

## The Effect of Diblock and Homopolymer Impurities on the Morphology of Triblock Polymers

L. J. FETTERS, B. H. MEYER,\* and D. McINTYRE,  
*The University of Akron, Department of Polymer Science,  
Akron, Ohio 44325*

### Synopsis

Commercial triblock polymers (Kratons) consisting of polystyrene and a polydiene were characterized via gel permeation chromatography and small-angle x-ray scattering in order to determine the amount of free polystyrene and diblock material and to clarify the effect of these polymeric impurities on the morphology of solvent-cast samples. Gel permeation chromatography measurements revealed the Kratons to consist of 80–85% triblock, 15–20% diblock, and trace amounts of free polystyrene. Pure triblocks, impurity-doped pure triblocks, the Kratons, and a postpolymerically degraded Kraton were examined with regard to the effect of polymeric impurities on morphology. Small amounts (<5%) of free polystyrene induce a regularization of the glassy domains, while increased amounts of this homopolymer apparently lead to diffuse phase boundaries. The presence of diblock polymer results in a loss of macrolattice details, indicating the presence of less ordered and more diffuse glassy domains.

### INTRODUCTION

The search for new elastomeric materials has led to the discovery<sup>1,2</sup> of "thermolastic" elastomers which are block polymers of the ABA type. These materials at ambient temperatures exhibit the properties of vulcanized rubber but can be remolded at elevated temperatures. These unusual properties are a reflection of the chain structure of these block polymers. The triblock materials consist of polystyrene and polydiene where the interior segment (B) is the polydiene ( $M_n \simeq 50\text{--}100,000$ ), while the exterior segments are polystyrene. In essence, the morphology of the materials can thus be described as a finely divided dispersion of a plastic in a rubber matrix. This morphology occurs spontaneously as a result of the incompatibility of the A and B segments, so that the A segments, which represent the lesser component, form domains within the elastic matrix formed by the B blocks. Thus, the two-phase system consists of glassy domains attached to a matrix of elastomeric polydiene chains.

\* Present address: Research Department, Koppers Co. Inc., 440 College Park Drive, Monroeville, Pennsylvania 15146

It has become increasingly evident that many investigators are now studying commercial triblock polymers (Kratons) (trademark of Shell Chemical Company) without (1) obtaining an analysis of other polymeric impurities, and/or (2) being aware of the profound effect these impurities have on morphologic conditions. In some studies solely devoted to physical properties, such as mechanical strength and creep, it is to be expected that the results can be reinterpreted, if these impurities are known. However, not all mechanical measurements can be easily re-evaluated, and many physical chemical studies must take these impurities into account at the planning stages of the experiments.

This report is to clarify by means of gel permeation chromatography (GPC) and small-angle x-ray scattering (SAXS) the measurements of the amount and effect of homopolymer and diblock polymer in the commercial Kratons. The morphology of the pure triblock polymers, impurity-doped pure triblocks, commercial Kratons, and postpolymerically reacted and slightly degraded Kratons are compared by SAXS. With only these two techniques of characterization, it is of course impossible to be definitive about all effects of these impurities on the morphology and physical properties.<sup>3</sup> It is possible, however, to make clear to all research workers that these impurities must be stated clearly in all reports of future work. This must be accomplished if there is to be meaningful comparison of interlaboratory data and the elucidation of a valid molecular model of the morphology.

The work of Meier<sup>4</sup> is perhaps the best overall analysis of the thermodynamic factors involved in diblock polymer morphology. Meier considered the equilibrium phenomena associated with the phase separation. In an attempt to achieve equilibrium in our samples, films of the block polymers were cast from 15–25% solutions and air dried. Complete removal of the residual solvent was done under vacuum at an elevated temperature (95°C).

## EXPERIMENTAL

**Pure Triblocks.** The polystyrene and triblock (SBS and SIS) polymers were synthesized in these laboratories under carefully controlled conditions. The synthetic methods of anionic polymerization used are described elsewhere.<sup>5,6</sup> Suffice it to say that the synthesis was carried out under conditions of rigorous purity under high vacuum. The mode of SBS and SIS synthesis involved the sequential addition of the monomers to yield a three-stage polymerization. Each polymer thus prepared was characterized as to number-average molecular weight and molecular weight distribution, using the GPC for the latter. The GPC measurements on the SIS and SBS samples did not detect, unlike the Kratons, the presence of polystyrene homopolymer and diblock material. The Kraton triblock polymers (101, 1101, 102, 1102, 107, and 1107) are apparently synthesized via a two-stage anionic polymerization followed by a coupling reaction to

yield triblock polymer.<sup>1,2</sup> As will be shown later, this mode of synthesis yields a product containing 15% to 20% of uncoupled diblock polymer in addition to the desired triblock material. The major disadvantage of the coupling technique compared to the three-stage process is that it requires high precision in the stoichiometry of the linking reactions as well as high efficiency in the reaction itself.

**Hydroxylated Kraton.** Monoperthalic acid was used to prepare the hydroxylated Kraton material. Hydrolysis was carried out in excess sodium hydroxide in aqueous methanol overnight at room temperature. The basic procedures are outlined elsewhere.<sup>7-10</sup> The polymer is designated as K-101-OH and was derived from lot number 70903.

**Gel Permeation Chromatograph.** The gel permeation chromatograms were obtained on a Waters Ana-Prep instrument equipped with five columns. These columns had permeability ranges of  $2-5 \times 10^3 \text{ \AA}$ , two columns with  $5-15 \times 10^3 \text{ \AA}$ ,  $1.5-5 \times 10^4 \text{ \AA}$ , and  $5-15 \times 10^4 \text{ \AA}$ . Solutions containing 0.25 wt-% of the polymers were used with tetrahydrofuran as the solvent. Flow rates of 0.25 ml/min and 1 ml/min were maintained at a temperature of 45°C. A linear relationship between  $\log M_w$  and elution volume was generated for these columns over a molecular weight range of  $5 \times 10^3$  to  $5 \times 10^5$ . The Pressure Chemical Co. polystyrene standards were used for this calibration, in addition to polystyrene samples synthesized and characterized in these laboratories. The amounts of triblock, diblock, and homopolymer in the Kraton samples were determined by measurement of the relative areas under the curve.

**Molecular Weight Measurements.** The number-average molecular weights were determined with toluene solutions at 37°C. The Hewlett-Packard high-speed membrane osmometers (Models 502 and 503) were used with the 450 gel cellophane membranes.

**Film Preparations.** The films used in this work were cast and partially dried at room temperature from tetrahydrofuran-methyl ethyl ketone mixtures (90%/10%). Residual solvent was removed under vacuum at 95°C. A constant weight was gradually obtained after six days of vacuum drying.

**X-Ray Measurements.** A Bonse-Hart<sup>11</sup> small-angle x-ray diffractometer manufactured by Advanced Metals Research, Burlington, Mass., was used in these experiments. The sample thickness was approximately 1.8 mm and consisted of several layers of cast film. The transmission coefficient was approximately 0.5. The generator was the ultrastable Phillips Model PW 1310. The exposure time for each angle varied as follows: (1) for scattering angles from 0 to 1000 sec, the readings were taken every 10 sec of angle and the counting times were 100 sec for each point; (2) for scattering angles greater than 1000 sec, the intensity of scattered radiation ( $\sim 3$  counts/sec) was so low that counting times of 1.5 hr were used for each point. The diffractometer can routinely be aligned to measure scattering within 20 sec of the incident beam.

The scattering data were corrected for slit smearing by the technique of Schmidt<sup>12</sup> using an infinite slit correction.<sup>13</sup>

## RESULTS

Representative GPC traces for each of the three types of Kratons are shown in Figures 1 to 3. These traces were run at a flow rate of 0.25 ml/min. Previous GPC measurements<sup>14</sup> on these samples at a flow rate of 1 ml/min reached similar results. However, the slower rate led to increased resolution and a more accurate determination of the respective amounts of di- and triblock material. The composition of the Kratons, along with the number-average molecular weights, are shown in Table I.

It can readily be seen that, irrespective of type, the Kratons contain 80–85% triblock chains and 15–20% diblock material. The small amount of polystyrene found in some of the samples undoubtedly results from termination during the addition of the diene monomer. The presence of the diblock fortifies the indication<sup>1,2</sup> that the synthesis procedure used for the preparation of the Kratons involves a coupling reaction between the polydienyllithium chain end and an alkyl dihalide species. The molecular weight ( $M_w$ ) of the polystyrene detected in Figure 1 is estimated to be  $1.5 \times 10^4$  from the calibration curve generated with standard polystyrene samples. Figures 4 and 5 show the SBS and SIS GPC traces run at the slow rate. It is apparent that these block polymers are quite pure. Neither trace gives any indication that homopolymer or diblock polymer is present in either sample.

Figure 6 shows the x-ray scattering carried out to 1000 sec of angle under relatively fast scanning for the pure SIS material and the same triblock

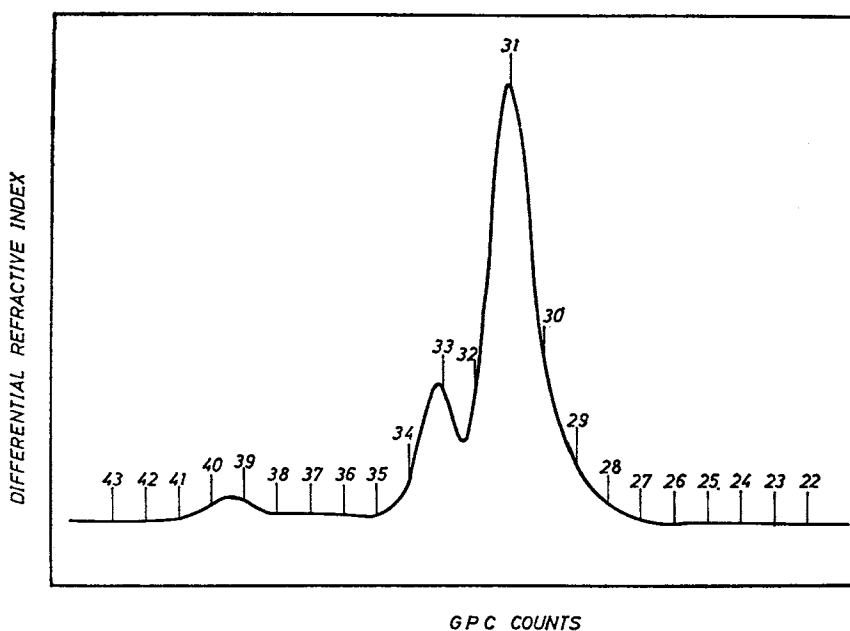


Fig. 1. Gel permeation chromatogram of Kraton 1101, lot no. 00211.

TABLE I  
GCP Characterization of Kraton Block Polymers at Slow Flow Rate<sup>a</sup>

Sample no.	Lot no.	$M_n \times 10^{-4}$ , g/mole	ABA, wt-%	A(0.5B), wt-%	A, wt-%	Poly-styrene, wt-% <sup>b</sup>
101	70903	10.0	80	19	1	30
101	80319	10.4	83	17		
1101	00211	9.4	78	21	1	
1101	90501	9.5	82	18		
102	80325	7.8	84	16		25
102	TR41-691	8.2	80	19	1	
102	70905	8.0	81	18	1	
1102	90514	7.8	84	16		
107	80201	12.5	81	18	1	12
1107	90428	14.3	75	25		
1107	91225	14.3	81	19		
K-101-OH <sup>c</sup>	70903		60	39	1	

<sup>a</sup> Experimental errors:  $M_n$ ,  $\pm 7\%$ ; A, A(0.5B), and ABA wt-%,  $\pm 5\%$ .

<sup>b</sup> Data given by the Shell Chemical Co.

<sup>c</sup> Flow rate of 1 ml/min.

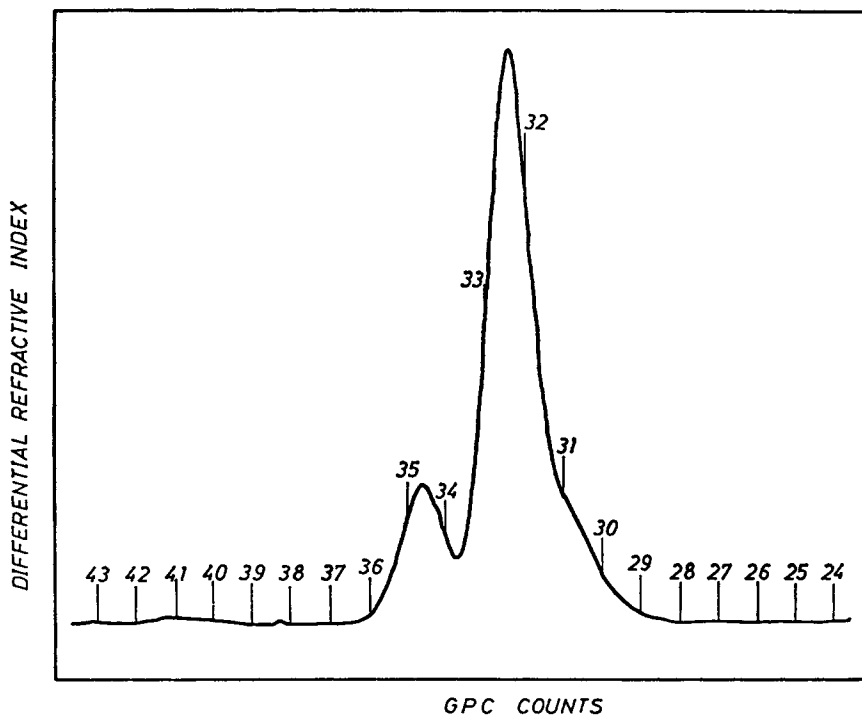


Fig. 2. Gel permeation chromatogram of Kraton 1102, lot no. 90514.

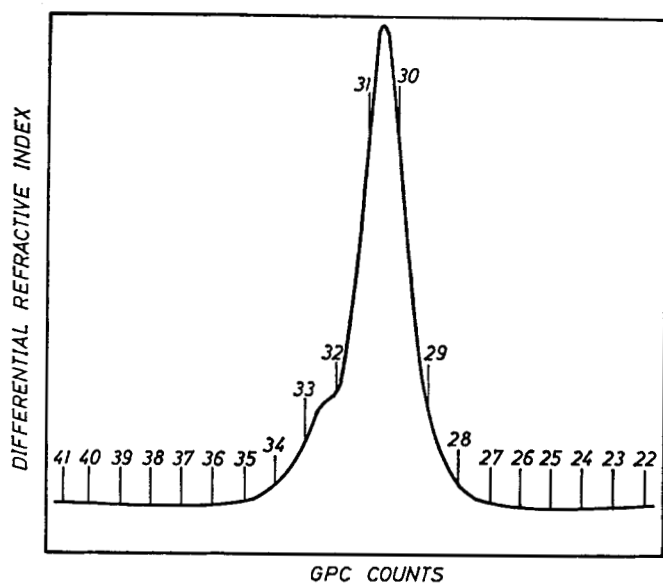


Fig. 3. Gel permeation chromatogram of Kraton 1107, lot no. 91225.

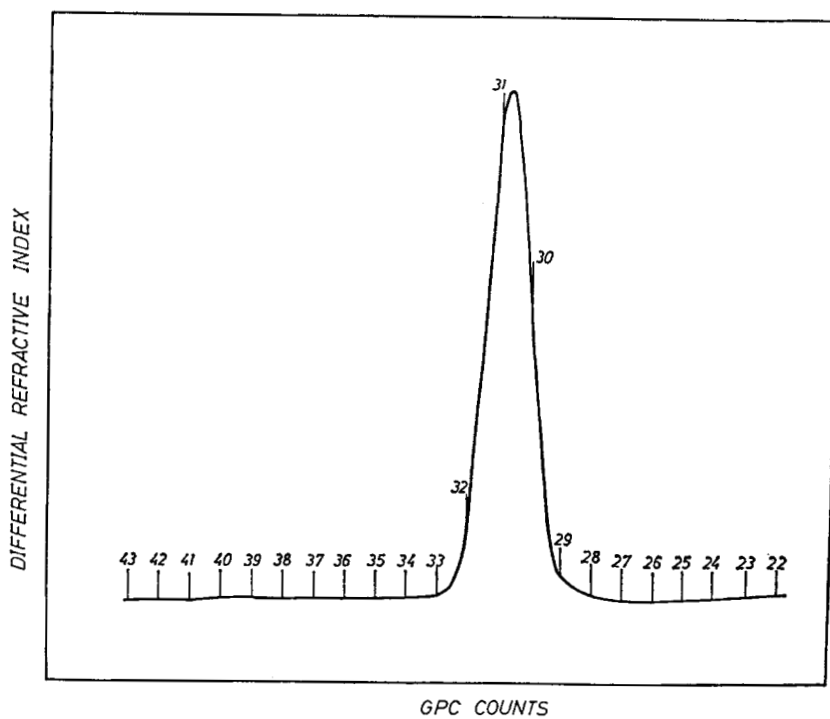


Fig. 4. Gel permeation chromatogram of SIS triblock polymer.

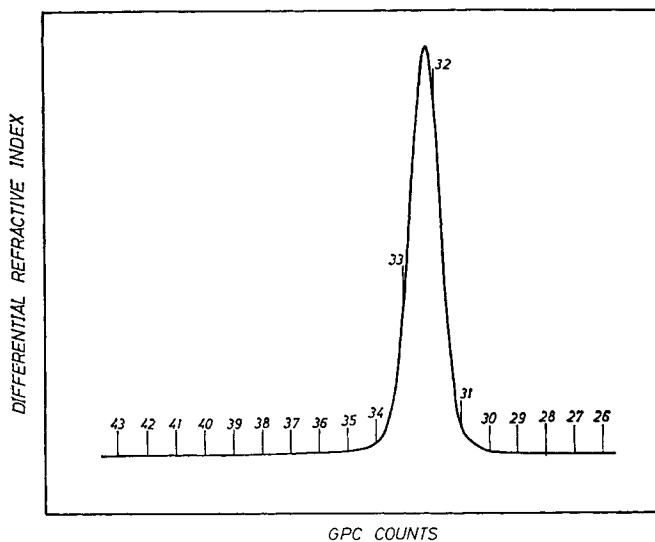


Fig. 5. Gel permeation chromatogram of SBS triblock polymer.

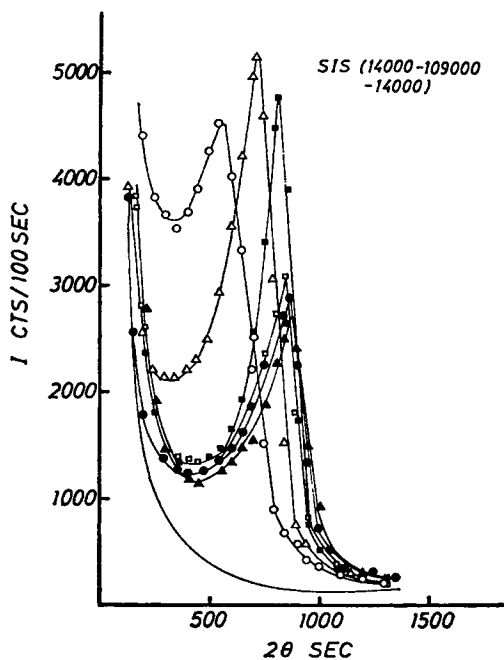


Fig. 6. Scattering from SIS polymer with blends of homopolymer. Per cent of added polystyrene: (-) background; (O) 0%; (Δ) 1%; (■) 2%; (□) 5%; (●), 10%; (▲) 20%.

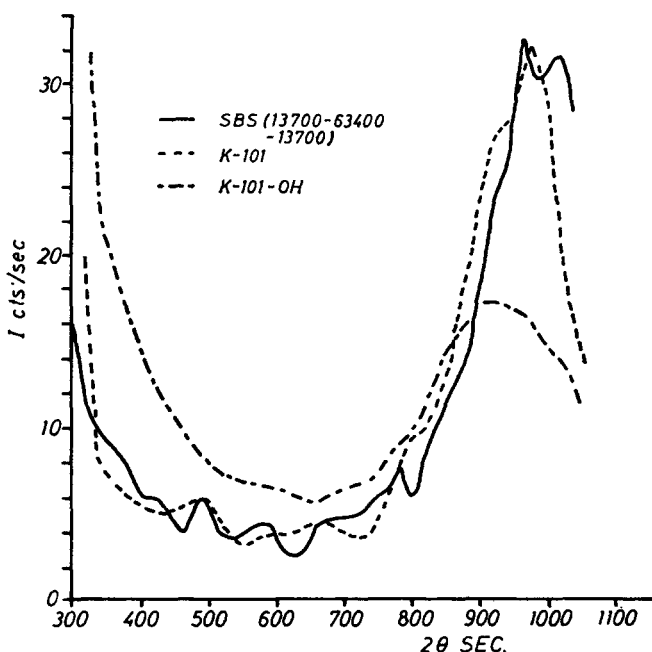


Fig. 7. Low-angle x-ray analysis of SBS, K-101 and K-101-OH block polymers. The Kraton materials were taken from lot no. 70903.

adulterated with various amounts of polystyrene. The homopolymer impurities were added to the samples in solution. The homopolymer had a molecular weight similar to the A block of the SIS triblock polymer. The main peak is the nearest neighbor peak, whether the phases are considered to be a liquid or macrolattice structure. The homopolymer has the effect of sharpening up the nearest neighbor peak initially. As more polystyrene is added, the nearest neighbor peak is partially smeared out.

The x-ray scattering of the SBS, K-101, and K-101-OH materials in the region of the main peak is compared in Figure 7. The SBS sample (similar in composition and molecular weight to the Kraton 101) has the clearest definition, namely, a series of pronounced small peaks throughout the whole region. The K-101 sample in the same range has a much more subdued series of peaks and is missing some peaks altogether in the same region. The K-101-OH, in which the triblock polymer content has gone down to 60%, has lost almost all the macrolattice details, and the nearest neighbor peak has been significantly reduced.

Figure 8 shows the drastic effect of the diblock impurity in the region of single-particle scattering. There is only one easily seen peak and one possible shoulder in Figure 8 for the SBS. The K-101 has a shoulder and a very broad peak around 2500 sec. In these comparative measurements, the SAXS measurements were not extended to higher angles because of the long counting times. However, even at the first particle scattering peak, the line width is considerably larger in the K-101 material.



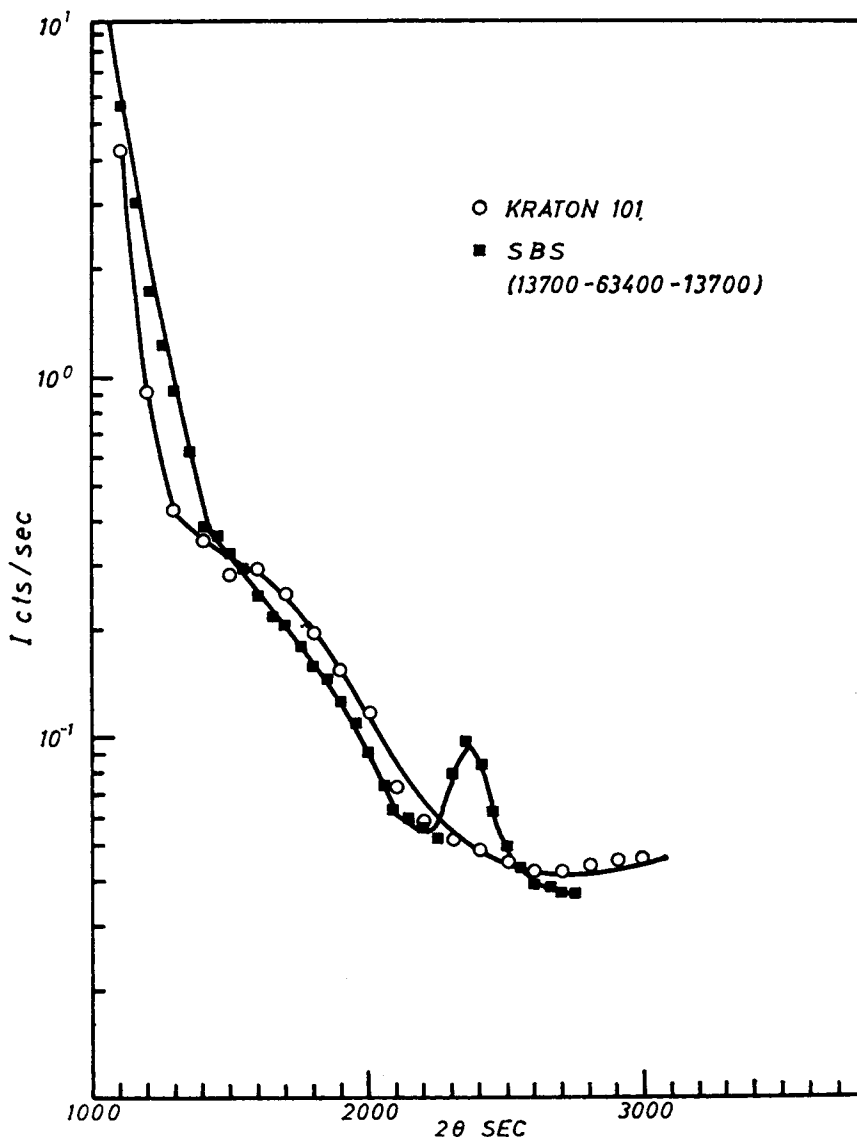


Fig. 8. Scattering of SBS and Kraton 101 (lot no. 70903) block polymers.

**DISCUSSION**

The existence of approximately 20% diblock content in the Kratons is certain. Fortunately, the amount of homopolymer (polystyrene) is ca. 1% or less. The SAXS experiments shown in Figure 4 reveal that the presence of 1% homopolymer can markedly sharpen up the nearest neighbor peak. Consequently, as long as the homopolymer impurity is kept below 5%, the distribution of glassy domains appears to become even more regular. This regularizing of the nearest neighbor distance

probably comes about by the easing of interfacial strains between glassy and rubbery domains. Mechanical measurements<sup>15</sup> show that at a given stress the strain is less in the SIS with the added homopolymer, while the tensile strength of the SBS is enhanced when the homopolystyrene is added. These mechanical effects may also be partly attributed to the improved reinforcement resulting from regularly placed spherical particles, although other morphologies are possible. Such an effect would have to be theoretically analyzed since it could not, of course, be evaluated experimentally in any other filler system but a triblock polymer.

However, as the homopolymer impurity becomes an ever greater portion of the total glassy phase, the smearing of the phase boundaries probably is sufficiently haphazard to eliminate the presence of a sharp scattering peak. Another possibility is that aggregates of several discrete phases are now tied together. The scattering pattern would become less sharply defined in such cases. It has been observed<sup>15,16</sup> that when a 20% SBS sample had additions of polystyrene until the total polystyrene content was 40%, there was less optical clarity than in a 40% triblock polymer. These visual observations indicate that larger scattering domains are present. The absence of marked blurring of small secondary peaks at smaller scattering angles from the main peak can be interpreted as the diminution of long-range order in the placement of glassy domains. Interestingly, mechanical measurements<sup>15,16</sup> show that the 20% homopolymer-doped SBS and the 40% undoped SBS are not significantly different in tensile strength or stress at equivalent elongation. Again, it is clear that the exact role of the regularly arranged domains in reinforcement is not presently known.

The SAXS measurements (Figs. 7 and 8) show the morphologic effect of the diblock component in Kraton in contrast with a pure SBS material where no homopolymer or diblock material is present. The expected single-particle scattering diagram would be a series of minima and maxima occurring with decreasing intensity. For uniform spherical domains, the peak in Figure 8 could be interpreted as spheres of 170 Å radius. As the nonuniformity of the sphere size increases, the Rayleigh sphere scattering peaks quickly vanish. If there is a macrolattice, all of these peaks, of course, can only occur where the convolution of the particle scattering factor and lattice distribution are non-zero. Figure 8 shows a very diffuse first Rayleigh peak. With the above scattering assumptions of a spherical radius of 170 Å and a close-packed cubic lattice, the entire volume amount of polystyrene in the SBS polymer can be accounted for. The Kraton evaluated in a similar manner as a two-phase system does not yield good agreement between the lattice volume and the stoichiometric polystyrene volume. Again, the simplest explanation is to assume a large interface in the Kraton. This interface may be of the order of 50 Å in Kraton instead of 10 Å for the SBS, and may thus contain most of the diblock polymer.

The x-ray scattering shows differences between SBS and Kraton cast films and consequently differences in their morphology. More recent

studies<sup>18-21</sup> have involved extruded samples of Kratons. The influence of diblock and homopolymer impurities on the morphology of extruded or molded triblock polymers has not been measured in this study. However, it may be reasonable to speculate that with extruded samples, small amounts of homopolymer impurity, particularly of very low molecular weight, might be even more effective in reducing interfacial strain by the nonequilibrium process of extrusion or molding. Extensive work by Morton<sup>15</sup> on the effect of impurities on mechanical properties deals with cast films only so that there is no possibility of making the comparison between cast and extruded samples.

In extruded samples, diblock polymer impurity may also be even more effective in maintaining a diffuse interface, thus leading to poorly defined spheres during phase separation, than in cast film samples. Nonuniform, smeared spherical patterns have been shown by electron microscopy.<sup>17</sup> These glassy domains seem to have a knob-like appearance in a Kraton 101 sample.

In brief, then, the morphology and mechanical properties do depend markedly on the amounts of homopolymer and diblock impurities. Consequently, these impurities should be characterized when new experimental studies are published.

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