THE CONSTRUCTION OF A MICROCALORIMETER AND MEASUREMENT OF HEATS OF SOLUTION OF STRETCHED GLASSY POLYSTYRENE

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SYNOPSIS

A conduction-type twin microcalorimeter was constructed in order to measure very small amounts of heat, and the microcalorimeter was applied to measure the heat of solution (ΔH) of stretched polystyrene (glassy state). The area of the thermogram was proportional to the supplied electric energy into the microcalorimeter in a range of 0 to 0.3 calory. As the calibration, ΔH for KCl was measured at 30°C in molar fraction, 1 : 5,500. The standard deviation was ± 0.4%. The ΔH of stretched glassy polystyrene was measured in toluene at 30°C. The specific volume of the samples was measured by floating method of each stretched sample and unstretched sample. The measured value of the specific volume did not depend on the stretched temperature and the draw ratio. However, the value of measured ΔH of stretched (at 110°C) samples decreased with the increase of the draw ratio: it decreased about 50 cal/mole at the draw ratio 3 as compared with that of unstretched sample.

INTRODUCTION

Flory and other researchers have developed the theory of rubber elasticity and revealed that the elasticity depended mainly on entropy of the randomly coiled molecules in the network and that the internal energy has only small effect on the elasticity.

A number of experiments of rubber elasticity have been carried out, and the amount of the internal energy was estimated based on those theories. The obtained values are scattered by researchers because of their indirect measurements. In this study, the internal energy contribution on stretching was estimated.
directly from the measurements of heat of solution for stretched glassy polymer by using the following equation:

\[
\Delta H^\Delta = \Delta E^\Delta + P \Delta V \\
= \Delta E^\Delta \left[ \frac{\partial E}{\partial V} \Delta V + \frac{1}{2} \left( \frac{\partial^2 E}{\partial V^2} \Delta V \right) + \frac{1}{6} \left( \frac{\partial^3 E}{\partial V^3} \Delta V \right) + \cdots + P \Delta V \right] \\
= \Delta E^\Delta \left[ P + P_i \right] \Delta V \\
\]

where,

\( \Delta H^\Delta \): the enthalpy difference between the stretched sample and the unstretched sample.

\( \Delta E^\Delta \): the difference of internal energy at constant volume.

\( P_i \): the internal pressure.

\( \Delta V \): the change of the specific volume.

\( P \): the external pressure.

According to equation (1) if the enthalpy difference of glass-transition is the same for the stretched sample with various draw ratios, the internal energy contribution caused by stretching, \( \Delta E^\Delta \), can be estimated from measurements of heats of solution, internal pressure, and specific volume.

Experimental

A microcalorimeter was constructed to measure very small quantities of heat as shown in Figure 1. It was a conduction type twin calorimeter based on the principle first developed by Tian and Calvet. On the construction of this microcalorimeter, the following modifications had been made in this laboratory. (1): In order to suppress the heat flow in the microcalorimeter as small as possible, the inside of microcalorimeter had not fans and shafts.