

Fractionation of a Statistical Copolymer in a Demixing-Solvent System: Theory and Experiment

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SYNOPSIS

It has been shown that, under specific conditions, a demixing-solvent fractionation according to chemical composition can be applied to statistical copolymers. Formally, identical expressions have been derived for the distribution of a copolymer between coexisting phases in precipitation (sol-gel) and demixing-solvent fractionations. Theory predicts that the effects of molar mass and chemical composition cannot be separated in either of the phase-equilibrium fractionations. With demixing solvents, the partition coefficient depends steeply on copolymer composition, which enables one, e.g., to separate homopolymers from a blend. Multistep demixing-solvent fractionation of a copolymer may proceed only in specific cases, e.g., immediately below the maximum of the coexistence curve. A feasibility study was performed with a chemically heterogeneous statistical copolymer of styrene and 2-methoxyethyl methacrylate; the experimental results have confirmed the theoretical predictions.

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INTRODUCTION

Determination of heterogeneity in the chemical composition of copolymers is a complex problem and, for an unknown material, cannot be done routinely. One method that can be used for such a determination is fractionation according to chemical composition. A theory of phase equilibria (Topchiev et al.,¹ Teramachi and Nagasawa²), which was derived for copolymers, leads to the conclusion that fractionation according to chemical composition is always accompanied by separation according to molar mass.

Kuhn³⁻⁵ suggested and performed demixing-solvent fractionations that were expected to proceed, for the copolymers studied, predominantly according to chemical composition. The practical applicability of the method requires finding a pair of solvents having the following properties: (i) both liquid components (solvents) are partially miscible at room temperature; (ii) they are completely miscible above a certain (elevated) temperature; and (iii) one of

the liquids is a thermodynamically good solvent for one of the copolymer constituents and, at the same time, is a poor solvent or a nonsolvent for the other (and vice versa). Thus, under favorable conditions, the copolymer will be distributed between the coexisting liquid phases. When systems like *N,N*-dimethylformamide/heptane or *N,N*-dimethylformamide/cyclohexane were applied to fractionations of various polystyrene-*block*-polydiene copolymers, integral chemical composition distributions (ICCD) were obtained,^{4,5} and good correspondence with the theoretical expectation was observed.⁶ Similarly, poly(methyl methacrylate)-*graft*-polydimethylsiloxane was fractionated in a dimethyl sulfoxide/tetrachloroethylene solvent pair, and the ICCD thus obtained agreed well with the prediction.⁷ The approach will be applied in a forthcoming paper⁸ to the system polystyrene-*block*-hydrogenated polyisoprene in the dimethylformamide/methylcyclohexane demixing-solvent system.

Demixing-solvent fractionation is almost ideally suited to separating blends of homopolymers into parent constituents or for removing homopolymer "impurities" from a crude graft copolymer.⁵ Under favorable conditions, one of the parent homopolymers may enter the upper phase, the other appears

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in the lower one, and the pure graft copolymer remains in the third, intermediate phase. Purification of a graft copolymer may therefore be carried out in a single fractionation step.

So far, no demixing-solvent fractionation of a copolymer synthesized by statistical copolymerization has been reported. In the present paper, a theoretical analysis of a demixing-solvent fractionation of statistical copolymers has been done. Moreover, a feasibility study has been performed. We decided to fractionate a statistical copolymer of styrene (ST) and 2-methoxyethyl methacrylate (MEMA), prepared by free-radical copolymerization up to a high degree of conversion, because this material and its chemical heterogeneity had been studied extensively also by other methods and approaches.⁹⁻¹² The dimethyl sulfoxide/tetrachloroethylene mixture was chosen as the demixing-solvent system. Instead of a straightforward successive decreasing-temperature fractionation,⁴ aimed at obtaining an experimental ICCD, we focused on the phase-separation behavior of the system and analyzed the conjugate phases.

THEORETICAL

A solution of a nonuniform and chemically heterogeneous binary copolymer (constituent units A and B) in a two-component solvent (components 1 and 2) will be dealt with. The copolymer (component 3) is composed of a large number of species differing in the degree of polymerization P and chemical composition w . It follows from the Flory-Huggins equation that, neglecting the ternary term, the change of chemical potentials of individual components, $\Delta\mu_{P,w}$, may be expressed by¹³

$$\begin{aligned} \frac{\Delta\mu_{P,w}}{RT} = & \ln \varphi_{P,w} + 1 - P \left(\varphi_1 + \frac{\varphi_2}{\xi} + \frac{\varphi_3}{\bar{P}} \right) \\ & - \varphi_1 \varphi_2 P \chi_{1,2} + \varphi_1 P \chi_{1,w} + \varphi_2 P (\chi_{2,w}/\xi) \\ & - \varphi_1 \varphi_3 P \bar{\chi}_1 - \varphi_2 \varphi_3 P (\bar{\chi}_2/\xi) \quad (1) \end{aligned}$$

where R , T , φ_i , P and \bar{P} are, respectively, the universal gas constant, absolute temperature, volume fraction of the component i , the degree of polymerization of a given copolymer species, and the number-average degree of polymerization of the whole copolymer; $\xi = V_2/V_1$ is the ratio of molar volumes of the solvent components; $\chi_{1,w}$ and $\chi_{2,w}$ are the Flory-Huggins parameters pertaining to interactions between the copolymer species of composition w and components 1 and 2, respectively; $\bar{\chi}_1$ and $\bar{\chi}_2$ are mean values obtained by averaging $\chi_{1,w}$ and $\chi_{2,w}$

over all values of w ; and $\chi_{1,2}$ quantifies the interaction between components 1 and 2.

For each individual copolymer species (w , P), distributed between two demixed liquid phases in equilibrium, it must hold that its chemical potentials in both phases are equal. It follows that, for infinite dilution of the copolymer component, the partition coefficient k may be expressed as

$$\ln k = \ln \frac{\varphi'_{P,w}}{\varphi''_{P,w}} = P(\varphi'_1 - \varphi''_1) \left[1 - \frac{1}{\xi} - \chi_{1,w} + \frac{\chi_{2,w}}{\xi} + \chi_{1,2}(1 - \varphi'_1 - \varphi''_1) \right] \quad (2)$$

Here, φ'_i and φ''_i are volume fractions of the component i in, respectively, the upper and the lower phases.

The Flory-Huggins interaction parameters of the copolymer, $\chi_{1,w}$ and $\chi_{2,w}$, are not easily accessible. It is possible to estimate them using the Hildebrand solubility parameters¹⁴ δ_i :

$$\chi_{i,w} \cong 0.35 + \frac{V_i}{RT} (\delta_w - \delta_i)^2 \quad (3)$$

Substituting for $\chi_{i,w}$'s in eq. (2) from the right-hand side of eq. (3), we obtain

$$\begin{aligned} \ln k = & P(\varphi'_1 - \varphi''_1) \left[\left(1 - \frac{1}{\xi} \right) 0.65 \right. \\ & + \chi_{1,2}(1 - \varphi'_1 - \varphi''_1) \\ & \left. - \frac{V_1}{RT} (2\delta_w - \delta_1 - \delta_2)(\delta_2 - \delta_1) \right] \quad (4) \end{aligned}$$

Let us now approximate the solubility parameter of the copolymer species, δ_w , by a linear combination of the solubility parameters of both parent homopolymers δ_A and δ_B , according to Krause¹⁵:

$$\delta_w = w\delta_A + (1-w)\delta_B \quad (5)$$

It has been assumed^{1,2} that the interaction parameters $\chi_{i,w}$ rather than the solubility parameters δ_w of the copolymer are linear functions of copolymer composition. Our assumption [eq. (5)] is justified by the fact that the Hildebrand solubility parameters of polymers may be relatively successfully estimated using the structural contribution method.¹⁵

Equation (4) may be then transformed into a simple relation:

$$\ln k = P(\sigma - \Omega w) \quad (6)$$

where

$$\sigma = (\varphi_1' - \varphi_1'') \left[\left(1 - \frac{1}{\xi} \right) 0.65 + \chi_{12} (1 - \varphi_1' - \varphi_1'') - (\delta_2 - \delta_1) (2\delta_B - \delta_1 - \delta_2) \frac{V_1}{RT} \right] \quad (7)$$

$$\Omega = 2(\varphi_1' - \varphi_1'') (\delta_2 - \delta_1) (\delta_A - \delta_B) \frac{V_1}{RT} \quad (8)$$

Topchiev et al.¹ derived an equation formally identical with eq. (6) for a copolymer in a single solvent, and later Teramachi and Nagasawa² generalized this approach also for a copolymer in a solvent/nonsolvent mixture. Though the definitions of the parameters σ and Ω are different in each case, the thermodynamic description of the distribution of a polymer between two coexisting phases in equilibrium does not depend on the nature of the phases, that is, it is the same for the precipitation (sol-gel) and the demixing-solvent mechanisms.

EXPERIMENTAL

Copolymer

A statistical ST/MEMA copolymer was prepared by a solvent-free radical copolymerization up to 99% degree of conversion (see Table I in Ref. 16, run II). Its mass average molar mass determined by light scattering is 2.8×10^6 g mol⁻¹; its mean chemical composition measured by ¹H-NMR spectroscopy and/or elemental analysis can be expressed by the mass fraction of ST, $w_{ST} = 0.76$. For this copolymer composition, theory predicts¹⁶ a maximum attainable conversional chemical heterogeneity; a compositional drift from $w_{ST} \sim 0.66$ (0%) to 0.88 (99% degree of conversion) is expected and observed. Owing to statistical chemical heterogeneity,¹⁷ the real ICCD will be somewhat broader.

Solvents

The components of the demixing-solvent mixture, i.e., tetrachloroethylene (TCE) and dimethyl sulfoxide (DMSO), were chosen because polystyrene is well soluble in TCE and insoluble in DMSO, whereas the opposite is true for poly(2-methoxyethyl methacrylate). Both solvents were distilled on a column and their purity was checked by gas chromatography (> ca. 99.8%). Auxiliary solvents (toluene and methanol) were used as received. Dichloromethane, an eluent for gel permeation chromatography

(GPC), was stored over KOH or NaOH and freshly distilled before use to suppress absorption in the UV region.

Cloud-point Curves

The copolymer and both liquid components (TCE and DMSO in varying ratios) were weighed individually into glass ampules to form ca. 1% (w/v) copolymer solutions and sealed. All mixtures in the sealed ampules were submerged in warm water and shaken until homogeneous solutions were formed. By allowing the temperature to slowly decrease, the cloud points were recorded for all mixtures, and the appearance and behavior of turbidity were observed.

Fractionations

Weighed amounts of TCE, DMSO, and the copolymer were mixed at elevated temperature to form a homogeneous solution that was then transferred into a reservoir equipped with a heated jacket. The hot mixture was then distributed from this reservoir into three to four graduated cylinders (25 cm³) submerged in a thermostat. Temperature of the thermostat was then slowly decreased until phase separation took place. The phases usually separated overnight; to improve the visibility of the phase boundary, a trace of fuchsin was added to the mixture so that the upper (DMSO-rich) phase became violet. (Fuchsin disappears after reprecipitation of the copolymer fraction.) The conjugate phases in one of the thermostated cylinders were then separated and analyzed (see below). The temperature of mixtures in the remaining cylinders was then decreased (as a rule, by 0.5–1.5°C); the procedure was repeated with another cylinder, etc.

Phase Analyses

After phase equilibrium had been established, the volumes of both phases were read off at a given temperature. Using a weighed syringe equipped with a polyethylene capillary, the entire upper phase was carefully collected and its mass determined. A few milliliters of toluene were added and mixed with the phase directly in the syringe to make the solution homogeneous at room temperature; the phase/toluene mass ratio was determined. The content of the syringe was then divided: a smaller aliquot part was injected into an ampule, sealed, and stored for further analysis by liquid chromatography (LC, determination of the TCE/DMSO mass ratio); the rest of a known mass was poured into a precipitant

(methanol) to isolate an aliquot of the crude copolymer fraction. Before drying, the precipitate was always extracted for 1 h with boiling methanol in a Soxhlet extractor; the aim of this step was removal of the residual DMSO that interfered with both NMR and elemental analysis. From the mass of the dry aliquot copolymer, the overall mass of the copolymer in the upper phase was calculated. A similar procedure was applied to the lower phase, but without the syringe operations. In both cases, the chemical composition of the isolated dry copolymer fraction was determined by $^1\text{H-NMR}$ spectroscopy and/or elemental analysis.

Liquid Chromatography

Reversed-phase HPLC was used for the determination of the TCE/DMSO mass ratio in individual samples of phases. A clear TCE/DMSO/toluene/copolymer solution, prepared as described in the preceding paragraph, was mixed directly in the ampule with methanol to precipitate the copolymer, and the clear supernatant was injected into the LC columns. When injecting the supernatant sample, pure water was used as the first LC eluent, which eluted DMSO only, leaving TCE and toluene on the start. A methanol/water 60/40 (v/v) mixture, applied as the second eluent, released toluene and TCE, well separated from one another.

Integrated peak areas of TCE and DMSO were recorded by a refractometric detector. Calibration was carried out by injecting seven copolymer-free TCE/DMSO/toluene mixtures with varying TCE/DMSO ratios. To check whether the presence of the copolymer in the mixture affects the shape of the calibration curve, four other TCE/DMSO/toluene mixtures, containing ca. 1% (w/v) copolymer, were included. Methanol was added to each of them to precipitate the copolymer, and the clear supernatant was analyzed under conditions identical to those for copolymer-free calibration mixtures. No effect was found and all 11 experimental points fitted well the same flat parabola. Thus, the experimental values of integrated peak areas of TCE and DMSO, obtained for an unknown phase sample by LC, could be used for calculating the TCE/DMSO mixture composition, defined by the mass fraction of TCE, y_T .

The LC analyses were carried out under isocratic conditions in glass columns (CGC type, 3.3 mm inner diameter and 150 mm length, Tessek, Czechoslovakia), packed with C 18-modified macroporous spherical silica gel (5 μm mean particle diameter). The columns were kept at 40°C; the injection volume

was 10 μL . The flow rate of the mobile phase was 0.5 $\text{cm}^3 \text{min}^{-1}$. The Spectra-Physics liquid chromatograph SP 8100 was used in connection with the SP 4200 integrator and the Waters R 401 differential refractometer.

Gel Permeation Chromatography

Double-detection GPC was assumed to be a method suitable for a direct analysis of the copolymer fractions present in both conjugate phases (determination of chemical compositions, concentrations, and molar masses of these fractions), as a logical counterpart of LC that actually gave the TCE/DMSO mixture composition.

The instrumental setup, used for GPC, was essentially the same as that used in LC, but was supplemented by the SP 8440 UV-VIS detector (254 nm wavelength), and the integrator was equipped with a special replay chip for simultaneous registration of the responses of both detectors. Three stainless-steel columns (4 \times 250 mm) were packed with macroporous spherical silica gel applicable in 10^3 – $2 \times 10^6 \text{ g mol}^{-1}$ molar mass range. Methanol, 10 vol %, was added to dichloromethane in the mobile phase to suppress any possible sorption of MEMA units onto the silica gel. The flow rate was 0.5 $\text{cm}^3 \text{min}^{-1}$ at 40°C; the injected volume was 0.1 cm^3 .

$^1\text{H-NMR}$ Spectroscopy

$^1\text{H-NMR}$ spectra were recorded with an AC-300 Bruker spectrometer at 300.1 MHz and 60°C. Solutions, 5–10%, of the copolymer samples in CDCl_3 (Merck) were measured. Integrated peak intensities of aromatic and nonaromatic protons were used to calculate the chemical composition of the ST/MEMA copolymers.

RESULTS AND DISCUSSION

Theoretical Results

It follows from eq. (6) also that demixing-solvent fractionation of copolymers proceeds according to both chemical composition and degree of polymerization. The effect of molar mass is always present and fractionation solely according to chemical composition is impossible.

Equation (6) also shows that the dependence of the partition coefficient k on the copolymer composition w is very steep. It may be more lucid to

plot—instead of k —the parameter $k/(k+1)$ (Fig. 1). If the volumes of both phases are equal, then $k/(k+1)$ represents the ratio of the mass of the copolymer species in the upper phase to that in both conjugate phases.

The width of the interval of w , in which a given copolymer species is present in both phases in comparable concentrations, is in most cases very narrow and decreases with increasing P [Fig. 1(a)]. Consequently, copolymer species of the same degrees of polymerization are present almost exclusively in one or the other phase, depending on its w [$P \sim 10^3$, curve 1 in Fig. 1(a)].

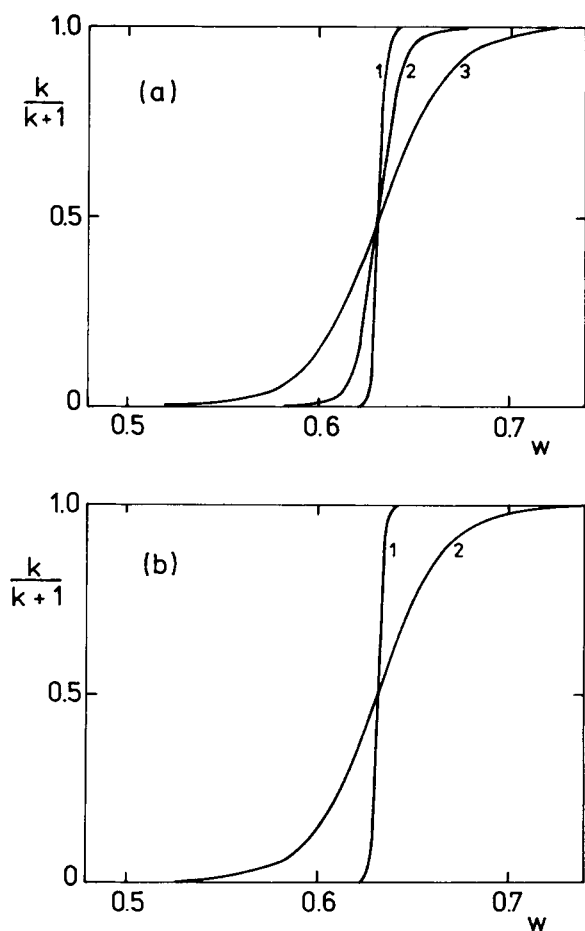


Figure 1 (a, b) Calculated dependence of the ratio $k/(k+1)$, in which k is the partition coefficient, on the copolymer chemical composition w [eq. (6)] for a hypothetical system: $\delta_1 = 18.4 \text{ J}^{1/2} \text{ cm}^{-3/2}$ ($9.0 \text{ cal}^{1/2} \text{ cm}^{-3/2}$), $\delta_2 = 24.6 \text{ J}^{1/2} \text{ cm}^{-3/2}$ ($12.0 \text{ cal}^{1/2} \text{ cm}^{-3/2}$), $\delta_A = 18.8 \text{ J}^{1/2} \text{ cm}^{-3/2}$ ($9.2 \text{ cal}^{1/2} \text{ cm}^{-3/2}$), $\delta_B = 22.7 \text{ J}^{1/2} \text{ cm}^{-3/2}$ ($11.1 \text{ cal}^{1/2} \text{ cm}^{-3/2}$), $V_1 = V_2 = 100 \text{ cm}^3$, $T = 298 \text{ K}$. (a) $P = 1000, 300, \text{ and } 100$ (curves 1, 2, and 3, respectively) at constant $\varphi_1'' - \varphi_1' = 0.6$; (b) $\varphi_1'' - \varphi_1' = 0.6$ and 0.06 (curves 1 and 2, respectively) at constant $P = 1000$. For explanation of the symbols, see text.

An exception is possible when both σ and Ω are very low. This can happen in any of the following three cases [eq. (8)]: (i) When the difference between φ_1' and φ_1'' is small, i.e., in close vicinity of the maximum on the coexistence curve [Fig. 1(b)]; (ii) when δ_2 approaches δ_1 (however, limited miscibility of the solvent components implies large χ_{12} and, consequently, large $\delta_2 - \delta_1$); and (iii) when copolymers having small $\delta_A - \delta_B$ are separated, i.e., for copolymers of two chemically similar constituent monomer units.

With demixing-solvent systems, the values of Ω and σ for common copolymers are expected to be high and, accordingly, the effect of chemical composition will be more pronounced than with common solvent/precipitant systems. This was expected also by Kuhn³⁻⁵ and used, e.g., for removing homopolymers from a crude graft copolymer. Unfortunately, this effect strongly limits the applicability of the demixing-solvent fractionation of copolymers, because of too steep dependence of k on w .

Phase Diagram

The cloud-point curve is given in Figure 2 (open circles). In a certain range of temperature below this curve and at $y_T < \text{ca. } 0.72$ (y_T being the mass fraction of TCE), the phase separation is governed by a sol-gel mechanism, i.e., by a separation of the copolymer-rich phase from a homogeneous TCE/DMSO mixture. Sol-gel separation has been recognized from the typical milky or even flocculent appearance of the demixed TCE/DMSO/1% copolymer systems existing in this region. Throughout the text, the small changes of y_T , caused by the presence or absence of polymer in the mixture, are neglected.

As an example, if cooling was started at $y_T = 0.66$ and $t = 60^\circ\text{C}$, phase separation appeared at 59°C , yielding a white, nonsedimenting turbid system containing undoubtedly a concentrated polymeric "gel" phase. Upon further decrease of temperature, this gel phase became less swollen and resembled a precipitate. However, when the temperature reached ca. 36°C , TCE and DMSO demixed, the precipitated copolymer redissolved exclusively in the lower, TCE-rich phase, and a system of two clear phases was formed.

On the other hand, a pure liquid-liquid demixing effect can be observed at $y_T > \text{ca. } 0.80$, accompanied by no precipitation of the copolymer: If cooling was started at, e.g., $y_T = 0.88$ and temperature $t = 40^\circ\text{C}$, the clear solution became turbid at $t = \text{ca. } 37^\circ\text{C}$, but liquid-in-liquid droplets were observed almost in-

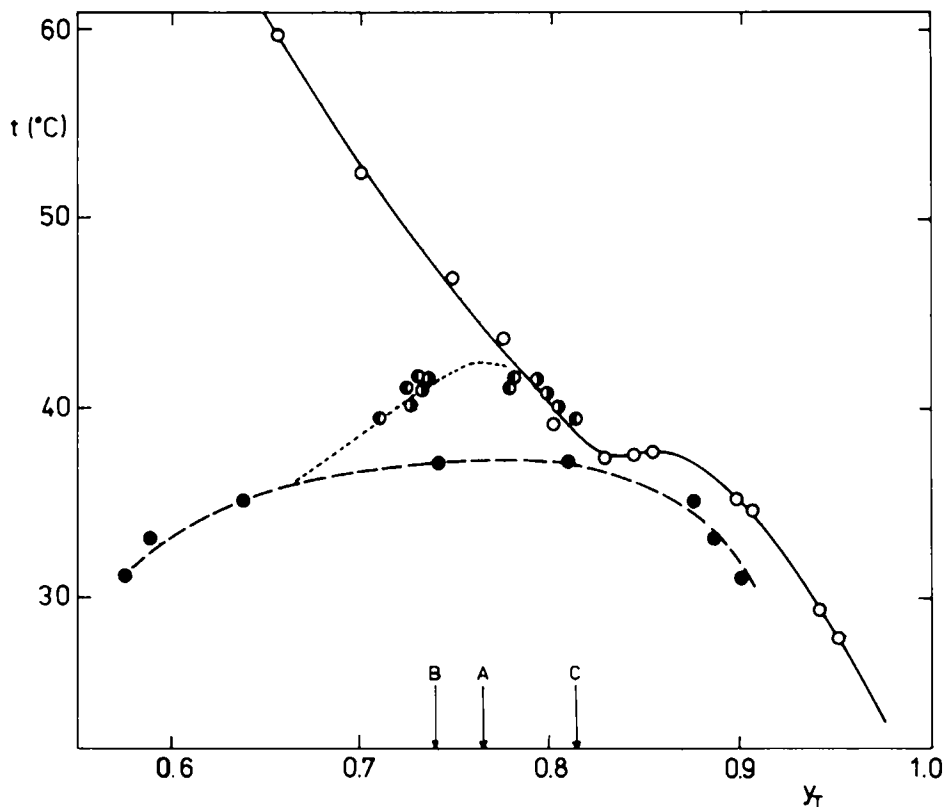


Figure 2 Phase diagram of statistical copolymer of styrene and 2-methoxyethyl methacrylate in tetrachloroethylene (TCE)/dimethyl sulfoxide mixture; t is temperature, y_T is a mass fraction of TCE in the mixture; (○, solid line) cloud-point curve (1% w/v of copolymer); (dotted line) coexistence curve (0.6% w/v of copolymer) pertaining to fractionation runs, the starting y_T 's of which are denoted by (●) A and (●) B; (●, dashed line) coexistence curve pertaining to phase separation, the starting y_T of which is denoted by C.

stantaneously and the system quickly formed two transparent layers (again, the copolymer was found in the lower phase only). As expected, no precipitation of the copolymer occurred even when this two-phase system was cooled down to 25°C because, apparently, the TCE-rich solvent mixture of the lower phase is a good solvent for the copolymer.

To explain the discrepancy between the cloud-point and the coexistence curves at $y_T > 0.8$ (some 3°C at $y_T = 0.88$, Fig. 2), we had first to exclude the effect of different copolymer concentrations (1% w/v for the cloud-point and 0.6% w/v for the coexistence curve). The result is shown in Figure 3 where the cloud-point temperature is plotted against the copolymer concentration. It is seen that an increase of the latter quantity from 0.6 to 1% w/v may cause a decrease of the former by some 0.2°C only. This effect is apparently too small and, moreover, its direction is opposite to that observed in Figure 2.

One of possible explanations of the discrepancy is the preferential sorption of TCE onto copolymer

chains. Methanol, added to the TCE-rich phase before injection into the LC columns, precipitates the copolymer from the solution. Undoubtedly, the precipitate retains a certain amount of TCE, thus diminishing the value of y_T in the supernatant. Only very strong preferential sorption could be fully responsible for such a relatively large shift of y_T (the difference in y_T between the cloud-point and the coexistence curves at a fixed temperature is as high as 0.02–0.03; cf. the right branch of the phase diagram in Fig. 2). On the other hand, this explanation is at variance with the fact that the presence of copolymer has no effect upon the LC calibration (cf. Experimental).

An alternative explanation of the discrepancy lies in different dynamics of the two processes: Liquid-liquid demixing proceeds much faster than does diffusion of macromolecules from one phase to the other.

The liquid-liquid and the sol-gel phase-separation mechanisms differ, i.e., in the velocity of the sedimentation of the lower phase: For TCE/DMSO

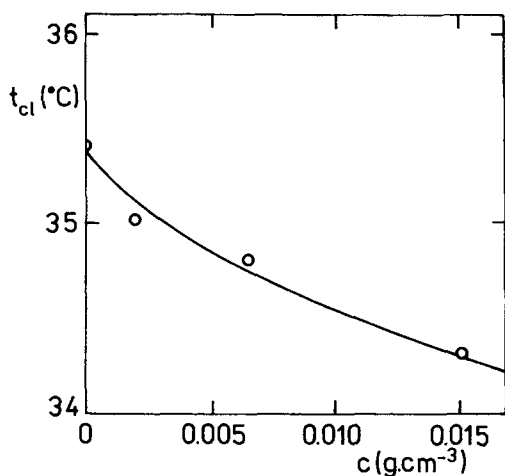


Figure 3 Dependence of cloud-point temperatures, t_{cl} , on the concentration of the copolymer, c , at constant composition of the mixed solvent $y_T = 0.905$.

solvent pair, the difference between the densities of conjugate phases is much higher (and, consequently, the sedimentation is faster) in case of the liquid-liquid demixing mechanism.

The most interesting region of the phase diagram in Figure 2 is limited by the inequalities $0.74 < y_T < 0.80$ and $37^\circ\text{C} < t < 43^\circ\text{C}$. It seems that a combined sol-gel and liquid-liquid demixing mechanism takes place here. Two fractionation runs were carried out in this region, viz., at $y_T = 0.765$ (run A) and $y_T = 0.740$ (run B) and a total of six pairs of

conjugate phases pertaining to six different temperatures was analyzed to obtain (i) the TCE/DMSO ratio in both conjugate phases (halved points in Fig. 2), (ii) the compositions of the copolymer fractions isolated from both phases (Fig. 4, discussed below), and (iii) mass ratio of the copolymer fractions pertaining to both conjugate phases (Fig. 5, discussed below).

For the sake of comparison, a phase separation outside this mixed-mechanism region was also done (at $y_T = 0.812$, run C), but since no true copolymer fractionation took place (the copolymer was always found in the lower phase only), the only results were the TCE/DMSO mixed-solvent compositions, determined at four different temperatures.

The presence and mutual position of two coexistence curves in the phase diagram (Fig. 2, the dashed line and the dotted line) is convincing evidence of the existence of two entirely different phase-separation mechanisms in the regions $0.7 < y_T < 0.8$ and $y_T > 0.8$. The existence of the dotted curve cannot be explained by a pure sol-gel mechanism. Liquid-liquid demixing definitely contributes to the overall effect and preferential sorption of TCE by the copolymer, which is undoubtedly different in either phase, may play a role as well. However, it was impossible to estimate the relative contributions of these effects.

The resulting complex mechanism may be considered to be either a liquid-liquid demixing separation influenced by the presence of the copolymer

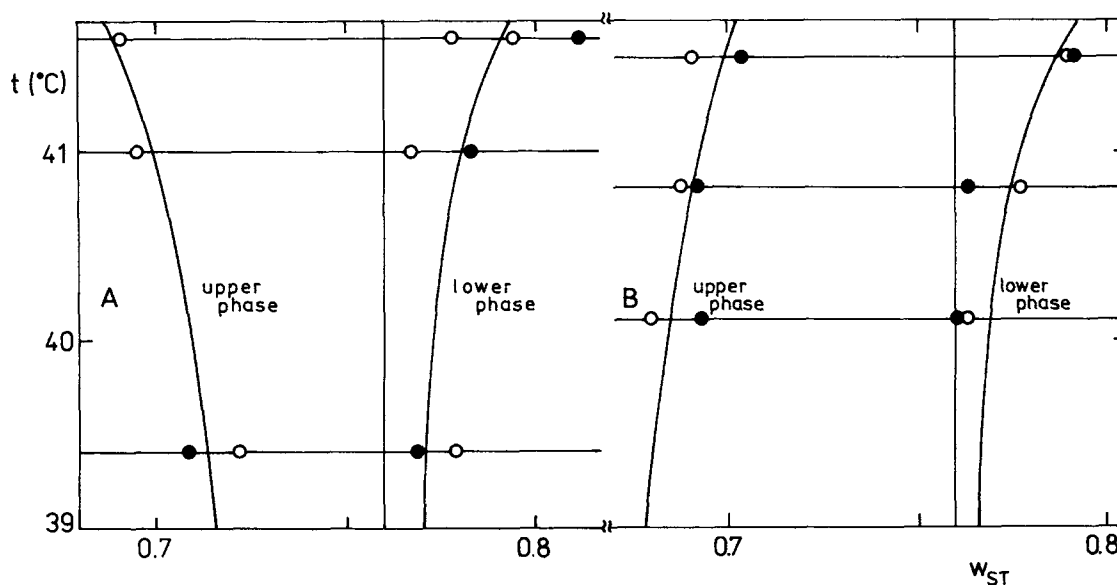


Figure 4 Chemical composition of copolymer fractions, w_{ST} , isolated from conjugate phases at different temperatures for fractionation runs A (left half) and B (right half); w_{ST} was determined by (○) $^1\text{H-NMR}$ spectroscopy and/or (●) elemental analysis; vertical lines denote w_{ST} of the original sample.

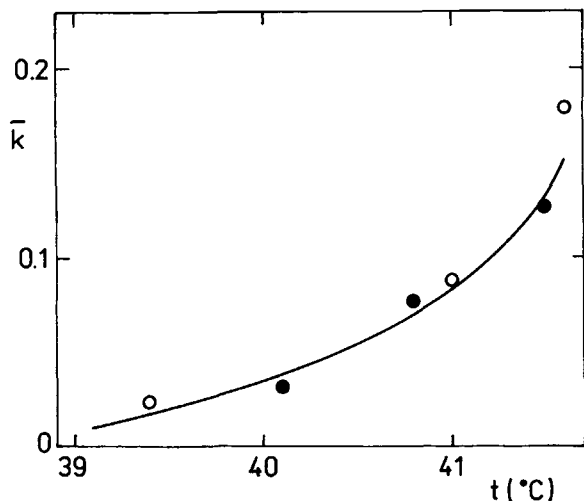


Figure 5 Dependence of the mean partition coefficient \bar{k} [eq. (9)] on temperature t for fractionation runs (○) A and (●) B.

or, conversely, a sol-gel separation affected by limited miscibility of the liquid components.

Fractionations

The results of the fractionation runs A and B are given in Figure 4. In all cases, the overall chemical composition of the original copolymer sample, calculated as a linear combination of w_{ST} 's of both "conjugate" fractions using a mass balance, is, within the limits of an experimental error, equal to that measured experimentally ($w_{ST} \approx 0.76$). Since with decreasing separation temperature the mass of the copolymer fraction in the lower phase approaches asymptotically the total mass of the original copolymer (cf. also the temperature dependence of the partition coefficient, as discussed below and also in Fig. 5), it is not surprising that also w_{ST} of that fraction approaches the limiting value of 0.76 for the unfractionated copolymer (right branches of Fig. 4). It is clear that the process fractionates (also) according to the chemical composition and that it must proceed close to the maximum of the coexistence curve. An attempt has been made to determine by GPC possible differences also in the molar masses of the fractions, but, as will be shown below, it failed because the resolving power of the GPC was not sufficient to discern these relatively minor effects. Also, the scale of our fractionations was five to 10 times smaller than that necessary to get a sufficient mass amount of fraction for, e.g., the light-scattering measurement.

The distribution of the whole copolymer between the phases is described by a mean partition coeffi-

cient \bar{k} [i.e., the coefficient k from eq. (2) averaged over all copolymer species]:

$$\bar{k} = \varphi'_3 / \varphi''_3 \cong c' / c'' \quad (9)$$

Here, c' and c'' are the copolymer concentrations (w/v) in the upper and in the lower phases, respectively. Its practical importance may be seen in Figure 5, where \bar{k} is plotted against temperature. The narrowness of the temperature range (some 2.5°C below the maximum on the coexistence curve), in which \bar{k} assumes non-zero values and multistep fractionation is feasible, seems to be a general feature of demixing-solvent fractionations, as has been predicted in the Theoretical part of the present paper and will also be demonstrated⁸ on an ST/hydrogenated isoprene diblock copolymer in an *N,N*-dimethylformamide/methylcyclohexane demixing-solvent system. Below this temperature range, the copolymer is concentrated in one phase only, leaving the conjugate phase empty.

GPC and Phase Analysis

An attempt was made to measure the quantities w_{ST} and c by double-detection GPC. The results showed very poor reproducibility and the experimental error seemed to be higher than the effect to be followed. The same was true for the determination of possible molar mass differences between "conjugate" copolymer fractions.

To explain this failure, an error analysis was carried out. If qualified estimates of the relative deviations of the integrated peak areas pertaining to refractometric and UV detections are taken into account (4% and 2%, respectively), then the calculation of the relative deviation of w_{ST} leads to values of some 8.5–10%, unacceptably high for our purpose.

Analogous error analysis yielding a similarly discouraging result was done for the concentration c and for the molar mass. Consequently, we had to rely solely on NMR (or elemental analysis) and gravimetry when determining, respectively, w_{ST} and c . The question as to what extent the "demixing" fractionation of statistical copolymers proceeds also according to molar mass thus remains open.

CONCLUSIONS

A theory has been developed describing an equilibrium distribution of a statistical copolymer between coexisting phases of a binary demixing-solvent sys-

tem. The theory predicts that the dependence of the corresponding partition coefficient on the copolymer composition is much steeper than in precipitation (sol-gel) fractionation. Consequently, an efficient multistep demixing-solvent fractionation is feasible only immediately below the maximum on the coexistence curve, where the compositions of the coexisting phases are close. A feasibility study has been carried out with a high-conversion, chemically heterogeneous statistical copolymer of styrene and 2-methoxyethyl methacrylate in tetrachloroethylene/dimethyl sulfoxide solvent mixture. A phase diagram of the system has been constructed and two fractionation runs have been done. The results confirm the theoretical expectation that if the separation temperature is decreased substantially (here, by more than some 2–2.5°C) below the maximum on the coexistence curve, the partition coefficient assumes immeasurably low or high value, i.e., almost all the copolymer is present in only one phase. On the other hand, it has been shown that, if the separation temperature approaches that of the maximum, comparable mass amounts of fractions of the statistical copolymer, substantially differing in their chemical composition, may be isolated from both conjugate phases.

Note Added in Proof. As illustrated by Figure 1(b), the sigmoidal curve steepens with increasing $\varphi'_1 - \varphi''_1$, i.e., equivalently, with decreasing separation temperature (under otherwise constant conditions). The steeper such a dependence, the “sharper” fractionation according to chemical composition takes place. For the hypothetical case described by curve 1 in Fig. 1(b), the model mixture of two homopolymers (having identical P , δ_A , and δ_B , but differing in ω) could almost perfectly be separated into its constituents, even if their values of ω are as close as 0.62 and 0.64. Such a powerful solvent system might seem to be also useful for a preparative multistep fractionation of a real copolymer. Unfortunately, as follows again from curve 1 in Fig. 1(b), only one fractionation step, yielding two fractions of comparable mass amounts, can be carried out with a copolymer having its mean value of ω ca. 0.63. Either resulting fraction could be fractionated again only if the corresponding inflection point (and the sigmoidal curve itself) is “shifted” toward higher or lower values of ω . Such a shift could not be achieved by changing temperature only; instead, another binary demixing solvent system would have to be

found or a third liquid component added in the next fractionation step. Needless to say, finding a suitable series of various demixing-solvent pairs is extremely difficult if not impossible; similarly, establishing proper conditions for the fractionation in a ternary demixing-solvent system would be very laborious, and the original method would lose its versatility and elegance. Thus, the practical applicability of the demixing-solvent multistep fractionation at high $\varphi'_1 - \varphi''_1$ values is strongly limited.

On the other hand, multistep fractionation at low $\varphi'_1 - \varphi''_1$ values is relatively easy to perform but, at the same time, fractionation according to chemical copolymer composition is much less efficient [the dependence of $k/(k + 1)$ on ω is less steep], and the effect of copolymer molar mass is more pronounced.

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