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Analysis of the Pressure Dependence of the Crystallization Kinetics of *cis*-Polyisoprene

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ABSTRACT: Published crystallization kinetics data for *cis*-polyisoprene at pressures up to 3 kbar have been analyzed by using regime III of the Lauritzen–Hoffman theory and experimentally determined values of the input parameters T_∞, U^*, and T_m°. This theory was found to be applicable to such an analysis, and values of the fold surface free energy σ_e calculated confirmed the large and sudden increase in σ_e at a pressure approaching 1 kbar, found earlier independently from lamellar thickness data. A model has been proposed, involving a pressure-induced change in adjacent reentry fold conformation, to explain this behavior. The low values obtained for σ_e and the work of chain folding q have been tentatively attributed to low adjacent reentry fold fractions, suggesting that cilia emerging from the fold surface in regime III crystallization have low excess energies due to minimization of amorphous chain overcrowding.

1. Introduction

Pressure is a thermodynamic variable of obvious theoretical importance. It is also of considerable practical significance in polymer crystallization, since fabrication processes such as injection molding and extrusion apply high pressures to the polymer during crystallization. While complicating factors such as molecular orientation and nucleation density undoubtedly play very important roles in this process, an investigation of the effect of pressure on crystallization kinetics is an essential first step to understanding the crystallization of polymers during processing.

Some studies on polymer crystallization under pressure have been made, but most of them have been concerned with the morphology, particularly the "chain-extended" crystals produced in some polymers such as polyethylene. Kinetics studies seem to have been relatively ignored.

Phillips and Edwards[1] studied the crystallization kinetics of *cis*-polyisoprene (as the *Hevea* form of natural rubber) at pressures ranging from atmospheric to 3.5 kbar. This polymer was chosen because it could be stained with osmium tetraoxide for transmission electron microscopy, this staining technique serving also to stop the crystallization process at any given instant. Moreover, the relatively slow rate of crystallization at convenient temperatures and pressures simplified the experimental procedure. Growth rate and lamellar thickness data were obtained by transmission electron microscopy of thin films. The growth rate curves at any given pressure were bell-shaped, as expected. The application of pressure resulted in moving the curves to higher temperatures and in increasing the maximum growth rate over the first 1.5 kbar.

In this paper, we present an analysis of the high-pressure crystallization kinetics data of Phillips and Edwards[1] for *cis*-polyisoprene. The analysis of atmospheric-pressure data[2] has been reported earlier.[3] We have previously determined[4-6] the pressure dependence of the required input parameters U^*, T_∞, and T_m°.

2. Input Parameters

We have used the high-pressure crystallization kinetics data of Phillips and Edwards,[1] reported as linear growth rate G as a function of crystallization temperature T and pressure P, at pressures from atmospheric to 2.5 kbar. At each pressure, the WLF temperature T_∞ and WLF energy term U^* were calculated from the fitted[4] polynomials

$$T_\infty = -122.7 + 17.78P - 0.673P^2 \tag{1}$$

$$U^* = 17.26 + 1.57P - 0.099P^2 \tag{2}$$

and the equilibrium melting temperature T_m° was calculated[6] from

$$T_m^\circ = 35.5 + 27.0P - 1.49P^2 \tag{3}$$

where T_∞ and T_m° are in °C, U^* is in kJ/mol, and P is in kbar. Equations 1 and 2 were fitted to dielectric data up to 3.8 kbar, and eq 3 was fitted to equilibrium melting data up to 2.6 kbar.

Values of the heat of fusion per unit crystal volume, Δh_f, are unavailable at high pressures and therefore had to be assumed invariant at the atmospheric-pressure value of 6.4×10^7 (J/m^3).[7] At least in the case of polyethylene this is a good approximation, as seen from the work of Karasz and Jones,[8] in which the heat of fusion per unit mass of crystal falls by no more than 2% over 1.6 kbar. Crystal dimensions, similarly, were assumed invariant at their atmospheric-pressure values: molecular width $a = 0.445$ nm and layer thickness $b = 0.623$ nm.[2] This is justified by the very low polymer crystal compressibilities normally encountered (typically ~1%/kbar).

The growth rate contours for *cis*-polyisoprene in the P–T plane are presented in Figure 1, together with the pressure dependence of the parameters T_∞ and T_m°. This figure clearly illustrates bounding of the crystallization temperature range by T_∞ and T_m°, as well as the movement of the entire range to higher temperatures with increasing pressure.

The temperature range $T_m^\circ - T_\infty$ available for crystallization increases with pressure at a rate of about 14 °C/kbar, which is presumably the reason for the much higher maximum growth rates at high pressures. This observation contrasts well with that for *trans*-polyisoprene,[9] where the reduction in maximum growth rate with pressure was attributed to a narrowing of the range $T_m^\circ - T_\infty$ at about 5 °C/kbar.

0024-9297/84/2217-0248$01.50/0

Table I
Analysis of High-Pressure Kinetics Data

input parameters				$K_g \times 10^{-5}$, K^2	$\sigma\sigma_e \times 10^3$,[a] J^2/m^4	σ_e,[b] J/m^2	SE, %
P, kbar	$T_m°$, K	U^*, kJ/mol	T_∞, K				
0.0001	308.7	17.26	150.7	2.56	0.29	0.021	1.6
0.5000	321.8	18.02	157.0	2.96	0.33	0.024	12.1
1.0000	334.2	18.73	163.3	5.55	0.59	0.042	5.1
1.5000	345.8	19.39	169.4	5.54	0.57	0.041	10.6
2.0000	356.7	20.00	175.3	5.72	0.57	0.041	14.2
2.5000	366.9	20.57	181.0	4.81	0.47	0.034	43.5

[a] $\sigma\sigma_e$ calculated from eq 8, with Δh_f independent of pressure. [b] σ_e calculated assuming σ invariant at 0.014 J/m².

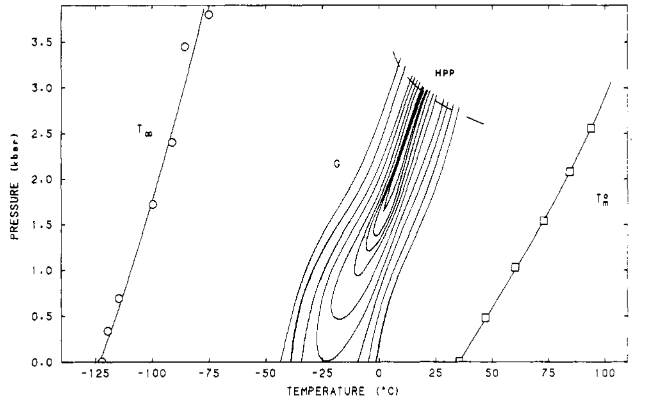

Figure 1. Growth rate contours G^1 for *cis*-polyisoprene bounded by the WLF temperature T_∞[4] and the equilibrium melting temperature $T_m°$.[6] Values of G are (inward) 0.05, 0.1, 0.25, 0.5, 1, 1.5, 2, 2.5, and 3 μm/h. The high-pressure phase (HPP) appears in the P–T region above the dashed line.

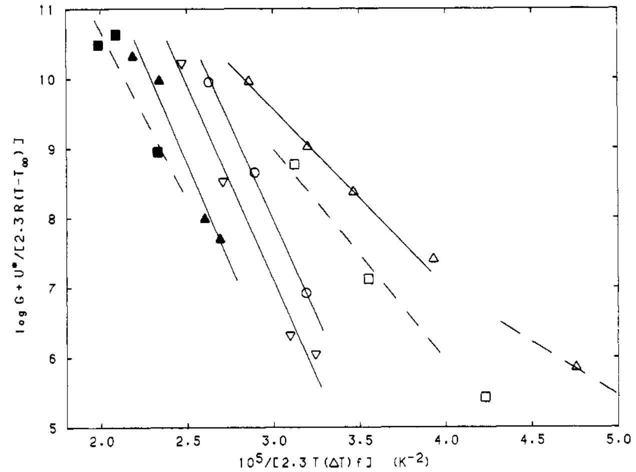

Figure 2. Plots of kinetics data at high pressures: (△) 1 bar; (□) 0.5 kbar; (○) 1 kbar; (▽) 1.5 kbar; (▲) 2 kbar; (■) 2.5 kbar.

3. Analysis of Crystallization Kinetics

We have analyzed the kinetic data in terms of the widely used Lauritzen–Hoffman (LH) theory,[10] which is relatively simple but has been successfully used for several polymers.[11] All of the kinetic theories available, including the LH theory, have been derived for atmospheric-pressure applications, and pressure does not explicitly enter into any of the resulting equations. They should be applicable at any pressure, however, if all of the parameters are corrected for the effect of pressure and if the fundamental crystallization mechanisms involved do not change.

According to the LH theory, the linear growth rate G of a chain-folded polymer crystal is given by

$$G = G_0 \exp\left(\frac{-U^*}{R(T - T_\infty)}\right) \exp\left(\frac{-K_g}{T(\Delta T)f}\right) \tag{4}$$

where $\Delta T \equiv T_m° - T$ is the undercooling and f is a correction term of the order of unity, usually represented by

$$f = 2T/(T_m° + T) \tag{5}$$

Equation 4 indicates that the kinetics data should be linear when plotted with abscissa X and ordinate Y, given by

$$X = 1/[2.303T(\Delta T)f] \tag{6}$$

$$Y = \log G + U^*/[2.303R(T - T_\infty)] \tag{7}$$

The high-pressure kinetics data are plotted in this manner in Figure 2.

An apparent regime II–regime III transition has been reported[3] for the crystallization kinetics of *cis*-polyisoprene at atmospheric pressure. This transition occurred at about −13.9 °C, corresponding to $X = 3.71 \times 10^{-5}$ K^{-2}. The high-pressure data are not extensive enough to analyze in terms of a regime transition, but it is reasonable to assume that the transition occurs at about the same undercooling at all pressures and hence at about the same value of X. Figure 2 indicates that all of the high-pressure data, except for one point, lie well below the X value of the transition. Hence all of them were considered to be on the low-temperature (regime III) side of the transition, this being further justified by the linearity of the plots. At atmospheric pressure, the data do lie on both sides of the transition, so only those points having X values below the break were analyzed in terms of regime III, the other two points being neglected.

The regression lines are shown in Figure 2. Some of these are poorly defined and are shown dashed. Values of the kinetic rate constants K_g of eq 4 are given by the negative slopes of these lines and are listed in Table I.

In regime III, recently proposed by Phillips[12] and Hoffman,[13] the niche separation during crystal growth is reduced to the extent that it approaches the molecular width a, and K_g is given by

$$K_g(\mathrm{III}) = (4b\sigma\sigma_e T_m°)/(k\Delta h_f) \tag{8}$$

where b is the layer thickness, σ and σ_e are the lateral and fold surface free energies, and Δh_f is the heat of fusion per unit volume of crystal at the equilibrium melting temperature $T_m°$. Values of the product $\sigma\sigma_e$, listed in Table I, were calculated from eq 8.

Since there is no obvious reason to expect σ to depend significantly on pressure, it was assumed to be independent of pressure. Its value was estimated[3] at atmospheric pressure to be 0.014 J/m². With this assumption, the kinetically determined values of the fold surface free energy σ_e were calculated and are listed in Table I. As is obvious from the curves in Figure 2, the data at some pressures are more comprehensive than at others. In some cases only three data points were available, leading to larger errors in estimation. Standard deviations (SE) were calculated for the K_g values and are also appropriate for the values of $\sigma\sigma_e$ and σ_e, which were derived directly from

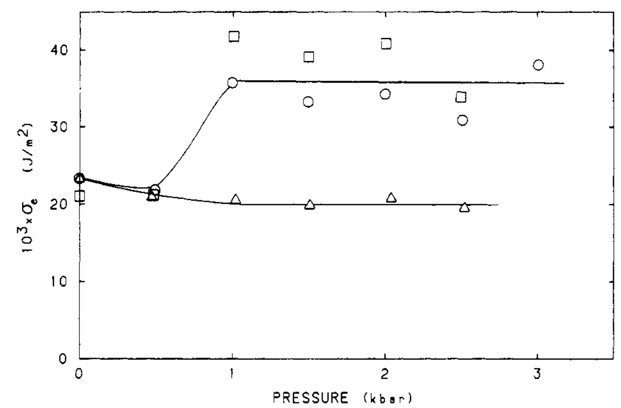

Figure 3. Pressure dependence of the fold surface free energy σ_e: (□) growth rate data, $P_c = P$; (○) lamellar thickness data, $P_c = P$;[6] (△) thermodynamic data, P_c = 1 bar.[6]

K_g. They are presented in Table I. Except for the 2.5-kbar data, errors were generally better than 15%.

A sudden increase in σ_e at and above 1 kbar, to almost double its atmospheric-pressure value, is clearly present. This is very similar to the pressure variation of σ_e determined from lamellar thickness.[6] The strong correlation existing between σ_e values from these two quite different sets of experimentation indicates clearly that, despite the major assumptions and the inherent errors involved, there is a major discontinuity in the end surface free energy. These two sets of σ_e data, obtained for samples crystallized under pressure, are compared in Figure 3. The points could be brought closer together if a slightly higher value of σ were chosen or if it were allowed to increase slightly with pressure. Figure 3 also shows σ_e for material crystallized at atmospheric pressure,[6] which, in contrast, is practically independent of pressure.

The values of the lamellar thickness and the growth rates were determined[1] on the same samples, but the measurements are quite independent of each other and so are the analyses. Consequently, the good correlation between the $\sigma_e(P)$ values from these data obtained from separate thermodynamic and kinetic experiments strongly supports the applicability of the basic LH theory to the high-pressure crystallization kinetics of *cis*-polyisoprene.

4. Pressure Dependence of σ_e

A pressure-induced change in σ_e such as that shown in Figure 3 has not been reported before for any polymer. Various possible explanations for the observed behavior are discussed below.

4.1. Change in Crystal Structure. Pressure-induced changes in crystal structure are well-known. Such a change would indeed explain the σ_e data obtained, with several mechanisms possible. One of these could be an actual change in σ_e, because a different fold conformation almost certainly would be required to connect adjacent stems in a different structure. The relation between fold conformation and σ_e will be discussed later in this paper. Another mechanism could involve changes in the heat of fusion and melting temperatures accompanying the structure change (see section 4.2).

There are, however, several reasons to believe that there is no change in crystal structure occurring at a pressure anywhere near that of the observed change in σ_e. First of all, Edwards and Phillips[1] have reported that electron diffraction studies of *cis*-polyisoprene crystallized under high pressures indicated that no change in crystal structure had occurred. This is not entirely conclusive evidence, because they had to quench their samples and then study them at atmospheric pressure, for lack of high-pressure diffraction facilities. It could be argued that a high-pressure structure, if present, might have reverted to the low-pressure form on release of pressure; however, the growth rate and lamellar thickness data are relatively free of this problem because the samples were stained in situ. Such a reversion is unlikely, however, since it is known that the reverse process certainly does not occur, as concluded from the insensitivity of σ_e to pressure for material crystallized at atmospheric pressure.[6]

Another argument against a change in crystal structure is the smooth variation of $T_m°$ with pressure,[6] which is apparently free of any perturbation which would most likely accompany the structural change.

High-pressure X-ray data are required to conclusively establish that a change in crystal structure does not occur, but at present such an assumption seems justified by the facts discussed above.

4.2. Change in Heat of Fusion. The apparent change in σ_e could be explained in terms of a change in the heat of fusion Δh_f, irrespective of whether any real change in σ_e takes place. This is true for the σ_e values determined from both the lamellar thickness and the growth rate.

The heat of fusion at high pressures is unknown and has been assumed invariant at the atmospheric-pressure value. Some dependence on pressure may certainly be expected, but this cannot be very large and, more importantly, should be gradual. A *step* change in Δh_f is most unlikely in the absence of any change in the crystal structure.

4.3. Change in Crystallization Regime. The value of σ_e obtained from a given experimental kinetic rate constant K_g is dependent on the crystallization regime assumed. However, the low-pressure data are being analyzed in terms of regime III. Regime II is unacceptable at high pressures, at least with experimental U^* and T_∞ values, because it would indicate that the value of σ is greater than or comparable to σ_e. If a sudden change were to occur from regime III at low pressure to regime II at high pressure, it would *decrease* the apparent value of σ_e by a factor of 2, not increase it.

In any case, the lamellar thickness is independent of the crystallization regime, and the pressure dependence of σ_e values obtained from such data cannot be explained in this manner.

4.4. Change in Growth Face. The conformation of a fold connecting two adjacent stems in a crystal depends on their relative separation and orientation, and hence, it depends on the crystallographic plane in which these stems lie. Since σ_e is a direct function of fold conformation, it can be altered by a change in the growth face, which need not involve a change in crystal structure.

Such an explanation has been offered for the lower melting β crystals in *cis*-polyisoprene.[2] However, this morphology is readily distinguished in the micrographs, and they are present at atmospheric pressure but gradually suppressed at higher pressures. No distinct morphological change was reported at 1 kbar.

4.5. Change in Fold Conformation Directly. It is possible for the fold conformation to be directly altered by the application of pressure, without any changes in crystal structure or growth face occurring. A model for this process is proposed and discussed below.

5. Effect of Pressure on Fold Conformation

There are two aspects of the pressure dependence of σ_e for *cis*-polyisoprene that need to be explained. One is the large increase in σ_e just below 1 kbar, which is distinctly shown by data obtained from two different analyses. The increase is probably discontinuous, or at least very steep, with a minimum slope of about 200%/kbar. The other aspect of this phenomenon is the relative insensitivity of σ_e to pressure, up to 2.5 kbar, for material crystallized at atmospheric pressure. Both of these features are compatible with a proposed model involving changes in the fold conformation of molecules in the crystalline phase.

The higher free energy of the fold surface has been attributed (see ref 11) entirely to the work of chain folding q, the relation being given by

$$\sigma_e = q/2A_0 + \sigma_{e0} \tag{9}$$

where $A_0 = ab$ is the cross-sectional area of each chain and σ_{e0} ($\simeq \sigma$) is the value that would result if no work were required to form the fold. Hoffman et al. have suggested that the value for polyethylene ($q \simeq$ 4–5 kcal/mol) is compatible with the approximate torsional energy of a geometrically feasible fold.

Consequently, the pressure dependence of σ_e should be a manifestation of the pressure dependence of q, and hence of that of the conformation of the fold. It is thus sufficient for the model to show the appropriate change in the fold conformation.

Some amount of adjacent reentry (AR) of the chains is assumed. It is true that with the high undercoolings and high sample molecular weights considered here (which are responsible for regime III crystallization) adjacent reentry is hindered. But it has been estimated[13] that the probability of nonadjacent reentry cannot exceed $^1/_3$, even in regime III, due to statistical analyses based on amorphous density considerations.

The model assumes that two (or more) molecular conformations are possible in forming the fold, each representing a local energy minimum, but that the lowest energy state at atmospheric pressure is not also the lowest volume state. Consequently, another state will have the lowest total energy at some higher pressure due to the reduction in volume.

While very involved numerical computations are required to obtain reliable conformational energy data, a qualitative idea of the problem can be obtained from a simple skeletal molecular model. Such a model provides an approximate analogue representation of a macromolecule.

A molecular model was constructed based on crystallographic data for *cis*-polyisoprene from Nyburg[14] and Natta and Corradini.[15] The (100) fold plane deduced by Edwards[2] for the α lamellae was used. The fold surface was assumed to be parallel to the basal plane, which is very nearly perpendicular to the chain axis (β = 92°).

Very little is known about the actual fold structure, even for simple polymers like polyethylene. However, it is clear that in *cis*-polyisoprene even the tightest fold must contain at least two monomer units. It was found that two adjacent stems in crystallographic register could be connected by a two-monomer length of chain by deforming it in torsion but without the need for significant bond angle or bond length alteration. Two separate conformations were found, with about the same strain level, but with one rising to a significantly larger height than the other. It was impossible to convert one conformation into the other without impossible bond angle deformation (e.g., 90° bend), indicating the presence of a very large energy barrier between the two. A fold surface projection of the two conformations is sketched in Figure 4. The height of the highest atom in each is indicated.

The model was quite crude in that there was almost no measure of torsional energies, and excluded-volume requirements had to be satisfied in large part visually. Moreover, an isolated fold was considered. But it did nevertheless mimic most of the required features. At least two relatively low-energy states were found, one of them occupying a greater volume and separated by a large potential energy barrier. It could not be established that the state with the greater volume had the lower strain energy.

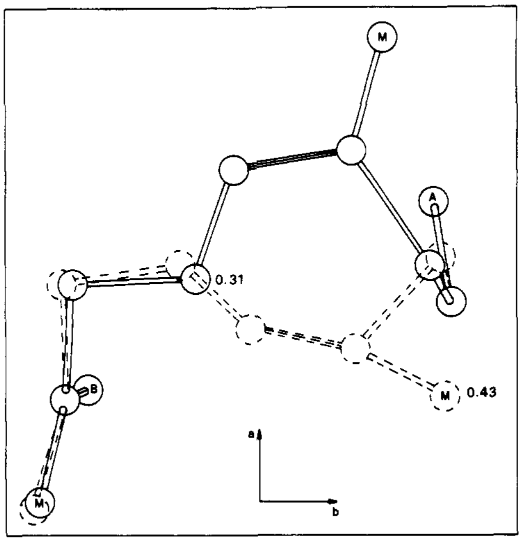

Figure 4. Fold surface projections of carbon atoms in two possible fold conformations in *cis*-polyisoprene. Numbers are heights (in nm) of highest carbon atoms from surface. Base (A, B) and methyl (M) carbon atoms are indicated.

Table II
Variation of the Work of Chain Folding q with Pressure[a]

	from l data		from G data	
P, kbar	σ_e, J/m^2	q, kJ/mol	σ_e, J/m^2	q, kJ/mol
0.001	0.024	3.3	0.021	2.4
0.500	0.022	2.7	0.024	3.4
1.000	0.036	7.5	0.042	9.6
1.500	0.033	6.5	0.039	8.5
2.000	0.034	6.8	0.041	9.2
2.500	0.031	5.8	0.034	6.8

[a] $\sigma_{e0} \simeq \sigma$ = 0.014 J/m^2 at all pressures. From ref 6.

No claim is made regarding the uniqueness of this model in satisfying the required features. In fact, it is noted that the two fold conformations need not have the same length, as assumed here. It is entirely possible that the lower energy state is longer and looser and hence occupies a greater volume.

The large energy barrier between the two conformations provides an explanation for the insensitivity of σ_e to pressure for material crystallized at low pressure. It is apparently necessary for the conformation to be adopted during the crystallization process; once crystallization has occurred, the energy barrier is so large as to forbid any significant conformational change even at high pressures.

The work of chain folding q was calculated by using eq 9 and the σ_e values of ref 6 and Table I of this work, which were found from lamellar thickness and growth rate data, respectively. As before, σ was considered invariant at 0.014 J/m^2. The resulting q values are listed in Table II.

The most noticeable feature of these values is that they are very low. In fact, they are certainly too low at atmospheric pressure to correspond to any kind of tight fold whatsoever and might well be too low even for a very loose adjacent reentry fold. One possible explanation for this could be that only a fraction of the folds are AR folds.

Lower limits of the AR fold fraction have been proposed. Frank[16] has suggested $\simeq$0.7, on essentially qualitative arguments. Hoffman[17] has suggested a value of 0.3–0.5. He has also pointed out that the AR fraction will be lowest at high molecular weights. The reason for the existence of a lower limit is basically the need to avoid anomalously high amorphous densities. It should be noted, as Frank[16] has pointed out, that the value depends on the tilt angle between the chain direction and normal to the fold surface. The above values assume no tilt, but at least some tilt is known to occur in, e.g., polyethylene, which if it occurred in *cis*-polyisoprene would further depress the lower limit.

Fringed-micelle-type chain exits from a crystal have been suggested (see ref 11) as having very high fold surface free energy σ_e due to chain overcrowding. However, if this problem is avoided by keeping above the lower limit of AR folding, such chain exits could have very low σ_e.

Considering the above arguments, as well as the very high molecular weight ($\bar{M}_w > 10^6$) of this polymer and the regime III crystallization process, it is possible that the AR fold fraction r is quite low and that this effect is responsible for the low σ_e values. If, as postulated above, σ_e is of the order of σ for a cilium or loose nonadjacent reentry fold, q is given by

$$q = (\sigma_e/r - \sigma_{e0})2A_0 \qquad (10)$$

instead of by eq 9, with σ_e being the effective (measured) surface free energy rather than that corresponding to an AR fold. Using Hoffman's "limiting" value of $r = 0.3$ gave $q \simeq 21.4$ kJ/mol = 5.1 kcal/mol at atmospheric pressure, which is a reasonable value for an essentially linear aliphatic chain, being slightly above that quoted for polyethylene.[11] This value would be even higher if r is lowered (by tilt) or if the heat of fusion is higher than the value used (6.4×10^7 (J/m^3)).

The high-pressure value of q, using $\sigma_e \simeq 0.035$ J/m^2 (see Figure 3) and $r = 0.3$ as before, was found to be 34.3 kJ/mol = 8.2 kcal/mol, which is an increase of ~60% over the low-pressure value.

6. Conclusions

The Lauritzen–Hoffman theory[11] was found to be suitable for the analysis of isobaric high-pressure crystallization kinetics data for *cis*-polyisoprene. The applicability of this theory is further justified by the similar σ_e values, and their pressure dependence, calculated from independent lamellar thickness data[6] and crystallization kinetics data.

The fold surface free energy σ_e for material crystallized under pressure increases suddenly between 0.5 and 1 kbar to a value significantly higher than that at low pressure. On the other hand, for material crystallized at atmospheric pressure, σ_e is practically independent of pressure.[6] A model involving a pressure-induced change in the fold conformation of a macromolecule in the crystal apparently satisfies these observations qualitatively. Several other possible explanations have been found to be inappropriate.

The σ_e values obtained for *cis*-polyisoprene are somewhat lower than typical values for other polymers, and the work of chain folding q, calculated as suggested by Hoffman et al.,[11] is unacceptably low. It is possible that this is because only a small fraction of the folds are of the adjacent reentry type.

Acknowledgment. This research has been supported by the Polymers Program of the National Science Foundation under Grants DMR 78-24696 and DMR 81-06033.

Registry No. Polyisoprene (homopolymer), 9003-31-0.

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Diffusion of Brownian Spheres in Semidilute Polymer Solutions

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Received June 21, 1983

ABSTRACT: We develop a theory of the dependence on polymer concentration of D/D_0, the diffusion coefficient of dilute Brownian spheres of radius R in a semidilute polymer solution relative to the pure solvent value. The result is $D/D_0 = \exp(-\kappa R)$, where κ is the screening constant of the semidilute polymer solution. For rodlike polymers, $\kappa = (\zeta_L n_L/\eta)^{1/2}$, with n_L and ζ_L the rod number density and friction coefficient, respectively, and η the fluid viscosity. For random coil polymers with Debye–Bueche screening, $\kappa = (\zeta_a n_a/\eta)^{1/2}$, with ζ_a and n_a the monomer friction and number density, respectively; thus $\kappa \sim n_a^{1/2}$. Other dependences of κ on n_a were obtained by Edwards and Freed and by de Gennes. Therefore, the above D/D_0 expression can serve as a probe of screening in the semidilute regime. Comparison with experiments for rod and coil solutions are made, and good agreement is found with the above D/D_0 expression with $\kappa R \sim n_a^{1/2}R$.

I. Introduction

In a dilute polymer solution the monomer density is very inhomogeneous since there are polymer–solvent and pure solvent regions. In the semidilute regime, where the polymer coils overlap extensively yet the monomer volume fraction $\phi \ll 1$, the monomer density is quite homogeneous. It has been suggested that it is useful to describe a semidilute polymer solution as a porous "sponge" through