

TABLE I
Thermal Diffusivity of Natural Rubber at 60°C.

	This work	Ref. 1	Ref. 3
Gum			
$k \times 10^3, \text{cm.}^2/\text{sec.}$	0.76	1.06	0.72
$-\frac{dk}{dT} \times 10^6, \text{cm.}^2/\text{sec.} \cdot ^\circ\text{C.}$	0.9	5.9	—
Black			
$k \times 10^3, \text{cm.}^2/\text{sec.}$	1.14	1.49	1.11
$-\frac{dk}{dT} \times 10^6, \text{cm.}^2/\text{sec.} \cdot ^\circ\text{C.}$	1.2	7.1	—

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Dependence of Activation Energy for Viscous Flow of Polyhydrocarbons on Bulk of Substituents

The temperature coefficient of the steady-state viscosity η of molten polymers is of importance in processing. It is usually represented by an apparent energy of activation for viscous flow E^* and defined by the Arrhenius equation

$$\eta = A \exp \{E^*/RT\} \quad (1)$$

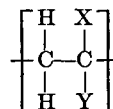
The higher value of E^* for low-density polyethylene, compared with that of high-density polyethylene, has been tentatively explained in terms of the hole theory¹ as being due to short-chain branches.^{2,3} The size of the segment of a polymer chain moving as a single unit in viscous flow may be increased by branches or substituents in two ways. First, their bulk hinders rotation around carbon-carbon bonds in the backbone, thereby rendering the chain stiffer. The influence of chain flexibility on the size of the flow unit is confirmed by the fact that a completely rigid chain can move only as a single unit. Second, branches and substituents increase the volume of the chain for any given length. According to the theory that E^* represents the energy required for hole formation,¹ substituents should increase the size of the flow unit in proportion to their volume and to their frequency of recurrence, thereby augmenting the size of the hole required for flow and consequently increasing E^* .

The purpose of this note is to correlate empirically the value of E^* of different polymers with the bulkiness of the substituents. Bulkiness is expressed as molar volume of the

substituents at the boiling point. This is simpler than detailed geometrical analysis. Concerning atomic models, their use can be misleading. For instance, the polyisobutylene molecule cannot be constructed with Taylor-Hirschfelder models because of the overcrowding of methyl groups and secondary hydrogen atoms, yet the properties of the polymer are indicative of a flexible chain.

Another factor likely to affect the magnitude of E^* is the attraction between chains by secondary valence forces. By limiting the considerations to polyhydrocarbons, the variation in interchain attraction from polymer to polymer is minimized. Below certain levels of molecular weight and temperature, increasing molecular weight and decreasing temperature usually cause increases in E^* . The values selected here were obtained with samples of molecular weight high enough and at temperatures high enough to fall in the range where E^* is practically independent of these factors. Where temperature is concerned, this means raising it to 100°C. or more above the glass transition. The activation energies for viscous flow either refer to zero shear or to fixed shear stress. It has been observed that the two are equal, i.e., that E^* at fixed shear stress is independent of shear stress.^{3,4}

For a series of polyhydrocarbons of the type



the sums of the molar volumes at the boiling point of the two substituents X and Y on the second carbon atom, V_{X+Y} , are listed in Table I together with the apparent energies of activation for viscous flow. Volume equivalents are those of Le Bas,⁵ namely, 3.7 ml. for the hydrogen atom, 14.8 ml. for the carbon atom, and 15.0 ml. subtracted for a benzene ring. The values of V_{X+Y} plotted against E^* give rise to a smooth curve which can be used as a guide for estimating the E^* values of unknown polyhydrocarbons. On a semi-logarithmic scale the relation is linear and can be expressed by

$$\log E^* = 0.784 + 0.0060 V_{X+Y} \quad (2)$$

Extrapolations can be made only if X and Y are smaller than the flow unit.

TABLE I
Energy of Activation for Viscous Flow of Molten Polyhydrocarbons as a Function of Molar Volume of the Substituents

Polymer	V_{X+Y} , ml.	E^* , kcal./mole	Ref.
Polyethylene	7.4	6.5	2
		7.0	3 ^a
Polypropylene	29.6	9.0 ± 1.0	6
		9.6	7
		12.0	4
Polyisobutylene	51.8	15.5	8 ^a
		16.2	9
		22.6	10 ^a
Polystyrene	96.0	22.6	10 ^a
Poly(α -methylstyrene)	118.2	32.0	11

^a Contains additional references listing similar values of E^* .

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 Å.), 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 Jong² and Philippoff³ 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:

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

where $\eta_{r1}(c_1)$ is the reduced viscosity (η_{sp}/c) that component i would have in a single-polymer solution of concentration $c_i = c_1 + c_2$. When the appropriate values for $\eta_{r1}(c_1)$ 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	
Methacrylate-copolymer	Polyisobutylene	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