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.

Acknowledgment. We are indebted to the U.S. Army Research Office for financial support of this work. We are grateful to G. D. Smith for making some of his molecular mechanics results available to us.

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

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Subglass Relaxation Processes. Dielectric Relaxation in Vinyl Acetate/Ethylene Copolymers

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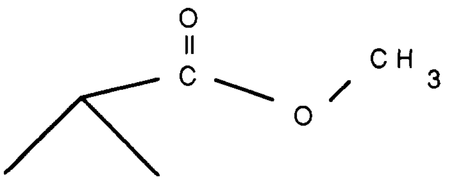
ABSTRACT: As part of an investigation of the nature of subglass relaxations, a pendant acetate group attached to a polyethylene chain has been selected as a model for the processes associated with flexible side-group motion in polymers. Dielectric measurements have been made on a series of vinyl acetate/ethylene (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



(1)

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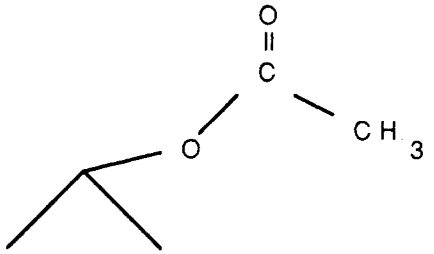

(2)

latter. It is thus of interest to find how their relaxation differs when the groups are attached to a polyethylene chain with the side groups in a dilute environment and, hopefully, to provide an explanation for why their behavior differs.

Experimental Section

Polymer Preparation and Characterization. The vinyl acetate/ethylene (VA/E) copolymers were purchased from the Scientific Polymer Products Co. The manufacturer gave the weight percent vinyl acetate of the 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 and listed in Table I were established by elemental C and H analysis with the O established by difference. The PVAc homopolymer was also purchased from the Scientific Polymer Products Co.

The copolymers contained a degree of crystallinity that depends on vinyl acetate content and was measured via thermal analysis in a Perkin-Elmer Co. differential scanning calorimeter, DSC II. The DSC scans were started at 285 K and continued through 400 K at 10 K/min. Both the degree of crystallinity and melting temperatures are highly depressed by increasing VA content, but all of the copolymers displayed detectable endotherms. In the higher VA content copolymers, the crystallinity is easily quenched to low values but was found to anneal back to higher levels at room temperature. The scans were made on samples that had remained at room temperature for some time. Degrees of crystallinity (weight percent) were calculated from the measured heats of fusion by using the approximation that the heat of fusion is the same as for polyethylene homopolymer. A value for 100% crystalline PE of 67 cal/g (ref 4) was used. Crystallinity values are reported in Table I along with the melting ranges.

Dielectric Measurements. The measurements were carried out via an ac bridge at 13 frequencies over the range 5 Hz to 50 KHz. The experimental details are very similar to those reported in the MA/E study[1] and previously.[5]

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. The data reduction in subsequent phenomemological fitting of isothermal complex-plane plots 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 copolymers, that for VA14, are plotted isochronally at the extrema frequencies and intermediate decade frequencies in Figures 1 and 2. Data for the PVAc homopolymer are plotted separately for the α and β regions in Figures 3–6.

Phenomenological Data Fitting. As will be commented on more fully in the ensuing Discussion section, there is definite evidence for structure in the subglass relaxation in the copolymers. At low frequency, isochronal loss plots show a splitting into two partially resolved processes. We have, therefore, in response to this observation designated them β and γ. There is a regime at low temperature where the characteristics of the γ relaxation can be separately determined. The relaxation parameters of the γ process were thus determined in a manner very similar to the subglass process in MA/E copolymers from isothermal complex-plane plots. However, for the intermediate β relaxation here this is not the case, and only an approximate loss map can be constructed from $T_{\max}$ values.

Table I
Copolymer Compositions and Degrees of Crystallinity

	vinyl acetate			
sample[a]	mol %	wt %	χ_c, %	melting range, K
VA09	4.7	13.2	30	320–380
VA14	6.7	18.1	29	305–380
VA18	7.2	19.2	21	310–365
VA25	9.3	23.9	18	305–360
VA28	12.0	29.5	16	310–360
VA33	12.5	30.5	13	310–355
VA40	20.0	43.4	6	305–345
VA50	19.4	42.5	4	315–335
PVAc	100.0	100.0	0	

[a] The two digits in the sample designation are the nominal weight percent vinyl acetate quoted by the manufacturer.

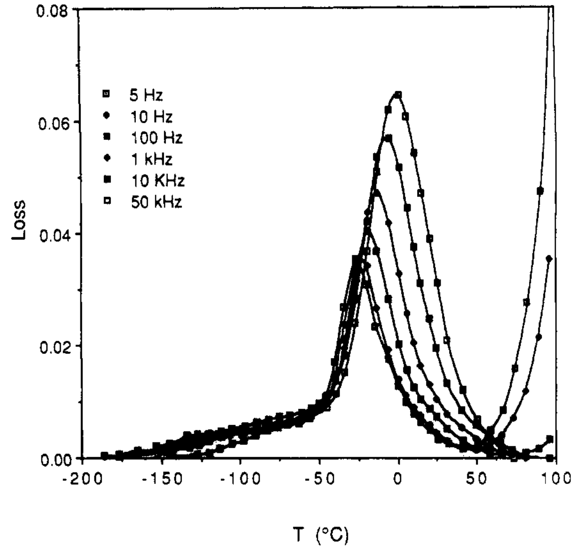

Figure 1. Dielectric loss plotted isochronally versus temperature at six frequencies for a vinyl acetate/ethylene copolymer, sample VA14.

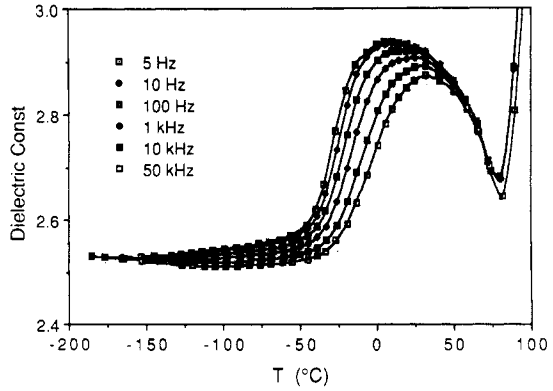

Figure 2. Dielectric constant plotted isochronally versus temperature at six frequencies for a vinyl acetate/ethylene copolymer, sample VA14.

For the α glass–rubber relaxation at high frequencies in the copolymers, there is overlap from the subglass relaxation region, and complete fits to isothermal complex-plane plots cannot be accomplished. This was also the case for MA/E copolymers, and it was handled by using the temperature-extrapolated relaxed subglass dielectric constant values as the unrelaxed dielectric constant for the α process, and these anchored the left-hand sides of the plots. Then only the highest several frequencies were used in the fitting. In the present case this was complicated by the fact that the β portion of the subglass region was not fit. However, as a rough estimate the β relaxation appears to have a strength of only ~5–10% of the α process. Thus we continued to use the relaxed γ process values as the unrelaxed α dielectric constant and included the small contribution of the β process in the strength

Table II
Relaxation Parameters for the γ Process[a]

sample	ϵ_u		ϵ_r		α		log τ			fitting range	
	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
VA09	2.77	−0.041	2.81	−0.014	0.177	0.16	2394	17.68	0	133	173
VA14	2.51	−0.042	2.56	−0.009	0.203	0.12	2021	15.34	0	143	173
VA18	2.60	−0.053	2.65	−0.003	0.166	0.12	2606	19.03	0	143	183
VA25	2.57	−0.072	2.65	−0.013	0.162	0.06	2366	17.91	0	143	173
VA28	2.72	−0.112	2.78	0.058	0.235	−0.10	2367	17.93	0	143	173
VA33	2.54	−0.053	2.65	−0.033	0.135	0.15	2500	18.65	0	133	173
VA40	2.60	−0.054	2.73	−0.021	0.159	0.09	2372	17.44	0	123	173
VA50	2.68	−0.126	2.76	0.033	0.224	−0.09	2239	17.20	0	143	173
PVAc	3.45	−0.054	3.63	−0.078	0.221	0.11	2064	13.47	0	133	213

[a] All values of T_0 = 133 K.

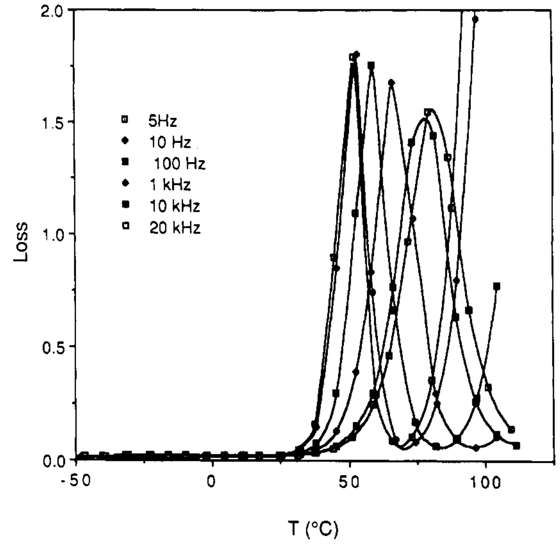

Figure 3. Dielectric loss plotted isochronally versus temperature at six frequencies for PVAc homopolymer.

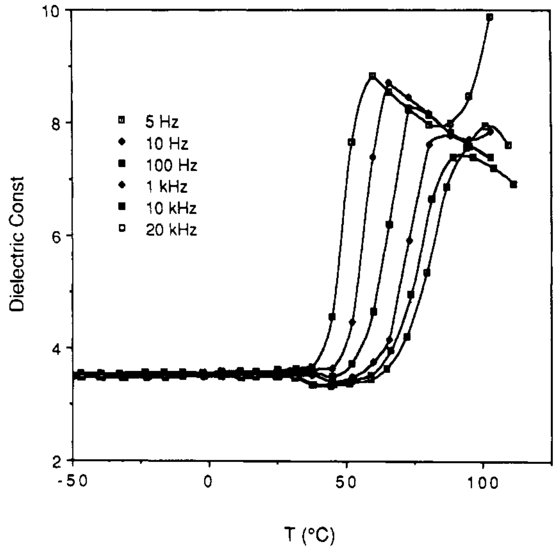

Figure 4. Dielectric constant plotted isochronally versus temperature at six frequencies for PVAc homopolymer.

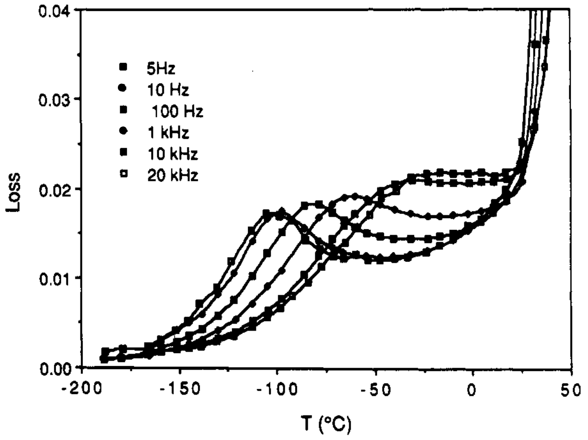

Figure 5. Blowup plot of dielectric loss in the β relaxation region for PVAc homopolymer.

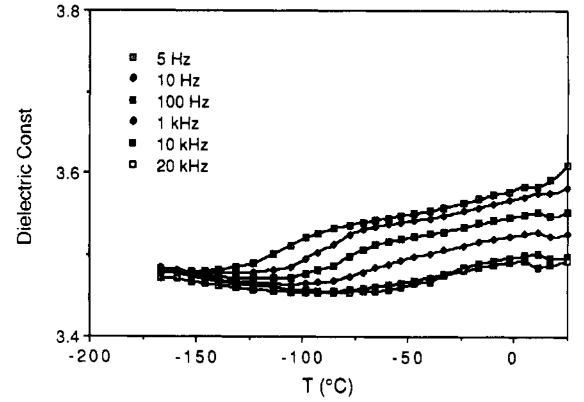

Figure 6. Blowup plot of dielectric constant in the β relaxation region for PVAc homopolymer.

of the α process in the isothermal complex-plane fits. In Figure 4, for PVAc homopolymer, it may be seen that there is a slight dip in dielectric constant at 30 °C. This is an artifact due to the sample remaining at this temperature in the apparatus for some time. As a result, the β and α regions were fit independently, and the $\epsilon_u(\beta)$ and $\epsilon_r(\alpha)$ do not join in Tables II and III.

As before, the parameters determined are defined by the Cole–Cole equation[6]

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

where ϵ_r and ϵ_u are the unrelaxed dielectric constants, $\bar{\alpha}$ is the width parameter, τ_0 is the central relaxation time, and ω is angular frequency. This equation was used for representing the subglass processes (γ relaxation) and, in the copolymers as they contain crystallinity, the amorphous fraction glass–rubber (α relaxation).[7] In the completely amorphous PVAc homopolymer, the Havriliak–Negami equation[8]

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

with the additional $\bar{\beta}$ parameter was used in representing the skewing found in the α process. The constants ϵ_r, ϵ_u, and, in addition, $\bar{\alpha}$, were represented as linear functions of temperature:

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

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

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

where the superscript 0 indicates the value at a conveniently chosen reference temperature, T_0, and the superscript s indicates a linear temperature coefficient.

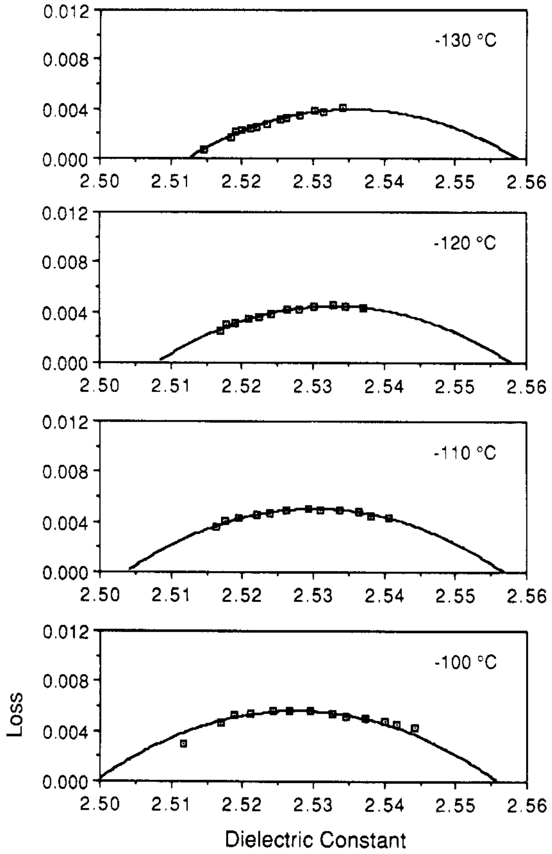

Figure 7. Complex-plane plots of dielectric loss versus dielectric constant for the γ subglass process in copolymer sample VA14. Curves are fits calculated by using the parameters of Table II.

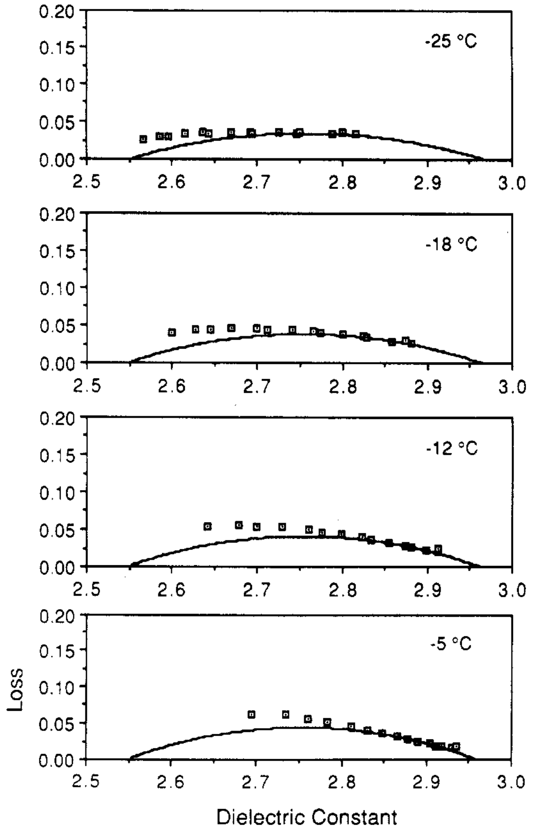

Figure 8. Complex-plane plots of dielectric loss versus dielectric constant for the α glass–rubber relaxation in copolymer sample VA14. Curves are fits calculated by using the parameters of Table III.

The parameters determined are listed in Table II for the γ process and in Table III for the α relaxation. Complex-plane plots showing the resulting fits for the α and γ processes in VA14 are shown in Figures 7 and 8 and in Figures 9 and 10 the α and β processes in PVAc homopolymer.

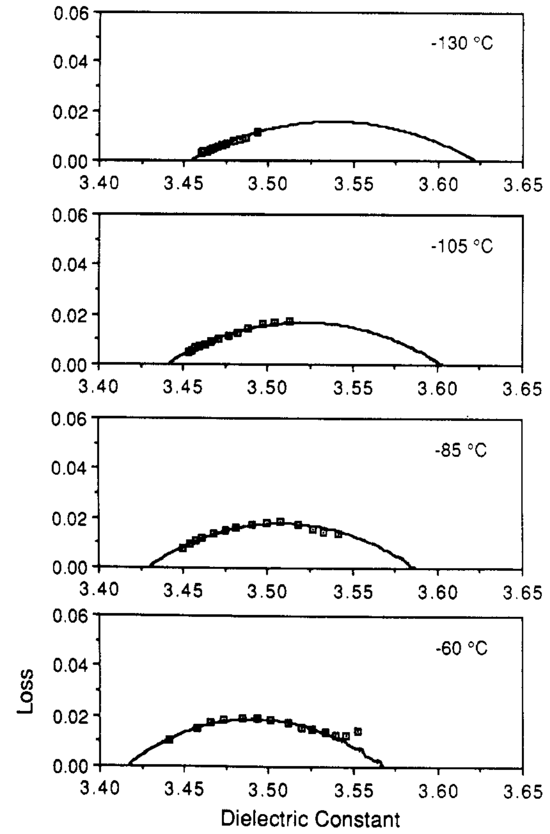

Figure 9. Complex-plane plots of dielectric loss versus dielectric constant for the β subglass process in PVAc homopolymer. Curves are fits calculated by using the parameters of Table II.

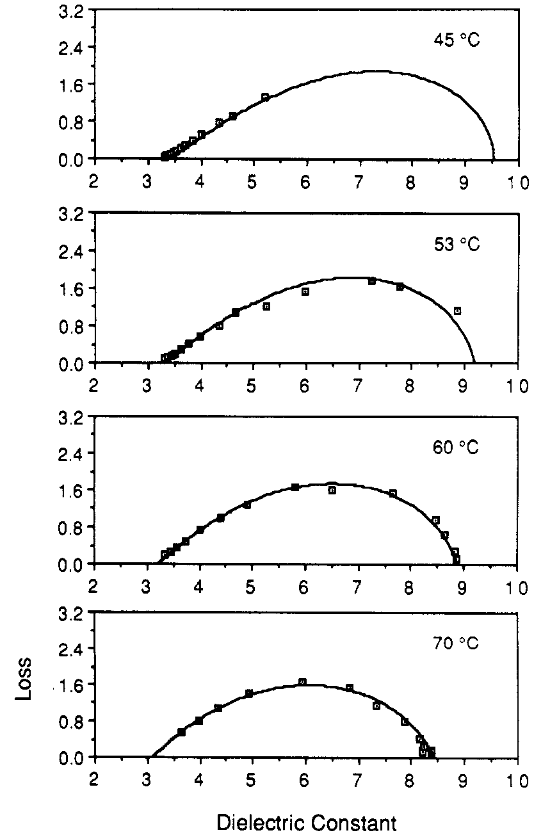

Figure 10. Complex-plane plots of dielectric loss versus dielectric constant for the α glass–rubber relaxation in PVAc homopolymer. Curves are fits calculated by using the parameters of Table III.

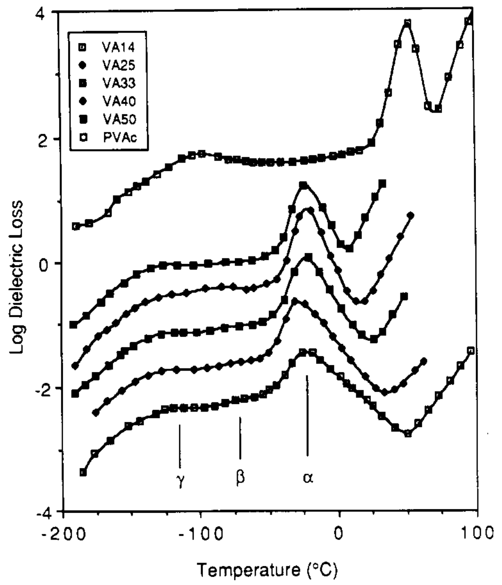

Figure 11. Comparison of loss curves at low frequency, 10 Hz, for several of the VA copolymers and PVAc homopolymer. Loss is plotted logarithmically, and the curves are shifted upward by 0.5 with respect to the preceding one starting at the bottom.

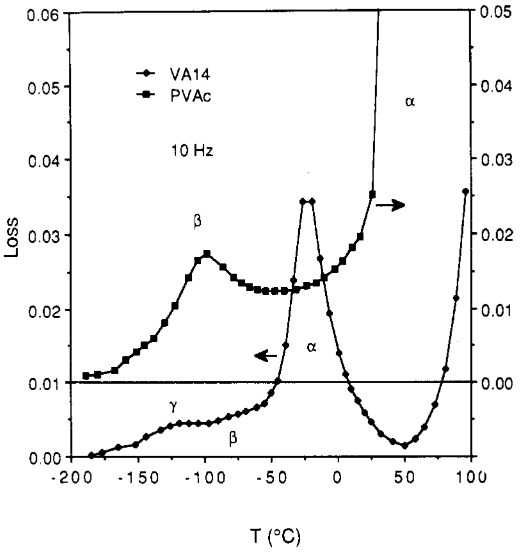

Figure 12. Comparison of loss at low frequency for a VA copolymer (VA14) and PVAc homopolymer.

For the γ processes in the copolymers (and β in PVAc homopolymer), the τ_0 values were fit to an Arrhenius relation

$$\log \tau_0 = A/T + B \tag{6}$$

and those for the α processes to WLF or Vogel behavior

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

These parameters are also listed in Table II and III.

Discussion of Results

The low-frequency dielectric loss isochrones for the copolymers show structure in the subglass region in the form of splitting into two partially resolved processes. Comparison of the loss curves at 10 Hz for all of the copolymers and the homopolymer is made in Figure 11. Figure 12 shows an expanded-scale 10-Hz isochrone for sample VA14 with the β, γ regions labeled and compared with the same region for the PVAc homopolymer. In Figure 13 a comparison is made with the relaxation in a methyl acrylate copolymer[1] of composition similar to VA14. Neither PVAc homopolymer nor MA copolymers[1] show evidence of this more complex structure.

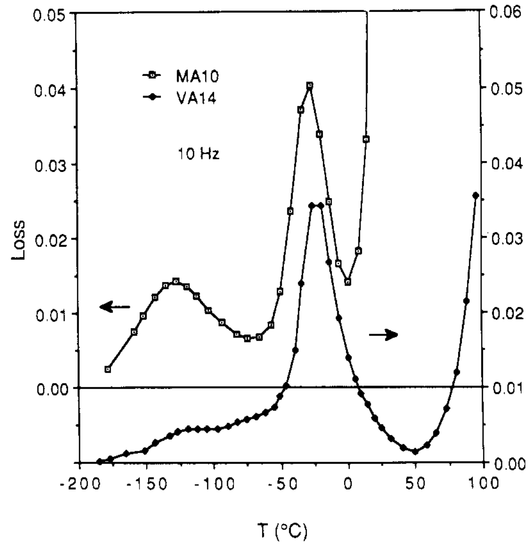

Figure 13. Comparison of loss at low frequency for a VA copolymer (VA14) and a methyl acrylate/ethylene copolymer of similar molar composition (5 mol % MA, ref 1).

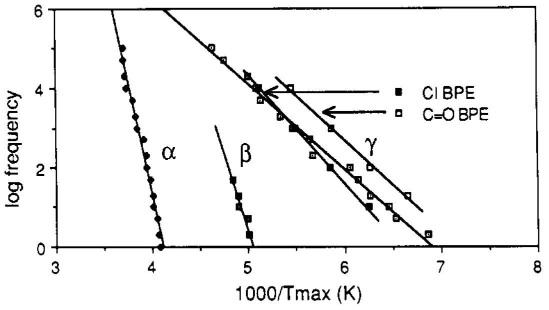

Figure 14. Relaxation map, log f versus $1/T_{\max}$, for sample VA14 copolymer. Plots are also shown for the γ relaxation in lightly dipole decorated (carbonyl and chlorine) branched polyethylene (ref 10).

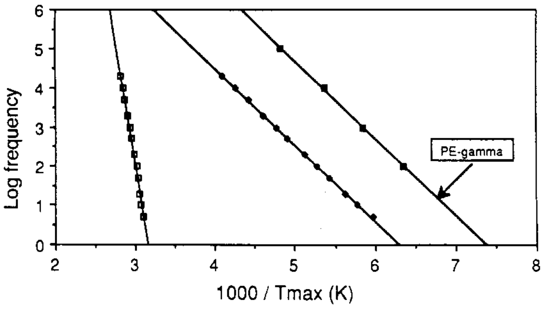

Figure 15. Relaxation map, log f versus $1/T_{\max}$, for PVAc homopolymer. For comparison, the γ relaxation in a branched (carbonyl decorated) polyethylene is also shown.

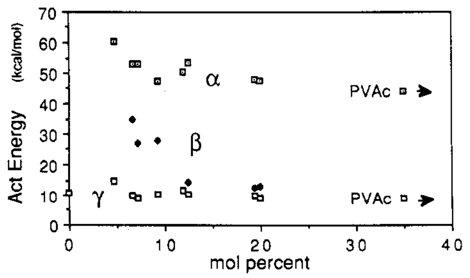

Figure 16. Activation energies from isochronal $T_{\max}$ relaxation maps (Figures 14 and 15, for example) for the three relaxation processes versus copolymer composition.

Table III
Relaxation Parameters for the α Process[a]

sample	ϵ_u		ϵ_r		α		log τ			fitting range	
	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
VA09	2.79	−0.014	3.07	−0.057	0.185	0.20	750.8	15.00	193.2	248	268
VA14	2.55	−0.009	2.97	−0.052	0.195	0.30	275.1	10.24	215.5	248	268
VA18	2.65	−0.003	3.26	0.002	0.210	0.46	588.8	13.96	199.1	243	263
VA25	2.63	−0.013	3.39	−0.156	0.240	0.40	539.1	13.17	198.4	243	263
VA28	2.85	0.057	3.85	−0.007	0.229	0.61	313.4	11.50	215.6	243	268
VA33	2.61	−0.033	3.66	0.011	0.243	0.50	540.8	13.19	201.2	243	268
VA40	2.71	−0.021	4.36	−0.139	0.281	0.80	475.8	12.56	205.5	243	273
VA50	2.72	−0.186	4.21	0.700	0.279	0.89	384.2	11.54	211.3	243	273
PVAc[b]	3.30	−0.610	9.76	−4.500	0.999	−0.67	1093.4	14.63	241.9	323	348

[a] For PVAc, $T_0 = 313$ K. For all other samples, $T_0 = 243$ K. [b] $\beta = 0.378 + 8.87 \times 10^{-3}(\text{temp} - 313\ \text{K})$.

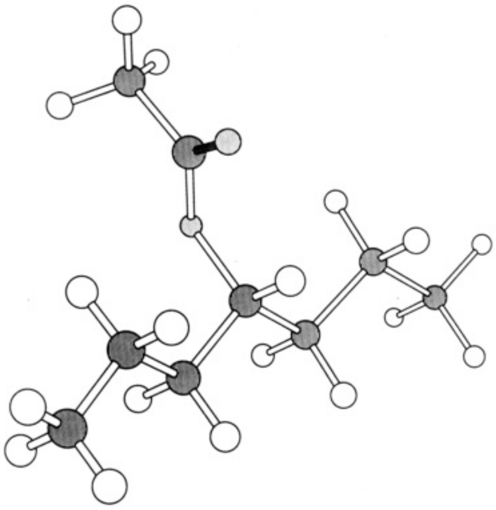

Figure 17. More stable side-group conformation calculated from molecular mechanics for an acetate group attached at carbon 4 in *all-trans-n*-heptane.

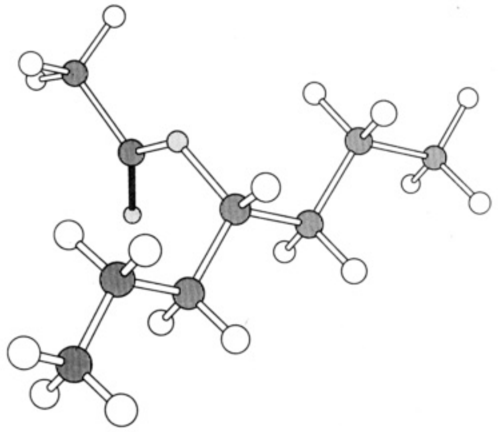

Figure 18. Less stable side-group conformation calculated from molecular mechanics for an acetate group attached at carbon 4 in *all-trans-n*-heptane.

A relaxation map of log f versus $1/T_{max}$ for sample VA14 is shown in Figure 14, where the location of the β, γ regions as determined from the maxima in isochronal loss versus temperature plots is indicated. A similar plot for PVAc homopolymer is shown in Figure 15. In general, the apparent activation energy of the β processes was found to be intermediate between those of the α and γ ones (see Figure 16).

In PVAc, the relaxation strength of the β subglass process is quite weak in comparison with the α glass–rubber relaxation. This is a situation that does not prevail in PMA or its copolymers. The subglass process is much stronger there. It is interesting to note that in the VA/E copolymers here, the subglass processes, β, γ, are still quite weak in comparison with the α relaxation but not as much so as in the homopolymer. The following explanation of the subglass relaxation behavior is offered on the basis of some very preliminary conformational energy calculations.[9] Taking an all-trans conformation of the polyethylene chain as a representative local environment for an acetate group in dilute copolymers, it is found from conformational energy calculations that two side-group conformers are stable. The more stable of the two is shown in Figure 17. It is doubly degenerate with respect to a slight torsional canting of the bond attaching the acetate group to the main chain. The other conformer is shown in Figure 18. Its energy is nearly 2 kcal/mol higher than the more stable one. This contrasts with the MA/E situation,[1] where the energy difference between the stable conformers is ~1 kcal/mol. In addition, due to a steric interference between the ester carbonyl and the main-chain methylene in the β position with respect to the attached group, the barrier to the transition between conformers in the VA/E case is significantly higher than for MA/E. From the high energy difference between conformers in VA/E, we conclude that the subglass process arising from side-group reorientation is greatly weakened through the Boltzmann populating effect in a site model context. What is observed from this source is the weak β relaxation, and it occurs at a higher temperature isochronally and with a higher activation energy in VA/E compared to MA/E because of the higher barrier in the transition. We propose that the γ process in VA/E is the result of the internally rigid side-group being driven through angular excursions by nearby localized main-chain motions similar to that responsible for the γ process in polyethylene. The relaxation map location is very similar (see Figure 14). The strength per polar group is also very similar to that in dipole-decorated BPEs.[10] In MA/E copolymers, it was speculated that the internal ester group motion and this main-chain-driven contribution overlap and only one subglass relaxation region results.[1]

For PVAc homopolymer, the conclusions are more speculative in the absence as yet of detailed conformational calculations. However, the mechanism involving the PE γ process driving the relaxation could be expected to be obviated since the localized main-chain motions should be quite different. The relaxation map location is displaced to higher temperature (Figure 15), but the activation energy is more similar to the VA/E γ process than it is to the VA/E β process (Figure 16).

A critical test of a more detailed molecular model for the subglass process will be its relaxation strength and how the combined relaxation strength is divided between the glass–rubber and subglass relaxations. For purposes of later comparison with detailed conformational energy

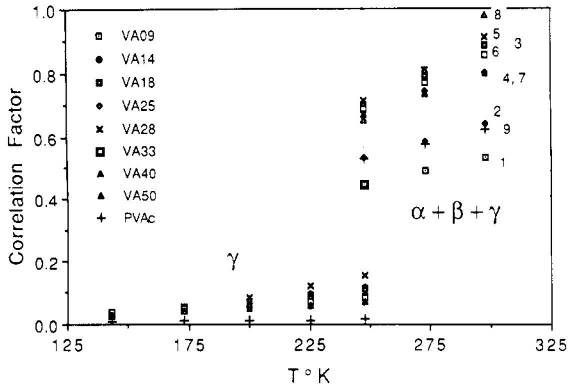

Figure 19. Correlation factors, *g*, from the the Kirkwood–Onsager equation and the relaxed and unrelaxed dielectric constants of Tables II and III for both the γ subglass process and the combined $\alpha + \beta + \gamma$ processes. The numbers alongside the points in the glass–rubber relaxation region refer to the samples VA09 (=1) through PVAc (=9).

calculations, the strengths represented as dipolar correlation factors, *g*, from the Kirkwood–Onsager equation

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

have been calculated. Details of this application have been presented in a similar calculation for the MA/E system.[1] The sample density needed to determine the dipole density, N/V in eq 8, was estimated from copolymer weight fractions (w_1, w_2) and the weight fraction degree of crystallinity, X_c, as

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

where the sample density is D, VA density $D_1 = 1.21$ g/cm^3,[11] amorphous ethylene density $D_2 = 0.855$ g/cm^3,[12] and crystalline density $D_c = 1.00$ g/cm. A value of the ester group dipole moment, $\mu_0 = 1.67$ D, was again taken.[1] Correlation factors calculated from the relaxed and unrelaxed dielectric constants of Tables II and III are shown in Figure 19. A blowup of the subglass region is shown in Figure 20.

It may be seen in Figure 19 that for the less crystalline copolymers the correlation factors for the combined $\alpha + \beta + \gamma$ processes are approaching unity but are more temperature dependent than those in MA/E copolymers. The reason for the greater temperature dependence is unknown, but this seems to be a real effect. An observation that may be related to this is the fact that the two lowest VA content copolymers, which are the most crystalline as well, have distinctly lower correlation factors. It has been noticed before that the amorphous-phase glass–rubber relaxation process correlation factor is sometimes lowered from that of the completely amorphous polymer.[7] The effect has been attributed to the restricting influence of the connections of amorphous chains to the crystal surfaces on segmental reorientation. This restriction can result in incomplete ability at lower temperatures for spatial dipole reorientation, which in turn leads to a lowered apparent correlation factor.

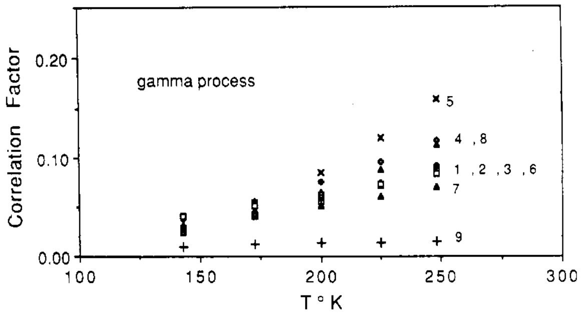

Figure 20. Correlation factors, *g*, from the the Kirkwood–Onsager equation and the relaxed and unrelaxed dielectric constants of Tables II and III for the γ subglass process. The numbers alongside the points have the same meaning as in Figure 19.

In PVAc, homopolymer, the correlation factor is distinctly smaller than unity, as was also found in PMA, indicating important nearby dipolar correlation in this dipole dense system.

For the subglass γ processes, the correlation factors are temperature dependent, Figure 20, but the slopes are less than the slopes for the subglass β process in MA/E, where the process is ascribed primarily to internal side-grou reorientation between conformer sites of somewhat different energy.

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Registry No. (VA)(E) (copolymer), 24937-78-8; PVAc, 9003-20-7.

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