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Direct measurement of polymer segment orientation and distortion in shear: semi-dilute solution behavior

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Abstract

The shear induced backbone segment orientation and deformation of the polymeric chromophore diacetylene 4-butoxycarbonylmethylurethane (4BCMU) in semi-dilute solution has been measured with an extended dichroism technique. At low shear rates the random coil, visco-elastic polymer shows orientation in the flow direction. At higher shear rates a reduction in the average conjugation length is observed with an increase in the number of segments orienting perpendicular to the flow direction. Novel behavior, which is not consistent with standard models, is observed for this visco-elastic polymer at high shear rates. The results presented are discussed in view of prior experimental and theoretical work.

Keywords: Polymer physics; Visco-elastic polymer; 4BCMU

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1. Introduction

Polymer solutions and melts show significant shear thinning and visco-elastic behavior in shear hence the name complex fluids [1]. While a significant number of theoretical works have modeled this complex behavior, significant discrepancies between theory and experiment still exist [2–4]. Of particular importance is the inability to predict shear thinning in simple flow [4]. The common basis of the models of semi-dilute solutions and melts is that the polymer is considered to reptate in a tube formed by neighboring molecules [2,3]. The 'tube' deforms and orients in the flow direction due to the shear force exerted on the system. The reptating chain in flow is then considered to undergo so called constraint release due to the motion of the surrounding chains [4]. These models develop the concept that the entropic nature of the random coil requires a shear force to stretch the polymer coil and reduce the entropy of the chain in a reversible manner [3,5]. The polymer is generally modeled as beads on springs to encapsulate the hydrodynamic friction and elastic deformation [6]. Recent Brownian dynamics simulations by Petera and Muthukumar have shown that the size of the chains shrinks for very high shear rates when hydrodynamic interactions are considered [7].

Prior experimental studies aimed at developing a molecular understanding of complex fluid flow have focused on light scattering, neutron scattering, NMR, birefringence, dichroism and fluorescence [1,8–19]. The excellent texts by Fuller [8], Nakatani and Dadmun [9], Larson [1] and the review of Wagner [10] are referred to for elegant reviews and summary of the prior optical rheometry studies. The light scattering works of Cottrell et al. [11], Link and Springer [12], Muller et al. [13] and Menasveta and Hoagland [14] have shown that the experimentally measured expansion ratios for coils in dilute solution are significantly less than predicted by basic theory [20,21]. The introduction of hydrodynamic interactions and excluded volume effects in simulations has done much to resolve this discrepancy [7]. These studies have recently been confirmed by rheo-optic measurements of the dilute solution behavior of 4BCMU which has shown that the prolate random coils in solution orient in the flow direction with no measurable segment deformation [22–27].

The notable works of Le Duc et al. and Smith et al. have used fluorescence tagged DNA to show single chain molecular deformation in flow [16–18]. These works have been limited to DNA (~56 μm contour length) as the relatively small size of most synthetic polymers is such that

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the spatial resolution of the fluorescence method prohibits measurements of the deformation for these systems. Bur et al. have used fluorescence anisotropy methods to measure the orientation of polyisobutylene in flow [19].

A number of works have measured flow induced birefringence in semi-dilute polymer solutions to assess the molecular models [8,9,28–39]. Birefringence measurements have generally shown that the polymers align in the flow direction. The observed birefringence arises from both intrinsic and form components that derive from segmental and coil contributions, respectively [2]. It should be noted that this single observable does not permit ready distinction between the segmental and coil components of the birefringence. In the present study the segment is defined as a short element (2–3 nm) of the polymer backbone which acts as a single optical unit.

We report the first quantitative results obtained for flow induced polymer chain segment orientation and deformation in semi-dilute solution. 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. 4BCMU is an optically active semiconducting polymer. Diurethane sidegroups render the otherwise insoluble conjugated polydiacetylene backbone soluble in some organic solvents [40]. 4BCMU solutions exhibit dramatic and reversible solvatochromism and thermochromism associated with backbone conformational changes [41]. These properties arise from the highly conjugated backbone which absorbs light in a manner such that the distribution of conjugated segment lengths correlates with the absorption spectrum [42–49]. The shorter segments absorb at shorter wavelengths while the longer segments absorb at longer wavelengths. The strong absorption in the visible region is due to the highly delocalized π-bonding system that extends along each segment length of the backbone. The transition dipole of the absorption is parallel to each segment length [46,47]. Polarized light is, therefore, selectively absorbed by the subset of segments oriented in the polarization direction. Therefore, any flow induced change in the orientation of the polymer backbone conjugation/segment lengths results in an absorbance magnitude change as observed in a classical dichroism measurement [8]. The measured spectral shift then corresponds to a change in the distribution of the conjugation/segment lengths. This experimental system is, therefore, an extended dichroism measurement which enables both orientation and distortion of the backbone segments to be determined in shear.

2. Experimental section

4BCMU used in these experiments was prepared by the method of Patel, Chance and Witt [40] to produce a polymer with an average molecular weight of 800,000 g/mol and a polydispersity of 1.8 as determined using Dawn Wyatt/Waters GPC light scattering apparatus. The critical overlap concentration is 0.007 g ml^{-1} and intrinsic viscosity is 300 ml g^{-1} in chloroform as measured with capillary viscometry ($C^*[\eta] = 2.1$) [50]. The Mark-Houwink exponent of 0.8 indicates that the 4BCMU is a random coil in $CHCl_3$ [41]. Lim and Heeger have used light scattering to show that the persistence length of the 4BCMU in chloroform is of order 2–3 nm consistent with values calculated from quantum mechanical arguments [41,46]. 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 [41,42,46]. Allegra et al. have also used light scattering to interpret a persistence length of the 4BCMU of order 20 nm in $CHCl_3$. This yields a ratio of contour length to persistence length of 40 which may still be considered a random coil [48]. A number of other studies using quasi-elastic light scattering, small angle neutron scattering and high-pressure optical absorption have also shown that the polydiacetylene chain is a random coil in chloroform solvent [46,47,49].

Optical rheometry measurements were undertaken in a custom-built Couette cell comprising a pair of co-axial quartz cylinders which were placed in the beam of a Cary 3E spectrophotometer [22,50]. A Glan-Taylor polarizer (Harrick) was included in the beam line in order to select light polarized either parallel or perpendicular to the shear direction as defined by a flow line. (See Fig. 1 for details of this geometry, also Fig. 3 of Ref. [22]). 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). An angular velocity range of 0–6.28 rad s^{-1} accurate to 1% was used. 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 [51]. Evaporative losses of chloroform during the course of an experiment were avoided using a sample reservoir above the cell. 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. The different shear rates were measured by random variation with reversibility 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 in the optical system is accounted for in these measurements since changes relative to the zero shear case were determined. Zero shear absorption spectra for this polymer are provided in Fig. 2. The absorption

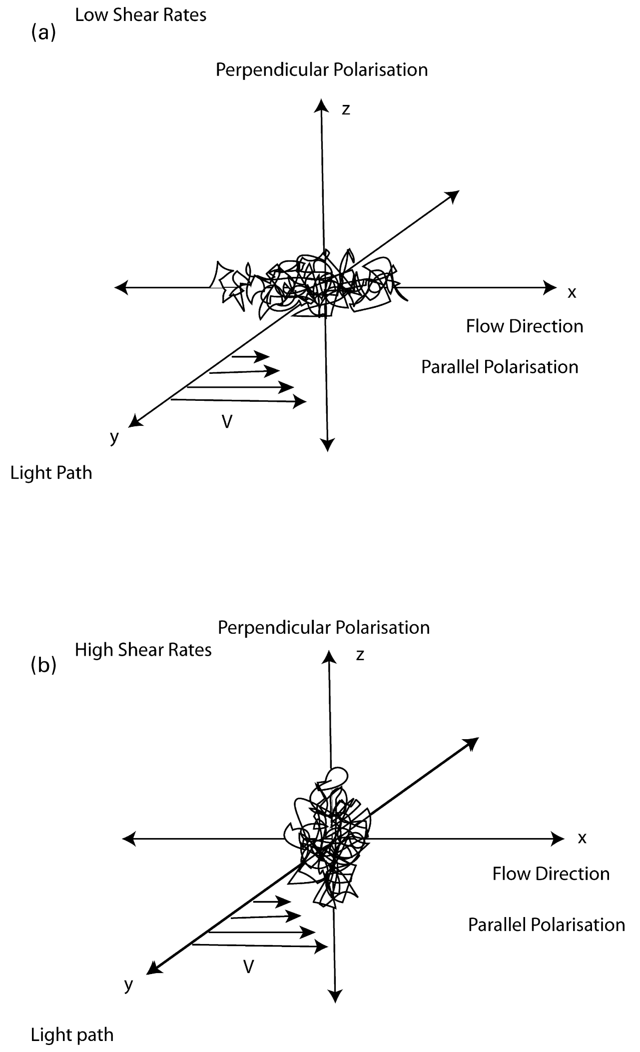

Fig. 1. Schematic diagram showing the interpreted orientation of the polymer relative to the shear plane and optical path at: (a) low shear rates and (b) high shear rates. The Couette cell axis of rotation is along the *z*-axis (the vorticity direction) and the shear direction is along the *x*-axis. The shear gradient is in the $x-y$ plane and the parallel and perpendicular polarizations are in the $x-y$ and $y-z$ planes, respectively.

maximum occurs at 468 nm 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.

3. Results and discussion

The rheological properties of 4BCMU have been previously measured at two concentrations in the semi-dilute range, namely 7 and 14 mg ml^{-1}, and exhibit visco-elastic behavior typical of polymers in semi-dilute solution [1,50]. Viscosity shear rate curves and mechanical spectra were measured using a solvent trap modified Carri-Med rheometer [50]. This behavior is shown in Fig. 3, and may be summarized as a significant reduction in viscosity with shear rate and substantial storage moduli which increase with measurement frequency. The data range is limited to less than 300 s^{-1} as the sample exited from the cone and plate geometry at higher shear rates.

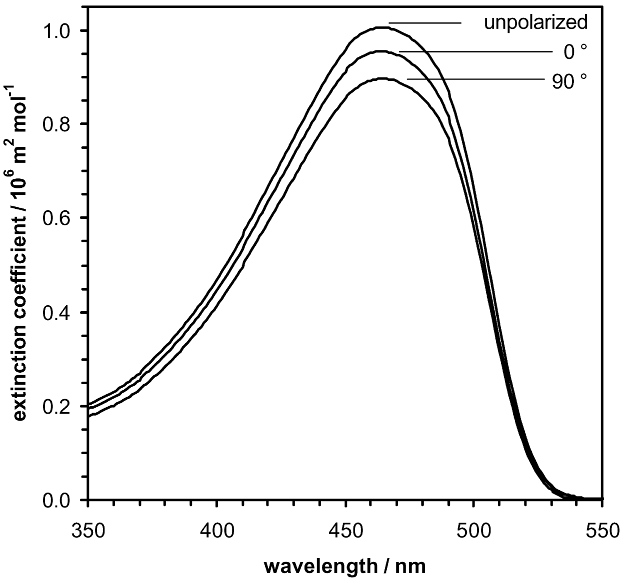

Fig. 2. Absorption spectra for concentrated 4BCMU in chloroform (11 mg ml^{-1}) collected with (a) unpolarized light, (b) 0° polarization (c) 90° polarization. No shear was applied.

Rheooptic measurements of semi-dilute solutions (8,11,13 mg ml^{-1}) of 4BCMU in CHCl$_3$ show complex orientational behavior as a function of shear rate as shown in Fig. 4(a) and (b). Within experimental error the extinction coefficient changes are the same for the three concentrations measured. The data show an initial increase (positive change) in the extinction coefficient parallel to the shear direction, with a complementary decrease in the perpendicular direction (negative change). This is consistent with an increase in the proportion of segments aligned parallel to the shear direction. 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. This is consistent with an increase in the proportion of polymer segments aligned perpendicular to the shear direction. This data uniquely shows 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 is consistent with prior birefringence studies on other polymer systems indicating that polymer alignment in the flow direction occurs [28–39]. Pearson et al. have shown using birefringence measurements on semi-dilute solutions of 4BCMU in chloroform that at low shear rates (<300 s^{-1}) the

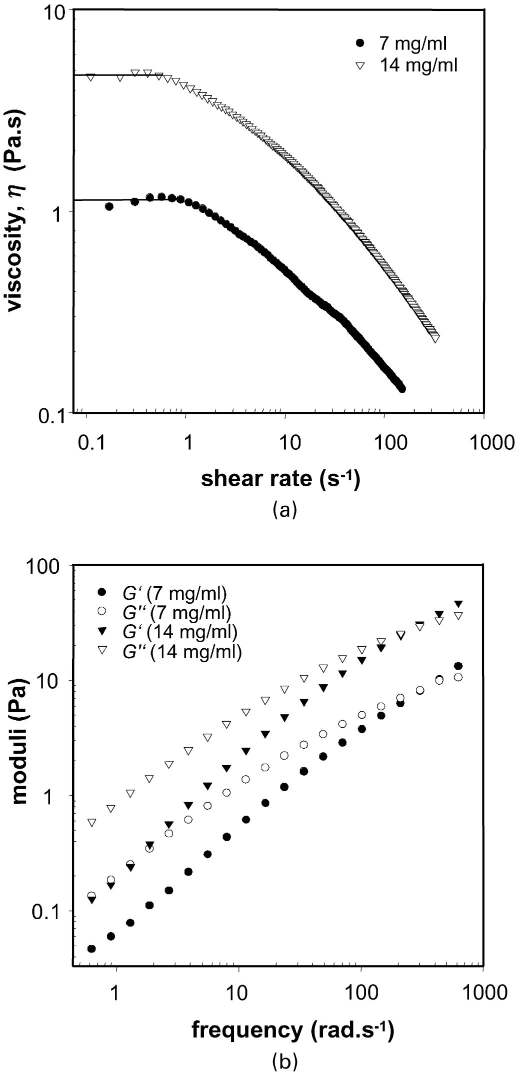

Fig. 3. Rheological data obtained for concentrated 4BCMU in chloroform. Taken from Ref. [48]. (a) Steady shear viscosity measurements for semi-dilute solutions of 4BCMU, at 7 mg ml^{-1} and 14 mg ml^{-1}, in $CHCl_3$, at 25 °C. (b) Small amplitude oscillatory measurements of the storage and loss moduli, G' and G'', for 4BCMU, conditions as above.

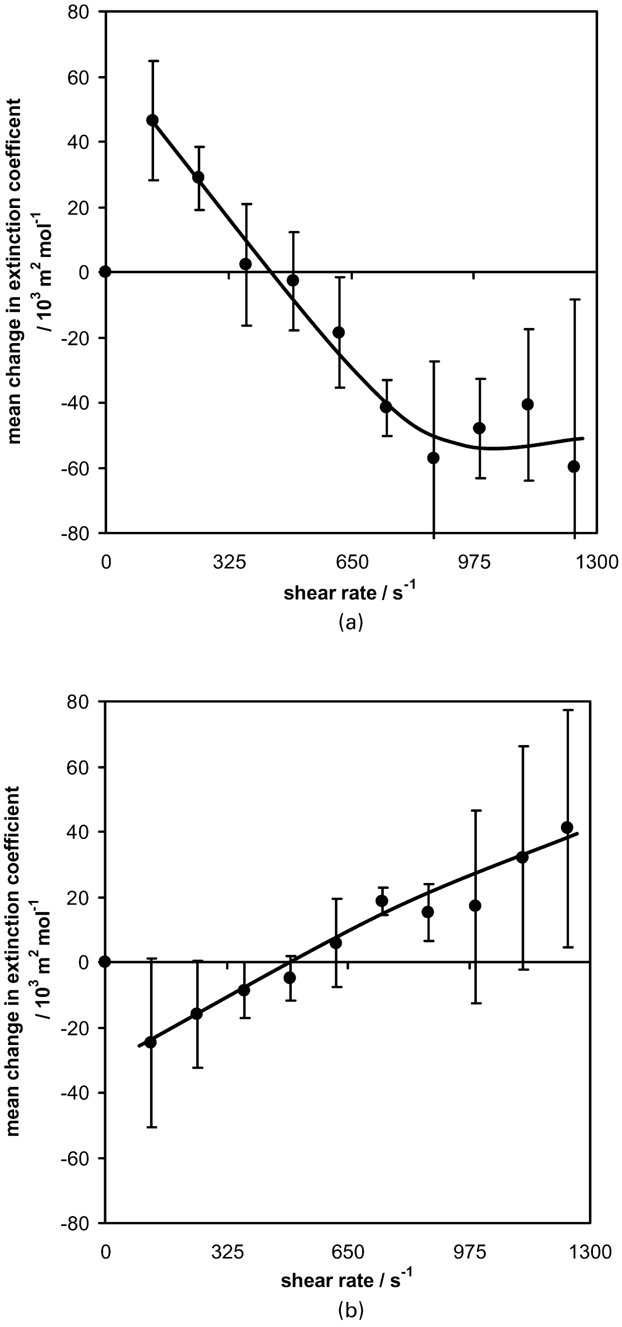

Fig. 4. (a) The measured change in extinction coefficient for concentrated 4BCMU in chloroform versus shear rate with 0° polarized light (parallel to the shear direction) at $\lambda = 468$ nm (λ_{max} in zero shear). The data points were determined as mean values from repeated measurements of three concentrations in the semi-dilute range (8, 11 and 13 mg ml^{-1}). 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 versus shear rate with 90° polarized light (perpendicular to the shear direction). All other conditions were as described above.

4BCMU orients in the flow direction [24]. This work is consistent with the results of the present study at low shear rates.

Interestingly, similar orientational behavior to that observed in the present work at high shear rates has previously been reported in one rheooptic birefringence study of high molecular weight polystyrene in dioxane in simple shear flow [52]. More recently Romo-Uribe et al. observed ‘log rolling’ effects in liquid crystalline polymers in shear [53]. While the present study is concerned with random coil polymers, the work of Romo-Uribe et al. shows that simple alignment of polymers in the flow direction is not always observed. Prior work by our group on cross-linked hydroxypropyl guar gelled under shear shows similar behavior to that reported here for 4BCMU. Atomic force microscope images of the polymers show alignment of the semi-flexible coils at low shear and ‘balling up’ of the HPG at high shear rates [54].

Further to the measured complex orientational behavior, the 4BCMU polymer coil exhibits a small shear-dependent spectral shift. Two alternative and independent data analysis methods were applied to absorption spectra recorded at a range of shear rates with unpolarized light. All spectra were smoothed using a standard Savitsky-Golay algorithm, and the first derivative was evaluated for each spectrum to determine the maximum absorption wavelength. Normalized difference spectra were also calculated. (See Fig. 5 caption for details of the method.) Both methods return similar outcomes, namely that a blue shift occurs with increasing shear rate. A spectral shift of this nature corresponds to a change in the distribution of conjugation lengths to shorter values. We conclude that 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 [45]. Fig. 5 shows the normalized difference spectrum for 4BCMU at 1240 s^{-1} and is characteristic for the range of studied shear rates. The spectrum in shear is normalized to the absorbance at λ_{max} for the zero shear spectrum and subtracted. Using this method the changes in extinction coefficient due to orientation are largely removed and the spectral shift induced in shear is revealed. There is an increased absorption at short wavelengths, relative to the zero shear case, and a concurrent decrease in absorbance at longer wavelengths. 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 [42]. The data show that there is an increase in the proportion of shorter conjugation lengths within the polymer ensemble, and a simultaneous reduction in the relative number of longer conjugation lengths in shear. The normalized change in extinction coefficient at 420 and 540 nm is plotted versus shear rate in Fig. 6. This data shows that the ensemble of polymer segments systematically reduces in size as the shear rate increases.

The Rouse/Zimm-type theories effectively assume fixed segment lengths, with non-local coil deformation arising at length scales above the segment size [2,3,20,21]. The current experiment senses local, segmental effects and shows that these systematically reduce in size in shear. Interpreting global polymer properties from local chain deformation is non-trivial. However, the data indicates that high shear induces a progressive reduction in the average polymer conjugation length and corresponding segment lengths. We hypothesize that this demonstrates that a reduction in the global polymer size is occurring in flow at high shear. As the segments orient perpendicular to the shear direction the average segment length decreases at high shear rates. The coil will, therefore, be reduced in size at the higher shear rates and not stretched as much of the theory would suggest [2,3] indicating that a new physics is occurring at high shear rates. The results presented in the current work confirm the recent Brownian dynamics simulations of bead-rod chains in shear flow by Petera and Muthukumar [7]. These simulations for chains which include hydrodynamic interactions and no excluded volume show that the expansion ratio of the chain reduces at high shear rates to values less than the non-shear values. The size of the chain is, therefore, shown to shrink at high shear rates.

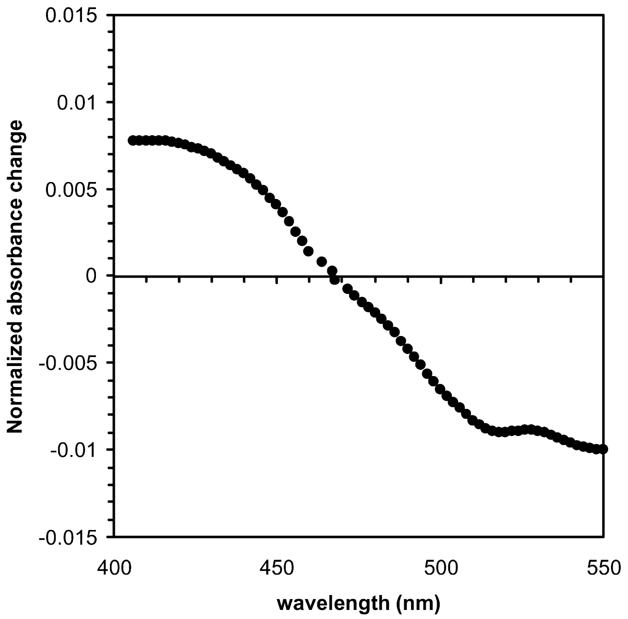

Fig. 5. Normalized absorbance difference spectra for concentrated 4BCMU in chloroform (11 mg ml^{-1}), measured at a shear rate of 1240 s^{-1}. The zero shear spectrum was rescaled and subtracted from the spectrum collected in shear. Unpolarized light was used for this experiment.

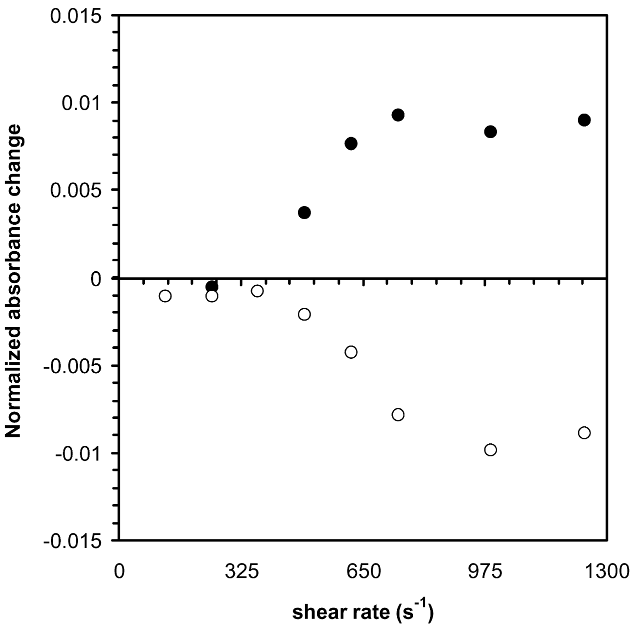

Fig. 6. The normalized absorbance change at 420 nm (filled circles) and 540 nm (open circles) versus shear rate showing a shift to shorter conjugation lengths at higher shear rates as the number of longer conjugation lengths decrease. This data was collected using unpolarized light, and the data processing method was as described for Fig. 5.

4. Conclusions

The experimental findings of this work demonstrate that, in semi-dilute solution, 4BCMU polymer segments align with the shear direction at low shear rates. At elevated shear rates (above $500\,\mathrm{s}^{-1}$) the proportion of segments aligned perpendicular to the shear direction increases. A measurable distortion, namely a reduction in the average conjugation lengths of the polymer, is observed for this visco-elastic polymer solution at high shear rates. We conclude that a reduction in the ensemble segment lengths occurs at high shear consistent with a reduction in the size of the polymer confirming the recent Brownian dynamics simulations [7].

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