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Conformational Energy Contributions to Energy Storage in Deformed Macromolecules

The stretching of a macromolecule by an external force results in an increase in the free energy of the macromolecule. Since this increase equals the work done on the polymer by the external force, it is usually referred to as energy storage.[1,2] Such free-energy storage in polymers deformed by shear and elongational flows has played an important role in models of turbulent drag reduction by polymeric additives by providing a mechanism through which energy transferred to the viscous sublayer can be dissipated even at very high Reynolds numbers.[2] Previous treatments[2-6] which used the Gaussian model for the free polymer chain addressed only the entropic contributions to free-energy storage, i.e., computed the reduction in the number of possible configurations of a macromolecule distorted by the flow, assuming that all the configurations are isoenergetic in the absence of the flow.

In this communication we estimate the importance of effects associated with the energetics of the conformational states of a macromolecule by using the rotational isomer state model[7] to analyze the free-energy storage in a deformed polyethylene-like chain. We assume that the polymer is free draining, i.e., that the flow interacts with all the monomers in the chain (no hydrodynamic screening effects[8]). Since for steady-state potential flow the frictional forces between the polymer segments and the flow field can be described by a potential,[9] we can associate a potential energy with each macromolecular conformation. Thus, assuming that a steady state is reached in the presence of the flow, the segment distribution will be given by the appropriate Boltzmann distribution. The analysis of the free-energy storage in semiflexible polymers in steady extensional flows is complicated by the fact that the potential energy associated with the monomer-flow interaction is a function of the vector $\vec{r}$ from the center of mass of the macromolecule to the monomer and the angle it makes with the extension axis of the flow.[10] (We hope to report the results of Monte Carlo calculations based on the exact model, in the near future.[11])

Here we consider a simpler model for the monomer-external field interaction which is appropriate for the stretching of the polymer by a homogeneous quadrupolar field[12]

$$v = -\frac{\alpha}{2}(3\cos^2\vartheta - 1) \qquad (1)$$

where α is a constant (independent of the location of the monomer) and ϑ is the angle the monomer makes with the extension axis. In this case, the steady-state distribution function is identical with the one obtained for a polymer chain dissolved in a nematic solvent.[13] In particular, the partition function Z for a polyethylene-like chain (the backbone bonds lie on a tetrahedral lattice) has been given in ref 13 as a matrix product

$$Z = \sum_{u,v=1}^{36} \mathbf{g}(u)\mathbf{W}^{N-3}(u,v) \qquad (2)$$

where $\mathbf{W}$ is a (36) × (36) matrix and $\mathbf{g}$ is a (36) vector, both evaluated in ref 13 (N is the number of monomers in the chain). The elements of the matrix consist of products of the factors F and G where $F = \exp(\alpha)$ is the Boltzmann factor containing the potential energy of the monomer-field interaction and $G = \exp(-E/k_BT)$ is the Boltzmann factor corresponding to the gauche state of a trimer[13] (E is the relative energy of the gauche with respect to the trans configuration). Notice that $F = 1$ at zero field and that the chain is purely entropic for $G = 1$, since $E = 0$ means that the gauche and trans states are randomly distributed.

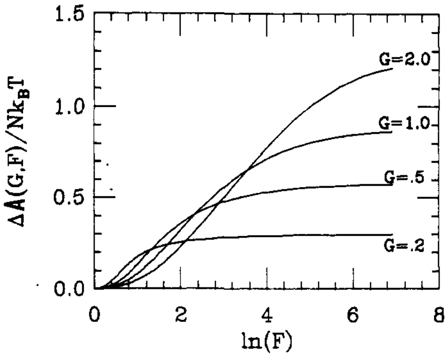

Figure 1. Free-energy storage per monomer (in units of k_BT) is plotted against the monomer-field interaction energy ln F for G = 0.2, 0.5, 1, and 2.

Taking the negative of the logarithm of the partition function, we obtain the Gibbs potential for a chain stretched by the external force.[14] This expression contains the (negative) energy of interaction with the external field that has to be subtracted in order to obtain the free-energy storage. The latter is given by the difference of Helmholtz free energies[14] in the presence and absence ($F = 1$) of the flow

$$\Delta A(G,F) = -k_BT \ln \frac{Z(G,F)}{Z(G,1)} + k_BT\langle n_z\rangle \ln F \qquad (3)$$

where $\langle n_z\rangle$ is the average number of monomers having a projection along the external field axis. Both ln Z and $\langle n_z\rangle$ have been computed by diagonalizing the $\mathbf{W}$ matrix and taking the limit $N \rightarrow \infty$ in which only the largest eigenvalue contributes.[7]

In Figure 1 the dimensionless free-energy storage per monomer is plotted as a function of ln F (interaction energy per monomer). As we have previously mentioned, the purely entropic behavior over the complete range of ln F is given by the $G = 1$ curve. The initial (small ln F) regime of all the other curves is also entropic; it corresponds to the redistribution of trans and gauche configurations in order to increase the projected chain length along the external-field direction— at *fixed* ratio of trans to gauche configurations.[15] In this regime the energy storage is a decreasing function of G (at constant F), since it is proportional to the unperturbed dimensions of the polymer which *decrease* with increasing G.[7] The nonentropic effects become important at higher values of ln F at which curves with $G < 1$ ($G > 1$) fall below (above) the $G = 1$ curve. Here the stretching due to redistribution is saturated and further stretching involves changing the ratio of gauche to trans configurations. This conformational energy effect tends to reduce the available free-energy storage capacity for chains with $G < 1$ (such as polyethylene) and to increase it for chains with $G > 1$ (which, qualitatively describes the behavior of poly(oxyethylene)).

As expected, the free-energy storage saturates at high values of ln F that correspond to a fully stretched state of the polymer. The asymptotic energy storage increases with G, i.e., with decreasing chain stiffness. In the extensional flow case, the average monomer–flow interaction is expected to increase faster than linearly with the strain rate since it is proportional to $\langle r^2 \rangle$ which increases rapidly with it.[10] Thus the asymptotic regime in ln F can be reached for moderate values of the applied strain rate.

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References and Notes

(1) More appropriately one should refer to free-energy storage. We shall use the latter term in the following.
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Spontaneous and Rapid Polymerization of Plasma-Exposed Monomer Crystals in the Liquid Phase

A plasma is a partially ionized gas composed of electrons, ions, radicals, and photons spanning a wide range of energy. Among them electrons particularly generated by the glow-discharge plasma gain energy from an imposed electrical field and lead to the formation of a host of chemically reactive species, some of which become precursors to the plasma polymerization as well as plasma-initiated polymerization.[1,2]

We report here an interesting polymerization process in which plasma is used to generate the active species with very long life on the crystal of water-soluble monomers. The active species thus formed cannot initiate the polymerization at all as long as the monomer remains in the solid state. However, when the monomer crystal is allowed to dissolve by introducing water in vacuo, it can initiate the polymerization very rapidly and gives a polymer with extremely high molecular weight.

Thus, once the monomer crystal has been exposed to the plasma beforehand for 60 s or less, one can obtain the polymer in situ only by dissolving the monomer crystal in water (or acid solution in some cases). This polymerization process was referred to as plasma-initiated solvopolymerization.

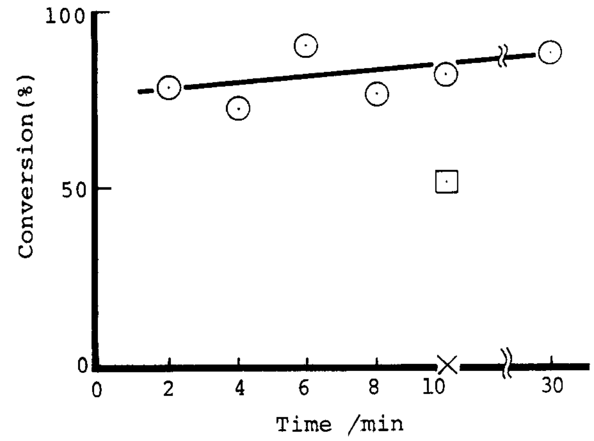

Figure 1. Monomer conversion–postpolymerization time profile for the polymerization of AMPS. AMPS 1.5 g, 4 mL of water (⊙), Me$_2$SO (□), or DMF (×) was added to the AMPS crystal immediately after plasma exposure. Postpolymerization, 25 °C.

The experimental apparatus and procedure used in the present investigation are similar to those reported previously,[3-6] i.e., 0.5–1.5 g of purified monomer crystal was evacuated several times in a 25-mL Kjeldahl flask under 1.0–0.1 Pa. The flask was inserted between a pair of parallel-plate electrodes connected to a plasma generator operating at 13.56 MHz. A glow discharge was initiated in the gas phase for 60 s at 100 W.

Four milliliters of water (or aqueous acid) previously degassed was then introduced in vacuo into the flask containing the monomer crystal, dissolved by shaking vigorously, and postpolymerized for 2–10 min at 25 °C. Obtained polymer solution was precipitated in a large amount of poor solvent, dried in vacuo, and weighed to determine the percent conversion. In some cases the plasma-exposed monomer crystal was allowed to stand for several days or weeks in vacuo, dissolved in water, and postpolymerized for 10 min.

The polymerization of the plasma-exposed crystal took place only by dissolving in water and no polymerization occurred in the crystalline state at all. Once water was introduced, the rate of polymerization was very high and appeared to occur almost simultaneously with dissolution in water. Figure 1 shows conversion–postpolymerization time profile for the polymerization of 2-acrylamido-2-methylpropanesulfonic acid (AMPS). It is seen that the polymer is obtained with 80% conversion only 2 min after water was introduced. Polymerization occurred also by dissolving in dimethyl sulfoxide (Me$_2$SO), but no polymer was obtained in dimethylformamide (DMF) in analogy with plasma-initiated solution polymerization in DMF.[7,8] The active species generated in the AMPS crystal had very long life. Polymerization occurred even when the plasma-exposed crystal was allowed to stand for several months in vacuo and then dissolved in water and postpolymerized for 10 min. The polymer yield decreased only slightly (Figure 2a). However, when the plasma-exposed AMPS crystal was left in aerobic condition, the polymer yield decreased from 80% to 50% in 10 h, which later remained constant (Figure 2b).

We reported previously that the polymers obtained by the plasma-initiated polymerization are un-cross-linked soluble polymers[3,4] having extremely high molecular weight as large as 3×10^7.[9] The molecular weight of polymers obtained by this method was also very high. For example, intrinsic viscosities of AMPS polymers obtained after 2 and 6 min of postpolymerization showed 18.0 and 16.5 dL/g, respectively, in 0.1 mol/dm^3 aqueous NaCl solution