

Rheoptical Studies of Polydiacetylene Solutions

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This work describes a rheoptical experiment with the ability to distinguish between orientation and deformation of polymers while quantifying the degree of deformation in shear using a polymeric chromophore. The chromophore used is poly(4-butoxycarbonylmethylurethane)diacetylene, referred to as 4BCMU, which is known to display varying optical properties that are attributed to conformational changes in the polymer backbone. The orientation may be measured by changes in the extinction coefficient both perpendicular and parallel to the shear field. The results obtained for dilute solutions of 4BCMU under shear are explained by an ellipsoidal random coil polymer in the quiescent state orientating in the shear field. In apparent contradiction to earlier theoretical models, no deformation of the polymer is observed within the range of shear fields used in this work. Extant theories have attributed the rheological behavior of polymer solutions to deformation of the spherical random polymer coils under shear.

Introduction

Polymers in solution give rise to a fascinating and diverse range of rheological properties that vary depending upon the intrinsic nature of the solution. Properties such as shear thinning, shear thickening, and normal stress differences can all be observed in polymeric systems and are understood to arise from changes in the microstructure of the solution.¹ It is of interest to study the microstructural changes of polymer solutions as knowledge of the response of the individual polymer molecules to the applied force will lead to further insights into the polymer physics governing the aforementioned properties. Utilization of this information will result in more effective control of polymer behavior in many applications. The response of the polymer molecules to the shear fields is postulated to include deformation.^{2–4} While a considerable body of theoretical work exists, well-defined experiments in this area are few. The experiments described herein are an attempt to quantify separately the changes induced in the conformation and orientation of the polymer molecules under shear.

In the quiescent state a polymer molecule is free to rotate and translate due to Brownian motion. Upon the application of a shear field, hydrodynamic forces are superimposed on the rotational and translational diffusion forces on the polymer. When the hydrodynamic forces begin to dominate the Brownian forces, both spatial organization and deformation occur.⁵ Brownian motion tends to randomize the orientation of the molecules, thereby opposing the alignment. The balance between the opposing effects of hydrodynamic and Brownian forces is characterized by the Peclet number (Pe), which is the ratio of the viscous to the Brownian forces acting on the molecules.⁶ We define the Peclet number as follows:

$$Pe = \dot{\gamma}/D_r \quad (1)$$

where $\dot{\gamma}$ is the shear rate and D_r is the rotary Brownian diffusion coefficient

$$D_r = 3kT(\ln 2p - 0.5)/\pi\eta_s L^3 \quad (2)$$

η_s is the solvent viscosity, p the axial ratio, L the major axis of the ellipsoid, k the Boltzmann constant, and T the temperature.

Predictions of the behavior of polymers under shear have been made by Kuhn² (elastic dumbbell), Rouse³ (spring–bead model), and Zimm⁴ (spring and bead model with hydrodynamic interactions of the beads). These theories, along with those of de Gennes⁷ and Bueche,⁸ rely on the assumption that the polymer chain is spherical in the unsheared state and under shear it is deformed and then oriented to give rise to the observed shear-induced anisotropy seen through scattering or birefringence. The reduced shear rate β , as defined in eq 3, predicts shear rates above which the shear forces on the polymer molecules can be expected to dominate their behavior. Springer⁹ argues that deformation may occur when the reduced shear rate, β , is greater than 1.

$$\beta = \tau\dot{\gamma} \quad (3)$$

where the characteristic relaxation time of the polymer molecule, τ , is given by

$$\tau = [\eta]\eta_s M/kT \quad (4)$$

in which $[\eta]$ is the intrinsic viscosity of the polymer and M is the molecular weight of the polymer.

Prior experimental studies of the deformation of polymer molecules under shear have focused on birefringence and scattering methods, such as light and neutron scattering.^{5,9–18} The orientation of the deformed radius of gyration may also be inferred from scattering techniques in addition to flow birefringence methods. Interpretation of the results obtained from these experiments enables the extent of deformation of the spherical radius of gyration of the enveloping volume to be calculated, from which the extent of deformation of the actual polymer molecules is inferred. These results show that large discrep-

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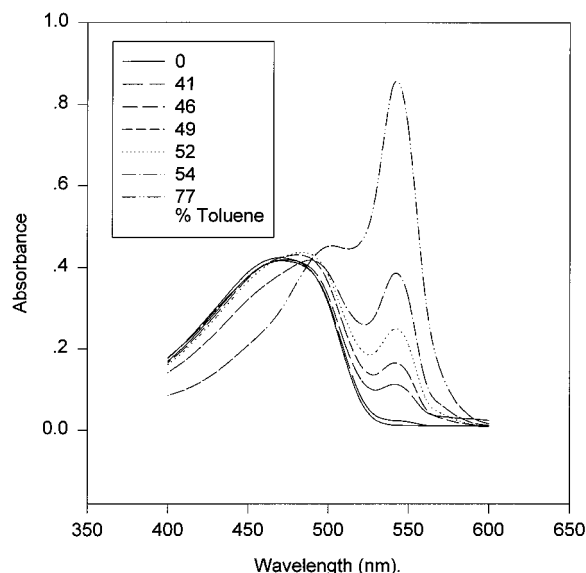


Figure 1. Spectra of 4BCMU (0.03 g/L) in increasing concentration of toluene characterized by the peak at 540 nm.

ancies exist between theoretical predictions and experimental data for polymer solution behavior. Scattering techniques rely on deconvolution of changes in the radius of gyration from the random ensemble in the quiescent state to the orientated case under shear. No information concerning any deformation of a single polymer molecule can be determined using birefringence. Interpretation of the data has assumed deformation of the spherical random coil to give rise to the observed anisotropy in the shear field.

The characteristic optical properties of soluble polydiacetylenes, in particular those with side groups such as nBCMU ((butoxycarbonyl)methylurethane) and nBMU (butoxymethylurethane), offer a unique experimental system in which both deformations may be quantified. The soluble polydiacetylenes are understood to undergo conformational changes at different temperatures and in different solvents. The observed color change has been attributed to a transition from a random coil chain to a semirod-like/lamellar polymer structure. The polymer is both solvatochromic^{19–23} and thermochromic²⁴ as characterized by a shift in λ_{\max} , which is observed as a color change between red and yellow as seen in Figure 1. It has been shown by light scattering and UV/vis spectroscopic measurement techniques that the spectral shift is accompanied by a change in the effective conjugation length of the polymer backbone.¹⁹ Both the above techniques show the polymer to be in the random coil configuration in the good solvent chloroform and a rigid rod configuration in the poor solvent toluene at 25 °C.^{19–23}

Given the difficulties in interpreting the scattering and birefringence techniques discussed above, combined with the limited number of experimental studies that have attempted to verify extant theories, we have designed experiments that utilize the spectral properties of poly((4-butoxycarbonyl)methylurethane)diacetylene, 4BCMU (Figure 2), in an attempt quantify the changes in the polymer under shear. Deformation of the polymer coil induced by the shear field would be expected to result in changes in the effective conjugation length and hence changes in the measured spectra. Thus, the extent of deformation of the polymer molecules in the shear field may be quantified.

Experimental Section

The spectroscopic technique employed uses a quartz parallel cylinder, as shown in Figure 3. The Couette geometry is used

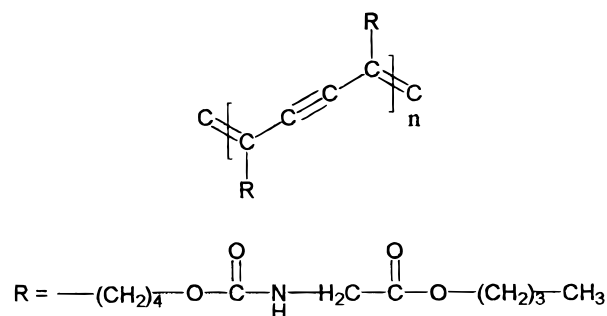


Figure 2. Poly((4-butoxycarbonyl)methylurethane)diacetylene.

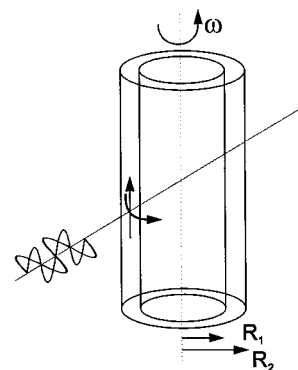


Figure 3. Couette geometry showing the path of the light beam and the axis of polarization.

to create a shear flow field that also allows spectroscopic measurements to be taken. The ratio of the radii of the two glass cylinders is greater than 0.95, and this ensures that a nearly constant shear rate is maintained across the gap. The outside cylinder is fixed, and the inside cylinder rotates at controlled speeds. The Couette cell is placed in the Cary 3E spectrophotometer and manually adjusted so as the flow field is perpendicular to the incident beam. Spectra were then collected with shear rates varying from 150 to 2000 s^{-1} . An important extension of the above experiments involves using polarized light whereby the anisotropy of the flow system can be observed. The incident beam is polarized by using a Melles Griot polarizer orientated either parallel or perpendicular to the flow field, allowing absorbance changes in either direction to be recorded as shown in Figure 3. The 4BCMU, as shown in Figure 2, used in this study was synthesized and polymerized following literature procedures²⁵ and is of average molecular weight 800 000 with a polydispersity of 1.8 as measured by GPC light scattering using a Dawn Wyatt system. The intrinsic viscosity at 25 °C in chloroform is $1.05 \times 10^{-2} M^{0.83}$.¹⁸ The rheoptical measurements were performed using three different solvents. Chloroform ($CHCl_3$) was used as a good solvent for 4BCMU. Dioctyl phthalate (DOP) was added to the $CHCl_3$ system in order to increase the solvent viscosity and attain higher reduced shear rates. Toluene was added to the $CHCl_3$ system to induce the transition to the rigid rod form of 4BCMU.

Results and Discussion

Spectra were collected using unpolarized light for solutions of 4BCMU in $CHCl_3$ and 30% DOP/ $CHCl_3$, and the absorbance at λ_{\max} was seen to increase with shear, as shown in Figure 4. Any distortion in the polymer, such as that seen with the solvatochromic and thermochromic changes which are attributed to conformational changes, would be expected to give rise to significant peaks after normalization and subtraction of the spectra obtained under shear and with no shear applied. No shift in λ_{\max} was observed when the 4BCMU was placed in the

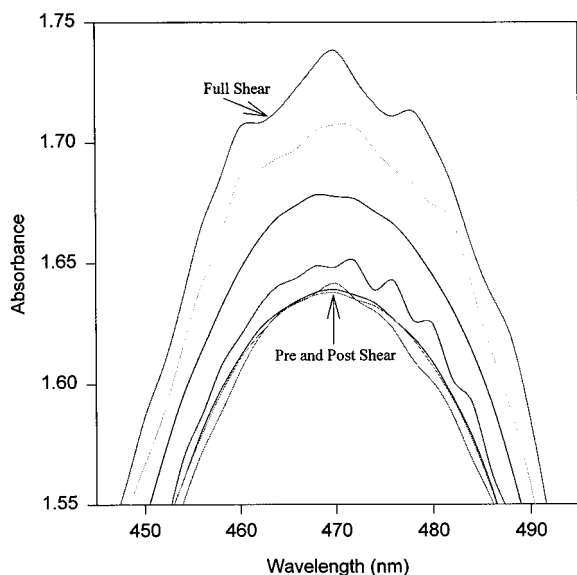


Figure 4. Absorption spectra of 4BCMU (1.5 g/l), under shear rates 0–2000 s^{-1} , showing no change in λ_{max} .

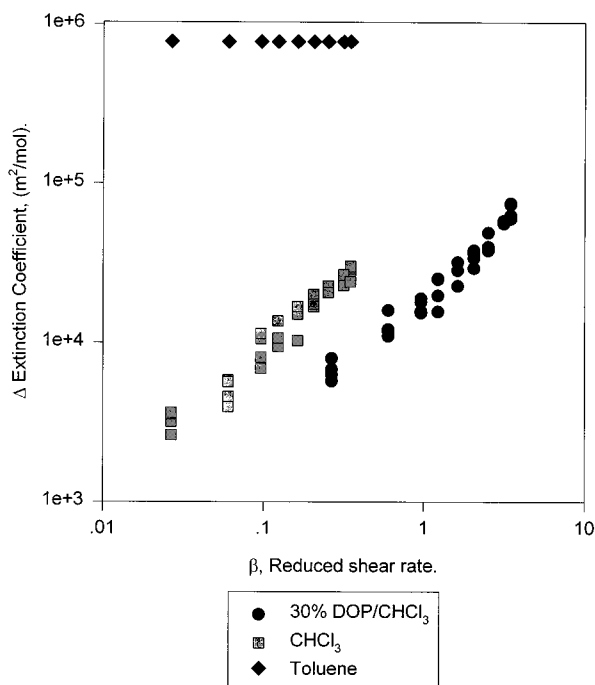


Figure 5. Change in extinction coefficient for 4BCMU (0.75–3.00 g/L) in $CHCl_3$ and 30% DOP/ $CHCl_3$ and 4BCMU (0.50 g/L) in toluene versus reduced shear rate using unpolarized light.

shear field up to the highest shear rates attainable with this apparatus (Figure 4). Given the nature of the spectral changes observed with differing solvent quality and temperature, it is concluded that the shear field induces no observable distortion of the polymer molecules. As will be discussed later, any change in conjugation length should be observed spectrally.

The Beer–Lambert law is employed to interpret changes in the absorbance to changes in the extinction coefficient, ϵ , of the molecules. Given the constant concentration and path length used in the experiments, the change in absorbance may be interpreted as a change in the extinction coefficient, as shown in Figure 5. The change in extinction coefficient yields a change in the surface area/molecule at any given shear rate. While deformation of the molecule could be expected to yield changes in λ_{max} , no such deformation was evident as discussed above. This effect may be attributed to orienting of the absorbing

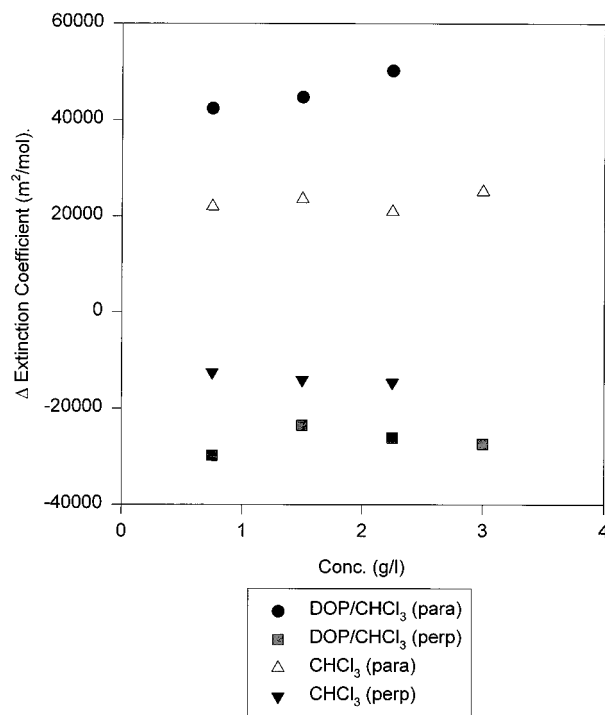


Figure 6. Change in extinction coefficient for 4BCMU in $CHCl_3$ and 30% DOP/ $CHCl_3$ versus concentration, using polarized light, at a shear rate of 2000 s^{-1} .

species relative to the light beam. The observed changes were completely reversible and time independent, indicating that concentration and temperature effects were not responsible for the changes seen.

The symmetry of the system enables both parallel and perpendicular absorbances to be measured. The change in extinction coefficient may be interpreted from the change in absorbance using the Beer–Lambert law, and it is positive parallel and negative perpendicular to the shear field. The changes in the extinction coefficient shown in Figure 6 are independent of concentration at a shear rate of 2000 s^{-1} , where negative and positive absorbances are observed perpendicular and parallel to the shear direction. This observation is consistent with the changes observed using the unpolarized incident beam.

The rigid-rod red form of 4BCMU was induced by adding toluene to a chloroform solution (3:8 (v/v) $CHCl_3$ /toluene).¹⁷ Flow spectra using the same protocol as described above were collected and show a large increase in the extinction coefficient and no change in λ_{max} . While the extinction coefficient, ϵ , increases linearly with shear rate for the 4BCMU/ $CHCl_3$ system, the change in the extinction coefficient, $\Delta\epsilon$, is observed to be independent of shear rate over the range that the spectra were taken for the 4BCMU/toluene solutions (Figure 5). Importantly, the extinction coefficient for the 4BCMU/toluene solutions increases for light polarized parallel to the shear flow and decreases for light perpendicular to the flow, as observed for the 4BCMU/ $CHCl_3$ and 4BCMU/ $CHCl_3$ /DOP systems. For shear rates above 150 s^{-1} using the 4BCMU/toluene solution, no changes in the absorbance with β were observed, which suggests that the polymer in this form has reached maximum alignment (see Table 1). These results show the effect the aspect ratio of the polymer has on the degree of orientation for a given reduced shear rate.

The experimental data obtained for 4BCMU in the three different solvents may be summarized as follows: no spectral shift with shear rate occurs, while ϵ increases parallel and decreases perpendicular to the shear field. Patel and Miller²⁶

TABLE 1: 4BCMU in CHCl₃/Toluene under Shear

shear, s ⁻¹	Δ(extinction coefficient) m ² /mol
150–2000	7.76 × 10 ⁵
2000 (parallel)	9.90 × 10 ⁵
2000 (perpendicular)	-1.76 × 10 ⁵

have used quantum mechanical calculations to predict the effective average conjugation length (l_{ec}) in the red and yellow form. The values obtained are $l_{ec} > 6$ repeat units for the yellow form and $20 > l_{ec} > 10$ repeat units for the red form. Simple division of the wavelengths associated with each form of the polymer yields a 7 nm shift in the absorption wavelength for a repeat unit change in the effective conjugation length. Given the sensitivity of the spectra to changes in the conjugation length and that no spectral shift is observed up to the highest shear rates attainable, no change in the average conjugation length of the polymer is induced by the shear field. From this analysis we conclude that no deformation of the polymer occurs in the shear field, up to the shear rates of 2000 s⁻¹ used in these experiments.

In order to explain these observations, we return to the random coil assumption of the polymer in the quiescent state. It has been postulated theoretically that the shape of the random coil of any polymer molecule in a good solvent is not spherical, but rather takes on a prolate shape with the principal components of the radius of gyration given approximately by $\langle L_3^2 \rangle : \langle L_2^2 \rangle : \langle L_1^2 \rangle = 11.7 : 2.7 : 1$.^{27–29} The ensemble of the prolate objects in quiescent solution is isotropic as Brownian rotation ensures all orientations are adopted. The shear field simply aligns the prolate objects to reduce drag and reduce viscosity. No deformation of the polymer coils is required to explain the experimental data obtained using scattering and birefringence methods. The data obtained in this study show that no measurable deformation takes place. The simple hypothesis that the random coil state is asymmetric explains the observed data. Alignment of the prolate polymer coils with their major axis parallel to the shear field increases the absorption cross section in the flow direction, while reducing the absorption perpendicular to the shear field. The above measurements indicate that the physical model used in prior theoretical interpretations of polymer flow behavior is incorrect. For the polymer system considered here, the concept of spherical polymers both deforming and orientating in the shear field appears to be a flawed description of the molecular changes induced by the shear forces in the system.

In order to characterize the extent of the polymer alignment with the flow field, a simple bimodal distribution is assumed. The molecules exist in either the random or aligned state, such that

$$\frac{\epsilon_{on}^{soln}}{\epsilon_{off}^{soln}} = f \left(\frac{\epsilon_{on}^{soln}}{\epsilon_{off}^{soln}} \right) + (1 - f) \quad (5)$$

where ϵ_{on}^{mol} and ϵ_{off}^{mol} are the molecular extinction coefficients of the molecules with the shear field on and off and were obtained from the 4BCMU/toluene data as limiting values. The ratio of solution extinction coefficients $\epsilon_{on}^{soln}/\epsilon_{off}^{soln}$ is obtained from the change in extinction coefficient from 4BCMU in CHCl₃ and 30% DOP/CHCl₃ solutions. The factor f , which describes the fraction of molecules that are aligned in order to give the change in extinction coefficient seen, is calculated as a function of $\epsilon_{on}^{soln}/\epsilon_{off}^{soln}$ and plotted against reduced shear rate to give the linear results described in Table 2.

TABLE 2: Orientation Factor of 4BCMU as a Function of Reduced Shear Rate

4BCMU solution	f
CHCl ₃	0.0901β
30% DOP/CHCl ₃	0.0221β

Conclusions

The results presented above are consistent with the picture that the polymer coil in the quiescent state is nonspherical, with the ellipsoidal polymer coil simply aligning in the shear field without further distortions. In contrast, previous models assume that the polymer coil is spherically symmetric, but under a shear field, it first distorts and is then orientated along the flow direction to give rise to the observed birefringence effects. The consequence of this work in our understanding of polymer flow behavior is immense. As suggested by Solc and Stockmayer,²⁸ "Appreciable corrections may be required to approximate theories based on an invariant spherical cloud as the molecular model". Extension of this work to higher concentrations of 4BCMU and other polymers is being pursued.

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