pears to provide a unified description of real-space configurational structures and their corresponding scattering functions for a wide variety of finite polymer systems in generally good agreement with simulated data.

The component scattering arising from centers $i,i+\nu$ is readily determined by means of the IC technique, and in conjunction with the associated weighting functions W_ν (Table I) provides a unified approach to the structure of the Kratky plot, regardless of polymer structure for systems of identical molecular weight. The W_0 factors are obviously independent of the molecular structure; the W_1, however, are already sensitive to the molecular geometry and appear responsible for the characteristic oscillation in ladder and star scattering functions. In all cases the components are oscillatory and there appears no evidence of the Gaussian transforms presumed responsible for the Debye plateau. This does not preclude the development of a plateau region in the scattering curve, but its appearance cannot be attributed to Gaussian behavior within the system.

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Intercomparisons of Dielectric Relaxation, Dynamic Light Scattering, and Viscoelastic Properties of the Local Segmental Motion in Amorphous Polymers

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ABSTRACT: Independent of the nature of the probe (e.g., longitudinal compliance by dynamic light scattering, shear compliance by dynamical compliance and modulus or by creep recovery, electric compliance by dielectric relaxation) near and above the glass temperature, the appropriate correlation or relaxation function of the local segmental motion in an amorphous polymer is well described by the Kohlrausch–Williams–Watts function $\exp\{-(t/\tau^*)^{1-n}\}$. The temperature dependence of the effective time τ^* is well represented by the Vogel–Fulcher–Tamann–Hesse equation $\tau^* \propto \exp\{B/(T - T_0)\}$. However, the fractional exponent n and the quantity B, *for a fixed* T_0, can depend on the nature of the probe. Through a compilation of the experimental data of a number of amorphous polymers, we have established an empirical correlation between n and B. Whenever the two quantities n and B are probe dependent in an amorphous polymer, we find the product $(1 - n)B$ remains invariant. An explanation of this empirical relation can be found from an extant prediction of the coupling model of relaxation.

Introduction

It has been noticed repeatedly[1-11] in the course of the study of local segmental motion (i.e., relaxation of small portions of backbone chain that is responsible for volume and enthalpy recovery near the glass temperature T_g often referred to as the α relaxation) in polymers that there can be a significant difference between its relaxation time determined dielectrically and its relaxation time obtained from either photon correlation spectroscopy or viscoelastic (mechanical) measurement. The same is true for nonpolymeric glass-forming liquids such as *o*-terphenyl.[12] Examples in polymers include poly(propylene glycol)[1]

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(PPG), poly(vinyl acetate)[2-5] (PVAc), poly(styrene)[6-9] (PS), poly(ethyl acrylate)[10] (PEA), poly(methyl acrylate)[11] (PMA), and others. In all these systems, the dielectric relaxation times have been found to be shorter than the light scattering relaxation time or the mechanical relaxation times. In some cases the difference can be as large as one or more than 1 order of magnitude. It is not surprising that relaxation times obtained by using these different probes are not the same, since time correlation functions of different dynamical variables (e.g., dipolar polarization, density fluctuation, and shear stress/strain) are involved. Even for two dynamic variables which are conjugate to each other, such as stress σ and strain ϵ or electric field E and dielectric displacement D, the relaxation time of one (τ_ϵ at constant ϵ and τ_D at constant D) can be quite different from that (retardation times τ_σ at constant σ and τ_E at constant E) of the other.[13] For exponential time correlation functions of stress and strain, it has been shown that $\tau_\sigma/\tau_\epsilon = G_U/G_R$ where G_U and G_R are the unrelaxed and relaxed modulus.[15] We are not interested in this difference between relaxation and retardation times. In fact we shall address only bulk compliance $B(t)$ or $B^*(\omega)$, longitudinal compliance $N(t)$ or $N^*(\omega)$, shear compliance $J(t)$ or $J^*(\omega)$, and dielectric compliance $D(t)$ or $\epsilon^*(\omega)$. Hence, in each case only the retardation time is involved. In comparing dielectric and mechanical data it has been pointed out that the electric field E corresponds to the mechanical stress σ and that the dielectric displacement D corresponds to the mechanical strain. It follows that $D(t)$, $\epsilon^*(\omega)$, and τ_E are analogous to $J(t)$, $J^*(\omega)$, and τ_σ, respectively. The time constant τ_E is generally known as the dielectric relaxation time. This can be confusing, because of the analogy of τ_E with τ_σ, it is more appropriate to call τ_E the dielectric retardation time. To avoid possible confusion, we depart from common usage of terminologies in this paper and refer to τ_E as the dielectric retardation time, and dielectric relaxation is dielectric compliance. Recent theoretical advances[13,2,3] have made clear that the time correlation function of density fluctuation measured in dynamic light scattering is associated with the longitudinal compliance (which to a good approximation can be identified[2,3] as the bulk compliance for amorphous polymers above the glass temperature T_g). Hence we can restate the above observation by many workers that the dielectric retardation times can be significantly shorter than either the bulk or the shear retardation times. The comparison between the bulk and shear retardation times is also of interest. It was the subject of a separate investigation in amorphous poly(propylene).[14] Naturally, the physical origin of the large difference between the dielectric and bulk viscoelastic retardation times is a basic problem that deserves an explanation.

A valuable attempt to explain this has been made by Fytas et al.[2] based on the Vogel–Fulcher–Tammann–Hesse (VFTH) equation[15] for the retardation time τ

$$\tau = \tau_0 \exp\{B/(T - T_0)\} \tag{1}$$

and the interpretation in terms of the free volume theory of Cohen and Turnbull.[16] The Cohen–Turnbull expression for B is given by

$$B = \gamma v^*/\alpha \bar{v}_\mathrm{m} \tag{2}$$

where γ is a constant ($0.5 \leq \gamma \leq 1$), v^* is the minimum required volume of the void in the theory, α is the thermal expansion coefficient, and $\bar{v}_\mathrm{m}$ is the mean volume of the polymer segment responsible for the relaxation. A larger value of the parameter B is experimentally observed for dynamic light scattering than that for dielectric relaxation, with the *same* reference temperature T_0 being used for both. Let us denote these two values of B by B_b and B_dr respectively for dynamic light scattering and dielectric compliance. We have chosen the subscript b for quantities obtained from light scattering because, if the approximation of identifying longitudinal compliance measured by light scattering with bulk compliance is valid, the quantities such as the retardation time τ_b and the VFTH parameter B_b are associated with the bulk compliance. If the difference in the B parameter dominates the determination of the two τ's (τ_b and τ_dr) from eq 1, then via eq 2 of the Cohen–Turnbull theory they have traced the physical origin of the problem in hand to a smaller $\bar{v}_\mathrm{m}$ (or the corresponding free volume $v_f = \alpha\bar{v}_\mathrm{m}(T - T_0)$) needed for bulk compliance than that for dielectric relaxation. Without an explicit microscopic model of the molecular motions responsible for bulk compliance and for dielectric relaxation, it is not possible to be assured that $(\bar{v}_\mathrm{m})_\mathrm{b}$ indeed is smaller than $(\bar{v}_\mathrm{m})_\mathrm{dr}$. Hence the explanation in terms of the Cohen–Turnbull theory is incomplete. In this work we extend the phenomenologies of this problem. In addition to the observation in several cases that

$$\tau_\mathrm{b} \geq \tau_\mathrm{dr} \tag{3}$$

as discussed, we point out that this situation is invariably accompanied by the inequality

$$n_\mathrm{b} \geq n_\mathrm{dr} \tag{4}$$

Here n_b and n_dr are the fractional (i.e., $0 < n < 1$) exponents that appear in the Kohlrausch–Williams–Watts (KWW) representations of the time correlation function[17-19] of density fluctuation

$$g(t) = \exp\{-(t/\tau^*_\mathrm{b})^{1-n_\mathrm{b}}\} \tag{5}$$

obtained in photon correlation spectroscopy[1-14] and of the dipole moment correlation function[19]

$$\phi(t) = \exp\{-(t/\tau^*_\mathrm{dr})^{1-n_\mathrm{dr}}\} \tag{6}$$

that appears in the calculation of the complex dielectric susceptibility $\epsilon^*(\omega)$ by the equation[19]

$$\frac{\epsilon^*(\omega) - \epsilon_\infty}{\epsilon_0 - \epsilon_\infty} = \int_0^\infty \left[\frac{-\mathrm{d}\phi(t)}{\mathrm{d}t}\right] e^{-i\omega t}\, \mathrm{d}t \tag{7}$$

The KWW exponents $\beta_\mathrm{b} \equiv 1 - n_\mathrm{b}$ and $\beta_\mathrm{dr} \equiv 1 - n_\mathrm{dr}$ can be very different. This is true for polystyrene, poly(vinyl acetate), and especially for poly(propylene glycol). The data sets that led us to this conclusion will be presented in the next section. For each polymer, by considering different dynamical variables of the local segmental motion we have also established an empirical correlation between the parameter B in the VFTH equation (1) for τ and the fractional exponent n in the KWW equations (5) and (6) based on the same data.

In the third section, we shall summarize the essence of a new description[20] of the coupling model[21] of relaxation for a physical interpretation of this inequality. We show how this inequality leads us, via the "second" prediction of the coupling model, to derive the relation

$$(1 - n_\mathrm{b})B_\mathrm{b} = (1 - n_\mathrm{dr})B_\mathrm{dr} \tag{8}$$

if the same T_0 is used in both VFTH representations of τ_b and τ_dr. Whence, it follows from inequality (4) that

$$B_\mathrm{b} \geq B_\mathrm{dr} \tag{9}$$

and the correlation between n and B is found. More importantly, we find the experimental data are in good

Table I
Values of the KWW Exponent β and the B Parameter of the VFTH Equation for the Temperature Dependence of the KWW Relaxation Time τ^* Taken from Experimental Data Obtained by Different Probes for Poly(propylene glycol)

					VFTH params for τ^*		KWW exponent	
type of probe	measd quant	authors	sample mol wt	T_g, K	T_0, K	B, K	$\beta = (1 - n)$	$(1 - n)B$, K
dynamic light scattering	longitudinal compliance	Wang et al.	425, 1025, 2025, 4000	198	170	1137	0.38 ± 0.02	432 ± 23
shear creep compliance and dynamic shear compliance	recoverable shear compliance and $J^*(\omega)$	Cochrane et al. Barlow & Erginsav	4000	*a*	171.2	1028.9	0.42 ± 0.02	432 ± 21
dielectric relaxation	electric compliance $\epsilon^*(\omega)$	Alper et al.	380, 3030	*a*	*a*	*a*	0.51 ± 0.02	
		Johari	4000	200	176	716.4	0.52 ± 0.02	
					170^b	$\sim 800^b$	0.52 ± 0.02	416 ± 16
		Williams	1.2×10^6	198	174^c	893	0.47 ± 0.02	420 ± 18

[a] Data not reported or not tabulated. [b] If T_0 is chosen to be the same as in the analysis of dynamic light scattering data, then we find $B \cong 800$ K to a good approximation. [c] No adjustment of T_0 has been made, the sample is of much higher molecular weight than that of PPO-4000.

quantitative agreement with the prediction given by eq 8. This is the major result of this paper. Furthermore, under certain condition to be specified, we arrive at the result given by inequality (3) that the bulk viscoelastic relaxation time is longer than the dielectric relaxation time.

Experimental Data. Establishing a Correlation

In this section we shall summarize the empirical evidence for several polymers from investigations of the local segmental motions by both dynamic light scattering and dielectric relaxation. In particular, we find the three inequalities (3), (4), and (9) hold simultaneously. We shall collect the experimental data of PPG, PVAc, PEA, and PMA. The light scattering data and dielectric data are augmented by shear creep compliance data, whenever available.

A. Poly(propylene glycol). Homodyne photon correlation spectroscopic measurements of PPG with molecular weights 425, 1025, 2025, and 4000 had been carried out.[1] The time correlation function of density fluctuation $g(t)$ probed in the photon correlation spectroscopic measurement had been well fit with the KWW fractional power exponential of eq 5 for each temperature. From the effective relaxation time τ^*_b, it is customary to consider also mean relaxation time $\bar{\tau}_b$ which is related to τ^*_b by

$$\bar{\tau}_b = \int_0^\infty dt \exp[-(t/\tau^*_b)^{1-n}] = \{\tau^*_b/(1-n_b)\}\Gamma(1/(1-n_b)) \quad (10)$$

where Γ is the Γ-function. Over the temperature range of −45 to −65 °C, the fractional exponent $\beta_b = 1 - n_b$ increases slightly. The temperature variation of $\bar{\tau}_b$ follows the VFTH equation

$$\bar{\tau}_b = \bar{\tau}_0 \exp\{B_b/(T - T_0)\} \quad (11)$$

For PPG-1025, $\bar{\tau}_0 = 7.29 \times 10^{-4}$ s, $B_b = 1137$ K, and $T_0 = 170$ K. The parameters for the temperature dependence of $\bar{\tau}_b$ in eq 11 are rather similar for PPG of various molecular weights. Representative values are entered into Table I.

The dielectric relaxation of the local segmental motion is observable in polymers containing dipoles transverse to the chain backbone and has been investigated by several workers.[22-30] This activity, started by Baur and Stockmayer[22] in PPG liquids with molecular weights from 1025 to about 3700, has been further pursued by others in PPG and many other polymers. Williams[24] studied an amorphous PPG sample of high number-average molecular weight, $>10^5$. Out of these many sets of data we select the ones by Alper et al.,[25] by Williams,[24] and by Johari[29] for our analysis because these data sets are presented in such a way that the fractional exponent $1 - n_{dr}$ in eq 6 and 7 can be determined with accuracy for each case. The dielectric spectrum $\epsilon^*(\omega)$ of the local segmental α-relaxation has been fitted to the theoretical curves given by eq 7 via the KWW function. In all cases the fits are satisfactory. The fractional exponent n_{dr} determined this way to within the error bounds of ±0.02 together with the parameters of the VFTH representation of τ_{dr}, eq 1, obtained from the analyses of the original authors are entered into Table I.

Shear creep and creep recovery measurements of PPG-4000 with $\bar{M}_n = 3030$ also had been made by Cochrane et al.[31] over the temperature range −76 to +10 °C and an experimental window of 0.1 to 10^5 s. Creep recovery measurements with the torque removed after steady-state flow conditions have been attained give directly the recoverable compliance $J_r(t)$ continuously from the glassy value of approximately 10^{-9} to 10^{-6} Pa^{-1}. In several previous publications[32-34,14] we have described a method of extracting the local segmental mode contribution to $J_r(t)$. For the amorphous polymers PS,[32,34] PVAc,[33,34] and atactic poly(propylene)[14] studied, the recoverable creep compliance from the glassy level up to a level between 10^{-8} and 10^{-7} Pa^{-1} can be satisfactorily fitted by theoretical creep compliance for the local segmental mode. The latter are generated by solving the linear viscoelastic relation between creep compliance and shear modulus, and the shear modulus contribution from the local segmental mode is assumed to have the Kohlrausch–Williams–Watts form

$$G(t) = G_R + (G_U - G_R) \exp[-(t/\tau^*_G)^{1-n_G}] \quad (12)$$

Where G_U and G_R are the unrelaxed and relaxed modulus from the local segmental mode. The best fit to the $J_r(t)$ data at each temperature determines the shear Kohlrausch exponent $1 - n_G$ and the effective relaxation time τ^*_G. Alternatively, we have fit the recoverable shear creep compliance data directly to the compliance function

$$J_r(t) = J_R + (J_U - J_R) \exp[-(t/\tau^*_J)^{1-n_J}] \quad (13)$$

where J_R and G_R^{-1} and $J_U = G_U^{-1}$. We find τ^*_J is longer than τ^*_G as in the case of exponential decay.[15] Also n_J is nearly the same as n_G to within the error bounds of ±0.02 found in fitting the experimental data via eq 12 or directly by eq 13. The KWW exponent for compliance $\beta_J \equiv 1 - n_J$ has the value of 0.42 ± 0.02 for best fit by using directly eq 13. On the other hand, the indirect approach to compliance based on the modulus eq 12 gives $\beta_G = 1 - n_G = 0.41 \pm 0.02$ for best fit. The temperature dependence of τ^*_G and τ^*_J are the same. Moreover they are the same as that found for the shift a_T along the time axis necessary for superposition of the recoverable compliance data in the glass–rubber transition region, as it should be. The shift factor a_T for reduction to −68 °C has been described by the VFTH equation[31]

$$\ln (a_T) = 129.71 + 1028.9/(T - 171.2) \qquad (14)$$

These values of the parameters of the VFTH equation (14) and the KWW exponent β_J are entered into Table I.

By inspection of the entries in Table I, it is evident that both the VFTH parameter B and the KWW exponent β depend sensitively on the nature of the compliance probe. On the other hand, their product remains almost invariant. Also it appears that they anticorrelate with each other: larger B is accompanied by smaller β. We point out in passing another interesting viscoelastic property observed also by Cochrane et al.[31] The steady-state (limiting long time) recoverable compliance J_e decreases as the temperature approaches the glass temperature from above. This property, shared at least by low molecular weight polystyrene,[36] has been addressed and explained by the coupling model in a separate paper.[34]

B. Poly(vinyl acetate). There are two sets of photon correlation spectroscopic (PCS) studies of PVAc above the glass temperature that have been published recently.[2-5] However, the results are not in agreement with each other. The most significant difference is the value of the Kohlrausch exponent β_b of the correlation function. At this time, it is not entirely clear what the causes for this difference in β_b are, although it is certain that the molecular weight and the glass temperature T_g of the samples used are quite different. The sample studied by the Max Planck–Utah (MP-U) group as a viscosity-average molecular weight of 1.5×10^4 and a T_g of 17 °C determined by DTA. The glass temperature is low compared with the generally quoted T_g values between 29 to 32 °C for higher molecular weight PVAc samples used in other studies. The low T_g value obtained by the MP-U group is due to the low molecular weight of their sample. The difference in molecular weight and its distribution and the presence of different amounts of plasticizers including water in samples will cause changes in T_g. The VFTH parameters, especially the reference temperature T_0, will change with T_g and they are not expected to be the same for the two studies.[2-5] However, a difference in the Kohlrausch exponent β_b is not expected. Shear creep compliance measurements of polystyrene[36,15] have shown that the shape of the recoverable compliance $J_r(t)$ versus log t curve is essentially independent of molecular weight in the glass–rubber relaxation region where the local segmental motion contributes. By use of eq 13 to describe $J_r(t)$, it follows that the Kohlrausch exponent β_J is the same for high and low molecular weight samples. Thus from the established literature of shear viscoelasticity[36,15] we are led to conclude large differences between the two light scattering measurements in β_b cannot be due simply to differences in the molecular weight of samples used. The MP-U group have pointed out that their T_g value is similar to that of the PVAc sample used in the dynamic compressibility measurements by McKinney and Belcher.[35] Thus, it is meaningful to identify approximately the time scale and spectrum of the bulk compliance measured in PCS[2,3] by the MP-U group with that determined from dynamic compressibility by McKinney and Belcher.[35] On the other hand, it is not surprising that the time scale of the PCS data of Tribone et al. can be very different from that of dynamic bulk compressibility data of McKinney et al., considering the large difference in the glass temperature.

Both groups have fitted the correlation function of density fluctuation obtained to the KWW function, eq 5. However, the β_b values ($\beta_b = 1 - n_b$) obtained are different. The MP-U group's β_b value is between 0.36 and 0.37, considerably less than the value of 0.45 found by Tribone et al. It has been suggested that this difference is caused by the use of a linear correlator to collect autocorrelation function data with different sample time segments and the matching of overlapping segments to obtain a composite function. This controversy has not been settled. If this procedure of data processing involving matching of the correlation function is not improper then we have to take seriously the β_b value of 0.45 of high molecular weight PVAc given by Tribone et al. However, the question of the cause of the large difference in the β_b value from that of the low-T_g sample still remains.

The MP-U group have fitted their data of $\bar{\tau}_b$ to a VFTH equation (11) and obtained $B_b = 2252$ K, $T_0 = 238$ K, and $\bar{\tau}_0 = 6.4 \times 10^{-15}$ s. Tribone et al. have not fitted their data to the WLF or the VFTH equation. Nevertheless it is evident from the plots given by these authors that the temperature variation of $\bar{\tau}_b$ from their PCS data is appreciably weaker than that of the MP-U group. It is also considerably weaker than the temperature dependences of dynamic shear compliance of Williams and Ferry,[37] volume recovery of Kovacs,[38,39] and shear creep compliance of Plazek.[40,41,33] This large difference has not been understood nor expected and is a problematic element already pointed out by the authors.[4]

Turning our attention to mechanical measurements, the storage shear modulus and loss tangent of PVAc with $M_w = 2 \times 10^6$ were made by Kovacs, Stratton, and Ferry[39] (KSF) at temperatures from 31 to 39 °C under conditions of voluminal equilibrium. The dynamic shear measurements above 33 °C can be reduced and the shift factors a_{TG} can be obtained in the usual way. Below 33 °C, the relaxation spectrum changes with temperature and the method of reduced variables become inapplicable. Above 33 °C, the a_{TG} values can be closely fitted by a WLF equation. This same WLF equation gives a satisfactory fit also to earlier dynamic shear compliance data of Williams and Ferry if the latter is limited for consideration to the lower temperature range from 45 to 57 °C. KSF have also found that the shift factor a_{TG} agrees almost exactly with the a_T calculated from the time-scale separation of the isothermal bulk contraction curves in ref 38. Plazek has made torsional creep measurements on PVAc samples ($M_w = 6.5 \times 10^5$) dried under vacuum in situ.[40,41] All other measurements on PVAc referred to in this work were made on samples that were in equilibrium with water vapor under ambient conditions.[40] Plazek has estimated that the T_gs of the wet samples were depressed by about 1.4 °C. Hence he has added 1.4 °C to the values taken from ref 37 and 39 to bring them into correspondence with the values obtained on the dried samples. In this way, Plazek has demonstrated (see Figure 1 of ref 41) that the dynamic mechanical shift factors determined by Williams and Ferry and by Kovacs, Stratton, and Ferry are in close agreement with his shift factor represented by

$$\log a_T = -7.425 + 928.13/(T - 248) \qquad (15)$$

From these discussions we are led to the values $B = 2137.5$ K and $T_0 = 248$ K for the parameters in the VTFH representation of the shift factors of shear[37,39-41] and bulk deformation[38,39,42] in high molecular weight dry PVAc.

The shear creep compliance $J(t)$ measurements on PVAc with $M_\omega = 6.5 \times 10^5$ by Plazek has been analyzed previously[33] by the methods discussed in the PPO section. From the analysis, the value 0.57 ± 0.02 for both coupling parameters n_J and n_G was determined. This is remarkably in good agreement with the coupling parameter n_v of the isothermal recovery of the specific volume v following a single rapid temperature change near T_g.[42] Earlier, it was

Table II
Values of the KWW Exponent β and the B Parameter of the VFTH Equation for the Temperature Dependence of the KWW Relaxation Time τ^* Taken from Experimental Data Obtained by Different Probes for Poly(vinyl acetate)

type of probe	measd quant	authors	sample mol wt	T_g, K	VFTH params for τ^*		KWW exponent $\beta = (1 - n)$	$(1 - n)B$, K
					T_0, K	B, K		
dynamic light scattering	longitudinal compliance	Fytas, Wang Meier, & Fischer	1.2×10^4	17	238 231.6[a]	2252 2450[a]	0.36 ± 0.02	882 ± 49
dynamic bulk compress	bulk compliance B^*	McKinney & Belcher	$\sim 10^4$	~ 17	~231.6[a,b]	~2450[a,b]	~0.36[b] ± 0.02	882[b] ± 49
dynamic mechanical	shear modulus $G^*(\omega)$	Kovacs, Stratton, & Ferry	2×10^6	32.0	248[c]	2137.5[c]	0.43[d] ± 0.02	919[a,c] ± 43
sheer creep recovery	shear compliance $J(t)$	Plazek	6.5×10^6	33.4	248	2137.5	0.42 ± 0.02	919 ± 43
dynamic mechanical	dyanmic shear compliance $J^*(\omega)$	Ferry & Landel; Williams & Ferry		32.0	248	2073	0.43[d] ± 0.02	919[a,c] ± 42
vol recovery	bulk vol deformation	Kovacs, Kovacs, Stratton, & Ferry	2×10^6	32.0	248[c]	2073[c]	0.44[e] ± 0.02	912[a,c] ± 42
dielectric relaxation	electric compliance $\epsilon^*(\omega)$	Nozaki & Mashimo	8×10^4	31.0	249.38 246.6[a]	1877 1970[a]	temp dep $0.62 \leq \beta \leq 0.47$ for $84.77 \geq T \geq 40.2$ °C	843[a,f] ± 59

[a] Values obtained after correction for the difference in T_g has been made, using Plazek's dry sample value of 33.4 °C.[41] [b] Taken to be the same as the corresponding quantity determined by dynamic light scattering, as shown by Fytas et al.[2] [c] Plazek has shown the shift factor is identical with his from shear compliance data after correcting 1.4 °C for the difference in T_gs of wet and dry samples.[41] [d] Taken to be the same as that determined by an analysis of Plazek's shear compliance data. [e] From analysis of the volume recovery data using the coupling model by Rendell et al.[42] [f] From analysis of dielectric relaxation data using the coupling model by Rendell et al., taking into consideration the variation of β with T.[49] See discussions in text.

found by another application[42] of the coupling model to the volume recovery measurements of Kovacs[38] that $0.55 \leq n_v \leq 0.57$.

Dielectric relaxation has been used to study the local segmental mode of PVAc by a number of workers, started as early as 1941 by Mead and Fuoss.[43] It was continued by Ishida and co-workers,[44] Saito and Nakajima,[45] Sasabe and Moynihan,[46] and more recently by Mashimo and coworkers.[47-49] Attempts to compare dielectric relaxation and mechanical data were made.[37] Williams and Ferry have made comprehensive comparison of their dynamical shear compliance J^* data with the dielectric data of Mead and Fuoss.[43] They found that the shift factors are practically the same. Reduction to a single curve is apparently successful for both the real and the imaginary parts of the dielectric constant for this study[43] with a limited expanse of the frequency window. Later works with progressively improved experimental equipment have significantly increased the size of the frequency window.[47,48] It is now possible to make isothermal dielectric measurements in the enormous frequency range $10^{-6} < f < 10^7$ Hz, with temperature being maintained constant to within ±0.02 °C. The extension at low frequencies have made possible the observation of the local segmental mode to lower temperatures.[47,48] The data show clearly that the shape of the frequency dependence changes with temperature, especially near T_g, as seen also through the shear modulus measurements.[39] At each temperature the KWW function via eq 6 and 7 gives a good description of the dielectric data.[49] The fractional exponent $\beta_{dr} = 1 - n_{dr}$ decreases with decreasing temperature. Nozaki and Mashimo[47] fitted the temperature dependence of the frequency of the dielectric loss maximum to the VFTH equation. They gave $B = 1877$ K and $T_0 = 249.38$ K from a least-square fit, but the error bounds on these values were not stated in their paper.[47] These values of B and T_0 are entered into Table II. The dielectric data were obtained over nine decades in frequency down to the ultralow frequency of 1 μHz. They were able to monitor the dielectric relaxation below T_g in samples which had been annealed at sufficient long times to attain equilibrium. It was found that the best-fit VFTH equation deviates significantly at low temperatures from the data. These two concurrent features, i.e., T-dependent β_{dr} and deviation of the empirical VFTH equation, are intimately related according to the predictions of the coupling model.[49] The coupling model will be discussed in the next section where the key prediction used in ref 49 appear as eq 6′. The dielectric Kohlrausch exponent β_{dr} being temperature dependent for PVAc is being made clear in Table II. There it is explicitly stated that β_{dr} decreases continuously from 0.62 to 0.42 as T decreases from 84.77 to 40.2 °C. The error bound for β_{dr} obtained by least-square fit to the dielectric loss data is ±0.01.

Using Plazek's $T_0 = 248$ K as a standard and assuming $T_g - T_0$ is molecular weight independent, we find the corresponding T_0 for other samples by correcting the difference in T_gs:

$$T_0 - 248 = T_g - 33.4 \tag{16}$$

In this manner we find $T_0 = 231.6$ K for the low molecular weight sample used in dynamic light scattering, and $T_0 = 246.6$ K for the sample investigated by dielectric relaxation.[47-49] Such a data set is refitted by the VFTH equation with the new T_0 and the new B value is determined. The results of these adjustments are entered into Table II together with other relevant information discussed earlier. It is now meaningful to compare directly the adjusted values of B from different compliance experiments, even though the samples used to obtained them have different T_gs. By inspection it is clear from Table II that, on varying the nature of the probe, an increase in B corresponds to a decrease in β (or an increase in n). This is true notwithstanding the fact that β_{dr} is temperature dependent. At all temperatures the anticorrelation between β and B,

$$\beta_{dr} > \beta_J > \beta_b \tag{17}$$

while

$$B_{dr} < B_J < B_b \tag{18}$$

continues to hold. The anticorrelation between β and B, or equivalently the correlation between n and B, have been seen before in PPO (Table I). Again, the product $(1 - n)B$ remains almost invariant to change in probe from bulk compliance to shear compliance or modulus. For dielectric

Table III
Values of the KWW Fractional Exponent β and the B Parameter of the VFTH Equation for the Temperature and Pressure Dependence of the KWW Relaxation Time τ^* Taken from Experimental Data Obtained by Different Probes for Poly(ethyl acrylate) and Poly(methyl acrylate): $\tau^* \propto \exp[(B + \alpha P)/(T - T_0)]$

				VFTH params for τ^*			KWW exponent
polymer	type of probe	measd quant	authors	T_0, K	B, K	αT, cm^3/mol	$\beta = 1 - n$
PEA	dynamic light scattering	longitudinal compliance	Fytas et al.	216	1249	37.4	0.38 ± 0.02
	dielectric relaxation	electric compliance	Williams & Watts	216[a]	1249[a]	not available	0.38 ± 0.02[b] 0.41 ± 0.02[c]
PMA	dynamic light scattering	longitudinal compliance	Fytas et al.	222	1814	39.7	0.42 ± 0.04
	dielectric relaxation	electric complixance	Williams	222[a]	1814[a]	~39.7[a]	0.41 ± 0.02

[a] Taken to be the same as the corresponding quantity from the dynamical light scattering data. This is based on the very good agreement of the temperature and pressure dependences of τ^* from dielectric and light scattering data. [b] From Williams and Watts.[50] [c] From Williams et al.[19]

relaxation the product $(1 - n)B$ does not have a unique value because n_{dr} is temperature dependent. B is not entirely meaningful either because of the deviation of the VFTH equation from the measurements.[47-49] As will be discussed in the next section, based on the coupling model the product $(1 - n)B$ is the parameter B_0 in the VFTH equation for the primitive or microscopic friction factor (see eq 20) provided n is temperature independent. If n is temperature dependent then we must deduce B_0 from a full analysis using the so-called second relation (eq 6 of ref 49) of the coupling model.[20,21] The relation $B_0 = (1 - n)B$ is only a special case of the second relation, being valid only if n is T independent. In ref 49 we have deduced B_0 = 843 K from a full analysis of the dielectric relaxation data. Nevertheless, this value is entered into Table II under $(1 - n)B$ for dielectric relaxation. It is close in value to the product $(1 - n)B$ for bulk and shear compliances.

C. Poly(ethyl acrylate). The correlation between the fractional exponent n in the KWW function and the parameter B of the VFTH equation observed in PPO and PVAc on varying the probe of the local segmental motion will be examined in the case of poly(ethyl acrylate) PEA. Polarized photon correlation measurements of the local segmental motion in bulk PEA has been measured at different temperatures and pressures by Fytas et al.[10,11] Again the density fluctuation correlation function from the PCS is well described by the KWW function, eq 5. The β_{b} parameter has the value of 0.38 ± 0.02 and is virtually independent of temperature and pressure. The experimental relaxation times τ^*_{b} and $\bar{\tau}_{\mathrm{b}}$ obey the VFTH equation. For example, the mean relaxation time $\bar{\tau}$ in seconds is well fitted by the equation[11]

$$\ln \bar{\tau}_{\mathrm{b}} = \ln (1.5 \times 10^{-12}) + 1249/(T - 216\ \mathrm{K}) \quad (19)$$

Dielectric relaxation of the local segmental motion (α relaxation) has been studied as a function of temperature and pressure by Williams and Watts (WW).[50] The time window $10^{-6} < t < 10^{-1}$ s of PCS corresponds rather well with the frequency window of $1 < f < 10^5$ Hz of dielectric relaxation. As a consequence the temperature range of PCS measurements overlaps almost completely that of dielectric measurements at any applied pressure. WW have found the KWW function eq 6 gives a good representation of the dielectric data for $\beta_{\mathrm{dr}} = 0.38$, independent of temperature and pressure. Also τ^*_{dr}, which is inversely proportional to $\omega_{\max}$ the angular frequency of maximum loss (the proportionality constant is approximately 0.65 for $\beta_{\mathrm{dr}} = 0.38$),[7] can again be fitted by the VFTH equation with the same B and T_0 as found for the temperature dependence of $\bar{\tau}_{\mathrm{b}}$ of PCS. After correcting the difference[7] between $\omega_{\max}^{-1}$ and $\bar{\tau}_{\mathrm{b}}$ and the relation between τ^*_{b} and $\bar{\tau}_{\mathrm{b}}$ for $\beta_{\mathrm{b}} = 0.38$, we find that τ^*_{dr} is shorter than τ^*_{b} by a factor of approximately 2 throughout the temperature range of measurement.

In this instance, the correlation between n and B is again obeyed in a special way: $n_{\mathrm{dr}} = n_{\mathrm{b}}$ and at the same time $B_{\mathrm{dr}} = B_{\mathrm{b}}$. The experimental data are summarized in Table III. Another example of this type of behavior is afforded by PMA. The photon correlation study[11] has determined the KWW exponent $\beta_{\mathrm{b}} = 0.42 \pm 0.04$ and the parameters B and T_0 of the VFTH equation for τ^*_{b} to be 1814 and 222 K, respectively. These values agree well with those determined from dielectric relaxation data[51] and from shear compliance data[15,52] (see Table III). Moreover the pressure dependence of τ^*_{b} reflected by the size of the activation volume is also in good agreement with the dielectric relaxation data.

The four amorphous polymers PPO, PVAc, PMA, and PEA discussed here together with atatic, completely amorphous polypropylene published elsewhere[14] all follow similar trends. The KWW function form $\exp[-(t/\tau^*)^{1-n}]$ gives a good representation of the relaxation function $\phi(t)$ of the local segmental motion, independent of the nature of the probe: dielectric, shear viscoelastic, bulk viscoelastic, and dynamic light scattering. The fractional exponent n and the effective relaxation time τ^* may depend on the probe. The temperature dependence of τ^*, at temperatures not too far above T_g, follow the WLF equation or the equivalent VFTH equation $\ln \tau^* = \ln \tau^*_0 + B/(T - T_0)$. If we choose the *same* T_0 for fitting the VFTH equation to the τ^* data sets obtained by different probes, then an interesting correlation has been established between n and B. We find that the data for a probe exhibiting a larger n (smaller β) will also have a larger B. On the basis of the observations made on only four amorphous polymers, it seems that the less bulky backbone polymer PPO has a larger spread in the values of either n or B for different probes. While polymer with bulkier backbone such as PVAc has a narrower spread, and PEA the bulkiest of the three has almost no spread.

Other than the four given examples of polymers in which both dielectric relaxation and dynamic light scattering have been measured, there are also polystyrene[6-9] and the poly(alkyl methacrylates)[7,53] including PMMA, PEMA, and PBMA. The methacrylates are not suitable for testing the correlation because of the difficulty of determining the KWW exponent of the local segmental (α) mode caused by the overlapping contribution from the β mode. Polystyrene has a small dipole moment and low dielectric loss. The dielectric spectrum could be distorted by contributions other than that from the local segmental motion. In fact the reported dielectric loss[45] appears to be anomalous, the loss peak first narrows and then broadens on lowering the temperature. This is one among several reasons that polystyrene is not considered at this time. There are a number of nonpolymeric glass-forming liquids on which both PCS and dielectric relaxation measurements of the primary relaxation have been made. Discussions of these results are beyond the scope of this work and will be presented elsewhere.

Coupling Model. Explanation of the Correlation

The basic approach to relaxation of a dynamic variable ψ (e.g., electric polarization, density, etc.) starts from Hamilton's equations of motion of the generalized phase-space coordinates q_i and momenta p_i. The dynamic variable ψ projected out from phase space is defined by a function $\psi(q_i,p_i)$ of the phase-space variables. The other faster variables play the role of what is conventionally called the heat bath, which enables the irrevisible processes of the dynamic variable to occur, such as the decay of correlation. The decay (relaxation) rate W is usually regarded as a constant of time and has been substantiated by theoretical developments under certain approximations.[54] For the local segmental mode, the dipole moment μ is its dynamical variable when considering dielectric relaxation in polymers having transverse dipole moment rigidly attached to the polymer backbone. The density fluctuation is the dynamical variable of the local segmental motion when the latter is monitored by dynamic light scattering. Several mechanisms may contribute to dynamic light scattering but we are concerned only with the "Mountain" line.[55,56]

The actual chain dynamics and the mode of conformational transitions that give rise to a local segmental motion have been clarified for a single chain in a frictional medium.[57] It has been determined that on varying the temperature while holding the friction constant fixed, the activation energy of the transition is approximately equal to one barrier height between the trans and a gauche state, as the experiments had indicated. In a bulk polymer, effects due to interchain interactions on the conformational transition are important especially near T_g. One obvious effect caused by molecular interactions is caused by their crowding. The change in the effect of the crowding as temperature falls has been modeled by either a decrease of configurational entropy or a reduction of free volume.[15] With reasonable assumptions, the temperature dependence of the frictional coefficient ζ_0 can be derived by either approach. The friction factor ζ_0 has the WLF or the equivalent VFTH form of

$$\zeta_0 \propto \exp[B_0/(T - T_0)] \tag{20}$$

Near T_g, ζ_0 varies rapidly with temperature and its inverse dominates the temperature dependence of the conformational transition rate W_0 in the bulk polymer.

Another effect of molecular interactions stressed by the coupling model[21,59–61] is the slowing down of the initially constant rate W_0 at times longer than a time t_c characteristic of the strength of the molecular interaction. We[20] have recently modeled the molecular interactions as time-dependent constraints in Dirac's formulation of classical mechanics with constraints.[58] A time-dependent contribution to the Liouville operator is shown to arise from the time development of the constraints. A standard method of statistical mechanics of an irreversible process generalized to include the time-dependent Liouville operator leads to the conclusion that for $t > t_c$, the primitive relaxation rate W_0 is reduced and assumes a time-dependent form, $W(t) = W_0 f(t)$ where $f(t) < 1$ for $t/t_c > 1$, and reflects the rate slowing down.[20] This rate slowing down is the central idea behind the coupling model. It is difficult if not impossible to calculate the function $f(t)$ from first principles. Although we have been able to derive the form of $f(t)$ from general and fundamental principles, the methods[59–61] used are rather special and not immediately transparent. However, now there is an easier way[20] to find $f(t)$. The functional form of $f(t)$ can be adduced from the requirement of time–temperature equivalence (e.g., thermorheological simplicity) of the relaxation function $\psi(t)$ for a single relaxation mechanism obtained by solving the rate equation $d\psi/dt = -W_0 f(t)\psi$. A relaxation function $\psi(t)$ is thermorheologically simple if $\psi(t)$ can be written as a function $\psi(t/\tau^*)$ of the reduced time t/τ^*, and a change of temperature modifies only τ^* but not the functional form ψ. A proof was given in ref 20 that $f(t)$ can only have the form of $(\omega_c t)^{-n}$, $0 < n < 1$, in order that the slowed relaxation function ψ be thermorheologically simple. For more details of this proof and the classical mechanic and statistical mechanic derivation of rate slowing down in this new approach of the coupling model we refer the reader to ref 20. The reason that this new approach is being stressed here is that its conceptual basis naturally implies that the magnitude of the coupling parameter n depends on the constraints which in turn depend on the dynamical variable. The constraints imposed on relaxation of a dipole transverse to the chain backbone need not be the same as those imposed on shear deformation or those imposed on bulk deformation. Hence in general the value of n for dipole relaxation (n_{dr}) may differ from that (n_J) for shear compliance and from that (n_b) for density fluctuation. In this short description of a constraint dynamics model,[20] we have tried to make the last conclusion as intuitively obvious as possible. An entropic reformulation of the model together with the use of generalized Kullback–Leibler[63] relations has enabled us[62] to arrive at the inequalities

$$n_{dr} \leq n_J \leq n_b \tag{21}$$

from fundamental principles. This theoretical work[62] will be submitted elsewhere for future publication. Its content is beyond the scope of this paper and will not be discussed any further.

The predictions of the coupling model now follow from the solution to the rate equation[21]

$$d\psi/dt = -W_0(\omega_c t)^{-n}\psi \tag{22}$$

where $\psi(t)$ can be identified with $g(t)$, the time correlation function of density fluctuation for dynamic light scattering, and with $\phi(t)$, the dipole moment correlation function for dielectric relaxation. If the coupling parameters n_{dr} and n_b as well as the primitive transition rates W_{0b} and W_{0dr} are permitted to differ, the solutions to eq 22 are the KWW functions given by eq 5 or 6, which are thermorheologically simple. This first prediction of the form of the relaxation function is followed by the second prediction that, if $\omega_c/W_0 \gg 1$,

$$\tau^*_b = [(1 - n_b)(\omega_c)^{n_b} W_{0b}^{-1}]^{1/(1-n_b)} \tag{5'}$$

and

$$\tau^*_{dr} = [(1 - n_{dr})(\omega_c)^{n_{dr}} W_{0dr}^{-1}]^{1/(1-n_{dr})} \tag{6'}$$

and a third relation of crossover[21,61] if $\omega_c/W_{0b} \ll 1$ or $\omega_c/W_{0dr} \ll 1$. From the model, the inverses of both W_{0b} and W_{0dr} are proportional to the primitive friction factor ζ_0, i.e., $W_{0b} \propto W_{0dr} \propto \zeta_0^{-1}$. Then on combination of the VFTH equation (20) for the primitive friction factor with eq 5′ and 6′, temperature dependences of the effective τ^*_b and τ^*_{dr} can be predicted to be

$$\tau^*_b \propto \exp\{[B_0/(1 - n_b)]/(T - T_0)\} \tag{23}$$

$$\tau^*_{dr} \propto \exp\{[B_0/(1 - n_{dr})]/(T - T_0)\} \tag{24}$$

On comparing these with eq 11 and a similar equation for τ^*_{dr}, we arrive at the additional "second" predictions

$$B_b = B_0/(1 - n_b) \quad (25)$$

$$B_{dr} = B_0/(1 - n_{dr}) \quad (26)$$

together with a similar relation for shear compliance

$$B_J = B_0/(1 - n_J) \quad (27)$$

These two results can be combined into an invariance relation

$$(1 - n_b)B_b = (1 - n_J)B_J = (1 - n_{dr})B_{dr} = B_0 \quad (28)$$

The invariance of the product $(1 - n)B$ has been discussed previously as eq 8 in the Introduction and tested for several polymers in electric dipole relaxation, shear compliance, and bulk deformation. Within the error bounds the invariance of the product is verified as can be judged by inspection of the tables. To avoid possible confusion we remind the reader that the last entry in the column under $(1 - n)B$ of Table II for PVAc is not obtained actually as a product of B and a value of $(1 - n)$. The strong temperature dependence of $(1 - n)$ in this case has preempted such a simple operation. Instead, a full analysis according to eq 6′ must be used to obtain B_0. The value entered, 843 ± 59 K, is taken from the analysis given in ref 49.

Thus, a natural explanation of the empirical correlation established in this work between the KWW exponent n and the B parameter in the VFTH equation can be found in the second prediction of the coupling model. The coupling model has the advantage of predicting also the KWW relaxation function. On the other hand, a free volume model would have to invoke inhomogeneous fluctuations in free volume and their ad hoc distribution to generate a KWW function. Although fluctuations in free volume are possible, recent experiments,[64-66] if interpreted this way, have all pointed to the sizes of the local free volumes being an order of magnitude too small compared with the molecular volume,[67] suggested to be responsible for the local segmental motion. The concept of free volume is useful but it is not fundamental[15] as compared with molecular interactions and constraints in classical mechanics. Finally, a polymer with a bulky backbone may tend to have the coupling parameter n averaged out to the same value, independent of the nature of the probe. This trend, expected from the concepts of the coupling model, has been observed empirically and discussed in the previous section.

Conclusions

The comparisons between the effective relaxation times τ^* of the local segmental mode probed by dynamic light scattering and by dielectric relaxation in some polymer systems have been made repeatedly in the past. In some polymer systems especially PPO their temperature dependences are not the same, while in others such as PEA and PMA they are similar. The temperature dependence of τ^* near the glass temperature is well fitted by the Vogel–Fulcher–Tamann–Hesse (VFTH) equation: $\tau^* = \tau_0 \exp(B/T - T_0)$. The same reference temperature T_0 has been chosen for analysis of data obtained from different probes on samples with the same T_g. Whenever samples with different T_gs are considered, the T_0s are adjusted such that the difference between T_g and T_0 is the same. Then if the temperature dependence of τ^* is probe dependent, it will be reflected genuinely by the dependence of B on the nature of the probe. In this work, additionally we examine the relaxation functions or correlations functions of the different relevant dynamical variables (e.g., dipole moment polarization for dielectric relaxation and density fluctuation for dynamic light scattering). The correlation functions are always well described by the Kohlrausch–Williams–Watts (KWW) form: $\exp[-(t/\tau^*)^{1-n}]$. We find the fractional exponent n in the KWW function is independent of (dependent on) the probe, then the B parameter in the VFTH equation for τ^* is also independent of (dependent on) the probe. Empirically we have established the product $(1 - n)B$ is invariant when a change of probe is made. We have considered all the polymer systems in which both dielectric relaxation and dynamic light scattering data are available and are unambiguous for determinations of the parameters B and $(1 - n)$. These include PPO, PVAc, PEA, and PMA. Shear compliance data whenever available have also been taken into account. Shear creep has been considered as another probe and again for a given material the invariance of the product $(1 - n)B$ is verified if dielectric relaxation, light scattering, and shear compliance data are all included for consideration. Such a result, of course, does not interrelate τ^* values from the different experiments since the preexponential factor τ_0 has not been considered in arriving at the constancy of $(1 - n)B$.

A theoretical explanation of the empirical invariance relation has also been given in the framework of the coupling model. The coupling model has the physical concepts and the predictions to explain the KWW form, the dependence of the KWW exponent β on the probed dynamical variable of the local segmental motion, and the invariance of the product βB established empirically in this work.

Registry No. PVAc, 9003-20-7; PEA, 9003-32-1; PMA, 9003-21-8; PPG, 25322-68-3.

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Test of the Reptation Concept: Crystal Growth Rate as a Function of Molecular Weight in Polyethylene Crystallized from the Melt

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ABSTRACT: The concept of reptation in high polymer melts is tested for the case of crystallization, where a strong force resulting from the free energy difference between the subcooled liquid and the lamellar crystal is envisaged as drawing a chain through a reptation tube onto the substrate. The presence of the strong force sets this process apart from the case of free curvilinear diffusion. The test is made by determining the dependence on molecular weight of the crystal growth rate at constant undercooling, $G_{\Delta T\mathrm{const}}$. According to the development presented, which combines nucleation and reptation theory, $G_{\Delta T\mathrm{const}}$ varies as $n^{-[y+f(\lambda)]}$, where the factor n^{-y} with $y = 1$ derives directly from the steady-state reptation concept where the overall friction coefficient in the tube is proportional to the number of monomer units n. The factor $f(\lambda)$ is of statistical mechanical origin and accounts for the free energy of first attachment of a chain to the substrate. On the basis of published growth rate data on 11 polyethylene fractions $n_z = 1590$ to $n_z = 14\,500$, it was determined that $y = 1.0 \pm 0.20$ in the vicinity of the regime I → II transition. This renders plausible the simple steady-state reptation tube model in this special application, where the molecule is reeled in quite rapidly allowing little time for lateral excursions of the tube, but not so rapidly that only short sections of "slack" can crystallize. Estimates are given for the reptation time. The paper contains results of interest concerning nucleation theory as it applies to chain-folded systems. Besides modifying the theory to account for the free energy of first attachment, the treatment is developed for regimes I and II along parallel lines first excluding the backward reaction, i.e., stem removal, in the "$\epsilon = 0$" case and then in the case denoted "$\epsilon = 1$" including it. The differences between the two are minimal, showing that neglect of the backward reactions is permissible under stated circumstances. It is significant that the improved theory (with either $\epsilon = 0$ or $\epsilon = 1$), coupled with improved input data, leads to a lower substrate completion rate g and a smaller substrate length ($L \simeq 210$ Å) than had been estimated previously.

I. Introduction

In its simplest form, the reptation concept proposed by de Gennes holds that under appropriate circumstances the overall friction coefficient of a linear polymer chain in the liquid state is proportional to its length.[1] Here we propose to test this idea by considerations based on the dependence on molecular weight of the rate of crystallization from the melt at constant undercooling.

At a fixed undercooling, the mean force $\bar{f}_c$ drawing the polymer molecule onto the growth front is constant av-

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