

TABLE I
SPHERULITE GROWTH RATES IN IRRADIATED POLYETHYLENE

T_1 (°C.)	T_2 (°C.)	Diametral growth rate (mm./min. $\times 10^3$)
Dose = 0 MR.		
191	120.7	1.34
192	122.9	1.24
193	125.1	0.218
196	127.0	0.013
168	122.4	1.06
153	122.5	1.21
Dose = 20 MR.		
195	114.0	1.21
195	116.4	2.59
195	118.6	0.51
Dose = 40 MR.		
195	113.1	3.5
195	113.8	2.7
195	114.6	2.6
195	115.8	0.79
195	117.0	.54
195	117.8	.028
Dose = 100 MR.		
195	100.0	.87
195	100.0	.74
195	101.8	.39
195	104.0	.095

able growth rates are observed is decreased. Melting points of 133, 128, 121 and 113° were determined for specimens receiving respectively doses of 0, 20, 40 and 100 MR. The melting point given here for the unirradiated polymer is lower than the usually accepted one (137.5° determined dilatometrically) presumably because of the rapid heating rate. In spite of the difference the melting point depression per unit of radiation is probably correct.² The dominant effect of ionizing radiation on molten polyethylene is the introduction of intermolecular crosslinks. These crosslinks result in decreased size and increased imperfection of the crystallites which form from the melt on cooling.² The net result is a decrease in the equilibrium value of both the crystal melting point and the degree of crystallinity. The spherulites that develop from such a cross-linked melt are thus forming in a medium of extremely high macroscopic viscosity and are composed of crystals of lowered melting point. If the growth of the spherulite were controlled by diffusion of material to the spherulite-melt boundary, then the increase in viscosity with dose would be expected to inhibit growth markedly. On the other hand, if the spherulite growth were controlled by a nucleation process, then it is to be expected that the growth rate would depend only on the supercooling below the crystal melting point. The data in the table indicate that comparable growth rates occur at equal degrees of supercooling, regardless of the dose. Thus, even though considerable disruption of the crystallites results from the radiation and even though the spherulites are developing in a crosslinked matrix, the predominant effect of that radiation on the spherulite growth rates seems to be due largely to the suppression of

the crystal melting point. As noted above this is consistent with the concept of nucleation control of spherulite growth.

SURFACE TENSION, INTERMOLECULAR DISTANCE AND INTERMOLECULAR ASSOCIATION ENERGY OF PURE NON-POLAR LIQUIDS¹

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An approximate linear relation between molar refraction R and the parachor P has been established empirically,²⁻⁶ which may be expressed as

$$R = k'P + C \quad (1)$$

in which k' and C are empirical constants. As C is small compared with $k'P$, it usually may be neglected without serious error.⁵ Thus, (1) may be written approximately

$$R = k_1P \quad (2)$$

in which k_1 is the slope of the least-squares line of regression forced statistically through the origin. The parachor may be expressed in the usual approximate form⁷

$$P = V_m \gamma^{1/4} \quad (3)$$

in which V_m is the molar volume and γ is the surface tension. The Clausius-Mosotti equation for molar refraction of visible light in non-polar liquids may be expressed as

$$R = \frac{4}{3} \pi N \alpha_E \quad (4)$$

in which N is Avogadro's number and α_E is the electron polarizability. Substituting (3) and (4) in (2) yields

$$\frac{4}{3} \pi N \alpha_E = k_1 V_m \gamma^{1/4} \quad (5)$$

To obtain an equation that yields γ as a function of molecular characteristics only, it is useful to employ an expression for V_m in terms of the average distance d between molecular centers in a liquid. Define V_{mol} as the effective volume per molecule. Confining attention to a pure non-polar liquid composed of spherical (or quasi-spherical) molecules, and thereby assuming spherical configuration of V_{mol}

$$V_{mol} = \frac{4}{3} \pi (d/2)^3 \quad (6)$$

and, therefore

$$V_m = k_2 N V_{mol} = k_2 \frac{4}{3} \pi N (d/2)^3 \quad (7)$$

in which k_2 is a constant the value of which depends only upon the structure of the liquid. By

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substitution of (7) in (5), division by $(4/3)\pi N$, and solution for γ

$$\gamma = (\alpha_E/d^3)^{1/4} k_3 \quad (8)$$

in which $k_3 = (8/k_1 k_2)^{1/4}$. From (8) it is clear that the temperature-dependency of γ for liquids of the considered type is due solely to the temperature-dependency of d . It is known that α_E is temperature-invariant,⁸ and k_3 is temperature-invariant since k_1 is known empirically to be independent of temperature and k_2 (which is structure-sensitive only) cannot be expected in this case to be a function of temperature.

London's approximation for the dispersion energy E_{dis} of a system containing molecules of one kind only may be stated⁹

$$E_{\text{dis}} = -\frac{3}{4} \frac{\alpha_E^2}{d^6} h\nu_0 \quad (9)$$

if it is assumed that $\alpha_E = \alpha$, the total polarizability. In (9), ν_0 is the frequency of a London oscillator and h is Planck's constant. Using (8) and (9)

$$E_{\text{dis}} = -\frac{3}{4} \frac{\gamma^{1/2}}{k_3^{1/2}} h\nu_0 \quad (10)$$

As $h\nu_0$ may be replaced by the molecular ionization potential without serious error,¹⁰ and as molecular ionization potentials are approximately the same for most organic molecules,¹¹ (10) may be written

$$E_{\text{dis}} = k_4 \gamma^{1/2} \quad (11)$$

for such liquids, in which $k_4 = -(3/4)h\nu_0 k_3^{-1/2}$. As this discussion is limited to non-polar liquids, the total molar intermolecular association energy $E_a = NE_{\text{dis}}$ and

$$k_5 = \frac{E_a}{\gamma^{1/2}} \quad (12)$$

is obtained for pure non-polar organic liquids composed of spherical molecules. In (12), $k_5 = Nk_4$. If the development of (12) is valid, the value of k_5 will have the following characteristics:

1. It will be of the same order of magnitude for all non-polar organic liquids composed of spherical or quasi-spherical molecules.

2. For a liquid composed of aspherical non-polar organic molecules it will in general be different from the k_5 value of a similar liquid composed of spherical or quasi-spherical molecules, and the magnitude of the difference will increase as the aspheric characteristic increases.

3. It will be temperature-invariant for non-polar liquids.

To test k_5 for these characteristics, the molar internal latent heat of vaporization is considered to be equal to the molar intermolecular association energy

$$E_a = \Delta H_v - RT \quad (13)$$

in which ΔH_v is the total molar latent heat of vaporization at absolute temperature T and R is the ideal

gas constant. Using (13), the Clausius-Clapeyron equation

$$\frac{dp}{dT} = \frac{\Delta H_v p}{RT^2} \quad (14)$$

the differentiated form of the Antoine equation

$$\frac{dp}{dT} = \frac{(\log_e 10)pB}{(T+C)^2} \quad (15)$$

and appropriate values of surface tension^{12,13} and Antoine constants,¹⁴ k_5 may be evaluated as a function of temperature for various compounds. In (14) and (15), p is the vapor pressure at absolute temperature T and B and C are Antoine constants, which depend empirically upon the compound only.

Values of k_5 for five representative non-polar liquids composed of quasi-spherical organic molecules are given in Table I. It is apparent that the prediction of constancy of k_5 with respect to spherical molecules is valid. It is to be noted that the value of k_5 does not depend upon the chemical nature, polarizability, or molecular weight of the molecule.

TABLE I

Compound	k_5 (20°)
CCl ₄	1.44
C ₆ H ₆	1.43
Cyclohexane	1.48
Cyclohexene	1.49
Cyclopentane	1.37

The prediction of progressive deviation of k_5 with increasing asphericity is validated by the data given in Table II.

TABLE II

Compound	k_5 (20°)
<i>n</i> -Pentane	1.51
<i>n</i> -Hexane	1.66
<i>n</i> -Heptane	1.84
<i>n</i> -Octane	2.02
<i>n</i> -Nonane	2.22

That k_5 is almost but not strictly temperature-invariant is indicated by the data in Table III, in which values of $\Delta k_5/\Delta T$ are given over temperature ranges from 40 to 85°.

TABLE III

Compound	$\Delta k_5/\Delta T$	Compound	$\Delta k_5/\Delta T$
CCl ₄	0.0014	<i>n</i> -Pentane	0.0027
C ₆ H ₆	.0012	<i>n</i> -Hexane	.0026
Cyclohexane	.0014	<i>n</i> -Heptane	.0007
Cyclohexene	.0013	<i>n</i> -Octane	.0018
Cyclopentane	.0033	<i>n</i> -Nonane	.0015

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