ADVANCES IN CLASSICAL LIGHT SCATTERING
FROM POLYMER SOLUTIONS

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Abstract - The following recent developments in and
applications of the classical light scattering from polymer
solutions are briefly reviewed: Light scattering photometers;
characterization of important polymers; combination of light
scattering with other methods; characterization of the degree
of branching, particle shape, aggregates, microgels,
copolymers, polyelectrolytes, and DNA; thermodynamics of
concentrated solutions; solutions of polymer mixtures;
interactions in polymer solutions; kinetic measurements;
depolarization of scattered light. Some topical problems of
the method are discussed, viz. interpretation of curved
angular dependences of Kc/R_θ on $\sin^2(\theta/2)$, coupling of light
scattering with GPC, and some frequent artefacts.

INTRODUCTION

In this review, only the classical elastic light scattering from polymer
solutions is dealt with, in which all information is inferred from the total
intensity of scattered light, regardless of some more subtle properties of
the scattered light due to the dynamics of the scattering system. The
investigation of these latter properties, e.g. spectral distribution of
scattered light, yielding information on various types of motion in the
scattering system, requires different methical approach; it has developed
to an autonomous branch of light scattering and is not included.

The elastic light scattering from dilute polymer solutions is one of the few
absolute methods, with rigorous theoretical basis, for the determination of
such fundamental molecular parameters of polymers as weight average molecular
weight, z-average radius of gyration, and the second virial coefficient. In
routine molecular weight determinations, viscometry and gel permeation
chromatography do preponderate over the absolute methods but, owing to the
necessity of calibration, the absolute methods are indispensable and light
scattering is, for a number of reasons, the most widely used one.

In addition to the three above fundamental molecular parameters, light
scattering yields, in particular cases, important information on the
structure of polymers, thermodynamics, interactions, kinetics, etc., of the
scattering systems and in a number of applications is, in fact, the only
method available.

The present paper intends to inform generally interested readers about some
recent developments, applications, and topical problems in the field of
classical light scattering from polymer solutions. Therefore, the topics are
dealt with in a purely qualitative manner. After a brief enumerative review
of some major accomplishments of the method in the past decade or so, a few
selected questions are discussed in more detail.

RECENT DEVELOPMENTS AND APPLICATIONS

In the following, the given references are meant merely as recent examples
expanding the point under consideration and should by no means be regarded
as an exhaustive list of relevant papers.

Advances in the classical light scattering from polymer solutions have
repeatedly been surveyed in competent reviews by Huglin (1-3). The light
scattering characterization of industrially important polymers has been
treated by Yearsley (4). In references 1 and 2 extensive lists of important
papers can be found.

Commercial instruments
The situation with commercial light scattering photometers has been
developing somewhat annoyingly. The production of the well-tried Fica
instruments, both of the classical Model 42000 and of its advanced version
Model 50, has reportedly been stopped. The low angle laser light scattering
photometer KMX-6 (Ref. 5), with a fundamentally new optical design and
a number of attractive features, has been marketed successfully since several
years. The experience with this apparatus hitherto accumulated in different
laboratories, including the author´s own, is very satisfactory in molecular
weight determinations. Its low angle version does not, however, cover
an angular range large enough for reliable determination of the radius of
gyration of the scattering particles. The announced wide angle accessory for
KMX-6, enabling the angular dependences of the scattering intensity to be
measured, is not on the market yet. Thus, a gap may appear in the capacity of
the commercially available light scattering photometers.

Adaptation and new design of photometers
A number of adaptations improving the performance of commercial light
scattering photometers have been suggested (e.g., Ref. 6-8). Some authors
prefer homemade photometers tailored to meet their specific needs (Ref. 4,
9-12). A noteworthy apparatus for continuous measurement of the angular
dependence of light scattered from systems changing their scattering power in
time has been developed by Morris et al. (Ref. 12). This photometer can
collect and store 120 complete angular dependences between 20 and 160° in one
minute and is thus suitable for studies of the kinetics of processes
progressing in time intervals longer than a few seconds.

The conventional light sources are widely being replaced by lasers, in both
commercial and homemade photometers (Ref. 8-13). The lasers simplify
considerably the optical system. The modification of the much used apparatus
Fica 42000 with a gas laser source has been described in detail by Millaud
and Strazielle (8). He-Ne lasers with red light of wavelength 633 nm are
employed most frequently (Ref. 5, 8, 11, 13). The application of a He-Ne
laser operating at a near infrared wavelength of 1086 nm makes lower values
of the ratio $\sin(\theta_{min}/2)/\lambda$ (θ_{min} being the minimum angle of measurement)
experimentally available, which improves the precision of the determination
of molecular weights and radii of gyration of particles with large dimensions
(Ref. 10). The considerably more expensive lasers with adjustable wavelength
solve the problem if systems absorbing light at different wavelengths, such
as suspensions of many types of biological particles, are to be studied
(Ref. 12).

Industrially important polymers
The absolute determination by light scattering of the weight average molecular
weight of some of the industrially most important polymers, such as poly-
olefins, poly(vinyl chloride), polyamides, etc., is connected with
experimental problems and traps in the interpretation of data. The main
source of trouble is the presence of small amounts of large supermolecular
structures in solutions of these polymers. The big particles increase
considerably the scattering intensity, particularly at small angles of
measurement.

With polyolefins, the difficulty is overcome by heating the solutions above
or close to the melting point of the polymer and by performing all the
clarification procedures and the proper measurement at rather high
temperatures, between 130 and 145°C, an obvious nuisance for the
experimenter (Ref. 14-17).

In the case of poly(vinyl chloride), the ability of syndiotactic sequences
longer than a critical length to tie many macromolecules into relatively
stable supermolecular structures gives rise to problems in light scattering
measurements. Sometimes, appropriate heat treatment of the solution prior to
measurement annuls the anomalous behaviour, or special evaluation procedures

supposedly eliminate the contribution of supermolecular structures to the scattered intensity (Ref. 14, 15, 18, 19).

The determination of molecular weights of polyamides by light scattering, and by other methods as well, is often complicated by the polyelectrolyte effect, the presence of aggregates, and hydrolytic splitting of the main chain. To suppress all these undesirable phenomena, binary or ternary solvent systems have to be used, the search for an appropriate system being rather a time-consuming job (Ref. 20).

Combination of light scattering with other methods
Whenever light scattering is combined with measurements of other solution properties, the information yield is much larger than a simple sum of partial information from the individual methods. Most frequently, light scattering is used along with viscometry. For the calibration of the dependences of intrinsic viscosity on molecular weight, light scattering is the most suitable method, the viscosity average and weight average molecular weights being close to each other. An important structural parameter of polymer chains, the unperturbed dimensions, is most conveniently determined by joint application of light scattering and viscometry. Coupling of these two techniques is apparently the most efficient method for the characterization of branched polymers (see below). Also, combination of light scattering with osmometry, sedimentation analysis, spectroscopy, measurements of diffusion, streaming birefringence, optical rotatory dispersion, circular dichroismus, etc., yields valuable structural information.

A very promising recent application of light scattering is its use as an absolute molecular weight detector in gel permeation chromatography (Ref. 21, 22). The commercial low angle laser light scattering photometer KMX-6 (Ref. 5), equipped with a special, small volume, flow-through cell, is well suited for this purpose. When on line with a concentration detector, the light scattering detector considerably augments the information extractable from a GPC experiment. A light scattering photometer as a second detector is particularly helpful in the GPC characterization of branched polymers (Ref. 23, 24). In this case, a number of assumptions can be dropped, which otherwise must be made for the evaluation of experimental data obtained in the conventional mode with only a concentration detector.

As mentioned above, the analyses of light scattering data obtained with some important polymers (e.g. polyolefins, poly(vinyl chloride), etc.) indicate the presence of a small amount of big particles in solution. This inter-pretation of the angular dependences of light scattering has been almost generally accepted but is occasionally challenged as an artefact due to dust or other impurities. MacRury and McConnell (25) measured the molecular weight distribution of polyolefins by GPC with an infrared concentration detector and a low angle light scattering photometer as an absolute molecular weight detector. With a low-density polyethylene sample, a sharp intense light scattering peak appeared at small elution volumes, without a corresponding infrared response (Fig. 1). This is a strong support for the interpretation of the static light scattering results as due to the presence of trace amounts of very high molecular weight polymer.

Branching
With macromolecules large enough to exhibit angular dependence of scattered light, information on branching can, in principle, be obtained from the shape of this dependence. A comparison of the theoretical particle scattering factors for star-branched or comb-like macromolecules with uniform architecture with experimentally determined angular dependences for carefully synthesized models yields usually satisfactory results (Ref. 26).

Systems more important in practice are products of the common branching and crosslinking polymerizations and/or reactions of polymers. These systems are always polydisperse both in molecular weight and with respect to the shape of macromolecules. Branching and polydispersity in molecular weight affect the angular dependence of scattered light always in opposite directions so that the resulting dependences do not strikingly differ from those for non-branched systems. Little information on branching can thus be extracted from the angular dependence alone of light scattered from solutions of statistically branched polymers. The theory of the particle scattering factors for statistically branched, polydisperse systems has been developed
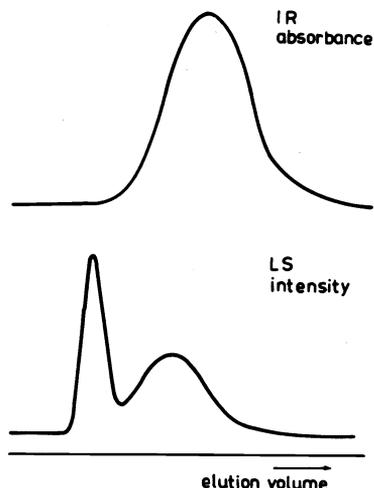
Fig. 1. GPC chromatogram of a low-density polyethylene
containing a small amount of microgel; infrared and light
scattering detectors on line (Ref. 25).

by an efficient and elegant application of the cascade theory to an
impressive degree of sophistication by Gordon, Burchard, and co-workers (Ref.
27-32). A difficult problem still to be solved is how to include into the
theory the effect of formation of intramolecular rings on the size and shape
of branched molecules, and on their molecular weight distribution functions.
In common branched polymers, the ring formation seems to be very important
(cf., e.g., Ref. 32) and it certainly affects the angular distribution of
scattered light.

Reliable, if only qualitative or semiquantitative, information on the degree
of branching of an unknown sample can be obtained by combination of light
scattering with viscometry (Ref. 33). If fractionation and GPC are employed
as further methods, the characterization becomes a time-consuming procedure
but yields a relatively good image of the sample.

Particle shape
The angular distribution of the intensity of scattered light depends on the
distances between the individual subunits and on their distribution within
the scattering particle, i.e., on the size and shape of the particle. For
particles large enough to show a pronounced angular dependence of the
scattering intensity, information on particle shape can, in principle, be
obtained by comparison of the experimental angular dependence with
theoretical dependences, calculated for a few particle shapes which the
polymer under investigation might assume. This method is more frequently
employed for biopolymers (Ref. 34, 35) since, with biopolymers, a larger
variety of particle shapes exist than among synthetic polymers.

The above method of particle shape determination is not free from a number of
pitfalls. First of all, the effect of polydispersity on the angular
distribution of the intensity of scattered light is comparable with that of
particle shape. In other words, the angular dependence can be interpreted in
terms of particle shape only if the polymer under investigation is strictly
monodisperse. Unfortunately, this prerequisite has not been respected by
too many authors.

Also, it has to be borne in mind that an agreement between the experimental
and calculated angular dependences is not a positive proof of a specific
particle shape. Model calculations show that virtually any experimental
dependence can be fitted, within the limits of experimental error, by a wide
spectrum of theoretical particle scattering factors for systems with
different particle shape and polydispersity. For instance, almost identical
angular distributions can be obtained for a large set of combinations of
different degrees of chain stiffness and polydispersity. Thus, in the
majority of cases, good agreement of the angular distribution of scattered

light for a model with an experimental dependence only means that the model under consideration ranks among the acceptable ones.

If a series of samples is available which consist of particles of the same chemical nature and shape but have different molecular weights, the dependence of the radius of gyration on molecular weight enables relatively safe conclusions on particle shape to be drawn.

Aggregates and microgels

The weight average molecular weight and, still more, the z-average radius of gyration are very sensitive to the presence of an even minute amount of large particles, such as aggregates or microgels, in the polymer. Therefore, the intensity of scattered light and its angular distribution indicate very sensitively the presence of large particles, in fact, at concentrations so small that they cannot be perceived by any other potentially appropriate experimental technique, such as sedimentation analysis or GPC.

The formation of aggregates, both reversible and irreversible, is frequent in solutions of biopolymers and bioanalogous polymers. As recent examples, the investigation of aggregates in solutions of denatured proteins (Ref. 36), proteoglycans (Ref. 37), pectic substances (Ref. 38), and oligopeptides (Ref. 39) can be introduced.

The solutions of many important synthetic polymers contain large super-molecular structures (cf. also above), as evidenced by the characteristic increase in scattering intensity at small scattering angles. The presence of these big particles has been observed mainly with crystalline polymers and polymers containing non-reacted double bonds in macromolecules, capable of intermolecular crosslinking. Sometimes, the big particles can be destroyed by heating, which is the case with, e.g., polyoxyethylene (Ref. 40). In solutions of some other polymers, e.g., poly(vinyl alcohol) (Ref. 41) or aromatic polyazomethines (Ref. 42), the supermolecular structures are formed after dissolution. The big particles observed in solutions of polyisoprene, polybutadiene, butadiene copolymers, polychloroprene, polyurethanes (Ref. 43), postpolymerized polyamides (Ref. 44), and other polymers seem to have the nature of chemically crosslinked microgels.

From the angular distribution of the intensity of scattered light, some information on the supermolecular structures can be obtained, as discussed in more detail below. Often, light scattering is the only method yielding this type of information.

Copolymers

The intensity of light scattered from dilute solutions of copolymers is affected not only by the molecular weight of the solute but also by its heterogeneity in chemical composition. The routine for light scattering characterization of the chemical heterogeneity of copolymers has frequently been applied inadequately, giving rise to a number of artefacts. Prior to using the method, the feasibility of the determination of the chemical heterogeneity for the given copolymer by light scattering should be scrutinized, because the procedure is, unfortunately, not as general as it is believed to be (Ref. 2, 45, 46).

The extension of the theory of light scattering from solutions of chemically heterogeneous binary copolymers to terpolymers is not too difficult, but an experimental quantitative characterization of the extent of chemical heterogeneity of ternary copolymers seems to be as good as unfeasible (Ref. 47).

The conformation of block and graft copolymers in solution is a topical problem. Under specific conditions, light scattering yields the radii of gyration of the parts of the macromolecule consisting of either monomer, and the distance between the centres of mass of both parts of the macromolecule (Ref. 48-51). The data must be interpreted with a great deal of caution, because the measurements have to be performed in a number of different solvents and the conformation of the copolymer molecules may vary with the nature of the solvent.

In the recent years, much attention was paid to block and graft copolymer micelles in solution, a structural variety of copolymers with many

interesting features (Ref. 52). Copolymer micelles have very high molecular
weights, of the order of magnitude 10^6-10^9, and light scattering is the
most appropriate method for the determination of such large particle weights.
Sometimes, an analysis of the angular distribution of the intensity of
scattered light yields information on the internal structure of copolymer
micelles (Ref. 53).

Polyelectrolytes

Polyelectrolytes dissolved in pure ionizing solvents scatter light in
a rather obscure manner due to the polyelectrolyte effect (Ref. 46, 54, 55).
From measurements on such systems, no information on the molecular parameters
of the polyelectrolyte can be obtained. The anomalous angular and
concentration dependences of the intensity of light scattered from dilute
polyelectrolyte solutions in pure solvents are probably caused by the inter-
molecular interference arising from the non-random arrangement of the polymer
in solution (Ref. 55). The reproducibility of experimental data in these
systems is rather poor, which may explain why attempts to interpret the
results in structural terms are scarce.

As is generally known, the polyelectrolyte effect in dilute solutions is
suppressed, if the ionic strength of the solution is increased by addition
of a neutral salt. Then, the polyelectrolyte solutions behave in a perfectly
tidy way, like the solutions of uncharged polymers. The only circumstance
which must not be forgotten is that salt solutions in ionizing solvents are,
in fact, multicomponent solvents and the experimental data have to be
treated accordingly.

Thermodynamics of multicomponent polymer solutions shows that correct values
of molecular weights and other molecular parameters are obtained from light
scattering measurements on polymer solutions in mixed solvents, and thus also
in salt solutions, if the refractive index increment, $(dn/dc)_\mu$, is measured
at equal chemical potentials for all solvent components both in polymer
solution and mixed solvent. In terms of experimental practice, this
requirement means that the osmotic equilibrium must be established between
the polymer solution and the solvent prior to the measurement of the
difference between the refractive indices. This fundamental precept of
thermodynamics has been disregarded by many authors investigating light
scattering from solutions of polyelectrolytes. Such data only yield apparent
values of molecular parameters which may considerably differ from the true
values (Ref. 54, 56).

Light scattering is an appropriate method for the characterization at
molecular level not only of polyelectrolytes with ionogenic groups chemically
attached to the polymer chain but also of polyelectrolytes which are
complexes of an uncharged polymer with an adsorbed ionogenic low molecular
weight compound (Ref. 57, 58).

Deoxyribonucleic acids

Light scattering and sedimentation equilibrium are the only two techniques
which can yield the absolute molecular weight of very large molecules without
any assumption on molecular shape. Therefore, light scattering has frequently
been utilized in the more profound characterizations of deoxyribonucleic
acids (DNA) samples (Ref. 59).

The light scattering characterization of DNA with very high molecular weight
(order of magnitude 10^7) is an experimentally most exacting operation,
mainly for two reasons: (1) Perfect clarification of DNA solutions is, for
a number of causes, still more important but also still more difficult than
with other polymers. (2) Reliable molecular weight and radius of gyration
values can only be obtained, if the range of angles of measurement is
extended well below the common lower limit (25˚-30˚), down to angles 6˚-10˚.

Measurements in the extended angular range require special light scattering
photometers, not commercially available. On the other hand, measurements in
the usual angular range often lead to erroneous values of both the molecular
weight and radius of gyration, which may be twice to three times smaller than
the correct values.

Thermodynamics of concentrated solutions

Thermodynamic analysis of concentration fluctuations both in solutions of
low molecular weight liquids and in polymer solutions shows that the
contribution of concentration fluctuations to the overall intensity of
scattered light is inversely proportional to the derivatives, at constant
temperature and pressure, of the chemical potential of the components of
a solution with respect to the composition of the system. The integration of
the dependence of these derivatives on the composition of the system then
gives the chemical potentials of the components at a particular composition
of the system and thus also the Gibbs free energy of mixing. The measurement
of the temperature dependence of the intensity of scattered light yields the
enthalpy and entropy of mixing of the system. In principle, light scattering
is one of the few methods providing complete thermodynamic description of
a solution in the entire range of composition (Ref. 60, 61).

There are a number of limitations, both of physical and experimental nature,
reducing the applicability of light scattering for the acquisition of
thermodynamic data. For instance, the components of the system must
sufficiently differ in their refractive indices. Solutions of polymers with
high molecular weights are very viscous even at moderate concentrations,
which creates serious experimental problems. For thermodynamic inter-
pretation, the overall scattering intensity has to be divided into
contributions due to the density fluctuations and concentration fluctuations.
To this end, data on density of the solutions and their isothermal
compressibility must be available. Unfortunately, the compressibility data
are very scarce for polymer solutions and isothermal compressibility
measurement is not a method commonly practiced in a polymer characterization
laboratory.

In spite of the above and some additional problems and limitations, it is
the present author´s opinion that the thermodynamic potentialities of the
light scattering method have been exploited by far not fully, particularly
in the investigation of concentrated polymer solutions.

Solutions of polymer mixtures

Light scattering measurements with dilute solutions of mixtures of polymers,
binary in most cases, have two main objectives: (1) Determination of the
molecular weights and, if need be, of other molecular parameters of the
components of a polymer blend. (2) Investigation of the thermodynamic
interaction of two different macromolecular species in solution (Ref. 46,
62-65).

Thermodynamic interaction of different polymers in solution is closely
related with the topical and unsolved problem of a rigorous quantitative
characterization of polymer compatibility, and this is the main reason why
growing attention has recently been paid to this question. Light scattering
and osmometry are the only two methods providing information on the purely
thermodynamic interaction of two polymers in solution. Both methods are
complementary since, depending on the nature of the system, one or the other
may be more appropriate.

The result of this type of measurement is an interaction parameter, similar
to the second virial coefficient, characterizing quantitatively the
intensity of thermodynamic interaction of two non-identical polymer
molecules and can easily be converted into, e.g., the more familiar
corresponding interaction parameter of the Flory-Huggins theory.

Physically analogous information can be extracted from the spinodals in
systems two polymers - solvent, the spinodals being determined by light
scattering (Ref. 66). The interaction of unlike polymers in solution can
sometimes also be interpreted, more graphically, in terms of mutual
selective exclusion of non-identical polymer molecules (Ref. 67, 68).

An analysis of equations describing light scattering from dilute solutions of
mixtures of polymers shows that the contribution due to the interaction of
non-identical polymer molecules to the total excess scattering intensity is
always a small fraction of the latter quantity. The determination of the
interaction parameter is, therefore, subject to a large relative experimental
error and ranks among the most exacting applications of the light scattering
method (Ref. 46).

Interactions in polymer solutions

The borderline between the content of the preceding paragraph and the present one is diffuse. Above, a particular type of interaction, related to the problem of polymer compatibility, was discussed. In this section, the interactions in a more general sense are briefly mentioned.

In a multicomponent polymer solution, any attractive or repulsive interaction between some components affects the concentration fluctuations and thus also the intensity of scattered light. Conversely, light scattering measurements enable us to make conclusions on the interactions operative in the system under investigation. Often, the information is not available by any other method.

Light scattering has been routinely used to measure the extent of preferential solvation of a polymer dissolved in a binary or multicomponent solvent (Ref. 46). This type of interaction can also be studied by other experimental techniques.

Strong interactions resulting in the formation of complexes between a polymer and a low molecular weight compound (Ref. 57, 58) or between two polymers (Ref. 69-71) are easily detected and, frequently, quantitatively described on the basis of light scattering measurements.

The diversity of interactions, both reversible and irreversible, is immense with biopolymers (Ref. 72, 73). Due to the highly organized structure of some biopolymers, the interaction may produce some fundamental structural changes, which also can be traced by light scattering. This happens, e.g., when a protein interacts with a low molecular weight denaturing agent (Ref. 74).

Kinetic measurements

Light scattering is, in principle, a convenient method for the investigation of systems in which processes connected with a change of molecular weight and/or size of macromolecular or colloid particles are in progress. The main advantage of light scattering consists in that the changes of the scattering intensity can be monitored continuously and without external interference with the system, such as taking off samples, adding reagents, etc..

The kinetics of polymerization can be followed by a continuous measurement of the intensity of scattered light, but the interpretation of the results in terms of molecular weight and size requires extensive additional data, which renders the procedure less attractive. On the other hand, the application of continuous light scattering measurement to kinetic studies and the interpretation of experimental data is rather simple and rewarding with systems in which macromolecular or colloid particles are present at the beginning and undergo some association, aggregation, crosslinking, dissociation, splitting, and so on. Valuable information has been obtained by light scattering on, e.g., kinetics of polymer photolysis (Ref. 76), kinetics of structural changes in biological particles with short duration of the process (more than a few seconds) (Ref. 12), etc..

A highly advanced kinetic application of light scattering enables molecular weight changes with a time resolution of about 1 μs to be followed (Ref. 77). The technique was used in studies of the kinetics of polymer degradation in solution by flash photolysis and yielded unique information, otherwise hardly accessible, on the rate of disentanglement of macromolecular fragments.

For some reason, light scattering has been utilized in kinetic investigations much less than it could and should be. There is hardly any more sensitive and rapid indicator of changes in particle weight and/or size.

Depolarization of scattered light

The depolarization of excess scattering due to the polymeric solute is generally low for synthetic polymers. Oligomers may show an appreciable depolarization of scattered light but its value decreases with increasing degree of polymerization and levels off at degrees of polymerization ca. 100-200 (Ref. 78).

Strikingly large depolarizations have been observed for some stereoregular polymers. From the measured depolarization, the molecular optical anisotropy, an important structural parameter, can be computed. A considerable difference

between the molecular optical anisotropies of atactic and isotactic polystyrene has been interpreted in terms of short range interactions in polymer chains, and conclusions on the preferred conformations of these chains in solutions were drawn (Ref. 79, 80).

Very recently, it has been observed in the author´s laboratory that also samples exhibiting fluorescence and samples, incidentally stereoregular, in which the unpolarized primary beam by accident impinged upon the meniscus in the solution cell behaved phenomenologically in exactly the same way as solutions of highly anisotropic polymers. Still more surprisingly, the application of the classical correction for anisotropy of the polymeric solute improved the data perfectly. Thus, high depolarization of scattered light need not necessarily mean large anisotropy of the polymer under investigation, and other potential causes should be checked on.

SOME TOPICAL PROBLEMS OF THE ART

Interpretation of strongly curved angular dependences
As mentioned in two of the preceding paragraphs, many industrially important polymers do not dissolve perfectly molecularly and the solutions contain large supermolecular structures. Due to the fundamental rules of light scattering from solutions of polydisperse systems, even a minute weight fraction of a component with molecular weight and dimension much larger than the bulk of the material strongly affects the intensity of scattered light and its angular distribution.

In a simplified manner, this phenomenon can be explained as follows: Large particles scatter light very intensely at small scattering angles, due to a large particle weight, but the intraparticle interference of scattered light makes the scattering intensity rapidly decrease with increasing angle of observation. On the other hand, individual macromolecules with common values of molecular weight scatter light less intensely than large particles at small angles but their scattering decreases much less, if at all, at larger scattering angles. Therefore, in solutions of mixtures of individual macromolecules with a small amount of large supermolecular particles, the scattering behaviour at small angles of observation can mainly be controlled by the big particles whereas, at large angles, the contribution to the total scattering intensity by the individual macromolecules predominates. When plotting the experimental results obtained with such a two-component system in the usual coordinates Kc/R_θ against $\sin^2(\theta/2)$, a characteristic, strongly curved dependence results (Fig. 2); here, K is an optical constant of the given polymer-solvent system, c is the weight per volume concentration of the solute, and R_θ is the Rayleigh ratio for the angle of observation θ, a quantity by which the intensity of scattered light is conveniently expressed.

As in any light scattering experiment, the two basic pieces of information are the weight average molecular weight, M_w, and the z-average radius of gyration, s_z, of the whole sample, i.e., the averaging includes both the individual macromolecules and microgel particles. Due to the averaging procedure, s_z mainly depends on the radius of gyration of the microgel particles. M_w is also strongly affected by the particle weight of the microgel, but the effect is much less than in the case of s_z. Anyhow, the molecular parameters of the bulk of the sample, i.e., of the molecularly soluble polymer, which are the point of our prime interest, cannot be obtained straightforwardly with such systems. Since the contribution of microgels to the scattering intensity at large angles of observation is often small, an extrapolation of the values measured at large angles to zero angle often yields a value close to the weight average molecular weight of the individual macromolecules (Fig. 2) and can be considered as a tolerable estimate of this important quantity.

An analysis of the whole angular dependence of the scattering intensity yields some additional information on the system. Several procedures have been suggested for the evaluation of light scattering data on microgel-containing systems (Ref. 41, 43, 81-83). All the procedures have a common denominator: Explicitly or implicitly, a model system is assumed and its parameters are adjusted to fit best the experimental data. It is important to remember that the parameters thus obtained may or may not be identical with those of the real system. Very often, a number of different model systems can be found, all of which fit the experimental data within the
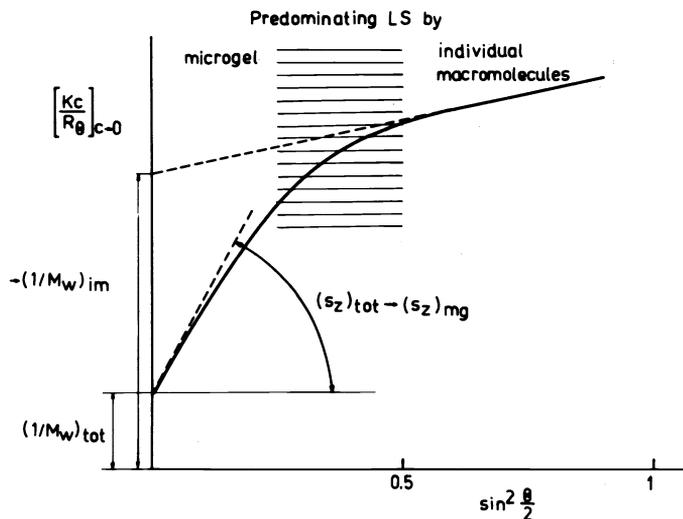
Fig. 2. Sketch of a typical angular distribution of the
intensity of scattered light from an infinitely dilute
solution of a polymer containing a small amount of microgel.
M_W and s_z are the weight average molecular weight and
the z-average radius of gyration; the indices im, mg, and
tot refer to the characteristics of individual macromolecules,
microgels, and the total sample, respectively.

limits of experimental error. If the data are evaluated in terms of different
models, the result may yield a useful estimate of the region in which the
true parameters of the system are likely to be included. The results of the
evaluation procedures obtained with individual samples should not be ascribed
too much absolute meaning. On the other hand, relative information deduced
from a comparison of results obtained with a series of similar samples is
fairly trustworthy.

The characteristics of the system which can be obtained from the analysis of
the angular distribution of the intensity of scattered light depend on the
particular procedure applied. Most frequently and most reliably, the
molecular weight of the molecularly dispersed polymer, the radius of gyration
of the microgel, and the weight fraction of the microgel can be evaluated.
The estimation of other parameters usually requires additional assumptions
and their values are much more conditional. Very often, light scattering is
the only method capable of yielding the above information on microgel-
containing systems.

The individual methods used for the evaluation of experimental data differ in
the definition of the model system. Usually, two-component model systems are
assumed, one component being the molecularly dissolved polymer and the other
one the microgel. In most cases, a two-component model satisfactorily
conforms to the experimental data within the limits of experimental error.
An increase in the number of components of the model system would certainly
further improve the fit between experimental and calculated data but the
information gain would be illusory, because the larger the number of
parameters describing the model system the more these parameters become
merely adjustable constants without much relation to physical reality.

For different model systems, different coordinates are advantageous for
graphical analysis of experimental data. For some procedures, the usual
coordinates Kc/R_θ against $\sin^2(\theta/2)$ are appropriate (Ref. 83). Lange (43, 81)
employs modified coordinates of the Zimm plot and Gruber (41, 82) recommends
the Guinier plot. An analysis of light scattering data according to the above
procedures for solutions of mixtures of two polystyrenes differing in
molecular weight by a factor of ca. 300, the small weight fraction of the
high molecular weight component simulating the microgel, yielded virtually
identical results, and the parameters calculated from the experimental data
for the mixtures were in good agreement with the values based on the
independently measured parameters for the individual components of the

mixture (Ref. 83).

The measurements on artificial mixtures of two polystyrenes with very different molecular weights (Ref. 83) were performed both in the usual angular range 30°-150° with a Fica light scattering photometer and at small angles, between 3° and 7°, by the low angle laser light scattering photometer KMX-6 (Ref. 5). The low angle measurement yields the correct weight average molecular weight of the mixture. On the other hand, the extrapolation of the Kc/R_Θ values from the angular range of $\Theta > 30°$ (Fig. 3) is very likely to result in much too high values of $Kc/R_{\Theta=0}°$ and, consequently, in incorrect, too small values of the weight average molecular weight of the mixture. The reason for the erroneous extrapolation is the rather strong curvature of the angular dependence of Kc/R_Θ in the angular range between 4° and 30°, which hardly can be guessed correctly. This result is a warning that the weight average molecular weights of microgel-containing systems estimated from measurements at angles larger than 25°-30° may not be correct.
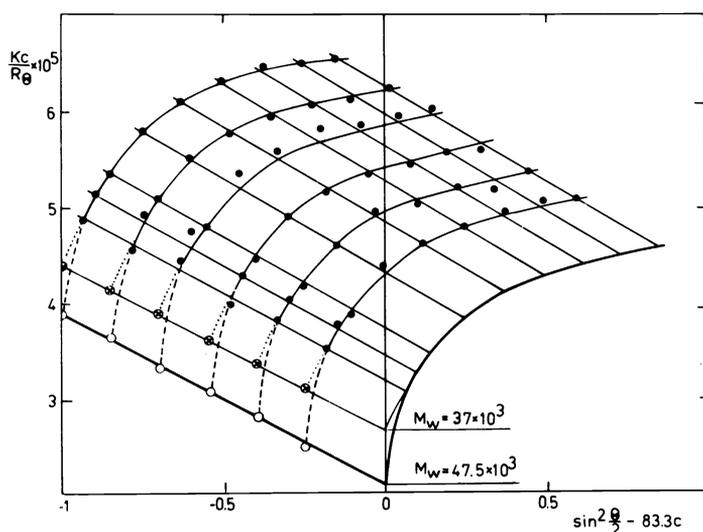
Fig. 3. Zimm plot for a mixture of 0.4 percent by weight of polystyrene with $M_w = 6.5 \times 10^6$ and 99.6 percent by weight of polystyrene with $M_w = 20.7 \times 10^3$; calculated M_w of the mixture is 46×10^3. ● are the experimental points for the usual angular range, ○ are the average experimental values for angles between 3° and 7°, and ⊗ are the probable points obtained by intuitive extrapolation to zero angle from $\Theta \geq 30°$. ----- correct extrapolation, ... probable extrapolation if the correct Kc/R_0 values are not known.

The credibility of the parameters of a microgel-containing system calculated from the angular distribution of the intensity of scattered light is considerably enhanced, if some additional information on the system is available by an independent method. Sometimes, e.g., the weight fraction of the microgel can be estimated from a sedimentation or GPC experiment. Also, the knowledge of the intrinsic viscosity of the polymer is very helpful. All these supplementary data enable the model system to be defined more realistically.

Moderately curved angular dependences
Very often, moderately curved dependences of Kc/R_Θ on $\sin^2(\Theta/2)$ (Fig. 4a) are observed, even with some samples of such polymers as common polystyrene or poly(methyl methacrylate), which are known for tidy solution behaviour and for which one rather would expect a rectilinear dependence. To publish this type of Zimm plot is considered almost bad taste, but an analysis of confidential private communications from laboratories all over the world shows that the moderately curved angular dependences are much more frequent in experimental practice than scanning of the literature indicates; in fact,

they seem to outnumber the well-behaved rectilinear plots.

Several reasons for the curvature can readily be suggested, e.g., the presence of not excessively large supermolecular structures or a small amount of dust, and/or incorrect optical adjustment of the photometer. With several polymers, it has been shown that none of these causes applies. The same polymer measured in the same photometer yielded a moderately curved angular dependence in one solvent (Fig. 4a) and a straight line in another (Fig. 4b), the calculated molecular weight being identical for both measurements.
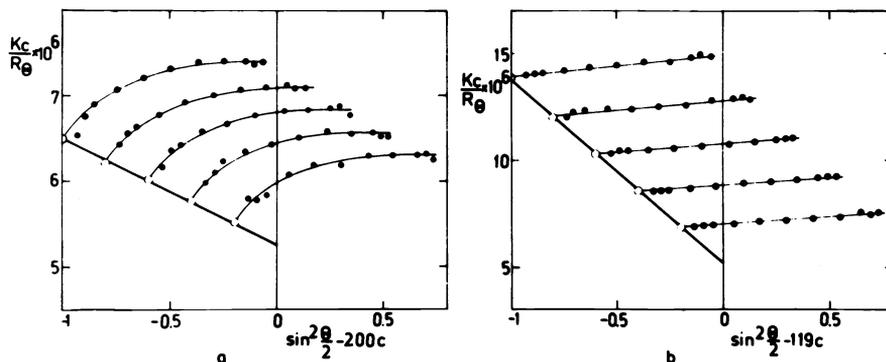
Fig. 4. Zimm plots for polystyrene, $M_w = 1.92 \times 10^5$, in (a) methyl ethyl ketone and (b) dioxane with 15 vol. percent of styrene, measured with the same photometer.

The moderate curvature of the angular dependences of Kc/R_θ is certainly a nuisance. It renders the extrapolation to zero angle less safe. In particular, the evaluation of the radius of gyration is less accurate, because there is a great deal of arbitrariness in the determination of the initial slope of the extrapolated part of a curve the shape of which has not been known in advance.

Some authors are anxious to get additional information on polymers yielding moderately curved angular dependences of Kc/R_θ and interpret the results in terms of the theory of the asymptotic properties of the particle scattering factors. Unfortunately, the application of the asymptotic theory to this type of Zimm plots is virtually never justified and, as a rule, leads to fallacious conclusions (Ref. 15).

The origin of the curvature in many angular dependences of Kc/R_θ is not clear. Due to the frequency of the phenomenon, it should become a subject of systematic investigation by experts in the field of light scattering from polymer solutions.

Light scattering detectors in GPC

Above, it has been mentioned that one of the modern and attractive applications of light scattering is the use of a low angle light scattering photometer as an on-line absolute molecular weight detector in GPC. Very probably, this combination of two powerful techniques will be widely employed in the near future. A number of experimental problems germane to the combined method have been discussed elsewhere (Ref. 21-25).

Here, attention is focussed on a potential serious experimental problem, which so far may not have been critically examined at desirable depth, viz., the accuracy with which the small excess scattering intensity, i.e. the contribution of the polymeric solute to the total intensity, of highly dilute solutions can be measured.

In a typical GPC experiment, 2 to 10 mg of polymer elute from the column in 25 to 75 ml of solvent (Ref. 84). Thus, the average concentration of the polymer during the elution is 10 to 100 times smaller than in a common static light scattering experiment. The situation is somewhat more favourable in the vicinity of the elution peak but much less favourable for both tails of the elution curve. Extremely small excess scattering intensities are to be

expected for the low molecular weight tail of the elution curve.

A rough estimate shows that, during the elution period, the contribution of the eluted polymer to the total intensity of light scattered from solution typically ranges from a few percent up to some 10 or 20 percent, the bulk of the scattering intensity being the scattering by the solvent. The crucial quantity, the excess scattering due to the polymer, is thus always a small difference of two large numbers and, therefore, is subject to a large relative error. For example, a drift in the signal of the solvent of only a few tenths of one percent can produce in the excess scattering intensity an error of tens of percent. Also, any small instability of the light scattering signal would result in a considerable relative error.

A thorough analysis of the effect of experimental error of light scattering detectors in GPC seems to be a topical problem. Otherwise, the term "absolute molecular weight detector" might tempt the users of this upsurging technique to ascribe to the results more absolute meaning than they actually possess.

Some frequent artefacts
The literature on light scattering from polymer solutions, particularly on its more exacting applications, is regrettably rich in artefacts. The reason is that in original papers and, still more, in reviews and monographs the limits of applicability of the individual techniques are often not sufficiently emphasized. Thus, the methods are considered as generally employable procedures and are used inappropriately. It may be pertinent to remember here some of the frequent artefacts as word of caution.

In the estimation of particle shape from the angular distribution of the intensity of scattered light, it is frequently forgotten that sensible conclusions can be drawn only for systems of particles in which there is no distribution of particle weight, size, and/or shape (Ref. 15).

The heterogeneity in chemical composition of copolymers has many times been measured using an inappropriate set of solvents. As it is well known, the measurement must be performed with three or more different solvents. If the individual solvents do not sufficiently differ in their refractive indices, the solution of the system of equations from which the heterogeneity parameters are computed becomes unstable and a small experimental error produces huge variation of the calculated heterogeneity parameters, resulting sometimes in physically inadmissible values (Ref. 45, 46).

Measurement of the depolarization of light scattered by dilute polymer solutions is a delicate job. A number of experimental errors can affect the results, most of them increasing the apparent value of depolarization (Ref. 85). Therefore, if the measured depolarization ratio for a polymer exceeds, say, 0.05, the experimental procedure should be critically examined whether some of the potential sources of error are not operative.

In certain cases, the experimental angular dependence of the intensity of scattered light can, in the region of large angles of observation, virtually coincide with its asymptote. If so, additional information on the polymer can be obtained, e.g., for linear Gaussian coils, the number average molecular weight and the number average end-to-end distance. Unfortunately, the conditions for the application of the theory of asymptotes of the angular distribution of the intensity of scattered light are only rarely fulfilled in experimental practice, although the shape of the angular dependence very often looks as if the true asymptote could be determined. In this way, a number of authors have arrived at fictitious conclusions. Special care has to be observed whenever interpreting the asymptotic behaviour of the angular distribution of scattering intensity (Ref. 15).

It may seem strange to conclude a review on advances in a certain field of science by a list of methodic pitfalls. But it is the author´s experience that excessive credulity in published instructions often results in misleading conclusions, and an appeal to certain temperance may really be one of the topical problems of the art. Hopefully, the paper has shown that, even with sober applications, light scattering is an indispensable tool for the solution of many challenging problems in the physical chemistry of polymers.

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