

SEC/Light Scattering Analysis of Multicomponent Polymer Systems

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We have shown several examples of characterization of multicomponent polymer systems by size exclusion chromatography coupled with a light scattering detector. Although SEC cannot provide a complete information for such systems due to its intrinsic limitation, one can extend its capability by combining multiple detection in order to get relevant information to some extent.

Introduction

Size exclusion chromatography (SEC) is one of the most widely used techniques for the characterization of polymeric materials.¹ The separation principle of SEC is the exclusion equilibrium of the polymer chains between the solvent in small pores (stationary phase) and the mobile phase. Therefore, macromolecules are separated in terms of their size in the solvent 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 easily obtain its molecular weight distribution (MWD).² For this purpose the calibration with standard samples of known molecular weights is most frequently employed.¹ In case that standard samples are not available, the universal calibration method can be used.³ With the development of viscosity detector, the universal calibration method can be carried out simultaneously with SEC separation.⁴ Furthermore, recent advances of light scattering detectors made it possible to determine directly the absolute molecular weight of polymer chains without relying on any type of calibration.^{5,6}

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.⁷ For an example, independent light scattering measurements have to be carried out in at least 3 different solvent systems to obtain the average molecular weight of a copolymer.⁸ SEC cannot be a solution of the problem either. Since SEC separates the macromolecules only in terms of their size, a fraction eluted from SEC column contains a mixture of polymer molecules having both MWD and CCD. Therefore SEC is unable to characterize either MWD or CCD except for several special cases; molecular size of each polymer component is different enough to yield a completely separated elution chromatogram or their composition is homogeneous and independent of molecular weight, so on.⁹ Due to this intrinsic limitation of SEC, many attempts to characterize multicomponent polymers with SEC had to rely on approximations to some extent.¹⁰⁻¹²

Another approach to the analysis of multicomponent polymeric systems is to separate the specimen according to its chemical composition. For this purpose solvent gradient HPLC has been widely used.¹³⁻¹⁵ However it generally suf-

fers from a limitation in the variety of applicable polymeric systems as well as in the detection due to the use of solvent gradient. A classical way to analyze such complicated systems is the cross-fractionation or orthogonal chromatography, which is rather difficult and time consuming yet to become a practical method.¹⁶⁻¹⁸

Previously we demonstrated that the both components in a binary polymer mixture could be characterized by use of SEC/multiple detection method.¹⁹ In this method, the use of multiple detection could not overcome the intrinsic limitation of SEC and the universal calibration method had to be employed in order to obtain the complete MWD of both components. In practice, however, it may not be necessary to obtain such detailed information but be sufficient to have a semi-quantitative measure of CCD as well as MWD. In this study we examined the applicability of SEC light scattering detection method for the characterization of two component polymeric systems.

Experimental

The SEC system consists of an isocratic pump (LDC, Constametric 3200), a 6 port injector (Rheodyne 7125), 4 columns (Showa Denko KF80M, 804, 8025, 801), a low angle laser light scattering (LALLS) detector (LDC, KMX 6), a refractive index (RI) detector (LDC, Refractomonitor IV) and a variable wavelength UV/Visible absorption (UV/Vis) detector (LDC, Spectromonitor 3200). Elution solvents are degassed by a membrane degasser (LDC) and filtered by an in-line filter (Alltech) before it reaches the columns. Columns are put in an oven (FIATron, CH-460) and the temperature was kept at 25 °C.

One polystyrene (PS), one poly(styrene-co-acrylonitrile) (SAN) random copolymer and two poly(methyl methacrylate) (PMMA) samples were used for this study. PS and SAN were provided from the Miwon Petrochemical Co. and PMMAs were acquired from Aldrich. All polymers have wide molecular weight distribution and were used as received without further purification. Tetrahydrofuran (THF) was used as the elution solvent. It was fractionally distilled after drying with sodium metal and filtered through 0.2 µm pore PTFE filter (Gelman) before use. The wavelength of the UV/Vis detector was set at 260 nm. The specific refractive index increments of PS, PMMA and SAN in THF were measured by a differential refractometer (LDC, KMX 16) at the

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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 The value for SAN was 0.163. SEC samples were prepared gravimetrically and the w/v concentration was obtained from the density of the materials. Typical sample concentration was 4 mg/mL and the injection volume was 100 μ L.

Analysis Scheme

First, consider the SEC analysis of a homopolymer. For a fraction eluted at a certain retention volume, output of three detectors are as follows.

$$RI : \Delta n_i = K_{RI} v c_i \quad (1)$$

$$UV/Vis : A_i = K_{UV} \epsilon c_i \quad (2)$$

$$LS : \Delta R(0)_i = K_{LS} v^2 c_i M_i \quad (3)$$

K_{RI} , K_{UV} and K_{LS} are the instrumental constants of three detectors, v 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 molar mass of the polymers in the i fraction, respectively. From a concentration detector, either RI or UV/Vis , c_i can be obtained if the instrumental constants and v 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* Eq. 3 from the excess scattered intensity, $\Delta R(0)_i$, and the pre-determined values of K_{LS} and v as follows.

$$M_i = \frac{\Delta R(0)_i}{K_{LS} v^2 c_i} \quad \text{and} \quad M_w = \frac{\sum_i M_i c_i}{\sum_i c_i} \quad (4)$$

Thus obtained M_w is the same as that from a batch light scattering measurement;

$$\begin{aligned} M_w &= \frac{\Delta R(0)}{K_{LS} v^2 c} = \frac{\sum_i \Delta R(0)_i}{K_{LS} v^2 \sum_i c_i} \\ &= \frac{K_{LS} v^2 \sum_i M_i c_i}{K_{LS} v^2 \sum_i c_i} = \frac{\sum_i M_i c_i}{\sum_i c_i} \end{aligned} \quad (5)$$

This is the typical SEC/LS analysis scheme to obtain the absolute molecular weight distribution of a homopolymer.

For a two component polymeric system, detector response is the sum of the contribution from each component A and B, *i.e.*,

$$UV/Vis : A_i = K_{UV} (\epsilon_A c_{A,i} + \epsilon_B c_{B,i}) \quad (6)$$

$$RI : \Delta n_i = K_{RI} (v_A c_{A,i} + v_B c_{B,i}) = K_{RI} v_i c_i \quad (7)$$

$$c_i = c_{A,i} + c_{B,i} \quad \text{and} \quad v_i = \frac{v_A c_{A,i} + v_B c_{B,i}}{c_i}$$

Therefore, in principle, one can obtain $c_{A,i}$ and $c_{B,i}$ by solving Eq. 6 and 7 simultaneously.¹⁹ On the other hand, the response of a light scattering detector is given as follows.

$$LS : \Delta R(0)_i = \sum_j \Delta R(0)_{ji} = K_{LS} \sum_j v_{ji}^2 c_{ji} M_{ji} \quad (8)$$

where the subscript j , i denotes the j species in the i fraction; j is *neither A nor B*. j species in i fraction is the species, among the copolymers eluted in the i fraction, having the molecular weight of M_{ji} , the concentration of c_{ji} , and its composition is such that its specific refractive index increment is v_{ji} . This somewhat complicated notation is required for $\Delta R(0)_i$; contrary to A_i or Δn_i since the total scattering intensity is the sum of the scattering intensity of individual macromolecule not of monomeric units. This is the reason why one cannot determine M_w of two component polymeric system from a single batch light scattering measurement in a solvent system. The molecular weight obtained from such a batch light scattering measurement of multicomponent polymeric system is commonly called as *apparent molecular weight* (M_{app}) since it depends on the refractive index of the solvent;

$$M_{app} = \frac{\Delta R(0)}{K_{LS} v^2 c} = \frac{\sum_i \Delta R(0)_i}{K_{LS} v^2 c} = \frac{\sum_i \sum_j (v_{ji}/v)^2 c_{ji} M_{ji}}{c} \quad (9)$$

where v is the average dn/dc of the whole specimen.

As mentioned earlier, SEC cannot provide the correct MWD, however, it is worth while to consider several special cases.

(1) If the composition is uniform for all the molecules in the specimen, *i.e.*, $v_{ji} = v_i = v$, Eq. 8 is reduced to $\Delta R(0)_i = K_{LS} v^2 c_i M_i$ which is equivalent to the case of homopolymer and then M_w can be obtained *via* Eq. 4. Therefore a copolymeric system with a homogeneous composition behaves just like a homopolymer with respect to the GPC/LS analysis. For an example the SEC/LS analysis of Cotts and Siemens was carried out under the assumption of the uniform composition.⁹ However such copolymers can only be obtained either by careful feed composition control or by stopping the polymerization at a low conversion before significant feed composition drift takes place.

(2) If all the molecules eluted in a given i fraction, not all of those in the specimen, have a homogeneous composition, *i.e.*, $v_{ji} = v_i \neq v$, Eq. 8 is reduced to $\Delta R(0)_i = K_{LS} v_i^2 c_i M_i$. The c_i and v_i can be obtained from Eq. 6 and 7, and the weight average molecular weight of the i fraction, M_i can also be obtained from $\Delta R(0)_i$. Then M_w can still be obtained as follows, which a batch light scattering measurement cannot provide.

$$M_i = \frac{\Delta R(0)_i}{K_{LS} v_i^2 c_i} \quad \text{and} \quad M_w = \frac{\sum_i M_i c_i}{\sum_i c_i} \quad (10)$$

Grinshpun and Rudin carried out SEC analysis of EPDM rubber under this assumption.¹¹ In general, SEC separation is not expected to meet this condition. On the other hand, interaction HPLC is sometimes able to separate copolymer molecules only in terms of the composition.²⁰ In this case, this analysis scheme may be used to obtain the absolute MWD although such an attempt has not been reported to our knowledge.

(3) If the composition of the polymers eluted in a fraction is not homogeneous, which is the general case in a chromatographic analysis of a copolymer sample, some approximation has to be made since exact information of each species (e.g., c_{ji} and v_{ji}) cannot be obtained by SEC analysis.

(3-1) If we use average specific refractive index increment of the whole specimen, ν in place of ν_{ji} , and calculate the concentration of i fraction from an RI detector response (Δn_i) and ν value, i.e., $\Delta n_i/\nu = c \sum \nu_{ji} c_{ji} / \sum \sum \nu_{ji} c_{ji}$, it is not c_i . Let such a concentration be denoted as c_i' . The reason of taking RI detector as the concentration detector in this example is due to its universality. However, it is not necessary to use RI detector and this analysis can be done by use of any concentration detector together with an LS detector. If we try to calculate the average molecular weight of i fraction (M_i') from c_i' , ν , and $\Delta R(0)_i$:

$$M_i' = \frac{\Delta R(0)_i}{K_{LS} \nu^2 c_i'} = \frac{\sum_j (\nu_{ji}/\nu)^2 c_{ji} M_{ji}}{c_i'} \quad (11)$$

Then the average molecular weight calculated from M_i' and c_i' is

$$M_w' = \frac{\sum_i M_i' c_i'}{\sum_i c_i'} = \frac{\sum_i \sum_j (\nu_{ji}/\nu)^2 c_{ji} M_{ji}}{c} \quad (12)$$

since $\sum_i c_i' = c = \sum_i c_i$.

It is interesting to note that Eq. 12 is identical to Eq. 9 so that the SEC/LS analysis of a multicomponent polymeric system according to the scheme (3-1) yields M_{app} .

(3-2) If we use the average specific refractive index increment of each fraction, ν_i in place of ν_{ji} , and calculate c_i by Eq. 6 and 7 then the molecular weight obtained from the excess scattering intensity is

$$M_i'' = \frac{\Delta R(0)_i}{K_{LS} \nu_i^2 c_i} = \frac{\sum_j \nu_{ji}^2 c_{ji} M_{ji}}{\nu_i^2 c_i} \quad (13)$$

This analysis requires two concentration detectors in addition to an LS detector. If one attempts to calculate the average molecular weight from M_i'' ,

$$M_w'' = \frac{\sum_i M_i'' c_i'}{\sum_i c_i'} = \frac{\sum_i \sum_j (\nu_{ji}/\nu_i)^2 c_{ji} M_{ji}}{c} \quad (14)$$

It is interesting to note that M_w'' is not M_{app} (eq 9) although M_i'' is identical to $M_{app,i}$. If one deals with a mixture of two homopolymers and if two components in the mixture are completely separated down to the baseline so that each fraction contains only one homopolymers, M_i'' becomes the weight average molecular weight of i fraction and M_w'' of individual component can be obtained by the analysis scheme (3-2).

Results and Discussion

The characterization results of PS and PMMA homopolymers are listed in Table 1. The weight average molecular weights of PS, PMMA10 and PMMA14 were determined by two independent methods. LS stands for the batch mode LALLS measurement which is a static low angle light scattering method. SEC/LS is the size exclusion chromatography analysis with an LALLS detector. These methods yielded practically identical results for 3 homopolymers.

We have tested 6 different PS/PMMA mixtures and a random copolymer (SAN) as summarized in Table 2. The first two digits in the binary mixture sample code identify the

Table 1. M_w of Polymers Used

Polymers	M_w ($\times 10^5$)	
	LS	SEC/LS
PS	243	237
PMMA10	97	93
PMMA14	141	138

Table 2. Average Molecular Weights Obtained by Various Methods ($\times 10^5$)

Sample	w_{PS}	SEC/LS		LS	Calculated	
		M_w'	M_w''	M_{app}	M_w	M_{app}
SM10 30	0.299	227	134		136	227
SM10 50	0.505	250	169		166	247
SM10 80	0.799	247	205		208	245
SM14 30	0.306	251	182		168	245
SM14 50	0.487	258	193		186	253
SM14 80	0.787	254	221		216	248
SAN			106	100		

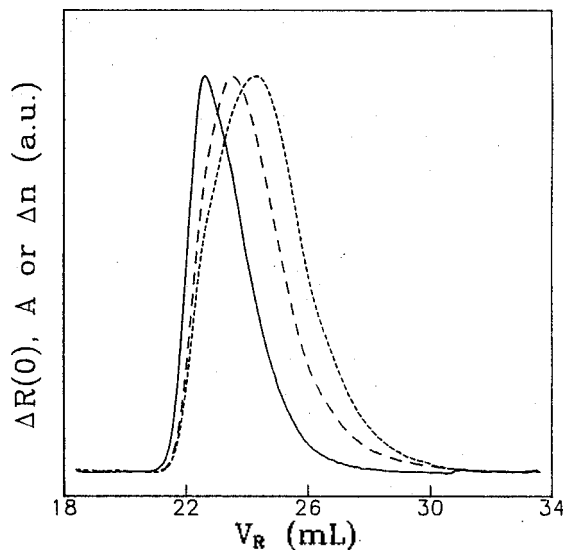


Figure 1. SEC chromatograms obtained by three detectors, RI (dotted line), UV/Vis (dashed line), and LS (solid line) of the SM10 50 chromatogram. The chromatograms are corrected for the lag time between the detectors and their intensities are normalized for visual aid.

PMMA used, while last two digits indicate the approximate weight percent of PS in the mixture. In Figure 1, a typical set of response curves from 3 detectors, RI (dotted line), UV/Vis (dashed line), and LS (solid line) of the SM10 50 chromatogram is shown. These chromatograms are corrected for the lag time between the detectors and their intensities are normalized for visual aid. The LS response curve shows up at the lowest retention volume, i.e., high molecular weight region, because the scattered light intensity depends upon not only the concentration but also the molecular weight. At the wavelength of 260 nm, PMMA does not absorb light

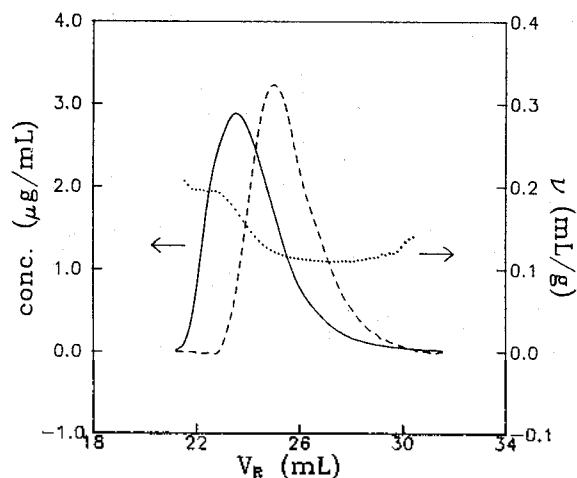


Figure 2. Isolated chromatograms of PS and PMMA in SM 10 50. The solid and dashed lines represent the concentration of PS and PMMA10 vs. retention volume, respectively. They are obtained by simultaneously analyzing the UV/Vis and RI response curves shown in Figure 1. The dotted line is the specific refractive index increment calculated by Eq. 7.

so that the UV/Vis chromatogram is practically the chromatogram of PS only. Since PS has a higher molecular weight than PMMA10 so being eluted earlier than PMMA10, UV/Vis response curve appears to be shifted toward the lower retention volume than RI response curve.

From the UV/Vis and RI response curves, the concentration of each components, $c_{PS,i}$ and $c_{PM,i}$ are obtained by solving Eqs. 6 and 7 simultaneously. The results are displayed in Figure 2 together with v_i deduced from $c_{PS,i}$ and $c_{PM,i}$. The solid and dashed lines represent the concentration of PS and PMMA10 vs. retention volume, respectively. We already have shown that thus determined $c_{PS,i}$ and $c_{PM,i}$ are quite reliable.¹⁹ The dotted line is v_i , which well represents the change of specific refractive index increment according to the composition of eluted fraction. The v_i value is higher at the low retention volume since PS having higher molecular weight is eluted. Before PMMA10 starts to come out, it shows the value of pure PS, and gradually changes toward the low value of PMMA. The increase of v_i value at the end of the chromatogram is due to the slight baseline drift at the low signal intensity region.

A mixture of two homopolymers can be regarded as a two component copolymeric system with extreme composition inhomogeneity so that only two species exist in a fraction, i.e., two pure homopolymers. Then Eq. 8 is reduced to

$$\Delta R(0)_i = K_{LS}(v_{PS}^2 c_{PS,i} M_{PS,i} + v_{PM}^2 c_{PM,i} M_{PM,i}) \quad (14)$$

and the analysis scheme (3-1) and (3-2) can be applied. As shown in Table 2, it is experimentally confirmed that M_w' obtained by the scheme (3-1) is identical with M_{app} . On the other hand, it is interesting to note that M_w'' by the analysis scheme (3-2) is very close to M_w , the real weight average molecular weight. This observation is common for all 6 mixtures indicating that it is not an accidental coincidence. As discussed previously, if two components in a mixture are completely separated down to baseline, M_i'' is the weight

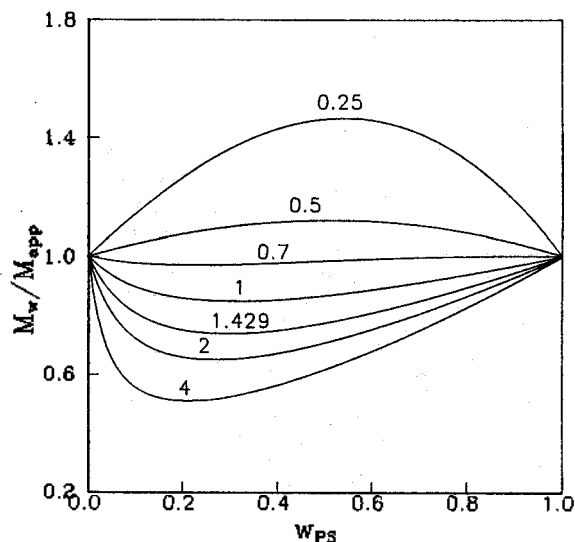


Figure 3. Simulation result of M_w/M_{app} as a function of the weight fraction of PS in mixtures of monodisperse PS and PMMA. The numbers in the plot indicate the values of M_{PS}/M_{PM} .

average molecular weight of i fraction and M_w should be obtained by the analysis scheme (3-2). This explains in part why M_w'' is closer to M_w than M_w' since there are some unoverlapped region of PS and PMMA peaks. As for the overlapped region, a simulation study was carried out for PS/PMMA mixture system and the result is shown in Figure 3. In the plot, the ratio of M_w to M_{app} of monodisperse PS and PMMA is plotted as a function of the PS weight fraction in the mixture. M_w and M_{app} are equivalent to M_i and M_i'' for the i fraction, respectively. The numbers in the plot indicate the values of M_{PS}/M_{PM} . As can be seen in the plot, M_w/M_{app} varies much with w_{PS} especially when M_{PS} is much different from M_{PM} . Since a fraction separated by SEC contains macromolecules of the same hydrodynamic volume, the molecular weights of two polymers should not be very far off and this is why M_w'' is close to M_w . More rigorously, from the Mark-Houwink constants of two polymers in THF ($K_{PS} : 11.0 \times 10^{-4}$ mL/g, $a_{PS} : 0.725$, $K_{PM} : 7.5 \times 10^{-4}$ mL/g, $a_{PM} : 0.72$) we find out that M_{PS} is about 30% smaller than M_{PM} for the polymers having the same hydrodynamic volume, thus eluted at the same fraction. As can be seen in Figure 3, M_w/M_{app} is close to 1 when $M_{PS}/M_{PM} \approx 0.7$. Therefore M_i'' should be very close to M_i , and M_w'' turns out to be practically identical to M_w . A 3 dimensional surface of the same plot as in Figure 3 is shown in Figure 4. In Figure 5 is also shown a 3 dimensional plot of M_w/M_{app} vs. weight fraction of one component (w_A) at various v_A/v_B . In this plot, M_A/M_B is kept at 0.7 like the case of PS and PMMA. As expected, one can easily notice that M_w/M_{app} is close to 1 when v_A is similar to v_B . In result, the simulation study tells us that M_i'' is not far off from M_i (i.e., $M_w'' \approx M_w$) if the specific refractive index increments and the molecular weights of two components are not much different at the same fraction.

In Figure 6 is shown RI and UV/Vis detector response curves of SAN and the ratio of two detector signal intensities. The constant ratio of two detector response over the whole retention volume range of the chromatogram peak in-

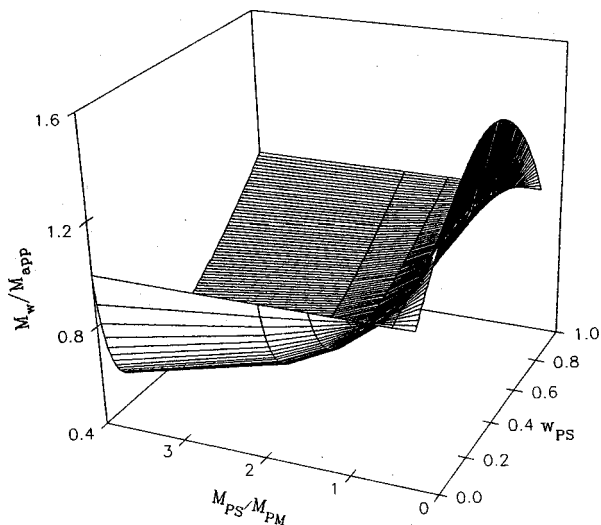


Figure 4. 3 dimensional representation of Figure 3.

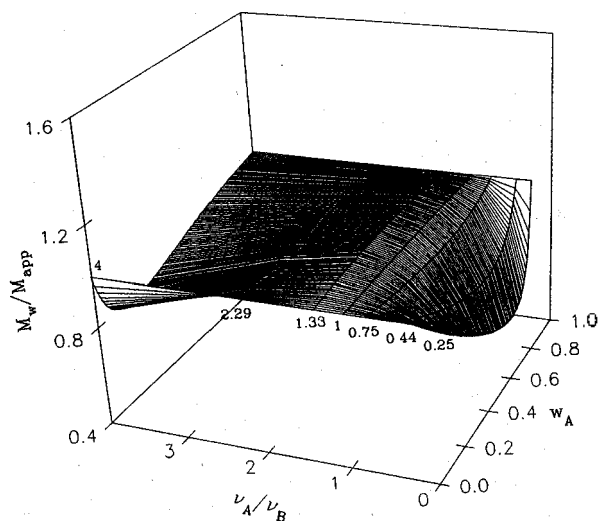


Figure 5. Simulation results of M_w/M_{app} as a function of weight fraction of component A in a binary polymer mixture of A and B, where $M_A/M_B=0.7$ like the case of PS and PMMA. The numbers in the plot is the value of ν_A/ν_B .

icates that the composition of the copolymer is homogeneous and independent of molecular size. This is the case (1) in the Analysis Scheme section. It was proven experimentally as shown in Table 2 that the molecular weight determined by SEC/LS is identical with the result of a batch LS measurement.

In summary, we have shown several examples of SEC/LS analysis of two component polymer systems. Although a complete information of MWD and CCD cannot be achieved for such systems by SEC due to its intrinsic limitation, one can extend its capability by combining multiple detection in order to get relevant information to some extent. At the same time one has to bear in mind the intrinsic limitation of SEC as well as the validity of the assumption employed in the analysis in order to acquire useful information from a multicomponent polymeric system.

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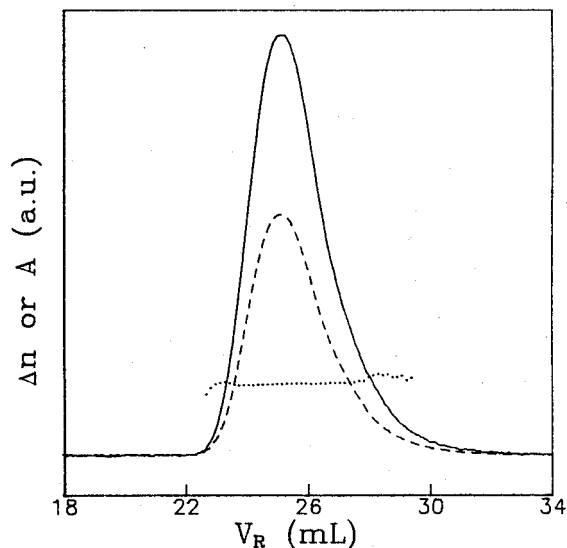


Figure 6. RI (solid line) and UV/Vis (dashed line) detector response curves in SEC analysis of SAN and the ratio (dotted line) of the detector signal intensity. The constant ratio of two detector response over the whole retention volume range of the chromatogram indicates that the composition of the copolymer is homogeneous and independent of molecular size.

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Correlation between the Reactant Complex or Transition State Conformations and the Reactivity of 4-Nitrophenyl Benzoate and Its Sulfur Analogues with Anionic Nucleophiles by Comparative Molecular Field Analysis (CoMFA)

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A comparative molecular field analysis (CoMFA) was carried out for the correlation of the transition state structures and the reaction rates for the S_N2 reaction of 4-nitrophenyl benzoate and its sulfur analogs with anionic nucleophiles. The CoMFA analysis showed that both steric and electrostatic effects are important, and the steric contribution increased when nucleophiles are alkoxides or arylsulfides. In this study, we have demonstrated that the CoMFA analysis can be expanded beyond the scope of dealing with reactants and products. The reactant complex and transition state conformations generated along the reaction path can be more appropriately used for the correlation of structures and reaction rates.

Introduction

In our previous works,¹ we have demonstrated that CoMFA is a powerful and valuable tool for describing the relationship between the LUMO energy and the rate constants of S_N2 reactions of benzyl benzenesulfonate with *p*-methoxybenzylamines and also for studying the substituent effects of the Pd(II) catalyzed rearrangement of allylic esters. However, in both cases, the conformations used for the CoMFA studies were either from reactants or products. In theory, however, it might be possible or more appropriate to use the conformations generated as the reaction proceeds along the reaction path for the CoMFA analysis to correlate with the reaction rates. For that purpose, we chose the kinetic data for a typical S_N2 reaction from the literature for our studies.

Recently Um *et al.*² carried out the kinetic study of the S_N2 reaction between 4-nitrophenyl benzoates and various anionic nucleophiles to investigate the effect of polarizability on the reaction rates. In the study, they found that the substitution of oxygen with more polarizable sulfur in the leaving group or in the carbonyl group of **1** changed the reactivity significantly, depending on the degree of polarizability of the attacking nucleophiles. The reactivity of the polarizable substrates **2** and **3** increases significantly toward the polarizable nucleophiles (ArS^-), and decreases toward the nonpolarizable nucleophiles (RO^-) indicating that the effect of polarizability on the rate is important in the system.

In our study, we investigated the same system theoretical-

ly to establish the relationships between the reactivity and the reactant complex and the transition state structures-reactivity relationship by the comparative molecular field analysis (CoMFA).³

Method

Starting geometries of the molecules were generated by the BUILD option in SYBYL (version 6.1a)⁴ and the geometry optimization for the reactants and the reactant complexes and the reaction path calculations were carried out by MO-PAC⁵ using the PM3 method.⁶ Locations and geometries of the stationary points on the potential energy surfaces were obtained by the reaction coordinate method⁷ refined by the NLLSQ (Non-Linear Least Squares) gradient norm minimization⁸ or EF (Eigenvector Following) routine⁹ and characterized by confirming only one negative eigenvalue in the Hessian matrix.¹⁰

Comparative Molecular Field Analysis (CoMFA). The optimized molecules were aligned by the least square fitting of the C_1 , Nu_2 , Y_3 , X_4 , and C_5 atoms of the molecule (Scheme 1). Then the CoMFA analysis was performed by using the QSAR option in SYBYL. The CoMFA grid spacing was 2.0 Å in all x, y, and z directions and the grid region generated automatically by the program was large enough to cover molecules completely with additional 4.0 Å in all directions. As a probe $sp^3 C^+$ ion was used.

A statistical analysis of the interaction energy and the target property ($\log k$ in Table 1)² was carried out by the partial