

Shear Degradation and Possible viscoelastic properties of High Molecular Weight Oil Drag Reducer Polymers

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ABSTRACT

High molecular weight polymers are susceptible to mechanical shear degradation. Oil soluble polymer drag reducers (DRA) are long chain molecules with average molecular weight in excess of $10 \cdot 10^6$, reaching an average of about $50 \cdot 10^6$. Polymer drag reducers exhibit Weissenberg effect, which is characteristic of viscoelastic behavior. Several mechanisms have been suggested for the drag reduction mechanism in turbulent flow. The extent of the shear degradation of DRA is studied when the polymer was exposed to 3395, 6790 and 13582 sec^{-1} . It is also studied the effect of the temperature on the shear degradation. The paper shows the effect of 5 and 60°C . Also, the effect of shear degradation on the viscoelastic properties of the polymers is addressed as shown from the G' trend as a function of scanned frequency (ω) between 0.01 to 10 sec^{-1} .

Polymer recovery after shear degradation is determined by the regain properties of the polymer.

Key words: Polymer drag reducers, shear degradation, viscoelastic properties of degraded polymers.

INTRODUCTION

There is very little work reported in literature that addresses the oil soluble drag reducers. However, there are a lot of studies done on water soluble drag reducers. A recent paper by Peiwen et al¹ (2001) has utilized the degradation phenomenon in their investigation with water/surfactant to enhance the heat transfer in drag-reducing flow. The paper presented her is an

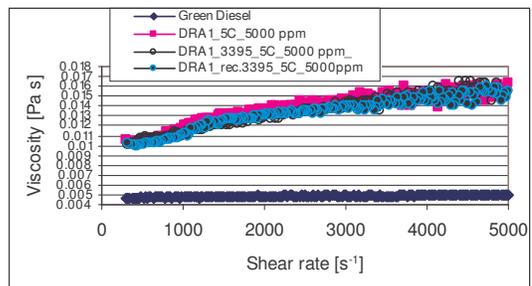
extension to our first reported effect of the temperature on degradation of the drag reducer polymers² at 20 and 40°C to 5 and 60°C . A comparison between the degree of degradation of two polymers are made based on their relative average molecular weight before and after being exposed to mechanical shear degradation rates of 3395, 6790 and 13581 sec^{-1} , where the average molecular weight of the polymers are estimated from the intrinsic viscosity.

Intrinsic viscosity $[\eta]$ of a polymer solution is generally determined by measuring relative viscosities at series of different concentrations. Rudin³ proposed determination of intrinsic viscosity from a single point. In most cases, $[\eta]$ can be evaluated conveniently using the graphic representations of Huggins⁴ and Kraemer⁵. Although, nonlinear least squares fitting of the actual curvilinear relation is a universal method for estimating $[\eta]$ from relative viscosity data at a series of concentrations⁵. In our previously work, the nonlinear least square was used by determining the average viscosity at low shear rates for different concentrations. However when this method of calculation was applied in this work, there was hardly any difference in the calculated intrinsic viscosity for some of the experiments, especially where the difference in the relative viscosity is not large enough. This may be due to the fact that the nonlinear best fit suppresses the real difference, hence overshadowed the small differences. Rudin's³ approach was followed after verification by another similar approach by Solomon et al⁶.

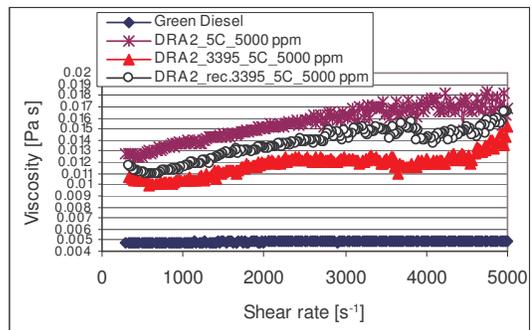
RESULTS and DISCUSSIONS

In order to address the shear degradation of the polymers, two main steps were followed in this work. The first is to establish the properties of the polymer (shear viscosity measurements) and then expose the polymer to different shear degradation at constant time, followed by assessing the change in the polymers' properties immediately after the shear degradation and after 72 hrs (recovered) where the polymers were kept with no disturbances under the same degradation temperature. The work has been done for several concentrations, however polymer concentration that is presented here is for 5000 ppm(w). When the DRA1 was exposed to low shear degradation 3395 sec^{-1} at 5°C , there was almost no difference between the sheared and the recovered status as shown in fig.1 a, except for DRA2 at 5°C , where it shows a partial regain of its property after 72 hrs at 5°C as shown in fig.1b. On the other hand at 60°C , the low shear degradation of 3395 sec^{-1} showed no change in DRA properties as shown in fig 2.a&b. When the polymers were exposed to high shear degradation rate of 13582 sec^{-1} , no regain of their viscoelastic properties was observed for the two temperatures, as shown in fig.1c&d and fig.2 c&d.

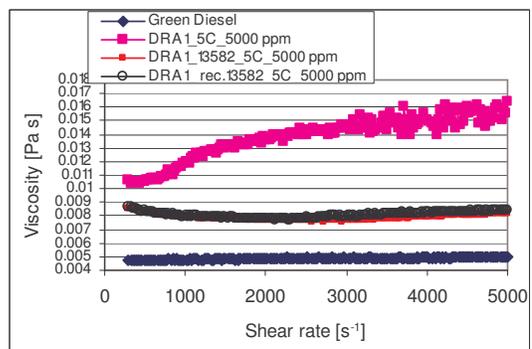
It is interesting to observe that the recovery tests show a slightly lower viscosity than the measured shear viscosity immediately after the shear degradation. More work is on going, however, this phenomenon is not clear on why it occurs at this stage.



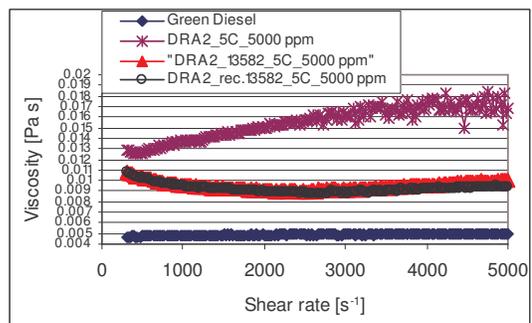
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b

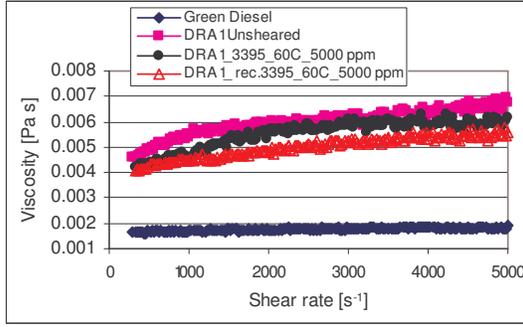


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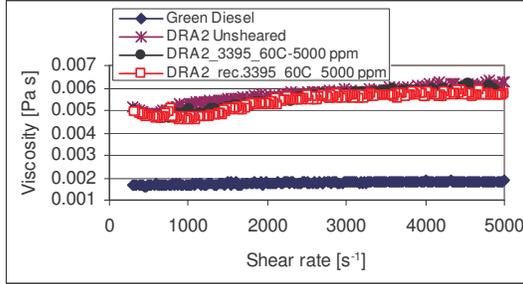


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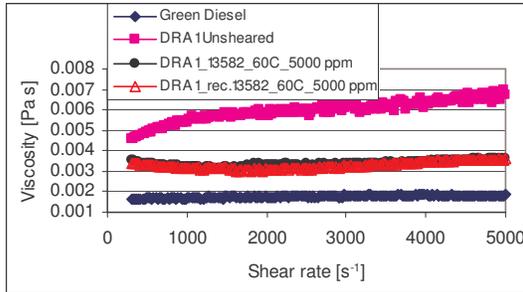
Fig.1 Shear viscosity of mechanical shear degraded polymers DRA1 and DRA2 at 3395 sec^{-1} for DRA1 (a) and DRA2 (b) and at 13582 sec^{-1} after 72 hrs for DRA1 (c) and DRA2 (d) at 5°C .



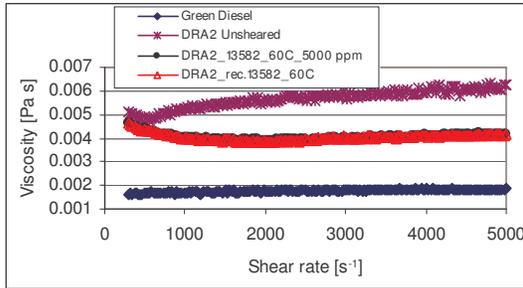
a



b



c



d

Fig.2 Shear viscosity of mechanical shear degraded polymers DRA1 and DRA2 at 13582 sec⁻¹ for DRA1 (a) and DRA2 (b) and at 13582 sec⁻¹ after 72 hrs for DRA1 (c) and DRA2 (d) at 60°C.

MOLECULAR WEIGHT

In order to determine the degree of degradation, a similar approach to our

previous work is followed here². This is done by relating the intrinsic viscosity to molecular weight for the sheared and un-sheared polymers. The intrinsic viscosity $[\eta]$ is defined by the following equation

$$[\eta]=[(\ln \eta_r)/c]_{c \rightarrow 0} \quad (1)$$

Huggins⁴ has pointed out that plots for a given polymer/solvent system vary approximately as the square of intrinsic viscosity as expressed by the following equation:

$$\frac{1}{C} \left(\frac{\eta}{\eta_0} - 1 \right) = [\eta] + k_H [\eta]^2 C \quad (2)$$

Where, η and η_0 are the viscosity of polymer solution and the solvent, respectively,

($\frac{\eta}{\eta_0} = \eta_r$, relative viscosity), C is the

polymer concentration expressed as g.dl⁻¹ and k_H is Huggins constant. In practice it is customary to measure the relative viscosity at two or more concentrations, chosen to give relative viscosities in the range of 1.1 to 1.5, and then extrapolated to $C=0$. Series of shear rates are then required in order to extrapolate to very low shear rate of zero. This practice may produce errors due to forcing a real curvilinear relation into a rectilinear form. In our previous work², the power series expressions are solved directly by non-linear regression analysis⁵ of the following equation

$$\frac{1}{C} \left(\frac{\eta}{\eta_0} - 1 \right) = [\eta] + k_H [\eta]^2 C + k_H' [\eta]^3 C^2 + \dots \quad (3)$$

This approach, has shown that the calculated $[\eta]$ in different cases of shear degradation and recovery did not show appreciable difference. This may be explained that the slight change in the shear viscosity occurs at a certain window of shear rates, hence overshadowed by the low differences.

Rudin³ proposed an approach to calculate intrinsic viscosity from a single point at low concentration and shear rate. The intrinsic viscosity $[\eta]$ is calculated by the following equations

$$[\eta] = \frac{\phi(1.31\rho - 2.5c)}{(c\rho)(0.524 - \phi)} \quad (4)$$

where ρ is the density of the solution ($\frac{g}{cm^3}$), and ϕ is the swelling factor obtained by

$$\frac{1}{\eta_r} = 1 - 2.5\phi + 11\phi^5 - 11.5\phi^7 \quad (5)$$

The obtained intrinsic viscosity was verified by a similar approach by Solomon et al⁵. The results were almost identical

Intrinsic viscosity can then be related to average molecular weight using Houwink-Sakurada's relation given by

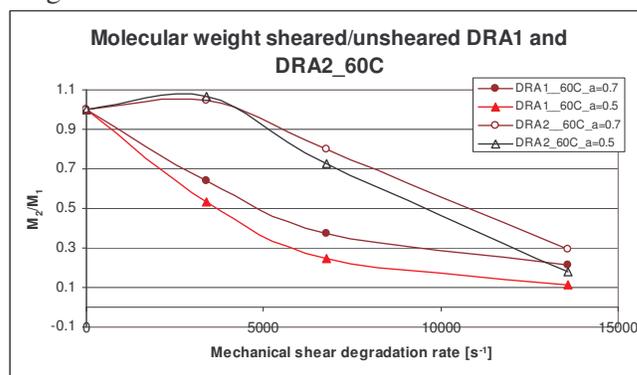
$$[\eta] = K \cdot \bar{M}^a \quad (6)$$

where K and a are polymer constants. Exponent a ranges from 0,1 to 1. Flory⁷ stated that this exponent does not fall below 0.5 and seldom exceeds 0.8.

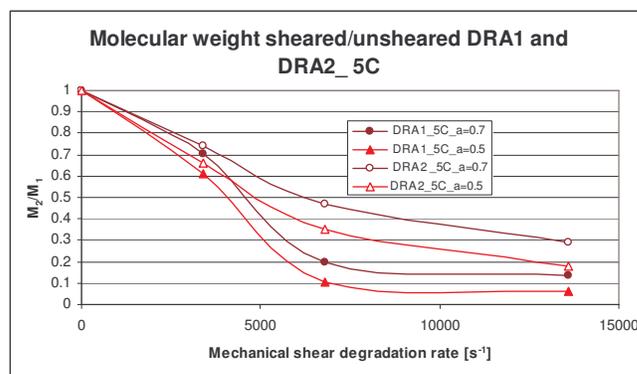
Rudin et al¹⁰ tested various polymers with different solvents, found that the exponent (a) is between 0.5 and 0.7. Park and Choi¹¹ found that for linear polymer system the Mark-Houwink exponent (a) is about 0.7 in a good solvent and 0.5 in the theta condition. In this work exponent (a) of 0.7 and 0.5 are used. The trend for the degree of degradation of the polymers is calculated relative to the un-sheared polymer. This relation is shown below.

$$\frac{\bar{M}_2}{\bar{M}_1} = \left(\frac{[\eta]_2}{[\eta]_1} \right)^{\frac{1}{a}} \quad (7)$$

where, the subscript 1 and 2 represent the un-sheared and the sheared polymer, respectively. As shown in fig 3a and b, for the un-sheared polymer at 60 and 5°C, respectively that DRA1 is more susceptible to shear degradation than DRA2 as expected, since it has higher molecular weight.



a



b

Fig. 3 Ratio of the molecular weight of the sheared to the un-sheared polymers DRA1 and DRA2 at 60°C (a) and 5°C (b) using exponent a of 0.5 and 0.7.

It also demonstrates that at high temperature 60°C the polymers are less susceptible to mechanical shear degradation rates. This phenomenon is not well understood, however, since this relation reflects the viscosity, it may, then be explained based on that the molecular activity at 60°C is higher than that for 5°C, the degradation may then be masked.

VISCOELASTIC PROPERTIES of the POLYMERS

Viscoelastic properties are dominated by rearrangements of molecular segments. Polymer molecular weight and molecular weight distribution have important effect on the viscoelastic properties of the polymer. Interpretation of polymer behaviour using the storage modulus (G') trend as a function of scanned frequencies from 0.01 to 10 sec^{-1} at strain amplitude of 50% is believed to give an insight to the molecular behaviour that may propose possible explanation to some of the observed phenomena. The measurements are done using Paar Physica rheometer (model Physica USD 200) Fig.4, 5, 6, 7 and 8 show plots of the storage modulus (dyn/cm^2) versus the angular frequency (sec^{-1}) for un-sheared polymers (DRA1 and DRA2), sheared polymers at 3395 sec^{-1} (5 and 60°C) and 13582 sec^{-1} (5 and 60°C), respectively for polymer concentration of. 5000 ppm(w).

At angular frequencies (ω) below about 0.01 sec^{-1} high fluctuation responses were obtained, it was therefore decided to stay within the shown frequencies for this work(0.01-10 sec^{-1}).

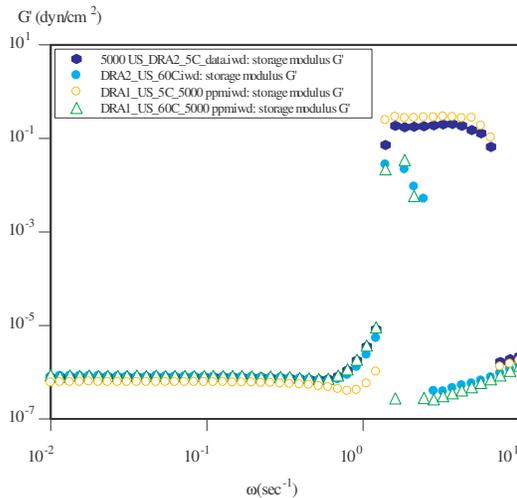


Fig.4 Storage modulus of polymer for DRA1 (open symbols) and DRA2 (filled symbols) at 60 and 5°C.

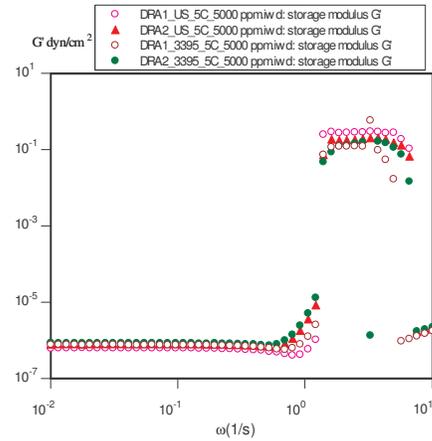


Fig.5 A comparison between G' for the un-sheared and sheared at 3395 sec^{-1} polymers DRA1 (open symbols) and DRA2 (filled symbols) at 5°C.

Oyanagi et al ⁸ from their work on narrow distribution polystyrenes identified three distinct zones, which are the terminal, plateau and transition zones.

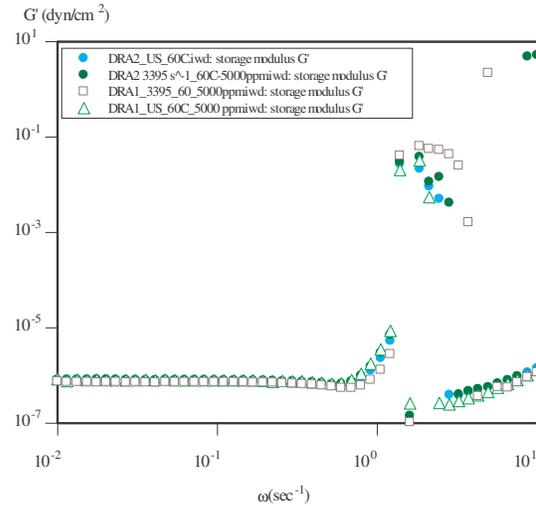


Fig.6 A comparison between G' for the un-sheared and sheared at 3395 sec^{-1} polymers DRA1 (open symbols) and DRA2 (filled symbols) at 60°C.

In this work here, there is a general feature in all the presented figures (4-8), where four zones were observed zones. The first is a long plateau zone. Within this zone, the polymer behaviour is shown not to be

much affected by differences in molecular weight or molecular weight distribution.

At frequency of about 0.2sec^{-1} a sharp increase of G' from about $5 \cdot 10^{-7}$ to about $3 \cdot 10^{-1} \text{dyn/cm}^2$ was observed, which is

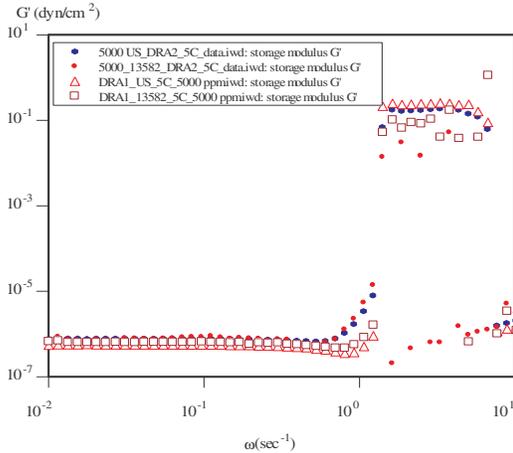


Fig.7 A comparison between G' for the un-sheared and sheared at 13582sec^{-1} polymer DRA1 and DRA2 at 5°C .

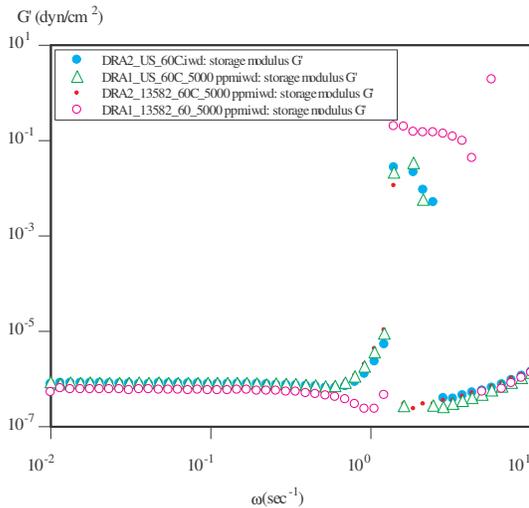


Fig.8 A comparison between G' for the un-sheared and sheared at 13582sec^{-1} polymer DRA1 and DRA2 at 60°C .

followed by a third zone with a plateau (low slope). The fourth zone shows a drop in G' after which all G' converged. The fourth zone has the same criteria as the reported transition zone in literature, where

all the curves converge. So the terminal is perhaps what is identified as second zone followed by the short plateau (zone 3) and then transition zone (zone 4). The difference between the transition zone in this work and the reported in the literature is that after the plateau G' decreased to the range of about 10^{-6}dyn/cm^2 where the curves converged.

In order to confirm that zone 3 is the equivalent to the reported plateau in literatures, this zone was further examined. Qyanagi and Ferry⁹ showed that in the plateau zone, the loss tangent ($\tan \delta$), passes through a minimum, where the minimum deepens with molecular weight. Plots of $\tan \delta$ and G' vs ω are shown in fig.9, where the minimum coincides with the third zone, hence it may represent the plateau.

The transition between the terminal and plateau and the magnitude and the shape of the plateau may give information on the polymer behaviour.

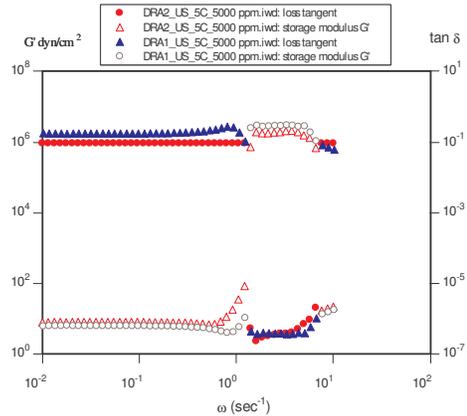


Fig.9 G' and $\tan \delta$ (filled symbols) for the un-sheared polymers DRA1 (open triangles) & DRA2 (open circles) at 5°C .

It is interesting to observe that the sheared and un-sheared polymers have longer plateau at lower temperature (5°C) than at the high temperature (60°C). This is true for both low and high shear rates, 3395 and 13582sec^{-1} , except that the sheared DRA1 at high shear rate 13582sec^{-1} (60°C) has long plateau that is comparable, to some

extent, with that obtained with the un-sheared polymer at the low temperature (5°C). The plateau, where G' changes only slightly with frequency may be explained to be due to entanglements^{8&9}, as a result, the polymer behaviour is not much affected by differences in molecular weight or molecular weight distribution. Fig 5, and 7 show that for shear degradation of 3395 and 13582 sec^{-1} , respectively at 5°C have slightly but consistently indication of higher molecular weight than the un-sheared polymers. However, at 60°C, the sheared DRA1 at 3395 and 13582 sec^{-1} , as shown in fig. 6 and 8, respectively show a comparable behaviour to the un-sheared polymers (DRA1 and DRA2) at 5°C in the plateau zone that may indicate that the sheared DRA1 (high average molecular weight) has large molecular distribution, hence promoting entanglement phenomenon to occur. This phenomenon has not been observed for the sheared DRA2 at 60°C

CONCLUSIONS

The tested polymer drag reducers seem to be less susceptible to shear degradation at 60°C than at the low temperature of 5°C. This may be explained based on that the degradation effect is masked by the higher level molecular activities at 60°C. At the high temperature the degraded DRA1, has indicated (from the plateau) possible occurrence of more entanglement when sheared at 13852 sec^{-1} . Combining the polymer activities and the wide molecular weight distribution after the shear degradation may enhance the entanglement phenomenon. On the other hand this phenomenon was not observed for DRA2, to the same extent as for DRA1. This, perhaps, is due to narrower molecular weight distribution than for DRA1. This is not unrealistic, since the average molecular weight of DRA2 is about 5 times less than that for DRA1.

The molecular weight ratio estimated from the intrinsic viscosity does give insight to molecular weight distribution but rather

average molecular weight ratio between the sheared and the un-sheared polymers.

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