esis (Fig. 3). First CO binds at a cluster Fe that is bridged to the Ni. Methyl transfer to the Ni is then followed by attack on the bound CO, forming an acetyl adduct, which might migrate from Fe to Ni. Transfer of the acetyl group to CoA completes the catalytic cycle. Alkyl attack on metal-bound CO is a well-precedented organometallic process that has been extensively studied (*21*). Usually the CO binds to the same metal atom that bears the alkyl group, following dissociation of another ligand. In the mechanism suggested in Fig. 3, the function of the Fe-S cluster is to provide access to CO at ambient temperature and pressure, by way of a binding site that is under redox control. Removal of an electron from a metal center has been found to strongly promote the CO insertion reaction (*22*). Thus, reoxidation of the Fe_4S_4 cluster in center A could accelerate acetyl formation. There is evidence for acceleration of the CO–acetyl-CoA exchange reaction upon addition of one-electron oxidants (*12*).

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Direct Observation of Tube-Like Motion of a Single Polymer Chain

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Tube-like motion of a single, fluorescently labeled molecule of DNA in an entangled solution of unlabeled lambda-phage DNA molecules was observed by fluorescence microscopy. One end of a 16- to 100-micrometer-long DNA was attached to a 1-micrometer bead and moved with optical tweezers. The molecule was stretched into various conformations having bends, kinks, and loops. As the polymer relaxed, it closely followed a path defined by its initial contour. The relaxation time of the disturbance caused by the bead was roughly 1 second, whereas tube-like motion in small loops persisted for longer than 2 minutes. Tube deformation, constraint release, and excess chain segment diffusion were also observed. These observations provide direct evidence for several key assumptions in the reptation model developed by de Gennes, Edwards, and Doi.

Understanding the behavior of a concentrated solution of flexible polymers is a challenging problem in condensed matter physics. Interactions between entangled polymer chains lead to a rich variety of unusual properties. On long time scales, these materials flow like a viscous liquid; on shorter time scales, they have the elastic response of rubber; and for still shorter times, they display glass-like behavior (*1*). These viscoelastic materials play an important role in many biological systems and have broad commercial applications.

The most popular and successful theoretical model for a concentrated polymer solution is the reptation model of de Gennes, Edwards, and Doi (*2*–*6*). The key assumption of the model is that an entangled polymer chain is confined to an imaginary tube through which it moves in snake-like fashion (Fig. 1). The notion of a tube, originally proposed by Edwards (*3*), is based on the idea that a chain is topologically constrained by its neighbors from undergoing transverse displacements. As a consequence, the chain behaves as if it were trapped in a small tube that follows its own contour. The motion of an individual chain is governed by one-dimensional diffusion within the tube. De Gennes originally modeled this motion as diffusion of a gas of noninteracting defects carrying stored length along the chain. The chain ends can diffuse or "reptate" out of the original tube, creating new portions of tube. He conjectured that the results might extend to the case of concentrated or molten polymers in which the tubes would be effectively frozen on time scales less than the characteristic time separating the viscous from the elastic domain. De Gennes (*4*) and Doi and Edwards (*5*) extended the basic reptation model to include tube deformation and constraint release, which would allow the tube to undergo limited transverse motion on longer time scales. Tube deformation is predicted to occur when a strained polymer relaxes its strain by deforming the surround-

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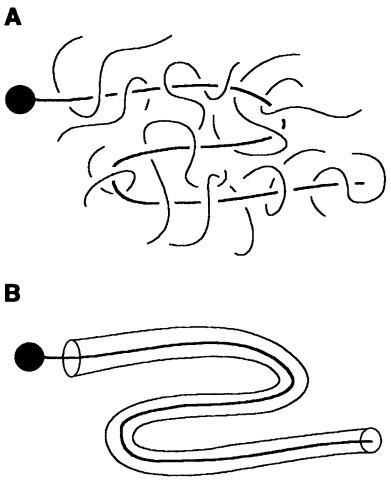

Fig. 1. Schematic representation of the experiment. (**A**) A stained DNA molecule in a concentrated solution of unstained λ-phage DNA was manipulated with optical tweezers by means of a 1.0-μm latex bead attached to one end of the molecule. (**B**) The topological constraints of all the background chains collectively act to confine the polymer to motion within a tube-like region along its own contour.

ing polymers. Constraint release refers to the release of topological constraints imposed by the reptation of the surrounding chains. The theoretical advantage of the reptation model is that it simplifies a many-body problem to the problem of a single body moving in an effective mean field.

Although experimental studies of the bulk properties of polymers have tested the predictions of reptation (*6*, *7*), the assumptions of the reptation model must be tested by probing the dynamics of individual chains. Neutron scattering measurements (*8*, *9*) involving deuterated polymers as test chains have shown that the dynamics are consistent with tube-like constraints on time scales faster than 10^{-8} s, but they were not used to investigate longer time behavior. Recently, Russell *et al.* (*10*) have shown that ends of a polymer at the interface of two layers diffuse more rapidly than the central portion of the chain by differentially labeling chains with deuterium and probing the motion across a boundary with secondary-ion mass spectroscopy. Although these methods yield results consistent with reptation, they have an inherent disadvantage: The detailed motion of a single chain cannot be measured, and its dynamics must be inferred from indirect measurements averaged over a macroscopically large number of chains.

We directly observed the tube-like motion of a single, flexible polymer chain in a solution of entangled polymers using fluorescence microscopy. This method of observing reptation by fluorescently staining a single DNA molecule embedded in a background unstained DNA was first suggested by Chu (*11*).

Solutions of DNA are an excellent system for studying polymer dynamics (*12*–*14*). Modern molecular biology techniques offer precise control in the preparation and manipulation of DNA molecules, facilitating the preparation of monodisperse polymer solutions. Single molecules of DNA are of sufficient size (tens of micrometers) that they can be directly visualized by fluorescence microscopy with efficient, tightly bound fluorescent dyes (*15*). Several groups have used fluorescence microscopy to observe individual DNA molecules undergoing gel electrophoresis (*16*).

For the test chain, we formed single DNA molecules up to 100 μm long by linking several λ-phage DNA molecules (16 μm). One end of the DNA molecule was biotinylated and attached to a streptavidin-coated polystyrene sphere (*17*, *18*). The concentrated, monodisperse polymer solution consisted of 600 μg/ml of highly purified λ-phage DNA (New England Biolabs) in a buffer solution of 12 mM tris-HCl (pH 8), 1.2 mM EDTA, 0.01% Tween-20, and 2 mM NaCl. This density of DNA corresponded to a concentration of 12 molecules per cubic micrometer. Because the radius of gyration of a single λ-phage DNA molecule is about 1 μm in dilute solution, there were about 50 polymers packed into the space that one would occupy in dilute solution, and a large degree of entanglement was expected. The chains are flexible because the contour length of λ-phage DNA is about 160 times longer than the Kuhn length of about 0.12 μm (*13*, *19*). Before using the concentrated DNA, we heated the solution to 70°C for a few minutes to linearize any circular DNA molecules. The experiment was carried out at room temperature.

In a modified optical microscope with a high power objective (Zeiss, numerical aperture 1.4, ×63), the 1-μm-diameter polystyrene beads were trapped and manipulated in an aqueous environment with optical tweezers (*20*). A yttrium-aluminum-garnet–Nd laser producing about 100 mW at the focus formed the tweezers. The fluorescently stained DNA was excited by an argon-ion laser operating at 488 nm (*21*), and the resulting fluorescent images were taken by a silicon-intensified target video camera (Hamamatsu), processed by an image processor (Hamamatsu Argus 10), and recorded by a VCR.

The fluorescently labeled test polymer chain was dragged through the entangled solution with optical tweezers at velocities from 5 to 100 μm/s. This allowed us to stretch the chain into various conformations in the focal plane of the microscope and produce kinks and loops on length scales smaller than the radius of gyration of the background polymers or the diameter of the bead. As the test chain was pulled or relaxed through the concentrated polymer solution, it closely followed the path of the bead, allowing for various conformations to be drawn with the test chain (Fig. 2). This tube-like motion is strikingly different from the motion of a polymer chain in a viscous Newtonian fluid. In a Newtonian fluid [25 centipoise (cP)], the chain moved in a direction perpendicular to its contour (Fig. 3A), even on the most rapid time scales investigated (1/30 s).

In our experiment, a primary concern was to understand the disturbance created by the trapped bead as it moved through a polymer solution. We were concerned that a path created in the entangled polymers would define a tube that was independent of the reptation model. Furthermore, if the tube collapsed back to molecular dimensions, there might still be a residual "weakness" in the entanglements that could survive for a long time. We conducted three experiments to investigate these two possibilities.

We measured the relaxation time for the

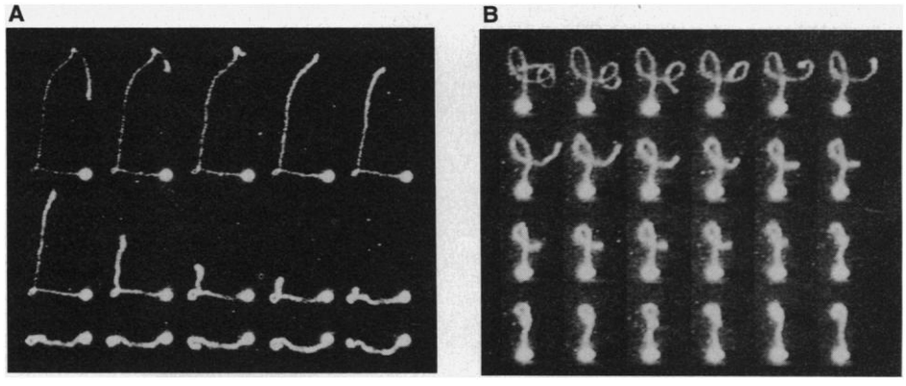

Fig. 2. (**A**) A series of tiled images showing the tube-like motion of a relaxing DNA molecule in a concentrated (12 molecules per cubic micrometer) polymer solution. The sequence starts when the bead was stopped, and the times are (row 1) 0, 2.3, 4.7, 7.0, and 9.3 s; (row 2) 11.6, 24.6, 37.7, 50.7, and 63.7 s; (row 3) 76.7, 89.7, 103, 115, and 128 s. The DNA was about 80 μm long, and the image of the 1-μm bead is 1.5 times its true size because of blooming in fluorescence. Topological constraints imposed by the background polymers persisted in excess of 120 s, as shown by the persistence of the small loop of DNA near the bead. The images in the first row show an increase in fluorescent intensity of the chain near the relaxing end, implying an increase in monomer or excess chain segment density, which slowly diffused, relieving tension in the chain, as shown in the subsequent images. As seen in the first three images, the tight loop at the top of the image showed a sharp increase in intensity at the loop and hindered this diffusion. In the bottom two rows, the middle section of the tube between the loop and the bead began to sag downward and developed small wiggles as excess length moved into it. This movement was most likely the result of constraint release caused by the reptation of surrounding chains in and out of the way of the chain. The more contorted section of the tube forming the loop hardly drifted at all. (**B**) A series of tiled images showing relaxation along a contorted path drawn with the optical tweezers by manipulation of the bead. Each image is separated by 1.5 s and the concentration of the polymer solution is 7 molecules per cubic micrometer.

background chains to interact with the test chain after the passage of the bead by comparing the relaxation of a linearly stretched-out test chain in the polymer solution to that in the solvent alone (buffer solution with a viscosity of ~0.9 cP). If the movement of the bead carrying the test chain formed a hole of pure solvent in the network of background chains, the test chain would be free of other entangling polymers, and one would expect the test chain to relax as if it were in pure solvent. The relaxation of the test chain stretched at 80 μm/s in the polymer solution became much slower than the relaxation in pure solvent in less than 1 s (*12*) (Fig. 4). The relaxation data were analyzed for a spectrum of decaying exponentials with an inverse Laplace transformation (*22*), which yielded peaks at a time constant of about 0.6 s in the pure solvent and 0.7 and 14 s in the concentrated polymer solution. After about 1 s, the background chains have become close enough to strongly interact with the test chain. Furthermore, the surrounding chains are about one-fifth the length of the longest test chain and, within the repation theory, should reptate 125 times faster and rapidly relieve any induced stress in the background polymers.

We made another estimate of the background polymer relaxation by stretching out the test chain linearly by moving the bead at constant velocity (10 μm/s) and then suddenly reversing the direction of travel so that the bead went back along its original path. After the change of direction, the trailing polymer chain was pulled back on itself by the bead. For a brief time, the section of chain following the bead was dragged along with the bead, but after about 1 s, the chain caught on an entanglement and became anchored at a particular point, around which it was pulled like a rope on a pulley. This experiment showed that the test chain was entangled with the background chains and the entanglement withstood the elastic forces of the stretched DNA. Thus, any path weakened by the passage of a bead through the polymer solution recovered in about 1 s.

Finally, we directly investigated the disturbance of the moving bead on the background chains by observing a fluorescently labeled chain entangled with other unlabeled background chains while rapidly moving a bead back and forth across the labeled molecule. Very little deformation of the entangled chain was observed, suggesting that the entangled chains are elastically deformed by the bead and relax very quickly without disentangling. Rarely, this test chain would elastically deform up to about 2 μm but would elastically retract back to its original conformation in less than 1 s.

To test for tube-like motion of the test chain on longer time scales, we drew small loops with the test chain that encircled a bundle of background chains using our joystick-controlled optical tweezers. Encircled chains imposed a topological constraint on the test chain, which could easily be visualized. The topological constraint of such a small loop persisted for at least 120 s (Fig. 2A). We were unable to observe the topological constraint at longer times because the test chain, relaxing inside the tube, went around the loop (*23*). We have shown that a stretched polymer relaxes to its equilibrium state in a tube defined by a configuration created with optical tweezers and that the tube lasts for times in excess of 120 s. Thus, the tube constraints in a concentrated polymer solution exist and are stable for long times. Tube-like motion is the dominant relaxation mechanism for an extended polymer, and the tube is robust against the elastic, entropic forces of an extended polymer.

Whereas the constraints of a small loop can stay fixed for very long times, straight sections of the tube may drift and fluctuate slightly. In the bottom two rows of Fig. 2A, one sees that at about 1 min, the middle section of the tube between the loop and the bead began to sag downward and develop small wiggles as excess length moved into the region. This was most likely the result of constraint release as surrounding chains reptated in and out of the way of the linear section of the chain. Constraint release near the more contorted section of the chain forming the loop, which hardly drifted at all, was evidently much slower.

Evidence for excess chain segment diffusion is also seen in Fig. 2A. The chain segment or monomer density can be inferred by the fluorescent intensity along the chain. The first row of images shows the sharp increase in the fluorescent intensity of the chain near the relaxing end without a corresponding increase in intensity of the chain close to the bead. These excess chain segments only slowly moved through the entanglements along the test chain. At 9.3 s after the bead stopped, in the last image in the first row, the last half of the chain is significantly brighter than the half closer to the bead. After 24 s, excess chain segment density has diffused along the full length of the chain, as evidenced by the increased fluorescent intensity along the whole length of the chain. This diffusion was driven by the tension within the chain and slowed by entanglements and contorted chain conformations. These results may support the idea of hindered defect diffusion (*24*). We also

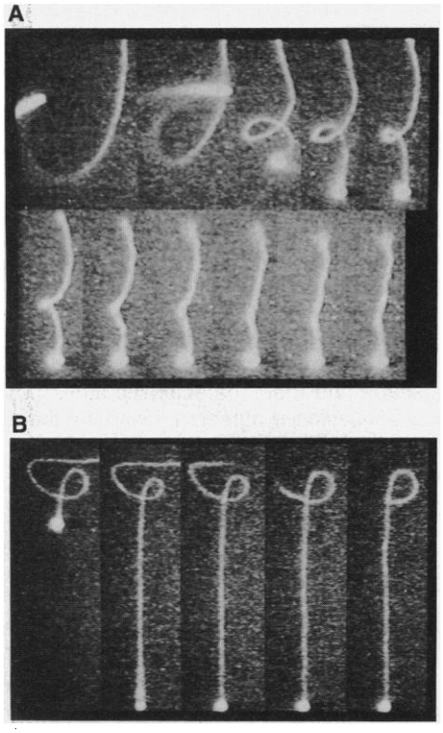

Fig. 3. (**A**) A series of tiled images showing that a loop formed in viscous (25-cP) Newtonian fluid rapidly disappeared as the DNA chain moved transverse to its contour. The times for the images are 0, 0.5, 1.7, 2.1, 2.9, 3.6, 4.4, 5.1, 5.9, 6.6, and 7.4 s. The solution was 55% (w/w) sucrose in an aqueous solution containing 5 mM NaCl, 1 mM tris-HCl (pH 8), 0.01% Tween-20, and 0.5 mM EDTA. (**B**) A tiled series of images showing tube deformation and stress recovery in a concentrated polymer solution. As the bead was rapidly moved away from the loop, tension in the chain increased, applying a stress that decreased the diameter of the loop. After the bead stopped, the loop recovered to its original size. The times for the images are 0, 1.3, 1.6, 2.3, and 3.0 s.

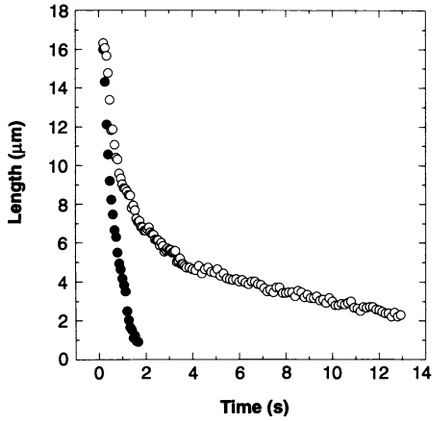

Fig. 4. Comparison of the relaxation of a 17-μm molecule linearly stretched to full extension at 80 μm/s in (○) a concentrated polymer solution of 12 molecules per cubic micrometer and in (●) pure solvent. The relaxation in the polymer solution became much slower than that in the pure solvent in a time of less than 1 s, indicating that background chains were strongly interacting with relaxing polymer in less than 1 s.

saw a ball of excess chain segments at the relaxing end until about 100 s (25).

Tube deformation and microscopic elasticity were also observed (Fig. 3B). After the loop was drawn, the bead was rapidly moved away from the loop, pulling the chain taught. This increased tension in the chain squeezed the loop down, deforming the original tube with an applied stress. The entangled polymers that form the constraint were deformed until they balanced the applied stress. After the bead was stopped, the stress applied by the loop decreased as excess chain segments diffused in from the relaxing free end and relieved the tension. With this reduction in stress, the loop grew back to its initial size. In contrast, loops formed in Newtonian fluids always decreased in time. Thus, we have shown the deformation of a tube with an applied stress and its subsequent recovery when the stress is relieved.

The experimental techniques presented in this paper allow for direct observation and controlled deformation of single DNA molecules. Using optical tweezers, one can go beyond passive observations of the Brownian dynamics of polymers by driving the dynamics with forces and stresses applied on the microscopic level of single chains. Quantitative measurements of the excess chain segment diffusion and tube deformation are examples of studies that are now possible. These techniques should allow detailed investigations of the microscopic origin of viscoelastic behavior and other collective effects displayed by solutions of entangled polymers.

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25. Although this is not visible in the photographic images, this local increase in intensity at the relaxing end was visible in the original video images.

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Relaxation of a Single DNA Molecule Observed by Optical Microscopy

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Single molecules of DNA, visualized in video fluorescence microscopy, were stretched to full extension in a flow, and their relaxation was measured when the flow stopped. The molecules, attached by one end to a 1-micrometer bead, were manipulated in an aqueous solution with optical tweezers. Inverse Laplace transformations of the relaxation data yielded spectra of decaying exponentials with distinct peaks, and the longest time component (τ) increased with length (L) as $\tau \sim L^{1.66 \pm 0.10}$. A rescaling analysis showed that most of the relaxation curves had a universal shape and their characteristic times (λ_t) increased as $\lambda_t \sim L^{1.65 \pm 0.13}$. These results are in qualitative agreement with the theoretical prediction of dynamical scaling.

An understanding of the static and dynamic properties of a single isolated chain forms the foundation of polymer physics (*1–3*). One can then ask questions about the behavior of dilute solutions and eventually consider more concentrated solutions, melts, and gels in which interactions between chains become important. The theoretical approach has involved many techniques: thermodynamic analysis, field theory, scaling, renormalization group theory, and computer simulation (*1–3*).

Many of the observable static properties of polymers in dilute solutions are well described by scaling relations. If A is an observable quantity, then $A \sim M^{\nu} \sim L^{\nu}$, where M and L are the molecular weight and length of the polymer and ν is the scaling exponent. The value of ν is independent of the local molecular structure of the polymer but does depend on temperature and monomer-solvent interactions (*2*). De Gennes (*4*) proposed that these scaling laws can be generalized to dynamical properties such as relaxation and elongation rates, but the experimental verification of this idea has been on less firm ground.

Measurements of rheology, light scattering, and birefringence of bulk samples have been used to study the dynamics of polymer chains (*5–7*). For example, Keller *et al.* (*5*) used birefringence measurements to determine the bulk orientational order in regions of dilute polymer solutions. A sharp increase in the birefringence is observed in an extensional flow at a critical strain rate $d\epsilon_c/dt$, and a relaxation time τ was extracted by assuming that $(d\epsilon_c/dt)\,\tau \approx 1$. In these experiments, it was found that $\tau \sim \eta L^{1.5}/kT$, where η is the solvent viscosity, k is the Boltzmann constant, T is absolute temper-

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