Dynamic light scattering (DLS) · FOQELS · Particle sizing · Polymer latices

Use of Fiber Optics Quasi-Elastic Light Scattering (FOQELS) in the particle sizing of Polymer Latices

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Dynamic light scattering (DLS) technique is used for characterizing the molecular changes in the physiological, chemical, polymer and colloidal systems. Since the first experimental use of the optical fiber in 1975, it has been increasingly important tool in the light scattering instrumentation. There had been a great amount of modification and development of this instrumentation during last couple of decades by so many researchers. Here we report the DLS study of polymer latices of different particle size and different concentration using various cells. The study shows that the quartz cell shows better efficiency than the acrylic cell for the latices of lower concentration. Analysis by FOQELS for concentrated solution of the latex of smaller particle size shows no deviation. Analysis of the latex of relatively larger particles shows negative deviation.

Verwendung von faseroptischer-quasielastischer Lichtstreuung (FOQELS) in der Partikelgrößebestimmung von Polymerkristallen

Dynamische Lichtstreuung (DLS) · FOQELS · Partikelgrößebestimmung · Polymerkristalle

Die Technik der dynamischen Lichtstreuung (DLS) wird zur Charakterisierung der Molekülwanderungen in physiologischen, chemischen, polymeren und kolloiden Systemen verwendet. Seit der ersten experimentellen Verwendung 1975 hat sich Glasfaser zunehmend zu einem wichtigen Werkzeug der Lichtstreuungsinstrumente entwickelt. Im Verlauf der letzten Jahrzehnte wurde diese Technik von zahlreichen Forschern verändert und weiterentwickelt. In diesem Beitrag wird über eine DLS-Untersuchung an Polymerkristallen unterschiedlicher Teilchengröße und unterschiedlicher Konzentration unter Verwendung verschiedener Zellen berichtet. Die Studie zeigt, daß die Verwendung von Quartz-Zellen bei Kristallen geringerer Konzentration eine bessere Leistungsfähigkeit als die Akryl-Zellen besitzen. Die Analyse von konzentrierter Latexlösung mit kleiner Teilchengröße durch FOQELS zeigt keine Abweichung. Die Analyse von Latex mit relativ größeren Teilchen zeigt negative Abweichung.

Dynamic light scattering (DLS), quasi elastic light scattering (QELS), photon correlation spectroscopy (PCS), intensity fluctuation spectroscopy (IFS) are all synonymous terms of noninvasive laser-light scattering technique that is used for characterizing the molecular changes in physiological, chemical, polymer and colloidal systems [1, 2]. After the first experimental use of the optical fiber by Tanaka and Benedek [3], it has been increasing important tool in LLS instrumentation. Optical fibers whether single mode, multi mode or in bundles are important tools for laser light scattering (LLS) experiments [1, 2].

The basic principle of optical fiber in using LLS instrumentation is that it transmits the laser light to the scattering medium as well as detects the back scattered laser light. The first backscattering fiber optic system, a fiber optic doppler anemometer (FODA) was described by Dyott [4] in 1978. The FODA was successfully used for DLS study of colloidal suspensions [5, 6]. Dhadwal et al [7] and Thomas [8] modified this system so that it can be used as very efficient and compact backscatter fiber optic probe which provided a self-beating detection of the scattered light. In this case the self-beating fiber optic probe comprises two optical fibers placed side by side but mounted in common ferrule.

Here we report the DLS study of different polymer latices of different particle size and of different concentration using different sample cells. This report explains the scope and limitations of use of optical fiber probe for the LLS study of polymer latex particles.

Experimental

Sample preparation

Polystyrene latex of different diameter (e.g 489 nm, 305 nm and 69 nm) was obtained from Seradyn Inc. (Indianapolis, IN). The sample was diluted to different concentration (i.e 1%, 0.1% and 0.01%) using doubly distilled deionized water (18.0 mΩ). The samples were filtered with different millipore membrane filters in order to remove dust particles (for 489 nm particle by 0.8 µm filter, for 305 nm by 0.5 µm and for 69 nm by 0.2 µm). In the experimental set up of FOQELS used for the DLS measurements with the probe is positioned just outside the sample cell. It is provided with the systems of statistical averaging of repeated measurements. A laser beam from 10 mw He-Ne operated at $\lambda = 671$ nm was transmitted to the sample solution by the transmitting optical fiber. The backscattered light was received by the receiving optical fiber. The optical fibers used here are all monomode. The end of receiving fiber is connected to the photomultiplier detection system. The volume of intersection of the transmitting and the receiving fiber is called scattering volume. The scattering angle in case of this FOQELS is 155°. In this study we have used size distribution analysis routines provided by the manufacturer of the digital correlator, Brookhaven Instruments Corporation, Holtsville, USA. The measurements were carried out using 10 mm square acrylic cell as well as quartz cell. The fiber optic probe was positioned just outside the sample cell. All measurements were performed at 25 °C.

Theoretical background[1]

A random motion of small particles in the solution gives rise to fluctuations in the time intensity of the scattered light. In this case the autocorrelation function can be written as

$$C(t) = A.e^{-2\Gamma t} + B \quad (1)$$

Where t is the time interval, A is an optical constant determined by the instrument. B is also a constant when t increases the correlation is lost and the correlation function approaches the constant B. Γ is the relaxation time of fluctuations.

$$\Gamma = Dq^2 \quad (2)$$

q is calculated from the scattering angle θ (here it is 155°), the wavelength of the laser light λ and the refractive index (n) of the suspending liquid.

$$q = \frac{4\pi n}{\lambda} \text{Sin} \frac{\theta}{2} \quad (3)$$

The translational diffusion co-efficient, D is the principal quantity measured by DLS. It is an inherently interesting property of the particle. According to Stoke-Einstein equation D can be expressed as

$$D = \frac{\kappa T}{6\pi\eta r} \quad (4)$$

where κ is Boltzman constant, T is the absolute temperature, η is the absolute viscosity of the medium, r is the hydrodynamic radius.

In this study FOQELS first measures the autocorrelation function and fits this function to eqn-1 to determine relaxation time Γ. D is calculated by using equation 2 & 3 which in turn calculates r, the size of the particles. A self-beating experiment involves a measurement of a normalized intensity-intensity temporal autocorrelation $g^{(2)}(\tau)$, which is related to $g^{(1)}(\tau)$

$$g^{(2)}(\tau) = A[1 + \beta|g^{(1)}(\tau)|^2] \quad (5)$$

where β describes the spatial coherence of the scattering volume.

For monodisperse sample the measured intensity-intensity autocorrelation decays exponentially with a time constant $2q^2D$, and a simple transformation yields the particle size. However for a polydisperse system the first order autocorrelation is

$$g^{(2)}(\tau) = \int_a^b p(D)e^{-q^2D\tau}\, dD \quad (6)$$

Where p(D) is the distribution in diffusion coefficient due to the species present in the solution; a and b are the lower and upper bounds on D respectively.

Result and discussion

Different concentration of polystyrene latex (PS) was analyzed with FOQELS at ambient temperature. The particle size of PS latex as well as the diffusion co-efficient of the latices was measured with FOQELS. *Fig. 1* shows an example of FOQELS analysis of a PS latex. Before taking the final data it was ensured that a satisfactory correlation curve was achieved. Fig. 1 shows a good correlation curve of a PS latex of 69 nm diameter. An example of the different analytical data of the PS latex of 69 nm is shown in *Tab. 1*. In each case, at least three measurements of the elapsed time 5 minutes were carried out and it was ensured that the sample quality was 9.8 to 10.0. *Tab. 2* indicates that as the concentration of polystyrene (PS) latex of 69 nm decreases as the particle size of the latex increases. This means there is positive deviation from the actual diameter of the latex when measured with quartz cell or acrylic cell (*Fig. 2*). For 1% PS latex both the quartz cell as well as the acrylic cell gives the concordant value with the actual diameter. For dilute solution (i,e for 0.08% and 0.008%) quartz cell gives more accurate result than the ac-

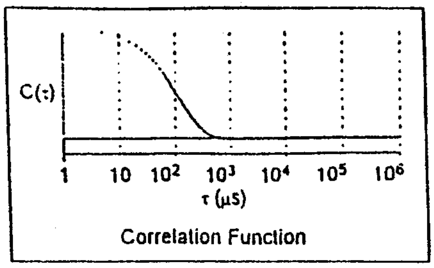

Figure 1. A Correlation diagram of FOQELS analysis of a PS latex of 69 nm using quartz cell (Q)

Table 1. An example of the different analytical data obtained during analysis (PS of 69 nm)

Run	Eff. Diam. (nm)	Half Width (nm)	Polysipersity	Sample Quality
1	66.1	15.2	0.053	9.9
2	66.4	13.3	0.040	9.9
3	66.3	14.4	0.047	9.8
Mean	66.3	14.3	0.047	9.9
Std Error	0.1	0.6	0.004	0.0
Combined	66.3	14.3	0.046	10.0

Table 2. Analysis of PS latex of 69 nm using FOQELS

Conc. (%)	Cell used	Avg. Count Rate (cps)	Poly-dispersity	Diffusion Coeff. ($\mu m^2/s$)	Effective Diameter (nm)	Deviation from actual diameter (%)
1.0	Acrylic	630.9	0.141	3.47	70.6	+2.3
0.08	Acrylic	119.5	0.005	2.84	86.3	+25.0
0.008	Acrylic	65.9	0.277	2.04	120.2	+71.1
1.0	Quartz	575.1	0.047	3.69	66.3	−3.9
0.08	Quartz	66.5	0.037	3.37	72.8	+5.2
0.008	Quartz	9.9	0.131	3.24	75.5	+9.4

Table 3. Analysis of PS latex of 305 nm using FOQELS

Conc. (%)	Cell used	Avg. Count Rate (cps)	Poly-dispersity	Diffusion Coeff. ($\mu m^2/s$)	Effective Diameter (nm)	Deviation from actual diameter (%)
1.0	Acrylic	977.7	0.131	1.76	139.1	−183.8
0.1	Acrylic	484.0	0.281	1.15	213.0	−30.1
0.01	Acrylic	65.2	0.148	0.67	364.2	+19.48
1.0	Quartz	1400	0.275	1.28	190.9	−37.4
0.1	Quartz	1100	0.173	0.79	308.5	+1.1
0.01	Quartz	46.4	0.030	0.76	328.3	+7.6

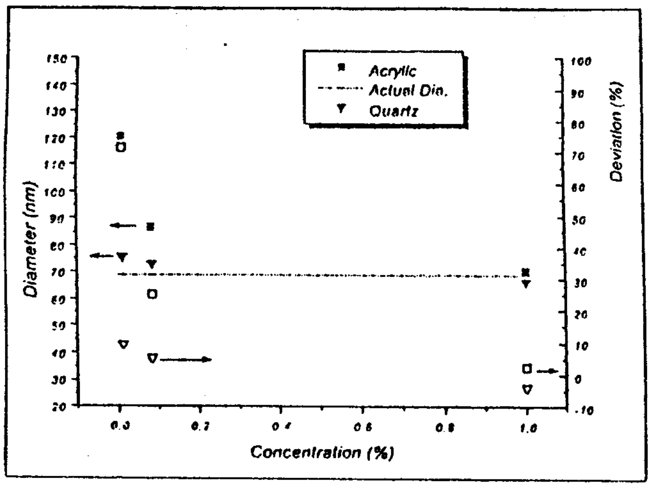

Figure 2. Plots of diameter measured with FOQELS vs concentration (filled symbols) and deviation (%) of the measured diameter from the actual one (open symbols) for PS latex of 69 nm

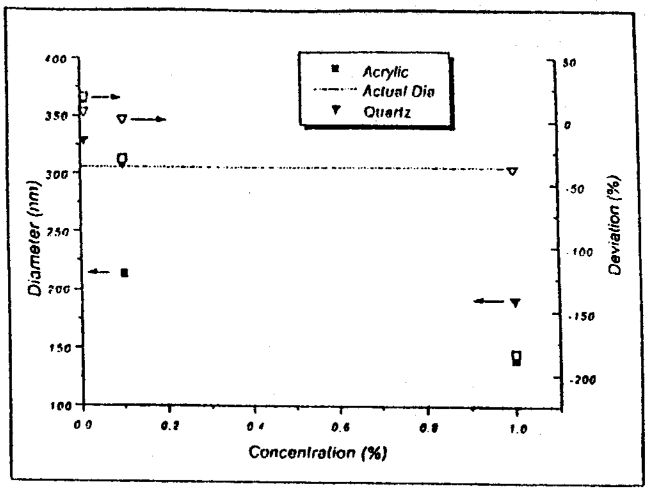

Figure 3. Plots of diameter measured with FOQELS vs concentration (filled symbols) and deviation (%) of the measured diameter from the actual one (open symbols) for PS latex of 305 nm.

rylic cell. *Tab. 3* indicates the experimental results of PS latex of 305 nm. For 1% latex acrylic cell shows large negative deviation (*Fig. 3*). As the concentration decreases the deviation decreases. For 1% PS latex the observed diameter is much less than the actual diameter. But for 0.1% and 0.01% solution the deviation is much less and almost shows the original diameter (*Fig. 4*).

The PS latex of 489 nm shows lower diameter in case of acrylic cell as well as quartz cell using 1% latex solution (*Tab. 4*). Though quartz cell shows excellent result for 0.1% and 0.01% latex solution, the acrylic cell shows appreciable deviation for these two solutions.

In case of concentrated latex there is multiple scattering, i.e the photons are scattered more than once before reaching the detector [7]. So. there is large uncertainty in determination of scattering angle. In case of smaller particle (like PS of 69 nm), the multiple scattering is absent. Hence it shows least deviation from the actual particle size. But PS of 308 and 489 nm the extent of multiple scattering is very large. So there is large deviation between the measured value and the original value of the particle size of latices.

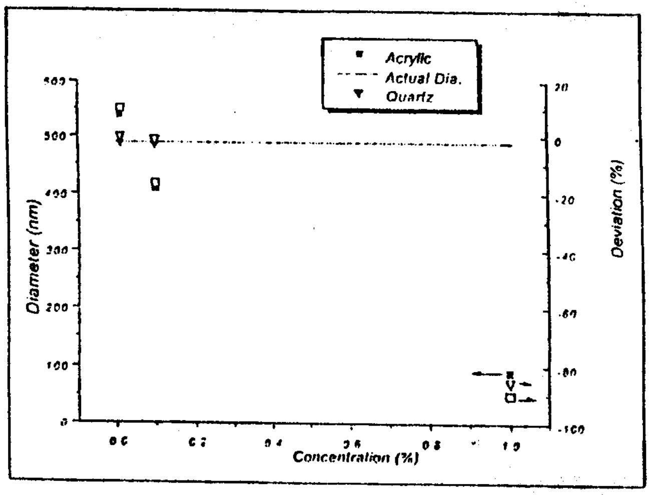

Figure 4. Plots of diameter measured with FOQELS vs concentration (filled symbols) and deviation (%) of the measured diameter from the actual one (open symbols) for PS latex of 489 nm

Acrylic cells are made of polymethyl methacrylate (PMMA) and have high chemical resistance. It is used for the analysis of blood and other fluids. Acrylic offers light transmission of 92% with particular clarity at lower wavelengths of 270 to 350 nm. Quartz glass can transmit light as low as 220 nm [9]. Acrylic has more imperfections than the quartz cell because of less order in packing compared to well-defined packing in quartz material. However, acrylic cells are much cheaper than the quartz cell. In acrylic cell the extent of local oscillation is more than in the quartz cell. It might lead to larger deviation from the actual value when measured with acrylic cell. Bremer et al [10] and Thomas [8] observed that in FOQELS pure homodyne and heterodyne detection could not be achieved in many situations. In homodyne method[2] the auto correlation function of the intensity of the scattered light is directly meas-

Table 4. Analysis of PS latex of 489 nm using FOQELS

Conc. (%)	Cell used	Avg. Count Rate (cps)	Poly-dispersity	Diffusion Coeff. (μm^2/s)	Effective Diameter (nm)	Deviation from actual diameter (%)
1.0	Acrylic	899.0	0.182	2.77	88.4	−89.92
0.1	Acrylic	494.2	0.266	0.60	408.4	−16.48
0.01	Acrylic	65.3	0.189	0.45	539.1	+10.22
1.0	Quartz	1100.0	0.280	3.43	71.3	−85.40
0.1	Quartz	602.2	0.206	0.50	484.7	−0.87
0.01	Quartz	38.7	0.017	0.50	487.4	−0.03

ured. In the heterodyne method[2] a small portion of the unscattered light (local oscillator) is mixed with the scattered light. The proportion of both contribution would be used to analyze the measurement of polymer latices.

Conclusions

FOQELS can be used for polymer latices of relatively lower concentration whereas in the conventional light scattering instrument 0.001% latex or emulsion can be used. For relatively smaller particle size FOQELS shows good result. But for latex of larger particle size shows appreciable deviation. When quartz cell is used in FOQELS it shows better result. The FOQELS unit is compact, portable and thus very handy instrument. Since FOQELS counts the backscattered light, the signals are not affected by dust. Because of the several advantages over conventional QELS, FOQELS is moving into quality control laboratory. It is being used in the chemical plant as process monitoring device.

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