Thermal Expansion Measurements and Transition Temperatures. II. An Automatic Recording System

A differential expansion apparatus useful for studying first- and second-order transitions in polymeric materials has been described previously.[1] This apparatus utilizes a tipping mirror arrangement as part of an optical lever to magnify the expansion of the polymer sample with a change in temperature. Readings of light spot position on a scale and of sample temperature had to be taken almost continuously to obtain useful curves. These readings were very tedious and time-consuming, limiting the usefulness of the technique. Hence, an automatic recording system was developed, greatly expanding the potentialities of this kind of analysis.

The apparatus currently in use is illustrated in Figure 1. An $X-Y$ recorder (Electronic function plotter, Minneapolis Honeywell, Brown Instrument Division) replaces the galvanometer scale shown in Figure 4 of reference 1. The carriage pen carries a pair of photoresistors (Powermaster Photocell No. CDS-10, Hupp Electronics Co.), chosen for their large surface area. These are part of a resistive bridge circuit powered by a dry cell. The output voltage of the bridge is applied to the input terminals on the pen carriage after its potentiometer power is opened. This rewiring replaces the normal error signal with the output of the bridge. The polarity is adjusted so that the pen movement reduces the error signal, thus keeping the photocell bridge at the center of the light spot. The pen motor thus moves the carriage system, both centering the photocell unit and tracing the X component. The thermocouple imbedded in the
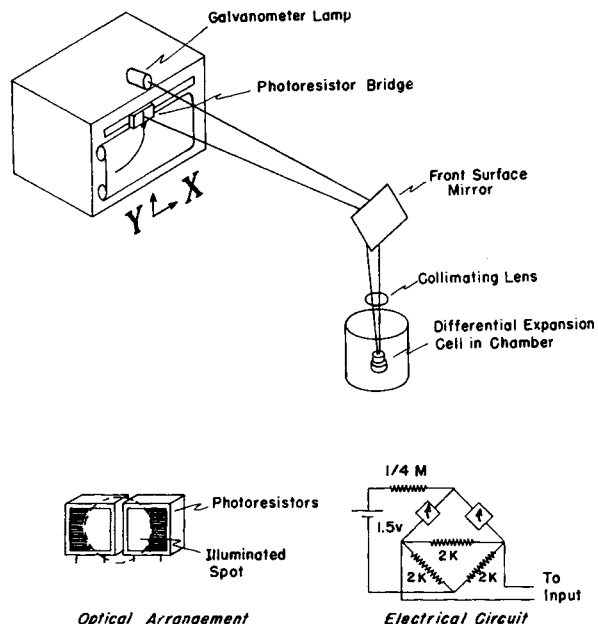

Fig. 1. Schematic arrangement of expansion apparatus with details of photoresistor arrangement.
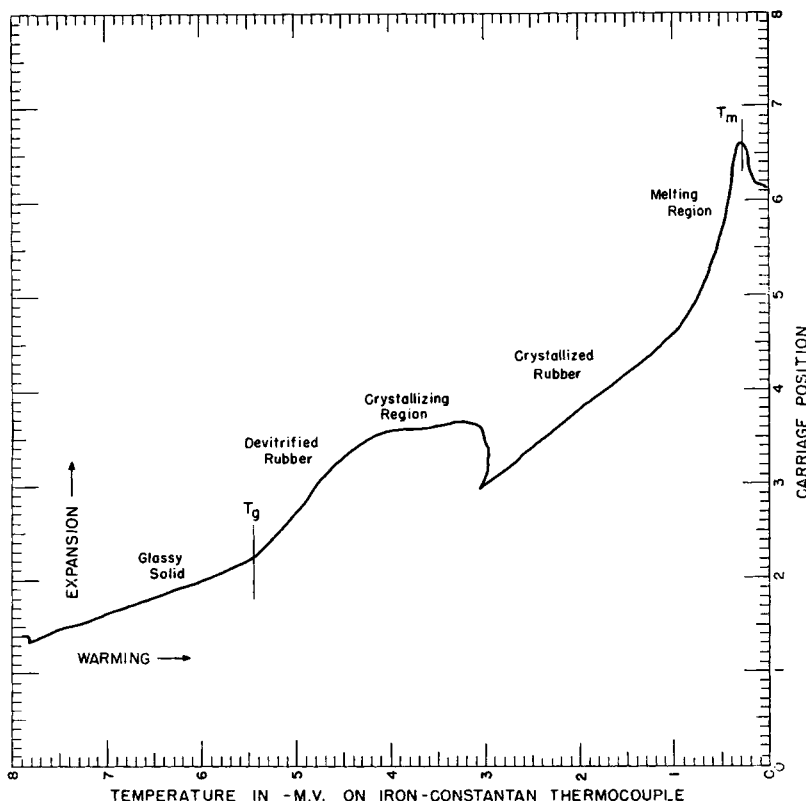

Fig. 2. Typical differential thermal expansion curve: polybutadiene rubber

sample is connected to the chart movement amplifier controlling the Y component in a standard manner.

The amplifier circuit in the pen servo circuit is sufficiently sensitive that it can easily be overloaded into mechanical oscillation. The potential applied to the photocell bridge is reduced to about 10 mv. by a drop resistor to eliminate this overdrive and subsequent hunting. Stray light must be reduced with appropriate baffles and shields; however, complete darkness is not required.

A typical expansion curve obtained from this revised apparatus is shown in Figure 2. This curve is for a sample of uncured polybutadiene, about 98% in the cis-1,4 configuration. The sample in the expansion cell was precooled with liquid air, beginning the run. Warmup from about −8 mv. to −5.4 mv. (−110°C.) is linear and typical of a glassy organic solid. The change in slope defines T_g. Warmup to about −4.5 mv. is characteristic of a devitrified rubber. At about −4 mv. (−85°C.) crystallization begins, with liberation of heat, which further accelerates the process to exhaustion. The warm sample cools slightly, then expands linearly to about −1 mv. (−20°C.), wherein melting begins. The melting point, T_m, is evident at −0.2 mv. (−4°C.), above which linear expansion again can be noted. Frozen stresses account for the apparent shrinkage just above the melting point.

While the work reported thus far in this note and in reference 1 has covered only the temperature range below room temperature, the range above room temperature can be studied easily by replacing the Dewar system with a small oven, heated at a controlled rate. Studies typical of this latter kind are illustrated by glassy changes in polyvinyl chloride at about +85°C. and by crystalline melting points in polyethylenes about 130°C. Most polymers studied at higher temperatures are too low in molecular weight to show simple rubbery expansion above either T_g or T_m. Instead, at the higher temperatures, they generally creep or flow rapidly, apparently indicating contraction. Cooling curves from very high temperatures can be obtained if the mirror tripod is properly adjusted or compensated for the expected creep.

References

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Gravimetric Dilution Viscometry

Frequently it is desired to estimate molecular weights of very small samples of polymer, e.g., a few milligrams. If viscometry is to be used, dilution viscometers requiring only about 1 ml. of polymer solution are desirable. At least two such viscometers have been reported. One was described by Hart,[1] and the other, which we have used in this laboratory, is commercially available.[2]

Such viscometers require the delivery of accurately known portions of solution and solvent. Volumetric methods require careful calibration of volumetric flasks and of pipets for both solutions and solvents, since drainage errors and reproducibility present serious difficulties. Even so, the precision of calibration is not as good as might be desired, particularly with volumetric flasks.

These problems can be overcome simply by using a purely gravimetric procedure. The initial polymer concentration is determined gravimetrically on a weight per cent basis. The polymer solution and successive solvent portions are introduced to the viscometer by means of a syringe which is weighed on a semiautomatic, single-pan, analytical balance before and after addition of liquid to the viscometer. We have used B-D Luer-Lok Multifit syringes (registered trademarks of Becton, Dickinson, and Company) with 17-gage stainless steel needles cut off square with the tips ground to a bevel. If stainless steel is to be avoided, the syringes can be modified by sealing on glass capillary tips as described by Thoburn.[3]

In addition to eliminating the need for calibration of volumetric glassware, the use of syringes confers several other advantages. Fewer sizes are needed to give the same precision—we have used only two sizes, although it is possible to use only one. Cleaning is easier; a large Soxhlet extractor is very satisfactory for this purpose. Control of amount delivered is easier when using volatile solvents. Less total time is required for equivalent accuracy and precision.

Calculation of results is no more tedious than with volumetric methods, but it must be modified slightly.

When kinetic-energy, end-effect, and shear corrections are unnecessary, and the solution densities differ insignificantly from that of the pure solvent, the procedure is particularly simple. Then we may use the usual definitions

$$\eta_{rel} = t/t_0$$

where t and t_0 are the fall times for solution and solvent, respectively, and

$$\eta_{sp} = \eta_{rel} - 1$$

We can denote weight per cent concentration as c', and without converting to volume concentrations, plot η_{sp}/c' vs. c' and $(\ln \eta_{rel})/c'$ vs. c' directly. The intercept at $c' = 0$ we denote as $[\eta']$, where $[\eta'] = d_0[\eta]$ if d_0 is density of pure solvent. Further, the Huggins constants are easily evaluated, since in the equations

$$\eta_{sp}/c' = [\eta'] + k[\eta']^2 c'$$

and

$$(\ln \eta_{rel})/c' = [\eta'] + k'[\eta']^2 c'$$

the values of k and k' are identical to those found from the usual relationships involving $[\eta]$ and c rather than $[\eta']$ and c'.

If molecular weights are to be estimated by this technique for a number of samples of the same polymer in the same solvent, it is simpler to use the Mark-Houwink equation modified as $[\eta'] = K'(\bar{M}_v)^a$, where $K' = d_0 K$, rather than convert $[\eta']$ to $[\eta]$ each time.

When the densities of the polymer solutions differ significantly from d_0, they may be estimated by measuring the density of the original solution by use for example, of a