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Applications of Refractive Index to Polymer Characterization

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ABSTRACT

The Lorentz-Lorenz formula (relating refractive index, molecular weight, and density to molar refractivity) was shown to give unreliable results when applied to polymers. A new equation has been derived relating refractive index to the total parachor and number of bonds of a molecule which can be applied to polymers as well as monomers. The ratio of total bonds to parachor approaches a limiting value for a given polymer system which in turn can be related to the limiting refractive index of that polymer. Applications are made to polymer molecular weights, tacticity, and copolymer composition.

INTRODUCTION

Our research was motivated by a desire to find organic compounds with large indices of refraction. The Lorentz-Lorenz formula, which correlates composition to molar refractivity, R, was an obvious starting point for examining this problem:

$$R = \frac{\eta^2 - 1}{\eta^2 + 2} \left[\frac{M}{\rho} \right] \tag{1}$$

Elemental composition or a selection between possible molecular structures can be made from density (ρ), refractive index (η), molecular weight (M), and tabular atomic and structural specific refractivities [1]. Solutions to Eq. (1) with high refractive index sought within an homologous series required a high density independent of molecular weight (Tables 1 and 2). Table 1 gives solutions for the hypothetical molecule polycubane (Fig. 1) showing that, in general, the index of refraction increases with density independent of molecular weight for $1.50 \le \eta \le 2.00$.

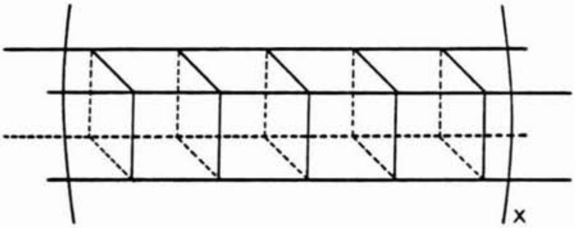

FIG. 1. Linear polycubane.

In Table 2 solutions for alkanes occurred independent of molecular weight within the experimental range $1.30 \le \eta \le 1.50$; in contrast, solutions for fluoroalkanes were found to occur over a wider range ($1.05 \le \eta \le 1.95$) but with unrealistically high densities (Table 3). Calculations carried out for linear polymers such as polyadamantane (Fig. 2) generally gave results independent both with respect to

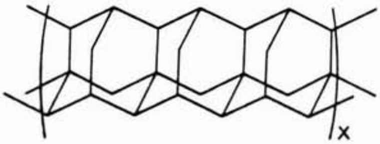

FIG. 2. Linear polyadamantane.

density and refractive index (Table 4). For example, the dimeric adamantane $C_{18}H_{24}$ was found as a solution for $1.50 \leq \eta \leq 2.20$.

The independence of refractive index from molecular weight and density, which gives poor correspondence to experimental observation, led us to seek other approaches.

THEORY

For low-density material without dipole-dipole interaction the Lorentz-Lorenz formula reduces to Eq. (2) [3]:

$$\eta - 1 = \frac{fN\rho\left[\frac{e^2}{M_e}\right]}{2\pi M(\nu_0^2 - \nu^2)} \tag{2}$$

The quantity ν_0 is the frequency of the absorption band having a mean oscillator strength f, and ν is the actual frequency of the light used to observe the index of refraction. The oscillator strength of an absorption band can be regarded as the effective number of electrons with mass M_e set into oscillation about their equilibrium positions in their respective normal modes when a group of molecules is placed in a radiation field (e.g., light of frequency ν) [4]. N is the number of molecules in 1 cm^2 of gas at 0°C and 1 atm; e is the electronic charge. Equation (2) can be rewritten for two empirical terms; α, the number of bonds per unit volume, and K_α, the refractive index per electron density (Eq. 3) which is obtained from the slope of the line correlating the refractive index and α.

$$\eta = K_\alpha \alpha + 1 \tag{3a}$$

$$\alpha = \frac{f\rho}{2M} = \frac{g}{V_m} \tag{3b}$$

V_m is the molar volume.

$$K_\alpha = \frac{Ne^2/M_e}{\pi(\nu_0^2 - \nu^2)} = \frac{2.428588956 \times 10^{31}}{\nu_0^2 - \nu^2} \tag{3c}$$

TABLE 1. Solutions to Lorentz-Lorenz Formula for Polycubane

K	Calculated K	Molecular weight	Density	Empirical formula	C/H ratio
		Index of Refraction = 1.50			
27.8483	28.1440	104.1526	1.1000	C_8H_8	1.0000
37.3032	37.8160	152.1970	1.2000	$C_{12}H_8$	1.5000
56.1733	57.1600	248.2858	1.3000	$C_{20}H_8$	2.5000
67.0430	66.8320	296.3302	1.3000	$C_{24}H_8$	3.0000
77.9128	76.5040	344.3746	1.3000	$C_{28}H_8$	3.5000
102.6277	105.5200	488.5078	1.4000	$C_{40}H_8$	5.0000
112.7210	115.1920	536.5522	1.4000	$C_{44}H_8$	5.5000
		Index of Refraction = 1.60			
27.4086	28.1440	104.1526	1.3000	C_8H_8	1.0000
37.1910	37.8160	152.1970	1.4000	$C_{12}H_8$	1.5000
56.6266	57.1600	248.2858	1.5000	$C_{20}H_8$	2.5000
67.5841	66.5320	296.3302	1.5000	$C_{24}H_8$	3.0000
78.5416	76.5040	344.3746	1.5000	$C_{28}H_8$	3.5000
83.9054	86.1760	392.4190	1.6000	$C_{32}H_8$	4.0000
94.1780	95.8480	440.4634	1.6000	$C_{36}H_8$	4.5000
104.4507	105.5200	488.5078	1.6000	$C_{40}H_8$	5.0000
114.7233	115.1920	536.5522	1.6000	$C_{44}H_8$	5.5000

		Index of Refraction = 1.70			
28.7538	28.1440	104.1526	1.4000	C_8H_8	1.0000
36.7654	37.8160	152.1970	1.6000	$C_{12}H_8$	1.5000
48.3712	47.4880	200.2414	1.6000	$C_{16}H_8$	2.0000
56.4489	57.1600	248.2858	1.7000	$C_{20}H_8$	2.5000
67.3721	66.8320	296.3302	1.7000	$C_{24}H_8$	3.0000
78.2952	76.5040	344.3746	1.7000	$C_{28}H_8$	3.5000
84.2617	86.1760	392.4190	1.8000	$C_{32}H_8$	4.0000
94.5780	95.8480	440.4634	1.8000	$C_{36}H_8$	4.5000
104.8943	105.5200	488.5078	1.8000	$C_{40}H_8$	5.0000
115.2106	115.1920	536.5522	1.8000	$C_{44}H_8$	5.5000
		Index of Refraction = 1.80			
27.8270	28.1440	104.1526	1.6000	C_8H_8	1.0000
38.2714	37.8160	152.1970	1.7000	$C_{12}H_8$	1.5000
47.5552	47.4880	200.2414	1.8000	$C_{16}H_8$	2.0000
55.8618	57.1600	248.2858	1.9000	$C_{20}H_8$	2.5000
66.6713	66.8320	296.3302	1.9000	$C_{24}H_8$	3.0000
77.4808	76.5040	344.3746	1.9000	$C_{28}H_8$	3.5000
88.2903	86.1760	392.4190	1.9000	$C_{32}H_8$	4.0000
		Index of Refraction = 1.90			
28.5035	28.1440	104.1526	1.7000	C_8H_8	1.0000
37.2675	37.8160	152.1970	1.9000	$C_{12}H_8$	1.5000
		Index of Refraction = 2.00			
28.9313	28.1440	104.1526	1.8000	C_8H_8	1.0000
27.4086	28.1440	104.1526	1.9000	$C_{12}H_8$	1.5000

TABLE 2. Solutions to Lorentz-Lorenz Formula for Alkanes

K	Calculated K	Molecular weight	Density	Empirical formula
		Index of Refraction = 1.40		
20.08658	20.67200	58.12430	0.70000	C_4H_{10}
24.93506	25.29000	72.15139	0.70000	C_5H_{12}
29.78355	29.90800	86.17848	0.70000	C_6H_{14}
34.63203	34.42600	100.20557	0.70000	C_7H_{16}
39.48052	39.14400	114.23266	0.70000	C_8H_{18}
44.32900	43.76200	128.25975	0.70000	C_9H_{20}
49.17749	49.38000	142.28684	0.70000	$C_{10}H_{22}$
54.02597	52.99800	156.31393	0.70000	$C_{11}H_{24}$
58.87446	57.61600	170.34102	0.70000	$C_{12}H_{26}$
63.72294	62.23400	184.36811	0.70000	$C_{13}H_{28}$
68.57142	66.85200	198.39520	0.70000	$C_{14}H_{30}$
73.41991	71.47000	212.42229	0.70000	$C_{15}H_{32}$
78.26839	76.08800	226.44938	0.70000	$C_{16}H_{34}$
83.11688	80.70600	240.47647	0.70000	$C_{17}H_{36}$

TABLE 3. Solutions to Lorentz-Lorenz Formula for Fluoroalkanes [2]

Compound	η_{calc}	η_{exp}	ρ_{calc}	ρ_{exp}
$FCH_2CH_2CH_2F$	1.30	1.3190^{26}	1.10	1.0057_4^{25}
$CF_3(CF_2)_4CF_3$	1.25	1.2515^{22}	3.65	1.6995_4^{25}
$CF_3(CF_2)_5CF_3$	1.25	1.2770	3.65	1.801_4^{25}
$CF_3(CF_2)_7CF_3$	1.26	1.2865^{25}	3.55	1.860_4^{25}
$CF_3(CF_2)_8CF_3$	1.25	1.2890^{25}	3.60	1.873_4^{25}
$CF_3(CF_2)_9CF_3$	1.25	1.2960^{25}	3.55	1.919_4^{25}

TABLE 4. Solution to Lorentz-Lorenz Formula for Polyadamantane

K	Calculated K	Molecular weight	Density	Empirical formula	C/H ratio
Index of Refraction = 1.50					
70.7033	69.9240	240.3911	1.0000	$C_{18}H_{24}$	0.7500
259.2136	266.9320	969.4590	1.1000	$C_{74}H_{80}$	0.9250
Index of Refraction = 1.60					
42.3708	41.7800	136.2385	1.1000	$C_{10}H_{16}$	0.6250
68.5325	69.9240	240.3911	1.2000	$C_{18}H_{24}$	0.7500
98.2252	98.0680	344.5436	1.2000	$C_{26}H_{32}$	0.8125
127.9178	126.2120	448.6962	1.2000	$C_{34}H_{40}$	0.8500
157.6104	154.3560	552.8488	1.2000	$C_{42}H_{48}$	0.8750
187.3030	182.5000	657.0013	1.2000	$C_{50}H_{56}$	0.8929
Index of Refraction = 1.70					
71.4707	69.9240	240.3911	1.3000	$C_{18}H_{24}$	0.7500
123.8732	126.2120	448.6962	1.4000	$C_{34}H_{40}$	0.8500
152.6270	154.3560	552.8488	1.4000	$C_{42}H_{48}$	0.8750
181.3807	182.5000	657.0013	1.4000	$C_{50}H_{56}$	0.8929
210.1345	210.6440	761.1539	1.4000	$C_{58}H_{64}$	0.9062
238.8883	238.7880	865.3064	1.4000	$C_{66}H_{72}$	0.9167
267.6421	266.9320	969.4590	1.4000	$C_{74}H_{80}$	0.9250

		Index of Refraction = 1.80			
41.5995	41.7800	136.2385	1.4000	$C_{10}H_{16}$	0.6250
68.5084	69.9240	240.3911	1.5000	$C_{18}H_{24}$	0.7500
98.1906	98.0680	344.5436	1.5000	$C_{26}H_{32}$	0.8125
127.8727	126.2120	448.6962	1.5000	$C_{34}H_{40}$	0.8500
157.5549	154.3560	552.8488	1.5000	$C_{42}H_{48}$	0.8750
187.2370	182.5000	657.0013	1.5000	$C_{50}H_{56}$	0.8929
216.9192	210.6440	761.1539	1.5000	$C_{58}H_{64}$	0.9062
259.0158	266.9320	969.4590	1.6000	$C_{74}H_{80}$	0.9250
		Index of Refraction = 1.90			
42.2558	41.7800	136.2385	1.5000	$C_{10}H_{16}$	0.6250
69.8998	69.9240	240.3911	1.6000	$C_{18}H_{24}$	0.7500
100.1848	98.0680	344.5436	1.6000	$C_{26}H_{32}$	0.8125
122.7951	126.2120	448.6962	1.7000	$C_{34}H_{40}$	0.8500
151.2987	154.3560	552.8488	1.7000	$C_{42}H_{48}$	0.8750
179.8022	182.5000	657.0013	1.7000	$C_{50}H_{56}$	0.8929
208.3057	210.6440	761.1539	1.7000	$C_{58}H_{64}$	0.9062
236.8092	238.7880	865.3064	1.7000	$C_{66}H_{72}$	0.9167
265.3128	266.9320	969.4590	1.7000	$C_{74}H_{80}$	0.9250
		Index of Refraction = 2.00			
42.5745	41.7800	136.2385	1.6000	$C_{10}H_{16}$	0.6250
70.7033	69.9240	240.3911	1.7000	$C_{18}H_{24}$	0.7500
95.7066	98.0680	344.5436	1.8000	$C_{26}H_{32}$	0.8125
124.6378	126.2120	448.6962	1.8000	$C_{34}H_{40}$	0.8500
153.5691	154.3560	552.8488	1.8000	$C_{42}H_{48}$	0.8750

(continued)

TABLE 4. Solution to Lorentz-Lorenz Formula for Polyadamantane (Continued)

K	Calculated K	Molecular weight	Density	Empirical formula	C/H ratio
182.5004	182.5000	657.0013	1.8000	$C_{50}H_{56}$	0.8929
211.4316	210.6440	761.1539	1.8000	$C_{58}H_{64}$	0.9062
240.3629	238.7880	865.3064	1.8000	$C_{66}H_{72}$	0.8167
269.2942	266.9320	969.4590	1.8000	$C_{74}H_{80}$	0.9250
		Index of Refraction = 2.10			
42.6331	41.7800	136.2385	1.7000	$C_{10}H_{16}$	0.6250
71.0464	69.9240	240.3911	1.8000	$C_{18}H_{24}$	0.7500
96.4688	98.0680	844.5436	1.9000	$C_{26}H_{32}$	0.8125
125.6305	126.2120	448.6962	1.9000	$C_{34}H_{40}$	0.8500
154.7922	154.3560	552.8488	1.9000	$C_{42}H_{48}$	0.8750
183.9539	182.5000	657.0013	1.9000	$C_{50}H_{56}$	0.8929
213.1156	210.6440	761.1539	1.9000	$C_{58}H_{64}$	0.9062
242.2773	238.7880	865.3064	1.9000	$C_{66}H_{72}$	0.9167
271.4390	266.9320	969.4590	1.9000	$C_{74}H_{80}$	0.9250
		Index of Refraction = 2.20			
42.4915	41.7800	136.2385	1.8000	$C_{10}\ _{16}$	0.6250
71.0297	69.9240	240.3911	1.9000	$C_{18}H_{24}$	0.7500
		Index of Refraction = 2.30			
42.1965	41.7800	136.2385	1.9000	$C_{10}H_{16}$	0.6250

From Eq. (3a) we predicted that η is a linear function of α with an intercept of unity. The electron density α included only valence bonds or one-half the number of valence electrons. Equation (3a) was verified for the n-alkanes (Table 5); and the calculated η agreed with experimental values as signified by the square of the correlation coefficient which was equal to 0.999893.

In addition to α, other parameters have been proposed such as the reciprocal of the molecular weight [6] (1/M) or the molar volume ($1/V_m$) (Eq. 4).

$$\eta_{1/M} = K_{1/M}\left[\frac{1}{M}\right] + b_{1/M} \tag{4a}$$

$$\eta_{1/V_m} = K_{1/V_m}\left[\frac{1}{V_m}\right] + b_{1/V_m} \tag{4b}$$

With these parameters, 1/M or $1/V_m$, the estimation of the refractive index was poorer (Table 5).

The residual variances that were obtained from linear determinations of measured refractive index and refractive index calculated by three different methods are

$$\sigma^2(\alpha) = 0.241819 \times 10^{-6}$$

$$\sigma^2(1/V_m) = 11.3608 \times 10^{-6}$$

$$\sigma^2(1/M) = 3.38508 \times 10^{-6}$$

Bartlett's test and Hartley's test [7] of the ratio of maximum to minimum variance both indicated differences in these variabilities at the 0.01 level of significance. It can therefore be concluded that the first linear relationship had a significantly lower residual variance than the other linear relationships. In addition, only with α was the theoretical value of the intercept obtained (Table 6). Employment of the parameter 1/M or $1/V_m$ necessitates neglect of density and oscillator strength.

Equation (2) was derived only for low-density substances without

TABLE 5. Parameter Estimate of Refraction Index for Alkanes [5]

Refractive index	C_4H_{10}	C_5H_{12}	C_6H_{14}	C_2H_{16}	$C_{10}H_{22}$	$C_{16}H_{34}$	$C_{20}H_{42}$	$C_{28}H_{58}$	$C_{30}H_{62}$	$C_{40}H_{82}$	Correlation coefficient
η_{exp}	1.3326	1.35748	1.37486	1.38764	1.41189	1.43453	1.4426	1.4520	1.4536	1.4593	1.000000
η_{α}	1.3325	1.3579	1.3755	1.3884	1.4125	1.4349	1.4430	1.4511	1.4538	1.4592	0.999893
$\eta_{1/M}$	1.3317	1.3564	1.3778	1.3910	1.4157	1.4371	1.4445	1.4527	1.4543	1.4593	0.998539
η_{1/V_m}	1.3326	1.3520	1.3669	1.3788	1.4041	1.4295	1.4399	1.4503	1.4518	1.4593	0.995260

TABLE 6. Calculated Intercepts and Slopes for Various Homologous Series

Homologous series	Parameter	K_α	Intercept
Alkane	α	2.7013	0.98224
Alkane	1/M	-8.2272	1.4732
Alkane	$1/V_m$	-14.9058	1.4801
Cycloalkane	α	2.6304	0.98802
1-Alkene	α	2.3857	1.0420
1-Alcohols	α	0.9142,[a] -1.9480[b]	1.3078
1-Alkyl iodides	1/M	1.9023,[a] 37.5553[c]	1.1265
Polyethylene oxide	1/M	-2.4094	1.4538
Nonconjugated dienes	1/M	-8.9033	1.5122

[a] K_α for the alkyl portion of the molecule.

[b] K_α for the oxygen of the alcohol group determined by assigning only that portion of the C—O bond represented by the difference in their electronegativities.

[c] K_α for the iodine atom; calculated similarly to that for oxygen.

dipolar groups. In alcohols and iodides there are two distinct sets of electrons. The first are found in the carbon-carbon, carbon-hydrogen skeletal orbitals whereas the second are in nonbonding and π-type orbitals. In order to accommodate the latter set, Eqs. (2) and (3) were expanded (Eqs. 5 and 6):

$$\eta - 1 = \frac{N\rho e^2/M_e}{2\pi M} \sum_i \frac{g_i}{\nu_{0_i}^2 - \nu^2} \tag{5}$$

$$\eta - 1 = \sum_i K_{\alpha_i} \alpha_i \tag{6}$$

As an example of the application of Eq. (6), consider alkyl iodides which possess two different sets of electrons; the three bonding pair associated with the iodide atom and the (3n + 1) valence electrons associated with the alkyl residue. Since the parameter α was defined as the number of bonds per unit volume, Eq. (6) can be rearranged to Eq. (6a):

$$\sum_i K_{\alpha_i} \alpha_i = \sum_i K_{\alpha_i} \frac{g_i}{V_m} = \frac{1}{V_m} \sum_i K_{\alpha_i} g_i \tag{6a}$$

By solution of simultaneous equations, the constants K_{α_i} were obtained.

With homoatomic molecules all bonds are alike, i.e., differences in the α-value depend only on the number of bonds. The assignment of an α-value in the case of heteroatomic molecules to the heteroatomic bond is not simply the number of bonds or fractional number of bonds adjacent to the heteroatom divided by the molar volume. A more general definition of α is the oscillator strength, f_{nk} per volume. The oscillator strength is a dimensionless quantity defined as being the ratio of the quantum mechanical and classical contributions of an optical transition n → k to the polarizability of the molecule. For strongly allowed transitions the oscillator strength is of the order of 1:

$$f_{nk} = \frac{8\pi^2 m a_{nk}^2 \nu_{nk}}{h}$$

The quantity a_{nk} is a measure of the probability of a transition connected with radiation of frequency ν_{nk} along, say, the Z-axis.

$$a_{nk} = \int Z \Psi_n \Psi_k \, d\tau$$

The size of the transition probability a_{nk} is dependent upon the symmetry of the wave functions Ψ_n, Ψ_k, and upon the overlap of the ground and excited vibrational states. The promotion of nonbonding electrons to a σ^* or π^*-excited state is symmetry disallowed and thus nonbonding electrons make little contribution to f or η. The overlap between ground and excited vibrational states generally increases the smaller the energy gap between ground and excited electronic states.

Consequently, in alkyl iodides or other heteroatomic molecules the assignment of α to the heteroatomic moiety requires more rigorous treatment than that given here. However, the following can be stated concerning alkyl iodides: the carbon-iodide bond is a stronger oscillator than carbon-carbon or carbon-hydrogen bonds, and the nonbonding electrons on the iodide atom make little contribution to f and η.

We recognize there are limitations to this approach; these will be considered in detail in future publications.

In order to calculate the refractive index of an homologous series by means of Eq. (3a), K_α, α, and the intercept must be obtained from a correlation of the refractive index with the parameter α, which was in turn obtained from density. It was not possible to calculate the refractive index of hypothetical molecules with Eq. (3a) unless the molar volume was known from other data.

Perhaps the most successful attempt to approximate molar volume was achieved by Sugden when he discovered a simple relationship between surface tension and density [8]:

$$\gamma = \frac{P^4(D - d)^4}{M^4} \tag{7}$$

where γ is the surface tension, D and d are the densities of a liquid and its vapor, respectively, M is the molecular weight, and P is a constant, the parachor. When the vapor density is negligibly small and the surface tension is unity, the relationship reduces to an equation of parachor and molar volume:

$$P = V_m \tag{8}$$

Although parachor has been criticized from time to time, this equation between parachor and molar volume has remained a useful empirical relationship [9]. More accurately, parachor was expanded in powers of V_m:

$$P = a_0 + a_1 V_m + a_2 V_m^2 + \dots \tag{9}$$

Truncation of the expansion after the second term was found to fit the alkane family (Fig. 3). A new parameter β was defined as

$$\beta = \frac{g}{P} = \frac{\text{number of bonds}}{\text{total parachor}}$$

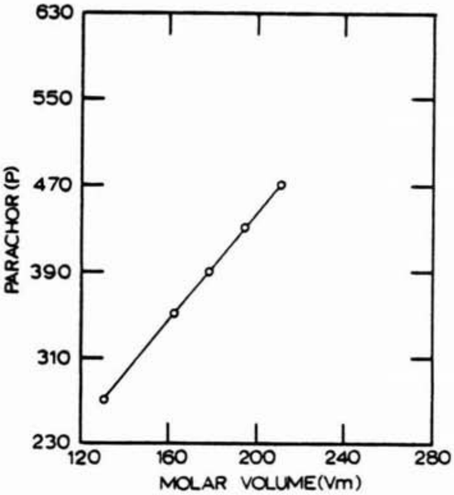

FIG. 3. The linear dependence of parachor on molar volume for the alkane family.

Substitution of β into Eq. (3a) yielded a new expression for the relative index:

$$\eta = K_{\alpha}\beta \frac{P}{V_m} + 1$$

where

$$\alpha = \beta P/V_m \tag{10a}$$

$$\eta = K_{\alpha}\alpha + 1 = \frac{d\eta}{d\alpha}\alpha + 1 = \frac{d\eta}{d \ln \alpha} + 1$$

Case I:

$$P = aV_m$$

$$\ln \alpha = \ln \beta + \ln (P/V_m) = \ln \beta + \ln a$$

$$d \ln \alpha = d \ln \beta$$

$$\eta = \frac{d\eta}{d \ln \beta} + 1 = k_{\beta}\beta + 1 \tag{10b}$$

Case II:

$$P = aV_m + b$$

$$\ln (P/V_m) = \ln \left[\frac{aV_m + b}{V_m}\right] = \ln \left[a + \frac{b}{V_m}\right]$$

$$d \ln \alpha = d \ln \beta + d \ln \left[a + \frac{b}{V_m}\right] = d \ln \left[a\beta + \frac{b\beta}{V_m}\right]$$

$$\eta = \frac{d\eta}{d \ln \left[a\beta + \frac{b\beta}{V_m}\right]} + 1 = k'_{\beta}\beta + 1 \tag{10c}$$

For small values of b, Case I applied. In most instances the value of b was not small and it was found simpler to employ β as the independent parameter, which resulted in a nonunity intercept. In Table 7 are presented values of a and b for a few representative compounds; and in Table 8 are data showing the index of refraction and β to be linearly correlated.

TABLE 7. Selected Values of a and b

Compound	V_m	P	a	b
$C_8H_{19}I$	189.5	425.8	2.199	8.931
$C_{28}H_{58}$	483.4	1151.0	2.615	-113.07
$C_{10}H_{22}O$	200.9	445.3	2.242	-5.349
$C_{18}H_{36}$	319.5	739.1	2.484	54.71

TABLE 8. Intercepts and Slopes for Selected Homologous Series for β

Compound	K_β	Intercept
n-Alkanes	20.675	-0.07458
Alkyl iodides	4.7724[a]	1.4666[a]
Alkyl aromatics	0.81147[a]	1.4767[a]
1-Alkenes	16.23762	0.25857
Diamond	35	-1.41
1-Alcohols	8.0105	0.861181

[a] These values were calculated by assuming only the nonbonding or π-electrons were undergoing oscillation.

The advantages of β are that the molar volume was not needed to calculate the index of refraction and that β depended directly upon the number of repeating units. As the number of repeating units increased, β approached a limiting value. As an example, in the alkane family C_nH_{2n+2} the number of bonds, g, was $(3n + 1)$. The total parachor P was $\left[(n - 2)P_{CH_2} + 2P_{CH_3}\right]$, where P_{CH_2} and P_{CH_3} were the parachor of the methylene and methyl groups, respectively:

$$\beta^{RH} = \frac{3n + 1}{(n - 2)P_{CH_2} + 2P_{CH_3}}$$

As n became large, β approached the β value of polyethylene:

$$\beta^{RH}_{lim} = \frac{3}{P_{CH_2}} = \frac{3}{40}$$

From β_{lim} the refractive index of polyethylene was calculated (see Table 9):

$$\eta^{RH}_{lim} = 20.675 \times \frac{3}{40} - 0.07458 = 1.48$$

As another example, the limiting β for 1-alkenes $\beta^{RC{=}CH_2}_{lim}$ was equal to β^{RH}_{lim} as expected:

$$\beta^{RC{=}CH_2}_{lim} = \frac{3n}{(n - 3)P_{CH_2} + P_{CH_2} + P_{CH{=}CH_2}}$$

$$\beta^{RC{=}CH_2}_{lim} = \frac{3}{P_{CH_2}} = \frac{3}{40}$$

TABLE 9. Limiting Refractive Indices for Selected Polymers

Polymer	Limiting β	Experimental refractive index	Calculated limiting refractive index
Polyethylene	0.075	1.49	1.476[a]
Polystyrene	0.080	1.59-1.60	1.597
Polybutadiene	0.075	1.5074-1.5159	1.5035
Diamond	0.111	2.4173	2.48

[a] Amorphous.

From $\beta_{\text{lim}}^{\text{RC=CH}_2}$ the refractive index of Δ^1-polyethylene was calculated:

$$\eta_{\text{lim}}^{\text{RC=CH}_2} = 16.23762\left[\frac{3}{40}\right] + 0.25857 = 1.476$$

The limiting refractive index for 1-alkyl iodides is 1.4666:

$$\beta^{\text{RI}} = \frac{3}{(n-1)P_{\text{CH}_2} + P_{\text{CH}_3} + P_{\text{I}}}$$

$$\beta_{\text{lim}}^{\text{RI}} = 0$$

$$\eta_{\text{lim}}^{\text{RI}} = 4.7724(0) + 1.4666$$

In Table 9 are the limiting β and refractive index for several polymers.

APPLICATIONS

Refractive Index and Molecular Weight

Any intermediate value of the refractive index can be calculated for a polymer system; e.g., suppose an alkane with a refractive index of 1.400 was required, the number of repeating units is calculated from

$$1.400 = 20.675 \left[\frac{3n + 1}{(n - 2)P_{CH_2} + 2P_{CH_3}} \right] - 0.07458$$

giving n = 8.23. This gives a molecular weight of 117.28 which corresponds to octane having a refractive index of 1.397. Similarly, from a determination of the refractive index within an homologous series the molecular weight can be obtained. In the case of alkanes the refractive index rapidly increases with n, the number of carbon atoms, and then approaches the limiting value of 1.476 (Fig. 4) with the inflection point occurring at about n equal to 500. This change in refractive index with respect to n for alkanes is

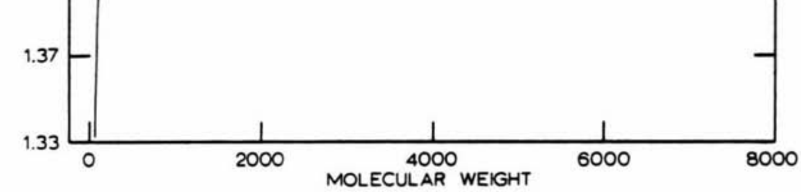

FIG. 4. Alkane refractive index.

$$\frac{d\eta}{dn} = \frac{1096}{(40n + 31)^2}$$

and is shown in Fig. 5.

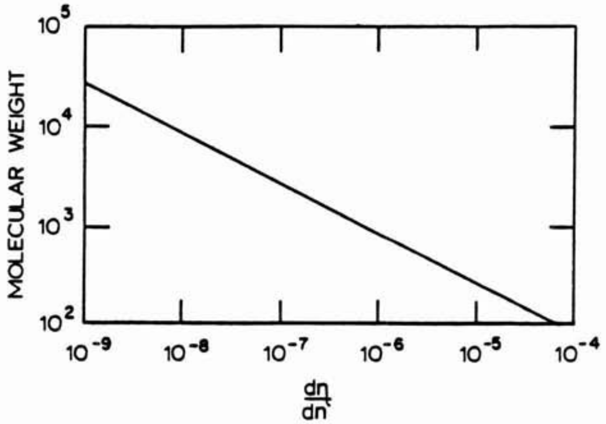

FIG. 5. Change in refractive index as a function of the number of polymer repeat units.

By means of interferometric methods, changes in refractive index as minute as 1×10^{-8} have been detected [10]. For this variation in refractive index with incremental increases of molecular weight, the maximum molecular weight determinable is 1×10^5. This technique can be used for any homopolymer system.

Besides linear polymers, the refractive index of cross-linked three-dimensional molecules can also be determined. Adamantane, diadamantane, and homologs are members of the diamondoid family, i.e., the last member of the family is diamond (Fig. 6). The parameter β as a function of the number of condensed adamantane units is given by

$$\beta = \frac{10R + 18}{(6 + 4R)(P_C + P_H) + 12P_H + 0.8(2R + 1)} \tag{11}$$

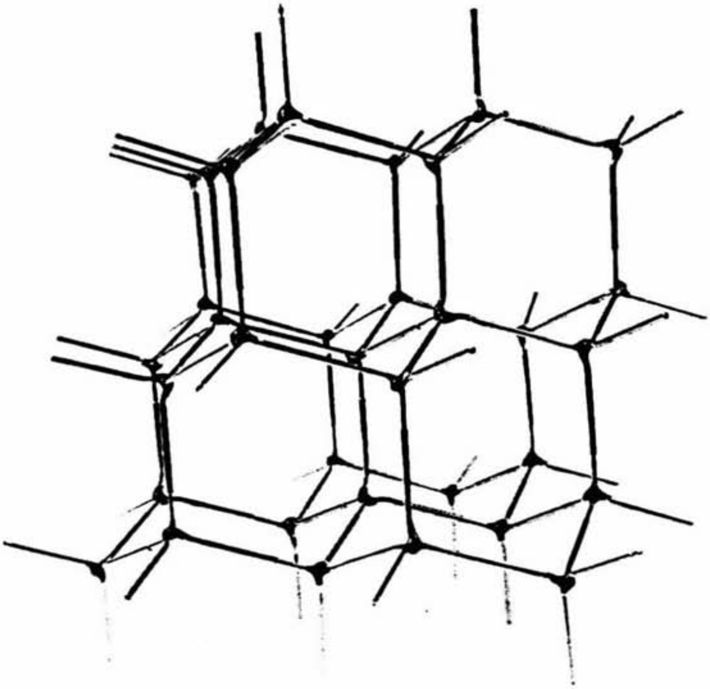

FIG. 6. Hexaadamantane.

The term 0.8(2R + 1) in the denominator contributes the influence of ring expansion on the parachor where R is the number of adamantane units. The limiting β for polyadamantane, $\beta^{\text{ADA}}_{\text{lim}}$, is 0.100:

$$\beta^{\text{ADA}}_{\text{lim}} = \frac{10}{4(24.5) + 1.6} = 0.100$$

The limiting structure of polyadamantane is a molecule, the interior of which resembles diamond and the exterior of which contains the hydrogen atoms. $\beta^{\text{ADA}}_{\text{lim}}$ is less than the theoretical limiting β value of diamond, 0.111, because of the uncertainty in the assigned values of P_C and P_H, the carbon and hydrogen atom parachors.

The theoretically limiting β value of diamond, 0.111, is the maximum β value for all carbon-hydrogen containing compounds. The parameter β is maximized with saturated compounds and with a large carbon-to-hydrogen ratio. Within a series of saturated compounds the smallest parachor is achieved with linear or fused ring cyclohexyl polymers (Fig. 7). The limiting βs for polyethylene, polymethine, and polyquaternary carbon are 0.075, 0.0816, and 0.111, respectively.

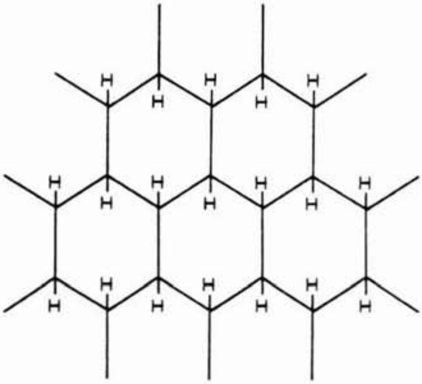

FIG. 7. Polymethine.

Tacticity

The measurement of refractive index can be applied to the sterochemistry of polymers. The differences in refractive index among isotactic, syndiotactic, and atactic isomeric polymers are reflected in the parameter β by variations in parachor. In particular the refractive index of polybutene-2 is a function of the sterochemistry of the repeating vicinal methyl groups which are on the same side, alternating, or randomly arranged along the polymer backbone. Each of these arrangements is characterized by a unique parachor and refractive index for the same molecular weight. From the model compounds cis- and trans-1,2-dimethylcyclohexane the parachor of the sterospecific repeating unit was extracted. The polymers were then constructed by adding the trans-1,2-dimethylethenyl units together to form the syndiotactic structure, the cis-1,2-dimethylethenyl forming the isotactic and equal numbers of the cis- and trans-dimethylethenyl groups randomly distributed to form the atactic isomer.

Figure 8 shows the relationship between β and the number of repeating units for the three isomeric poly-2-butenes; hence, for the same number of repeating units each steroisomer has a different refractive index. In polymers with mixed sterochemistry the measured refractive index falls in between the syndio- and isotactic curves. The fraction of isotacticity is given by the tie line rule:

$$\frac{\beta - \beta_{st}}{\beta_{it} - \beta_{st}} = \text{fraction isotacticity}$$

Alternatively, refractive index can be plotted against the number of repeating units for the same calculation.

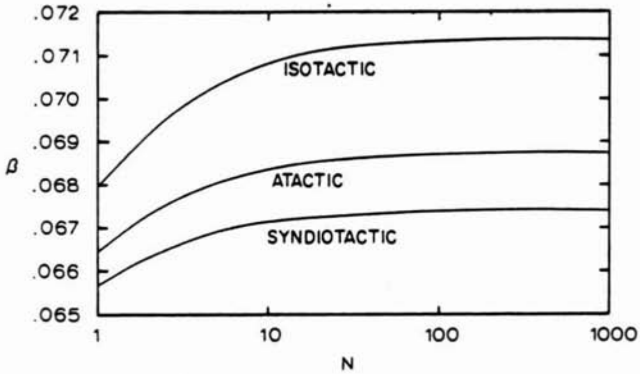

FIG. 8. Dependance of tacticity on β for an increasing number of repeat units.

Copolymer Composition

The weight fraction of each component of a copolymer $(AB)_x$ can be obtained from the copolymer refractive index and the refractive indices of the homopolymers $(A)_x$ and $(B)_x$, respectively.

The refractive indices of copolymers $(AB)_x$ and $(BA)_x$ are equivalent since reading the unit sequences along the backbone of polymer $(AB)_x$ from right to left is the same as reading the repeating units of $(BA)_x$ from left to right.

Furthermore, the sequence read ABABAB or BABABA depends upon the point at which the sequence reading commences; i.e., B or A. Thus the sequence segments (AB) are indistinguishable from the sequence segment (BA). By selectively replacing AB with its equivalent BA, or BA with the equivalent AB, the copolymer ABABABA can be converted into the block copolymer AAAABBB. Therefore the refractive indices of the copolymer ABABABAB and the block copolymer AAAABBBB are identical:

ABABABABA

ABABABAAB

ABABAABAB

ABABAAABB

.
.
.

AAAAABBBB

Assuming the blocks $(A)_x$ and $(B)_x$ are large, the index of refraction for each block can be calculated from

$$\eta = K_\beta \beta_{\text{lim}} + \text{constant} \tag{12}$$

The refractive index, η_{AB}, of the copolymer $(AB)_x$ can be calculated from

$$\eta_{AB} = \eta_A X_A + \eta_B X_B = (1 - X_B)\eta_A + X_B \eta_B \tag{13}$$

where X_i is the respective weight fractions. Since η_A and η_B are constants obtained from Eq. (12), a single measurement of the copolymer refractive index gives the copolymer composition. For example, the fraction of component B in the copolymer $(AB)_x$ is given by

$$X_B = \frac{\eta_{AB} - \eta_A}{\eta_B - \eta_A} \qquad (14)$$

To illustrate this technique the calculated compositions of a butadiene-styrene copolymer are compared to experimentally obtained values [11] in Table 10. It is clear that small inaccuracies in refractive index measurements can result in large errors in the calculated composition.

TABLE 10. Copolymer Composition

X_{PS}^{exp}[a]	X_{PS}^{calc}[b]	η_{PS-PB}
0	0	1.5148
2.1	2.3	1.5166
7.9	8.8	1.5217
22.6	24.7	1.5342
36.3	39.1	1.5456
53.1	58.8	1.5611

[a] Experimental weight fractions of polystyrene (PS).

[b] Weight fraction of PS employing experimental refractive indices for PS and polybutadiene (PB).

Future Applications

We are currently studying the applications of the theory developed in this paper to: (a) hardness and softness of molecular fragments, molecules and molecular sites with application to the reactivities of monomers and polymers; (b) hydrodynamic volume and end-to-end distance; and (c) ionomers.

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