

Ionic Heterogeneities in Sulfonated Polysulfone Films

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Synopsis

Measurements of glass transition temperature, small-angle x-ray scattering (SAXS), and transmission electron microscopy (TEM) have been applied to the study of ionic heterogeneities in sulfonated polysulfone (SPS) films. The SAXS study confirms the existence of heterogeneities in the electron density distribution, whose appearance for the Cs^{+1} , Ca^{+2} , and Fe^{+3} forms of SPS but not for H^{+} suggests that the scattering centers are ion-containing regions. However, a TEM study could not detect the existence of microseparated regions down to a level of 50 Å, and the T_g behavior as a function of IEC was more typical of that for random copolymers. A Mössbauer study, performed earlier by Heitner-Wirguin et al. on samples of our material, indicated the existence of clusters ~35–40 Å in diameter.

INTRODUCTION

Sulfonated polysulfone (SPS) is a linear copolymer of a bisphenol A type, polyarylether sulfone, combined with repeat units which have undergone sulfonation of one of the bisphenol A aryl rings, as shown in Figure 1.

Depending on its degree of sulfonation and the method of preparation,^{1,2} this material can display remarkably selective water vs. ion passage, which suggests its use as a permselective membrane for reverse osmosis.^{1,2} Since the ion exchange sites in ion-containing polymers often aggregate to form clusters and multiplets,³ a preliminary attempt was undertaken to study the spatial disposition of ionic species in SPS in order to establish a possible link between aggregation phenomena and the physicochemical factors effecting the transport properties.⁴ The experimental techniques chosen, which have often been used to elucidate the structure of ionomeric materials, included small-angle x-ray scattering (SAXS), measurements of the glass transition temperature (T_g), and transmission electron microscopy (TEM). The present work is an expansion of the data reported earlier⁴ and helps to more clearly define the physical disposition of the ions in SPS membranes.

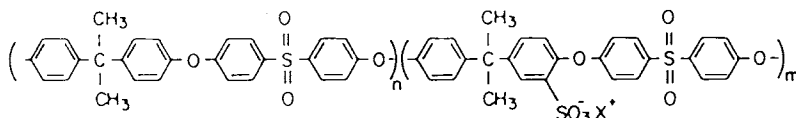


Fig. 1. General structure of sulfonated polysulfone.

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EXPERIMENTAL

Materials

Polysulfone resins grade P-1700 and P-3500 were obtained from Union Carbide. Their weight-average molecular weight \bar{M}_w , determined by ultracentrifuge measurements of dilute solutions in dimethyl formamide (DMF), was $\bar{M}_w = 35,400$ for P-1700 and $\bar{M}_w = 38,600$ for P-3500.

The sodium salt of sulfonated polysulfone, Na-SPS, was obtained by reaction of polysulfone resin (P-1700 or P-3500) with chlorosulfonic acid in 1,2-dichloroethane.¹ This was followed by dissolution in DMF, precipitation in 10% NaCl, and rinsing with large volumes of water until the washings were free of NaCl.

The ion-exchange capacity (IEC) of the samples was determined by potentiometric titration with sodium hydroxide of the SPS-H⁺ form in a solution of 90% dimethylformamide, 10% water.

The polymer film was cast on glass plates from a 20% (by weight) solution of polymer in dimethylformamide. After the film was dried at 50°C for 40 min, it was removed from the glass plate by immersion in water. No difference was found in the properties of sulfonated products based on the P-1700 resin or P-3500 resin.

Methods

Glass Transition Temperature Study

Glass transition temperature measurements were carried out using a Perkin-Elmer thermomechanical analyzer (TMS-1) in the penetration mode. The sample thickness was 30–40 μm , the penetration loading was 10 g, the rate of heating was 5°C/min, and all trials were made in a helium atmosphere. The T_g temperature was determined by drawing tangents to the thermomechanical curve.

SAXS

Small-angle diffraction patterns were obtained at room temperature using a "Searle" x-ray camera with $\text{CuK}\alpha$ (1.54 Å) radiation (35 kV, 25 mA). The exposure times were about 65 h. The photographs were microdensitometered using a Joyce-Lobel double beam microdensitometer.

Transmission Electron Microscopy

Thin Film Preparation. A thin film was cast on a glass plate from a 0.2% (w/v) solution of the sodium form of SPS in DMF. The pure polysulfone film was cast from a dilute solution in chloroform. After the film was air dried, it was removed from the glass plate and float cast on the water surface. Grids were placed on the film surface and removed from the water with the help of a piece of paper. For better contrast, grids were placed into a 2% salt solution (cesium chloride or lead chloride) and after that washed with water.

Thin Section Preparation. Prior to embedding, the 20 μm thick polymer film was converted by ion exchange to its Cs⁺ or Fe⁺³ form. A mixture of vin-

ylcyclohexene dioxide (10 g), diglycidyl ether of polypropyleneglycol (6 g), nonenyl succinic anhydride (26 g), and dimethylaminoethanol (0.4 g) was used as an embedding material.

Ultrathin sections ($\sim 800 \text{ \AA}$) were cut with an ultramicrotome MT-2, using a diamond knife. In both methods of preparation, micrographs were obtained using a Phillips EM 300 electron microscope at an accelerating voltage of 80 kV.

RESULTS AND DISCUSSION

Glass Transition Measurements

The effect of ion concentration on the glass transition of ionomers has been extensively investigated by various authors,⁵⁻⁹ but no general agreement exists with respect to the question of whether the system simply obeys the copolymer equation⁵ or whether ionic domains act as crosslinks,⁹ or if these two effects overlap. Nevertheless, two important conclusions may be still drawn from a T_g study as a function of ion concentration: (i) The presence of only a single T_g shows that only a small fraction of the ions can exist in the form of large ionic domains; otherwise two T_g 's should be detected, one for the nonpolar phase devoid of ion content and a second for the ionic phase; (ii) deviation from linearity in the dependence of T_g vs. ion content may be interpreted as *prima facie* evidence that some change in the state of ion aggregation, e.g., transition from multiplets to clusters, has occurred at this ion content.¹⁰

In light of these generalizations it is interesting to examine the results obtained for various values of IEC, for SPS in the sodium form, which are shown in Figure 2. In the range of IEC examined, a linear increase is found similar to that determined for other ionomeric materials.³ No difference was found between SPS samples prepared by sulfonation of PS-1700 and PS-3500, which are nominally of differing molecular weight.

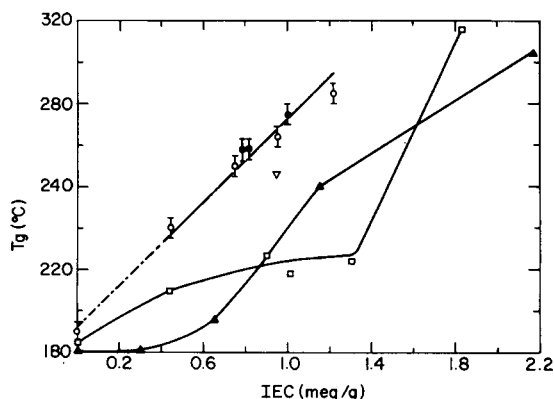


Fig. 2. T_g vs. IEC for various samples of sulfonated polysulfone: (O) SPS obtained by sulfonation of PS-1700 (TMS method, heating rate $5^\circ\text{C}/\text{min}$); (●) SPS obtained by sulfonation of PS-3500 (TMS method, heating rate $5^\circ\text{C}/\text{min}$); (▽) SPS obtained by sulfonation of PS-1700¹ (T_g was determined by differential thermal analysis, heating rate $10^\circ\text{C}/\text{min}$); (▲) SPS obtained by sulfonation of PS-1700² (T_g was determined by mechanical loss temperature measurements); (□) SPS¹⁰ T_g was determined by DSC, heating rate $40^\circ\text{C}/\text{min}$.

From Figure 2 it appears that sulfonated polysulfone behaves as a random copolymer of nonsulfonated and fully sulfonated (i.e., one sulfonic acid group per each repeat unit) polysulfone. However, a lack of knowledge of the T_g for the fully sulfonated polysulfone does not permit us to verify whether the increase in T_g obeys the simple random copolymer equation. For this reason, it is difficult to decide whether the increase in T_g is only due to a change in composition or if, in addition, ion-exchange sites act as crosslinkages. However, if ion-rich domains (or clusters according to Eisenberg's classification³) exist in SPS, they are not sufficiently large or numerous to show up as a separate phase with respect to T_g measurements made by the penetrometer technique.

For the purpose of comparison, T_g values reported by other authors for the sodium form of SPS are shown on the same figure. It can be seen that strong discrepancies exist between the data. There are several possible reasons that different authors have obtained different T_g results for the sodium form of SPS. To begin with, a significant part of the observed discrepancy may be due to the fact that different techniques were used to detect T_g and to measure the IEC. Since it is a second-order transition, T_g depends, for example, on such experimental parameters as heating rate. This might explain the difference between our data and that of Brausse et al.¹ However, if this was the only major factor, we would not expect to find a difference in the form of the dependence of T_g on IEC as in the data of Refs. 2 and 11.

One important difference which exists between the sets of data is the fact that the polysulfone samples in Refs. 2 and 11 were sulfonated with an SO_3/TEP complex, as opposed to the HSO_3Cl sulfonation agent used by ourselves and Brausse et al.¹ The SO_3/TEP complex is claimed to avoid acidic hydrolysis of the polysulfone backbone which can occur with HSO_3Cl .

Since T_g values found in our case and that of Brausse et al.¹ are higher than those cited in Refs. 2 and 11 for the same values of IEC, it is not possible to account for the observed difference on the basis of acid hydrolysis in the PS backbone. One may speculate that the use of the HSO_3Cl sulfonation agent in our case and that of Brausse et al.¹ vs. the SO_3/TEP complex used by Noshay and Robeson² and Lloyd et al.¹¹ results in a difference in the statistical distribution of the sulfonic acid groups along the chain, and therefore in a different ionomeric structure.

Small-Angle X-Ray Scattering

A small-angle scattering peak, $2^\circ < 2\theta < 3^\circ$, was observed for the Cs^{+1} , Ca^{+2} , Fe^{+3} forms of SPS for high and moderate IECs (Fig. 3). Since the peak disappears when the SPS is ion exchanged to the H^+ form (curve d, Fig. 3), there can be no question that the scattering arises due to the presence of heterogeneities in the electron density from counterions in the material. However, the difficulty arises in attempting to interpret the scattering angle.

A scattering maximum, corresponding to a Bragg spacing of 20–40 Å, was also observed for the salt forms but not for the acid form of other ionomers.³ Several models have been proposed to interpret this peak in terms of molecular structures, among them: (i) the existence of some periodicity inside of ion-rich domains, 150–200 Å in diameter¹²; (ii) an infinite paracrystalline model with a spacing between scattering centers calculated according to a Bragg equation¹³;

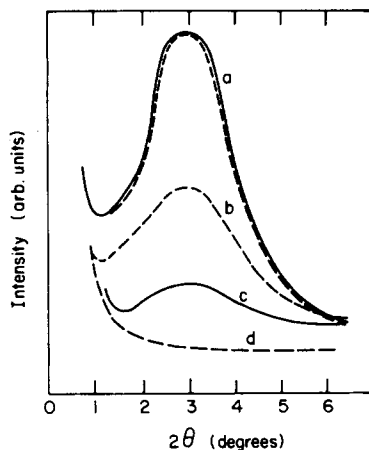


Fig. 3. Comparison of the intensities of the SAXS peak for the acid, and its salts of SPS, IEC = 1.2 meq/g: (—) 92% RH; (---) 32% RH. (a) $-\text{Cs}^{+1}$ form; (b) $-\text{Fe}^{+3}$ form; (c) $-\text{Ca}^{+2}$ form; (d) $-\text{H}^{+}$ form (reproduced from Ref. 4).

and (iii) local order models: (a) a shell-core model in which a 3–13-Å ionic core is separated from a surrounding ionic shell by a distance corresponding approximately to the Bragg spacing¹⁴ and (b) a lamellar model in which ion-rich layers are separated by an organic matrix.¹⁵

In the later work by Roche et al.,¹⁵ calculations based on the different models were compared with experimental data for nondeformed and deformed samples. It was shown that, for nondeformed samples, local models given a much better fit than any of the others. The data for deformed samples are in best agreement with the lamellar model. However, even for this model a further calculation is needed, i.e., a 3-dimensional model, to approach a complete coincidence between the theoretical and the experimental data. Therefore, at present it is as yet impossible to construct a definite molecular structure of an ionomer material based solely on the SAXS data. For this reason we limited the scope of our investigation and we shall present our experimental data without attempting a fit to the various models.

One aspect of the question regarding the spatial arrangement of scattering centers was brought to light from a combination of small-angle x-ray scattering and ion-exchange data. The fact that the *scattering angle is independent of the valence of the counterion* (Fig. 3) showed that SPS can be regarded as a rigid matrix of ionic sites within which the counterion may be exchanged. Thus, while monovalent ions should display no problems for exchange, multivalent ions may be expected to experience some difficulty in effecting complete exchange (due to the problem of satisfying all their valence sites), depending on the spatial distribution of the $-\text{SO}_3^-$ functionalities.

Ion exchange experiments were carried out on a 1.2 meq/g IEC sample of SPS, and Table I demonstrates that Fe^{+3} indeed experiences just such difficulty, as it is able to exchange *only half of the available sites*. Most interesting, however, is the fact that the Fe exchanged shows a gram equivalent weight of 37, which indicates an apparent valence of 1.5, i.e., the Fe must be present in approximately equal amounts of a trivalent and a monovalent form (probably FeCl_2^+). Hence,

TABLE I
Conditions and Results of Ion Exchange for an SPS Sample with a Total IEC = 1.21 meq/g

Ion form of SPS used for exchange	Conditions of exchange	Amount of initial counterion left after exchange (meq/g)	Amount of the new counterion introduced during ion exchange (meq/g)	Apparent valence of counterion
Na	0.5N CsCl	0.0 ^a	—	1
Na	0.5N CaCl ₂	0.0 ^a	1.2 ^c	2
H ⁺	0.5M FeCl ₃ + HCl, pH = 1	0.6 ^b	1.15 ^{c,d}	1.5

^a Determined by ashing and atomic absorption.

^b Determined by titration with NaOH.

^c Determined by ashing and titration with EDTA.²²

^d Assuming valence of + 3.

in this sample only 25% of all the $-\text{SO}_3^-$ groups are at a distance able to accommodate the Fe^{+3} ion. A Mössbauer study performed on a sample of this same material in the Fe^{+3} form¹⁶ revealed that the Fe^{+3} exists in almost equal amounts of monomers (28%), dimers (36%), and clusters (36%), with an average diameter of 34 Å for the latter. On this basis, only 8–10% of the $-\text{SO}_3^-$ ionic groups exist in the form of ionomeric clusters out of a total ion exchange capacity of 1.2 meq/g.

The question which will require resolution in future work is which, if any, of the scattering models mentioned earlier is appropriate to the present case. As may be seen from Figure 4, the scattering angle does show some dependence on the ion exchange capacity, but seems to remain constant above an IEC of ~ 1 meq/g. In contradistinction to the general behavior of other ionomeric systems,¹³ the scattering angle does *not* disappear when the sample is maintained at 100% humidity (Fig. 3).

If the correct morphological description of the source of the scattering is still beyond our reach, at least the latter phenomenon may be explicable in terms of the high T_g of the SPS material. An ionic aggregate is formed due to dipole-dipole interactions between different ion pairs of the bound anion and cation. When water is added, a dissociation of these ionic pairs occurs, and instead of attractive forces the repulsive forces between charged anionic groups operate. These forces may destroy an ionic aggregate if they exceed those forces which are cohesive.

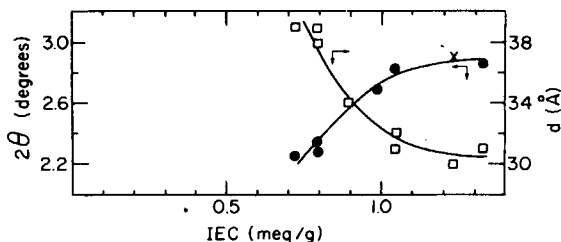


Fig. 4. Position of the SAXS peak (●) and distance between scattering centers (□) calculated according to the Bragg equation (reproduced from Ref. 4).

The copolymers examined in earlier studies^{12,13} contain COOH groups, and possess, in general, much lower T_g 's than the salts of SPS. For example, for the copolymer of polyethylene with acrylic acid¹⁷ and for the copolymer of polystyrene with methacrylic acid,¹⁸ the T_g 's were found equal to -10 and 143°C , respectively, while for SPS the T_g is equal to 275°C (all three systems are in the sodium form and ionic concentration ~ 1 meq/g). The T_g may be regarded as a measure of the energy required for segmental mobility. Thus, even if it is difficult to predict the plasticization effect which water can induce on T_g , it is still possible to surmise that, even in the wet state, SPS will possess a higher T_g than materials which are copolymers of polyethylene or polystyrene with acrylic and methacrylic acids. Therefore, a greater osmotic pressure is needed to bring about structural rearrangements for SPS, so that such effects are probably only present (if at all), at IECs much higher than the samples we examined.

Transmission Electron Microscopy (TEM)

While the T_g and SAXS techniques are indirect methods, whose interpretation are dependent on model assumptions, it is natural that TEM has been used by several authors to attempt a direct visual examination of the structure of ionomers.^{12,19}

However, as Handlin et al. have pointed out²⁰ (and as the present authors had already learned independently²¹), the potential simplicity for drawing conclusions from this technique is marred by the number of artifact phenomena which may be observed, so that TEM results must be evaluated with great caution.

In order to obtain better contrast between the organic polymer and the ion-rich cluster regions, it has become accepted practice to ion exchange the mobile cations for heavy atoms such as Cs^+ or Pb^{+2} . Thus, utilizing SPS material examined in the SAXS and Mössbauer study, thin, solvent evaporated films of 1.2 meq/g IEC and ~ 1000 Å thick were placed into a 2% solution of PbCl_2 or CsCl , after which they were washed with water. Dark regions, 500–1500 Å in diameter, could be observed, as seen from Figure 5 (only the samples with the CsCl treatment are shown, as the PbCl_2 results were very similar). These pictures are rather similar to those observed in the case of ethylene-methacrylic acid copolymers (e.g., Ref. 12, Fig. 5). Those authors considered only the dark regions whose size

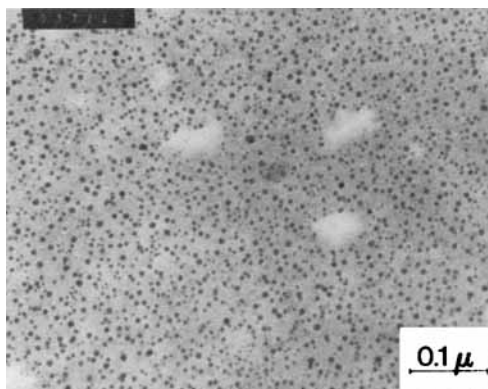


Fig. 5. Thin film of SPS, IEC = 1.2 meq/g, treated with 2% solution of CsCl .

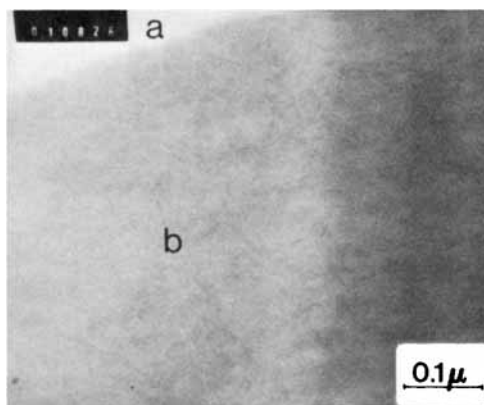


Fig. 6. Thin section of SPS, IEC = 1.2 meq/g, Cs⁺ form: (a) embedding material; (b) SPS, Cs⁺ form.

was around 50 Å in diameter and which were therefore assumed to be clusters. The origin of darkened regions of much greater magnitude was explained as the result of thickness variation. In a review of TEM in the examination of ionomers,¹⁹ no such distinction was made according to size, and it was assumed that "ionic clusters along chains aggregate to form grains or regions about 100–1000 Å in diameter."

To exclude the possibility that the structure observed in Figure 5 was specific to a thin evaporated film or that it was an artifact of the sample preparation, two additional samples were examined: (a) thin sections were prepared by embedding and microtoming a 20 μm thick film from the identical sample used in both the SAXS and the Mössbauer study¹⁶ (cf. Fig. 6) and *which were already in the Cs⁺ form*; and (b) thin, solvent evaporated films of pure (nonsulfonated) polysulfone were treated with CsCl or PbCl₂ as in the original manner (Fig. 7). Figure 6, which was obtained by TEM of the microtomed sections, shows that the electron density of the membrane is higher than that of the embedding material, as the membrane is much darker. However, the membrane is dark in a very homogeneous fashion, and *no regions of elevated electron density can be observed down to a resolution of 50 Å.*

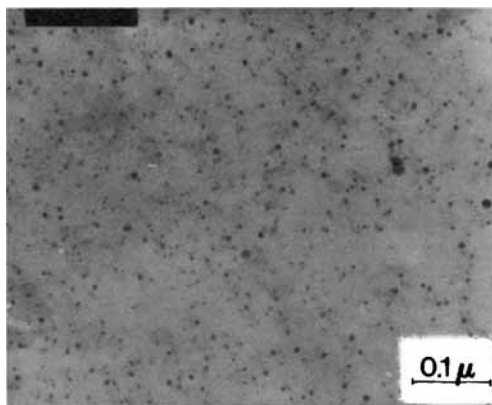


Fig. 7. Thin film of PS treated with 2% solution of CsCl.

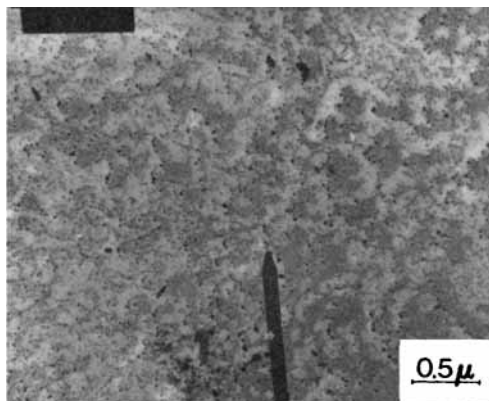


Fig. 8. Thin film of PS treated with 2% solution of CsCl, at point of diffraction.

On the other hand, photomicrographs of the CsCl-solution-treated, pure polysulfone film (Fig. 7) show circular dark regions identical to those observed in Figure 5. Furthermore, by the use of the microscope's electron diffraction mode, and focusing on a dark region, we observed that the *dark regions in both samples are crystalline with a diffraction pattern identical to that of the pure CsCl salt used for ion exchange* (Figs. 8 and 9). This unusual property of polysulfone to adsorb salts is most interesting; however, we have no explanation for such behavior. It is clear that one accepted procedure for sample preparation for TEM inspection, namely treating a thin film by a salt solution of a heavy metal, seems to be a source of artifacts, at least in the present case. Therefore, the method of microtoming thin sections when a sample is already in the proper ion form seems to be more reliable. However, even in this safer procedure of sample preparation, artifacts may appear. Thus, in the course of the TEM study we learned that if a sample is left under the electron beam for some period of time, for example, during the 3 min or so required for focus adjustments in order to take a picture, beam damage sometimes occurs (Fig. 10). This picture is very similar to those (e.g., Fig. 18 of Ref. 19), which were considered to prove the existence of microphase separation in ionomers.

To void this phenomenon, we had to set the focus and move the grid to take



Fig. 9. Electron diffraction pattern of black area at arrow tip in Figure 8.

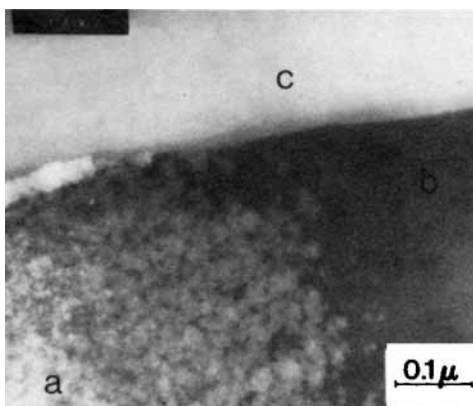


Fig. 10. Thin section of SPS, IEC = 1.2 meq/g, Cs^{+1} form, result of beam damage: (a) a part of the sample that was left under the electron beam during ca. 3 min; (b) a part of the sample that was not left under electron beam; (c) embedding material.

the picture from a portion that was not under the beam. A comparison of the two such regions is shown in Figure 10.

It is clear then that the results from examining the thin microtomed sections are in fact in agreement with the Mössbauer work already mentioned in the previous subsection, which predicted clusters whose average diameter is about 34 \AA , well below the 50 \AA resolution we were able to attain. While higher resolution in TEM is achievable with other types of samples, one must keep in mind the fact that in this case 65% of the IEC material is in the form of monomers and dimers, which decrease the electron density difference between the clusters and rest of the matrix, so that the TEM sensitivity decreases. Finally, one also has to take into account the fact that the sectioned sample is much thicker than the cluster diameter (800 \AA vs. 34 \AA), which also decreases the sensitivity. For these reasons, we were probably unable to increase our resolution and photographically verify the existence of the 34 \AA cluster.

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