Determination of Compositional Heterogeneity in Copolymers by Thin Layer Chromatography. I. Preliminary Results for Styrene–Acrylate Copolymers

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ABSTRACT: The feasibility of determining the compositional heterogeneity of copolymers by thin layer chromatography (tlc) has been demonstrated. Homopolymers and copolymers of styrene (ST) and methyl acrylate (MA) prepared at various monomer feed ratios were used as test samples. Seven solvents, chosen appropriately from the eluotropic series, were used to develop the chromatograms. No intermediate R_f value was observed, since some species remained immobile while others reached the solvent front. Similar, unfavorable results were observed using solvent mixtures. Good separation was achieved by developing in a concentration gradient, using the system carbon tetrachloride–methyl acetate. By this procedure, the composition distribution curve of a high-conversion ST–MA copolymer was determined. The result agreed well with a calculated curve, based on radical copolymerization kinetics. The limitations of the new technique are discussed briefly. Finally, preliminary data are presented indicating that, under suitable conditions, separation of copolymers with respect to differences in steric monomer arrangement is also possible.

During the copolymerization of two monomers different degrees of reactivity exist between the radical chain ends and the two monomers. This gives rise to compositional heterogeneity among the copolymer molecules, in most cases depending upon the degree of conversion. This heterogeneity is an important factor in characterizing the physical properties of the product, in addition to the average composition and the degree of polymerization. Furthermore, knowledge of the complete composition distribution curve allows experimental proof for the theory of copolymerization kinetics. For these reasons it is desirable to establish a rapid method for the determination of this distribution.

Experimental methods available to date for this purpose[1] are fractional precipitation and dissolution,[2] light scattering in dilute solution,[3] density-gradient ultracentrifugation,[4] and high-resolution nuclear magnetic resonance and infrared spectroscopy.[1,5,6] Fractionation is, of course, the most direct technique; however, for thermodynamic reasons it is impossible to obtain separation on the basis of composition only, without interference due to polydispersity in molecular weight. In addition, this method is very time consuming. Light scattering can give limited information on compositional distribution and has been applied by several Russian workers.[7] Nuclear magnetic resonance and infrared spectroscopy allow the determination of sequence length distributions in the copolymer chains. None of these methods permits direct and rapid visualization of the entire composition distribution curve without any influence of heterogeneity in molecular weight.

The present communication deals with an application of thin layer chromatography (tlc) for this purpose which completely fulfills the above requirements. Langford and Vaughn[8] have probably introduced the use of chromatographic techniques for separating high polymers of different chemical compositions. Extending this idea, tlc was applied to styrene (ST)–methyl acrylate (MA) copolymers prepared at various monomer feed ratios. Suitable eluotropic solvent mixtures were found, allowing complete separation of the copolymers with respect to composition.

Experimental Section

Preparation and Characterization of Polymer Samples. Polymerization. Styrene (ST) and methyl acrylate (MA) monomers were purified by distillation and polymerized with azobisisobutyronitrile. Copolymerization runs at different monomer feed ratios were made at 60 and 75°. The conversion was varied for the purpose of obtaining copolymers with different compositional heterogeneities. Experimental details have been described in a previous paper;[9] polymerization conditions are listed in Table I.

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(2) O. Fuchs, *ibid.*, **70**, 267 (1966).

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(5) Y. Yamashita, private communication.

(6) F. Kamiyama, H. Matsuda, and H. Inagaki, *J. Phys. Chem.*, **71**, 4153 (1967).

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(9) H. Matsuda, K. Yamano, and H. Inagaki, *J. Polym. Sci.*, in press.

TABLE I
POLYMERIZATION CONDITIONS AND CHARACTERIZATION OF STYRENE–METHYL ACRYLATE COPOLYMERS

Sample code	Monomer feed ratio ST, mol %	Initiator concn, wt %	Monomer concn,[a] wt %	Temp, °C	Conversion, %	Compn ST, mol %	$M_v \times 10^{-4\,b}$
SM76-1	76.0	0.10	11.2	75	15.3	77.6	11.1
SM76H	76.7	0.30	33.0	60	71.0	78.8	7.98
SM65	60.0	0.10	24.8	75	2.3	65.8	13.8
SM50-1	37.6	0.10	25.0	75	3.5	52.7	14.5
SM50-2	34.4	0.30	33.0	60	17.9	48.9	15.8
SM40	21.1	0.10	25.2	75	2.2	42.5	17.0
SM35H	34.4	0.30	33.0	60	97.8	34.2	38.9
SM25	9.98	0.10	32.6	75	6.1	25.8	14.5

[a] In benzene. [b] Estimated using eq 1 in the text.

In addition to these copolymers, fractionated samples of polystyrene (PST) and of poly(methyl acrylate) (PMA) were used. Intrinsic viscosities of these samples in butanone at 30° were 0.42_8 and 1.46 (dl/g), respectively.

Fractionation. A whole copolymer, SM40, was fractionated into seven fractions at 30° using butanone and methanol–water as solvent and precipitant, respectively. Details of this procedure are also given in a previous paper.[9] These fractions were used to determine the molecular weight dependence of the rate of flow, R_f, in tlc. Intrinsic viscosities, $[\eta]$ (deciliters per gram), were measured in benzene at 30° and converted into molecular weights, M_v, using an equation proposed by Matsuda, *et al.*[9]

$$[\eta] = 6.15 \times 10^{-5} M_w^{0.78} \qquad (1)$$

Thin Layer Chromatography. Stationary Phase. One part of silica gel, Yamanilayer-G (Yamani Pharm. Co., Kyoto), containing approximately 13% gypsum, was slurried with two parts of distilled water, and applied as the stationary phase onto a thick glass plate (20 × 10 cm²). The thickness of the layer was adjusted to 0.25 mm, using a commercially available device. Immediately before use, the gel layer was activated by heating the plate at 110° for 1 hr.

Development Procedure. Stock solutions for tlc tests were prepared by dissolving 40 mg of each sample in 10 ml of butanone. With the aid of a microsyringe a spot of each solution, containing *ca.* 20 μg of polymer, was formed on the layer. The position of each spot, *i.e.*, the starting points, was 2.0 cm from one edge of the glass. The plate was dried for several minutes and placed into a desiccator containing the developing solvent at room temperature. After the solvent front had risen 10 cm from the starting point, the plate was removed from the container and kept in an oven at *ca.* 100° to prevent further ascent of the solvent front. Then, a 1% methanol solution of iodine was sprayed unto the gel, marking the position of the polymer as brown spots. Because this color faded after 20–30 min, the chromatograms were photographed on high-contrast film.

Composition Dependence of Blackness of Film. A relation was established between blackness of film and amount and composition of polymer on the layer. For this purpose, dilute butanone solutions of PST, PMA and copolymer samples SM 76-1 and SM40 were prepared at identical concentrations of 4 g/l. By means of a microsyringe 3 drops of each solution were formed on a thin layer plate, each containing exactly 10 μl. After the solvent was evaporated, the spots were marked with iodine–methanol and photographed. A sample picture is shown in Figure 1. It has frequently been observed that the blackness is more intense at the periphery of a spot than at the center; at decreasing polymer concentration this trend is less pronounced. Therefore, blackness determinations were made at different positions on each spot, using a densitometer with an aperture sufficiently smaller than the spot. The reading of the densitometer will hereafter be called the apparent blackness and denoted by *B*. An average value of *B* was evaluated and corrected further considering the area of the corresponding spot (see Table II). The final value represents the blackness produced by 40.0 μg of polymer and will be designated by B^0. A linear dependence with a negative slope is found when

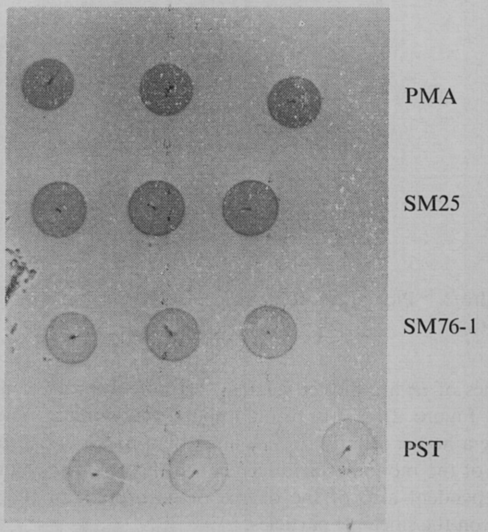

Figure 1. Determination of composition dependence of blackness on photographic film.

TABLE II
RELATIONSHIP BETWEEN PHOTOGRAPHIC BLACKNESS AND COPOLYMER COMPOSITION

Sample	Compn ST, mol %	App blackness, *B*	Relative area of spot	Blackness, B^0
PMA	0	5.74	0.94	5.26
		5.20	1.00	
		5.21	1.00	
SM40	42.5	3.58	1.00	3.72
		3.44	1.07	
		3.89	1.00	
SM76-1	77.6	1.55	0.94	1.57
		1.40	1.00	
		1.81	1.00	
PST	100	0.80	1.07	0.83
		0.86	1.00	
		0.77	1.00	

Table III
Chromatographic Development with Single Solvents

Developer	Dielectric constant	R_f[a] PST	SM65	SM25	PMA
n-Hexane	1.89	0	0	0	0
Carbon tetrachloride	2.22	0	0 (u)	0 (u)	0
Chloroform	4.62	>0.90	0 (u)	0	0
Ethyl acetate	6.02	>0.90	>0.90	>0.90	0
Methyl acetate		0 (u)	>0.90	>0.90	>0.90 (d)
Acetone	21.3	0	>0.90	>0.90	>0.90 (d)
Acetonitrile	87.5	0	0	>0.90	0.42 (u, d)

[a] u and d indicate "tailing up" and "tailing down" of the spot, respectively.

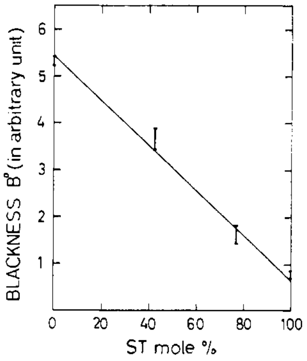

Figure 2. Plot of photographic blackness against ST mole fraction.

values of B^0 are plotted against the mole fraction of ST, m_1 (see Figure 2). This result implies that iodine molecules have a higher affinity to MA units than to ST units, regardless of the monomer arrangement in the polymer chain and independent also of the degree of adsorption of the polymer on the silica gel particles.

Concentration Gradient Development. This technique has been described by Rybicka[10] and was utilized unmodified in the present study. A vacuum desiccator was used, containing in advance a developing solvent. After the solvent front had arrived at a height of 2 cm above the starting line, a second solvent was added from a buret. The rate of addition was adjusted so that the desired final composition of solvents was attained when the solvent front had moved to a height of 10 cm. For copolymers with broad composition distributions the rate of addition was not constant, but increased with elution time. A magnetic stirrer was used to keep the solvent mixture homogeneous. More detailed descriptions of the procedure in each case will be given below.

Results and Discussion

Tlc Development with Single Solvents and Their Mixtures. Guided by published rules for the selection of eluotropic series,[11] seven solvents with different dielectric constants—*n*-hexane, carbon tetrachloride, chloroform, ethyl acetate, methyl acetate, acetone and acetonitrile—have been used as developing agents for polymer samples PST, SM65, SM25, and PMA. The R_f values for each set of polymer and solvent were determined and the results summarized in Table III.

It is seen that in the case of single solvent development some polymer species remain on the starting line, while others reach the solvent front without showing any intermediate R_f values. This indicates that a high dissolving power of any solvent may be a necessary but not a sufficient condition for an appropriate chromatographic development. For example, chloroform is known to be a good solvent for PMA but cannot develop this polymer at all. Thus the developing power of a solvent may be rated by the extent to which the solvent can reduce interactions (dipole–dipole or dipole–hydrogen bonds) between solute and silicic acid.

On the basis of the above results, two solvents with intermediate developing and dissolving powers, *i.e.*, chloroform and ethyl acetate, were selected and their mixtures at various compositions used for further tlc experiments. Again, negative results were obtained as seen in Table IV. This led to the conclusion that no individual solvent mixture exists which can give complete separation of these species. However, for samples SM76-1 and SM65 Table IV indicates a favorable trend in the case of mixtures having variable compositions in the range of 0.04–0.20 (volume fraction of ethyl acetate).

Concentration Gradient Development. On the basis of these results, the concentration gradient method was applied to the present problem. This method had been shown to be effective for several low molecular weight compounds that could not be separated with single solvents.[10]

A preliminary test was made on PST, SM76-1, SM76H, SM65, SM50-1, SM40 and SM25 using chloroform and ethyl acetate. At the beginning of the experiment, 30 ml of chloroform was placed into the container. After the solvent front had reached a height of 2 cm from the starting line, ethyl acetate was added dropwise until its volume fraction in the mixture was 0.14 (5 ml was added). The experiment took approximately 30 min and yielded the chromatogram shown in Figure 3. It indicates that with increasing concentration of ethyl acetate, the composition of migrating components becomes increasingly rich in MA content. Consequently, a chromatogram was obtained giving higher R_f values with increasing ST content. To confirm this result, a butanone solution containing identical amounts of PST, SM76-1, SM65 and SM50 was subjected to concentration gradient development. This test showed complete separation of these polymers with respect to ST content.

Molecular Weight Dependence of R_f. It is necessary to know whether the R_f values depend upon the molecular weight of the polymer. It has been reported in the

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(10) S. M. Rybicka, *Chem. Ind.* (London), 308 (1962).

(11) H. Strain, "Chromatographic Adsorption Analysis," Interscience Publishers, New York, N. Y., 1951; H. S. Knight and S. Groennings, *Anal. Chem.*, **26**, 1549 (1954); E. Stahl, *Angew. Chem.*, **73**, 646 (1961).

TABLE IV
DEVELOPMENT WITH INDIVIDUAL SOLVENT MIXTURES OF ETHYL ACETATE AND CHLOROFORM

Volume fraction of ethyl acetate	Dielectric constant	R_f PST	SM76-1	SM65	SM40	SM25	PMA
0	4.62	>0.90	0	0	0	0	0
0.048	4.66	>0.90	0.89	0.07	0	0	0
0.200	4.80	>0.90	>0.90	>0.90	0	0	0
0.500	5.15	>0.90	>0.90	>0.90	>0.90	0	0
1.000	6.02	>0.90	>0.90	>0.90	>0.90	>0.90	0

TABLE V
MOLECULAR WEIGHT DEPENDENCE OF R_f FOR FRACTIONS OBTAINED FROM SM40

Fraction sample	Compn ST, mol %	$[\eta]^{30°}_{\text{benzene}}$	$M_v \times 10^{-4}$ [a]	R_f
3	46.3	0.727	16.6	0.44
4	46.4	0.590	12.7	0.44
5	45.0	0.475	9.64	0.45
6	44.6	0.371	7.05	0.43

[a] Estimated using eq 1 in the text.

literature that the adsorption equilibrium of polymers on a surface can be affected by molecular weight,[12] and oligomers have been fractionated in this manner with respect to molecular weight.[13]

Several fractions obtained from SM40 were subjected to concentration gradient development. For the purpose of emphasizing the effect of molecular weight upon R_f as much as possible, methyl acetate and carbon tetrachloride were used for developing, because their dielectric constants are considerably different from each other. The results are summarized in Table V. It can be seen that the R_f values are almost independent of molecular weight within the molecular weight span studied here.

Determination of the Composition Distribution Curve. Procedure. A copolymer sample, SM35H, prepared by polymerization up to a conversion of 97.8%, was subjected to the concentration gradient method. At the beginning of the experiment a mixture of methyl acetate and carbon tetrachloride (1:5 at a total volume of 30 ml) was present in the container. Methyl acetate (30 ml) was added dropwise to the mixture in such a way that the rate of addition increased with development time. The final composition of the mixture was seven parts of methyl acetate and five parts of carbon tetrachloride. The amount of SM35H in the test solution was adjusted so that each drop of 3 μl contained 100 μg, as compared to 20 μg in the preliminary experiments. Samples SM50-1, SM50-2, SM40, SM25 and PMA were developed under identical conditions in order to determine relative R_f values corresponding to each copolymer composition.

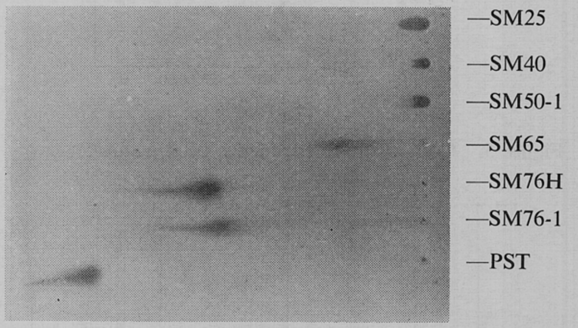

Figure 3. Chromatogram obtained by concentration gradient development of copolymers with different compositions and PST with chloroform–ethyl acetate mixture.

Quantitative Evaluation of the Chromatogram. A photograph of the chromatogram is shown in Figure 4. It indicates clearly that sample SM35H is developed not as a spot but as a band extending from the starting line, and showing a definite distribution of blackness. In order to determine whether this distribution can be correlated with different migration rates for different components in SM35H, the following test was made. Sample SM35H was developed under the same conditions as in the previous run, and the chromatogram was stained to visualize the band. The thin layer, on which the band is located, was scraped off the glass plate, and separated into three portions, *i.e.*, an upper, middle and lower portion. Each portion was treated with acetone to extract adsorbed polymer, and the composition of the extracts was determined using intensity ratios of the 1730- and 1498-cm^{-1} infrared bands characteristic of MA and ST units,[6] respectively. The results indicated that the upper portion contained copolymer species rich in ST units while the lower portion was rich in MA units. In this connection it should be noted that despite the high conversion (71.0%), the chromatogram of SM76H shows only a spot, as seen in Figure 3. This result can be explained readily

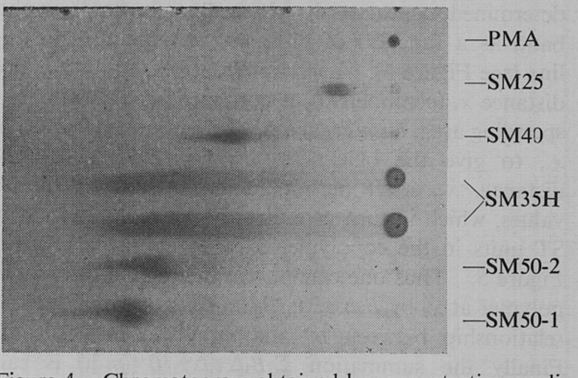

Figure 4. Chromatogram obtained by concentration gradient development of SM35H prepared at high conversion (97.8%) with carbon tetrachloride and methyl acetate.

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[12] F. Patat, E. Killmann, and C. Schliebener, *Fortschr. Hochpolym. Forsch.*, **3**, 332 (1964); R. R. Strombery, *J. Phys. Chem.*, **69**, 3955 (1965).

[13] K. Bürger, *Z. Anal. Chem.*, **169** (4), 259 (1963); K. Konishi and S. Yamaguchi, *Anal. Chem.*, **38**, 1755 (1966).

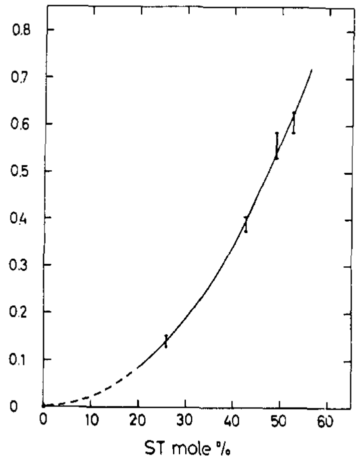

Figure 5. Composition dependence of R_f values.

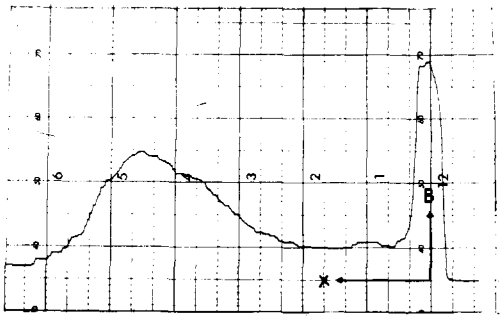

Figure 6. Photometric recording curve of blackness of the chromatographic band obtained for SM35H.

TABLE VI

COMPOSITION DEPENDENCE OF R_f

Sample	Compn ST, mol %	$R_f{}^a$
SM50-1	52.7	$0.58_4 \sim 0.62_5$
SM50-2	48.9	$0.53_0 \sim 0.58_5$
SM40	42.5	$0.371 \sim 0.48_6$
SM25	25.8	$0.12_8 \sim 0.15_2$
PMA	0	0

[a] Upper and lower limits are given.

TABLE VII

DETERMINATION OF THE COMPOSITION DISTRIBUTION CURVE FROM DENSITOMETRIC DATA

R_f	ST mole fraction, $[m_1]_i$	$B_i\Delta x_i$-Δy_i $= B_i{}^0$	$B_i{}^0/B^0$-$([m_1]_i)$ $= X_i$	(X_i/Σ_iX_i) $\times 100^a$
0.000	0.00	9.68	1.773	11.3
0.033	0.12	1.40	0.286	1.8
0.045	0.14	1.20	0.250	1.6
0.052	0.16	1.27	0.270	1.7
0.069	0.18	1.50	0.326	2.1
0.085	0.20	1.42	0.315	2.0
0.102	0.22	1.60	0.362	2.3
0.121	0.24	1.48	0.342	2.2
0.142	0.26	1.37	0.324	2.1
0.164	0.28	1.41	0.352	2.2
0.188	0.30	1.48	0.366	2.3
0.214	0.32	1.41	0.357	2.3
0.242	0.34	1.51	0.391	2.5
0.273	0.36	1.58	0.410	2.6
0.306	0.38	1.71	0.455	2.9
0.342	0.40	1.93	0.527	3.4
0.372	0.42	2.22	0.639	4.1
0.425	0.44	2.60	0.769	4.9
0.470	0.46	4.20	1.278	8.1
0.514	0.48	5.17	1.620	10.3
0.562	0.50	5.30	1.711	10.9
0.610	0.52	4.03	1.342	8.5
0.660	0.54	2.70	0.928	5.9
0.706	0.56	0.88	0.313	2.0

[a] $\Sigma_iX_i = 15.656$.

by the fact that this copolymer was prepared under nearly azeotropic conditions, as expected from the reactivity ratios reported by Alfrey, *et al.*,[14] for this monomer pair.

Before analyzing the band, the R_f values of the other copolymer samples were determined. Each spot on the thin layer is smeared to a certain extent due to tailing and other effects; consequently, for each spot, values of R_f were read off at two opposite sides. The results are given in Table VI and Figure 5, in which the R_f values are plotted against the mole fraction of ST units in the copolymer.

Figure 5 serves as a calibration curve in connection with Figure 2, in which the blackness, $B^0(m_1)$, for 40 μg of polymer, is plotted against the mole fraction of ST units. In the evaluation, apparent blackness, B, is determined continuously along the chromatographic band as a function of distance, x, from the starting line (see Figure 6). Each apparent blackness, B_i, at a distance x_i (centimeters), is corrected against the corresponding area, *i.e.*, $\Delta x_i\Delta y_i$, Δy_i being the band width at x_i, to give the blackness, $B^0{}_i$ $(= B_i\Delta x_i\Delta y_i)$. The distance, x_i, itself permits determination of the R_f values, which in turn give directly the mole fraction of ST units in the copolymer existing at x_i, $[m_1]_i$, using Figure 5. Thus one can express the relative amount of polymer at x_i by $B_i\Delta x_i\Delta y_i/B_0([m_1]_i)$ with the aid of the relationship between B^0 and m_1 given in Figure 2. Finally the summation $\Sigma_iB_1\Delta x_i\Delta y_i/B^1([m_1]_i)$ is carried out, and the relative fraction of polymer species with a known mole fraction of ST can be calculated. As is apparent from the above description, this determination can be carried out without requiring the difficult determination of the absolute blackness of the photographic plate. Table VII demonstrates the process of constructing the composition distribution curve for SM35H and the final result.

Comparison between Experiment and Theory. In Figure 7 the relative amount of each copolymer species in SM35H is plotted against the mole fraction of ST units in the form of a histogram. The arithmetic mean of the mole fractions of ST units calculated from the histogram is 0.355, in good agreement with a value of 0.342 determined by elementary analysis of this sample. In the following part this result will be confirmed by comparing it with that predicted by the theory of radical copolymerization.

The instantaneous mole fraction of monomer 1 (ST) in the monomer mixture, f_1, can be related to that

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(14) T. Alfrey, Jr., E. Merz, and H. Mark, *J. Polym. Sci.*, **1**, 37 (1946).

entering the copolymer, F_1, through the well-known equation[15–18]

$$F_1 = (r_1f_1^2 + f_1f_2)/(r_1f_1^2 + 2f_1f_2 + r_2f_2^2) \qquad (2)$$

where r_i is the reactivity ratio, and the subscripts 1 and 2 refer to ST and MA for the present case, respectively. On the other hand, the compositional changes with conversion may be described by a differential equation first derived by Skeist[19]

$$2.303 \log \frac{[M]}{[M]_0} = \int_{f_1^0}^{f_1} \frac{1}{F_1 - f_1}\, df_1 \qquad (3)$$

where [M] represents the appropriate monomer concentration, and the zero sub- or superscripts refer to initial concentrations.

Introducing literature values, $r_1 = 0.75$ and $r_2 = 0.20$,[14] the relationship between F_1 and f_1 is first established according to eq 2. Using these sets of F_1 and f_1 the integrand in eq 3 is calculated and plotted against f_1. This curve is then integrated graphically from $f_1^0 = 0.35$ (experimental condition) to a proximity of $f_1 = 0$. The upper limit of integration in this case was 0.98, making the calculated conversion, $1 - [M][M]_0^{-1}$, coincide with the experimental value. The relationship between F_1 and conversion is thus established and can be related readily to the composition distribution curve. In Figure 7 the distribution curve calculated in this manner is indicated by a fine line, while the solid line represents the experimental values. It is seen from the figure that experiment and theory are in excellent agreement. Thus it may be concluded that tlc combined with concentration gradient development can be used for determining the composition distribution curve of copolymers.

Conclusions

The last part of this paper will be devoted to a brief discussion as to what kind of copolymers tlc can be applied successfully. As has been investigated intensively by Howard and McConnell,[20] and also pointed out in this paper, the amount of macromolecules adsorbed on the silica gel surface will depend upon a competitive balance of interactions of three types, *viz.*, polymer–solvent, solvent–silica and silica–polymer.

On the other hand, for systems of copolymer and solvent, the polymer–solvent interaction generally changes with the composition of copolymer. However, it was found that this dependence was not pronounced if a fairly good solvent is used.[9,21,22] Thus one may assume that under some limited conditions, polymer–solvent interactions remain constant, independent of any compositional change.

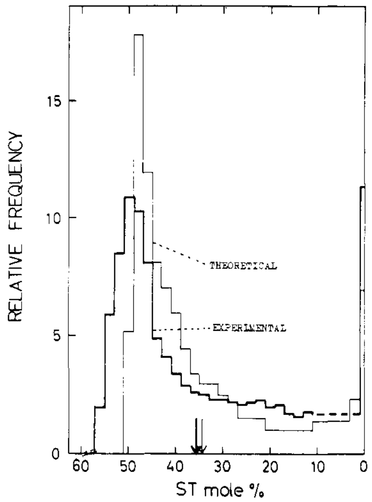

Figure 7. Composition distribution curves (histograms) obtained experimentally and theoretically for SM35H. For details, see text.

If the above assumption is valid, the conditions required for separating a copolymer with compositional heterogeneity into components having different compositions may be summarized as follows. Each component must exhibit a different silica–polymer interaction for a given composition. This means that only copolymers consisting of a combination of polar and nonpolar monomers can be resolved successfully by tlc. The degree of adsorption of such copolymers on silica gel will vary widely with any change in composition. This assumption readily explains the succcess achieved with the present copolymer.

In this connection it should be pointed out that ST–methyl methacrylate (MMA) copolymers with the same composition but different sequence lengths, *i.e.*, block, random and alternating copolymers,[23] can be separated with respect to sequence length. Preliminary experiments show that under suitable developing conditions the block polymer remains on the starting line, while the other components develop in such a way that the alternating portion exhibits a lower R_f value than the random polymer. Another interesting application of tlc is the separation of steric copolymers with respect to stereospecificity and -regularity. It was found that an atactic PMMA can be developed while an isotactic PMMA remains on the starting line. Thus it may be expected that this method will be useful for the analysis of chemical as well as steric copolymers.

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