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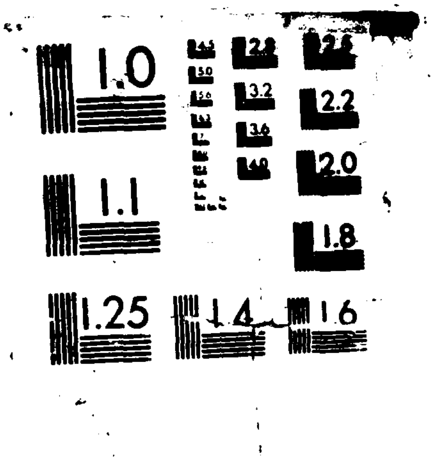

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Observation of Cluster Growth in an Ionomer

by

A. F. Galambos, W. B. Stockton, J. T. Koberstein, A. Sen,
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In this communication, we report the results of an experiment in which an ionomer with a microdomain structure characterized by the absence of a small-angle x-ray scattering maximum (herein interpreted as being void of ionic clusters) is heated to elevated temperatures. Using the high x-ray flux afforded by a synchrotron radiation source, the formation of the cluster morphology in this material was observed as a function of temperature through small angle x-ray scattering measurements. To our knowledge, this represents the first time that the development and growth of microphase separation in an ionomer has been reported.

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OBSERVATION OF CLUSTER FORMATION IN AN IONOMER

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INTRODUCTION

Ionomers exhibit unique mechanical and rheological properties as a consequence of strong associations between the ionic species. Although the spatial arrangement of the ionic groups in ionomers is still an unresolved question, it is now generally agreed that in most ionomers microphase-separated ion-rich aggregates, termed clusters[1], are the dominant morphological feature. The primary evidence for ionic clusters comes from small angle x-ray (SAXS) and neutron scattering (SANS) experiments where a maximum corresponding to distance of 2 - 4.5nm is observed for most ionomers[2,3].

We have been studying the effects of thermal history and low molecular weight diluents on the structure-property relationships of ionomers, particularly lightly sulfonated atactic polystyrene (SPS). In several recent publications[4-6] we showed by electron spin resonance spectroscopy and SAXS experiments that polar solvents, such as alcohols or water, can preferentially solvate the ionic interactions in SPS ionomers in solution or in the

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solid state. This result suggested that solvent history might be used for controlling the structure and properties of ionomers. In fact, when films of an SPS ionomer were cast from different solvents, very different morphologies occurred, as is demonstrated by the SAXS data for a Mn(II) salt of 7.6 mol% SPS shown in Fig. 1. Similar results were obtained for other metal salts of SPS.

The most striking observation in Fig. 1 is the absence of the SAXS maximum for the sample cast from a mixture of 90% tetrahydrofuran (THF) and 10% water. This result suggests the absence of ionic clusters in this sample. We should point out, however, that an alternative interpretation might be that the characteristic size for the cluster morphology is sufficiently large that the scattering maximum is positioned too close to the beam stop for adequate resolution. Such a conclusion might be based on the fact that a high degree of zero angle scattering was observed for this sample (as it was for most ionomer samples studied by us as well as other laboratories) and that the addition of water to a compression molded SPS ionomer tends to shift the SAXS peak to lower scattering angle[7,8]. It should be emphasized, however, that no water could be detected in the sample used to generate the data in Fig. 1 by either gravimetric techniques or infrared spectroscopy. Although this does not exclude the possibility of trace amounts of water, we have found that detectable water concentrations of several percent cannot account for the disappearance of the SAXS maximum in this SPS ionomer.

In this communication, we report recent results of an experiment in which an ionomer with a microstructure characterized by the absence of a SAXS maximum (herein interpreted as being void of ionic clusters) is heated to elevated temperatures. Using the high flux afforded by a synchrotron radiation source the formation of the cluster morphology in this material was observed as a function of temperature. To our knowledge, this represents the first time that the development and growth of microphase separation in an ionomer has been reported.

EXPERIMENTAL

SPS containing 7.6 mol% sulfonic acid groups was prepared by the homogeneous sulfonation of polystyrene (Mn=100,000 and Mw=260,000) in dichloroethane solution with acetyl sulfate[9]. This was neutralized with the equivalent amount of manganese acetate. A 25 μm film was prepared by casting a 10% solution of the ionomer in a mixed solvent of 90% THF and 10% deionized water onto glass. The solvent was evaporated in air and the film was dried under vacuum for 5 days at 60°C.

The x-ray scattering experiments were performed at Beam Line I-4 of the Stanford Synchrotron Radiation Laboratory (SSRL), Palo Alto, CA. The ionomer film was placed in an aluminum sample cell that was fashioned from a conventional DSC pan. The pan contained thin Kapton windows in the top and the bottom so as to maximize the transmission of x-rays. The sample assembly was placed in a Mettler FP82 Hot Stage that controlled the heating of the sample at a rate of 10°C/min between 40° and 240°C. SAXS curves were collected every 26 seconds, which corresponded to every 4°C.

The sample-to-detector distance was 35 cm. The wavelength of the incident radiation was 0.143 nm and the detector covered a range of scattering angles, 2θ from 0.6 to 3.3°. This corresponded to Bragg spacings from 13 to 2.5 nm. Additional information on the experimental setup can be found elsewhere[10].

RESULTS AND DISCUSSION

The SAXS data corrected for variations in the main beam intensity and differences in sample thickness and absorption are given in Fig. 2. The unheated film exhibited no scattering maximum, though substantial zero angle scattering is evident. This intense zero angle scattering has been observed in many ionomer samples with no agreement as to its origin. From the changes in the zero angle scattering observed in these experiments as a function of temperature it is evident that this scattering must be associated with the presence of ions. As discussed above, the as-cast ionomer film possessed a micro phase structure significantly different from that usually observed for similar SPS ionomers[11-13]. We feel that these data are indicative of the absence of microphase-separated ion-rich clusters in the as-cast ionomer.

As the ionomer film was heated, a broad SAXS peak centered at a scattering vector ($s = 2 \sin \theta / \lambda$) of about $0.27 nm^{-1}$ developed at 165°C and increased in intensity with increasing temperature. This corresponds to a characteristic spacing of ca.3.7 nm, which is consistent with that measured for compression molded SPS ionomers[11-13]. It appears that the usual microstructure observed for these ionomers forms upon heating the cast film. The ions that are present in the as-cast ionomer as contact ion-pairs or small multiple ion-pairs (i.e., multiplets, in the terminology of Eisenberg[1]) aggregate when the ionomer is heated. That the ions initially exist as associated ion-pairs and not isolated ion-pairs was confirmed by the electron spin resonance spectrum of the cast film shown in Fig. 3. The broad single line spectrum in which the hyperfine structure is unresolved is characteristic of associated Mn(II) ions[14]. No differences were observed between spectra measured at 25°C and 150°C, which indicates that the local environments of the cations are similar both below and above Tg.

The fact that the SAXS peak first appeared at about $.27nm^{-1}$ and remained at that position throughout the experiment argues against the explanation that the absence of the peak in the as-cast film could be due to residual water. If the presence of water had shifted the SAXS peak to very low angles, we would have expected the SAXS peak to develop at a lower scattering vector and shift towards $0.27nm^{-1}$ as water diffused from the sample during heating. The growth of the SAXS peak at a constant scattering angle is similar to the behavior we have observed for disorder-order transitions in other microphase separated polymers such as block copolymers[15].

Another interesting observation associated with the data in Fig. 2 concerns the zero-angle scattering. As the SAXS peak developed, there was a corresponding decrease in the intensity of the zero-angle scattering. This suggests that the latter phenomenon is also associated with the spatial arrangement of the ions. These two features in the SAXS curves, the peak and the zero-angle scattering, suggest the existence of two distinct environments for the ions (e.g., clusters and multiplets), though at this point we do not have sufficient information for such assignments.

The SAXS invariant is plotted against temperature in Fig. 4. Due to the limited angular range of the experimental detector configuration, it was not possible to correct the scattering intensity for background contributions arising from thermal density fluctuations[16]. For this reason, the reported invariants are not absolute values, but they are self-consistent. A small increase in the invariant for temperatures above Tg (∿100°C) is probably associated with the expected increase in thermal density fluctuations with temperature.

A distinct transition in the scattering invariant occurs at ca. 180°C. The invariant increases, coincident with the emergence of a scattering maximum suggesting the development of ion-rich microdomains or clusters. Future experiments will consider temperature jumps to above Tg in order to assess the kinetics and, perhaps elucidate the mechanism of microphase separation.

The effect of the changing morphology on Tg is shown by the DSC thermograms in Fig. 5. The as-cast film had a Tg of about 97°C, which increased to 116°C and 123°C on the second and third DSC heating scans, respectively. This result was somewhat surprising in that one might have expected that by analogy to other phase-separated polymers, the Tg would decrease upon phase-separation. One could also argue that since the ionic domains are essentially multifunctional crosslinks, the mobility of the matrix chains, which is responsible for Tg, is inherently coupled to that of the microdomains. Unlike block copolymers where the chains have a single coupling between phases, or idealized immiscible blends where there is no connectivity between phases, an ionomer chain may be anchored to more than one domain. For example, for the SPS used in these studies, the molecular weight between ionic groups (or between crosslinks if one assumes that all ionic groups participate in the clusters) is about 1300. Thus, one would expect chain mobility to be highly restricted in such a system, and the rise in Tg upon cluster formation is understandable.

CONCLUSIONS

These results represent our initial attempts at studying the kinetics of phase separation in ionomers as well as establishing structure-property relationships in these systems. These types of experiments hold out promise for answering a number of outstanding questions in this field, namely the structure of these materials, the origin of the zero-angle scattering, and the origin of the increase in Tg for ionomers.

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Figure Captions

Fig. 1. Scattered x-ray intensity vs. scattering vector for 7.6 mol% MnSPS samples prepared by (●) compression molding,

(○) casting from THF solution, (□) casting from DMF solution,

(△) casting from 90% toluene/10% methanol, and

(◇) casting from 90%THF/10% water.

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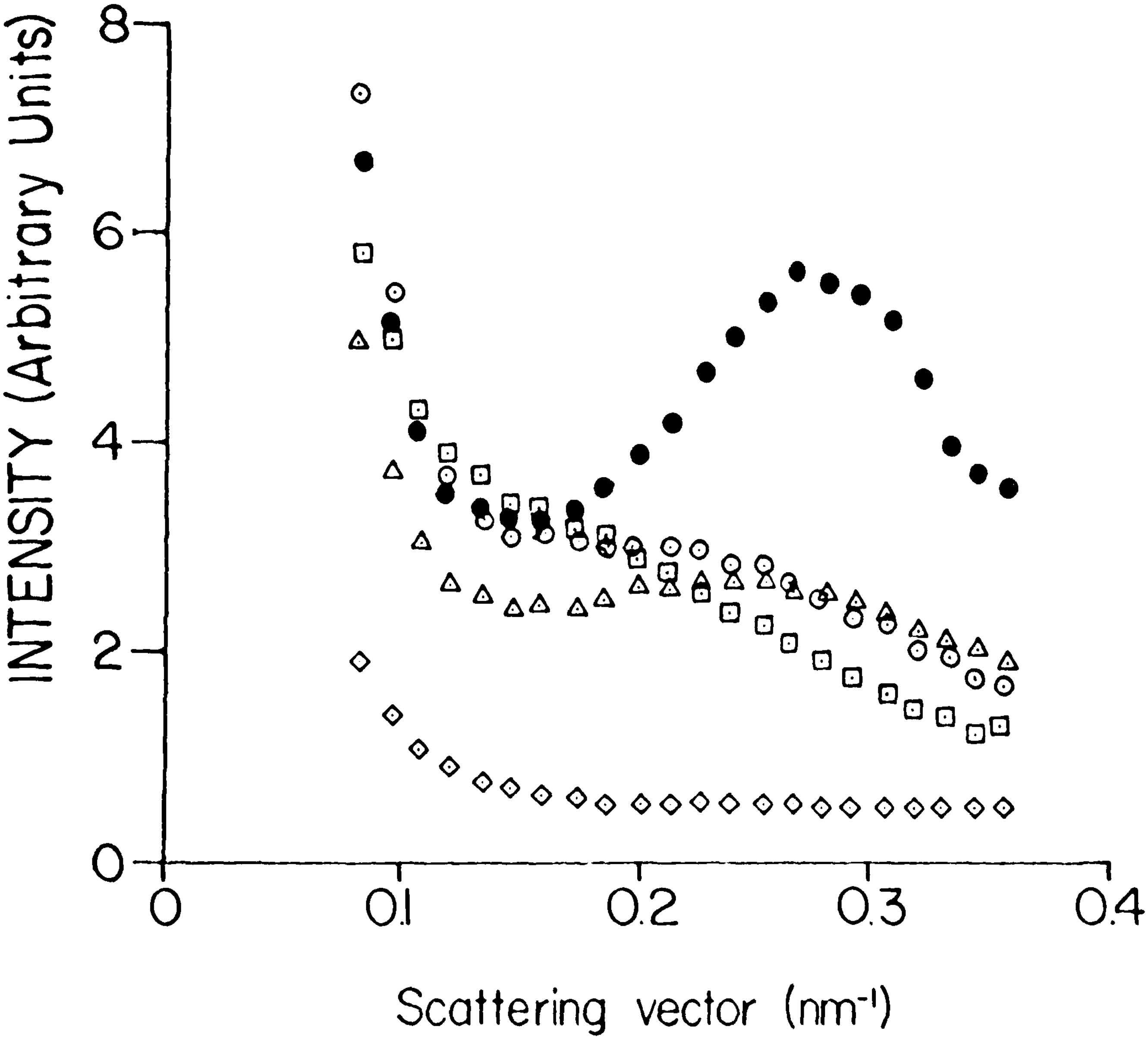
Fig. 2. SAXS intensity vs. scattering vector for 7.6 mol% MnSPS film cast from THF/water as a function of temperature. Heating rate was 10°/min.

Fig. 3 ESR spectra of 7.6 mol% MnSPS cast from THF/H_2O: (---) 25°C and (—) 150°C.

Fig. 4. SAXS invariant vs. temperature for 7.6 mol% MnSPS film cast from THF/water.

Fig. 5. DSC thermograms of 7.6 mol% MnSPS film cast from THF/water: (-) first heat, (---), second heat, (°°°) third heat.

Fig 1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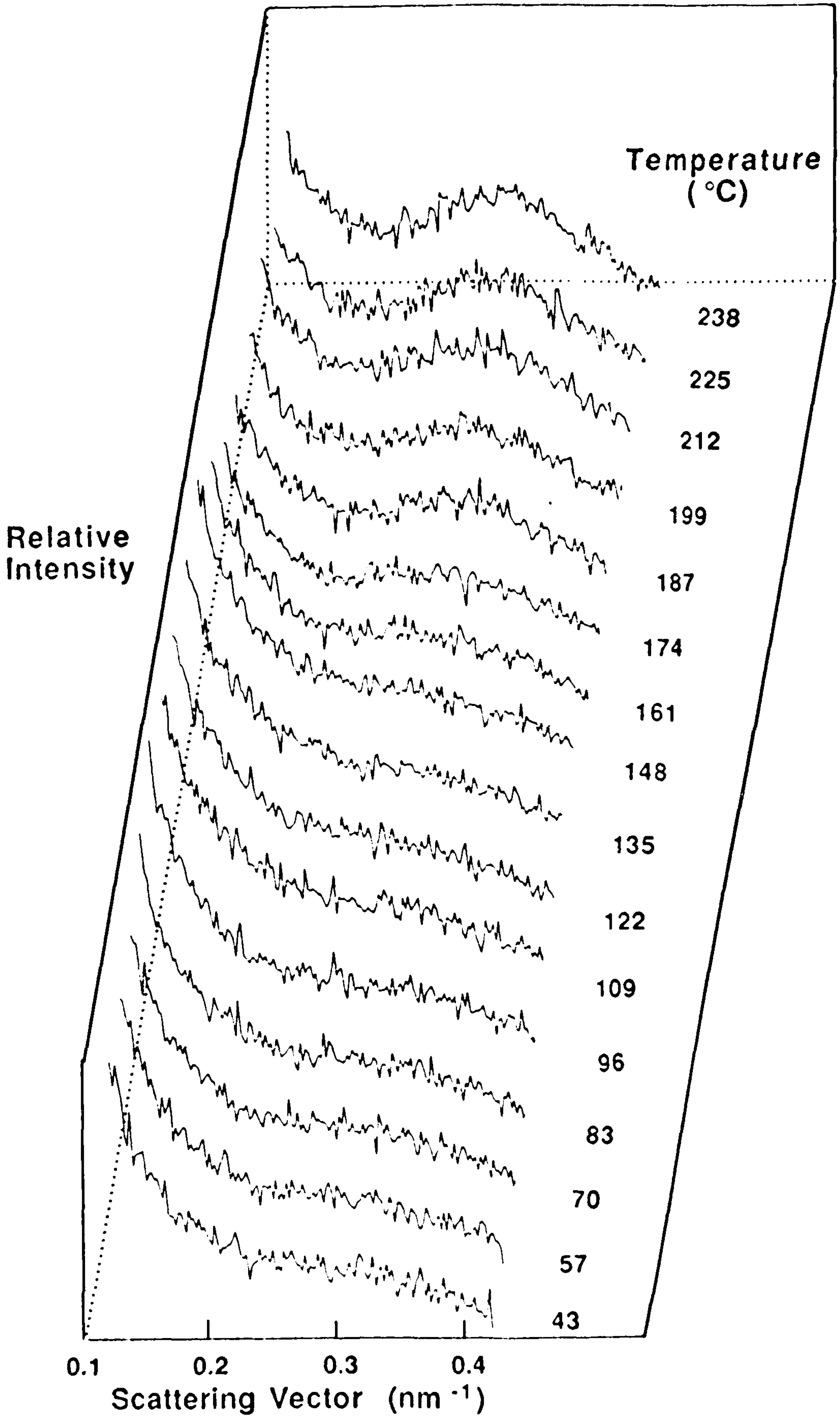
0.4
Scattering vector (nm⁻¹)

FIG.2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Relative
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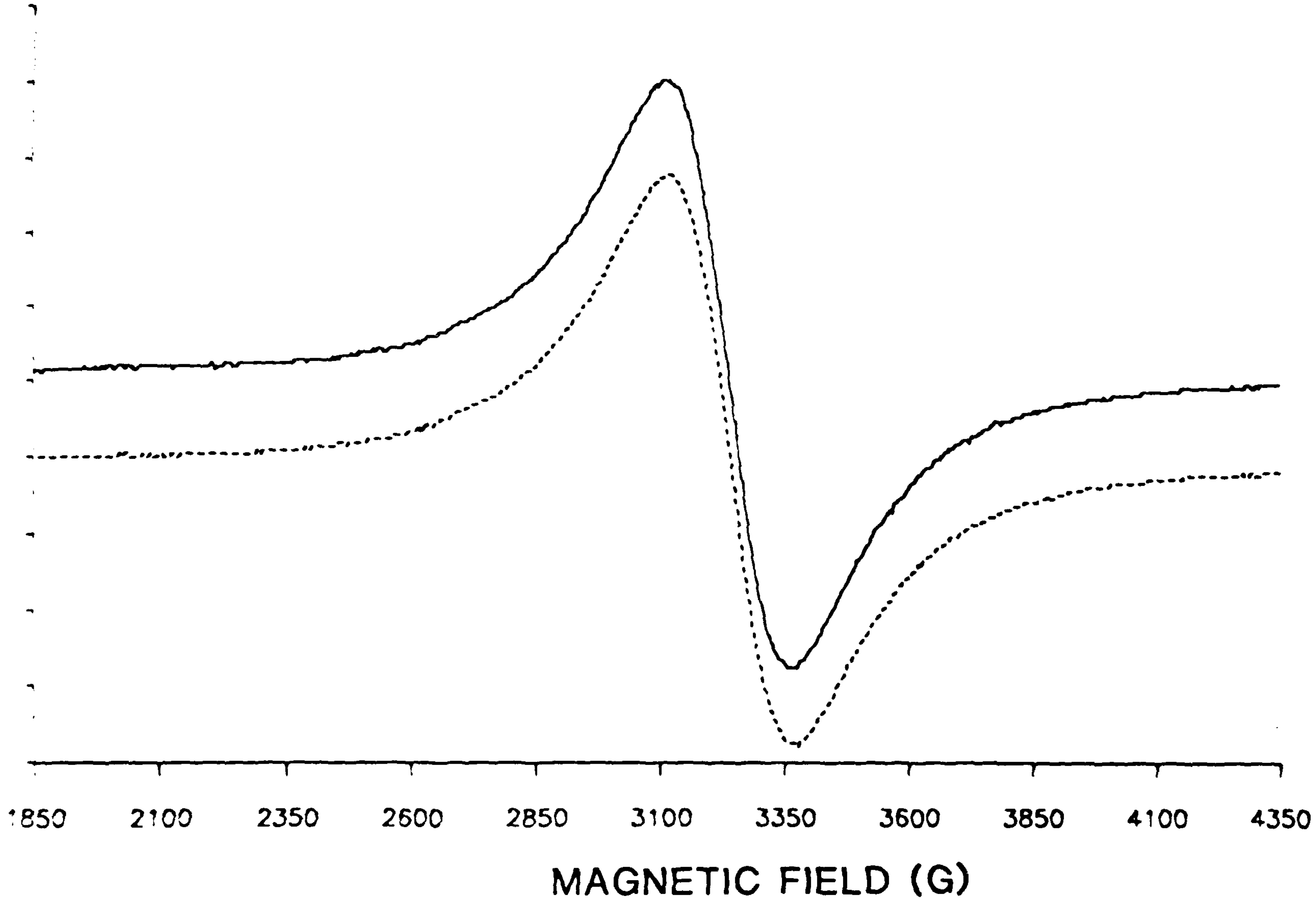
0.3
0.4
Scattering Vector (nm⁻¹)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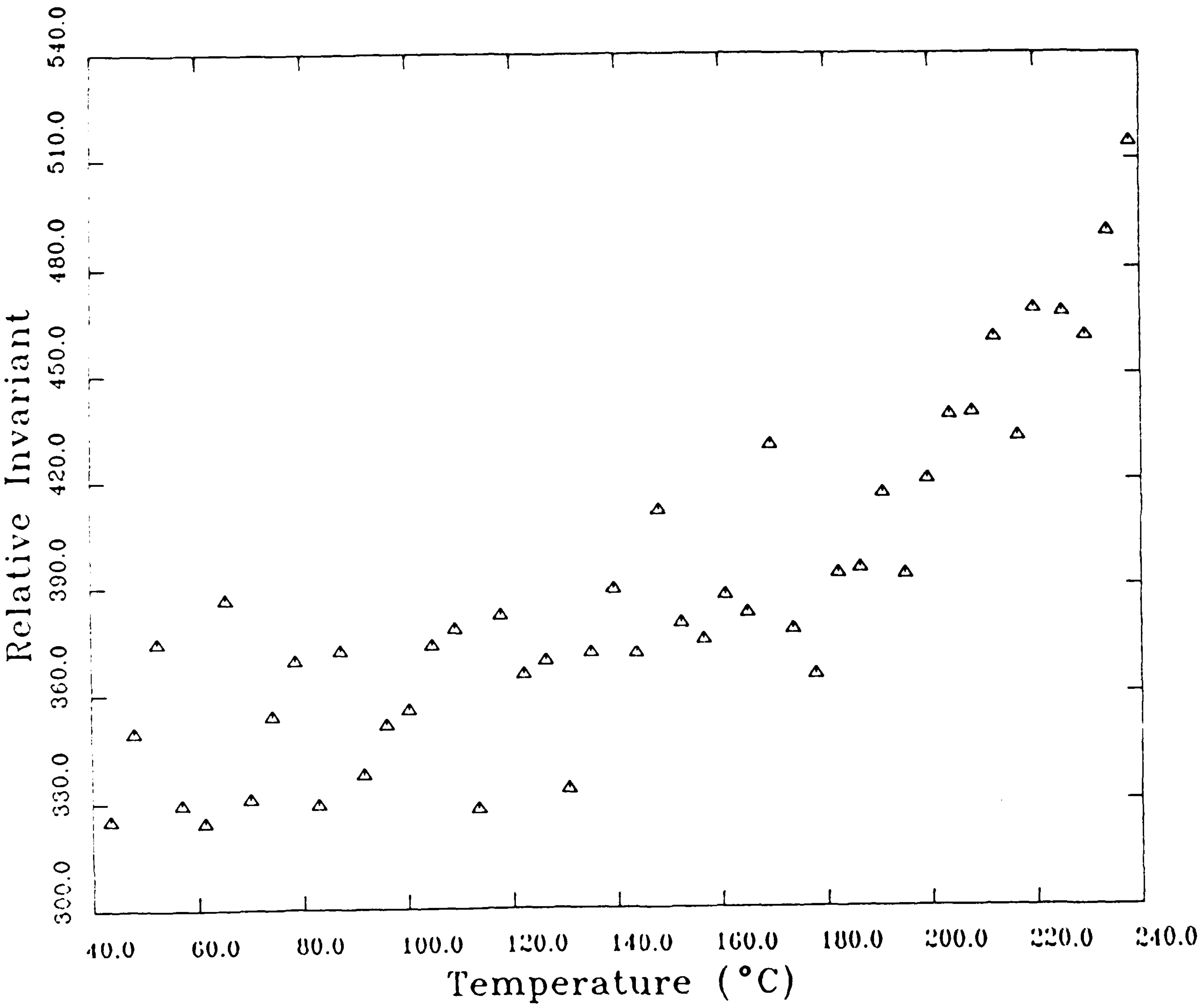
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Relative Invariant
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100.0
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200.0
220.0
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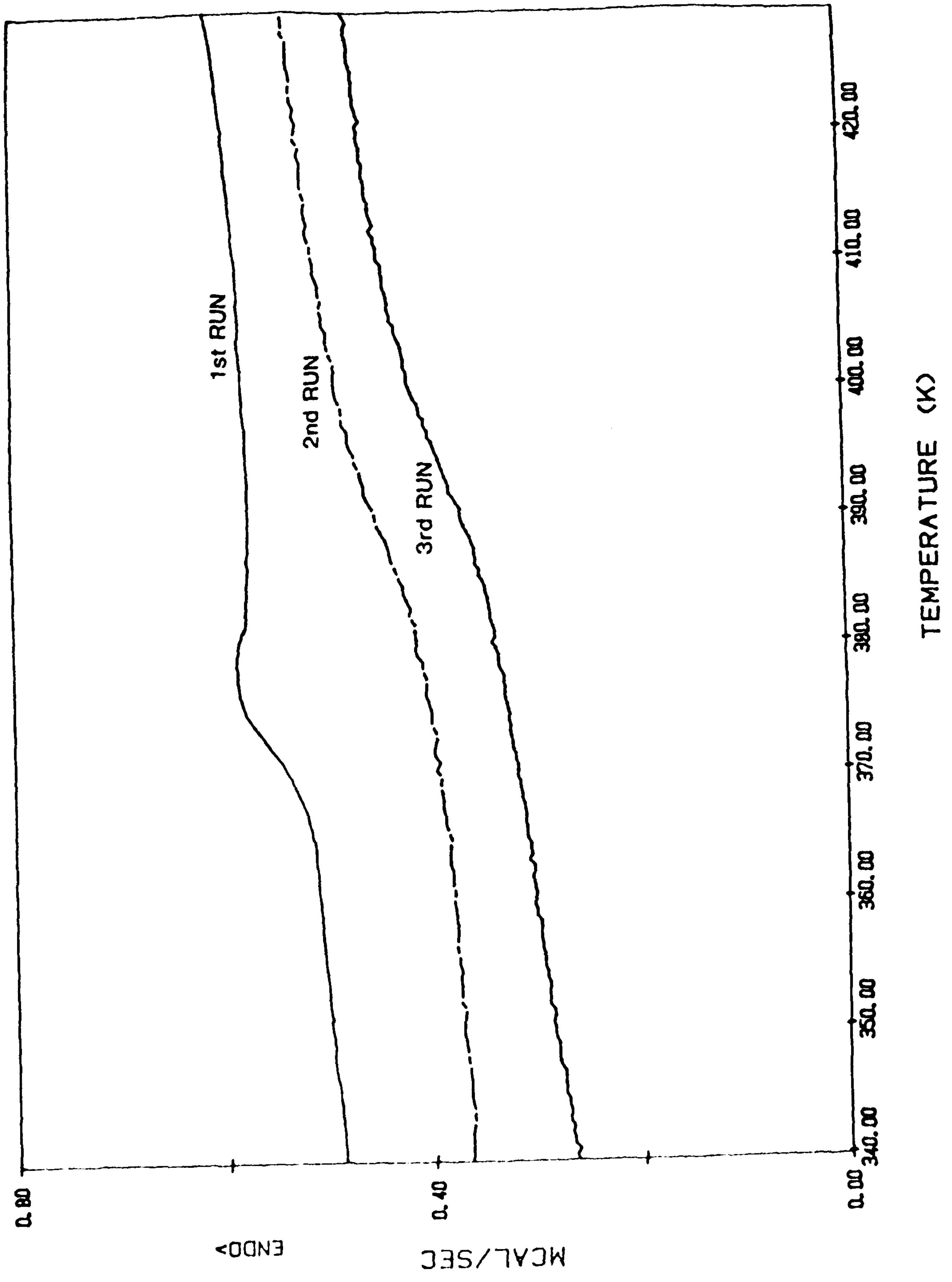
Temperature (°C)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