

TABLE IV  
Intrinsic Viscosities and Interaction Parameters;  
Methacrylate Copolymer and Polyisobutylene in Mineral Oil  
(Quadratic Smoothed Data)

Parameter	100°F.	210°F.
$[\eta]$ Methacrylate copolymer	0.245	0.419
$[\eta]$ -Polyisobutylene	0.360	0.323
$b_{11}$ -Methacrylate copolymer	0.0272	0.0521
$b_{22}$ -Polyisobutylene	0.0648	0.0518
$k'_1$ -Methacrylate copolymer	0.453	0.297
$k'_2$ -Polyisobutylene	0.501	0.495
$2b_{12}$	0.089	0.102
$2(b_{11}b_{22})^{1/2}$	0.084	0.104
$2[(b_{11} + b_{22})/2]$	0.0920	0.1039
rms deviation ( $\eta_{sp,m} - \eta_{sp,calc}$ )	0.0058	0.0062

tight coil, its polar backbone largely covered up by the long-chain fatty alcohol residues. Consequently, the effective interaction behavior of the methacrylate copolymer is that of a hydrocarbon, and the ideal additivity becomes quite reasonable. Even at 210° F., although the methacrylate copolymer coil has expanded considerably, the intrinsic viscosity remains quite small in relation to the molecular weight, so we may surmise that the 50 wt.-% long-chain residues continue to function as a hydrocarbon sheath for the more polar backbone. By contrast, such other nonelectrolyte polymer pairs<sup>6,8</sup> as polystyrene-poly(methyl methacrylate) and natural rubber-SBR present to each other (and to the solvent) a homogeneous averaged surface, so that their polarity differences are made immediately effective.

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### The Thermal Conductivity of Poly(methyl Methacrylate)

The relative scarcity of data on the thermal conductivity of bulk polymers has recently been noted by Kline.<sup>1</sup> As a result of his own work and that of others, principally Cherkasova,<sup>2</sup> he has concluded that the thermal conductivity of amorphous polymers generally increases with temperature, as a result of increasing segmental mobility. We should like to point out that our work on poly(methyl methacrylate) which is not included among the polymers considered by Kline, shows that above the glass transition temperature the conductivity decreases, at least up to temperatures of 160°C.

The data on the thermal conductivity of PMMA in the literature are not in good agreement. Figure 1 shows the results of Hölmüller and Münx<sup>3</sup> on otherwise unspecified "Plexiglas," of Woodside and Wilson<sup>4,5</sup> on (presumably cast) Lucite two inches thick, and data reported by Bernhardt<sup>6</sup> on Lucite 140 molding powder. The molecular weights of these materials may differ widely, although all must have viscosity average molecular weights greater than 100,000; there may be small amounts of other monomers in some of the materials. Notwithstanding these possible differences, the divergence of values seem large, and the erratic nature of the temperature dependence of Hölmüller and Münx's results, which are claimed to be reproducible, is surprising.

We have recently measured the thermal conductivity of cast PMMA sheets (Plexiglas II UVA) using an apparatus of the "guarded hot-plate" type, which can be briefly described as follows: a central heater element is embedded in a well distributed manner in a circular brass disk, 3 in. in diam. and 1/2 in. thick. An annular brass guard ring of identical thickness and 1 1/2 in. wide, containing a second heater element, surrounds the central disk with a gap 1/16 in. wide separating them. Two identical samples of the material to be tested cover both brass pieces, and these in turn are covered by two aluminum "cold plates," honeycombed with interior channels through which a coolant, pumped from a reservoir at constant temperature, circulates rapidly. A measured power input is sent to the central heated plate, and sufficient power input is sent to the guard ring to bring to zero the temperature difference across the small air gap. This temperature difference is measured using four copper-Constantan thermocouple in series. The energy flow from the central plate is thus forced to pass normally through the sample plates to the cold plates. The temperature difference across each sample is measured using four thermocouples in series, and the thermal conductivity can be easily calculated after a steady state is reached. An important feature of the apparatus is that the "sandwich" of plates is held between the platens of a stationer's press, and after bringing the samples to a temperature of 120°C. the press is tightened to insure good contact between the plates and the samples before equilibrating at a new test temperature. The temperature difference across each sample is normally about 7°C.

Our results for seventeen separate pairs of samples of 3/16 in. and 1/4 in. thick material, cut from four separate cast sheets, are shown in Figure 2. The precision of measurement is estimated as about 2%, and nearly all of the data points are within  $\pm 2\%$  of two fairly well-defined straight lines intersecting near the glass transition. The thermal conductivity is almost constant in the glassy

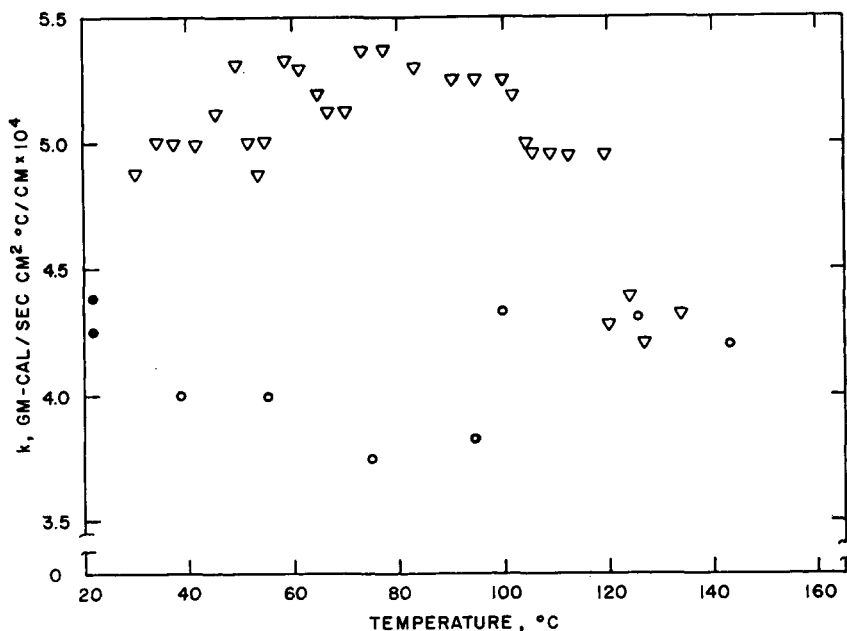


Fig. 1. Thermal conductivity of poly(methyl methacrylate): data of (●) Woodside and Wilson,<sup>4</sup> (○) Bernhardt,<sup>6</sup> (▽) Hölzmüller and Münx.<sup>3</sup>

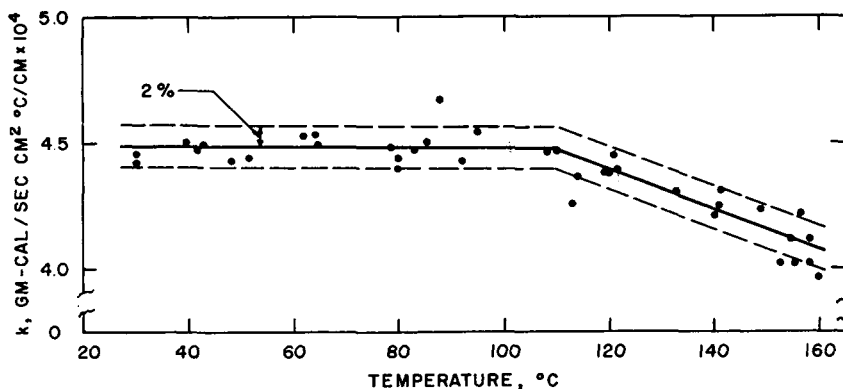


Fig. 2. Thermal conductivity of poly(methyl methacrylate).

region, but decreases continuously in the rubbery region (above ca. 105°C.). This decrease is also apparent in Hölzmüller and Münx's work, and it is of interest to note that these authors also found that the conductivity of polystyrene (PS) decreases slightly above 80°C.

Überreiter and Nens<sup>7</sup> examined the thermal conductivity of PS of degree of polymerization 33 and found a maximum at the brittle point (ca. 70°C.). They suggest that below the brittle point conduction is due to longitudinal waves propagated along the main chains. These propagate more easily as the temperature rises. Above the brittle point transverse vibrations start, and tend to dampen the longitudinal wave motion. However, they believe that at temperatures higher than they investigated, the conductivity would again increase. It may be that examinations of the thermal conductivity of PMMA above 160°C. would reveal an upturn, but it appears that in the temperature region just above the glass transition other effects, perhaps primarily an increase in free volume, offset the increased segmental mobility and decrease the conductivity.

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