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GRADIENT ADSORPTION THIN-LAYER CHROMATOGRAPHY OF STYRENE–ACRYLONITRILE RANDOM COPOLYMERS*

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SUMMARY

The compositional inhomogeneity of styrene–acrylonitrile random copolymers has been investigated by gradient adsorption thin-layer chromatography. The compositional distributions obtained this way are in good agreement with those calculated from the kinetics of the copolymerization.

INTRODUCTION

This paper deals with the investigation by thin-layer chromatography (TLC) of the compositional inhomogeneity (CI) of styrene (St)–acrylonitrile (AN) random copolymers synthesized by radical copolymerization under various conditions of conversion and temperature. The use of this method for the investigation of the CI of St–AN copolymers has been described previously[1–4]. Mixtures of chloroform and methyl acetate (isocratic elution)[1,2], benzene (toluene) and acetone[3] and tetrachloroethane and ethyl acetate[4] (gradient elution) were used as separating systems. It has been shown[4] that the compositional distributions obtained by gradient TLC for St–AN copolymers are in good agreement with those calculated from the kinetics of the copolymerization. Commercial copolymers with St contents above the azeotropic composition investigated in this manner had a bimodal compositional distribution.

To separate the St–AN copolymers, TLC with solvent programming was used: 3 ml of acetonitrile were added to a mixture of 5 ml of dichloromethane and 2 ml of carbon tetrachloride. This system permitted the separation of copolymers containing 4.5–44.7 wt.-% (8–61.4 mole-%) of AN. Chromatograms were developed by spraying with a 3% solution of potassium permanganate in concentrated sulphuric acid, the intensity of darkening being proportional to the St content in the copolymer. This type of detection is more sensitive than treatment of plates with a solution of iodine in methanol or with iodine vapour, as used previously[1–4], and gives a colour that is stable for an unlimited period.

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EXPERIMENTAL

Materials

The following samples of St–AN copolymers were investigated:

(a) samples obtained by radical copolymerization in bulk at an initiator (azobisisobutyronitrile, AIBN) concentration of 0.0125 mole l^{-1}, a temperature of 50 ± 0.1°C and a conversion of 4–5%;

(b) samples obtained by radical heterophase copolymerization in a precipitant (*n*-heptane) under similar conditions with a conversion from 2.2 to 70%;

(c) fractions of a heterophase sample synthesized by method (b) with 70% conversion obtained by preparative fractionation according to molecular mass in a dichloromethane–methanol system proposed by Glöckner *et al.*[5];

(d) samples obtained by radical homophase copolymerization in bulk at the initial azeotropic composition of the monomers and a conversion from 5 to 60%;

(e) samples obtained by thermal initiation (40 and 140°C) with a conversion of 5–100% (of azeotropic composition). Copolymers were synthesized under conditions simulating industrial conditions.

Intrinsic viscosity, composition and molecular mass (M) were determined for all copolymers. The characteristics of samples (a)–(e) are given in Tables I–V.

TABLE I
CHARACTERISTICS OF St–AN COPOLYMERS WITH CONVERSIONS OF 4–5%

Sample No.	*Proportion of AN (elemental analysis) (wt.-%)*	*$[\eta]$ at 25°C (dl/g) (DMF*)*	$M_{S_\eta} \cdot 10^{-5}$
1	4.5	2.60	2.4
2	12.2	2 62	2 3
3	18 7	2 32	3.7
4	25 4	2 03	2 5
5	31 0	1.90	3.3
6	37.4	1.59	3.1
7	44 7	1.09	4 0

* Dimethylformamide.

Methods

The composition of copolymers was determined from their nitrogen content. Intrinsic viscosity ($[\eta]$) was measured in an Ubbelohde viscosimeter in methyl ethyl ketone at 30°C. The molecular weights of fractions and samples were estimated on the basis of the Flory–Mandelkern invariant $\Phi^{1/3}P^{-1} = 2.5 \cdot 10^6$ (ref. 6) according to the equation

$$\bar{M}_{S_\eta}^{2/3} = \frac{S_0 \eta_0 [\eta]^{1/3} N_A}{\Phi^{1/3} P^{-1} (1-\bar{V}\varrho)},$$

where S_0 is the sedimentation constant, η_0 is the viscosity of the solvent, N_A is Avogadro's number, $\bar{V}$ is the specific partial volume determined with a pyknometer, ϱ

TABLE II
CHARACTERISTICS OF HETEROPHASE St–AN COPOLYMERS OBTAINED IN A PRECIPITANT (*n*-HEPTANE)

Sample No.	*Conversion (%)*	*Proportion of AN (wt-%)*		*[η] at 30°C (MEK*)*	$\bar{M}_{S\eta}\ 10^{-5}$
		Elemental analysis	*TLC*		
1	2.2	27.3	25–31	0 86	1.5
2	25	27 8	25–33	2 8	4 0
3	50	28.4	25–33	4 15	7.5
4	70	28.4	25–33	4 7	9 3

* Methyl ethyl ketone

TABLE III
CHARACTERISTICS OF FRACTIONS OF A HETEROPHASE St–AN COPOLYMER WITH 70% CONVERSION

Sample No	*Proportion of AN (wt-%)*		*[η] at 30°C (MEK*)*	$\bar{M}_{S\eta}\ 10^{-5}$
	Elemental analysis	*TLC*		
I	30 7	30 0	8 15	12
II	29 4	30.0	7 33	9.0
III	29 4	30 0	5 62	—
IV	29 8	30 0	4 76	7.1
V	29 4	29 5	4 10	5 5
VI	29.6	29 5	2 85	—
VII	30 1	29 0	1 72	2 2
VIII	27 3	27 0	0 58	1 0

* Methyl ethyl ketone

TABLE IV
CHARACTERISTICS OF HOMOPHASE St–AN COPOLYMERS OBTAINED IN BULK

Sample No	*Conversion (%)*	*Proportion of AN (wt-%)*		*[η] at 30°C (MEK)*	$\bar{M}_{S\eta}\ 10^{-5}$
		Elemental analysis	*TLC*		
1	5 6	23 5	29.0	1.45	2.1
2	27	23 5	23 0	1.70	2 4
3	55	25 7	23 0	2 40	3 2

TABLE V
CHARACTERISTICS OF St–AN COPOLYMERS OBTAINED BY INITIATION IN BULK

Sample No	*Temperature (°C)*	*Conversion (%)*	*Proportion of AN (wt-%)*		*[η] at 30°C (MEK)*	$\bar{M}_{S\eta}\ 10^{-5}$
			Elemental analysis	*TLC*		
1	110	3 8	23 1	24 0	1 68	2 72
2		21 6	23 5	24.0	1 44	1 9
3		69.7	23 5	24 0	1 55	2 7
4		97.0	23 1	24 0	1.53	2 4
5	140	7 0	23.5	23 0	1 32	1.74
6		23.0	22 7	23 0	1 06	1 62
7		96 0	25 4	23 0	0 96	1 30

is the density of the solvent. Sedimentation coefficients were measured by high-speed sedimentation in a MOM-3170 ultracentrifuge equipped with Dippot–Swenson's optics. Measurements were carried out in methyl ethyl ketone at 20°C at a rotor speed of 40,000 rev/min.

TLC was carried out on 5 × 10 cm plates coated with KSK silica gel (pore diameter 100 Å, particle diameter 15 μm) containing 5% of gypsum (500 mg of silica gel + 1.75 ml of water per plate). Prior to chromatography the plates were activated for 30 min at 120°C. Copolymer samples were spotted on the plates from solutions in methylene chloride. Gradient TLC was used for separation according to the composition of the copolymers, as follows.

The chromatographic plate was placed in a chromatographic chamber 7 cm in diameter and 10 cm in height mounted on a magnetic stirrer unit. A mixture of 5 ml of methylene chloride and 2 ml of carbon tetrachloride was poured on to the bottom of the chromatographic chamber, which was closed with a cover that had an opening in the centre. A 3-ml volume of acetonitrile was added through this opening at a rate of 0.12 ml/min. The chromatographic chamber was thermostated at 17°C and, after chromatography, the plate was dried for 10 min at 150°C, sprayed with a 3% solution of potassium permanganate in concentrated sulphuric acid and heated for *ca.* 10 min at 180°C.

The copolymers developed as black spots on the light background of the sorbent. Photographs of the chromatograms were taken by a contact method on reflex photographic paper. The sensitivity of detection was 0.2–1.0 μg of the copolymer.

RESULTS AND DISCUSSION

As samples with a low degree of conversion were used, it was possible to develop an efficient TLC system for the separation of St–AN copolymers according to composition (Fig. 1a). The dependence of R_F on the composition of the copolymer was linear in the range 4.5–44.7 wt.-% of AN (Fig. 1b) and the best separations of the

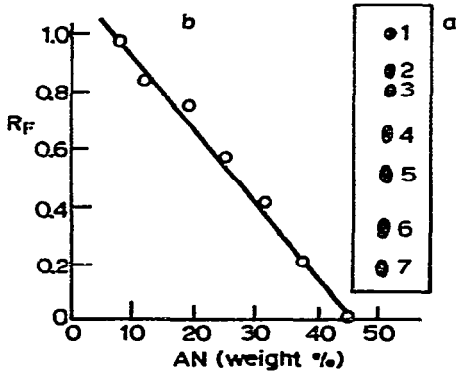


Fig 1. (a) Gradient TLC of St–AN random copolymers of various compositions with 4–5% conversion using methylene chloride–carbon tetrachloride (5.2) plus acetonitrile (3 ml), the acetonitrile being added at a rate of 0.12 ml/min. The St–AN copolymers contained the following proportions of AN. (1) 4.5, (2) 12.2, (3) 18.7, (4) 25.4, (5) 31.0, (6) 37.4 and (7) 44.7 wt.-% (b) R_F value of St–AN random copolymer *vs* their AN content (wt.-%).

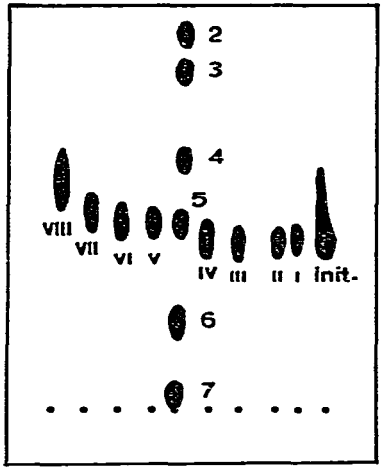
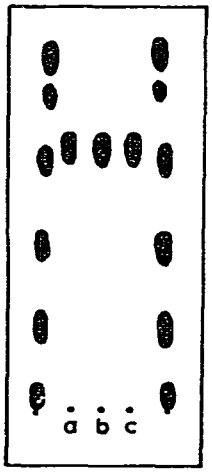


Fig 2. Gradient TLC of a heterophase St–AN copolymer with 70% conversion and its fractions (I–VIII) using the system as in Fig 1 A mixture of samples 2–7 (Fig 1a) was spotted in the middle of the plate

copolymers were obtained in this range. It should be noted that the reproducibility of the method is not high, but the above linear dependence is maintained on a particular plate.

It has been established[7,8] that in adsorption TLC random copolymers with $M > 50 \cdot 10^3$ are separated according to composition. However, as this phenomenon has no rigorous theoretical explanation, when new polymers are separated this feature of adsorption TLC of random copolymers should be checked experimentally. Consequently, the TLC of fractions of a heterophase sample with 70% conversion (Fig. 2) was investigated. As can be seen from Table III, these fractions do not differ greatly in composition but the values of $[\eta]$ vary from 0.58 to 8.15. Fig. 2 shows the TLC of the initial sample and its eight fractions. It is clear that all fractions, except low-molecular-weight fraction VIII with $[\eta] = 0.58$, migrate to approximately the same extents. This indicates that the system chosen separates the copolymers precisely according to composition, regardless of M. Table III gives the composition of the fractions obtained from the TLC data and the corresponding composition established from elemental analysis. Fig. 2 shows that the width of the chromatographic spots of the fractions is smaller than that of the unfractionated (initial) copolymer and that the average composition depends on M, especially in the low-M region. Probably the composition of the macromolecules formed under the conditions of heterophase copolymerization depends on their length. In TLC the R_F value of the substance is strongly dependent on concentration. This dependence is complex owing to the convex shape of the adsorption isotherm and specific viscosity effects[9]. Hence, it was necessary to choose concentrations (ensuring detection at the required sensitivity) that would not lead to concentration effects. For polymers with $[\eta] > 2$ this concentration corresponded to sample weights of 0.3–0.5 μg used in our investigations. By using the method developed here, St–AN copolymers obtained under different conditions, in a precipitant and in bulk, were investigated. Their characteristics are given in Tables II and IV.

According to the theory of radical copolymerization, azeotropic copolymers obtained under homophase conditions (in bulk) should have narrow compositional distributions. This is confirmed by the chromatograms shown in Fig. 3, which indicate that azeotropic copolymers exhibit compositional homogeneity over the range of conversions investigated (up to 60%). Copolymerization in a precipitant occurs simultaneously in several phases of a complex reaction system, each phase being characterized by its own chain propagation and termination constants. This inevitably leads to the appearance of the polydispersity of copolymers according to both their chemical composition and M[10].



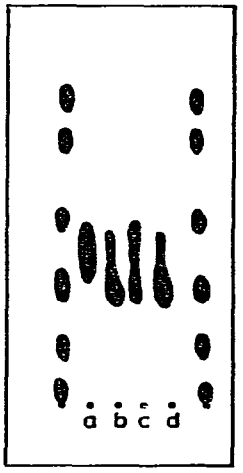


Fig 3 Gradient TLC of homophase St–AN copolymers with conversions of (a) 5 6%, (b) 27% and (c) 55%. Conditions as in Fig. 1. A mixture of samples 2–7 (Fig 1a) was spotted near the edges of the plate (Figs 3–5)

Fig 4 Gradient TLC of heterophase St–AN copolymers with conversions of (a) 2%, (b) 25%, (c) 50% and (d) 70% Conditions as in Fig 1

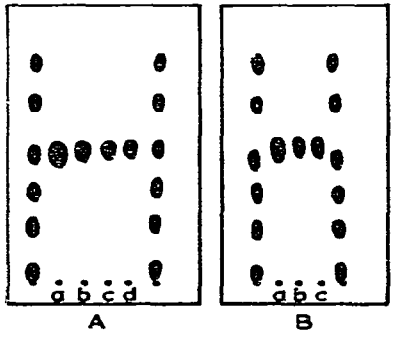


Fig 5 Gradient TLC of St–AN copolymers synthesized at (A) 110°C with conversions of (a) 3 8%, (b) 21% and (c) 69.7% and (B) at 140°C with conversions of (a) 7%, (b) 23% and (c) 96%. Conditions as in Fig 1

Fig. 4 shows the chromatogram of copolymers synthesized in a precipitant with the characteristics listed in Table II. It can be clearly seen that at low conversions the process occurs with the formation of copolymers with a broad distribution according to composition (25–31 %). As the conversion increases, a bimodal compositional distribution becomes apparent. Evidently, this is related to simultaneous chain propagation in both solid and liquid phases.

Copolymers obtained by thermal initiation in bulk at 110 and 140°C over a wide range of conversions under conditions simulating those of industrial synthesis were also investigated (Table V). Fig. 5 shows that these copolymers are characterized by a high homogeneity of composition regardless of conversion and the temperature of the synthesis.

The compositions of all of the copolymers calculated from the TLC data are in good agreement with those obtained by elemental analysis (Tables I–V). These experiments show that TLC is a highly sensitive technique for studying fine differences in the compositions of copolymers. Hence, it can be concluded that TLC can be used successfully as a simple, rapid and sensitive method for evaluating the homogeneity of composition in studies of the mechanisms of the copolymerization of St–AN random copolymers

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