Fractionation of a Model Random Copolymer in Various Solvent Systems

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ABSTRACT: A copolymer with a broad chemical composition distribution was modelled by a mixture of ten chemically homogeneous random styrene–2-methoxyethyl methacrylate copolymers of different composition. The sample was fractionated in solvent systems of various types selected on the basis of cloud-point determinations. The distribution functions of chemical composition obtained from fractionation in binary systems are compared with the known original distribution function of the unfractionated sample. Fractionation purely by molecular weight was suggested and verified in a more complex ternary solvent system. The distribution functions of chemical composition obtained from fractionation in binary systems are compared with the known original distribution function of the unfractionated sample. The distribution function of chemical composition obtained by cross-fractionation of the sample is in good agreement with the original distribution function; partition of the copolymer by this method proceeds almost exclusively by chemical composition of copolymer chains. The results permit one to formulate a few qualitative rules about the precipitation fractionation of copolymers, heterogeneous both in molecular weight and chemical composition.

The problem of fractionation of copolymers is frequently often encountered in practice. To determine a number of basic characteristics of copolymers (e.g., the relation between intrinsic viscosity and molecular weight), it is advantageous to have at one's disposal several fractions of different molecular weight, but with the same average chemical composition. In other cases fractionation is employed in the detection of the copolymer chemical heterogeneity or in the estimation of the chemical composition distribution.

Theoretical analysis of phase equilibria in systems containing copolymers has been carried out by several authors,[1–4] but the results do not provide direct instruction on how to perform the actual fractionation of copolymers. A suitable solvent system for fractionation (i.e., in most cases a solvent–precipitant system) is usually selected empirically, using the determination of the cloud points of consituent homopolymers. As a rule, two solvent systems are looked for; in one of them fractionation should proceed predominantly by chemical composition of copolymer chains, while in the other it should, if possible, depend only on their molecular weight. The results of fractionation of a chemically heterogeneous copolymer in such solvent systems could then be used in constructing, e.g., distribution functions of chemical composition and molecular weight, which would relatively satisfactorily characterize the fractionated copolymer.

The main criterion recommended in the literature for a proper choice of a fractionation system to separate by molecular weight is that the cloud points of the constituent homopolymers should be identical or close to each other.[5] In more sophiticated papers, the slope of the dependence of the critical volume fraction of precipitant, φ_c, on chemical composition of the copolymer at the point corresponding to the average copolymer composition is required to be nil.[6] On the contrary, for fractionation by chemical composition, solvent systems are sought in which the cloud points of the two homopolymers differ markedly, or in which the slopes of the dependence of φ_c on copolymer composition have the highest values.

It is usually not possible to verify the fractionation efficiency, especially with respect to chemical composition, because fractionated copolymers have an unknown distribution of chemical composition; the majority of authors do not even attempt to calculate the distribution function of chemical composition from the copolymerization conditions. For this reason, we prepared a model random copolymer of styrene and 2-methoxyethyl methacrylate with a known distribution of chemical composition, using it to verify the validity of simple criteria of the choice of solvent systems suitable for various types of fractionation. This is done by comparing the known distribution function of chemical composition with experimental results of fractionation in various solvent systems. We have also tried to improve the separation effect by using ternary solvent systems in the fractionation by molecular weight, or more complicated fractionation procedures (cross-fractionation) in the partition by chemical composition.

Experimental Section

Preparation and Characterization of Copolymers. The styrene used was a commercial product of Lachema, Czechoslovakia; 2-methoxyethyl methacrylate was prepared by esterification of methacrylic acid with 2-methoxyethanol.[7] The monomers were distilled at reduced pressure and their purity (>99.9%) was checked by gas chromatography.

Random copolymers of styrene and 2-methoxyethyl methacrylate were obtained by radical copolymerization in toluene (50 vol%) at 60 °C to 20–30 wt % conversion. The initiator, azobis(isobutyronitrile), was twice recrystallized from methanol. The copolymerization products were twice reprecipitated from acetone into methanol and dried in vacuo at 50 °C to constant weight. The conversion chemical heterogeneity of the samples, characterized by the calculated statistical variance of the chemical composition of copolymer macromolecules, σ^2 (cf. eq 2), is low ($\sim 10^{-5}$), so that from the viewpoint of fractionation these samples can be regarded as chemically homogeneous.[8]

A model copolymer with a broad distribution of chemical composition was prepared by mixing ten copolymers with different chemical composition (Table I). The mixture was homogenized by dissolution in acetone and reprecipitation into methanol. Further treatment was the same as above.

The molecular weight of the copolymers (in some cases also of fractions) was determined by light scattering from butanone solutions with the Photo-Gonio-Diffusomětre Sofica employing a method described elsewhere.[9] The refractive index increments were measured with a Brice-Phoenix differential refractometer, Model BP-2000-V. Copolymer composition was determined by elemental analysis. The experimental error of determination of chemical composition was ca. 1 wt % of styrene.

Cloud Points. The solutions of homopolymers or copolymers were placed at 25 ± 0.1 °C in a double-jacket thermostated titration vessel; precipitant was added with a microburet. The appearance of first turbidity was followed visually. The polymer concentration and volume fraction of the precipitant at the cloud

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Table I
Copolymer with a Model Distribution of Chemical Composition[a]

i	W_i	w_i	$M_w \times 10^{-5}$
1	0.378	0.203	1.64
2	0.265	0.245	1.72
3	0.114	0.288	1.63
4	0.072	0.318	1.61
5	0.049	0.347	1.64
6	0.034	0.376	1.73
7	0.028	0.405	1.73
8	0.023	0.432	1.97
9	0.022	0.468	1.93
10	0.014	0.510	1.96

[a] W_i is the weight fraction of the ith component with a chemical composition given by the weight fraction of styrene, w_i, and with the molecular weight M_w. Average composition, $\bar{w} = 0.27$.

point, φ, were calculated from the known initial concentration of the polymer solution (0.2 to 2.0 wt % of polymer) and from the known volumes of polymer solution and precipitant added. Extrapolation of the concentration dependence of cloud points φ to pure polymer yielded critical volume fractions of the precipitant,[10,14] φ_c.

Fractionation. The model copolymer was fractionated at 25 ± 0.1 °C by precipitation fractionation in the common experimental arrangement. The polymer concentration during the isolation of the first fraction was ca. 1 wt %. The isolated gel phase was dissolved in a small amount of solvent, and the solvent was removed by evaporation and drying. The composition of the fractions was determined by elemental analysis.

Treatment of Experimental Fractionation Data. The integral weight distribution function of chemical composition, $G(w)$, can be defined as the sum of the weight fractions of copolymer having a content of styrene equal to or less than w. A sample calculation is given in Table IV and plotted in Figure 6. A function of the type $G(w) = A + B\,w^C$, where A, B, and C are adjustable parameters, was fitted to the data by the least-squares method. The parameter C was varied, until the maximum value of the correlation coefficient was obtained.

The differential weight distribution function of chemical composition, $g(w)$, was then obtained by differentiating the analytical form of the integral distribution function $G(w)$, i.e., $g(w) = BCw^{C-1}$. The area under this distribution function in an interval between w and $w + \Delta w$ gives the weight fraction of macromolecules with chemical composition within this interval.

Results and Discussion

Choice of Copolymer for Fractionation. Random copolymers of styrene (S) and 2-methoxyethyl methacrylate (MEMA) were intentionally chosen for the investigation of fractionation. While PS is a typical representative of nonpolar polymers, PMEMA exhibits a considerably polar character.[7] Hence, sufficiently large differences in the solubility of the two polymers may be expected. We were directed to the choice of these copolymers also by a number of other requirements, such as, e.g., the feasibility of an easy and sufficiently accurate determination of their chemical composition, defined conditions of copolymerization, low probability of branching, etc.

Owing to the copolymerization parameters of the monomer pair S–MEMA[11] ($r_S = 0.50$, $r_{MEMA} = 0.58$) and to the properties of MEMA, it is difficult to prepare linear copolymers with a high chemical heterogeneity by radical copolymerization. The maximum conversion heterogeneity,[8] expressed by the statistical variance of chemical composition σ^2 (cf. eq 2 below), which can be attained by the copolymers S–MEMA, is ca. 1×10^{-5} at a 10 wt % conversion of copolymerization, and 4×10^{-4} at a 50 wt % conversion. Many practically important copolymers have much broader distributions of chemical composition (σ^2 with an order of magnitude 10^{-3} and higher). Unfortunately, most of these copolymers are for a number of reasons (e.g., inaccurate determination of composition, presence of supermolecular structures in solution, small differences of solubility of corresponding homopolymers) little suited to a rigorous fractionation study.

For the above reason, and also since it was desirable to have at our disposal a copolymer with a known distribution of chemical composition, it was decided to model a continuous broad distribution of chemical composition by a discrete mixture of chemically homogeneous copolymers differing by their chemical composition (Table I).

Such a procedure has some advantages in further experiments: (a) The individual components of the model copolymer thus prepared may be chosen so as to have similar distributions and close average of molecular weights. In this way, mutual independence of the distributions of molecular weight and chemical composition of the copolymer chains is attained. With real and especially high-conversion copolymers, these two distributions may correlate (e.g., chains with a higher content of one type of monomer unit may have a higher average molecular weight than chains with another chemical composition), thus rendering the interpretation of results more difficult. (b) The distribution function of chemical composition of products of copolymerizations may be estimated by calculation, the copolymerization mechanism being known, but the latter may be affected by the reaction conditions, or be more complex than it is assumed. On the contrary, the distribution function of chemical composition of the model copolymer prepared by the mixing of components is well defined.

The amount of the individual constituent copolymers and their composition (Table I) were chosen so as to make the distribution of chemical composition correspond to a distribution met in practice. The modelled distribution of chemical composition conforms with that of a copolymer of monomers A and B with the copolymerization parameters $r_A = 0.23$ and $r_B = 1.68$, for the initial content of A in the monomer mixture 30 wt %, and for a 92 wt % conversion. The above copolymerization parameters correspond to, e.g., the monomer pair vinyl acetate–vinyl chloride.[12] The shape of the distribution function of chemical composition was calculated using Myagchenkov's and Frenkel's[13] equations. Since the number of components of the model copolymer is sufficiently high, the distribution of chemical composition of this sample (Table I) is treated as if it were continuous.

Choice of the Solvent System. Binary Systems. The first step was the search for suitable fractionation solvent systems. In the first approximation, the difference between the critical volume fractions of precipitant,[10] ϵ, for the respective homopolymers was taken as a rough criterion of the type of solvent system (Figure 1):

$$\epsilon = \varphi_c(\mathrm{PS}) - \varphi_c(\mathrm{PMEMA}) \qquad (1)$$

To start with, solvent systems were looked for in which the cloud points (or the critical volume fractions of precipitant) were almost identical for the two homopolymers, i.e., $\epsilon = 0$. With such systems, a relatively small sensitivity to the composition of copolymer chains may be expected, and the fractionation of copolymers should proceed predominantly by their molecular weight. After that, we tried to find solvent–precipitant pairs with which the difference between the cloud points of the two homopolymers would be as high as possible; in such systems fractionation could be carried out prevailingly by chemical composition.

Of a whole number of solvent systems tested[14] (com-

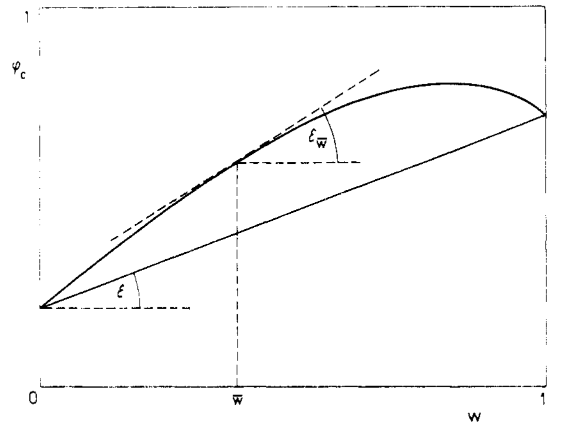

Figure 1. Schematic example of the dependence of critical volume fraction of the precipitant, φ_c, on the chemical composition of copolymer, w, and definition of the parameters ϵ and $\epsilon_{\bar{w}}$.

Table II
Some Characteristics of Solvent Systems[a]

solvent	precipitant	φ_c PS	φ_c PMEMA	ϵ	$\epsilon_{\bar{w}}$
butanone	methanol	0.11	0.79	−0.68	−0.76
ethyl acetate	diisopropyl ether	0.43	0.45	−0.02	0.21
benzene	cyclohexane	0.96	0.31	0.65	0.64
butanone	n-heptane	0.42	0.33	0.09	0.27
butanone	ethanol	0.18	0.70	−0.52	−0.46

[a] Cloud points φ_c are critical volume fractions of the precipitant[10] for homopolymers, ϵ is the difference between these cloud points, and $\epsilon_{\bar{w}}$ is the slope of the dependence of φ_c on the copolymer composition at $\bar{w} = 0.27$.

binations of four solvents and six precipitants), a few representatives of different types are characterised in Table II; the dependence of critical volume fraction of precipitant on copolymer composition in some systems was determined (Figure 2).

The majority of the φ_c vs. w dependences are slightly curved; therefore, a further characteristic considered for the solvent system was the derivative of this dependence, $\epsilon_{\bar{w}}$ (Figure 1), at the point corresponding to the average composition of the model copolymer, $\bar{w} = 0.27$.

In the solvent systems consisting of a common solvent and precipitant of the two homopolymers, the maximum attainable value of ϵ is usually not higher than 0.8 in order for the system to be effective in the fractionation of copolymers with any composition ranging between both homopolymers. For other types of solvent systems, e.g., when both components are solvent for one of the homopolymers and precipitant for the other, very steep φ_c vs. w dependences may be obtained (Figure 2, system acetone–acetonitrile). The quantification of steepness by ϵ then loses its meaning, and $\epsilon_{\bar{w}}$ must be employed instead. The application of such systems in fractionations is somewhat restricted by the fact that only copolymers with compositions within a limited range are separated into two phases. Copolymers whose chemical composition lies beyond this interval are always either completely soluble or insoluble in the solvent system, irrespective of its composition. For this reason, no fractionations of the model copolymer were carried out in the acetone–acetonitrile system; here, components with a low styrene content would be always soluble.

Ternary Systems. When looking for a solvent system possessing specified properties, with a binary system it will be more or less a matter of chance whether or not it fulfils the requirements put on it. An example can be seen in, e.g., the condition of identical cloud points for two different homopolymers in the same solvent system, i.e., $\epsilon = 0$. In several of the systems tested this condition was almost fulfilled; not one could be found, however, in which it would be met completely. An even approximate fulfilment of the requirement $\epsilon_{\bar{w}} = 0$ is still more difficult. Since systems satisfying the condition $\epsilon = 0$ or $\epsilon_{\bar{w}} = 0$ are sought for fractionation of copolymers by molecular weight, this case was investigated in more detail.

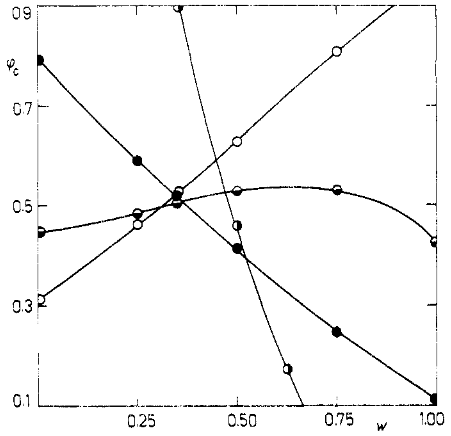

Figure 2. Dependence of critical volume fraction of precipitant, φ_c, on chemical composition, w, of random S-MEMA copolymers. The composition w is expressed as the weight fraction of styrene. Solvent systems follow: butanone–methanol (●), ethyl acetate–diisopropyl ether (◒), benzene–cyclohexane (○), and acetone–acetonitrile (◑).

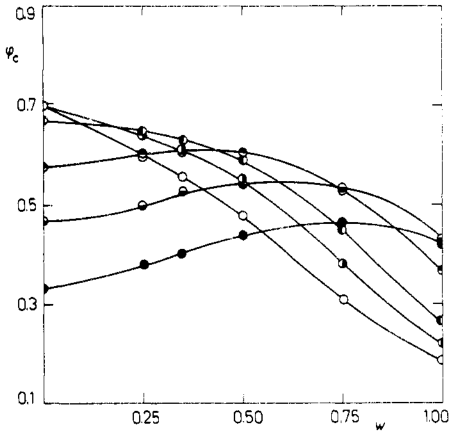

Figure 3. Dependence of critical volume fraction of precipitant, φ_c, on chemical composition, w, of the S-MEMA copolymers in the ternary solvent system butanone–n-heptane–ethanol. The composition w is expressed as the weight fraction of styrene. The volume fraction of n-heptane in the mixed precipitant n-heptane–ethanol follows: 0 (○); 0.2 (◑); 0.4 (◐); 0.6 (◓); 0.8 (◒); 1.0 (●).

One of the relatively passable routes for finding such systems appears to consist in the use of more complicated ternary solvent systems.[6] It is appropriate to choose the individual components of the ternary solvent system so that one of them is a common solvent for both homopolymers; each of the other two components should be a more effective precipitant for one of the homopolymers than for the other, or in other words, the ϵ values of the two binary systems should have opposite signs. Butanone–n-heptane–ethanol was selected on the basis of preliminary experiments (Table II; the apparently better suited pair of precipitants, namely, methanol and cyclohexane, was not used because of the limited miscibility of these precipitants).

Copolymer solutions in butanone were titrated until the first turbidity appeared by a mixed precipitant n-hep-

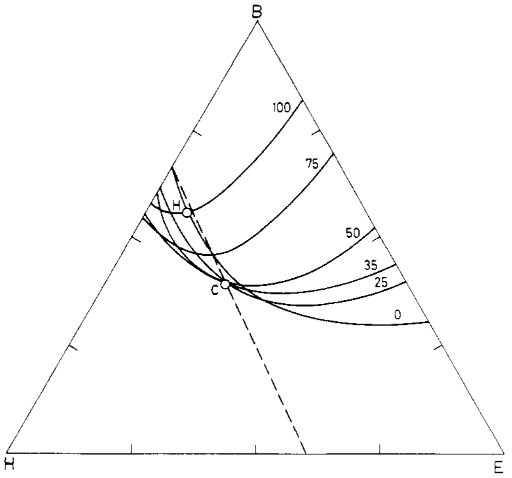

Figure 4. Dependence of cloud points, φ, of the S-MEMA copolymers on the composition of the ternary solvent system butanone (B)-*n*-heptane (H)-ethanol (E). The composition of copolymers in wt % of styrene is given on the individual curves. The broken straight line shows one of the possible choices of the solvent system for fractionation by molecular weight.

tane–ethanol with different compositions.

The results obtained in ternary solvent systems (Figure 3) are more adequately represented in triangular coordinates (Figure 4). The plot shows that identical cloud points for both homopolymers will be observed for any system (mixed) solvent–(mixed) precipitant, if the connecting line of their composition in the triangular diagram passes through the point H in which the curves linking the cloud points of the two homopolymers cross each other. The condition under which not only the parameter ϵ but also $\epsilon_{\bar{w}}$ would be nil for all copolymer compositions (i.e., the cloud points are independent of the copolymer composition) is met when the curves for all copolymer compositions intersect at a single point. In most cases this requirement cannot be generally satisfied. In the system under investigation there is only a single point (C, Figure 4) at which, within the limits of experimental error, more than two curves intersect (for 25, 35, and 50 wt % of styrene). Hence, the solvent and precipitant (generally, both mixed ones) chosen so that the connecting line of their compositions passes through the point C (e.g., broken straight line in Figure 4) form a solvent system, which has prerequisites permitting fractionation of a copolymer with chains containing 25–50 wt% of styrene to proceed only by molecular weight. Verification of this assumption is dealt with below.

Fractionation of a Model Copolymer in Solvent Systems of Various Types. In order to verify the fractionation efficiency and to compare its results with the qualitative prediction obtained from the cloud points (i.e., to find out to what extent fractionation in a given solvent system proceeds "by molecular weight" and to what extent "by chemical composition"), a sample with model distribution of chemical composition was fractionated in a few solvent systems of different type: (1) in the binary system ethyl acetate–diisopropyl ether, in which the fractionation should proceed preferentially by molecular weight; (2) in the ternary system butanone–*n*-heptane–ethanol, where the molecular weight is expected to play the decisive role in fractionation; (3) in the binary system butanone–methanol, in which the copolymer is separated predominantly by chemical composition; and (4) by cross-fractionation, the first fractionation in benzene–cyclohexane followed by refractionation of the fractions obtained in butanone–methanol. This last procedure should provide effective separation of the copolymer by chemical composition.

Table III
Results of Fractionation of the Model Copolymer[a]

n	W_n	w_n	n	W_n	w_n
		Ethyl acetate–diisopropyl ether			
1	0.017	0.225	9	0.046	0.261
2	0.015	0.226	10	0.069	0.263
3	0.097	0.233	11	0.087	0.262
4	0.065	0.240	12	0.084	0.277
5	0.038	0.238	13	0.118	0.286
6	0.069	0.244	14	0.166	0.311
7	0.032	0.245	15	0.053	0.333
8	0.043	0.248			
		Butanone–*n*-heptane–ethanol			
1	0.191	0.257	6	0.114	0.265
2	0.067	0.262	7	0.096	0.259
3	0.105	0.268	8	0.138	0.259
4	0.078	0.266	9	0.038	0.251
5	0.111	0.266	10	0.062	0.260
		Butanone–methanol			
1	0.010	0.440	13	0.049	0.235
2	0.012	0.442	14	0.062	0.233
3	0.024	0.438	15	0.049	0.226
4	0.074	0.394	16	0.045	0.229
5	0.031	0.368	17	0.041	0.227
6	0.025	0.336	18	0.042	0.220
7	0.047	0.318	19	0.039	0.217
8	0.047	0.306	20	0.042	0.222
9	0.063	0.283	21	0.037	0.223
10	0.057	0.268	22	0.019	0.220
11	0.065	0.258	23	0.099	0.219
12	0.066	0.248			

[a] W_n is the weight fraction of the *n*th fraction and w_n is its chemical composition expressed as the weight fraction of styrene.

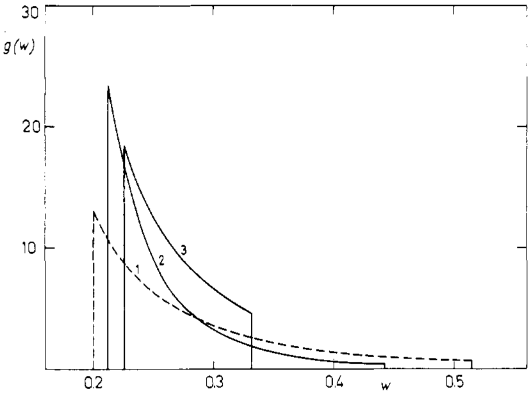

Figure 5. Comparison of differential weight distribution functions of chemical composition, $g(w)$, obtained from experimental fractionation data in binary solvent systems with the distribution function of the model copolymer: 1, model copolymer; 2, butanone–methanol; 3, ethylacetate–diisopropyl ether.

Fractionation in a Binary Solvent System by Molecular Weight. Judging from a preliminary analysis of the solubility behavior of random copolymers of styrene with 2-methoxyethyl methacrylate in the solvent system ethyl acetate–diisopropyl ether, and according to common criteria[5] ($\epsilon \simeq 0$), it could be expected that fractionation would proceed almost exlusively by molecular weight and that the chemical composition of copolymer chains would have a negligible effect on it. If so, the distribution function of chemical composition would be represented by an infinitely high peak with zero width. However, the chemical compositions of the individual fractions obtained by fractionation of the model copolymer in this solvent system extend over a fairly wide range (Table III). Such separation can hardly be regarded as fractionation exclusively by molecular weight (curve 3, Figure 5). Apparently, the solvent system is more adequately characterized by the parameter $\epsilon_{\bar{w}}$ than ϵ, at least in those cases in which the dependence of cloud point on chemical composition of the copolymer is curved, and the two parameters may differ substantially.

Fractionation in a Ternary Solvent System. For fractionation of the model copolymer in a ternary solvent system, a mixture butanone–*n*-heptane (2:1 by vol) was chosen rather arbitrarily as a solvent and *n*-heptane–ethanol (2:3 by vol) as precipitant (cf. broken straight line in Figure 4).

The results of fractionation show that the composition of all fractions obtained may be regarded as identical within the limits of experimental error (Table III). Consequently, fractionation in this solvent system proceeded only by molecular weight of copolymer chains, regardless of their chemical composition. Thus it is possible to provide such conditions of fractionation which make separation of polymer molecules proceed virtually only by molecular weight.

It is of course laborious to find a suitable multicomponent system for fractionation by molecular weight; preliminary measurements require a large number of copolymers of various composition. In spite of this, ternary solvent systems are advantageous for fractionation of copolymers and cannot be fully replaced by simpler ones.

Fractionation in a Binary Solvent System by Chemical Composition. Owing to the comparatively steep dependence of the cloud points of S-MEMA copolymers on their composition in butanone–methanol (Figure 2), it may be expected that fractionation of a chemically heterogeneous sample will proceed preferentially by chemical composition. Experimental results corroborate this assumption (Table III, curve 2 in Figure 5). If, however, the shape of the distribution function of chemical composition of the unfractionated sample is compared with the distribution function constructed on the basis of fractionation data, it can be seen that the original distribution function is nonzero within a considerably broader range of chemical compositions (Figure 5). Obviously, the conclusive role in the separation of the copolymer is played not only by the chemical composition of copolymer chains, but also by their molecular weight. A similar conclusion also holds for fractionation in ethyl acetate–diisopropyl ether (Fig. 5), but the extent to which both variables affect the separation of the copolymer is different in different solvent systems.

The fact that the distribution of chemical composition obtained from fractionation data is always narrower than the actual distribution of chemical composition is easy to understand. Thus, e.g., in our case during the establisment of the first phase equilibrium in butanone–methanol the majority of copolymer chains with the highest content of styrene pass into the gel phase. In addition, the gel phase also contains minor quantities of all types of macromolecules with a lower styrene content, which decreases the average content of styrene in this phase. The average styrene content in the first fraction is therefore lower than that of macromolecules with the highest content of styrene present in the original sample. A similar argument applies to the other fractions.

Since the separation of the copolymer by chemical composition using butanone–methanol is not satisfactory, we examined a potentially more effective fractionation procedure, called cross-fractionation.

Cross-Fractionation. Cross-fractionation as a method of fractionation of copolymers by chemical composition was suggested in the early 50's.[15] The experimental and time requirements of this method are comparable with those of classical precipitation fractionation. Nonetheless cross-fractionation is employed only rarely, and papers dealing with its theoretical analysis[16,17] or experimental application[15,18-22] in the study of chemically heterogeneous copolymers have, so far, been sporadic.

Table IV

Results of Cross-Fractionation of the Model Copolymer[a]

n	W_n	w_n	n	W_n	w_n
I-1	0.043	0.463	III-3	0.056	0.241
I-2	0.032	0.422	III-4	0.044	0.225
I-3	0.037	0.332	III-5	0.059	0.235
I-4	0.049	0.355	IV-1	0.038	0.298
II-1	0.019	0.350	IV-2	0.062	0.216
II-2	0.086	0.316	IV-3	0.033	0.203
II-3	0.062	0.293	IV-4	0.033	0.232
II-4	0.040	0.275	V-1	0.030	0.197
II-5	0.086	0.239	V-2	0.036	0.207
III-1	0.033	0.286	V-3	0.037	0.197
III-2	0.062	0.254	V-4	0.023	0.192

[a] W_n is the weight fraction of the nth fraction and w_n is its chemical composition expressed as the weight fraction of styrene. Roman numerals denote primary fractions obtained by fractionation in benzene–cyclohexane. Arabic numerals denote fractions obtained by refractionation of primary fractions in butanone–methanol.

The principle of cross-fractionation consists in the separation of a copolymer into a number of primary fractions in a solvent system with a steep dependence of cloud points on chemical composition of the copolymer. The fractions thus obtained are then refractionated in another solvent system, also with a steep dependence of the cloud points on chemical composition; the two systems are usually chosen so that the parameters ϵ or $\epsilon_{\bar{w}}$ have an opposite sign in each.[17]

In our case, the system chosen for the first fractionation was benzene–cyclohexane, in which copolymers with a high content of MEMA are preferentially precipitated; the following refractionation was carried out in butanone–methanol, in which preferential precipitation involves copolymer chains with a major amount of styrene (Table II, Figure 2). Other solvent systems might suit as well, e.g., pairs butanone–*n*-heptane and butanone–ethanol (Table II), that is the systems consisting of the same components as the ternary one used in the fractionation of the model copolymer by molecular weight (cf. above).

Results of cross-fractionation (Table IV) show that primary fractions are chemically quite heterogeneous, because their refractionation yielded secondary fractions with very different composition. The chemical composition of these secondary fractions does not decrease monotonically with ordinal number of the fraction. The last one of a series of secondary fractions resulting from a given primary fraction might be expected to have lowest styrene content. In the system under investigation, however, the lowest styrene content was mostly observed with the penultimate fraction.

Figure 6 illustrates the determination of the integral distribution function of chemical composition from the experimental data. The shape of the distribution of chemical composition of the model copolymer justifies a purely concave plot through experimental points (cf. Experimental Section). Deviations of experimental values from the plotted curve mostly do not exceed the experimental error of determination of chemical composition. Of course, it is possible, in principle, to correlate experimental data by polynomials of a higher order. As a result, the fit of the plotted integral distribution curve would be im-

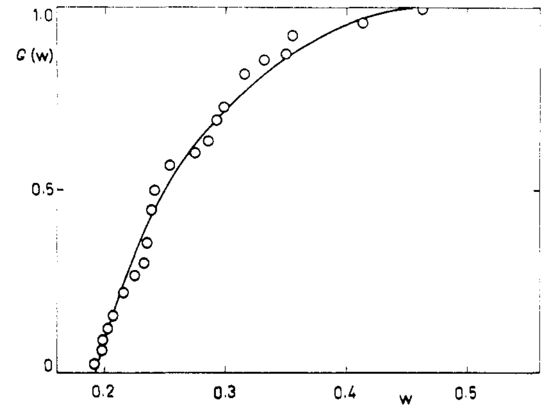

Figure 6. Fitting the integral distribution function of chemical composition of the type $G(w) = A + Bw^C$ to experimental points obtained from cross-fractionation.

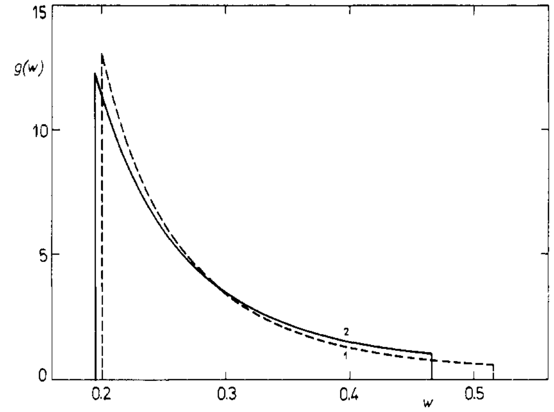

Figure 7. Comparison of the differential weight distribution function of chemical composition, $g(w)$, obtained from cross-fractionation with the distribution function of the model copolymer: 1, model copolymer; 2, experimentally obtained curve.

proved, but the differential distribution function of chemical composition might exhibit imaginary extremes.

The agreement between the original and experimentally obtained distribution function of chemical composition is very good (Figure 7). A major difference can be seen in the part of the distribution function corresponding to high contents of styrene. The amount of macromolecules with a higher styrene content in the model copolymer is small (Table I) and comparable to, or even smaller than, the weight of fractions. A better agreement between the two distribution functions could be reached if the number of fractions were adequately raised.

Cross-fractionation also yielded fractions with a content of styrene as low as 19.2 wt % S (Table IV), even though the model copolymer was prepared using samples with the styrene content 20.3 wt % and more (Table I). Although the difference observed is within the limits of experimental error of the analytical determination of chemical composition, the phenomenon just described may be explained through the chemical heterogeneity of the copolymers constituting the model sample. The calculation of the conversion heterogeneity[13] shows that a copolymer with an average styrene content of 20.3 wt % prepared up to a 30 wt % conversion may contain copolymer chains with 19–21 wt % S. This finding is in accordance with experimental results, indicating a high efficiency of cross-fractionation.

Empirical Correlation of the Results of Fractionation with the Properties of Solvent Systems. The experimentally obtained distribution functions of chemical composition are always narrower than the distribution function of an unfractionated model copolymer (Figures 5 and 7). The width of distribution of chemical composition, apparent or real, may be described by, e.g., the statistical variance of chemical composition, defined as

Table V
Some Characteristics of the Model Copolymer Obtained from Fractionation Data in Various Solvent Systems[a]

solvent system	$\bar{w}$	$\sigma_e^2 \times 10^5$	D
butanone–methanol	0.264	351	0.627
ethyl acetate–diisopropyl ether	0.269	104	0.186
butanone–*n*-heptane	0.263	4	0.007
benzene–cyclohexane/butanone–methanol	0.271	492	0.878
unfractionated copolymer	0.266	560	1.000

[a] $\bar{w}$ is the weighted average copolymer composition and σ_e^2 is the statistical variance of chemical composition obtained experimentally by fractionation. The parameter D is defined by eq 3.

$$\sigma^2 = \sum_n (w_n - \bar{w})^2 W_n \qquad (2)$$

where w_n and $\bar{w}$ are the chemical composition of the nth fraction and the average copolymer composition, respectively, and W_n is the weight fraction of the nth fraction. If σ^2_e and σ^2_0 are the experimentally obtained and true variance of chemical composition, respectively, then their ratio

$$D = \sigma^2_e/\sigma^2_0 \qquad (3)$$

may be regarded as a measure of the efficiency of fractionation by chemical composition (Table V). Assuming mutual independence of the molecular weight and chemical composition distributions, $D = 0$ would correspond to fractionation exclusively by molecular weight, regardless of the composition of copolymer chains. $D = 1$ would be reached at a hypothetical ideal fractionation by chemical composition.

There is obviously a connection between the properties of a solvent system (e.g., steepness of the dependence of cloud points on the chemical composition of a copolymer, $\epsilon_{\bar{w}}$, Table II) and the efficiency of fractionation by chemical composition expressed through D. It appears that in our case one may, purely empirically, correlate experimentally obtained $\epsilon_{\bar{w}}$ and D values by the relation (Figure 8)

$$D = \tanh |\epsilon_{\bar{w}}| \qquad (4)$$

If this relation were of more general validity, it would be possible, from the experimentally obtained apparent value of the variance of chemical composition, σ^2_e, and the known value of $\epsilon_{\bar{w}}$ (by employing eq 3 and 4), to estimate the actual value of the parameter of chemical heterogeneity, σ^2_0, which is an important characteristic of chemically heterogeneous copolymers.

It should be stressed that the above correlation could be used only with copolymers having mutually independent distributions of molecular weights and chemical compositions. If these distributions were not independent, even fractionation exclusively by molecular weight (i.e., at $\epsilon_{\bar{w}} = 0$) generally would yield fractions differing in their chemical composition, and thus also $D \neq 0$. Under these conditions, the D value would be some measure of mutual dependence of the two distributions.

Conclusions

Experimental fractionations of a model copolymer with mutually independent distributions of molecular weight

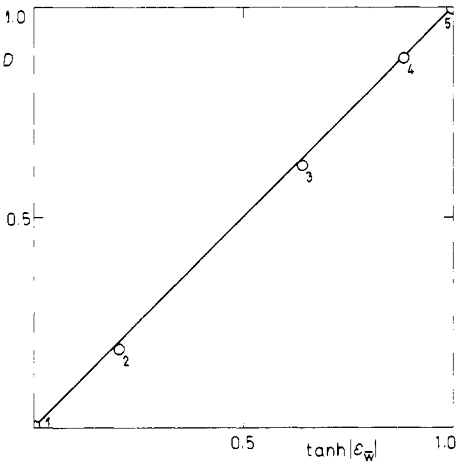

Figure 8. Correlation of the efficiency of fractionation by chemical composition with the properties of solvent systems according to the equation $D = \tanh|\epsilon_{\bar{w}}|$: 1, ternary solvent system; 2, ethyl acetate–diisopropyl ether; 3, butanone–methanol; 4, cross-fractionation; 5, hypothetical ideal solvent system. For cross-fractionation, the sum of the absolute values of $\epsilon_{\bar{w}}$ of both binary solvent systems used was taken instead of $|\epsilon_{\bar{w}}|$.

and chemical composition in various solvent systems have shown that:

(a) The fractionation process in binary solvent systems is usually affected both by molecular weight and by the chemical composition of copolymer chains. The effect of the two variables is operative in various solvents to different extents. Binary systems are not suited for the determination of the distribution functions of molecular weight or of chemical composition, but they may help in a qualitative detection of the chemical heterogeneity of copolymers.

(b) Fractionation by molecular weight only is experimentally feasible, if more complex, e.g., ternary, solvent systems are used. Results of such a fractionation allow one to draw conclusions about the character of the molecular weight distribution of copolymer chains by the same procedure as used for homopolymers.

(c) Cross-fractionation gives a relatively realistic picture of the distribution of chemical composition of copolymer macromolecules. The separation efficiency of copolymers by chemical composition is higher in this case than with the common binary solvent systems.

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