

Rapid Communication

COMPOSITION DETERMINATION OF BINARY POLYMER MIXTURES BY SIZE EXCLUSION CHROMATOGRAPHY WITH LIGHT SCATTERING DETECTION*

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Abstract Base on the principle of absolute quantification of size exclusion chromatography (SEC), a light scattering (LS) detector coupled with a concentration detector (refractive index detector) is utilized to determine the compositions of complicated binary mixtures. A theoretical analysis predicts that the response factors for both LS and RI detectors are linear functions with the composition of any specified polymer mixtures in the binary polymer mixtures. Two pairs of complicated binary mixtures were used to test the theory mentioned in the present paper, and the experimental results show an excellent accordance with the theory.

Keywords: Size exclusion chromatography; Light scattering; Composition of binary mixture; Absolute quantification; Response factor.

Since the binary mixture composed of two kinds of industrial complicated materials is directly related to composition designs and properties of the mixture in practice, crucial attention has been paid to the analysis of the composition of the mixture. Size exclusion chromatography (SEC), which is mainly employed in determining molar masses (MW) and molar masses distribution (MWD) of macromolecules, can also be utilized to estimate the compositions of copolymers or blends^[1–7]. Usually the composition of mixtures is determined by SEC coupled with concentration detectors such as ultraviolet absorption (UV) detector^[8–10], differential refractive index (RI) detector^[11, 12], density detector^[13], etc. However, there are barely any reports about the analysis by non-concentration detectors. In the present work, based on the principle of absolute quantification of SEC^[14–16], a novel method of SEC-LS is described to decide the composition of complicated binary mixtures. In this case, the composition of the mixture can be calculated even more accurately than the concentration detector.

If dividing $H(V)$ at elution volume V by the injected mass w_{inj} , we can get the mass normalized chromatograms

$$H_w(V) = \frac{H(V)}{w_{\text{inj}}} \quad (1)$$

where $w_{\text{inj}} = \int C(V)dV$ for samples dissolved well in the eluent. Hence, the response factors of a single solute could be defined as the ratio of the total area A with the injected mass w_{inj}

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$$K = \frac{A}{w_{\text{inj}}} = \frac{\int H(V) dV}{w_{\text{inj}}} = \int H_w(V) dV \quad (2)$$

According to the principle of absolute quantification of SEC, the signal of RI detector $H^{\text{RI}}(V)$ is proportional to the sample concentration $C(V)$ at elution volume V

$$H^{\text{RI}}(V) = k^{\text{RI}} \nu(V) C(V) \quad (3)$$

where k^{RI} is the instrument factor of RI detector that does not depend on the kind of polymer, and $\nu(V)$ is the refractive index increment at elution volume V . Therefore, the response factor of RI detector can be deduced as

$$K^{\text{RI}} = \frac{A^{\text{RI}}}{w_{\text{inj}}} = \frac{\int H^{\text{RI}}(V) dV}{\int C(V) dV} = k^{\text{RI}} \int \nu(V) \frac{C(V)}{C(V) dV} dV = k^{\text{RI}} \int \nu(V) w(V) dV = k^{\text{RI}} \nu \quad (4)$$

where $w(V)$ is weight fraction of the sample at elution volume V , $w(V) = \frac{C(V)}{\int C(V) dV}$; the refractive index

increment of the whole sample ν is decided by the kind of polymer, although it is varied with the MW of the sample^[17, 18]. Hence, K^{RI} is a constant for a kind of polymer.

Owing to existence of axial dispersion effect of the SEC process, the concentration at elution volume V is much lower than the injected concentration. Thus the signal $H^{\text{LS}}(V)$ of the detector at elution volume V , which is proportional to the Rayleigh ratio, can derive from extrapolating them to the detected angle $\Theta = 0$ ^[19, 20]

$$H^{\text{LS}}(V) = K' \nu(V)^2 M(V) C(V) \quad (5)$$

where $M(V)$ is the molar mass at elution volume V ; K' is defined as the optical constant, $K' = \frac{4\pi^2 n_0^2}{\lambda_0^4 N_A}$ ^[19]; n_0 is the refractive index of the solvent at λ_0 , the wavelength of incident beam in vacuum; N_A is Avogadro's number. Then the response factor of LS detector can be obtained

$$K^{\text{LS}} = \frac{A_{\text{LS}}}{w_{\text{inj}}} = \frac{\int H^{\text{LS}}(V) dV}{\int C(V) dV} = K' \frac{\int \nu^2(V) M(V) C(V) dV}{\int C(V) dV} \quad (6)$$

For not too board homo-polymers, $\nu(V) = \nu$, Eq. (6) can be written as

$$K^{\text{LS}} = \frac{A^{\text{LS}}}{w_{\text{inj}}} = K' \nu^2 \frac{\int M(V) C(V) dV}{\int C(V) dV} = K' \nu^2 M_w \quad (6-1)$$

where $M_w = \frac{\int M(V) C(V) dV}{\int C(V) dV}$ is the definition of weight average molar mass for polymers, and M_w is a specified value for a single polymer.

For copolymers and blends, $\nu(V) \neq \nu$. By defining $M^*(V) = \frac{\nu^2(V)}{\nu^2} M(V)$, we can get the analogous form as Eq. (6-1)

$$K^{\text{LS}} = \frac{A^{\text{LS}}}{w_{\text{inj}}} = K' \nu^2 \frac{\int M^*(V) C(V) dV}{\int C(V) dV} = K' \nu^2 M_w^{\text{app}} \quad (6-2)$$

where $M_w^{\text{app}} = \frac{\int M^*(V)C(V)dV}{\int C(V)dV}$, can be defined as the apparent weight-average molar mass. It is also invariable for a single polymer.

Hence, we can conclude that K^{LS} is a constant for a specified polymer, while K^{RI} is a constant for a kind of polymer. This specified polymer could be homo-polymers, copolymers or blends. According to Eqs. (2), (4), (6-1) and (6-2), the signal areas of both RI and LS detectors can meet the relation for quantification

$$A = Kw_{\text{inj}} \quad (7)$$

It is pointed out that K is a constant for a specified polymer, which can be homo-polymers, copolymers or blends.

For complicated binary mixtures, the signal areas of component 1 and component 2 should be

$$A_1 = K_1 w_{\text{inj}} W \quad (8-1)$$

$$A_2 = K_2 w_{\text{inj}} (1 - W) \quad (8-2)$$

where W is the weight fraction of component 1 (denoting polystyrene in the experiment); K_1 and K_2 are the response factors of polymer 1 and polymer 2. For RI detector they can be written as

$$K_1^{\text{RI}} = k^{\text{RI}} v_1^1 \quad (9-1)$$

$$K_2^{\text{RI}} = k^{\text{RI}} v_2 \quad (9-2)$$

For LS detector they can be expressed as

$$K_1^{\text{LS}} = K' v_1^2 M_{w1} \quad (10-1)$$

$$K_2^{\text{LS}} = K' v_2^2 M_{w2} \quad (10-2)$$

Where v_1 and v_2 , M_{w1} and M_{w2} are the refractive index increments and weight-average molar masses of components 1 and 2, respectively. If there are no strong interactions or reactions between the two components, the relation $A = A_1 + A_2$ is obvious. Thus, with the Eqs. (7), (8-1) and (8-2) we can calculate the response factor of the mixture

$$K = K_1 W + K_2 (1 - W) \quad (11)$$

According to Eqs. (9-1), (9-2), (10-1) and (10-2), the response factors of RI and LS detectors can be written as

$$K^{\text{RI}} = K_1^{\text{RI}} W + K_2^{\text{RI}} (1 - W) = k^{\text{RI}} v_1^1 W + k^{\text{RI}} v_2 (1 - W) \quad (11-1)$$

$$K^{\text{LS}} = K_1^{\text{LS}} W + K_2^{\text{LS}} (1 - W) = K' v_1^2 M_{w1} W + K' v_2^2 M_{w2} (1 - W) \quad (11-2)$$

It indicates that the response factors of both LS and RI detectors should be linear with the composition W . Hence, the composition of the mixture can be calculated by

$$W = \frac{K - K_2}{K_1 - K_2} \quad (12)$$

For RI detector and LS detector we have

$$W^{\text{RI}} = \frac{K^{\text{RI}} - K_2^{\text{RI}}}{K_1^{\text{RI}} - K_2^{\text{RI}}} = \frac{v - v_2}{v_1 - v_2} \quad (12-1)$$

$$W^{\text{LS}} = \frac{K_1^{\text{LS}} - K_2^{\text{LS}}}{K_1^{\text{LS}} - K_2^{\text{LS}}} \quad (12-2)$$

It is first reported by us that the response factors of LS detector for binary blends can meet the relation as mentioned in Eq. (11) and can be used to calculate the composition of complicated binary mixtures by Eq. (12-2).

EXAMPLES

In this work, in order to examine the applicability of the above principle, the analyses of SEC were investigated on mixtures of polystyrene/poly(methyl methacrylate) (code PS/PMMA) and of polystyrene/poly((ethylene oxide)-*block*-(ϵ -caprolactone))(code NPS4/MPEO-PCL). Detailed information of the samples can be seen in Table 1. We have drawn the mass normalized chromatograms for the two blends in Figs. 1–2, using $H_w^{\text{LS}}(V)$ and $H_w^{\text{RI}}(V)$ for LS and RI detectors, respectively. Measurements of SEC were performed at $(25.0 \pm 0.5)^\circ\text{C}$ on a 515 pump (Waters Corporation, USA) equipped with a Multi-angle Laser LS detector (DAWN EOS, Wyatt Technology Corporation, USA) and a RI detector (Optilab rEX, Wyatt Technology Corporation). The wavelengths of the laser in LS detector and the LED in RI detector were 690 nm and 685 nm, respectively, without necessary of wavelength correction. The columns were STYRAGEL HR3, HR4 and HR5 (300×7.8 mm, Waters Corporation). HPLC grade THF (TS2121, Tedia, USA) was used as eluent at a flow rate of 1.0 mL/min. Samples in THF were filtered over a filter with a pore size of $0.45 \mu\text{m}$ (Millipore, USA) into a 200 μL loop. Software of ASTRA (Wyatt Technology Corporation) was employed for exporting data after the correction of band broadening. The areas of the SEC peaks were integrated by software of ORIGIN (OriginLab Corporation, USA) with the baselines carefully subtracted.

Table 1. Detailed information for the four polymers in the two mixtures

Code	$K^{\text{RI}} \times 10^4$	K^{LS}	ν^* (mL/g)	$M_w \times 10^{-4}$ *	$M_n \times 10^{-4}$ *	D^*
PS	1.84	14.2	0.184	25.4 (0.2%)	9.33 (3%)	2.72 (3%)
PMMA	0.834	0.943	0.0830	8.02 (0.3%)	4.69 (3%)	1.71 (3%)
NPS4	1.83	1.32	0.183	2.25 (0.2%)	2.23 (2%)	1.01 (2%)
MPEO-PCL	0.707	0.151	0.0705	1.73 (2%)	1.31 (6%)	1.53 (6%)

* The refractive index increments ν , molecular weights and polydispersities D are calculated by the software ASTRA; The values in the parentheses are the errors estimated by the software.

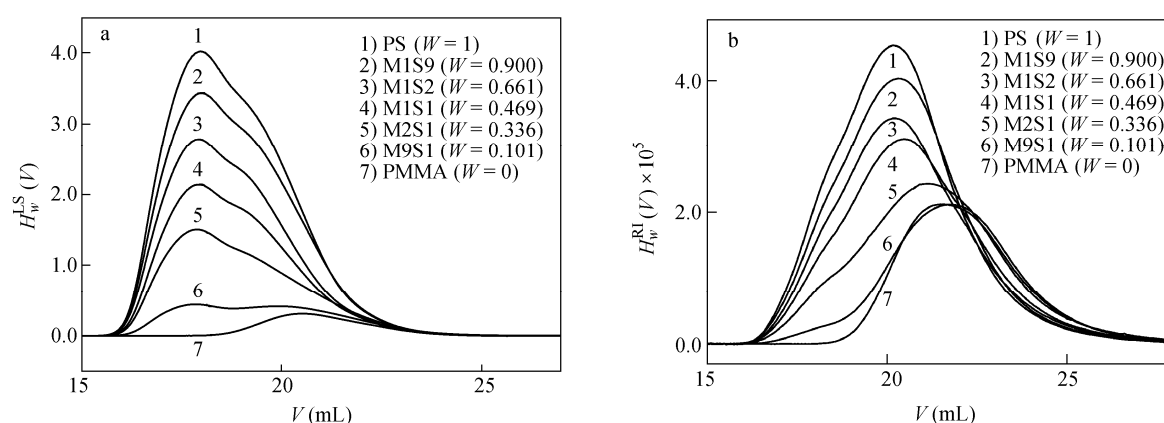


Fig. 1 Mass normalized chromatograms of mixtures PS/PMMA
a) LS signals at 90° ; b) RI signals

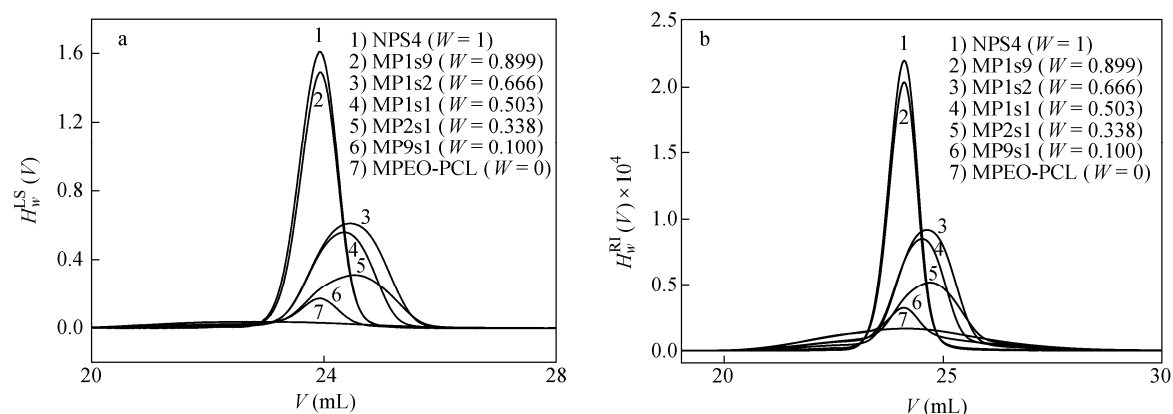


Fig. 2 Mass normalized chromatograms of mixtures NPS4/MPEO-PCL
a) LS signals at 90° ; b) RI signals

Figures 3 and 4 show the response factors of both detectors for the two mixtures are linearly varied with the composition W . It indicates that the relation predicted by Eq. (11) is totally correct for complicated binary blends.

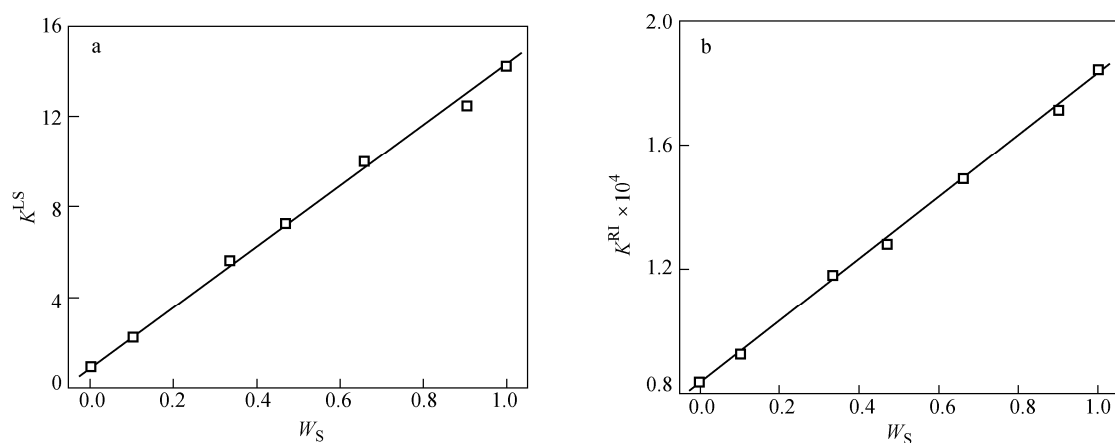


Fig. 3 The linear relation of the response factors of (a) LS detector and (b) RI detector versus compositions for mixtures PS/PMMA

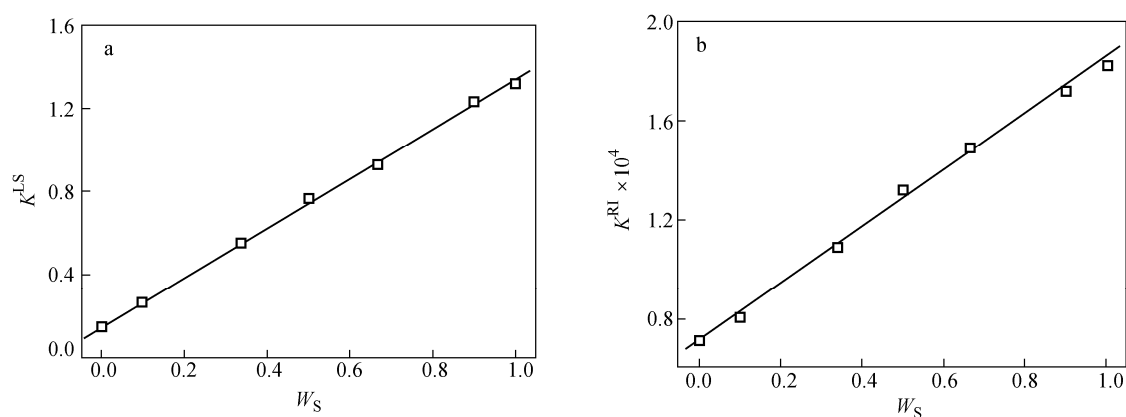


Fig. 4 The linear relation of the response factors of (a) LS detector and (b) RI detector versus compositions for mixtures NPS4/MPEO-PCL

Table 2. Determination of the compositions of binary mixture PS/PMMA

Code*	W_s	$K^{RI} \times 10^4$	K^{LS}	W_s^{RI}	W_s^{LS}	$\frac{W_s^{RI} - W_s}{W_s}$	$\frac{W_s^{LS} - W_s}{W_s}$
				Eq. (12-1)	Eq. (12-2)	W_s	W_s
M1S9	0.900	1.71	12.5	0.871	0.872	-0.03	-0.03
M1S2	0.661	1.49	10.0	0.652	0.683	-0.01	0.03
M1S1	0.469	1.28	7.24	0.443	0.475	-0.06	0.01
M2S1	0.336	1.18	5.62	0.343	0.353	0.02	0.05
M9S1	0.101	0.928	2.24	0.093	0.098	-0.08	-0.03

* M and S represent homo-polymers PMMA and PS, respectively; The code Mn_1Sn_2 is interpreted as a mixture consisting of n_2 part of PS and n_1 part of PMMA.

Table 3. Determination of the compositions of binary mixture NPS4/MPEO-PCL

Code*	W_s	$K^{RI} \times 10^4$	K^{LS}	W_s^{RI}	W_s^{LS}	$\frac{W_s^{RI} - W_s}{W_s}$	$\frac{W_s^{LS} - W_s}{W_s}$
				Eq.(12-1)	Eq.(12-2)	W_s	W_s
MP1s9	0.899	1.72	1.23	0.902	0.923	0.00	0.03
MP1s2	0.666	1.49	0.929	0.697	0.666	0.05	0.00
MP1s1	0.503	1.32	0.764	0.546	0.524	0.08	0.04
MP2s1	0.338	1.09	0.555	0.341	0.346	0.01	0.02
MP9s1	0.100	0.805	0.265	0.087	0.097	-0.13	-0.03

* MP and s represent the copolymer MPEO-PCL and the homo-polymer NPS4, respectively; The code MPn_1sn_2 is interpreted as a mixture consisting of n_2 part of NPS4 and n_1 part of MPEO-PCL.

We calculate the compositions from the response factors according to Eqs. (12-1) and (12-2). The results for the two pairs of mixtures are listed in Tables 2 and 3. We can see that the determined compositions (the 5th and 6th columns) are in fair agreement with the original feeds of the mixtures (the 2nd column). And the results calculated by LS detector with Eq. (12-2) are more exact than the ones determined by RI detector, as the errors shown in the 7th and 8th columns of Tables. 2–3. The reason for this is that the difference between K_1^{LS} and K_2^{LS} is always larger than the one between K_1^{RI} and K_2^{RI} . As seen in Eq. (12), the larger the denominator ($K_1 - K_2$) in the right side is, the smaller the errors for calculating W are. Hence, the LS detector has performed well in the determination of composition, which is hardly expected without our theory and experiments. The method would show a productive prospect in the methods of SEC-LS due to its validity and easy manipulation.

REFERENCES

- Balke, S.T., "Journal of chromatography library: quantitative column liquid chromatography, Vol. 29", Elsevier, Amsterdam, 1984
- Scott, R.P.W., "Journal of chromatography library: liquid chromatography detectors, Vol. 33", Elsevier, Amsterdam, 1986
- Mori, S., "Size exclusion chromatography: high performance liquid chromatography of polymers", Kyoritsu Shuppan Co., Tokyo, 1991
- Potschka, M. and Dubin, P.L., "Strategies in size exclusion chromatography, ACS Symposium Series 635", American Chemical Society, Washington DC, 1996
- Mori, S. and Barth, H.G., "Size exclusion chromatography", Springer, Berlin, 1999
- Pasch, H. and Trathnigg, B., "HPLC of polymers", Springer, Berlin, 1999
- Wu, C.S., "Handbook of size exclusion chromatography and related techniques, 2nd ed", CRC Press, New York, 2003
- Runyon, J.R., Barnes, D.E., Rudd, J.F. and Tung, L.H., J. Appl. Polym. Sci., 1969, 13: 2359
- Mori, S. and Suzuki, T., J. Liq. Chromatogr., 1981, 4: 1685
- Medrano, R., Laguna, T.R., Saiz, E. and Tarazona, M.P., Phys. Chem. Chem. Phys., 2003, 5: 151

- 11 Stejskal, J., Strakova, D., Kratochvil, P., Smith, S.D. and McGrath, J.E., *Macromolecules*, 1989, 22(2): 861
- 12 Chen, Z.N., Xie, H.F., Yang, H., Wang, Z.L. and Cheng, R.S., *Acta Polymerica Sinica*(in Chinese), 2007, (8): 689
- 13 Trathnigg, B., *J. Chromatogr. A.*, 1991, 552: 507
- 14 Cheng, R.S. and Zhao, S.L., *ACS Sym. Ser.*, 1993, 521: 113
- 15 Wang, Z.L., Zhou, C.H., Qian, J. and Cheng, R.S., *Acta Polymerica Sinica*(in Chinese), 1995, (2): 189
- 16 Cheng, R.S., Wang, Z.L. and Zhao, Y., *Acta Polymerica Sinica*(in Chinese), 1991, (5): 560
- 17 Cheng, R.S. and Yan, X.H., *Acta Polymerica Sinica*(in Chinese), 1989, (6): 647
- 18 Itakura, M., Sato, K., Lusenkov, M.A., Matsuyama, S., Shimada, K., Saito, T. and Kinugasa, S., *J. Appl. Polym. Sci.*, 2004, 94(3): 1101
- 19 Radke, W., Simon, F.P.W. and Muller, A.H.E., *Macromolecules*, 1996, 29: 4926
- 20 Netopilik, M., Bohdanecky, M. and Kratochvil, P., *Macromolecules*, 1996, 29: 6023