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Study on the Feasibility of TLC/FID to Reveal Chemical Composition Distributions of Copolymers Obtained by Emulsion Processes

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Synopsis

The CCD (chemical composition distribution) of poly(styrene-co-ethyl methacrylate) has been determined by thin layer chromatography/flame ionization detection (TLC/FID). It appeared that a mixture of five reference copolymers obtained by solution polymerization each having a narrow CCD, could be separated in five distinct peaks, provided a modified spotting procedure and a concentration gradient elution technique were applied. All copolymers prepared by solution polymerization could be successfully characterized. Copolymers obtained by emulsion techniques using nonionic or anionic surfactants containing oxyethylene groups, or in the absence of chain length modifier behaved anomalously and appeared to have spurious CCD's. Also the average composition calculated from these CCD's did not agree with the average composition determined by $^1\text{H-NMR}$. This anomalous behaviour disappeared when using sodium lauryl sulfate as surfactant or when applying a chain length modifier (*n*-dodecyl mercaptan) during the preparation of the polymer. Several possibilities have been proposed in order to explain these phenomena. The most probable explanation seems to be reaction of a growing polymer chain with surfactant molecules resulting in a quasi-terpolymer. This polymer containing highly polar oxyethylene groups, remains strongly adsorbed on the silica surface during elution, thus disturbing the separation process.

INTRODUCTION

The molecular structure of copolymers is a very complicated matter since the macromolecules may not only differ in chain length and chemical composition (intermolecular structure), but also in sequence lengths and tacticity (intramolecular structure). Since the microstructure of copolymers will influence the properties of the resulting materials¹⁻⁶ there is a still growing emphasis on the development of research tools to reveal reliable information about the chain structure.

Widely used and advanced methods of determining intramolecular structures are $^1\text{H-}$ and $^{13}\text{C-NMR}$. $^1\text{H-NMR}$ has been used extensively, especially in the case of styrene-methacrylate copolymers.⁷⁻⁹ NMR results also revealed relations between sequence arrangement of the monomers and the glass transition temperature of copolymers with a narrow CCD.²⁻⁵

In order to obtain a more detailed view of the molecular structure, aimed at understanding relations between material properties and structure of copoly-

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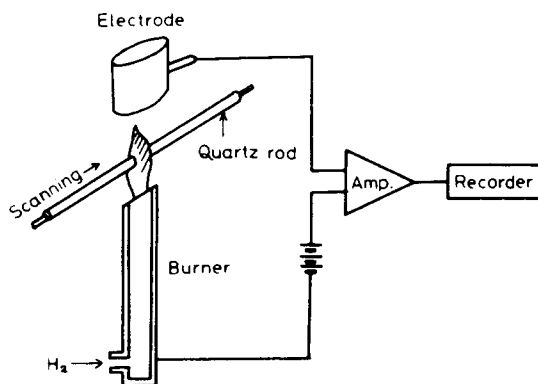


Fig. 1. Schematic diagram for FID for TLC.

mers obtained at very high conversion, it is a necessity to determine the CCD without interference caused by the molar mass distribution (MMD).

In the classical approach, this requires the laborious and time consuming fractionation using a suitable selected solvent-precipitant pair. Moreover, the MMD almost inevitably interferes with the CCD obtained by these methods.

However, with the introduction of fast and flexible chromatographic separation techniques a significant improvement could be achieved in the characterization of copolymers. For instance, thin layer chromatography (TLC) was successfully applied by Inagaki.^{12,13} Since then other chromatographic techniques were developed, e.g., high performance precipitation liquid chromatography (HPPLC) by Glöckner^{14,15} and adsorption liquid chromatography (ALC).^{16,17} The advantages of separation and detection by TLC were easily recognized. Unfortunately, the quantification of chromatograms obtained by conventional plate TLC is accompanied by several error sources.¹⁸

To cope with these difficulties, Padley¹⁹ proposed the TLC/FID technique, in which rods instead of plates were used to perform the analysis. During the last decade a scanning apparatus equipped with FID for detection and quantification has become commercially available. A schematic diagram of the instrument (Iatroscan TH-10) is shown in Figure 1. After proper reconditioning, the rods can be reused after each run, up to 40 analyses. The method was successfully applied by Min,^{20,21} Ogawa,²² and Tacx.²³

However, during our investigation serious problems, dealing with nonlinear detector response and repeated deactivation of the rods resulting in unreliable CCD's, urged us to carry through major modifications. The applicability of TLC to copolymers made by emulsion polymerization, also depends on the type of emulsifier used.

These novel findings and the feasibility of applying TLC/FID to copolymers obtained by various emulsion processes are discussed.

EXPERIMENTAL

Purification of Chemicals

The specifications of the monomers styrene (STY) (Merck) and ethyl methacrylate (EMA) (Merck), and the radical initiator AIBN (Merck p.a.) and

TABLE I
 Characteristics of Reference Styrene(1)-Ethyl Methacrylate(2) Copolymers^a

	Sample				
	S-37	S-48	S-53	S-59	S-68
Composition (mol% STY)	37	48	53	59	68

^aTotal conversions < 15%; $r_1 = 0.49$, $r_2 = 0.40$ at 335 K in toluene; cf. Ref. 26.

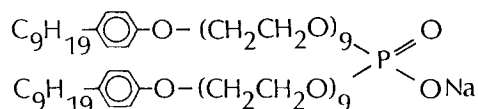
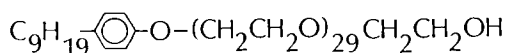
solvent have been described in detail elsewhere.²³ The other radical initiator, potassium persulfate (Merck), and the chain transfer agent, i.e., *n*-dodecyl mercaptan (Fluka), were used as supplied. The water was distilled twice and degassed by boiling before use.

Preparation of Low Conversion Solution Samples Reference Copolymers

The reference copolymers, required for calibration of the TLC/FID method of determining the chemical composition, were prepared in a stainless steel reactor (SFS). The total monomer concentration in the reactor, thermostated at 335 K, was 3 mol dm⁻³ and the initiator concentration ranged from 1.5 to 12 mmol dm⁻³ depending on the initial feed ratio. Both conversion and feed ratio were calculated from quantitatively monitoring the monomer concentration by means of GLC during the reaction. The GLC conditions have been described elsewhere.²³ The characteristics are given in Table I.

Preparation of High Conversion Emulsion Copolymers

The copolymerizations were carried out in a 1 L glass vessel. The monomers were pre-emulsified by adding them dropwise to the soap solution (Antarox CO-880 (GAF) or RE-610 (GAF) or sodium lauryl sulfate (Fluka)). The formula of these surfactants is given in Scheme 1. The pH, measured using a radiometer pHM80, was reset at pH = 8 by adding a few drops of potassium hydroxide solution (0.1*N*). Subsequently, the initiator solution (Potassium persulfate in 25 mL water) was added to the monomer emulsion, thermostated at 335 K ± 0.5. The total weight conversion was determined by solid content analysis. The feed ratio was again monitored by means of GLC. A detailed description of the GLC conditions and working-up procedures of copolymers have been given elsewhere.²³



Scheme 1.

TABLE II
Optimum-scanning Conditions for Iatroscan in the Quantification of High Molar Mass
Styrene-Ethyl Methacrylate Copolymers

Hydrogen pressure	1.1 atm
Air flow	1800 mL min ⁻¹
Scanning speed	0.42 cm s ⁻¹

RESULTS AND DISCUSSION

Calibration of FID

It appeared that extreme heating (red glow of quartz) of the rods during detection must be prevented in order to prolong reuse and maintain reproducibility. On the other hand, sufficient heating is required to ionize part of the components. So preliminary experiments were carried out, aimed at the establishment of the optimum Iatroscan scanning conditions. These results are presented in Table II.

It is a well-known phenomenon that the presence of hetero-atoms in molecules decrease the response in FID. Furthermore, during our investigation it appeared that the detector response might be a function of the development distance of the components as also reported by Parrish.²⁴

As a consequence, the response of the FID of the Iatroscan is a complex matter involving mechanical as well as chemical effects. By means of calibration, these effects must be taken into account properly in order to reveal reliable CCD's of copolymers.

After the optimum scanning conditions were established, the calibration, i.e., relative detector response versus composition, was performed. A stock solution containing four polymers, polystyrene, polyethyl methacrylate, and two copolymers were prepared. Ten rods were spotted with various amounts

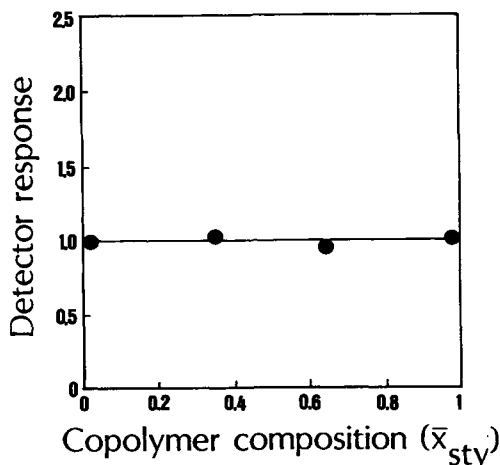


Fig. 2. Detector response in arbitrary units versus copolymer composition. The amount of each polymer ranged from 0.2 to 1.2 μ g.

ranging from 0.2 to 1.2 μg of each copolymer. Subsequently, the rods were developed under conditions mentioned elsewhere.²³ The peak areas were measured using a calibrated planimeter. The results are presented in Figure 2, where it appears that under these conditions the detector response is nearly independent of composition.

This result, which was most convenient but unexpected, must be explained by the occurrence of two competitive effects. On the one hand, the FID response is reduced when hetero-atoms are present (oxygen in ethyl methacrylate). On the other hand the component which migrated the longest distance along the rod, is detected with reduced response as compared with components that migrated a relatively short distance.

Activity of Chromarods

In conventional plate TLC, the following procedure is usually applied to accomplish separation and detection. First, the plates are activated at 110–140°C for 0.5 h and then spotted with 20–50 μg of components. After drying off the solvent, the (gradient) elution is performed. Finally, the solvent is evaporated and the spots are visualized and detected. In principle, no problems concerning the activity of the plates are met. .

Unfortunately, the activity of the rods may decrease as the number of analyses increases. In our investigation we paid much attention to maintain the appropriate activity as required for the separation of high molar mass species. The optimum conditions we found will be described in the following.

New rods are being scanned twice and then stored under nitrogen atmosphere in a water saturated vessel. After at least 24 h of storage under these conditions, the rods are activated at 140°C for 20 min, subsequently scanned twice, and then spotted with 0.2 μL solution, using four successive spotting actions. From FID scans of undeveloped rods, it appeared that the peaks pertaining to the starting material prior to separation were relatively sharp and *not* split-up. In contrast with conventional TLC spotting procedures, used in the analysis of low molar mass components, the spotted rods were not dried after spotting and prior to elution. This anomalous procedure appeared to be a prerequisite of reliable copolymer compositional separation. Since evaporation of the solvent is prevented, precipitation of the copolymer on the silica surface is avoided. Thus the copolymer remains in equilibrium with solvent and adsorbent, and as a consequence, slow redissolution leading to an apparent CCD does not occur. Furthermore, the rack containing 10 spotted rods must be placed in a vessel saturated with initial eluent. This vessel was specially designed in our laboratory for the purpose of gradient elution. A diagram is presented in Figure 3. The chamber outside the development tank guarantees a thorough mixing of solvents and prevents liquid surface waves in the development tank which might cause disturbances in the separation process. After the elution is completed the rods are dried and scanned on the Iatroscan.

The activity of the chromarods remains practically constant during the first 20 analyses and then decreases rapidly. The latter phenomenon causes a strong baseline drift, high noise level and peak broadening atypical of the actual CCD. Moreover, the average compositions calculated from those experi-

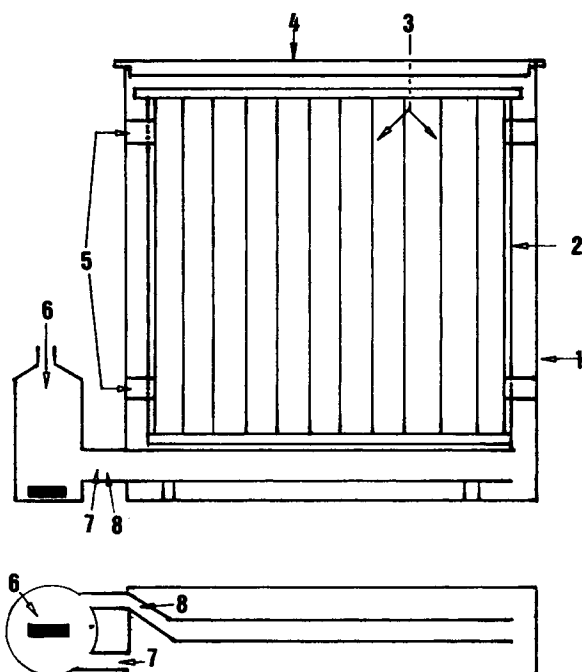


Fig. 3. Specially designed developing tank for gradient elution of 10 chromarods. (1) tank; (2) rack of 10 rods; (3) chromarods; (4) cover; (5) rack holder; (6) mixing chamber with aperture for addition of second solvent; (7) and (8) supply and discharge of solvent.

mentally observed distributions were totally unreliable. To cope with this difficulty, the rods were reactivated with chromic acid during 2–3 h. Longer treatment was found to be detrimental to the rods. In the majority of cases, this major reactivation could be carried out twice. After that, further treatment did not result in the required separation. In general a total of 30–35 analyses per rod could be carried out. All these precautions appeared to be of paramount importance to obtain reproducible and reliable separations of our high molar mass copolymers of styrene and ethyl methacrylate.

Reproducibility

The advantages of conventional TLC include flexibility, simplicity, and sensitivity. However, a rather serious disadvantage of the method lies in the quantification and reproducibility. Both drawbacks may be overcome by application of the TLC/FID technique.

In order to investigate the reproducibility of the TLC/FID in conjunction with the chromarods, four rods were spotted with a solution containing a mixture of five reference copolymers, each with a known average composition and also a narrow distribution according to chemical composition. On the remaining six rods 1.0 μg of azeotropic copolymer (53% STY) was spotted. The spotting procedure and elution were performed as described above. The chromatograms obtained from this run are presented in Figures 4(a) and 4(b).

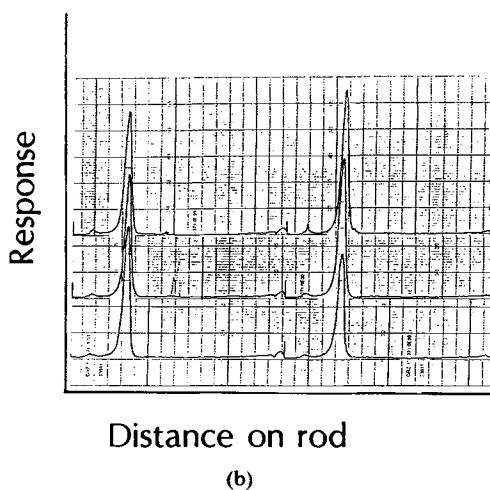
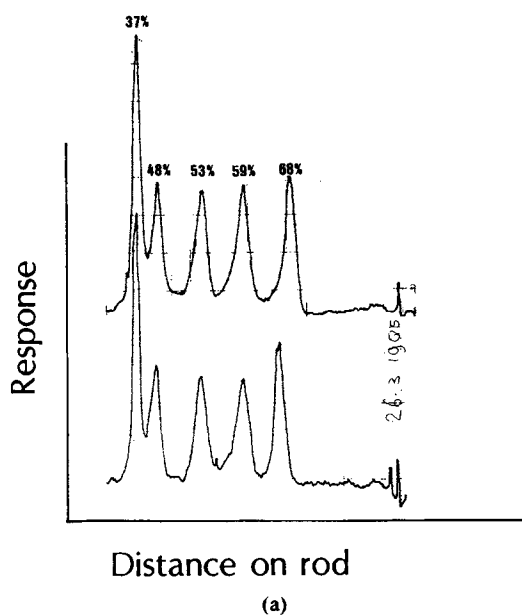


Fig. 4. (a) Reproducibility of the separation of a mixture of five reference copolymers each having a narrow distribution according to composition (duplicate measurements). Conditions: 125 mL toluene and 6 mL acetone; at solvent front positions of 2 and 4 cm, 6 and 2 mL acetone have been added successively. (b) Reproducibility of the elution of azeotropic copolymer (sixfold measurements).

From Figure 4(a), it becomes obvious that the reproducibility and resolution are beyond expectation. The R_f values calculated vary approximately 3% only. Furthermore, from Figure 4(b), one can easily verify that not only the position of the top, but also the shape of the distribution is undoubtedly reproducible.

These results unequivocally indicate that the TLC/FID technique is a very powerful tool in revealing reliable and very detailed information about the

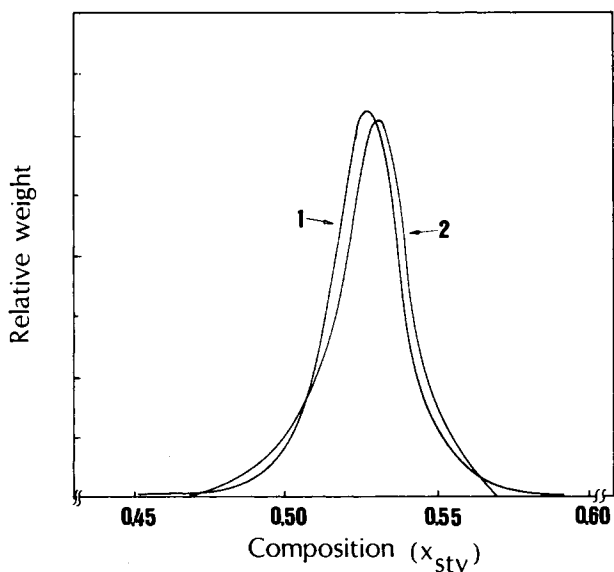


Fig. 5. Predicted (1) and observed (2) CCD of an azeotropic copolymer (STY-EMA) obtained by solution process.

intermolecular structure of copolymers provided all necessary precautions have been taken. It should be emphasized that the half peak width at the baseline is approximately 4% composition.

Now, this raises the question whether the observed chromatograms in Figure 4(b) represent the actual CCD of the copolymer. To answer this question, the chromatogram was transformed to a normalized differential weight distribution i.e., CCD. The predicted CCD was calculated using a model proposed by Tacx et al.²³ This model takes into account the conversion [Alfrey-Mayo (AM) model] as well as the instantaneous heterogeneity according to composition (extended Stockmayer model²⁵). From a separate study on the high conversion copolymerization kinetics of styrene and ethyl methacrylate, it appeared that the AM model is valid here. The theoretically predicted and experimentally observed CCD's are presented in Figure 5.

From Figure 5, it becomes clear that predicted and observed CCD's are in favorable agreement. Furthermore, it appears that the chromatographic separation causes no additional peak broadening even in the case of the rather narrow CCD's of the random copolymers. The agreement between calculated and observed CCD was also reported by Inagaki, when applying classical TLC to the characterization of styrene-methylacrylate copolymers,¹² and by Ogawa²² for styrene-acrylonitrile copolymers, although these samples were obtained by high conversion processes. Furthermore, their calculation procedures did not take into account the instantaneous CCD. In our case this would lead to unreliable predictions, since the CCD due to composition drift is relatively small as compared with the instantaneous CCD.

TABLE III
 Conditions for Emulsion Polymerization of Styrene and Ethyl Methacrylate
 (All Amounts Indicated, in grams)

	Copolymer					
	a	b	c	d	e	f
STY	153	153	40	153	153	153
EMA	146	146	—	146	146	146
Antarox CO-880	35	—	—	35	—	—
RE-610	—	15	—	—	15	—
SLS	—	—	—	—	—	3.9
K ₂ S ₂ O ₈	3.5	3.5	3.00	3.5	3.5	1.15
Water	700	700	1000	700	700	700
RSH	—	—	—	5.01	2.01	—
Temperature (°C)	67	67	62	67	67	67
Time (h)	4	4	36	4	4	4

Analysis of Copolymers Obtained by Various High Conversion Processes

The reaction conditions for the products obtained by high conversion emulsion copolymerization are summarized in Table III. In a first attempt to characterize the copolymers (a) and (b), each having an average composition of 51% STY, we observed that nearly all copolymer remained on the starting point of the rod. These copolymers were expected to show up at a value of R_f approximately 0.46 as was indeed observed for the copolymer of the same average composition but made by a solution process.

This leads to the assumption that the emulsion copolymers a and b are physically bound to the silica surface. This might be attributed to possible evaporation of solvent or the presence of very polar groups in the copolymer. Several possibilities have been considered to explain this unexpected result, viz.: (a) too high a viscosity of the solution, preventing the copolymer to migrate; (b) polar initiator end groups; (c) partial saponification of ethyl methacrylate units; and (d) highly polar surfactant molecules chemically bounded to the polymer chain.

To discriminate between the several possibilities an additional set of copolymers were prepared and characterized. Polystyrene (c) was made by soapless emulsion polymerization with persulfate as radical initiator. Under these conditions the polystyrene is expected to have a relatively high number of sulfate end groups per polymer chain. Copolymers (d + e) were prepared having the same average composition as copolymers (a) and (b) but a significantly lower molar mass. This could be achieved by addition of *n*-dodecyl mercaptan. Finally, a copolymer (f) was prepared using sodium lauryl sulfate (SLS).

The first possibility as a cause of anomalous behavior must be ruled out since copolymer (f) made by an emulsion process using SLS, migrates on the rods as would be expected on the ground of its composition, whereas solutions of polymers (f), (a), and (b) had comparable viscosities. The high polarity of

the sulfate end groups is not likely to be the cause since polystyrene (c) containing a relatively high number of sulfate end groups migrated similarly along the rod as polystyrene made by solution polymerization (initiator, AIBN). Partial saponification of em groups, resulting in highly adsorbing methacrylic acid cannot be completely ruled out, although this certainly does not play a dominant role since the elution of copolymer (f), made by an emulsion process, using SLS, was not affected by excessive adsorption.

The final possibility is regarded the predominant factor, determining the adsorption of copolymer to the silica surface. This explanation can only be true if the pure emulsifiers Antarox and RE-610 do not migrate when submitted to the elution process. This was indeed verified and leads to the conclusion that the emulsifiers Antarox and RE-610 become chemically bound to the polymer chains during emulsion polymerization. The susceptibility of hydrogen atoms of the oxyethylene groups to hydrogen abstraction is well-documented in the literature.²⁷ The relevant energy of activation is high as compared with the activation energy of the hydrogen abstraction from the mercaptan. This explains why in the presence of mercaptans during the reaction [copolymers (d) and (e)] no significant amounts of surfactant will become chemically bound. Under these conditions, the polymer will migrate along the rod exclusively according to the difference in polarity between the two monomeric units, without interference caused by a third unit, i.e., the surfactant.

In a forthcoming paper,²⁸ the influence of other conditions, like different polymerization techniques, high conversion, and compositional drift will be presented.

CONCLUSIONS

It has been shown that the TLC/FID technique is a very powerful tool in determining reliable CCD's of STY-EMA copolymers, provided some serious precautions are taken into account. Copolymers obtained by low conversion solution processes, using AIBN as radical initiator, appeared to have a very narrow distribution according to chemical composition, in complete agreement with the distribution predicted from AM kinetics. This clearly indicates the validity of the separation and quantification.

Copolymers obtained by batch emulsion processes using nonionic or anionic surfactants containing very polar oxyethylene groups, exhibited anomalous CCD's while the average compositions determined from these CCD's did not agree with the ones determined by ¹H-NMR. This behavior disappeared when using *n*-dodecyl mercaptan or when using SLS as surfactant.

This behavior was explained by transfer reaction of the growing polymer chain with the surfactant containing oxyethylene groups. In the presence of mercaptan predominant transfer to modifier occurred. When applying SLS, no transfer leading to unreliable separations showed up.

It may be concluded that TLC/FID may also supply important information about the CCD of copolymers obtained by a batch emulsion process. The reliability of the observed CCD may be checked by comparison of the average composition determined from the CCD with the one determined by, e.g., ¹H-NMR. For the present copolymers, very good agreement was found be-

tween the average compositional data obtained by these two analytical techniques.⁹

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