

Thermal Conductivity of Polymer Melts

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Synopsis

Thermal conductivities were measured for melts of a series of polypropylene and a series of polyethylene samples that had been characterized by GPC. Results indicate that thermal conductivity depends upon the molecular weight distribution and degree of branching of the polymers. The results of this work can probably be used to predict the thermal conductivity of a commercially available polypropylene or polyethylene to within 25%.

INTRODUCTION

Fairly extensive studies have been made of the thermal conductivity of solid polymers; however, this information is of little use for the analysis of polymer processes that involve polymer melts. Reported determinations of thermal conduction through polymer melts are meager and, with a few exceptions,¹⁻⁵ of dubious accuracy. As pointed out by Fuller,⁵ there are often significant differences in thermal conductivity for the same polymer, even as determined in these more accurate studies, that cannot be explained except by assuming that they result from differences in polymer molecular weight or configuration characteristics. Unfortunately, the possible importance of these effects generally has not been recognized, and the polymers studies were not characterized sufficiently.

Two studies of the effect of molecular weight on thermal conductivity have been reported. Hanson and Ho⁴ developed a theory for the effect of molecular weight on thermal conductivity of polymer melts, and the theory was reportedly tested for linear polyethylene. The theory predicts that thermal conductivity will increase proportionally with increase in molecular weight to the two-thirds power and that the effect of molecular weight on thermal conductivity will be negligible at high molecular weights.

The data⁶ for a polyethylene system indicated that thermal conductivity varied proportionally with molecular weight to the one-half power and that the effect of molecular weight was negligible at molecular weights above 90,000. However, the validity of Hanson and Ho's results is doubtful. Molecular weight was varied by blending a paraffin wax with a molecular weight of about 367 and a polyethylene with a molecular weight of about

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132,000, producing molecular weight distributions that were distinctly bimodal, particularly for the low molecular weight mixtures. At high molecular weights, the amount of wax added to the polyethylene to reduce the molecular weight was very small. Whether such a small added quantity of a low molecular weight component would affect the thermal conductivity of the polymer significantly is questionable. In any case, this work might more properly be considered to be a study of the effect of a diluent on the thermal conductivity of a polymer melt.

Lohe³ determined the effect of molecular weight on the thermal conductivity of polyethylene glycol for degrees of polymerization ranging from 9 to 455 and found that thermal conductivity increased with increasing molecular weight. His results showed a linear dependence of reciprocal thermal conductivity on the reciprocal degree of polymerization to the one-third power. Lohe's results, however, are for a low molecular weight material with a rather narrow distribution.

The purpose of the work reported here was to determine the effect of temperature on the thermal conductivity of a series of polyethylenes and of a series of polypropylenes that are commercially available, and then to deduce the effect of molecular weight on the thermal conductivity of these polyolefins from the results.

EXPERIMENTAL

Experimental Method and Procedure. The experimental apparatus used in this work was a concentric cylinder device with guard heaters which was described in detail previously.⁵ The apparatus is constructed so that polymer can be melted and loaded into the conductivity cell in the absence of air and so that the melt can be held under pressure in the cell. These features minimize polymer degradation and ensure good thermal contact of the melt with cylinder walls. The experimental procedure used in this work and the method of determining thermal conductivity, including a correction for radiant heat transfer, have also been described in detail previously.⁵

Polymers. Five polypropylene samples from the same supplier and six polyethylene samples from the same supplier were studied. These were industrial-grade samples of varying molecular weight. The polymers used were characterized by density, melt flow or melt index, and gel permeation chromatography. Values determined for each polymer used, including long-chain branching coefficients by the method of Drott and Mendelson⁷ and moments about the mean as recommended by Miller,⁸ are given in Tables I and II. Polyethylene sample D is the same as sample C except that a few per cent of a low molecular weight plasticizer had been added to increase the melt flow.

By obtaining samples that had been made by the same process by one manufacturer, it was expected that the molecular weight distribution and configuration might remain constant or at least vary in a regular manner. As can be seen, this was only partially true. The second and third moments of the polymer samples vary with M_n as shown in Figures 1 and 2.

TABLE I
Properties of Polypropylene Samples^a

Sample	Melt flow	Density, g/cc	$M_n \times 10^{-4}$	$M_w \times 10^{-4}$	$M_z \times 10^{-4}$	$M_p \times 10^{-4}$	M_w/M_n	$\sigma_2 \times 10^{-10}$	$\sigma_3 \times 10^{-15}$
A	12.0	0.902	3.47	28.5	101	24.4	8.20	0.868	7.67
B	5.5	0.902	4.93	38.6	101	33.7	7.82	1.66	16.65
C	5.5	0.902	5.37	39.9	102	35.1	7.44	1.80	18.58
D	0.5	0.902	6.96	54.0	116	48.4	7.76	3.28	36.3
E	5.5	0.902	7.06	47.5	101	42.7	6.73	2.86	27.5

^a σ_2 = Second moment about the mean for the number distribution; σ_3 = third moment about the mean for the number distribution.

TABLE II
Properties of Polyethylene Samples^a

Sample	Melt index	Density, g/cc	$M_n \times 10^{-4}$	$M_w \times 10^{-4}$	$M_z \times 10^{-4}$	M_w/M_n	$\lambda \times 10^4$	$\sigma_2 \times 10^{-10}$	$\sigma_3 \times 10^{-15}$
A	21.0	1.024	0.943	12.72	95.42	13.48	1.54	0.111	0.111
B	44.0	0.924	1.051	24.76	200.8	23.57	2.69	0.250	5.25
C	27.0	1.024	1.211	28.07	233.9	23.17	2.52	0.325	7.95
D	27.0-33.0	0.923-1.024	—	—	—	—	—	—	—
E	10.0	0.919	1.384	38.30	279.7	27.68	2.32	0.511	14.6
F	1.9	0.922	1.546	17.00	84.62	10.99	1.27	0.239	2.11

^a λ = Long-chain branching coefficient; σ_2 = second moment about the mean for the number distribution; σ_3 = third moment about the mean for the number distribution.

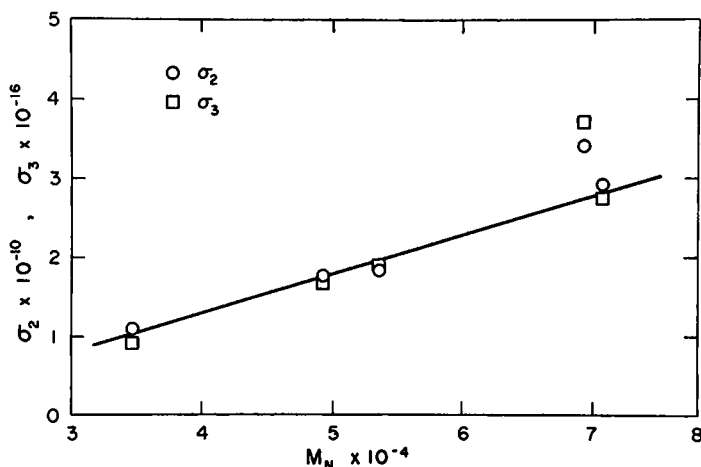


Fig. 1. Effect of number-average molecular weight on the second and third moments of the distribution about the mean for polypropylene samples.

From Figure 1, it can be seen that both dispersion and skewness of the molecular weight distribution of the polypropylenes studied increase with increasing M_n and that the increase is linear except for sample D. All samples exhibit distributions that are quite broad and skewed. Dispersion and skewness also increase with increasing M_n for the polyethylenes, as shown in Figure 2, but long-chain branching affects the distributional parameters. With more branching, the distribution broadens, and increases in dispersion and skewness with increases in M_n are greater. Since

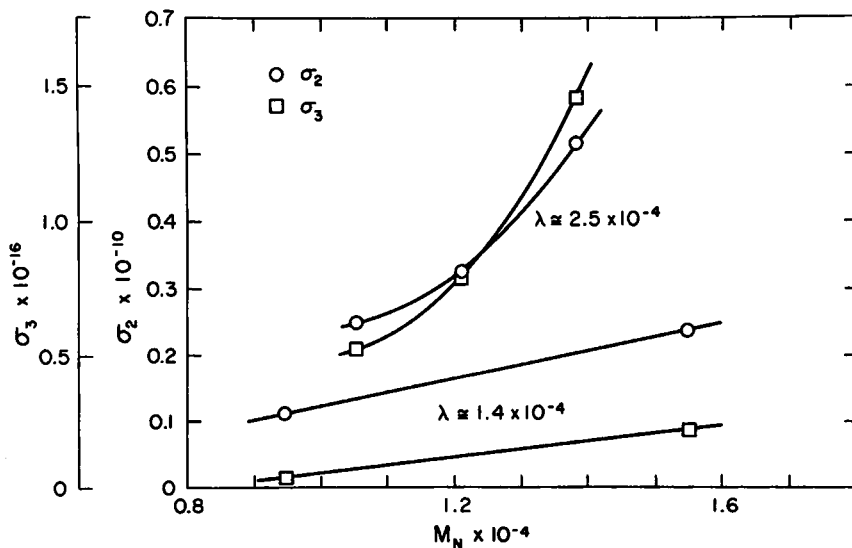


Fig. 2. Effect of number-average molecular weight on the second and third moments of the distribution about the mean for polyethylene samples.

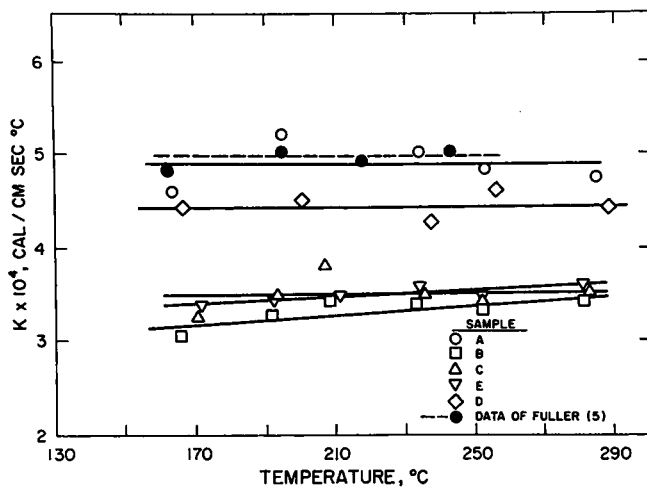


Fig. 3. Effect of temperature on the thermal conductivity of polypropylene.

branching is only approximately constant and the data are limited for either set of polyethylene samples, the curves shown in Figure 2 can be considered to be only approximate. However, it can be seen that two sets of polyethylene samples with distinctly different characteristics have been used in this study.

RESULTS AND DISCUSSION

Thermal conductivities as a function of average melt temperature for each of the polymers investigated are shown in Figures 3, 4, and 5. As can be seen from Figure 3, temperature has almost no effect on thermal

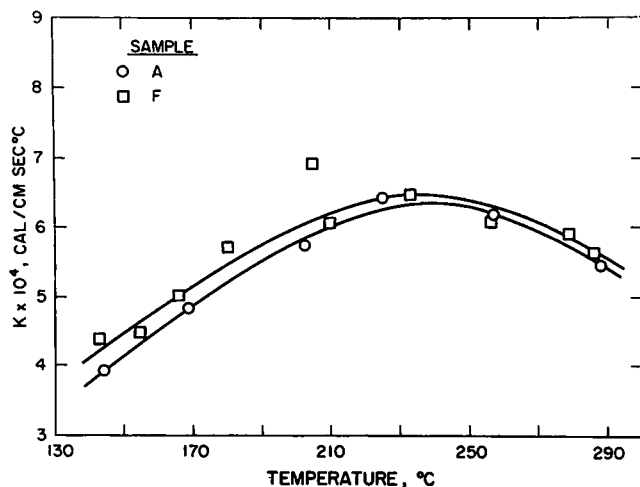


Fig. 4. Effect of temperature on the thermal conductivity of polyethylene ($\lambda = 1.4 \times 10^{-4}$).

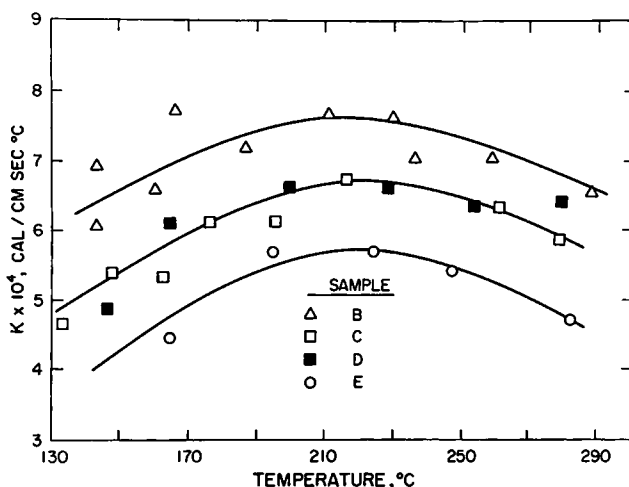


Fig. 5. Effect of temperature on the thermal conductivity of polyethylene ($\lambda = 2.5 \times 10^{-4}$).

conductivity of any of the polypropylene melts; the effect could be considered as statistically significant in only one case. However, molecular weight characteristics appear to have a large effect, because the thermal conductivities of different samples differ by more than 50%, based on the lower value. This difference is much larger than the estimated limit of error of the data, which is about 10% maximum and much more than the experimental error in precision of the data. Therefore, the effect of molecular weight parameters is significant.

The effect of temperature on the thermal conductivity of the polyethylene samples is shown in Figures 4 and 5. In all cases, the thermal conductivity is temperature dependent and exhibits a maximum with respect to temperature. The effect of temperature on the thermal conductivity of the polymer melts is not difficult to explain, but impossible to predict. The thermal conductivity should decrease with decreasing density; however, increased segmental mobility of the polymer chains resulting from increased temperature should cause an increase in thermal conductivity. Since these are competing effects and are generally nonlinear functions of temperature, the dependence of thermal conductivity on temperature could take almost any form. However, one would expect the same type of relationship for samples of the same polymer, and the results do show this. Even though the data for polyethylenes are more scattered than the data for polypropylenes and the maxima for the polyethylene thermal conductivities are rather flat, the maximum does appear to be shifted to a lower temperature with increase in long-chain branching or broadening of the distribution. Results for polyethylene samples A and F, shown in Figure 4, exhibit a maximum at about 240°C. These samples have long-chain branching coefficients of 1.27×10^{-4} and 1.54×10^{-4} , respectively, and are less disperse than the other polyethylene samples. Results for the

other polyethylenes, shown in Figure 5, exhibit a maximum at about 210°C. These samples have branching coefficients above 2.3×10^{-4} , and all are much more skewed than samples A and F.

The molecular weight distribution and long-chain branching of the polymers studied do not appear to affect the general shape of the temperature versus thermal conductivity curve, but do shift the curve. The general effect of temperature of the thermal conductivity of polymers determined by Fuller and Lohe agree with the results of this work on polyethylenes and polypropylenes, and with some additional results on nylons⁹ that are not reported here since the nylon polymers were not completely characterized. However, the values of thermal conductivity determined at any temperature for a given type of polymer vary by as much as 50%, based on the lower value, for samples used in different studies or for different samples used in this study. Obviously, thermal conductivity is not insensitive to molecular weight characteristics at high molecular weight.

The thermal conductivity decreases with increasing M_w for the polypropylenes, except sample D, and for the polyethylenes exhibiting the higher branching coefficients, as shown in Figures 6 and 7. In these two cases, the molecular weight distribution parameters vary in a regular manner with change in M_n . However, the relationship between molecular weight and thermal conductivity for polymers is much more complex than this. Polypropylene sample D, whose distribution is broad compared to the other samples, exhibits a high thermal conductivity. The thermal conductivity of the polypropylene sample studied by Fuller⁴ is higher than would be predicted by the curve shown in Figure 6, but the distribution appears to be broader. Further, the thermal conductivities of polyethyl-

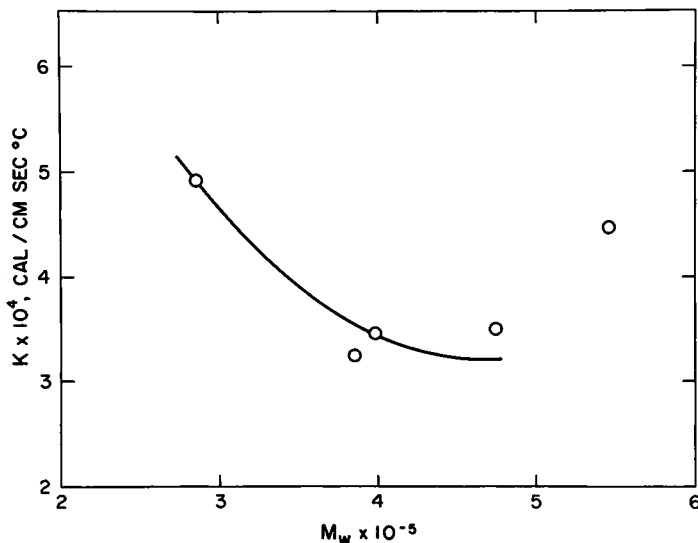


Fig. 6. Variation of thermal conductivity of polypropylene samples with weight-average molecular weight.

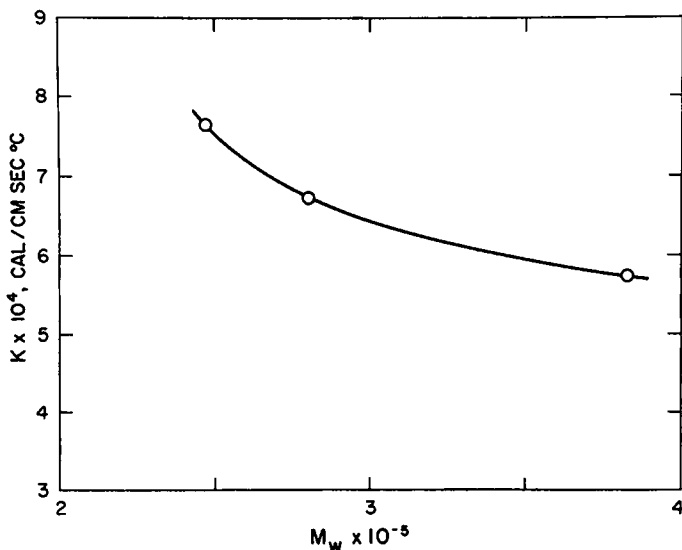


Fig. 7. Variation of thermal conductivity of polyethylene samples ($\lambda = 2.5 \times 10^{-4}$) with weight-average molecular weight.

ene samples A and F are almost identical, even though the difference in M_n is greatest for these two samples. However, change in distribution moments with change in M_n for these samples is small, compared to the changes for the other samples. Finally, the addition of small amounts of a low molecular weight component appears to have little effect. Polyethylene sample D is identical to sample C, except that a small amount of a low molecular weight plasticizer has been added to increase the melt index from 27 to 33. As can be seen in Figure 5, the thermal conductivities of these two samples are identical. This agrees with our interpretation of the results of Ho⁶ as discussed previously.

It is not possible to develop a model of the effect of molecular weight distribution or branching on thermal conductivity from our results. However, small amounts of a low molecular weight additive do not appear to affect the thermal conductivity. Also, the thermal conductivity appears to depend upon the higher moments of the molecular weight distribution and upon branching. This is the primary utility of the results of this work, since it demonstrates that thermal conductivity is probably a complex function of the molecular weight distribution and that sample distributions must be controlled if data useful for developing a model of the dependence of thermal conductivity of molecular weight is to be collected. The results of this work do have a practical value, however. It has been demonstrated that the functional relation between thermal conductivity and temperature is the same for samples of the same polymer and thermal conductivities versus temperature for all samples of the same polymer fall within a band, regardless of the distribution. Therefore, the mean curve for the band can be used as an estimate (\pm about 25%) of the thermal con-

ductivity for commercial samples of the polymer. For many purposes, such an estimate is sufficiently accurate.

CONCLUSIONS

Thermal conductivities of polyolefin melts appear to be complex functions of molecular weight distribution and possible long-chain branching. Thermal conductivity of polypropylene is independent or nearly independent of temperature, while thermal conductivity of polyethylene exhibits a maximum with respect to temperature. The results of this work can be used as an estimate ($\pm 25\%$) of the thermal conductivity of commercial polyethylene or polypropylene.

The authors are grateful to Dr. F. C. Stehling of Esso for assistance in characterizing the samples.

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Received September 15, 1972

Revised October 24, 1972