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 $\eta_{rel} = dt/d_0t_0$ 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.

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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 CO_2 and
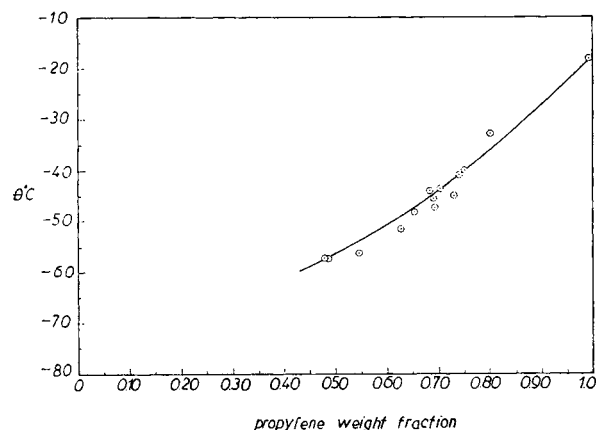
TABLE I
Second-Order Transitions of Ethylene–Propylene Copolymers

Sample	Propylene content, weight fraction	No. of measure-ments	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 Reding[4] 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 Wood[7] 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:

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

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 $\beta_{1(rubber)} = 9 \times 10^{-4}$ cm.^{3}/g./°C. (value reported for linear polyethylene in the liquid state[8-10]). Assuming, following the suggestion of Gordon and Taylor, that $\beta_{1(glass)} = 2 \times 10^{-4}$, 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

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

TABLE II

	$\Delta\beta$	$\Delta\beta_2/\Delta\beta_1$	K
Polyethylene	7×10^{-4} ⎫	0.57	0.49
Polypropylene	4×10^{-4} ⎬		

should be equal to the value of K (Table II); in this case there is only a fair agreement.

If transition temperatures are plotted against molar copolymer compositions, one can obtain a linear relationship, in agreement with the results of Natta and Crespi[11] obtained by minimum rebound temperatures measurements.

Because of the good reproducibility (Table I) of the dilatometric second-order transition temperature determinations, the propylene content of such a copolymer could be evaluated in this way.

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Low Temperature Bath

Several low temperature baths are described in the literature. Many designs call for elaborate and expensive refrigeration equipment. We have found none that meet the need for a bath requiring little capital outlay and capable of operating for several months at low cost. To meet these requirements, a bath has been designed and constructed from materials which should be available to any laboratory. The bath was used in crystallization studies described in this journal,[1] involving exposure of samples in dilatometers for periods of several weeks at various temperatures between 0 and $-45°C$. Cooling was accomplished by using metal conductors to transfer heat from the controlled bath to a cold source.
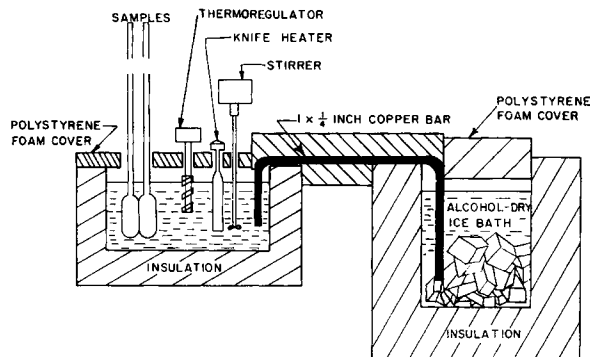

Fig. 1. Low temperature bath.

Referring to Figure 1, it can be seen that the controlled bath is cooled by conduction along $1 \times \frac{1}{4}$-in. copper bars to an alcohol–Dry Ice mixture. This is similar in principle to the operation of a device called a cold bar described by Mooney and Wolstenholme.[2] The copper bars were bent to the shape indicated and their ends inserted in the controlled bath and cold source. Any well insulated container may be used for the controlled bath. In the work mentioned above, a 1-gal. Dewar flask was employed. Foamed polystyrene was found to be a convenient material for lids and for insulating the copper bars and other portions of the apparatus. The Dry Ice bath consisted of a 10-gal. bucket inside a 30-gal. can, the air space being filled with vermiculite insulation. A stirrer in the controlled bath was the only moving part. The number of copper bars needed to maintain a given temperature was determined experimentally. It was found, for example, that one copper bar conducted enough heat to maintain an equilibrium temperature of about $0 \pm 1°C$. Two bars resulted in an equilibrium temperature of about $-20°C$., three bars $-35°C$., and four bars $-45°C$. Equilibrium temperature was reached in about one day without any additional cooling.

More precise control was obtained by using a greater heat leak than necessary and opposing this with a controlled heater. This also permitted operation at intermediate temperatures. For example, to operate the bath at any temperature above $-45°C$., four copper bars were employed and temperature maintained with a 125-w. knife heater. The heater was controlled by a standard thermoregulator arrangement, which provided $\pm 0.1°C$. temperature control.

The bath seems ideally suited to long-term exposure of materials that impose only a small heat load on the apparatus. Thermal losses from the bath were found to be quite low, and Dry Ice consumption was minimal. For example, a 10-gal. Dry Ice–alcohol cold source was sufficient to maintain bath temperature over a Friday-to-Monday weekend.

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