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Pressure- and Temperature-Dependent Photon Correlation Study of Bulk Poly(ethyl acrylate) above the Glass Transition Temperature

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ABSTRACT: We report polarized photon correlation measurements of bulk poly(ethyl acrylate) (PEA) in the temperature range between −8.3 and +26.4 °C, above the glass point (T_g = −24 °C), and in the pressure range between 1 and 2000 bar. The temperature dependence of the mean relaxation time conforms to a Vogel–Fulcher–Tamann equation involving a divergence at $T = T_0$. For the pressure dependence, we use an empirical equation (eq 7 in the text) which is interpreted in terms of the free volume model and of the rotational isomerization model. The temperature dependence of the apparent activation energy and activation volume can be described on this basis. The quantities as hole volumes, hole formation energies, and isomerization energy barriers calculated from both models have physically meaningful values. The physical picture suggested by these findings is that of a local segment motion involving the cooperative rearrangement of a small number of monomer units.

1. Introduction

The dielectric behavior of amorphous polymers has been extensively studied over the past 20 years as a function of temperature and pressure.[1-3] One important feature that has emerged from these studies is the existence of two relaxation regions in some polymers known as α and β, which tend to coalesce at higher temperatures. The α relaxation has been ascribed to collective motions of the chain involving several segments, and the freezing of this motion has been related to the glass transition of the polymers. On the other hand, the assignment of the β motion to the dynamics of polar side groups or to local intrachain motions is a question still open to debate. Recently, photon correlation spectroscopy[4-8] has been established as an important technique to contribute to the elucidation of the dynamics of amorphous polymers from a different viewpoint, i.e., by probing the isotropic and the anisotropic polarizability dynamics within the polymer. These two components are selected through the direction of polarization of the scattered light relative to that of the incident laser beam.

All the photon correlation spectroscopic studies of bulk polymers have been so far performed at 1 atm as a function of temperature. The time correlation functions obtained so far in the temperature range above T_g show no molecular weight dependence and no angular dependence,[7] with, until now, one remarkable exception.[6] Furthermore the light scattering and the dielectric relaxation times have very close values and both exhibit a significant deviation from the Arrhenius temperature dependence. This has been generally interpreted in terms of a decrease of the available free volume beyond a critical value required for the molecular motion, thus leading to increasing cooperativity and hence to larger relaxation times. This interpretation suggests strongly to study the effect of high pressure on the relaxation times of the polymer melt.[9]

In this line of thought we present a pressure- and temperature-dependent light scattering study of poly(ethyl acrylate) $(-CH(COOC_2H_5)CH_2-)_n$ (PEA), with the objective to study the pressure effects on the time correlation function and to obtain the energy and volume activation parameters describing the dynamics of a bulk polymer near T_g. We then compare the results with dielectric relaxation data[2,10] and theoretical predictions based on conformational transitions of the chain[11] and free volume considerations.[12]

2. Experimental Section

Photon correlation functions at different temperatures (−9 to +26 °C) and pressures (1–2000 bar) were taken at a scattering angle θ = 90°, using the apparatus described elsewhere.[13] The light source was an argon ion laser (Spectra-Physics) operating at λ_0 = 488.0 nm and at 400-mW power. Both the incident beam and the scattered light were polarized perpendicular (V) to the scattering plane. This geometry gives the so-called VV-spectral component of the scattered light, I_{VV}. The single-clipped photocount autocorrelation function was measured with a 96-channel Malvern correlator. The measurements were performed with the high-pressure light scattering cell at 90 °C shown in Figure 1, which was designed for pressures up to 3 kbar. The high-pressure cell can be used in the temperature range from −50 to +200 °C, mainly limited by the material of the O-rings used. The high-pressure cell, 15 cm in diameter and 19 cm high, was constructed of stainless steel 4057. The cylindrical cell body (3) had an axial hole, where a rectangular (12 mm × 12 mm) glass cell could be placed. Cylindrical light scattering cells of 10-mm o.d. were also used with a black metal sample holder (8). The plate (2) on the top of the central hole was sealed to the main body via a Viton O-ring and the pressurizing medium—in the present case nitrogen—entered the cell at the inlet (1). Three optical windows in 90° geometry, two of these drawn in Figure 1, were incorporated into the main body. The saphire windows (4) placed into the window holders (5) were made pressure tight in a way that the applied high pressure compresses the Teflon ring (6). At the same time the Teflon ring (7) is sealed to the cell body. To minimize the volume of nitrogen and additionally to have refractive index matching conditions, n-hexane was filtered into the main hole up to the top of the sample cell. The thermostating liquid was circulated through a jacket surrounding the main cell body and the temperature was measured by means of a thermocouple (9) located very close to the sample position. The pressure was generated with a Nova Swiss membrane compressor and was measured with a Heise gauge having a resolution of ±3 bar.

The PEA sample was prepared by thermal polymerization at 90 °C of monomer ethyl acrylate purchased from Merck. The monomer, after vacuum distillation to remove the inhibitor and after addition of ~0.1 wt % 2,2′-azobis(isobutyronitrile) as initiator, was filtered through a 0.22-μm Millipore filter into the dust-free light scattering cell (10-mm o.d.) and, after degassing, was flame sealed under vacuum. This monomer sample was polymerized at 90 °C for 1 week, heated to 150 °C for 1 day to complete the reaction, and then slowly cooled to room temperature to minimize strains. The polymer conversion was checked by Raman spectroscopy.[14] The low Landau–Plazcek intensity ratio (~4 at 25 °C) computed by recording the Rayleigh–Brillouin spectrum constitutes an additional confirmation of the suitability

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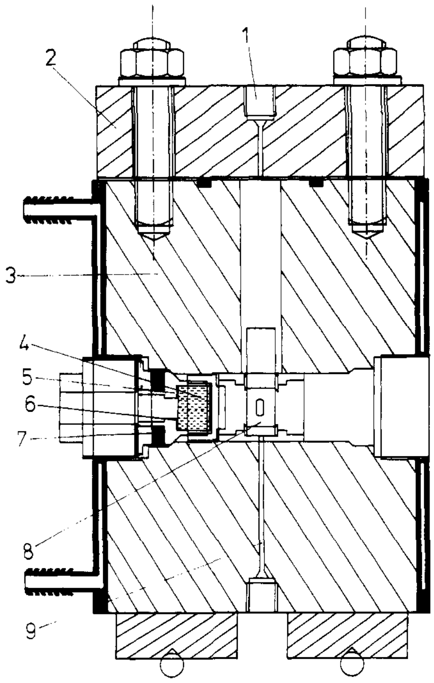

Figure 1. High-pressure light scattering cell: (1) inlet of pressurizing nitrogen; (2) high-pressure cover; (3) main high-pressure vessel body; (4) saphire window; (5) window holder; (6, 7) Teflon rings; (8) sample; (9) thermocouple.

of the PEA samples for photon correlation measurements as far as optical homogeneity is concerned. The top of the optical cell was opened before the high-pressure measurements were started.

3. Data Analysis

The measured single-clipped photocount autocorrelation function for a detector of finite effective photocathode has the form

$$G_k^{(2)}(t) = A(1 + b|g^{(1)}(t)|^2) \qquad (1)$$

where $g^{(1)}(t)$ is the normalized correlation function of the scattered electric field, k is the clipping level, A is the background, and b is an unknown parameter used in the fitting procedure, depending mainly on the clipping level, the coherence area, and the delay time. t $(=I\Delta\tau)$ is the delay time, with I and $\Delta\tau$ being the channel number and the increment delay time, respectively.

In order to describe the origin of the observed decay times, which do not conform to a single-exponential scheme, we have chosen for the correlation function $g^{(1)}(t)$ the empirical form[10]

$$g^{(1)}(t) = \exp(-t/\tau_0)^{\beta} \qquad (2)$$

where β $(0 < \beta \leq 1)$ is a measure of the width of the distribution of decay times. The mean relaxation time $\bar{\tau}$ is given by

$$\bar{\tau} = \frac{\tau_0}{\beta}\Gamma(\beta^{-1}) \qquad (3)$$

where $\Gamma(\beta^{-1})$ is the gamma function.

Figure 2 shows four normalized correlation functions $|g^{(1)}(t)|^2 = [G_k^{(2)}(t)/A - 1]/b$ at 16.5 °C for different pressures (1, 600, 1200, and 1500 bar), obtained by superimposing two successive sections obtained with different delay times $\Delta\tau$ (by a factor of 10). The equation

$$G_k^{(2)}(t)/A - 1 = a + b \exp[-2(t/\tau_0)^{\beta}] \qquad (4)$$

has been fitted to the combined correlation function thus obtained, where a accounts for a small nonzero background (10^{-3}). The β parameter obtained from the correlation functions in Figure 2 was equal to 0.38 and is virtually independent of temperature and pressure. The section of the experimental correlation function with the largest $\Delta\tau$ has been taken under the condition $\bar{\Gamma}\tau_{\max} \sim 2.5$, with $\tau_{\max} = 92\Delta\tau$ and $\bar{\Gamma}$ being the average line width as computed by the cumulant method.[15] A fit of eq 1 and 2 with a fixed base line A measured with the four last channels to this section of the correlation function leads to almost the same mean value of the relaxation time $\bar{\tau}$ as the two-section fits covering about 3 decades in time, but with a slightly different β value. Thus for $\beta \geq 0.4$ the one-section correlation function with $\bar{\Gamma}\tau_{\max} \sim 2.5$ seems to comprise the same information in terms of $\bar{\tau}$ and β as the composite correlation function. Nevertheless, in order to ensure a unified data procedure we have always measured two sections as described above.

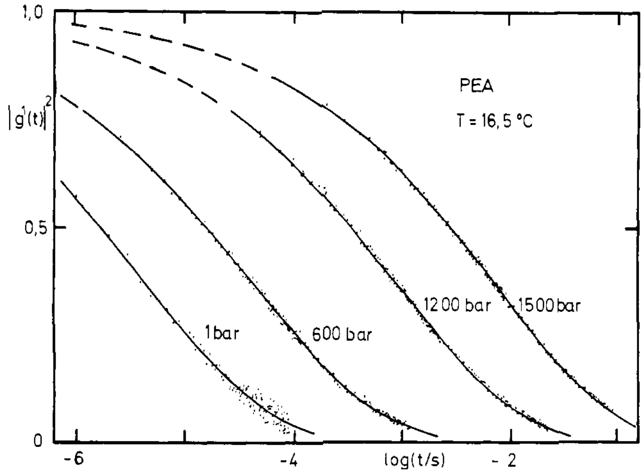

Figure 2. Normalized VV-correlation functions of poly(ethyl acrylate) plotted vs. log t at 16.5 °C for different pressures. The dots are experimental points and lines are the best fits to eq 4.

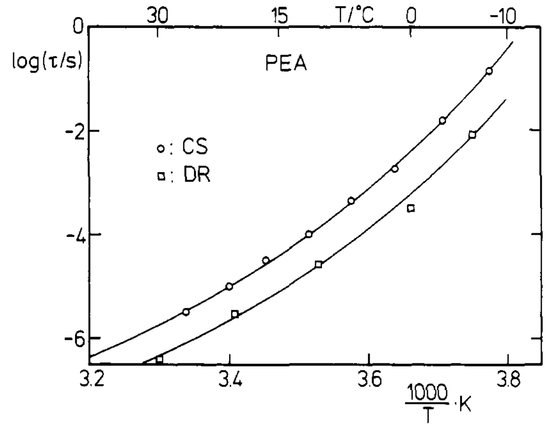

Figure 3. Temperature dependence of relaxation times of poly(ethyl acrylate) as probed by correlation spectroscopy (CS) (○) and dielectric relaxation (DR) (□) (ref 10) at 1 bar.

4. Results and Discussion

1. Temperature Dependence of the Relaxation Time. The values of $\bar{\tau}$ and β of PEA as a function of temperature at different external pressures are listed in Table I. The mean relaxation time $\bar{\tau}$ is a decreasing function of temperature as shown in Figure 3. By fitting a Vogel-Fulcher-Tamann (VFT) equation of the form

$$\ln \bar{\tau} = \ln \tau_0 + B/(T - T_0) \qquad (5)$$

to the experimental data at 1 bar of Table I, we obtained $\bar{\tau}_0 = 3.4 \times 10^{-13}$ s, $B = 1404$ K, and $T_0 = 213$ K. (The relaxation times at 26.4 and 21 °C are extrapolated values from Figure 4 and are also included in the fit of eq 5.)

Table I
Mean Relaxation Time $\overline{\tau}$ and the Relaxation Time Distribution β Obtained from the Polarized Time Correlation Functions of PEA

T/°C	P/bar	$\overline{\tau}$/s	β
−8.3	1	0.15	0.35
−3.4	1	1.7×10^{-2}	0.37
1.6	1	1.9×10^{-3}	0.36
6.5	1	4.0×10^{-4}	0.38
	400	5.0×10^{-3}	0.36
11.4	1	1×10^{-4}	0.36
	400	1.2×10^{-3}	0.38
	600	4.0×10^{-3}	0.40
	800	1.9×10^{-2}	0.35
16.5	1	3.2×10^{-5}	0.38
	400	4.3×10^{-4}	0.37
	600	1.1×10^{-3}	0.37
	800	3.7×10^{-3}	0.36
	1200	2.6×10^{-2}	0.38
	1500	0.17	0.38
21.0	400	7.9×10^{-5}	0.38
	600	2.9×10^{-4}	0.40
	800	6.6×10^{-4}	0.39
	1200	8.7×10^{-3}	0.35
	1500	2.8×10^{-2}	0.39
	1700	0.10	0.35
26.4	800	1.8×10^{-4}	0.39
	1200	1.4×10^{-3}	0.38
	1500	9.3×10^{-3}	0.35
	2000	7.8×10^{-2}	0.38

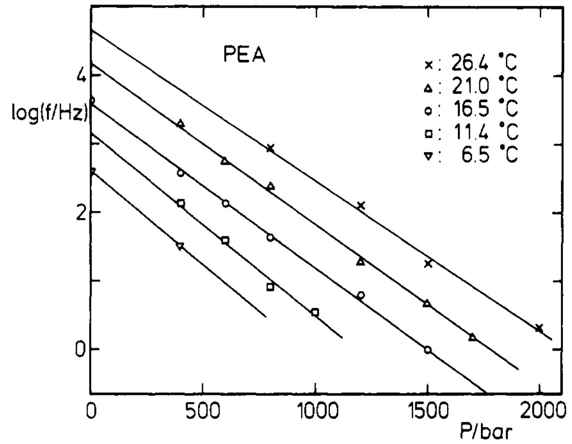

Figure 4. Pressure dependence of the relaxation frequency ($=1/(2\pi\overline{\tau})$) at different temperatures.

An Arrhenius fit of the $\overline{\tau}$ data at 1 bar would give an activation energy equal to 48.1 kcal/mol, which is similar to the activation energy value reported for polystyrene (PS)[4,5] and poly(propylene glycol) (PPG)[7] near T_g. Besides the fact that the Arrhenius equation is not suited for the representation of the data, it does not bring forth the basic physical picture associated with the temperature variation of $\overline{\tau}$. On the other hand, the values of the parameters B and T_0 of eq 5 can be rationalized in terms of the conformational motions of the polymers. In fact, using a simple three-state rotational isomer model, Miller has related B to the rotational activation energy of the rotation about the main-chain bonds ($E_0 = RB$, with R being the gas constant) and T_0 to the conformational entropy and furthermore to the energy difference between the rotational states.[11,16] On the basis of this model, the relaxation process as viewed through the polarized correlation function $g^{(1)}(t)$, which monitors the density fluctuations, is considered to be due to the concerted center-of-mass motion of chain segments.[7] The motion involving the whole macromolecule does not affect the time correlation function observed here, as clearly demonstrated by the independence of $\overline{\tau}$ on the molecular weight in PPG.[7] According to this rotational isomerization model, the energy E_0 of rotation about the chain backbone for PEA at 1 bar is equal to 2.8 kcal/mol, similar to the value found for PPG[7] and those found in the corresponding polymers from viscosity and α-dielectric relaxation data.[11,16]

The dielectric relaxation times exhibited in Figure 3 are calculated from the relation $\tau_D = 1/(2\pi f_m)$, where f_m is the frequency in cycles/s of the maximum dielectric loss ϵ'' for the α process at 1 bar as taken from Figure 9 of ref 10. The difference between τ_D and $\overline{\tau}$ (at 20 °C, $\overline{\tau}/\tau_D \simeq 5$) is a common feature in polymer systems. It is interesting to mention that the comparison of photon correlation light scattering and dielectric relaxation times for the polymers PS[4] and PPG[7] yields similar deviations between $\overline{\tau}$ and τ_D. The α-dielectric relaxation in PEA has been attributed to the rotation of the dipole moment component perpendicular to the main chain.[10] The direction of this dipole moment is supposed to vary via local isomerization of short main-chain segments,[17] which also may involve translation of scattering segments which will be monitored by polarized light scattering too. Thus photon correlation and dielectric measurements may yield similar but not necessarily identical relaxation times near T_g. A prima facie comparison of the relaxation data in Figure 3, apart from the fact that the two techniques here are basically probing different correlation functions and hence $\tau_D < 1/(2\pi f_m)$ for a broad distribution,[18] suggests that dielectric relaxation and light scattering reflect different aspects of essentially the same molecular motion. The similar temperature dependence of the times $\overline{\tau}$ and τ_D in Figure 3 adds credence to this suggestion. Additionally, we surmise that the temperature dependence arises for the most part from chain-to-chain interactions, whereas the individual relaxation times responsible for the broad distribution with values of β almost independent of temperature have an intrachain origin.[1] Thus the conclusions of this section confirm those drawn from the study of the molecular weight independence of PPG.[7]

2. Pressure Dependence. The large pressure effect on the time correlation function is demonstrated in Figure 2 and quantitatively expressed in terms of the times $\overline{\tau}$ in Table I. The relaxation frequency f_r ($=1/(2\pi\overline{\tau})$), frequently used in dielectric relaxation, is plotted in Figure 4 as a function of the pressure. If we consider the α relaxation as an activated process involving an activation volume, which reflects the volume requirements of the transition state, we obtain

$$\left(\frac{\partial \ln f_r}{\partial P}\right)_T = -\frac{\Delta V^*}{RT} \tag{6}$$

ΔV^* denotes the activation volume, i.e., the difference in the molar volume of the equilibrium conformation and the one corresponding to the transition state between two equilibrium conformations. The value of 130 cm^3/mol at 26.5 °C for ΔV^* corresponds to the molar volume of roughly four monomer units. This suggests that only a few repeat monomer units are involved in the activation process. This is in accord with the physical picture of local segmental motion stated above and the conclusion of PPG work[7] based on the invariance of $\overline{\tau}$ on molecular weight down to 425. This simple model has to be supplemented so as to allow for additional experimental features. Thus we find that ΔV^* increases with decreasing temperature from 130 cm^3/mol at 26.5 °C to 157 cm^3/mol at 6.5 °C, in agreement with the temperature trend that has been reported from dielectric relaxation studies.[10]

Before we proceed further, it is necessary to state the main experimental results of this study: (a) ln f_r varies linearly with pressure up to 2000 bar; (b) the shape of the measured correlation functions does not change either with pressure or with temperature as shown by the invariance of β (=0.38) with respect to these state variables; and (c) the temperature dependence of $\bar{\tau}$ at 1 bar is well described by eq 5.

In the frequency range accessible to photon correlation measurements, the experimental dynamics conform to hydrodynamics and hence the central position of the viscosity as a link between the macroscopic behavior of the polymer and the relaxation times observed, as illustrated by the Debye equation. Viscosity in liquids (and polymers) has been generally viewed as determined by the free volume available to enable molecules or parts of molecules to move from one equilibrium position to another.[12] Since this motion entails the passage of the system over an energy barrier, the pertinent rate constants will be expressible both in terms of an activation volume ΔV^* and activation energy ΔE^*. In this situation we have to decide whether we prefer to stress the energetic or the steric argument in our model consideration. An empirical relation for the relaxation times which leads to the observed divergence at T_0 and to a temperature dependence of the apparent activation energy and volume is

$$\bar{\tau}(P,T) = \bar{\tau}_0 \exp[(B + aP)/(T - T_0)] \qquad (7)$$

where $\bar{\tau}_0$ accounts for the distribution of relaxation times. This quantity is found to be independent of T and P. We thus conclude from the experimental facts a, b, and c that the second factor on the right-hand side of eq 7 is responsible for the T and P dependence of $\bar{\tau}$ in the form given by this equation. We thus obtain

$$\Delta V^* = aR/(1 - T_0/T) \qquad (8a)$$

$$\Delta E^* = (B + aP)R/(1 - T_0/T)^2 \qquad (8b)$$

Both quantities diverge for $T \rightarrow T_0$; however, the divergence of ΔE^* is more marked. The results in the narrow range between −8 and +26 °C do indeed confirm the trend manifested in these expression. As we shall see below, eq 7 is an approximation to the results of two apparently different approaches to interpret the Vogel constants B and T_0. Additionally, eq 7 has a convenient form for extrapolation and interpolation purposes.

From the fit of the temperature dependence of $\bar{\tau}$ at 1 bar to eq 5 in the previous section, we obtained $B = 1404$ K, $T_0 = 213$ K, and $\bar{\tau}_0 = 3.4 \times 10^{-13}$ s. Using these values, we computed via eq 7 and the data of Table I $a = 0.45 \pm 0.02$ K/bar. In agreement with eq 8a we thus obtain for the activation volume per rotating segment the constant value $\Delta V_1 = aR \simeq 37.5$ cm^3/mol over the whole temperature range of these measurements. Figure 5 depicts the fit of the relation (7) to the experimental data in a semilog plot. According to eq 8a the activation volume ΔV^* increses with decreasing temperature. As $T \rightarrow T_0$ we should observe a divergence. Two different attempts to connect the quantities $B(P)$ (=$B + aP$) and T_0 to the free volume theory[12] and to the more recent conformational[11,16] transition model of polymer chains have been reported in the literature. We show below the results obtained by applying these two models to our data.

According to the Cohen–Turnbull theory, the viscosity is given by[12]

$$\ln (\eta/\eta_0) = \gamma(v^*/v_f) \qquad (9)$$

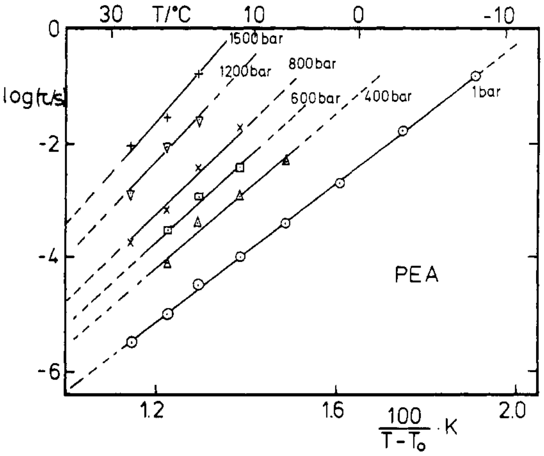

Figure 5. Mean relaxation time $\bar{\tau}$ of poly(ethyl acrylate) vs. $1/(T - T_0)$ at different pressures.

where v_f is the average free volume of a "cage" containing one molecule, v^* is the critical volume of the hole which must be available to the molecule to allow mobility, and γ is a numerical factor between $^1/_2$ and 1 accounting for the overlap of free volume between adjacent holes. Alternatively, empirical eq 7 has been proved to be suitable to represent the temperature dependence of the viscosity. Sanchez[12] has obtained an optimized approximation of the VFT eq 5 to the free volume eq 9 using the results of the hole theory of liquids. The quantity B is given by[12]

$$B(P) = 4.53\left(\gamma\frac{v^*}{v_s}\right)(E_h + Pv_h)/R \qquad (10)$$

with $E_h = 2RT_0$. In the original paper[12] the external pressure has been taken equal to zero. In eq 10, E_h, the energy required to form a hole in the polymeric melt, is related to the intersegmental interaction energy, v_h denotes the average hole volume, and v_s is the hard-core volume of the mobile segment. If the temperature dependence of the relaxation time $\bar{\tau}$ is the same as that of the viscosity,[7] then eq 10 predicts also a linear pressure dependence for $\bar{\tau}$, as found experimentally. By identifying $B(P)$ in eq 10 with $B(P)$ of eq 7, we obtained the values $E_h = 0.84$ kcal/mol, $\gamma(v^*/v_s) = 0.73$, and $v_h = 11.4$ cm^3/mol, corresponding to a hole diameter of 3.3. Å. The value of v_h compares reasonably to 7 cm^3/mol, the value found for poly(vinyl acetate) from compressibility measurements at T_g.[12] Also the value of the parameter $\gamma(v^*/v_s)$ should lie between $^1/_2$ and 1 in the case of full ability of the polymer to utilize the available free volume, i.e., $v = v_s$. However, values larger than 1 should not be excluded.

The second approach to the mobility of bulk polymers above T_g as a function of P and T is a molecular interpretation connecting the parameters $B(P)$ and $T_0(P)$ to the conformational energetics of transitions around main-chain bonds.[11] Ignoring the pressure dependence of T_0 for $P >$ 1 bar, we find that eq 6 of ref 11 reduces to

$$B(P) = B + (\partial \ln \bar{\tau}/\partial P)_T(T - T_0)P \qquad (11)$$

Since $B(P)$ depends only on the pressure, $(\partial \ln \bar{\tau}/\partial P)_T$ should be proportional to $1/(T - T_0)$ so that eq 10 has the form of eq 7. In the light of this interpretation the overall activation energy $E_0 = RB$ is related to the energy difference $U = 4.2RT_0$ between gauche and trans states and the energy barrier V between these states via the equation

$$E_0 = V - fU \qquad (12)$$

where f is the fraction of gauche bonds depending on temperature and U.

The strong pressure dependence of the relaxation times apparently reflects the intermolecular interaction of the polymer segments, exerting a profound influence on the energy V. This changes from 2.95 kcal/mol at 1 bar to 3.85

kcal/mol at 1000 bar, as calculated by eq 12 with $f = 0.09$ at 25 °C. If we give some credence in a more qualitative sense to the estimates of the "isolated-chain" values of the quantities E_0, V, and U,[11] it appears that our values are, as expected, much larger.

These calculations show that with both models we obtain reasonable results for quantities like hole volumes and hole formation energies or isomerization energy barriers. This is not unexpected since the physical basis of both models is simple and not too different. The isomerization model gives to the hole model a more precise interpretation which, however, cannot be validated or invalidated by this kind of measurement.

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Light Scattering Study of a Series of Xanthan Fractions in Aqueous Solution

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ABSTRACT: A series of fractions of xanthan polysaccharide (Kelco Keltrol) has been prepared by ultrasonic degradation and subsequent molecular weight fractionation on preparative-scale size exclusion chromatography columns packed with controlled pore glass (Electronucleonics CPG-10). The samples were converted to the sodium salt form and studied in 0.1 M aqueous NaCl solution. They were characterized by NMR, ORD, and UV absorption spectroscopy and are believed to be chemically equivalent to the undegraded starting material. Twelve xanthan samples covering a range of $\bar{M}_w$ from 0.8×10^5 to 19.5×10^5 were studied by Rayleigh light scattering. The radii of gyration and second virial coefficients were found to depend on molecular weight in the way expected for samples of molecularly dispersed, semiflexible macromolecules. For the samples of higher molecular weight the angular dependence of the scattering intensity exhibited asymptotic behavior at high angle and could be analyzed directly to give a linear mass density of about 2000 daltons/nm. Assuming that the samples of lower molecular weight behave as rigid rods, it was also possible to analyze the scattering curves for these samples in the limiting (low angle) region to yield the linear mass density. Although these data are more scattered due to uncertainties arising from the correction for molecular weight heterogeneity, they yield a linear mass density fully consistent with the value obtained from the asymptotic behavior of the high molecular weight samples. These results support the proposal by Holzwarth that xanthan exists in aqueous solution as double-stranded helical chains.

The bacterial polysaccharide xanthan is of interest not only for its commercial applications,[1,2] but also because it is known to undergo transitions in conformation which can be driven by changes in temperature, ionic strength, and the degree of ionization of the polymeric carboxyl groups.[3-9] Although the chemical constitution of the polymer now seems firmly established (cellulosic backbone with ionic three-sugar side chains on alternating backbone residues),[10,11] the polymer chain conformation remains a matter of some discussion [3-9,12-21] The present work has been undertaken in an attempt to deduce from Rayleigh light scattering some additional information about the stiffness of the xanthan chain in dilute solution and the linear mass density of the molecule.

The limiting (low angle) dependence of Rayleigh scattered light from an infinitely dilute solution of macromolecules, chemically homogeneous but heterogeneous with respect to molecular weight, is well-known to yield the mean-square z-average radius of gyration $\langle s^2\rangle_z$ regardless of particle shape, provided certain basic conditions are met.[22] The same experiment yields the weight-average molecular weight $\bar{M}_w$ of the particles and, if the concentration dependence of the scattering at zero scattering angle is analyzed, a complicated average of the osmotic second virial coefficient A_2' may be obtained.[23] If the solvent comprises more than one component, then special experimental procedures are required in general to obtain the true molecular weight and virial coefficient of the macromolecular component.[24] Data of this sort are normally analyzed by using the equation

$$\frac{Kc_2}{\alpha i(\theta)} = \frac{1}{\bar{M}_w}\left[1 + \frac{\mu^2\langle s^2\rangle_z}{3}\right] + 2k^{-1}A_2'c_2 \qquad (1)$$

where K and α are standard optical parameters defined elsewhere,[25,26] c_2 is the polymer concentration in g/mL, $i(\theta)$ is the excess scattering at angle θ due to dissolved polymer, μ is the magnitude of the scattering vector defined by μ

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