# Dynamics of Conformational Transitions in Polymers

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Polymeric systems exhibit an extraordinarily broad range of relaxation times. Well known are the unusual viscoelastic properties, evident to the casual observer, associated with relaxation times of order seconds or greater. Microscopically, disentanglement of whole macromolecules is required for these relaxations, a process peculiar to polymers. Rapid relaxation processes also occur in these molecules on a time scale similar to that for small molecules, typically nanoseconds in solutions. Thus, a dipole moment rigidly attached to a polymeric backbone lags somewhat in response to a microwave field, causing dielectric loss. These rapid motions are the subject of the present article. Although they take place on the same time scale as small-molecule rearrangements, and involve essentially a limited number of atoms, the dynamics of these motions are strongly influenced by the fact that they are occurring in a macromolecule. An excellent earlier review of the subject was given by Stockmayer (1).

Microscopically, a polymer backbone, typically a chain of carbon atoms, has a geometric structure as illustrated schematically in the inset to Fig. 1. The state of the backbone is specified by giving the length of each bond, the bond (valence) angle formed at each atom, and the rotational (torsional, dihedral) angle of each bond. (The rotational angle of a bond i is defined as the angle between two planes, the first defined by bonds i - 1 and i, the second by bonds i and i + 1. Alternatively, regard planar zigzag, that is, trans, as 0°. Point the right thumb up bond *i* in the sense from bond i - 1 to i + 1, the order of numbering being arbitrary but consistent along the chain. Now determine the angle bond i + 1must be rotated about the thumb in the direction of the curled fingers to bring it from the trans to the given position.) The bond lengths and angles vary little, being held in a single, rather narrow potential well. However, bond rotational states 9 NOVEMBER 1984

can vary widely since they are governed by a potential of the form of Fig. 1 (which might be appropriate for polyethylene). This potential has three stable positions (conformations). The central one is termed trans (t). Displaced by about  $\pm 120^{\circ}$  are the gauche plus (g<sup>+</sup>) and gauche minus (g<sup>-</sup>) conformational states (see Fig. 1 inset). Separating the conformational states are barriers with heights several times the thermal energy,  $k_BT$ , so that residence in a state can be adequatefluorescent tags (such as anthracene) are incorporated in, or rigidly attached to, the backbone. The groups are excited by a short pulse of polarized radiation, as from a synchrotron. If the tags remain stationary the fluorescence will be polarized. However, reorientation of the tags, a reflection of rotations in the backbone, leads to depolarization of the fluorescence. Other techniques such as light and neutron scattering, acoustic attenuation, excimer fluorescence, and electron spin resonance (ESR) have also been used to study rapid relaxations in macromolecules.

I shall return to a discussion of experiments later, but let me now point out a few of the features which they have revealed. Rates of the fast relaxations in solution are independent of molecular weight and inversely proportional to solvent viscosity, except for very low viscosity solvents. The temperature dependence is partly due to the viscosity factor. The remainder is Arrhenius-like with an activation energy about equal to the barrier height between trans and gauche states, as in small molecules.

Summary. Conformational transitions in polymers involve large angle rotations about bonds. The process must proceed in a way that does not require gross movements of the macromolecules. The dynamics have been investigated by computer simulation and kinetic theory. The rate-determining step in the transition is found to occur in a mode which is kept local by distortion of nearby parts of the molecule. One especially important type of cooperativity, crank-like counterrotation of second-neighbor bonds, is identified. Experiments which provide evidence about the dynamics of conformational transitions are discussed.

ly defined, its lifetime there being much longer than vibration periods or relaxation times in the wells. The rotational isomeric state of the chain (also termed the chain's conformation) is given by the sequence of the bonds' conformations. The major contributor to the rapid relaxations is conformational transitions over the energy barriers separating rotational states.

There are a number of means of determining rapid relaxation rates in polymers (2) besides dielectric relaxation, which was mentioned above. Nuclear magnetic resonance (NMR), which is particularly sensitive to the orientation of carbonhydrogen bonds, is a useful tool. Relaxation times  $T_1$  as a function of magnetic field (the frequency variable being Larmor frequency) can be calculated if one knows the time correlation function of orientation (3). Going in the other direction is difficult. However, such time correlation functions have recently been extracted from fluorescence depolarization measurements (4). Consider that a few

Yet, considering the physics of the situation, there must be important differences between conformational transitions in macromolecules and small molecules. Referring to the model depicted in Fig. 1, consider the consequences of some bond, say the middle one, being rotated, with all other bond states being held fixed. The attached material, only a small part of which is shown in the figure, would undergo a large, swinging motion. If this motion were to take place in a solvent or melt there would be an enormous frictional resistance. Such a motion would be exceedingly slow, with a rate dependent on molecular weight. This cannot be the way in which the transition proceeds, except in a small molecule. How do conformational transitions occur in polymers? We have obtained an insight into the process by means of computer simulations (5, 6) and by application of a kinetic theory (7, 8).

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### **Computer Simulations**

Brownian motion simulations have been performed on a polymer model with 200 bonds and periodic boundary conditions extending the molecule indefinitely. Quadratic potential terms keep the bond lengths close to 0.153 nm and the bond angles close to 0.153 nm and the bond angles close to tetrahedral. The rotational potential of Fig. 1 defines three conformational states per bond between which there are occasional transformations. One could refine the potential to include even more detailed aspects of real polymers, but these are not essential for answering the question posed earlier of how the transitions proceed.

The computer simulates the polymer's Brownian motion in a frictional medium by solving simultaneous Langevin equations for the 600 degrees of freedom:

$$m \frac{d^2 x_i}{dt^2} = -\frac{\partial V}{\partial x_i} - \zeta \frac{d x_i}{dt} + A_i(t) \quad (1)$$

The acceleration of each carbon center is equal to the sum of three forces. The first is the force associated with the potential energy V. The second is a frictional force proportional to a friction constant  $\zeta$  and the velocity. Finally, there is white-noise random force, arising from random impulses of the medium, with variance proportional to the temperature, so as to maintain the mean kinetic energy constant. Since this last term is stochastic there is no definite trajectory; but by an appropriate numerical technique (9) a representative trajectory, statistically accurate over long times, can be generated.

Looking at the trajectory for one bond's rotational angle, one sees long periods of motion largely near the bottom of one of the conformational wells. and occasionally a transition to a different well. These transitions are the events of interest. By statistical analysis of the first passage times from one well bottom to another, transition rates have been determined. Varying the temperature, while holding the friction constant fixed, one determines that the activation energy for the transitions is approximately equal to one barrier height between the trans and a gauche state, as the experiments had indicated. This would not be surprising except for one other finding: the transitions frequently occur in pairs. It is this observation of cooperativity which we shall examine in greater detail, because it is a manifestation of the special dynamical aspect of conformational transitions in large chain molecules.

The statistical method used to extract transition rates, hazard analysis, enabled us to observe the time dependence of reaction rates. We discovered that im-



Fig. 1. Bond rotational potential energy used in simulations and calculations. The cis barrier at 180° has been made artificially high to eliminate transitions across this barrier. If the bonds of the molecular model inset are labeled from left to right, then the black bonds 2, 4, and 6 are  $g^+$ ,  $g^-$ ,  $g^+$ , respectively, and bonds 3 and 5 are t.

mediately following the transition of one bond there was a strong increase in the transition rate of its second-neighbor bonds, lasting for a short period of time. Here the special virtue of computer simulations as a research tool emerged. In the plethora of data that a trajectory presents is the information needed to look at processes in ways beyond the reach of experiments. A tabulation was made of every pair of transitions of second-neighbor bonds that occurred within that short correlation period. These could be broken down into types according to (i) the initial and final states of the two transforming bonds and (ii) the unchanged state of the intermediate bond. Examination of the tabulation revealed that two types of transitions overwhelmingly dominated the list (occurring ten or more times as often as the other types). accounting for almost all the cooperativity. They are, as illustrated in Fig. 2,

$$\cdots g^{\pm} tt \cdots \rightleftharpoons \cdots ttg^{\pm} \cdots \qquad (2)$$

 $\cdots ttt \cdots \rightleftharpoons \cdots g^{\pm} tg^{\mp} \cdots \qquad (3)$ 

The significance of this observation emerges upon examination (7) of a geometric property of these two transitions, not shared by other second-neighbor pair transitions. In both cases the first two and last two bonds have translated relative to each other. In other words, the final state of every bond, except the central one, is parallel to its initial state. This is also true of all the bonds of the long tails (not shown) attached to each end of the illustrated segment. For all other pairs of transitions of second neighbors (except for strongly disallowed transitions in which the high cis barrier at 180° would have to be crossed) one finds that the tails rotate, as is the case for a single bond's transition. Thus,

the frequently observed pair transitions of Eqs. 2 and 3 greatly reduce the motion of the tails and the frictional resistance which the tails present to the transition.

The parallel displacement of the tails is related to the fact that, as a result of bond 3 of the chains in Fig. 2 being trans, the (black) transforming bonds, 2 and 4, are parallel. The transitions represented by Eqs. 2 and 3 involve a crank-like counterrotation of bonds 2 and 4; that is, one rotates by  $+120^{\circ}$  while the other rotates  $-120^{\circ}$ . The resultant is no rotation of the attached tails.

Three issues must still be addressed. (i) Even though the motion of the long tails has apparently been reduced it has not been eliminated. There would still be an enormous, molecular weight-dependent frictional resistance should the tails be forced to translate rigidly. (ii) Individual transitions and pair transitions, seemingly involving tail rotation, are observed. (iii) If two transitions frequently occur cooperatively, why is the activation energy about one barrier height? Further light is cast on the physics of conformational transitions by performing a kinetic theory analysis of the problem.

## **Kinetic Theory**

Let us consider the application of kinetic theory (7, 8) to a single bondtransition. One cannot achieve a satisfactory description in terms of the single variable  $\phi$  characterizing that bond's rotational state. Rather one must introduce all the degrees of freedom of the chain into the analysis. Figure 3 schematically depicts the potential as a function of all the coordinates. Each conformation corresponds to a multidimensional energy well, these wells being separated by generalized saddle passes.

A many-variable kinetic theory has two important elements. First, one must identify a reaction coordinate. This is the central path followed by the reaction. The true paths may be regarded as fluctuations about the reaction coordinate. Second, one applies an appropriate onedimensional theory along the reaction coordinate. The freedom of motion orthogonal to the reaction path enters as an entropy, changing the energy of activation to a free energy of activation  $F^{\dagger}$ . The rate of transition is composed of two factors. There is the Arrhenius factor  $\exp(-F^{\dagger}/k_BT)$ , related to the probability of being near the saddle point. This is multiplied by a factor which reflects how fast the saddle is traversed. The essential step for completing a transition is to get from a free energy of order  $k_B T$  below



Fig. 2. Molecular models illustrating the transitions of Eqs. 2 and 3.

the barrier height on one side to a similar energy level on the other side. From below such an energy spontaneous fluctuations back over the barrier become unlikely. In reaction rate theory (low friction) the rate of passage over the barrier is the mean positive velocity. For high friction, the present case, the flow over the barrier is diffusional with many changes of direction along the way. As Kramers has shown (10), a quantitative analysis of the dynamics near the barrier is possible because in this region the potential may be regarded as quadratic in the position variables. One way to proceed is to solve the Smoluchowski equation. In the multidimensional case, solution involves determination of a separable coordinate system. Of the various normal modes just one is unstable, and this can be identified as the reaction coordinate. When all friction constants are equal the reaction coordinate is along the path of steepest descent from the saddle point.

One finds that the reaction coordinate is always a localized mode; that is, as rotation of the transforming bond across its barrier occurs, the amount that remote carbon atoms move falls off exponentially with distance along the chain. This is as it must be to avoid having a large frictional resistance, which grows with increasing chain size. However, in order to localize the mode the central bond's transition must be accompanied by distortion of neighboring degrees of freedom. Because the system is attempting to move optimally down in energy from the saddle point it distorts mostly other bond rotations, these being the softest degrees of freedom. As noted above, if a first-neighbor bond to the transforming bond is trans, counterrotation of the second-neighbor bond goes a long way toward localizing the motion. A large-scale rotation of the tail is transformed into a much smaller translational motion. Other bond rotations, as well as a small but important (11) amount of bond-angle bending and bond stretching, can be used to complete the localization. These features are quite evident in calculated reaction coordinates (8).

The theory does not say anything about what happens to the distortion after the rate-determining part of the transition is completed, because the theory applies only in the neighborhood of the saddle point. The distortion probably spreads out among many degrees of freedom to lower the associated energy. Other transitions may also occur in such a way as to relieve part of the distortion. In particular, the simulations indicate that frequently before the distortion has had much opportunity to spread, the counterrotation of the second-neighbor bond is brought all the way to the point of its own transition, as the first transforming bond continues its descent to the bottom of the new conformational well. The fact that the activation energy is one barrier height indicates that the two processes must be taking place in a coherent, sequential fashion.

Sometimes the second bond is not brought over its own barrier but descends back to the former conformation. This accounts for the fact that both cooperative pair and individual transitions are observed. An effort is being made to produce a theory of the branching ratio.

The kinetic theory predicts transition rates in rather good accord with simulations (5, 8), but we shall not discuss this here. Quantitative prediction of the rates for real molecules would require much greater knowledge of potentials and friction constants and more elaborate models.

#### **Time Correlation Functions**

The discussion above has focused on the mechanism of conformational transitions. Unfortunately, experiments do not examine such matters directly. Frequently experiments measure a time correlation function for the orientation of some direction (a dipole, a C-H bond, a transition moment, and so on). Thus, one is motivated to investigate how the special aspects of the conformational dynamics may be reflected in experiments. First we shall consider the implications of the counterrotational cooperative pair transitions for the functional form of time correlation functions.

A paradigm, which has been exactly analyzed by Hall and Helfand (12), is the



Schematic Cartesian coordinates

Fig. 3. Schematic representation of the potential energy as a function of the molecules' atomic Cartesian coordinates. [Reprinted by permission of *Journal of Chemical Physics*]

following. Consider a chain of elements, each of which can exist in one of two states (rather than the three states of many polymer bonds). The state of an element will be labeled  $\mu_i = \pm 1$  (denoted simply + or - below). Individual transitions of the form  $+ \rightleftharpoons -$  can occur at a rate  $\lambda_0$ . Also, a pair of neighbors can undergo a transition of a compensatory nature,  $+ - \rightleftharpoons - +$ , at a rate  $\lambda_1$ . The time correlation function for the state of a bond can be shown to be given by

$$\langle \mu_i(t)\mu_i(0)\rangle = \exp[-2(\lambda_0 + \lambda_1)t]I_0(2\lambda_1 t)$$
(4)

where  $I_0$  is a modified Bessel function. This result can also be derived in a heuristic way (12) by saying that the information about the initial state of element *i* diffuses along the chain by virtue of the counterrotational pair processes. A correlation function with two  $I_0$  terms approximately describes the three-state polymer chain (6, 12). The function on the right of Eq. 4 has been used with considerable success to fit data on fluorescence depolarization by Viovy et al. (4), NMR relaxation by Connolly et al. (3), and correlation functions determined in computer simulations by Weber and Helfand (6).

#### **Other Experiments**

The picture described above helps in the qualitative interpretation of a number of other observations. Activation energies are generally found to be about equal to one barrier height (after removing the temperature dependence of the friction constant). Morawetz and coworkers (13) have found that the rates for transitions involving reorientation have the same temperature dependence whether the group is in a small molecule or in the backbone of a macromolecule. A comparison has also been made of the relaxation rates of labels attached to polymers in the chain, in side groups, and at the chain ends (14-16). The picture in this case is less clear, the indication being that activation energies may be somewhat lower for chain end transitions.

Liang et al. (17) have looked at conformational transition rates in polymer chains adsorbed on surfaces. The molecules contain rigidly attached nitroxide labels, so the ESR line shape can be used to determine backbone rotation rates. When the solvent is removed the transitions become slow because the molecules completely adsorb. When solvent is added the molecules partially desorb in the sense that loops of several monomer units come off the surface between adsorbed units. One then finds that part of the ESR line shape is close to that of molecules in solution. This indicates that the conformational transitions can take place at nearly the same rate in short sections of chain with fixed, rather than free, boundary conditions. Frictional resistance may be nearly as effective as adsorptive pinning. In both cases the rate-determining step proceeds via a localized mode.

Jelinski et al. (18) have made interesting observations on polybutylene terephthalate



by using solid-state NMR techniques. The ring is relatively immobile, forcing sequence to proceed in a localized fashion. Call the carbons in this sequence C1, C2, C3, and C4. By selective deuteration of C2 and C3 they were able to show that the C2-H and C3-H directions relax, in the sense of reorienting, faster than the C1-H and C4-H directions. This is in accord with a picture of the major conformational transition being a counterrotational pair of transitions of the carbon bonds C1-C2 and C3-C4 (see Fig. 2). As mentioned earlier, in such a transition the material attached to C1 and C4 translates, hence does not contribute to NMR relaxation. The bonds between H's and C3 and C4 do reorient.

Counterrotational crank-like pairs of transitions similar to those described above have been proposed as pathways for transitions and relaxations in various molecules of biological interest such as DNA (19), polypeptides (20), and lipid bilayers (21).

A few years ago, when observational techniques were less acute and theoretical guidelines vague, it seemed sufficient to interpret data on relaxation controlled by conformational transitions in terms of a single, exponential process. Now we see that this leads to a set of relaxation rates and activation energies with contradictions, especially when measured by different techniques (15). Viewed positively, we can hope that in resolving

these inconsistencies (at least those that are real) we may gain a better understanding of the dynamics.

#### **References and Notes**

- W. H. Stockmayer, Pure Appl. Chem. Suppl. Macromol. Chem. 8, 379 (1973).
   R. A. Pethrick and R. W. Richards, Eds., Static
- and Dynamic Properties of the Polymeric Solid State (Reidel, Dordrecht, Netherlands, 1982).
- J. J. Connolly, E. Gordon, A. A. Jones, *Macromolecules* 17, 722 (1984).
   J. L. Viovy, L. Monnerie, R. Brochon, *ibid.*, in press; J. L. Viovy, L. Monnerie, J. C. Morola, *ibid.*
- *ibid.*, in press. E. Helfand, Z. R. Wasserman, T. A. Weber, *ibid.* 13, 526 (1980). 5. 6.
- T. A. Weber and E. Helfand, J. Phys. Chem. 87, 2881 (1983). 7
- 2001 (1983).
  E. Helfand, J. Chem. Phys. 54, 4651 (1971).
  J. Skolnick and E. Helfand, *ibid.* 72, 5489 (1980);
  E. Helfand and J. Skolnick, *ibid.* 77, 3275 (1982). 8.
- E. Helfand, Bell Syst. Tech. J. 58, 2289 (1979); H. S. Greenside and E. Helfand, *ibid.* 60, 1927 9
- 11.
- H. A. Kramers, *Physica* 7, 284 (1940).
   E. Helfand, Z. R. Wasserman, T. A. Weber, J. Skolnick, J. H. Runnels, *J. Chem. Phys.* 75, 4441 (1981).
- C. K. Hall and E. Helfand, ibid. 77, 3275 (1982).
- H. Morawetz, *Science* **203**, 405 (1979).
   A. Morawetz, *Science* **203**, 405 (1979).
   A. T. Bullock, G. G. Cameron, N. K. Reddy, *J. Chem. Soc. Faraday Trans. 1* **74**, 727 (1978).
   C. Friedrich, R. Lauprêtre, C. Noël, L. Monnerie, *Macromolecules* **14**, 1119 (1981).
   C. S. P. Sung, I. R. Gould, N. J. Turro, *ibid.*, in press

- Liang, P. N. Dickenson, W. G. Miller, in Polymer Characterization by ESR and NMR, A. E. Woodward and F. A. Bovey, Eds. (ACS Symposium Series 142, American Chemical So-ciety, Washington, D.C., 1980).
   L. W. Jelinski, J. J. Dumais, A. K. Engel, Macromolecules 16, 492 (1983).
   W. Olcon, in Biomedical Stateodynamics.
- 19.
- Macromolecules 16, 492 (1983).
  W. K. Olson, in Biomolecular Stereodynamics, R. H. Sarma, Ed. (Adenine, Guilderland, N.Y., 1981), vol. 1, pp. 327-343.
  M. R. Pear et al., Biopolymers 20, 629 (1981).
  T. H. Huang, R. P. Skarjune, R. J. Wittebort, R. G. Griffin, E. Oldfield, J. Am. Chem. Soc. 102, 7277 (1990) 7377 (1980
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