

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. ($-110^{\circ}\text{C}.$) 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. ($-85^{\circ}\text{C}.$) 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. ($-20^{\circ}\text{C}.$), wherein melting begins. The melting point, T_m , is evident at -0.2 mv. ($-4^{\circ}\text{C}.$), 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 $+85^{\circ}\text{C}.$ and by crystalline melting points in polyethylenes about $130^{\circ}\text{C}.$ 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

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

and

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

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 $K' = d_0K$, 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

semimicro Sprengel pycnometer, a linear relationship between density and concentration over the range used being assumed. The values of η_{rel} obtained from the relationship $\eta_{rel} = dt/dt_0$ should be used with the volumetric concentrations c rather than with c' if the Huggins constants are to be evaluated. If only $[\eta]$ is sought, the density corrections for η_{rel} may be safely ignored and the data used as above.

When kinetic-energy, end-effect, and/or shear corrections are necessary, each experimental point must be corrected much as in volumetric dilution viscometry.

Although these techniques are ideally suited for semimicro quantities, they may be used equally well with larger volumes.

References

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Second-Order Dilatometric Transition Temperatures of Ethylene-Propylene Copolymers

Second-order transition temperatures were determined dilatometrically for ethylene-propylene copolymers. The composition of the copolymers, as determined by infrared^{1,2} and mass spectrometric methods,³ ranged from about 100 to 50 wt.-% of propylene; such a range is probably the most interesting for practical uses. Measurements were made only on amorphous polymers previously fractionated by extraction with solvents. We employed capillary dilatometers (containing liquid *n*-propanol) which were immersed in Dewar flasks containing petroleum ether and solid CO₂ and

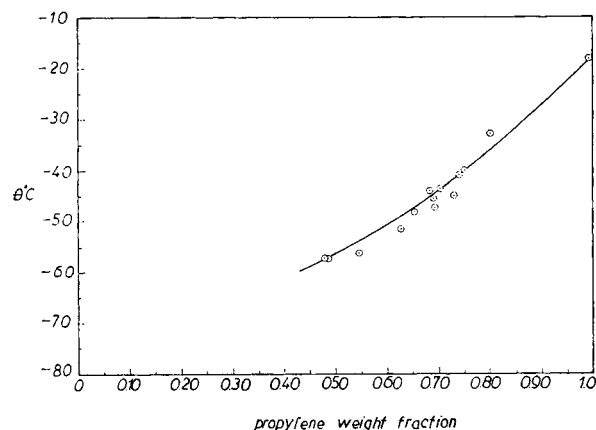


Fig. 1. Plot of second-order transition temperature against copolymer composition for ethylene-propylene copolymer.

TABLE I
Second-Order Transitions of Ethylene-Propylene Copolymers

Sample	Propylene content, weight fraction	No. of measurements	Mean transition temperature, °C.	Range, °C.
1	1.000	4	-18.4 ^a	1.3
2	0.805	3	-33.1	1.1
3	0.753	3	-40.3	1.3
4	0.742	6	-41.1	3.6
5	0.732	3	-45.2	0.3
6	0.706	3	-44.2	0.6
7	0.694	7	-47.6	1.1
8	0.693	3	-45.8	0.5
9	0.685	5	-44.2	5.1
10	0.655	3	-48.5	1.2
11	0.627	3	-51.8	0.4
12	0.565	3	-55.0	1.4
13	0.486	3	-57.5	0.4
14	0.481	3	-57.5	1.6

^a Value similar to data of Reding⁴ and Dannis.⁵

liquid air for lower temperatures in order to extend the measurements to about -120°C. The temperatures were recorded with a Pt thermocouple. The mean cooling rate was 5°C./10 min.; identical results were obtained also with lower rates.

Figure 1 and Table I show the dilatometric second-order transition temperatures as a function of the copolymer composition.

From the experimental data of Table I, if one applies the Gordon and Taylor theory,⁶ developed by Wood⁷ for amorphous copolymers, eq. (1):

$$\theta = [\theta_1 + (K\theta_2 - \theta_1)c_2]/[1 - (1 - K)c_2] \quad (1)$$

where θ denotes the transition temperature of the copolymers, θ_1 is the transition temperature for homopolymer 1 (polyethylene), θ_2 is the transition temperature for homopolymer 2 (polypropylene), c_2 is the weight fraction of homopolymer 2 in the copolymer, and K is a constant, becomes:

$$\theta = (-75.1 + 66.1c_2)/(1 - 0.51c_2) \quad (2)$$

The curve of Figure 1 was drawn according to this equation. The constant K represents, according to Gordon and Taylor, nearly the ratio of the differences of the specific volume-temperature coefficients above and below the glass transitions of the homopolymer:

$$K = \frac{\Delta\beta_2}{\Delta\beta_1} = \frac{(\beta_{2(\text{rubber})} - \beta_{2(\text{glass})})}{(\beta_{1(\text{rubber})} - \beta_{1(\text{glass})})} \quad (3)$$

For the amorphous polypropylene we have experimentally determined the value of $\Delta\beta_2$ (see Table II).

We may assume for the completely amorphous and linear polyethylene that $\beta_{1(\text{rubber})} = 9 \times 10^{-4} \text{ cm.}^3/\text{g.}^\circ\text{C.}$ (value reported for linear polyethylene in the liquid state⁸⁻¹⁰). Assuming, following the suggestion of Gordon and Taylor, that $\beta_{1(\text{glass})} = 2 \times 10^{-4}$, we can calculate $\Delta\beta_1 = 7 \times 10^{-4}$. Therefore the ratio $\Delta\beta_2/\Delta\beta_1$ has a value of 0.57. Following the theory of Gordon and Taylor, the value of such a ratio