The γ Relaxation Of A Poly(ethylene-*co*-methacrylic acid) Polymer and Its Salts

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ABSTRACT: The dynamic mechanical behavior of a poly(ethylene-*co*-methacrylic acid) polymer containing 4.1 mol % methacrylic acid groups and its sodium, lithium and calcium salts was studied at 110 Hz in the temperature range −180 to −60°. It was found that the γ relaxation occurring in this region consists of two overlapping peaks. It is shown that the low-temperature peak, occurring at −163°, arises in the crystalline phase, while the high-temperature peak, occurring at −129°, arises in the amorphous phase. It is proposed that the motion responsible for the −163° peak arises around defect points in the crystal. It is further shown that the carboxylic acid groups or salt groups, which are entirely present in the amorphous phase, do not take part in the molecular motion responsible for the −129° peak. It is thus concluded that the amorphous relaxation is due to local motions of polyethylene segments.

Despite the considerable amount of reported work, there is no completely satisfactory explanation for the low-temperature ($T \simeq -120°$) γ relaxation in semicrystalline ethylene polymers. Schmieder and Wolf,[2a] Oakes and Robinson[2b] and Woodward and collaborators[3,4] all observed the γ relaxation in polyethylene of varying crystallinity and attributed it to short-range motion in the amorphous areas. Wilbourn[5] demonstrated that the γ transition is more general, occurring in polymers of widely differing types containing at least four methylene sequences. Schatzki[6] then proposed his now famous "crankshaft" model for γ relaxations in the amorphous regions. Boyer,[7] summing up the work done to 1963, favored this model and concluded that the γ peak does indeed arise in the amorphous areas, a conclusion also reached by Bohn.[8] More recently, Andrews and Hammack[9] presented a new model for the γ transition, assigning it to amorphous phase motions. Iwayanagi and Sakurai[10] have given additional support to a local mode amorphous motion but discount the Schatzki model.

On the other hand, Pechold, *et al.*,[11] Sinnott,[12] Illers[13] and Takayanagi[14] have all presented evidence for a γ relaxation mechanism involving defects in the crystalline regions. Peterlin and coworkers[15,16] have given evidence which they suggest shows that the relaxation is related to crystallinity, not through internal defects, but due to disordered regions in the chain fold plane. This is also claimed by Wada, *et al.*,[17] for single crystals.

The available evidence thus leads to the reasonable hypothesis that in semicrystalline systems the γ relaxation may, in fact, consist of contributions from both the amorphous and crystalline regions. This suggestion was first made by Cole and Holmes[18] and later by Boyer.[19] Sinnott[12] pointed out an unresolved shoulder on the low-temperature side of the γ peak for both melt-crystallized and solution grown single crystals of high-density polyethylene and suggested that the γ region may be a superposition of two peaks. Hoffmann, *et al.*,[20] have shown that the γ relaxation in polychlorotrifluoroethylene can be decomposed into γ_a and γ_c regions which are associated with the amorphous and crystalline phases, respectively, and suggest that polyethylene should show similar behavior. Matsuoka and coworkers[21] have proposed that the γ relaxation in polyethylene may arise in either, or both, the crystalline or amorphous regions, depending on the method of preparation of the sample.

We have been studying a unique semicrystalline ethylene copolymer containing a small amount of copolymerized methacrylic acid. By ionizing the acid moieties with group I and II cations, large changes in the properties of this material are observed. These groups

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exist exclusively in the amorphous regions and show their influence on mechanical relaxations arising in the amorphous regions. Thus their presence allows a method of distinguishing processes with amorphous and crystalline contributions. In this report, we examine the unusual behavior of the γ relaxation region and submit evidence for the coexistence of two distinct γ relaxation mechanisms, one arising in the crystalline regions and the other due to motions in the amorphous areas.

Experimental Section

The parent poly(ethylene-*co*-methacrylic acid) polymer was prepared from a commercial material supplied by E. I. du Pont de Nemours and Co., and is identical with that used in our previous studies.[22,23] This material has a weight average molecular weight of about 300,000, a methacrylic acid content on the purified material of 4.1 mol % (by oxygen analysis), and a degree of methyl branching (by infrared) similar to low-density branched polyethylene (approximately 25 branches per 1000 carbon atoms).

The acid groups were ionized to various levels (generally about 20, 50 and 75% ionization) with lithium, sodium and calcium salts. We have described the ionization procedure in previous reports.[22] Films were prepared by pressing at 150° (~180° for the calcium salts) for 5 min at ~10,000 psi. Samples were quenched by direct immersion of the mold in a Dry Ice–ethanol bath immediately after removal from the press. Annealed films were prepared by heating the quenched material in nitrogen at 95° for 24 hr and cooling slowly.

The real and imaginary parts of Young's modulus were obtained on a Vibron dynamic viscoelastometer in the temperature range −180 to −60° which completely encompasses the γ transition spectrum. The data reported in this work is for determinations made at a constant, forced frequency of 110 Hz.

Crystallinities were determined by an X-ray radial scan method using both copper and molybdenum targets. The per cent crystallinity was calculated by decomposition of the peaks in a plot of intensity *vs.* Bragg angle into crystalline and amorphous contributions.[24]

Results

Plots of log E'' *vs.* $1/T$ in the γ relaxation region are given in Figure 1 for annealed samples of the un-ionized polymer and a calcium-ionized derivative. These plots are typical of all the samples studied. It can be shown[25] that the strength of the relaxation mechanism taking place in the γ region should be proportional to the area under the curve, assuming the process is of the Arrhenius type. In this case, the relaxation times are described by eq 1. Then, the relaxation strength, ΔE, is

$$\tau = \tau_0 \exp(-\Delta H^*_a/RT) \qquad (1)$$

given by eq 2, where E_i' and E_f' are the storage moduli

$$E'_i - E'_f = \Delta E = \frac{2\Delta H_a^*}{\pi R}\int E''\, d(1/T) \qquad (2)$$

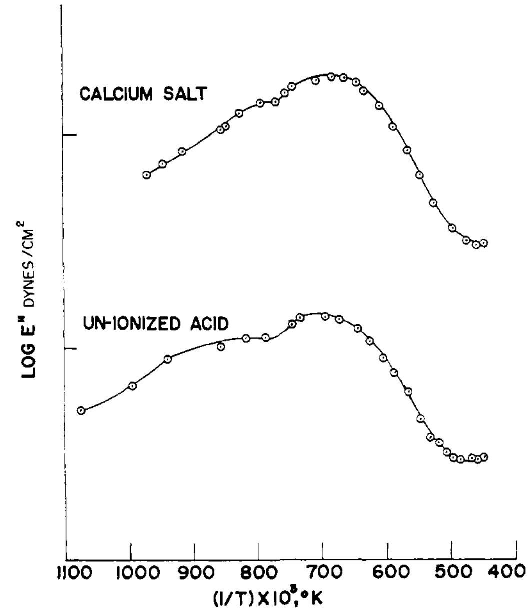

Figure 1. E'' *vs.* $1/T$ for a calcium salt and the un-ionized copolymer in the γ relaxation region.

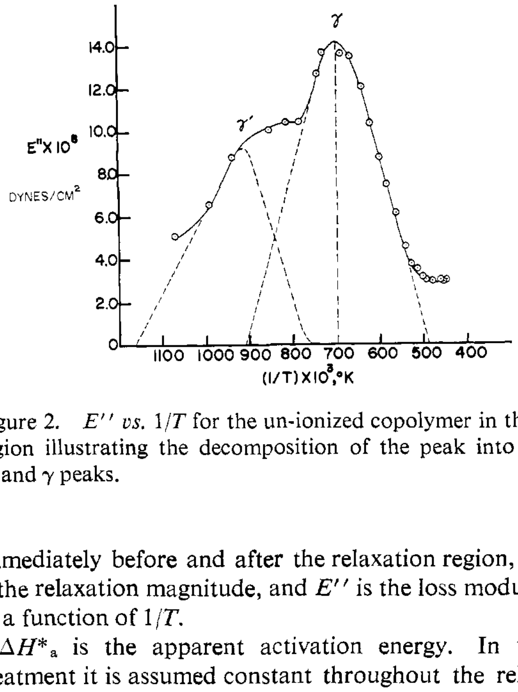

Figure 2. E'' *vs.* $1/T$ for the un-ionized copolymer in the γ region illustrating the decomposition of the peak into the γ' and γ peaks.

immediately before and after the relaxation region, ΔE is the relaxation magnitude, and E'' is the loss modulus as a function of $1/T$.

ΔH^*_a is the apparent activation energy. In this treatment it is assumed constant throughout the relaxation region. Dielectric determinations,[26] coupled with the mechanical data presented here, confirm that the γ relaxation processes have an Arrhenius dependency and that ΔH^*_a has about the same value for each process.

If the relaxation process takes place in either the crystalline or amorphous regions exclusively, there should be some straightforward relationship between the peak area, as given by the value of the integral, and either χ, the degree of crystallinity, or $1 - \chi$. Analysis of the areas and comparison with crystallinities did not uncover any such relationship. Moreover, since the γ peak is far removed from the perturbing influence of any other

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transitions, we would also expect a symmetrical distribution of relaxation times if only one mechanism is involved. It is clear, however, that the peaks are asymmetric and, in fact, show a prominent shoulder on the low-temperature side. These features suggest that the γ relaxation is, in reality, two closely related mechanisms partially superimposed on each other.

We then decomposed the γ peak into two separate peaks by assuming symmetry around a line drawn through the high-temperature peak maximum and constructing the second peak by differences. The method is illustrated in Figure 2 for the un-ionized polymer. This procedure results in two separated peaks, which we designate as γ_a, the high-temperature peak, and γ_c, the low-temperature peak. The maximum in γ_c coincides with the shoulder on the undecomposed curve.

The area of γ_c for all the samples is plotted in Figure 3 as a function of χ. The area increases linearly in a manner directly proportional to χ only, and does not depend on the level of ionization, type of cation, or thermal history, except insofar as the latter affects the over-all degree of crystallinity. Recent studies on these copolymers in our laboratory and by others[26] have uncovered large changes in the amorphous phase behavior, particularly in the β transition region, caused by changes in ionization level, cation type and thermal treatment. Thus the independence of the γ_c area with these variables leads us to conclude that this is a relaxation occurring exclusively in the polyethylene crystalline regions. That the crystalline regions are composed only of the polyethylene segments of the chain is supported by the findings of Otacka[27] on poly(ethylene-*co*-acrylic acid) systems and by the results of Bodily and Wunderlich[28] using polyethylene copolymers containing vinyl acetate groups. Both conclude that the comonomer is excluded from the crystalline regions.

The γ_a peak area is plotted in Figure 4 as a function of $1 - \chi$. Again, there is a linear relation between the strength of the absorption and the amount of amorphous material, with some apparent dependence on the chemical nature of the groups in the amorphous areas. We therefore assign the γ_a relaxation to the amorphous regions of the polymer.

Discussion

Although we cannot assign specific mechanisms to these processes, several features should be pointed out. Our preliminary microscopic and DSC examinations suggest that the nature of the crystalline morphology is complex and is significantly different depending on whether the samples are quenched or annealed. Furthermore, this work, as well as more complete electron microscopy studies by Davis, *et al.*,[29] on similar systems, show drastic changes in the crystalline morphology on ionization. Since the γ_c relaxation is unaffected by thermal treatment or degree of ionization *per se*, this mechanism must involve motions in the crystal phase.

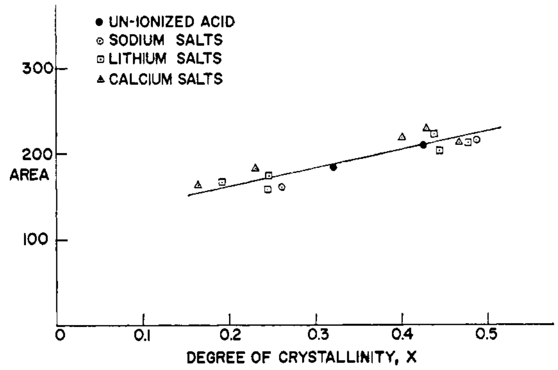

Figure 3. Area of the γ_c peak *vs.* degree of crystallinity, χ, for the un-ionized copolymer and its sodium, lithium, and calcium salts.

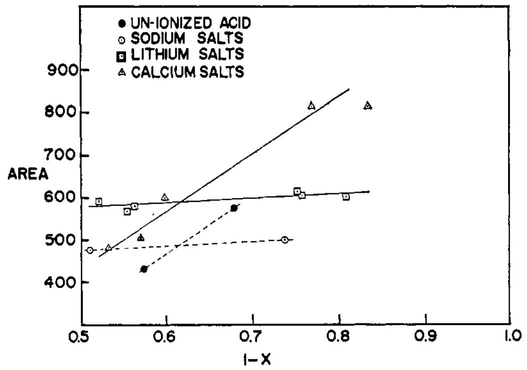

Figure 4. Area of the γ_a peak *vs.* amorphous fraction $(1 - \chi)$ for the un-ionized copolymer and its sodium, lithium, and calcium salts.

Our data contain one disturbing but highly interesting aspect with regard to the γ_c transition—the failure of the line in Figure 3 to extrapolate to zero area at $\chi = 0$. It is possible that this is a result of some systematic error in area and crystallinity measurements. However, we feel this is not the case based on reexamination of the data and the possible errors involved. Sinnott, in his examination of polyethylene single crystals,[12] plotted the area of the γ peak against the nmr mobile fraction and found a similar failure to extrapolate to zero area. He suggested this may be due to an unresolved lower temperature relaxation. No evidence for a lower temperature peak in the neighborhood of the γ relaxation was found in our work.

We believe it more likely that the data shown in Figure 3 is a demonstration of the origin of the γ_c relaxation in more than one kind of crystal defect. In the discussion that follows, we will advance the hypothesis that the γ_c relaxation occurs both in the interior of the crystal lattice and in the side surfaces. Hoffmann has suggested that the γ_c mechanism in polychlorotrifluoroethylene (PCTFE) may involve twisting of chain segments adjacent to row defects in the crystal. This model is appealing since it explains the observed increase in γ_c with annealing by showing that the additional insertion of chain ends drawn into the crystal during annealing increases the row vacancy defect concentration. These defects result in an unsymmetrical potential field around the chain segments

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adjacent to the vacancy. The γ_c relaxation is a result of these local chain segments twisting or flip-flopping in and out of the vacancy. We add to this concept the suggestion that there will also be a similar unsymmetrical potential field for chains on the side surfaces of the crystallites as a result of vacancies at the crystal-amorphous boundary plane. These vacancies may exist as imperfections on the growth faces of the crystal where many chains are entering and leaving the ordered lattice structure. Alternatively, there may be vacancies in the amorphous areas adjacent to the crystal face which provide sites for twist motions of segments of crystallized chains. The important consequence of this postulated model is that the contribution of surface defect motion to the total γ_c relaxation strength should be large at small crystal volumes where the ratio of surface area to volume is large. However, as the crystal size increases due to lateral growth, the contributions of surface defect motions will become proportionately smaller and eventually interior defect motions will swamp the effects of surface defects. When this occurs, the relaxation strength is then a linear function of crystal volume.

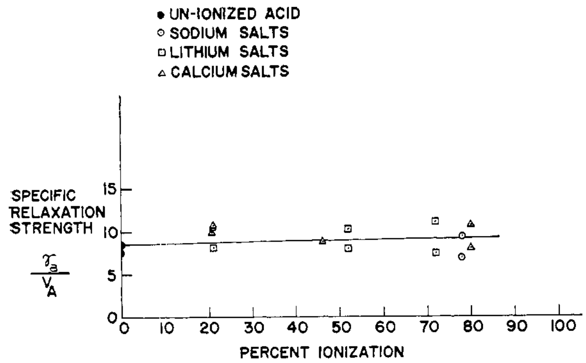

Figure 5. Specific relaxation strength of the γ_A peak *vs.* per cent ionization for the un-ionized copolymer and its sodium, lithium, and calcium salts.

The form of the contributions of each of these motions can be represented in a qualitative way by the relationship $\psi(E'') = f(\text{internal defect motion}) + g(\text{side surface defect motions})$, where $\psi(E'')$ is some function of the total relaxation strength of the γ_c region in a plot of the loss modulus *vs.* reciprocal temperature. The functions f and g should involve both the specific strength of the relaxation modes and the concentration of defects of each type. It becomes apparent, then, that f is proportional to the volume of the crystal, while g is proportional to the side surface area. Thus

$$\psi(E'') = f(\text{crystal volume}) + g(\text{side surface area}) \quad (3)$$

At this time it is not possible to calculate quantitatively the dependence of the two functions on the degree of crystallinity. It may be stated, however, that the crystal volume is just proportional to the degree of crystallinity, χ. Although admitting that this is a tenuous identification, we justify it by the fact that all samples were prepared from the melt in exactly the same way and, therefore, should have approximately the same number of crystal nuclei. Thus we can identify differences in degree of crystallinity with differences in crystal size. The problem of the relationship between the side surface area and the degree of crystallinity is more complex, especially in the absence of data points in the region where the surface to volume ratio becomes large and the second term in eq 3 would be expected to dominate. We are attempting to develop a technique for preparing samples of lower crystallinity to check this region experimentally.

The γ_a mechanism appears to arise only from short-range local motions of polyethylene segments in the amorphous phase. The specific relaxation strength, calculated as the γ_a area per unit volume of a morphous material, is plotted against degree of ionization in Figure 5. It is seen that there is no dependency on either the ionization level or the chemical nature of the comonomer groups. This is in dramatic contrast to the behavior of the β region where the longer range motions of amorphous phase polyethylene segments are controlled by ionization and comonomer structure. It is interesting to note that the γ_a mechanism occurs at a higher temperature than the γ_c motions [$T_{\max}(\gamma_a) = -129°$; $T_{\max}(\gamma_a) = -163°$]. The same result was also observed for PCTFE.[20] This must indicate that the size of the vacancies in the amorphous regions are somewhat smaller than those in the crystal.

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