CHARACTERIZATION OF COPOLYMERS BY MEANS OF LIQUID CHROMATOGRAPHY

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Abstract - Poly(styrene-co-acrylonitrile) and their SEC frac-
tions were separated according to composition by means of
gradient elution using HPLC equipment. The influence of the
shape of gradient has been investigated as well as that of
temperature and sample concentration. The effect of molar
mass on retention is small in comparison with the influence
of copolymer composition. Evidence is given for the mechanism
of the separation which involves precipitation and redissolu-
tion of the polymer sample.

INTRODUCTION

When studying the complex molecular structure of copolymers it is common
practice to investigate these materials by size exclusion chromatography
(SEC, GPC) with two (or more) detectors. In the ideal case, one detector
should indicate the total amount of polymer, whereas the other should
measure its composition. All methods of SEC with multiple detection have
in common that heterogeneity in composition is judged by the degree of simi-
larity between the traces of the different detectors. In the event of
correspondence, the copolymer is assumed to be homogeneous in chemical com-
position. In case of discrepancy, the opposite is held to be true and the
average composition of the fractions is derived from the signal ratio at
corresponding values of elution volume. A closer examination of the sepa-
ration mechanism in SEC of copolymers shows that such conclusions may
sometimes be erroneous.

To know more about a copolymer one must remember the principles of cross
fractionation. This procedure requires fractionation in one direction and
subsequent analysis of the fractions in a second direction which should
diverge from the first one as far as possible. With classical techniques
of fractionation this requires a lot of work.

This paper deals with copolymer analysis according to the principles of
cross fractionation and with the help of methods and instruments which
can make investigation more efficient. The basic idea is straightforward -
the distribution in the fractions of the initial separation should be
evaluated by means of a rapid micromethod. If the latter reveals the chemi-
cal composition distribution (CCD), the initial separation can be perfor-
med by SEC. One of the advantages of SEC is its ability to yield fractions
each containing about 20 to 50 µg of polymer.

The combination of SEC with a complementary analytical method has been
realized (Ref. 1 - 6), but either still required a lot of work or reached
only limited resolution. Column adsorption chromatography was recently
used by several authors investigating copolymers (Ref. 7 - 9) but combi-
nation with SEC, to the best of our knowledge, has not yet been reported.

HIGH PERFORMANCE PRECIPITATION CHROMATOGRAPHY OF SAN COPOLYMERS

We intended to characterize poly(styrene-co-acrylonitrile) (SAN) and their
fractions by means of high performance liquid chromatography (HPLC). In
devising a chromatographic technique, one of the most important decisions
is the choice of the packing. For separating copolymers by composition, the
stationary phase should be the same for all constituting macromolecules
irrespective of their size. With porous packing materials, the pores must

not exclude a certain fraction of the solute. This condition can be fulfilled either by using a packing material with very large pores, which is capable of housing even the largest solute molecules, or by using a packing with pores so small that none of the solute molecules can enter. At a first glance the latter choice seems to be rather unfavourable because the sample under investigation remains outside the grains and does not come into contact with the vast internal surface of the packing which is so important in most chromatographic processes. But with a grain size small enough, this is not too severe a drawback. Silica spheres of 5 µm uniform diameter and a pore volume of 1.2 cm^3g^{-1} have an external surface area of 1.2 m^2g^{-1}, which is about 20 % of the total surface of a packing material having 400 nm pores. In order to avoid unwanted size exclusion effects we used columns packed with LiChrosorb[R] RP 18, which is based upon silica with a 10 nm pore size, or LiChrospher[R] 1000 with 100 nm pores and a C-8 bonded phase.

Solvent/nonsolvent combination

Concerning the mobile phase, we had searched for the combination of a chromatographically strong solvent with a weak one which would yield retention due to composition as well as complete elution of all constituents of a copolymer within a reasonable period of time, but have not yet found such a combination of solvents which are transparent in the UV region needed for the detection of the polymer. So we tried another approach on the basis of our experience in the field of SAN solubility behaviour. With an alkane hydrocarbon as a precipitant, dilute solutions of SAN samples differing in acrylonitrile content (AN) yield turbidity curves as shown in Fig. 1.
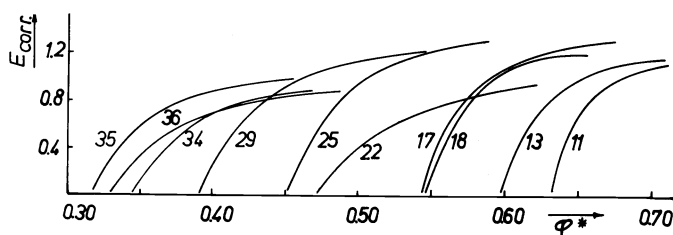

Fig. 1. Turbidimetric titration of SAN copolymers in dichloromethane. Extinction (corrected for dilution) vs. volume fraction of precipitant (a kind of light gasoline, b.p. range 70 - 100). The figures at the curves indicate copolymer composition - 36: 36.4 wt % AN; 35: 35.4 %; 34: 33.9 %; 29: 29.0 %; 25: 25.1 %; 22: 22.4 %; 18: 17.9 %; 17: 17.5 %; 13: 12.9 %; 11: 10.5 %.

The intersection with the abscissa gives the volume fraction of the precipitant at the cloud point. Figure 2 shows the continuous reduction in this value with increasing acrylonitrile content. With an alcohol as a precipitant, the solubility behaviour is quite different: the corresponding curve has a maximum at about 30 wt % AN in the copolymer.

Using n-hexane or a corresponding kind of light gasoline (b.p. range 70 - 100°C) it was possible to fractionate SAN copolymers by their composition (Ref. 10). The drawbacks of our early fractionation technique were (i) the preparation of the sample outside the column with the polymer as a thin film on glass beads (a procedure which required dismantling of the column for the insertion of each specimen), (ii) the cumbersome isolation and characterization of the fractions and (iii) the necessity for rather large amounts of sample (about 200 mg).

The cloud points of SAN copolymers dissolved in tetrahydrofuran (THF) also were strongly dependent on the acrylonitrile content when titrated with n-hexane (see Fig. 2). We used THF as a chromatographically powerful solvent in HPLC because this solvent is successfully used in SEC of SAN. The THF solvent was complemented by n-hexane or iso-octane as a chromatographically weak precipitant. Like in classical precipitation chromatography (BAKER-WILLIAMS fractionation) we started with an eluent rich in precipitant and gradually changed the composition to higher contents in solvent.
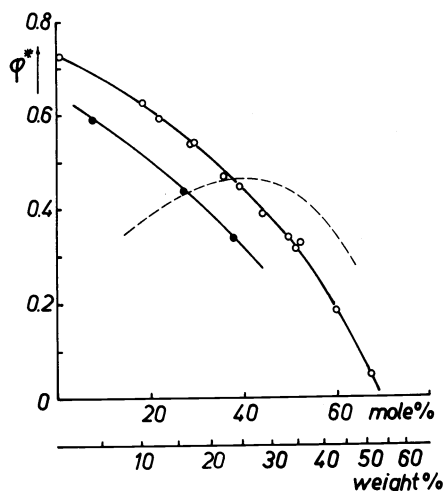
Fig. 2. Volume fraction of nonsolvent vs. acrylonitrile con-
tent of SAN copolymers; o - solvent dichloromethane, precipi-
tant light gasoline (data from Fig. 1); ● - solvent tetrahydro-
furan, precipitant n-hexane.
The dashed line represents a cloud-point curve as obtained with
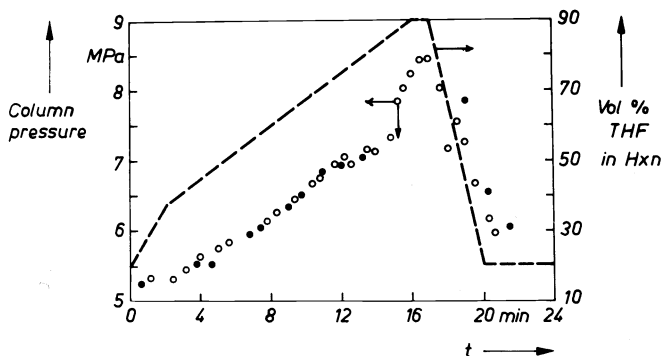alcohol as a precipitant.

Fig. 3. Solvent gradient (20⟶90% of tetrahydrofuran in n-
hexane) and column pressure vs. time; o - blank run, ● - run
with injection of 20 µg SAN copolymer in 50 µl THF; 40°C; flow
rate 2 ml/min; column: L = 25 cm, d_C = 4.6 mm, packed with

silica (10 µm). (Reprinted from Ref. 11 with permission of
Akademie-Verlag Berlin).

An example of such a gradient is shown by the dashed line in Fig. 3. The sample
was dissolved in THF and injected into the running eluent at its starting
composition of 80 % hexane. This must cause precipitation of the polymer in the
column where the polymer molecules are stripped off the solvent which brought
them into the apparatus. Such precipitation might block the column, but the
registration of column pressure showed no alarming effect. The increase in
the course of the run was due to the difference in viscosity between n-hex-
ane and THF. Using iso-octane as a precipitant whose viscosity is similar to
that of THF, we observed scarcely any pressure change. So we felt encour-
aged to run precipitation chromatography with HPLC equipment.

The mechanism of separation
Any chromatographic separation requires multistage distribution between
stationary and mobile phase. In a precipitation mechanism, the stationary

phase is the precipitated polymer (= the gel phase) and the mobile phase
is the related sol phase. As already stated, we postulate the precipitation
of the injected polymer and its fixation to the packing material at the top
of the column. From polymer adsorption data it can be concluded that an area
of about 200 cm^2 would be sufficient to keep an amount of 20 µg injected
polymer in a monomolecular layer. This area is provided by the outer surface
of about 35 mg silica microspheres (d_p = 10 µm) which fill only 3.5 mm of a
column being 4.6 mm in diameter. From this film, the polymer molecules are
successively extracted by an eluent, the dissolution power of which is steadily
increased by an appropriate programme. Although this dissolving process meets the
conditions for gaining sharp fractions very well, it is only a one-stage sepa-
ration. A chromatographic separation would require reprecipitation and redis-
solution. In BAKER-WILLIAMS fractionation this is realized by a temperature
gradient along the column. Provided normal temperature dependence of solubil-
ity, any fraction dissolved at the high temperature at the top of the column
will be reprecipitated in the cooler parts below. In this way it will again
become part of the stationary phase until it is redissolved by a more power-
ful mixture for the next migration step.

One might think of HPLC with temperature gradient, but the use of porous
support materials offers the possibility of gaining chromatographic separa-
tion without additional complication. Let us assume a polymer completely
excluded from the pores of the packing. Such a polymer is restricted to the
interstitial volume V_I of the column. If dissolved, the polymer is trans-
ported at a linear velocity of

$$u_p = L \, / \, (V_I/v) \tag{1}$$

Here, L is the length of the column, and v the flow rate.

In contrast to the polymer, the eluent has access to the pore volume of the
packing. With the internal porosity ε_p and the empty column volume V_C, the
eluent volume in the column is

$$V' = V_I + \varepsilon_P(V_C - V_I) \tag{2}$$

This gives for the eluent a linear velocity of

$$u_E = L/(V'/v) \tag{3}$$

As $V' > V_I$, the velocity of the eluent is smaller than the velocity of the
dissolved polymer. The polymer bypasses the pores and thus always overtakes
the eluent having solvent power enough to keep the polymer in solution. It
rushes into the poorer solvent running in front, and consequently precipitates.
This gives the opportunity for multistage separation according to the prin-
ciples of chromatography.

The solvent gradient

The characteristics of such a HP precipitation chromatogram are represented
by the example given in Fig. 4. It shows the record of a UV detector at 259 nm
for two gradient cycles the first of which with the injection of 20 µl of a SEC fraction
containing about 4 µg SAN copolymer, the following one without any injection. The column[R]
was 15 cm in length, 4.6 mm in inner diameter, and packed with LiChrosorb
RP 18, grain size 10 µm. From these geometrical data, the flow rate of 1 ml/min
and a total porosity of ε = 0.8 the eluent hold-up time is estimated to be
t' = 2 min. At this time, the record showed always a sharp inflection which
was caused by the solvent injected. For the example shown in Fig. 4, this
was stabilized THF, the eluent used in SEC. Its additives are responsible
for the consecutive inflections. It is essential that no peak appears at
the leading edge of the solvent trace, i.e. with a retention time shorter
than the eluent hold-up time. This would indicate unretained polymer.

In Fig. 4, the gradient shows up at t_e = 5.6 min. The pattern of the blank
run demonstrates the baseline inflection caused by the increase in solvent
"B" from 10 to 90 % and the rapid return to starting conditions. The injection
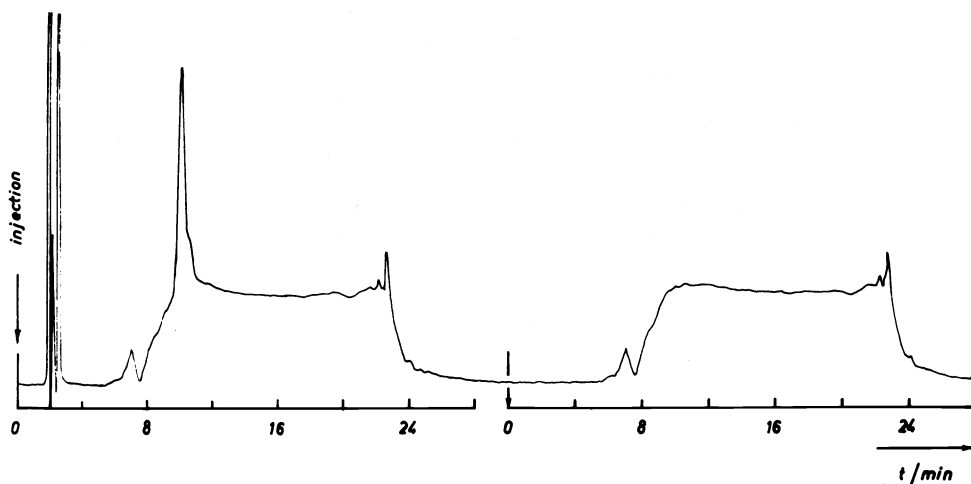of a pure, transparent solvent (THF or dichloroethane) showed no influence

Fig. 4. UV record of two consecutive gradient cycles, the second
being a blank run without injection. For the first cycle, the sample
was a SEC fraction of a SAN copolymer with 16.1 wt % AN.
The abscissas indicate the time elapsed since the start of each cycle.
Solvent "A" - iso-octane; "B" - tetrahydrofuran with 10 % methanol.

Programme:

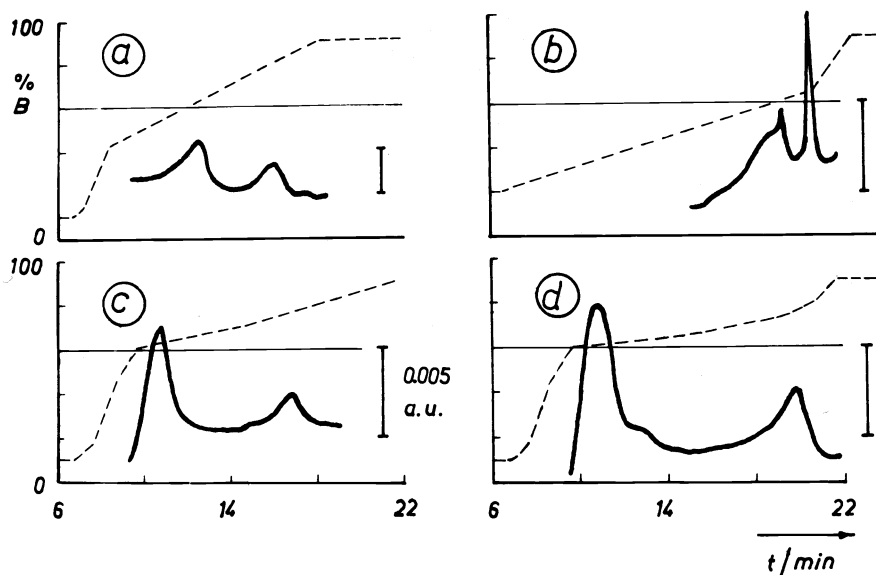| t:	0	1	2	3	8	11	13	14	15	17	18	21.9	22	25	25.1 min
"B":	10	18	46	60	65	70	75	80	90	90	10				10 %
v.	1											1	2	2	1 ml/min

Fig. 5. Influence of the gradient used on the elution of SAN
copolymers containing 19 wt % (1st peak) and 30 wt % AN (2nd
peak).The dashed lines indicate the eluent composition at the
detector;solvents "A" and "B" were the same as in Fig. 4.
The vertical bars indicate 0.005 absorption units at 259 nm.
The amount of sample was 20 μg in each case.

on the pattern of a blank run. The shape of the gradient markedly influenced
the chromatographic pattern of the polymer under investigation. Figure 5
shows the traces of a 1 : 1 mixture of two SAN samples as obtained using
four different gradient programmes. It shows that the separation of these
two samples occurred between 60 and 80% of "B". Since azeotropic SAN copolymers
contain about 23 % of acrylonitrile the composition area spanning from 19 to
30 % AN will be of main interest. We therefore mostly applied the gradient
5d. Its final rise to 90% "B" and the isocratic period on this level aimed
at the cleaning of the column. The introductory part with only 10 % "B" made
sure that the polymer adhered to the column. The initial precipitation of
the polymer as a thin film onto the packing material is an essential prerequisite
for the eventual separation.

While the retention time of a given specimen was strongly influenced by the
shape of the gradient used, the corresponding eluent composition was almost
the same. In Fig. 6a the eluent composition of n-hexane/THF mixtures at peak
position of four SAN samples is plotted vs. AN content of these copolymers.
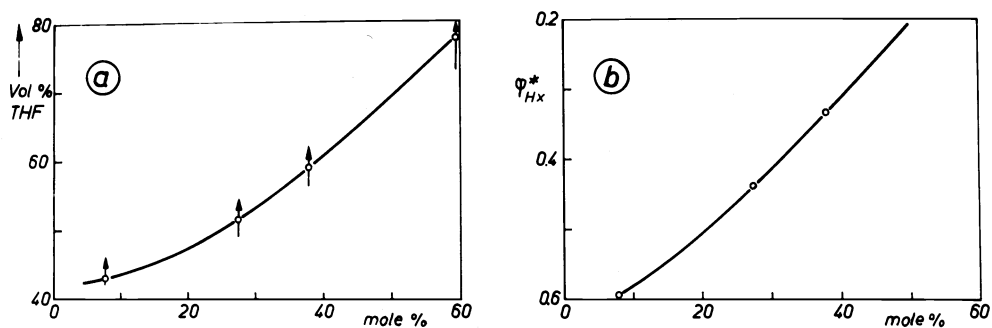With the same samples, Fig. 6b shows the volume fraction of n-hexane

Fig. 6. Eluent composition at peak position vs. acrylonitrile
content of SAN copolymer samples (a), and cloud-point curve of the
same samples as estimated by means of turbidimetric titration (b).
(Reprinted from Ref. 11 with permission of Akademie-Verlag, Berlin).

which causes precipitation of THF solutions containing 40 mg/l polymer. The
chromatographic data was obtained at 40 °C whereas the titrations were per-
formed at 20 °C. Both plots are identical in scale. The similarity of the
curves corroborates the assumption that precipitation and redissolution are
involved in the mechanism of the separation.

Effect of temperature

The significance of solubility can also be concluded from the temperature
dependence of the retention. Figure 7 shows the chromatogram of a mixture
of three SAN copolymers at 25 and 50 °C. At the higher temperature, the peaks
are shifted towards shorter retention times by 0.6 to 0.85 minutes, which
is in accordance with increased solubility. The temperature effect made us
aware of the need for temperature control of the column. Aiming at high
diffusion rates, we increased the column temperature to 50 °C.

Precipitation and redissolution are responsible for separation in the well-
known classical column fractionation technique called precipitation chromato-
graphy (BAKER-WILLIAMS fractionation). This paper deals with a kind of high
performance liquid chromatography (HPLC) based upon the precipitation of the
polymer solute and yielding retention due to the redissolving power of the
eluent. For this technique the designation HP precipitation LC (HPPLC)
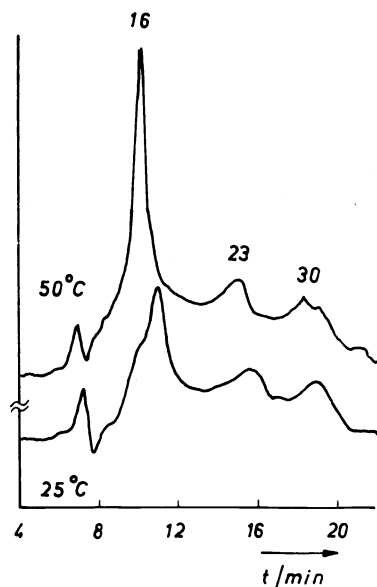seems to be appropriate.

Fig. 7. Chromatogram of a mixture of 3 SAN samples (16.1, 23 and 30 wt % AN) at 50 and 25°C. Column: L = 15 cm, d_C = 4.6 mm, packed with LiChrosorb$^{(R)}$RP 18, d_p = 10 μm. Solvents and gradient as in Fig. 4; total amount of sample 20 μg dissolved in 50 μl dichloroethane.

Molar mass effect

In general, the solubility of any polymer is dependent on molar mass. With copolymers, both the influence of composition x and of degree of polymerization P is expressed by the equation

$$\varphi''_{P,x} / \varphi'_{P,x} = \exp P (\sigma + Kx) \tag{4}$$

Here, $\varphi''_{P,x}$ and $\varphi'_{P,x}$ are the volume fractions of the macromolecules with the degree of polymerization P and the composition x in the gel phase and the sol phase, respectively. x is the concentration of A units in a A/B copolymer (volume fraction), and K a quantity determined by the differences in interaction parameters of solvent and copolymer constituents (Ref. 12). If separation by chemical composition is the main goal of a fractionation, the factor regulating molar mass dependence should be as small as possible. But even for σ = 0, solubility fractionation by composition will always be linked to a certain separation in molar mass.

By means of turbidimetric titration we found that lower alcohols solely precipitate SAN copolymers according to molar mass (Ref. 13). This also held true for the fractionations in the more or less level part of the solubility curve at the maximum (see Fig. 2). In this region of copolymer composition, the fractions precipitated, for example, by addition of methanol did not differ in acrylonitrile content (Ref. 10). Their cloud points varied according to molar mass and fulfilled the relation

$$\varphi^* = a + b/M^{0.5} \tag{5}$$

which was originally found using homopolymers as samples (Ref. 15). In Eq. (5) φ^* is the volume fraction of precipitant at the cloud point. The quantity b is characteristic of the efficiency of a certain solvent/nonsolvent combination in fractionating by molar mass. Using the combination dichloromethane/ methanol and SAN we found b = 40 (Ref. 13).

In order to learn about the molar mass effect in HPPLC with alkane hydrocarbons as a precipitant we investigated fractions obtained by SEC. We attempted to use homogeneous copolymers as initial materials. Prepared by azeotropic copolymerization to a low degree of conversion, our samples should not have greater inhomogeneity than the small contribution of instantaneous spread in composition (Ref. 14). But in HPPLC, consecutive SEC fractions from such samples always showed slightly decreasing retention values. This could indicate either an unexpected decrease in acrylonitrile content with decreasing hydrodynamic volume, or a straightforward dependence of HPPLC retention on molar mass. In order to decide whether the former or the latter held true, we selected pairs of azeotropic SAN copolymers with partly overlapping SEC curves. At a certain elution volume in the overlapping range we separately took slices

from both samples and injected them in HPPLC. For one pair of samples the retention times differed by 0.3 %. This close correspondence of data from unlike samples made clear that the differences in retention of consecutive fractions were due to a molar mass effect. To be able to judge this effect on the base of Eq. (5) we plotted the volume fraction of nonsolvent "A" at peak position vs. $M^{-1/2}$. The results shown in Fig. 8a conform to the prediction of Eq. (5). The average slope value is about 13 and, as an initial estimate, independent of the composition in the range 16 to 30 wt % AN.
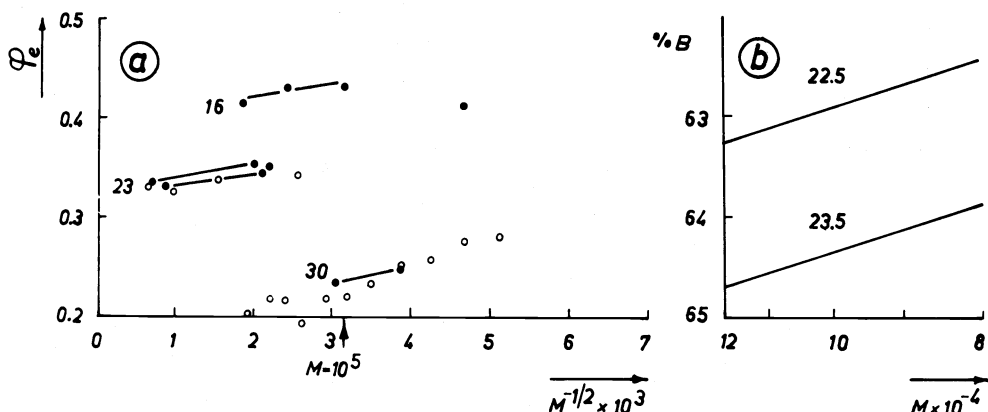

Fig. 8. Molar mass effect in HPPLC: a - solvent composition at peak position of SEC fractions vs. inverse of the square root of molar mass (16 - sample with 16.1 wt % AN, 23 - three samples of azeotropic composition, 30 - sample with 30 wt % AN); the points refer to runs using THF/n-hexane gradient, the circles to THF/iso-octane; b - enlargement of the region around M = 100,000 g/mol.

With b = 13 and the shift due to composition as shown in Fig. 8a, the characteristic lines of two copolymers in the azeotropic region were calculated. In Fig. 8b, they are plotted vs. M. (Note: the abscissa scale is linear in $M^{-1/2}$.) An 1 % change in composition (22.5 - 23.5 wt % AN) has a stronger influence upon peak position than a 20 % change in molar mass. Because of the greater effect of composition, HPPLC is really useful for evaluation of CCD in SEC fractions, especially if the dependence on M can be taken into account by calibration.

Effect of sample concentration
An example of the influence of sample concentration is shown in Fig. 9. A specimen with 30 weight % acrylonitrile and M_n = 71,000 was used for preparation of solutions in dichloroethane containing 0.1...1.0 g/l of copolymer. The peak elution time just slightly increased with sample mass m_o. The peak area A varied directly with concentration:
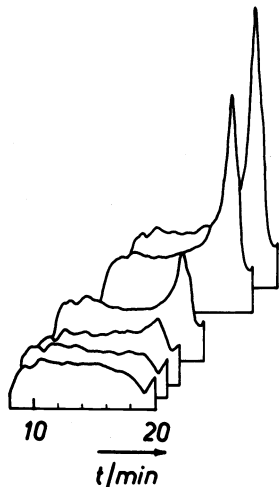
$$A = f \times m_o \tag{6}$$

Fig. 9. Influence of the amount of sample injected. The curve in front is the UV record of a blank run. The curves behind are from runs with injection of 5, 10, 20, 40, or 50 μg copolymer, respectively. Each curve shows the same section of the chromatogram (8 to 20 min). The gradient was the same as in Fig. 4, but with pure THF as solvent "B".
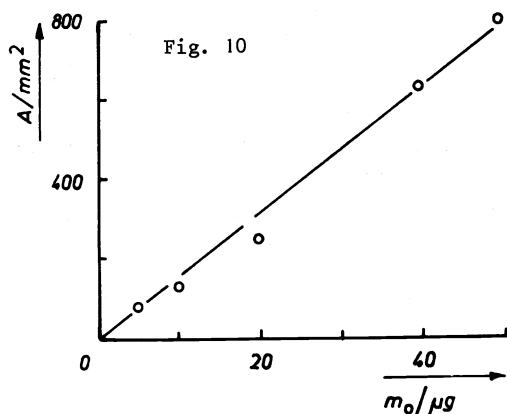
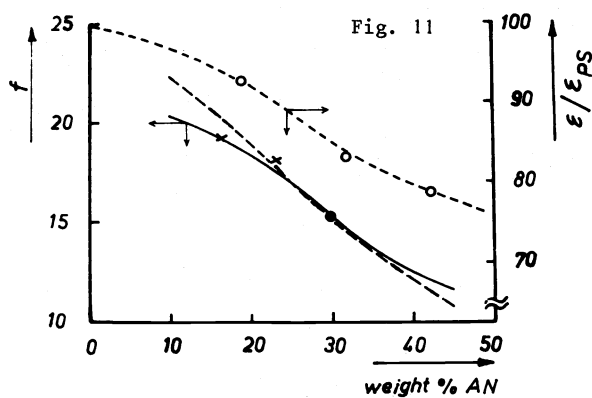Fig. 10. Peak area vs. sample mass injected (data from Fig. 9).

Fig. 11. Hypochromic effect with SAN copolymers; o – normal-
ized extinction coefficient at λ = 261 nm vs. AN content,
SAN in THF, data from Ref. 15; ● – value of the factor f in
Eq. (6) as derived from Fig. 10; x – experimental f at other
copolymer compositions; —— composition dependence of the
factor f (experimental calibration line); - - ● - - compo-
sition dependence as estimated from the normalized extinc-
tion coefficient and the copolymer composition.

Figure 10 shows a linear signal response. Samples with less acrylonitrile
have steeper calibration lines because at 259 nm the styrene units only are
the source of the UV absorption of the copolymer. The slope f of the cali-
bration lines is not simply proportional to styrene content. This is partly
due to the sequence length effect which leads to the hypochromism in styrene
absorption via adjacent acrylonitrile units.

Figure 11 shows experimental data of the calibration factor f vs. copolymer
composition. This data has been obtained by runs using the system iso-octane/
tetrahydrofuran and the gradient explained in Fig. 4. They indicate a de-
creasing value of f with increasing acrylonitrile content of the copolymer.
The dashed line is drawn on the basis of the experimental value f = 15.3
from Fig. 10, of the data concerning the hypochromic effect published by
Brüssau and Stein (Ref. 15), and of the plain influence of the styrene content
of the copolymer samples. This curve represents the dependence of the cali-
bration factor f on copolymer composition in good agreement with the experi-
mental results of this work.

CROSS FRACTIONATION OF SAN COPOLYMERS
BY MEANS OF HP PRECIPITATION CHROMATOGRAPHY AND SEC

During the development of the HPPLC method we always injected 20 µg of poly-
mer dissolved in 20 or 50 µl of solvent. Using SEC fractions as samples, at
first we adjusted their concentration in order to have similar injection con-
ditions. With an amount of about 0.9 mg starting material in SEC, this meant
evaporation of about 50 % of the solvent from the fractions at the centre
of the SEC chromatogram, and of 95 % or even more from the limiting fractions
containing only a small portion of solute.

We investigated a mixture of two SAN copolymers. By SEC using µ Styragel[(R)]
columns, this mixture was first subdivided into six fractions of about 2.5 ml
eluate volume each. As mentioned above, these fractions were concentrated
so that an injection of about 20 µl would bring about 10 µg solute into the
HPPLC apparatus. Figure 12 shows the HPPLC patterns of four fractions. Al-
though the difference in the acrylonitrile content of the components of the
initial mixture was only 4 %, a distinct separation was obtained. The high-
molecular fractions (fr. 2 and fr. 3) clearly showed the component which was
richer in acrylonitrile and eluted after about 15 minutes , whereas in the
low-molecular fractions (fr. 4 - 6) the material with the lower AN content
dominated which exited from the column after 9 - 10 minutes.

The remaining question was to what extent the separation according to compo-
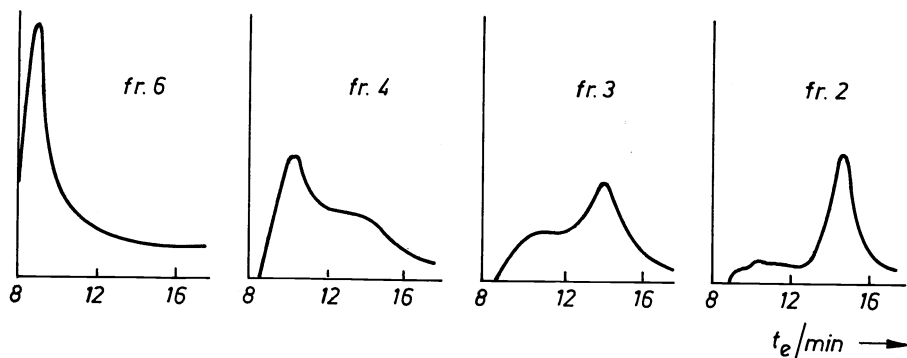sition was favoured by the difference in molar mass. Therefore we mixed a

Fig. 12. Cross fractionation of the mixture of two SAN co-
polymers by SEC and HPPLC. SAN I: 23.0 wt % AN, M_n = 480,000;
SAN II: 19 wt % AN, M_n = 41,000.

UV record of SEC fraction 2 (elution volume 32.3 - 34.8 ml),
fr. 3 (34.8 - 37.3 ml), fr. 4 (37.3 - 39.8 ml) and fr. 6 (42.3 -
50.3 ml). From each chromatogram the section 8 - 18 minutes
is shown.

high-molecular polymer of low AN content (M_n = 325,000; 16.1 wt % AN) with
one of lower molar mass but containing more AN (M_n =71,000; 30 wt % AN). In
this mixture the molar mass effect would diminish the solubility difference
due to composition. As in the first example, about 0.87 mg of the mixture
were subdivided into six SEC fractions. From these fractions, injections con-
taining about 10 µg of polymer showed very distinct HPPLC patterns with the
16.1 % component dominating in the high-molecular fractions.

We always observed sharper HPPLC peaks from SEC fractions than from unfrac-
tionated samples. The explanation is straightforward: the prefractionation
by SEC diminishes the influence of molar mass distribution. The smaller a
slice from the SEC eluate is, the more narrow its representation can be in
HPPLC, provided that the initial sample is homogeneous in composition. It is
possible to obtain very clear HPPLC patterns by injection of SEC eluate
without any further treatment.

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