Changes in dissymmetry of light scattering in aggregating latex

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Received 15 March 1988

Dedicated to Academician V Kellö, in honour of his 70th birthday

The method of dissymmetry of scattering of light radiation applied to monodisperse PS latices with particle diameters of 98 or 215 nm was used for modelling the course of their rapid coagulation. The changes in dissymmetry found experimentally during aggregation were in good agreement with theoretical values and on the basis of them some information about the apparent size of aggregates is to be obtained. It has simultaneously been shown that the presence of aggregates does not affect the determination of size of primary latex particles from dissymmetry data performed at a characteristic pair of angles and wavelength.

Для монодисперсных ПС латексов с диаметром частиц 98 или 215 нм был применен метод асимметрии рассеяния оптического излучения с целью моделирования процесса их быстрой коагуляции. Опытно обнаруженные изменения асимметрии в процессе агрегации очень хорошо согласовались с теоретическими предсказаниями, причем, исходя из этих данных, можно судить о кажущемся размере агрегатов. Одновременно было показано, что при определенной паре углов и длине волны присутствие агрегатов не влияет на определение размеров первичных латексовых частиц, исходя из данных по асимметрии.

The aggregation of particles to larger units is an incidental phenomenon in different biological, chemical, and physical processes. From the theoretical standpoint, the growth of aggregates may be investigated by two different methods.

The first method was formulated by *Smoluchowski* [1] while the second method is represented by the Flory—*Stockmayer* theory [2]. Recently, *Cohen* and *Benedek* [3] analyzed both approaches from the viewpoint of statistical mechanics and achieved that their theory was applicable to classical coagulation as well as to formation of *n*-mer molecules.

Several experimental procedures are available for studying aggregating systems. Since the scattering of light represents the most preferred method, this communication is concerned with the changes in dissymmetry of light scattering during fast coagulation of some monodisperse systems containing spherical particles.

Method of dissymmetry

The coefficient of dissymmetry is defined in this method [4] as a ratio of two fluxes of the optical radiation scattered by isolated monodisperse spherical particles at angles Θ_1 and Θ_2 (nonpolarized primary beam)

$$Z(\Theta_1/\Theta_2) = \frac{\Phi(\Theta_1)}{\Phi(\Theta_2)} = \frac{i_1(m, a, \Theta_1) + i_2(m, a, \Theta_1)}{i_1(m, a, \Theta_2) + i_2(m, a, \Theta_2)}$$

where i_1, i_2 are the Lorenz—Mie [4] intensity functions for vertically or horizontally polarized primary beam, m stands for the relative refractive index (the ratio of the refractive indices of the particle and medium). Parameter $a = \pi d/\lambda$ (d and λ are diameter of particles and wavelength of radiation in the system, respectively). Then a comparison of the theoretical relationship $Z = f(a)$ with the experimental values of Z enables us to determine the size of particles [4] or the distribution of their sizes [5]. Besides, as it follows from the presented paper, the method of dissymmetry may also be used for investigating light scattering in an aggregating system.

For modelling the changes in angular dependence of light scattering in a system of aggregating latex particles, we started from the Smoluchowski description of fast coagulation of monodisperse systems.

Assuming the formation of linear, planar, and three-dimensional aggregates, the light scattering in a system with a certain degree of coagulation E may be expressed according to paper [6] by the equation

$$\Phi_\Theta(E) = \Phi_\Theta(0)\left[1 + 2\sum_{k=2}^{\infty} \frac{n_k(E)}{n_0} A_\Theta(k)\right]$$

where $\Phi_\Theta(0)$ is flux of the light scattered at the angle Θ by a system without aggregation and $E = t/t_{1/2}$ ($t_{1/2}$ is half-value period of coagulation). The symbols $n_k(E)$, n_0, and $A_\Theta(k)$ stand for the number of aggregates containing k particles in a volume unit at the extent of aggregation E, the initial number of non-coagulated particles, and the factor corresponding to Rayleigh—Gans—Debye (RGD) geometry of the aggregate, respectively. Thus we obtain for the dissymmetry of light scattering at varying extent of coagulation

$$Z_E(\Theta_1/\Theta_2) = \Phi(\Theta_1, E)/\Phi(\Theta_2, E) = \frac{\Phi_{\Theta_1}(0)\left[1 + 2\sum_{k=2}^{\infty} \frac{n_k(E)}{n_0} A_{\Theta_1}(k)\right]}{\Phi_{\Theta_2}(0)\left[1 + 2\sum_{k=2}^{\infty} \frac{n_k(E)}{n_0} A_{\Theta_2}(k)\right]}$$

where $\Phi_{\Theta_1}(0)/\Phi_{\Theta_2}(0) = Z_0(\Theta_1/\Theta_2)$ is the dissymmetry of the nonaggregating system.

Experimental

The polystyrene latices were obtained from the Institute of Macromolecular Chemistry of the Czechoslovak Academy of Sciences in Prague. Both samples were practically monodisperse, the particle size determined by electron microscope was 98 nm for sample PSL 1 and 215 nm for sample PSL 2.

For measuring light scattering the latex dispersions were so diluted that the disturbing effect of multiple scattering was minimum. This condition was fulfilled if the number of particles in 1 cm^3 varied within the range 5×10^8—1×10^9 In order to produce coagulation, the optically pure 1 M solution of KCl was added into the latices.

The measurements of light scattering were carried out in a usual way by using a photogoniodiffusiometer Sofica. The corresponding time variations were recorded up to 6 min for PSL 1 and 45 min for PSL 2. The time in which the experimental ratio $\Phi_\Theta(t)/\Phi_\Theta(0)$ was identical with the corresponding theoretical ratio at $E = 1$ was taken as half-time of aggregation.

Results and discussion

Figs. 1*a, b* show an evident effect of the degree of aggregation of the investigated latices on light scattering for selected angles of observation and two wavelengths. It can be seen that the agreement between theoretical and experimental values of light scattering is excellent for latex PSL 1, similarly as it has been described in paper [6] for PS latices with particle size of 126 nm. This statement cannot be sustained for the second latex, especially for the angle of 135° and the blue line of optical radiation at higher degrees of aggregation. We must realize that the theoretical calculations of light scattering in aggregating system have been built on the RGD theory the use of which for large particles and great angles of observation is inadequate as stated in paper [7]. However, this statement is also valid for the model of the Mie equivalent sphere. On the other hand, it is worth noticing that the determination of the half-time of aggregation on the basis of experimental investigation of the kinetics of coagulation is loaded by greater error for larger particles than for smaller particles. As a matter of fact, the relative changes in light scattering in an aggregating system are smaller for larger particles and unsuited to determination of the half-time of aggregation at some angles or wavelengths (Figs. 1*a, b*).

We observed the changes in light scattering at the angle of 90°. The light scattering increases with aggregation for latex PSL 1 and decreases for latex PSL 2. These results are in agreement with the results published in paper [8] which have shown in harmony with theoretical assumptions that the values of i_{90} decreased with increasing number of the particles of aggregate for latex with particle diameter $d = 264$ nm.

Now we shall pay attention to the changes in dissymmetry of light scattering in aggregating system for two pairs of angles and two wavelengths (Figs. 2*a*, *b*). In this case represented in Fig. 2*b* in accordance with Fig. 1*b* a certain disagreement (rather acceptable) appears between the theoretical and experimental

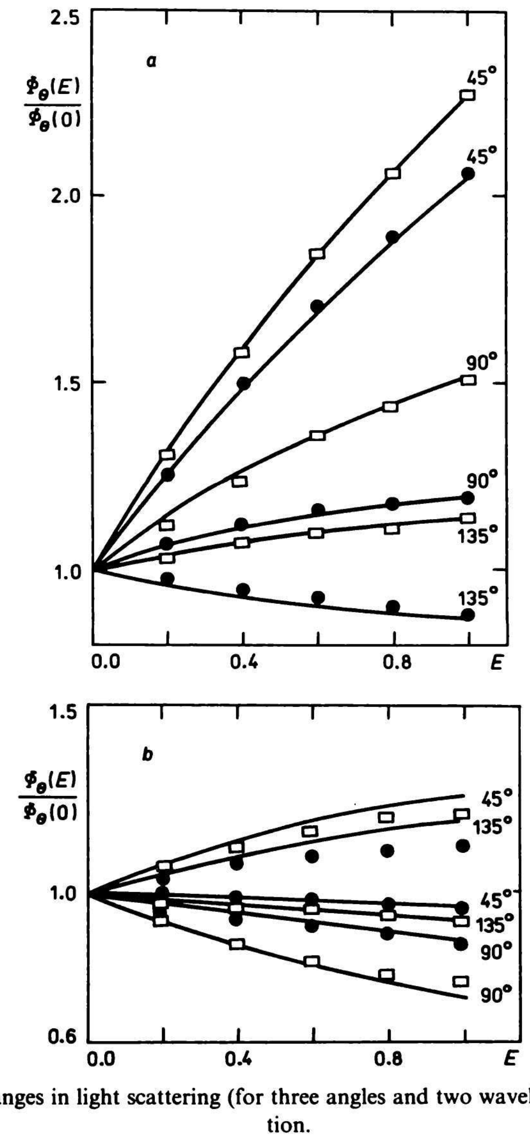

Fig. 1. Relative changes in light scattering (for three angles and two wavelengths) during aggregation.

● $\lambda_0 = 436$ nm, □ $\lambda_0 = 546$ nm (experimental values) — theoretical relationship. Dispersion of PSL 1 (*a*); dispersion of PSL 2 (*b*).

values. It results from a comparison of Fig. 2*a* with Fig. 2*b* that the dissymmetry of light scattering in aggregating system is greater at a smaller wavelength for latex PSL 1 while it increases with wavelength for latex PSL 2. At the blue line, $Z(45°/135°)$ decreases in the course of aggregation and the influence of particle

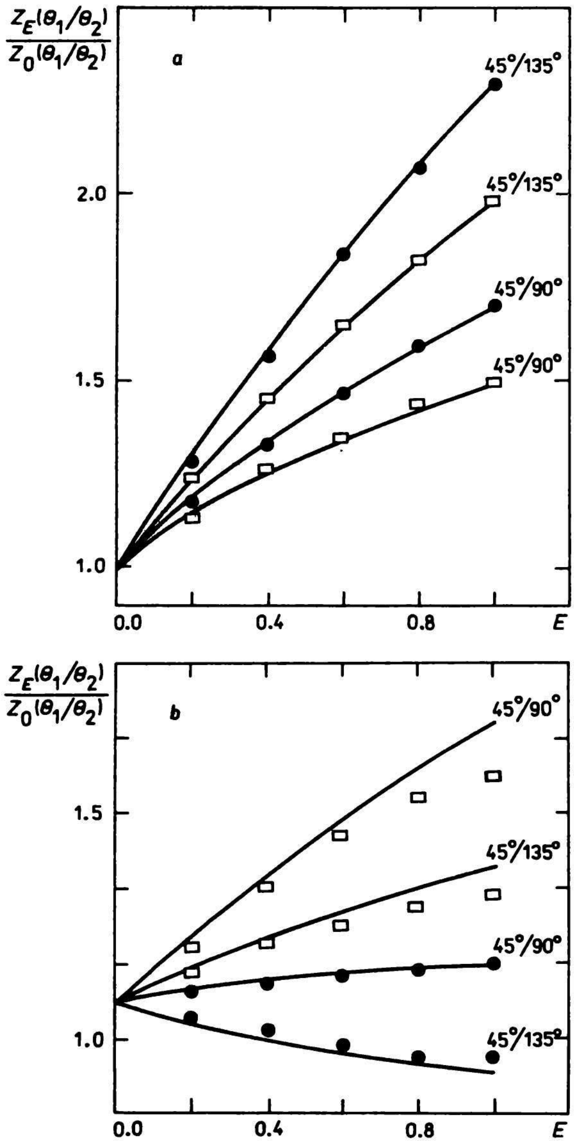

Fig. 2. Relative changes in dissymmetry (for two pairs of angles and two wavelengths) during coagulation (denotation as in Fig. 1). Dispersion of PSL 1 (*a*); dispersion of PSL 2 (*b*).

aggregation on the values of $Z(45°/90°)$ is small. On the basis of these facts we may state that the method of dissymmetry may be used for diagnostic of aggregation. The dependence of $Z(45°/90°)$ or $Z(45°/135°)$ on the degree of aggregation at different wavelengths gives information about the relative size of building units of aggregating system. The theoretical relationship $Z(\Theta_1/\Theta_2) = f(d)$ at a characteristic wavelength enables us to determine not only the

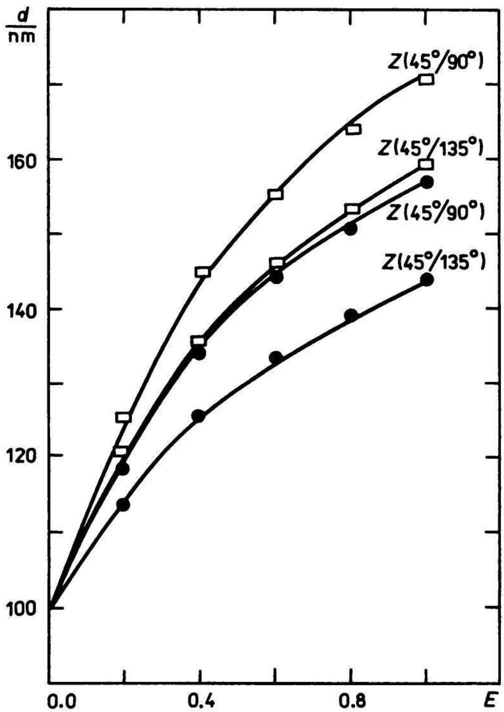

Fig. 3. Varying apparent size of aggregates at different degrees of aggregation (denotation as in Fig. 1).

apparent size of aggregates (diameter of equivalent sphere) in particular stages of aggregation but also the real size of building units of grouping. That is illustrated in Fig. 3 for latex PSL 1 and given in Table 1 for latex PSL 2. Simultaneously it results from this table that the measurements of $Z(45°/90°)$ at $\lambda_0 = 436$ nm may be conveniently used for determining the size of constituent particles of such latices because the presence of aggregates does not interfere in

Table 1

Apparent size of aggregate (on the basis of $Z(45°/90°)$) in the process of aggregation — sample PSL 2

		E				
		0.2	0.4	0.6	0.8	1
$\frac{d}{nm}$	theor.[a]	216.5	217.5	218.3	219	219.6
	exp.[a]	210.0	211.0	212.0	213.0	214.0
	theor.[b]	227.8	238.5	246.3	251.8	255.8
	exp.[b]	220.0	230.0	238.0	244.0	246.0

a) $\lambda_0 = 436$ nm; *b)* $\lambda_0 = 546$ nm.

this case. An extension of the investigated relations for further pairs of angles, other sizes of particles, and other wavelengths will be the topic of subsequent communication.

Acknowledgements. The authors are thankful to Dr. B. Sedláček (Institute of Macromolecular Chemistry, Czechoslovak Academy of Sciences, Prague) for interest in realization of this work.

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Translated by R. Domanský