

Refractive Index Increments of Polyethylene

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Synopsis

The refractive index increments of linear and branched polyethylene were determined for several solvents and various wavelengths (403, 436, 546, and 633 nm), mainly at 135°C. Differences were observed between values for linear and branched samples. Data obtained in this investigation are compared with the reported ones.

INTRODUCTION

The refractive index increment of a polymer in a given solvent and at a particular temperature is the basic parameter which must be known to make molecular weight determinations by light scattering. This quantity is also of importance in gel-permeation chromatography and sedimentation analysis of macromolecular compounds. The first papers dealing with the light scattering from polyethylene solutions, and thus also with the determination of the refractive index increments, date back to the early 1950s¹; in spite of this, the determination of molecular weights and/or refractive index increments of this polymer has not yet become a routine matter. Although many papers have been published on the determination of the molecular weight of polyethylene, only some of them give experimental values of the refractive index increments¹⁻²⁵; most of the authors use published values. Data reported in the literature cannot be regarded as complete, for the following reasons:

1. A substantial part of published refractive index increments of polyethylene has been determined at temperatures below 130°C.²⁻¹² At present, however, the prevailing trend is to use temperatures above 130°C (i.e., above the melting point of fully crystalline polyethylene), where polyethylene is soluble in the given solvent regardless of the degree of crystallinity and where one may rule out the existence of residues of the crystalline structures and associates in solution.

2. Although most of commercial light-scattering photometers are equipped for measurements at various wavelength (usually, intense lines of the mercury spectrum: 365, 436, 546, and 578 nm), the refractive index increments are usually measured only for green light of 546 nm; values for 436 nm^{2-4,12,13} are reported only exceptionally. Recently, a small-angle light-scattering photometer, Chromatix KMX-6 (working also at high temperatures), has been introduced into the market. For this apparatus operating at the wavelength of the He-Ne laser (633 nm), only a few increments given by the manufacturer are available.¹⁴

3. The choice of solvents in which the refractive index increments were determined is virtually limited to 1-chloronaphthalene,^{1-9,11,12,14-22} tetralin,^{2-5,7-11,13,17} and *n*-decane.^{5,17,21,25} A few values are given for chloro-

benzene,¹³ 1,2-dichlorobenzene,^{10,14} 1,2,4-trichlorobenzene,^{14,20} diphenyl,²⁴ and xylene.²¹ A number of other solvents have been utilized in the characterization of polyethylene by other methods, e.g., diphenylmethane (viscometry²⁶) 1-methyl naphthalene (GPC²⁷), or 1-bromonaphthalene (sedimentation²⁸). These, as well as some other solvents, may also be used in light-scattering measurements. It appears desirable to extend the number of solvents used so far, and especially to include Θ solvents.

4. From the formal viewpoint it should be noted that many refractive index increments are reported in the literature with a positive sign,^{1-3,6,7,9,10,13,21} although in fact they are negative.

5. Differences in values obtained for the same solvent by different authors are sometimes considerable.

For all these reasons, we regarded it as useful to summarize the existing values of the refractive index increments of polyethylene, especially at elevated temperatures (data at lower temperatures have been summarized in, for example, refs. 20 and 29), and to extend these data so as to include determinations at other wavelengths and in some other solvents.

EXPERIMENTAL

Differential Refractometer

The Brice-Phoenix differential refractometer, model BP-2000-V, has been adjusted for measurements at elevated temperatures as in the literature.³⁰ The cell was placed in a metallic block, but no immersion liquid was used. In addition to a mercury lamp, a tungsten lamp (250 or 500 W) placed in the slide projector was used as an external light source. The required wavelength of light was isolated by interference filters. A condensing lens increasing the intensity of incident light was placed in front of the slit of the apparatus.¹⁹

The differential refractometer was calibrated at 25°C by aqueous solutions of potassium chloride. The refractive indices of these solutions for various wavelengths were taken from the literature.³¹ The calibration constant, $k = (0.932 \pm 0.003) \times 10^{-5}$, was independent of the wavelength. It may be inferred from the original paper describing the construction of the differential refractometer³² that the calibration constant should be independent of temperature, because its value is given only by the geometry of the apparatus. For the temperature range between 25 and 70°C, this fact was experimentally proved by Ehl et al.¹⁷

In our case, the temperature independence of the calibration constant was verified indirectly by the molecular weight determination of a standard polystyrene sample (Chemical Pressure Company, Inc., USA, $M_w = 97\,200$), using light scattering from dibutylphthalate solutions at different temperatures. Light scattering was measured with a Fica 50 in unpolarized primary light of wavelength 546 nm. The results of light scattering were used for the calculation of the refractive index increments, whose values were then compared with the differential refractometric determination (Table I). The refractive index increments obtained by both procedures are identical within the limits of experimental error.

TABLE I
Refractive Index Increment of Polystyrene in Dibutylphthalate at Different Temperatures and at 546 nm

Method	Refractive index increment, ml/g	
	25°C	135°C
Differential refractometry	0.108 ± 0.001	0.120 ± 0.001
Light scattering	0.111 ± 0.004	0.120 ± 0.004

Preparation of Polyethylene Solutions

Most of the differential refractometric measurements were carried out with one linear polyethylene (PE), Hizex 2200J (Mitsui Petrochemical, Japan), and one branched PE, Bralen FA-7-15 (Slovnaft, Czechoslovakia). In some cases, the determination of the refractive index increments was performed with linear PE SRM 1475 (Standard Reference Material, National Bureau of Standards, USA), DMDJ 3472 and DMDJ 5140 (Union Carbide, USA), branched PE SRM 1476 (National Bureau of Standards, USA), and samples α and β distributed under the scheme of the IUPAC Working Party on the Molecular Characterization of Commercial Polymers.³³ The samples were not reprecipitated or otherwise treated.

The solvents were either common commercial chemicals or were purified by recommended procedures so as to achieve a purity of at least 99.5 wt. % (checked by gas chromatography).

A weighted amount of PE granules and a known amount of solvent were sealed in a glass ampul. The latter was placed in a bath of silicone oil heated to 145–160°C. Its content was mildly shook until the sample dissolved (2–4 hr, as a rule). The solutions were transferred from ampuls into the cell of the differential refractometer in all-glass syringes preheated to 160°C. After each measurement the cell was cleared by repeated rinsing with boiling xylene followed by rinsing with toluene. The syringes were purified by condensing xylene vapors.

The refractive index difference was measured with at least five solutions at concentrations between 4×10^{-3} and 1.5×10^{-2} g/ml. An example of the evaluation of differential refractometric data is shown in Figure 1. The relative error of determination of the refractive index increments varies about 1%.

RESULTS AND DISCUSSION

The published values of the refractive index increments of polyethylene (PE) in various solvents are reviewed in Table II; our results are summarized in Tables III and IV, where the boiling points of the particular solvents are also given in Table III. Most of these compounds are liquid at room temperature; only diphenylmethane (mp 26°C), *p*-dibromobenzene (mp 87°C), and diphenyl (mp 69°C) are crystalline.

The solvent densities at the temperatures of measurement were obtained by the interpolation of reported data. Solutions used in the measurements are usually prepared by weighing the PE and solvent at room temperature; if the concentration in g/g thus obtained is recalculated to the more usual g/ml units, the solution density (or at least the solvent density) at the elevated working temperature should be known. In papers dealing with the determination of the refractive index increments or molecular weights of PE by light scattering, the

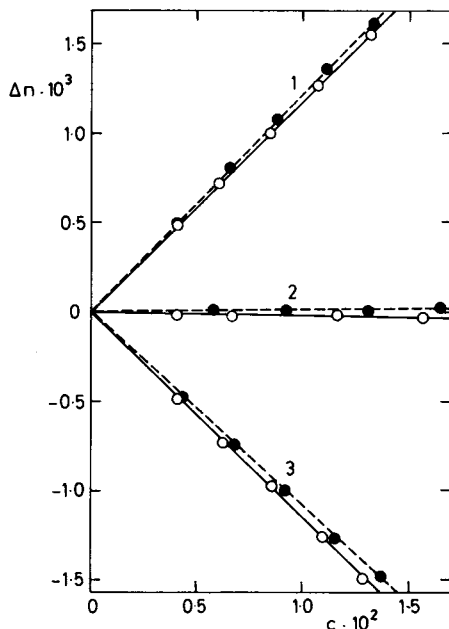


Fig. 1. An example of the determination of refractive index increments by differential refractometry at $\lambda_0 = 546$ nm, $t = 135^\circ\text{C}$: ○, linear PE Hizex 2200 J; ●, branched PE Bralen FA-7-15. Solvents: 1, *n*-decane; 2, paraffin oil; 3, 1,2,4-trichlorobenzene. Δn is the difference between refractive indices of solution and solvent; c is the polymer concentration in g/ml.

solvent densities are usually not given. The use of incorrect densities, or even the neglect of density changes with temperature, may lead to errors in the evaluation of experimental data.

1-Chloronaphthalene as Solvent

1-Chloronaphthalene is undoubtedly the solvent most in use in light-scattering measurements of PE. For this reason, the determination of the refractive index increments with this solvent are extensive both in the literature (Table II) and in this study (Table IV). Most authors give results almost identical within the limits of experimental error, which is probably related, among other things, to the mild temperature dependence of this refractive index increment.^{16,17} In carefully performed measurements, the refractive index increment was found to increase somewhat with increasing molecular weight.^{19,20,22} A similar phenomenon was also observed for other polymers³⁵⁻³⁸; it is explained by a decrease in the partial specific volume of the polymer with increasing molecular weight or with increasing degree of branching,³⁹ and for low-molecular-weight samples by the effect of end groups on the refractive index of the polymer.⁴⁰

Our own results (Table IV) show that the refractive index increments of branched PE are higher (i.e., in absolute value lower, because the values are negative) than those of linear samples. Since industrial samples of branched PE usually exhibit a higher weight-average molecular weight M_w , than linear ones (the number average values M_n , being comparable), superimposing effects may exist of molecular weight and branching on the partial specific volume, and thus on the refractive index increment. It is difficult to decide which effect predominates.

TABLE II
Reported Refractive Index Increments, dn/dc , of Polyethylene at 546 nm and $t \geq 120^\circ\text{C}^a$

Solvent	t , $^\circ\text{C}$	dn/dc , ml/g	Ref.
<i>n</i> -Decane	125	+0.093	17
	130	+0.094	17
	138	+0.096	17
	140	+0.098	21
	143	+0.099	17
Tetralin	120	-0.075	8
	125	-0.074	8
		-0.094	3
	128	-0.084	17
	129	-0.094	2
	138	-0.081	17
	144	-0.080	17
		-0.078	10
1,2-Dichlorobenzene	120		10
1,2,4-Trichlorobenzene	135	-0.109 to -0.106 ^b	20
Biphenyl	123	-0.174	10
1-Chloronaphthalene	120	-0.192	8
	125	-0.191	1, 8
		-0.195	4, 7, 11
	127	-0.197	17
	135	-0.190	16
		-0.191	15
		-0.193	18
		-0.195 to -0.192 ^b	19
		-0.193 to -0.188 ^b	20
	139	-0.196	17
	140	-0.190	21, 22
		-0.191	4
145	-0.196	18	
	-0.197	17	
151	-0.194	17	

^a In some cases the incorrect positive sign in the reported value was replaced by the negative one.

^b dn/dc depends on the molecular weight of the polymer.

Measurements in blue light, 436 nm, are less reliable. The refractive index of 1-chloronaphthalene at this wavelength is only a little smaller than that at which the beam is totally reflected from the inclined partition of the differential refractometric cell.⁴¹

Our results are in good agreement with the reported ones at 546 nm. At 436 nm, the difference between our values (Table IV) and those reported (e.g., -0.245 at 125°C¹² and -0.275, also at 125°C²) is considerable. Since different results have been obtained for branched and linear PE in 1-chloronaphthalene, measurements in the other solvents were always carried out for one linear and one branched PE sample (Table III).

Other Solvents

Paraffin oil can be formally regarded as low-molecular-weight polyethylene. For this reason, both PE and this solvent can be expected to have close refractive index values and similar dispersions of the refractive index. The results indeed

TABLE III
Boiling Points t_b and densities ρ_t of Selected Solvents for Polyethylene and Refractive Index Increments, dn/dc , for Linear (L) and Branched (B) Polyethylenes at Temperatures t for Various Wavelengths λ_0

Solvent ^a	t_b , °C	t , °C	ρ_t , g/ml	Polymer ^b	dn/dc at λ_0 , ml/g				
					403	436	546	578	633
<i>n</i> -Decane	174	135	0.640	L	0.119	0.117	0.114	0.113	0.112
Paraffin oil ^c	—	135	0.794	B	0.122	0.120	0.118	0.117	0.116
				L	-0.001	-0.001	-0.001	-0.001	-0.001
Tetraline	208	135	0.883	B	0.001	0.001	0.001	0.001	0.001
				L	-0.091	-0.087	-0.077	-0.075	-0.074
<i>o</i> -Dichlorobenzene	180	135	1.167	B	-0.089	-0.085	-0.075	-0.073	-0.071
				L	-0.101	-0.095	-0.083	-0.080	-0.078
Bromobenzene	156	135	1.338	B	-0.099	-0.091	-0.081	-0.078	-0.076
				L	-0.107	-0.101	-0.089	-0.085	-0.083
1,2,4-Trichlorobenzene	213	135	1.316	B	-0.101	-0.095	-0.083	-0.080	-0.078
				L	-0.130	-0.125	-0.110	-0.108	-0.107
				B	-0.122	-0.117	-0.105	-0.103	-0.102

<i>p</i> -Dibromobenzene	219	135	1.777	L	-0.184	-0.179	-0.162	-0.159	-0.155
Diphenyl	255	135	0.939	B	-0.182	-0.176	-0.159	-0.157	-0.153
1-Methylnaphthalene	245	135	0.936	L	-0.209	-0.195	-0.172	-0.168	-0.163
1-Bromonaphthalene	281	135	1.374	B	-0.207	-0.192	-0.167	-0.163	-0.158
				L	-0.220	-0.206	-0.177	-0.172	-0.167
				B	-0.211	-0.199	-0.170	-0.164	-0.159
				L	e	e	-0.208	-0.207	-0.205
				B	e	e	-0.210	-0.208	-0.206
1-Dodecanol ^d	256	137	0.746	L	0.049	0.048	0.046	0.046	0.045
Diphenylmethane ^d	262	142	0.911	B	0.050	0.049	0.047	0.047	0.047
				L	-0.155	-0.146	-0.129	-0.127	-0.126
				B	-0.142	-0.135	-0.120	-0.118	-0.116
Diphenyl ^d	255	127	0.944	L	-0.215	-0.202	-0.176	-0.172	-0.166
				B	-0.212	-0.199	-0.173	-0.169	-0.165

^a The boiling points of solvents at 0.1 MPa were taken from ref. 34. The solvent densities were calculated from available data.

^b Linear polyethylene, Hizex 2200J; branched polyethylene, Bralen FA-7-15.

^c Tamson Oil 150, Mobil Oil Corp., Benelux.

^d θ solvents; θ temperatures taken from ref. 26.

^e Beyond the measuring range of the differential refractometer.

TABLE IV
Refractive Index Increments, dn/dc , for Polyethylenes in 1-Chloronaphthalene at 135°C for Various Wavelengths λ_0

Polymer	$10^{-5} M_w^a$	dn/dc^b at λ_0 , nm			
		436	546	578	633
Linear polyethylenes					
SRM 1475	0.53	-0.214	-0.193	-0.188	-0.183
Hizex 2200 J	0.88	-0.212	-0.193	-0.187	-0.183
DMDJ 5140	1.40	-0.216	-0.192	-0.187	-0.182
DMDJ 3472	1.80	-0.216	-0.191	-0.189	-0.182
Average		-0.215	-0.192	-0.188	-0.183
Branched polyethylenes					
IUPAC β	1.98	-0.213	-0.189	-0.184	-0.178
SRM 1476	2.40	-0.209	-0.188	-0.183	-0.178
Bralen FA-7-15	4.70	-0.213	-0.191	-0.185	-0.179
IUPAC α	7.80	-0.211	-0.189	-0.184	-0.178
Average		-0.212	-0.189	-0.184	-0.178

^a Molecular weights determined by light scattering in this laboratory. 1-chloronaphthalene as solvent, 135°C, 546 nm. ρ_{135} for 1-chloronaphthalene taken as 1.096 g/ml.

^b Error of determination ± 0.002 ml/g.

indicate (Table III) that paraffin oil is virtually an isorefractive solvent at all the wavelengths. This solvent could be employed with advantage, e.g., in the study of the copolymers of ethylene with monomers having a different refractive index.

Sufficiently pure tetralin is comparatively difficult to obtain. Available commercial products were of poor quality (tetralin content of 70 wt. % and less). Carefully purified tetralin (>99 wt. %) changed during measurements at elevated temperatures; its refractive index varied with time. The refractive index increments thus obtained should be regarded as approximate values.

n-Decane is one of the few solvents for which the refractive index increment of PE is positive. The results of our measurements with this solvent are at variance with reported data. All the authors^{11,15,17,21} who measured the refractive index increments of PE in *n*-decane obtained values between 0.087 and 0.099 ml/g (for temperatures between 75 and 143°C). Our values are much higher (Table III). It is also of interest that the refractive index increment of branched PE is higher than that of linear PE (Fig. 1, Table III). This difference cannot be explained as with 1-chloronaphthalene, i.e., through different partial volumes of the two polymers in solution. An obvious conclusion seems to be that both linear and branched PE may differ from each other not only in their partial specific volumes, but also in their refractive indices.

No commentary is needed for the other solvents given in Table III. For light-scattering measurements of polyethylene solutions, one may recommend as solvents 1,2,4-trichlorobenzene, *o*-dichlorobenzene, *n*-decane, 1-methylnaphthalene, diphenyl, and diphenylmethane, in addition to the usual 1-chloronaphthalene. In calculations of the light scattering constant, one should respect whether the sample is a linear or branched polymer and carry out the calculation with the corresponding refractive index increment (Table III).

Partial Specific Volume

If the partial specific volume v_P , and the refractive index of PE n_P , are evaluated from the equation

$$\frac{dn}{dc} = \bar{v}_P(n_P - n_S) \quad (1)$$

where dn/dc is the refractive index increment of PE in the given solvent (Table III) and n_S is the refractive index of this solvent at the given temperature and wavelength, it can be seen that the partial specific volume of branched PE is lower and its refractive index is higher compared with the linear sample (Fig. 2 and Table V). These conclusions should be regarded as preliminary, because the refractive indices of solvents at 135°C and at 546 nm were calculated from molar refractions according to the Lorenz-Lorentz equation and may be subject to a certain error. Figure 2 also shows that our values of the refractive index increment of PE in *n*-decane depart from the linear dependence given by eq. (1), while the reported data (Table II) satisfy this dependence. No explanation for this finding can be offered. Also, the refractive index increment of PE in 1-bromonaphthalene departs somewhat; measurements in this solvent with a high re-

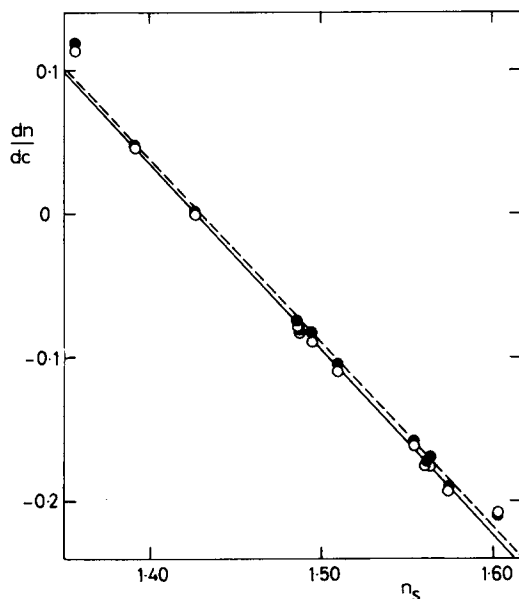


Fig. 2. The dependence of the refractive index increment, dn/dc , in ml/g, on the refractive index of the solvent n_S at $\lambda_0 = 546$ nm, $t = 135^\circ\text{C}$: O, linear PE Hizex 2200 J; ●, branched PE Bralen FA-7-15.

TABLE V
Partial Specific Volumes \bar{v}_P , and Refractive Indices n_P , of Polyethylene at 135°C and 546 nm
Calculated from Eq. (1)

	Linear PE	Branched PE
\bar{v}_P , ml/g	1.295 ± 0.012	1.280 ± 0.017
n_P	1.426	1.428

fractive index lie at the limit of applicability of the differential refractometer and may therefore be less reliable.

The validity of eq. (1) is generally restricted to low values of the refractive index increments⁴²; in the range of higher dn/dc , the application may fail. The evaluation of data by more sophisticated procedures⁴² does not lead to essentially different conclusions. The lack of data on the partial specific volumes of PE does not make any comparison with our results possible. (For linear PE, the following values are reported: 1.264 ml/g in 1-chloronaphthalene at 110°C and 1.28 ml/g in diphenyl at 123°C⁴³; 1.29 ml/g in 1-chloronaphthalene at 135°C and 1.30 ml/g in 1,2,4-trichlorobenzene at the same temperature.⁴⁴)

The solution properties of polyethylene and of some other polyolefins do not seem to have been adequately described so far. Due to the prime importance of these polymers, a thorough investigation is most desirable.

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