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A REVIEW OF THE GLASS TRANSITION IN SURLYNS AND POLYPENTENAMER IONOMERS

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ABSTRACT. The Surlyn family of ionomers consists of poly(ethylene co-methacrylic acids) partially neutralized with either sodium or zinc. These ionomers are thus based on a semi-crystalline backbone. Polypentenamers are highly unsaturated elastomers formed from the metathesis polymerization of cyclopentene. They may be modified to form ionomers by derivitization to form carboxylates, thioglycolates, phosphonates, and sulfonates. All of these are thus ionomers based on a rubbery backbone. The glass transition (T_g) behavior of both these classes of ionomers is interpreted on the basis of the presence of salt group aggregates which act as physical crosslinks and/or microphase separated ionic clusters.

1. INTRODUCTION

Despite the existence of a considerable body of literature,⁽¹⁾ there remain a number of questions and uncertainties about the influence of salt groups on glass transition behavior. Specifically, there are two issues of overriding importance. (1) How does the presence of salt groups affect the glass transition temperature of the backbone and the relaxations accompanying it. (2) To what extent and under what circumstances can the aggregation of salt groups lead to their presence as a separate microphase possessing its own glass transition temperature. Although the situation appears to be confused, it is the thesis of this article that the glass transition behavior of ionomers can be understood at least qualitatively in terms of a model, discussed elsewhere in this volume. That is, it is postulated that salt groups in ionomers aggregate to form two distinct families termed multiplets and clusters.⁽²⁾ The multiplets consist of isolated ion pairs or associations containing up to approximately 8 ion pairs while the clusters contain 50 to over 100 ion pairs. The multiplets remain homogeneously dispersed in the matrix while the clusters form microphase separated entities consisting of both ion pairs and hydrocarbon. These microphase separated clusters are usually less than 10 nm in size. The partitioning of the ion pairs between multiplets and clus-

ters depends on the nature of the hydrocarbon backbone, the primary distribution of the salt groups along the chain, the type of cations and anions present, and the presence or absence of polar impurities such as water. In what follows, the glass transition behavior of Surlyn and Polypentenamer Ionomers will be discussed in the context of this model.

2. SURLYN IONOMERS

The group of partially neutralized poly(ethylene-co-methacrylic acids) known as Surlyns has been commercially available since the mid-1960's.⁽³⁾ Most of these polymers are neutralized to less than 50% and are either sodium or zinc salts. The investigation of glass transition temperatures and associated relaxation behavior in Surlyns is complicated by the presence of poly ethylene backbone crystallinity and unneutralized carboxylic acid groups. As a result, traditional thermodynamic techniques such as calorimetry have not been particularly fruitful for investigating glass transition behavior. The method which has been most widely utilized is dynamic mechanical relaxation.

The dynamic mechanical properties of surlyn ionomers have been investigated by many workers.⁽³⁻⁹⁾ In general the response for both the parent acid copolymers and their salts resembles that of low-density polyethylene. At the lowest temperatures, there is a large loss peak, the γ relaxation, occurring near -120°C . This relaxation can be decomposed into two peaks for both the acid copolymer and its salt. The relaxation strength of the lower-temperature peak correlates with the degree of crystallinity while the higher-temperature peak is proportional in size to the amount of amorphous material. Since the degree of crystallinity in ethylene-carboxylic acid copolymers and ionomers is low, the γ relaxation is best described as due to a crankshaft motion of short hydrocarbon segments in the amorphous phase.

In the acid copolymers a relaxation occurs at a temperature between 0 and 50°C , increasing in temperature with increasing fraction of comonomer. This peak, labeled β' , is assigned to micro-Brownian segmental motion accompanying the glass transition temperature. The increase in temperature of the β' peak over the β relaxation temperature of branched polyethylene, -20°C , can be attributed to the crosslinking effect of dimerized carboxyl groups.

As the acid groups are neutralized, the intensity of the β' peak diminishes and a new relaxation, labeled β , appears at lower temperatures, from -20 to 0°C , near that of the β relaxation in branched polyethylene. As more and more of the acid groups are neutralized the β' peak disappears completely and the β relaxation shifts to lower temperatures. The β peak is therefore assigned to a relaxation occurring in the amorphous branched polyethylene phase from which most of the ionic material has been excluded.

It should be recalled here that the location of the β relaxation in polyethylene is strongly dependent on the degree of crystallinity.⁽¹⁰⁻¹¹⁾ As the percent crystallinity increases, the temperature of the β relaxation increases. However, the β peak remains at about the

same position as a function of neutralization for quenched samples. This result is more likely attributable to incomplete phase separation rather than as a consequence of lower crystallinity. The annealing process allows better separation of phases and consequently the amorphous branched polyethylene phase contains less ionic material and therefore has a lower β -relaxation temperature.

For dry, annealed 95% sodium salts of ethylene-methacrylic acid copolymers, the β peak decreases in temperature and increases in magnitude as the amount of comonomer increases.⁽⁷⁾ The increase in intensity reflects the increasing fraction of amorphous material as the amount of crystallinity is reduced at higher comonomer contents. As discussed above, the decrease in temperature for the β relaxation in the annealed ionomers results from enhanced phase segregation at higher ion contents. Water saturation, which destroys the small-angle x-ray "ionomer peak" shifts the β relaxation to lower temperatures and greatly increases its magnitude. These results indicate that water breaks up the ionic phase, therefore creating more amorphous phase.

Somewhat contradictory findings have been reported.⁽⁴⁻⁶⁾ These authors give evidence for a regular increase in the β -relaxation temperature for ethylene-acrylic acid copolymer salts as a function of increasing ion content and therefore conclude that a separate ionic phase does not exist. The thermal history of the materials studied by these workers is not discussed and may have had a significant effect on the subsequent results and analysis. As discussed above, annealing ethylene ionomers causes the β relaxation to decrease in temperature.

The differences in the behavior of the β relaxation could be the result of several factors of which one is certainly the influence of thermal history. In the case of ethylene ionomers one must keep in mind that the β relaxation involves chain motion near branch points and that comparison of polymers having different molecular architecture is somewhat risky. Considering all of the evidence for concentrations between 1 and 10 mole % it appears that the β relaxation for a given ethylene ionomer occurs above that of the same polymer converted to its methyl ester (i.e., branched polyethylene), but its location does not change significantly with temperature as a function of ion content.

In the acid copolymers containing relatively small amounts of comonomer, a high-temperature relaxation occurs that is related to the crystalline α peak in polyethylene. At higher concentrations (lower crystallinity) this relaxation is not observed. A new relaxation, also labeled α , becomes observable as the acid groups are neutralized. This relaxation occurs near 50°C and moves to higher temperatures as a function of neutralization and as a function of increasing ion content. Neutralization with divalent cations causes a further increase in the temperature and magnitude of this relaxation. The α peak has been assigned to motions involving the ionic phase and can be considered as a glass transition temperature of the ionic domains.

Assuming that the β relaxation is associated with the glass transition of the hydrocarbon (polyethylene) phase, it may be concluded from the above results that the surlyn ionomers exhibit a high degree of clustering. Most of the salt groups are microphase separated from

Carboxylate derivative

Sulfonate derivative

In contrast to the polyethylene ionomer case, backbone crystallinity is either not present or at a very low level in the polypentenamer derivatives and thus there is no difficulty in determining glass transition temperatures by calorimetry. At low substituent concentrations (up to 10 mole% or 2/100 backbone carbon atoms) there is a linear dependence of T_g on salt content with the slopes increasing in the order thioglycolate $\approx$ carboxylate $<$ sulfonate $<$ phosphonate. In the context of the model described above this would imply that the substituents are mostly present as multiplets in this concentration range. The differences in slopes would then be explained on the basis of a combination of a copolymer effect and a crosslinking effect. For instance, the bulky phosphonate group would be expected to elevate the glass transition temperature more efficiently than the smaller carboxylate salt groups. The sulfonates, based on a strong acid, would be expected to form higher order multiplets more effectively than either carboxylates or phosphonates and thus to achieve a greater "degree of crosslinking" at a given concentration than the other derivatives. Unfortunately, due to preparative difficulties, no data are available for thioglycolate, carboxylate, and phosphonate derivatives at concentrations above 10 mole %. A study has been made, however, of sulfonate derivatives up to 20 mole % (4/100 backbone carbon atoms).

Table I summarizes the calorimetric glass transition temperatures for the sulfonate derivatives.⁽¹⁷⁾ It can now be seen that the apparent linear dependence of T_g on concentration is an artifact resulting from the restricted concentration range available. There is one well documented case where T_g 's of ionomeric polymers have been measured over a wide concentration range, and that is in poly(ethyl acrylate co-sodium acrylate).⁽¹⁸⁾ The concentration dependence of T_g in these ionomers is sigmoidal in shape. It cannot be ascertained if the sulfonated polypentenamers exhibit similar behavior because the concentration range is still not large enough. However, it may be assumed that this is the case. The most likely explanation for a change in slope of the T_g -concentration curve is that it reflects the onset of clustering. If a system is completely phase separated the glass transition of one phase should be independent of the concentration of the other. It is clear that this is not the case for ionomers. In addition to the presence of multiplets there is presumably a considerable degree of interfacial interaction between the clusters and the matrix. Both these factors can be expected to influence the glass transition behavior. The quantitative interpretation of this influence must await further morphological and properties

investigations over a much wider concentration range of salt groups.

The glass transition of the clusters in the substituted polypentenamers can be observed using the dynamic mechanical relaxation technique. As with the Surlyn family of ionomers the cluster glass transition cannot be determined by calorimetry. There is no clear evidence for a mechanical relaxation peak associated with motions within the clusters for the thioglycolate, carboxylate, and phosphonate derivatives. This is most probably due to the low concentration of salt groups available in these polymers. Therefore, we shall restrict the discussion of the cluster glass transition to the sulfonate derivatives. We have already indicated that the departure of the concentration dependence of the matrix glass transition temperature from linearity at around 10 mole % substituent concentration is indicative of the presence of clusters. This is further substantiated by the appearance of a mechanical relaxation region associated with motions in a microphase separated ionic rich phase.⁽¹⁷⁾ This relaxation appears at -13°C at 11 Hz in the 10% derivative and is very small. In the 15% derivative, the relaxation has moved to 25°C and has significantly increased in magnitude. In the 20% derivative, the cluster relaxation moves to 50°C and becomes the dominant feature of the mechanical relaxation behavior.

If this relaxation is indeed related to the cluster glass transition it should be susceptible to the phenomenon of preferential plasticization discussed earlier. Such is actually the case. In the 20% derivative, saturation with water (23 H₂O per SO₃) leads to a large reduction in the temperature of the cluster relaxation, leaving the relaxation associated with the hydrocarbon matrix essentially unchanged. Table I summarizes available glass transition data for the sodium sulfonate derivatives.

The unsaturated polypentenamer backbone can be hydrogenated⁽¹⁹⁾ and this changes its character and that of its derivatives from essentially elastomeric to thermoplastic. Because of its linear nature and the fairly low substituent concentration range studied, hydrogenation leads to a high degree of crystallinity. This makes the detection and interpretation of glass transitions difficult. The original publications should be consulted for more details.

Despite the disparity in the backbone chain structure and the presence of differing substituents, it is possible to trace a common pattern in the transition behavior of both Surlyns and polypentenamer ionomers. Although many details remain to be worked out, the basic concept of two families of ionic aggregates, multiplets and clusters, provides the unifying theme for the understanding of transitions and relaxations in ionomers generally.

TABLE I. Glass Transition Temperatures (T_g 's) for Sulfonated Polypentenamers.

Mole %		"Ionic Cluster"
Sodium Sulfonate	T_g^a ($^{\circ}\text{C}$)	T_g^b ($^{\circ}\text{C}$)
1.9	-95	-
6.7	-85	-
10.8	-72	-13
14.3	-38	+25
17.6	+31	+50

^a By Differential Scanning Calorimetry (DSC).

^b Temperature of mechanical relaxation at 11 Hz. in dried samples.

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- DISCUSSIONS -

G. WILKES :

I am concerned in your calculations with these spherical fillers, you put a volume fraction in contrast to consideration of sizes and when one gets down a very small size of particles there is often some very strong effect on modulus. This has been shown in indeed if there is a phase or some kind of interacting regions, that size would probably make a big difference.

W. MACKNIGHT :

I fully agree with you. I made the calculations only as a sort of baseline saying that one could not just apply standart macroscopic ideas and account for the phenomena that we see.

C. BAILLY :

What is your feeling for this "water peak" that is seen so often in ionomers ?

W. MACKNIGHT :

When we first saw it, we immediately did the analogy to a similar phenomenon which one sees in nylon and segmented polyurethanes where at least back some years ago the common interpretation was that it has to do with motion of hydrogen bonded in water to the carbonyl or NH groups and any more detail on that I don't know the answer.

B.E. READ :

I think we concluded that it was actually the water molecule itself rotating within the ionic domains and we did a few calculations. Water as you know has a very high permittivity, about 80, and it only requires a very small concentration of rotating water molecules to give a fairly big effect.

W. MACKNIGHT :

It is again one of the opened question which perhaps has to be addressed in a meeting like this.

R. WEISS :

You have shown some data on the effect on the glass transition of the concentration of the ion groups, can you make any comment on the width of that transition.

W. MACKNIGHT :

Yes, in general when we were able to measure, the matrix glass transition broadens considerably as you increase the concentration of the ionic substituents. That's would seem to be a pretty general statement as far as I know, I am talking about DSC measurements now, it is certainly true in those sulfonated cases and it is also true in some of the work that Dr Bailly has done on these sodium sulfonates PEK for example. That's definitely does occur which might suggest a range of microenvironments as you increase the sulfonate substituents content.