

CHARACTERIZATION OF COPOLYMERS BY TLC, GPC AND OTHER METHODS

Hiroshi Inagaki and Takeshi Tanaka

Institute for Chemical Research, Kyoto University, Uji, Kyoto-Fu 611, Japan

Abstract - This article describes three topics related to molecular characterization of copolymers having different chain architecture. The first topic is concerned with the feasibility of thin-layer chromatography (TLC) in separation of mixtures of the homopolymers having chemical differences only in the terminal groups. Applications of this technique to characterization of graft copolymerization products are described. The second topic involves a review of the determination of composition heterogeneities of statistical and block copolymers by gel permeation chromatography and TLC. Emphasis is put on the specific feature of the composition heterogeneity of block copolymers. Finally another possibility for the composition heterogeneity determination is described, which is achieved by using light scattering in a modified way. The limits of its applicability are discussed in detail.

INTRODUCTION

The molecular characteristics of copolymers with any chain architectures, such as the number- and weight-average molecular weights (M_n and M_w), and the molecular weight distribution (MWD), are obtainable with the same instrumentation as applied to homopolymers; although, except for osmometry, the experimental procedures and/or the data treatment are much more complicated. However there are other characteristics, specific to copolymers, for which no routine method has yet been established: these are the composition heterogeneity, the homogeneity in chain architecture for block and graft copolymers, the chain structure for graft copolymers, etc. Difficulties in the determination of these characteristics originate principally from lack of means for polymer separation, as will be discussed below.

For determining the composition heterogeneity, especially the composition distribution curve (CDC), cross fractionation is a most basic method. In practice, however, one encounters a difficulty in selecting pairs of solvent and precipitant, in addition to the time-consuming nature of this method (Ref. 1). A unique method similar to the counter-current distribution method (Ref. 2) has been proposed by Kuhn (Ref. 3) and the turbidimetric (and cloud-point) titration methods have been extensively worked out and discussed by Elias (Ref. 4). Despite these efforts it may be obvious that for thermodynamic reasons, these methods do not allow one to fractionate copolymers solely by their composition without interference from molecular weight effects. Thus to cope with the difficulty, the application of various chromatographic methods has attracted attention, and this will be discussed as one of the main subjects in this article.

It is a rare case that a given block- or graft-copolymerization product is perfectly free from polymeric impurities even after it has been refined by an appropriate procedure. For example, a graft product is usually composed of true graft copolymer, unreacted mother polymer and attendant homopolymer. Isolation of true graft copolymer from crude product is thus the most important task to be done in advance of the molecular characterization. However the isolation is often hindered by the so-called emulsifying effect (Ref. 5) even when the graft product is soluble in some solvents. The same is also true for block products. Therefore, establishment of appropriate fractionation techniques which guarantee homogeneity in chain architecture is of primary importance.

In this article we will deal with three topics related to molecular characterization of various copolymers. The first topic involves a potentiality of thin-layer chromatography (TLC) in separating polymer species by differences in their terminal groups, and its application for characterizing graft-copolymerization products of vinyl monomers onto cellulose. The second topic will be concerned with the determination of composition heterogeneities of statistical and block copolymers by gel permeation chromatography (GPC) and a column adsorption-chromatography. Finally another possibility for the determination

of composition heterogeneities without the aid of separation procedure will be described, which is achievable by using classical light scattering in a modified way.

SEPARATION OF POLYMERS BY DIFFERENCE IN THEIR TERMINAL GROUPS

The feasibility of applying TLC to this type of problem was first demonstrated by Taga and Inagaki for graft-copolymerization products of styrene onto cellulose prepared by simultaneous gamma-ray irradiation (Ref. 6). The graft product was acid-hydrolyzed to recover polystyrene (PS) produced within the cellulose matrix. The PS species thus obtained was subjected to TLC. It was found that the sample was separated into two components: one of them remained immobile on the chromatogram ($R_f = 0$) because of some sugar residue attached to the PS-chain end, while the other migrated up to the solvent front ($R_f = 1$) so that it was regarded as the attendant PS. This observation indicates that TLC enables one to distinguish the true grafted side-chain PS from the attendant PS according to the difference in their terminal groups.

Effects of terminal groups upon polymer separation by TLC were further examined by Min et al., using three types of polystyrenes, namely with two, one or no carboxyl terminal groups (Ref. 7). The samples were prepared mainly by anionic polymerization techniques. It was concluded that when a sample polymer is of low polarity and carries polar terminal groups and/or a small number of polar side-groups, TLC separation by the difference in the number of these polar groups was possible by the polarity-controlled adsorption mechanism (Ref. 8). This finding was then successfully applied to the determination of functionality distributions in telechelic prepolymers, especially, commercial liquid rubbers of various types of α, ω -difunctional polybutadienes (Ref. 9).

With the aid of the aforementioned TLC technique we investigated in detail the mechanism for simultaneous graft copolymerization of styrene onto cellulose induced by gamma-rays (Ref. 10). Various graft products were prepared by changing the monomer content in the reaction medium, the total irradiation dosage, the amount of chain transfer agent (CCl_4) and the dose rate. Then, TLC and GPC were applied to determine the true percentage grafting (Y) and the molecular weight (M) of true grafted side-chains for the graft products, respectively.

Highly activated silica gel was used as the stationary phase in TLC and the development was made with benzene. Quantification of chromatograms was made by a method, similar to that proposed by Padley (Ref. 11), which may be called 'thin layer-FID chromatography' (FID: flame ionization detector). The procedure has been reported elsewhere (Ref. 9). This analysis allowed evaluation of the quantity, P_g , which is defined by:

$$P_g = R_2 / (R_1 + R_2)$$

where R_1 and R_2 are the FID responses due to the attendant homopolymer and the side-chain polymer, respectively. Once we know the apparent increase Y_a of the cellulose matrix after graft copolymerization,

$$Y_a (\%) = \frac{(\text{wt of graft product}) - (\text{wt of cellulose})}{(\text{wt of cellulose})}$$

we can estimate the true percentage grafting through

$$Y = Y_a \times P_g$$

By way of example, some results will be shown below. In Table 1 are given graft-co-

TABLE 1. Radiation graft copolymerization data obtained under variation of styrene content*

Sample code	St/MeOH/H ₂ O (by vol)	Produced PS (g)		Y _a (wt%)
		F-PS ^a	B-PS ^b	
G05	0.5/10/1	0.020	0.050	5.0
G1	1/10/1	0.058	0.075	7.5
G5	4/10/1	0.072	0.247	24.7
G7	7.3/10/1	0.136	0.281	28.1

^a Polystyrene produced in reaction medium.

^b Polystyrene produced within cellulose matrix.

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polymerization data obtained at a constant dosage (3.8×10^5 rad) under variation of styrene content. Table 2 summarizes values of P_g and Y for the graft products, and characterization

TABLE 2. Characterization results of graft products and polystyrenes recovered as hydrolysis residue*

Sample code			G.p.c. results			
Graft Product	PS	P_g	$(Y_a \times P_g)$	$M_n \times 10^{-4}$	M_w/M_n	G_s^a
G05	PSH-05	0.49	2.5	3.2	2.0	2.2 (4.4)
G1	PSH-1	0.46	3.5	5.1	2.1	2.0 (4.3)
G5	PSH-5	0.44	10.8	13.6	4.9	2.2 (5.1)
G7	PSH-7	0.41	11.5	15.3	4.8	2.3 (5.4)

^a Values in parentheses were calculated on the basis of Y_a .

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data for the polystyrene species recovered as the hydrolysis residue. The last column in the table contains the chemical yield of irradiation for cellulose, G_s , which is estimated from:

$$G_s = Y \times N_A / \bar{M}_n^s \times D \times A$$

where \bar{M}_n^s is the number-average molecular weight of side chains, N_A is the Avogadro number, D is the total dosage (rad), and A is the energy conversion factor, 5.8×10^{13} [eV/(g.rad)]. As seen from the table, the G_s -values thus estimated are effectively constant (2.1 ± 0.1) independent of the styrene content. This means that \bar{M}_n^s is proportional to Y , and the linearity suggests that the increase in Y was caused uniquely by the propagation of each side chain. In sharp contrast to this finding it should be noticed that G_s -values deduced from Y_a rather than Y are much larger than 2.1, scattering in an irregular manner (see values in parentheses in the same column of Table 2).

Another regularity in the graft copolymerization data may be confirmed by inspecting Table 3, which shows the influence of changing the total dosage (irradiation time). This series

TABLE 3. Characterization results of graft products obtained under variation of irradiation dosage and polystyrenes recovered as hydrolysis residue*

Sample code	Graft products			Polystyrenes	
	Irradiation (rad $\times 10^{-5}$)	P_g	Y (wt %)	$M_n \times 10^{-4}$	G_s
G5-04	1.8	0.38	5.1	13.9	2.1
G5-08	3.5	0.44	10.8	13.6	2.3
G5-16	7.0	0.35	22.0	15.5	2.1
G5-20	8.8	0.31	32.6	16.8	2.3
G5-24	10.5	0.23	33.0	16.6	1.9

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of experiments were carried out by keeping the styrene content and other conditions constant. The sample code given in the table refers to each PS hydrolysis-residue recovered from the graft product relevant to each irradiation time. A result to be noticed in Table 3 is that the M_n -values for side-chain PS are practically kept constant over the range of total dosage tested. This allows us to conclude that the number of side chains having nearly the same length increased with increasing dosage so that the Y -value was enhanced. As seen in the last column in the table, G_s -values may be again regarded as

constant (2.1 ± 0.2), implying that a constant number of side chains having nearly the same length was produced by unit irradiation energy. Before closing this section, it should be emphasized that such consistent results found for graft copolymerization in an heterogeneous system would have hardly been deduced without the aid of the TLC separation technique. Moreover, this technique was successfully applied by Taga et al. to elucidating the reaction site in graft copolymerizations of styrene and methyl methacrylate onto cellulose initiated with ceric ammonium nitrate in the absence of mineral acid (Ref. 12,13).

COMPOSITION-HETEROGENEITY DETERMINATION BY GPC AND ADSORPTION-CHROMATOGRAPHIC METHODS

A copolymer of any chain architecture has a heterogeneity in molecular weight as well as in composition, and the determination of composition heterogeneity can never be completely free from the complications of molecular weight heterogeneity, as discussed in 'Introduction'. A general way to cope with this complexity may be as follows: a given copolymer sample is first fractionated on the basis of molecular size using GPC, although GPC does not strictly guarantee fractionation by molecular weight, and then each fraction is separated by composition using an appropriate method, which can be fractionation by solubility, turbidimetric titration or adsorption chromatography. A typical example of this approach is seen in the instrumentation proposed by Hoffmann and Urban, in which GPC was combined with turbidimetric titration (Ref. 14). In this section we will review the variety of efforts made to establish composition heterogeneity for statistical and block copolymers.

Statistical copolymers

The composition heterogeneity in statistical copolymers can, in principle, be calculated in a form of composition distribution curve (CDC) if all elementary reactions taking place during copolymerization are known, as has already been discussed in the 1940's (Ref. 15,16). The well-known copolymerization equation based on the terminal model became available, and integration of this equation was made first by Skeist (Ref. 17) to predict the CDC and later by several authors (Ref. 18,19) to calculate the average composition as a function of the conversion of monomer to polymer.

Several attempts to judge the validity of the terminal model have been made. Some authors reported results which support its validity (Ref. 20-24), whereas others cast doubts on it (Ref. 25,26). On reviewing these papers we notice that disagreement between theory and experiment has been found for copolymer samples obtained in bulk at high conversions. This finding means that the composition heterogeneity, especially, of commercial products, cannot be predicted theoretically and can only be determined experimentally. We discuss below some experimental methods presently available for this purpose.

The simplest method may be use of GPC furnished with a dual detector system, the utility of this method was first demonstrated by Adams (Ref. 27). The principle is that use of a dual detector system can yield the composition at each elution volume (hereafter denoted as the point-by-point composition) so that information of the composition heterogeneity can be deduced. However it should be remembered that this method gives only information on the composition drift as a function of apparent molecular weight but not the CDC, unless a unique correlation exists between the composition and the chain length for a given copolymerization system. This means that the CDC of radical copolymerization products cannot be obtained by this method, since the composition and the chain length may roughly be regarded as independent of each other.

Mirabella et al. applied this method to investigate the composition heterogeneity of poly-(vinyl chloride-co-vinyl stearate) prepared in bulk at a high conversion (Ref. 25). For this work GPC equipped with RI- and IR-detectors was used. It was found that the drift in composition thus observed was far wider than expected from the terminal model. A study similar to the above was made by Teramachi et al. for a statistical copolymer of styrene and methyl acrylate at a high conversion (Ref. 26). Using GPC having RI- and UV-detectors, they determined the MWD and the point-by-point composition. A discrepancy was found between theory and experiment for a high conversion sample, in contrast to the fact that the molecular characteristics of this copolymer prepared at a low conversion were well described in terms of the terminal-model kinetics.

Somewhat differing from the foregoing studies, Elgert and Wohlschiess tried to estimate the CDC of poly(α -methyl styrene-co-butadiene) by GPC using a dual detector system (Ref. 28). Their analysis was possible because the sample was obtained by anionic polymerization; in other words, a correlation between composition and chain length exists since butadiene is preferentially enchaind at an early stage of the propagation reaction while the chain length tends to increase with time. However it should be pointed out that the true CDC can be broader than estimated by this analysis.

In contrast to the single use of GPC described above, TLC based on the polarity-controlled adsorption mechanism (Ref. 8) has been proved to be applicable directly to the CDC determination by Belenkii and Gankina (Ref. 29) and independently by Inagaki et al. (Ref.

23). A variety of successful applications of TLC to the present purpose have been reviewed by the aforementioned authors (Ref. 8,30). At the very beginning of the TLC application, this technique had been considered to be useful mainly for copolymers whose comonomer pairs have a large difference in polarity, such as between styrene and acrylates. Later, however, it was recognized that TLC was applicable even to copolymers of styrene and dienes which have small polarity differences (Ref. 31,32). Drawbacks in the application of TLC are experienced at present rather in visualization and quantification of chromatograms.

To avoid such drawbacks Teramachi et al. attempted recently to introduce a high-speed liquid chromatograph for separation of poly(styrene-co-acrylate) by composition (Ref. 33). However it is not yet affirmed whether or not this method is widely applicable to copolymer separation solely by composition. Although adsorption liquid chromatography (ALC) and TLC should give the same separation result if the same adsorbent and eluent are adopted, there is an essential difference between these methods in the action of adsorbent upon separation: TLC uses adsorbent in its activated state whereas ALC does not, as discussed in detail by Tanaka et al. (Ref. 34). This may be the reason why TLC can be superior to ALC in separability.

In connection with separability it is noteworthy that Kohjiya et al. found a prominently high performance of TLC in separating copolymers of styrene and 1-chloro-1,3-butadiene (CB) by composition (Ref. 35). Samples having different CB-content were chromatographed on highly activated silica gel by a gradient development with cyclohexane and tetrahydrofuran as the initial and secondary developer, respectively. Separation was achieved for samples having extremely low CB-contents so that TLC was utilized to determine the CB-contents which were not detectable with NMR and elementary analysis, as shown in Table 4.

TABLE 4. Determination of CB-content in poly(CB-co-styrene)*

Sample code	CB-content in feed (mole %)	Conversion (wt %)	CB-content in polymer			
			¹ H NMR	Elementl analysis of Cl	TLC	Calc ^a
1	0.102	32.5	- ^b	0	0.40	0.35
2	0.156	32.1	-	0	0.65	0.60
3	0.180	6.82	-	1.55	(1.55) ^c	-
4	0.450	6.13	-	2.11	(2.11) ^c	-
5	3.51	80.0	-	4.70	(4.70) ^c	4.8

^a Calculated by the Skeist method (Ref. 15) with the reactivity ratios and the conversion.

^b Undetectable.

^c Samples No. 3, 4 and 5 were used as the reference for TLC. For the detail, see original text.

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Block copolymers

The composition heterogeneity in a block copolymer generally results from the heterogeneity in the chain lengths of the constituent sub-chains, and hence, it is closely correlated with the MWD, differing from the case of statistical copolymers. Thus it must be noted that the MWD of block copolymers can be narrower than those of their precursors, as predicted theoretically (Ref. 36-38). This prediction can be derived from a theory based on an assumption, called the 'random coupling model', which will be described below.

For the sake of simplicity, we will consider a diblock copolymer of A-B type since the theory can be easily extended to any multiblock copolymer (Ref. 39). A randomly coupled diblock copolymer is characterized by the equation:

$$N(M_A, M_B) = N_A(M_A) \times N_B(M_B) \quad (1)$$

where $N(M_A, M_B)$ is the probability density of finding copolymer molecules with molecular weight M_A and M_B for the A- and B-subchains, respectively, and $N_K(M_K)$ is the number-based MWD for the K precursor (K = A or B). More detailed discussion on this model has been made by Vorlicek and Kratochvil (Ref. 37) and Kotaka et al. (Ref. 38).

In the following we will describe some features to be expected on the basis of this model.

First, the weight-based MWD is written by using $N(M_A, M_B)$ in a form:

$$W(M_A, M_B) dM_A dM_B = [(M_A + M_B) / \bar{M}_n] N(M_A, M_B) dM_A dM_B \quad (2)$$

Or in terms of the total mass, $M = M_A + M_B$, and the composition, $x_K = M_K / \bar{M}_n$ ($K = A$ or B), we have

$$W(M, x_A) dM dx_A = (M^2 / \bar{M}_n) N(x_A M, x_B M) dM dx_A \quad (3)$$

Then, by referring to Eqs. (1) and (2), the \bar{M}_w of a block copolymer is given by

$$\bar{M}_w = \int_0^\infty \int_0^\infty (M_A + M_B) W(M_A, M_B) dM_A dM_B = (1 + \bar{x}_A^2 Y_A + \bar{x}_B^2 Y_B) \bar{M}_n \quad (4a)$$

hence

$$Y = \bar{x}_A^2 Y_A + \bar{x}_B^2 Y_B \quad (4b)$$

with

$$Y_K = (\bar{M}_w^K / \bar{M}_n^K) - 1, \quad K = A \text{ or } B \quad (5)$$

and

$$\bar{x}_A + \bar{x}_B = 1$$

where \bar{M}_w^K and \bar{M}_n^K refer to the K -subchains and \bar{x}_A^K is the average weight fraction for the K -subchains.

Similarly the composition distribution function of a block copolymer is expressed by

$$W(x) dx = \left[\int_0^\infty W(M, x) dM \right] dx \quad (6)$$

which is computable if the $N_K(M_K)$ is given. Equation (6) can be analytically integrated provided that the Schulz distribution or the log-normal distribution is assumed for the $N_K(M_K)$. For the resultant expressions, the reader is referred to Tanaka et al. (Ref. 34,39). The important points are that the $W(x)$ for a block copolymer can be calculated only with knowledge of x , Y_A and Y_B if the hypothesis of 'random coupling' is valid, and that the $W(x)$'s derived from the above two distributions differ little from one another.

Now we will discuss the validity of the random coupling model. The hypothesis has been recently verified by a direct experimental test for block copolymers of styrene and butadiene prepared by an anionic living polymerization method via a sequential addition procedure (Ref. 40), after the previous, indirect observations which implied the random coupling nature of copolymers obtained with such a preparation method (Ref. 36, 41, 42). On the other hand, applicability of the hypothesis to copolymers prepared by a coupling reaction itself may be somewhat problematic, since the rate constant of a coupling reaction will depend on the chain lengths of precursor polymers largely for physical reasons. However, the MWD calculated under neglect of such a dependence approximates well to the actual MWD of a free-radical polymerization product in many cases. This may suggest that random coupling statistics are also valid approximations for the latter type of copolymers.

Turning back to the calculation problem of $W(x)$, we will consider the determination of Y_A and Y_B . In many cases, one may obtain only one or none of the precursor polymers. For example, by an anionic copolymerization in which a living poly-A initiates the polymerization of monomer B, one can gain one precursor poly-A but not the other poly-B unless there is a method that selectively degrades poly-A (Ref. 40). Light scattering is particularly useful for characterizing such a copolymer, if the measurement is made in a solvent giving zero refractive increment v_A . In this way we can determine \bar{M}_w^B , from which we know the polydispersity Y_B of the B-subchain, since we usually know \bar{M}_n^B with more ease. However it should be remembered that this method may become impractical when Y_B is small, and also, the large effects of intermolecular interference often observed in such a system (Ref. 43,44) can lead to a poorly defined value of \bar{M}_w^B . The drawbacks may be eliminated by carrying out light scattering measurements in a modified way, as will be described in the next section.

Now we will review some examples of CDC analyses of block copolymers made by adsorption chromatography. In a previous section we have mentioned that the retention behaviour of statistical copolymers in TLC based on the polarity-controlled adsorption mechanism depends

very little on sample molecular weight if it is sufficiently large, e.g. for $M > 5 \times 10^5$. Kotaka et al. applied this principle to the CDC analysis of block copolymers of styrene and methyl methacrylate (MMA) (Ref. 41). It was confirmed that the TLC separation occurred predominantly by the difference in composition and the diblock copolymer could be chromatographically distinguished from the triblock one. The CDC thus constructed were very broad in sharp contrast to the narrow MWD of these samples, and this feature was interpreted successfully in terms of the random coupling statistics.

Another attempt to separate a diblock copolymer of PS-PMMA by composition on a semi-preparative scale was made by Donkai et al. (Ref. 34). Their method is based on the principle of adsorption TLC but analogous to column fractionation from the aspect of instrumentation. A glass column, as sketched in Figure 1, was packed with activated silica gel. In advance, sheets of filter paper to which sample polymer had been loaded were placed

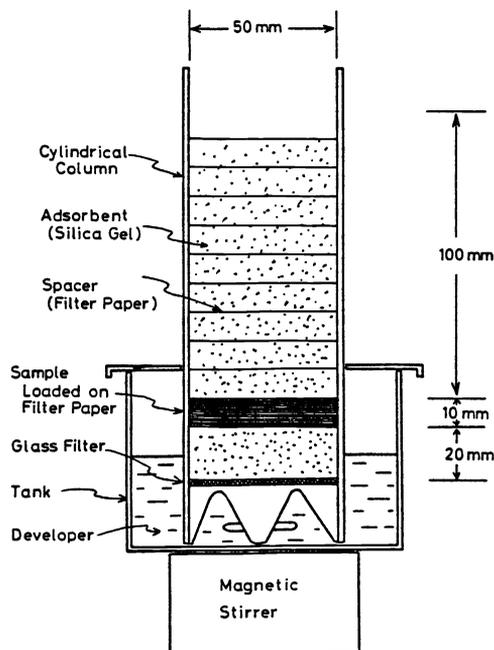


Fig. 1. Schematic sketch of fractionation column. Reproduced from Ref. 34 by courtesy of Marcel Dekker, Inc.

at ca. 2 cm above the bottom (starting level), and the entire column space above the starting level was divided into nine compartments by eight sheets of filter paper, as shown in the figure. The column thus prepared was immersed in an eluent, and elution was continued in the same manner as in TLC. Then, the silica gel in each compartment was taken out, and the polymeric component in it was extracted and recovered.

About 300 mg of the PS-PMMA sample, coded 74B, whose characteristics and GPC-result are respectively given in Table 5 and in Figure 2, was subjected to this separation. Elution

TABLE 5. Molecular characteristics of PS-PMMA diblock copolymers*

Sample Code	\bar{x}_{PS}	$10^{-5} \bar{M}_n^a$	Y_{PS}^b	Y_{PM}	\bar{M}_w/\bar{M}_n^c
74B	0.47	7.39	0.06	0.38	1.12
63B50	0.49	6.89	0.12	0.37	1.13

^a Osmometry.

^b Values for the precursor PS.

^c Calculated from Eq. (4a).

* Reproduced from Ref. 34 by courtesy of Marcel Dekker, Inc.

was carried out for ca. 5 hrs. to separate the sample into nine fractions. Each fraction thus obtained was characterized by GPC to determine the average composition and the elution

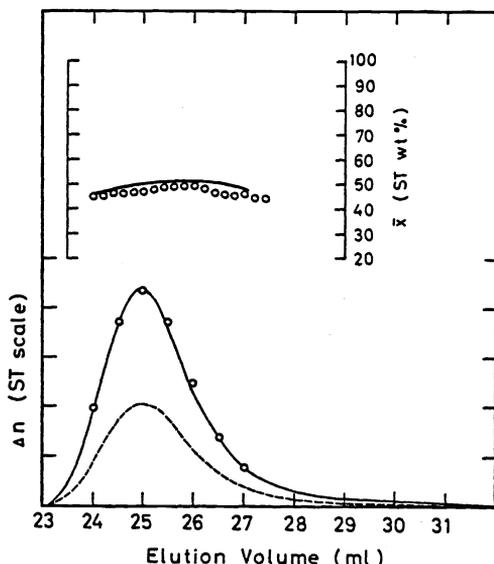


Fig. 2. GPC elution and point-by-point composition curve for diblock sample 74B. Reproduced from Ref. 34 by courtesy of Marcel Dekker, Inc.

volume at the peak maximum, V_e^* . The result indicated that separation was achieved predominantly by the composition difference. The resultant CDC is shown by open circles in Figure 3 in a form of integral distribution, and its three-dimensional indication is given

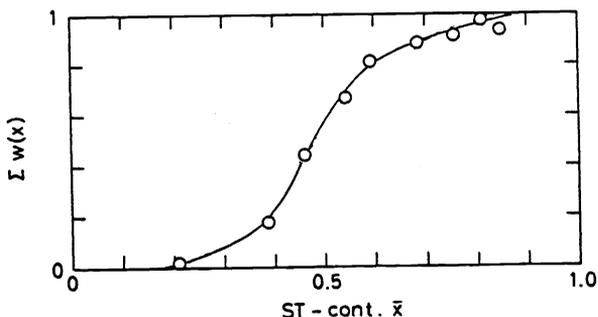


Fig. 3. Integral CDC for 74B obtained by adsorption column chromatography.

in Figure 4. Again it should be noted that the CDC is very broad in contrast to the MWD. A more detailed discussion on this problem has been made elsewhere (Ref. 39).

The last topic to be mentioned in this subsection is concerned with information derivable from the GPC point-by-point composition for block copolymers. Let us express by $\langle x_A \rangle_M$ the average composition of copolymer species having apparent molecular weights, M . For a randomly coupled block copolymer, the average value of the first moment with respect to the composition can be written as:

$$\langle x_A \rangle_M = \frac{\int_0^1 x_A N_A(x_A, M) N_B(x_B, M) dx_A}{\int_0^1 N_A(x_A, M) N_B(x_B, M) dx_A} \quad (7)$$

When the Schulz distribution is assumed for N_K , the M -dependence of $\langle x_A \rangle_M$ can be given by

$$d\langle x_A \rangle_M / dM = (y_B - y_A) \{ \langle x_A^2 \rangle_M - (\langle x_A \rangle_M)^2 \} \quad (8)$$

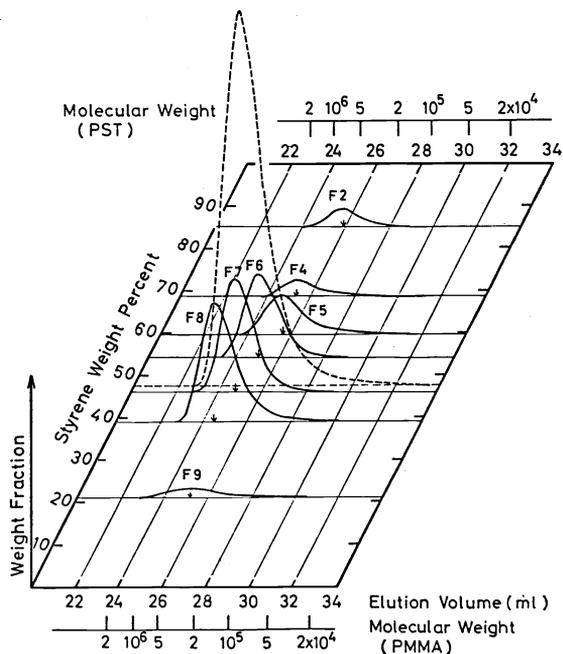


Fig. 4. Three-dimensional indication of CDC and MWD for 74B.

with $y_K \equiv (\bar{M}_n^{K} Y_K)^{-1}$ for $K = A$ or B . As $\langle x_A \rangle_M^2 - (\langle x_A \rangle_M)^2 \geq 0$ holds, the sign of the M -dependence will be decided by that of $(y_B - y_A)$. This prediction may qualitatively be correct for MWD-functions other than the Schulz distribution. In this connection it should be emphasized that no variation of the GPC point-by-point composition does not necessarily guarantee uniformity in composition for a sample copolymer, as already demonstrated by Figures 2 and 3.

NEW APPLICATION OF CLASSICAL LIGHT SCATTERING

In light scattering from an A-B copolymer, one conventionally measures the apparent molecular weight \bar{M}_{app} in at least three solvents and evaluates the weight average molecular weight \bar{M}_w and the heterogeneity parameters P and Q through the relation (Ref. 45,46),

$$\bar{M}_{app} = \bar{M}_w + 2P[(v_A - v_B)/\bar{v}] + Q[(v_A - v_B)/\bar{v}]^2 \quad (9)$$

Here v_K ($K = A$ or B) is the refractive index increment of the K homopolymer, \bar{v} is the average increment of the copolymer, and P and Q are given by

$$P = \sum_i w_i M_i \Delta x_i \quad (10)$$

$$Q = \sum_i w_i M_i \Delta x_i^2 \quad (11)$$

with w_i being the weight fraction of species i have molecular weight M_i and composition deviation Δx_i from the mean.

This method usually provides fairly reliable values of \bar{M}_w for copolymers with broad as well as narrow distribution in composition. However, it has been pointed out that the method is not necessarily sensitive enough to permit its routine use for determination of P and Q (Ref. 47,48). For example, values of Q which are much too large to be theoretically explained have been obtained for certain copolymers (Ref. 46,49). In most cases, such copolymers are those with relatively narrow composition distribution. This indicates that the method is insensitive to small heterogeneity, and can even lead to an erroneous conclusion when employed beyond the sensitivity limit. However, it is obvious from Eq. (9) that the smaller Q is, the smaller \bar{v} must be, so that the relative magnitude of the last term becomes large enough. It seems to us that this condition has not been met in most of the experiments which gave unreasonable results.

Experiments made in an isorefractive solvent, i.e., a solvent in which $\bar{v} = 0$, are distinguished from those in other conditions: scattering therein arises solely from the

fluctuation of composition about the mean (Ref. 50), and the forward scattering intensity becomes proportional directly to Q . One may thus expect to determine Q with enhanced accuracy. The feasibility of this kind of measurement has been examined firstly by Kratochvil and co-workers. (Ref. 48,51) and subsequently by us (Ref. 34,52). In what follows, we discuss the feasibility and limitations of this special technique referring mainly to the recent work of Tanaka et al. (Ref. 52).

We begin with the general theory of light scattering from multi-component systems (Ref. 53). For small concentration c , the forward scattering intensity R_0 is given by the following equation (Ref. 54):

$$R_0/K^*c = \sum_i \nu_i^2 w_i M_i - 2c \sum_{i,j} \nu_i \nu_j w_i w_j M_i M_j B_{ij} + \dots \quad (12)$$

where K^* is a constant, ν_i is the refractive index increment of species i , and B_{ij} is the osmotic second virial coefficient between species i and j .

If ν_i is assumed to be linear in copolymer composition, as is usually the case, the first term in Eq. (12) can be expressed in a form equivalent to Eq. (9),

$$\lim_{c \rightarrow 0} R_0/K^*c = \bar{\nu}^2 \bar{M}_w + 2\bar{\nu}(\nu_A - \nu_B)P + (\nu_A - \nu_B)^2 Q \quad (13)$$

but unlike Eq. (9), this equation is defined for all $\bar{\nu}$. The difference $(\nu_A - \nu_B)$ for a given polymer pair is nearly independent of solvent, so is the last term in Eq. (13). In general, determination of $\bar{\nu}$ would be subject to an absolute error $\Delta\bar{\nu}$, whose magnitude is approximately independent of $\bar{\nu}$ if $\bar{\nu}$ is small. Accordingly, the value Q_{obs} which is experimentally obtained from measurements of R_0 , $(\nu_A - \nu_B)$, etc. would be in error as much as

$$\frac{Q_{\text{obs}} - Q}{Q} = \frac{\Delta\bar{\nu}}{(\nu_A - \nu_B)^2} [(2\bar{\nu} + \Delta\bar{\nu})(\bar{M}_w/Q) + 2(\nu_A - \nu_B)(P/Q)] \quad (14)$$

Clearly, the error from this source is minimum when $\bar{\nu} = 0$, whereas it can be destructively large when $\bar{\nu}$ and \bar{M}_w/Q are large. Thus, Eq. (14) with $\bar{\nu} = 0$ represents one limit of feasibility of light scattering. Since P is similar to or smaller than Q (or $P/Q \lesssim 1$) in most cases, the last term in brackets in Eq. (14) becomes less and less important as \bar{M}_w/Q increases, or composition heterogeneity becomes smaller. In such a limit, we have

$$(Q_{\text{obs}} - Q)/Q = [\Delta\bar{\nu}/(\nu_A - \nu_B)]^2 / (Q/\bar{M}_w) \quad (15)$$

If we legitimately set $\Delta\bar{\nu} \sim 2 \times 10^{-3}$ (ml/g), and require the relative accuracy in Q_{obs} to be 20%, then we have

$$(\nu_A - \nu_B)^2 (Q/\bar{M}_w) \gtrsim 2 \times 10^{-5} \quad (16)$$

Another limitation would be the lowest intensity $R_{0,\text{cri}}$ that can be determined with sufficient accuracy. Following Vorlicek and Kratochvil (Ref. 51), we assume $R_{0,\text{cri}}$ to be 10% of R_{90} for benzene and the solvent refractive index to be 1.5. The last term in Eq. (13) which we want to determine must be larger than $R_{0,\text{cri}}$, and thus we have the following relation for the V_v scattering with 436-nm light:

$$Qc(\nu_A - \nu_B)^2 \gtrsim 1 \times 10^{-1} \quad (17)$$

Equation (16) and (17) represent the applicability limits of light scattering in terms of Q , Q/\bar{M}_w , $(\nu_A - \nu_B)^2$, and c . These limits would be reached only by use of isorefractive solvents, as we have pointed out repeatedly.

There is another large advantage in using an isorefractive solvent, which may be understood when the second term in Eq. (12) is examined. For $\bar{\nu} = 0$, the equation may be cast into the form,

$$R_0/K^*c(\nu_A - \nu_B)^2 = Q[1 - 2\langle B \rangle (P^2/Q)c + \dots] \quad (18)$$

where $\langle B \rangle$ is an average virial coefficient defined by

$$\langle B \rangle = \frac{\sum_i \sum_j w_i w_j M_i M_j \Delta x_i \Delta x_j B_{ij}}{\sum_i \sum_j w_i w_j M_i M_j \Delta x_i \Delta x_j} \quad (19)$$

Equations (18) and (19) should be compared with the following equations, which describe the magnitude of concentration dependence in a thermodynamically equivalent system with $v_A = v_B = v (\neq 0)$:

$$R_0/K^*v^2c = \bar{M}_w(1 - 2\bar{B}\bar{M}_w c + \dots) \quad (20)$$

$$\bar{B} = \frac{\sum_i \sum_j w_i w_j M_i M_j B_{ij}}{\sum w_i w_j M_i M_j} \quad (21)$$

Since $\langle B \rangle \sim \bar{B}$ and $P < Q$ in order of magnitude, the second term in brackets in Eq. (18) differs by about a factor Q/\bar{M}_w from the corresponding term in Eq. (20). Clearly, the concentration dependence in an isorefractive system is less significant than in the conventional system, since Q is always much smaller than \bar{M}_w (typically, $Q/\bar{M}_w < 10^{-2}$). For somewhat more rigorous treatments of this problem, the reader is referred to the original paper (Ref. 52).

Incidentally, we note that when composition heterogeneity is extremely large as in a mixture of homopolymers, a considerable magnitude of concentration dependence may be observed depending on the interactions between unlike polymers. This in turn suggests a simple and reliable method to determine the Flory interaction parameter χ_{AB} (Ref. 55). Based on this principle, Tanaka and Inagaki (Ref. 56) have recently succeeded in determining χ_{AB} as small as about 3×10^{-3} with sufficient accuracy.

The above theoretical predictions have been experimentally tested by Tanaka et al. (Ref. 34, 52), who investigated copolymers of styrene and methyl methacrylate (MMA) in bromobenzene. In this solvent, both $v_{PS} (> 0)$ and $v_{PMMA} (< 0)$ vary with temperature so that the condition of isorefractivity could be met by adjusting temperature. Some of their results will be reproduced below.

Figure 5 shows the R_0/K^*c vs. $[\sin^2(\theta/2) - c]$ plot for a diblock copolymer of PS-PMMA type (sample 74B, see Table 5). To be noted in the figure is that: (i) even though bromo-

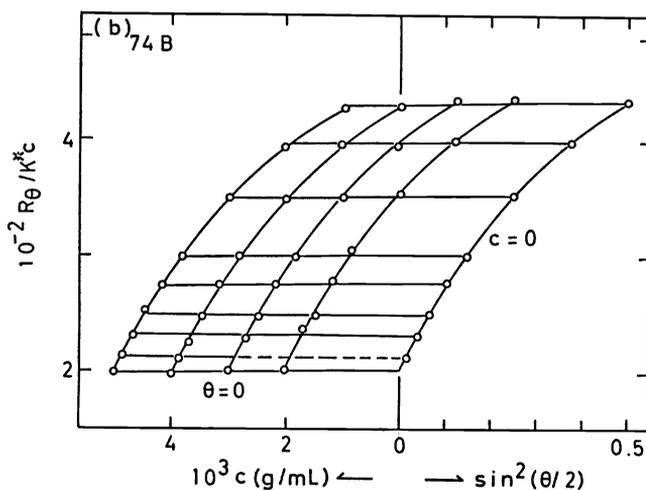


Fig. 5. Plots of R_0/K^*c vs. $\sin^2(\theta/2)$ minus c for PS-PMMA block copolymer 74B in bromobenzene at 38°C . Reproduced from Ref. 52 by courtesy of Hlthig and Wepf Verlag.

benzene is a good solvent for both PS and PMMA the concentration dependence is nearly zero, as if in a theta solvent; and (ii) contrary to usual cases, R_0 increases with increasing angle θ . A quantitative analysis of the angular envelope has shown physical consistency of this result with the light scattering result obtained under the conventional (i.e., $v \neq 0$) condition (Ref. 57).

In Figure 6, the forward intensity R_0 is plotted against c for various copolymers: Curve 1 is for a mixture of PS and PMMA, Curves 2-4 are for diblock copolymers, Curve 5 is for a mixture of low-conversion statistical copolymers with different compositions, and Curve 6 is for a low-conversion statistical copolymer of azeotropic composition. In all the cases, the concentration dependence is negligibly small in the examined ranges of concentration. Thus one of the above predictions has been verified. The values of Q obtained for the mixture

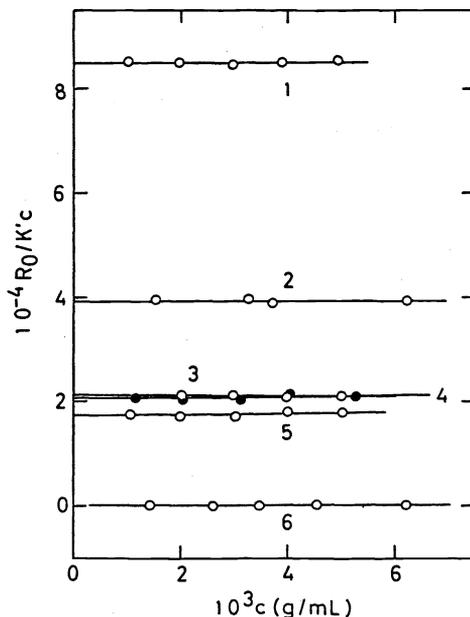


Fig. 6. Plots of $R_0/K'c$ vs. c ($K' = K*(v_A - v_B)^2$) for (1) an equi-weight mixture of PS ($\bar{M}_w = 3.6 \times 10^5$) and PMMA ($\bar{M}_w = 3.1 \times 10^5$), (2) PS-PMMA block copolymer ($\bar{M}_n = 3.6 \times 10^5$ and $\bar{x}_{PS} = 0.51$), (3) sample 74B (see Table 5), (4) sample 63B50 (see Table 5), (5) an equi-weight mixture of two SM statistical copolymers ($\bar{M}_n = 3.6 \times 10^5$ and $\bar{x}_{PS} = 0.29$, $\bar{M}_n = 2.1 \times 10^5$ and $\bar{x}_{PS} = 0.69$), and (6) SM azeotropic copolymer ($\bar{M}_n = 7.7 \times 10^5$ and $\bar{x}_{PS} = 0.52$). Reproduced from Ref. 52 by courtesy of Hülthig and Wepf Verlag.

samples (Curves 1 and 5) agreed well with the calculated values, whereas those for the block copolymers (Curves 3 and 4) were shown to be consistent with the values estimated from other information. As an example, we show in Figure 7 the integral CDC of a block co-

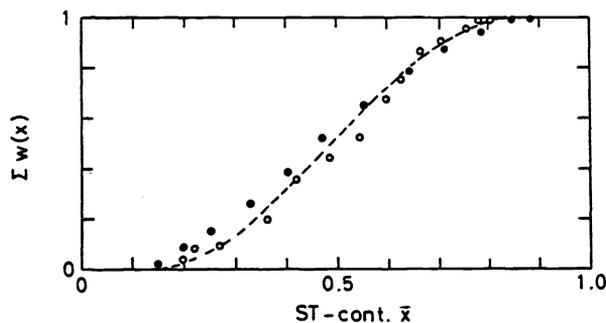


Fig. 7. Integral composition distribution of sample 63B50, calculated (broken curve), and evaluated by TLC (circles, Ref. 41). Reproduced from Ref. 34 by courtesy of Marcel Dekker, Inc.

polymer (sample 63B50, see Table 5). The circles in the figure were obtained by the TLC analysis (Ref. 41), whereas the broken curve was calculated, based on the random coupling statistics (see the previous section), from the light scattering Q-value along with the already known \bar{y}_{PS} - and \bar{x}_{PS} -values. The agreement between them is satisfactory. Finally, the Q-value of the azeotropic copolymer (Curve 6) should be, according to the kinetics (Ref. 16), of order 10. This figure is far beyond the sensitivity limit of light scattering of any form. The present experiment could only show that its Q-value is not

greater than about 2×10^2 .

From all the above analyses, we conclude that the parameter Q can be determined with the highest possible precision when $v = 0$, and that the concentration dependence then is insignificant. The smallness of concentration dependence permits measurements at concentrations higher than usual, and thus the problem of low scattering intensities may be largely circumvented by increasing concentrations. When Q is sufficiently small, concentrations around 10^{-2} (g/ml) may be permissible. With this figure into Eq. (17), we have

$$Q(v_A - v_B)^2 \gtrsim 10 \quad (22)$$

Equations (16) and (22) indicate that if $v_A - v_B = 0.1$, which approximates the PS/PMMA system, determination of Q is possible for $Q \gtrsim 1 \times 10^3$ and $Q/\bar{M}_w \gtrsim 2 \times 10^{-3}$. These limiting values suggest feasibility of light scattering to most block and graft copolymers, certain statistical copolymers and polymer blends.

The special light scattering technique thus far discussed is obviously of limited applicability, insofar as we confine ourselves to single-solvent systems. As has been demonstrated by Tuzar et al. (Ref. 51), use of mixed solvents will give more flexibility to realize the required condition of vanishing v and, in certain cases, a large difference ($v_A - v_B$) between the pair of polymers whose refractive indices are close to each other.

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