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- (17) The uncertainty in the measurement of proton relaxation times is greater than the expected or observed change after blending with small amounts of either blend component.
- (18) The PMMA- d_8 was synthesized by Dr. Claude Picot, CNRS, France. Cumylpotassium was used as an initiator and the MW was determined by GPC to be 100 000.
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Activation Energies of Local Conformational Transitions in Polymer Chains

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In recent years, much effort has been devoted to understand the mechanism for rapid relaxation processes in polymers. Various theoretical and experimental studies have accumulated on the dynamics of local orientational motions. The fact that these local motions result from conformational transitions of the skeletal bonds from one isomeric state to another is now well established. However, still some controversy remains as to the exact nature and extent, along the chain, of these motions. High frictional resistance naturally prevents the propagation of the configurational rearrangements beyond a finite sequence. However, crankshaft^{1,2} or three-bond³ motions, which leave the tails of the motional unit unchanged, necessitate the passage through at least two barriers between conformers, which is incompatible with the experimentally observed activation energies. Although the scale of motions probed depends on the specific experimental technique (NMR, ESR, fluorescence depolarization, dielectric relaxation, etc.), most experiments reveal an activation energy of about 5 kcal/mol for rapid relaxation processes.⁴ Simulation studies by Helfand and collaborators⁵ demonstrated that isolated single-bond motions accompanied by the translation of chain ends dominate the relaxation behavior. The activation energies associated with those motions, referred to as type 2 motions, are slightly larger than the barrier height between the gauche and trans states. Also, relying on an activation energy of 2.6 kcal/mol measured by NMR for aryl aliphatic esters, Tékely et al.⁶ concluded that type 2 motions are highly probable in long aliphatic subchains, while the higher activation energy (5.6 kcal/mol) for molecules with shorter motional sequences was attributed⁶ to the occurrence of three-bond or crankshaft-like motions. Skolnick and Yaris calculated,⁷ on the other hand, an activation energy of about 2 kcal/mol for the dissipation of the diffusive mode, by parameterizing the Bendler-Yaris⁸ and Skolnick-Yaris⁹ models to NMR experiments on PVA; in comparison, an activation energy of 4 kcal/mol

was measured¹⁰ by dielectric relaxation.

More investigation is clearly required to elucidate the relative contributions of (i) barriers through conformational isomeric states, (ii) frictional resistance of the surroundings, and (iii) constraints imposed by chain connectivity to the observed activation energies. The first two effects are present in small molecules, too, while the latter is characteristic of polymeric chains. The fact that temperature dependence of the excimer fluorescence intensity parallels that in a small molecule analogue, as pointed out by Liao et al.,¹¹ suggests that the apparent activation energy is independent of effect (iii). In fact, calculations reported below yield, invariably, a definite activation energy slightly larger than the barrier to internal rotation of a skeletal bond, regardless of the degree of constraints imposed by the connected tails.

The internal orientational autocorrelation function (OACF) is given by

$$M_{2,\text{int}}(t) = \frac{1}{2} \langle 3 \cos^2 \theta(t) - 1 \rangle \quad (1)$$

where $\theta(t)$ denotes the angular separation between the initial and final (at time t) orientations of the bond investigated and the brackets represent the ensemble average. The subscript int indicates that the global or external reorientation of the sequence to which the bond belongs is not considered. Calculations are performed by keeping the first two bonds of the sequence fixed relative to a laboratory-fixed coordinate system. In experiments such as NMR, ESR, and fluorescence depolarization, $M_{2,\text{int}}(t)$ is measured, during the short time windows of observation.

In recent work,¹² the OACF of the central bond of a finite motional sequence was investigated, with special emphasis on the influence of factors such as first neighbor interdependence and strength of constraints imposed by chain connectivity. The evaluation of the ensemble average in eq 1 necessitates the analysis of all possible transitions between conformers. To this end, the complete set of sequences with various configurations was generated, and normalized stochastic weights or time-delayed joint probabilities were assigned to each transition between those configurations. In accordance with the scheme first introduced by Jernigan,¹³ joint probabilities were obtained as the solution of a master equation describing local dynamics. The parameters such as the chain geometry, the height of saddles between isomeric states, etc., were determined from real chain characteristics. The method allows for the calculation of any dynamic property associated with local conformational transitions. For the complete description of the calculation scheme, the reader is referred to ref 12.

In this note, the above simulation method¹² is used to calculate the activation energy associated with conformational transitions. A finite sequence of n bonds belonging to a polyethylene chain is considered. $M_{2,\text{int}}(t)$ for the last bond of the sequence, whose first bond is held fixed, is calculated for various degrees of constraints: In one extreme case, only transitions conserving the coordinates of the end point of the sequence are allowed. In the other extreme, possible constraints on the motion of the sequence imposed by the connected tail are ignored; i.e., all transitions of the sequence are considered. Neither of the two extremes is a realistic representation of the chain behavior. The end of the motional sequence is not necessarily fixed at its original position during conformational transition (e.g., type 2 motions), while, on the other hand, large swinging motions of the tails are precluded by high frictional resistance. In the intermediate case, only those

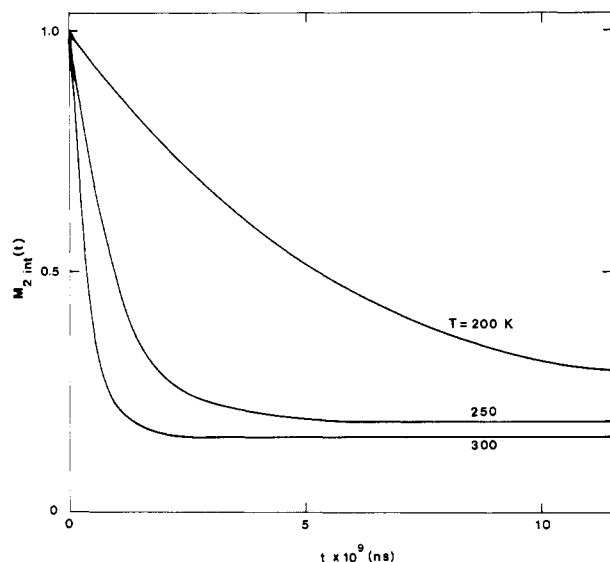


Figure 1. Dependence of $M_{2,int}$ on time for $n = 8$ and $\delta = 2 \text{ \AA}$ at three different temperatures.

transitions resulting in the displacement of the free end within a spherical domain of radius δ are considered. The magnitude of δ is a measure of the severity of constraints imposed by chain connectivity. Larger δ values are physically equivalent to longer sequences undergoing configurational rearrangements since subsequent bonds along the chain will necessarily reorient to accommodate the new position of the displaced end.

Calculations were carried out for $n = 6$ and 8 . The typical time dependence of $M_{2,int}(t)$ is depicted in Figure 1 for $n = 8$ and $\delta = 2 \text{ \AA}$. The curves are drawn for the temperatures $T = 200, 250$, and 300 K . They are found to converge to finite autocorrelation values, depending on the strength of constraints and the temperature. Complete relaxation occurs only when no constraint due to chain connectivity operates. The asymptotic values, $M_{2,int}(\infty)$, to which the internal OACF converges and the relaxation times, τ , corresponding to $1/e$ of the full relaxation are determined. The Arrhenius plot of $\ln(1/\tau)$ vs. $1/T$ is shown in Figure 2. The solid and dashed lines are for $n = 8$ and 6 , respectively. Results are shown for three different degrees of constraint, represented by $\delta = 0$ and 2 \AA and δ_{max} , where the latter denotes the maximum possible displacement of the end. $\delta_{max} = 9.2 \text{ \AA}$ for $n = 6$ and 14.2 \AA for $n = 8$. Lines for $n = 6$ parallel those for $n = 8$ but are slightly shifted below as a result of their longer relaxation time. As pointed out previously,¹² in the absence of the frictional resistance of the surroundings, the relaxation process is more rapid with longer sequences due to the larger number of available paths to relaxation. Nevertheless, it is interesting to note that all curves yield a constant activation energy equal to $3.25 \pm 0.10 \text{ kcal/mol}$ regardless of the sequence size and constraints due to chain connectivity. Thus, although these factors strongly influence the time and extent of relaxation, no effect on apparent activation energies is discernible.

In their Brownian dynamics study, Helfand and collaborators determine the rates from first passage times and hazard analysis.⁵ They extract information about the transitional kinetics from the trajectory generated in simulations of a 200-bond chain, whereas in the present treatment a complete enumeration technique of all possible configurations of a finite sequence is employed. Although the two approaches are different, the calculated activation energies are of the order of one barrier height, in both cases. The value 3.3 kcal/mol obtained in their work⁵ by

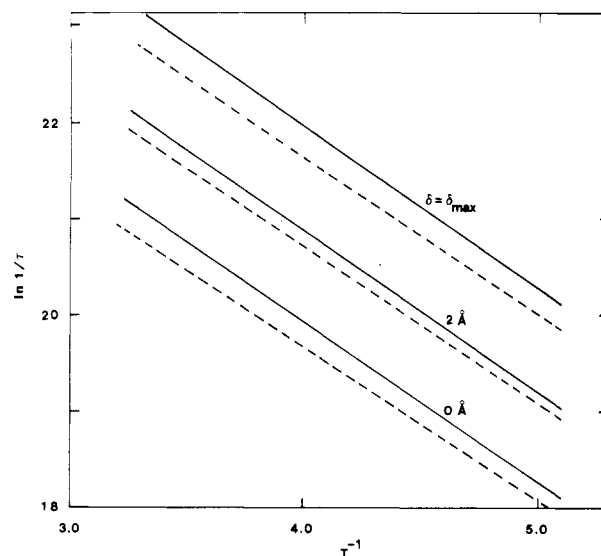


Figure 2. Arrhenius plots, $\ln(1/\tau)$ vs. $1/T$, for various degrees of constraints. Solid lines are for $n = 8$, dashed lines for $n = 6$. τ is in seconds.

using the torsional potential parameters proposed by Ryckaert and Bellemans¹⁴ exactly coincides with our result of $3.25 \pm 0.1 \text{ kcal/mol}$.

The value $3.25 \pm 0.1 \text{ kcal/mol}$ compares favorably with results of NMR experiments on perfluoroalkane chains by Matsuo and Stockmayer¹⁵ where mean orientational correlation times for C-F and C-H bonds are found to have equal activation energies of about 3 kcal/mol . The barrier for internal rotation about typical $\text{CH}_2\text{-CH}_2$ bonds is slightly over 3 kcal/mol , from spectroscopic data and conformational analysis.¹⁶⁻¹⁸ This value is exactly reproduced in the present theoretical treatment. It is thus confirmed that, of the experimentally measured activation energies, a quantity equal to the barrier height for single-bond internal rotation accounts for the energy associated with local conformational transitions, while the remaining quantity corresponds to frictional effects.

Registry No. Polyethylene, 9002-88-4.

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