RECENT TRENDS IN CLASSICAL LIGHT SCATTERING FROM POLYMER SOLUTIONS

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Abstract - Extension of usable wavelengths to the near i.r. by means of
laser sources enables the molecular weights and dimensions to be measured
for exceptionally large macromolecules and bacteria. Comparisons have been
made between experimental and theoretically predicted behaviour of solutions
subjected to external constraints such as temperature, applied pressure and
hydrodynamic shear. Scission and molecular motion can be analysed via
light scattering in polymers subjected to laser or pulse degradation;
kinetics of anionic polymerisation may be clarified by estimating the
association of the living polymer. Problems associated with compositional
heterogeneity in copolymers and terpolymers are discussed as is the anomalous
behaviour of block copolymers in which one portion is optically masked. In
principle, the compatibility between two polymers in a common solvent can be
determined quantitatively, but the techniques demand an exceptionally high
level of care and accuracy.

INTRODUCTION

Despite rapid advances in quasi-elastic light scattering, the literature reveals no diminu-
tion of effort expended on conventional Rayleigh light scattering (L.S.) from polymer
solutions. In the period 1969-76 there are ca. 60 references listed each year in Chem.Abs.,
which are specifically identifiable from their titles with this topic. Since characterisa-
tion and solution properties frequently involve L.S., but not obviously so from the title,
the number of annual publications is probably at least twice the figure mentioned. On the
commercial scale there have been few instrumental developments except for the 'Bleeker SAL
Photometer' (Ref. 1), which has an angular range of $0^\circ\ 30' - 130^\circ$ and does not require a
secondary calibration standard, since energies rather than intensities are obtained. The
instrument is geared to solid thin specimens, but special cuvettes are available for liquids
and solutions. Non-commercial instrumentation includes (i) the Uppsala apparatus for normal
and quasi-elastic L.S., (Ref. 2-4); (ii) the pulsed induced critical scattering (P.I.C.S.)
equipment (Ref. 5); (iii) modification of an existing photomer (Ref. 6,7), construction of a
new instrument (Ref. 8) and construction of a differential refractometer (Ref. 8,9) all for
near i.r. incident light; (iv) modification of the Sofica and using synchronous summation of
intensities for measuring extremely small polymer dimensions; (v) useful practical tips for
L.S. measurements at temperatures considerably below ambient have been reported recently
by Wolf et al. (Ref. 10). .

Characterisation (including L.S.) of distributed polymer samples in Japan (Ref. 11) has given
far more consistent results than in earlier 'round-robin' investigations conducted in Japan
and internationally. Current emphasis is on multicomponent systems (copolymers, polymer
mixtures and mixed solvents) (Ref. 12) and seems likely to continue so in view of the
technological interest in blends and compatibility generally.

WAVELENGTH OF LIGHT

There are certain advantages to be gained by extending the range of wavelength in vacuo, λ_o.
For a polymer having a particular mean square radius of gyration $<S^2>$, the reciprocal intra-
molecular scattering factor $P^{-1}(\theta)$ increases in value as λ_o decreases. Theoretical scatter-
ing functions for different shapes are difficult to distinguish by experiment, since the
practically realisable range of $P^{-1}(\theta)$ covers mainly the initial portion common to all
particle shapes. X-ray scattering is preferable in this respect and in general the low (u.v.)
region is not used because of (i) absorption, (ii) poorer response of photomultiplier cf. the
visible and (iii) the need to use quartz cells for $\lambda_o <$ ca. 320 nm.

Within the visible and near i.r. a large number of possible wavelengths can be selected by the
use of lasers. Thus the cheap Ar Kr ion yields eleven values of λ_o between 529 and 647 nm;

with the He–Ne λ_o = 633 and 1086 nm and the expensive Nd–YAG affords λ_o = 1064 nm (Ref. 13).
With a frequency doubler the value of λ_o can be halved. None of these is pulsed, although
pulsed lasers can be employed to effect scission as indicated in a later section. Some
applications will be discussed.

Zimm plot with variable λ_o

The usual L.S. equation for estimating the weight average molecular weight M, the second
virial coefficient A_2 and $<S^2>$ is

$$Kc/R_\mu = M^{-1} (1 + \mu^2 <S^2>/3 + ...) + 2A_2C \qquad (1)$$

where $\mu = (4\pi n_o/\lambda_o) \sin (\theta/2)$ and the optical constant K is $2\pi^2 n_o^2 \nu^2/N_A\lambda_o^4$ for unpolarised
light or twice this value for vertically polarised light (n_o, ν, N_A, θ and $R\mu$ denote
respectively the refractive index of solvent, specific refractive index increment (s.r.i.i.)
of solution, the Avogadro number, the angle of observation and the Rayleigh ratio appropriate
to this particular μ). In the normal procedure λ_o is kept constant and θ is varied thereby
yielding μ = 0 by extrapolation to θ = 0. A neat verification of the Debye expression,
Eq(1), has been demonstrated (Ref. 14) and consists of making measurements at constant θ
(= 90°), but at various values of λ_o ranging from 365 to 1086 nm with a Hg lamp and lasers.
Hence μ = 0 is achieved by extrapolation to λ_o = ∞. In this form of Zimm plot the ascissa
is μ^2 + (constant)(c) instead of $\sin^2 (\theta/2)$ = (constant)(c). Excellent agreement has been
obtained when the values of M, A_2 and $<S^2>$ were compared with those yielded by several
conventional plots each at a particular λ_o and variable θ. Of course this procedure is
better suited to samples of high M in view of the low intensity at higher values of λ_o.

Absorbing and insoluble polymers

To avoid corrections for fluorescence and excessive absorption at normal wavelengths it is
sometimes imperative to employ higher λ_o (e.g. red laser giving 633 nm). Such is the
situation for pyrrone prepolymers or poly (amic acid) which are precursors of polyimides.
The latter are rather new, thermally stable, heterocyclic aromatic polymers of desirable
engineering properties.
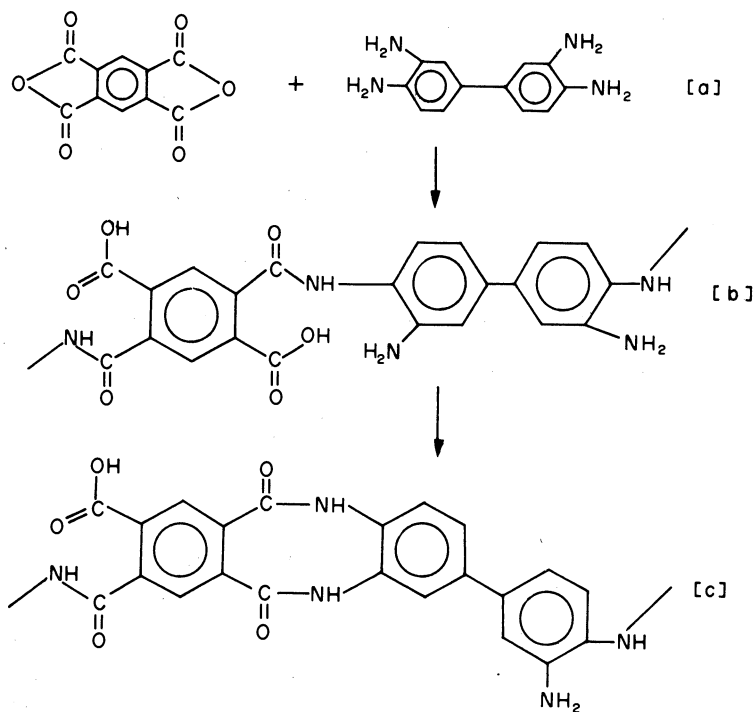
The preparation is in two stages (Fig. 1)

Fig. 1. Preparation of insoluble, cyclised polyimide (c) from soluble
reactants (a) and soluble intermediate (b). L.S. is measured directly on
solution (b) at a high λ_o due to extensive absorption.

The soluble poly(amic acid) (b) may be processed to any desired shape required for the final application. It is converted subsequently by ring closure to the final infusible, insoluble poly (imide) (c). L.S. at high λ_0 is conducted directly on the solution (b) without isolation of the solid (Ref. 15). It is inferred reasonably that there is no change in chain length in the step (b)→(c) (Ref. 15,16).

Near i.r. L.S.
Rayleigh-Gans-Debye L.S. is bounded by the restraints:

$$\left| n_r - 1 \right| <<1 \quad \text{and} \quad (2\pi D/\lambda)\left| n_r - 1 \right| <<1 \tag{2}$$

where n_r is the refractive index of polymer relative to that of solvent (commonly ca. 1.07 for many polymer solutions), $\lambda \simeq \lambda_0/n_0$ is the wavelength in the medium and D is the major dimension of the dissolved particle. If the dissolved particle is too large, the angular scattering profile exhibits oscillations and a Zimm plot cannot be constructed (Ref. 6). Solution and implementation of Mie theory is only practicable for large monodisperse spheres.

Two groups of workers (Ref. 6-8) have demonstrated elegantly how to treat systems for which Eq(2) does not hold under normal circumstances, because the dimensions D are exceptionally large, e.g. bacterial suspensions which scatter light enormously and require only extremely low concentrations. Effectively, the rationale is to reduce the value of D/λ by increasing λ to about twice its normal magnitude; this is accomplished with near i.r. radiation (Nd : YAG, λ_0 = 1064 nm (Ref. 7) or He-Ne, λ_0 = 1086 nm (Ref. 8,14)). For many bacterial suspensions $n_r \simeq 1.06$ (Ref. 17), although it can be as high as ca. 1.12 for spores. The behaviour is thus restored to the Rayleigh-Gans-Debye region so that the usual parameters can be derived from a Zimm plot. Table 1 illustrates some results for particularly large particles in water:

TABLE 1. Near i.r. L.S. results for an aqueous bacterial suspension (Ref. 7)

Bacterium	T. ferrioxidans
λ_0	1.06 μm
A_2	slightly negative
M	1.6×10^{11} g/mol
Bacterial mass	$M/N_A = 2.6 \times 10^{-13}$ g
$<S^2>^{1/2}$	1.05 μm
Semi-major (b) and semi-minor (a) axes assuming prolate ellipsoid	a = 0.7 μm b = 2.1 μm

Advantages include (i) applicability to non-spherical, polydisperse particles, (ii) possibility of monitoring variations in mass and size of bacteria in various interactions and (iii) extensions to bacteria of size up to ca. 4.5 μm, using low angles and λ_0 = 1.06 μm.

Using λ_0 = 1.08 μm, polystyrene and cellulose trinitrate of M up to 39×10^6 and 9×10^6 respectively (with correspondingly large dimensions) have been characterised by this means (Ref. 8)).

Specific refractive index increment
Attention has been drawn (Ref. 18) to the fact that, in isolated reports, experimental values of $\nu(436 \text{ nm})$ are smaller than those of $\nu(546 \text{ nm})$, which is contrary to the direction of normal dispersion for a polymer or a solvent. Calculated and observed s.r.i.i. values are in very good accord both for the systems mentioned and for those in which $\nu(436) > \nu(546)$. Apparently, the unusual relationship $\nu(436) < \nu(546)$ holds only when the solvent molecule contains a phenyl group and it is a characteristic of its dispersion which weights that of the polymer in such a way in the expression for the s.r.i.i. so as to give rise to the final unusual dispersion in ν for the solution. Examples of the value of $\nu(436) - \nu(546)$ are -0.010, -0.010, -0.006 and -0.005 ml/g for poly (propylene oxide) in benzene and chloroform, poly (methyl methacrylate) (PMMA) in benzene and toluene respectively.

Some consideration might be given in future to examining the feasibility of effecting changes in ν solely by varying λ_0. Normally the desired refractive properties (Ref. 19-23) of a

solution of a copolymer, terpolymer or polymer mixture are achieved precisely by altering the solvent medium (frequently by including a second or third solvent), or even by changing the temperature. Both of these are thermodynamic in nature and hence some concomitant variation in chain expansion is unavoidable; such is not the situation with dispersion of ν, achievable in principle by varying λ_0. Unfortunately, like the photochemist, the polymer chemist still awaits the time when L.S. embracing the wide range of λ_0 referred to earlier can be accomplished in a single apparatus.

EXTERNAL CONSTRAINTS

External pressure
The influence of external pressure (p), usually coupled with that of temperature (T), has been pioneered (Ref. 24) and reviewed (Ref. 25) by Schulz and Lechner. Specially constructed apparatus (Ref. 2-4, 24-26) as well as modified commercial instruments (Ref. 27-29) have been employed. The variables studied include M, nature of solvent and composition of mixed solvent (Ref. 26), the prime experimentally derived quantities being A_2 and $<S^2>^{1/2}$. Determination of the latter does not require a knowledge of the s.r.i.i., but that of the former does. ν can be evaluated (not measured) at any p and T from the common intercept in the Zimm plot using the value of M previously measured at atmospheric pressure, on the assumption that M is independent of pressure (Ref. 25,26).

Measurements allow both A_2 and $(\partial A_2/\partial p)_T$ to be compared with theory. Moreover, they afford a means of evaluating the volume of dilution ΔV_1 since, for a fixed concentration, $-\Delta V_1 \propto (\partial A_2/\partial p)_T$. Thus, for PS in toluene at atmospheric pressure and room temperature the pressure coefficient is positive and ΔV_1 negative, whereas with trans-decalin as solvent but otherwise identical conditions the coefficient is negative and ΔV_1 positive (Ref. 26).

Since the solvent is compressed more than the polymer, the free volume difference between these two components is reduced when pressure is applied and solubility enhanced with a widened miscibility gap between the lower critical solution temperature (LCST) and the upper critical solution temperature (UCST); the effect is more pronounced for the LCST. A typical value of d(LCST)/dp is ca. 0.4 deg/bar. There is reasonable agreement between theory and experiment for the magnitude of this pressure coefficient, although the absolute value of the LCST observed at any p is less than predicted by theory (Ref. 28,29).

A single curve of $<S^2>^{1/2}$ vs. A_2 is yielded irrespective of whether changes in these quantities are effected via p or T. Effectively, the radius is the same whether p or T is used to cause it to depart from its unperturbed value by a factor $\alpha(\mathfrak{z})$, the expansion factor. This factor is obtained from the radius and its value when $A_2 = 0$. The excluded volume function $\mathfrak{z}h(\mathfrak{z})$ may be obtained from A_2; several theoretical forms of excluded volume function exist. As before, data points obtained for different p and T yield a unique curve of $\alpha(\mathfrak{z})$ vs. $\mathfrak{z}h(\mathfrak{z})$, which affords a comparison with proposed excluded volume theories. The results accord well with all excluded volume theories particularly at low chain expansion ($\alpha(\mathfrak{z}) = 1.0 - 1.2$) (Ref. 27).

The theory referred to in connection with A_2 and the LCST is that due to Flory and Prigogine. Patterson (Ref. 27,30) has expressed it concisely to give $\chi(p, T)$ as a function of two types of quantity - (i) reduced parameters of the solvent and (ii) parameters characteristic of both solvent and solute, e.g. contact energies. Insofar as this expression does furnish a value of the interaction parameter χ or A_2, such a value may be regarded as 'theoretical'. However, there are several quantities in the relevant expression which appertain to experimental data unrelated to L.S. Hence, irrespective of the validity of the theory, the so-called 'theoretical' value itself could be in error. It may well be that the agreement between 'theory' and practice is actually better than is supposed.

Hydrodynamic shear field
Theoretical treatments exist on the conformation of randomly coiled macromolecules subjected to hydrodynamic shear stress (Ref. 31-33), but rather few investigations via L.S. have been reported (Ref. 34-36). Heller et al. (Ref. 34,35) have constructed an elaborate apparatus with a laser light source, the disturbance in recorded scattering due to minute air bubbles being overcome by filling the cell slowly under gravity feed. Cottrell et al. (Ref. 36) have modified a Sofica photometer and used it in conjunction with a normal mercury lamp.

Polymer solutions are sheared in the anulus of a co-axial shear cell in which the inner and outer cylinders respectively rotate and are kept stationary. Analysis of the specific increment in scattering due to shear as a function of observation angle with respect to direction of flow allows one to establish if the effect is purely one of orientation or, as for aqueous poly (acrylamide), mainly due to deformation. The mode of differentiation involves the use of polarised light (Ref. 34). The technologically important drag-reducing property of poly (acrylamide) results from energy dissipation by deformation of the polymer as evidenced by the hydrodynamic increment in L.S. intensity. Supporting evidence is the exceptionally long

relaxation time observed for the increment after stopping the flow,

For solutions of poly (isobutylene) (Ref. 36), corrected Zimm plots have been devised to calculate a specified extension ratio ϵ, where

$$\epsilon = <S^2_x> \text{ (shear)}/<S^2_x> \text{ (rest)}$$

The subscript x indicates that the mean square radius of gyration is projected in a particular direction x defined by a unit vector $\underline{A}$ in the incident beam direction and a unit vector $\underline{B}$ along the direction of observation such that $\underline{x} = \underline{A} - \underline{B}$. Complete L.S. information yields (i) three independent extension ratios of the coil and (ii) the orientation angle in the field. The major axis extension ratio, for instance, only varies from 1.00 to ca. 1.28, whilst the orientation angle ranges from 45° to 91°. The exact form of the latter dependence accords with predictions based on complete chain flexibility. However, the extension ratios do not and are more in accord with the Cerf model (Ref. 31), which assumes a finite internal viscosity.

CHEMICAL PROCESSES

Association
Association and aggregation of polymers in solution have been reviewed (Ref. 37) and continue to be studied, particularly in connection with biochemical systems (Ref. 38). Regarding non-terminated polymers, interest has centred around the state of aggregation of hydrocarbon polymers polymerised in hydrocarbon solvents via an anionic mechanism (Ref. 39-41). The kinetics and especially the precise mode of propagation necessitate a knowledge of the association number N of the living polymer for their elucidation. The value of N is found by measuring M for the living polymer and comparing it with the value of M for the terminated species. Values of N = 2, 4 and 4 over a wide range of concentration have been obtained thereby for polystyryl-, polyisoprenyl- and polybutadienyl- lithium (PS, PI and PBD) (Ref. 40).

Complex, grease free, high vacuum apparatus is used, the concentration of living polymer being measured by u.v. absorption. The L.S. cell, with its cumbersome appendage associated with the preparative operations, is inserted via a collar and magnetic seal into a Sofica photometer (Ref. 40). M is evaluated readily for PS in cyclohexane at 35°C(θ-conditions). However, there are no θ- solvents for PI and PBD, which are suitable media for anionic polymerisation. The finite virial coefficients for these polymers in cyclohexane introduces much uncertainty in extrapolating L.S. data to c = 0. The problem has been overcome neatly by adding a little isoprene or butadiene to the living polymer PS. From the standpoint of association the living products possess associative characteristics of PI and PBD. Since they consist preponderantly of poly (styrene), they behave thermodynamically as this polymer, i.e. $A_2 = 0$ in cyclohexane at 35°C. Their molecular weights are thus obtained directly by L.S. at any concentration.

Degradation and molecular processes
Continuous L.S. techniques have been established for monitoring molecular weight changes during free radical (Ref. 42,43) and ionic (Ref. 44) polymerisations as well as during photolysis. Recent experimental refinements have increased the time resolution by five orders of magnitude so that molecular weight changes can be followed with a time resolution of ca. 1 μs (Ref. 45-47). The method has been applied to study the degradation of several polymers and copolymers in solution, the scission being effected by either a laser flash or an electron pulse from an accelerator. Changes in L.S. intensity are monitored on an oscilloscope, the incident source also being a different laser. The scattered intensity is proportional to signal voltage so that the process can be followed in terms of this voltage at different times. For first order degradation the signal voltage falls exponentially with a half-life $t_{\frac{1}{2}}$ (LS). Since this is inversely proportional to the rate constant, large and small values of $t_{\frac{1}{2}}$ (LS) signify slow and fast processes respectively.

The main requirements are (i) ability of polymer to absorb light of the λ_0 produced by the laser light source; when this does not hold, a sensitiser such as benzophenone can be incorporated; (ii) reasonably large value of ν to maintain a high signal/noise ratio, (iii) polymer which undergoes scission exclusively (with poly (vinyl methyl ketone) the initial drop of signal voltage in the μsec. region, indicating scission, is followed by an increase in the sec. region, indicating subsequent cross-linking (Ref. 48)); (iv) rate of scission to be much greater than rate of subsequent disentanglement of scinded chains.

The influence of the following has been investigated: concentration and M of polymer, composition of copolymer, viscosity of solvent, added quencher which reduces the number of polymer molecules in the excited triplet state i.e. the number capable of undergoing scission, and the rate of decay in the triplet state (by optical absorption). Inter alia, the findings indicate that disentanglement diffusion can be distinguished from translational diffusion,

and that the former proceeds more easily for loosely coiled macromolecules than for tightly coiled ones.

COPOLYMERS

L.S. studies on copolymer solutions continue to constitute a major field, with emphasis on di- and tri-block copolymers, graft copolymers, micelle formation and, to a somewhat lessening extent, random copolymers.

Compositional heterogeneity parameters (P and Q)
Determinations of the molecular weights M_A and M_B of constituents A and B as well as the true molecular weight M of the copolymer are made most reliably from the experimentally observed apparent molecular weight M^* of the copolymer, if the A or B parts are optically masked by the use of a solvent of appropriate n_0. In practice the number of suitable solvents is restricted and more versatility is provided by mixed solvents. The appropriate s.r.i.i. under these circumstances is the value at constant chemical potential of low molecular weight solvents (Ref. 12,19,23).

Accurate determinations of the parameters P and Q (Ref. 49) pose a far more formidable problem; the topic has been reviewed (Ref 12). Solutions of the relevant expressions (Ref 49) via simultaneous equations can yield values of P and Q which vary according to the selection of equations if more than three solvents are used, may afford values that are inconsistent with the mode of preparation or which exceed their theoretical maxima, or may even yield negative values for M. Frequently, the range of $(\nu_A-\nu_B)/\nu$ cannot be extended sufficiently for P and Q to be obtained from the Benoit parabola (Ref. 49). A least squares fitting programme by computer (Ref. 50) does indeed yield a parabola, but this statistical expedient offers no great advantage if the actual data points display considerable scatter about the least squares curve. The way of effecting dissolution has also been shown to influence the L.S. data considerably (Ref. 51).

The expression for P and Q is

$$d = ax + by + c\mathcal{z} \tag{3}$$

where $a = 1$; $b = 2(\nu_A-\nu_B)/\nu$; $c = (\nu_A-\nu_B)^2/\nu^2$; $d = M^*$, and the required quantities are $x(= M)$; $y(= P)$; $\mathcal{z}(= Q)$. Experiments with three solvents each of different n_0 yield different sets of values for b, c and d distinguished by subscripts 1, 2 and 3. Solution of Eq(3) by determinants gives Q, for example, as:

$$Q = \mathcal{z} = 4 \left[\frac{b_2(d_3 - d_1) + b_3(d_1 - d_2) + b_1(d_2 - d_3)}{b_2b_3(b_3 - b_2) + b_3b_1(b_1 - b_3) + b_1b_2(b_2 - b_1)} \right] \tag{4}$$

The relative error in Q cannot be estimated from Eq(4), but the expression does emphasise the numerous arithmetic operations involved each of which is influenced by the presence of errors of ca. $\pm1\%$ for ν, ν_A, ν_B and ca. $\pm5\%$ for M^*. That differences such as (d_3-d_1) and (b_3-b_2) must be significant is also apparent.

When data covering only part of the Benoit parabola are available, the following device may sometimes be useful for determining P and Q: Experiments 1, 2 ...... n yield values of (d_1, b_1), (d_2, b_2) ..... (d_n, b_n). Thus for experiments n and $(n-1)$,

$$d_n = M + Pb_n + Qb_n^2/4$$
$$d_{n-1} = M + Pb_{n-1} + Qb_{n-1}^2/4$$

Subtraction and division by (b_n-b_{n-1}) give

$$(d_n-d_{n-1})/(b_n-b_{n-1}) = P + Q(b_n + b_{n-1})/4 \tag{5}$$

Thus a plot of the left hand side of Eq(5) vs. (b_n+b_{n-1}) should be linear with a slope equal to $Q/4$ and intercept on the ordinate axis equal to P. Illustrations are shown in Fig. 2.

One source of inaccuracy consists of taking $(\nu_A-\nu_B)/\nu$ to be constant for a particular copolymer in a series of solvents. This implies that the slopes of Gladstone-Dale plots (Ref. 55) are the same for homopolymers poly-A and poly-B, which is certainly not true for the pair PMMA/poly(n-butyl methacrylate), for example (Ref. 56). In any particular solvent the absolute values of ν_A, ν_B and ν should be measured directly for better accuracy.

The critical relevance of $|\nu_A-\nu_B|$ in estimating P and Q has been discussed by Vorlíček and Kratochvíl (Ref. 57), who have devised a nomogram, which is useful when the composition is independent of M. It has been used to examine the feasibility of determining Q accurately by
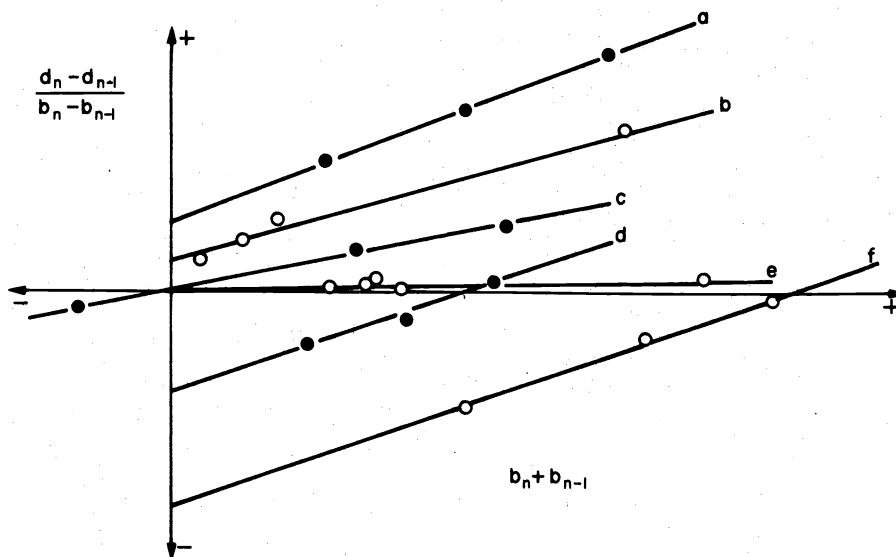
Fig. 2. Estimation of P and Q from plots according to Eq (5). (a) and (b)
- nylon-6/poly (methyl acrylate) graft (Ref. 23,52); (b) - PS/PMMA random
(Ref. 53); (c) PS/poly (di-n-butyl itaconate) random (Ref. 54); (e) - PS/
PMMA block (Ref. 53); (f) - nylon-6/poly (methyl acrylate) mixture (Ref.
23, 52).

L.S.. In general, for (Q/M) <10% of its maximum possible value, this quantity is only
obtainable reliably if M > ca. 10^5, according to the exact magnitude of Q/M and $|v_A-v_B|$.
Calculations (Ref. 58) for model graft copolymers disclose that $(Q/M)/(Q/M)_{max}$ is actually
less than 0.1 with 2-3 grafts/molecule, provided the heterogeneities of backbone and graft
are similar. In the presence of residual homopolymer(s) from the preparation, the composi-
tional heterogeneity is greater. Such homopolymer at levels down to 1% (wt.) is detectable
by density gradient ultracentrifugation (Ref. 20,59). For highly grafted copolymer in the
absence of homopolymer, Q/M is very small. For extremely high heterogeneity or for mixtures
of polymers, excellent agreement has been obtained between theoretical and experimental
values of Q/M. Careful distinction should be made between the reported term "negligibly
small heterogeneity" and "too small a heterogeneity to be estimated accurately by L.S." The
latter may be the more correct.

Distorted Zimm plots for block copolymers
Anionic polymerisation is the most convenient means of preparing AB block copolymers of high
monodispersity of molecular weight and low levels of contamination by homopolymer. L.S.
studies offer a means of assessing the interpenetration or segregation of one block with the
other, i.e. it gives some (although not unequivocal) indication of the degree of compatibility.
If block B, for instance, is optically masked, one obtains the dimensions $<S_A^2>$ of the block A
directly, which can be compared with the dimensions $<S_A^2>$ (homo) of A uninfluenced by B, i.e.
those of homopolymeric poly-A of the same molecular weight. Moreover the overall dimensions
of the copolymer or of a block (accessible or otherwise) can be compared with those calculated
from the intrinsic viscosity via the Flory-Fox relationship (Ref. 20-22).

When the whole copolymer scatters light, the Zimm plots are usually normal, but in a solvent
for which v_B is zero (or practically so) gross distortion is usually displayed. The scatter-
ing envelopes have a markedly upward curvature at low θ, which becomes especially pronounced
as C and M increase. The effect has been explained (Ref. 20,21) as arising from intermole-
cular interference due to very large excluded volumes for the unmasked portion. To a large
extent the abnormality ensues from applying normal L.S. laws to a system in which the
optically observable part is smaller than the whole. In terms of the intramolecular and
intermolecular factors $P(\theta)$ and $\Phi(\theta)$, the L.S. equation reads

$$Kc/R_\theta = 1/MP^*(\theta) = 1/MP(\theta) + 2A_2C \Phi(\theta)/P(\theta) \qquad\qquad (6)$$

Guinier analysis (Ref. 20, 60) invoking a form of Eq(6) yields the whole excluded volume β and the mean square radius $<r^2>$ of the scattering portion ($\beta \neq <r^2>3/2$). Experimentally, the required ratio in the appropriate plot, $P(\theta)/P^*(\theta)$, (where $P^*(\theta)$ is the apparent intramolecular scattering function) is obtained as $(c/R_\theta)_{c=c}/(c/R_\theta)_{c=o}$. In a block copolymer when $\nu_B = 0$ and ν_A is finite, $P(\theta)$ reflects only the size of A and therefore remains closer to unity than expected for the total size of the whole molecule. However, $\Phi(\theta)$ is determined by the excluded volume for the whole molecule and hence falls in value below unity more rapidly at high θ:

$$P(\theta) = 1 - (\mu^2/3)<S^2> + \cdots \qquad (7)$$

$$\Phi(\theta) = 1 - (\mu^2/6)<r^2> + \cdots \qquad (8)$$

This effect is very pronounced when $<r^2>$ is large. Hence there is an exaggerated decrease in $\Phi(\theta)/P(\theta)$ which produces the effect referred to. Rather unusually, PS(A)/poly (dimethyl siloxane)(PDMS)(B) block copolymers exhibit this behaviour even when $\nu_B \neq 0$. An explanation invoking $P(\theta)$ and $\Phi(\theta)$ has been proposed (Ref. 61). This system and others also display the unusual feature that the extrapolated line at c=0 can be of positive, zero or negative slope, which means that the apparent dimensions $<S^2_*>$ are of corresponding sign or magnitude. This actually is what has been predicted by Benoit (Ref. 49) and follows from the interrelation among $<S^2_*>$, $<S^2_A>$, $<S^2_B>$, y and (1-y), where $y = W_A\nu_A/\nu$ (W_A is the weight fraction of A in the copolymer). The PS/PDMS copolymers at various values of W_A are rather convenient for examining these predictions since, in many solvents ν_A has a positive value and ν_B a comparable negative one. Most systems studied have PS as component A (Ref. 20-22, 61-64). More detailed discussion has been provided by Tanaka et al. (Ref. 21), who have noted and commented on the onset of blue coloration and iridescence at quite high concentrations for copolymers in which M_A was constant, but M_B variable and ν_B=0.

In more recent work, Tanaka et al. (Ref. 22) have examined the conformational properties of AB block copolymers via two different approaches, viz (i) computer simulation by the Monte Carlo method and (ii) analysis of their own and other L.S. data particularly for the case of ν_B=0. Both (i) and (ii) lead to the conclusion that the radii of gyration of A and B blocks are almost the same as those of the homopolymers of the same molecular weight. On the other hand, (i) indicated that the mean square distance between the centres of gravity of A and B increases markedly with inter-block repulsive interaction, thus rendering the conformation of the blocks and of the whole copolymer more asymmetrical. The effect of this on heterocontacts diminishes with increasing expansion due to excluded volume effects, i.e. with improving solvent quality towards A and B.

Particularly pertinent observations have been made (Ref. 22) on the influence of the ostensibly masked portion B. A solvent is selected so as to yield ν_B=0, but invariably this is only approximately true. Thus PMMA in toluene, in toluene/furfuryl alcohol (40/60 wt.), PI in chlorobenzene have ν_B = 0.004, 0.007 and -0.004 ml/g respectively. Calculations based on equal expansion of the two blocks and invoking both Gaussian coil and hypothetical segregation models show that $<S^2_*>/<S^2_A>$ is equal to unity at low contents of B in the copolymer, but the influence of finite small ν_B can introduce very considerable departure from unity when the weight fraction of B is high (Fig. 3).

Micelles

In block copolymers either A or B can undergo phase separation to form a micellar core, depending on the affinity for the solvent. 2-butanone is a selective solvent for PS/PBD block copolymers, i.e. a non-solvent for PBD. In this solvent (but not in others) L.S. on di- and tri-blocks has indicated micelle formation as evidenced by an abnormally high value of M^* (4×10^6 cf. true value of ca. 4×10^4) (Ref. 65). Reasonable estimates can be made of the number of molecules per micelle. Often L.S. yields useful information in conjunction with temperature variation or measurement of intrinsic viscosity $[\eta]$. Thus, for poly (acrylic acid), the characteristic temperatures for cluster formation and for coil → globule transition have been established (Ref. 66).

Fig. 4 illustrates schematically the reported behaviour (Ref. 67) of a PS-g-PI graft copolymer at different temperatures. n-decane is a poor solvent for PS, but not for PI; methyl cyclohexane is a poor solvent for PI, but not for PS. In (a), M increases greatly on cooling, whereas $<S^2>^{1/2}$ and $[\eta]$ both fall, indicating intermolecular micellation with pronounced segregation of PS and PI at low temperature. The radius of the hydrodynamically equivalent sphere R_η (calculated from $[\eta]$ and M) remains constant, consistent with the supposition that the micelles are compact at low temperature. In (b), M remains constant and $[\eta]$ falls as does $<S^2>^{1/2}$ to a lesser extent. Hence there is no aggregation and $<S^2>^{1/2}$ remains considerably higher than R_η. The intramolecular micelles are concluded to have an open structure with only some slight segregation of components PS and PI.
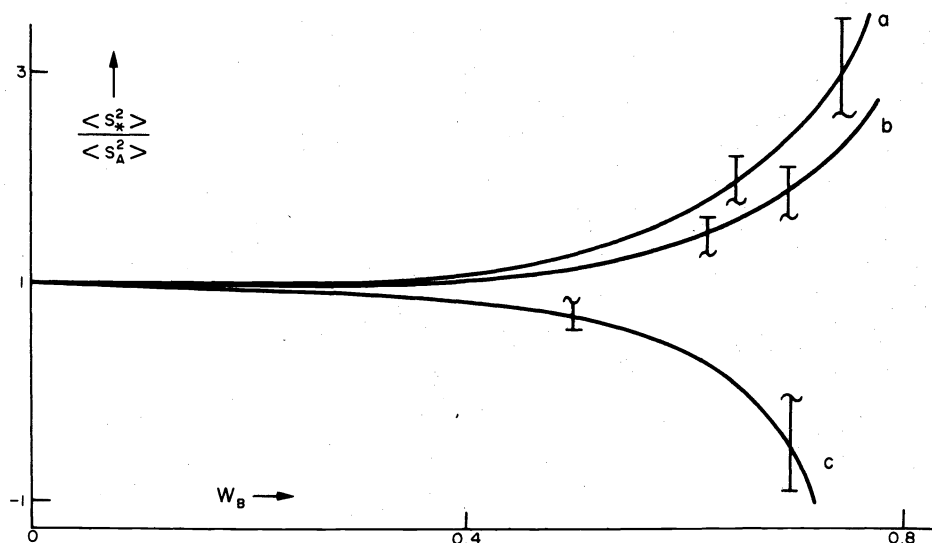
Fig. 3. Departure of the ratio $\langle S_*^2\rangle/\langle S_A^2\rangle$ from unity for A/B block copolymers of different weight fraction (W_B) of B (Ref. 22). Plots are according to model calculations based on equal expansions of A and B, and show the influence of the small finite visibility of almost optically masked B block. Extrema of points are based on a random flight model ($\sim$) and a hypothetical segregation model (-). Values of ν_B/ν_A - (a) 0.007/0.114, PS/PMMA (Ref. 63); (b) 0.004/0.113, PS/PMMA (Ref. 21); (c) - 0.004/0.083, PS/PI (Ref. 20). For nature of solvents - see text.
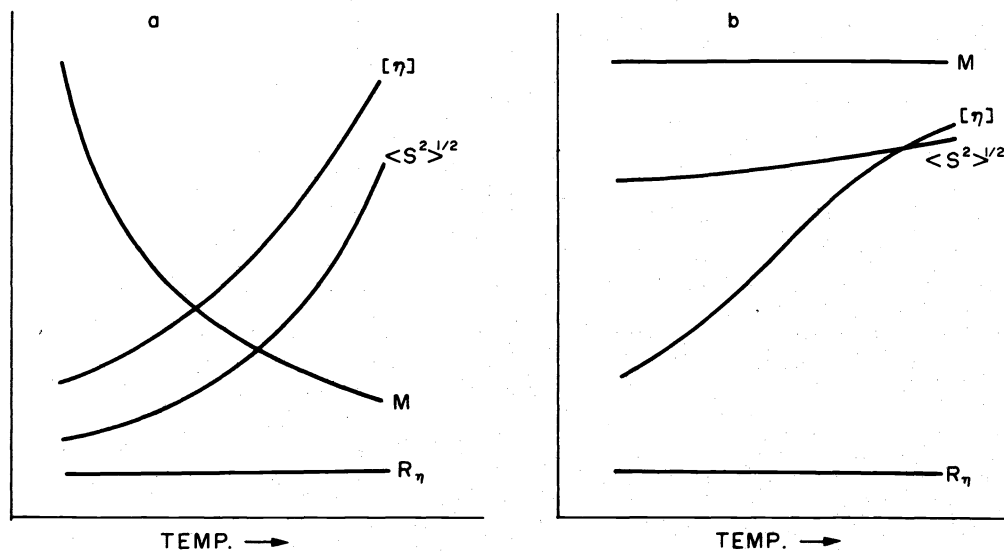

Fig. 4. Influence of cooling on the conformational behaviour of a sample of poly (styrene)-g-poly (isoprene); shown schematically from data in Ref. 67; (a) - highly segregated, compact, intermolecular micelles in n-decane, (b) slightly segregated, open, intramolecular micelles in methyl cyclohexane.

TERPOLYMERS

Characterisation of A/B/C terpolymers by L.S. is in its infancy and present indications suggest that it will pose considerable difficulties. The dependence of the s.r.i.i. (ν) of the terpolymer on its composition was reported by Mächtle (Ref. 68). A variation of ν with conversion is expected and has been demonstrated for PS (A)/poly (acrylonitrile) (B)/PMMA(C). However, for azeotropic composition of feed and terpolymer, ν remains constant up to ca. 50% conversion (Ref. 69). Similarly, for the azeotrope, $M^*/M \not> 1.1$, but M^*/M can attain values up to 1.54 for the non-azeotrope, when solvents affording a range of n_0 values are used (Ref. 56,70).

The interrelation between M^* and M, corresponding to the Benoit expression for copolymers is (Ref. 70):

$$M^* = M + 2P_A(\nu_A-\nu_C)/\nu + 2P_B(\nu_B-\nu_C)/\nu$$

$$+ Q_A(\nu_A-\nu_C)^2/\nu^2 + Q_B(\nu_B-\nu_C)^2/\nu^2$$

$$+ 2R_{AB}(\nu_A-\nu_C)(\nu_B-\nu_C)/\nu^2 \tag{9}$$

By putting B = C, Eq(9) reduces to the expression for an A/B copolymer. There is actually a variety of compositional heterogeneity parameters indicating the deviation of composition from the average (P_A, P_B, P_C, Q_A, Q_B, Q_C) as well as cross-parameters (R_{AB}, R_{BC}, R_{CA}). Moreover, in addition to the molecular weights of the constituents (M_A, M_B, M_C), the molecular weights of constituent pairs (M_{AB}, M_{BC}, M_{CA}) are invoked in expressing the molecular weight in terms of composition and molecular weights of portions comprising the terpolymer (Ref. 71). At present it appears likely that Eq(9) will be used primarily to determine M, but the selection of solvents yielding the appropriate s.r.i.i. values will undoubtedly prove troublesome. Clearly, iso-refractive components B and C within the terpolymer would simplify the implementation of Eq(9). Kambe (Ref. 56) lists the following requisites: (i) homopolymers of A, B and C should be soluble in at least six solvents of widely different n_0 so that ν_A, ν_B, ν_C can be measured directly; (ii) the terpolymer should be soluble in these solvents so that ν can be measured in them; (iii) the differences $|\nu_A-\nu_B|$ etc. should be large; (iv) the sample must, of course, be heterogeneous enough to afford large values of M^*/M.

COMPATIBILITY

Gross effects of incompatibility are clearly discernible, and are thermodynamically definable for phase separation in solutions. However, more subtle and less clear-cut partial compatibility is not yet really quantified. On the basis of several (possibly arbitrary) criteria, Krause (Ref. 72) has listed pairs of polymers with respect to their compatibility; extremely few pairs of common polymers exhibit compatibility within her frame of reference. In L.S. studies on two polymers in a common solvent, the polymers are usually designated by 2 and 4 (rather than A and B). Such studies have been reviewed fully by Hyde (Ref. 73) and discussed by Kratochvíl (Ref. 12). In continuation of their earlier work, Kuhn et al. (Ref. 74) have proposed a new method for estimating incompatibility from Zimm diagrams that are anomalous in the respect that at $\theta = 0°$, the second virial coefficient changes from positive to zero to negative values with increasing concentration of one polymer. Optical masking of one polymer is employed. Optical masking has also been used (Ref. 75) to study polymer mixtures in solution at temperatures in the vicinity of the critical temperature.

Using Stockmayer's theory of multicomponent systems, Kratochvíl et al. (Ref. 76) have re-examined systems already studied and have carried out numerous experiments (mainly on PS + PMMA + liquid). The primary aim was to quantify polymer 2-polymer 4 compatibility in terms of the interaction parameter A_{24}, which is the analogue of the second virial coefficients A_{22} (for polymer 2 in the liquid) and A_{44} (for polymer 4 in the liquid). Two main approaches have been adopted, viz (i) The ratio of the concentrations (C_2/C_4) is kept constant and the solution is diluted with the liquid. Provided the appropriate information (e.g. A_{22}, M_2, A_{44} M_4 etc.) is obtained first from separate experiments on 2 and 4, the value of A_{24} may be isolated from the slope in a plot of:

$$K(C_2 + C_4)/R = \text{Intercept} + \text{Slope} (C_2 + C_4)$$

where K is an optical constant not containing the s.r.i.i. and R is the Rayleigh ratio at $\theta = 0$ (ii) The concentration C_4 is kept constant. Hence the solvent is regarded as (polymer 4 + liquid) and C_2 alone is varied by dilution with this solvent of constant composition. Provided the same preliminary information as for (i) is established, the value of A_{24} may be isolated from the intercept at $C_2 = 0$ in a plot of:

$$Kv_2^2C_2/R = \text{Intercept} + \text{Slope} (C_2)$$

The range of concentration over which the theory and approximations made are valid has been examined. In particular it has been noted that the region of low overall $(C_2 + C_4)$ is subject to considerable error, because the contribution of the interaction between dissimilar polymers to the total L.S. is small.

An interesting comparison has been made (Ref. 77) between selective adsorption or desorption in systems comprising one polymer in a binary liquid mixture and the situation obtaining for a mixture of 2 + 4 in one solvent. The interaction between dissimilar polymers is regarded as selective desorption of one polymer by the other. A relation is derived between the coefficient of selective adsorption and A_{24}. It is noted that under certain condition, the introduction of 4 into a solution of 2 may produce a decrease in the L.S. from the solution. Qualitatively, the limited interpenetration of dissimilar polymers, still strongly suppressed by their incompatibility (selective desorption), reduces the concentration fluctuations in solution and thus the intensity of scattered light. Zero and negative excess L.S. intensities for several (2 + 4 + solvent) systems are scheduled to be reported (Ref. 77, 78).

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