Size Exclusion and High-Performance Precipitation Liquid Chromatography of Styrene-Acrylonitrile Copolymers†

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ABSTRACT: The molecular structure of poly(styrene-*co*-acrylonitrile) samples (SAN) was investigated by cross fractionation employing two different chromatographic techniques. From mixtures of SAN copolymers, samples containing less than 1 mg of solute were first fractionated according to hydrodynamic volume by means of size exclusion chromatography (SEC). Next, the chemical composition distribution of the SEC fractions was analyzed by means of high-performance precipitation liquid chromatography (HPPLC) using commercially available instruments. HPPLC is a gradient technique based upon solubility differences. The method is dependent on the availability of a suitable solvent/nonsolvent combination. We used tetrahydrofuran (with 10% methanol) as a solvent and isooctane as a precipitant. The eluate was monitored by UV detection at 259 nm. The HPPLC technique yielded clear UV patterns after injection of about 100 μL of the crude SEC eluate. In these chromatograms, the components of the mixture showed distinctly separate peaks.

Introduction

Copolymers exhibit a complex molecular structure because they have distributions of chemical composition (CCD) and sequence length (SLD) in addition to the molar mass distribution (MMD) and the other kinds of structural inhomogeneities which are also present in homopolymers. Even without taking into account monomer consumption or alteration in reactivity by changing conditions, a growing copolymer molecule will have an instantaneous spread in composition.[1] The extent to which this instantaneous spread will be manifested in a CCD detectable by fractionation depends on the size of the copolymer molecules. At a high degree of polymerization, sections which are produced at consecutive instants and which possibly differ in composition, merge into one large final particle. The composition of the latter is the average of the sections included. For this reason, small variations in chemical composition due to instantaneous spread are more likely to be detected in a sample with a low degree of polymerization than in one with a high degree of polymerization.

Copolymers obtained at higher degrees of conversion usually exhibit an additional contribution to the spread in chemical composition caused by the exhaustion of a certain monomer species in the course of the reaction (and possibly further changes in polymerization conditions). This CCD is much more pronounced than the heterogeneity due to the instantaneous spread and is often accompanied by a change in MMD.

The instantantous spread is linked to variations in sequence length. Thus, the SLD is a distribution along the polymer molecules. Like the CCD due to the instantaneous spread, differences in average sequence length of various molecules are leveled by increasing degree of polymerization. *Differences in the average value of sequence length are normally connected with differences in composition.*

For basic research as well as for plant control and product development, it is necessary to know the exact mean values of molar mass and chemical composition, but the ultimate goal of copolymer analysis is to obtain information about CCD and MMD. Investigation by size exclusion chromatography (SEC and GPC) with two detectors is common practice. In the ideal case, one detector should measure the total amount of copolymer and the other its composition. But even then only the average composition of a certain eluate is known. One should be cautious in drawing conclusions concerning the chemical homogeneity of the copolymer under investigation.

To know more about CCD and MMD, the principles of cross fractionation must be applied. With classical techniques of fractionation this means a large amount of work. With the help of modern methods and instruments the investigation can be performed more efficiently. The basic idea is straightforward—the distribution in the fractions of an initial separation should be evaluated by means of a rapid micromethod. If the latter reveals the CCD, the initial separation can be performed by SEC.

The principle of cross fractionation has been realized by SEC investigation of copolymer fractions obtained by thin-layer chromatography (TLC)[2] or an analogous technique using a column packed with dry silica.[3] Polyethylene has been fractionated by crystallization, and the fractions obtained have been analyzed by SEC.[4] SEC fractions have been investigated by turbidimetric titration.[5] Application of TLC has also been mentioned.[6] Balke and Patel[7] fractionated poly(styrene-*co*-*n*-butyl methacrylate) by means of a two-dimensional chromatographic setup. By this column-switching technique the authors succeeded in the separation of the azeotropic copolymer (containing 55.3 wt % styrene) from both parent homopolymers and the separation of a copolymer with either 26.5 or 23.5 wt % styrene from admixed polystyrene. Column adsorption chromatography was recently used in analyzing copolymers,[8-10,16] but combination with SEC, to the best of our knowledge, has not yet been reported.

The aim of the present work was the investigation of SEC fractions of poly(styrene-*co*-acrylonitrile) by means of a HPLC technique sensitive to copolymer composition. We used the solubility-based high-performance precipitation liquid chromatography (HPPLC) technique.[11,12]

Experimental Section

High-Performance Precipitation Chromatography. The liquid chromatographic equipment consisted of a Varian liquid chromatograph Type 5020 suited for gradient elution. The instrument was modified with two serial mixing chambers (10 cm in length and 5 cm in length, respectively, both with an internal diameter of 4.6 mm), the first of which was filled with glass spheres

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† Dedicated to Professor W. H. Stockmayer on the occasion of his 70th birthday.

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Table I
Poly(styrene-*co*-acrylonitrile) Samples

sample	AN content, wt %	M_n(osm), kg/mol	M_w(LS), kg/mol	M_n*(GPC), kg/mol	M_w*(GPC), kg/mol
I	23	480	830		
II	19			49	130
III	16.1	325			
IV	30			86	190

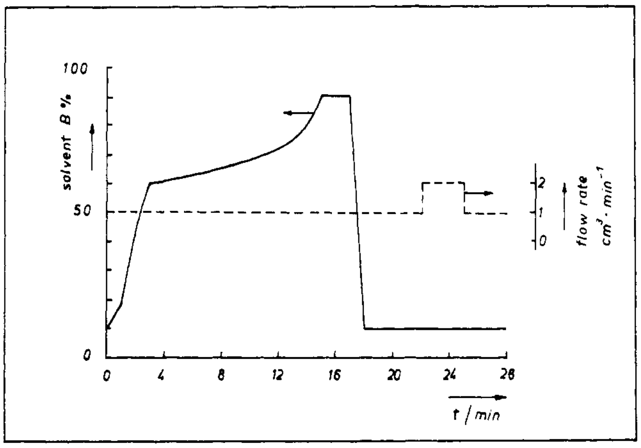

Figure 1. Gradient elution and flow program pattern.

(about 3 mm in diameter). An injection valve, Rheodyne Type 7105, with a loop volume of 175 μL was used to introduce the samples on the column. The loop can be filled partially. Detection was carried out with a variable-wavelength flow-through UV detector, Schoeffel Type SF 770, at a wavelength of 259 nm. The reference cell was filled with 2,2,4-trimethylpentane. Mixtures of 2,2,4-trimethylpentane (isooctane), tetrahydrofuran (THF), and methanol were used as mobile phases. 2,2,4-Trimethylpentane (purum quality, Fluka) was used with the addition of a suitable trace amount of toluene (pa, Merck) (solvent A). Tetrahydrofuran (pa quality, Baker) was distilled under nitrogen to remove the stabilizer butylhydroxytoluene. The distilled tetrahydrofuran was mixed with 10 vol % methanol (HPLC grade, Fisons) (solvent B). The gradient elution pattern and the flow program of an analytical run are shown in Figure 1.

The column (150 mm in length, 46-mm i.d., 316 stainless steel) was packed by means of a balanced density slurry technique with reverse-phase packing material Lichrosorb RP 18 (Merck) with a mean particle size of 10 μm. Column temperature was maintained at 50 °C.

High-Performance Size Exclusion Chromatography. A Waters ALC/GPC Model 244 instrument was used for the size exclusion chromatography. The instrument is equipped with a high-pressure pump (Model M 6000 A), an injection device U 6 K with a loop volume of 0.5 mL, a fixed-wavelength UV detector Model 440 (254 nm), and a differential refractometer Model R 401.

Five columns (300-mm length, 7.8-mm i.d.) packed with μStyragel (5×10^2, 10^3, 10^4, 10^5, and 10^6 Å) with a mean particle size of 10 μm were used. The mobile phase was THF with a flow rate of 1 cm³/min. Diffusion of oxygen into the THF was prevented by means of a nitrogen blanket. The experiments were done at ambient temperature.

Samples. The poly(styrene-*co*-acrylonitrile) samples I and III were prepared by bulk polymerization, and samples II and IV by suspension polymerization, all at a low degree of conversion. M_n was determined by osmometry, M_w by light scattering, and the apparent values M_n* and M_w* by GPC with polystyrene calibration. The acrylonitrile (AN) content was obtained by elemental analysis. Table I gives a survey of the samples used.

Results

SAN copolymers can be separated according to their composition by means of gradient elution with the solvents listed, with the amount of solvent B increasing from 60 to 80%. The higher the acrylonitrile content of a given specimen, the longer its retention time. The interval 60–80% of solvent B is well suited for separation of SAN containing 16–30 wt % AN. Having passed this interval, the content of solvent B was further increased to 90% and maintained at this level for 2 min. The aim of this flushing was the removal of all polymer traces off the column.

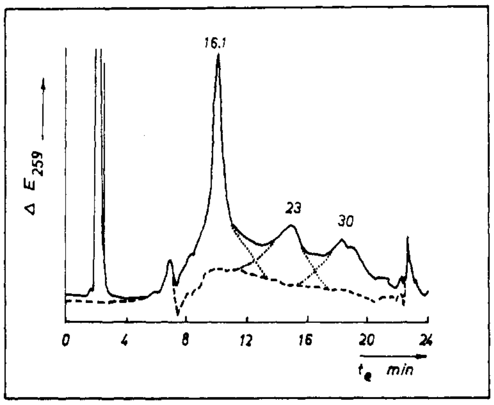

Figure 2. HPPLC chromatogram of a mixture of three SAN copolymers (16.1, 23, and 30 wt % acrylonitrile, respectively; total amount of sample 20 μg) and base line record of a blank run. Conditions as reported in the Experimental Section.

The base line pattern of a gradient cycle was dependent on the UV transmittance of the solvents used and on the refractive index gradient. At 259 nm the transmittance of isooctane is higher than that of pure tetrahydrofuran; thus the base line would rise with increasing THF content. To compensate for this effect, the solvent A was stained by traces of toluene, which shows high UV absorption and is inert with respect to the chromatographic process. An addition of about 20 ppm lifted the base line of solvent A to the level of B. But in spite of the absorbances balanced in this way, a gradient blank run with the solvents described always exhibited distinct deflections, especially at the instant of steep changes in composition. This was due to the difference in refractive index of THF (n_D = 1.405) and isooctane (n_D = 1.392) and could be suppressed a good deal by addition of methanol n_D = 1.329) to the THF. The sharp solvent peak about 2 min after an injection is likewise due to the rapid change in refractive index between the starting eluent (10% B) and the solvent of the sample injected. Solvent additives, e.g., the stabilizer in the THF which was used as an eluent in SEC, often give rise to similar deflections following that of nonretained solvent. Under well-defined conditions, this pattern has no connection with the polymer under investigation, which only appeared after the gradient had become effective. With the program used in this work, this was the interval ranging from 8 to 20 min.

Figure 2 shows the chromatogram of a mixture of three SAN copolymers. In the mixture, the peak position of each component is the same as that obtained by single injections. Therefore, the calibration (determination of the relation between elution time and AN content) can be performed in one experiment as indicated in Figure 2.

The calibration curve is presented in Figure 3. In addition to the peak position of each component, the average

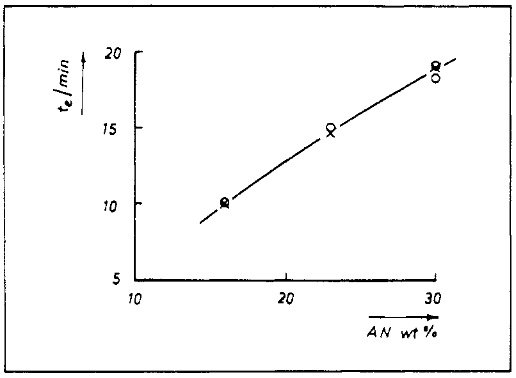

Figure 3. Calibration curve as derived from Figure 2: (O) peak position calibration; (×) mean area calibration.

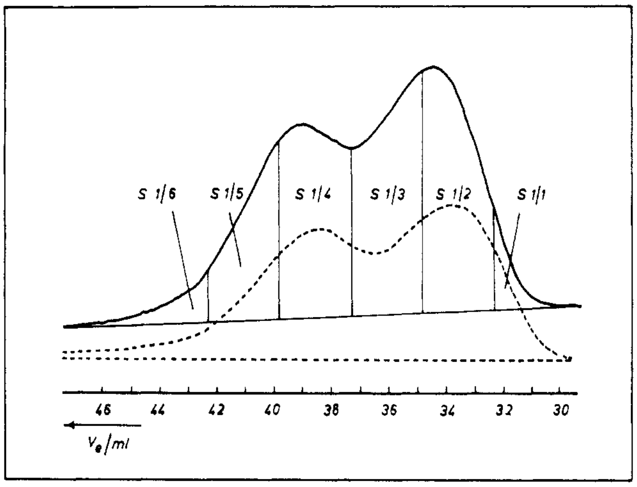

Figure 4. SEC fractionation S 1 of the mixture containing 63.3 wt % SAN sample I (see Table II) and 36.7 wt % II: (—) signal from the differential refractometer; (- - -) UV signal at 254 nm. Sample mass m_0 = 0.95 mg.

elution time $\bar{t}_e$ is likewise plotted vs. AN content in Figure 3. These data are calculated from the differences between the chromatographic patterns for each component and the blank (see Figure 2), using the equation

$$t_e = \sum h_i t_{e,i} / \sum h_i \qquad (1)$$

Here, h_i is the difference in UV signal of the sample and the base line at the elution time $t_{e,i}$.

Another calibration showing proportionality between peak area and sample mass with a proportionality factor changing linearly with AN content was also derived.[12]

Figure 4 shows the SEC fractionation (separation S 1) of the mixture of two SAN samples (I and II) which differ in composition and in molar mass. The difference in M was sufficient for a bimodal elution curve with two distinct maxima. The dashed curve indicates the UV trace of the run. The data characteristic of the fractions are compiled in Table II.

The apparent MMD of the mixture is plotted in Figure 5. It has been calculated from the refractometer signal in Figure 4 by means of the calibration

$$\ln M^* = A + BV_e + CV_e^2 + DV_e^3 \qquad (2)$$

Here, M^* is the molar mass of a polystyrene standard exiting from the column with the peak elution volume V_e. Conversion of this apparent MMD into the real MMD requires knowledge of the AN content of each M^* value. The relative amount of polymer at each M^* value must be divided by the refractive index increment (or UV absorption coefficient) of the copolymer with that AN content, and from M^* the true molar mass M can be derived by use of the Mark–Houwink equations of polystyrene[18] and SAN[19] with that AN content. This has not been done in the present work.

From separate SEC investigation the apparent MMD of component sample II was known. Its contribution to the apparent MMD of the mixture is presented in Figure 5. The MMD curve of the other component is the difference. From these curves it follows that the fractions S 1/3 and S 1/4 contain portions from both samples I and II, whereas the other fractions only consist of material from either I or II.

The HPPLC chromatograms of the fractions are shown in Figure 6. They meet the expectations and show a

Table II
Cross Fractionation S 1 of the Mixture of Two SAN Copolymers (I and II)

	fraction no.					
	S 1/1	/2	/3	/4	/5	/6
initial vol, cm^3	2.5	2.5	2.5	2.5	2.5	8.7
percentage of total sample	3.8	26.9	26.1	24.1	14.9	4.1
apparent molar mass (M_n*), kg·mol^{-1}	2400	1030	412	150	65.5	16.8
solvent evaporated, %	90.6	80	82	41	62	98.6
vol injected, (μL)	50	20	10	50	50	85.5
amt of sample injected, μg	9.0	10.3	5.3	8.0	8.0	10.2

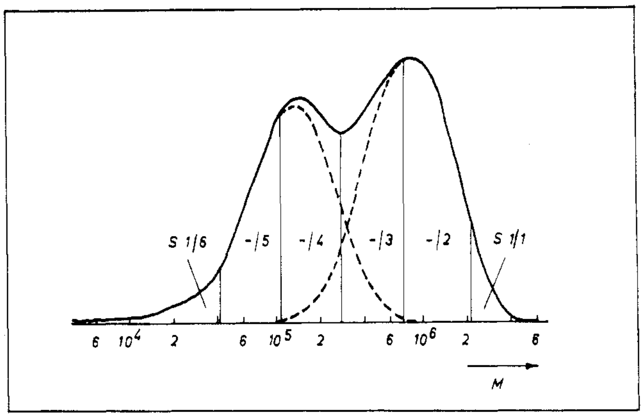

Figure 5. Apparent molar mass distribution of the mixture S 1 as derived from the SEC separation shown in Figure 4 and apparent molar mass distributions of the components of the mixture.

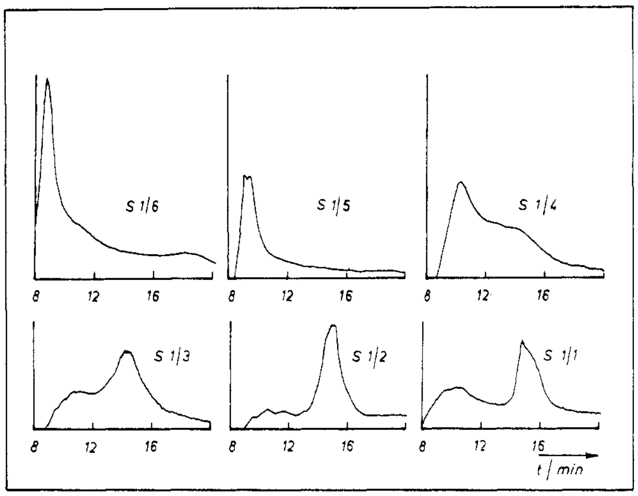

Figure 6. Cross fractionation S 1: HPPLC chromatograms of the SEC fractions indicated in Figure 4; for data see Table II.

Table III
Cross Fractionation S 2a of the Mixture of Two SAN Copolymers (III and IV)

	fraction no.					
	S 1/1	/2	/3	/4	/5	/6
initial vol, cm^3	3	2	2	2	3	8
percentage of total sample	2.9	17.0	27.2	27.9	21.5	3.7
apparent molar mass (M_n*), kg·mol^{-1}	1440	710	338	157	67.4	16.5
solvent evaporated, %	91	72	44	44	75	98.4
vol injected, μL	40	20	50	80	50	50
amt of sample injected, μg	3.9	10.7	10.0	16.9	12.5	10.1

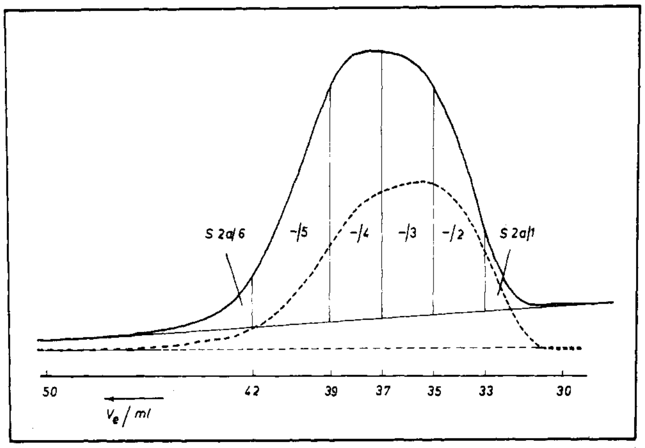

Figure 7. SEC fractionation S 2a of the mixture containing 59.3 wt % SAN sample III (see Table III) and 40.7 wt % IV: (—) signal from the differential refractometer; (- - -) UV signal at 254 nm. Sample mass m_0 = 0.87 mg.

relatively narrow peak at about 15 min for the first three fractions, indicating copolymer with an AN content of 23 wt%, and another peak at a smaller elution time (9–11 min) for the later fractions. The fact that the elution time is lower than the expected value of 12 min for 19% AN (according to the calibration given in Figure 3) might be attributed to the relatively low molar mass of sample II, which acts in the same way on the solubility as a lower AN content. This is increasingly the case for the fractions S 1/4, S 1/5, and S 1/6. In addition, the pattern of fraction S 1/1 exhibits a broad peak at about 10-min elution time which indicates material having a rather high styrene content. This result is in accordance with the conclusion drawn from the ratio of the UV and the RI detector signal.

Table III presents data characteristic of the investigation S 2a of another mixture of two SAN copolymers. Here, sample III having a high molar mass is poorer in AN content than the admixed sample IV, which has a lower molar mass. The selection of these samples was intentional in that the influence of composition on solubility should act against the influence of molar mass. In this case a HPPLC separation is more difficult than it was in the first example S 1.

Figure 7 shows the SEC fractionation S 2a of this mixture. The difference in hydrodynamic volume of both component samples is not sufficient for a bimodal curve. The same holds true for the apparent molar mass distribution. The MMD curves of the constituents (samples III and IV, each multiplied with its relative amount in the mixture) coincide with the respective edges of the chromatogram of the mixture, just as in example S 1.

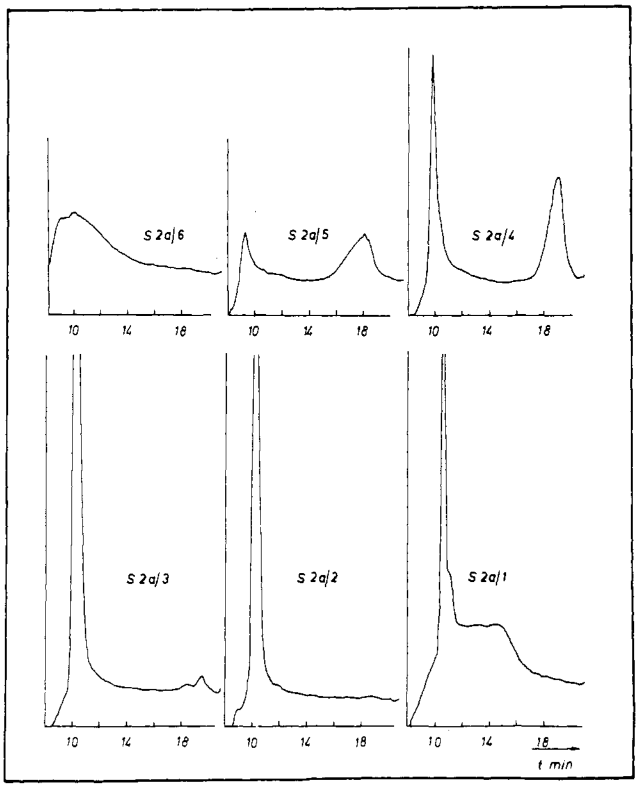

Figure 8. Cross fractionation S 2a: HPPLC chromatograms of the SEC fractions indicated in Figure 7. Data listed in Table III.

The HPPLC chromatograms of the fractions are shown in Figure 8. The sample component IV has an elution time of about 18 min. This component is to be seen in the patterns of the fractions S 2a/4 and S 2a/5. In fractions S 2a/3 a very small amount is present. The component sample III with 16.1 wt % AN gives rise to the sharp peak at about 10-min retention time, which predominates in the fractions S 2a/2 and S 2a/3. Here also, we find a tendency of a small shift to lower elution times with lower molar masses (for both components). Concerning the HPPLC pattern of fraction S 2a/6, the large initial volume of this fraction (8 mL) must be taken into account. It contains all low molecular weight components of the initial mixture.

In investigations S 1 and S 2a, the SEC fractions had been concentrated by solvent evaporation in order to obtain injection conditions similar to those used in the development of the HPPLC technique. In the course of these experiments, we learned that SEC fractions can yield very distinct HPPLC chromatograms even with less sample material. We therefore performed another investigation using fractions from SEC eluate without any further treatment (separation S 2b). The sample mixture was the same as in S 2a. The SEC eluate was subdivided into slices of 0.5 mL each, which covered the most interesting region of the elution curve corresponding to the fractions 4 and 5 of the separation S 2a. Injections of 100 μL each yielded the HPPLC chromatograms shown in Figure 9. They exhibit two peaks. The first one at about 10-min retention time is again due to component III, and the other at higher retention to copolymer IV. From the area between the base line and the record of the peaks mentioned, the portion of component sample IV (based on the contribution to the UV absorption signal) was estimated. In Figure 10 the results are presented as a block diagram inside the eluate slices investigated.

Discussion

The chromatographic technique used here for composition analysis of SEC fractions is based on solubility effects and involves precipitation of the polymer inside the

Table IV
Cross Fractionation S 2b of Nonpreconcentrated Fractions of the Mixture of Two SAN Copolymers (III and IV) (Same Mixture as in Table III)

	fraction no.										
	S 2b /2	/3	/4	/5	/6	/7	/8	/9	/10	/11	/12
percentage of total sample	6.9	7.1	7.1	6.9	6.5	6.0	5.1	4.1	3.2	2.4	1.9
apparent molar mass (M_n*), kg·mol^{-1}	254	209	162	142	117	97.0	80.3	66.4	55.0	45.6	37.8
vol injected, μL	100	100	100	100	100	100	100	100	100	100	175
amt of sample, μg	18.6	12.3	12.3	12.1	11.4	10.5	8.8	7.2	5.6	4.2	5.7

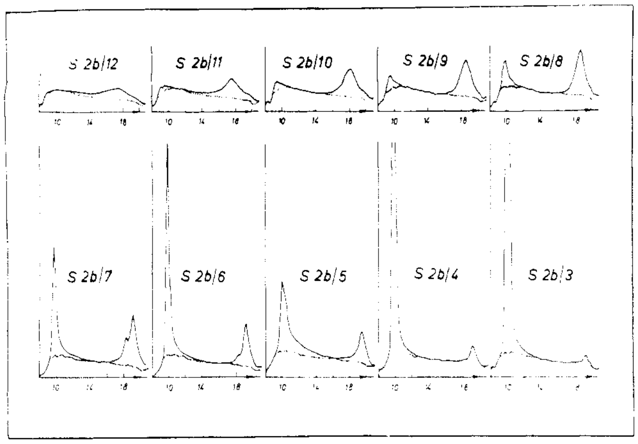

Figure 9. HPPLC chromatograms of the cross fractionation S 2b using slices of 0.5 mL each from the SEC separation of another 0.87-mg sample of the mixture which was investigated in the separation shown in Figure 7; data listed in Table IV.

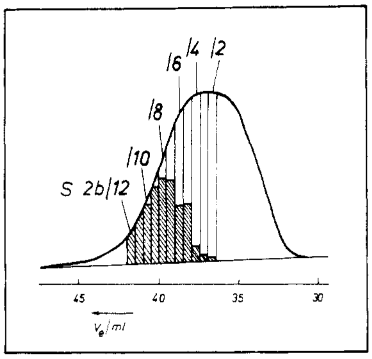

Figure 10. SEC curve of separation S 2b with indication of the slices and of the portion of the sample IV as estimated from the peak areas of the HPPLC patterns shown in Figure 9.

column. This statement is corroborated by the following facts:

(i) A species of a given AN content always emerges from the column with a definite composition of the eluent irrespective of the shape of the gradient, which, of course, determines the elution pattern of the sample under investigation. The graph relating eluent composition and AN content of the copolymer is similar to the solubility curve obtained by turbidimetric titration.[11]

(ii) The solubility of polymers is generally dependent on molar mass, according to[13]

$$\varphi^* = a + bM^{-0.5} \tag{3}$$

Here, φ^* is the volume fraction of nonsolvent at the cloud point. This equation has also been found valid in molar mass dependence of both SAN cloud points as well as in that of their peak position in HPPLC.[12] With THF as a solvent and either n-hexane or isooctane as a precipitant, we found $b = 13$ (g/mol)$^{1/2}$ by both turbidimetric titration and gradient elution chromatography.

(iii) Increasing column temperature caused shorter retention times. This is in accordance with the increase in solubility with rising temperature, and thus a strong argument in favor of the postulated solubility mechanism. A polymer adsorption mechanism would require stronger retention at higher temperature due to the generally observed increase in polymer adsorption with increasing temperature.[17]

The aim of the method used here was separation by composition. It is well-known that solubility methods cannot separate without an effect of molar mass.[14] In the system investigated, this effect is small as compared with the chemical composition effect, but it is still advantageous to fractionate the copolymer under investigation first by SEC. In a small slice uniform in hydrodynamic volume the remaining molar mass effect on the width of the peak can be neglected, especially at higher values of molar mass. This is clearly demonstrated by comparison of the very narrow peaks of fractions of sample III in Figures 8 and 9 and the less narrow peak of the whole sample in Figure 2. In the determination of AN content from the HPPLC elution time according to the calibration curve, the effect of molar mass must be taken into account. This can be done with the help of eq 3.

It is essential that the separation by composition not be superimposed by any size exclusion effect. For this reason the packing material used should have pores which are either large in comparison with the solute molecules or so small that none of the solute molecules can enter. Only under this condition can all components of a sample (irrespective of their size) interact with exactly the same stationary phase. Here we used Lichrosorb RP 18, which is a small-pore packing material (100 Å). With fine particles, this material has an external surface which is still about 20% of the total surface area of a packing material with pores large enough for all solute molecules.

Small pores are accessible to the eluent only. The macromolecular solute is restricted to the interstitial volume of packing. This has two consequences, both of which are essential for effective separation. The first is that the sample solvent is stripped from the polymer injected right at the top of the column.

Let us consider the injection of a SEC fraction in 100 μL of THF into the streaming eluent at its starting composition (90% isooctane). Let us further assume the total pore volume to be equal to the interstitial volume of the column and the distribution coefficient of THF to be equal to one. Then the eluent available from a pore volume of about 200 μL should suffice to reduce the THF content in the sample volume to 40% (v/v). At this composition the SAN copolymer is no longer kept in solution. With spheres of 10-μm diameter and porosity $\epsilon_p = 0.4$, a pore volume of 200 μL is provided by a packing with an external surface area of about 1800 cm^2. The amount of polymer injected was 20 μg at most, or 0.11 mg/m^2 of surface area. This is a small fraction of the value typical of a monomolecular layer in polymer adsorption (1 mg/m^2). The film thickness corresponding to 1 mg/m^2 is less than 100 nm. Although this consideration ignores the more gradual alteration in solvent composition, it explains why we never observed blocking of the column. (The gradualness is due to the simultaneity of transport and distribution. It already causes some fractionation of the polymer during the initial precipitation.)

The higher the THF content of the eluent, the later the precipitating composition is reached. With 40% THF or more in the initial eluent, it is quite impossible to surpass the precipitation threshold. Thus the sample is likely to rush through the column and to show up in the detector signal earlier than the sharp inflection due to the solvent.

The second consequence concerns the mode of separation. The characteristics mentioned above in points i–iii indicate that HPPLC is based on solubility phenomena such as the Baker–Williams fractionated.[15] The distinctness of the peaks suggests a multistage separation mechanism. In Baker–Williams fractionation this is caused by the antiparallel temperature gradient along the column. In HP precipitation chromatography a similar effect can be brought about by differences in the accessibility of the pores. Since the macromolecules are restricted to the interstitial volume of the column, whereas the eluent can enter the pores, any change in solvent properties due to a gradient program moves along the column with only about half the speed of that of a polymer solute. The polymer bypasses the pores and thus overtakes the eluent having sufficient solvent power to keep the polymer in solution. It rushes into the poorer solvent running in front an consequently precipitates. In this way it is transformed into a part of the stationary phase. When precipitated, it is retained at that zone of the column until an eluent of sufficient solvent power reaches this position. Then the polymer is redissolved and transferred back to the mobile phase.

The HP precipitation chromatography described here has advantages and drawbacks. One drawback is that solubility fractionation of copolymers is always linked to a separation by molar mass. The paper gives evidence of the possibility of fitting conditions so well that the sensitivity to composition overrides the sensitivity to molar mass. Nevertheless, it is advantageous to investigate copolymers by the combination of SEC and HPPLC according to the principles of cross fractionation. Fractions obtained by SEC can be nicely analyzed with respect to their composition distribution. Another drawback is the restriction to polymers visible by the detector and to solvents which do not disturb the detector signal.

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Notes

Corresponding States in Polymer Mixtures[†]

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Recently, it was pointed out by Dayantis[1] that the Flory–Huggins (FH) theory of polymer solutions predicts a corresponding-states behavior for polymer/solvent mixtures that is similar to the scaling predictions of Daoud and Jannink.[2] In this brief note it is shown that the FH model implies that all binary polymer mixtures satisfy a generalized corresponding-states principle. In polymer/solvent mixtures this general corresponding-states principle is similar to that predicted by scaling arguments.

Free Energy Expansion

A Landau-type expansion of the Gibbs free energy, $G(C,T)$, about the critical temperature (T_c) and concentration (C_c) may be used to obtain quantitative relationships for phase equilibria near a critical point. Ignoring gradient terms and retaining only a minimum number of terms, one obtains the expansion[3]

$$G = G(T_c,C_c) + G_C\Delta C + G_T\Delta T + G_{CT}\Delta C\Delta T + \frac{1}{2}G_{TT}(\Delta T)^2 + \frac{1}{2}G_{CCT}\Delta T(\Delta C)^2 + \frac{1}{4!}G_{CCCC}(\Delta C)^4 \quad (1)$$

where the subscripts on G denote partial differentiation, $\Delta C \equiv C - C_c$, and $\Delta T \equiv T - T_c$. All derivatives are evaluated at the critical point. Second and third powers of ΔC are absent from eq 1 because $G_{CC} = G_{CCC} = 0$.

Coexistence Curves

In a two-component, two-phase (α and β) liquid system, equilibrium is characterized by the tangent condition

$$(\partial G/\partial C)|_{C=C_\alpha} = (\partial G/\partial C)|_{C=C_\beta} \quad (2)$$

For the Landau model near the critical point, C_α and C_β are equidistant from C_c; therefore, with $C_\alpha - C_c \equiv \Delta C_e \equiv C_c - C_\beta$, eq 1 and 2 yield

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[†] Dedicated to Professor Walter H. Stockmayer on the occasion of his 70th birthday.