Translated from *Uspekhi Khimii*, 53, 880-895 (1984) U.D.C. 541.64 : [illegible]39.199 : 532.72

Dynamic Light Scattering and Thermal Motion of Macromolecules in Solutions

V.S.Skazka

The theory and practice of a new method of studying the translational and rotational mobility of macromolecules in solution by dynamic light scattering are briefly outlined. Experimental assemblies are described, and results obtained by this method for macromolecules of different chemical structure are reported. The possible applications of the method and its likely future developments are discussed.
The bibliography includes 47 references.

CONTENTS

I. Introduction 506
II. Theoretical foundations 506
III. Measurement principles 508
IV. Some experimental results 510
V. Further developments of the method 513

I. INTRODUCTION

In diffusion, sedimentation, and viscosity phenomena the organised translational and rotational motion of macromolecules in solutions takes place as a result of their interaction with an external field of force: in diffusion, the field of the chemical potential gradient, in sedimentation, the centrifugal force field, and in viscous flow, the field of the flow velocity gradient. The presence of these fields (external to the macromolecule) can perturb the results. Therefore in many experiments allowance must be made for these perturbing effects, usually by extrapolating the results to zero values of the fields or gradients.

However, we can approach the study of the mobility of macromolecules in a different way: by using the dynamic light scattering method. Macromolecules in solution are in a state of continuous thermal motion. The displacement of their centre of gravity, which characterises the "macro-Brownian" motion[1], can be described according to Einstein's theory in terms of the translational diffusion coefficient D. The "micro-Brownian" motion of the individual segments of the macromolecule is determined by the rotational diffusion coefficient D_r and by the spectrum of relaxation times for the small-scale intramolecular motions[2]. The Brownian motion causes fluctuations in the concentration of the macromolecules in solution, and these fluctuations can scatter the electromagnetic energy when a light wave is passed through the solution. Therefore the light scattered by a solution of a polymer must contain (in principle) information on the kinetic characteristics of the macromolecules.

II. THEORETICAL FOUNDATIONS

The classical theory[3] deals with the scattering of light on time-averaged fluctuations of the concentration of the solution $\overline{(\Delta c)^2}$. This treatment leads to formulae giving the molecular weight of the dissolved macromolecules, their size, and the thermodynamic parameters of the solution–solvent system from the intensity of the scattered light[3].

In practice, however, the fluctuations are time-dependent owing to the presence of thermal Brownian motion, and therefore the time dependence of the fluctuations is determined by the kinetic parameters of the macromolecules in solution. Concentration fluctuations arise, grow, and disappear with time: this produces a modulation of the frequency of the scattered light, i.e. a shift of its frequency with respect to the incident frequency. The frequency shift can be interpreted as the manifestation of the Doppler effect during light scattering by moving macromolecules whose velocity in the solution is determined by the intensity of the Brownian motion. The light scattered by the solution will have a distribution of frequency (of variable width) with a profile centred on frequency of the incident light. Thus the width of the scattering spectrum carries information on the statistical distribution of the kinetic parameters of the macromolecules in solution.

The molecular theory of the spectral distribution of the intensity of light scattered by liquids was formulated by Komarov and Fisher[4], who used the mathematical framework of space–time correlation functions proposed by van Hove[5]. For any system of N particles we can define the probability density G_1 of finding a given particle at time $t = 0$ at a point in the solution having the coordinate r_0, and at time $t > 0$ at the point r, irrespectively of the position of the other particles. Another characteristic quantity (G_2) defines the probability density of finding a particle at the point r in the solvent at time $t > 0$ when another particle is at the point r_0 at time $t = 0$.

The functions G_1 and G_2 are the internal and the external autocorrelation function respectively. The internal autocorrelation function G_1 describes the probability of displacements of a given particle in the solution, the external function G_2 describes the probability of the relative displacement in the solution of two particles whose motions are assumed to be mutually independent.

The time autocorrelation function $G(\tau)$ for any function $x(t)$ is given by the expression

$$G(\tau) = \lim_{T\to\infty} \frac{1}{2T} \int_{-T}^{T} x(t)\, x^*(t+\tau)\, \mathrm{d}t = \langle x(t)\, x^*(t+\tau) \rangle ,$$

where $x(t)$ is the value of the function at time t, and $x^*(t + \tau)$ is the complex conjugate value of this function at time $t + \tau$: the angle brackets denote averaging with respect to time. The autocorrelation function differs from other averages in being independent of the variable τ.

The spectral density of the intensity of scattered light is found by a Fourier transformation of the space–time function for the scattering system:

$$\mathcal{J}(\omega) = \int_{-\infty}^{\infty} G(\tau) \exp(i\omega\tau)\, d\tau .$$

The theory of dynamic light scattering by solutions of polymers was developed by Pecora[6–8]. The theory is too complex to be reviewed in detail, and we shall confine ourselves to describing the main physical postulates on which it is based. Pecora considers two independent correlation functions. The first [the autocorrelation functions for the centre of gravity of the macromolecule, $G_\phi(\tau, \mathbf{r})$] is defined as the probability of finding the centre of gravity of a molecule at the point r at time $t > 0$ if at time $t = 0$ the centre of gravity of the same molecule is at the origin of the coordinate system. The second correlation function is the space–time correlation function $G_A(\tau, \mathbf{r})$, which defines the probability of a second segment of a macrmolecule being found at the point r at time $t > 0$ if an arbitrarily chosen segment of the same macromolecule is at the origin at time $t = 0$. Thus the quantity $G_A(\tau, \mathbf{r})$ defines the correlation between the motions of the segments within the macromolecule.

The optical spectrum of the scattered light is found by Fourier transformation of the correlation functions $G_\phi(\tau, \mathbf{r})$ and $G_A(\tau, \mathbf{r})$:[9]

$$\mathcal{J}(\omega) = \frac{N}{2\pi} \int_{-\infty}^{\infty} G_A(\tau, \mathbf{r})\, G_\Phi(\tau, \mathbf{r}) \exp[i(\omega - \omega_0)\tau]\, d\tau ,$$

where

$$G_A(\tau, \mathbf{r}) = \langle A(t) A^*(t+\tau) \rangle$$
$$G_\Phi(\tau, \mathbf{r}) = \langle \exp\{-i[\mathbf{q}, \mathbf{r}(t)]\} \exp\{i[\mathbf{q}, \mathbf{r}(t+\tau)]\} \rangle .$$

The vector q is the difference between the wave vectors of the incident and the scattered wave. Its numerical value is

$$q = \frac{4\pi n_0}{\lambda_0} \sin\frac{\vartheta}{2} .$$

In this expression n_0 is the refractive index of the medium, λ_0 is the wavelength of the incident light in a vacuum, and ϑ is the scattering angle.

The physical meaning of the quantity $A(t)$ can be explained as follows. The light wave scattered by every jth particle (of a total number N of particles) is defined by the equation

$$E_j = A_j(t) \exp\{-i[\mathbf{q}, \mathbf{r}_j]\} \exp(i\omega_0 t) ,$$

where $A_j(t)$ is the amplitude of the wave scattered from the jth particle.

The aggregate field of the light wave from N scattering elements is

$$E_s = \sum_{j=1}^{N} E_j = \sum_{j=1}^{N} A_j(t) \exp\{-i[\mathbf{q}, \mathbf{r}_j(t)]\} \exp(i\omega t) . \qquad (1)$$

The intensity of the scattered light is proportional to the square of the amplitude of the light wave:

$$\mathcal{J}_s = \langle |E_s|^2 \rangle , \qquad (2)$$

On the assumption that the light scattering events from all the particles in solution are mutually independent, carrying out the summation of Eqn.(2) after inserting Eqn.(1) into it gives

$$\mathcal{J}_s = \left\langle \sum_{j=1}^{N} |A_j|^2 \right\rangle = N \langle |A|^2 \rangle .$$

Thus the parameter $A(t)$ is the average amplitude of the scattered light wave.

If we ignore the intramolecular thermal motion of the macromolecules, i.e. if we neglect the rotational motion and the mutual displacement of the segments, the autocorrelation function takes it simplest form:

$$G_A(\tau, \mathbf{r}) = N |A|^2 .$$

The optical spectrum is given by the equation

$$\mathcal{J}(\omega) = N |A|^2 \frac{1}{2\pi} \int_{-\infty}^{\infty} \exp[i(\omega - \omega_0)\tau]\, G_\Phi(\tau)\, d\tau .$$

The autocorrelation function $G_\phi(\tau)$ can be calculated by noting that it describes a time dependence analogous to that of a large concentration fluctuation artificially imposed on the system at time $t = 0$.[10] Concentration changes in such a fluctuation obey Fick's law, which for $G_\phi(\tau)$ can be written as

$$\partial G_\varphi(\tau)/\partial\tau = D\nabla^2 G_\varphi(\tau) , \qquad (3)$$

where D is the translational diffusion coefficient of the macromolecule. Solving Eqn.(3) by the method of Fourier transforms in space gives

$$G_\varphi(\tau) = \exp(-Dq^2\tau) . \qquad (3')$$

Hence

$$\mathcal{J}(\omega) = \frac{N|A|^2}{2\pi} \int_{-\infty}^{\infty} \exp[i(\omega - \omega_0)\tau] \exp(-Dq^2\tau)\, d\tau =$$
$$= \frac{N|A|^2}{2\pi} \frac{q^2 D}{(\omega - \omega_0)^2 + (q^2 D)^2} . \qquad (4)$$

The shape of the spectral line is Lorentzian, centred on the frequency ω_0. The half-width of the Lorentz outline, $(\Delta\omega)_{1/2} = (\omega - \omega_0)_{1/2}$, is simply related to the translational diffusion coefficient:

$$(\Delta\omega)_{1/2} = q^2 D . \qquad (5)$$

Usually in dynamic light scattering experiments the solution is irradiated with polarised light, with the electric vector of the light wave in a vertical plane, and the intensity of the scattered light with the same polarisation is measured. The intensity of this component can be denoted $\mathcal{J}_{VV}$, and identified with the the quantity given by Eqn.(4). It is also possible to determine the intensity of the component of the scattered light in which the polarisation of the light wave is horizontal ($\mathcal{J}_{HV}$).

Formula (4) applies if the size of the macromolecule $(\overline{h^2})^{1/2}$ is much less than the wavelength λ_0 of the incident light. The criterion of smallness for a molecule in dynamic light scattering is the same as the criterion adopted in the classical theory of light scattering[3]: $(\overline{h^2})^{1/2} \leq \frac{1}{20}\lambda_0$. Under these conditions the internal interference (Debye) function is $P(\theta) = 1$. For large molecules, when $P(\theta) < 1$, the intensity of the light scattered by isotropic spherical symmetrical molecules is obtained by multiplying the right-hand side of Eqn.(4) by $P(\theta)$.[8] In this case the $\mathcal{J}_{VV}(\omega)$ spectrum is unaffected by intramolecular motion.

On the other hand if the macromolecule is asymmetrical the scattering spectrum is affected by the internal thermal motion (molecular rotation). Assuming that the translational and the rotational motion of the macromolecule are mutually

independent we obtain the following equation for the spectrum of the scattered light:

$$\mathcal{J}_{vv}(\omega) = \frac{4NA}{\pi}\alpha^2\left\{\left|\frac{1}{n}\sum_{j=1}^{n/2}J_0(qb_j)\right|^2\frac{q^2D}{(\omega-\omega_0)^2+(q^2D)^2} + \right.$$
$$\left. + 5\left|\frac{1}{n}\sum_{j=1}^{n/2}J_2(qb_j)\right|^2\frac{q^2D+6D_r}{(\omega-\omega_0)^2(q^2D+6D_r)^2} + \ldots\right\}. \qquad (6)$$

The scattered light spectrum is the sum of two Lorentzian curves whose relative statistical weight is determined by the squares of sums containing the spherical Bessel functions J_0 and J_2 (zero-order and second-order respectively). In Eqn.(6) n is the number of segments, b_j is the distance of the jth segment from the centre of gravity of the macromolecule, and α is the polarisability of the macromolecule.

The intramolecular Brownian thermal motion affects the spectral distribution of the intensity of scattered light. The micro-Brownian motion in a group of macromolecules has been calculated[11] by using the sub-chain model (see, for example, Ref.12), in which the macromolecule is assumed to contain a number of linearly arranged, freely interconnected segments, each of which acts as a flexible "sub-chain". The hydrodynamic interaction with the solvent is transmitted by beads at the ends of the sub-chains, which have a significant mass and a coefficient of friction ξ. Each bead experiences highly elastic forces from the neighbouring sub-chains. The action of these forces is similar to that of a spring with linear characteristics, and the distance between the ends of sub-chains is assumed to have a Gaussian distribution.

Thus by studying the dynamics of motion of the segments in real macromolecules we are studying the dynamics of motion of a set of beads interconnected by elastic springs and immersed in a viscous medium. The motion of the jth bead determines the jth mode of the intramolecular motion, and is characterised by a relaxation time (τ_j). Unfortunately the theory does not allow us to calculate τ_j for all j. Only τ_1 (which refers to the rotation of the macromolecule as a whole) is theoretically calculable. For the two extreme cases of negligibly small and of maximum possible hydrodynamic interaction (penetrable and impervious group of macromolecules respectively) the following formulae have been obtained[11] for τ_1:

$$\tau_1 = \frac{6M[\eta]\eta_0}{\pi^2RT} \text{ and } \tau_1 = \frac{0.422M[\eta]\eta_0}{\pi^2RT}.$$

The spectrum of the scattered light with allowance for the intramolecular thermal motion by the Rouse and Zimm theory is described by the equation[13]

$$\mathcal{J}_{vv} = P_0(x)\frac{q^2D}{(\omega-\omega_0)^2+(q^2D)^2} + \sum_{j=2}^{\infty}P_1(x)\frac{q^2D+1/\tau_j}{(\omega-\omega_0)^2+(q^2D+1/\tau_j)^2} +$$
$$+\sum_{j=1}^{\infty}P_2(x)\frac{q^2D+1/\tau_j}{(\omega-\omega_0)^2+(q^2D+1/\tau_j)^2}. \qquad (7)$$

The argument z of the scattered light amplitudes P_0, P_1, and P_2 depends on the size of the macromolecules: $x = q^2\bar{h}^2/6$. For $0 \leq x \leq 1$ the only contribution to $\mathcal{J}_{vv}(\omega)$ is that of the diffusional motion of the centre of gravity of the macrmolecules, given by the first term in the right-hand side of Eqn. (7). The contribution of the internal motion to the spectral distribution of the intensity of scattered light becomes significant only when $x \gg 1$. These values of x are reached only in macromolecules having a mass $>10^6$ and in measurements with large scattering angles θ.[14]

If the macromolecule has a significant optical anisotropy the spectral distribution of scattered light intensity shows contributions from the translational motion of the centre of gravity of the macromolecules (D) and from the rotation of the molecule as a whole, characterised by the rotational diffusion coefficient D_r. The rotation of the macromolecules modulates the intensity of the scattered light at a frequency equal to the rotation frequency of the group of macromolecules: this effect is directly observable in the spectrum of the scattered light. The intensities of the $\mathcal{J}_{vv}$ and $\mathcal{J}_{Hv}$ components in the scattered light are given by

$$\mathcal{J}_{vv}(\omega) = \frac{NA}{9\pi}(\alpha_\parallel + 2\alpha_\perp)^2\frac{q^2D}{(\omega-\omega_0)^2+(q^2D)^2} + \frac{4}{3}\mathcal{J}_{Hv} \qquad (8)$$

$$\mathcal{J}_{Hv}(\omega) = \frac{NA}{9\pi}(\alpha_\parallel - \alpha_\perp)^2\frac{q^2D+6D_r}{(\omega-\omega_0)^2+(q^2D+6D_r)^2}, \qquad (9)$$

where $\alpha_\parallel$ and $\alpha_\perp$ are the polarisabilities of the macromolecules in directions parallel and perpendicular to the molecular axis respectively.

Eqns.(4), (6), (8), and (9) form the basis of all methods of determining D, D_r, and τ for macromolecules in solution from experimental measurements of the dynamic scattering of light.

In its present state of development the theory of the dynamic scattering of light does not allow for concentration effects in the system, i.e. it is strictly applicable only to solutions at infinite dilution. However, some experimental studies of the concentration dependence of the shape of the scattered line have been reported[15,16]. It is assumed implicitly that the equations which relate the shape of the spectrum to the parameters of the molecular motion remain valid at finite concentrations, but this assumption has no theoretical justification.

III. MEASUREMENTS PRINCIPLES

When using the dynamic light scattering method in practice we should note that the frequency shift of the scattered light for polymer solutions is of the order of $\Delta\omega \cong 10^3$–10^4 Hz. Therefore in order to distinguish these frequencies in the optical spectrum ($\omega_0 \cong 10^{15}$ Hz) we need a spectroscopic equipment with a resolving power of $\omega_0/\Delta\omega \cong 10^{11}$ or better. The resolving power of ordinary optical methods is far from being adequate for this purpose. Furthermore the spectral width of the incident light should be less than $\Delta\omega$: this condition can be met by using laser light.

The spectral distribution of the intensity of scattered light is studied by optical mixing methods, which are an extension to the optical frequency range of methods commonly used at radio frequencies[9,17]. The wanted signal is transmitted by using waves having a carrier frequency $\omega_0 \cong 10^6$ Hz, modulated at the frequency of the signal ($\Delta\omega$). In the detector these waves are mixed with a reference signal of frequency comparable to that of the carrier wave: the interference between the reference and the carrier frequency reveals the wanted signal $\Delta\omega$. By using a laser as the light source in conjunction with an FEU photoelectric amplifier and a spectrum analyser the same procedure can be applied to waves in the optical frequency range.

The optical mixing used in these measurements consists in the destructive interference of two light waves (reference, and carrier) incident on the cathode of the FEU. The result is a modulation of the current taken from the FEU. The modulation frequencies correspond to the frequencies in the wanted signal, and the signal is centred on the frequency difference between the reference wave and the information-carrying wave. If the frequency of the reference wave is comparable to that of the wave carrying the information (i.e. the light scattered by the polymer solution) the current taken from the FEU will display the frequencies of the wanted

signal. The dependence of the photocurrent on $\Delta\omega$ will be determined by the shape of the spectral line of the incident light, with the important difference from the normal optical methods (for example, the Fabry–Pérot interferometer or other similar apparatus) that the changes in photocurrent are now in the audio frequency range, whereas the frequency changes which define the shape of the spectral line are centred on the optical frequency $\omega_0 \cong 10^{15}$–10^{16} Hz.

The procedure can be illustrated as follows. Let a light wave of amplitude E_0 and frequency ω_0 fall on the scattering particles 1 and 2 in a state of Brownian motion with velocities v_1 and v_2. The light scattered by these particles (observed at an angle θ) will contain the Doppler frequency shifts $\Delta\omega_1$ and $\Delta\omega_2$ with respect to the base frequency ω_0. To simplify the discussion we shall assume equal amplitudes E_1 and E_2 of the components scattered by particles 1 and 2 in the light wave incident on the FEU photocathode. Since the current at the output of the FEU is proportional to the square of the amplitude of the light wave, and the FEU cannot resolve frequencies above 10^9 Hz, we can express the current I by the formula

$$I = \text{const} + E^2 \cos(\Delta\omega_1 - \Delta\omega_2)t .$$

Since $\Delta\omega_1$ and $\Delta\omega_2$ are ~10^3–10^4 Hz it follows from this equation that the photocurrent at the FEU output is modulated by two audio frequencies. In practice, of course, the shifted frequencies of the light wave ($\Delta\omega$) form a complex spectrum which characterises the system and is reflected in the frequency dependence of the photocurrent. Since the beat frequencies of the photocurrent are in the audio region they can be analysed with standard spectral frequency analysers used in radio technology. Their resolving power is usually better than 10 Hz, which is several orders better than the resolving power of ordinary optical spectroscopy equipment.

Two experimental arrangements can be used[9] to extract from the scattered light spectrum the signal carrying information on the kinetic parameters of the scattering macromolecules. In the first (homodyne) assembly the beam of scattered light strikes the surface of the photocathode, where interference between the frequencies contained in the spectral line can take place. In this case the wave whose frequency corresponds to the maximum of the spectral line of the scattered light acts as the reference wave. A beat signal centred on the frequency 0 Hz appears at the output of the FEU. In the second (heterodyne) scheme a reference (base) beam of light of frequency ω_b, obtained from a separate source, is directed at the photocathode together with the experimental beam of scattered light. In this case the beat signal is centred on the frequency $\omega_0 - \omega_b$. If the same laser is used as the base source and for generating the signal, $\omega_0 - \omega_b = 0$, and the signal is centred on the frequency 0 Hz (as in the homodyne variant).

We note that the description "centred" is applied to the beat signal on the understanding that only frequencies $\omega > 0$ have a real significance, i.e. the beat signal has only one branch. We should also stress that so far no really ambiguous names have been proposed for the two variants described above. In particular, the homodyne method has been called the self-beat method[10].

At present the homodyne method of producing beat signals is the more widely used. In the homodyne scheme the photocurrent duplicates the outline of the scattered line (except for a d.c. component and the shot noise of the FEU), but with double the width:

$$I(\omega) = C_1 \frac{2q^2 D}{(\Delta\omega)^2 + (2q^2 D)^2} , \qquad (10)$$

In the heterodyne scheme the outline of the photocurrent line exactly duplicates that of the scattering line of the spectrum.

A typical homodyne assembly[19] for measuring $\mathcal{J}_{vv}$ at different scattering angles θ is shown in Fig. 1. It consists of a circular photoelectric nephelometer in which the intensity of scattered light can be measured for angles in the range $\theta = 30$–$150°$. The experimental solution is placed in the cylindrical cell K, on which the light of a He–Ne laser ($\lambda_0 = 632.8$ nm) is focussed by the diaphragms D_1 and D_2 and the lens L_1. To optimise the signal-to-noise ratio the scattering volume and its reflection on the photocathode should be as small as possible[9]. By focussing the laser radiation the beam diameter can be reduced to 0.2–0.3 mm. The scattered light is focussed on the photocathode of the FEU by the diaphragm D_3 and L_2, whose focal length is chosen to give an image on the photocathode smaller than the diameter of the light beam in the measuring cell K. The photocurrent from the output of the FEU is taken to the KP amplifier, which has linear frequency characteristics and a stable gain at audio frequencies. The d.c. component of the FEU output is eliminated by a capacitor and the current from the KP is led to the input of the spectrum analyser SA (standard radiotechnical model).

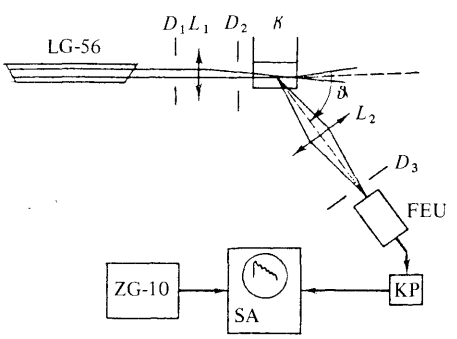


Figure 1. Homodyne variant of the apparatus for studying the dynamic scattering of light in polymer solutions[19]

The spectral distribution of the intensity of scattered light is displayed by analysing the frequency dependence of the photocurrent, $I(\omega)$, at the output of the SA. The photocurrent is characterised by comparing it with the mathematically expected signal and its frequency dependence. The audio frequency generator ZG-10 is used to calibrate the frequency scale of the scan of the SA oscilloscope. The frequency at which the signal is 3 dB down is measured for $\Delta\nu = (\Delta\omega)/2\pi \to 0$. This frequency $(\Delta\nu)_{1/2}$ is assumed to be equal to the half-width of the photocurrent line. In the

homodyne variant the parameter $(\Delta\nu)_{1/2}$ is related to the diffusion coefficient by the equation

$$2\pi(\Delta\nu)_{1/2}=(\Delta\omega)_{1/2}=2q^2D\ , \qquad (11)$$

measured at different values of θ and extrapolated to $\theta = 0$ the intercept on the vertical axis is

$$(\Delta\omega)_{1/2}=6D_r\ , \qquad (12)$$

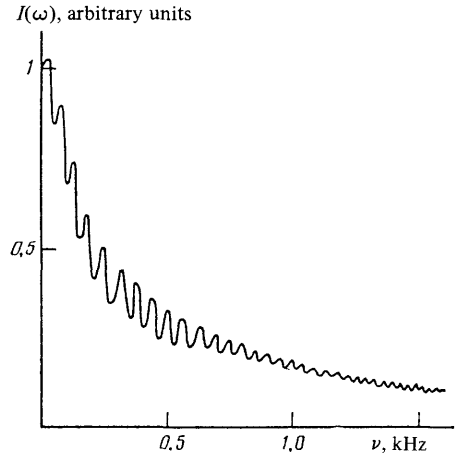


Figure 2. Outline of the photocurrent line on the screen of the spectrum analyser for a solution of the $M = 10^7$ fraction of polystyrene in toluene; $c = 0.05\%$, scattering angle $\theta = 60°$.[19]

A typical plot of the photocurrent against frequency at the FEU output, photographed from the screen of the spectrum analyser, is shown in Fig.2.

IV. SOME EXPERIMENTAL RESULTS

Measurements of $(\Delta\omega)_{1/2}$ as a function of θ are shown in Fig.3 for some polymer solutions. The D values calculated from the slope of the lines are given in Table 1 together with the D values obtained by an independent method (polarisation interferometry). The concentration of the solutions were the same in both sets of measurements (~0.05%). As Table 1 shows, the agreement between the D values obtained by the two methods is acceptable.

We note that the extrapolation of curve *2* in Fig.3 does not pass through the origin. This effect is due to the anisotropic component of the light scattered by polystyrene (PS) solutions. It follows that at the highest molecular weights the amplitude modulation of the light scattered by PS solutions is large enough to be experimentally detectable. Amplitude modulation of the scattered light results from the rotational motion of macromolecules showing optical anisotropy.

The $\mathcal{I}_{VV}$ spectrum of the scattered light for an anisotropic molecule is the sum of at least two Lorentzian curves according to Eqn.(8). The half-width is determined by the parameters D and D_r, and the contribution from the translational diffusion decreases as the scattering angle decreases. In principle this allows us to separate the component due to molecular rotation from the overall spectrum. If $(\Delta\omega)_{1/2}$ is

Table 1. Diffusion coefficients D for some polymers, determined by dynamic light scattering and by measurements of longitudinal diffusion in solutions[19].

Polymer	Solvent	$10^{-6}M$	$10^{11}D$, $m^2 s^{-1}$	
			light scattering	longitudinal diffusion
Polystyrene	toluene	1.0	1.3	1.4
Polystyrene	»	13.0	0.6	0.5
Styrene–methyl methacrylate block copolymer	butyl acetate	0.6	1.6	1.8
Polyvinyltrimethylsilane	cyclohexane	0.5	1.0	1.04

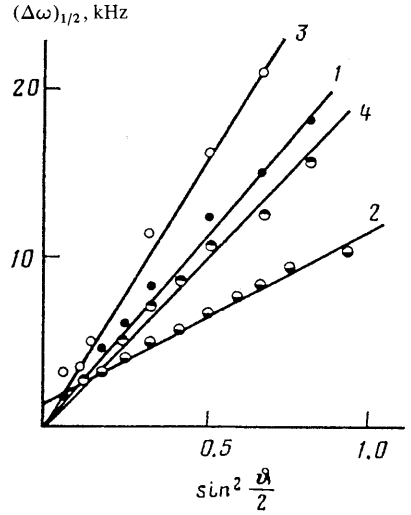


Figure 3. Plots of the half-width of the scattering angle $(\Delta\omega)_{1/2}$ against $\sin^2\theta/2$ for polystyrene (*1*, *2*), the styrene–methyl methacrylate block copolymer (*3*), and polyvinyltrimethylsilane (*4*).[19]

Experiments of this type for F-actin are reported in Ref. 20. The D_r values calculated by Eqn.(12) were close to the values given by other methods for this polymer.

An analysis of the frequency dependence of $\mathcal{I}_{VV}$ has been reported[21] for the PS fraction with $M = 10^7$ in benzene and decalin. An appropriately oriented Frank–Ritter prism was inserted into the scattered light path of the apparatus shown in Fig.1 to separate $\mathcal{I}_{VV}$ from the overall scattered intensity. The root mean square radius of inertia of the PS molecule in benzene was found to be $(\overline{R^2})^{1/2} = 140$ nm from the light scattering results. This value of $(\overline{R^2})^{1/2}$ accounted for a change from 6 to 1 in $x = q^2\overline{h^2}/6 = q^2\overline{R^2}$ for solutions in benzene over the working range of scattering angles. The range of x values for solutions of PS in decalin was calculated from the radius of inertia of the PS macromolecules

obtained by Flory's formula from the characteristic viscosity. The choice of these solvents was dictated by the difference in their thermodynamic properties in relation to PS and by the large difference in their viscosities.

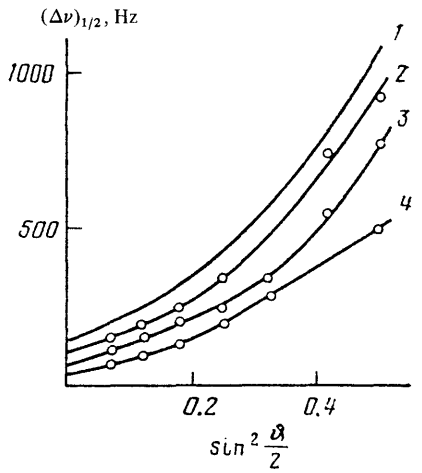


Figure 4. Plots of the half-width of the scattering line $(\Delta\nu)_{1/2}$ against $\sin^2\theta/2$ for solutions of the $M = 10^7$ fraction of polystyrene in toluene at different concentrations: *1*) 0; *2*) 0.06; *3*) 0.12; *4*) 0.18 g/100 cm^3.[21]

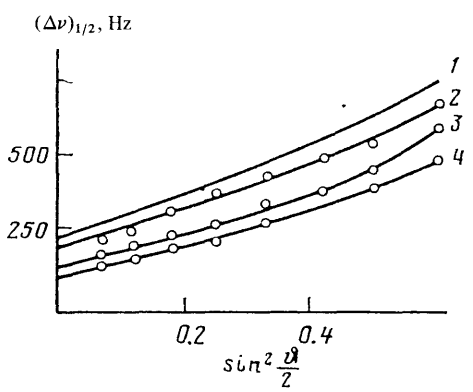


Figure 5. Plots of the half-width of the scattering line $(\Delta\nu)_{1/2}$ against $\sin^2\theta/2$ for a solution of the $M = 10^7$ fraction of polystyrene in decalin at different concentrations: *1*) 0, *2*) 0.05, *3*) 0.12, *4*) 0.17 g/100 cm^3.[21]

The dependence of $(\Delta\nu)_{1/2}$ on $\sin^2\theta/2$ for solutions of PS in benzene and in decalin at different concentrations is shown in Figs.4 and 5. The shape of the scattering line at all the concentrations can be described as the sum of at least two Lorentz curves, as indicated by the non-linearity of the plots in Figs.4 and 5. The width of the spectral distribution of the scattered light intensity increases as the concentration of the solution decreases. The results were therefore extrapolated to zero concentration. Fig.6 shows the dependence of $(\Delta\nu)_{1/2}$ on the concentration of the solution c for the scattering angle $\theta = 0$: the plot is linear within experimental error. Linear plots of $(\Delta\nu)_{1/2}$ against c were obtained also for other (non-zero) scattering angles. Plots of $(\Delta\nu)_{1/2}$ against $\sin^2\theta/2$ for $c = 0$ are shown as the upper lines in Figs.4 and 5. Extrapolation of the data in Fig.6 to $\theta = 0$ gave the $(\Delta\nu)^0_{1/2}$ values: the half-widths of the scattering spectra for $\theta = 0$ and $c = 0$. The $(\Delta\nu)^0_{1/2}$ values were used to calculate the rotational diffusion coefficients of the PS molecules in benzene and decalin by the equation

$$2\pi(\Delta\nu)^0_{1/2} = (\Delta\omega)^0_{1/2} = 2 \cdot 6D_r \,. \qquad (13)$$

The D_r values and some physical parameters of the PS solutions are given in Table 2.

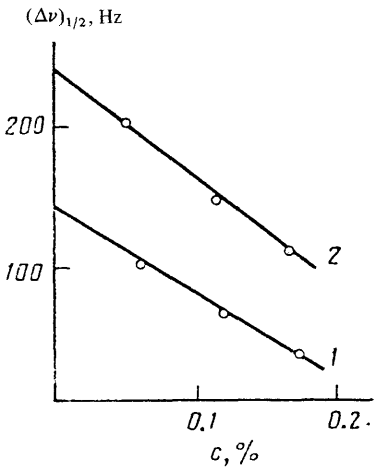


Figure 6. Dependence of $(\Delta\nu)_{1/2}$ at the scattering angle $\theta = 0$ on the concentration of the solution (c) for the $M = 10^7$ fraction of polystyrene in toluene (*1*) and in decalin (*2*).[21]

Table 2. Physical characteristics of solvents and of the solutions of the $M = 10^7$ fraction of polystyrene[21]

Solvent	$10^3\eta_0$, Pa s	x	D_r, s^{-1}	
			light scattering	FBR
Benzene	0.64	1—6	120	100
Decalin	2.07	0.6—3.4	80	—

At low values of the scattering angle θ the parameter $\mathcal{J}_{vv}$ is controlled by the first term of Eqn.(8). Under these conditions the dependence of $(\Delta\nu)_{1/2}$ on $\sin^2\theta/2$ is described by a straight line whose slope is proportional to the translational diffusion coefficient D. Using the homodyne method of detecting the scattered light we find, for small θ,

$$2\pi[(\Delta\nu)_{1/2} - (\Delta\nu)^2_{1/2}] = 2q^2D \,. \qquad (14)$$

The diffusion coefficients of the PS fraction calculated for $c = 0$ from the initial slope of the curves in Figs.4 and 5 are $D = 0.4 \times 10^{-11}$ m^2 s^{-1} in benzene and 0.2×10^{-11} m^2 s^{-1} in decalin.

It is interesting to compare the D_r values obtained in this way with data on the rotational diffusion coefficient of PS in benzene calculated from measurements[22] of flow birefringence (FBR). According to those measurements, $D_r = 100$ s^{-1} for the $M = 10^7$ fraction of PS. This is acceptably close to the value $D_r = 120$ s^{-1} given by the dynamic light scattering method (see Table 2). The difference between the two values is probably due partly to the difference between the methods of determining D_r and partly to the dependence of $\mathcal{I}_{VV}$ on the mode of dispersion of the sample. The effective spectral broadening (and therefore also the D_r value) for $x < 10$ is greater for polydispersed than for monodispersed samples[23].

The role of the second term in Eqn.(8), which according to Eqn.(9) is proportional to $(\alpha_\parallel - \alpha_\perp)^2$, increases markedly with the anisotropy of the macromolecules. In principle, the anisotropic component $\mathcal{I}_{HV}$ can be measured at the scattering angle $\theta = 0$. This allows complete elimination of the Doppler effects due to the translational motion of the macromolecules on the spectral distribution[24,25]. From Eqn. (9) for $\theta = 0$ we obtain

$$\mathcal{I}_{Hv} = \frac{NA}{9\pi}(\alpha_\parallel - \alpha_\perp)^2 \frac{6D_r}{(\Delta\omega)^2 + (6D_r)^2} .$$

Under these conditions the scattering spectrum has a simple Lorentz outline. The half-width of the spectrum is determined by Eqn.(12). Hence there are at least two possible ways of decoupling the component contributed by the rotation of an anisotropic molecule from the scattering spectrum: extrapolation of the data obtained from measurements of $\mathcal{I}_{VV}$ to zero angle of scattering and direct measurements of $\mathcal{I}_{HV}$ at $\theta = 0$.

Parallel measurements of the angular dependence of $\mathcal{I}_{VV}$ and of the parameter $\mathcal{I}_{HV}$ at $\theta = 0$ have been made on solutions of three samples of poly-γ-benzyl-*L*-glutamate (PBG) in dimethylformamide (DMFA).[21] Because of their rigidity the molecules of this polymer have a high segmental anisotropy: $(\alpha_\parallel - \alpha_\perp) = 400 \times 10^{-23}$.[26] This is almost two orders of magnitude higher than typical values for polymers with flexible chains. Hence in the case of solutions of PBG in DMFA we can extract the anisotropic component from the overall spectrum with confidence.

The parameter $\mathcal{I}_{VV}$ for solutions of PBG in DMFA was measured at different angles of scattering by the apparatus shown in Fig.1. On the other hand, for measurements of $\mathcal{I}_{HV}$ at $\theta = 0$ the following optical assembly was used. The experimental solution was placed in a glass cell in the shape of a tube 15 mm in diameter and 10 cm long in the path of the light beam. The cell was located between crossed Frank–Ritter prisms, one of which (at the point of entry of the beam into the cell) polarised the laser light in a vertical plane, while the other (following the cell) separated the $\mathcal{I}_{HV}$ component of the scattered light. Because the polarisation by the prisms was not perfect, part of the primary beam reached the photocathode of the FEU. The horizontal component of this primary beam, which had an elliptical polarisation, was used as the reference beam in the heterodyne detection method. The current from the FEU was taken to a specially designed amplifier, assembled from micro-modules, incorporating high- and low-frequency corrections and having a high gain at audio frequencies. The signal was then passed to the input of the spectrum analyser. The spectral distribution of the photocurrent observed on the SA screen had the same width as the scattering spectrum[9]. All the recorded spectrograms were similar to those shown in Fig.5.

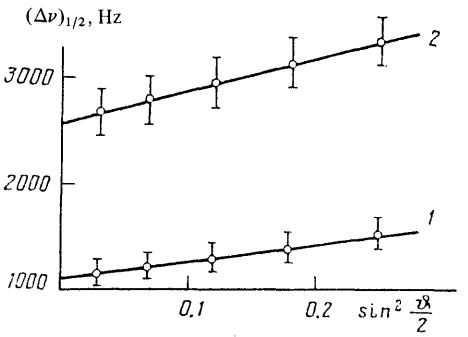


Figure 7. Dependence of $(\Delta\nu)_{1/2}$ on $\sin^2\theta/2$ for solutions of PBG samples 1 and 2 in DMFA.[21]

Table 3. Experimental data for solutions of PBG in DMFA.[21]

Sample	$10[\eta]$, m^3 kg^{-1}	$10^{13}s$, s	$10^{-3}M_\eta$	$10^{-3}M_{s\eta}$	$10^{11}D$, m^2 s^{-1}	$10^{-3}M_{sD}$	D_r, s^{-1} from $\mathcal{I}_{Hv}$	D_r, s^{-1} from $\mathcal{I}_{vv}$	D_r, s^{-1} from FBR
1	8.2	3.5	370	330	0.84	360	630	570	580
2	3.7	3.0	220	180	1.30	220	1160	1400	1350
3	0.8	2.2	83	70	—	—	5900	—	6600

Symbols: $[\eta]$ is the characteristic viscosity; s is the sedimentation coefficient; M_η is the molecular weight of PBG calculated from the $[\eta]$ value by the Mark–Koene equation; $M_{s\eta}$ is the molecular weight calculated from $[\eta]$ and s using the hydrodynamic constant A_0; M_{sD} is the molecular weight calculated from sedimentation and diffusion data.

Fig.7 shows the dependence of $(\Delta\nu)_{1/2}$ on $\sin^2\theta/2$ for PBG samples 1 and 2, plotted from measurements of the angular dependence of the $\mathcal{I}_{VV}$ spectrum. We note that the plots do not go through the origin. A corresponding plot for sample 3 could not be obtained because of the high noise level and the large width of the spectrum. The curves in Fig.7 were used to calculate the translational diffusion coefficients D of samples 1 and 2 by formulae (14). The results are given in Table 3 with the molecular weights of the PBG samples. The M values were determined in various ways: from characteristic viscosity $[\eta]$ data, inserted into the equations of Mark and Koene[26], from sedimentation and viscosimetric data, using the hydrodynamic constant $A_0 = 4.1 \times 10^{-17}$ J K^{-1}, and in the case of samples 1 and 2 from measurements of D and s, where s is the sedimentation coefficient[26]. The similarity between the M values obtained by different methods suggests that the PBG samples are not significantly polydispersed.

The rotational diffusion coefficient D_r is calculated from the intercept on the vertical axis of the plot of $(\Delta\nu)_{1/2}$ against $\sin^2\theta/2$ (Fig.7). In the homodyne variant of the detection system the quantities $(\Delta\nu)^0_{1/2}$ and D_r are related by Eqn.(13). It follows from Fig.7 that for the PBG samples

1 and 2 the $(\Delta\nu)^0_{1/2}$ values are (respectively) 1100 ± 100 and 2600 ± 200 Hz. The D_r values derived from these[21] by formula (13) are given in Table 3.

The second method of determining D_r consists in finding $(\Delta\nu)_{1/2}$ for the scattering angle $\theta = 0$ for the $\mathcal{J}_{H\nu}$ spectrum[24]. In the heterodyne detection variant the quantity $(\Delta\nu)_{1/2}$ is related to the rotational diffusion coefficient by the expression

$$2\pi(\Delta\nu)_{1/2} = (\Delta\omega)_{1/2} = 6D_r \ . \qquad (15)$$

The values of $(\Delta\nu)_{1/2}$ determined from the photocurrent spectra for the PBG samples 1, 2, and 3 were 600 ± 50, 1100 ± 100, and 5600 ± 500 Hz respectively at $\theta = 0$. These values were used to calculate the rotational diffusion coefficients D_r (also given in Table 3).[21] It is evident that the two methods of calculating D_r give similar results.

These values can be compared also with measurements[26] of the rotational diffusion coefficient of PBG in DMFA by the dynamic flow birefringence method. Values of D_r calculated from those measurements for PBG fractions of molecular weight corresponding to samples 1, 2, and 3 are also given in Table 3. We note that the D_r values calculated from the dynamic flow birefringence are close to those obtained by the dynamic light scattering method.

The measurement of D by the dynamic light scattering method has some important advantages over the conventional refractometric methods. Firstly, the principle of the measurement is more rational: we observe "self-diffusion" rather than diffusion across a boundary. Thus the creation of a solvent–solution diffusion boundary becomes unnecessary. The measurements of D are carried out under conditions of strict thermodynamic equilibrium. The measurement time is much shorter: a measurement of the angular dependence of $\mathcal{J}_{\nu\nu}$ and calculation of D can be completed in 15–20 min, whereas a refractometric determination of D usually requires at least 24 h. Because of the shorter experimental times the requirements on the temperature stability of the experimental cell are less demanding. On the other hand, like all light scattering experiments, the method requires painstaking purification of the solutions and cleaning of the cells[3].

V. FURTHER DEVELOPMENTS OF THE METHOD

The dynamic light scattering method has been used not only to determine the hydrodynamic characteristics of macromolecules (D,[27,28] D_r,[29] and the parameters of the intramolecular motion and of the relaxation processes in polymer chains[30,31]), but also to study cooperative diffusion in concentrated polymer solutions[32] and chain mobility in polymer gels[33], and to monitor the dynamics of the formation of critical fluctuations in polymer solutions[34] and molecular motion in polymer networks[16] and in polymer films adsorbed on a different polymer[35]. Attempts have been made to apply the dynamic light scattering method in studies of the kinetics of chemical reactions[8,17,18,36].

Dynamic light scattering assemblies incorporating minicomputers (correlometers) for direct calculation of the correlation function $G_\phi(\tau)$ are now widely used[9,37]. In the homodyne method of recording the photocurrent the autocorrelation function $G_\phi(\tau)$ is simply related to the autocorrelation function of the photocurrent $G_I(\tau)$ by the expression[37]

$$G_I(\tau) \approx 1 + f|G_\varphi(\tau)|^2 \ , \qquad (16)$$

where the constant $f \leq 1$ is a correction for incoherent effects and for the finite time of flight of electrons. Inserting the expression (3′) for $G_\phi(\tau)$ into Eqn.(16) gives

$$G_I(\tau) = 1 + f\exp(-2q^2D\tau) \ . \qquad (17)$$

This equation applies to small isotropic particles for $x < 1$. In the case of anisotropic molecules the spectrum of the scattered light ($\mathcal{J}_{\nu\nu}$) is given by Eqn.(8). The autocorrelation function of the photocurrent $G_I(\tau)$ in this case becomes, to a first approximation,

$$G_I(\tau) = 1 + C_1\exp(-2q^2D\tau) + C_2\exp[-(q^2D + 6D_r)\tau] \ , \qquad (18)$$

where C_1 and C_2 are constants. We note from formulae (17) and (18) that the autocorrelation function of the photocurrent is a simple exponential or the sum of two exponentials. This greatly simplifies the interpretation of the results and the calculation of D and D_r.

The most noteworthy of the assemblies developed for analysing the spectral distribution of the light it is the quadratic detection spectrometer described in Ref.38. It can be used to analyse the spectral distribution of light intensity in scattered light. A special attachment to this spectrometer for calculating the autocorrelation function $G_\phi(\tau)$ has also been developed[39].

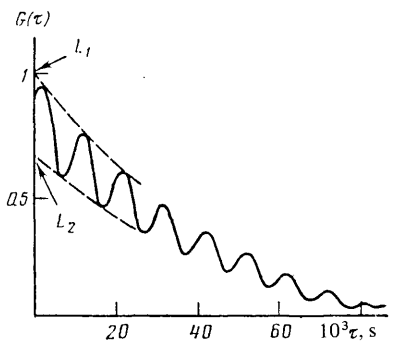


Figure 8. Autocorrelation function for the light scattered by a polystyrene suspension in a vibrating cell[40].

We should note a further potential application of dynamic light scattering. Japanese workers[40] have proposed a new method of determining the sedimentation coefficient of dissolved particles. Vibrational acceleration is applied to the polymer solution by setting the cell and the solution in vibrational motion with a frequency ω_V and amplitude a_V. The autocorrelation function of the photocurrent in this case is an exponential [given, for example, by Eqn.(17) with a superimposed sinusoidal oscillation of frequency ω_V produced by the sedimentation motion of the particles (Fig.8)]. The amplitude of these oscillations is proportional to the amplitudes a_i of the relative displacement of the particles in the solution. On the spectral distribution of the photocurrent this autocorrelation function corresponds to two maxima with a Lorentz outline and centred on the frequencies $\omega = 0$ and $\omega = \omega_V$. The parameter a_i can be evaluated from the ratio of the heights of these maxima. The average sedimentation coefficient is given by the expression

$$(\bar{s}^2)^{1/2} = \frac{1}{a_V\omega_V}\left(\sum A_i a_i^2\right)^{1/2} \ , \qquad (19)$$

where A_i is the relative intensity of the light scattered by the *i*th particle. Formula (19) applies to the heterodyne variant of the method of light detection. The degree of polydispersion of the dissolved particles can also be obtained if the homodyne variant of the apparatus is used.

By solving the equation of motion for the *i*th particle of a solution in a vibrating cell in terms of the autocorrelation function $G_I(\tau)$ and averaging over all the particles the authors[40] converted Eqn.(19) into

$$s = \frac{1}{a_v \omega_v} \frac{L_1 - L_2}{L_1} \quad (20)$$

where L_1 and L_2 are the intercepts obtained by extrapolating to the ordinate axis the envelopes of the sinusoidal modulation of the autocorrelation function $G_I(\tau)$ shown in Fig.8. Formula (20) is valid for small vibration amplitudes a_v, and it offers a practical method of calculating *s* from dynamic light scattering data. The criterion for smallness of the vibration amplitude of the cell is a displacement a_i during one vibration period smaller than the wave length of the laser radiation.

As well as *s* we can determine the translational diffusion coefficient *D* from the upper envelope of the autocorrelation function $G_I(\tau)$, using (for example) Eqn.(17). Of course, this parameter can also be determined by studying light scattering without vibration of the cell.

The original paper[40] describes a study of the sedimentation of a suspension of polystyrene latex in water by this method. The sedimentation coefficient of the latex measured in an ultracentrifuge was $s = 2.81 \times 10^{-7}$ s, and the value calculated by Eqn.(20) from the autocorrelation function of the scattered light was 3.0×10^{-7} s. Thus the effectiveness of the proposed method of determining *s* from measurements of dynamic light scattering was convincingly demonstrated. There is no evidence that the method has been adopted in other laboratories so far, but any attempt to develop new methods of determining sedimentation coefficients without resorting to the traditional ultracentrifuge techniques cannot fail to attract interest.

To conclude this review we should mention one more method, developed during the past 2 or 3 years: the use of holography in studies of dynamic light scattering[41]. The holographic correlometer with phase modulation has been used successfully in studies of ultra-slow molecular motions in very viscous scattering media[41].

The dynamic light scattering method offers some important advantages over the traditional methods of studying the translational and rotational mobility of macromolecules. These advantages are discussed above. However, the apparatus which has to be used to analyse the frequency dependence of the photocurrent is fairly complex. The experimenter must have had some previous experience of working with a spectrum analyser, and he must be familiar with modern methods of correlation analysis, including the use of correlometers (a highly specialised form of digital computer).

New fields of application of dynamic light scattering have been identified in recent years. In addition to the existing studies of the mobility of polymeric molecules[42], the properties of polyelectrolyte solutions at different ionic strengths have been investigated[43,44]. Dynamic light scattering is being studied in concentrated solutions and in gels[45], and the transition temperature in macromolecular systems (polystyrene[46] and poly(methyl methacrylate)[47]) are being determined. Additions to this list in the near future are likely. Thus we may conclude that the dynamic light scattering method is being successfully developed.

REFERENCES

1. T.Alfrey, "Mechanical Behaviour of High Polymers" (Translated into Russian), Inostr.Litd., Moscow–Leningrad, 1952.
2. S.Middleman, "The Flow of High Polymers", Wiley, New York, 1968 (Translated into Russian), Izd.Mir, Moscow, 1971.
3. V.E.Eskin, "Rasseyanie Sveta Rastvorami Polimerov" (Light Scattering by Solutions of Polymers"), Izd. Nauka, Moscow, 1973.
4. L.I.Komarov and I.Z.Fisher, Zhur.Eksper.Teor. Fiz., 1962, **43**, 1927.
5. L.Van Hove, Phys.Rev., 1954, **95**, 249.
6. R.Pecora, J.Chem.Phys., 1964, **40**, 1604.
7. R.Pecora, J.Chem.Phys., 1965, **43**, 1562.
8. R.Pecora, Discuss. Faraday Soc., 1970, **49**, 222.
9. H.Z.Cummins and H.L.Swinney, "Progress in Optics", North-Holland, Amsterdam–London, 1970, Vol.8, p.135.
10. N.C.Ford, R.Gabler, and F.E.Karasz, Adv.Chem. Series, 1973, **4**(125), 25.
11. B.H.Zimm, J.Chem.Phys., 1956, **34**, 269.
12. P.E.Rouse, J.Chem.Phys., 1953, **21**, 1272.
13. J.D.G.McAdam and T.A.King, Chem.Phys.Letters, 1974, **28**, 90.
14. T.A.King, A.Knox, and J.G.D.McAdam, Chem.Phys. Letters, 1973, **19**, 351.
15. R.M.Johnsen, Chem.Scripta, 1972, **2**, 31.
16. J.D.G.McAdam, T.A.King, and A.Knox, Chem.Phys. Letters, 1974, **26**, 64.
17. J.Benedek, Uspekhi Fiz.Nauk, 1972, **106**, 481.
18. N.C.Ford, Jr., Chem.Scripta, 1972, **2**, 193.
19. V.S.Skazka, Vysokomol.Soed., 1975, **17A**, 2507.
20. S.Fujime, J.Phys.Soc.Japan, 1970, **29**, 751.
21. V.S.Skazka, Thesis, Syktyvkar, 1978.
22. V.N.Tsvetkov and S.M.Savvon, Zhur.Tekh.Fiz., 1956, **26**, 348.
23. B.E.A.Saleh and J.Hendrix, Chem.Phys., 1976, **12**, 25.
24. A.Wada, W.Suda, T.Tsuda, and K.Soda, J.Chem.Phys., 1969, **50**, 31.
25. C.C.-C.Han and H.Yu, J.Chem.Phys., 1974, **61**, 2650.
26. V.N.Tsvetkov, I.N.Stennikova, V.S.Skazka, and E.I.Rjumtsev, J.Polymer Sci., 1968, C, 3205.
27. M.E.McDonnel and A.M.Jamieson, J.Macromol.Sci.-Phys., B, 1977, **13**, 67.
28. D.B.Sellen, Polymer, 1975, **16**, 561.
29. A.Wada, N.C.Ford, Jr., and F.E.Karasz, J.Chem. Phys., 1971, **11**, 1798.
30. Wu-Nan Huang and J.E.Frederick, Macromolecules, 1974, **7**, 34.
31. D.R.Bauer, J.I.Brauman, and R.Pecora, Macromolecules, 1975, **8**, 443.
32. M.Adam, M.Delsanti, and G.Jannink, J.Phys.Letters, 1976, **37**, 53.
33. K.L.Wun and F.D.Carlson, Amer.Chem.Soc.Polymer Preprints, 1975, **16**, 303.
34. Q.H.Lao and B.Chu, J.Chem.Phys., 1975, **62**, 2039.
35. E.E.Uzgiris and H.P.M.Fromageot, Biopolymers, 1976, **15**, 257.
36. A.Soda and A.Wada, Internat.J.Quantum Chem., 1969, **3**, 153.
37. J.G.D.McAdam and T.A.King, Chem.Phys., 1974, **6**, 109.
38. M.L.Gurari, I.I.Lushchikov, G.I.Rukman, and V.K.Sakharov, Metrologiya, 1975, **29**.
39. I.K.Yudin, Thesis, Moscow, 1978.

40. A.Wada, I.Nishio, and K.Soda, Rev.Sci.Instr., 1979, **50**, 458.
41. M.L.Gurari, A.A.Magomedov, V.K.Sakharov, A.B.Davydova, I.M.Bel'govskii, and N.S.Enikolopyan, Vysokomol.Soed., 1980, **22A**, 1900.
42. D.E.Kranbuehl and P.H.Verdier, Polymer, 1983, **24**, 383.
43. R.S.Koene and M.Mandel, Macromolecules, 1983, **16**, 231.
44. R.S.Koene, T.Nicolai, and M.Mandel, Macromolecules, 1983, **16**, 227.
45. E.J.Amis, P.A.Janmey, J.D.Ferry, and Hyuk Yu, Macromolcules, 1983, **16**, 441.
46. G.D.Patterson, P.J.Carroll, and J.R.Stevens, J.Polymer Sci., Polymer Phys.Ed., 1983, 21, 605.
47. G.D.Patterson, P.J.Carroll, and J.B.Stevens, J.Polymer Sci., Polymer Phys.Ed., 1983, 21, 613.

"50th Anniversary of the USSR"
Syktyvkar State University