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Determination of Compositional Heterogeneities for Acrylonitrile-Styrene Copolymers by Thin-Layer Chromatography

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Thin-layer chromatography was applied for determining the compositional heterogeneity of acrylonitrile-styrene (AS) copolymer systems. Good separation according to the composition was achieved by a concentration-gradient development with a binary tetrachloroethane + ethyl acetate. A compositional distribution thus found for a radically prepared high-conversion AS copolymer with an AN-content lower than the azeotropic composition was in good agreement with that calculated from copolymerization kinetics assuming the terminal model. While, a bimodal compositional distribution was obtained for a commercial AS copolymer product which had a higher AN-content than the azeotropic composition.

INTRODUCTION

Thin-layer chromatography (TLC) has been widely applied to different problems on polymer separation.[1] One of the most important and useful TLC applications to copolymer systems is the determination of compositional heterogeneities,[2] and this method may be superior in its rapidness and simplicity over those available for this purpose.[3~5] However, there are only a few copolymer systems whose compositional heterogeneity has so far been investigated quantitatively by TLC.[2,6,7] Recently, Teramachi and Esaki have made a TLC experiment on acrylonitrile–styrene (AS) copolymer but their purpose was not to determine the compositional heterogeneity of this copolymer but to transfer TLC-data to column adsorption chromatography.[8]

This paper deals with various problems on TLC application for determining the compositional heterogeneity of AS copolymer, which is one of the most important products in polymer industry. The characteristics of this copolymer system are as follows: (i) AS copolymer is specific in its large polarity difference between the comonomer units, (ii) adequate eluents for TLC development are limited because of the poor solubility of acrylonitrile-rich components and (iii) even for high conversion, the compositional heterogeneity may be extremely small as expected from radical copolymerization kinetics. Taking these characteristics into consideration, we investigated separation possibilities of this copolymer system according to the composition.

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The experimental results thus obtained were discussed on the basis of the theoretical prediction from radical copolymerization kinetics assuming the terminal model.

<div align="center">EXPERIMENTAL</div>

Sample Polymers and Fractionation

Acrylonitrile (AN) and styrene (ST) were purified by distillation. Copolymerization runs at different monomer feed-composition were carried out in bulk at 60°C under nitrogen, using azobisisobutyronitrile as initiator. In each polymerization run, the conversion of monomer to polymer was kept below 10% on purpose to minimize the compositional heterogeneity, except for the two runs. The polymerization conditions are summarized in Table I. The monomer reactivity ratios for random AS copolymers were evaluated from our experimental data by the method

Table I. Polymerization Conditions and Characterization of Styrene-Acrylonitrile Copolymers

Sample code	ST in feed, mole %	Initiator, wt. %	Time, min	Conv, %	ST in copolymer, mole %	$\bar{M}_{GPC}$ [a] $\times 10^{-4}$	R_f
AS80	91.7	0.298	30	3.4	80.4	18.5	0.63–0.71
AS70	76.8	0.300	40	6.9	68.0	22.3	0.37–0.43
AS70–H	76.8	0.301	250	69.6	71.9	21.5	0.47 (d)
AS60 (b)	61.7	0.300	40	8.3	61.6	24.0	0.25–0.31
AS60–H (b)	61.7	0.301	240	75.7	62.3	19.8	0.33 (d)
AS55	46.7	0.300	30	6.9	56.0	29.0	0.18–0.25
AS50	28.0	0.301	15	2.6	49.4	22.0	0.09–0.16
CAS60–H(c)	—	—	—	high	60.0	18.5	0.39 (d)
CAS50–H(c)	—	—	—	high	52.2	8.8	0.31 (d)

(a) Molecular weight determined by GPC, on the styrene scale
(b) Azeotropic conditions
(c) High-conversion commercial samples
(d) Approximate peak position of densitometric reading

Table II. Characterization Results on Fractions Obtained from AS60

Sample code	$[\eta]$, dl/g	$\bar{M}_w \times 10^{-4}$ [b]	ST mole %	R_f
AS60–1	1.053	38.9	61.6	0.33
AS60–2	0.849	27.5	61.5	0.31
AS60–3	0.734	21.8	61.3	0.34
AS60–4	0.648	17.8	62.4	0.35
AS60–5	0.516	12.3	61.7	0.37
AS60–6	0.382	7.6	61.5	0.37
AS60–7	0.218	3.0	61.6	—
AS60 [a]	0.792	24.6	61.6	0.35

(a) Original sample with azeotropic composition
(b) Calculated with a viscosity equation $[\eta] = 3.60 \times 10^{-4} M_w^{0.62}$ established for azeotropic AS copolymer in butanone at 30°C: Y. Shimura et al., J. Polymer Sci., **B2**, 403 (1964).

<div align="center">(81)</div>

of Finemann and Ross,[9] and found to be $r_1=0.38$ for ST and $r_2=0.06$ for AN monomer. It follows that the azeotropic composition lies at 61.3 ST mole%. In addition, two commercial samples of random AS copolymer, CAS50–H and CAS60–H, were tested in the present study. Purification of the samples was carried out by precipitating the sample from tetrahydrofuran (THF) solution with methanol.

A low-conversion azeotropic sample (AS60) was fractionated into seven fractions at 30°C by a successive fractional precipitation method, using THF and methanol as solvent and precipitant, respectively. The characterization result on fractions thus obtained is shown in Table II. The fractions were used as reference samples for subsequent TLC experiments.

TLC Procedure

TLC experiments were performed in the same manner as previously described.[1] Adsorbent used in this study was Kieselgel H (E. Merck AG., Darmstadt, West Germany). The thickness of this layer was adjusted to 0.30 and 1.2 mm for conventional and semi-preparative experiments, respectively. Each sample was dissoved in THF at a concentration of 0.5 g/dl and applied with a microsyringe onto the chromatoplate. For the semi-preparative experiment, the sample was spotted on a chromatoplate of 20×20 cm² size not in a circular form but in a narrow band having a width of 5 mm and a length of 19 cm. Thus each band contained ca. 40 mg of the sample. Chromatograms were stained by iodine vapor and photographed on high contrast film. The picture of each chromatogram was analyzed by a recording microphotometer MP–3 (Rigaku Denki Co., Ltd., Japan) to determine the compositional distribution for each sample. The detail of this procedure has been described before.[1,2] Two linear calibrations were established: one is for the relation between the amount of sample applied and the response of microphotometer, and the other for that between the composition of sample, *i.e.*, ST mole%, and the response of microphotometer. It should be mentioned that the above calibrations were independent of the molecular weight of sample within an experimental error. Further experimental details will be given together with the results relevant to each.

GPC Technique

A Shimadzu Gel Permeation Chromatograph Model 1A was used for the determination of "point-by-point" composition expressed in ST content, $<x>$, at each elution count. For this purpose, a uv-detector, LKB Uvicord II (LKB, Stockholm, Sweden), was connected in series with a differential refractometer built in the GPC apparatus. The uv-detector was set at 260 nm. The relative response of AN and ST units on the differential refractometer was estimated by using AS copolymers with known ST contents, because polyacrylonitrile (PAN) is insoluble in THF: The refractometer response for the AN unit was calculated from two types of plots between the response area and the sample concentration constructed for a homopolystyrene and an AS copolymer with a known ST content. The uv-detector response for the ST unit was also determined by using the same AS copolymer as above in order to minimize the underestimation of $<x>$ due to the hypochromic effect in uv absorption.[10] Calculation of $<x>$ was carried out according to a method proposed by

Runyon et al.[11]

RESULTS AND DISCUSSION

TLC Separation According to Chemical Composition

TLC experiments on samples with different AN content were conducted with single solvents as developer and the values of R_f (rate of flow) thus found are listed in Table III. No single solvent had ability to allow separation of AS copolymers

Table III. Results for TLC Developments with Single Solvents

Solvent	Dielectric constant	Solubility parameter	Values of R_f		
			PST	AS80	AS50
Methanol	32.6	14.28	0^n	0^n	0^n
2-Butanone	18.5	9.27	1	1	1
Ethylene dichloride	10.65	9.8	1	0.2	0
TCE	8.2	9.7	1	0.2	0
THF	7.42	9.1	1	1	1
Amylchloride	6.6	8.3	a	0	0^n
Ethyl acetate	6.02	9.1	1	1	1
Chloroform	4.8	9.3	1	0.7	a
Benzene	2.28	9.2	1	a	0^n

a) Tailing upward from the starting position.
b) 0^n means that $R_f = 0$ because the sample is insoluble in this solvent.

according to chemical composition. In such a case, a binary solvent mixture chosen from search for single solvents is generally used as developer. A necessary condition required to such binary mixtures is their good dissolving power toward copolymer samples.[12] In the case of AS copolymers, this condition is particularly important for copolymer samples with high AN contents, because they have usually low solubilities. Teramachi and Esaki have applied a mixture of chloroform and methyl acetate to AS copolymers.[8] However, it is seen in the table that the solvent strength i.e., eluting power of chloroform, is a little bit too strong for AS copolymers with lower AN contents. In the present case, a binary mixture of tetrachloroethane (TCE) and ethyl acetate was employed as developer. The solvent strength of TCE is weaker than that of chloroform, despite the fact that the solubility parameter of the former is higher than that of the latter (see Table III). In this case, ethyl acetate plays a role equivalent to methyl acetate. In practice a concentration-gradient development technique was applied, using 75 ml of TCE and 32 ml of ethyl acetate as the initial and adding solvent, respectively. A photograph of the chromatograms thus obtained is shown in Fig. 1, in which one sees that the R_f values for standard samples decrease with increasing AN content. The R_f values determined from Fig. 1 are listed in the last column of Table I.

In order to examine the effect of molecular weight upon R_f, the fractions obtained from a low-conversion azeotropic sample AS60 were subjected to TLC under the same
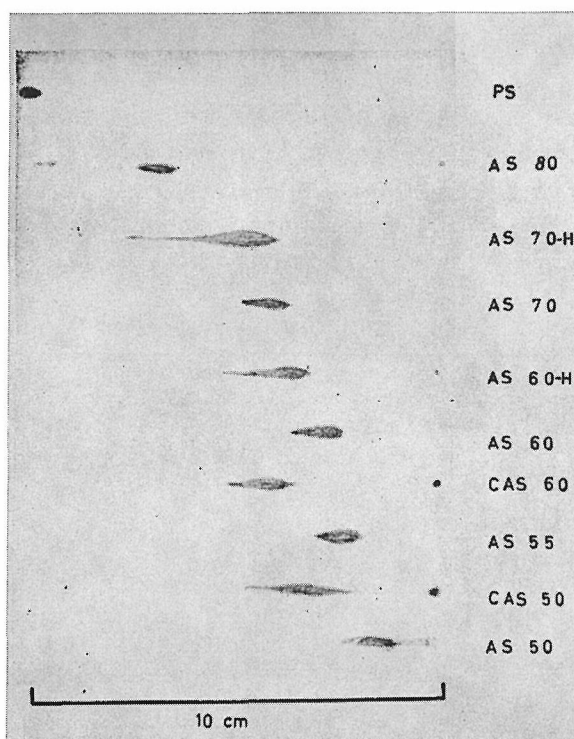
Fig. 1. Chromatograms obtained by a concentration gradient development with TCE–ethyl acetate for AS copolymers with different ST contents. For the detail, see text.

development condition as applied to obtain Fig. 1. The result, listed in Table II, shows that the R_f values are almost independent of molecular weight within the molecular weight span studied here.

We are now in a position to calculate the average composition and compositional distribution of test copolymers from the chromatograms. For this purpose, the visualization-and-photodensitometer-tracing method[1,2] was adopted. Quantitative analysis by this method can be readily done by using the two calibrations, the relative specific darkness vs. ST content relation and the R_f vs. ST content relation for the standard samples. At first, we attempted to analyze a chromatogram for a sample AS70–H, prepared by polymerization up to a conversion of 70%. The compositional distribution curve obtained for this sample is shown in Fig. 2, in which the relative amount of each copolymer species is plotted against the mole fraction of ST units in the form of a histogram. The arithmetic mean of the mole fraction of ST units calculated from the histogram is 0.72, which is in excellent agreement with a value of 0.719 determined by elementary analysis of this sample.

Next we will compare the compositional distribution curve obtained from TLC with that predicted from the radical copolymerization theory.[13,14] Calculation of the compositional distribution was carried out by using the conversion-composition equation proposed by Skeist.[14] The details of this calculation procedure was already reported in a previous paper.[2] For this calculation, the values of 0.696 and 0.768
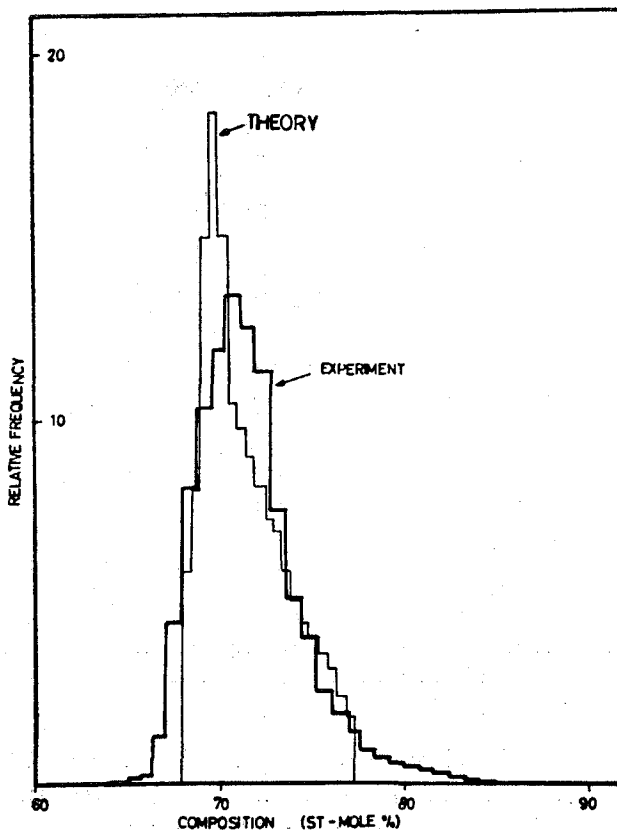
Fig. 2. Compositional distribution curves (histograms) obtained experimentally and theoretically for sample AS70-H.

were used as the conversion of monomer to polymer and the initial mole fraction of ST in feed, respectively (see Table I). In Fig. 2, the calculated compositional distribution curve is shown together with the experimental one. The experiment and theory are fairly in good agreement. The small tailing of the experimental curve can probably be attributed to an artifact of TLC. It turns out in any case (even for high conversion) that the compositional heterogeneity of the radically prepared AS copolymers is very low.

Application to Commercial Products

Using the same procedure as described above, we attempted to determine the compositional heterogeneity of commercial products, CAS50-H and CAS60-H. The chromatograms are already shown in Fig. 1. By inspecting the chromatograms it is found that the compositional distributions for the both samples are rather narrow, although the sample products must have been prepared at a sufficiently high conversion. The same is revealed by the result calculated from the chromatogram for CAS50-H, as shown in a histogram in Fig. 3. However, the average ST mole fraction calculated from the histogram was 0.59 for this sample, which is inconsistent with
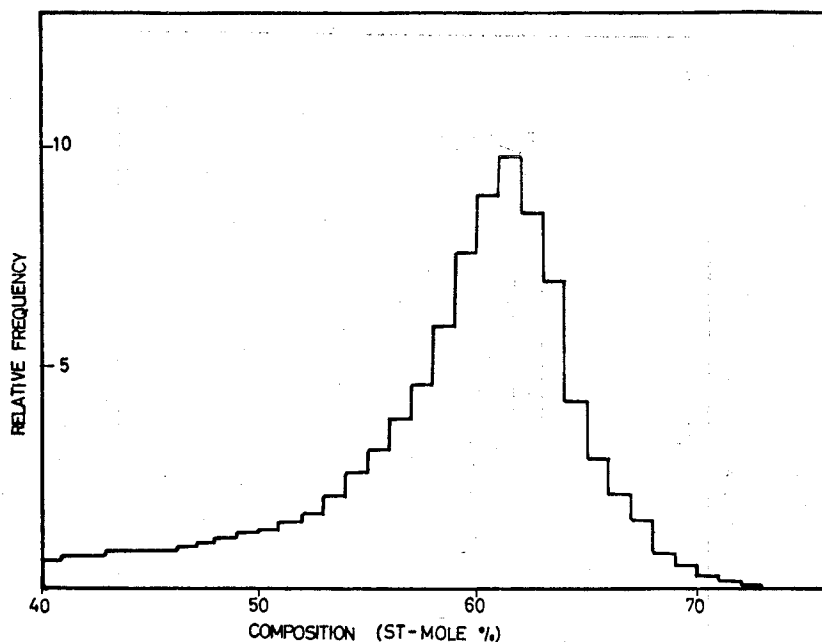
Fig. 3. Compositional distribution curve obtained experimentally for commercial sample CAS50-H. The immobile component species (see Fig. 1) was neglected in this determination.

that of 0.52 determined by elementary analysis. The average ST mole fraction obtained from TLC and elementary analysis for CAS60-H were also 0.67 and 0.60, respectively. These differences in the average ST content suggest that the commercial products might contain some component species having higher AN contents because such species will remain immobile at the starting point due to their insoluble nature toward the developer employed here. In fact, both the commercial products, CAS50-H and CAS60-H, showed distinctly an immobile spot on the starting line (see Fig. 1), which may be assigned to copolymer species with higher AN contents and/or PAN. In sharp contrast to the above, almost no sample polymer remained untravelled in the case of our standard samples. To explore this phenomenon, a semi-preparative TLC separation of CAS50-H was carried out. About 40 mg of the sample was developed on a chromatoplate with 1.2 mm thickness layer by the binary developer of a constant composition (TCE/ethyl acetate=75/25, v/v). This experiment was made twice. The sample was thus separated roughly into two components, which were located around $R_f=0.5$ and the starting level. The latter component was extracted from the silica gel with boiling THF. The isolated polymer (~ 7 mg) was reprecipitated, and its AN content was found to be about 85 mole% by elementary analysis. The true average AN content of the species remaining on the starting line is probably higher than 85 mole%, but it was impossible to detect the presence of PAN by the extraction method described above.

In Fig. 4 is shown a GPC elution curve, which was taken simultaneously with the refractometer (RI) and the uv-detector at 260 nm for a sample CAS50-H. The point-by-point composition of this sample increased with increase in elution count,
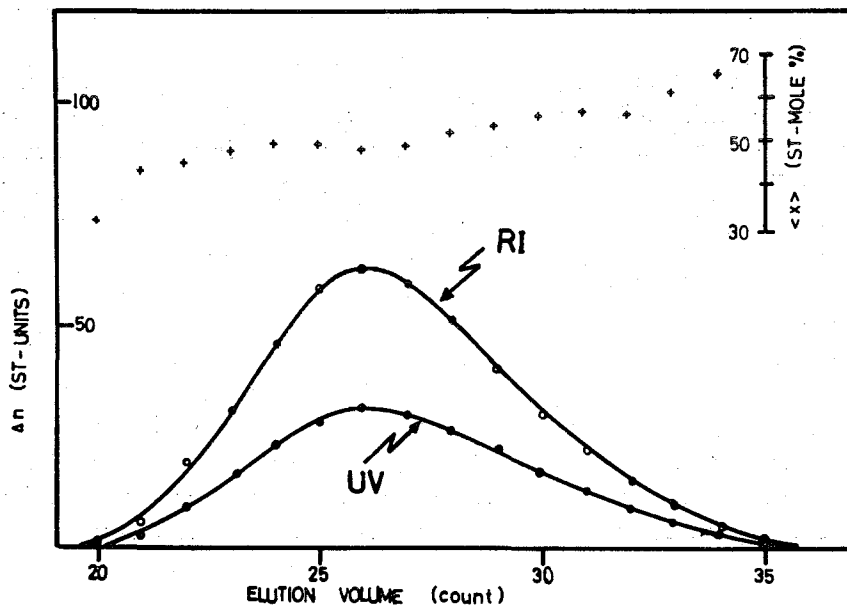
Fig. 4. GPC elution curves obtained with refractometric (RI) and ultraviolet (UV) detectors for a commercial sample CAS50–H and plots of point-by-point ST content against elution volume V_e, indicated by $<x>$.
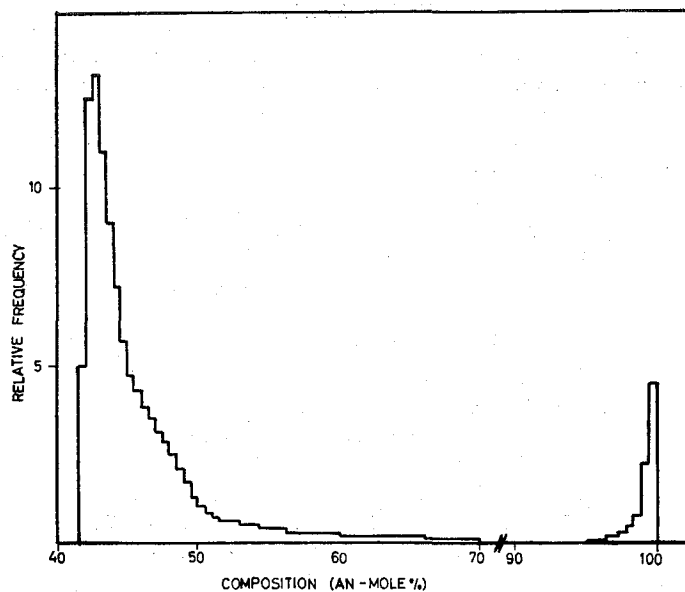

Fig. 5. Compositional distribution curve to be expected theoretically for an AS copolymer obtainable at an initial monomer feed-composition of 46.7 mole ST (below the azeotropic composition) and at 100% conversion.

indicating that higher-molecular-weight species have higher AN contents. The result, however, yields no information on such a bimodal compositional distribution as mentioned above.

On the other hand, it is predicted from the radical copolymerization mechanism that a high-conversion AS copolymer with an average ST content higher than the azeotropic composition will have a bimodal compositional distribution. This is due to the large difference in reactivity ratios for the present monomer pair. For example, let us consider a system of initial monomer feed-composition of ST/AN=46.7/53.3 (mole/mole). Up to about 90% conversion, the copolymer product has a single compositional distribution, which is relatively narrow. However, toward the end of polymerization, i.e., after most ST monomer has been consumed, the species with very high AN contents and finally homo-PAN will be formed. Figure 5 shows a theoretical compositional distribution of the copolymer sample obtained at 100% conversion under the polymerization conditions mentioned above. The result gives a strong evidence of a bimodal compositional distribution of the commercial samples. However, further consideration on these commercial products cannot be made because the details of copolymerization conditions for these samples are unknown.

ACKNOWLEDGMENT

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