

11. COCHRAN M.A., DUNBAR J.H., NORTH A.M. & PETHRICK R.A. (1974) *J. Chem. Soc. Faraday Trans. II* **70**, 215, and references quoted therein.
12. CONNOR T.M. & HARTLAND A. (1968) *Polymer* **9**, 591, and references quoted therein.
13. STOCKMAYER W.H. (1967) *Pure appl. Chem.* **15**, 539; DAVIS J.E. (1960) Ph.D. thesis, MIT; NORTH A.M. & PHILLIPS P.J. (1968) *Trans. Faraday Soc.* **64**, 3235.
14. COCHRAN M.A., JONES P.B., NORTH A.M. & PETHRICK R.A. (1972) *J. Chem. Soc. Faraday Trans. II* **68**, 1719.
15. NORTH A.M., RHONEY I. & PETHRICK R.A. (1974) *J. Chem. Soc. Faraday Trans. II* **70**, 223.
16. NORTH A.M. & SOUTAR I. (1972) *J. Chem. Soc. Faraday Trans. II* **68**, 1101.
17. FERRY J.D. (1973) *Accounts Chem. Res.* **6**, 60, and references quoted therein.
18. LAMB J. & MATHESON A.J. (1964) *Proc. Roy. Soc. A* **281**, 207.
19. SHEN M.C., HALL W.F. & WAMES R.E. (1968) *J. Macromolec. Sci.* **C2**, 183.
20. MOORE R.S., McSKIMIN H.J., GNIKIEWSKI C. & ANDREATCH P. (1969) *J. Chem. Phys.* **50**, 466, 5088.
21. BATES T.W., IVIN K.J. & WILLIAMS G. (1967) *Trans. Faraday Soc.* **63**, 1894; DAVIS M., WILLIAMS G. & LOVELUCK G.D. (1960) *Z. Electrochem.* **64**, 575.
22. STOCKMAYER W.H. (1973) *Macromolecular Chemistry*, Vol. 8, p. 379. Butterworth, London.
23. JENNINGS B.R. (1969) *Br. Polymer J.* **1**, 70.
24. ALLEN G., HIGGINS J.S. & WRIGHT C.J. (1974) *J. Chem. Soc. Faraday Trans.* **70**, 348.

Bibliography

Viscoelastic relaxation

- FERRY J.D. (1970) *Viscoelastic Properties of Polymer Solutions*. Wiley, New York.
 YAMAKAWA, H. (1971) *Modern Theory of Polymer Solutions*. Harper & Row, New York. This is an excellent survey of the theoretical aspects of the static and dynamic properties of polymer chains in solution.
 BERRY G.C. & FOX T.G. (1968) *Advanc. Polym. Sci.* **5**, 261. This review deals with the dynamic behaviour of concentrated polymer solutions.
 FERRY J.D. (1973) *Accounts Chem. Res.* **6**, 60. A summary of the most recent aspects of viscoelastic behaviour of polymers in solution.

Dielectric relaxation

- BLOCK H. & NORTH A.M. (1970) *Advances in Molecular Relaxation Processes*, Vol. 1, p. 309. An extensive review of the relaxation behaviour of synthetic and bio-polymers in solution.
 NORTH A.M. (1972) *Chem. Soc. Rev.* **1**, 49.

Acoustic relaxation

- PETHRICK R.A. (1973) *Rev. Macromol. Chem.* **C9**, 91. A survey of the relaxational properties of polymers in solution.

Nuclear magnetic resonance

- SCHAEFER J. & NATUSCH D.F.S. (1972) *Macromolecules* **5**, 416.
 CONNOR T.M. (1969) *Br. Polymer J.* **1**, 116.
 ALLENBAND A. & HAILSTONE R.K. (1972) *J. Chem. Phys.* **56**, 3718.

Light scattering (dynamic)

- JENNINGS B.R. (1969) *Br. Polymer J.* **1**, 70, and papers quoted therein.

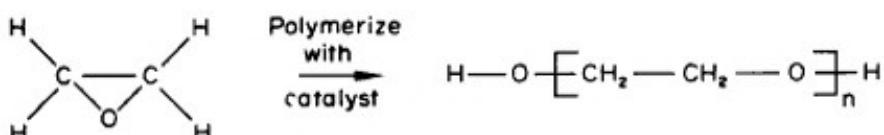
Molecular motion of polymers in solution

R. A. Pethrick

Certain aspects of the molecular motion found in polymers in solution are considered in detail. The correlation of the intrinsic flexibility of a polymer and its intramolecular potential surface are highlighted.

Introduction

The relative ease of manufacture of synthetic polymeric materials in the last 20 years has produced a technological revolution in the lubrication and textile industries. Polymers are long chain organic molecules usually pictured as strings of 'poppit' beads. The production of such materials involves the reaction of smaller molecular units (monomer) in such a way that bridging chemical bonds are formed between the sub-units.



The physical properties of the polymers formed are found to be sensitive to changes in the chemical composition of the original monomer used. In more recent years polymers have become commercially important and this has been amply demonstrated by the current public concern over the use of petroleum as a fuel rather than as a feed stock for the polymer industry. The appeal of polymeric materials to industry lies in their ease of fabrication into complex shapes and also the wide variety of physical properties which can be obtained from what are relatively simple chemical modifications of a basic structure.

The unique properties associated with synthetic and biological polymers arise from their spatial extension and relative degree of flexibility. In a rigid solid the polymer chains may be forced into a stable highly entangled structure which possesses a high Young's modulus and poor fracture properties. Changes in the flexibility and resistance to fracture in a solid may be achieved by in-

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creasing the mobility of the polymer chains and opening of the chain structure. Polymers are often cross-linked into a matrix structure which has greater high temperature stability and improved stress-strain characteristics. A non-cross linked structure of flexible chains will have a marked tendency to flow at high temperatures and be unable to recover having once been deformed beyond some limiting value. Rubber elasticity and flow are both associated with the ease of movement of the constituent chains, the former associated with changes in the degree of order and extension within particular areas of the solid, the latter to the relative movement of chains in a spaghetti-like structure. Studies of the physical properties of polymeric materials have revealed that many of their properties such as ductility and impact strength may in part be associated with the intrinsic flexibility possessed by the polymer chains. The apparent importance of an understanding of the factors which influence the flexibility of polymer chains has prompted a number of molecular physicists to attempt to quantify this property and correlate it with features associated with the basic chemical structure of the macromolecules. Flexibility or the ease of motion of one part of the chain relative to another—segmental motion—may be expected to be determined by similar factors to those influencing internal rotation in small molecules. Studies of small molecules have indicated the desirability of performing such investigations in the gas phase.¹ Such measurements are impossible for macromolecules and the alternative approach of studying the isolated chains in solution is usually adopted. In this situation polymer-polymer are replaced by polymer-solvent interactions which in turn are usually assumed to be of minor importance in determining the observed motions. In a solid the dynamic behaviour will be influenced by both intermolecular (chain entanglement, packing of the chains in crystalline regions or simply immobilization by strong intermolecular forces) and intramolecular (non-bonded closest neighbour and multipole interactions) effects. In solution the dominant interactions influencing chain flexibility may be expected to be of an intramolecular origin and studies of the dynamic behaviour enable correlation of the intrinsic chain flexibility with chemical structure.

Motion of a polymer molecule in solution

(a) *Whole molecule rotation and translation*

The simplest motions which a polymer may execute in solution are those of overall rotation and translation of the whole molecule. These processes are directly analogous to those observed in small rigid molecules and are influenced by changes in the moments of inertia and shape with molecular weight. Whole molecule rotation and translation are usually defined assuming the internal molecular geometry of the polymer remains constant during the period of observation. In certain rigid or highly regular polymers this approximation is

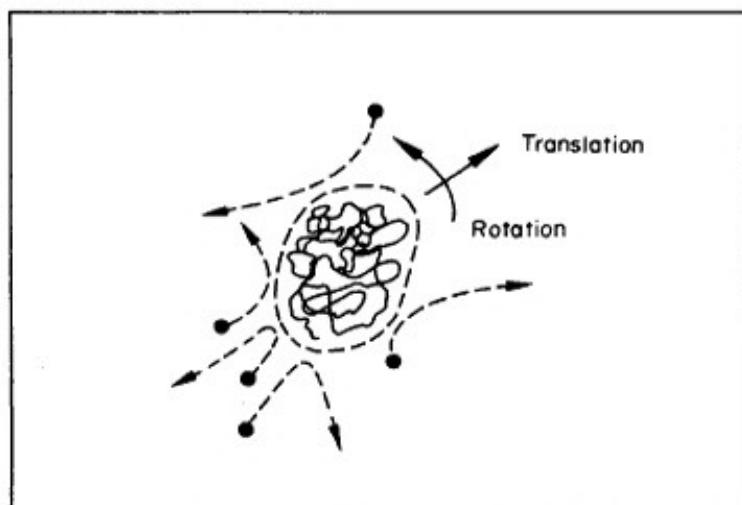
valid. However, in the large majority of polymers the internal motion of elements of the chain may occur during the time of whole molecule rotation or translation.

(b) *Segmental and normal mode motion of a polymer chain*

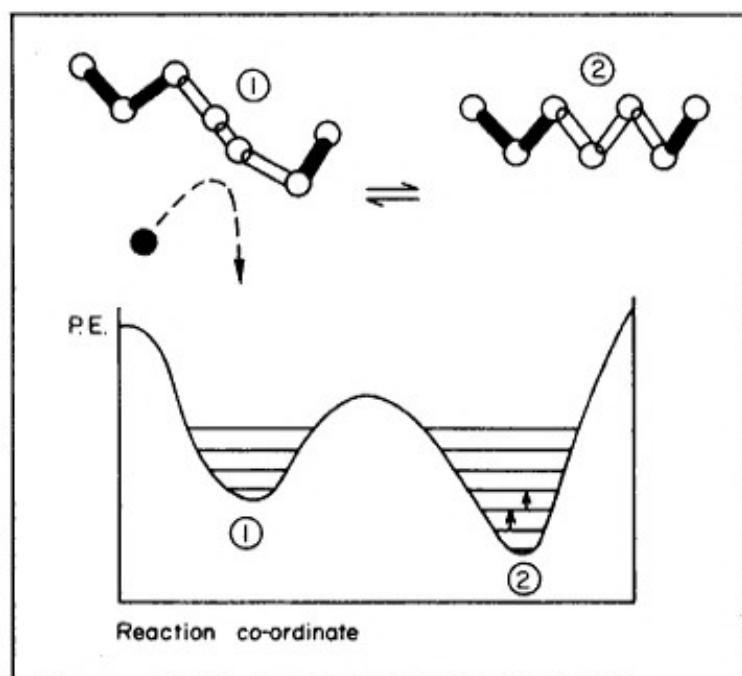
At equilibrium a polymer chain will experience a continuous bombardment from the surrounding solvent molecules. The collisions may be either elastic or inelastic. An elastic collision occurs when a solvent molecule collides with the polymer and is scattered with a possible change of momentum. The result of such collisions will be similar to those between molecules of the solvent and ultimately leads either to whole molecule rotation or translation of the polymer. In an elastic collision, momentum must be conserved during the period of the collision. Alternatively an inelastic collision is one in which momentum is not conserved and provides a mechanism for conversion of translational energy into internal vibrational energy of the solvent or polymer. The reverse process will also be possible and the combination of the forward and reverse inelastic processes is often referred to as vibrational to translational relaxation. In an inelastic collision conservation of energy is required. A vibrational analysis of the polymer reveals that small angle rotation or displacements of elements of the backbone, such as torsional oscillation, are associated with the lowest vibrational energy transitions. Inelastic collisions will tend to activate preferentially the lowest energy modes. Successive activation of torsional oscillations may ultimately lead to changes occurring in the conformations of the chain elements (Fig. 1). In general the more sterically crowded the conformation the higher its energy. Subsequent inelastic collisions will activate an energetically unstable conformation and enable the polymer to return to its original lowest energy state. The rate of internal rotation of elements of the backbone will be influenced by the magnitude of the intramolecular interactions and the efficiency of activation. The intramolecular interactions are usually of a non-bonded form and thus a function of the chemical structure of the polymer. A detailed study of the activation of a particular element of the backbone must also allow for accumulation of energy in sub units of the chain by vibrational energy transfer from neighbouring sites as well as by direct collisional activation. In general the higher the temperature the more energetic and hence efficient the collisions and subsequently the greater the probability that internal rotation will occur. The Brownian nature of the motion of the solvent molecules provides a random probability for the activation of any given element of the polymer backbone.

The random occurrence of inelastic collisions may be expected to lead to a complex pattern of displacements of the polymer chain. The overall motion of the chain may be described by a superposition of two forms of displacement: segmental and normal mode motion. The former is usually associated with the movement of a block of the chain relative to the main backbone (Fig. 1)

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Elastic collisions



Inelastic collisions

Fig. 1. Collision between solvent and polymer molecules. The dotted lines in the above diagrams indicate the trajectories followed by the solvent molecules during their collision with the polymer. The heavy arrows in the upper diagram indicate the directions of overall rotation and translation of the polymer. The lower diagram depicts a conformational change accompanying an inelastic collision between a solvent molecule and a section of the polymer chain. The arrows between energy levels for conformation (2) depict torsional transitions of the chain backbone.

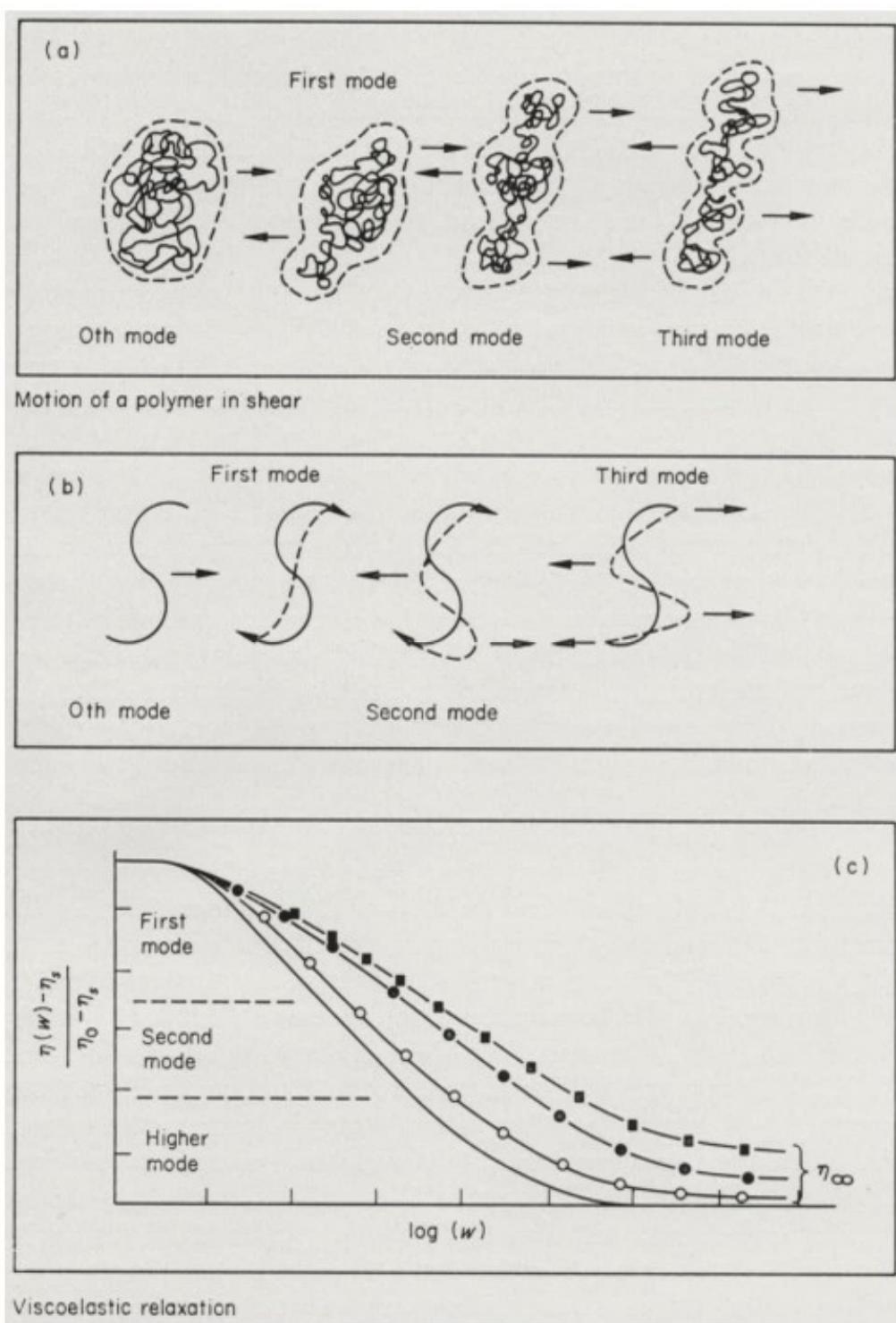


Fig. 2. The effects of shear on a polymer in solution. (a) Motion of a polymer molecule when subjected to an oscillating shear field. (b) Diagrammatic representation of the motion of an ideal flexible chain when in an oscillating shear field. (c) Viscoelastic relaxation of a polymer in solution. η_∞ the high frequency limiting value, η_0 the zero frequency and η_s the dynamic shear viscosity. Curves for the ideally flexible free draining coil (—), the ideally flexible non-free draining coil (\circ), partially flexible free draining coil (\bullet), partially flexible non-free draining coil (\blacksquare).

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change from structure (2) to (1). The only restriction placed on such a motion is that sufficient energy should be available from inelastic collisions for the intramolecular interactions restricting free rotation of the polymer backbone to be overcome. It is implicit in this definition of segmental motion that the relaxation process involves direct activation from the lowest energy state via a cascade mechanism which may lead to excitation of the other thermal vibrational states.

Normal mode behaviour may be considered as that part of the molecular displacement which may be described in terms of a phase coherent motion of the whole polymer chain (Fig. 2). The normal mode motion is in fact an eigenvalue solution of the stochastic perturbation of the flexible random chain and requires a phase coherence of the overall displacement in space and time of the macromolecule. Using this framework, segmental motion may be considered as the phase incoherent movements of the microscopic elements of the polymer backbone and usually is considered to involve a random jump of one stable conformation to another (Fig. 1). In high molecular weight polymers the distinction between segmental motion and the higher normal modes, whilst still being precise, may appear to become blurred since a suitable summation of a series of segmental motions may on average approximate closely to a normal mode displacement. This apparent confusion is implicit in the stochastic formulation but, as will be shown later, does not lead to any real contradiction in terminology.

The normal mode description of the polymer motion is most frequently encountered in the discussion of the displacement of a flexible polymer molecule under the influence of a shear gradient. The effects of establishing a shear gradient (Fig. 2) in a liquid will lead to the production of a regular distribution of momentum between the shearing boundaries. If this shear field is further required to oscillate then the direction of average momentum transfer will similarly oscillate. In a field at equilibrium the random collisions of solvent with the polymer will result in an averaging of the momentum transfer to zero. In a shear field the distribution will be biased in one direction and a net transfer of momentum will occur. The effect of a resultant in terms of the momentum transfer will lead to a greater probability of activation of a given conformation in one region than in another. This probability will be influenced by the magnitude and rate of change with time of the shear gradient. If the period of oscillation is low, the rates of activation and deactivation are close to their equilibrium values, little momentum is lost and the net effect is the overall translation of the polymer. This motion is often referred to as the zeroth normal mode (Fig. 2). At higher rates of oscillation, activated conformations are unable to return momentum to the solvent during the period of oscillation with the net result that a distortion of the polymer occurs and momentum is lost. Analysis of the complex pattern of conformations adopted by the polymer is possible in terms of the normal mode motion which by definition requires a

certain phase coherence of the overall distortion of the polymer. Since the degree of momentum transfer is reflected in the viscous drag which the polymer exercises on the solvent, the first normal mode plays a major role in determining the polymer viscosity increment. At very high frequencies of oscillation the change of direction of the momentum is so fast that it is unable to influence the polymer conformations and the observed viscosity of the solution approaches that of the solvent. The distortion of the polymer visualized at high frequencies leads to a picture which contains motions of chain blocks similar to those associated with segmental motion.

In recent years attention has been drawn to the fact that the addition of small amounts of polymer to fluids experiencing high shear fields suppresses the onset of turbulence. Analysis of the hydrodynamic equations describing the motion of a fluid under a shear gradient indicates that a value of the stress must exist at which the equations become unstable. Physically, small fluctuations in the density—eddies—build up in such a way that lamellar flow will no longer exist in the fluid. The limiting condition is a function of the form of the shear dependence of the viscosity coefficient, the effectiveness of the heat transfer between specific volume elements in the fluid and the non-linear terms in the hydrodynamic tensors. The effects of the polymer in this situation may be envisaged as averaging out the density fluctuations by effecting energy transfer from one element to another. The polymer stores energy in terms of activated conformations which it releases after a short delay. The polymer has two effects on the local viscosity of the solution: firstly it modifies the flow behaviour due to its interaction with neighbouring solvent molecules and secondly it influences the energy terms through its ability to store energy. The suppression of the onset of turbulence can be associated with the polymer damping the eddies which if they are allowed to build up lead to long-range fluctuations which ultimately increase the viscosity of the solution. The effectiveness of the polymer in suppressing turbulence will be a function of the volume which it occupies, its chemical composition and its efficiency in achieving energy transfer.

Theoretical considerations of the motion of a polymer chain in solution

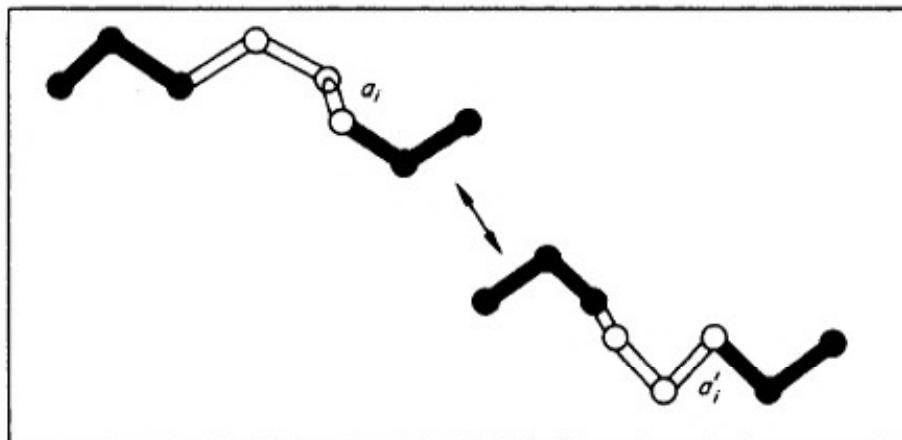
No unique description of the dynamic behaviour of a polymer molecule exists; however the principal modes of motion can be easily identified from a simple 'poppit' bead model.² The polymer molecule may be considered to be constructed from $N+1$ beads, joined by N links (bonds) each of length b . The direction of the bond from bead $i-1$ to bead i is given by the unit vector a_i . If the spatial position vector of the zeroth bead is r_0 , the location and conformation of the chain is then specified by the set of $N+1$ vectors $\{r_0, a_1, a_2, \dots, a_n\}$ (Fig. 3).

As mentioned earlier, the chain conformation will vary as a function of time

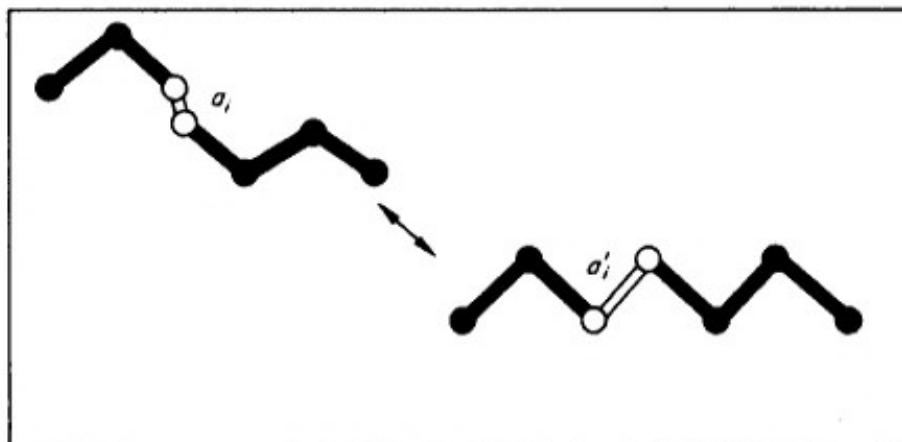
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as a result of random activation by collision with solvent molecules. This type of process may be considered in terms of the movement of beads one at a time. For interior beads ($i \neq 0$ or N) the motion consists of a jump or 'flip' whereby the vector a_i and a_{i+1} exchange values. In order to differentiate between the bond vectors before and after a flip, primes are used for the latter and the process corresponds to

$$a'_i = a_{i+1} \text{ and } a'_{i+1} = a_i \quad (1)$$



Local mode motion without translation



Local mode motion with translation

Fig. 3. Two possible forms of local motion of a polymer chain. Motion in each case is achieved by a series of bond flips.

Such an approximation is only strictly valid for the ideally flexible polymer chain, real chains may involve simultaneous activation of a number of chain units. In this simplified model the chain is assumed to be sufficiently long for the effects of end groups to be neglected. If this is correct then the probability that the chain has a conformation $\{a_1, a_2, a_3, \dots, a_n\} = \{a^n\}$ may be designated

as $p\{a^n, t\}$. The dynamic experiment is concerned with the probability $w_i dt$ that bead i will execute a flip during the time interval dt to form a new conformation which may be considered in terms of the master equation

$$dp(a^n, t)/dt = p(a^n, t) \sum_i w_i + \sum_i w_i p(\dots, a_{i+1}, a_i, \dots, t) \quad (2)$$

If the end groups were involved the above equation would require to be of a somewhat more complex form. In practice the dynamics of the end groups can often be considered in terms of the motion of the analogous freely rotating top attached to an infinite mass. For a freely jointed chain the flip probability may be written as

$$w_i = \alpha(1 - g a_i \cdot a_{i+1}) \quad (3)$$

where $|g| \leq 1$, which permits weighting the mobility of a bead according to its instantaneous bond angle. The overall effect of such a weighting on a three-dimensional chain would be simply to increase the rates of all the flips by a factor of $1 + (g/3)$. The chain may also be expected to show a weak correlation due to the effects of the intramolecular potential on the nearest neighbour link motions. This correlation may be given by the form

$$\langle a_i \cdot a_{i+1} \rangle_{eq} = \beta \quad (4)$$

and may be related to the equilibrium mean square length of the chain by

$$\langle r^2 \rangle_{eq} = Nb^2(1 + \beta)/(1 - \beta) \quad (5)$$

The above correlation is a first step to the consideration of a real polymer where specific angular geometries may be expected to be favoured over others. In the application of the above formulation it is assumed that β is small, restricting the application of this analysis to semi-flexible chains. Using equation (4) the flip probability for a bead may be written as

$$w_i = \alpha(1 + 3\beta a_{i-1} \cdot a_{i+1} + 3\beta a_i \cdot a_{i+2}) \quad (6)$$

The above relationship has to be consistent with the requirement of microscopic reversibility. In the practical experimental observation of the motion of a polymer chain one is usually concerned with the time required for a change of conformation as reflected in terms of the average value of one bond vector $q_i(t)$ which may be expressed by

$$dq_i/dt = \langle a_{j-1} w(a_{j-1} \cdot a_j) + a_{j+1} w(a_j \cdot a_{j+1}) - a_j w(a_{j-1} \cdot a_j) - a_j w(a_j \cdot a_{j+1}) \rangle \quad (7)$$

where

$$q_j(t) = a_j(t) = \int \dots \int_{\text{all } a, N} a_j p(a^N, t) d\{a^N\} \quad (8)$$

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where the averages are non equilibrium ensembles. The above may be combined with the condition for a bead flip occurring and yields

$$\begin{aligned} dq_j/dt = & -2a_j + a_{j-1} + 3\beta [\langle a_{j-1}(a_{j-2} \cdot a_j) \rangle + \langle a_{j-1}(a_{j-1} \cdot a_{j+1}) \rangle \\ & + \langle a_{j+1}(a_{j-1} \cdot a_{j+1}) \rangle + \langle a_{j-1}(a_j \cdot a_{j+2}) \rangle - \langle a_j(a_{j-2} \cdot a_j) \rangle \\ & - \langle a_j(a_j \cdot a_{j+2}) \rangle - 2 \langle a_j(a_{j-1} \cdot a_{j+1}) \rangle] \end{aligned} \quad (9)$$

If all terms in $O(\beta^2)$ are neglected the triple correlations are those of a freely jointed chain which may be easily evaluated in terms of linear averages and yields the result

$$\alpha^{-1} dq_j/dt = -2q_j + (1+\beta)(q_{j-1} + q_{j+1}) - \beta(q_{j-2} + q_{j+2}) \quad (10)$$

The above equation may be written as

$$\alpha^{-1} dq/dt = -Bq \quad (11)$$

where q is a column vector whose elements are all the q_i and B is a square $N \times N$ matrix with elements

$$\begin{aligned} B_{jj} &= 2 \quad B_{ij} = -(1+\beta) \text{ for } i = j+1 \\ &= \beta \text{ for } i = j+2 \\ &= 0 \text{ otherwise} \end{aligned} \quad (12)$$

The matrix B is diagonalized by the transformation $Q^{-1}BQ = \lambda_p$ where

$$Q_{jp} = (2/N)^{\frac{1}{2}} \sin(jp\pi/N) \quad (13)$$

and the eigen values of B are

$$\lambda_p = 4(1-3\beta)\sin^2(p\pi/2N) + 16\sin^4(p\pi/2N) \quad (14)$$

The above results are derived assuming that the value of N is large and that any distinction between N and $N+1$ may be ignored. It is usual to consider the motion of the chain in terms of the normal coordinate $X_p(t)$ which are related to the average chain coordinates and form a column vector A defined by the orthogonal transformation

$$A = Qq \quad (15)$$

The time dependence or relaxation of such modes may be assumed to have the form

$$A_p(t) = A_p(0) \exp(-t/\tau'_p) \quad (16)$$

where

$$\tau'_p = 1/\alpha\lambda_p \quad (17)$$

The above analysis indicates that for the first few (slower normal modes) ($p \ll N$) the relaxation spectrum of the freely jointed chain possesses values of λ_p which are proportional to p^2 , however deviations from this relationship will occur for the faster modes. The ratio of the longest to the shortest relaxation time is given by

$$\tau_1/N^2\tau_N = 4(1+4\beta)/\pi^2 \quad (18)$$

and the overall relaxation spectrum is broadened as the energetic preference for the extended conformation (β positive) is increased.

In the above formulation the time dependence of r_0 has been neglected and describes the displacement of the chain as a whole—translational diffusion. The mean square displacement per unit time of the centre of mass as a result of the random perturbation of the beads may be described in terms of the translational diffusion coefficient D ,

$$6D = \sum_{i=0}^N \frac{\langle w_i(\Delta r_i)^2 \rangle_{eq}}{(N+1)^2} \quad (19)$$

in which the displacement of bead i at a flip is

$$\Delta r_i = b(a'_i - a_i) = b(a_{i+1} - a_i) \quad (20)$$

which can be shown to be equal to

$$D = b^2(1 - \beta/N) = kT/N\xi \quad (21)$$

where the last quantity illustrates the connection between the basic flip frequency α and the effective friction coefficient ξ of a bead in the chain and leads to the result for slow relaxation that

$$1/\tau'_p = 3\pi^2 p^2 D / \langle r^2 \rangle_{eq} \quad (22)$$

In summary, the above treatment indicates that the normal mode and segmental processes are closely related, the former being a consequence of the summation of the effects of the latter. The above stochastic model is useful in indicating how the average motion of a molecular property of the sub-unit can provide information on the whole and component motions of the polymer chain. A variety of different approaches have been used to derive similar results to those outlined above. In the original formulations of a flexible chain the analysis was based on a system of beads linked by a spring, their motions being modulated by a frictional damping force. This approach due to Rouse and Zimm³ enables the effects of both intra and intermolecular damping on the motion of the polymer to be considered. The results obtained for the shear behaviour yields curves similar to those in Fig. 2. Discrepancies between the observed and predicted high frequency behaviour of the shear viscosity are usually attributed to the effects of segmental motion.

How may experimental data and theory be compared?

In the above section the discussion was concerned with a molecular formulation of the time dependent behaviour of the system. An experimental observation will usually be concerned with either the observation of the effects of some motion of the ensemblage or of a sub-unit of the whole molecule. In order that the information on the motion of the polymer may be abstracted from the experiment a detailed understanding of the observed phenomena is required. In general information on the motion of a molecular system can neither be obtained from time dependent spectroscopic or dynamic perturbation experiments.

The common forms of spectroscopy used for the investigation of polymers involve a resonance interaction with a nuclear or electric moment characteristic of a particular chemical environment. For example, an electromagnetic field can interact with a collection of dipoles in such a way that the ensemblage gains or loses a quantum of vibrational energy. The detailed process will involve a photon with the required energy changing the vibrational state of the molecule. The change of state produced by the interaction will itself be influenced by the dynamic motion of the polymer and is reflected in the shape of the observed vibrational curve. In recent years a number of workers have measured the detailed band shapes of various molecular interactions and information abstracted on the motion of a molecule on the time scale of the vibrational transition. This type of analysis will usually only provide information on the motion of the polymer on a very short time scale and reflects librational and rotational motions of sub-units of the polymer. Due to the short time scale of the interaction a system consisting of rotational isomers is composed of a mixture of apparently static conformations.¹ Raman spectroscopy provides similar information to that described in the infrared experiment outlined above. In this case the mechanism of the interaction involves the scattering of a 'virtual' photon. The analysis of the line shape in this situation is concerned with the rotational or librational motion of the molecule during the period of the virtual state. In both the infrared and Raman experiments a system in which dynamic conformational changes can occur often appears as an average of distinct structural types; in other words, on the time scale of the interaction the structures are frozen. Nuclear magnetic interactions have a considerably longer time scale than the photon interaction experiments and if the conformational changes are sufficiently rapid will lead to an averaged or collapsed spectrum. In this latter case the environment seen by the nuclei during the time in which they are in the excited state will be the average of all the possible states of the molecule. In certain cases it is possible to cool the sample down so that the condition of an apparently frozen structure is once more observed. In the nmr experiment, cooling a system of rotational

isomers usually leads initially to a broadening and ultimately a splitting of the resonances into components characteristic of the conformations present. Electron spin resonances may also be observed to show features characteristics of rotational isomerism; however, in this latter case the interaction time is usually significantly shorter than the exchange rates and averaged environments are not always achieved. In spectroscopic studies the important feature with regard the type of information obtained on the dynamics of a polymer in solution is the lifetime of the excited state. Studies of the effects of temperature on band intensities may also be used to obtain an indication of the energy difference between conformational states.

In addition to distinct quantal transitions associated with the interaction of radiation with specific atom groups, gross interaction can also be observed in systems containing permanent dipoles. The application of an electromagnetic field to such a system will lead to an alignment of the dipoles in the direction of the applied field. In the usual situation the electromagnetic field oscillates and the dipoles will attempt to follow the fluctuations in the field; this is shown schematically in Fig. 4. At high rates of fluctuation the dipoles are unable to reorientate and follow the applied field and the polarization which can be achieved on the system is dropped proportionately. At a frequency where the dipoles are just about able to follow the field a certain number will lag behind the applied field and lead to an energy dissipation. The frequency dependence of the dielectric properties of a material will reflect the ease of reorientation of the constituent dipoles, their magnitude, the distribution of environments to be found in the system and any anisotropy of the motion which may be present. A variety of other forms of perturbation are available to the physicist and include stress, pressure (acoustic waves) and oscillatory hydrodynamic fields. Such studies are termed 'relaxation' experiments.

In both the spectroscopic and relaxation studies the interpretation of the detailed motion of the polymer chain involves a correlation of the microscopic properties with the macroscopic observable which usually involves assumptions with regards to the form of the ensemble average describing the system. For example, in the case of dielectric relaxation (reorientation of dipoles) the observed dielectric dispersion is assumed to arise from the motion of relatively unconnected dipoles. In practice the motion of one dipole may be expected to some extent to be coupled with that of neighbouring dipoles and the resultant behaviour must be considered to be described by a cooperative motion of the system. Since the motion of one isolated dipole is not being observed, it is often somewhat difficult to accurately ascribe the detail of the molecular motion being monitored. The interrelationship of the microscopic behaviour and the macroscopic observable is a problem in all types of experiment and will be discussed in detail later.

The application of correlation theory to the description of a relaxation

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experiment can be illustrated in terms of the bead and spring model of a polymer being distorted by a shear field. This model was first proposed by Rouse and Zimm and was later modified by Kirkwood & Riseman⁴ who acknowledged the effects of hydrodynamic interactions on the motion of the elements of the

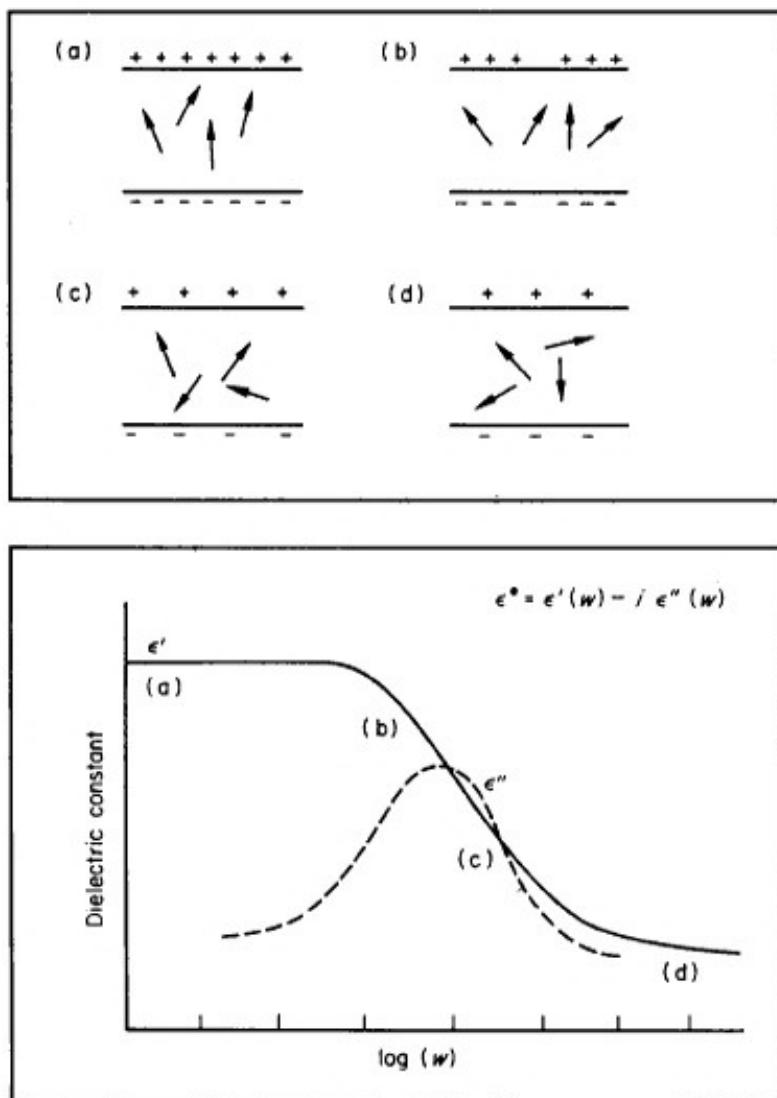


Fig. 4. Motion of a dipole in an oscillating electric field. (a) At low frequency almost complete alignment of the dipoles in the slowly reversing field is possible, as the frequency is raised (b) and (c) fewer of the dipoles are aligned in the field direction until at very high frequency (d) the dipoles maintain an almost random distribution of alignments. The residual high frequency polarization arises from atomic and electronic contributions.

chain. In order to simplify the mathematical manipulation the hydrodynamic interaction is usually introduced in a pre-averaged form. This premature averaging has the effect of maintaining linearity in the chain coordinates and preserves the normal coordinate transformation which paves the way

to simple analytical results. This re-averaging can sometimes lead to unrealistic results but when used with care produces a formulation for transport coefficients and relaxation times which agrees well with experimental observation. An alternative to the pre-averaged Oseen (hydrodynamic) tensor has recently been put forward but is considered more difficult to apply and does not tend to lead to any significant new results.⁵

An illustration of the way in which an experiment may be modelled will now be considered. The bead and spring model is widely used for the study of the viscoelastic properties of the polymer solution and is based on a matrix formulation for the diffusion equation. The position and conformation of the polymer chain may be defined in terms of a distribution function $f(r,t)$ at a time t with the coordinates of the $N+1$ beads being expressed by $\{r_0, r_1, r_2, \dots, r_N\}$. The symbol r denotes the column vector whose elements are the beads' cartesian coordinates. The hydrodynamic interactions may be introduced in terms of a column vector v_0 which describes the fluid velocity of a bead with root mean square displacement length b and friction constant ξ . The bead is itself subjected to a potential energy U_e from the external field. The diffusion equation will then have the form

$$df/dt = -\nabla^T f v_0 + \nabla^T (kT/\xi) H \cdot [\nabla f + f \nabla U_e/kT + 3b^{-2} f A r] \quad (23)$$

where A is an $N \times N$ matrix with elements $A_{jj} = 2A_{jj \pm 1} = -1$, otherwise zero, and expresses the linear sequences of spring forces between the beads. The hydrodynamic interaction matrix H has the structure

$$H_{jk} = \delta_{jk} + (1 - \delta_{jk})(1/6\pi\eta_0) \langle r_{jk}^{-1} \rangle \quad (24)$$

$$= \delta_{jk} + (1 - \delta_{jk})(6\pi^3)^{\frac{1}{2}} b \eta_0 |j - k|^{\frac{1}{2}} \quad (25)$$

The viscosity of the polymer solution may be described in terms of an appropriate time correlation function

$$\eta = (1/YkT) \int_0^\infty J^{xy}(t) J^{xy}(0) \exp(-iwt) dt \quad (26)$$

in which

$$J^{xy} = \sum_i m_i \dot{x}_i \dot{y}_i + \sum_i y_i F_i(x) \quad (27)$$

the summation being over all particles in the volume V . The i th particle has mass m_i , velocity components \dot{x}_i and \dot{y}_i , and is acted on by the x component of the force $F_i(x)$. The time correlation function J^{xy} is over an equilibrium ensemble and the viscosity is for an oscillating shear circular frequency w .

In consideration of the effect of the polymer on the solvent viscosity it may be recognized that only the difference in J between the solution and the pure solvent need be considered. It should, however, be remembered that in certain

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situations the 'structure' of the solvent may be significantly altered by the introduction of the polymer and whilst the above approximation is valid for consideration of shear relaxation behaviour it is not valid for the discussion of equilibrium thermodynamic properties of polymer solutions. It follows from the separation of the time correlation functions that

$$[\eta] = (N/M\eta_0 kT) \int_0^\infty \Delta J^{xy}(t) \Delta J^{xy}(0) \exp(-iwt) dt \quad (28)$$

where N is Avogadro's number, M is the molecular weight of the polymer and η_0 is the solvent viscosity. Physically the integral is entirely concerned with the mutual interaction among the elements of a single chain of the polymer. It is further possible to define J^{xy} as

$$J^{xy} = \sum_i y_i [F_i^{(x)\prime} + F_i^{(x)\prime\prime}] \quad (29)$$

where the sum is over all elements of a polymer chain and the two forces are respectively called 'diffusion' and 'bond interactional' contributions. The former is directly related to the velocity term and may be written as

$$F_i^{(x)\prime} = -kT(d\ln f/dx_i) \quad (30)$$

while the second is

$$F_i^{(x)\prime\prime} = -dU_{int}/dx_i \quad (31)$$

in which U_{int} is the intramolecular potential energy governing the bonding in the chain. In the limit of field free zero flow the 'diffusion' term vanishes and

$$\langle J^{xy}(t) J^{xy}(0) \rangle = (kT)^2 \sum_p \exp(-t/\tau_p) \quad (32)$$

in which the relaxation times τ_p are given by

$$\tau_p = b^2 \zeta / 6kT \lambda_p \quad (33)$$

The use of the correlation theory approach presents a method of interrelationship of the data from experiment to that obtained from molecular dynamic theories. These correlations are at present in their infancy and it is hoped that with their wider application the role of intermolecular interactions in the determination of the molecular correlation times may be quantified.

Some aspects of molecular motion in linear polymer chains

In the previous section the interplay of the molecular model and the form of the correlation function obtained was illustrated. It is this realization of the importance of the correlation theory in the interpretation of experimental data which has led to a better understanding of a number of apparently contradictory

experimental observations. The forms of the correlation functions for a number of experiments are summarized in Table 1.

Table 1. Time correlation function and experiment

| Experimental observation | Dynamic quantity | Time correlation function |
|----------------------------------|--|---|
| Neutron scattering | r_i , position of the i th nucleus in a fluid | $\frac{1}{N} \sum_{i=1}^N \langle e^{ik.r_i(0)} e^{ik.r_i(t)} \rangle$ |
| Raman scattering | u , unit vector along molecular transition vector | $\langle P_2(u(0) \cdot u(t)) \rangle$ |
| Infrared absorption | u , unit vector along molecular transition dipole | $\langle u(0) \cdot u(t) \rangle$ |
| Diffusion coefficient | v , centre of mass velocity of tagged molecule | $\langle v(0) \cdot v(t) \rangle$ |
| Spin-rotation relaxation | J , angular momentum about molecular centre of mass | $\langle J(0) \cdot J(t) \rangle$ |
| NMR lineshape | M_x , x component of the magnetization of the system | $\langle M_x(0) \cdot M_x(t) \rangle$ |
| Rotational diffusion coefficient | Ω angular velocity about molecular centre of mass | $\langle \Omega_a(0) \Omega_b(t) \rangle$ |
| Fluorescence depolarization | r_{fi} , the intensity of a line in fluorescence | $r_0 \langle \frac{1}{2}(3\cos^2\alpha(t) - 1) \rangle_{fi}$ |
| Sound absorption | $\zeta(\omega)$ frequency dependent bulk viscosity | $\frac{1}{18VkT_0} \int_0^\infty dt e^{-i\omega t} \langle \sum_i (T_{ii}(0) - \bar{T}_{ii}) \cdot \sum_j T_{ij}(0) - (\bar{T}_{ij}) \rangle$ |
| Dielectric relaxation | $\gamma(t)$ the correlation function of a dipole at time t | $\frac{\langle \mu(0) \cdot \mu(t) \rangle}{\langle \mu(0) \cdot \mu(0) \rangle}$ |

Key to symbols: N number of molecules per unit volume, k the wave vector, $r_{fi} = (I_{II}^f - I_{\perp}^f)/(I_{II}^f + 2I_{\perp}^f)$, where I_{II}^f is the intensity of a line in fluorescence when the emitted light has its electric field parallel to the electric field of the exciting light, and I_{\perp}^f is the corresponding emission intensity for perpendicular electric fields, Ω the angular momentum vector and r_0 is the polarization index for light emitted by an undisturbed molecule, T_{ij} is the momentum flux tensor and V is the volume, $\mu(t)$ moment of the dipole at time t .

A survey of the data available on the motion of polymers has enabled certain characteristic types of behaviour to be identified. A polymer being a long chain-like structure may be expected to show changes of its relaxation behaviour with changes in the molecular weight. The effects of increase in the chain length of a polymer have been illustrated by dielectric relaxation.⁶ At low molecular weight the relaxation which reflects the rate of reorientation of a dipole vector within the polymer will be approximately proportional to the chain length.⁷ This observation suggests that the relaxation is associated with what is essentially whole

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molecule rotation. For higher molecular weights the relaxation becomes independent of the chain length and is constant at a particular temperature for a specific polymer sample. This type of behaviour is illustrated in Fig. 5. It is assumed that for the high molecular weight material the reorientation of the dipole is achieved by a process which does not involve overall rotation of the whole polymer chain-segmental motion. The value of the molecular weight at which the relaxation behaviour changes from being dominated by overall

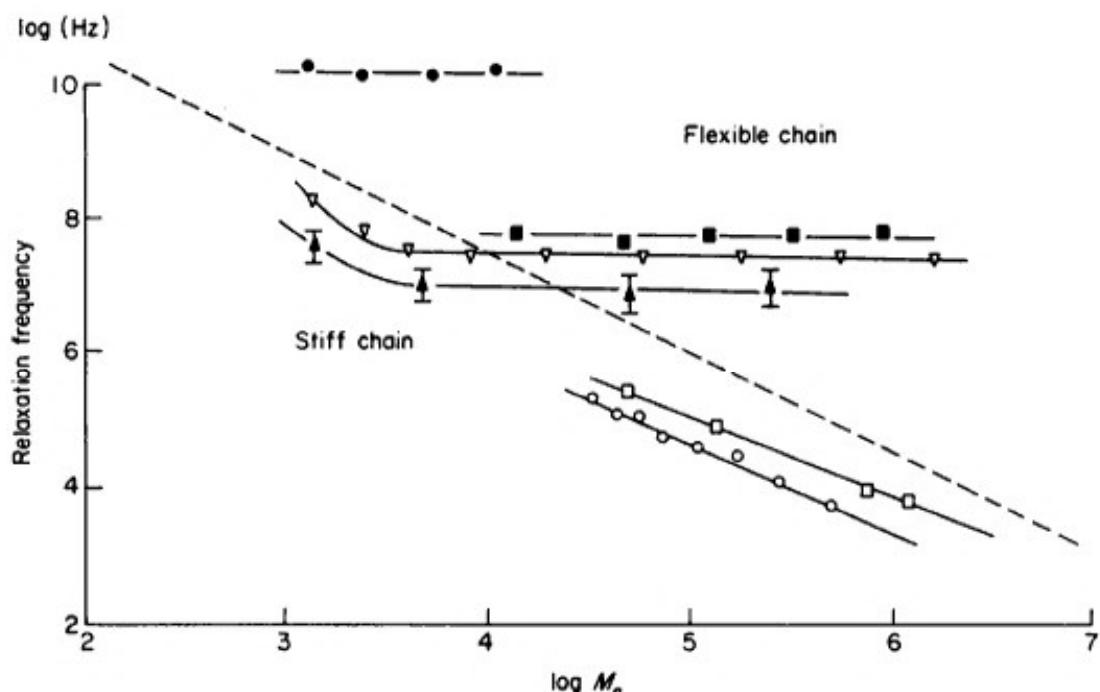
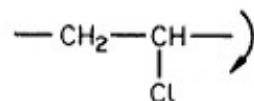
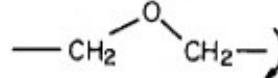
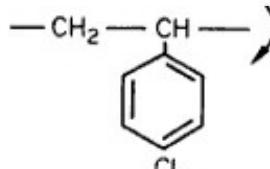
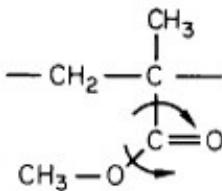
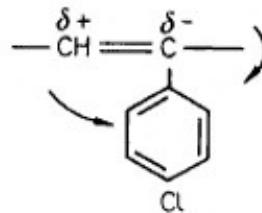
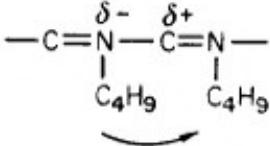


Fig. 5. Molecular weight dependence of the dielectric relaxation frequency. Polymers lying above the dotted line may be considered to behave as flexible chains, those below as stiff coils. Key: ●, Poly(ethyleneoxide) (Stockmayer W.H., 1967, *Pure appl. Chem.* 15, 539); ■, poly(methylmethacrylate), ▲, poly(N-vinyl carbazole) (North A.M. & Phillips P.J., 1968, *Chem. Comm.* 1340); ▽, poly(p-chlorostyrene) (Matsuo K., 1960, Ph.D. thesis, MIT); □, Poly(σ -benzyl L-glutamate) (Block H., Hayes E.F. & North A.M. 1970, *Trans. Faraday Soc.* 66, 1095); ○, poly(hexane-1-sulphone) (Bates T.W., Ivin K.J. & Williams G., 1967, *Trans. Faraday Soc.* 63, 1976).

rotation to becoming determined by the ease of segmental motion is a function of the magnitude of the intramolecular potential governing internal rotation. It will be appreciated that a molecular weight will exist where overall rotation and segmental motion are equally probable and a complex relaxation mechanism must be used to describe the observed dynamic behaviour. In general the dielectric relaxation behaviour of a polymer molecule in solution will be dominated by the energetically easiest process. In the case of a stiff polymer, whole molecule rotation will dominate to high values of the molecule weight; in a very flexible polymer, solvent viscosity will inhibit whole molecule rotation and as a conse-

quence segmental rotation dominates at low values of the molecular weight. The detailed interpretation of the data presented in Fig. 5 requires consideration of the selection rules for the relaxation of a particular dipole component. The allowable motion for a dipole will depend upon the method of attachment of the polar group to the main backbone and also the direction of the dipole

Table 2. Relaxations of molecular dipoles in polymers

| Polymer | Dipole geometry | Structure and motion |
|--------------------------------|-------------------------------------|---|
| Poly(vinyl chloride) | rigid perpendicular |  |
| Poly(ethyleneoxide) | rigid perpendicular |  |
| Poly(p-chlorostyrene) | rigid perpendicular |  |
| Poly(methyl methacrylate) | flexible parallel and perpendicular |  |
| Poly(p-chlorophenyl acetylene) | rigid perpendicular and parallel |  |
| Poly(n-butyl isocyanate) | rigid parallel |  |

relative to the main persistence vector for the polymer. Various possible configurations are illustrated in Table 2. If the dipole is perpendicular to the backbone the behaviour described above is observed and reflects the mobility of the chain segments. If, however, the dipole has its major component in the direction

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of the backbone, rapid segmental motion will not relax the dipole and effective relaxation can only be achieved by whole or normal mode processes. Various combinations of these two extremes are possible in practice and the observed dispersion requires a complex mechanism of dynamic behaviour for its complete description. The observation of a dispersion curve which is broader than would be predicted by theory for a single relaxation process is often indicative of multiple relaxation behaviour in the system. However, it should be noted that a broader than Debye relaxation curve can also arise from the effects of the breadth of the molecular weight distribution of the polymer sample used in the study. A detailed analysis of the shape of the dielectric relaxation curves has suggested that the observed dispersion arises in many cases from cooperative motion of the constituent dipoles of the polymer.⁸ It will be appreciated that the dipole-dipole interactions in such a system will in the absence of any other interaction lead to a tendency for the motion of the dipoles to be weakly coupled. A detailed study of the potential surfaces associated with the internal rotation would suggest that reorientation of any one element would be easiest if neighbouring groups are weakly coupled enabling minimum energy conditions to be achieved at all stages of the relaxation process. In concentrated solutions other restrictions on the motion of a dipole such as limitations of the volume, expansivity of the local environment and intermolecular potential require to be discussed and lead to an observed relaxation behaviour which may only be interpreted in terms of cooperative motions of the dipoles. A number of studies of the temperature dependence of the relaxation times have been used to yield activation energies for the internal rotation process. Such an interpretation assumes that the nature of the relaxation process does not change significantly with temperature; this is not necessarily so. It would appear logical to expect that changes in temperature would influence the local environment as well as the probability of activation of the intramolecular motion of the polymer sub-units, and as a result a simple Arrhenius type of behaviour is surprising in such systems.

Dielectric relaxation provides information on the average motion of an ensemble of dipoles and therefore does not always provide the detailed information on the motion of individual dipoles. It is clear that, in general, a complete interpretation of the form of relaxation of spectroscopic data in terms of the motion of a sub-unit of the polymer requires a detailed knowledge of the potential surface associated with such motion. At the present time such information is only available for a relatively few small molecule systems.

Molecular weight effects have been recognized in a number of experiments,⁹⁻¹¹ ¹³C nuclear magnetic resonance relaxation behaviour, spin labelled relaxation and acoustic dispersion studies have enabled these effects to be investigated further. Studies of the relaxation of the induced nuclear polarization associated with the ¹³C nucleus naturally found in polymers provides a powerful tool for a detailed study of the effects of chain length on the relaxation

behaviour. In the typical experiment the nuclei are firstly aligned by a large magnetic field and then rotated through an angle of 180° by an applied radio frequency field. The induced polarization will be randomized by a number of molecular processes and ultimately would adopt an equilibrium distribution. In the usual experiment a pulse of r.f. is applied after a known delay which rotates the residual induced magnetization into the xy plane and gives rise to a signal of reduced amplitude in comparison with the original signal being detected. The amplitude of the detected pulse will depend on the length of the delay and the rate of relaxation of the particular nucleus being studied. After the application of the first pulse (180°) a non random component will exist in the xy

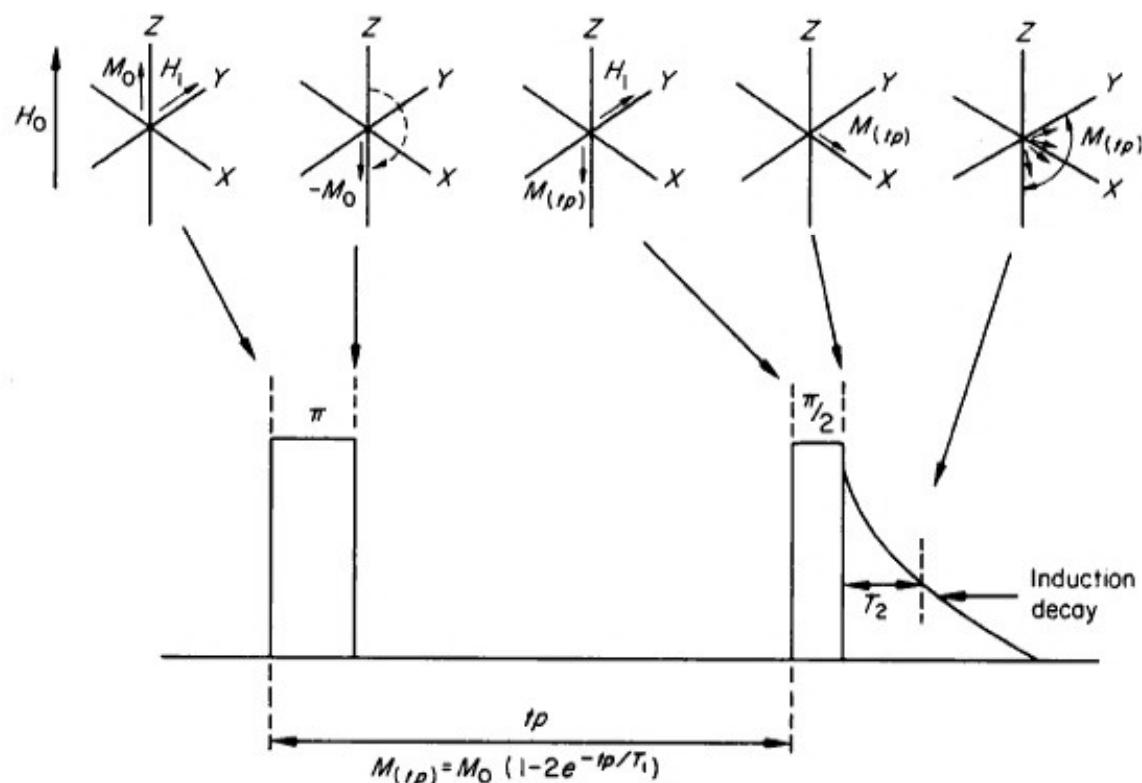


Fig. 6. Vectorial representation of the induced magnetization during a pulsed experiment. H_0 applied magnetic field in the z direction. H_1 radio frequency field.

plane and this will give rise to the so-called free induction decay which is controlled by the spin-spin coupling of the various nuclei (T_2). The randomization of the total magnetization is determined by the dissipation processes of the nuclei coupling with the thermal fluctuations of the local environment and is termed the spin-lattice (T_1) relaxation (Fig. 6). It will be appreciated that the two relaxation times are not always separable in all experimental systems and assumptions are usually required for the analysis of the experimental data.¹² A transformation of the free induction decay is used in Fourier transformation spectro-

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scopy and yields the usual resonance spectrum. In brief, the relaxation of the total magnetization may be achieved by magnetic dipole-dipole, electric quadrupole, chemical shift anisotropy, scalar coupling and spin rotation interactions. In the case of a protonated carbon atom the dominant process is of a magnetic dipole-dipole origin. In a simple liquid the magnetic dipole-dipole coupling arises from long-range hydrodynamic fluctuations which have a component at the natural resonance frequency of the particular nucleus being considered (Larmor frequency). In a polymer segmental motion and whole molecule motions will tend to have larger components at the Larmor frequency than the normal hydrodynamic fluctuations. It is found in practice that the dominant mechanism for the relaxation in polymer solutions is in fact directly related to the motions of the polymer chain at the frequency of observation. A study of the molecular weight dependence of the relaxation of polystyrene suggests that below a molecular weight of 20,000 the processes responsible for the relaxation are molecular weight dependent. This observation is in good agreement with dielectric studies of chlorinated polystyrene.¹³

One of the major advantages of ¹³C studies is that due to its low natural abundance the effects of nuclear coupling may be neglected and the relaxation may be considered to be indicative of the true motion of that site. This type of study is in its infancy but shows considerable potential for the future. For instance, studies of the normal alkanes have indicated that the relaxation of carbon atoms at various distances from the chain centre will possess significantly different relaxation times and thence possibly different mechanisms of motion. A similar observation has recently been made for alkyl side chains of various length when attached to polymethylacrylate backbone. For the low molecular weight alkanes the effects of whole molecule rotation dominate the relaxation spectrum up to a chain length of approximately six units. Above this the relaxation process contains an increasing component from internal rotation and normal mode processes. A similar explanation has been put forward for the apparent molecular weight dependence of the relaxation times in polystyrene.

Similar effects to those described above have been identified from ultrasonic studies of the normal alkanes,¹⁴ polystyrene,¹¹ (Fig. 7) and poly(α -methylstyrene-alkane) copolymers.¹⁵ In the ultrasonic experiment the mean velocity of the solvent is perturbed by the application of a sinusoidally varying pressure wave. Elastic and inelastic collisions between solvent and polymer enable coupling of the perturbation of the solvent with the internal modes of the polymer. If the internal modes activated by inelastic collisions are not immediately deactivated by subsequent collisions a mechanism is established for energy storage and hence damping of the applied perturbation. The position of the associated relaxation behaviour is determined by the detailed balance of energy uptake and return. For a molecular process to be acoustically active there must exist a difference in either volume or energy between the states involved.

Application of this selection rule to the observed molecular weight dependence of the relaxation in polystyrene solutions in toluene suggests that isoenergetic whole molecule rotation of the polymer which contributes to the ^{13}C studies should not influence the acoustic measurements. In the acoustic studies it is inferred that the molecular weight dependence arises from three effects. Firstly normal mode type of relaxation processes may be expected to extend into the low megahertz frequency region and in fact will be centred in this region for low molecular weight materials. Calculation of the contribution to the observed dispersion behaviour would suggest that normal mode processes contribute typically 10–20 per cent to the total relaxation behaviour. At high molecular

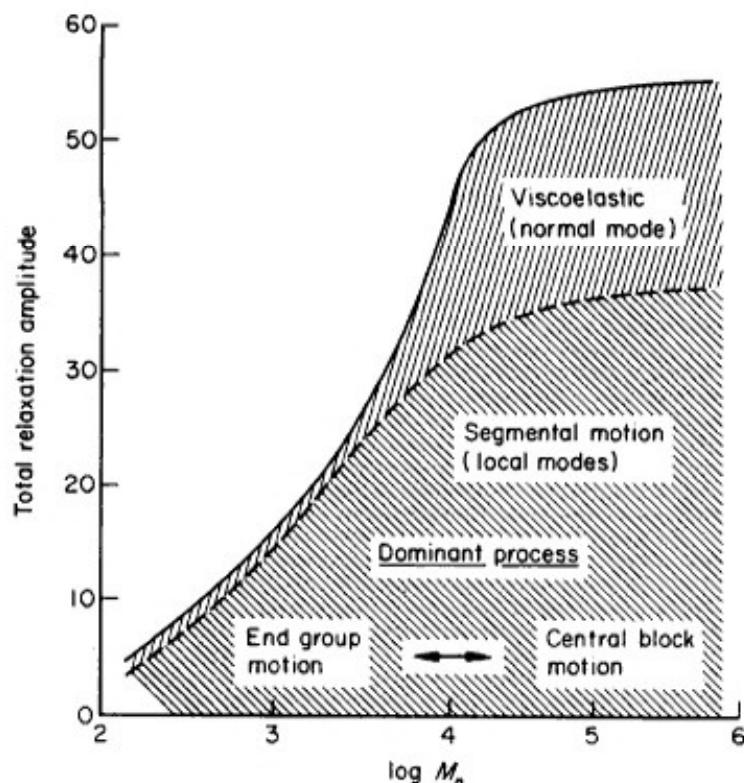


Fig. 7. Molecular weight dependence of the acoustic relaxation of polystyrene in toluene.

weights the normal mode processes will have moved to low frequency and will make a negligible contribution to the observed dispersion. The molecular weight dependence must therefore be explained in terms of either changes in the mobility of the polymer with the chain length or from effects associated with intermolecular contacts.

The ease of motion of the end groups of a polymer chain relative to those of the centre of the polymer has recently been demonstrated using a study of the depolarization of the fluorescence of a dye tagged polymer.¹⁶ The experiment involves the dye molecule absorbing a quantum of polarized light, the wave-

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length is chosen to correspond to that of the normal singlet-singlet transition. The fluorescence will occur at a somewhat different frequency and it is therefore possible to observe the emission independent of the absorption. The photo-selected fluorescent molecules will during their excited state lifetime execute some degree of molecular motion. The degree of depolarization of the emitted light will reflect the degree to which motion has occurred during the lifetime of the excited state. This experiment may only be performed on polymers in which the dye is attached rigidly to the polymer backbone and in which effective internal energy transfer down the chain does not compete with the normal radiative processes. Studies of polymers tagged both at the middle and at their ends indicates that the motion of the terminal units are significantly faster than those of the central units and supports the previous hypothesis with regards the molecular weight dependence of the relaxation behaviour of polymers. This technique has a severe limitation on its general application to the study of the flexibility of polymers, this is the finite size of the dye used. The dye is often larger than the polymer sub-unit to which it is attached and the motion influencing the depolarization data reflects the effects of the local viscosity rather than some facet of the mobility of the polymer backbone. A further problem associated with the interpretation of the fluorescence depolarization data arises from the fact that in order to attach the dye a chemical bond has to be formed usually of a saturated nature, and which is often as not more flexible than that of the backbone. In this situation reorientation of the pendant group need not reflect the motion of the backbone of the polymer chain. This technique has the advantage of providing considerable sensitivity and enables studies to be performed on very dilute polymer solutions where the isolated polymer may truly exist. The molecular correlation times obtained from this technique agree well with those obtained from other relaxation studies.

Normal mode relaxation is usually studied by the frequency dependence of the shear viscosity. An extensive literature exists on this topic¹⁷ and a number of features have been successfully identified which can be used to characterize such motion. For a flexible polymer the shape of the relaxation curve and its position will primarily be determined by the strength of the interaction of the polymer with the solvent, the length of the chain and its flexibility as defined by the intramolecular interaction constants. Theoretical analysis has been developed for the flexible coil with virtually no interaction with the solvent, with interaction of the solvent and the chain and also for the partially rigid polymer. Numerous examples of polymer-solvent combinations which possess the desired characteristics can be found in the literature. In general the theory predicts the initial shape of the low frequency viscoelastic behaviour of the polymer quite well but fails to describe the limiting high frequency properties. This apparent departure from theory is yet another manifestation of the way in which the interplay of segmental and normal mode relaxation influences the observed behaviour.

In the discussion so far the experimental conditions have been chosen so that the polymer is isolated, flexible and in a good solvent and reasonable agreement between theory and practice is observed. In a poor solvent the polymer will be less spatially extended than in a good solvent and deviations from the ideal behaviour outlined above may be expected. Contraction of the polymer and the effects of excluded volume may become apparent in a poor solvent or at high concentrations of polymer. The excluded volume is defined as the volume occupied by the polymer which is not available for the movement of neighbouring backbone elements and arises from the physical impossibility of two chemical bonds to pass through one another. This type of restriction on the free motion of the polymer chains is obviously required for any flexible polymer of significant chain length and is both theoretically and practically difficult to study. Observation of the zero shear viscosity and visco-elastic properties of polymer solutions have been suggested to show evidence for these effects; however, a quantitative estimation of such effects is often lacking or of dubious merit. There are, however, exceptions and one such case is the zero shear studies of semi-flexible polymers in theta and good solvents. A theta solvent is one in which at a defined temperature, the theta temperature, the polymer possesses interactions with the solvent which are essentially identical with those of the polymer—with the polymer. A major problem with this latter type of study is the magnitude of the experimental uncertainty involved in the determination of the magnitude of the excluded volume effects.

Change of solvent will in general influence the polymer in two ways. Firstly it will change the strength of the hydrodynamic interaction and hence the whole molecule and normal mode relaxation behaviour. Secondly it will influence the size of the polymer through its effects on the distribution between the various possible conformational states. The influence of the solvent on the hydrodynamic interaction can be observed by comparison of the viscoelastic relaxation of polystyrene in toluene,¹⁸ decalin¹⁹ and araclor.²⁰ In the latter, a highly viscous solvent, the relaxation is considerably broader than in toluene and takes place more slowly than in the less viscous solvents. The effects of solvent can also be seen in dielectric studies of polypropyleneoxide which exhibits a relaxation spectrum in a good solvent which is characteristic of free internal rotation of independent local units of the backbone.²¹ In a highly viscous solvent, the relaxation processes correspond to a considerably broadened relaxation process with a much slower time constant. A broadening of the relaxation distribution is usually attributed to a greater number of possible sites or mechanisms required to describe the time dependent behaviour. It is envisaged that in highly viscous materials the dominant relaxation processes will be those which involve long-range motion of a cooperative origin. As the viscosity of the solvent increases both whole molecule and normal mode motions are considerably slowed down. The reduction in the translational momentum of the solvent molecules will lead

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to a net lowering of the average momentum transfer per collision. As a result, the number of activations which occur in unit time will be reduced and change in conformation by a series of small displacements which ultimately leads to large elements of the polymer moving in space may be expected to be of a cooperative nature. This longer range motion is favoured in the situation found in medium and high molecular weight polymers over the local single segmental motion often proposed to explain the high energy low viscosity conditions often used in relaxation studies due to the stoichiastic nature of the process. Cooperative motion has been proposed as an explanation for a number of experimental observations in which the activation energy exceeds the single bond dissociation energy and is a situation often met in highly viscous media.²² Similar conditions are often to be found in liquid polymers and it is assumed that the relaxation involves a defect diffusion type of description which essentially requires the cooperative motion of a number of sites for relaxation of a particular element to occur.

The solvent can play an important role in the determination of the size of the polymer and also influence its flexibility through its effects on the internal rotational profile. The effects of solvent on the relative stabilities of various conformations of a molecule have been extensively studied in small molecules through various spectroscopic techniques and in macromolecules through light scattering.²³ Changes in the relative stabilities of gauche and trans isomers within a polymer will lead to modification of the spatial extension. The more polar the solvent the greater the stability of the more polar form of the molecule. Whilst there exists an extensive literature on the effects of solvent change on the conformation preference in small molecules,¹ little is known quantitatively about the behaviour of macromolecules. Gross effects have been inferred from light scattering and thermodynamic studies but their relationship to the detailed changes in the microstructure are somewhat obscure.

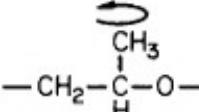
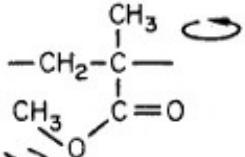
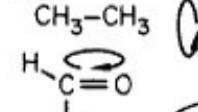
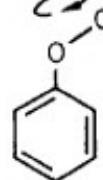
It may be anticipated that the solvent will act both through its effects on the relative stability of the various conformations and also through its effects on the stability of the transition state involved in the internal rotation process. In specific systems such as the polypeptides, the solvent may have a very marked effect on both the shape and energetics of the polymer. In these systems water is often incorporated into the helix structure and its removal destroys the stability and increases the relative flexibility of these structures.

Polymers with side groups

Many polymers possess side groups which are themselves capable of undergoing relaxation processes. In a molecule such as poly(methyl methacrylate) (Fig. 8), the motion of the carbonyl dipole in an applied electric field will not only be influenced by the internal rotation of the side group but also will be influenced

by motions of the polymer backbone. The polar side group in PMMA can be relaxed partially by the internal rotation process of the polymer backbone and partially by whole molecule or normal mode combined with internal rotational motion. In practice the observed relaxation is found to be somewhat broader than the ideal and is influenced by the tacticity of the polymer. It is generally assumed that in this system the motion of the side group is loosely coupled to the rotation of the motion of the backbone. This type of behaviour is generally referred to as cooperative motion and is found in a number of polymers with

Table 3. Activation energies for methyl and related top rotation

| Polymer/Molecule | Activation energy (kJ/mole) | Structure | Reference |
|--|--------------------------------|---|-----------|
| Poly(propyleneoxide) | 15 |  | a |
| Poly(methyl methacrylate) (I) (II) | 4 34 |  | a a |
| Ethane | 12 |  | b |
| Benzaldehyde | 18.4 |  | c |
| Anisole | 14.4 |  | d |

References: (a) HIGGINS J.S., ALLEN G. & BRIER P.N. (1972) *Polymer* **13**, 157. (b) WEISS S. & LEROI G. (1968) *J. Chem. Phys.* **48**, 962. (c) MILLER F.A., FATELEY W.G. & WITOWSKI R.E. (1967) *Spectrochim. Acta* **23A**, 891. (d) FEWSTER S. (1970) Ph.D. thesis, University of Manchester.

bulky side groups. It can be envisaged that the relaxation by internal rotation of the side group is most easily achieved if the motion is coupled to that of the backbone. In this case the transition state involved in the internal rotation process is achieved by a slight rotational displacement of the chain backbone which in turn alleviates the strain induced by nearest neighbour interactions. The motion of substituted phenyl groups in analogues of polystyrene has been suggested to exhibit cooperative motion and it would appear reasonable to expect that this type of phenomenon may be expected in most polymers containing

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side groups. A possible exception to this rather broad generalization is that of the motion of methyl groups. Studies of the motion of the methyl rotor in a series of polymers (Table 3), indicates that whilst the activation energy approaches that of ethane, which may be taken to be indicative of 'free' rotation, a number of higher activation energies have been observed. The methyl group may not be studied by either dielectric or acoustic relaxation techniques and has been observed almost exclusively by either nuclear magnetic or vibrational spectroscopic methods.

The infrared and Raman activity of the internal rotation (torsional oscillations) of the methyl group are spectroscopically forbidden. The motion of polar groups may be observed by infrared spectroscopy but may also be studied by dielectric relaxation. In recent years neutron inelastic scattering has been used with some success for the investigation of the torsional transitions.²⁴ In the neutron experiment a pulsed beam of mono-energetic neutrons is scattered from the polymer sample. Two types of interaction can occur, inelastic and elastic scattering. In the former the neutron loses some of its energy in exciting an internal vibrational mode into its excited state. Hydrogen atoms, because of their relatively light mass, have large amplitudes of motion; they also possess large neutron scattering cross-sections. The torsional motion involves a large displacement of the hydrogen atoms of the methyl group and since the intensity of the scattering is the product of the amplitude and the scattering cross-section these motions dominate in the observed spectrum. The detail of the energy transfer process is obtained by measuring the time of arrival of the neutrons at the detector. As a result of the interaction of the neutron beam with the polymer individual neutrons will gain or lose energy and hence arrive at the detector at different times. The result of this time domain experiment is very similar to that obtained from Raman spectroscopy. This similarity is further emphasized in the elastic scattering peak which in both cases is broadened by the effects of small amplitude high frequency fluctuations in the system. Analysis of the shape of the elastic scattering curve should be performed in terms of the velocity auto-correlation function which in its infinite limit would yield information on the hydrodynamic behaviour of the system as reflected in the translational and rotational diffusion of the individual molecules of the system.

A necessary condition for the observation of an infrared band is the existence of a dipole moment which changes on vibration; similarly a Raman band can only be observed if there is a change in polarization on vibration. Neutron scattering has somewhat different selection rules; a molecular vibration can be detected if the motion has a large amplitude of vibration and if the atoms involved have significant scattering cross-sections. Torsional motions with their high angular displacements will in general possess a high neutron scattering activity and may be readily identified in the overall scattering profile.

Calculation of the activation energy for internal rotation requires firstly an

accurate value for the torsional vibration and also a knowledge of the shape of the energy profile involved in the process. In the usual approach the torsional mode is assumed to have small angular displacements and to be accurately described by a simple harmonic potential function.¹ This approximation is possibly quite valid for the consideration of the first torsional transition but may be expected to fail for the higher order transitions. As the rotor attains the higher activated states corresponding to the eclipsed structure, distortions from the ideal geometry may be expected and departures from the harmonic approximation must be anticipated. If the torsional levels corresponding to states near the top of the activation profile were observed then it should be possible to calculate exactly the energy profile describing internal rotation. In practice only the first torsional transition is usually observed and the calculated values of the activation energy are often larger than those obtained from relaxation measurements.¹⁴ This apparent discrepancy can in part be attributed to the fact that the barrier in the spectroscopic study is derived from an assumed potential profile whereas the relaxation experiment senses the 'actual' form of the profile which allows for distortion in the transition state. In the case of a methyl top, quantum mechanical tunnelling between neighbouring conformations has been suggested as a possible explanation for the observed discrepancy between spectroscopic and relaxational determined activation energies.

Studies of the activation energies for internal rotation of the methyl top indicates that tacticity has an influence on the motion of this side group and it may be expected that in polymers where the tops are relatively close cog wheel motion may be expected to be very prevalent. Coupling of the motion of methyl tops is well known in small molecules and may be expected to be responsible for an increase in the degree of correlated motion of the backbone of certain methyl top containing polymers.

The relaxation of poly(methylmethacrylate) has recently been studied by acoustic relaxation techniques. This molecule can exist in a series of stereoregular forms (Fig. 8). Studies of syndiotactic, heterotactic and isotactic polymers in solution in toluene indicate that these polymers exhibit distinctly different relaxation behaviour. The syndiotactic is similar to that of the heterotactic which is in turn different from that of the isotactic polymer. The observed differences may be related to the greater steric constraints on the internal rotational isomeric process. It is also interesting to note that the amplitude of the energy absorption reflects the magnitude of the changes in energy states and temperature dependence of the relaxation frequency parallels the increased steric interactions going from the syndiotactic to the isotactic polymer. The differences in the stereoregularity of the polymers may readily inferred in the case of the methyl substituted backbone by analysis of their 220 MHz¹H nuclear magnetic spectra. A combination of the spectroscopic studies of the stereo-regularity of the polymers and changes in their relaxation properties may

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in the future provide a powerful method for the characterization of the effects of detailed changes in side group structure on the dynamics of a polymer chain.

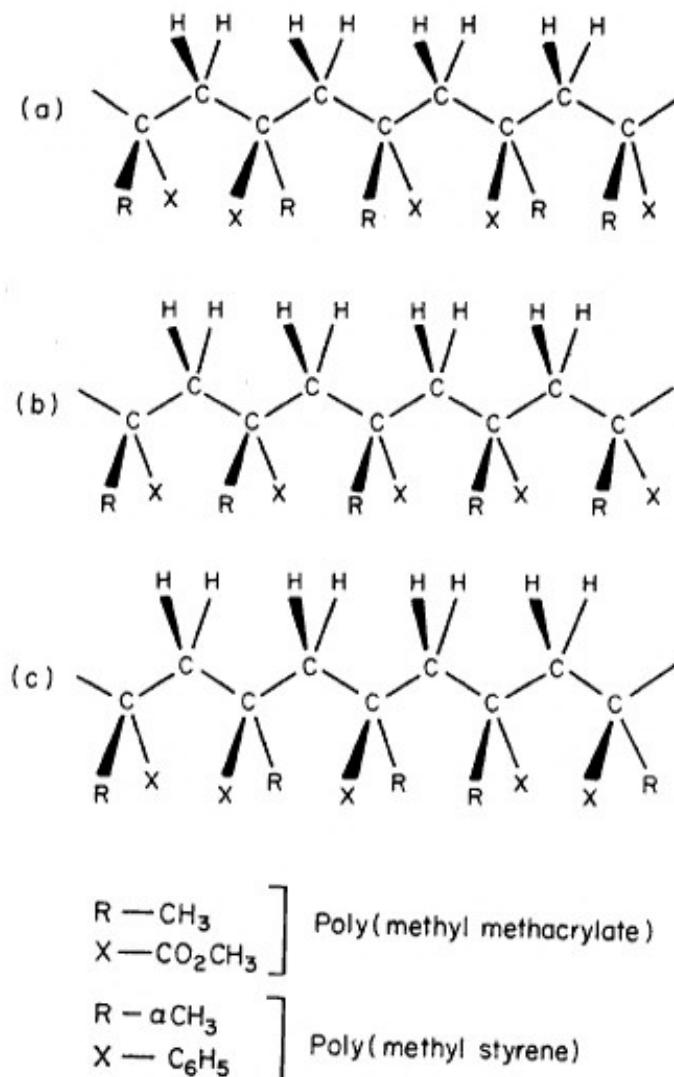


Fig. 8. Structural isomerism in vinyl polymers $-(\text{CH}_2-\text{CXY})_n-$. Tacticity in poly(methylmethacrylate): (a) syndiotactic, (b) isotactic, and (c) atactic.

Branched chain polymers

Branched chain polymers have recently received some attention as possible models for the characterization of the dynamic properties of cross linked polymer structures. The viscoelastic behaviour of a linear polymer may be described in terms of the simple normal mode picture. The addition to a linear polymer of a side group of substantial mass leads to the requirement that the dynamic behaviour of the resultant polymer must be described in terms of processes with nodes at the chain branches. The modified theory is essentially that of the simple

normal mode description with the added restriction that only those modes with nodes at the chain branches are allowed. Dilute solution studies of branched chain polymers of varying flexibility and complexity have confirmed the correctness of this analysis. In practice slight deviations from ideal behaviour have been observed and these can in part be associated with restrictions on the free motion of the chain in the neighbourhood of the chain branches due to steric crowding. The higher the degree of branching the larger the deviation and this is borne out by observations of the dynamic viscosity of the polymers in a good solvent. The type of solvent will influence the dimensions of the polymer and thence the ease of motion of the constituent chains.

Conclusion

It will be apparent to the reader that whilst it is possible to discuss the 'activation energy' for a segmental or normal mode process a considerable gap exists in our knowledge of the detailed shape of the potential surface governing the detailed dynamics of the motion of the polymer chain. Spectroscopic measurements will tend to provide information on a very local part of the potential surface whereas relaxation techniques will be weighted by longer range interactions and provide data on the average interaction potential. A combination of experiment and theory may in the future provide a means of obtaining additional information on the form of the interaction potential and the distribution parameters required to inter-relate the local dynamics with the longer range more cooperative motions of the chain. Recent advances in molecular dynamic calculations have made considerable advances in this direction and it may be anticipated that these studies may in the near future provide estimates of the magnitude of cooperative motion in a variety of polymers. This type of generalized approach is the ultimate aim of many of the current studies in molecular dynamics and it may be expected that one-three intramolecular interactions will be found to play a major part in the determination of the detailed dynamics of the polymer chain in dilute solution.

As a rough guide to the expected amplitudes of various relaxation processes, Fig. 9 depicts the approximate analysis of the overall dynamic behaviour of an ideally flexible chain into the processes discussed earlier. The amplitude as sensed by a particular relaxation experiment will depend on the form of the probe used to monitor the motion (Table 1), its correlation with the motions of the chain and the magnitude of the polymer-solvent and intramolecular potential energy surfaces. A detailed knowledge of the motion of an isolated polymer chain may be expected to ultimately yield charts of the above type which may assist the easy comparison of data on different polymers.

This review has of necessity been restricted in its coverage of the subject of polymer dynamics to those aspects of the subject which the author feels are of

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general interest. As a result certain aspects of this broad subject have received scant coverage and a selection of reviews are presented at the end of the reference section to assist the reader in gaining a more detailed understanding of this most fascinating subject.

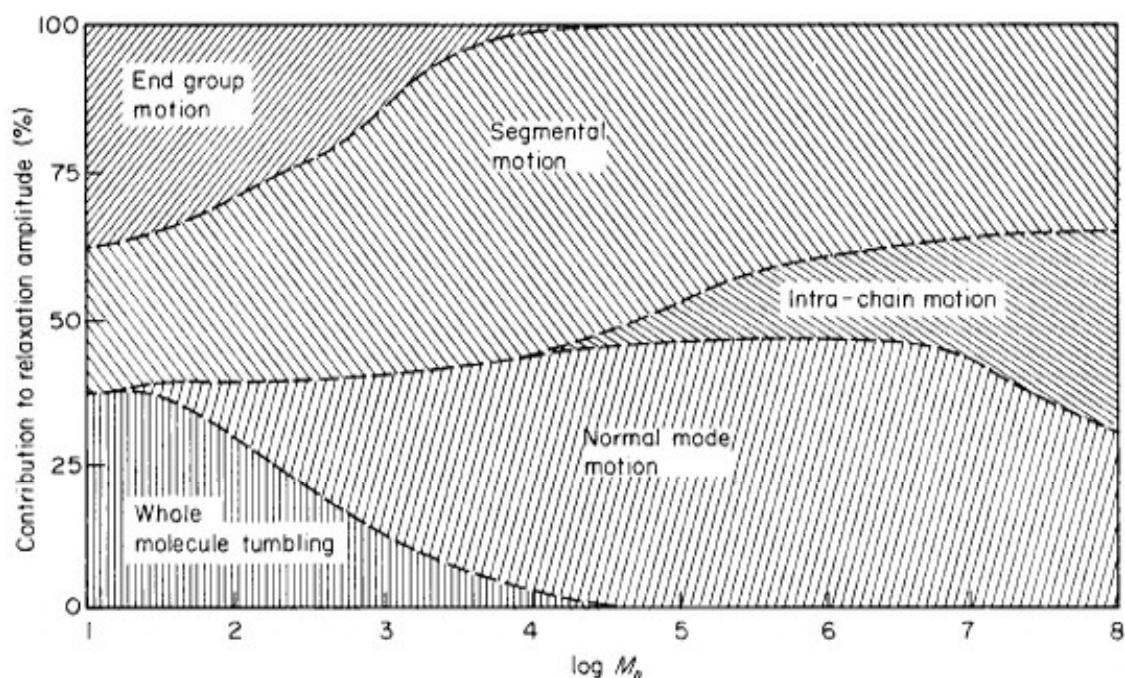


Fig. 9. Analysis of the molecular weight dependence of various relaxation processes. The analysis presented above is typical of the motion of an ideally flexible polymer. It should be remembered that in a particular relaxation experiment not all of the above processes will contribute to the observed relaxation and the prediction of a molecular correlation time requires consideration of the type of motions which will be 'active' in achieving relaxation. Intra-chain motions will refer to intra-chain entanglement in an isolated chain and entanglement in concentrated solutions.

References

1. ORVILLE-THOMAS W.J. (Ed.) (1973) *Internal Rotation in Molecules*. Wiley, New York. This volume contains a series of articles which cover both the experimental and theoretical aspects of the study of internal rotation in small molecules.
2. STOCKMAYER W.H., GOBUSH W. & NORVICH R. (1971) *Pure appl. Chem.* **26**, 537.
3. ROUSE P.A. (1953) *J. Chem. Phys.* **21**, 1272; ZIMM B.H. (1956) *J. Chem. Phys.* **24**, 269. Numerous modifications of this simple theory have appeared but the final results are essentially the same.
4. KIRKWOOD J.G. & RISEMAN J. (1948) *J. Chem. Phys.* **16**, 565.
5. PAUL E. & MAZO R.M. (1968) *J. Chem. Phys.* **48**, 2378.
6. MATSUO K. (1972) Ph.D. thesis, Dartmouth College.
7. NORTH A.M. (1972) *Chem. Soc. Rev.* **1**, 49.
8. WILLIAMS G. (1972) *Chem. Rev.* **1**.
9. SCHAEFER J. (1969) *Macromolecules* **2**, 210.
10. BULLOCK A.T., BUTTERWORTH J.H. & CAMERON G.G. (1971) *Europ. Polymer J.* **7**, 445.