The lowest E^* value recorded[12,13] for high polymers is that of polydimethylsiloxane, namely, 3.6 or 4.3 kcal./mole. This is in keeping with its highly flexible chain. Among the factors contributing to this chain flexibility are (a) lack of substituents on every other chain atom, (b) the greater length of silicon-carbon than of carbon-carbon bonds (1.88 versus 1.54 A.), meaning that the methyl groups of polydimethylsiloxane are farther removed from the backbone than are those of polyisobutylene, for instance, and interfere less with rotation about the bonds in the backbone, (c) that silicon-oxygen bonds are longer than carbon-carbon bonds, and that, moreover (d) the attraction between silicon-oxygen dipoles is considerably reduced through shielding by the methyl groups.

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The Interaction of Two Dissimilar Polymers in Solution

The viscosity of moderately dilute solutions of polymer mixtures has been studied by several investigators.[1-8] The theory of viscosity of such mixtures, as formulated by Krigbaum and Wall,[4] concentrates attention upon a single interspecific interaction parameter. For ideal mixtures, this is defined as the geometric average of the intraspecific interaction parameters for single-polymer solutions. For several polymer pairs, Krigbaum and Wall found that this quantity, b_{12} in eq. (1), varied substantially from the geometric average $b_{12} = (b_{11}b_{22})^{1/2}$:

$$\eta_{sp,m} = [\eta_1]c_1 + [\eta_2]c_2 + b_{11}c_1^2 + b_{22}c_2^2 + 2b_{12}c_1c_2 \quad (1)$$

where $\eta_{sp,m}$ = specific viscosity of mixed-polymer solution,

$[\eta_1]$, $[\eta_2]$ = intrinsic viscosities of components 1 and 2 respectively, c_1, c_2 = concentration of components 1 and 2 respectively, in mixed-polymer solution, and b_{11}, b_{22} = intraspecific interaction parameters of components 1 and 2 respectively, in single-polymer solutions.

Cragg and Bigelow,[5] Mikhailov and Zelikman,[6] Voyutsky et al.,[7] and Dogadkin et al.[8] also emphasized the nonadditivity of mixed-polymer solution viscosities, except at concentrations below 1% total solids. The apparent success of additivity laws reported by Bungenberg de Jong[2] and Philippoff[3] could be ascribed to high dilution or great similarity of chemical species.

While studying the solution properties of certain polymeric lubricating-oil additives some years ago, one of us observed that mixed-polymer solution viscosities could be predicted by a relatively simple additivity law, valid up to a total solids content of nearly 4% (i.e., well above the range at which most other polymer pairs begin to show a deviant interspecific interaction parameter). The successful additivity law was originally represented as:

$$\eta_{sp,m} = c_1\eta_{r1}(c_t) + c_2\eta_{r2}(c_t) \quad (2)$$

where $\eta_{ri}(c_t)$ is the reduced viscosity (η_{sp}/c) that component i would have in a single-polymer solution of concentration $c_t = c_1 + c_2$. When the appropriate values for $\eta_{ri}(c_t)$ are inserted into eq. (2), it can be readily converted to eq. (1), with $b_{12} = (b_{11} + b_{22})/2$, that is, the *arithmetic* average of the intraspecific interaction parameters b_{ii}. (For the particular pair of polymers studied, the geometric and arithmetic averages of the b_{ii}'s are sufficiently close together that no choice can be made between them. The geometric average remains preferable on theoretical grounds, of course.) The polymers studied were chemically rather dissimilar; their single-polymer solution-viscosity properties were also markedly dissimilar. Hence, nearly ideal additivity seemed particularly noteworthy.

TABLE I
Solution Viscosities of Methacrylate Copolymer and Polyisobutylene in Mineral Oil

Polymer, wt.-%		Viscosity, cstoke	
Meth-acrylate-copolymer	Polyiso-butylene	100°F.	210°F.
—	—	34.67	5.38
0.75	—	41.6	7.21
1.00	—	44.2	7.91
1.25	—	46.7	8.65
—	1.5	58.8	8.65
—	2.0	68.1	9.92
—	2.5	80.1	11.49
0.75	1.5	68.8	11.09
0.75	2.0	80.1	12.66
0.75	2.5	92.4	14.30
1.00	1.5	72.6	11.93
1.00	2.0	84.3	13.64
1.00	2.5	97.1	15.43
1.25	1.5	74.8	12.71
1.25	2.0	88.2	14.59
1.25	2.5	101.8	16.40

Materials. *1.* A methacrylate copolymer containing lauryl, stearyl, and methyl methacrylates, and a small percentage of 2-methyl-5-vinylpyridine, with a weight-average molecular weight of about 800,000. *2.* Polyisobutylene of molecular weight about 90,000; (solvent) a mineral oil of the following properties:

$$\eta_{100°F.} = 34.7 \text{ cstokes}; \quad \eta_{210°F.} = 5.38 \text{ cstokes}$$

The single-polymer and mixed-polymer solution viscosities are given in Table I. From the single-polymer solution viscosities, $[\eta_1]$, $[\eta_2]$, b_{11}, b_{22}, k_1', and k_2' can be evaluated by several methods; the values given in Table II were obtained by the simplest and best known technique, that of extrapolating the reduced viscosity η_{sp}/c to zero concentration. k_i' is the well-known Huggins[9] constant, defined by

$$k_i' = b_{ii}/[\eta_i]^2 \tag{3}$$

Also given in Table II are similarly obtained quantities in which, for example, the solution of 0.75 wt.-% methacrylate copolymer in mineral oil is regarded as the solvent, and polyisobutylene as solute. These $[\eta_i]$'s may be regarded as analogous to the intrinsic viscosity at concentration c suggested by Yamakawa[10] as a measure of polymer chain extension at finite concentrations of single-polymer solutions. We propose the terms *differential inherent viscosity, partial intrinsic viscosity,* and *partial differential inherent viscosity,* defined respectively as follows:

$$[\eta]_c = d \ln \eta_r/dc \quad \text{at} \quad c_i = c, c_j = 0$$

$$[\eta_i]_{c_j} = d \ln \eta_r/dc_i \quad \text{at} \quad c_i = 0, c_j = c_j$$

$$[\eta_i]_{c_i c_j} = d \ln \eta_r/dc_i \quad \text{at} \quad c_i = c_i, c_j = c_j$$

The quantities given in Table II(a) thus are the partial intrinsic viscosities of the methacrylate copolymer in various polyisobutylene solutions, $[\eta_1]_{c_2}$; Yamakawa's term "intrinsic viscosity at concentration c" is identical with our differential inherent viscosity, $[\eta]_c$.

Inspection of Table II shows that (*a*) mineral oil is a poor solvent for the methacrylate copolymer but a good one for polyisobutylene and (*b*) the use of unsmoothed data leads to rather irregular anomalies in the partial intrinsic viscosities and related slope parameters. Further, as shown in Table III, the observed values of b_{12} at both temperatures

TABLE IIA
Partial Intrinsic Viscosities of Methacrylate Copolymer in Polyisobutylene Solutions in Mineral Oil
(Unsmoothed Data)

Poly-iso-butyl-ene, wt.-%	Partial I.V.[a] of methacrylate copolymer		Huggins k' of methacrylate copolymer		b_{11}	
	100°F.	210°F.	100°F.	210°F.	100°F.	210°F.
0	0.253	0.403	0.34	0.41	0.022	0.066
1.5	0.232	0.379	0.02	−0.01	0.001	−0.001
2.0	0.237	0.354	0.02	0.16	0.001	0.020
2.5	0.188	0.310	0.65	0.33	0.023	0.032

[a] Units of I.V. = hectograms solvated polymer per gram dry polymer.

TABLE IIB
Partial Intrinsic Viscosities of Polyisobutylene in Methacrylate Copolymer Solutions in Mineral Oil
(Unsmoothed Data)

Methacry-late copolymer wt.-%	Partial I.V.[a] of polyiso-butylene		Huggins k' of polyiso-butylene		b_{22}	
	100°F.	210°F.	100°F.	210°F.	100°F.	210°F.
0	0.370	0.328	0.44	0.46	0.060	0.050
0.75	0.360	0.309	0.40	0.37	0.052	0.035
1.00	0.356	0.280	0.39	0.52	0.049	0.041
1.25	0.336	0.258	0.48	0.62	0.054	0.041

[a] Units of I.V. = hectograms solvated polymer per gram dry polymer.

scatter rather erratically, and differ noticeably from the (theoretical) geometric average. Other methods of evaluating $[\eta_1]$, $[\eta_2]$, etc., from single-polymer solution data yielded somewhat different values of b_{12}. Such procedures obviously concentrate all the experimental error into the deviation of b_{12} from the geometric mean. To avoid this, we decided to smooth the data from all solutions, fitting it to eq. (1), b_{12} being treated as a constant independent parameter (the data from the solution containing 1.25% methacrylate copolymer and 1.5% polyisobutylene was eventually rejected, however). The parameters listed in Table IV are those which minimize the root-mean-square deviation of $\eta_{sp,m}$ giving all points equal weight. The values in Table II were obtained by a graphical method which weights points in inverse ratio to concentration; the disagreement between Tables II and IV reflects this fact.

Most noteworthy in Table IV is the near ideality of b_{12} at both temperatures. This is rather surprising in view of the marked chemical dissimilarity of the two polymers. Presumably, it can be ascribed to the tendency of the methacrylate copolymer, in a nonpolar solvent, to form a relatively

TABLE III
Observed Interaction Parameters (b_{12}); Solutions of Methacrylate Copolymer and Polyisobutylene in Mineral Oil

Polymer, wt.-%			$2b_{12}$ Observed	
Meth-acrylate copolymer	Poly-iso-butylene		100°F.	210°F.
0.75	1.5		0.082	0.104
0.75	2.0		0.085	0.105
0.75	2.5		0.087	0.099
1.00	1.5		0.086	0.096
1.00	2.0		0.088	0.105
1.00	2.5		0.090	0.107
1.25	1.5		0.062	0.080
1.25	2.0		0.085	0.100
1.25	2.5		0.091	0.099
		Observed average:	0.084	0.099
		Geometric average:	0.073	0.115
		Arithmetic average:	0.082	0.116

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[5,8] 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.[1] As a result of his own work and that of others, principally Cherkasova,[2] 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 Hölzmüller and Münx[3] on otherwise unspecified "Plexiglas," of Woodside and Wilson[4,5] on (presumably cast) Lucite two inches thick, and data reported by Bernhardt[6] 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 Hölzmüller 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 ±2% of two fairly well-defined straight lines intersecting near the glass transition. The thermal conductivity is almost constant in the glassy