Light Scattering from Polyethylene Solutions

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Synopsis

The technique of measurement of light scattering from dilute polyethylene (PE) solutions is reviewed. Conditions are discussed under which various PE samples can be characterized. The choice of the solvent affects the accuracy of molecular weight determination. It appears that measurement with thermodynamically poorer solvents yields results subjected to a smaller error. The interpretation of light scattering data is often disturbed by the presence of supermolecular structures in PE solutions. The effect of reprecipitation on the behavior of PE samples is described. The measurements were mostly performed on PE standards and on the Czechoslovak sample Liten Macro.

INTRODUCTION

Polyethylene (PE) is one of the most important industrial polymers. Unlike many other macromolecular compounds of comparable importance, the methods of PE characterization, and in particular the investigation of its solutions properties, have not been treated in sufficient detail.

Light scattering from dilute polymer solutions is the most important method for the absolute determination of the weight average molecular weight M_w. Moreover, the light scattering measurements provide also some other data on the polymers involved, e.g., on the thermodynamic interaction between the polymer and solvent (second virial coefficient A_2), or on the dimensions of polymer chains in solution (z-average radius of gyration, $\langle R^2 \rangle_z^{1/2}$).

Problems involved in the light scattering measurements can be divided into several basic groups:

Choice of the Temperature of Measurement and of Suitable Solvents

The temperature at which PE dissolves differs for various samples. It depends on the molecular weight of PE and its degree of branching and on the thermodynamic quality of the solvent. In the early studies, there was a tendency to work at the lowest possible temperatures, where the samples were still soluble[1-5] (approx. from 80°C upwards) because any rise in temperature means also increased requirements on the experimental equipment. Since, at such temperatures, the existence of, e.g., associates or residues of crystalline structures cannot be completely ruled out,[2] contemporary studies are usually carried out at temperatures between 130°C and 140°C, or even at higher temperatures, i.e., above the melting point of crystalline PE. The temperature most frequently used in light scattering measurements is 135°C.

The choice of solvents is limited. In the overwhelming majority of papers, 1-chloronaphthalene (CN)[1,2,6–37] has been used as the solvent in light scattering measurements followed by 1,2,4-trichlorobenzene (TCB)[22,38,39] and tetralin.[3–8,27] Exceptionally, the light scattering measurements were also carried out in chlorobenzene,[27] o-dichlorobenzene,[3,27] n-decane,[40] and biphenyl.[27,41] In other methods of PE characterization, further solvents have been used, in addition to those already mentioned. Thus, e.g., diphenylmethane,[42] diphenyl ether,[9,42] decalin,[9] and higher aliphatic alcohols were used in viscometry, 1-methylnaphthalene was employed in GPC,[43] 1-bromonaphthalene was the solvent in sedimentation analysis,[44] and xylene was used in osmometry.[5] This list is by no means complete. Many of the solvents quoted above are utilized in several methods simultaneously (e.g., in addition to light scattering,[22,38,39] TCB is employed in viscometry, osmometry, and GPC,[29,45–49] diphenyl ether is utilized in, e.g., the investigation of the phase separation behavior,[50,51] etc.).

In recent studies, especially those regarding light scattering, the choice of solvents is restricted almost exclusively to 1-chloronaphthalene and 1,2,4-trichlorobenzene. Tetralin has been completely abandoned. Also, there is a tendency to use the same solvent in various methods of the investigation of solution properties so as to make the results obtained by the individual methods easier to compare.

Refractive Index Increments

For the evaluation of light scattering data, the knowledge of the refractive index increment of the polymer in a given solvent at a chosen temperature and wavelength is required. This quantity is usually determined at elevated temperatures[52] with modified commercial differential refractometers. The refractometric cells are heated either with a heating element incorporated in the cell housing[53,54] or with liquid from the thermostat; in the latter case, the heat transfer between the thermostating jacket and the cell is mediated through a suitable immersion liquid.[15,55] It is assumed that the calibration constant of the apparatus is temperature-independent within the limits of experimental error.[53] This assumption seems to be justified.[52]

Another method frequently used to estimate the refractive index increments is their calculation,[8,53,56] e.g., from molar refractions of solvents. The values thus obtained, however, cannot match the experimental ones. The refractive index increments for PE in different solvents have been collected[57,58] and critically analyzed.[52] An unpronounced dependence of the refractive index increments on the molecular weight[59] of PE and on its branching[52] have also been observed.

Clarification of Polyethylene Solutions

One of the methods used in the clarification of solutions is their filtration. The filter pores must be large enough not to trap high molecular weight fractions of the polymer (which, because of the usually broad molecular weight distribution of PE, are often present in a significant amount) and, at the same time, small

enough to remove foreign particles. The application of various filters has been reported (membrane, mainly Millipore,[9,11,17,35] or of other origin,[36] porcelain,[1,10,14] sintered glass filters,[3–5,15,60] sand columns,[13,37] and others), having a broad range of porosities[3,12] (from 5 μm down to 0.1 μm). A decrease in the filter permeability or even filter clogging during filtration have often been observed,[1,3,10,60] which suggests undesirable fractionation of the polymer on the filter.

The filtration apparatus is maintained at elevated temperature by a suitable jacket with circulating liquid from the thermostat[8] or a jacket with direct electric heating.[9,16] In some cases, centrifugation at higher temperature was used in the clarification.[4,7,25] The observed sedimentation of the polymer also indicates its potential fractionation.

Light Scattering Measurements

Commercial photometers (Brice-Phoenix,[2,4,5,10,13,15,21,60] Sofica[3,9,17,18]) have been adapted for light scattering measurements at elevated temperatures, or devices of special construction have been developed.[16,55] In devices of the Sofica type, a suitable immersion bath for the cell is to be found. The refractive index of the immersion should be close to that of the cell glass to minimize the reflections; e.g., 1,2,4-trichlorobenzene[25] and silicone oil[18,34,35] were used.

The commercial photometer FICA 50 (manufactured by Fica, France) has been designed for light scattering measurements at elevated temperatures. A high-temperature cell suited for measurements of PE solutions is also supplied as an accessory to the low-angle laser light scattering photometer (LALLSP), KMX-6 (produced by Chromatix Inc., USA). The apparatus has already been successfully used in the molecular weight determination of PE.[38,39]

Polyethylene Standards

Standard samples play an important role in the characterization of PE. As a rule, suitably chosen and adequately described industrial PE samples or their fractions are used for this purpose. Table I summarizes data reported on PE standards (Standard Reference Materials) distributed by the National Bureau of Standards, U.S.A., and on PE samples, well characterized by the IUPAC Working Party on Molecular Characterization of Commercial Polymers.[22]

Usually, the molecular weight determination does not involve any major problems and the results obtained by various authors are in good agreement (cf., e.g., SRM 1475, Table I). If, however, the sample is of more complex nature, as SRM 1476, which contains a small amount of a fraction of very high molecular weight,[29] the results obtained by various authors are inconsistent (Table I).

This paper is mainly concerned with the accuracy of the molecular weight determinations of PE by light scattering with respect to the solvent used. Some phenomena which impede the interpretation of data and are related to the often complex nature of industrial PE samples are also mentioned. Samples of linear PE are the main object of this paper, while branched PE is dealt with only marginally.

$M_w \times 10^{-3}$ (g/mol)	Method[a]	Solvent[b]	Reference
SRM 1475 (linear PE, whole polymer)			
52.5 ± 1.8	LS	CN	31
52.0 ± 2.0	LS	CN	32
52	LS	CN	35
52.4	LS	CN	36
54.6 ± 1.1	LALLSP	TCB	38, 39
50.5	LALLSP/GPC	TCB	39
55.8	LALLSP/GPC	TCB	38
53.0	GPC	TCB	33
55.9	GPC	TCB	61
SRM 1476 (branched PE, whole polymer)			
140	LS	CN	29
221 ± 9	LALLSP	TCB	38
100.4	LALLSP/GPC	TCB	38
$91 - 105$	GPC	TCB	29
SRM 1482 (linear PE, narrow fraction)			
13.6 ± 0.13	LS	CN	34
SRM 1483 (linear PE, narrow fraction)			
32.1 ± 1.6	LS	CN	34
32.6 ± 0.7	LALLSP	TCB	38
SRM 1484 (linear PE, narrow fraction)			
119.6 ± 2.2	LS	CN	34
118.0 ± 3.0	LALLSP	TCB	38
109.5	LALLSP/GPC	TCB	38
IUPAC α (branched PE, whole polymer)			
$774 \pm ^{176c}_{134}$	LS	CN, TCB	22
$920 \pm ^{240}_{263}$	GPC	TCB, DCB	22
IUPAC β (branched PE, whole polymer)			
$191 \pm ^{57c}_{48}$	LS	CN, TCB	22
$213 \pm ^{28}_{43}$	GPC	TCB, DCB	22

[a] LS, conventional light scattering (e.g., Sofica 42.000, Fica 50); LALLSP, low-angle laser light scattering photometer (KMX-6); GPC, gel permeation chromatography.

[b] CN, 1-chloronaphthalene; TCB, 1,2,4-trichlorobenzene; DCB, o-dichlorobenzene.

[c] Superscript and subscript mean the maximum deviation to the higher and to the lower sides, respectively.

EXPERIMENTAL

Polymer Samples

Of the NBS polyethylene standards, only SRM 1475 and SRM 1476 have been studied by light scattering. IUPAC samples α and β, characterized in 1977 under the scheme of the IUPAC Working Party on Molecular Characterization of Commercial Polymers, were also measured.

Since we considered useful to have a major amount of well-characterized polyethylene for experimental purposes, we chose an industrial PE sample of Czechoslovak origin, Liten 22 402 (denoted also as Liten MB 62, ČSSP Chemical Works, Litvínov, Czechoslovakia). According to manufacturer's information, this sample is an injection molding type of linear polyethylene with basic addi-

tivation and narrow molecular weight distribution. In this study, the sample is referred to as Liten Macro, in order to distinguish it from other batches of the same PE type which may possess somewhat different characteristics.

Other industrial PE samples, specified in the text, were also used in the measurement. Unless stated otherwise, granulated samples were employed in the preparation of solutions.

Refractive Index Increments

Refractive index increments were determined at a chosen temperature and wavelength 546 nm with a modified differential refractometer Brice-Phoenix, model BP-2000-V, as described in detail earlier.[52] Values given in Table II were used in the evaluation of the light scattering data.

Preparation of Solutions and Their Clarification

Both PE sample and solvents were weighted into glass ampoules. The solvents (Fluka, Switzerland) were distilled on a laboratory column and their purity (>99%) was checked by gas chromatography. The ampoules were sealed and placed in an oil bath at 145°C under stirring. The agitation was continued for about an additional hour after the macroscopic dissolution of the sample (usually less than 3 h). The polymer concentration (g/mL) was calculated from weighed amounts of the polymer and solvent, and from their densities at the temperature of measurement; the solvent densities were taken from literature.[52]

The solutions were clarified by filtration through a G4 sintered glass filter (VEB Jenaer Glasswork, GDR), with porosity ca. 3 μm, sealed into a double-jacket all-glass construction with circulating oil heated to approximately 140°C. If needed, the solutions were forced through the filter by nitrogen pressure up to 10 kPA chosen so as to make the rate of filtration about 0.03 mL/s (at the filter diameter 50 mm); at higher rates of filtration the clarification is usually less perfect. The cells for light scattering measurements were cleaned and at the same time heated with condensing xylene vapors. The filter was cleaned with boiling xylene after each PE sample, and with a mixture of concentrated sulphuric acid with 30% hydrogen peroxide (vol 1:1) as needed.

Light Scattering Measurements

Light scattering was measured with the commercial apparatus FICA 50 using unpolarized primary beam of wavelength 546 nm, in the angular range 30–150° and at 135°C (142°C in diphenylmethane). Paraffin Tamson Oil 150 (Mobil

TABLE II
Refractive Index Increments of Polyethylene, dn/dc, for $\lambda_0 = 546$ nm

| Solvent | t (°C) | dn/dc (mL/g) | | |
		Liten Macro	Linear PE[a]	Branched PE[a]
1,2,4-Trichlorobenzene	135	−0.111	−0.110	−0.105
1-Chloronaphthalene	135	−0.192	−0.192	−0.189
Diphenylmethane	142	−0.126	−0.129	−0.120

[a] Taken from Ref. 52.

Oil Corp., Benelux) was filtered through a G4 filter and then used as immersion liquid in the apparatus. The immersion bath was kept under argon during the measurement to prevent oxidation.

The apparatus was calibrated with benzene as a primary standard. The Rayleigh ratio for benzene was taken 16.3×10^{-6} cm^{-1} (Refs. 62 and 63) at 546 nm and 25°C. Since the benzene standard cannot be employed at higher temperatures, a working glass standard was used. The intensity of light scattered from this standard remained constant between 25°C and 150°C within the limits of experimental error (cf. also Ref. 53). Experimental data are represented below in the usual plot Kc/R_θ vs. $\sin^2(\theta/2) + kc$ (K is the optical constant, R_θ is the Rayleigh ratio, θ is the angle of observation, c is the polymer concentration, and k is an arbitrary constant). To make the plots better organized, we chose[64] $k < 0$.

RESULTS AND DISCUSSION

Polyethylene Standards

The molecular weights of the NBS standards SRM 1475 and SRM 1476 and of IUPAC samples determined independently with two different solvents (Table III, Fig. 1) are in fair agreement with the reported data (Table I).

The fact that, for standard SRM 1475, the molecular weights determined by most authors agree very well with each other is not surprising. The methods of measurement and evaluation of data are usually chosen so as to make the experimental and reported values coincide. The agreement is to some extent regarded as a criterion of "correctness" of the measurement, and therefore we feel that the set of reported data may not quite reflect the actual variance of the data. For samples the molecular weight of which has not been declared in advance, the scatter of data obtained in different laboratories is higher, as expected (Table I, IUPAC samples).

In the case of the SRM 1476, which contains a small fraction of particles of a very high molecular weight, our M_w value is closer to that obtained by light scattering by MacRury and McConnell[38] (Table I) than to that given by NBS. The cause of the conflicting results lies in the different ways of sample preparation for light scattering measurements. The high molecular weight fractions are removed to various degree during the clarification. The discrepancies are also partly connected with the mode of extrapolation of the angular dependences

TABLE III
Weight Average Molecular Weights M_w of PE Standards Determined by Light Scattering in the Authors' Laboratory

Polymer	$M_w \times 10^{-3}$ (g/mol)	
	TCB	CN
SRM 1475	50	53
SRM 1476	215	254
IUPAC α	618 (> 1000)[a]	613 (784)
IUPAC β	—	176 (198)

[a] For IUPAC samples, quadratic extrapolation of the concentration dependence of Kc/R_θ was used; values resulting from linear extrapolation are given in parentheses.
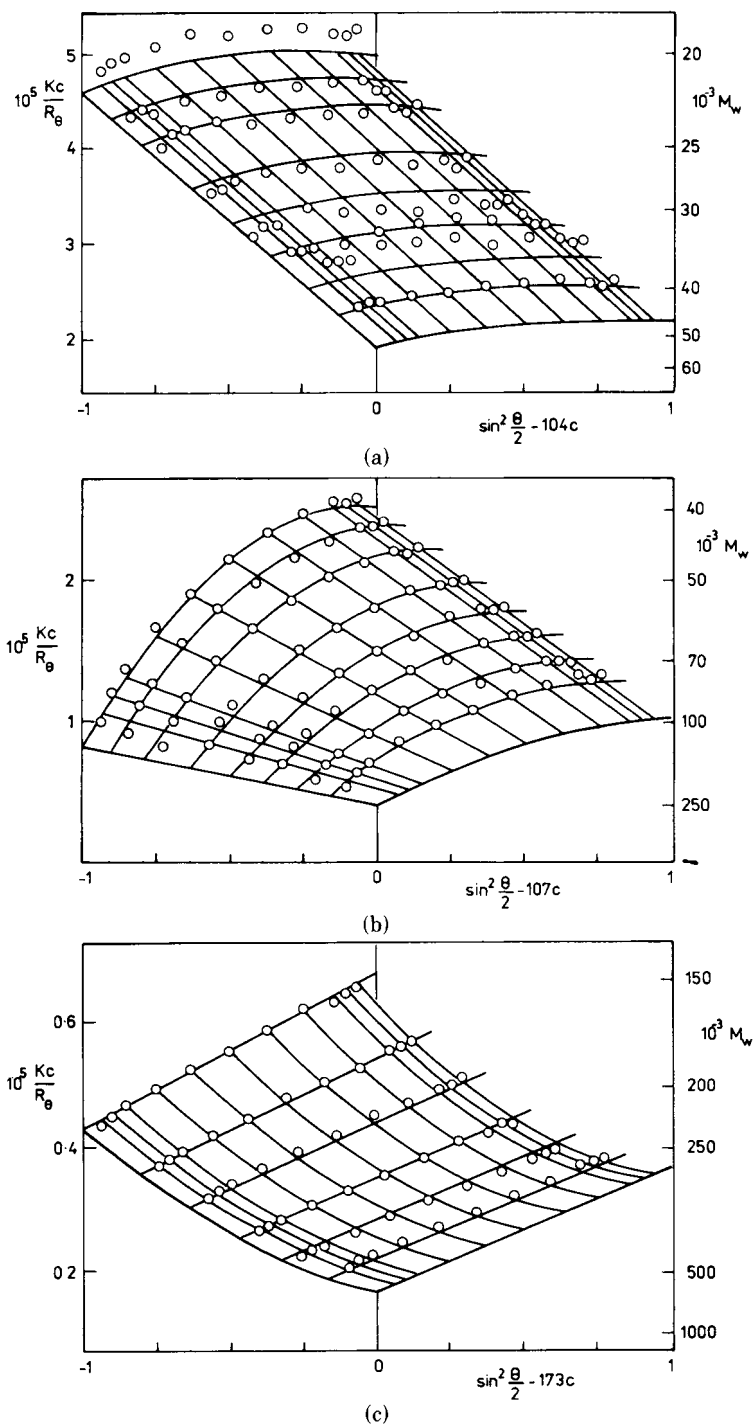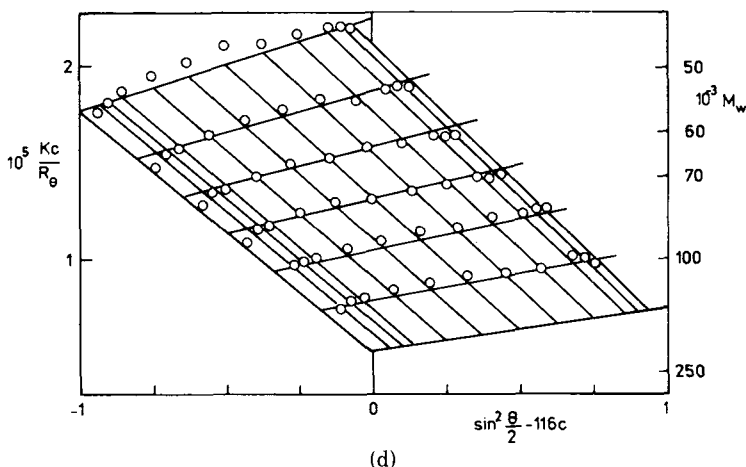
Fig. 1. Zimm plots for PE standards in 1-chloronaphthalene at 135°C: (a) NBS 1475, (b) NBS 1476, (c) IUPAC α, (d) IUPAC β.

(d)

Fig. 1. (*Continued from previous page.*)

of light scattering. The M_w values given at Table III were calculated assuming a quadratic character of the angular dependences. Figure 1(b) indicates that the curvature of the angular dependences is larger than that represented by the plotted curve. Hence, the true molecular weight is probably still higher than the result given in Table III.

The observed differences in the molecular weight determination of the IUPAC samples and the problem of extrapolation of the concentration dependences of light scattering are discussed below.

Some Problems of Data Evaluation

In the determination of molecular weights of polyethylene, we have encountered several problems. One of them consists in the extrapolation in the Zimm plots for polymer solutions in very good solvents. This problem has a general character and is not specific of polyethylene; however, with this polymer it becomes crucial. Another set of problems is related to the complex nature of PE. Here, only the effect of reprecipitation of the sample on the resulting molecular weight will be examined.

### Extrapolation of the Zimm Plots

At elevated temperatures, both 1-chloronaphthalene (CN) and 1,2,4-trichlorobenzene (TCB) are thermodynamically very good solvents for PE. In the usual range of molecular weights, the second virial coefficients A_2 assume in these solvents values of the order of 10^{-3} mol·mL/g^2, thus higher by 1 or 2 orders of magnitude compared with the common polymer–solvent systems. As shown by statistical analysis,[65] the error of the molecular weight determination steeply increases at high A_2 values. The error in the molecular weight determination by light scattering is typically about 5% for A_2 of an order from 10^{-5} to 10^{-4} mol·mL/g^2. If A_2 is of a higher order of magnitude, errors counted in 10's percent are no exception in the determined M_w value.

In order to demonstrate experimentally the conclusions of this analysis, we determined the molecular weight of Liten Macro (Table IV) independently four
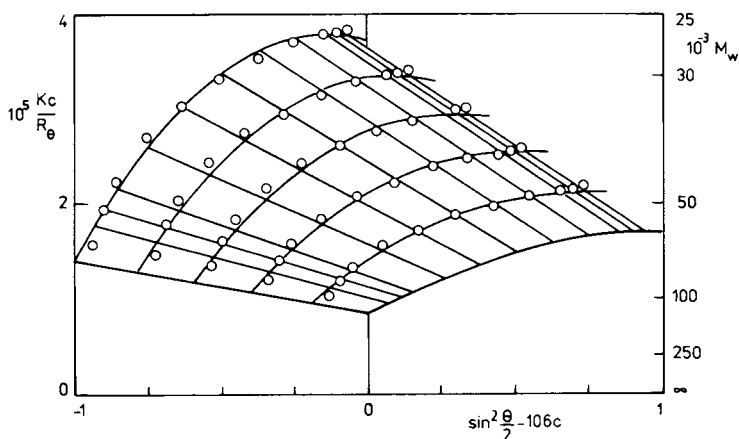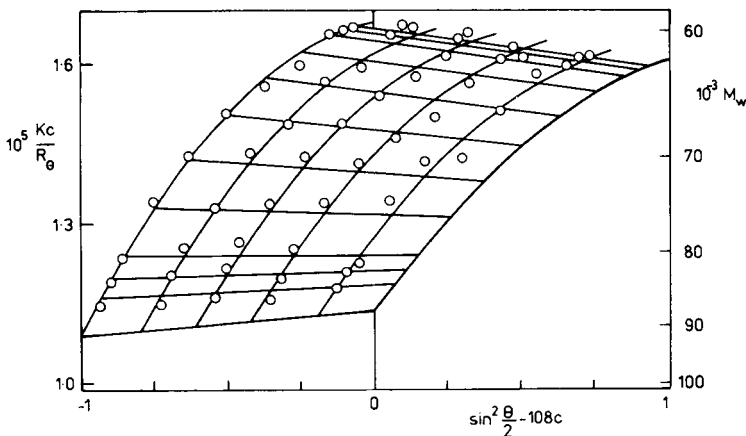
Fig. 2. Zimm plots for Liten Macro (a) in 1-chloronaphthalene at 135°C and (b) in diphenyl-methane at 142°C.

times in each of the solvents used, viz., TCB, CN [Fig. 2(a)] and diphenylmethane DPM [Fig. 2(b)]. According to the literature data,[42] the latter solvent is a θ-solvent for polyethylene at 142.2°C, in general agreement with our results (Table IV). Table V also presents the molecular weight averages of Liten Macro obtained by methods other than light scattering. Molecular weight $M_w = 88000$ g/mol seems to be an acceptable average for Liten Macro.

Although the results (Table IV) cannot be regarded as statistically conclusive, they still exhibit the expected trend. In our case, the standard deviation in the M_w determination in TCB was about 33%, in CN about 12%, and in DPM some 4%. These conclusions can be intuitively seen also in Figure 3, where the results of measurements in TCB and DPM are plotted together. The ordinate of the intercept on the Kc/R_θ axis (proportional to $1/M_w$) in the case of TCB will sensitively react to changes in the positions of the experimental points in the Zimm plot. For instance, the angular dependence corresponding to the highest polymer concentration in TCB exhibits a characteristic curvature indicating the presence
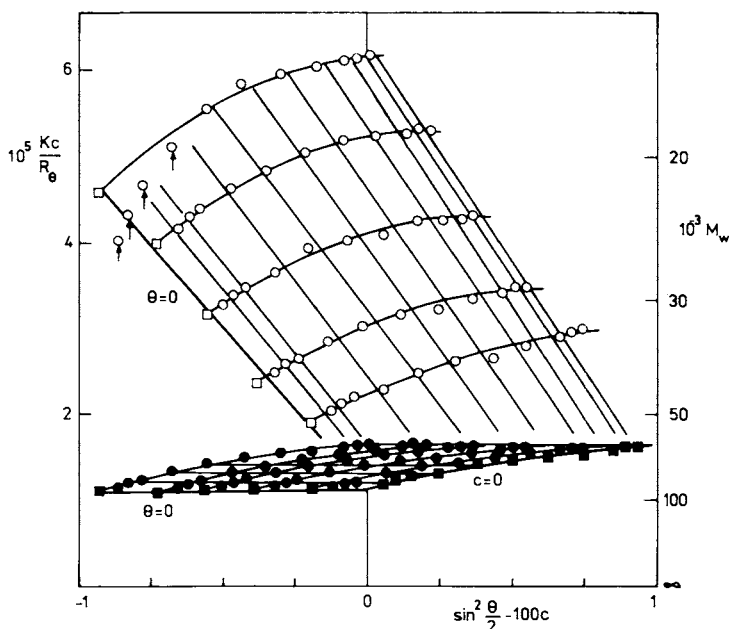
Fig. 3. Superimposed Zimm plots for Liten Macro in 1,2,4-trichlorobenzene (O, □) and diphen-ylmethane (●, ■). For the explanation of the arrows see text.

of impurities (points denoted with arrows in Fig. 3). When all the points are considered in the calculation, $M_w = 68,000$ is obtained. If, more correctly, the points denoted with arrows are disregarded, $M_w = 91,000$. The example demonstrates that the molecular weight thus obtained is strongly dependent on the subjective approach to the data treatment and more sensitive to the experimental procedure used (i.e., e.g., to the temperature fluctuations, various degrees of purity of solutions, accidental concentration changes caused by evaporation of the solvent, and the like) than usual. If thermodynamically poorer solvents are used, such as DPM [Figs. 2(b) and 3], the situation becomes much more favorable.

The high values of the second virial coefficients bring along also the undesired curvature of the concentration dependences of light scattering owing to the not negligible contribution of higher terms of the virial expansion. Increasing curvature of the concentration dependences is met mainly with high molecular weight samples ($M_w > 300,000$ g/mol). There is a wide choice of extrapolation procedures, ranging from purely empirical to statistically sophisticated ones, and the molecular weight values obtained by various extrapolation procedures may differ considerably. As can be demonstrated on the IUPAC α sample [Fig. 1(c), Table III], the curvature of the concentration dependences should be respected. With linear extrapolation, we usually arrive at significantly different M_w values in different solvents (Table III); on the other hand, a simple quadratic extrapolation largely improves the coincidence of molecular weights in both cases under examination.

To sum up, thermodynamically very good solvents (CN, TCB) bring forth trouble in the molecular weight determination of PE by light scattering. The difficulties may be avoided by using thermodynamically poorer solvents (e.g.,

TABLE IV

Weight Average Molecular Weights M_w, Second Virial Coefficients A_2, and z-Average Radii of Gyration, $\langle R^2 \rangle_z^{1/2}$, of Polyethylene Liten Macro Obtained by Light Scattering in Various Solvents

Solvent	t (°C)	Expt no[a]	$M_w \times 10^{-3}$ (g/mol)	$A_2 \times 10^4$ (mol·mL/g²)	$\langle R^2 \rangle_z^{1/2}$ (nm)
1,2,4-Trichlorobenzene	135	1	55	21.0	27
		2*	91	19.0	51
		3	99	18.8	90
		4	131	23.5	38
		Average	94 ± 31	20.6 ± 2.2	51 ± 27
1-Chloronaphthalene	135	1	141	5.6	75
		2	113	3.9	70
		3	107	3.5	66
		4*	120	3.0	69
		Average	120 ± 15	4.0 ± 1.1	70 ± 4
Diphenylmethane	142	1	82	0.93	37
		2*	88	−0.25	40
		3	89	−0.13	48
		4	87	0.04	38
		Average	87 ± 3	0.15 ± 0.53	41 ± 5

[a] The results of experiments denoted by an asterisk are also presented in the figures.

TABLE V
Molecular Weight Averages, M_n, M_w, and M_z, of Liten Macro Obtained by Membrane
Osmometry and Gel Permeation Chromatography

Method	Solvent	t (°C)	$10^{-3} \times$		
			M_n (g/mol)	M_w (g/mol)	M_z (g/mol)
Osmometry	p-Xylene	95	25	—	—
GPC	o-DCB	135	13	88	—
GPC	TCB	135	11	90	530

DPM). The use of CN and TCB in the light scattering measurements has become quite common. When various PE samples are compared on a merely relative basis (which is often the case in industrial laboratories), no serious objections can be raised against these solvents. On the other hand, studies requiring exact knowledge of the absolute values of molecular weights M_w (e.g., in the determination of constants of the Mark–Houwink equation, unperturbed dimensions, etc.) would call for thoughtful choice of a suitable solvent.

Effect of Reprecipitation of the Sample

Table IV, summarizing the molecular weights of Liten Macro determined in various solvents, seems to indicate that the molecular weight in CN is somewhat higher than in the other solvents (M_w = 120,000 in CN compared with 87,000 in DPM). Figure 2(a) shows that even the quadratic extrapolation of angular dependences does not adequately fit the experimental data. By using, e.g., a hyperbolic extrapolation of angular dependences,[66] which reflects the experimental data much more adequately, we obtain M_w = 188,000; manual graphical extrapolation can even yield infinite molecular weight [Fig. 4(a)]. A similar type of the Zimm plot would be expected for a sample containing a small amount of particles of very high molecular weight. In CN, for instance, such particles could arise by association of PE macromolecules. This hypothesis has been suggested earlier[2,6] in order to elucidate differences in molecular weights obtained in various solvents (molecular weights determined in CN were always higher than in other solvents). This explanation alone is unsatisfactory, because many other PE samples do not exhibit such behavior.[8]

TABLE VI
Weight Average Molecular Weights M_w of the Original and Reprecipitated PE Samples
Determined by Light Scattering

Sample	Solvent	t (°C)	$M_w \times 10^{-3}$ (g/mol)		Catalytic system
			Original	Reprecip.	
Liten Macro	CN	135	1.20	0.92	UCC[a]
	DPM	142	0.87	0.82	
DMDJ 3472	CN	135	4.34	1.92	UCC
	DPM	142	1.63	1.55	
DMDS 3190	CN	135	4.91	2.31	UCC
Hizex 2200J	CN	135	0.88	0.98	Ziegler
Hostalen GF 7740	CN	135	1.75	2.20	Ziegler

[a] Union Carbide Corp.
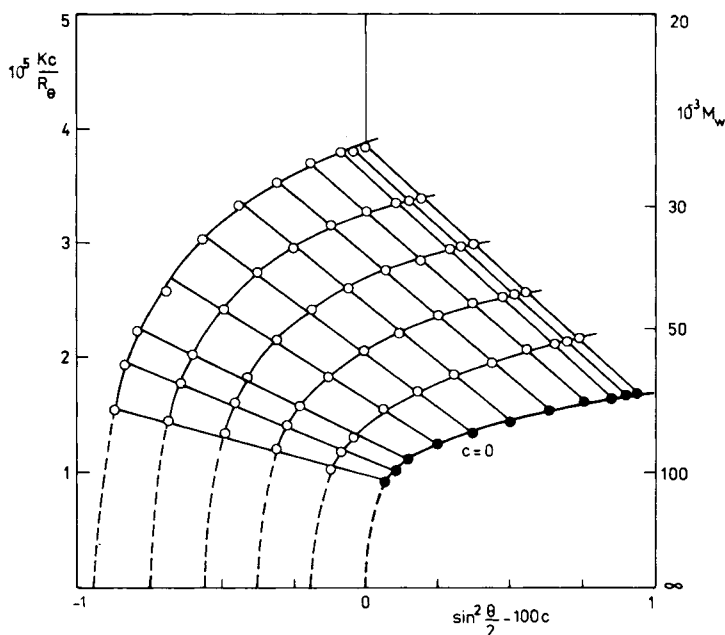
(a)
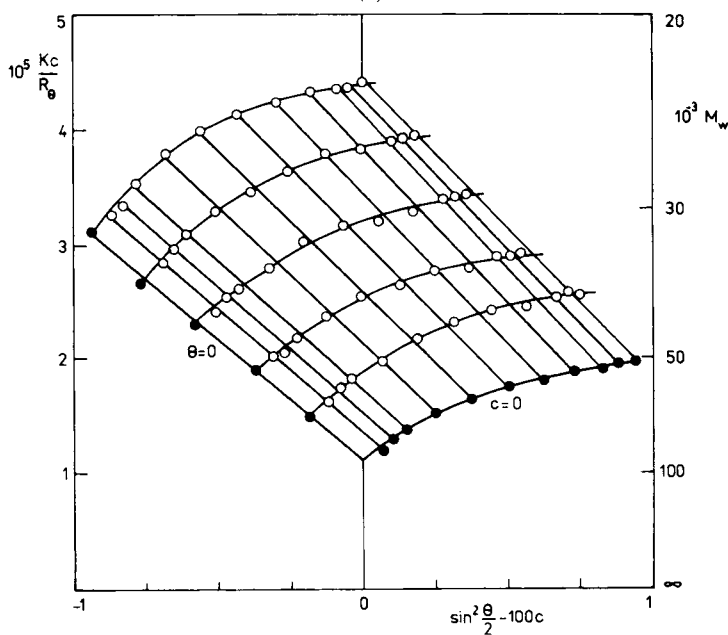
(b)

Fig. 4. Zimm plot for Liten Macro in 1-chloronaphthalene at 135°C: (a) the original sample (an example of manual graphical extrapolation); (b) the reprecipitated sample.

If Liten Macro is reprecipitated from xylene solution into methanol and the molecular weight is determined after isolation and drying, the Zimm plot obtained is both quantitatively and qualitatively different [Fig. 4(b)]. The angular dependences of light scattering are less curved and virtually parallel with each other. The molecular weight of the reprecipitated sample is lower and much

closer to the results obtained with the other solvents (Tables IV and VI). The second virial coefficient increases to $A_2 = 1.05 \times 10^{-3}$ mol·mL/g^2, in accordance with the assumed very good thermodynamic quality of 1-chloronaphthalene as solvent for PE.

Similar and even more pronounced behavior has also been observed with other industrial linear PE samples, such as DMDJ 3472. The molecular weight of the nonreprecipitated polymer in CN (but also in 1-methylnaphthalene and 1-bromonaphthalene) was more than double that determined in other solvents (TCB, DPM, tetralin, bromobenzene, o-dichlorobenzene); after reprecipitation of the samples, no differences of this kind were observed (Table VI). Chiang[13] also described clogging of the filter during the clarification of PE solutions in CN, whereas decaline solutions could be readily filtered. Filtration of PE solution through a sand column followed by precipitation of the polymer was also recommended as a part of the clarification procedure.[13]

The decrease in molecular weight occurring after reprecipitation of the sample has been observed only with polyethylenes produced on chromium type catalytic systems on silica support. One potential explanation of the effect could be that these polymers contain particles in which the macromolecular chains are physically or chemically bound on the residues of the catalytic sites. This bond survives in, e.g., 1-halogenonaphthalenes, but is destroyed in other solvents or after reprecipitation into methanol. Some technologies of PE production include the catalyst removal from the polymer and some do not. Therefore, reprecipitated PE may or may not exhibit a change in its molecular weight. Analytical determination of catalytic residues in original and reprecipitated samples showed, however, no correlation between the amount of these residues and the decrease of molecular weigh on reprecipitation. With polyethylenes prepared with the Ziegler catalysts, the molecular weight seems to increase slightly after reprecipitation (virtually within the limits of experimental error, Table VI). This may partly be due to the loss of a part of the low molecular weight fraction in this operation. No change in molecular weight after reprecipitation was observed with the SRM 1475 sample.[36]

With industrial samples, several complicating effects may operate simultaneously. The assumed presence of the polymer bound on residues of the catalytic sites may be accompanied by the presence of chemically crosslinked microgel, etc. Although a decrease in molecular weight was observed with some samples after reprecipitation, the angular dependences of light scattering remained curved (unlike Liten Macro), though less than with the corresponding nonreprecipitated samples.

In this paragraph, we merely tried to demonstrate, along with the complex solution behavior of industrial PE samples, one of many possible effects which may be met in practice, and to emphasize certain caution which should be exercised in the evaluation and interpretation of the light scattering data.

Note: A sample of linear polyethylene Liten Macro is available gratis on request.

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