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Subglass Relaxation Processes. Dielectric Relaxation in Methyl Acrylate/Ethylene Copolymers

D. E. Buerger and R. H. Boyd*

Department of Materials Science and Engineering and Department of Chemical Engineering, University of Utah, Salt Lake City, Utah 84112.
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ABSTRACT: A pendant methyl ester group attached to the polyethylene chain has been chosen as a model system for studying the subglass relaxation process associated with flexible side-group motion in polymers. Dielectric measurements have been made on a series of methyl acrylate/ethylene (MA/E) copolymers of varying polar group concentration, including PMA homopolymer. Phenomenological analysis of the data has been carried out to establish the strength, activation, and width parameters of both the α glass-rubber relaxation process and the β subglass process. The subglass process in PMA is known to have a relatively strong β process compared to the α glass-rubber relaxation. In MA/E copolymers, the relative strength is found to be even greater. Preliminary conformational energy calculations indicate that the relaxation involves reorientation between two side-group conformers of slightly different energy.

It is well-known that there are three general types of molecular motions and attendant relaxation processes commonly observed in polymers.[1,2] The highest temperature one isochronally is found in some semicrystalline polymers and is associated with a rotational-translational motion about and along the chain "*c*" direction in the crystal. Successful molecular models exist for describing the process.[3,4] The next process in descending temperature is the glass-rubber relaxation that occurs in amorphous polymers. It is characterized by WLF temperature behavior of the relaxation times and, dielectrically, by a modestly wide but skewed distribution of relaxation times. It also occurs in the amorphous fraction in semicrystalline ones but with a much broader distribution of relaxation times. Although no comprehensive molecular theory exists for the dynamics of the process, it can be regarded as understood conceptually as the achievement of the ability to visit the conformational space of individual polymer chains through cooperative segmental motions that are long range in nature. Much less well understood is the class of motions that occur in most polymers at temperatures below the glass transition. These processes are characterized by Arrhenius temperature behavior of the relaxation times and by an extremely broad distribution of relaxation times. In many cases, the polymer in question contains a pendant side group that can be regarded as conformationally flexible. Accordingly, there has been great motivation to associate the subglass process with motions in the side group. However, most polymers without flexible side groups also show subglass relaxations. Thus it is of importance to demonstrate that, in fact, the observed process can be associated on the one hand with side-group motion or on the other hand with local main-chain motions.

One way to increase confidence in the concepts would be to develop molecular models that successfully account for the experimental observations. Since the proposed motions are essentially localized in nature, there is some hope of molecular mechanics calculations giving rise to successful models. However, if this is to be the case, then it is important that there be appropriate experimental data available for systems that can be effectively modeled molecularly. We have selected the pendant ester group as the basis for model systems that give rise to dielectrically active subglass relaxations and can also be effectively modeled by conformational energy or "molecular mechanics" calculations.

The present work reports dielectric data on methyl acrylate/ethylene (MA/E) copolymers. This system presents the opportunity to investigate a structural environment where the flexible side group is attached to the main chain in a dilute or isolated condition and is not interacting with adjacent side groups. This then allows experimental observation of the effect of nearby intramolecular environment on the relaxation process as well as provides data for a situation for which it is inherently easier to develop a molecular conformational energy model. A further advantage to the ester group is that the subglass processes appear to display a sensitivity to side-group molecular structural details that is welcome in the context of being able in general to connect structure to process. The homopolymer, poly(methyl acrylate) (PMA), is well-known to have a prominent subglass process whose strength is an appreciable fraction in comparison with that of the glass-rubber relaxation and furthermore is reasonably well separated from the latter in time-temperature.[5] In contrast, the chemically isomeric poly(vinyl acetate) (PVAc), which also possesses a pendant ester group, has a much weaker subglass process,[6] and its copolymers with ethylene are more complex in that they show evidence of splitting into two processes in low-frequency isochrones.[7]

Experimental Section

Polymer Preparation and Chracterization. The methyl acrylate/ethylene copolymers were prepared by derivatizing acrylic acid/ethylene copolymers. The latter were purchased from the Scientific Polymer Products Co., Ontario, NY. The esterification utilized a two-step synthesis[8] by way of chlorothioformate intermediates (III) (see Figure 1). In the first reaction, a 5× molar excess of thionyl chloride (II) was added to a 10% by weight solution of the copolymer (I) in toluene. The reaction was allowed to proceed at 70 °C for 12 h, after which the excess thionyl chloride was boiled off. A 10× molar excess of methanol was then added and allowed to react at 70 °C for 5 h. The esterified product(IV) was precipitated in methanol, filtered, dried, and finally weighed. Reaction progress was monitored in both steps in infrared spectroscopy. The frequencies in Figure 1 indicate the peak position of the carbonyl absorption ($\nu_{C=O}$) for the species involved.

The manufacturer gave the weight percent acrylic acid of the parent polymer, and these nominal values gave rise to the sample nomenclature used in Table I. The actual copolymer compositions used in the dielectric data analysis were established by elemental C and H analysis and direct O analysis (by Galbraith Laboratories, Inc., Knoxville, TN). The resulting mole percent compositions are listed in Table I.

The PMA homopolymer was purchased already synthesized from the Scientific Polymer Products Co.

The copolymers are semicrystalline. The effect of copolymerization and the fact that they are effectively copolymers with branched polyethylene serve to limit the degree of crystallinity, even at the lower copolymer contents. At the higher MA contents, the level of crystallinity is low but detectable. The degrees of crystallinity were measured via thermal analysis in a

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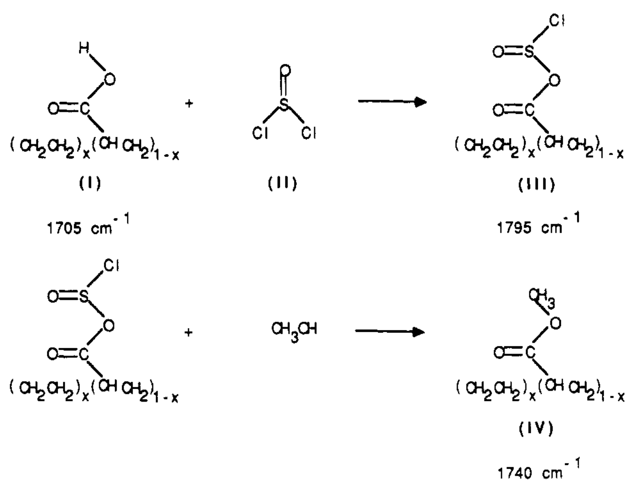

Figure 1. Reaction scheme for esterification of poly(acrylic acid).

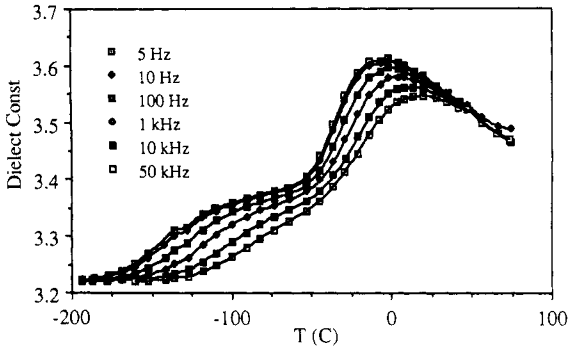

Figure 2. Dielectric constant plotted isochronally versus temperature at six frequencies for sample MA05.

Table I
Copolymer Compositions and Degrees of Crystallinity

sample^a	methyl acrylate mol %	methyl acrylate wt %	χ_c, %	melting range, K
MA05	2.7	7.9	31	330–375
MA10	4.8	13.4	28	310–370
MA15	7.7	20.3	19	305–365
MA20	9.2	23.6	12	310–365
PMA	100.0	100.0	0	

[a] The two digits in the sample designation are the nominal weight percent acrylic acid in the parent copolymer quoted by the manufacturer.

Perkin Elmer Co. differential scanning calorimeter, DSC II. Degrees of crystallinity were calculated from the measured heats of fusion by using a value for 100% crystalline PE of 67 cal/g,[9] and these are reported in Table I.

Dielectric Measurements. The measurements were carried out via an ac bridge at 13 frequencies over the range 5 Hz to 50 KHz. The apparatus has been previously described.[10] The sample cell is similar to one previously used[10] but has a larger area sample space (2-in. 50.8-mm diameter). The samples were pressed films of ~0.6-mm thickness, 2.25-in. (57.2-mm) diameter and were coated in an evaporator with gold/palladium. The various guard and air space rings[10] were scribed in the coatings.

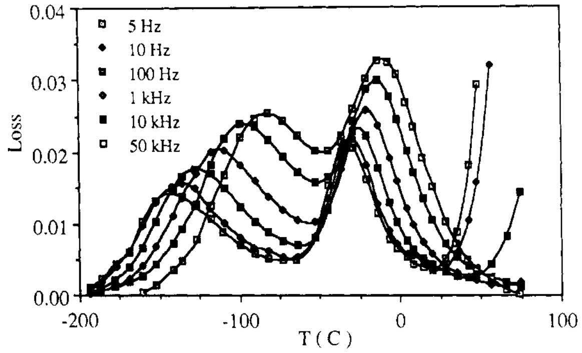

Figure 3. Dielectric loss plotted isochronally versus temperature at six frequencies for sample MA05.

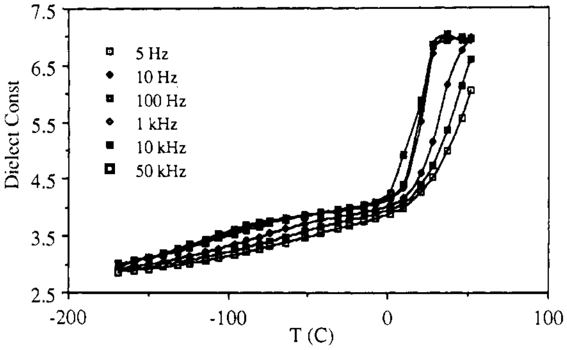

Figure 4. Dielectric constant plotted isochronally versus temperature at six frequencies for PMA homopolymer.

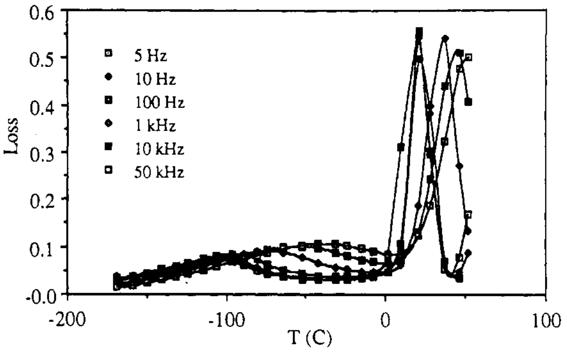

Figure 5. Dielectric loss plotted isochronally versus temperature at six frequencies for PMA homopolymer.

The temperature ranges started at −180 °C and continued through an upper temperature appropriate to capturing the glass–rubber relaxation region. The frequency scans were taken under approximately isothermal conditions about every 7 °C, but a measured temperature was recorded at each frequency point. All isothermal data reduction in subsequent phenomemological fitting involved using spline fits to the temperature dependence at each frequency and interpolation to desired fixed temperatures.

Representative dielectric constant and loss data, for the MA05 copolymer and the PMA homopolymer, are plotted isochronally at the extrema frequencies and intermediate decade frequencies in Figures 2–5.

Table II
Relaxation Parameters for the β Process^a

sample	ϵ_u: ϵ^0_u	ϵ_u: $\epsilon^s_u(\times 10^2)$	ϵ_r: ϵ^0_r	ϵ_r: $\epsilon^s_r(\times 10^2)$	α: α_0	α: $\alpha_s(\times 10^2)$	log τ: A	log τ: $-B$	log τ: T_∞, K	fitting range: T_{min}, K	fitting range: T_{max}, K
MA05	3.21	−0.052	3.34	0.056	0.304	0.046	1577.0	13.94	0	123	183
MA10	2.91	−0.101	3.10	0.027	0.175	0.178	2199.0	17.87	0	123	193
MA15	2.90	−0.096	3.20	0.076	0.0233	0.171	1826.0	15.70	0	113	173
MA20	2.56	−0.050	2.84	0.110	0.228	0.148	1819.0	15.10	0	108	193
PMA	2.75	0.0	3.90	0.060	0.110	0.237	1777.0	13.36	0	133	213

[a] For all samples, T_0 = 133 K.

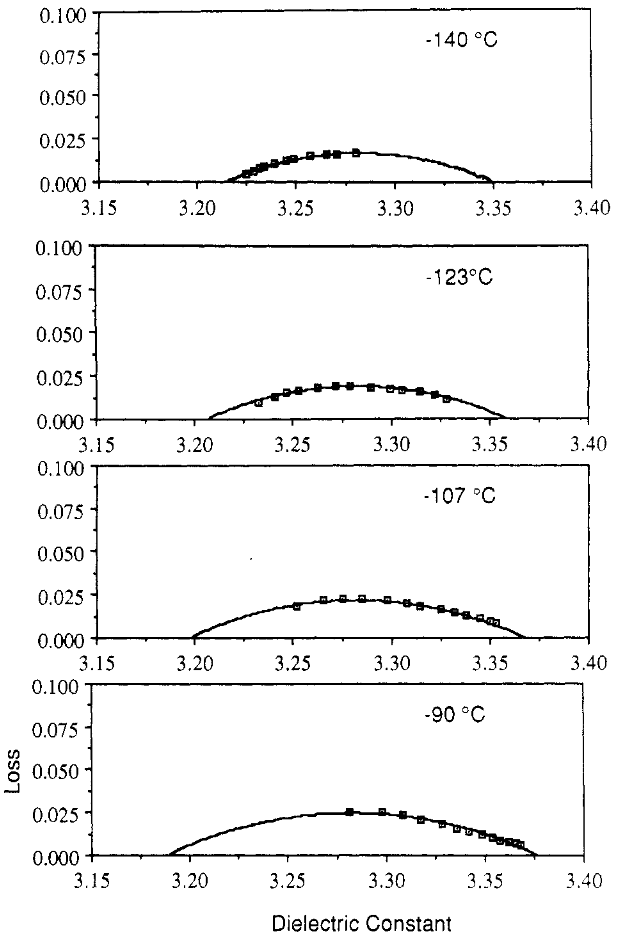

Figure 6. Complex-plane plots of dielectric loss versus dielectric constant for the β subglass process in sample MA05. Curves are calculated fits obtained by using the parameters of Table II.

Phenomenological Data Fitting. In order to quantify the relaxation characteristics, the parameters in phenomenological equations were determined by fitting to the data. The Cole–Cole equation[11]

$$\epsilon^* = \epsilon_u + (\epsilon_r - \epsilon_u)/(1 + (i\omega\tau_0)^{\bar{\alpha}}) \qquad (1)$$

where ϵ_r and ϵ_u are the unrelaxed and relaxed dielectric constants, $\bar{\alpha}$ is the width parameter, τ_0 is the central relaxation time, and ω is angular frequency, appears to be appropriate for representing the subglass processes (β relaxation), and, in the crystalline copolymers, the glass–rubber (α relaxation).[2] In wholly amorphous polymners such as the PMA homopolymer, the more general Havriliak-Negami equation[12]

$$\epsilon^* = \epsilon_u + (\epsilon_r - \epsilon_u)/(1 + (i\omega\tau_0)^{\bar{\alpha}})^{\bar{\beta}} \qquad (2)$$

with the additional $\bar{\beta}$ parameter is required in representing the skewing in the α process.[2,10,12,13] In the copolymers, the β low-temperature process is well resolved isochronally from the α process at low frequency, but the processes merge at higher frequencies (Figure 3). There is a significant temperature regime, however, where isothermal complex-plane plots can be constructed for the β process without interference from the α process. Therefore, β subglass processes were fit first and in this region. Relaxed and unrelaxed dielectric constants and Cole–Cole width parameters were determined from isothermal complex-plane plots by using Marquardt's method.[14] Since the β processes are extremely broad in the frequency domain at most temperatures, there is insufficient information to allow paramter determination from a single isothermal plot. However, by determining the relaxed and unrelaxed dielectric constants globally among the several temperature plots, parameter determination can be accomplished. This was effected by regarding ϵ_r, ϵ_u, and in addition, $\bar{\alpha}$, as linear functions of temperature:

$$\epsilon_u = \epsilon^0_u + \epsilon^s_u(T - T_0) \qquad (3)$$

$$\epsilon_r = \epsilon^0_r + \epsilon^s_r(T - T_0) \qquad (4)$$

$$\bar{\alpha} = \bar{\alpha}^0 + \alpha^s(T - T_0) \qquad (5)$$

where the superscript 0 indicates the value at a conveniently chosen reference temperature, T_0, and the superscript s indicates a linear temperature coefficient. After fitting the above parameters, values of τ_0 were back-calculated from eq 1 for each experimental point at a single temperature and a value of τ_0 selected at that temperature by averaging. For PMA homopolymer, the slope ϵ^s_u was constrained to zero to avoid a physically unrealistic positive value as a best fit. It is to be emphasized that the temperature coefficients of ϵ_u and ϵ_r are significantly influenced by the fitting procedure and do not necessarily accurately reflect, for example, the expected density dependence of ϵ_u. Complex-plane plots showing the resulting fits for the β processes in MA05 and PMA homopolymer are shown in Figures 6 and 7.

For the α processes in the copolymers, there is too much overlap from the β processes to allow parameter determination as above. However, by use of the relaxed ϵ_r (eq 4) determined for the β process as ϵ_u for the α process and considering only the lowest several frequency points, ϵ_r and $\bar{\alpha}$ for the α process could be determined. The resulting complex-plane fits for MA05 are shown in Figure 8. PMA homopolymer has a higher glass transition temperature than the copolymers, and the α process complex-plane plots are not influenced by the lower temperature one. As indicated, eq 2 has to be used to represent the skewing found in wholly amorphous polymer glass–rubber relaxations. Parameter optimization was carried out for several fixed values of $\bar{\beta}$ and the best one selected. The fits are shown in Figure 9.

For the β processes, the τ_0 values were fit to an Arrhenius relation

$$\log \tau_0 = A/T + B \qquad (6)$$

and those for the α processes to WLF or Vogel behavior

$$\log \tau_0 = A/(T - T_\infty) + B \qquad (7)$$

All of the determined relaxation parameters are listed in Tables II and III. A relaxation map of log f versus $1/T_{\max}$ constructed from the isochronal plots is shown in Figure 10 (where the temperature scale is too compressed to show WLF curvature for the α processes) for sample MA05 and PMA homopolymer. Activation energies for all of the specimens determined from such plots are shown in Figure 11.

Discussion of Results

It is our belief that the most sensitive test of a molecular model for a subglass process will be its relaxation strength and how the total relaxation strength is apportioned between the glass–rubber and subglass relaxations. Thus, we paid special attention above to careful determination of relaxation strength from the data. For the purposes of later comparison with detailed conformational energy calculations now under way, the strengths are probably best represented as dipolar correlation factors, g, from the Kirkwood–Onsager equation:

$$\epsilon_r - \epsilon_u = \frac{3\epsilon_r}{2\epsilon_r + \epsilon_u}\left(\frac{\epsilon_u + 2}{3}\right)^2 \frac{4\pi}{3} \frac{N}{V} g \frac{\mu_0^2}{kT} \qquad (8)$$

In applying this equation, attention needs to be paid to the question of morphological heterogeneity due to the presence of some crystallinity. It is no doubt true that virtually all of the polar ester groups reside in the amorphous fraction. Properly, the dielectric constant of the amorphous fraction should be used in eq 8. For certain morphologies, the amorphous phase constant can be calculated from the measured specimen value. However, in the present case, the dielectric constants of the two phases are similar enough and the degree of crystallinity low enough that this is not necessary. Exploratory calculations using the dielectric lamellar bounding equations[15] showed essentially identical results are obtained assuming that the

Table III
Relaxation Parameters for the α Process[a]

	ϵ_u		ϵ_r		α		log τ			fitting range	
sample	ϵ^0_u	$\epsilon^s_u(\times 10^2)$	ϵ^0_r	$\epsilon^s_r(\times 10^2)$	α_0	$\alpha_s(\times 10^2)$	A	$-B$	T_∞, K	T_{min}, K	T_{max}, K
MA05	3.41	0.056	3.66	−0.135	0.209	0.32	457.1	11.70	197.8	238	263
MA10	3.13	0.028	3.65	−0.43	0.181	−0.39	521.8	13.03	199.9	238	263
MA15	3.28	0.077	4.14	−0.61	0.220	−0.35	642.9	14.42	192.7	238	263
MA20	2.96	0.111	3.87	−0.69	0.226	−0.43	417.9	12.18	204.1	243	263
PMA[b]	3.98	1.0	7.43	−1.0	0.418	0.46	775.4	13.55	232.6	288	303

[a] For PMA, T_0 = 273 K. For all other samples T_0 = 243 K. [b] $\bar{\beta}$ = 0.55 (eq 2).

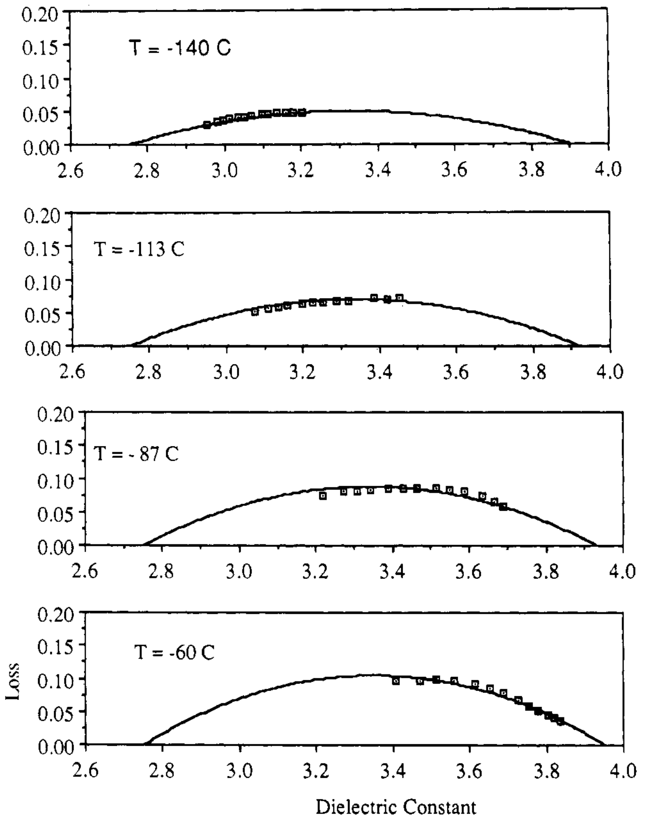

Figure 7. Complex-plane plots of dielectric loss versus dielectric constant for the β subglass process in PMA homopolymer. Curves are calculated fits obtained by using the parameters of Table II.

sample is homogeneous and using the measured sample dielectric constants directly in eq 8. Sample density is required to determine the dipole density, N/V, in eq 8. These were calculated under the assumption that the volumes of the monomers are additive, and therefore a weight fraction (w_1, w_2) averaging can be taken

$$1/D = w_1/D_1 + (w_2 - X_c)/D_2 + X_c/D_c \qquad (9)$$

where the sample density is D, the the MA density D_1 = 1.07 g/cm^3,[16] the ethylene amorphous density D_2 = 0.855 g/cm^3,[17] and the crystal density D_c = 1.00 g/cm^3. On the basis of conformational energy calculations of the inductive effect of a hydrocarbon chain environment on the ester group dipole moment,[18] a value of μ_0 = 1.67 D was adopted. Correlation factors calculated from the relaxed and unrelaxed dielectric constants of Tables II and III are shown in Figure 12.

It may be seen in Figure 12 that for all the copolymers the correlation factors for the combined $\alpha + \beta$ processes are near unity and relatively temperature independent. This is not surprising since the dipolar concentration is low enough that direct intramolecular correlation is expected to be small, and the segmental motion allows visiting all spatial configurations. However, for the PMA homopolymer where the dipole concentration is not low, the correlation factor is distinctly smaller than unity, indicating important nearby dipolar correlation.

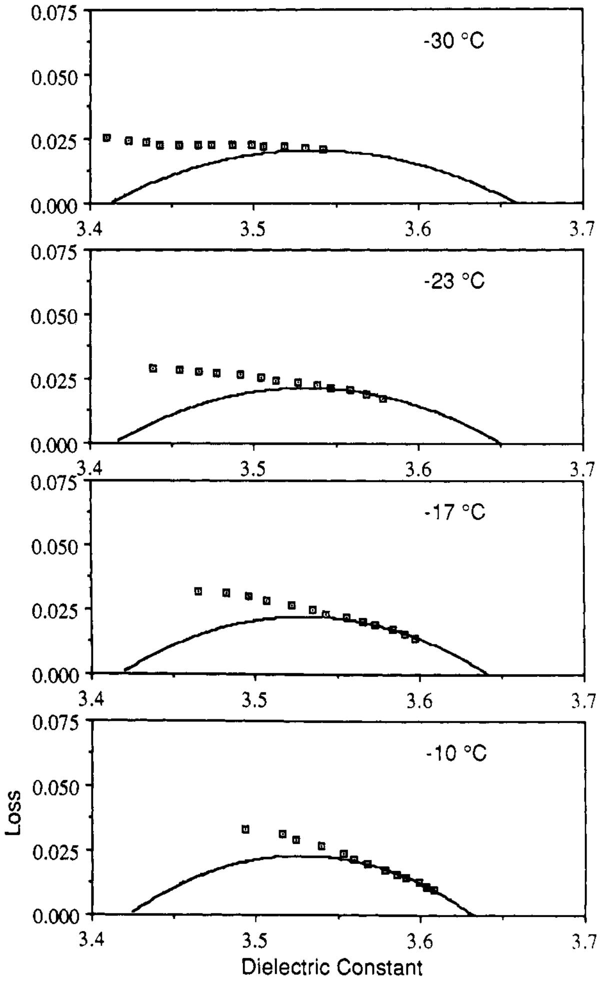

Figure 8. Complex-plane plots of dielectric loss versus dielectric constant for the α glass–rubber relaxation in sample MA05. Curves are calculated fits obtained by using the parameters of Table III.

For the subglass β processes in the copolymers, the correlation factors (Figure 12) and the activation parameters are very similar, indicating the polar groups are dilute enough that their environments are similar. The correlation factors are relatively strongly temperature dependent, increasing with increasing temperature. This is suggestive of a pendant group having at least two conformational states of unequal energy, and the increasing population of the higher states with temperature gives rise to increasing relaxation strength and hence apparent correlation factor. This information should then provide a sensitive test for any conformational model for the side-group reorientation.

Although we intend to present more detailed molecular mechanics calculations later, it is interesting to make a preliminary speculation concerning the molecular process

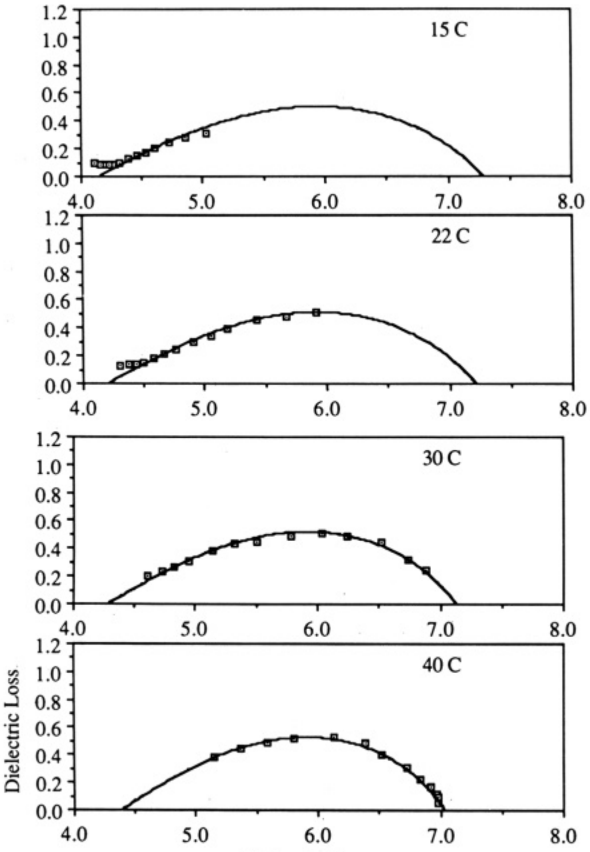

Figure 9. Complex-plane plots of dielectric loss versus dielectric constant for the α glass–rubber relaxation in PMA homopolymer. Curves are calculated fits obtained by using the parameters of Table III.

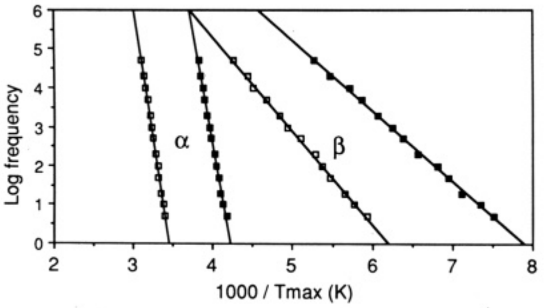

Figure 10. Relaxation map, log f versus $1/T_{\max}$, for PMA homopolymer (open points) and sample MA05 (solid points).

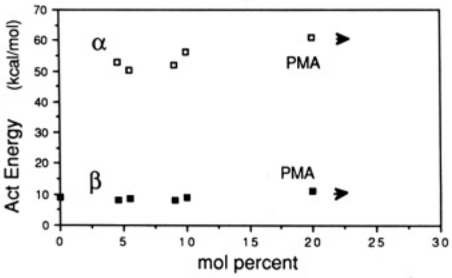

Figure 11. Activation energies for the α and β processes from log f versus $1/T_{\max}$ for all of the samples.

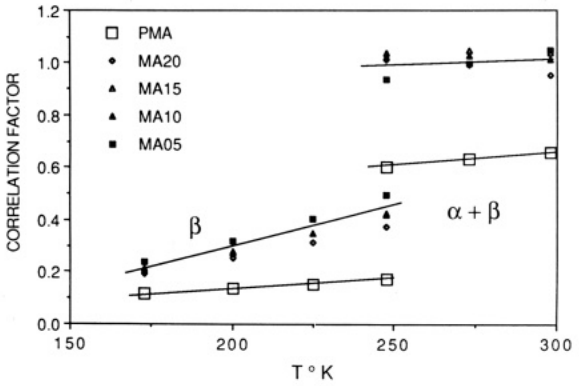

Figure 12. Correlation factors, g, from the the Kirkwood–Onsager equation and the relaxed and unrelaxed dielectric constants of Tables II and III for both the β subglass process and the combined $\alpha + \beta$ processes.

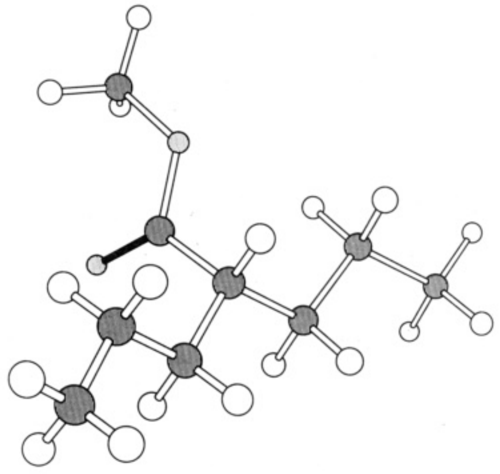

Figure 13. More stable side-group conformation calculated from molecular mechanics for a methyl ester group attached at carbon 4 in *all-trans-n*-heptane.

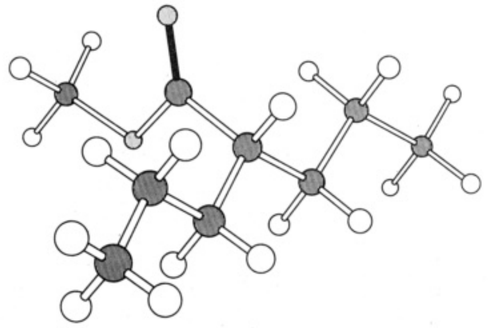

Figure 14. Less stable side-group conformation calculated from molecular mechanics for a methyl ester group attached at carbon 4 in *all-trans-n*-heptane.

associated with the β relaxation. Taking the *all-trans*-polyethylene chain as a typical environment for an isolated methyl ester group, conformational energy calculations on an isolated chain show that there are two stable positions or conformers with respect to the internal rotation about the bond attaching the group to the chain (Figures 13 and 14). They are separated in energy by slightly less than 1 kcal/mol. This energy difference is sufficiently low for both states to have appreciable population and therefore lead to an internal rotation reorientation process. The difference is high enough, however, to lead to temperature dependence of the populations and therefore to a temperature-dependent relaxation strength or apparent correlation factor as observed. The calculated intramolecular barrier for the reorientation is modest. Thus the relatively low temperature of the relaxation is reasonable. Another source of relaxation in the β region could come from localized main-chain motions such as those that give rise to the γ process in polyethylene homopolymers. These motions could give rise to angular excursions of the ester group without internal rotation taking place. Presumably,

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the relaxation from this source would lie in the PE γ region. The observed relaxation location in the copolymers does lie in this region. However, the observed strength of the β process is great enough, with g rising to above 0.4, that this source is probably only a relatively small part of the overall strength if the internal ester group and main-chain-driven contributions happen to fortuitously overlap and give a single process. The γ process in dilute dipole-decorated PEs has relatively temperature-independent g values in the range 0.05–0.20[19] and 0.02–0.1 in linear aliphatic polyesters[20] where the ester group lies in the main chain.

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Registry No. PMA, 9003-21-8; (acrylic acid)(ethylene) (copolymer, methyl ester), 119454-66-9.

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D. E. Buerger and R. H. Boyd*

Department of Materials Science and Engineering and Department of Chemical Engineering, University of Utah, Salt Lake City, Utah 84112.
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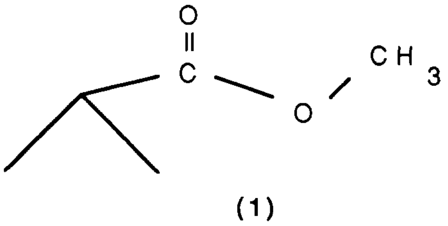
ABSTRACT: As part of an investigation of the nature of subglass relaxations, a pendant acetate group attached to a polyethylene chain has been selected as a model for the processes associated with flexible side-group motion in polymers. Dielectric measurements have been made on a series of vinyl acetate/ethylene (VA/E) copolymers of varying vinyl acetate concentration including PVAc homopolymer. The lower VA concentrations afford the opportunity to examine the acetate group relaxation under conditions where the groups relax independently of each other. It is found that the dielectric loss of the subglass relaxation in the copolymers plotted isochronally versus temperature is split at lower frequencies into two partially resolved (β, γ) processes. Phenomenological analysis of the data has been carried out to establish the strength, activation, and width parameters of both the α glass–rubber relaxation process and the γ subglass process. A tentative assignment is made of the β relaxation to the hindered internal motion of the acetate group and the γ process to the side-group angular displacement induced by main-chain motions similar to the γ process in PE homopolymer. The subglass process in PVAc homopolymer is known to be weak compared to the α glass–rubber relaxation. The β and γ processes are found to be also relatively weak in the copolymers but not as weak as in the homopolymer. Conformational reasons for this are suggested.

Subglass relaxation processes in polymers are not well understood in terms of molecular mechanism. They have been associated with both flexible side-group motion and with localized main-chain motions, but no successful molecular models yet exist for these motions. As part of an effort to obtain experimental data that can be compared against conformational energy calculations, we have selected a pendant ester group attached to the polyethylene chain as a model system for flexible side-group motion. It can be modeled by molecular mechanics and appears to lead to welcome significant differences in experimental behavior depending on its chemical environment and the direction of attachment to the chain. A study of the pendant methyl ester group in methyl acrylate/ethylene copolymers has been completed.[1] Here the results of a study of the chemically isomeric but differently attached pendant acetate group in vinyl acetate/ethylene copolymers are reported. It is already known that the homopolymers poly(methyl acrylate) (PMA) and poly(vinyl acetate) (PVAc) differ significantly in their subglass relaxation behavior.[2,3] The process is much weaker in the



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