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MOLECULAR-WEIGHT DISTRIBUTIONS OF FRACTIONS OF A COPOLYMER OF METHYL METHACRYLATE WITH STYRENE

(Presented by Academician N. N. Semenov, November 26, 1963)

As was shown by calculation ([1,2]), the form of the molecular-weight distributions (m.w.d.) of samples isolated during fractionation of copolymers depends substantially on the properties of the precipitant/solvent system. With increasing sensitivity of the system to composition (i.e., with increasing influence of the composition of macromolecules on their distribution between the phases during fractionation), the asymmetry of the differential m.w.d. of the fractions increases, and under certain conditions the fractions may have bimodal m.w.d.

For experimental verification of this and other conclusions of the theory, a copolymer of methyl methacrylate with styrene, with characteristic viscosity $[\eta] = 0.65$ and composition $\alpha = 0.23$ (α is the molar fraction of styrene units in the copolymer), was fractionated in two precipitant/solvent systems ([3]). According to preliminary data, the distribution of the copolymer between phases during fractionation in the system (n-hexane–methanol–0.8 : 1.0 by volume)–toluene (experiment 361) depends only weakly on the composition of the macromolecules, whereas in the acetonitrile/toluene system (experiment 359) it depends strongly on the composition of the macromolecules in the range of values $\alpha = 0$–0.5. It was to be expected that the m.w.d. of the fractions from experiment 359 would be considerably more asymmetric than those of the fractions from experiment 361. Since, as calculation showed, such differences are especially evident in the case of middle and light fractions, in the present work the m.w.d. of fractions 6, 11, and 14 from experiment 359 and 8 and 11 from experiment 361 were studied by the method of velocity sedimentation in an ultracentrifuge (in all, 18 fractions were isolated in each system).

The general theory of determining the m.w.d. of polymers with the aid of an ultracentrifuge and the methods for calculating sedimentation diagrams have been considered in detail in the literature ([4]); therefore we shall confine ourselves to several remarks connected with the specific nature of the samples studied. Fractions of copolymers are nonuniform both in size and in composition. If, within a fraction, the average composition α of macromolecules of the same molecular weight M does not remain constant with change in M, the form of the sedimentation diagram will not strictly correspond to the true distribution of concentrations in the cuvette, since polystyrene and polymethyl methacrylate have different refractive indices. In addition, experimentally determined values of the diffusion coefficients D have an averaged character, and their use for calculating sedimentation diagrams may be associated with distortion of the form of the m.w.d. in cases where, within a fraction, α depends on M. Thus, in the general case, it is apparently impossible to establish the exact form of the m.w.d. of copolymer samples with the aid of an ultracentrifuge. But a comparative characterization of a series of fractions is possible, since within the framework of such a task the distorting effects are of secondary importance.

Sedimentation diagrams were obtained at 17.5–18.5° on a large oil ultracentrifuge of the LKB system at 40 thousand rpm, using the Philpot–Svensson optical system (a phase-contrast plate was used) (^{5}). Diffusion coefficients at 20.9° were measured on a Lamm apparatus with a scale optical system, equipped

an automatic system of temperature control and photography (^{6}). The sedimentation coefficients s and diffusion coefficients D were reduced to the standard temperature of 20°.

It is advisable to carry out sedimentation measurements in a θ-solvent. This increases the resolving power of the method (^{7}), and also eliminates the concentration dependence of the sedimentation coefficients, making it possible to work at comparatively high concentrations, i.e., under conditions of increased sensitivity of the instrument, and considerably reduces the amount of experimental and computational work. For the samples studied, a mixture of n-propanol with methyl ethyl ketone (9 : 11 by volume) proved to be close in properties to a θ-solvent. We give the dependence of the sedimentation coefficients s on the concentration C for fraction 6 from experiment 359 at 18°.

C, g/100 ml	1.00	0.70	0.50	0.25	0.10
$s \cdot 10^{13}$, cm/(s · dyne)	7.54	7.71	7.75	7.71	7.55

From the data given it is clear that the values of s remain practically constant over a wide concentration range. Subsequently all sedimentation and diffusion measurements were carried out at $C = 0.7$ g per 100 ml of solvent.

The diffusion coefficients needed for calculating the molecular-weight distribution were determined for a series of fractions from experiment 361, which were comparatively close to one another in composition and to the unfractionated copolymer. The partial volume of these fractions at the experimental temperatures in the solvent used, determined by the pycnometric method, was $V = 0.83$. Viscosity measurements were carried out in a viscometer with a suspended level. The characteristics of the samples and the measurement results are presented in Table 1.

Table 1

Results of sedimentation and diffusion measurements

Sample	Content of styrene units, mol. %	$[\eta]$, dl/g	$s \cdot 10^{13}$, cm/(s · dyne)	$D \cdot 10^7$, cm^2/s	$M \cdot 10^{-5}$
Experiment 361, fraction 5	20.7	0.98	12.31	2.85 ± 0.11	3.19
Experiment 361, fraction 6	22.6	0.88	10.92	3.30 ± 0.06	2.44
Experiment 361, fraction 7	23.0	0.80	10.25	3.34 ± 0.07	2.27
Experiment 361, fraction 8	28.7	0.71	9.35	–	–
Experiment 361, fraction 11	24.5	0.57	7.40	4.82 ± 0.17	1.13
Experiment 361, fraction 12	23.4	0.46	6.82	4.98 ± 0.16	1.01
Experiment 359, fraction 6	24.7	0.78	7.96	–	–
Experiment 359, fraction 11	23.8	0.74	6.43	–	–
Experiment 359, fraction 14	22.0	0.60	5.11	–	–

The dependence between s and M in logarithmic coordinates is rectilinear and corresponds to the equation $s = 1.93 \cdot 10^{-2} M^{0.51}$. The exponent of M, within the experimental error, is close to 0.5, which is characteristic of linear polymers

Fig. 1. Molecular-weight distributions of copolymer samples. Experiment 361, fractions: a −8; −11. Experiment 359, fractions: −6; −11; −14

Figure 1: Fig. 1. Molecular-weight distributions of copolymer samples. Experiment 361, fractions: a −8; −11. Experiment 359, fractions: −6; −11; −14

in a θ-solvent.

Figure 1 presents the molecular-weight-distribution curves calculated from the sedimentation diagrams and the data of Table 1. As can be seen from the figure, the fractions from experiment 361 have almost symmetrical molecular-weight distributions. The molecular-weight distributions of the fractions from experiment 359 are sharply asymmetric, extended toward larger M, and in the case of fraction 14 the curve has a weakly expressed second maximum in the region $M = 3.5 \cdot 10^5$.

Thus, the results obtained confirm one of the conclusions of the theoretical analysis of the regularities of copolymer fractionation.

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Fig. 1. Molecular-weight distributions of copolymer samples.
Experiment 361, fractions: **a** −8; −11. Experiment 359, fractions: −6; −11; −14.

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