

SEPARATION AND CHARACTERIZATION OF BLOCK AND GRAFT COPOLYMERS BY THIN-LAYER CHROMATOGRAPHY

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Abstract—Feasibilities of thin-layer chromatography (TLC) and its combination with gel permeation chromatography in characterization of block and graft copolymers are discussed. The simplest application of TLC is to test the purity of block and graft samples having been subjected to purification treatment. TLC allows further to determine the compositional heterogeneity of block copolymers without interference of molecular weight, and to distinguish block samples by the difference in block sequence even on the same composition level. The latter applicability is illustrated for styrene-butadiene copolymers with different chain architecture. Finally two applications of TLC as a tool for characterization of graft systems are described: one is to isolate side-chain polymers truly grafted on mother polymer chains, and the other to isolate true graft copolymers from reaction products.

1. INTRODUCTION

Since polymer chemistry was established by Staudinger by introducing the concept termed as the "polymolecularity" or "polydispersity", polymer chemists have been inclined to characterize a given polymeric substance in terms of average quantities. This is in sharp contrast to chemistry of low-molecular-weight compounds. The reason may be attributed to lack of the knowledge of adequate separation technique for polymeric substances. Especially, various separation problems specific to copolymers are remaining still unsolved even after the successful introduction of gel permeation chromatography (GPC).¹ The difficulty in separating copolymers originates largely from unfavorable effects due to the superposition of heterogeneities in composition and molecular weight. Hence, cross fractionation is needed but impractical because of its time-consuming nature and the difficulty in selecting appropriate pairs of solvent and nonsolvent.

Most of reaction products of block and graft copolymers are contaminated by unreacted and partially reacted mother polymers, and/or attendant homopolymers. For the purpose of characterizing block and graft copolymers, therefore, a method for isolating the aimed component from a given reaction product should be worked out. However, such isolation is, often, hardly achievable not only for the general reason just mentioned above but also for another reason specific to block and graft copolymers. That is to say: in solution state, block and graft copolymers are apt to act as emulsifier to reduce the incompatible nature of different polymer species.² This action makes the isolation hazardous, especially, when fractional precipitation or dissolution technique is employed.

Our main concern in this contribution is to describe some applications of two chromatographic methods, namely thin-layer chromatography (TLC) and GPC, to the separation and characterization of block and graft copolymers. Although TLC has been in existence for a long time,³ no attempt to introduce it to polymer separation had appeared before Russian investigators⁴ and our research group⁵ independently proved its favorable utilities. This article will begin with a brief introduction to

TLC as applied to polymer chemistry since this experimental method might be fairly new for most polymer chemists.

2. SEPARATION MECHANISMS IN TLC

A TLC system is composed of three elements: a stationary phase, which is a thin layer formed mostly on a glass plate with adsorbent like silica gel, a mobile phase, which is any solvent used as the developer (carrier of sample), and a sample. TLC separation of a sample mixture is effected because the migration of each component relative to the mobile phase is retarded preferentially by the stationary phase. Of such retarding actions, those which are most important for polymer separation may be classified into three mechanisms,⁶ which involve adsorption-desorption process, "phase-separation" or precipitation process, and molecular sieving process.

2.1 Adsorption mechanism

To discuss the adsorption mechanism, three types of interactions among the adsorbent (*A*), the developer solvent (*D*) and the sample polymer (*P*) are considered, being abbreviated as the interaction [*A-D*], [*A-P*] and [*D-P*]. When the interaction [*A-D*] is stronger than [*A-P*], the active sites on adsorbent will be occupied predominantly by the solvent molecules so that the sample polymer molecules are desorbed from adsorbent. This means that the sample polymer migrates to the moving direction of mobile phase. The migration rate of sample on a given adsorbent is decided therefore by a balance between the strengths of [*A-D*] and [*A-P*]. The most important quantity to characterize a given sample in TLC, is this migration rate normalized to that of the mobile phase, which is often denoted by R_f . The value of R_f is zero when no sample migration takes place, while it goes to unity when the sample migrates at the same rate as that of the mobile phase.

The strength of [*A-D*] for a given developer solvent may be preestimated roughly for the so-called "elutropic series",^{3b} which is an arrangement of various solvents according to their increasing polarities represented by dielectric constant, and more exactly from a series of "solvent strength parameters", which were defined semi-empirically by Snyder based on his theory of adsorption

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chromatography.⁷ On the other hand, the strength of [A-P] is correlated to the adsorption energy and area of sample molecule on a given adsorbent surface, which were elucidated by Snyder in terms of the molecular structure of samples.⁷ For polymeric samples, the interaction [A-P] may be preestimated on the basis of the molecular structure of their monomeric units.⁸

The preestimate of these interactions will serve as a great help in selecting appropriate developer solvents or mixtures. However, the interaction [D-P] should also be taken into account in such a way that the developer can dissolve the sample polymer well.⁸ In addition it should be mentioned that inorganic adsorbents, e.g. silica gel and alumina, can be brought to any activity grade by the activation treatment.^{3b} An "active" adsorbent can attract sample molecules so strongly that the sample migration is retarded to a great extent.

In application of TLC to polymer separation, this polarity-controlled adsorption mechanism leads to separation of copolymers according largely to the chemical composition with minimal interference of the molecular weight.^{4,5,9-11} The characteristics of the molecular weight dependence of R_f is the most favorable feature of TLC application. However, Belenkii *et al.* reported recently that when a "macroporous" silica gel was used, an appreciably high dependence was observed by conducting the development in a transition region that the molecular sieving process was just supplanted by the adsorption process on changing the polarity of developer.¹² Its general validity is still open for discussion.

The compositional distribution of a styrene-methyl acrylate statistical copolymer, prepared at ca. 98 wt % of monomer to polymer, was determined by adsorption TLC and proved to be in good agreement with that predicted from the classical copolymerization kinetics.⁵ Further applicabilities of the adsorption mechanism have been shown on separation of binary copolymers with different chain architecture by their sequence length,¹³ and on those of polymethyl methacrylates (PMMA) and polybutadienes, respectively by their steric isomerism^{14,15} and stereoregularity,¹⁶ and by their geometric isomerism.¹⁷

2.2 Phase-separation mechanism

When poor solvents or solvent mixtures toward sample polymers are used as developer, "phase-separation" or precipitation of polymer takes place, which causes fractionation of sample by molecular weight in TLC.⁶ The phase-separation retards the migration of sample at different rate which is larger for a component of larger molecular weight, thus giving a smaller value of R_f for a higher-molecular-weight component. The fractionation mechanism according to this process has been elucidated in terms of the decrease in the phase ratio during the progress in the development.¹⁸ Here the phase ratio is defined as the weight of developer retained per unit weight of adsorbent.

Experimental conditions for TLC separation of polystyrene (PS) and polyethylene oxide by molecular weight was investigated by Otsuka and Hellman.¹⁹ In a subsequent work Otsuka made TLC separation of a commercial PS to determine the molecular weight distribution.²⁰ The result was in good agreement with that from GPC. A similar work was reported independently by our research group.²¹ This group achieved also the fractionation of PMMA by this mechanism.^{6,18}

Polymer fractionation by the molecular sieving mechanism can be realized even in TLC when a "macroporous" adsorbent is used and the polarity of developer

is so adjusted that the adsorption mechanism is eliminated completely.^{4,22-24} However, the resolution of separation with respect to the molecular weight, attained by this mechanism, is often inferior to that by the phase-separation mechanism.

3. TLC AND GPC APPLICATION TO BLOCK COPOLYMERS

3.1 Purity test of samples isolated from reaction products

Preparative isolation of block-copolymer species from the reaction product may be effected by a suitable extraction or dissolution-precipitation procedure, if the solubility difference between true block copolymer and attendant impurities is fairly large. A difficulty often associated with such operations is to know how far the purification treatment should be continued. On the removal of impurities, their absence in the extractant cannot simply be regarded as the end point of extraction because of the emulsifying effect of block copolymers.² This situation is, of course, the same for graft copolymers.

TLC technique has been recognized to be a simple as well as sensitive method for testing the purity of block and graft copolymer samples having been subjected to isolation treatment.^{25,26} An example of such purity tests²⁷ will be described below. For the experiment, a PS-PMMA diblock-copolymer product, coded 61B, was prepared by anionic polymerization at -78°C in THF with K-cumyl as initiator.²⁸ The styrene content and apparent molecular weight were 0.6 in mol fraction and 2.35×10^6 , respectively. After treated by twofold precipitation from benzene solution into methanol, the crude sample was further purified by extraction with boiling cyclohexane and then with acetonitrile to remove free PS and PMMA, respectively.²⁹ Both purities of the crude and purified sample, which will be designated respectively as 61B(c) and 61B(p), were compared by using TLC technique.

To this end, the above two samples are preliminarily chromatographed on activated thin layer of silica gel with chloroform, which has been known to allow migration of only PS up to the solvent front, leaving the block copolymer immobile on the starting point. A continuous development procedure^{3b} was applied for 1 hr in order to separate free PS completely from the sample. The chromatogram, stained by the thymol blue method,²¹ is shown in Fig. 1. In the chromatogram of each sample we see two final spots in the proximity of solvent front and at the starting point, which should be identified as the separated PS and the block copolymer, respectively. It is also recognized intuitively that the amount of PS separated from 61B(c) is much larger than that from 61B(p), as expected.

On the other hand, the same TLC experiments were carried out to determine the amount of free PS separated

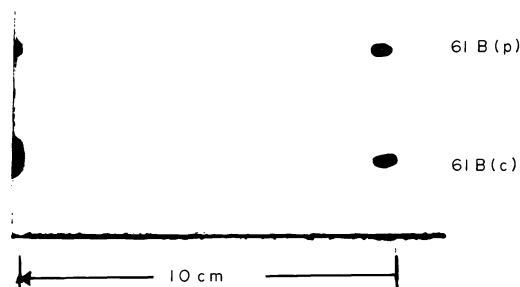


Fig. 1. Chromatograms prepared to test the purity of SM-diblock copolymers, sampled before and after purification treatment, coded as 61B(c) and 61B(p), respectively.

from the samples. The quantitation was made by scanning the chromatogram at a light wavelength 210 nm with a Dual-Wavelength TLC Scanner Model CS-900 (Shimadzu Seisakushyo Co. Ltd., Kyoto, Japan). The detail of this procedure has been described in our previous paper.³⁰ First, the removal efficiency of free PS was tested. For the purpose, three specimens were prepared by mixing the precursor PS, coded as 61H, to 61B(p) at different, known PS concentrations, and chromatographed as before. By quantifying the chromatogram it was found that the removal efficiency was at a minimum of 95% for each mixture. The result suggests that the emulsifying effect² does not exert any appreciable influence upon TLC separation of PS from the block copolymers. For the purity test of 61B(c) and 61B(p), chromatograms for these samples were prepared and quantified by the ultraviolet scanning. The sample size was adjusted exactly to 50 μg for each sample. Thus the amounts of free PS in 61B(c) and 61B(p) were determined to be 1.5 and 0.4 μg , respectively. This indicates, in turn, that the purities of the crude and purified sample are 97.0 and 99.2%, respectively. In this connection it should be mentioned that no free PMMA was detected by TLC, made in a similar manner by using a binary benzene + 2-butanone as developer,³¹ with which R_f values of PMMA and the block copolymer can be adjusted to zero and 0.5, respectively.

The minimum amount of free PS detectable by TLC depends on the sensitivity of TLC scanning photometer used. In our case this was found to be about 0.3 μg , which corresponds to a few per milliliter for the content of free PS if a 100 μg sample is loaded for the development. However, for such a high sample load as 100 μg , one encounters usually so called over-load effects which lead to poor separation. To avoid this difficulty, Horii *et al.* recommended a method for the sample spotting: Stock solution of sample is spotted on thin layer not in a circular form, as usually done, but in a narrow band with a length of 3 ~ 4 cm, extending from the starting point.²⁶ By this means they could detect by-products, which were occluded on a level of several per milliliter in various graft copolymers even after purification treatment.

3.2 Heterogeneity of pure block copolymers

After thorough removal of homopolymer impurities from block copolymerization product, still one should face the problem of testing the heterogeneity of isolated block-copolymer species. Conclusions drawn from GPC analysis are often misleading, since the technique allows one to look at the favorable side of the problem, i.e. the molecular weight distribution (MWD), but not the compositional heterogeneity (CH) of the resultant block copolymer. In general, block copolymerization proceeds preponderantly to yield species of narrow MWD, but does not necessarily do so in the compositional distribution.

Block copolymers may be synthesized through condensation of active end groups of precursor-homopolymer molecules. The reactivity of the end groups is probably independent of the length of the chains to which they are attached. The molecular weights of the precursor chains in a resultant block-copolymer molecule should be independent of one another. The block-copolymer synthesis through anionic "living" polymer technique may also be regarded as a sort of random coupling process, although the reaction mechanism is entirely different from the condensation technique. In such random coupling processes, a longer precursor chain will find a larger chance of coupling with a shorter chain of the other kind, simply

because the shorter chains exist in relatively larger population than the longer ones. Coupling of a longer A-chain with a shorter B-chain and vice versa automatically narrows the MWD but apparently not the CH of the resultant block-copolymer species. The situation should be contrasted to the case of, e.g. radical copolymerization at the azeotropic composition.

Employing the concept of random coupling, Kotaka *et al.* derived the CH- and MWD-function of pure block copolymer from the MWDs of precursor homopolymers.³² The theory may be easily generalized to include mixed block copolymers.³² Even without explicitly knowing the MWDs of the precursors, we can derive some interesting relations among various average quantities of the block copolymer. For example, for the weight-average to number-average molecular weight ratio we have the following relation:^{32,33}

$$M_w/M_n = 1 + \bar{x}^2 Y_A + (1 - \bar{x})^2 Y_B \quad (1)$$

where \bar{x} is the average A-content (by weight fraction) of the block copolymer; and Y_K ($K = A$ or B) is a MWD-index defined by $Y_K = (M_w^K/M_n^K) - 1$ for the K -precursor. If the sample is a multiblock copolymer, Y_K is the value of individual blocks divided by the number of K -blocks in a block-copolymer molecule.³² Apparently the M_w/M_n ratio is always smaller than that of its most polydisperse precursor and often can be smaller than either of the two precursors.³³ Accordingly the MWD of the block copolymer, and hence the GPC-chromatogram can be narrower than those of the precursors. These results are due to the selfcompensating effect of the random coupling mechanism in block copolymerization.

For compositionally heterogeneous copolymers, use of a conventional single detector GPC often leads to erroneous conclusions. Therefore, use of a dual- or multiple-detector GPC, which is furnished, e.g. with a refractometric (RI) and an ultraviolet absorption (u.v.) detectors, is recommendable for the analysis of such materials. By a dual-detector GPC, we can determine the variation of point-by-point composition (x) with elution volume V_e , besides the true chromatogram corrected for the detector responses.³⁴ The variation (x) with V_e may be approximated by the (x) vs log (molecular weight) relation.

For block copolymers we can show by assuming the random coupling mechanism that the (x) vs long M relation may be related with the light-scattering P parameter,³⁵ which is in turn given as:

$$P = \bar{x}(1 - \bar{x})[\bar{x}Y_A - (1 - \bar{x})Y_B]M_n \quad (2)$$

As opposed to statistical copolymers of low conversion or of azeotropic composition, the P parameter is not generally zero for block copolymers. However, it is zero, if $\bar{x}Y_A - (1 - \bar{x})Y_B$ is zero. Then depending on whether $P \geq 0$ or $\bar{x}Y_A \geq (1 - \bar{x})Y_B$, the (x) vs log M relation increases, stays constant, or decreases with increasing M .³²

Experiments with a dual-detector GPC were carried out to discuss the foregoing prediction by using PS-PMMA diblock samples, coded as 63B30 and 63B70, which were prepared by anionic "living" polymer technique.²⁸ The results of characterization and GPC experiment are shown in Table 1, and Fig. 2, respectively. Values of Y_A for the PS-blocks given in Table 1 were deduced from the M_w/M_n of precursor PS; while those of Y_B for the PMMA-blocks from the values of M_w/M_n of the block

Table 1. Characteristics of SM-diblock copolymers^a

Sample code	\bar{x} ST wt. fr.	$M_w \times 10^{-4}$	$1 + Y_A$	$1 + Y_B$	$\bar{x}Y_A$	$(1-\bar{x})Y_B$
63B30	0.24	150	1.20	1.40	0.05	0.3
63B70	0.69	64	1.20	1.41	0.35	0.12

(a) Y_A and Y_B refer to the MWD-index for PS- and PMMA-block, respectively. For the definition, see text.

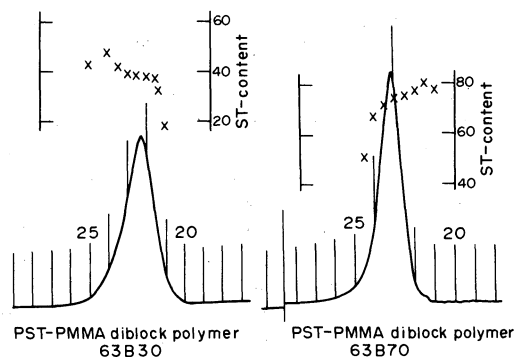


Fig. 2. GPC elution curves obtained by refractometry for SM-diblock copolymers and plots of point-by-point styrene content against elution counts V_e , indicated by (x).

samples with the aid of eqn (1). From the figures it is seen that the $\langle x \rangle$ vs V_e relations observed for each sample are interpreted quantitatively in terms of the theoretical prediction. In connection to this experiment it should be emphasized that the invariance of $\langle x \rangle$ vs M (and presumably with V_e) is insufficient to guarantee the compositional homogeneity of the block copolymer. Apparently the information from a dual-detector GPC is limited to the MWD and the correlation of composition and molecular weight. It tells us nothing about the broadness of the compositional heterogeneity itself. Therefore a need for devising an experimental technique applicable to the CH-analysis of block copolymers is evident.

For this purpose, again TLC appears to be promising, although it has inherent difficulties of its own when applied to block copolymers. The main difficulties arise from the emulsifying effects² and the possible conformational anomalies of block copolymers in developer solvents.³¹ Clear-cut separation of block-copolymer components according only to composition is often hampered by these effects,³¹ as opposed to the cases of statistical copolymers.⁵ Also in many cases, block copolymers of different type, e.g. AB-, ABA-types etc., show different chromatographic behavior, as will be described in the next section. For the latter reason, one needs to have well-defined samples of the desired block type as the elution standards, which are often not readily available.

The first difficulty may be avoided by adequate choice of developer solvents. They must be common good solvents toward the both precursors, and may cover a wide range of polarity upon varying solvent composition. The second difficulty may be avoided, if the constituent precursors show different responses to the available TLC scanning photometer. Specifically for the CH-analysis of PS-PMMA block copolymers of SM- and MSM-types, we were able to show that a binary carbon tetrachloride + 2-butanone allows reasonably good separation according only to composition.³⁰ Utilizing the fact that PS and

PMMA exhibit different responses to 225 and 265 nm scanning, we could deduce the CH-functions of these block copolymers without the aid of any elution standard. Figure 3 shows typical examples of integral CH-functions for three SM-diblock samples coded as 63B30, 63B50 and 63B70, which have $\bar{x} = 0.24, 0.49$ and 0.69 , respectively.³⁰ The CH-distributions of these samples are fairly broad: This is consistent with the results of fractionation and density-gradient ultracentrifugation. In Fig. 3, the circles are the TLC results, while the solid curves are the theoretical ones calculated by assuming the Schulz MWD-functions³⁶ for the precursor PS($Y_A = 0.2$) and PMMA($Y_B = 0.4$). We find a reasonably good agreement between the theory³² and the TLC experiments.

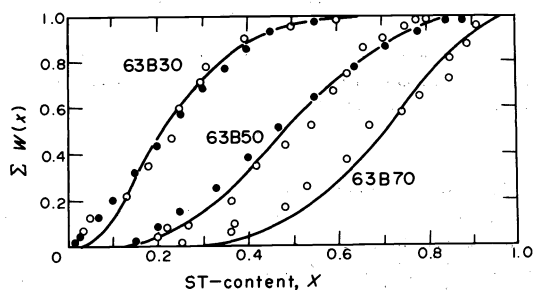


Fig. 3. Integral composition distribution curves for SM-diblock copolymers: Open and closed circles for data points obtained by TLC, and solid curves for computer simulation. For the detail, see Ref (30). Reprinted from Ref (30) by permission of Hüthig & Wepf, Basel.

The above results suggest two things: First, the CH-analysis of block copolymers is possible by adequately designed TLC; secondly, the CH-broadness and MWDs of block copolymers may be predicted reasonably well by assuming the random coupling mechanism. Because of this mechanism, the CH-control of block copolymers is very difficult even in the case of anionic "living" polymerization methods. Nevertheless we should hasten to add that the anionic "living" polymer technique is one of the most promising routes to obtain compositionally homogeneous and structurally well-defined block copolymer samples.

3.4 Separation by the difference in block sequence

One of our previous papers has dealt with the effect of monomer arrangements in styrene-methyl methacrylate copolymer chains upon TLC separation.¹³ The result was confined, however, to indicate that under an appropriate development condition, the random and alternating polymers can be migrated, while the block polymer remains immobile on the starting level. In the course of determining the compositional heterogeneity of PS-PMMA block copolymers by TLC, we observed that the SM-diblock polymer could be distinguished chromatographically from the MSM-triblock polymer even on the same composition level.³⁰ The TLC experiment was performed by using a concentration gradient development^{3b} with carbon tetrachloride and 2-butanone as the initial and adding solvent, respectively. Special caution had to be paid upon the rate of addition of the second solvent (2-butanone) in order to achieve good separation. The result³⁰ is reproduced in Fig. 4, from which it is seen that the R_f values for the triblock samples are higher than those for the diblock samples at every composition.

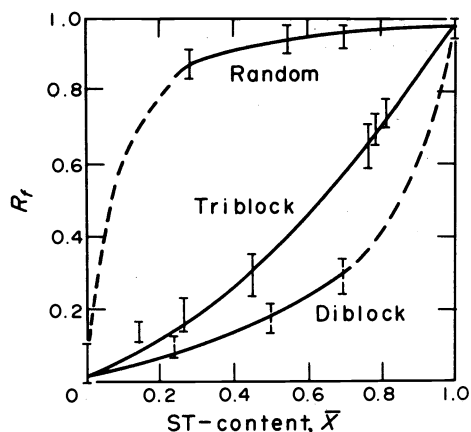


Fig. 4. Dependence of R_f on styrene content found for SM-block and random copolymers by TLC using binary 2-butanone + CCl_4 as developer. Reprinted from Ref (30) by permission of Hüthig & Wepf, Basel.

The above finding motivated us to investigate TLC separation of styrene-butadiene (SB) block copolymers with different block sequence, whose importance in industrial applications has nowadays increased steeply.³⁷ The result³⁸ will be reviewed below. On the outset of this study, three reference samples were prepared by anionic polymerization techniques, which were a SB-diblock and a SBS-triblock polymer, and a so-called "tapered" SB-copolymer. The characterization results by osmometry, GPC and others are listed in Table 2-A and 2-B, in which data for commercial products of SB-block copolymers tested here are also included.

Preliminary experiments were carried out to establish

the development condition which allows one to distinguish the reference samples according only to the chain architecture. Moderately good and good solvents toward the both precursor polymers have been tested as the developer, which were listed in Table 3. In addition, actions of silica gel and alumina, used as adsorbent, upon polymer separation have been investigated, since it is expected that the double bonds of butadiene would exert much more specific interactions with the latter adsorbent than with the former.⁷ The experimental results are summarized in Table 3.

In the table it is seen that no single solvent can give different R_f for different polymer species, except for carbon tetrachloride; experiments with this solvent and alumina will be described later. Therefore the reference samples were chromatographed by a concentration gradient technique on silica gel thin-layer activated at 120°C for 2 hr. A binary cyclohexane + chloroform (9:1 by volume), and chloroform were used tentatively as the initial and adding solvent, respectively. The chromatogram thus obtained is shown in Fig. 5. This proves a possibility of chromatographically distinguishing the triblock sample from either the diblock or the tapered sample, though the difference among the R_f values for each sample was not large enough for the complete separation, and also the tailing phenomena in the chromatogram could not completely be suppressed. A feature specific to this separation was that the R_f for the diblock sample was higher than that for the triblock, this being just the opposite to the case of PS-PMMA block copolymers.³⁰ The reason is still open for discussion.

The above TLC procedure was applied, with some alternations, to the identification for the chain architecture of various commercial SB-products. First, five commercial products having different chain architecture (see

Table 2-A. Characteristics of reference and commercial SB-samples tested

Sample code	Chain Architecture	$M_n \times 10^{-4}$	M_w/M_n^a	ST wt %		Producer
				NMR	UV(GPC)	
Reference samples						
Tap-SB	tapered	3.7	1.09	28.1	32.5(34)	
Di-SB	SB-block	3.4	1.13	26.4	28.5(29)	
Tri-SB	SBS-block	3.8	1.10	29.6	32.5(33)	
Commercial samples						
FRS 206	random	4.13 ^b	9.5 ^b	—	31.6(33)	Firestone
Solprene 300	random or tapered	10.4 ^b	2.4 ^b	—	26.5(36)	Phillips
Solprene 301		12.2 ^b	1.7 ^b	—	24.6(30)	
Solprene 1205		5.1 ^b	1.5 ^b	—	29.2(32)	
Kraton 1101	SBS-block	7.9	—	—	28.7(30)	Shell

(a) Determined by GPC.

(b) Data obtained by Kotaka and White [see Ref. (11)].

Table 2-B. Chain microstructures of butadiene parts in SB-samples^a

Sample code	Microstructure wt. % ^b		
	1,2-vinyl	cis-1,4	trans-1,4
Tap-SB	12.5	27.7	27.3
Di-SB	12.3	25.5	33.7
Tri-SB	11.0	30.6	25.9

(a) For the data of commercial products used in this study, see Ref. (11).

(b) Indicated on the basis of wt % of total polymer.

Table 3. R_f values for reference SB-samples obtained with single solvents as developer

Solvent	Dielec. const.	$\epsilon^{\circ a}$	R_f for silica					R_f for alumina				
			PS	PB	Tap-SB	Di-	Tri-	PS	PB	Tap-	Di-	Tri-SB
Cyclo-hexane	2.02	0.04	0	0	0	0	0	0	0	0	0	0
CCl_4	2.24	0.18	0	1 ^b	0	0	0	0	1 ^b	1	1	0
Amyl-Chloride	6.6	0.26	0	1 ^b	1	1	1	1	1 ^b	1	1	1
<i>p</i> -Xylene	2.27	0.26	1	1	1	1	1	1	1	1	1	1
Benzene	2.28	0.32	1	1	1	1	1	1	1	1	1	1
CH_2Cl	4.31	0.40	1	1	1	1	1	1	1	1	1	1
THF	7.42	0.45	1	1	1	1	1	1	1	1	1	1

(a) Solvent strength parameter defined by Snyder [see Ref (7)].

(b) R_f changes from zero to unity according to the microstructure [see Ref. (17)].

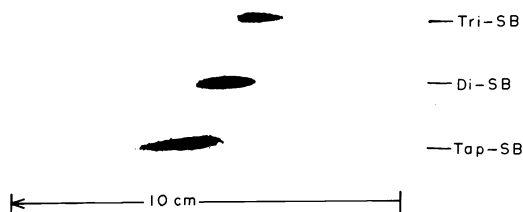


Fig. 5. Chromatograms obtained by adsorption mechanism for reference SB-samples of tapered, diblock and triblock type.

Table 2-A) were chromatographed by the same gradient development technique as before. The result showed that no appreciable separation by the difference in chain architecture was observed except for a random SB-copolymer (FRS 206), which gave $R_f = 0.6$.

Recalling that TLC developments with single solvents or mixtures often result in better separations than do those by gradient technique,^{8,16} we chromatographed the above commercial products by using the same binary but with a fixed composition, i.e. 140:75 (cyclohexane:chloroform) by volume. The chromatogram is shown in Fig. 6. Apparently two samples Solprene 300 and 301 can be identified as tapered type; while Solprene 1205, and Kraton 1101 roughly as SB-diblock and SBS-triblock type, respectively. The identifications thus deduced from TLC are in agreement with those given by the producer relevant to each sample, though Solprene 300 and 301 are nominated both as random type by the producer. This conclusion was further justified by a series of additional experiments made on the composition and molecular weight dependence of R_f for SB-copolymers:

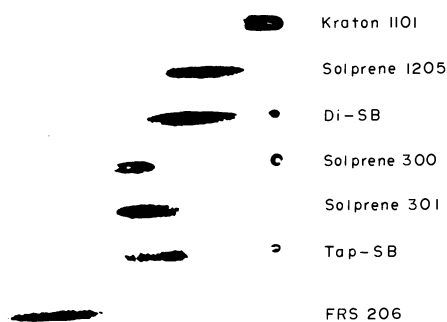


Fig. 6. Chromatograms obtained by adsorption mechanism for commercial SB-products and reference samples.

the experiments ensured that the differences in the composition and molecular weight among the commercial products used here did not exert any essential influence upon such chromatographic behavior as shown in Fig. 6.

Our next concern is to elucidate the chain architecture of Kraton 1101, which gave a little different elution curve in GPC from the other products. Figure 7 shows the elution curves obtained by a dual-detector GPC for this product. The elution curves, taken with the refractometric and ultraviolet (260 nm) detectors, both exhibit three peaks, denoted as P(a), P(b) and P(c), at elution counts, 27.3, 29.0 and 33.0, respectively. The peaks, P(a) and P(c), may be assigned immediately to a main component species of this product and homopolystyrene, respectively, by referring to the point-by-point compositions, $\langle x \rangle$, indicated by open circles in the figure. As to the component species appearing at P(b), we can only say that this species should have the almost same styrene content as that of the main component species.

To investigate the chain architecture of the component species at P(b), Kraton 1101 and its equiponderant mixture with our diblock sample were chromatographed together with Solprene 1205, identified to SB-diblock type, under the same condition as that applied to obtain the chromatogram given in Fig. 6. The result is shown in Fig. 8. As is seen from the figure, Kraton 1101 shows the chromatographic behavior similar to that of our triblock sample, and no symptom is observed that the sample contains any diblock component. Therefore it seems

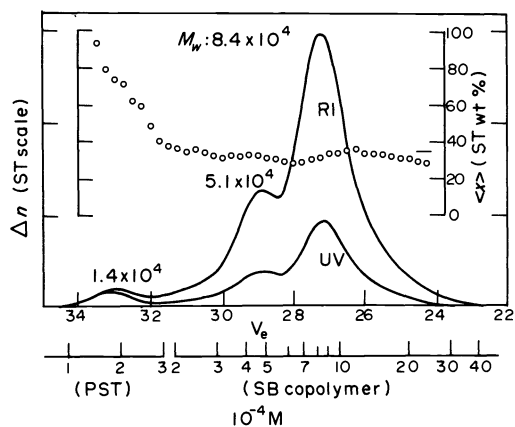


Fig. 7. GPC elution curves gained with refractometric (RI) and ultraviolet (UV) detector for a commercial SB-product, Kraton 1101. Open circles indicate plots of point-by-point styrene content against elution count.

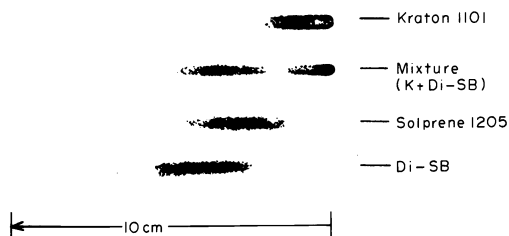


Fig. 8. Chromatograms obtained by adsorption mechanism for Kraton 1101, Di-SB, an equiponderant mixture of the former two, and Solprene 1205.

reasonable to conclude that the chain architecture of the component species at P(b) does not differ from triblock type.

The above conclusion was drawn from the observations obtained by the polarity-controlled adsorption mechanism.^{6,18} Further to confirm it we have applied the other separation mechanism to Kraton 1101, i.e. the solubility-controlled phase-separation mechanism,^{6,18} which allows fractionation largely by molecular weight. A gradient development with silica gel thin-layer was carried out at ca. 20°C: 100 ml of a 3:2 binary of chloroform and methanol was placed in a development chamber as the initial solvent, and during the development, 80 ml of methanol was added at a constant rate. A chromatogram shown in Fig. 9 was obtained, in which Kraton 1101 is separated into three components, though, in the figure, the fastest component located at $R_f = 0.85$ is too faint to be visualized by the staining method with thymol blue.²¹ Apparently the fastest and faster component, and the slow component on the chromatogram should correspond to those appearing at P(a), P(b) and P(c) in Fig. 7, respectively.

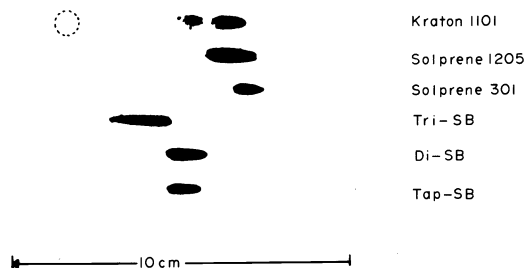


Fig. 9. Chromatograms obtained by phase-separation mechanism for Kraton 1101 and others. A dotted circle indicates the final spot for the fastest component separated from Kraton 1101.

Our next task was to assign the chain architecture of the faster component thus separated as above. To this end, a two-dimensional TLC development technique was utilized. The experimental detail has been described elsewhere.¹⁷ The result is shown in Fig. 10. As is seen in the figure, Kraton 1101 was spotted on a lefthand lower corner of the chromatoplate to prepare the main chromatogram. Besides, two reference chromatograms were prepared on the righthand, and the lefthand upper space of chromatoplate. After Kraton 1101 has been separated by molecular weight in the direction (A), the secondary development perpendicular to (A), i.e. (B), was made by the adsorption mechanism in the same manner as that used to obtain Fig. 8. Comparison of the main chromatogram with the reference one, allows us to justify

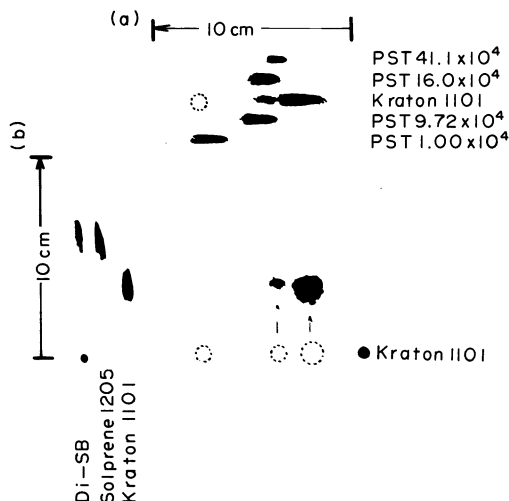


Fig. 10. Two-dimensional chromatograms prepared to determine the chain architecture of Kraton 1101. For the detail, see text.

the foregoing conclusion that Kraton 1101 does not contain any diblock component.

Last topic to be mentioned is the results observed by the use of alumina. As was shown in Table 3, the combination of alumina, as the adsorbent, with carbon tetrachloride, as the developer, lead us to complete separation of triblock from diblock (and also tapered) SB-copolymers. An additional TLC experiment was made on the commercial products under the same development condition as before. Figure 11 shows the chromatogram. Since this separation procedure could not make it possible to give different R_f value for the random, tapered and diblock samples, we have further looked for a condition for distinguishing them chromatographically.

To this end, the development characteristics obtainable with alumina and a binary cyclohexane + chloroform (7:3 by volume) was first investigated. The resultant chromatogram did not indicate any appreciable difference in R_f among the tapered, diblock- and triblock samples, except for a finding that a long upward tailing was exhibited by the tapered sample. This trend was similar to that observed with silica gel and the same binary as before. After a number of TLC runs with various solvent combinations we found that a binary carbon tetrachloride + *n*-hexane (9:1 by volume) was useful to

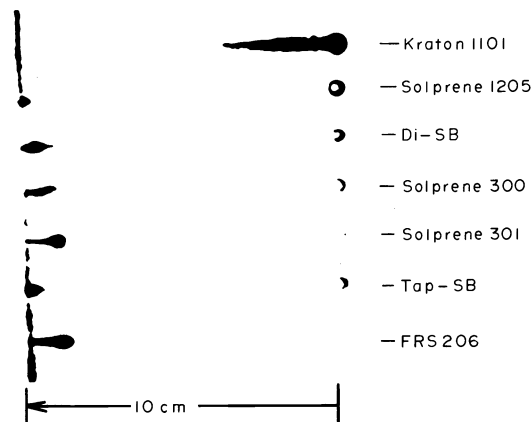


Fig. 11. Chromatograms obtained for commercial SB-products by using alumina thin-layer and CCl_4 as adsorbent and developer, respectively.

distinguish the tapered from the diblock- and triblock samples: The tapered sample migrated up to the solvent front and the diblock sample showed an upward tailing, while the triblock sample remained immobile. As this result implies, the use of carbon tetrachloride and other solvents having polarities lower than carbon tetrachloride is an essential prerequisite to achieve the separation. Another condition for the separation is that alumina is highly activated. Since the latter condition is quite sensitive to the humidity, it should be kept in mind that the reproducibility of the separation with alumina is not high enough for the routine work.

4. TLC APPLICATION TO GRAFT COPOLYMERS

4.1 Separation of side-chain polymers

The most important application of TLC to characterization of graft systems may be to isolate "truly" grafted copolymer species from a given reaction product. Before we deal with such a separation problem, we will describe another approach to characterize cellulose grafts by TLC. Usual separation techniques, such as extraction and/or fractional precipitation,³⁹ and density-gradient ultracentrifugation,⁴⁰ are inapplicable to cellulose grafts unless the cellulose substrate is brought into solution either by chemical modification or by appropriate choice of solvent. Therefore, attempts have been made to isolate the side-chain polymer,^{41,42} based on the fact that the cellulose backbone can be degraded chemically to low-molecular-weight sugars. Despite the simple and straightforward nature of this technique, a problem is still left behind whether or not the specimen isolated in this way be completely free from the attendant homopolymer remaining even after purification treatment of the graft product.

To solve this problem we have applied TLC in the following way.⁴³ Our samples were cellulose-styrene graft products, prepared by heterogeneous mutual irradiation with γ -rays in the absence of a chain-transfer agent for styrene. First, the cellulose grafts were subjected to extraction with boiling benzene to remove the attendant homopolystyrene (PS), and then the cellulose backbone was acid-hydrolyzed. The hydrolytic degradation will yield two types of PS, namely, the side-chain PS which carries a low-molecular-weight sugar at one of the chain ends, and homo-PS with no such end group.

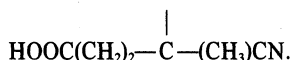
TLC separation of these types of PS was effected using highly activated silica gel, as adsorbent, and THF or benzene, as developer. The chromatogram thus obtained consisted of two final spots, which were located in the proximity of solvent front (the upper component) and starting point (the lower component). The upper component was identified as the attendant homo-PS by simultaneous development with a conventional PS. On the other hand, the lower component, after recovery from the thin layer, was investigated by infrared spectroscopy, and found to exhibit an absorbance around at 3620 cm^{-1} , which is attributable to the stretching vibrations of free OH-groups; while the upper component showed no such absorbance. Since this absorbance was pertinently ascribed to a sugar residue derived from cellulose by hydrolysis, the lower component was identified as the side-chain PS. Quantitation of the chromatogram by photodensitometry yielded the ratio of the side-chain to the occluded PS. It was demonstrated that in spite of the most careful extraction treatment, the graft products still occluded appreciable amounts of attendant PS.

The same TLC procedure was further extended to the

preparative purpose to collect the side-chain and occluded PS separately. Some unique findings on cellulose grafts were gained by this study.⁴³ First, it was found that the weight-average molecular weights of the side-chain and occluded PS were not identical, and the former molecular weight was distinctly higher than the latter. From the standpoint of polymerization kinetics, this cannot be explained in terms of the so-called gel effect.^{39,44} However we observed recently that no such difference in the molecular weight existed for cellulose-styrene grafts, prepared in the same manner as before, but in the presence of a chain-transfer agent for styrene.⁴⁵ Further study on this problem is in progress in our laboratory. Another finding was that the molecular weight distribution of each PS-component was unexpectedly narrow in comparison with those reported previously.

4.2 End-group effect upon polymer separation

TLC experiments,⁴⁷ made to reexamine the forgoing result, i.e. the end-group effect upon polymer separation, will be described below. In the experiment, we used an anionically prepared PS with a carboxyl end group, which has much more a well-defined structure than that of PS derived from the cellulose-styrene graft, mentioned in the previous subsection. To obtain the sample, polystyryl anions, prepared in THF with *n*-butyllithium,²⁸ were carboxylated with carbon dioxide,⁴⁸ and the resultant polymer was subsequently treated with anhydrous hydrogen chloride to liberate lithium from the chain end (coded as C-5). Sample C-5 obviously carries one carboxyl group at one of the chain ends. On the other hand, an aliquot of the living polymer solution was terminated with a methanol-THF solution to obtain a reference sample (coded as M-5). In addition we used one of our stock samples, which were prepared by radical polymerization of styrene with γ,γ' -azo-(γ -cyano-*n*-valeric acid) as initiator, and by subsequent fractionation⁴⁹ (coded as D-4). For this sample, two things should be noted for later discussion. The one is that the polymer chain was proved to carry two carboxyl end groups, and the other is that each end group involves a cyano group in addition to the carboxyl group, as anticipated from the structure of initiator fragments:



The TLC experiment has been designed that separation takes place according to the difference in chemical composition (refer to Section 2.1). To this end, good solvents toward PS were employed as developer. Samples M-5, C-5 and D-4 were chromatographed on thin layer of highly activated silica gel. The result is summarized in Table 4. As is seen in the table, toluene and benzene allow migration of only M-5 (conventional PS) up to the solvent front, leaving C-5 and D-4 completely immobile on the starting point. While, chloroform enables us chromatographically to distinguish C-5 (with one carboxyl group) from D-4 (with two carboxyl and cyano groups per chain). This result was obtained on a relatively lower-molecular-weight level ($\sim 5 \times 10^4$), where the end-group effect should still be prominent. Despite the fact, it must be emphasized that such a slight change in the over-all chemical composition as induced by the end group can be amplified to the drastic change in the sample migration in TLC, as revealed by $R_f = 0$ and 1.

Table 4. TLC results for polystyrenes having nearly the same molecular weight ($\sim 5 \times 10^4$) but different end-groups

Developer	$\epsilon^{\circ a}$	Dielectric constant	R_f		
			M-5	C-5	D-4
CCl_4	0.18	2.22	0	0	0
Toluene	0.29	2.38	1	0 ^b	0 ^b
Benzene	0.32	2.28	1	0 ^b	0 ^b
CHCl_3	0.40	4.62	1	1	0 ^b

(a) Solvent strength parameter [see Ref. (7)].

(b) Slightly upward tailing from the starting point.

In summary: when sample polymers are of low polarities and carry polar end groups and/or a small number of polar side groups, TLC separation by the difference in end- and/or side-group is possible by applying the adsorption mechanism. For this reason, the basic idea presented here may be applicable to other types of polymers, e.g. binder prepolymers whose functionality determination is now of industrial interest.⁵⁰

4.3 Separation of graft products

From the foregoing descriptions it is obvious that TLC will serve as a tool for separating a given graft product into component species. In fact, Horii *et al.* succeeded in such TLC separations for grafted products of cellulose triacetate, polyvinyl acetate, nylon and others,²⁶ and one of the results has been transferred to absorption column chromatography for the preparative purpose.⁵¹ In this subsection we will present our preliminary result on an acetylated cellulose-styrene graft product.⁴⁶

The cellulose graft sample was prepared in almost the same manner as briefly described in Section 4.1, except for the presence of carbon tetrachloride used as a chain-transfer agent. After subjected to extraction treatment of homo-PS, the sample was chemically modified to the triacetate in order to bring it in solution. The acetylated cellulose graft was separated by a "stepwise" development technique^{17,36} into three components, namely, the grafted and ungrafted cellulose triacetate (CTA-g and CTA), and attendant PS (A-PS). As the name implies, this technique allows migration of each component of a given sample to different level in a stepwise manner by multiple development runs for the same chromatoplate.

First, a sample stock solution was prepared with chloroform and spotted on a thin layer of highly activated silica gel. The primary development was made with a binary chloroform + dioxane (3:7 by volume) in such a way that the components, CTA-g and A-PS, migrate up to the solvent front whereas the component CTA remains on the starting level. In practice, we settled the solvent front at 5 cm above the starting level. After the primary development run, the chromatoplate was once dried up and subjected to the secondary development up to 10 cm above the starting point, for which chloroform was used as developer. By this procedure we could obtain a chromatogram consisting of three final spots at the level of 0, 5 and 10 cm above the starting point. The two spots, located at 0 and 10 cm, were assigned respectively to CTA and A-PS by a simultaneous development of their reference samples. The chromatogram was scanned at 210 nm with a TLC scanning spectrophotometer. No absorbance at this wavelength was observed on the

starting level, whereas it was observed on the levels of 5 and 10 cm. This result suggests, at least, that any PS component does no longer exist on the starting level, indicating complete separation of CTA-g and A-PS from the ungrafted CTA. Although we have no direct evidence, we may identify the final spot at 5 cm as the true graft copolymer. Scanning-spectrophotometric quantitation of these chromatograms is not yet successful due to a following phenomenon: An appreciable portion of spotted sample often migrates not only on the thin-layer surface but toward the glass-silica gel interface becoming hardly visible from the silica gel side. As discussed by Hezel,⁵² however, this difficulty will be overcome by minimizing the sample size and enhancing the sensitivity of photometer.

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