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Effect of Pressure on Diffusion in Polymer Solutions*

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Diffusion measurements have been made using two molecular weights of polysulfide polymer at 25°C and 59°C in toluene solution. One isotherm for the low molecular weight was obtained in chloroform solution. The results indicate that there are two mechanisms of motion in solution. At low pressure the dominant mode involves the expulsion of a solvent molecule from the coiled polymer. At high pressure the motion is segmental.

PREVIOUS work in this laboratory[1–5] on diffusion in liquids under pressure has indicated that high pressure is a very useful tool in the study of the structure of the liquid state and the nature of molecular motion. In particular the concept of the activation volume has proven useful for the elucidation of the mechanism of diffusion.

This paper presents some measurements of diffusion of high polymer in solution. The polymer used was polysulfide of the forms $[S-(CH_2)_6-S]_n$. Two molecular weight fractions were made (5500 and 42 000). Four isotherms were obtained using the low molecular weight polymer [1 percent (by weight) solution in toluene at 25° and 50 percent C, 5 percent solution in toluene at 59°C, and 2 percent solution in chloroform at 25 percent C]. The upper limit of the pressure range, 5000-6000 atmospheres, was determined by the point at which the viscosity of the solution interferred with the operation of the cell.

EXPERIMENTAL PROCEDURE

A. Synthesis of the Polymer

The synthesis of the polymer was made in three steps. The methods used were those described in the literature[6–9] modified slightly to insure maximum yield on sulfur. The radioactive sulfur was obtained as BaS from Oak Ridge National Laboratory. H_2S was generated and bubbled through an aqueous cyanamide solution to form thiourea. This was reacted with hexamethylene dibromide to form the dimercaptan. This was polymerized in an emulsion with KOH and lauric acid. The length of time determined the average molecular weight. Larger batches of nonradioactive polymer were prepared by exactly the same procedure. These were carefully fractionated and molecular weights were determined by light scattering.† The results from light scattering were correlated against intrinsic viscosity measurements on the same fractions. The molecular weights of the fractions used in diffusion measurements were obtained from these correlations.

B. Measurement of Diffusion

The apparatus and method of operation was substantially identical with that used in previous diffusion measurements.[1–5] Because of the slow diffusion it was necessary to shorten the cell length substantially. The upper part consisted of a slice of medium porosity fritted glass 0.088 cm thick. The lower layer consisted of two pieces of Whitman No. 1 filter paper. The effective path length was established by runs with 0.1-N

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