Thin-Layer Chromatographic Separations of Butadiene–Styrene Copolymers on the Basis of Composition and Molecular Weight

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ABSTRACT: Experimental methods have been developed for thin-layer chromatographic (tlc) separation of butadiene–styrene copolymers according to (i) composition and (ii) molecular weight. The technique of separation according to composition is based upon exploiting the adsorption of polymers from their solutions with less polar solvents through the greater adsorptivity of the relatively polar styrene units. The specific method involved is an elution gradient procedure based upon addition of a good relatively polar solvent for both polymers ($CHCl_3$) to the nonpolar solvent CCl_4. Adsorption onto silica gel during the development increases with styrene content so that high R_f values are associated with low styrene contents. The separation method for determining molecular weight distributions is based upon using solvents of marginal solubility and involves adding a highly polar nonsolvent to an initial polar solvent which precipitates the polymer during the development. Specifically CH_3OH is used as the nonsolvent and a CH_3OH–tetrahydrofuran mixture is the initial solvent. Methods of quantitatively interpreting the tlc smears to obtain compositional heterogeneity and molecular weight distribution are described. Detailed calculations for several copolymers are included.

Thin-layer chromatography (tlc) is one of the older branches of chromatography dating back about 35 years.[2a,b] It has been widely used for separating mixtures of low molecular weight organic compounds and has been the subject of treatises.[3] In the polymer industry, a common use has been the separation of low molecular weight oligomers and various additives from commercial polymers.[4] The idea that tlc might be used to separate macromolecules themselves can be traced to work reported on paper chromatography by Langford and Vaughn[5] in the late 1950's. However, the potentialities of tlc to separate polymer systems was not fully realized for another decade when a series of papers by Inagaki, Matsuda, and Kamiyama showed the ability of this technique to separate copolymers on the basis of composition[6] and extent of blocking.[7] This was soon confirmed by other research groups[8-11] on a variety of copolymer systems. Other applications of tlc to polymer systems were soon forthcoming. Poly(methyl methacrylates) were separated on the basis of tacticity[12] and polystyrenes on the basis of molecular weight.[13,14] The mechanism of tlc separations of macromolecules which seems to involve a mixture of mechanisms of adsorption and phase separation has been studied by Kamiyama and Inagaki.[15]

No commercial copolymer system is more important than that of butadiene and styrene and its many applications need not be considered here.[16-18] The very importance of butadiene–styrene copolymers has led to the commercial availability of materials of varying styrene content, butadiene microstructure, and extent of styrene blocking. Considerations of the polymerization kinetics (especially by anionic mechanisms) and reactor design for this system suggest that compositional heterogeneity may arise.[19] They are thus an opportune system for study. From a purely scientific viewpoint, butadiene–styrene copolymers present a considerable challenge in tlc for the difference in polarity between the structural units is considerably less than in the styrene–acrylate copolymers which have been previously successfully separated.[6-8] Not surprisingly the characterization of butadiene–styrene copolymers has a long history, though most effort has been associated with the measurement of molecular weight distribution and branching.[20-24,11] Investigations of compositional and microstructural heterogeneity in this copolymer system are of recent date and have utilized two different techniques, one based upon the analysis of the effluent from a gel permeation chromatograph (GPC)[25,26] and a second involving tlc.[9-11,27] The GPC method is based upon differences in molecular size[11,28,29] and one is thus unable to determine compositional and microstructural heterogeneities at constant molecular size. In other words, for example, one is unable to distinguish a mixture of two homopolymers from a copolymer even with a dual-detection system, when they are eluted at the same elution vol-

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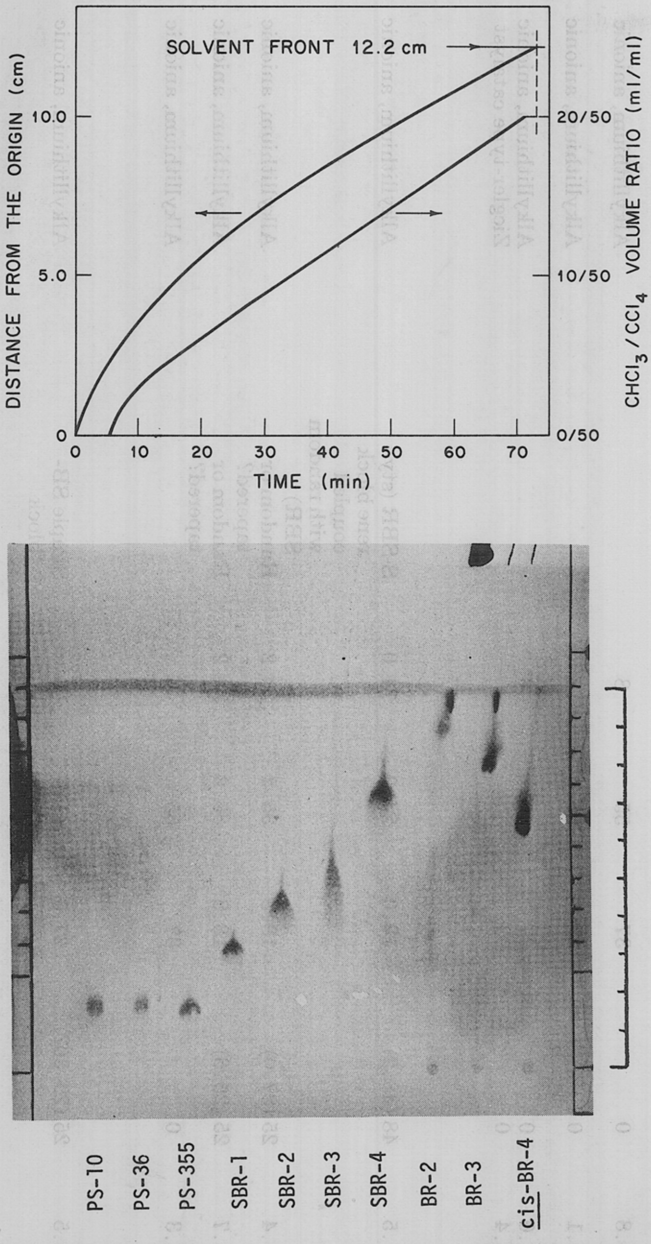

Figure 1. (a, top) A typical example of solvent front rising and a mixing pattern in a $CHCl_3$–CCl_4 elution gradient development, and (b, bottom) the chromatogram obtained in the particular run.

ume. The tlc studies while noteworthy have had incomplete success. Our purpose here is to develop a new tlc technique which can successfully separate butadiene–styrene copolymers on the basis of both composition and molecular weight.

Experimental Section

Materials. A large series of commercial polybutadienes, polystyrenes, and butadiene–styrene copolymers with range of compositions and microstructures have been studied. The polymers, their manufacturers, and approximate microstructures including styrene content, and cis-1,4, trans-1,4 and 1,2 (vinyl) content are summarized in Table I. Nominal styrene contents supplied by the manufacturers are given as well as styrene contents separately determined using uv absorption at a wavelength of 260 mμ. For preliminary tests a few other commercial polymers such as poly(methyl methacrylate) (Du Pont Lucite 147), polystyrene (Dow Chemical Styron 678), and polyisobutylene (Enjay Vistanex L100) were also used.

Procedure. GPC traces were obtained on each of the polymers studied using standard experimental techniques. The solvent was tetrahydrofuran and the experiments were carried out at 25°C using a bank of 10^6, 10^5, 10^4, and 10^3 Å columns.[11]

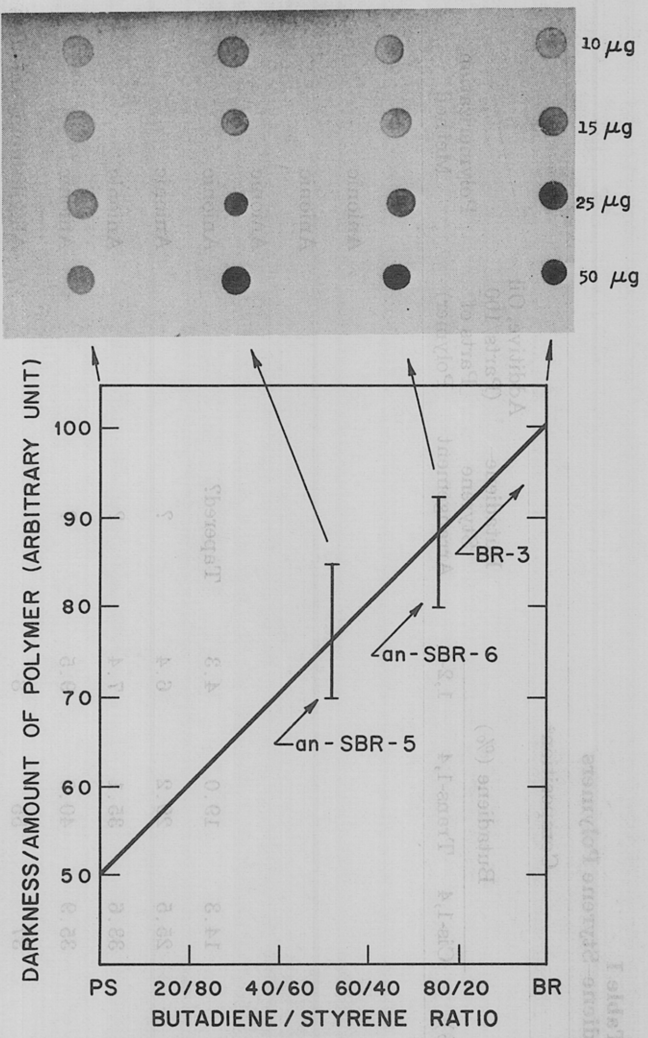

Figure 2. Plot of darkness intensity per unit mass *vs.* styrene content for SBRs on tlc plates.

The stationary phase for the tlc experiments was Merck silica gel G which contains gypsum. One part (10 g) of this was slurried with two parts (20 ml) of water and applied as the stationary phase on a thick glass plate. A commercially available apparatus was used to adjust the thickness of the layer to 250 μ. The gel phase was activated by heating to 120° for more than one hour before use. Usually 20–50 μg of polymers was spotted on the gel layer at a 2-cm distance from the edge, by means of drops of a stock solution from a microsyringe. The tlc stock solutions were 1% by weight in toluene. The plate was dried for several minutes and then placed into a vessel containing the developing solvent. The developing solvent rose through the gel layer by capillary action. The solvent front was usually allowed to travel a distance of 15 cm from the edge. The plate was then removed from the vessel, dried in a hood at room temperature, and/or heated in an oven at 60–100°. The choice depended upon the solvents employed.

In many experiments, a gradient elution technique[6] was used. Here a second solvent was added after the front of an initial solvent (or solvent mixture) reached a distance of 5 cm from the edge. The second solvent was added first rapidly and then gradually in such a way that as the solvent front advanced 1 cm, a roughly equal amount of the second solvent was added and that by the time when the front reached the distance of about 15 cm from the edge the desired final composition has been achieved. A typical elution pattern is shown in Figure 1a, in which 20 ml of $CHCl_3$ was added to 50 ml of CCl_4 during the total developing time of about 70 min. Figure 1b shows a chromatogram obtained in this particular run.

In order to visualize the polymer spots various solutions were sprayed onto the plates. These included: (i) a 1% I_2–methanol solution; (ii) a saturated solution of Thymol Blue in a 50:50 volume mixture of ethanol and water followed by spraying with a 3 *N* H_2SO_4 solution; (iii) 5% $KMnO_4$–8 *N* H_2SO_4 solution; (iv) 3 *N*

Table I
Structure of Butadiene–Styrene Polymers

				Composition[a]						
					Butadiene (%)					
Designation	Source of Polymer	$10^{-3} M_n$	M_w/M_n	Styrene (%)	Cis-1,4	Trans-1,4	1,2-	Butadiene–Styrene Arrangement	Additive, Oil (Parts/100 Parts of Polymer)	Polymerization Method
Reference polymers										
PS-10	Pressure chemical polystyrene	9.6	1.1	100						Anionic
PS-36	Pressure chemical polystyrene	36	1.1	100						Anionic
PS-355	Pressure chemical polystyrene	355	1.1	100						Anionic
SB-1	Phillips Petroleum experimental polymer	146	1.3	62.4	14.3	19.0	4.3	Tapered?		Anionic
SB-2	Phillips Petroleum experimental polymer	104	1.3	38.9	25.5	29.2	6.4	?		Anionic
SB-3	Phillips Petroleum experimental polymer	61.5	1.3	23.9	33.6	35.1	7.4	?		Anionic
SB-4	Phillips Petroleum experimental polymer	102	1.4	14.6	35.9	40.0	9.5	?		Anionic
BR-1-8	Fraction from Phillips Petroleum Solprene 245	16.2	3.2	0	37	55	8			Alkyllithium, anionic
BR-1-5	Fraction from Phillips Petroleum Solprene 245	86.7	2.2	0	37	55	8			Alkyllithium, anionic
BR-1-1	Fraction from Phillips Petroleum Solprene 245	87.3	2.8	0	37	55	8			Alkyllithium, anionic
BR-2	Phillips Petroleum Solprene 201	109	3.1	0	37	55	8			Alkyllithium, anionic
BR-3	Firestone Diene 55	101	3.0	0	37	55	8			Alkyllithium, anionic
Cis-BR-4	Phillips Petroleum cis-4, Solprene 1203	119	3.4	0	93					Ziegler-type catalyst
Alkyllithium polymers. I										
an-SBR-5	Phillips Petroleum Solprene 303	102	1.5	48 (48.2)	19.0	24.0	14.0	S-SBR (styrene block coupled with random SBR)		Alkyllithium, anionic
an-SBR-6	Phillips Petroleum Solprene 300	104	2.4	25 (27.0)	18.8	35.2	20.2	Random or tapered?		Alkyllithium, anionic
an-SBR-7	Phillips Petroleum Solprene 301	122	1.7	25 (25.6)	18.8	35.2	20.2	Random or tapered?		Alkyllithium, anionic
an-BR-5	Phillips Petroleum Solprene 203	109	4.3	0	37	55	8			Alkyllithium, anionic
Alkyllithium Polymers. II										
an-SBR-8	Phillips Solprene 1205 simple SB block copolymer	51.9	1.5	25 (29–30?)	27.5	41.5	6	Simple SB-block		Alkyllithium, anionic

an-SBR-9	Firestone Stereon 700	88.5	2.6	20.5 (22.2)	31.8	41.5	6.4	Tapered?		Alkyllithium, anionic
an-SBR-10	Firestone Stereon 720	84.5	2.3	10 (13.4)	36	46.8	7.2	Tapered?		Alkyllithium, anionic
an-SBR-11	Shell Chemical Kraton 1101, mixed SBS block copolymer	56.1	1.4	(33.5–36)	24	36	5	Mixed block styrene–butadiene styrene		Alkyllithium, anionic
Emulsion polymers										
em-SBR-12	Firestone FRS 206	41.3	9.5	23 (29–34?)	17.0	46.0	14.0	Random		Hot (50°) emulsion free radical
em-SBR-13	Texas US Chemical Synpol 8227	149	6.4	34.5	10.0	44.5	11.0	Random	37.5	Cold (5°) emulsion free radical
em-SBR-14	Texas US Chemical Synpol 1500	72	5.4	23.5	11.5	52.0	13.0	Random		Cold (5°) emulsion free radical
em-SBR-15	Texas US Chemical Synpol 1712	115	7.1	23.5	11.5	52.0	13.0	Random	37.5	Cold (5°) emulsion free radical
em-SBR-16	Texas US Chemical experimental polymer	102	6.4	15.5	12.5	57.5	14.5	Random	37.5	Cold (5°) emulsion free radical
em-BR-6	Texas US Chemical Synpol 8407	85	8.0	0	10	70	20		37.5	Cold (5°) emulsion free radical

[a] Microstructures are on the basis of weight per cent of total polymer.

H_2SO_4 solution followed by charring at 120°C. All of these techniques worked well for polybutadiene, butadiene-styrene copolymers, and poly(methyl methacrylate). They were rather poor for polystyrene and not too good for polyisobutylene depending upon the developing solvent, drying conditions, etc. System ii (Thymol Blue-methanol-water + 3 N H_2SO_4) was concluded to be the best for the polybutadiene-(butadiene-styrene copolymer)-polystyrene system and was generally used. Visualized chromatograms were recorded on high contrast film, each with a few different exposure speeds.

For quantitative analysis of spot darkness (recorded on a film), we proceeded in the following manner. First we must establish a calibration of darkness intensity versus amount of polymer, which might not be a linear function over a wide range of polymer quantity. Secondly the darkness intensity of a specific amount of polymer may vary with styrene content. To investigate these, stock solutions each containing a known amount (5 g/l.) of the polymers, polystyrene (PS), 48% styrene SBR (an-SBR-5), 25% styrene SBR (an-SBR-6), and polybutadiene (BR-3) were placed on chromatoplates in some cases to give spots having nearly the same size but different amounts of the polymers (*e.g.*, Figure 2), and in some other cases to give spots having different sizes but nearly the same mass density (*i.e.*, the amount of polymer per unit area). The plates were dried, and the spots were visualized and photographed each with a few different speeds. Then the darkness of each spot was determined by photodensitometric tracings. In one trial each spot was scanned using a thin rectangular slit of relatively large width (comparable to the largest spot size). Then the intensity profile was graphically integrated to obtain the darkness of the spot. In the other trial, intensity determinations were made at several different positions on each spot with a square aperture sufficiently smaller than the smallest spot. Then the average value of the intensities was multiplied by the spot area to obtain the darkness of the spot. This latter method is essentially the same as the one employed earlier by Inagaki *et al.*[6] in the first successful attempt at quantitative analysis of compositionally heterogeneous (styrene-methyl acrylate) copolymers.

Obviously absolute values of the darkness of a spot or a series of comparable spots varied somewhat from one tracing to the next depending on various factors such as visualization condition, exposure speeds, scanning procedures, etc. However we found that a series of tracings for each polymer species yield a fairly linear darkness *vs.* amount of polymer relationship which does not level off until the spot density reaches to a very high level. Since the spot density on a film involves two factors, *i.e.*, the actual mass density and the film density, the latter can be adjusted to accommodate fairly high mass density spots (perhaps up to about 200-μg/cm^2 level or more), by sacrificing the sensitivity toward very low-density spots. Furthermore we noticed that when the specific darkness (– the darkness/amount of polymer) is compared for different polymer spots in the same series of tracings, they invariably give nearly the same dependence on styrene content. The specific darkness *vs.* styrene content relation is shown in Figure 2. In short the relation is relatively insensitive to the particular visualization, photographing, and tracing procedures when the conditions are adequately chosen (*e.g.*, adequate choice of sample size, uniform spraying of visualizing agent, adequate choice of exposure speed, etc.). As to the two tracing procedures we should give the following comments here. The tracing with a thin rectangular aperture shows poor response toward a spot of very high density and small size (compared with the aperture width). The amount of polymer often tends to be underestimated. On the other hand, the multiple tracing with a very small aperture often shows poor performance for a spot with nonuniform blackness in the direction perpendicular to the scanning direction, which is often the case for spots or smears on an actual chromatogram. Neither of the methods works well for a spot of highly distorted shape and nonuniform density. This should be avoided by choosing adequate elution conditions, in the first place. We should add one more comment here. Namely, we have just mentioned that even fairly high mass density spots can be handled adequately by the photodensitometric tracing in the calibration experiments. This does not at all imply that one can place a large amount of sample in the actual tlc experiments. An overloading of a sample will surely result in an artifact yielding a highly irregular spot.

Results and Discussion

GPC Analysis of Molecular Weight Distributions. The GPC traces for the different polymers and homopolymers studied were converted to molecular weight distributions. For the polystyrenes investigated the conversion was carried out directly using the polystyrene calibration standards supplied by Waters Associates. For the polybutadienes and low styrene (25% or less)-butadiene copolymers, the conversion was carried out using a factor of 0.6 of the polystyrene molecular weight as recommended by our earlier work.[11] No correction for axial dispersion[30-32] was made. (It is our experience that such corrections are of the same order (or less) as the accuracy of measurements for molecular weight distribution in polydisperse polymers.) The results are summarized in Table I. Certain general but well-known conclusions can be drawn, in particular, the broad molecular weight distributions of the emulsion-polymerized elastomers as opposed to those polymerized by alkyllithium catalysts, and the intermediate molecular weight distributions of the Ziegler catalyst polymerized high *cis*-polybutadienes.[11]

Tlc Studies with Single Solvents, General. The tlc data are expressed in terms of R_f values which represent the movement of the polymeric species along the plate relative to the solvent front. Values of R_f are in the range from 0 to 1.0. Table II summarizes data for R_f values of poly(methyl methacrylate), polystyrene, butadiene–styrene copolymers (SBR) of different styrene content, polybutadienes (BR) of different microstructure, and polyisobutylene in single solvents. The list is more extensive than that of other works and we summarize the data in terms of the ordering of dielectric constant, ϵ, and solubility parameter δ.[33,34]

For all solvents above methyl ethyl ketone and below CCl_4 there is no development of any polymer except polyisobutylene in the chromatogram. Intermediate solvents like tetrahydrofuran (H_4furan), toluene, benzene, and xylene which are good solvents for both polystyrene and polybutadiene completely develop all polymers except poly(methyl methacrylate) giving R_f values of about 1.0. Partial development is found for solvents in the upper solubility parameter and dielectric constant range such as ethyl acetate. It is also seen to a lesser extent in CCl_4 on the low-solubility parameter side. Ethyl acetate is the best individual solvent for optimizing differential development of the polymers studied.

Interpretation of Single Solvent Tlc Experiments. These results may be interpreted in the following manner. For a polymer to be completely developed (R_f 1), two criteria must be satisfied. First the polymer must be soluble in the solvent. Otherwise the polymer spot will simply remain at its starting point. Secondly the solvent must be as polar or more polar than the polymer, so that the solvent molecules will be adsorbed to a greater extent on the silica gel substrate, releasing the polymer molecules from the substrate to be developed. Thus consider polystyrene in the series of solvents investigated. No development is possible in CH_3OH, acetone, or *n*-heptane because the polymer does not dissolve in these solvents. Polystyrene is soluble in CCl_4 but no development is possible because its greater polarity results in it being strongly adsorbed by the silica gel. In *p*-xylene, benzene, toluene, $CHCl_3$, H_4furan, ethyl acetate, and methyl ethyl ketone, the polystyrene is soluble and is fully developed because the solvents are as polar or more polar than the polymer. The same tendencies may be seen in the considerably more polar poly(methyl methacrylate) which is (i) insoluble and undeveloped in CH_3OH, *n*-heptane, and cyclohexane; (ii) soluble but is not developed in the less polar CCl_4, *p*-xylene, benzene, toluene, and $CHCl_3$; (iii) soluble and developed in the very polar H_4furan, ethyl acetate, methyl ethyl ketone, and acetone. An extreme case showing the same behavior is the very nonpolar polyisobutylene which is insoluble and undeveloped in CH_3OH, methyl ethyl ketone, and ethyl acetate; but is fully developed in every listed solvent in which it dissolves for these are all as polar or more polar.

Two criteria may be seen to exist for choosing developing solvents to separate different polymeric species spotted on a thin silica gel layer. These are distinctions in solubility and distinctions in polarity. The choice of solvents for the different types of separation may be based upon classifying them (relative to each polymer) in the following four groups: (1) more polar (larger dielectric constant, ϵ) and nonsolvent (large difference solubility parameter $|\delta_{\text{solv}} - \delta_{\text{polymer}}| = \Delta\delta$); (2) more polar (larger ϵ) and solvent (moderate $\Delta\delta$); (3) less polar (smaller ϵ) and solvent (moderate $\Delta\delta$); (4) less polar (smaller ϵ) and nonsolvent (large $\Delta\delta$). Tlc separations based upon phase separation due to solubility would use solvents which are in group 1 (or 4) for one of the polymers and group 2 for the other. Separations based upon adsorption would involve a solvent in group 2 for one polymer and group 3 for the other. The use of solubility may be seen in separation of polystyrene and poly(methyl methacrylate) with acetone, which is in group 1 for the former and group 2 for the latter and polystyrene and polyisobutylene with *n*-heptane which is in group 4 for the former and in group 2 for the latter. The adsorption mechanism may be used in separating the same two pairs of polymers with benzene and CCl_4, respectively. Benzene is in group 2 for polystyrene and group 3 for poly(methyl methacrylate) while CCl_4 is in group 3 for polystyrene and group 2 for polyisobutylene.

The problem of separating the butadiene–styrene copolymer system should now be very clear. There are only very minor differences in solubility and polarity between polystyrene and polybutadiene. Methyl ethyl ketone and ethyl acetate are in group 2 for polystyrene and group 1 for polybutadiene and thus allow solubility based separations. The copolymers are partially developed by ethyl acetate, but exhibit no development in the methyl ethyl ketone. CCl_4 which is in group 3 for polystyrene and in group 3 but near the group 2 interface for polybutadiene allows some adsorption based separation.

There is a serious possible aberration of solubility based tlc separations of copolymers according to composition for the solubility of copolymers varies considerably with molecular weight as well as composition. Indeed solubility has long been known as method of fractionation of polymers on the basis of molecular weight[35] and this technique has been frequently used on polybutadienes and butadiene–styrene copolymers.[20-22] Kamiyama and Inagaki[15] have argued that tlc separations of polystyrene according to molecular weight proceed by a solubility-phase separation mechanism. In our earlier paper we proposed ethyl acetate based systems to separate butadiene–styrene copolymers according to composition.[11] However our increased realization of possible molecular weight effects has led us to be wary of problems in this procedure.

What may we say about adsorption mechanism schemes for tlc separations according to composition. While there have been some studies[36-40] of molecular weight effect in adsorption onto various adsorbents including silica[37,39,40]

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Table II
R_f Values for Single Solvent Systems[a]

			Values of R_f						
Solvent	Dielectric Constant, ε	Solubility Parameter,[b] δ	PMMA 8.9 ~ 12.7[e]	PS 8.5 ~ 10.6[e]	an-SBR-5 B–S = 52:48 8.5 ~ 9.0[e]	an-SBR-6 B–S = 76:24 8.1 ~ 8.6[e]	BR-3 8.1 ~ 8.6[e]	cis-BR-4[e]	PIB 7.1 ~ 8.3[e]
CH_3OH	32.6	14.5	0 (N)[c]	0 (N)	0 (N)	0 (N)	0 (N)	0 (N)	0 (N)
Acetone	21.3	9.9	0.9–1.0	0 (N)	0 (N)	0 (N)	0 (N)	0 (N)	0 (N)
Methyl ethyl ketone	18.5	9.3	0.9–1.0	1.0	0 (N)	0 (N)	0 (N)	0 (N)	0 (N)
Ethyl acetate	6.02	9.1	1.0	1.0	0.7–0.9[d]	0–0.4[d]	0 → (N)	0 → (N)	0 (N)
Tetrahydrofuran	7.42	9.4	1.0	1.0	1.0[d]	1.0[d]	1.0[d] (?)	1.0[d] (?)	1.0 (?)
$CHCl_3$	4.62	9.3	0	1.0	0.8–1.0[d]	0.8–1.0[d]	0.7–1.0[d]	0.8–1.0[d]	1.0
Toluene	2.38	8.9	0	1.0	1.0[d]	1.0[d]	1.0[d]	1.0[d]	1.0
Benzene	2.28	9.2	0	1.0	1.0[d]	1.0[d]	1.0[d]	1.0[d]	1.0
p-Xylene	2.27	8.8	0 (θ)	1.0	1.0[d]	1.0[d]	1.0[d]	1.0[d]	1.0
CCl_4	2.238	8.6	0 (N)	0	0	0	0 → 0.4	0 → 0.1	1.0
Cyclohexane	2.023	8.2	0 (N)	0 (θ)	0	0	0	0	1.0
n-Heptane	1.9	7.4	0 (N)	0 (N)	0 (N)	0	0	0	0.8–1.0

[a] Materials are: PMMA = DuPont Lucite 147; PS = Dow Styron 678; PIB = Enjay Vistanex L100. [b] Solubility parameter values were taken from ref 34. [c] (N) indicates the polymer is not soluble; (θ) indicates θ solvent. [d] Also spot at zero. [e] Solubility parameters of polymers studied.

Table III
R_f Values for $CHCl_3$–CCl_4 and H_4furan–CH_3OH Systems with Fixed Composition

Solvent (v/v)	PMMA	PST	an-SBR-5 B–S = 52:48	an-SBR-6 B–S = 76:24	BR-3	cis-Br-4	PIB
$CHCl_3$–CCl_4							
0:100	0	0	0	0	0	0	1.0
10:90	0	0	0	0–0.24	0.66–0.9[a]	0.8–0.9[a]	1.0
20:80	0	0	0.1–0.35[a]	0.6–1.0[a]	0.8–1.0[a]	0.8–1.0[a]	1.0
40:60	0	0.9–1.0	0.9–1.0[a]	0.7–1.0[a]	0.7–1.0[a]	0.8–1.0[a]	1.0
H_4furan–CH_3OH							
100:0	1.0	1.0	1.0[a]	1.0[a]	1.0[a]	1.0[a]	1.0
80:20	0.9–1.0	0.8–1.0	0.6–0.7[a]	0.5–0.6[a]	0.3–0.5[a]	0.3–0.6[a]	0
75:25	0.9–1.0	0.8–1.0	0.6–0.7[a]	0.4–0.6[a]	0.25–0.5[a]	0.25–0.5[a]	0
70:30	0.9–1.0	?	0.4[a]	0.25[a]	0.25–0.6[a]	0.25–0.6[a]	0
60:40	0.9–1.0	0.1–0.3	0	0	0	0	0
50:50	0.9–1.0	0	0	0	0	0	0
30:70	0.9–1.0	0	0	0	0	0	0
0:100	0	0	0	0	0	0	0

[a] Also spot at zero.

the situation is not entirely clear because of molecular sieving effects[38,41] and apparent differences in molecular weight dependence upon adsorption rates and equilibrium.[42] However after a study of the literature, one can only conclude that the dependence of adsorption upon molecular weight is considerably weaker than that of solubility, as far as the tlc separation is concerned.

Tlc Separation of Styrene–Butadiene Copolymers, Preliminary. It was clear to us that no individual solvent that we studied was good enough to carry out a separation of butadiene–styrene copolymers according to composition. Ethyl acetate or methyl ethyl ketone based schemes seem questionable because of the solubility mechanisms involved. Only CCl_4 has the proper level of polarity to distinguish at all between the polymers with respect to adsorption. However the adsorption of the polymers is too strong. It thus seemed reasonable to look at mixtures of a solvent in group 3 (*e.g.*, cyclohexane or CCl_4) and a second solvent which is in group 2 with respect to both polystyrene and polybutadiene. Such a second solvent should decrease the strength of adsorption of both styrene and butadiene units.

From Table II we selected several binary solvent mixtures to check the adequate level of composition for separating the polymers. They included H_4furan–cyclohexane, toluene–cyclohexane, benzene–cyclohexane, H_4furan-CCl_4, and $CHCl_3$–CCl_4. From these systems we have chosen $CHCl_3$ as a suitable second solvent to add to a first solvent CCl_4. Table III summarizes R_f values for the several reference polymers developed with $CHCl_3$–CCl_4 mixtures with varying compositions.

Tagata and Homma[19] have applied a system based upon cyclohexane and benzene to butadiene–styrene copolymers. Here cyclohexane plays a role similar to CCl_4 as the low polarity solvent and benzene a role equivalent to $CHCl_3$. We have tested this solvent system and found that the R_f values of polystyrenes are slightly dependent on molecular weight. Empirically this seems to be related to the small difference in dielectric constant between the two solvents and has been observed by Inagaki[27] in other systems. The reasons for this are not obvious.

To devise a tlc scheme to separate polymers according

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Table IV
Summary of Quantitative Tlc Studies

				Results of $CHCl_3$–CCl_4 Systems				Results of H_4furan–CH_3OH Systems			
	Characteristics				Compositional Heterogeneity				Mol Wt Distribution		
Designation	10^{-3} M_n	M_w/M_n	% Styrene	R_f Values ($CHCl_3$–CCl_4) = 0:50, 20:50	ST	% Variance	Residue at Origin (%)	R_f Values (H_4furan–CH_3OH) = 30:20, 70:20	10^{-3} M_n	M_w/M_n	Residue at Origin (%)
Reference polymers											
PS-10	9.6	1.1	100	0.18 (0.10–0.22)			0	[0.76–0.83]			0
PS-36	36	1.1	100	0.16 (0.12–0.22)			0	[0.67–0.70]			0
PS-355	355	1.1	100	0.16 (0.12–0.22)			0	0.51 (0.49–0.53)	339	1.01	0
SBR-1	146	1.3	62.4	0.31 (0.24–0.36)^{a}	63.1	0.003	8.3	0.46 (0.42–0.52)^{a}	109	1.04	24
SBR-2	104	1.3	38.9	0.41 (0.32–0.49)^{a}	38.2	0.006	7.9	0.38 (0.34–0.44)^{a}	101	1.05	49
SBR-3	61.5	1.3	23.9	0.45 (0.31–0.61)^{a}	28.2	0.012	7.2	0.30 (0.26–0.36)^{a}	102	10.6	33
SBR-4	102	1.4	14.6	0.71 (0.62–0.79)^{a}	12.9	0.000	6.0	0.26 (0.22–0.35)^{a}	101	1.08	51
BR-1-8	16.2	3.2	0	0.96 (0.80–1.00)^{a}				[0.20–0.37]^{a}			
BR-1-5	86.7	2.2	0	0.96 (0.80–1.00)^{a}				[0.80–0.23]^{a}			
BR-1-1	87.4	2.8	0	0.96 (0.80–1.00)^{a}				[0.80–0.26]^{a}			
BR-2	109	3.1	0	0.96 (0.82–1.00)^{a}				0.14 (0.08–0.28)^{a}	187	1.4	68
BR-3	101	3.0	0	0.95 (0.73–1.00)^{a}				0.14 (0.07–0.28)^{a}	194	1.4	129
cis-BR-4	119	3.4	0	0.63 (0.54–0.80)^{a}				0.15 (0.06–0.30)^{a}	175	1.5	110
Alkyllithium polymers. I											
an-SBR-1	102	1.5	48.2	0.34 (0.25–0.41)^{a}	55.4	0.006	17.6	0.45 (0.40–0.50)^{a}	85.4	1.1	100
an-SBR-6	104	2.4	27.0	0.45 (0.34–0.61)^{a}	26.9	0.007	13.2	0.39 (0.32–0.45)^{a}	67.5	1.2	157
an-SBR-7	122	1.7	25.6	0.42 (0.28–0.55)^{a}	35.0	0.011	41.3	0.38 (0.32–0.45)^{a}	81.1	1.1	63
an-BR-5	109	4.3	0	0.96 (0.82–1.00)^{a}				0.16 (0.08–0.27)^{a}	339	1.7	117
Alkyllithium polymers. II											
an-SBR-8	41.3	9.5	25 (29?)	0.43 (0.29–0.54)^{a}	32.9	0.009	10.4	0.34 (0.26–0.43)^{a}	58.6	1.2	32
an-SBR-9	88.5	2.6	22.2		19.4	0.012	8.5	0.28 (0.18–0.44)^{a}	57.6	2.3	48
			(22.3%)	0.40 (0.33–0.49)^{a}	38.2	0.005					
			(77.7%)	0.72 (0.60–0.81)	13.8	0.000					
an-SBR-10	84.5	2.3	13.4		15.6	0.012	8.2	0.23 (0.11–0.40)^{a}	70.6	2.6	38
			(64.8%)	0.49 (0.36–0.68)^{a}	23.0	0.003					
			(35.2%)	0.96 (0.92–1.00)	0	0.000					
an-SBR-11	56.1	1.4	33.5	0.42 (0.30–0.51)^{a}	35.3	0.006	8.5	0.38 (0.35–0.50)^{a}	45.1	1.3	48
Emulsion polymers											
em-SBR-12	41.3	9.5	25 (29?)	0.70 (0.54–0.83)^{a}	14.1	0.001	42.7	0.39 (0.28–0.56)^{a}	9.9	2.5	144
em-SBR-13	149	6.4	39.5	0.39 (0.22–0.63)^{a,b}	43.4	0.023	36.5^{b}	0.34 (0.21–0.52)^{a,b}	63.8	3.8	43^{b}
em-SBR-14	72	5.4	23.5	0.50 (0.32–0.83)^{a}	22.5	0.012	20.7	0.26 (0.14–0.52)^{a}	63.6	3.5	64^{b}
em-SBR-15	115	7.1	23.5	0.44 (0.27–0.74)^{a,b}	27.0	0.014	41.6^{b}	0.27 (0.10–0.47)^{a,b}	61.3	5.4	94^{b}
em-SBR-16	102	6.4	15.5	[0.69–0.95]^{a,b}			*b*	0.21 (0.09–0.39)^{a,b}	98.3	3.8	110^{b}
em-BR-6	85	8.0	0	0.82 (0.79–1.00)^{a,b}			*b*	0.16 (0.04–0.39)^{a,b}	101	5.2	110^{b}

[a] Also spot at zero. [b] Also spot at an R_f of 1 due to additives.

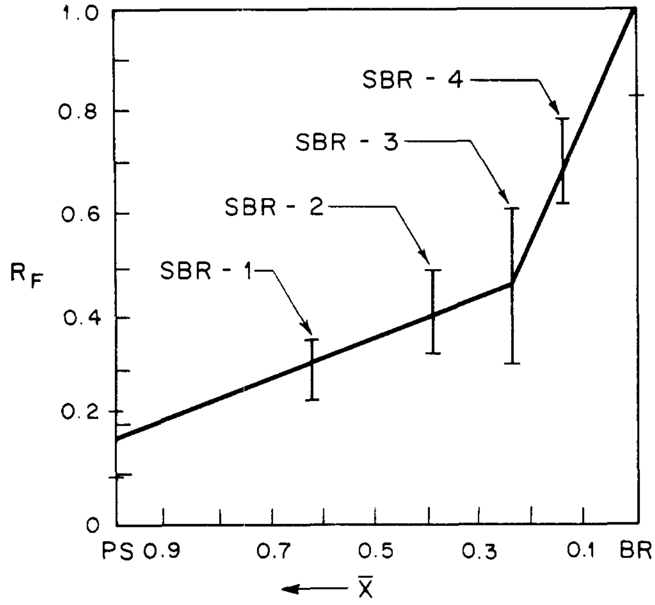

Figure 3. Establishment of calibration of tlc plate with narrow compositional and molecular weight distribution samples for the purpose of studying compositional heterogeneity.

to molecular weight rather than composition, one must use a solubility mechanism. Polystyrenes have been separated by different researchers on the basis of molecular weight using mixtures of group 1 and group 2 solvents. Otocka and Hellman[13] have used acetone-$CHCl_3$, while Kamiyama, Matsuda, and Inagaki[14] have shown that acetone-benzene has utility. The latter authors have shown that a much better separation is possible using a quaternary system acetone-ethanol-butanone-benzene, all of which are group 1 or group 2 solvents with respect to polystyrene. Separations might also be possible using group 2 and group 4 solvents. However adsorption phenomena would certainly become involved. As the molecular weight dependence of adsorption is as we have mentioned much weaker than solubility, such a solvent mixture would probably not be effective. Our interest in this paper is in copolymers where we may have compositional as well as molecular weight heterogeneity and thus adsorption phenomena are to be avoided. Again we tested several binary mixtures from Table II and have chosen to use CH_3OH, a group 1 solvent together with H_4furan a group 2 solvent. Table III also summarizes R_f values for the reference polymers developed with H_4furan-CH_3OH mixtures of varying compositions.

A crucial problem which arises during the development of the diene polymers is that usually two (or more) spots were observed, one always located at the origin (R_f 0). The same observation was made earlier by Quisenberry[10,11] who argued that the spot at zero is an impurity, probably gels. Exposure to light during the development was suspected to be a cause of such gels. Therefore development was attempted in a darkroom to avoid exposure to light. The attempt however did not help reduce the spot at zero. The presence of this spot may cause difficulty in making a quantitative analysis, in the sense that the polymer eluted to form the main spot might not be representative of the whole polymer samples placed initially at the origin.[9]

Another interesting detailed observation in the development using H_4furan-CH_3OH systems was that polystyrene migrated toward the interface between the glass plate and the silica gel layer and often becomes hardly visible from the silica gel side, but you can locate the spot by looking from the reverse side. This could be a drawback for using this eluting system. Similar behavior has been found for other systems.

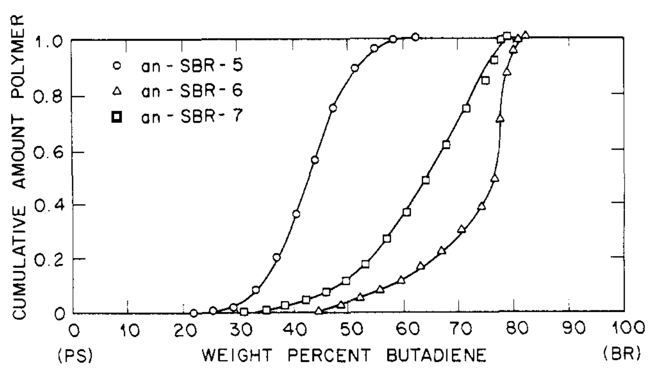

Figure 4. Integral compositional distribution curves for some alkyllithium-polymerized SBRs from tlc experiments.

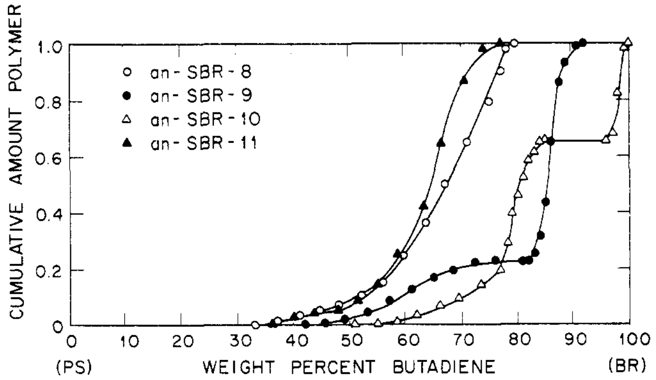

Figure 5. Integral compositional distribution curves for some alkyllithium-polymerized SBRs of block or tapered structure from tlc experiments.

Tlc Method for Determining SBR Compositional Heterogeneity. We will now attempt to apply this technique as an analytical tool to study compositional heterogeneity in the copolymers investigated. A limited number of narrow compositional and molecular weight distribution copolymers were available to us. These included Pressure Chemical anionically polymerized polystyrenes (PS-10, 36, 355) of varying molecular weight and butadiene-styrene copolymers (SBR-1, 2, 3, 4) kindly supplied to us by G. Kraus of Phillips Petroleum. Three fractions of a commercial polybutadiene were supplied to us by N. Donkai of Kyoto University who prepared them by fractionation with benzene and methanol. Various commercial polybutadienes and SBRs with different butadiene microstructures were available. An elution gradient technique was used in which $CHCl_3$ was added to CCl_4 until it reaches a 20:50 ratio. It can be seen from Table IV that with this $CHCl_3$-CCl_4 development system all of the polystyrene samples are bunched together in a narrow R_f range independent of molecular weight. The specially prepared Phillips Petroleum samples similarly have narrow R_f bands. A uniform variation of R_f with styrene content may be noted if one contrasts the polystyrenes, the samples from Kraus and the polybutadienes. It is worthwhile to note that the $CHCl_3$-CCl_4 system allows us to separate high *cis*-polybutadiene (cis-BR) from other anionically and/or radically polymerized polybutadienes. This suggests that an adequate adjustment of the elution gradient along this line would enable one to make analysis of the polybutadiene microstructures.

Let us now turn to a quantitative view. It is first necessary to obtain a calibration curve. The polybutadienes, polystyrenes and SBRs 1–4 were used as standards. In each run a few commercial polymers (test samples) were developed on a chromatoplate simultaneously with the standard polymers. After visualization photometric tracings were run over the standards as well as the test polymers. For a few cases the two methods of tracings were tested. In one run, darkness of a chromatographic smear was determined continuously along the elution direction as a function of distance r from the origin with a slit very narrow in the r direction but sufficiently wide to accommodate the widest part of the smear in a single run. The recorded intensity multiplied by Δr gives the darkness at the location r. In the other run the same smear was scanned along three different lines, one passing through nearly the center line of the smear in the elution direction, with a very narrow aperture. Three intensity readings were adequately averaged, $I_{\text{av}}(r)$, and corrected against the corresponding area, $\Delta y \Delta r$, Δy being the smear width at r. Then $I_{\text{av}}(r)\Delta y \Delta r$ gives the darkness at r. When these two darkness *vs.* r functions were normalized, we found that the both functions gave practically the same result. However, since even slight distortion and nonuniformity (particularly in the y direction) of smears which were often inevitable gave rise to a difficulty in processing the data of the triple-scanning method with the narrow aperture, we employed the single scanning method with the wide slit. This in turn might have caused inaccurate readings especially of the leading threadlike portion of a smear (*cf.* Figure 1b). However hopefully this might not cause a serious error, since it is rather inconceivable that this leading portion would have an extremely high mass density and have contained a large amount of polymer comparable to that of other wider portions of the smear.

A calibration curve for the R_f *vs.* styrene content relation was developed as follows. First the average value of R_f, *i.e.*, $\bar{R}_f$ for the standards was calculated by assuming the standards have no compositional heterogeneity

$$I(R_f = r/r_s) = (\text{intensity at } r) \quad (1a)$$

$$\overline{R_f} = \int R_f \mathrm{d}I(R_f) / \int \mathrm{d}I(R_f) \quad (1b)$$

where r_s is the distance of the solvent front and the integration was taken only over the main smears migrated from the origin. Then the $\bar{R}_f$ values were plotted against the weight per cent styrene X of the standards (see Figure 3 and Table IV).

We are now in a position to compute average composition and compositional distributions from the R_f smears for the test copolymers. This can be readily done by using the two calibrations, the relative specific darkness *vs.* styrene content X relation (Figure 2) and the $\bar{R}_f$ *vs.* X relation for the standard samples (Figure 3).

$$W(X) = [\text{amount of polymer with composition } X] \propto [I(R_f), \text{ intensity at } R_f \text{ corresponding to } X \text{ from Figure 3}] \cdot [\text{amount of polymer per intensity corresponding to } X \text{ from Figure 2}] \quad (2a)$$

$$\overline{R_f} = \int_0^{W_T} R_f \mathrm{d}W(X) / \int_0^{W_T} \mathrm{d}W(X) \quad (2b)$$

$$\text{tlc } \overline{X} = \int_0^{W_T} X(R_f) \mathrm{d}W(X) / \int_0^{W_T} \mathrm{d}W(X) \quad (2c)$$

$$\text{tlc variance} = \overline{X^2} - (\overline{X})^2 = \left[\int_0^{W_T} X^2 \mathrm{d}W(X) / \int_0^{W_T} \mathrm{d}W(X)\right] - (\overline{X})^2 \quad (2d)$$

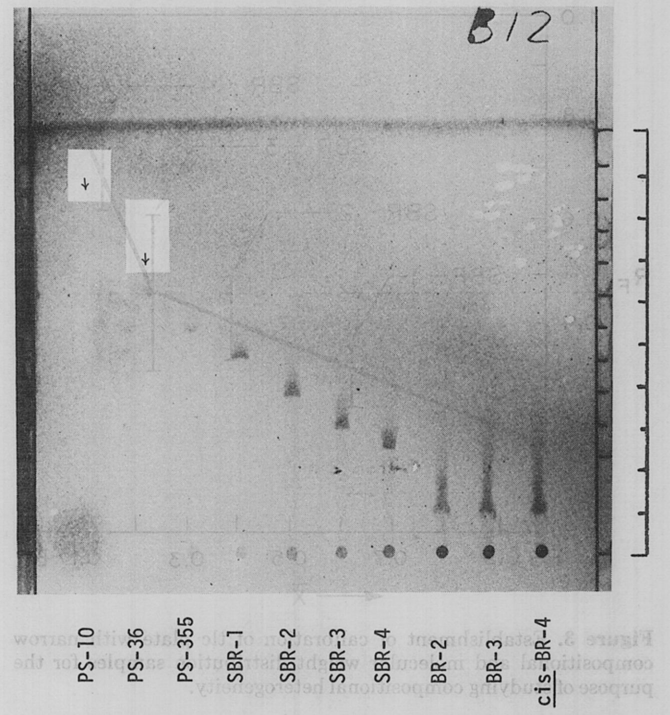

Figure 6. A typical chromatogram obtained by a H_4furan–CH_3OH elution gradient development. The samples tested were the same as shown in Figure 1b.

where W_T is the mass of the copolymer developed from the origin and does not include the mass of the undeveloped copolymer. These equations were applied to each chromatogram obtained by the $CHCl_3$–CCl_4 elution gradient system. Needless to say, the use of these equations does not require any explicit knowledge of absolute darkness of the spots at all, but only of relative darkness as a function of r together with the knowledge of Figures 2 and 3. These tlc values of $\bar{X}$ and the variance are listed in Table IV. On carrying out the calculation, we have neglected the contribution of the spot at zero, but simply evaluated its amount relative to the main R_f smear, W_O/W_T, where

$$W_O = [\text{total amount of polymer in the spot at origin}] \propto [\text{intensity integrated over the spot at origin}] \cdot [\text{amount of polymer per intensity corresponding to } \overline{X} \text{ from Figure 2}] \quad (3)$$

The values $100 \times W_O/W_T$ are listed as the per cent residue at origin. There is general agreement between the tlc and uv $\bar{X}$ values. Figures 4 and 5 show compositional (integral) distribution curves for some of the commercial copolymers studied.

Some of the results are of considerable interest especially the apparently bimodal distributions in an-SBRs-9 and -10, which are made by the same company. Certainly the manufacture of an-SBRs-9 and -10 involve much different reactor designs than the other alkyllithium SBRs. This is also suggested by their butadiene microstructure and apparently more random character than an-SBR-8. There are also differences between the emulsion SBRs. The em-SBR-12 has less heterogeneity than em-SBRs-13, -14, and -15. The em-SBR-12 is a hot-SBR polymerized at 50° while the em-SBRs-13, -14, and-15 are cold 5° polymerized copolymers. The em-SBR-12 would be expected to have more long-chain branching and a low molecular weight tail[20] as well as a lower trans-1,4 and higher cis-1,4 content.[43,44] Only limited studies related to compositional heterogeneity exist for emulsion SBR[16,44] and these imply

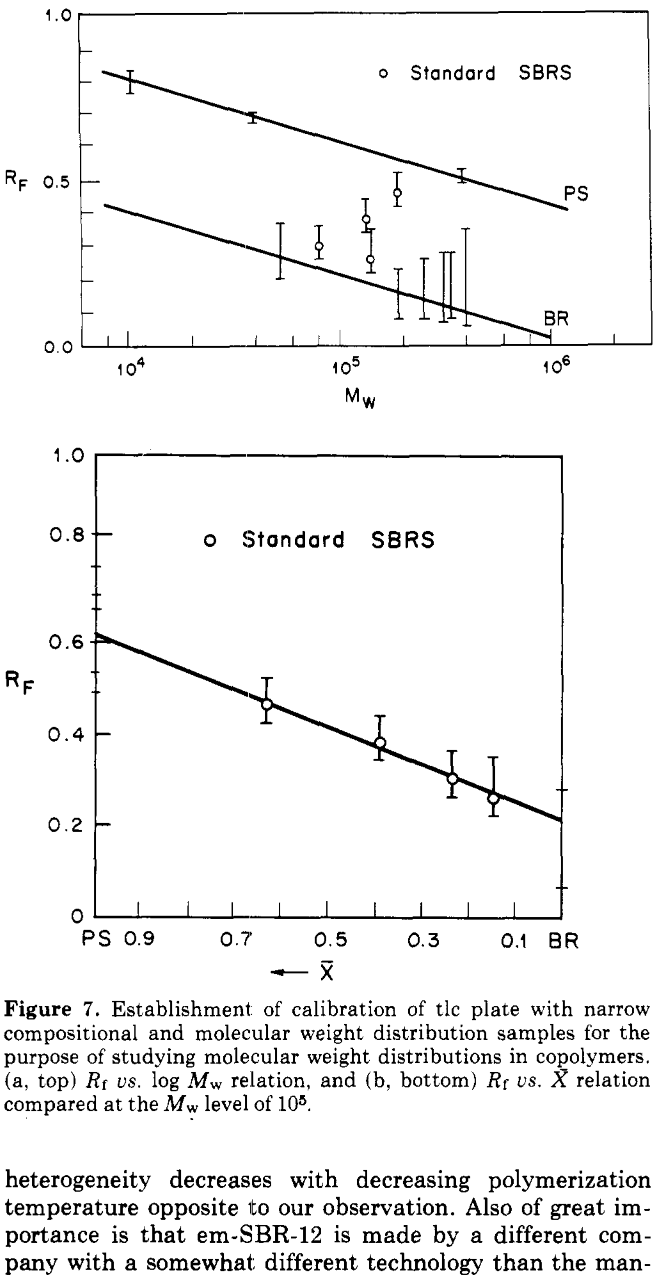

Figure 7. Establishment of calibration of tlc plate with narrow compositional and molecular weight distribution samples for the purpose of studying molecular weight distributions in copolymers. (a, top) R_f *vs.* log M_w relation, and (b, bottom) R_f *vs.* $\bar{X}$ relation compared at the M_w level of 10^5.

heterogeneity decreases with decreasing polymerization temperature opposite to our observation. Also of great importance is that em-SBR-12 is made by a different company with a somewhat different technology than the manufacturer of em-SBR-13, -14, and -15.

The above findings must be considered approximate because of the errors inherent in (1) the $\bar{R}_f - X$ calibration method; (2) the photodensitometer tracings; and perhaps most importantly (3) dispersion processes in the tlc which lead to tailing of the spot toward the styrene rich side. At the moment we know nothing about the effects of various other factors such as the heterogeneity in the microstructures, the extent of blocking, the branching and even the molecular weight which might influence the broadness of R_f smears.

Tlc Method for Molecular Weight Distribution. In the solubility-based separation also it was obvious that no individual solvent or binary mixture was sufficient to attain good separation. Again an elution gradient technique was used in which H_4furan was added to a 30:20 H_4furan-CH_3OH (v/v) ratio until it reaches a 70:20 ratio. The mixing pattern was similar to the $CHCl_3$-CCl_4 system (*cf.* Figure 1) except the total development time required was usually about 40 min. Figure 6 shows a typical example of the chromatograms. Table IV also summarizes R_f values obtained by the H_4furan-CH_3OH system for the various polymers tested in this program. The R_f values for the reference polymers are plotted against log (molecular weight) and also against average composition $\bar{X}$. The results are shown in Figure 7.

In contrast to the $CHCl_3$-CCl_4 system, polystyrenes are developed more than polybutadienes and the copolymers are developed to an intermediate extent by the H_4furan-CH_3OH system. However if we contrast only the polystyrene samples, we see that the narrow molecular weight distribution Pressure Chemical samples only exist in a limited R_f range with the higher molecular weight polymers possessing smaller R_f values. The Phillips Petroleum narrow compositional and molecular weight distribution copolymers are also narrow spots. The emulsion copolymers develop into broad smears, while the commercial alkyllithium polymerized copolymers form relatively narrow spots. This is in general agreement with GPC data discussed earlier, which indicated the emulsion polymerized polymers had broad molecular weight distributions and the alkyllithium copolymers rather narrow distributions.

The above discussion is qualitative and we must now turn to a quantitative analysis. The problem we face is more difficult than that considered by earlier tlc researchers for we seek to determine molecular weight distributions in copolymers possessing compositional heterogeneity. In a solubility-based development the R_f value of any particular copolymer species depends both upon its molecular weight M and its styrene content X. This is certainly the case for the present systems.

By comparing the R_f and molecular weight values for the narrow distribution polystyrenes we found that R_f varied almost linearly with the logarithm of the molecular weight

$$R_f = C_1 - C_2 \log M \qquad (4)$$

where C_1 and C_2 are constants in agreement with the observations of Otocka[13] and Kamiyama, Matsuda, and Inagaki.[14] For polybutadienes, although the samples available do not have very narrow distributions, similar logarithmic dependence of R_f on molecular weight appears to hold, if the weight-average values M_w are compared with R_f (*cf.* Figure 7). From inspection of Figure 7b we see that R_f varies in an approximately linear fashion with composition X, if the values are compared at a same molecular weight level. This suggests that, for copolymers, eq 4 could be modified or rather generalized to

$$R_f = (A_1 + B_1X) - (A_2 + B_2X)\cdot\log M \qquad (5)$$

where A_1, B_1, A_2, and B_2 are constants. Values of these constants were assigned using the various narrow distribution polystyrenes, SBRs and polybutadiene fractions. In a typical case (*cf.* Figure 7) it was found that

$$R_f = (1.16 + 0.40X) - 0.19 \log M \qquad (6)$$

In calculating molecular weight distributions for a copolymer sample from its R_f smear, we assumed that the smear is primarily due to its molecular weight distribution and used the average composition $\bar{X}$ instead of X in eq 5. Again undeveloped residue at the origin was neglected. Thus the distribution is

$$W(M) = [\text{amount of polymer with molecular weight } M] \propto [\text{intensity at } R_f = R_f(M,X) \text{ corresponding to } M \text{ and } X \text{ from eq 5}] \qquad (7).$$

Table IV summarizes the results of the H_4furan-CH_3OH system and the calculated molecular weight dis-

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(43) R. R. Hampton, *Anal. Chem.*, 21, 923 (1949).
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tributions from the tlc together with the GPC results cited earlier. There is certainly qualitative though not quantitative agreement here.

Comparing the tlc and GPC results, we notice that the former always predicts much narrower distribution than does the latter. Previous reports[13,14] showed good agreement between the two results at least for polystyrenes. The disagreement found here for a narrow distribution polystyrene, PS-355, is presumably due to the observation mentioned earlier that polystyrene developed by H_4furan–CH_3OH system migrated toward the glass-silica gel interface becoming hardly visible from the silica gel side. On the other hand, the disagreement found for various SBRs and polybutadienes may be partly due to the undeveloped residue at the origin. The amount of the residue is substantially larger in this H_4furan–CH_3OH system than in the $CHCl_3$–CCl_4 system.

Several comments are necessary here. First, no corrections for dispersion have been made and there would certainly seem to be upward tailing. Furthermore our calibration standards are much better at higher styrene than at lower styrene levels. Specifically we had to narrow distribution polybutadienes at our disposal. This will probably lead to greater errors in polybutadienes and low styrene SBRs. The H_4furan–CH_3OH system shows a large dependence of R_f on X. This could be improved by employing a more adequate system probably consisting of three or four solvent mixtures.

Concluding Remarks

Copolymers may be separated by tlc according to composition or molecular weight. We have in this paper developed tlc techniques for separating one particular copolymer system, butadiene–styrene, which had industrial importance. It was shown that using elution gradient techniques based upon relatively nonpolar solvents leads to separation according to composition by an adsorption mechanism. Use of very polar solvent–nonsolvent mixtures leads to separation primarily according to molecular weight. By suitable calibration the tlc smears may be interpreted quantitatively as compositional heterogeneity and molecular weight distribution. This procedure should be applicable to other copolymer systems.

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Induced Decomposition of Some Azo Sulfones with Polymer Radicals and Telomerization with Azo Sulfones

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ABSTRACT: Radical polymerizations of styrene and of methyl methacrylate (MMA) initiated by some azo sulfones were investigated to determine chain-transfer constants to azo sulfones with polystyryl and poly(MMA) radicals, respectively; with the former radical the constants at 70° were found to be 9.7 (*p*-methoxyphenyl phenylazo sulfone) to 23.4 (methyl phenylazo sulfone, MPAS) comparable to those of mercaptans, but with latter radical, the constant was practically zero. Thus, the relative rate constants for induced decomposition of azo sulfones with the polystyryl radical at 70° were correlated with Hammett's σ values of $\rho = +0.5$. Telomerizations of styrene, 1-hexene, and MMA, except a phenyl phenylazo sulfone (PPAS)-1-hexene system, were also studied by using an excess of the azo sulfone over monomer concentration; reaction of PPAS with styrene gave a hydrazone type product, $C_6H_5SO_2CH_2C(C_6H_5){=}N{-}NHC_6H_5$, suggesting that chain-transfer reaction to PPAS with the polystyryl radical could occur to give a hydrazone-type end group *via* hydrogen transfer from azo-type ending. On the other hand, the azo-type product, $CH_3SO_2CH_2CH(C_6H_5){-}N{=}NC_6H_5$, was obtained from the reaction of MPAS with styrene. The implications with respect to the reaction mechanism of azo sulfone with monomers are discussed on the basis of the results of the polymerization and telomerization.

In the course of a study of the radical copolymerization of sulfur dioxide and styrene,[1,2] it seemed interesting to investigate the induced formation of sulfonyl radicals from the reaction of sulfonyl compounds with polystyryl and other carbon radicals. It is well known that sulfonyl radicals can be generated easily from the homolytic scission of azo sulfones. The thermal decomposition of azo sulfones in solvents was extensively studied by Overberger,[3,4] Kice,[5,6] and Kojima,[7] and their collaborators. They determined the rate constants for unimolecular decomposition of azo sulfones and identified the decomposition products. We have used azo sulfones ($R{-}SO_2{-}N{=}N{-}C_6H_5$, containing R = CH_3, $C_6H_5CH_2$, C_6H_5, and p-X—C_6H_4) to homolytically decompose to yield both sulfonyl and phenyl radicals and nitrogen. Benzylsulfonyl radical which

$$R{-}SO_2N_2C_6H_5 \longrightarrow R{-}SO_2\cdot + C_6H_5\cdot + N_2 \qquad (1)$$

may result from the homolysis of benzyl phenylazo sulfone, $C_6H_5CH_2SO_2N_2C_6H_5$, further decomposes to benzyl radical and sulfur dioxide.[6] Overberger and Rosenthal[3,4]

$$C_6H_5CH_2SO_2\cdot \longrightarrow C_6H_5CH_2\cdot + SO_2 \qquad (2)$$

also studied the polymerization of styrene initiated by phenyl phenylazo sulfone and they confirmed the incorporation of both phenylsulfonyl ($C_6H_5SO_2$–) and phenylazo ($C_6H_5{-}N{=}N$–) groups at the polystyrene endings. Ueha-

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