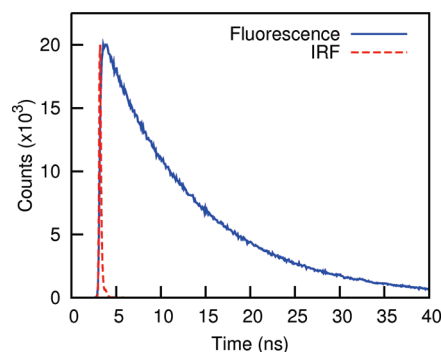
Figure 2. Fluorescence decay curve of RAFT-PMMA$_{50}$ in DMF solution at rest. The fluorescence lifetime of this sample was calculated to be 7.12 ± 0.05 ns.

radius corresponds to the separation at which the Coulombic energy transfer rate is equal to the rate of the other excited state depletion processes, or where fluorescence emission is exactly half the maximum intensity.[20,21] The Förster critical radius is given by eq 3.[20]

$$R_0{}^6 = 8.8 \times 10^{23} \kappa^2 \eta^{-4} Q_0 J(\lambda) \qquad (3)$$

where κ^2 is the dipole orientation factor, η is the refractive index of the solvent, Q_0 is the quantum yield of the donor fluorescent tag, and $J(\lambda)$ is the spectral overlap integral between the donor fluorescence emission and acceptor absorbance. κ^2 is typically assumed to be 2/3 for freely rotating fluorophores.[20,22]

A monodisperse 49 kg/mol molecular weight sample of PMMA with an anthryl and a dithiobenzoyl group attached to alternate ends, referred to as RAFT-PMMA$_{50}$, was used for the following experiments. The dithiobenzoyl group quenches the fluorescence emission from the anthryl group, with a calculated Förster critical distance of 1.34 nm for the current system.[20] In the current system, the dithiobenzoyl acceptor is nonemissive.

Time-resolved fluorescence measurements were used to measure the fluorescence decay of the RAFT-PMMA$_{50}$ in solutions of dimethylformamide (DMF) with added nonfluorescent PMMA at rest, under constant Couette shear for 15 min, and after relaxation for 15 min. The reference value for the donor-only fluorescence lifetime was 7.19 ± 0.02 ns, measured from a sample with the dithiobenzoyl fluorophore removed.[23]

The fluorescence decay curve of RAFT-PMMA$_{50}$ (i.e., with the dithiobenzoyl acceptor group present) at rest is shown in Figure 2, and the fluorescence lifetime was found to be 7.12 ± 0.05 ns. The reduction in fluorescence lifetime (compared with 7.19 ns) shows that FRET is occurring, and results in a donor−acceptor tag distance of 2.89 nm from FRET calculations assuming the critical transfer distance discussed above. The hydrodynamic radius of RAFT-PMMA$_{50}$ measured by dynamic light scattering was 1.65 nm, which gives an estimated end-to-end distance of 6.0 nm, assuming a random polymer coil conformation in solution.[24]

The fluorescence lifetime of RAFT-PMMA$_{50}$ decreases upon exposure to shear, to a minimum of 6.71 ± 0.05 ns at the highest experimented shear rate of 2464 s^{-1}. This reduction in fluorescence lifetime, relative to the lifetime in the
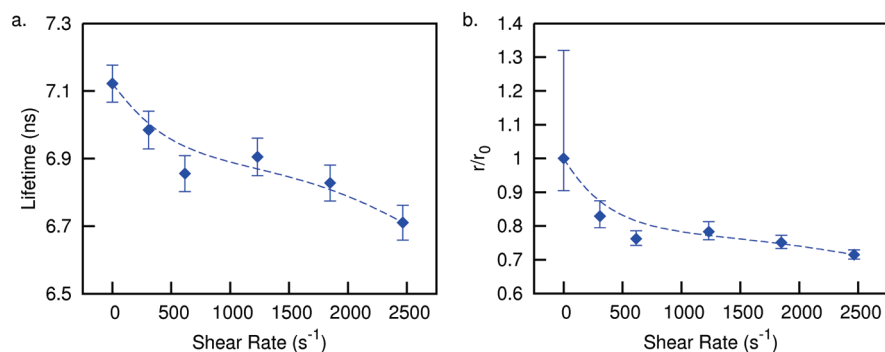
Figure 3. (a) Measured fluorescence lifetimes of RAFT-PMMA$_{50}$ in DMF solution after constant shearing at various shear rates from 308 to 2464 s^{-1}. (b) FRET distances.

quiescent state, is attributed to increased FRET between the donor and acceptor and corresponds to a FRET distance of 2.08 nm, or a 30% decrease in end-to-end distance. The fluorescence lifetime of the polymer returned to the original value (to within 0.04 ns) after cessation of shear for 15 min in all cases measured. The fluorescence lifetimes of the RAFT-PMMA$_{50}$ after exposure to various shear rates are shown in Figure 3a. The FRET distances are calculated as a function of shear rate from the observed decreases in fluorescence lifetimes (Figure 3b). There is a large uncertainty in the distance for the zero shear case, since the lifetime recorded is very close to the donor-only reference. There is, however, a significant steady reduction in fluorescence lifetime and corresponding FRET distance as a function of the applied shear rate. Control experiments with donor-only polymer samples prepared at identical concentration shows that the donor lifetime has no dependence on the applied shear rate or shear exposure time.

Rather than assuming a single discrete distance between the donor and acceptor groups, a distribution of distances might be expected to be a more appropriate model for fluctuating polymer molecules. The time-resolved fluorescence decay profiles were analyzed and modeled[25] to give a Gaussian distribution of energy transfer distances with a median distance and distribution width, as shown in Figure 4. Similar to the plot of the discrete fluorescence lifetimes (Figure 3b), the FRET distance is seen to decrease significantly with shear rate. The distribution width of the Gaussian model is also shown, and was largely independent of shear rate. The energy transfer distances determined from the distribution analyses are somewhat larger than those recovered from the discrete decay time analysis, but the trend is the same. The difference in the magnitude of the FRET distances calculated is attributed to the finite width of the distribution and the analysis process. Considering that we would expect a distribution of distances in such a system, in the following discussion we will refer to the data shown in Figure 4. We reiterate that the trend in the FRET distance as a function of shear rate, which is the key finding of this work, is the same whichever analysis method is used.

Complementary experiments were also performed with steady-state fluorescence measurements. Fluorescence intensity values from steady-state measurements were also used to calculate FRET distances based on eqs 1 and 2. These experiments were able to monitor the changes in fluorescence
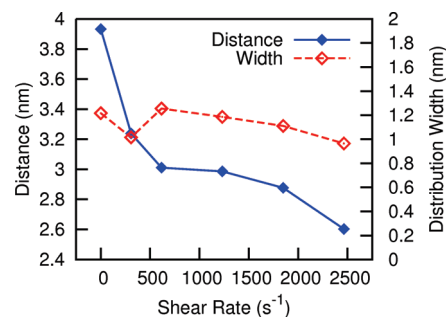
Figure 4. Median FRET distance and Gaussian distribution width of RAFT-PMMA$_{50}$ in DMF solution after constant exposure to shear at shear rates from 308 to 2464 s^{-1}.

intensity over time as shear was applied, and show very similar results to the time-resolved FRET measurements.[26] The current results with time-resolved fluorescence support and further substantiate the conclusions reported in the previous work.[26]

The time-resolved fluorescence experiments show a decrease in fluorescence lifetime with increasing shear rate for the PMMA solutions measured. This result is interpreted as resulting from a decrease in FRET tag distance, resulting in an increase in FRET transfer efficiency. Since the fluorescent tags were attached to the ends of the polymer molecules, it is concluded that the end-to-end distance and therefore the overall molecule dimensions are reduced in flow.

It is postulated that, at polymer concentrations above critical overlap, the extension of the chain is restricted by the presence of the neighboring chains and the net hydrodynamic force becomes compressive, rather than extensive as previously assumed for polymers in flow. The dumbbell model developed by Kuhn shows that compressive hydrodynamic forces occur as the chains precess in the Jeffrey orbits.[9]

Time-resolved fluorescence lifetime measurements are less affected by small changes in localized concentration, for example, those caused by phase separation, than steady-state measurements. Scattered light, which can interfere with steady-state measurements, is also measured in the time-correlated single photon counting (TCSPC) experiments, but its contribution can be accounted for during decay analysis. The disadvantage of the time-resolved experiments is the time required to perform each measurement, which means it is difficult to accurately measure the changes in lifetime in

small intervals of time, but rather only the preshear, steady state, and post shear systems were experimentally accessible. A Gaussian distribution was used to model the FRET distances for the time-resolved fluorescence data. It is possible that the polymer sizes instead had a biased distribution, such as an increased contribution from molecules with smaller end-to-end distances. Therefore the median distances calculated should serve as comparative values rather than absolute results.

The distances obtained from the Gaussian analysis are on the scale of 2.5–4 nm for the RAFT-PMMA$_{50}$ sample. These distances are smaller than the estimated 6.0 nm end-to-end distance of the polymer molecule obtained from photon correlation spectroscopy (PCS) measurements in dilute solution. This could suggest that the fluorescence tags attached to the ends of the polymer molecule were not completely random in space and that there may be attractive forces between the end tags. This is consistent with the observation that the hydrodynamic radius of the RAFT-PMMA$_{50}$ was 1.65 nm, which is smaller than a similar molecular weight untagged PMMA molecule of 44 kg/mol, at 2.4 nm. Inaccuracies in the FRET calculation assumptions could also account for some of this difference, such as the assumption of the orientation factor at 2/3 for a freely rotating fluorophore,[22] plus the tendency for FRET measurements to bias toward shorter distances for samples that may be fluctuating[20,27,28] and dynamic light scattering to bias toward larger radii.[29] The data obtained for the current systems shows a reduced coil size for the sheared case relative to the quiescent systems. While the absolute distances may have some uncertainty due to the discussed effects, the changes induced by flow singularly show a reduction in the end-to-end distances of the FRET tagged probe molecules in flow.

The observed reduction in polymer end-to-end distance after shear exposure is counter to expectations based on previous theories regarding polymer deformation in flow.[2,3] Polymer elasticity has previously been attributed to chain extension in flow,[2,3] but the results of this work suggest that elasticity is a result of compression of the molecules in Couette flow in a manner similar to that found in rubber elasticity on compression. The model posed by chain compression in flow accounts for the observed rheological properties where shear thinning and reduced first normal stress are measured with increasing shear rate. The reduced coil volume in compression readily accounts for shear thinning and a reduction in coil size with increasing shear rate is also consistent with the measured reduction in first normal stress with shear.[30]

Compression of polymer chains during shearing leads to a reduction in the entropy of the molecules in a manner similar to extension.[16] The observation of polymer compression during shear suggests that the molecules are not entangled in solution. Due to the relatively long time scales observed in the experiments, it is unlikely for the reduction in polymer sizes to be a direct compression effect. It is proposed that the mechanism for polymer size reduction is a balling effect, where molecules adopt a rearranged conformation when exposed to shear that results in reduced polymer end-to-end distances.

EXPERIMENTAL METHODS

Shear experiments were performed with a custom built quartz Couette rheofluorescence cell described previously,[26,31] with a radius-to-gap ratio of 28.5.[32] Polymer solution samples were injected into the gap between the quartz cell and quartz inner cylinder, and the cell was mounted in the beam path of a Varian Cary Eclipse fluorescence spectrometer for steady-state fluorescence measurements, or in the excitation beam path of the TCSPC system for time-resolved measurements.

The FRET-tagged polymer used in the experiments was a RAFT polymerized PMMA with 49 kg/mol molecular weight, as estimated by gel permeation chromatography (GPC) performed in toluene solution and compared to known polystyrene standards. The hydrodynamic radius of the polymer was measured by PCS, and the Förster distance was calculated using the results of steady-state fluorescence and absorption spectroscopy. The RAFT-PMMA$_{50}$ was dissolved in DMF solution (1.3 wt %) with a background of nonfluorescent 44 kg/mol PMMA (18.7 wt %). The critical overlap concentration c^* for PMMA at 49 kg/mol is 9.5%, and 10.0% for PMMA at 44 kg/mol. The sample used in experiments was at approximately $2c^*$. A sample of the RAFT-PMMA$_{50}$ with the acceptor dithiobenzoyl group removed, prepared with the same conditions, was used as the reference for the donor-only lifetime. The removal of the dithiobenzoyl end group was achieved by using a radical induced addition–fragmentation process as reported previously.[23]

A picosecond TCSPC system (based on an Edinburgh Instruments, TCC900 card) was used for the fluorescence decay measurements using a microchannel plate photomultiplier (Eldy, EM132-1). The pulsed excitation (790 nm) source was a cavity-dumped mode-locked titanium sapphire laser (Coherent Mira 900, APE PulseSwitch, ~120 fs) pumped by a solid state laser (Coherent Verdi 10). After reduction of the pulse frequency to 5.4 MHz and frequency doubling (to 390 nm), the laser beam was attenuated to reduce the detected photon count rate to less than 0.5% of the excitation source repetition rate. The fluorescence data were analyzed using the Globals software package developed at the Laboratory for Fluorescence Dynamics at the University of Illinois at Urbana–Champaign.

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