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Properties of Some Diblock Copolymers

Based on 1,3 Butadiene Monomer

by

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The properties of three series of diblock copolymers are discussed. One series of polymers is comprised of two diblock copolymers of polystyrene and 1,2 polybutadiene in which the polybutadiene microstructure is essentially pure 1,2 addition. Hydrogenation of these polymers leads to a second set of block copolymers of polystyrene and polybutene-1. The polybutene-1 segments are atactic and therefore exhibit amorphous, rubbery behavior. A third series of samples contains four diblock copolymers of 1,4 polybutadiene and 1,2 polybutadiene; microphase separation is observed for these 1,4 polybutadiene/1,2 polybutadiene materials. Results of		

small amplitude forced oscillation mechanical tests and of large deformation constant rate of strain measurements are reported and discussed.

A

INTRODUCTION. Owing in part to the potential for application as thermoplastic elastomers, certain triblock copolymers and segmented block copolymers have received more attention in the literature than corresponding diblock copolymers. On the other hand well characterized diblock copolymers are relatively easy to synthesize, and the equilibrium organization of diblock molecules in a bulk specimen is rather well understood; thus diblock copolymers are excellent candidates for use in obtaining a better understanding of how various molecular and morphological parameters influence bulk physical properties of multicomponent polymer systems. In previous studies, diblock copolymers of polystyrene and 1,4 polybutadiene (S/1,4B) were blended with a corresponding triblock to investigate the role of terminal chains in elastomeric materials (1). More recently diblocks of cis-1,4 polyisoprene and 1,4 polybutadiene (1,4I/1,4B) were shown to be homogeneous materials (2) which in certain cases had the ability to homogenize incompatible homopolymers of butadiene and isoprene (3, 4). The present work represents a continuation of our interest in such diblock copolymers in which at least one of the blocks is based on the monomer 1,3 butadiene.

MATERIALS. There are three series of diblock copolymers under investigation (Table 1). These were generously provided to us by Dr. A.F. Halasa of the Firestone Tire and Rubber Co. The first two sets of polymers were obtained directly as products of the various anionic polymerizations described below; the polymers of Series 3 in Table 1 were obtained by hydrogenation of the diene blocks of the polymers from Series 1, using procedures described below. The hydrogenated products of Series 2 will be discussed elsewhere.

The 1,2 polybutadiene/polystyrene (1,2B/S) diblocks were prepared by anionic polymerization in hydrocarbon media using n-butyllithium initiator modified with

dipiperidene ethane at a ratio of $\text{Li/DPE} = 4.0$; the 1,2 polybutadiene block was synthesized first keeping the temperature below 14°C . The 1,4 polybutadiene/1,2 polybutadiene (1,4B/1,2B) diblocks were made in hydrocarbon solvent using n-butyllithium initiator; the 1,4 polybutadiene block was synthesized first followed by addition of the polar modifier dipiperidene ethane and fresh monomer to change the microstructure of the second block to 99% 1,2 addition. Hydrogenations (5) of the 1,2B/S diblocks were carried out in toluene after the polymers were purified by precipitation from toluene solutions with methanol. The hydrogenation catalyst was soluble nickel octanoate reduced with triisobutyl aluminum. A mild hydrogenation procedure was employed at 100°C using a ratio of $\text{Al/Ni} = 3.0$. GPC and osmometric analyses indicated essentially no change in molecular weight of these diblocks (and of numerous 1,2 polybutadiene homopolymers prior to and following hydrogenation) due to the hydrogenation procedure. The amount of unsaturation remaining in the polybutene-1 blocks of the B1/S diblocks was about 10% as determined by proton NMR.

RESULTS. Dynamic mechanical properties of the various polymers were examined on a Rheovibron viscoelastometer at 3.5 Hz. Representative results are shown in Figures 1-5. Figures 1 and 2 clearly reveal the shift in location of the glass transition of the rubbery phase as a result of the hydrogenation procedure. This shift of about 13°C (from about -1°C to 12°C in Figures 1 and 2) is consistent with results of differential scanning calorimetry (DSC) experiments on these same samples, although the transitions appeared at lower temperatures (around -23°C and -1°C) in the DSC tests. Figures 3 and 4 reveal the influence of mechanical properties of the solvent employed in the spin casting (4,6) of film specimens of the B1/S diblocks. Although results are not shown here, we also found that for a given solvent, the temperature maintained during

slow (2-4) and spin (6) casting procedures had a strong influence on mechanical behavior; lower casting temperatures tended to favor sharper peaks in plots of $\tan \delta$ against temperature. On the other hand, post-casting annealing had very little effect on the dynamic mechanical properties of the B1/S copolymers. Figure 5 is a plot of the dynamic mechanical properties of one of the 1,4B/1,2B diblocks; two viscoelastic transitions are clearly revealed. Only the lower (1,4B) transition was clearly resolved in DSC measurements on these copolymers although hints of a second transition, as evidenced by changes in the baseline slope of the DSC trace, appeared in the region in which the 1,2 polybutadiene transition was expected.

Large deformation mechanical properties have also been measured for the various polymers listed in Table 1, both in the as-cast state and after cross-linking with various doses of low energy electrons. In Figure 6, the stress-strain behavior of the series of 1,4B/1,2B block copolymers is shown in comparison with the behavior of a 1,4 polybutadiene homopolymer and a 1,2 polybutadiene homopolymer; all samples were crosslinked with a 4 Mrad dose of electrons.

DISCUSSION. In a previous investigation (2-4) it was found that cis 1,4 polyisoprene/1,4 polybutadiene diblocks were homogeneous materials even though the corresponding homopolymers formed heterogeneous blends in essentially all proportions. The results presented in Figures 5 strongly suggest that diblocks of 1,4 polybutadiene/1,2 polybutadiene are heterogeneous materials. Further evidence for the presence of a two phase structure in the 1,4B/1,2B diblocks was obtained from transmission electron micrographs shown in Figure 7. Cross-linked samples of the 1,4B/1,2B diblocks were stained using the ebonite method

(7) which had been successful in supplying adequate phase contrast in other diene/diene binary systems (2-4); clear evidence of microphase separation, characteristic of block copolymers, is seen in the micrograph. The two-phase nature of the 1,4B/1,2B diblocks may help to explain the interesting stress-strain behavior shown in Figure 6. In particular, we are exploring various reasons for the observation that the envelope of stress-strain curves described by the four 1,4B/1,2B diblocks is much wider than that described by the two homopolymers.

The 1,2B/S and B1/S 'parent-child' pairs also offer interesting comparisons. The essentially pure (>99%) 1,2 nature of the polybutadiene prior to hydrogenation offers a major advantage in minimizing chain degradation during the hydrogenation process. Furthermore the anionic synthesis of 1,2 polybutadiene leads to an atactic polymer so that the polybutene-1 obtained as the hydrogenation product is therefore also atactic. All of our dynamic mechanical data and DSC experiments indicate that the polybutene-1 is an amorphous saturated rubber entirely devoid of crystallinity. What is most striking about the diblock copolymers containing these polybutene-1 moieties is the fact that they appear to behave rather more like triblock copolymers. For example, in Figure 3, there is a pronounced rubbery plateau covering the entire region of temperature between the polybutene-1 glass transition to the softening of the polystyrene near 100° C. This is in marked contrast to other diblocks of this type which begin to soften and flow at temperatures only slightly above the glass transition of the rubbery phase; a diblock of 1,4B/S (51000/9000) studied earlier, for example, lost all stress bearing capacity at temperatures near -50° C (about 40° C above T_g of the 1,4 B block) in dynamic mechanical tests similar to those conducted in this work (1). The unusual stress-bearing capability of the B1/S

diblocks is also evident in the large deformation stress-strain behavior of heptane and cyclohexane cast samples. Present work is aimed at elucidating a molecular or morphological explanation for this observation.

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TABLE 1

<u>Sample</u>	<u>Code^(a)</u>	<u>Block Molecular Weights in Thousands^(b)</u>	<u>Block Microstructure^(c)</u>
1-a	1,2B/S	84/16	>99% 1,2/atactic
1-b	1,2B/S	108/12	>99% 1,2/atactic

2-a	1,4B/1,2B	65/41	medium cis/>99% 1,2
2-b	1,4B/1,2B	100/36	medium cis/>99% 1,2
2-c	1,4B/1,2B	159/29	medium cis/>99% 1,2
2-d	1,4B/1,2B	195/30	medium cis/>99% 1,2

3-a	B1/S	84/16	atactic/atactic
3-b	B1/S	108/12	atactic/atactic

a. In these codes B indicates polybutadiene, B1 polybutene-1, S polystyrene.

b. An overall average of values determined from various methods including GPC, osmometry, infrared and NMR. The major source of uncertainty in these figures is in regard to the molecular weight of the second block which could not readily be obtained separately for analysis.

c. Diene microstructures from infrared analysis; medium cis indicates around 11% 1,2, 53% trans 1,4 and 33% cis 1,4.

FIGURES

Figures 1 and 2. Temperature dependence of the storage modulus (MPa) and loss tangent at 3.5 Hz for diblocks 1-a and 3-a (See Table 1). Film specimens prepared from 5% solution in cyclohexane.

Figures 3 and 4. Effect of casting solvent on the dynamic mechanical properties of sample 3-a.

Figure 5. Temperature dependence of the storage modulus and loss tangent at 3.5 Hz for diblock 2-a crosslinked with a 2 Mrad dose of electrons.

Figure 6. Stress-strain curves (23°C , $1.67 \times 10^{-3}\text{m/sec}$ elongation rate) obtained on diblocks 2-a to 2-d (Table 1) and on homopolymers of 1,4 polybutadiene ($\overline{M}_n = 100000$) and 1,2 polybutadiene ($\overline{M}_n = 90000$). All samples were crosslinked with a 4 Mrad dose of electrons.

Figure 7. Transmission electron micrographs sample 2-a stained by the ebonite method (7). Magnifications are indicated on the figures.

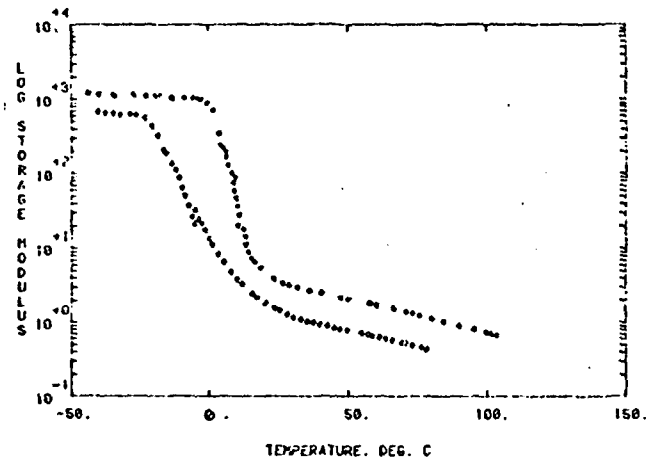


Figure 1

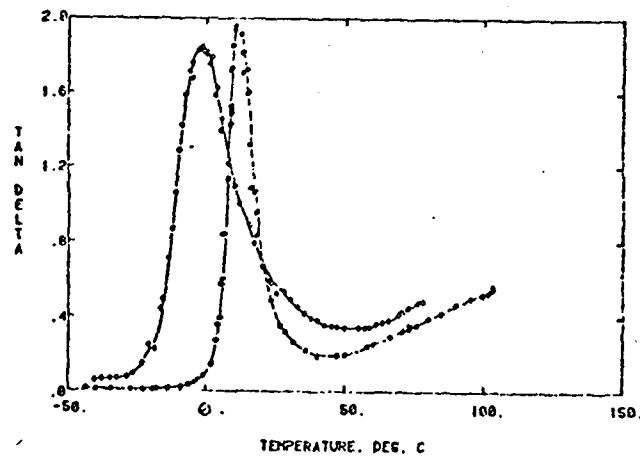


Figure 2

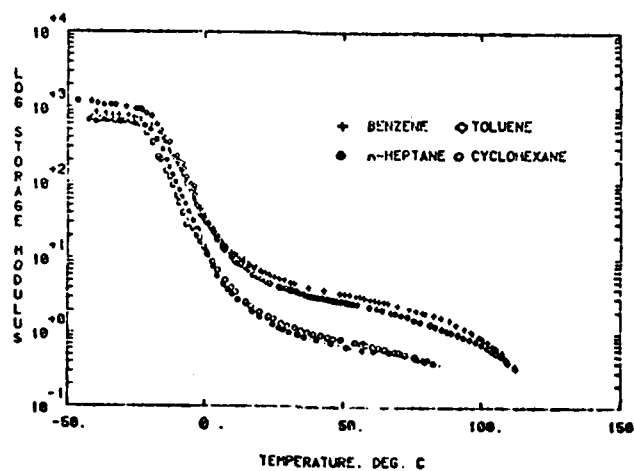


Figure 3

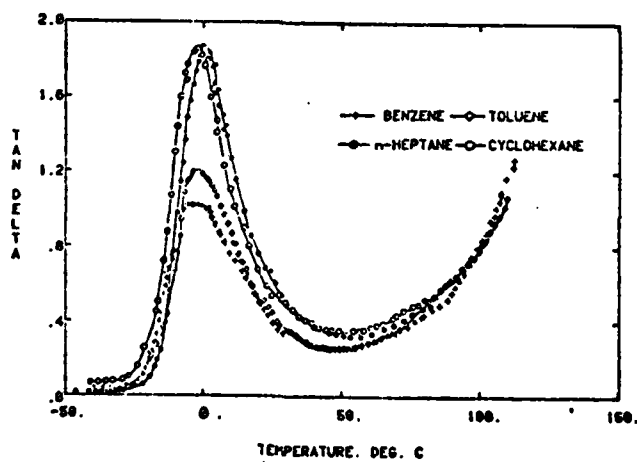


Figure 4

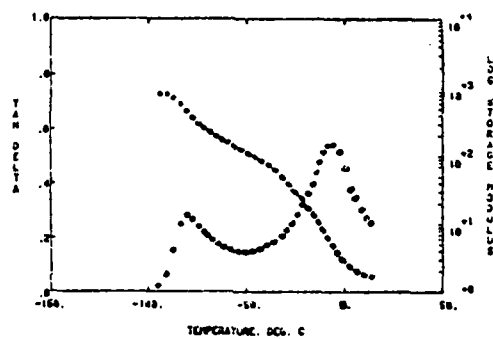


Figure 5

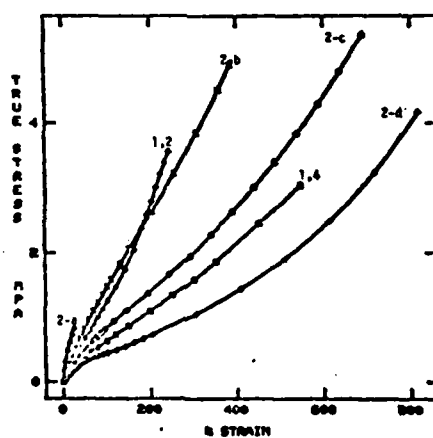
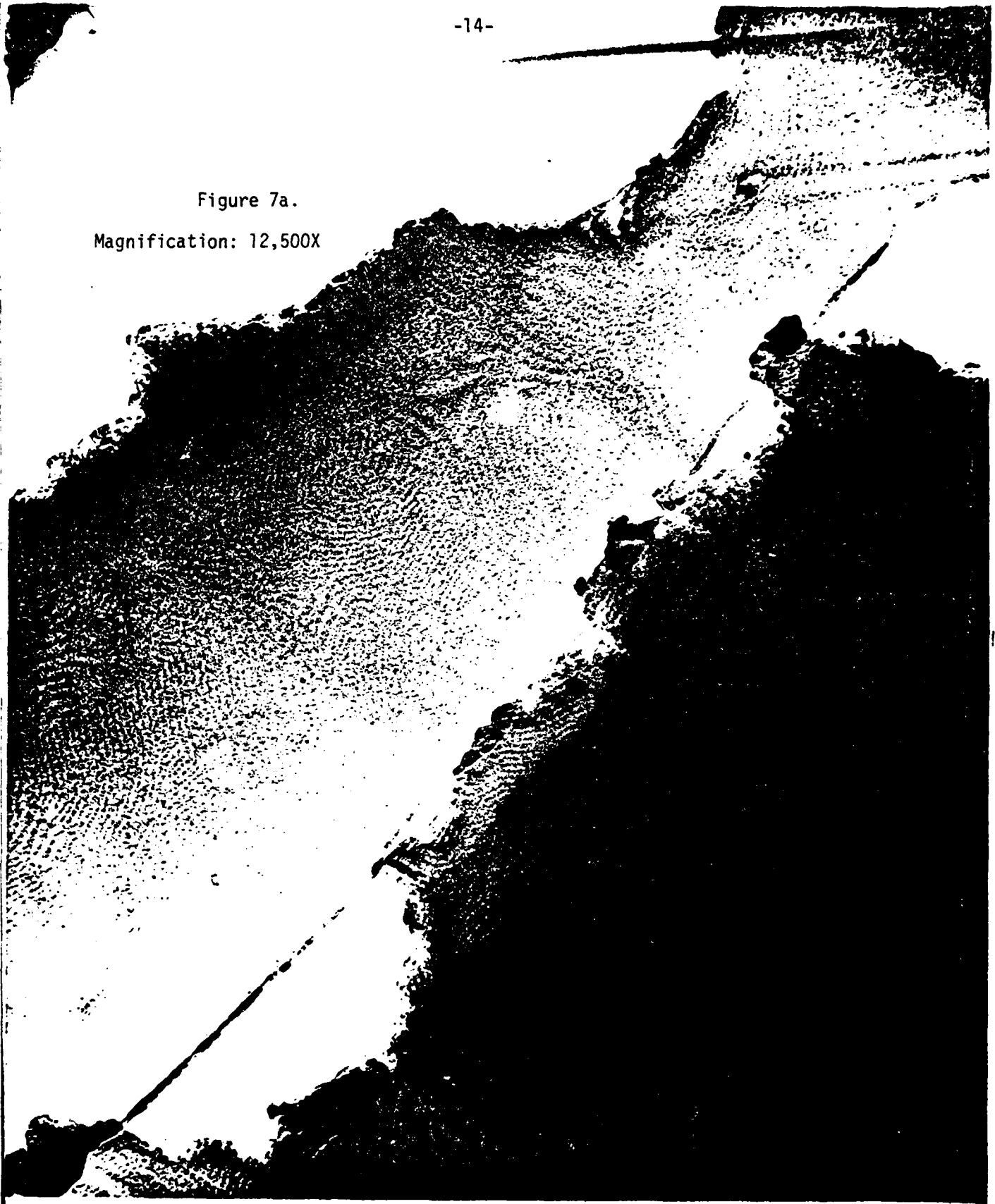


Figure 6

Figure 7a.

Magnification: 12,500X



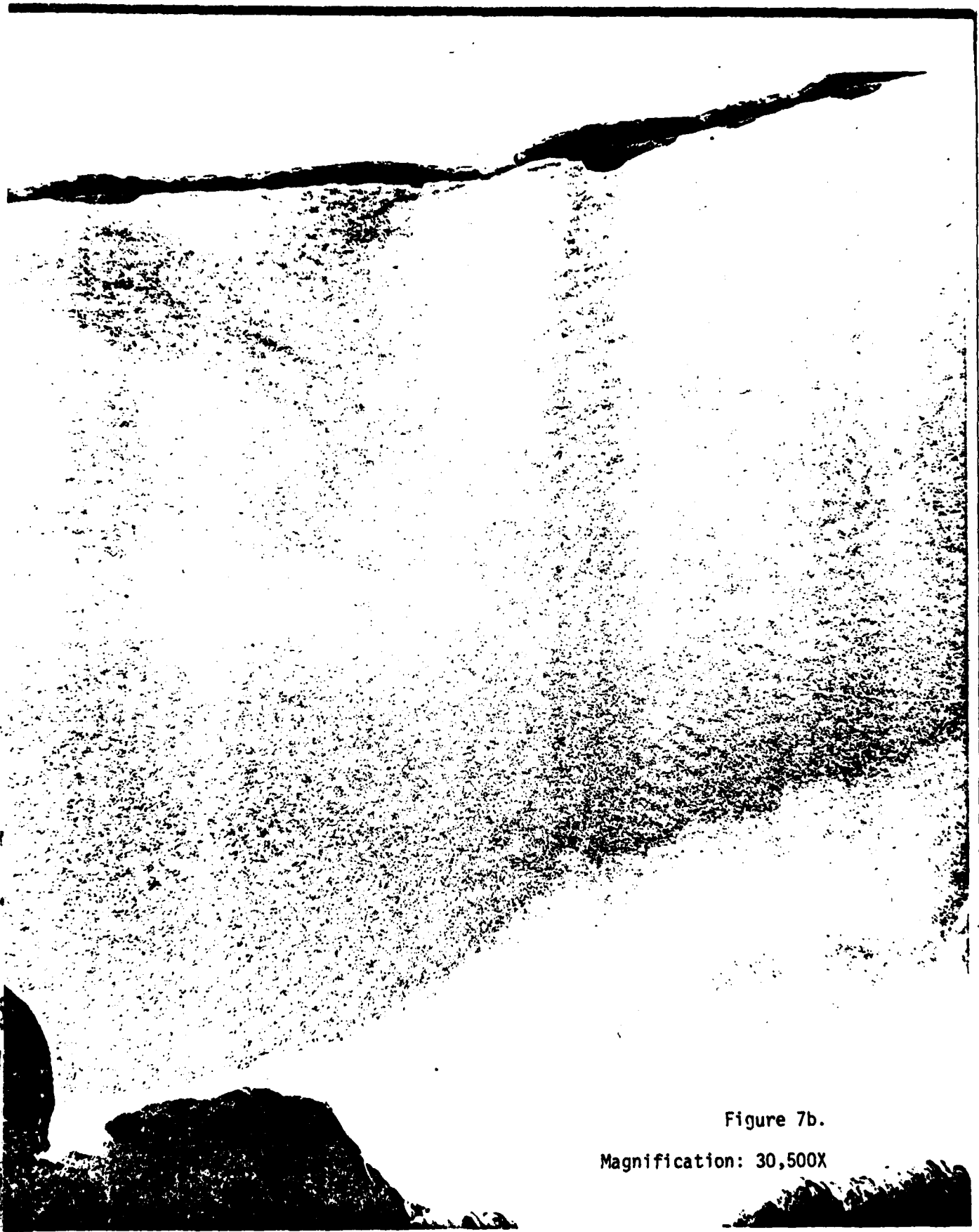


Figure 7b.

Magnification: 30,500X