Fatigue Behavior of Ionomers. 2. Effect of Counterion on Sulfonated Polystyrene Ionomers

M. Hara,* P. Jar, and J. A. Sauer

Department of Mechanics and Materials Science, Rutgers, The State University of New Jersey, Piscataway, New Jersey 08855-0909

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ABSTRACT: The effect of counterion type on the fatigue properties of sulfonated polystyrene ionomers was studied. It was found that the fatigue resistance of samples of the divalent Ca salt is ca. 3 times that of samples of monovalent K and Cs salts. This may be due to a more "effective" ionic cross-linking network in the Ca salt, which tends to suppress crazing in favor of shear deformation. This effect is similar to that found in Na salt ionomers of high ion content, in which the presence of ionic clusters leads to a more stable ionic cross-linking network rather similar to that found in covalently cross-linked PS.

Introduction

The introduction of ionic groups into polymer chains gives a unique opportunity to modify various physical properties, such as glass transitions, melt rheology, and mechanical properties.[1-5] This is due to the fact that among various physical bonds (interactions), the ionic interactions are the strongest; therefore, they can cause significant morphological changes and modifications of physical properties. The polymers having these ionic interactions are called ionomers. They have a relatively small number of ionic groups (up to 10–15 mol %) distributed usually along nonionic organic backbone chains. Because of the low dielectric constant of the medium in which ionic groups are embedded, ionic groups tend to form ion pairs which further coalesce (due to attraction between ion pairs) to create ionic aggregates. Two types of ionic aggregates are proposed to exist according to the environment (ion content, dielectric constant of the medium, etc.):[2] (1) multiplets consisting of a small number of tightly packed ion pairs, which dominate at low ion content level; (2) ionic clusters, larger aggregates than multiplets, consisting not only of ion pairs but also of some hydrocarbon chains, which bear many of the characteristics of microphase separation. The ionic clusters dominate at higher ion content levels above a critical ion content. In general, it is thought that the most critical (essential) factor modifying physical properties is the existence of ionic clusters and their size/amount. Therefore, understanding of the role of ionic clusters and the control of ionic clusters are most important aspects of the study of ionomers for both basic and application research.

Recently, we have worked on deformation and fracture behavior, including fatigue properties, of glassy ionomers to understand the role of ionic aggregates in modifying the mechanical properties of polymers.[6-8] Studies of deformation and fracture modes of thin films under simple tension by transmission electron microscopy (TEM)[7] provide basic information for developing an understanding of the deformation/fracture behavior of bulk ionomer samples subject to cyclic loading (fatigue). Fatigue is a failure phenomenon of a material due to repetitive (cyclic) loading.[9-12] Under cyclic loading, materials tend to fail at stress levels much lower than they can withstand under monotonic loading. Since all types of materials fail by fatigue loading of one kind or another, it is very important to improve the resistance of polymers to fatigue failure. In order to do so, it is essential to understand the mechanism of fatigue failure in terms of the microstructure of polymers and to determine how to modify the structure for maximum property enhancement.

The fatigue behavior of polymers is significantly influenced by various molecular variables, such as molecular weight, physical entanglement, cross-linking, rubbery phase inclusion, etc. The effect of molecular variables on deformation/fracture under fatigue loading is discussed in detail in a recent review article.[12] Another interesting molecular variable that can change fatigue performance of polymers is the existence of ionic groups. The creation of ionic aggregates (i.e., multiplets and ionic clusters) may lead to a significant modification of mechanical properties, including fatigue properties, as has been found for various physical properties.[2-5]

Recently, we have reported the results of a systematic study of ion content effects on fatigue properties of sulfonated polystyrene ionomers (Na salts).[8] It was shown that the fatigue performance of the ionomers at low ion content level (below 5 mol % where multiplets appear to play a dominant role) decreased with ion content. On the other hand, the fatigue performance of ionomers at high ion content level (above 6 mol %) was better than that of the ionomer precursor (i.e., PS). This was attributed to the effect of ionic clusters dominating at high ion content level. The ionic clusters may work not only as reinforcing fillers but also as more "effective" cross-links than multiplets, thereby suppressing (or stabilizing) crazing in favor of shear deformation, as is the case in covalently cross-linked PS.[13] The stabilizing effect on crazes (and enhancement of shear deformation) by ionic clusters at high ion content level was also confirmed by TEM observation of ionomer thin films subjected to simple tension.[7]

If the influence of an "effective" ionic cross-linking on craze stability is the major factor for the improvement of fatigue properties, it is suggested that a strengthening of the ionic bonding could lead to ionomer samples with even better fatigue properties. For this purpose, we have studied the effect of the nature of counterions on fatigue properties of ionomers since, in general, it is known that divalent ions form stronger ionic bonding than monovalent ions.[2] In this study, we have explored the fatigue properties of two ionomers with monovalent counterions (K, Cs) and an ionomer with a divalent counterion (Ca). The results obtained are discussed on the basis of the above-mentioned hypothesis and compared with previous results obtained for Na salt systems.

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* To whom correspondence should be addressed.

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Table I
Effect of Counterion on the Average Number of Cycles to Fracture, N_f(av), for Ionomer Samples Subject to a Stress Amplitude of 11 MPa at 5 Hz

counterion	N_f(av)
K	2.2×10^4
Cs	2.3×10^4
Ca	6.3×10^4

Experimental Section

Materials. Lightly sulfonated polystyrene samples were made by solution sulfonation according to the method developed by Makowski et al.[14] The polystyrene was obtained from Mobil Chemical (Mobil PS 1800) and had molecular weight of $M_w = 3.09 \times 10^5$ and $M_n = 1.41 \times 10^5$ ($M_w/M_n = 2.2$). After the sulfonation reaction was terminated by adding methanol, a proper amount of metal hydroxide dissolved in methanol (for K and Cs) or water (for Ca) was added to neutralize acid groups. The resulting ionomer (i.e., salt) samples were recovered by steam stripping in boiling water. The ion content of the sample was 4.1 mol %, i.e., 4.1 ionic groups on average per 100 repeating units. The recovered samples were dried at high temperature (120 °C) under vacuum for at least a week.

Fatigue specimens were made by compression molding. The ionomer samples were first molded into rectangular bars (15 cm × 1.6 cm × 1.6 cm) and then machined into hourglass-shaped round samples with threaded ends (3 in. long, $^1/_5$-in. diameter at the middle, and $^1/_2$-in. diameter at the grip ends). After machining, the specimens were thoroughly polished by using both emery papers and lens-polishing papers to remove surface scratches. Several specimens were made for each ionomer with different counterions.

Measurements. Fatigue testing was conducted by using an Instron Servohydraulic testing machine (Model 1350) at room temperature. Testing conditions were similar to those used for study of the ion content effect of Na salt ionomers:[8] tension–compression cycling with a maximum stress amplitude of 11 MPa and a sinusoidal waveform with a frequency of 5 Hz. Fatigue fracture surfaces were examined by a scanning electron microscope (SEM) (Etec) after the surfaces were coated with a thin layer of gold. Pictures were taken from various angles by tilting the sample. The temperature rise, due to hysteresis, of the ionomer specimens as well as of the PS specimens is expected to be negligible, because of the low stress level and the known very low tan δ value of polystyrene at room temperature. Hence failure of these specimens is a result of mechanical fatigue, involving a crack initiation phase and a crack propagation phase.

Results

Table I summarizes the fatigue data obtained on the various ionomer samples. It is evident that the average number of cycles to fracture, N_f(av), is essentially the same for the ionomer samples containing monovalent ions (K and Cs) and that the average fatigue lifetime for the divalent Ca ion is ca. 3 times higher.

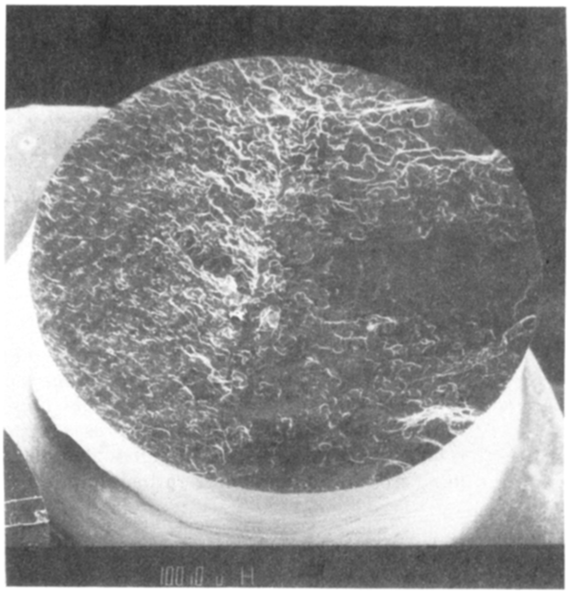

Figure 1. Fatigue fracture surface of K salt ionomer with 4.1 mol % ion content tested at a stress amplitude of 11 MPa and at 5 Hz.

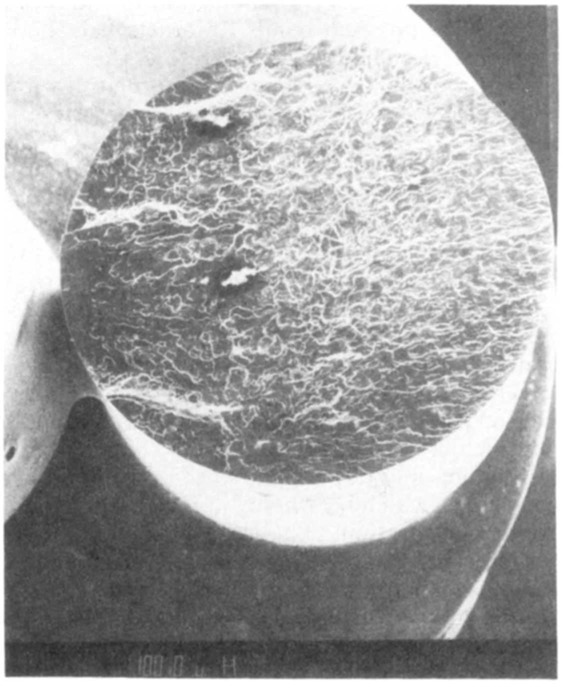

Figure 2. Fatigue fracture surface of Cs salt ionomer with 4.1 mol % ion content tested at a stress amplitude of 11 MPa and at 5 Hz.

The fatigue fracture surface morphology also shows some dependence on the nature of the counterion that is present. Low-magnification scans of the entire fracture surface for samples of each of the three different types of ionomers are shown in Figures 1–3. In many polymers, the fatigue fracture sulface, at low or moderate stress amplitudes, is transverse to the stress axis and consists of a comparatively smooth, slow-growth region in the vicinity of the fracture source, generally a microcrack that developed from a small surface craze, followed by a rougher region of more rapid crack growth.[9,15] This latter region develops after the fatigue-induced crack has reached some critical size. For the ionomer samples, in which some degree of ionic cross-linking is present, the transition zone from the region of relatively slow crack growth to that of catastrophic crack extension is not as clearly defined as in homogeneous polymers. It appears, however, that in the divalent Ca salt ionomer, the slow-growth region of the fracture surface is larger and somewhat better defined than that for the monovalent ionomers.

Other differences in fracture surface morphology appear in high-magnification SEM scans. For example, Figure 4 shows that several discontinuous crack growth (DCG) bands are present on the fracture surface of the monovalent K salt. These bands are similar to but not as well defined as those seen in PS.[9,15] They are indicative of periodic crack extension, over a rather broad front, through fatigue-damaged area crazes that advance essentially in a single transverse plane. In the divalent Ca salt ionomer, no comparable DCG bands have been observed. A high-magnification scan of a portion of the fracture surface for this ionomer taken in the vicinity of the surface fracture source is shown in Figure 5. Here it appears that craze

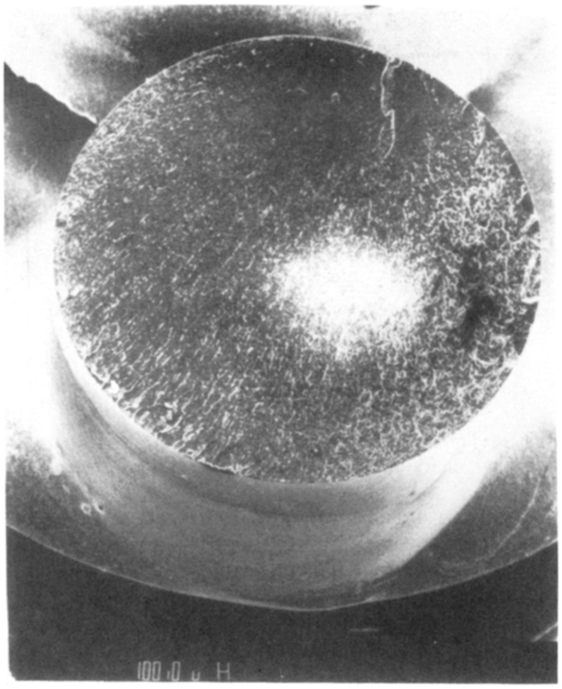

Figure 3. Fatigue fracture surface of Ca salt ionomer with 4.1 mol % ion content tested at a stress amplitude of 11 MPa and at 5 Hz.

Figure 4. Portion of fatigue fracture surface of K salt ionomer with 4.1 mol % ion content tested at a stress amplitude of 11 MPa and at 5 Hz.

growth and subsequent crack extension have not occurred along a single broad transverse plane but that crack growth has occurred in a more irregular manner. The fracture surface contains both relatively smooth areas, indicative of crack propagation through crazes, and inclined surfaces that may arise from crack advance through shear deformation zones or bands. The fatigue fracture surface observations thus provide indirect evidence that some shear deformation, as well as craze deformation, may occur in ionomers containing less than 5 mol % ion content, provided that divalent counterions are present.

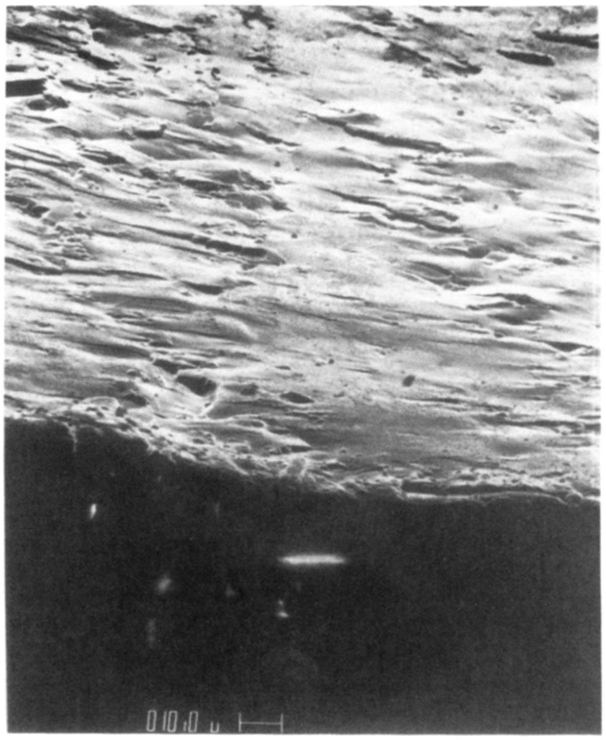

Figure 5. Portion of fatigue fracture surface of Ca salt ionomer with 4.1 mol % ion content tested at a stress amplitude of 11 MPa and at 5 Hz. SEM scan taken from direction almost parallel to fracture surface.

Discussion

Before we consider the implications of these results to ionomer microstructure, it is desirable to briefly summarize some of the information already obtained on Na salt ionomers with various ion contents (1.7, 2.5, 4.8, 6.1, and 8.5 mol %).[7,8] Fatigue tests on samples of all these ionomers were carried out under the same test conditions as in the present experiments involving different types of counterion. In the previous fatigue investigation[8] it was observed that both the fatigue life, N_f, and cycles to observation of the first observable defect, N_i, tended to decrease with increasing ion content up to 4–5 mol %. Thereafter, both N_f and N_i increased sharply in the 5–6 mol % range and then continued to increase up to the 8.5 mol % ion content level. These results were attributed to a change in microstructure of the ionomers, with ion pairs and multiplets dominating behavior below a critical ion content of ca. 5 mol % and ionic clusters dominating behavior at higher ion contents. In other words, ionic type cross-linking, associated primarily with multiplet formation, appeared to be adverse to fatigue performance, while the ionic interactions associated with the presence of large ionic aggregates or clusters led to a more effective type of ionic cross-linking and to an enhancement of resistance both to defect initiation and to fatigue fracture, probably by increasing craze stability.

The results of the present study show that an increased resistance to fatigue crack initiation and fracture, as also observed in the prior studies involing Na salts of high ion content (above 6 mol %), can be obtained even at the lower ion content of 4.1 mol % by changing from a monovalent type counterion to a divalent type counterion. In fact, the fatigue fracture surface morphology of the divalent Ca salt ionomer (Figure 5) displays some similar features to those noted in the Na salt ionomer containing 8.5 mol % ion content. An SEM scan of a portion of the fracture surface of this latter ionomer is shown in Figure 6. Here

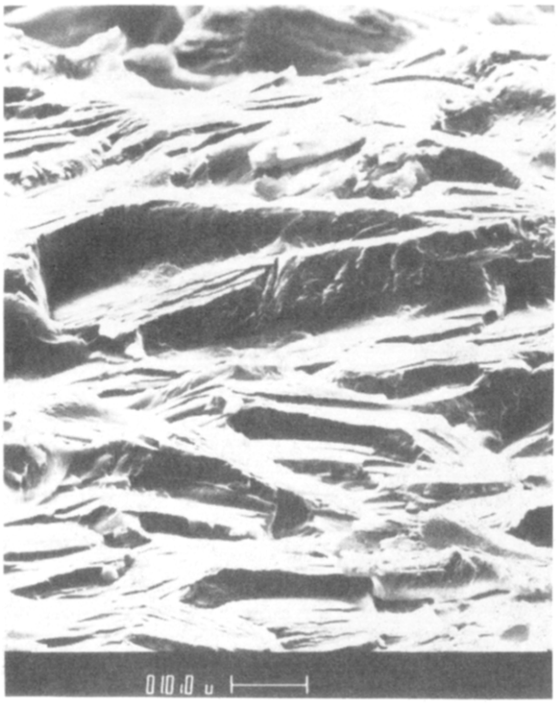

Figure 6. Portion of the fatigue fracture surface of Na salt ionomer with 8.5 mol % ion content tested at a stress amplitude of 11 MPa and at 5 Hz. SEM scan taken from direction almost parallel to fracture surface.

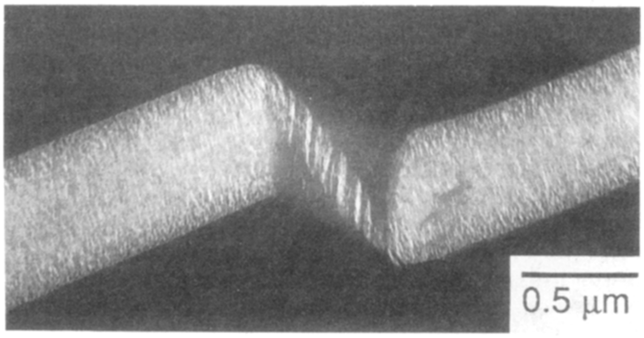

Figure 7. TEM micrograph of thin film of Na salt ionomer with 8.5 mol % ion content cast from DMF solution with heat treatment and deformed in tension.

too the fatigue crack has passed through both relatively flat areas (crazes) and lies perpendicular to the stress direction, as well as through inclined areas. This suggests that some localized shear deformation, as well as crazing, was present during the fatigue fracture process: a conclusion already drawn from examination of the fracture surface of the 4.1 mol % divalent Ca salt ionomer.

That shear deformation, as well as craze deformation, can become an effective mode of deformation in ionomers that possess a strong ionic cross-linking network is evident from TEM examination of deformed thin films of the Na salt ionomer.[7] In these studies it was noted that at low ion contents where microstructure was dominated by ion pairs and multiplets, pear-drop-shaped cavities readily formed at craze boundaries, craze stability decreased, and early crack development and fracture resulted. However, at high ion contents (above 6 mol %) where the presence of larger ionic aggregates (clusters) led to a more effective type of ionic cross-linking, craze stability increased, shear deformation began to compete with crazing as the more likely deformation mode, and the material became more resistant to fracture. Figure 7 shows a TEM micrograph of a deformed sample of the Na salt ionomer containing 8.5 mol % ion content. Here we see an inclined shear band that has interacted with two crazes that possess typical craze microstructure. The presence of shear bands can inhibit craze growth, enhance craze stability, and improve resistance to fracture.

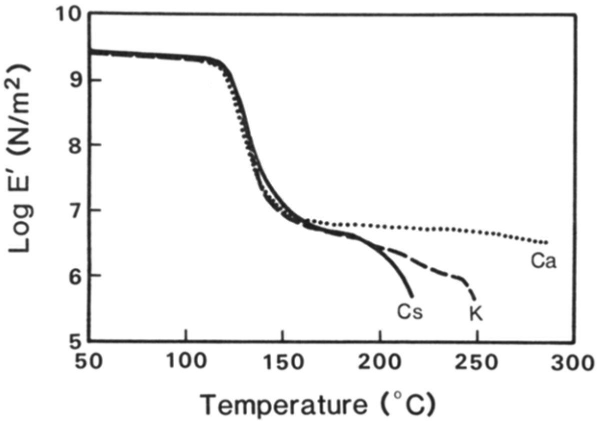

Figure 8. Tensile storage modulus, *E*′, vs temperature for K, Cs, and Ca salt ionomers with 4.1 mol % ion content.

Additional thin-film studies, which will be discussed more fully in a subsequent publication,[16] have recently been carried out in our laboratory on the 4.1 mol % ionomers containing K, Cs, and Ca counterions. These studies show that crazing is the only observable form of deformation in the monovalent ionomers (K and Cs), as noted earlier for the Na ion ionomers having an ion content of less than 5 mol %; but for the divalent Ca salt ionomer, both shear deformation bands and crazes were observed even though the ion content was only 4.1 mol %. This result is another strong indication that at a given ion content, the ionic cross-linking effect due to the presence of divalent counterions is more effective than that arising from the presence of monovalent counterions.

Other pertinent information about the strength and relative stability of the ionic bonding for the three different types of ionomers used in the present study has recently been obtained from dynamic mechanical tests made over a broad tempertaure range on samples of the K, Cs, and Ca salts.[17] Some of the results of this study are presented in Figure 8. A large modulus drop, associated with the glass transition temperature of the matrix material, occurs at essentially the same temperature for all three types of ionomers. However, the rubbery plateau modulus, attributed to the presence of ionic cross-linking, decreases appreciably with increasing temperatures above 150 °C for the monovalent salts but, for the divalent Ca salt, it remains almost unchanged up to the temperature limit of the instrument (300 °C). This behavior indicates that the ionic interactions, due to the presence of ionic aggregates or clusters, are much stronger in the divalent Ca salt than in the monovalent salts. These stronger ionic interactions are believed to be largely responsible for the threefold increase observed in fatigue lifetime, an effect that may arise from an enhanced craze stability and the presence of shear deformation.

The absence of discontinuous crack growth bands on the fatigue fracture surface of the divalent Ca salt ionomer is, indirectly, still another indication of the presence of a more effective ionic cross-linking network. For example, it is known that in many low molecular weight homogeneous polymers like PMMA and PVC, where there are few molecular entanglements per chain, DCG bands are present on the fatigue fracture surface; but, in high molecular weight samples, where there is a much greater degree of chain entanglement, no DCG bands are observed.[12,15] It thus appears that changing from a monovalent counterion to a divalent counterion in the 4.1 mol % ionomers, and thereby introducing a greater degree of ionic association, is rather akin, in the case of homogeneous polymers, to increasing the molecular weight and obtaining more intermolecular entanglements.

Conclusions

Fatigue properties of sulfonated polystyrene ionomers with three different counterions (K, Cs, and Ca) were studied. It was found that the fatigue performance of the divalent Ca salt was 3 times better than that of monovalent K and Cs salts. This was attributed to the formation of more "effective" ionic cross-linking in the Ca salt, which suppressed crazing in favor of shear deformation and probably enhanced the crack initiation phase, as was observed for Na salt ionomers with high ion content. Although it is too early to generalize our results to other counterions, it is encouraging to know that the use of Ca salt significantly enhanced fracture properties; hence it may be possible to create ionomers with even better fatigue performance by using other multivalent counterions (e.g., Al). This is an interesting problem to study not only for applications of ionomers as engineering plastics but also for basic understanding of the effect of the strength of ionic interactions on fracture properties.

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