Macromolecules **2004,** *37,* 1663−1665

Direct Measurement of Polydiacetylene 4-Butoxycarbonylmethylurethane Segment Orientation and Distortion in Shear: Semidilute Solutions

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Received August 4, 2003

Polymer solutions and melts show viscoelastic behavior in flow; hence the name complex fluids.[1] A number of prior studies have examined both theoretical and experimental aspects of polymers in flow.[2−6] In the present work the unique optical properties of the polymeric chromophore diacetylene 4-butoxycarbonylmethylurethane (4BCMU) have been exploited to measure both polymer segment orientation and distortion in flow in an extended dichroism measurement. 4BCMU solutions exhibit dramatic and reversible solvatochromism and thermochromism associated with backbone conformational changes.[7] These properties arise from the conjugated nature of the backbone which absorbs light in a manner such that the distribution of conjugated segment lengths correlates with the absorption spectrum. Changes in the spectra of the polymer with temperature and solvent are directly related to changes in the coil size and conjugation lengths of the polymer backbone.[8−15] The transition dipole of the absorption is parallel to each segment length.[12,13] Polarized light is therefore selectively absorbed by the subset of segments oriented in the polarization direction. Thus, the segmental orientation and distortion in flow may be characterized by measurement of the polarized absorption spectrum. The spectral shift and magnitude changes in the extinction cross section yield information regarding the distortion and orientation of the segments, respectively.

4BCMU was prepared by the method of Patel, Chance, and Witt[16] to have an average molecular weight of 800 000 and a polydispersity of 1.8 as determined using a Dawn Wyatt/Waters GPC-MALLS apparatus. The critical overlap concentration is 0.007 g/mL, and intrinsic viscosity is 300 mL/g in chloroform as measured with capillary viscometry ($C^*[\eta] = 2.1$). The Mark−Houwink exponent of 0.8 indicates that 4BCMU is a random coil in $CHCl_3$.[7] Lim and Heeger have also used light scattering to show that the persistence length of 4BCMU in chloroform is of order 2−3 nm, consistent with values calculated from quantum mechanical arguments.[7,12] A contour length of 800 nm is calculated from the monomer size and molecular weight. The ratio of the contour length to persistence length of order 250 indicates that the chains exist as a random coil in this good solvent.[7,8,12] Allegra et al. have used light scattering to interpret a persistence length of 4BCMU of order 20 nm in $CHCl_3$.[14] A number of other studies have shown that the polydiacetylene chain is a random coil in chloroform solvent.[12,13,15] It should be noted that 4BCMU has short side chains ($n = 14$) which will render the backbone stiffer than most synthetic polymer chains. Both the experimental evidence and scaling arguments indicate that the 4BCMU is a random coil under the experimental measurement conditions used in the current study.

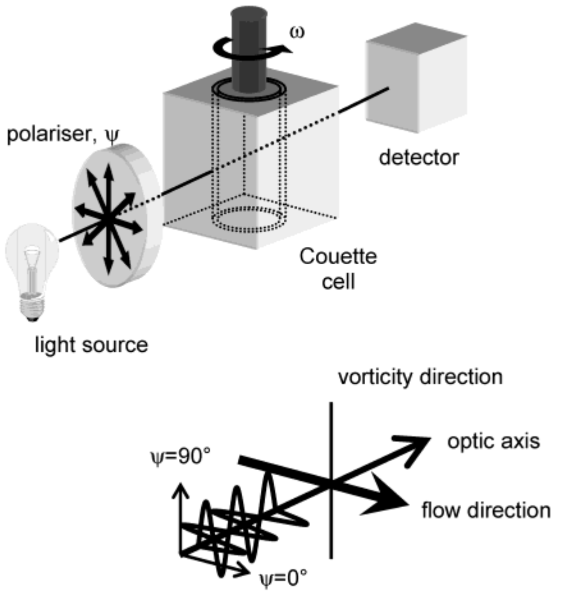

Figure 1. Schematic diagram of the optical train used in the experiments showing the light beam orientation (and polarization directions) relative to the Couette geometry and flow direction.

Optical rheometry measurements were undertaken in a custom-built Couette cell comprising a pair of coaxial quartz cylinders which were placed in the beam of a Cary 3E spectrophotometer as shown in Figure 1. (See also refs 17 and 18 for further details.) The Couette cell was placed vertically in the sample compartment of the spectrometer. A Glan Taylor polarizer (Harrick) was placed in the beam before the Couette cell for the polarization measurements. The beam was projected through the cell normal to the flow plane. Two polarization directions, parallel (along the flow direction) and perpendicular (along the vorticity direction), were measured. The gap-to-radius ratio in the Couette cell was maintained such that the shear was uniform across the gap (gap = 0.025 mm, outer radius = 4.925 mm, giving a cylinder radius ratio of 0.995). All measurements were performed in laminar flow as confirmed by direct visual observation of 0.3 μm tracer particles in the polymer solutions. Laminar flow was observed for shear rates significantly higher than those reported in this work in accord with theory.[19] The absence of thermal effects that could markedly affect the spectra was demonstrated by reproducing the data three times with fresh solution, using short shear periods and long equilibration intervals between measurements. No systematic trends with time indicative of shear-induced temperature increases were observed.

Segmental orientation within the polymer system was analyzed by monitoring shear-induced absorbance changes in each polarization direction and converting these values to extinction coefficient changes using the Beer−Lambert law. Any inherent polarization bias in the optical system and monochromators is accounted for in these measurements since changes relative to the zero shear case were determined for each polarization direction. The absorption maximum occurs at 468 nm

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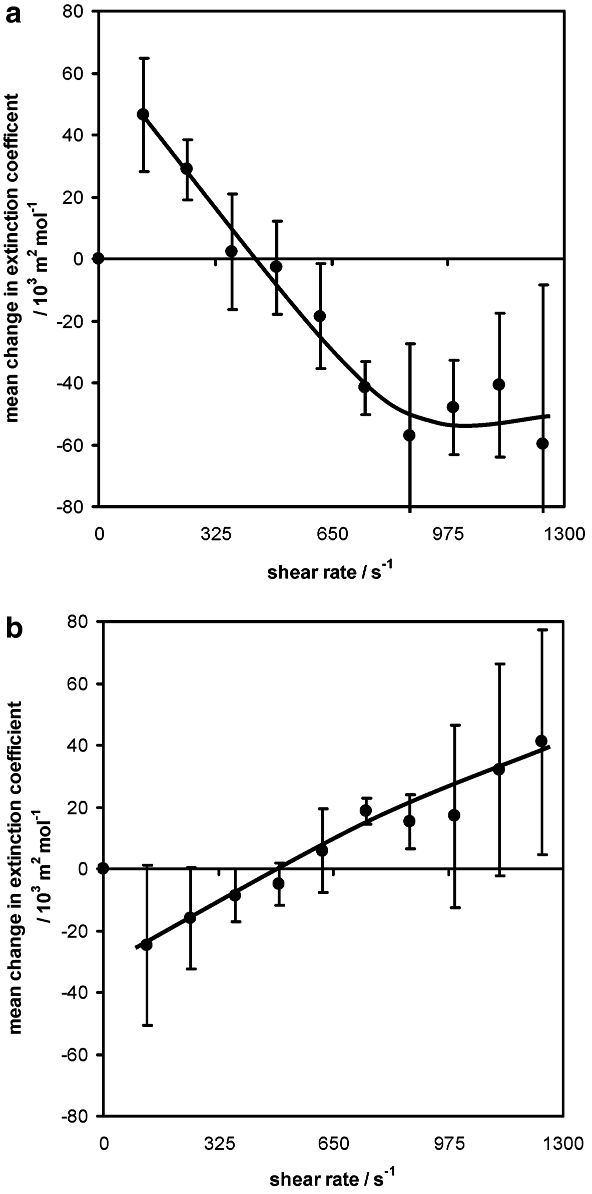

Figure 2. (a) The measured change in extinction coefficient for concentrated 4BCMU in chloroform vs shear rate with 0° polarized light (parallel to the shear direction) at $\lambda = 468$ nm (λ_{max} in zero shear). The data points were determined as mean values from repeated measurements of three concentrations in the semidilute range (8, 11, and 13 mg/mL). All samples yield similar data within the error bars shown. The curve drawn through the points serves merely to guide the eye. (b) The change in extinction coefficient for concentrated 4BCMU in chloroform vs shear rate with 90° polarized light (perpendicular to the shear direction). All other conditions were as described above.

and is characteristic of 4BCMU in its random coil form. The effect of small spectral shifts on the extinction coefficient values was modeled with simple quadratic curve-fitting procedures. It was confirmed that, because the spectrum exhibits a broad flat peak, small changes in the maximum absorption wavelength (<8 nm) do not introduce significant errors to the measured absorbance changes.

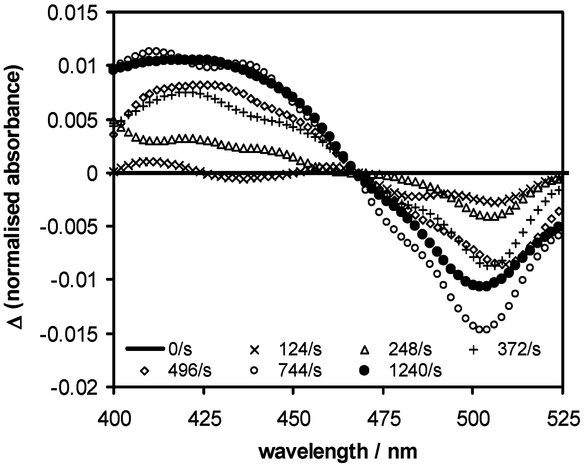

Figure 3. Normalized absorbance difference spectra for concentrated 4BCMU in chloroform (11 mg/mL), measured at a range of shear rates. The zero shear spectrum was rescaled and subtracted from the spectrum collected in shear. See text for detailed description of the analysis method. Unpolarized light was used for this experiment.

Rheooptic measurements of the semidilute solutions of 4BCMU in $CHCl_3$ (8, 11, and 13 mg/mL) show complex segmental orientational behavior as a function of shear rate as shown in Figure 2a,b. The data show a low shear increase (positive change) in the extinction coefficient parallel to the shear direction, with a simultaneous decrease in the extinction coefficient in the perpendicular direction (negative change). The proportion of segments aligned parallel to the shear direction is shown to increase at low shear rates. At shear rates greater than 500 s^{-1} the trend is reversed. A decrease is observed in the parallel extinction coefficient, whereas the perpendicular extinction coefficient increases relative to the zero shear case. An increase in the proportion of polymer segments aligned perpendicular to the shear direction is occurring at high shear. These data uniquely show that the ensemble of polymer segments orient parallel to the shear direction at low shear rates and align perpendicular to the shear at high shear rates. It should be noted that these shear-induced changes in extinction coefficient represent up to 8% of the measured quiescent values. The low shear data are consistent with prior birefringence studies on other polymer systems, indicating that polymer alignment in the flow direction occurs.[20-24] Pearson et al. used birefringence measurements on semidilute solutions at low shear rates (<300 s^{-1}) to show that the yellow form 4BCMU orients in the flow direction consistent with the results presented here.[10]

Further to the measured segment orientational behavior, the 4BCMU polymer coil exhibits a small shear-dependent spectral shift. Unpolarized spectra in shear were smoothed using a six-point FFT filter to remove small periodic oscillations due to rotation of the inner cylinder. These smoothed spectra were each peak normalized to a value of 1 at λ_{max}. The zero shear spectrum was subtracted from each normalized shear spectrum to yield the normalized difference spectra presented in Figure 3. Orientation-induced changes in extinction coefficient are largely removed using this method, and the spectral shift due to shear is revealed. At low shear rates little or no spectral shift is observed, indicating that the polymer is not distorted. At higher shear rates an increased absorption at short wavelengths, relative to the zero shear case, and a concurrent decrease in absorbance at longer wavelengths are observed. Significantly, the trend with increasing shear appears systematic within experimental error and when combined with the zero trend at low shear rates demonstrates the robust nature of the analysis method. A spectral shift of the nature observed at high shear corresponds to a change in the distribution of conjugation lengths to shorter values. This is a shear-induced effect, since thermal effects have been eliminated from these experiments and shear-induced polymer aggregation would lead to a red shift in the spectra.[11] It should be noted that a change in the conjugation length by one monomer unit corresponds to a 7 nm shift in the absorbance wavelength.[8]

Both the measured segmental alignment and the reduction in the conjugation length occur simultaneously. A reduction in the segment length and commensurate reduction in the global polymer coil size would lead to a reduction in the absorption cross section. We hypothesize that the prolate random coils initially align with the flow direction. This is consistent with the observed changes in extinction at low shear, i.e., positive and negative changes in extinction in the parallel and perpendicular directions, respectively. The coil shrinkage at high shear or balling up of the coils would then result in a reduction in the measured extinction in the parallel polarization direction and an increase in the perpendicular direction as is observed. This model yields a self-consistent interpretation of the data. Any attempt to separate the alignment and shrinkage contributions to the observed behavior requires sophisticated modeling which will be the basis of future work. In practice, the interpretation of the spectra has largely separated these components by using the normalized difference spectra.

The Rouse/Zimm-type theories assume fixed segment lengths, with nonlocal coil deformation arising at length scales above the segment size.[2,3,25,26] The current experiment senses local, segmental effects and shows that these systematically reduce in size in shear at high shear rates. Recent Brownian dynamics simulations do allow for segment deformation.[27−29] The simulations by Petera and Muthukumar for isolated coils in infinite dilution show that when hydrodynamic interactions are considered in the absence of excluded volume, the coils undergo “shrinkage” at high shear rates. The data presented in the current work confirm the model predictions, indicating that the 4BCMU is a polymer in which hydrodynamic interactions are important and excluded-volume effects negligible. The rationale for this is that the strong backbone attraction occurs while the side chains on the backbone (required for solubility) give rise to significant hydrodynamic interactions. Recent work by our group using atomic force microscopy on hydroxy propyl guar gels formed under shear shows “balling” of the polymers at high shear rates.[30] We are currently undertaking experiments on other polymer systems to substantiate the generality of these results.

Acknowledgment. Y.W. gratefully acknowledges the University of Melbourne for the award of a postgraduate scholarship. We thank John Sader, Trevor Smith, Franz Grieser, Gareth Price, Paul Mulvaney, and Derek Chan for helpful comments.

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MA030413V