Colloid & Polymer Science Colloid Polym Sci 267:1113–1116 (1989)

Automated determination of particle-size distributions of dispersions by analytical ultracentrifugation*)

H. G. Müller

Central Research Division, Bayer AG, Leverkusen, FRG

Abstract: The ultracentrifugation method for determining the particle-size distribution of dispersions has been automated and its precision and capacity improved.

A mixture of seven monodisperse calibration latices can be analysed and two lattices with a difference in diameter of 10% can be resolved by a base-line separation.

Key words: Particle-size distribution, ultracentrifugation, dispersions, emulsions.

1. Introduction

Dispersions play an important role in chemical industry, as illustrated in Table 1.

The greater number of polymers is produced by emulsion polymerization, that means by production of polymer lattices. The particle size and particle-size distribution (PSD) is fundamental in numerous areas of great practical importance, e. g., for the viscosity of such dispersions.

Pressure agglomeration used in the production of foam lattices is used to produce a special type of PSD. The degree to which viscosity depends on PSD is proven by the fact that latex with the same solid content can show extreme differences in viscosity. This can be clearly demonstrated by dispersion A and B, which differ only in their PSDs. Dispersion A has a high viscosity, whereas B has the same solid content, but a different PSD, and exhibits a low viscosity, compare Fig. 1.

The PSD of dispersions is not only important for rheology, but also for gloss of films, for grafting reactions onto lattices (ABS), and for the speed of resorption of pesticidal and pharmaceutical emulsions.

For the determination of PSD of such dispersions the ultracentrifugation method of Cantow [1], Scholtan and Lange [2] has been improved [3, 4] and automated, resulting in one of the best methods to determine PSD, compare Fig. 2.

2. Basic principle of the method

The specific feature of this method is that there is an integral fractionation before measurement takes place.

This is shown in Fig. 3. The upper part of the figure shows the cell of an analytical ultracentrifuge and the sedimentation of particles during a run.

Table 1. Dispersions in chemical industry, characterized by ultracentrifugation

Poly (butadiene-co-styrene)-latex Poly (butadiene-co-acrylonitrile)-latex Polychloroprene-latex
Polybutadiene and polyacrylates, seed latex, and graftlatex (ABS, ASA)
Polyurethane-dispersions, siliconoil-emulsions
Pesticidal and pharmaceutical emulsions
Pigments: Ironoxides, titaniumdioxide
Dispersed dyes

*) This paper was presented at the "VI. Symposium on Analytical Ultracentrifugation", Marburg, FRG, February 16–17, 1989.

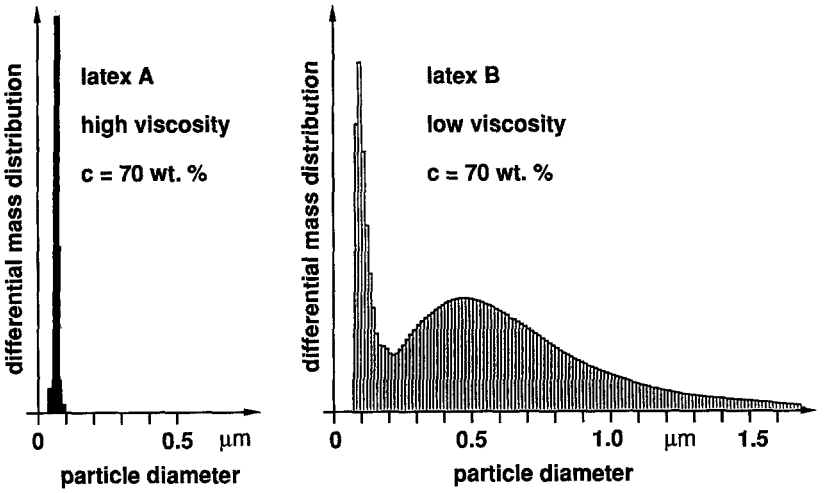

Fig. 1. Particle-size distributions of two latices with identical solid content but different viscosity. The high viscosity of latex A is of a Bingham-type. Product A, high viscosity: Narrow PSD, d: 0.04–0.10 µm; Product B, low viscosity: Broad PSD, d: 0.08–1.7 µm

It is well known that in a latex larger particles sediment faster than smaller ones. This means that at the end of the run, only the smallest particles are still dispersed in the cell. The intensity of a laser beam passing through the middle of the cell increases stepwise, when, at t_1 the large-sized, at t_2 the medium-sized, and at t_3 the small-sized particles leave the middle of the cell. From this change of intensity the concentration in the middle of the cell can be calculated, and from that the PSD, if the Mie scattering theory is taken into account.

3. *Improvements of the methods and results*

Figure 4 shows a cross-section of the automated preparative ultracentrifuge, Beckmann L 5–75.

Fig. 2

A multicell rotor constructed of titanium is the heart of the improved apparatus, which makes it possible to investigate up to seven different dispersions in one run. A He-Ne laser serves as light source, the beam of which is detected by a fast semiconductive receptor (with a resolution time of about 0.1 µs) when it has passed through the middle of the analytical cell. The seven signals are attributed to each cell by a light

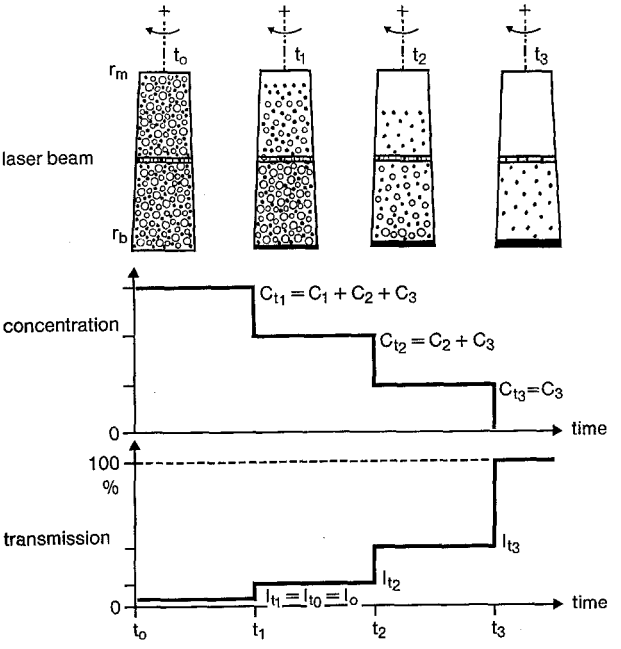

Fig. 3. Schematic presentation of the concentration and transmission profile in the ultracentrifugal cell during a sedimentation run

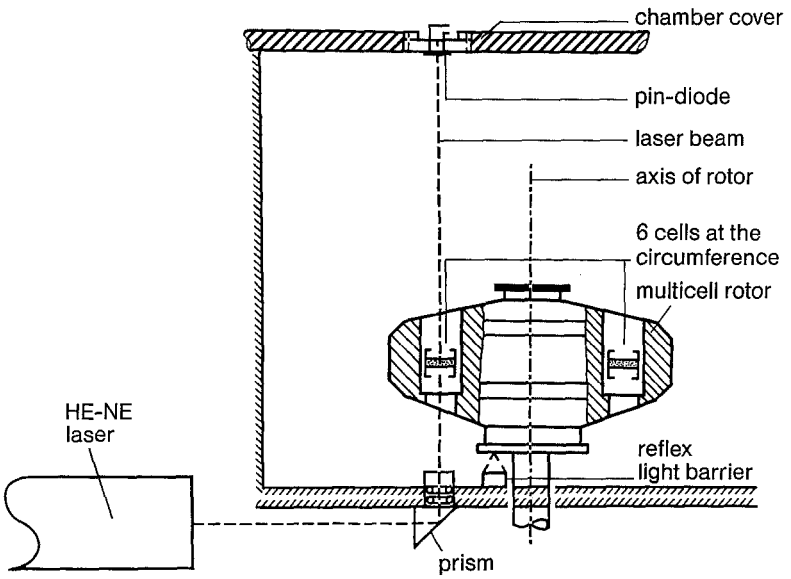

Fig. 4. Experimental set up; Rotor chamber and optical equipment for the preparative Beckman ultracentrifuge L 5–75

barrier which produces one signal per revolution of the rotor coupled with a computer. The excellent performance of the improved method is demonstrated by the separation of a mixture of seven calibration lattices. The result of this measurement is given in Fig. 5.

In Fig. 5 the relative mass of particles is given as a function of particle diameter. It can be seen that all seven single components of the mixture have been detected. In addition, the diameter and the mass fraction of these components can be compared with the actual values; this has been done in Table 2.

From table 2 it becomes obvious that the diameter and mass fraction of the seven components have been determined correctly.

Another advantage of this method is its high resolution. To elucidate the resolving power, two calibration lattices have been mixed 1 : 1 with a difference in diameter of only 10 %. The result of this measurement is given in Fig. 6.

In Fig. 6 the relative mass of particles is given as a function of particle diameter in an expanded scale; the

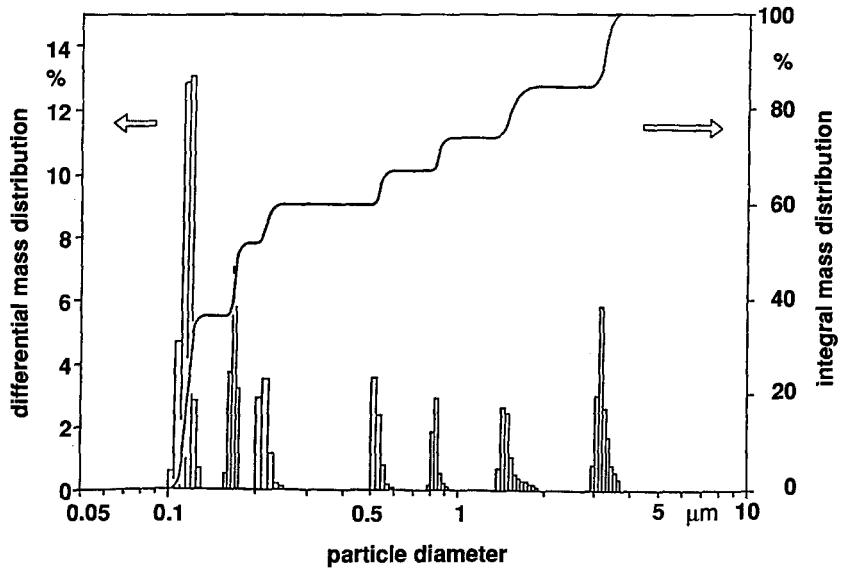

Fig. 5. Particle-size distribution of a mixture of seven calibration lattices in differential and integral representation

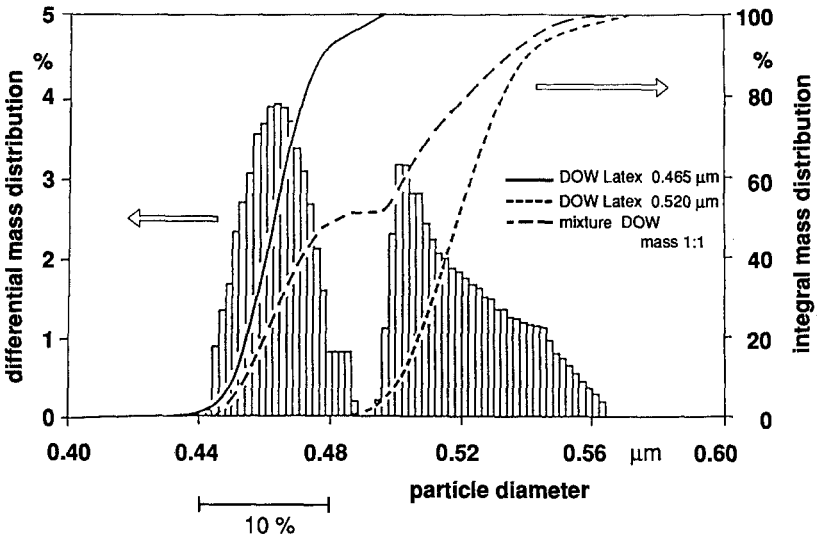

Fig. 6. Resolution power of the automated ultracentrifuge: Result of a mixture in differential and integral representation

Table 2. Comparison of known and experimentally determined mass fractions and diameters in a mixture of seven calibration lattices. The known diameters have been determined individually by ultracentrifugation

Concentration		Diameter	
Known wt%	Experimental wt%	Known[a]) µm	Experimental µm
40.4	36	0.115	0.115
17.0	15	0.165	0.167
8.3	8	0.215	0.215
8.0	7	0.520	0.530
6.0	8	0.800	0.820
8.0	10	1.380	1.460
12.8	15	2.990	3.100

[a]) determined individually

figure shows that this mixture can be resolved by a base-line separation.

These two examples show the high performance of the automated method for determining PSD. The increase in accuracy is due to cell centerpieces made from titanium with a sector angle of 1.5°.
This method for determining PSD is absolute one, no calibration is necessary, and its range is extremely wide at 0.02–10 µm.

Compared to electron microscopy, the ultracentrifugation method has the advantage of counting statistically relevant numbers of particles (in spite of dilution 10^8–10^{10} particles in each experiment), however, electron microscopy can answer questions of morphology.

Table 3. Advantages of the improved ultracentrifugation method in the determination of particle-size distributions

- Distributions can be determined accurately
- High precision
- High resolution power
- High statistical reliability
- High capacity by automation

Compared to laser correlation spectroscopy the ultracentrifugation method is far more precise and has a far better resolving power, but it cannot be carried out on-line in a production process. The Table 3 shows the advantages of the improved and automated ultracentrifugation method for the determination of PSD.

References

1. Cantow HJ (1964) Makromol Chem 70:130
2. Scholtan W, Lange H (1972) Kolloid-Z u Z Polymere 250:782
3. Mächtle W (1984) Makromol Chem 185:1025
4. Mächtle W (1988) Angew Makromol Chem 162:35

Received July 5, 1989
accepted August 22, 1989

Author's address:

Dr. Hans Georg Müller
Bayer AG, ZF-TPP 5; E-41
5090 Leverkusen, F.R.G.