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Characterization of binary polymer mixtures by size exclusion chromatography with multiple detection

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We demonstrated that both components of binary polymer mixtures of polystyrene and poly(methyl methacrylate) can be characterized simultaneously by size exclusion chromatography equipped with multiple detectors. In this analysis scheme, the individual peaks of the two components are separated from the overlapped chromatogram by simultaneously solving the response signal intensities from two concentration detectors, i.e. a refractive-index detector and an ultra-violet/visible absorption detector. Then the absolute molecular-weight distribution of each component is obtained from the response of a light-scattering detector in conjunction with universal calibration. This method can be applied to binary mixture systems the two components of which have a distinguishable difference in refractive index as well as in absorptivity.

(Keywords: binary mixtures; size exclusion chromatography; multiple detection)

INTRODUCTION

Size exclusion chromatography (s.e.c.) is perhaps the most widely used technique for the characterization of polymeric materials. The technique has a number of advantages over other characterization methods, such as (1) it provides not only the average value but also the distribution, (2) it is fast and relatively easy to use, and (3) the amount of sample required for the analysis is very small (for example, see ref. 1). The underlying principle of the technique is the exclusion equilibrium of macromolecules between the mobile phase and the stationary phase inside small pores. Therefore the macromolecules are separated in terms of their size in the mobile phase, not their molecular weight. For homopolymers, however, the correlation between the size and the molecular weight of a polymer chain is relatively simple, so that one can obtain information about the molecular-weight distribution (MWD). Furthermore, with the development of light-scattering detectors, it has become possible to determine directly the absolute molecular weight of polymer chains in each s.e.c. fraction[2,3].

Unlike the characterization of homopolymers, where MWD is the only major concern, copolymers or polymer mixtures have chemical composition distribution (CCD) also. As a result, the characterization of a copolymer or a polymer mixture is not trivial[4]. For instance, a light-scattering experiment has to be carried out in at least three different solvent systems to obtain the absolute molecular weight of a copolymer[5]. The situation is not much better for s.e.c. analysis either. Since s.e.c. separates the molecules only in terms of their size, not their chemical nature, it is impossible to characterize either MWD or CCD except for some special cases such as that in which their CCD is homogeneous and independent of molecular weight, etc.[6].

Owing to such intrinsic limitations of s.e.c., many attempts to characterize copolymers with s.e.c. have had to rely on approximations to some extent[7-9]. For example, in the work of Fodor *et al.*[7] all the copolymers eluted at a given retention volume were assumed to be a single species, i.e. identical composition and molecular weight. Also the molecular weight seemed to be assigned by calibration with standard polymers. However, copolymer chains of the same molecular size, which thus elute at the same retention volume, usually have variations in molecular weight as well as in composition[4]. Therefore, the obtained copolymer composition of an s.e.c. fraction is nothing but an average over the copolymers of the same size but of finite composition as well as molecular-weight distributions. For the same reason, the molecular weight determined relative to standard polymers cannot be a good measure of the absolute molecular weight. In the work of Grinshpun and Rudin, absolute polymer concentration in an s.e.c. fraction was measured by an evaporation detector, and d*n*/d*c* of the fraction was determined in conjunction with the refractive-index detector response[8]. The d*n*/d*c* value thus determined was used to obtain the absolute molecular weight from the light-scattering detector response. Although this method acquired the absolute molecular weight by use of a light-scattering detector, it still overlooked the variation of the composition and molecular weight in the s.e.c. fraction eluted.

Another approach to the analysis of polymeric systems having both CCD and MWD is to separate the polymers

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according to chemical composition. For this purpose, gradient h.p.l.c. has been widely used[10,11]. In this method the copolymers are separated according to their chemical composition, and then the average molecular weight at each elution volume, which has a homogeneous CCD, can be determined. Contrary to s.e.c., h.p.l.c. analysis cannot determine MWD but average molecular weight only. It can be more powerful for polymer mixtures than for copolymers since it is more probable to separate each component completely; then the MWD can also be obtained[12]. However, it generally suffers from a limitation in the variety of detection methods owing to the use of solvent gradient as well as of applicable polymeric systems. One of the classical ways to analyse both MWD and CCD is cross-fractionation or orthogonal chromatography, which is the combination of two chromatographic systems[13-15]. However, it is too complicated and time-consuming to become a practicable method at the moment.

In this paper, we would like to demonstrate the possibility of the characterization of each component in a binary polymer mixture by use of an s.e.c./multiple detection method.

EXPERIMENTAL

The s.e.c. system used consists of an isocratic pump (LDC, Constametric 3200), a six-port injector (Rheodyne 7125), four columns (Showa Denko KF80M, 804, 8025, 801), a low-angle laser light-scattering (l.s.) detector (LDC, KMX 6), a variable-wavelength ultra-violet/visible absorption (u.v./vis.) detector (LDC, Spectromonitor 3200) and a refractive-index (r.i.) detector (LDC, Refractomonitor IV). The three detectors are connected in the sequence l.s., u.v./vis. and r.i. to avoid damage caused by back-pressure. The lag volumes between detectors are determined from the elution time of a small amount of toluene, which was injected in the absence of s.e.c. columns while all other plumbing was kept the same. The lag volume was found to be 30 μl between l.s. and u.v./vis., and 70 μl between l.s. and r.i. Carrier solvents were degassed by a membrane degasser (LDC) and filtered by an in-line filter (Alltech) before reaching the columns. Columns are put in an oven (FIAtron, CH-460) and the temperature was kept at 25°C.

Tetrahydrofuran (THF) was used as the mobile-phase solvent. It was fractionally distilled after refluxing with sodium benzophenone complex and filtered through 0.2 μm pore PTFE filter (Gelman) before use. The solvent did not show any absorption at the wavelength of 260 nm, at which the wavelength of the u.v./vis. detector was set. The specific refractive-index increments of polystyrene (PS) and poly(methyl methacrylate) (PMMA) in THF were measured by a differential refractometer (LDC, KMX 16) at the wavelength of 633 nm. At 25°C we obtained 0.192 and 0.084 for PS and PMMA, respectively. These values are in good agreement with the literature values[16].

One PS and two PMMA samples were used for this study. PS was a gift from the Miwon Petrochemical Co. and PMMA were acquired from Aldrich. Both polymers have wide molecular-weight distribution and were used as received without further purification. S.e.c. samples were prepared gravimetrically and the concentration (w/v) was obtained from the density of the materials. Typical sample concentration was 4 mg ml^{-1} and the injection volume was 100 μl.

ANALYSIS SCHEME

In the case of homopolymer analysis by s.e.c., for a fraction i eluted at a certain retention volume, the outputs of the three detectors are as follows:

$$\text{r.i.}\qquad \Delta n_i = K_{\text{ri}}\nu c_i \tag{1}$$

$$\text{u.v./vis.}\qquad A_i = K_{\text{uv}}\varepsilon c_i \tag{2}$$

$$\text{l.s.}\qquad \Delta R(0)_i = K_{\text{ls}}\nu^2 M_i c_i \tag{3}$$

K_{ri}, K_{uv} and K_{ls} are the instrumental constants of the three detectors, ν is the specific refractive-index increment, ε is the specific absorptivity of the sample, and c_i and M_i are the concentration and the molecular weight of the polymer in the i fraction, respectively.

From a concentration detector, either r.i. or u.v./vis., c_i can be obtained if the instrumental constants and ν or ε are known. Or, more commonly, c_i is calculated from the amount of injected sample and the peak area of the concentration detector response. Once c_i is known, M_i can be obtained via equation (3) from the excess scattered intensity, $\Delta R(0)_i$, and the predetermined values of K_{ls} and ν. This is the typical s.e.c./l.s. analysis scheme to obtain the absolute molecular-weight distribution of a homopolymer sample[2].

For a binary polymer mixture, detector response is the sum of the contributions from each component, i.e.:

$$\text{r.i.}\qquad \Delta n_i = K_{\text{ri}}(\nu_1 c_{1,i} + \nu_2 c_{2,i}) \tag{4}$$

$$\text{u.v./vis.}\qquad A_i = K_{\text{uv}}(\varepsilon_1 c_{1,i} + \varepsilon_2 c_{2,i}) \tag{5}$$

$$\text{l.s.}\qquad \Delta R(0)_i = K_{\text{ls}}(\nu_1^2 M_{1,i} c_{1,i} + \nu_2^2 M_{2,i} c_{2,i}) \tag{6}$$

Then the concentration of each component, $c_{1,i}$ and $c_{2,i}$, can be deduced from r.i. and u.v./vis. chromatograms by solving equations (4) and (5) simultaneously provided ν and ε values are known. Therefore, it is in principle possible to isolate the chromatogram of each component.

Nonetheless, the absolute molecular weight of each component cannot be obtained because there is only one formula (equation (6)) for two unknowns ($M_{1,i}$ and $M_{2,i}$). In order to obtain both $M_{1,i}$ and $M_{2,i}$, one needs another formula relating the molecular weights of the two components. Here we suggest the use of a relationship that is frequently used in the universal calibration method for s.e.c. analysis[17].

It is well known that the intrinsic viscosity of a polymer chain is proportional to the volume occupied by unit mass of the chain, i.e. V/M. Since s.e.c. separates the polymer molecules in terms of the chain volume, the polymer chains eluted at a certain retention volume are supposed to have the same volume. This leads to the relation:

$$V_{1,i} \propto [\eta]_{1,i} M_{1,i} = [\eta]_{2,i} M_{2,i} \propto V_{2,i}$$

Together with the Mark–Houwink equation:

$$[\eta] = KM^a$$

it turns out that:

$$K_1(M_{1,i})^{a_1+1} = K_2(M_{2,i})^{a_2+1} \tag{7}$$

This relation serves as the second formula to obtain both $M_{1,i}$ and $M_{2,i}$. Solving equations (6) and (7) simultaneously, the molecular weights of the individual components can be obtained if the Mark–Houwink constants, K and a values are available for both components. It is not a difficult task to solve the simultaneous equations numerically.

RESULTS AND DISCUSSION

Basic parameters and the characterization results of PS and PMMA are listed in *Table 1*. The weight-average molecular weights of PS, PMMA10 and PMMA14 were measured by three different methods. L.s. stands for the batch-mode l.s. measurements, which is the static low-angle laser light-scattering method. S.e.c./l.s. is the size exclusion chromatography analysis with the l.s. detector. U.c. is the universal calibration analysis with respect to polystyrene standard materials. The three methods give practically identical results for the three polymers, which indicates that (1) the characterization results of the three polymers are reliable and, more importantly, (2) the Mark–Houwink constants for PS and PMMA are reliable, which is indispensable for the analysis scheme described above. The Mark–Houwink constants are quoted from the literature[16].

We have tested six different PS/PMMA mixtures as summarized in *Table 2*. The first two digits in the sample code identify the PMMA used, while the last two digits indicate the approximate weight per cent of PS in the mixture. In *Figure 1* are shown a typical set of response curves for SM10 50 from the three detectors. These chromatograms were corrected for lag volumes between detectors. The intensities of the three detector response curves are normalized for visual aid. The l.s. response curve (full curve) comes out at the lowest retention volume because the scattered light intensity depends not only on the concentration but also on the molecular weight as shown in equation (3). At the wavelength of 260 nm, PMMA does not absorb light, so that the u.v./vis. chromatogram is practically the chromatogram of PS only. Since PS has a higher molecular weight than PMMA10, so being eluted earlier than PMMA10, the u.v./vis. response curve (broken curve) appears to be shifted to lower retention volume than the r.i. response curve (dotted curve).

Table 1 Mark–Houwink constants[16] and M_w of the polymers used

Polymers	K ($\times 10^{-4}$ ml g^{-1})	a	M_w ($\times 10^3$) L.s.	S.e.c./l.s.	U.c.
PS	11.0	0.725	243	237	236
PMMA10	7.5	0.72	97	93	102
PMMA14	7.5	0.72	141	138	140

Table 2 The on-line characterization results of polymer mixtures

Sample[a]	w_{PS}	M_w ($\times 10^3$) PS	PMMA10	PMMA14
SM10 30	0.299	225	86	
SM10 50	0.505	232	93	
SM10 80	0.799	233	102	
SM14 30	0.306	225		147
SM14 50	0.487	228		141
SM14 80	0.787	233		142

[a] For instance, SM10 30 indicates the mixture of PS and PMMA10 whose PS content is near 30%

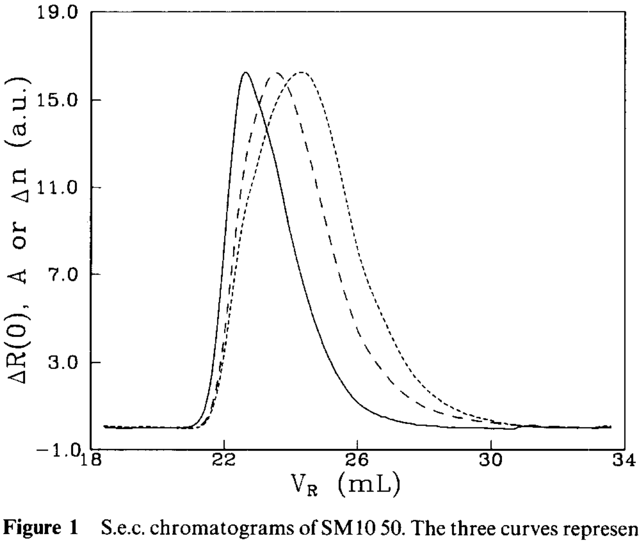

Figure 1 S.e.c. chromatograms of SM10 50. The three curves represent the response curves of the three detectors: r.i. (···), u.v./vis. (– – –) and l.s. (——). The intensities of the three detector response curves are normalized for visual aid. See the text for details

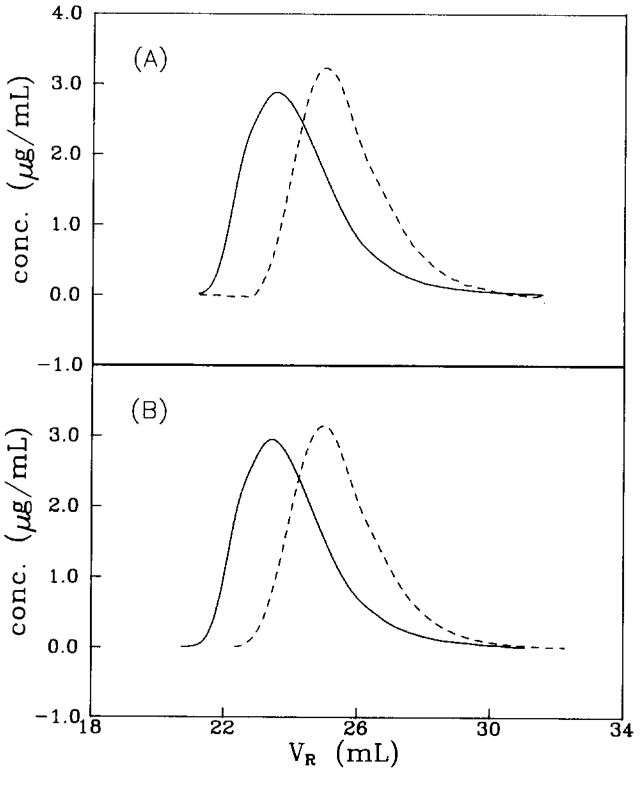

Figure 2 Plots of concentration vs. retention volume of PS (——) and PMMA10 (– – –) in SM10 50: (A) the curves obtained from the u.v./vis. and r.i. response curves in *Figure 1* by solving equations (4) and (5) simultaneously; (B) chromatograms of independent runs of PS and PMMA10 under the same experimental conditions as (A)

From the u.v./vis. and r.i. response curves, the concentrations of each component, $c_{1,i}$ and $c_{2,i}$, are obtained by solving equations (4) and (5) simultaneously, and are displayed in *Figure 2A*. The full and broken curves

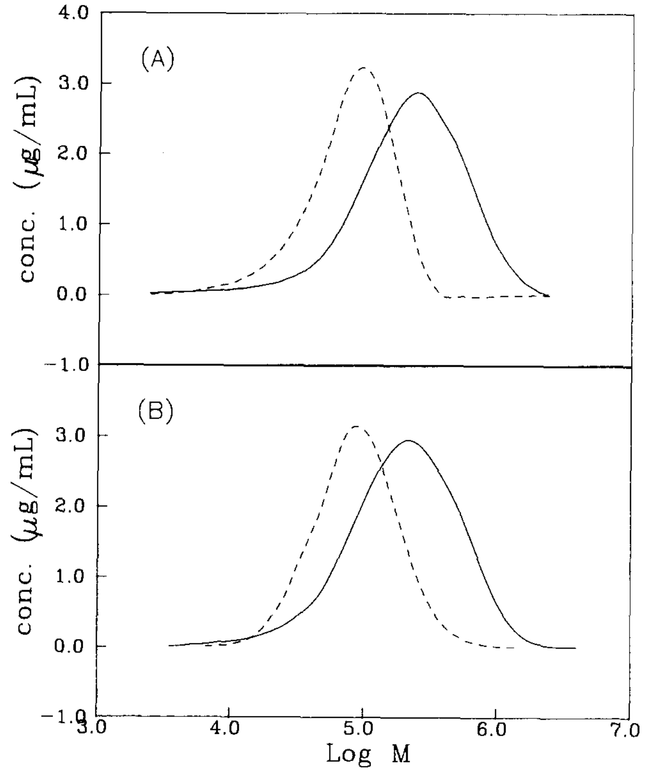

Figure 3 Molecular-weight distributions of PS (——) and PMMA10 (– – –) in SM10 50: (A) the curves obtained by solving equations (6) and (7) simultaneously; (B) molecular-weight distributions of PS and PMMA10 obtained from separate s.e.c./l.s. analysis of individual components under the same experimental conditions as (A)

represent the PS and PMMA10 concentration vs. retention volume, respectively. This result can be compared with *Figure 2B*, which shows composite chromatograms of independent runs of PS and PMMA10 under the same experimental conditions. At this point it is clear that we can obtain practically identical concentration chromatograms as expected.

The $c_{1,i}$ and $c_{2,i}$ thus obtained are used to solve the simultaneous equations (6) and (7). We have used the literature values of the Mark–Houwink constant as listed in *Table 1*. Then we obtained the final result of molecular-weight distribution of PS (full curve) and PMMA10 (broken curve) as shown in *Figure 3A*. This result again can be compared with *Figure 3B* in which the results from separate s.e.c./l.s. analyses of individual components are displayed. The agreement of the two results appears quite satisfactory except for a small distortion at the low-molecular-weight end of PMMA10 in *Figure 3A*. This is probably due to the low scattering intensity from low-molecular-weight PMMA, which is one of the persistent problems with light-scattering detection.

Analysis results of the six mixtures are summarized in *Table 2*. It is obvious that the obtained weight-average molecular weights are quite close to the real values. This result demonstrated that a binary homopolymer mixture can be analysed with reasonable precision without physical separation of the two components. In order to apply this analysis scheme, it is necessary that the two components have a distinguishable difference in refractive index as well as difference in absorptivity. This limitation can be relieved if one finds a greater variety of detection methods such as i.r. detector, mass detector and so on. Although this is a simple demonstration that such simultaneous characterization of a binary polymer mixture can be accomplished by use of s.e.c. with multiple detection, one may find a practical use of this method for the characterization of polymer blend systems.

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REFERENCES

1 Yau, W. W., Kirkland, J. J. and Bly, D. D. 'Modern Size-Exclusion Liquid Chromatography, Practice of Gel Permeation and Gel Filtration Chromatography', Wiley, New York, 1979
2 Ouano, A. C. and Kaye, W. *J. Polym. Sci., Polym. Chem. Edn.* 1974, **12**, 1151
3 Jackson, C., Nillson, L. and Wyatt, P. J. *J. Appl. Polym. Sci.* 1989, **43**, 99
4 Balke, S. T. in 'Modern Methods of Polymer Characterization' (Eds. H. G. Barth and J. W. Mays), Wiley, New York, 1991, Ch. 1
5 Benoit, H. and Froelich, D. in 'Light Scattering from Polymer Solutions' (Ed. M. B. Huglin), Academic Press, New York, 1972, Ch. 11
6 Cotts, P. M. and Siemens, R. *Polymer* 1991, **32**, 3052
7 Fodor, Zs., Fodor, A. and Kennedy, J. P. *Polym. Bull.* 1992, **29**, 689
8 Grinshpun, V. and Rudin, A. *J. Appl. Polym. Sci.* 1986, **32**, 4303
9 Dumelow, T., Holding, S. R., Maisey, L. J. and Dawkins, J. V. *Polymer* 1986, **27**, 1170
10 Teramachi, S., Hasegawa, A., Shima, Y., Akatsuka, M. and Nakajima, M. *Macromolecules* 1979, **12**, 992
11 Glöckner, G. *J. Appl. Polym. Sci., Appl. Polym. Symp.* 1992, **51**, 45
12 Pasch, H. *Polymer* 1993, **34**, 4095
13 Balke, S. T. and Patel, R. D. *Adv. Chem. Ser.* 1983, **203**, 281
14 Dawkins, J. V. and Montenegro, A. M. C. *Br. Polym. J.* 1989, **21**, 31
15 Glöckner, G. *Makromol. Chem.* 1989, **190**, 427
16 Brandrup, J. and Immergut, E. H. (Eds.) 'Polymer Handbook', 3rd Edn., Wiley, New York, 1989
17 Grubisic, Z., Rempp, P. and Benoit, H. *J. Polym. Sci. (B)* 1967, **5**, 753