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The Apparent Compressibility of High Polymers in Solutions

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I. Introduction

The rigidity of high polymer solutions has been measured by several authors in order to study the nature of the high polymer in solution, but only few workers⁽¹⁾⁽²⁾⁽³⁾ have examined it by measuring the velocity at which the longitudinal wave propagates in a solution of high polymer. Since the compressibility of the solvent and that of the solute high polymer are of the same order, it is difficult to ascertain, from the measured compressibility, the property of the solute high polymer itself.

We analysed our data and calculated the compressibility of solute high polymer by the equation

$$K = k_p C_p + k_s (1 - C_p), \quad (1)$$

where

K : Compressibility of solution,

k_p : „ solute,

k_s : „ solvent,

C_p : Volume concentration of polymer.

The compressibility K calculated by this formula is not intrinsic compressibility, but depends both on the nature of the polymer itself and on the interaction of solvent with the polymer; so it may be called "apparent compressibility". This apparent compressibility strongly depends upon the temperature, the concentration of solution and the kind of solvent.

II. Apparatus and method of experiment

The sound velocity V is measured by puls method of frequency 1MC/sec, by comparing with the velocity in water as standard. The compressibility is then calculated by the relation

$$K = \frac{1}{\rho V^2} \quad (2)$$

A quartz crystal which should serve as both the wave source and the receiver, is attached to the wall of the vessel. The temperature of the solution, which is kept constant by thermostat, is measured by a thermocouple inserted in it. Commercial polystyrene is used as sample. The volume concentration C in Eq. (1) is calculated by the formula

$$C_p = 1 - \frac{\rho}{\rho_s} (1 - \bar{C}_p),$$

where

ρ : Density of solution,

ρ_s : „ solvent,

$\bar{C}_p$: Weight concentration of polymer.

III. Results and discussion

The relation between the concentration and the compressibility of benzene solution of polystyrene at several temperatures is shown in Fig. I. As is seen in this figure the compressibility decreases with concentration. The same relation for the apparent compressibility, which was calculated from Eq. (1), is shown in Fig. II. It decreases suddenly at the concentration of about 10–20%, and afterwards attains constant value; furthermore it seems that the higher the temperature, the more remarkable becomes this behavior.

If chlorobenzene is used as solvent instead of benzene, the relation between the concentration and the apparent compressibility becomes different, as is shown in Fig. III. Here one sees that at low temperatures the compressibility keeps constant value even if the concentration changes, while at high temperature it depends slightly upon the concentration.

Since benzene is a good solvent for polystyrene, it is natural to consider that in benzene solution the polystyrene molecules will fully expand, as far as the concentration is comparatively small. When the concentration becomes larger, however, the molecules will begin to interact each other. Chlorobenzene is, on the contrary, a poor solvent for polystyrene. Therefore, the solute molecules not only coil up by themselves but entangle with each other even in dilute solutions. When the temperature is raised

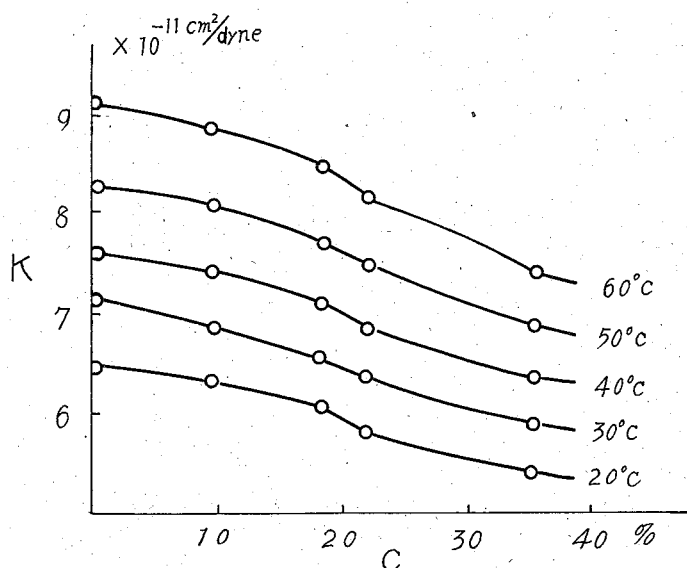


Fig. I. The relation between the concentration, C , and the compressibility, K , of the Benzene solution of polystyrene.

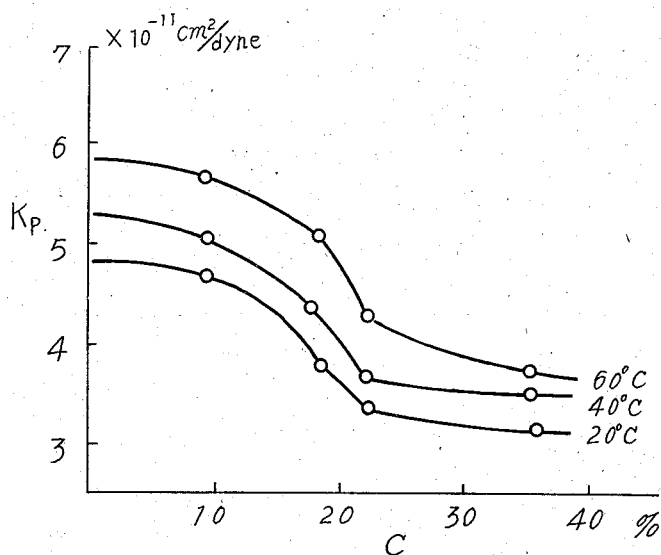


Fig. II. The relation between the concentration, C , and the apparent compressibility, K_p , of the polystyrene in the Benzene.

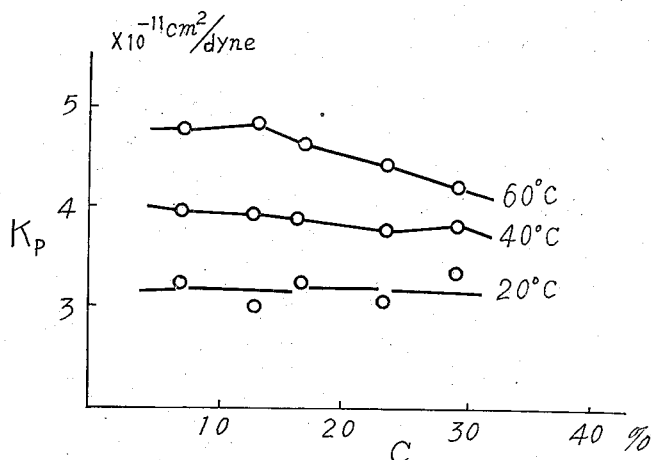


Fig. III. The relation between the concentration, C , and the apparent compressibility, K_p of the polystyrene in the Chlorobenzene.

and the thermal motion becomes active, the solute molecules will become to expand considerably, the degree of expansion being larger for smaller concentration.

Thus the above experimental results can be explained reasonably if we suppose that the apparent compressibility decreases when either intra- or inter- molecular interaction becomes large. We could conversely conclude that our experiment suggests strongly such a dependence of the apparent compressibility on the molecular interactions.

IV. Conclusions

An attempt was made to ascertain the property of a dissolved polymer by the measurement of the velocity of longitudinal wave. As was suggested above the behavior of solute polymer molecules can be inferred by its apparent compressibility. It seems for us very useful to study the nature of dissolved polymer by measuring the velocity of the longitudinal wave and by analysing it by means of Eqs. (1) and (2).

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