

INVESTIGATION ON THE RESPONSE FACTORS OF CONCENTRATION DETECTORS WITHIN SEC PROCESS*

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Abstract The response factors of refractive index (RI) and ultraviolet (UV) detectors of size exclusion chromatography (SEC) defined as the ratio of area of output signal to the mass of injected sample are studied and analyzed by using five narrowly distributed polystyrene (PS) standard samples with known molar masses. It is found that the individual response factor for a given sample varies with the concentration of the injected solution within a limited range bounded by an upper and a lower limiting response factor values. This variation reveals the conformational change of the polymer chains with the concentration of the injected solution. The dynamic contact concentrations c_s of the PS samples derived from the response factor data are in good accordance with those reported earlier by other methods. The physical meanings of the signals of the two detectors are further analyzed and theoretically formulated. The solvation of the polymer chain and the conformation changes play an important role in these detecting systems. Both of the solvation number of the structural repeating unit and the extra embedded solvent due to cluster forming in higher concentrations could be deduced from the variation of response factor with the concentration of the injected solution.

Keywords: Dynamic contact concentration; Entanglement; Response factors; Size exclusion chromatography (SEC); Solvation.

INTRODUCTION

Size exclusion chromatography (SEC) has been broadly employed in the separation and characterization of macromolecules^[1–10]. The differential refractive index (RI) detector and ultraviolet absorption (UV) detector are the two mostly adopted concentration detectors for polymers in SEC. Usually for not too broad homopolymers, the output signals H of these detectors at elution volume V are proportional to the concentration of the testing solution c in the detector cell, and the proportional coefficient is termed as response factor K . Owing to existence of axial dispersion effect of the SEC process, the maximum concentration in the detector cell is always smaller than the concentration without this effect, which also means lower than the injected concentration c_{inj} . However, the total area A under an SEC concentration detecting profile $H(V) = Kc(V)$ should be proportional to the mass of injected solute w_{inj} ^[11, 12]

$$A = \int H(V)dV = K \int c(V)dV = Kw_{inj} \quad (1)$$

Hence, the response factor of a single solute could be defined as the ratio of the total area with the injected mass

* This work was financially supported by the National Natural Science Foundation of China (No. 50633030).

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Received March 10, 2010; Revised April 27, 2010; Accepted April 28, 2010

doi: 10.1007/s10118-010-1010-x

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

In principle the response factor obtained for a given sample should be a constant regardless of the injected concentration. It implies that a plot of area versus injected mass should be linear and passing through the origin as the injected mass approaches zero. Adopting this principle, we have suggested a dynamic method to determine the specific refractive index increment of polymer by the use of the response constant of RI detector signals of SEC^[13–15]. However, an ideal zero intercept of the area versus injected mass plots may only hold for small molecules, while for polymers a very small positive intercept always definitely exists. It reveals an unknown systematic source of error exists, though the response constant derived from the slope of the area versus injected mass plots does not influence the evaluation of the refractive index increment. In the present paper a thorough investigation was paid to solve these unknowns by using five PS standard samples with different molar masses. It was found that the individual response factor calculated by Eq. (2) was dependent on the concentration of injected solution within two boundary limits and the controlling factors are the variation of the conformation and the states of solvation with the polymer concentration.

EXPERIMENTAL

Materials

Five narrowly distributed PS samples prepared by butyl-lithium initiated anionic polymerization at Nanjing University were used as standards in the present study. The weight-average molar mass (M_w), number-average molar mass (M_n), degree of polymerization (x) and polydispersity index (D) are listed in Table 1. The samples were originally characterized by the calibration of other PS standards (Waters, USA). The degree of polymerization x was calculated from the number average molar mass by

$$M_n = M_E + xM_0 \quad (3)$$

where M_E and M_0 are the molar mass of the end group compound and structural repeating unit, respectively. $M_E = 58$ for 1-butane, and $M_0 = 104$ for styrene.

HPLC-Spectro TS-2121 Tetrahydrofuran (Tedia, USA) was newly bought as the solvent without further purification. All solutions were prepared by mixing and weighing a stock solution with known concentration and the diluted solvent. The concentrations of the injected solution lay in a range from 10^{-5} g·mL⁻¹ to 3.1×10^{-3} g·mL⁻¹.

Table 1. The molar masses of PS standard samples

Code	$M_w \times 10^{-4}$	$M_n \times 10^{-4}$	x	D
NPS10	105.00	97.40	9.36×10^3	1.08
NPS8	34.10	31.80	3.06×10^3	1.07
NPS7	16.80	16.40	1.58×10^3	1.02
NPS4	2.09	2.03	1.95×10^2	1.03
NPS1	0.29	0.28	2.60×10^1	1.04

Measurements

SEC Measurements were performed at $(25.0 \pm 0.1)^\circ\text{C}$ on a 515 pump (Waters, USA) equipped with a 2487 UV detector (Waters) and an Optilab-rEX RI detector (Wyatt, USA). Fresh columns of STYRAGEL HR2, HR5E (7.8×300 mm, Waters) were employed to avoid the column absorption of foreign impurities. HPLC grade THF was used as eluent at a flow rate of 1.0 mL/min. Samples in THF were filtered over a filter with pore sizes of $0.45 \mu\text{m}$ (Millipore, USA) into a 200 μL loop. The pump pressure was $(2.76 \pm 0.02) \times 10^6$ Pa. Before testing the detector cell was flushed with clean solvent until a stable baseline was achieved.

Software of ASTRA (Wyatt) was employed for exporting data after the correction of band broadening. The areas of the SEC peaks were integrated by software of ORIGIN (Originlab, USA) with the baselines carefully subtracted. Thus the errors of areas are less than $\pm 1\%$.

RESULTS AND DISCUSSION

Regression Analysis

Plots of the area of RI and UV signals versus injected sample mass for each PS standards are shown in Fig. 1 which reveals good linearity passing through the origin as required at the first sight. However, applying the linear regression analysis to the data yields a straight line with perfect linearity but a very small nonzero intercept always exists for both detector and all PS standards. It means the response area of the concentration detector in SEC for polymers exactly obeys

$$A = \delta + Kw_{\text{inj}} \quad (4)$$

instead of Eq. (1). Alternatively the data also satisfy the logarithmic form of the equation

$$A = K \cdot w_{\text{inj}}^{\gamma} \quad (5)$$

$$\lg A = \lg K + \gamma \cdot \lg w_{\text{inj}} \quad (6)$$

as shown in Fig. 2 with a perfect linearity also in the first sight. The numerical results of the regression analysis for all PS standards and both detectors are listed in Table 2, in which all of the correlation coefficients R are equal to 1 (> 0.999). This perfect linearity is adequate for analytical purpose however the physical reasons of the appearance of non-zero intercepts and non-unity exponents of Eqs. (4)–(5) are not explored yet.

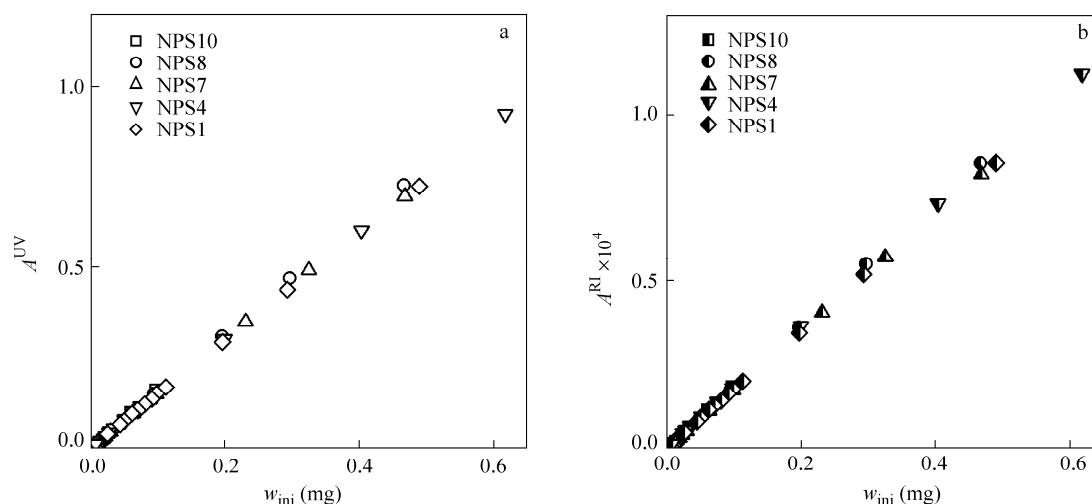


Fig. 1 Plots of A versus w_{inj} of the five PS standard samples: (a) UV detector and (b) RI detector

Table 2. The numerical results of the linear regression analysis for the area versus injected mass plots of UV and RI detectors

Code	UV detector				RI detector			
	$\delta \times 10^3$	K	$\lg K$	γ	$\delta \times 10^7$	$K \times 10^4$	$-\lg K$	γ
NPS10	0.4	1.678	0.207	0.988	0.5	1.935	3.719	0.991
NPS8	1.2	1.566	0.191	0.989	1.3	1.840	3.744	0.984
NPS7	2.1	1.497	0.164	0.976	2.2	1.756	3.771	0.971
NPS4	2.2	1.496	0.168	0.983	3.5	1.813	3.744	0.984
NPS1	2.4	1.480	0.168	0.989	4.1	1.747	3.764	0.980

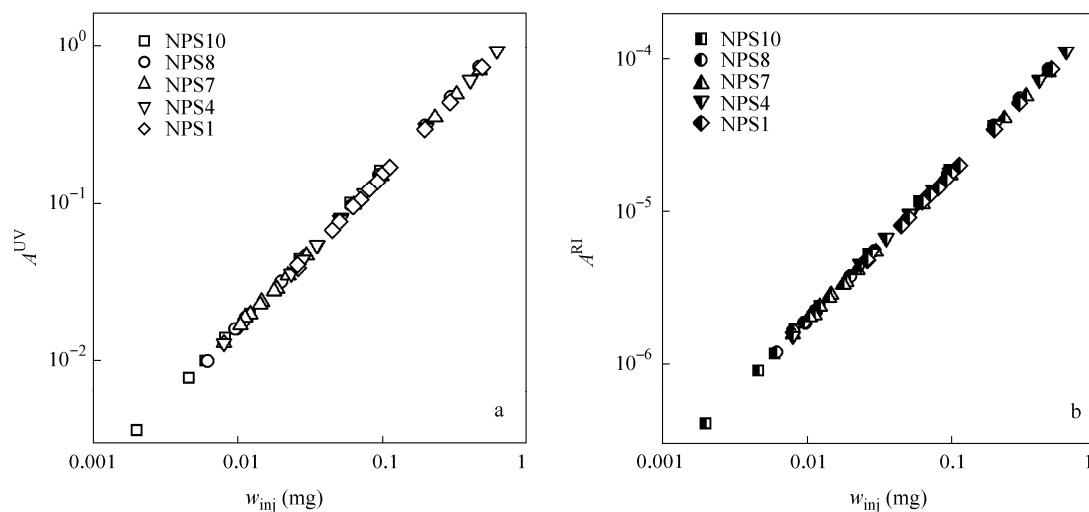


Fig. 2 Plots of A versus w_{inj} in the logarithmic form for the five PS standard samples: (a) UV detector and (b) RI detector

The non-zero intercept δ and the non-unity scaling factor γ in Table 2 vary systematically with the degree of polymerization of PS standards as shown in Figs. 3 and 4. These variations are parallel and almost equal (without consideration of the magnitude of the values) for both RI and UV detectors except that of the samples with lowest molar masses (NPS1 and NPS4) showing a greater difference. This difference indicates that the measuring principles of the RI and UV detectors for concentration are different and are more remarkable in the low molar mass region. Therefore a thorough investigation of the effect of the injected concentration on the individually determined response factor of the detectors is first required. On the other hand, the variation of the exponential scaling factor (γ) with chain length (x) expressed in Fig. 4 evidently demonstrates the effect of transition of the states of chain entanglement. Polystyrene has a critical molar mass of entanglement at $M_c = 35000$ which corresponds to a critical chain length $x_c = 336$. This value is also marked in Figs. 3 and 4. The entanglement effect of PS chains reported here occurs at a much lower concentration of solution than expected, but this effect does exist in dilute concentration of solutions as verified by some experiments^[16–18].

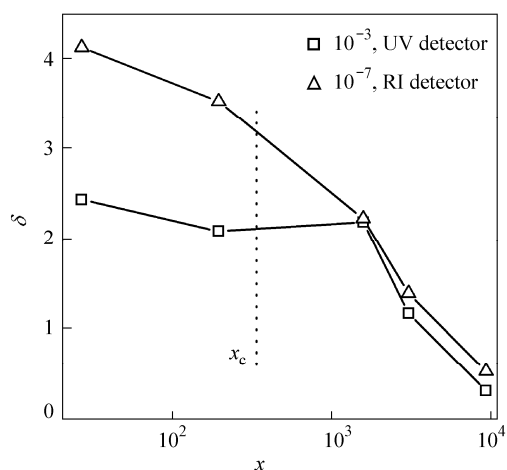


Fig. 3 Variation of the intercept δ of the area versus injected mass plot with the degree of polymerization of the PS standards for both detectors

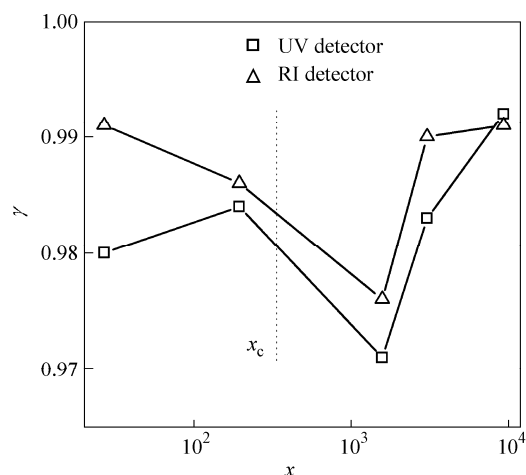


Fig. 4 Variation of the exponential scaling factor γ with the degree of polymerization x of the PS standards for both detectors

Concentration Dependency

Plots of the individually determined response factors expressed as $K = A/w_{\text{inj}}$ versus the concentration of the injected solution c_{inj} both for RI and UV detectors are shown in Fig. 5. It is presumed that the response factor should be a constant regardless of the concentration of injected solution. However, in this enlarged diagram the response factor K^{RI} and K^{UV} varies systematically with the concentration of the injected solution covering two and a half orders of magnitudes from 10^{-5} g/mL to 3.1×10^{-3} g/mL. For a given sample, it changes from a limiting value K_U at extremely dilute concentration region to a lower extreme limiting value K_E at higher concentrations. Such variation within a narrow range of K between two extreme limits certainly demonstrates the state of macromolecules in solution depends on the locus of the concentration regime it laid. The macromolecules in the extremely dilute concentration regime are in an individually dispersed state in the absence of intermolecular interaction while in the dilute concentration regime the existence of intermolecular interaction (self-association) will lead to cluster formation^[17, 18]. Hence, a characteristic state transition concentration should exist. Denoting this transition concentration as the dynamic contact concentration c_s as proposed by Qian^[19], the variation of the response factor of a given polymer with the concentration of the injected solution c may be expressed by

$$K = K_U e^{-\frac{c}{c_s}} + K_E (1 - e^{-\frac{c}{c_s}}) = K_E + (K_U - K_E) e^{-\frac{c}{c_s}} \quad (7)$$

Fitting the data of response factors of both detectors for each PS standards in Fig. 5 by Eq. (7), the evaluated values of the parameter K_U , K_E and c_s are listed in Table 3. All the correlation coefficients of the fitting curves are more than 0.95.

Table 3. Values of K_U , K_E and c_s for both detectors

Code	UV detector			RI detector		
	K_U	K_E	$c_s \times 10^4$ (g/mL)	$K_U \times 10^4$	$K_E \times 10^4$	$c_s \times 10^4$ (g/mL)
NPS10	1.75 ± 0.02	1.68 ± 0.01	0.7 ± 0.3	2.04 ± 0.02	1.94 ± 0.01	0.8 ± 0.3
NPS8	1.66 ± 0.01	1.58 ± 0.01	1.6 ± 0.4	2.02 ± 0.03	1.85 ± 0.01	1.0 ± 0.2
NPS7	1.67 ± 0.02	1.51 ± 0.01	2.3 ± 0.6	2.04 ± 0.02	1.77 ± 0.01	1.2 ± 0.2
NPS4	1.59 ± 0.02	1.50 ± 0.01	4.6 ± 1.0	1.98 ± 0.01	1.82 ± 0.01	3.7 ± 0.5
NPS1	1.54 ± 0.03	1.48 ± 0.01	6.8 ± 2.0	1.86 ± 0.02	1.75 ± 0.01	5.0 ± 2.0

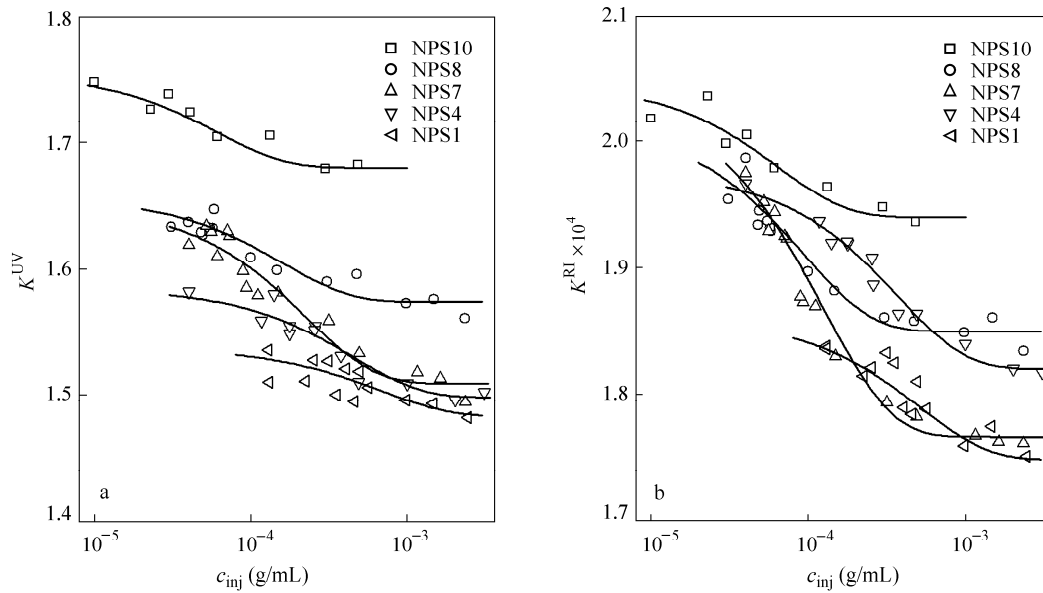


Fig. 5 Plots of response factors versus c_{inj} for the five PS standards: (a) UV detector and (b) RI detector

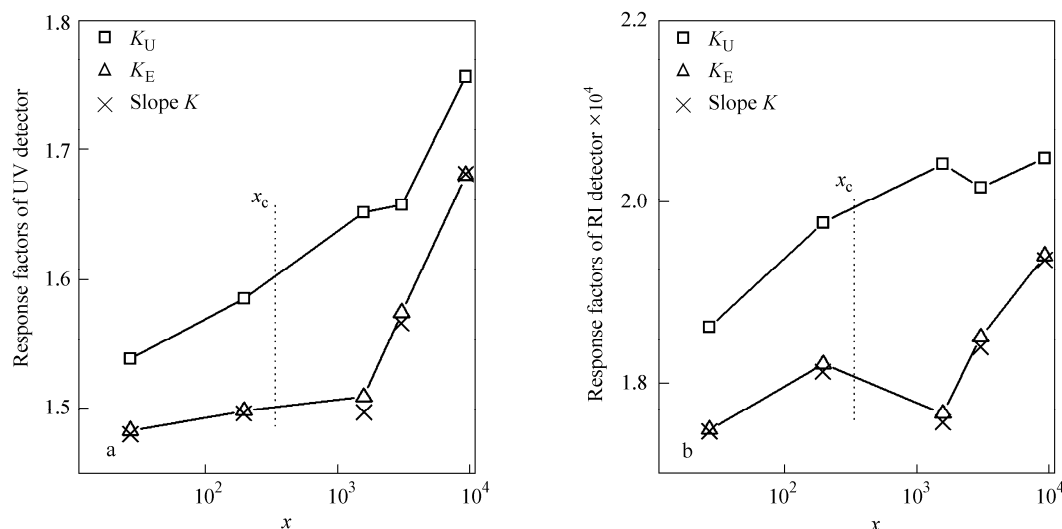


Fig. 6 The chain length dependency of K_U , K_E and slope K for: (a) UV detector and (b) RI detector

All these parameters are dependent on molar mass. The variations of the two extreme limiting response factors K_U and K_E with the chain length x are shown in Fig. 6. Two important facts should be noted. First, the slope of the linear regression line of the area of the detector signal versus the injected mass plot is identical to the K_E value, which means that this slope refers to the polymer in a cluster forming state. The second fact is that the critical chain length of PS also plays an important role, which divides the molar mass dependency into two distinct regions.

The K_U value refers to the response factor of polymer chain in the single chain state as the polymer concentration below the dynamic contact concentration c_s . The c_s derived from this work listed in Table 3 agrees well with the results of previous works derived by other methods^[20–22] as shown in Fig. 7. This agreement reveals the present interpretation of the response factor in terms of conformation change is reasonable.

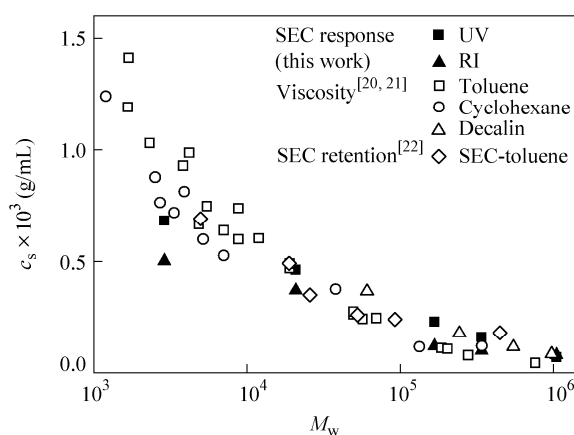


Fig. 7 Plot of c_s versus M_w for the five PS standards in THF at 25°C and comparison with the results by other methods

Solvation and Cluster Formation

It has been proven that the solvated solvent molecules contact with polymer chains firmly, and act as a part of the polymer chains^[23]. When the eluent flows during the SEC process, the “dressed” polymer chains with a solvated solvent shell will flow together with some trapped solvent inside^[24]. Accordingly, the observed solution

properties are the summation of the ‘naked’ polymer chain and solvated solvent. Considering these, the signal of RI detector can be written as

$$H^{\text{RI}}(V) = k^{\text{RI}} \left(\frac{dn}{dc} \right)_{\text{obs}} c(V) \quad (8)$$

where k^{RI} is the instrument constant of the detector, $(dn/dc)_{\text{obs}}$ is the observed specific refractive index increment of the solute and $c(V)$ is the concentration of the solute at elution volume V .

Integrating $H^{\text{RI}}(V)/w_{\text{inj}}$ over entire V , yields the response factor of RI detector

$$K^{\text{RI}} = \frac{A^{\text{RI}}}{w_{\text{inj}}} = \frac{\int H^{\text{RI}}(V) dV}{w_{\text{inj}}} = k^{\text{RI}} \left(\frac{dn}{dc} \right)_{\text{obs}} \quad (9)$$

It indicates that the response factor K^{RI} should be constant if all of the factors in the right side of Eq. (9) remain constant. The variation of K^{RI} with the concentration of injected solution must be originated from the unconstancy of any factor in the right side. In the present case the predominate factor is $(dn/dc)_{\text{obs}}$. Thus it can be represented by^[23]

$$\left(\frac{dn}{dc} \right)_{\text{obs}} = w_p \left(\frac{dn}{dc} \right)_p + w_s \left(\frac{dn}{dc} \right)_s \quad (10)$$

where w_p , w_s are the weight fraction of the polymer and solvated solvent, and have $w_s + w_p = 1$. $(dn/dc)_p$, $(dn/dc)_s$ are the refractive index increments of ‘naked’ polymer chain and the solvated solvent respectively. In a single solvent system, $(dn/dc)_s = 0$, so we have

$$\left(\frac{dn}{dc} \right)_{\text{obs}} = w_p \left(\frac{dn}{dc} \right)_p \quad (11)$$

w_p is calculable from M_0 , M_E , the molar mass of solvent M_s and the total number of solvent molecules ($m + xn + N$) involved in a solvated macromolecule by the formula^[23, 25]

$$w_p = \frac{M_E + xM_0}{M_E + xM_0 + (m + xn + N)M_s} \quad (12)$$

where m and n are the solvation number of the end group compound and that of a structural repeating unit respectively. N is the number of extra embedded solvent molecules per chain due to single chain looping or self-association of the chains. The specific refractive index increment of non-solvated polymer $(dn/dc)_p$ depends on the chain length x due to end group effect^[8, 13], and could be expressed by^[13]

$$\left(\frac{dn}{dc} \right)_p = \left(\frac{dn}{dc} \right)_{p(x \rightarrow \infty)} \left[1 + (K_v - 1) \frac{M_E}{xM_0} \right] \quad (13)$$

where $\left(\frac{dn}{dc} \right)_{p(x \rightarrow \infty)}$ is a constant for a given polymer and represents the extrapolated $(dn/dc)_p$ as the molar mass

approaches to infinity *i.e.* the reciprocal of x approaches to zero; K_v is also a constant representing the ratio of dn/dc of the end group with that of structural repeating unit and could be evaluated theoretically or determined experimentally. For PS in tetrahydrofuran at 25°C, $K_v = -0.778$ ^[13].

Substituting Eqs. (11)–(13) into Eq. (9), and denoting the product of the two constants k^{RI} and $(dn/dc)_{p(x \rightarrow \infty)}$ as K_0^{RI} , we have

$$K^{\text{RI}} = K_0^{\text{RI}} \left[\frac{M_E + xM_0}{M_E + xM_0 + (m + xn + N)M_s} \right] \cdot \left[1 + (K_v - 1) \frac{M_E}{xM_0} \right] \quad (14)$$

Eq. (14) is a complete formula which involves both the effect of chain length and solvation on the response factor of RI detector. Inspecting this formula, for a given polymer with a definite chain length the only factor which may vary with concentration is N , the extra-embedded solvent. As discussed in previous section, the extra-embedded solvent disappears as $c < c_s$, then the upper limiting K_U for RI detector will be

$$K_U^{\text{RI}} = K_0^{\text{RI}} \left[\frac{M_E + xM_0}{M_E + xM_0 + (m + xn)M_s} \right] \cdot \left[1 + (K_v - 1) \frac{M_E}{xM_0} \right] \quad (15)$$

For a given polymer sample, the solvation numbers m , n and the concentration independent response constants K_U^{RI} can be evaluated by numerical iteration of the plot of K_U^{RI} versus x with Eq. (15). The estimated results are $m = 2$, $n = 0.1$, and $K_0^{\text{RI}} = 2.14 \times 10^{-4}$. The correlation coefficients of the fitting curves are 0.94. The determination of the solvation number of polymer in solution is a somewhat troublesome task. However, the problem seems solvable using the concentration dependency of response factor as discussed in this section.

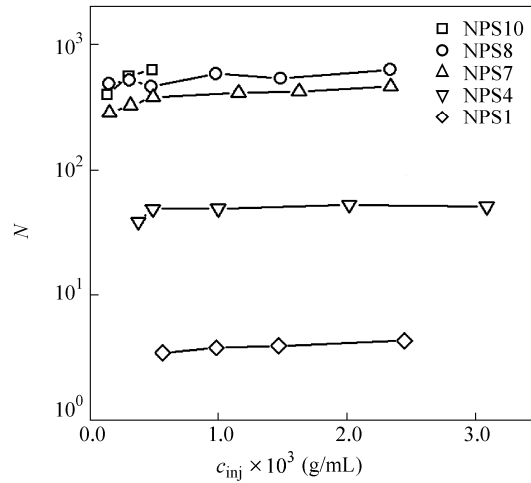


Fig. 8 The number of extra-embedded solvent molecules calculated from the response factors of RI detector in the dilute region of the five PS solutions

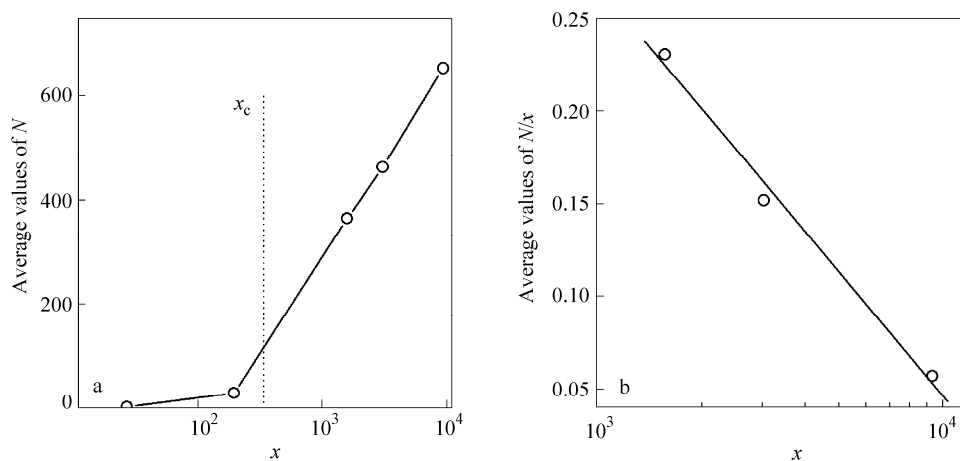


Fig. 9 The average extra-embedded solvents per chain (a) and per repeating unit (b) of PS standard samples below and above the critical entangling point $x_c = 336$ for RI detector

Substituting these determined m , n and K_U^{RI} values into Eq. (14), the number of extra-embedded solvent molecules N for each sample could be solved for solutions with $c_{\text{inj}} > c_s$. The plots of calculated results of N versus c_{inj} for RI detector are shown in Fig. 8. Taking the mean value of the extra-embedded solvents for each sample, a plot of N versus $\lg x$ is shown in Fig. 9(a). This plot indicates that the extra-embedded solvents increase with increasing molar mass as $x > x_c$. However, if the data are taken as the ratio of N/x , which representing the number of extra-embedded solvent per repeating unit, an inverted plot will be presented, as shown in Fig. 9(b).

As a concentration detector, RI detector measures a bulk property of a solution, while UV detector is detecting a molecular property of the object. It is well known that deviations of the Beers-Lambert law in absorptivity coefficients (namely response factors K^{UV}) at high concentrations (> 0.01 mol) are mainly due to electrostatic interactions between molecules in close proximity. In the PS solution, the entanglement and cluster formation mentioned above will generate proximities of styrene units. Hence, the response factor of UV detector at the injected concentration c_{inj} could be expressed as

$$K^{\text{UV}}(c_{\text{inj}}) = \frac{A^{\text{UV}}}{w_{\text{inj}}} = K_0^{\text{UV}} - a(c_{\text{inj}}) \quad (16)$$

where K_0^{UV} is the response factor of UV detector for the sample without chain-chain interactions; $a(c_{\text{inj}})$ represents the magnitude of deviation of K^{UV} due to all the loops formation at different c_{inj} of the sample, which can be written as

$$a(c_{\text{inj}}) = p(c_{\text{inj}}) \cdot a_0 \quad (16-1)$$

here $a_0 (\geq 0)$ is defined as the magnitude of deviation of K^{UV} when forming one loop (We simply assume a loop is corresponding to an entanglement point), which should be a constant for a certain kind of entanglement point; $p(c_{\text{inj}})$ is the amount of the entanglement points at different c_{inj} of the sample. Hence, the more the entanglement points formed in the solution are, the larger the deviation of the Beers-Lambert law becomes.

In analog to RI detector, $a(c_{\text{inj}})$ in Eq. (16) will vanish in the regime of $c < c_s$, thus the upper limiting K_U for UV detector will be

$$K_U^{\text{UV}} = \frac{A^{\text{UV}}}{w_{\text{inj}}} = K_0^{\text{UV}} \quad (17)$$

and so

$$a(c_{\text{inj}}) = K_U^{\text{UV}} - K^{\text{UV}}(c_{\text{inj}}) \quad (17-1)$$

If the value of a_0 is known, we can calculate the amount of entanglement points by

$$p(c_{\text{inj}}) = \frac{K_U^{\text{UV}} - K^{\text{UV}}(c_{\text{inj}})}{a_0} \quad (17-2)$$

Unfortunately, we couldn't get to know the absolute value of a_0 . According to the values of $a(c_{\text{inj}})$, we could assume $a_0 = 10^{-4}$, with a unit of mg^{-1} as the response factors'. Then the relative number p of entanglement points at different concentration can be determined. The data are not shown here. And if the data are taken as the form of $Nc_{\text{inj}}/(px)$, we can obtain the relative number of extra-embedded solvent per loop formed by PS chains at c_{inj} (Nc_{inj}/x means the relative trapped solvent numbers by all loops at c_{inj}). The plot of $Nc_{\text{inj}}/(px)$ versus c_{inj} is shown in Fig. 10. It indicates that the extra-embedded solvents per loop increase linearly with increasing c_{inj} for the samples of NPS10, NPS8 and NPS7. However, the trapped solvents per loop at a certain concentration are almost the same, because the lines of $Nc_{\text{inj}}/(px)$ versus c_{inj} for the three PS samples are parallel and close to each other, as seen in Fig. 10. Therefore, we can conclude that the size of loops and the trapped solvent per loop at a specified concentration are restricted to the chain structure of PS, such as the length of styrene unit and the angle of two adjacent units.

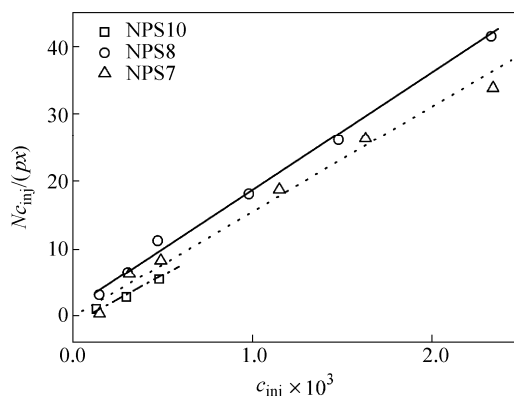


Fig. 10 The relative numbers of extra-embedded solvents per loop in the dilute regions of NPS10, NPS8 and NPS7

The data presented here indicate the solvation of polymer and the effect of chain's entanglement above the critical molar mass play an important role in the SEC process. We have suggested that the polymer in extremely dilute concentration regime is in an individually separated state holding an ideal solution property, and as the concentration increases to exceed the dynamic contact concentration, the polymer chains in solution will tend to self-association and cluster forming thus leading to the imperfection of the solution. The present results suggest that certain numbers of extra-embedded solvents and entanglement points will be involved in the course of this state transition.

CONCLUSIONS

The non-zero intercept of the total area of concentration detector signal versus the injected solute mass plot is originated from the individually determined response factor (ratio of area with injected solute mass) depending on the concentration of injected solution.

For a given polymer sample, the response factor varies with the concentration of injected solution within a narrow range bounded by two limiting values which correspond to two conformational states existing in low and higher concentration regimes respectively.

Mathematical treatment of the response factor data in the view of conformational state transition leads to the evaluation of dynamic contact concentration of polymer samples.

The response factors of RI for polymers are theoretically formulated in terms of the effect of chain length and solvation. The solvation numbers of the end group and the structural repeating unit could be estimated from the upper limiting boundary of the response factor. The controlling key factor of the concentration dependency is the number of extra embedded solvent which increases with chain length, and this number could be derived from the response factor in combination with the knowledge of solvation number.

The variation of the response factors of UV detector with concentrations is related to the cluster formation and the generation of entanglement points. The entanglement points and the trapped solvents per loop in different concentrations of the samples could be determined according to the Beers-Lambert law and the solvation. The size of loops and the trapped solvent per loop at a certain concentration are decided by the PS chain's structure, not the molar mass.

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