Thermal Conductivity of Polymer Melts

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Synopsis

A concentric cylinder conductivity cell with guard heaters was constructed and used to determine the thermal conductivity of polymer melts. Thermal conductivity was found to be a linear function of temperature for the melts studied, and the thermal conductivity decreased as the complexity of the polymer chain increased. The polymers studied were a linear polyethylene, branched polyethylene, polypropylene, polystyrene, nylon 6, and nylon 6,10. The measurements are precise to within ±6%.

INTRODUCTION

Studies of thermal conduction through polymers at low temperatures have led to development of theoretical models for conduction through solid polymers. In at least one case,[1] such a model developed for solids has been applied with some success to a linear polymer melt. However, reported measurements of thermal conduction through polymer melts are meager and, with a few exceptions,[1-3] of dubious accuracy. Therefore, general models for conduction through polymer melts cannot be applied with confidence until more experimental data are available for testing the models proposed. The purpose of this work was to construct an apparatus suitable for determining the thermal conductivity of polymer melts and of concentrated melt solutions accurately at high temperatures, and to use it to determine the thermal conductivity of melts of some common polymers.

EXPERIMENTAL

Selection of Experimental Method

The experimental methods used to determine thermal conductivity were reviewed, and the concentric-cylinder steady-state method was selected as the most appropriate for polymer melts, since this method affords ease of operation with minimum error. Ziebland[4] and others have presented arguments regarding the relative merits of various methods. Steady-state methods are usually more accurate than nonsteady-state methods for determining thermal conductivity, the concentric cylinder geometry is more adapt-

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able to liquids than the parallel plate geometry, and concentric cylinders can be aligned more easily than concentric spheres. Finally, polymer melts can be loaded easily in the absence of air and can be maintained under pressure easily in a concentric cylinder device. These features minimize polymer degradation and ensure good thermal contact of the melt with the cylinder walls.

Calculation of Thermal Conductivity

Steady-state heat transfer by conduction through a liquid confined between concentric cylinders follows Fourier's law, which states:

$$q_c = \lambda 2\pi r L \, dt/dr \tag{1}$$

where q_c = rate of heat transfer, by conduction, cal/sec; λ = thermal conductivity, cal/sec-°C-cm; r = radius, cm; L = cylinder length, cm; and t = temperature, °C, if there is heat transfer only in the radial direction, i.e., if there is no axial heat transfer. Axial heat transfer can be eliminated by using guard heaters at the ends of the measuring cylinder and adjusting the heat input to the guard heaters so that the axial thermal gradient is zero. Integrating from the inner wall, R_i, to the outer wall, R_0, and solving for λ, we obtain

$$\lambda = \frac{q_c}{2L} \frac{\ln(R_0/R_i)}{(t_0 - t_i)} \tag{2}$$

where R_i, R_0 = inner and outer radii of melt, respectively, cm; and t_i, t_0 = wall temperatures of the inner and outer cylinders, respectively, °C. Thus, the thermal conductivity of a liquid can be determined by measuring the heat transferred by conduction for a temperature drop across the liquid, $t_0 - t_i$. Unfortunately, not all of the measured heat input is transferred by conduction; some is transferred by radiation. Thus, the heat transfer by conduction is

$$q_c = q - q_R \tag{3}$$

where q = total heat transferred, cal/sec; and q_R = heat transferred by radiation, cal/sec.

The heat transferred by radiation was calculated, assuming that the polymer was transparent, by

$$q_R = 2\pi R_0 L \sigma (T_0^4 - T_i^4) \left[\frac{1}{\left(\dfrac{1}{\epsilon_i}\right) + \left(\dfrac{1}{\epsilon_0}\right) - 1} \right] \tag{4}$$

where σ = Stefan-Boltzmann constant, 1.356×10^{-12} cal/cm²-sec-°K; ϵ = emmissivity of heated stainless steel, 0.30; and T_i, T_0 = wall temperatures of inner and outer cylinders, respectively, °K.

The heat transfer by radiation calculated from eq. (4) was then subtracted from the measured heat input to determine the heat transferred by

conduction.   The effect of uncertainties in calculating the heat transfer by radiation is discussed later.

Description of Apparatus

A schematic diagram of the melt apparatus and the guarded, concentric-cylinder conductivity cell constructed and used in this work is shown in Figure 1.   A flanged length of steel pipe (A), wrapped with resistance wire for electrical heating and equipped with a piston (B), was used for melting the polymer and for forcing it into the conductivity cell (C).   Gases were removed from the melt cylinder and the conductivity cell by a vacuum pump (D).

The cell consisted of two 316SS concentric cylinders, separated by a 0.075-in. gap that held the melt.   The inner cylinder (E), 2.950-in. (O.D.) × 15.0 in. (length), was divided into three sections, one 6.0-in. guard heater section, one 3.0-in. guard heater section, and one 6.0-in. measuring section, with a 0.50-in.-diameter cartridge heater (F) centered axially in each section to serve as heat sources.   The inner cylinder was made from a single block of metal that was cut, faced, and pinned, and then the outer surface was machined to a ±0.0005-in. tolerance.   Holes for thermocouples and heaters were drilled, heaters and thermocouples were installed, and the cylinders were cemented together with refractory cement and reassembled.   The

A - MELT CYLINDER
B - PISTON
C - CONDUCTIVITY CELL
D - TO VACUUM SYSTEM
E - INNER CYLINDER
F - HEATERS
G - OUTER CYLINDER
H - SEAL RING
I - BASE PLATE
J - RESISTANCE HEATER

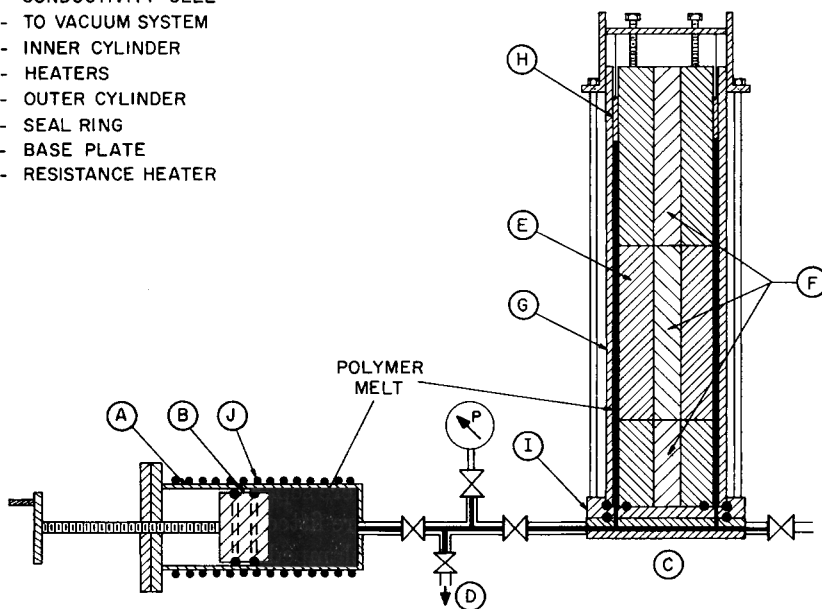Fig. 1. Schematic diagram of experimental apparatus.

| GUIDE | |
thermo-couple no.	radial distance
3	0.350 in.
4	0.500
5	0.700
6	0.900
7	1.100
8	1.300
1	1.600
2	1.670
10	0.750
11	0.750
12	1.250
13	1.250
15	0.750
16	0.750
17	1.250
18	1.250

Fig. 2. Location of thermocouples.

outer cylinder (G) was made from a 15-in. length of 316SS pipe machined to an O.D. of 1.550 in., with a wall thickness of 0.100 in. To ensure concentric alignment, the tops of the cylinders were separated by a spacer ring (H) that also served as a seal, the bottoms were fitted into machined grooves in the base plate (I), and the cylinders were clamped into place.

Power to each of the three heaters was adjusted by variacs, and the line voltage for each heater was stabilized. Power to the center (measuring) cylinder was measured to within ±0.25% with a wattmeter. Tempera-

tures within the cylinders were measured with calibrated thermocouples placed as shown in Figure 2.   The thermal gradients in the outer and inner cylinders were measured with thermocouples 1 and 2 and 3 through 8. Axial thermal gradients were measured with thermocouples 9 through 17. All thermocouple leads were perpendicular to the radial gradient to minimize heat flow at the junction.

Procedure

Polymer pellets or powder was placed in the melt cylinder, the apparatus was assembled and evacuated, and the polymer was melted.   The cell was preheated, the melt was compressed, and the melt was forced into the conductivity cell.   Suitable steady-state conditions were established by adjusting guard heater power to eliminate axial gradients.   Radial temperature gradients and power input to the inner cylinder were then measured.   The temperature drop across the polymer gap was taken as the difference in wall temperatures, determined by extrapolation of the thermal gradients.   The temperature corresponding to the experimentally determined thermal conductivity was taken as the arithmetic average of the wall temperatures.

The power input to the measuring cylinder was changed, steady state was reestablished, and the measurement was repeated.   Four to six measurements were made with each melt.

Polymers

Four vinyl polymers—low-density polyethylene, high-density polyethylene, polypropylene, and polystyrene—and two nylons—nylon 6 and nylon 6,10—were studied.   Descriptions of the polymers used are given in Table I.

TABLE I
Polymer Description

Type	Manufacturer	Designation	$\bar{M}_n$ $\times 10^{-3}$	$\bar{M}_w$ $\times 10^{-3}$
Linear polyethylene	Phillips Petroleum	Marlex 6002, Lot 0152046	12.3	174.2
Branched polyethylene	du Pont	Alathon, Lot 500613-10	26.0	300.0
Polypropylene	Enjay Chemical	Escon 103G, Lot 566	47.0	453.0
Polystyrene	Dow	Styron, Lot No. PT 61009	23.0	375.0
Nylon 6	Dow-Badische	Polycaproloctam B-300, Lot 2971	13.0	28.0
Nylon 6,10	du Pont	Zytel	18.0	37.0

RESULTS AND DISCUSSION

Thermal conductivities for each of the polymers investigated, along with the results of Lohe[2] and Hennig,[3] are shown in Figures 3 and 4.   Thermal conductivity of these melts is either independent of temperature or in-
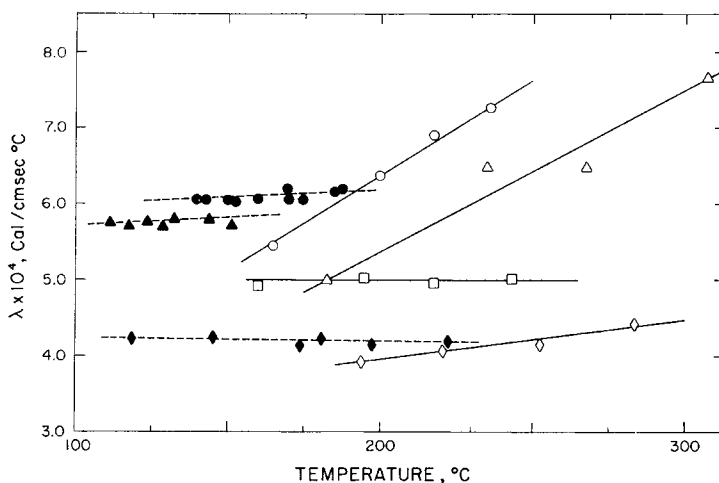
Fig. 3. Thermal conductivity of vinyl polymer melts: (O) linear polyethylene; (△) branched polyethylene; (□) polypropylene; (◇) polystyrene. Solid symbols are data of Lohe and co-workers.[2,3]
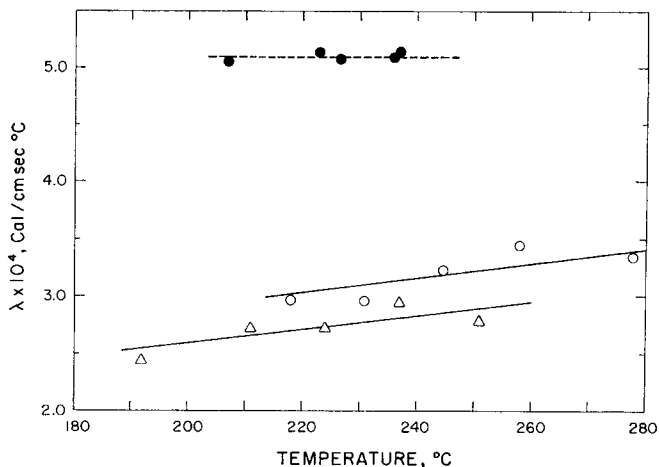

Fig. 4. Thermal conductivity of nylon melts: (O) nylon 6; (△) nylon 6,10. Solid symbols are data of Lohe.[2]

creases linearly with increasing temperature. Constants for the best straight line relationship,

$$\lambda = a + bt$$

where λ = thermal conductivity, cal/cm (°C) sec; and t = melt temperature, °C, are given in Table II for each polymer.

As can be seen in Figures 3 and 4, there is not complete agreement with Lohe's and Hennig's results. Our results indicate a more rapid increase in conductivity with increasing temperature than indicated by the results of

TABLE II
Constants for Equation (5)

Polymer	a, (cal/cm-sec-°C) $\times 10^4$	b, (cal/cm-sec-(°C)^2) $\times 10^6$
Linear polyethylene	1.37	2.50
Branched polyethylene	1.09	2.13
Polypropylene	5.00	0.0
Polystyrene	2.94	0.510
Nylon 6	1.69	0.621
Nylon 6,10	1.42	0.593

Lohe[2] and Hennig.[3] In fact, Lohe reports a slight decrease in thermal conductivity of polystyrene with increasing temperature. However, inspection of the data in Figure 3 shows little basic disagreement for polystyrene. Differences for the polyethylenes are more pronounced. Our results indicate a much greater effect of temperature on thermal conductivity, although the ranges of our data for polyethylenes do bracket Lohe's results. These differences may be due to differences in polymer branching, molecular weight, molecular weight distribution, and to differences in the temperature ranges of the data. However, as will be discussed later, our results for polyethylene are consistent with our results for other polymers. Finally, it can be seen from Figure 4 that the thermal conductivity of nylon 6 determined in this study differs from the value obtained by Lohe by nearly a factor of 2. There is no apparent reason for this gross difference.

The thermal conductivity of a polymer should decrease as the density decreases. However, it has been proposed[1,5] that increased segmental mobility of the polymer chains with increased temperature causes an increase in thermal conductivity. Apparently, this effect on thermal conductivity is greater than the effect of decreased density for most polymers.

Thermal conductivity decreases as the polymer chain becomes more complex, since conductivity decreases in the following order: linear polyethylene > branched polyethylene > polypropylene > polystyrene > nylon 6 $\simeq$ nylon 6,10. Hattori[6] found similar behavior for amorphous polymers at low temperatures. However, this must be considered only as a qualitative ranking, since the molecular weights are not the same, and it has been shown that conductivity varies with molecular weight.[1]

Hattori[7] found that solid linear polyethylene exhibited higher conductivity than solid branched polyethylene, and the melts exhibit similar behavior. Decrease in chain-to-chain density, as suggested by Hattori, is probably the effect causing this difference, rather than segmental mobility differences. Segmental mobility appears to be nearly the same, since the slopes of conductivity versus temperature curves for these polymers are almost equal. This reasoning is further supported by the observation that the polymers with lowest segmental mobility, polystyrene, and polypropylene, exhibit only a very slight increase in conductivity with increased temperature.

The cell was designed to minimize errors. Of particular concern was the melt gap thickness, since this parameter determines the relative importance of errors in alignment and in determining wall temperatures, and the relative importance of transfer by radiation and convection. For this cell, the maximum total error in thermal conductivity arising from misalignment, errors in determining wall temperatures, and error in measuring total heat input was estimated to be 6%. Convection was absent, but radiant heat transfer was significant. The polymer was assumed to be transparent, and radiant heat transfer was calculated to be 1% to 13% by eq. (4), depending upon temperature and temperature drop across the melt. The observed heat transfer rates were corrected by deducting the transfer by radiation to obtain the transfer by conduction. While the polymer melts may not be totally transparent, they are more transparent than opaque, and the error introduced by assuming transparency should be small. Also, this error should be systematic, increasing with temperature for a given polymer, which does not affect the conclusions reached above. Therefore, assuming steady-state was established, measurements should be precise to within 6% and accurate to within at least 12%, even if the assumption of total melt transparency is considerably in error.

CONCLUSIONS

Thermal conductivity of polymer melts increases linearly with temperature, or is independent of temperature, and decreases with increased complexity of the polymer structure. While the thermal conductivity varies consistently with polymer structure and the differences are significant, there is apparently less variation with composition and structure for polymers than for other classes of materials, such as metals or simple liquids.

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