Table V
Characteristics of the α Relaxation

Sample	$T_\alpha(E'')^a$	$T_\alpha(\tan\delta)^a$	tan δ magnitude^a
HYC3^b	−20	−8	0.45
HYC4^b	−12	0	0.46
HYC5^b	8	30	0.50
HYC6	20	76	0.13
HYC7	63	118	0.16
HYC8	70	127	0.18

^{a} At 110 Hz. ^{b} α relaxation and β relaxation overlap.

the great influence of the crystal phase in polyethylene-like materials on this motion.

The α Relaxation. The characteristics of the α relaxation are collected in Table V. The overlap of the α and β relaxations in samples HYC3, HYC4, and HYC5 makes a quantitative discussion difficult. However, there seems little doubt that in these derivatives of very low crystallinity, the α relaxation originates in motions accompanying the melting of small imperfect crystals and not from the conventional polyethylene α mechanism involving intracrystalline chain motions prior to melting. Table V indicates that the melting range in these derivatives encompasses the temperature of the α relaxation. On the other hand, the α relaxation in samples HYC6, HYC7, and HYC8 very probably does originate in intracrystalline motions and perhaps partially in interlamellar slip mechanisms as well.

Conclusions

The series of studies on the polypentenamer derivatives together with those of other workers on a number of other polymers begin to point toward the general conclusion that the two-phase model is an adequate representation of polymer behavior only in the case where the "amorphous phase" is of a sufficiently different structure from the "crystalline phase" that it cannot crystallize under any circumstances. Thus in isotactic polystyrene, crystallinity has no effect on the glass transition temperature or relaxations accompanying it and the same is true of polypropylene (and the cis–trans isomers of polypentenamer). On the other hand, polyethylene terephthalate and the polypentenamer derivatives have glass transition behavior which is greatly affected by crystallinity. The mechanism of the interaction of the "crystalline" and "amorphous" phases is by no means clear. The elucidation of the nature of this interaction will require extensive additional investigation.

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Dynamics of Stretched Polymer Chains

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ABSTRACT: We consider the internal modes of a strongly stretched chain ($\overline{Z}/R_0 \gg 1$, $\overline{Z}$ is the average end-to-end length, and R_0 is the radius of the free coil) including both excluded volume effects and hydrodynamic interactions. It is shown that the tensile screening length $\xi_t = (\beta f)^{-1}$ for excluded volume effects[1] also plays a similar role for the hydrodynamic interactions.[2] Scaling arguments are then employed to derive expressions for the width of the quasi-elastic incoherent neutron scattering peak. All our results are restricted to dimensional power laws and lack precise numerical coefficients.

I. Introduction

The purpose of this investigation is to study the internal dynamics of deformed, isolated, flexible polymers. The deformation is achieved by an external tensile force **f** applied to the ends of the chain. Such a situation might obtain, for example, (a) with polar molecules in electric fields (assuming that the monomer moment has a component along the backbone axis), (b) in the presence of strong velocity gradients[3] (although the nature of the force is slightly more complex in this case), (c) for a chain portion between cross-links in a stretched network.

In a previous paper,[1] we demonstrated that a long, stretched, flexible polymer in the presence of excluded volume interaction could be considered as an ideal coil of "tensile blobs" of radius $\xi_t = (\beta f)^{-1}$ [$\beta = (k_BT)^{-1}$]; i.e., for distances

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exceeding ξ_t the excluded volume effects are effectively screened out while within a blob they are maintained. In particular, it was determined that for $\xi_t < R_F$ ($R_F = aN^\nu$ is the Flory radius where N is the polymerization index, a is the monomer size, and $\nu = \frac{3}{5}$ in three dimensions) the stress–strain relationship became nonlinear. The scaling equation for the average end-to-end length $\overline{Z}$ in response to a tension $\mathbf{f}$ directed along the z axis is

$$\overline{Z} = R_F \Phi(R_F/\xi_t) \tag{1}$$

where $\Phi(x) \sim x$ for $x \ll 1$ and $\Phi(x) \approx x^p$ for $x \gg 1$ where $p = \nu^{-1} - 1$. This leads to $\overline{Z} \propto f^{2/3}$ in the strongly stretched regime.

The present paper deals with quasimacroscopic movements of a polymer in the strongly stretched limit ($\xi_t \ll R_F$). The slow motions of a long flexible molecule are often discussed in terms of two cases: (1) Rouse[4] or "free draining limit" where all hydrodynamic interactions between monomers are neglected; (2) Zimm[5] regime where these interactions are taken into account. For ideal chains, i.e., excluded volume effects are neglected, the width $\Delta\omega_q$ of the quasielastic neutron scattering peak for momentum transfer $\hbar q$ has been calculated for both limits.[6,7] In the free draining case,[6] the result is

$$\Delta\omega_q \approx 10^{-2} W (qa)^4 \tag{2}$$

where a is the monomer–monomer separation and

$$W = 3k_B TB/a^2 \tag{3}$$

B is the mobility of a single monomer. In the Rouse limit, deformation of the coil has little effect in the incoherent scattering but modifies the coherent width to vary as q^2. Because incoherent scattering dominates in highly protonated systems, we shall restrict our attention to this case. For a coil with hydrodynamic interactions (hydrodynamic radius b comparable to a), the long-range character of the velocity field dramatically modifies the wave vector dependence of the width to give[7]

$$\Delta\omega_q \approx 10^{-1}(b/a)\tau_0^{-1}(qa)^3 \sim \frac{k_B T}{\eta} q^3 \tag{4}$$

where the relaxation rate[8] is

$$\tau_0^{-1} = k_B T/2\pi\eta a^2 b \tag{5}$$

It is useful to note that in the Zimm limit $\Delta\omega_q$ is independent of both microscopic lengths a and b. In section II, we show that for stretched ideal chains in the presence of hydrodynamic interactions, the situation is intermediary between the Rouse[2] and Zimm[3] cases, depending on $q\xi_t$. The tensile screening length ξ_t also appears as the characteristic distance beyond which the hydrodynamic interactions between monomers give only logarithmic corrections to free draining results. Thus, for $q\xi_t \gg 1$, Zimm behavior is maintained, while for $q\xi_t \ll 1$ we have effectively a Rouse chain but with the beads of radius a replaced by blobs of radius ξ_t.

More recently, de Gennes[9] has rederived the Rouse and Zimm modes for unstretched molecules taking into account excluded volume effects. He finds that the q^4 dependence of $\Delta\omega_q$ in the free draining limit is renormalized to vary as q^p where $p = 2 + \nu^{-1} = 3.67$; in the Zimm limit the q^3 behavior remains unchanged. In section III, we generalize the results of section II to include the excluded volume effects using scaling arguments similar to those employed by de Gennes.[9] For large momentum transfer the q^3 behavior is again recovered. For $q\xi_t \ll 1$, we find a modified Rouse spectrum with $\Delta\omega_q \sim q^r$ ($r = 2/\nu = 3.33$). The difference between the exponents p and r caused by stretching is a result of the nonlinear stress–strain relationship[1] for $\xi_t < R_F$.

II. Ideal Chains

In this section, we consider the dynamics of an ideal stretched chain ($0 < \overline{Z} \ll Na$, N is the number of monomers in the chain). If $\mathbf{r}_n$ denotes the position of the nth monomer, we may write its equation of motion in the form

$$\frac{\mathrm{d}\mathbf{r}_n}{\mathrm{d}t} = B\boldsymbol{\phi}_n + \Sigma_m \delta\mathbf{v}_m(\mathbf{r}_n) \tag{6}$$

where $B \simeq (6\pi\eta b)^{-1}$ is the mobility of a single monomer (recall we shall later treat b as indistinguishable from a), $\boldsymbol{\phi}_n$ is the net force on the nth unit, and $\delta\mathbf{v}_m(\mathbf{r})$ is the velocity field in the solvent generated by the motion of the mth monomer. To first order in ϕ_m, the long-range part of $\delta\mathbf{v}$ which concerns us here is[10]

$$\delta\mathbf{v}_m(\mathbf{r}) \cong \frac{3bB}{4|r - r_m|}[\boldsymbol{\phi}_m + \mathbf{U}_m \cdot \boldsymbol{\phi}_m \mathbf{U}_m] \tag{7}$$

where U_m is a unit vector in the direction $\mathbf{r} - \mathbf{r}_m$. We now evaluate (7) with respect to the distribution function appropriate for a stretched ideal coil, i.e., defining $\mathbf{a}_n = \mathbf{r}_{n+1} - \mathbf{r}_n$,

$$\langle a_n^z \rangle = a^2/3\xi_t;\ \langle a_n^x \rangle = \langle a_n^y \rangle = 0$$
$$\langle (a_n^z)^2 \rangle = \frac{1}{3}a^2 + \frac{2}{45}a^4/\xi_t^2$$
$$\langle (a_n^x)^2 \rangle = \langle (a_n^y)^2 \rangle = \frac{1}{3}a^2 - \frac{1}{45}a^4/\xi_t^2 \tag{8}$$

The most important effect of stretching is to modify the average distance between a given pair of monomers to give

$$|\mathbf{r}_n - \mathbf{r}_m| = \left[|n - m|a^2 + \frac{(n-m)^2 a^4}{9\xi_t^2}\right]^{1/2} \tag{9}$$

i.e., for $\xi_t \gg (a/3)(|n - m|)^{1/2}$, the usual $r \sim n^{1/2}a$ random walk behavior is maintained, while for $\xi_t \ll (a/3)(|n - m|)^{1/2}$, $r \approx (na^2/3\xi_t)$. Thus, the mean distance between a given pair of monomers for strong stretching varies linearly with their chemical separation. Taking the force on the nth monomer as simply the entropic restoring force,

$$\boldsymbol{\varphi}_n = (3k_B T/a^2)(\mathbf{a}_n - \mathbf{a}_{n+1}) \tag{10}$$

the equation of motion (eq 6) has the form

$$\frac{\mathrm{d}\mathbf{r}_n}{\mathrm{d}t} = \tau_0^{-1}\left\{\mathbf{a}_n - \mathbf{a}_{n-1} + \frac{3}{4}b\sum_{m \neq n}\frac{1}{|\mathbf{r}_n - \mathbf{r}_m|} \times [\hat{\imath}(1 + U_x^2)(\mathbf{a}_m - \mathbf{a}_{m-1})_x + \hat{\jmath}(1 + U_y^2)(\mathbf{a}_m - \mathbf{a}_{m-1})_y + \hat{k}(1 + U_z^2)(\mathbf{a}_n - \mathbf{a}_{n-1})_z]\right\} \tag{11}$$

where the deformation is taken to be along the z axis. To find the eigenmodes of (11), we assume

$$x_n = x_0 e^{ipn} e^{-t/\tau_p} \tag{12}$$

for each component of $\mathbf{r}_n$. The relaxation spectrum is then given by

$$\tau_p^{-1} = \tau_0^{-1}\left\{2(1 - \cos p) + \sum_{s=1}^{\infty} F(s)\cos(ps)(1 - \cos p)\right\} \tag{13}$$

where $s = |n - m|$ and $F(s) \approx s^{-1/2}$ for $s \ll 9(\xi_t/a)^2$ and $F(s) \approx s^{-1}$ for $s \gg 9(\xi_t/a)^2$. There is an anisotropy in the relaxation spectrum generated by the deformations, i.e., there exists $\tau_z \neq \tau_x, \tau_y$. However, the dependences on such physical variables as the momentum transfer remains identical. Since it is these features which interest us here, we shall not explicitly discuss this anisotropy, but it should be kept in mind when experiments are performed. In the long-wavelength, lowfrequency limit $p \ll 1$, there are now two regimes depending on the product $ps_{\max}$ where $s_{\max} = 9(\xi_t/a)^2$. For $ps_{\max} \gg 1$, we find

$$\tau_p^{-1} \approx \alpha\tau_0^{-1}p^{3/2} \tag{14}$$

where α is a constant of order unity. This is the Zimm[5] and Dubois-Violette–de Gennes[7] result and leads to (4) for the width of the quasielastic neutron peak. For $pS_{\max} \ll 1$,

$$\tau_p^{-1} \approx \beta\tau_0^{-1}p^2 \tag{15}$$

where β is of order unity with some weak logarithmic corrections ($\ln pS_{\max}$) which we shall ignore. This p^2 dependence is characteristic of Rouse (eq 2) behavior. We are then led to the result that ξ_t is an effective screening length for the hydrodynamic interactions. The q dependence of the width of the quasielastic peak may then be calculated by using the standard correlation function approach of ref 7 or by the following scaling argument. Let us write

$$\Delta\omega_q \sim \tau_0^{-1}(qa)^3H(q\xi_t) \tag{16}$$

where H is a scaling function to be determined. For $x \gg 1$, $H(x) \rightarrow 1$ in order to obtain agreement with (4). For $x \ll 1$, $H(x) \rightarrow x$ to reach the Rouse q^4 behavior with[11]

$$\Delta\omega_q \sim \tau_0^{-1}q^4a^3\xi_t \sim k_BT\xi_tq^4/\eta \tag{17}$$

For long wavelengths $q\xi_t \ll 1$, this result may be interpreted as the spectrum of an ideal Rouse chain but with beads of radius ξ_t. The blobs of radius ξ_t move rigidly because of the strong internal hydrodynamic interactions, but distant blobs are effectively decoupled.

Another simple method to rederive these results using the blob concept is based on the consideration of the fundamental relaxation made of the stretched coil. As we have previously seen, the coil may be considered as a Rouse chain of blobs of radius ξ_t. Within each blob, the coil motions are strongly coupled by the hydrodynamic interactions and behave in a Zimm-like manner. Suppose that there exists a small fluctuation δR of the radius of the coil representing an expansion. This creates an elastic restoring force $F_{\text{el}} \simeq k_BT(\delta R)/R_0^2$; $R_0 = N^{1/2}a$ is the ideal coil radius, which is balanced by a viscous damping proportional to the time rate of change of the fluctuation amplitude and inversely proportional to the total mobility which for a Rouse chain is the mobility of each unit (B_b for each blob) divided by the number (N_b) of blobs;

$$-k_BT(\delta R)/R_0^2 = N_bB_b^{-1}(\delta\dot{R}) \tag{18}$$

Assuming that $\delta R = (\delta R)_0e^{-t/\theta}$, the fundamental relaxation time θ is given by

$$\theta^{-1} \cong k_BTB_b/N_bR_0^2 \tag{19}$$

Suppose that there exist g monomers per blob. Then the number of blobs is $N_b = N/g$. Within each blob of radius ξ_t, the coil is ideal, leading to $\xi_t = g^{1/2}a$ which determines g and gives $N_b \approx N(a/\xi_t)^2$. Each blob is assumed to behave as a rigid Stokes sphere with $B_b \simeq (6\pi\eta\xi_t)^{-1}$. Inserting these values in (19) gives

$$\theta^{-1} \simeq k_BT\xi_t/6\pi\eta R_0^4 \tag{20}$$

[Note that this result is consistent with (17) if we take $q \simeq R_0^{-1}$.] We then assume that the internal modes are related by scaling on θ by

$$\Delta\omega_q \cong \theta^{-1}F_1(qR_0)F_2(q\xi_t) \tag{21}$$

where F_1 and F_2 are scaling functions. For the internal modes of interest ($qR_0 \gg 1$) $\Delta\omega_q$ must be independent of the molecular weight; i.e., on the scale of the probe wavelength, the coil is effectively infinite. Assuming a power law [$F_1(x) \propto x^p$, $x \gg 1$] this gives $p = 4$ for N to cancel in (21). For $\xi_t \ll q^{-1} \ll R_0$ the coil behaves as a Rouse chain and we must find (2)–(3) for $\Delta\omega_q$ with $a \rightarrow \xi_t$ and $B \rightarrow B_b$. This gives $F_2(x) \rightarrow 1$ as $x \rightarrow 0$, which is indeed precisely (17). For even shorter wavelength $q^{-1} \ll \xi_t$, $\Delta\omega_q$ should become independent of the blob radius. Assuming that $F_2(x) \propto x^m$ for $x \gg 1$, this condition is fulfilled for $m = -1$, leading to

$$\Delta\omega_q \approx k_BTq^3/6\pi\eta \tag{22}$$

which agrees with (16) in this limit. We thus see that the scaling properties may be reproduced by a very simple argument based on the blob concept. In the next section, this method will be generalized to take into account excluded volume effects.

III. Excluded Volume Effects

In order to extend these results to chains in the presence of excluded volume interactions, it is useful to consider the analogue of (18) which describes the balance between the elastic restoring force and viscous drag for small fluctuations about the distorted equilibrium conformation. We discuss separately the modifications of each of these terms by the excluded volume effects.

The elastic restoring force might be strongly anisotropic because of the nonlinear stress–strain behavior, discussed in the Introduction. We shall first show that to within a numerical factor the spring constant is isotropic, i.e., identical dependence on the physical parameters. First along the stretching direction, from (1) for $\xi_t \ll R_F$,

$$f = (k_BT/R_F)(\bar{z}/R_F)^{\nu/(1-\nu)} \tag{23}$$

For a small fluctuation $(\delta z)[\bar{z} \rightarrow \bar{z} + (\delta z)]$ this leads to a restoring force,

$$\begin{aligned}\delta f_z &= \nu(1-\nu)^{-1}(k_BT/R_F^2)(\bar{z}/R_F)^{(2\nu-1)/(1-\nu)}\delta z \\ &= \nu(1-\nu)^{-1}(k_BT/R_F^2)(R_F/\xi_t)^{(2\nu-1)/\nu}\delta z\end{aligned} \tag{24}$$

For a transverse fluctuation $\delta r_\perp$, linear response theory gives

$$\delta f_\perp = \chi^{-1}\delta r_\perp \tag{25}$$

where the "susceptibility" is

$$\chi \approx \langle R_\perp^2\rangle/k_BT \tag{26}$$

and $\langle R_\perp^2\rangle$ is the mean square radius of the distorted chain.

As in ref 1, this may be determined in terms of the blob concept. The deformed coil may be considered as an ideal chain of tensile blobs each of radius ξ_t. Then $\langle R_\perp^2\rangle \approx \tilde{N}_b\xi_t^2$ where $\tilde{N}_b$ is the number of blobs renormalized to take into account excluded volume forces. Within a blob, distances scale with the Flory excluded volume exponent ν. Thus $\tilde{N}_b = N/\tilde{g}$ (*where* $\tilde{g}$ *is the renormalized number of monomers in a blob*) which in turn is given by $\xi_t \approx g^\nu a$, leading to $\tilde{N}_b \approx N(a/\xi_t)^{1/\nu}$. Using $R_F = N^\nu a$, we find

$$\langle R_\perp^2\rangle \cong R_F^2(R_F/\xi_t)^{(1-2\nu)/\nu} \tag{27}$$

Substituting into (26), we find $(\delta f)_\perp$ which apart from a numerical factor is identical with (24). (Note that for an ideal chain $\nu = ½$, the usual purely entropic elastic force is obtained.) In either case the elastic constant scales as N^{-1}.

The viscous force, as in the last section, is given by $(\tilde{N}_b/B_b)(\delta\dot{R})$ where we use the renormalized number of blobs, but the blob mobility B_b is unchanged because it depends only on the blob radius.

Balancing the two forces, we are led to the fundamental renormalized relaxation time

$$\tilde{\theta}^{-1} \sim \frac{k_BT}{6\pi\eta}R_F^{-2/\nu}\xi_t^{(2-3\nu)/\nu} \tag{28}$$

Notice that both θ and $\tilde{\theta}$ scale as N^2 but have different dependences on the tensile force. The spectrum is now determined by using scaling arguments analogous to the end of section II. For $\xi_t^{-1} \gg q \gg R_F^{-1}$

$$\Delta\omega_q \approx \tilde{\theta}^{-1}\tilde{F}_2(qR_F) \tag{29}$$

where $\tilde{F}_2(x) \sim 1$ for $x \sim 1$ and $\tilde{F}_2(x) \sim x^p$; $x \gg 1$; the exponent p is determined by the condition $\Delta\omega_q$ and should be independent of the chain length N. This immediately leads to $p = 2/\nu = {}^{10}\!/_{3}$ and

$$\Delta\omega_q \approx (k_BT/6\pi\eta)q^{10/3}\xi_t^{1/3} \tag{30}$$

which differs from both the ideal q^4 chain dependence and the de Gennes $q^{2+1/\nu}$ behavior for unstretched ($\xi_t \rightarrow \infty$) Rouse chains with excluded volume. For shorter wavelengths, $q \gg \xi_t^{-1}$, we expect to find $\Delta\omega_q$ independent of the screening length; i.e., $F_1(q_t) \sim 1$ for $q\xi_t \sim 1$ and $\tilde{F}_1(q\xi_t) \sim (q\xi_t)^r$ for $q\xi_t \gg 1$ where r is found from the condition that $\Delta\omega_q$ is dependent of ξ_t. This leads to $r = -{}^1\!/_3$ and the usual Zimm q^3 form (eq 4).

IV. Conclusion

In summary, we have shown that for stretched polymers the parameter $\xi_t = (\beta f)^{-1}$ in addition to being the screening length for the excluded volume effects is also the characteristic distance beyond which the hydrodynamic interactions lead to only logarithmic corrections to free draining behavior. Then, using scaling arguments, we found functional dependences for the width of the incoherent inelastic neutron scattering peak. For sufficiently short wavelengths, $q\xi_t \gg 1$, the ideal chain q^3 behavior obtains, characteristic of complete hydrodynamic coupling between the monomers. For $R_F^{-1} \ll q \ll \xi_t^{-1}$, Rouse-like behavior modified by the excluded volume interactions to give $\Delta\omega_q \propto q^{10/3}$ is found. The rather small difference between 3 and ${}^{10}\!/_3$ might be difficult to detect experimentally.

In principle, the quantity $\Delta\omega_q$ may be determined by quasielastic neutron or light scattering. Indeed recently Adam and Delsanti[12] have observed the q^3 law for undeformed coils in light scattering.

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(9) This work[2] has been submitted to *Macromolecules* in two parts: (I) deals with the Rouse limit while (II) includes the hydrodynamic interactions.

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Calculation of Phenyl Group Rotation in Polystyrene by Means of Semiempirical Potentials

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ABSTRACT: By means of a set of semiempirical potentials the activation energies of phenyl group rotation in polystyrene have been calculated. The backbones (isotactic and syndiotactic, isotactic with kink) have been given a high degree of flexibility. The activation energies have been determined by consecutive rotation of the rotational angle of the phenyl group between 0° and 180° in steps of 20° and by minimizing the energy with respect to all other variables. The lowest activation energy of 10.3 kcal/mol was found in the isotactic 3/1-helix. For other conformations the activation energies do not exceed ca. 20 kcal/mol. Higher values do not occur because of conformational changes of the flexible backbone.

Recently, Tonelli has summarized the efforts to interpret mechanical relaxation processes in polystyrene.[1] By means of semiempirical atomistic calculations he investigated the rotation of the phenyl group in syndiotactic polystyrene chain segments. In accordance with Reich and Eisenberg[2] he stated that phenyl group rotation with activation energies of as low as 10 kcal/mol is permitted only if the backbone adopts sterically unfavorable conformations.

In this paper, atomistic calculations with well tested semiempirical potentials, already performed on isotactic polystyrene,[3] have been extended to phenyl group rotation in isotactic as well as in syndiotactic polystyrene. During minimization of the conformational energy the flexibility of the backbone was explicitly taken into account. Due to the high degree of freedom of the chain segment considered we got new detailed results concerning phenyl group rotation and its coupling to the backbone.

Method of Calculation

The conformational energy and its gradient have been calculated by an effective matrix algorithm which allows a fast computation with minimal computer core storage.[6] In order to determine minima of the energy, the algorithm of Fletcher and Powell[7] has been used.

The representative chain segment containing the phenyl group to be rotated consists of flexible repeating units (ru) and of adjacent ru at both sides of the variable region, which are fixed to the ideal structure considered[3,8] (cf. Table I).

All nonbonded (steric) interactions between the atoms have been taken into account, except interactions between the