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Toward Absolute Chemical Composition Distribution Measurement of Polyolefins by High-Temperature Liquid Chromatography Hyphenated with Infrared Absorbance and Light Scattering Detectors

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Ⓢ *Supporting Information*

ABSTRACT: Chemical composition distribution (CCD) is a fundamental metric for representing molecular structures of copolymers in addition to molecular weight distribution (MWD). Solvent gradient interaction chromatography (SGIC) is commonly used to separate copolymers by chemical composition in order to obtain CCD. The separation of polymer in SGIC is, however, not only affected by chemical composition but also by molecular weight and architecture. The ability to measure composition and MW simultaneously after separation would be beneficial for understanding the impact of different factors and deriving true CCD. In this study, comprehensive two-dimensional chromatography (2D) was coupled with infrared absorbance (IR5) and light scattering (LS) detectors for characterization of ethylene–propylene copolymers. Polymers were first separated by SGIC as the first dimension chromatography (D1). The separated fractions were then characterized by the second dimension (D2) size exclusion chromatography (SEC) with IR5 and LS detectors. The concentrations and compositions of the separated fractions were measured online using the IR5 detector. The MWs of the fractions were measured by the ratio of LS to IR5 signals. A metric was derived from online concentration and composition data to represent CCD breadth. The metric was shown to be independent of separation gradients for an "absolute" measurement of CCD breadth. By combining online composition and MW data, the relationship of MW as a function of chemical composition was obtained. This relationship was qualitatively consistent with the results by SEC coupled to IR5, which measures chemical composition as a function of logMW. The simultaneous measurements of composition and MW give the opportunity to study the SGIC separation mechanism and derive chain architectural characteristics of polymer chains.
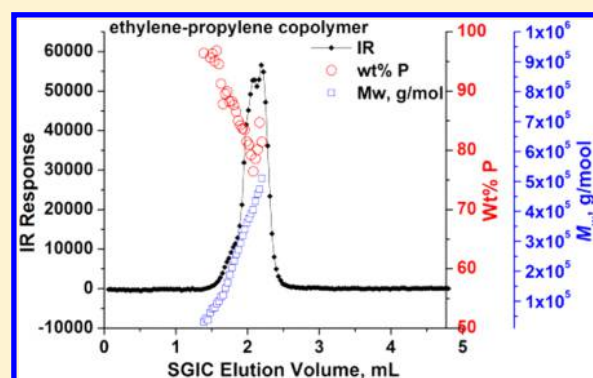
Molecular weight and chemical composition distributions (MWD and CCD) are two fundamental characteristics for representing the structures of copolymers. They are measured to connect the performance of polymeric materials to the reaction and process conditions.[1] MWD is routinely determined by size exclusion chromatography (SEC), where different sizes of polymer chains are separated in the order from large to small size. A concentration detector, such as differential refractive index detector (dRI), is connected to SEC column(s) to record weight fractions of polymer chains as a function of elution time, giving rise to a SEC chromatogram. The chromatogram is then converted to a MWD curve through a calibration curve established by polymer standards with known MW and polydispersity.[2] In the case of polymers with complex architecture, polymer chains with different MW will coelute if

they have the same size. MW-sensitive detectors, typically a light scattering photometer and/or a viscometer, are used with a concentration detector to determine absolute MW, radius of gyration (R_g), and/or intrinsic viscosity ($[\eta]$) online after SEC fractionation. The conformation of polymer chains can then be derived from either the MW vs R_g or the MW vs $[\eta]$ relationship.[3]

A separation based on chemical composition is required to obtain CCD. Chemical-composition-sensitive recognition can be achieved in high-performance liquid chromatography (HPLC) by finding a stationary phase having different enthalpic

interaction energies to different monomers.[4,5] The separation is then realized by employing a solvent gradient or a temperature gradient. In solvent gradient interaction chromatography (SGIC), the eluent strength is gradually increased by varying the composition of solvents so that the polymer chains having stronger interaction with the stationary phase will elute later.[6] In temperature-gradient interaction chromatography (TGIC), the elution power is manipulated by temperature. Highly interactive polymer chains are eluted at high temperature.[7,8]

It is an exception rather than the norm that polymer chains in SGIC and TGIC are separated only according to their chemical compositions. MW and chain architecture are the other two factors that have been demonstrated to affect polymer elution in both SGIC and TGIC.[9,10] To understand the impact of multiple factors, it would be desirable to determine composition and MW online after fractionation. Similar to SEC with MW-sensitive detectors, the hyphenation of chemical composition and MW-sensitive detectors with SGIC or TGIC would allow derivation of absolute chemical composition distribution as well as information about the architecture of polymer chains.

Attempts to make online chemical composition measurement have been carried out by hyphenation of HPLC with NMR (nuclear magnetic resonance spectrometer) and FTIR (Fourier transform infrared spectrometer). The use of NMR as an online detector has to overcome the interference of solvents on detection of analytes.[11] Examples have been given in the literature to apply wet solvent suppression to minimize the interference.[12−14] This technique was used mostly under isocratic elution conditions. The recent development of hyphenation of NMR with comprehensive two-dimensional liquid chromatography (X-2D) showed promise for using NMR as a detector for gradient separations.[15]

There are two ways to connect HPLC with FTIR.[16] One way is to have the eluent run through a flow cell inside of a FTIR spectrometer.[17] Another way is to evaporate solvents and deposit analytes on a disc for subsequent FTIR detection.[18,19] The flow-cell-based approach faces similar challenges as HPLC-NMR, where signals of HPLC solvents often dwarf signals of analytes. Therefore, solvent background correction is required for gradient elution separations.[20,21] The disc-based approach removes the interferences of solvents. The lack of interferences leads to higher sensitivity compared with the signals obtained by the flow-cell-based approach. The disc approach also allows for more choices of solvents and is thus more broadly practiced in the polymer industry.[22] The drawback of the disc approach is that variations in the deposited film result in less quantitative and reproducible data.

So far the research has been devoted to use NMR and FTIR as selective detectors to measure chemical compositions. In addition to chemical compositions, the concentrations of separated fractions must also be determined for measurement of absolute CCD. The simultaneous measurements of chemical compositions and concentrations require the hyphenation of a selective detector with a concentration detector. To avoid interference from the gradient, an evaporative light scattering detector (ELSD) is often used in SGIC and TGIC as a universal mass detector. Several studies have shown that the responses of ELSD are not linear and dependent on chemical compositions of polymers.[23,24] These are undesired characteristics for a concentration detector. Understandably, the hyphenation of ELSD with NMR or FTIR detector has never

been reported, although ELSD and FTIR are often used separately for the same HPLC separations.[25,22]

One possible way to overcome the challenge of concentration detection with a gradient is to run X-2D with SGIC as the first dimension (D1) and SEC as the second dimension (D2). In this mode of separation, analytes and solvents from D1 are separated in D2 so that the concentration detector for isocratic elution can be used. This concept was successfully demonstrated in high-temperature SGIC using a decane−trichlorobenzene (TCB) gradient in D1 separation and trichlorbenzene as the D2 SEC eluent.[26] A blend of isotactic polypropylene (iPP), ethylene−propylene copolymer, and polyethylene was separated and the recovered mass showed good agreement with the blend ratio. An infrared absorbance detector (IR5) was used for concentration measurement. Compared to a dRI detector, an IR5 detector has higher sensitivity for polyolefins.[27] The high sensitivity makes it a better choice for X-2D as the analytes are typically diluted by 2 orders of magnitude before detection.

IR5 is not only a concentration detector but also a composition detector for polyolefins. It is equipped with band-pass filters that are sensitive to the aliphatic C−H stretch and aliphatic CH_2 and CH_3 asymmetric stretch regions of the spectrum.[28] The band from C−H bonds is used for concentration measurement. The ratio of CH_3 over CH or CH_2 band can be calibrated for composition measurement. Therefore, the detector itself satisfies the requirement of simultaneous measurements of both concentrations and compositions for absolute CCD determination. When an LS detector is hyphenated with an IR5 detector, the ratio of light scattering signal over CH signal of the IR5 can be used to determine absolute weight-average molecular weight (M_w). The purpose of this study is to explore the properties of online measured composition and M_w as a function of SGIC elution time. Experiments are designed to investigate if a metric from online concentrations and compositions could be derived to represent the breadth of chemical composition distribution. The correlation of M_w−chemical composition from SGIC will be compared with the correlation obtained from SEC with IR5 and LS detectors.

■ EXPERIMENTAL SECTION

Polymers and Solvents. Isotactic polypropylene (iPP), ethylene−propylene random copolymer (E/P) of different compositions, and high density polyethylene (HDPE) were prepared by single-site catalysts for calibration and blend experiments. The E/P standards had the propylene contents at 20.0, 28.0, 50.0, 86.6, 92.0, and 95.8 wt % P (propylene), respectively. The compositions were determined by NMR.[29] Another E/P copolymer with broad CCD was produced using a continuous solution polymerization process. The M_w, polydispersity index, and composition of the sample were 261 kg/mol, 1.8, and 83.6 wt % P, respectively.

HPLC grade trichlorobenzene (TCB) was purchased from Fisher Scientific (Pittsburgh, PA, U.S.A.). Decane with 99+ % purity was from Acros Organics (NJ, U.S.A.). 2,6-Di-*tert*-butyl-4-methylphenol (Ionol) was also from Acros.

Instrumentation. A Waters GPCV2000 was reconfigured to run X-2D.[30] Two Shimadzu LC-20AD pumps (Columbia, MD, U.S.A.) were connected to the injector inside of the column oven of GPCV2000. The SGIC column was connected between the injector and a 10-port and 2-position switching valve from Valco Inc. (Houston, TX, U.S.A.). The SEC column

Table 1. Concentrations and Compositions of the Components in Blend Experiments

	component	mass (g)	concentration (wt %)	IR$_{measure}$ (× 10^5 mV)	concentration by IR$_{measure}$ (%)	concentration difference^a (%)	composition by NMR (wt % P)	composition by IR (wt % P)	composition difference^b (wt % P)	$M_w{}^c$ (kg/mol)
blend A	iPP	0.0114	28.4	4.52	26.2	−2.2	100	101	1	274
	E/P-50	0.0161	40.0	7.00	40.1	0.1	50.0	50.3	0.3	197
	E/P-28	0.0127	31.6	5.90	33.8	2.2	28.0	28.8	0.8	137
blend B	E/P-96	0.0127	34.2	5.86	35.0	0.8	95.8	96.9	1.1	290
	E/P-87	0.0109	29.4	4.50	26.7	−2.7	86.6	86.8	0.2	308
	E/P-20	0.0135	36.4	6.46	38.3	1.9	20.0	15.4	−4.6	78.1

^{a}Concentration determined by IR minus concentration in the physical blend. ^{b}Composition determined by IR minus composition determined by NMR. $^c M_w$ determined by X-2D with LS15 and IR$_{measure}$.

was connected between the 10-port valve and a PD2040 LS detector (Agilent, Santa Clara, CA, U.S.A.). An IR5 detector (Polymer Char, Paterna, Spain) was connected between the LS detector and a waste container. The isocratic pump of GPCV2000 was connected to the 10-port valve. The symmetrical configuration was adopted in the connections to the valve.[31]

SGIC × SEC 2D Chromatography. The SGIC column was Hypercarb from ThermoFisher. The column had a dimension of 2.1 × 100 mm, packed with 3 μm porous graphitic particles. The average pore size was 25 nm according to the manufacturer. The D1 flow rate was at 0.01 mL/min. The initial solvent composition was 100% decane. Ten minutes after injection, a typical gradient would have the mobile phase composition linearly changed from 0 to 60% TCB between 10−489 min. Other gradients used in this study will be described with the results. The TCB contained 200 ppm ionol as the radical scavenger. After SGIC separation, the column was washed by running 100% TCB at 0.2 mL/min for 10 min, followed by running 100% decane at 0.2 mL/min for another 10 min as the equilibration step before next injection.[32]

The SEC column was a PLRapide-M column purchased from Agilent. The column had a dimension of 10 × 100 mm, packed with 5 μm porous polystyrene-divinylbenzene (PS-DVB) particles. The D2 eluent was TCB running at 2.51 mL/min. The eluent from D1 SGIC separation was fractionated in 30 μL aliquots continuously into the two 60 μL sample loops equipped with the 10-port valve. As a practice of safe operation, the loop volume was two times larger than the collected volume for the complete recovery. When one loop was collecting the D1 effluent, the collected fraction in the other loop was loaded onto the SEC column for separation. The collection time and the SEC run time had to be synchronized. The time was 3 min. The temperature of SEC column was set at 140 °C.

The signals from LS and IR5 detectors were collected by EZchrom software through SS420X analog/digital converter (Agilent). The collection frequency was 10 Hz. The collected chromatograms were exported in ASCII format and imported to Matlab (Mathworks, Natick, MA, U.S.A.). A custom-made routine in Matlab was used to reduce the data.[30]

To prepare a sample solution for injection, 20−25 mg of sample was usually weighed into a 10 mL vial. The exact sample masses used in the blend experiments are given in Table 1. Decane with 400 ppm ionol was pipetted into the vial afterward. The volume of decane was 8 mL at room temperature. The vial was then heated at 160 °C with gentle shaking for 2 h. The vial was then transferred to the autosampler of GPCV2000. The temperatures of carousel, injector, column, and detectors were all set at 140 °C. The injection volume was 311 μL. The injection volume was

calibrated by the manufacturer and was required to operate the instrument. The method itself did not require injection volume having three significant figures. The injection volume was large for a 2.1 × 100 mm column. Larger injection volume was desired for better signal intensity. It had been demonstrated that large injection volume did not overload the column.[33] This is likely because the polymer samples were injected in decane, the solvent with weak elution strength. As a result, polymer samples were concentrated at the top of the column without significant band broadening.

SEC Chromatography. Three PL-gel Mixed-B (Agilent) columns were connected between injector and detectors, by passing the 10-port valve. Each column had a dimension of 7.5 × 300 mm. The columns were packed with 10 μm porous PS-DVB particles. TCB with 200 ppm ionol was the eluent, and the flow rate was 1.0 mL/min. A sample of 10−15 mg was dissolved in 8 mL of TCB with 200 ppm ionol at 160 °C. The injection procedure was the same as that of X-2D experiment. The chromatograms were collected by EZchrom and exported as AIA format. The exported chromatograms were imported to Cirrus (Agilent) for data reduction. The temperatures of all chromatograph components were set at 140 °C.

IR5 Calibration. Composition calibration was done the same way as before.[26] HDPE, iPP, and E/P standards made by single-site catalyst were prepared in TCB with 200 ppm ionol. The concentrations of sample solutions were between 1−2 mg/mL. The standard solutions were injected into a PLRapid-H column (Agilent). The column had a dimension of 10 × 100 mm, packed with 10 μm porous PS-DVB particles. All the other conditions were the same as those described in SEC chromatography experiments. The composition calibration curve, shown as the ratio of IR$_{methyl}$/IR$_{measure}$ as a function of wt % P, is given in Figure 1. Here IR$_{methyl}$ refers to the signal from CH$_3$ band and IR$_{measure}$ stands for the IR signal from C−H stretching. The terminology is from the manufacturer. Note that the signal of IR$_{methyl}$ also has the contribution from C−H bond. The IR$_{methyl}$/IR$_{measure}$ ratio is not at 0 for iPP.

LS Calibration. The calibration of LS over IR signals was used to obtain M_w of the separated fractions. The calibration details were reported in a previous study.[26] Briefly, the HDPE standard with known M_w and M_n (number-average MW) was run by SGIC × SEC 2D chromatography. SGIC was running in isocratic mode with 100% TCB so that the standard was eluted without retention by the column. The elution volume of the polymer peak appeared at around 0.6 mL in D1 chromatogram. The LS signals at 15° of all the fractions were summed as A_{LS15}:

$$A_{LS15} = \sum_n \sum_i LS15, i \tag{1}$$
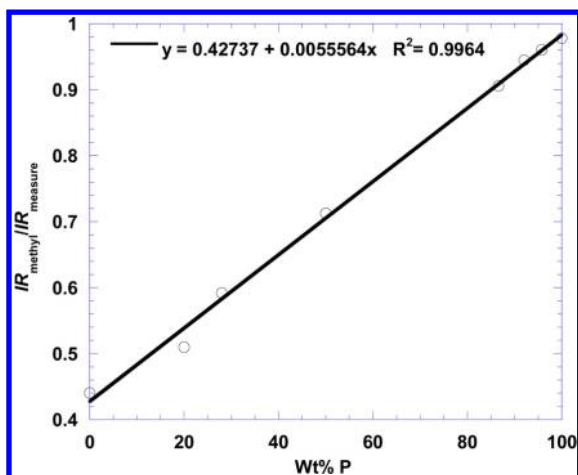
Figure 1. Composition calibration of IR5 by iPP, HDPE, and E/P standards.

where LS15,i represents the signal response of slice i in LS15 D2 chromatogram and n represents the fraction number. The "measure" signals of all the fractions were summed as $A_{measure}$:

$$A_{measure} = \sum_n \sum_i IR_{measure,i} \qquad (2)$$

where $IR_{measure,i}$ represents the signal response of slice i in $IR_{measure}$ D2 chromatogram The calibration constant, Ω, was then obtained by the following equation:

$$\Omega = \frac{A_{LS15}}{A_{measure}M_w} \qquad (3)$$

The M_w of separated fractions were then determined by the ratio of LS to $IR_{measure}$ signals and Ω, assuming the same dn/dc (differential refractive index increment) for E/P of different compositions.[34]

RESULTS AND DISCUSSION

SGIC × SEC Chromatography. The 2D chromatogram of a physical blend sample (blend A in Table1) is shown in Figure 2. The signal intensity of $IR_{measure}$ in the clolor scale is plotted
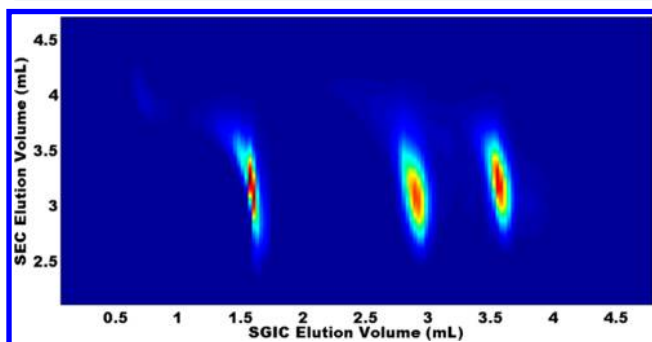

Figure 2. SGIC × SEC two-dimensional chromatogram of a blend. The blend has iPP, E/P with 50.0 wt % P, and E/P with 28.0 wt %P.

as a function of both SGIC and SEC elution volumes. The blend has three components. The concentrations and compositions of the three components are given in Table 1. The three components are eluted in the order of increasing propylene content in SGIC separation. The SEC chromatograms of individual fractions are plotted as a function of SGIC

elution volume to make the 2D chromatogram. By showing the data on 2D scale, both MWD and CCD of individual components can be evaluated. However, it is challenging to derive online composition or M_w data by taking the ratio of $IR_{methyl}/IR_{measure}$ or LS15/$IR_{measure}$ in 3D matrix format. All the data reported in this study were calculated from the reduced 1D chromatograms.

Simultaneous Concentration and Composition Measurements. The D1 SGIC chromatograms of two physical blend samples are shown in Figure 3. The SGIC chromatogram
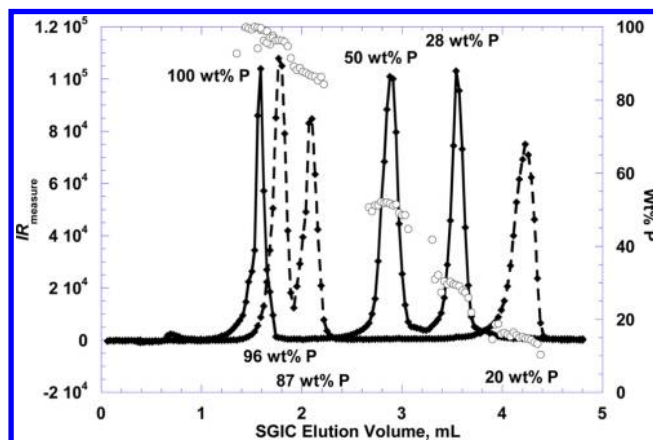
Figure 3. Summed D1 SGIC chromatograms of blend A (rhombus connected by solid line) and blend B (rhombus connected by dashed line). Blend A is a physical blend of iPP, E/P of 50.0 wt % P, and E/P of 28.0 wt % P. Blend B is a blend of E/P of 95.8 wt % P, 86.6 wt % P, and 20.0 wt % P. The circles represent the compositions referring to the right y-axis.

is reconstructed from 2D matrix data by plotting the summed SEC signals of individual fractions as a function of D1 elution volume. The summed signal of fraction n ($IR_{measure,n}$) can be represented as

$$IR_{measure,n} = \sum_{D2\ peak\ start}^{D2\ peak\ end} IR_{measure,i} \qquad (4)$$

The signals in the defined integration range are summed to obtain $IR_{measure,n}$. Note that the summation is by the signal heights so that the unit of $IR_{measure,n}$ is detector output voltage. The D1 elution volume (V_{D1}) is calculated as

$$V_{D1,n} = F_{D1} \times n \times t_{D2} \qquad (5)$$

where F_{D1} is the SGIC flow rate, 0.01 mL/min., and t_{D2} is the D2 SEC time. It is also the fraction collection time. The circles in Figure 3 represent the chemical compositions, determined by the $IR_{methyl}/IR_{measure}$ ratio and the calibration curve (Figure 1).

The mass of the components in sample blend A and B are shown in Table 1. Concentrations in weight percentage are determined from the mass. The $IR_{measure}$ signals of individual components are also listed in Table 1. The percentage of individual component by IR is obtained by normalization of the signal of individual component with respect to the total signal intensity. The difference of the percentage by IR to that by mass is in the range between −2.7 to 2.2%. There is no bias in the measured concentration by IR with respect to the chemical composition. This is in contrast to the results by ELSD, where results previously reported in the literature suggested that the ELSD response is dependent on chemical composition.[24]

The following three columns in Table 1 are for the evaluation of the chemical compositions determined by IR. Compared to the composition values determined by NMR, the compositions by IR show the differences equal to or less than 1 wt % P except standard E/P-20. The point corresponding to E/P-20 in Figure 1 shows the largest deviation from the fitted linear curve, indicating that there might be an error with the value from NMR. The result of E/P-20 by IR actually agrees well with what the calibration curve would predict. In summary, the data in Table 1 indicate that SGIC X SEC with IR5 detector is able to measure concentration and chemical compositions simultaneously.

The last column in Table 1 has the M_w of the individual components measured by 2D with online LS and IR5 detectors. The numbers are in agreement with the D2 SEC elution order shown in Figure 2.

Evaluation of the Online Chemical Composition by Varying the Gradient. The chromatograms in Figure 4 are
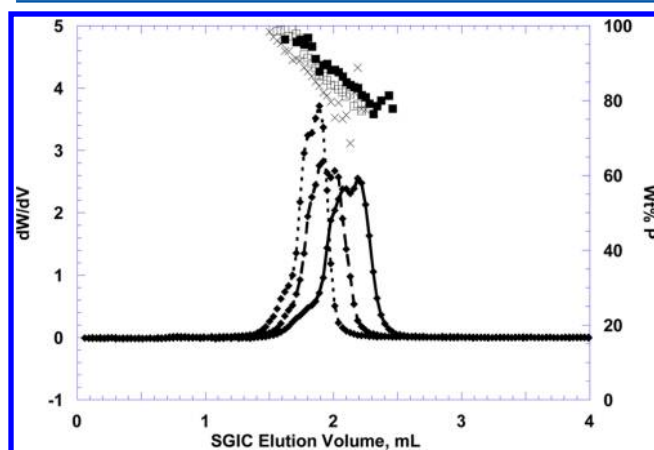
Figure 4. Normalized SGIC chromatograms of sample E/P-Broad obtained by running different gradients. The gradient slopes were 12.5 (solid line), 14.6 (dashed line), and 16.7%TCB/mL (dotted line), respectively. The filled squares, open squares, and crosses represent the online compositions for the solid, dashed, and dotted chromatograms, respectively.

obtained by running an E/P sample using gradients of different slopes. The E/P sample has a broader CCD compared to those of standards prepared by a single-site catalyst. It is named E/P-Broad. The gradients have the slopes of 12.5, 14.5, and 16.7 TCB/mL of elution volume, generated by increasing TCB from 0 to 60, 70, and 80% between 0.1 to 4.89 mL. The sample eluted under steeper gradient appears at lower elution volume with a narrower peak width. The online measured chemical compositions, shown as the symbols on the top of the chromatograms, change their slopes with respect to the elution volume. Sample eluted by faster gradient shows a larger degree of decrease in propylene contents as elution volume increases.

The composition of the sample is determined by the online IR measurement. It is 86.8 ± 0.8 wt % P from the three experiments (Table 2). A metric is proposed to represent the CCD breadth by calculating the chemical composition difference between 25 wt % polymer chains eluted early at low elution volume ($Comp_{25\%, early}$) and 25 wt % polymer chains eluted late ($Comp_{25\%, late}$) at high elution volume:

$$\Delta P_{quantile} = Comp_{25\%,early} - Comp_{25\%,late} \qquad (6)$$

Table 2. Properties of Online Chemical Compositions Obtained by Gradients of Different Slopes

	slopes of gradients (%TCB/mL)	average composition (wt % P)	$\Delta P_{quantile}$ (wt % P)
E/P-Broad	12.5	85.6	11.7
	14.6	87.0	12.3
	16.7	86.8	11.5
E/P 87	8.35	87.4	5.6
	12.5	87.7	4.9

The results of these calculations are shown in Table 2. The metric for E/P-Broad is 11.8 ± 0.4 wt % P from the three experiments. Notably, $\Delta P_{quantile}$ is independent of the gradients used in the separations.

The chromatogram of E/P-Broad is compared with that of E/P-87 in Figure 5. The chromatograms in Figure 5A are obtained using the same gradient (12.5%TCB/mL). The peak of E/P-87 is narrower compared to that of E/P-Broad, suggesting a narrower CCD of the sample prepared by single-site catalysts. $\Delta P_{quantile}$ in Table 2 indicates that the
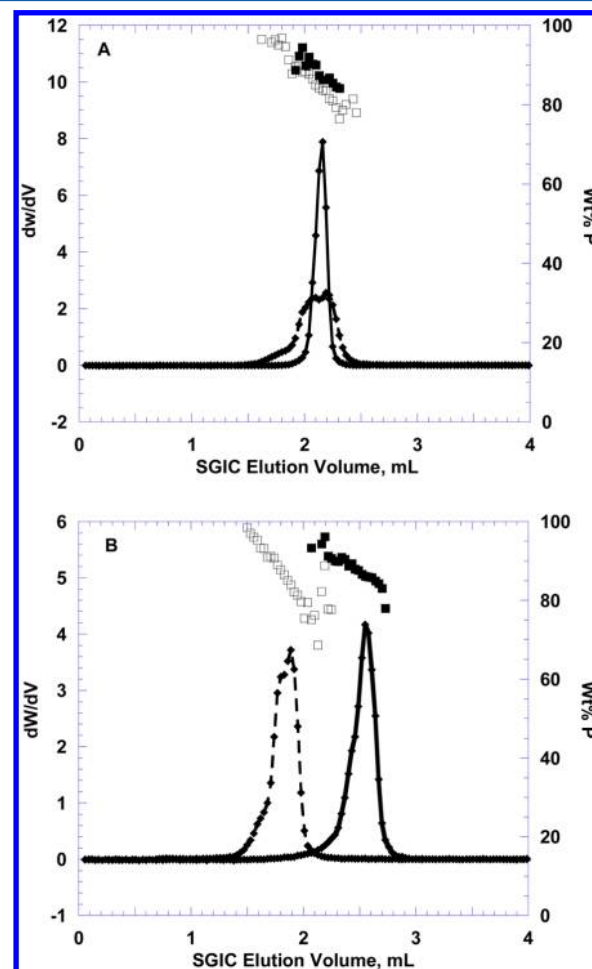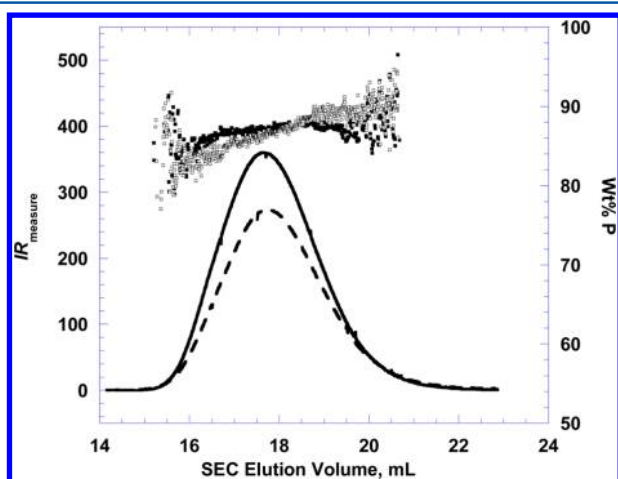

Figure 5. Comparison of SGIC chromatograms of E/P-87 (solid line) and E/P-Broad (dashed line). The filled squares and open squares are online compositions for E/P-87 and E/P-Broad, respectively. The chromatograms in Figure A were obtained by the same gradient, slope = 12.5%TCB/mL. The chromatograms in Figure B were obtained using the gradient of slope = 8.35%TCB/mL for E/P-87 and the gradient of slope = 16.7%TCB/mL for E/P-Broad, respectively.

CCD breadth of E/P-Broad is approximately twice the CCD breadth of E/P-87.

The chromatograms in Figure 5B are obtained using gradients of different slopes. The chromatogram of E/P-87 is obtained by a slow gradient with slope at 8.35%TCB/mL (0 to 40% TCB between 0.1–4.89 mL), whereas the chromatogram of E/P-Broad was obtained by a fast gradient with slope at 16.7%TCB/mL. E/P-Broad is eluted earlier than E/P-87 by the faster gradient. The peaks for the two samples show similar peak width, meaning that CCD cannot be compared when different elution conditions are used. The $\Delta P_{quantile}$ metric, however, is 11.5 wt % P for E/P-Broad by the fast gradient and 4.9 wt % P for E/P-87 by the slow gradient. The numbers correctly reflect the difference of CCD breadth between the two samples. This experiment further proves that the metric from online composition is independent of the tested gradients. The independency of the metric to gradient conditions suggests that absolute CCD could be derived from online measured concentration and chemical composition data.

Online Chemical Composition by SEC-IR5. SEC connected with concentration- and composition-sensitive detectors is commonly used to study chemical composition drift as a function of MW in copolymers. The ratio of UV to RI signals after SEC separation, for example, was used to study composition variation of styrene in poly(styrene-co-methyl methacrylate) copolymers.[35] Similarly, SEC with IR5 detector was used to measure chemical composition as a function of MW in polyolefins.[27] A comparison of the two techniques, SEC with IR5 and LS detectors versus SGIC × SEC with IR5 and LS detectors, is worthwhile for appropriate selection of techniques to address different kinds of problems.

The SEC chromatograms of E/P-87 and E/P-Broad are shown in Figure 6. The online compositions are also given on


Figure 6. SEC chromatograms of E/P-87 (solid line) and E/P-Broad (dashed line). Solid squares and open squares represent the online compositions for E/P-87 and E/P-Broad, respectively.

the top of the chromatograms. Early-eluting polymer chains have lower propylene content than those eluting later. The slope of propylene content versus elution volume is larger for E/P-Broad than for E/P-87. Using eq 6, $\Delta P_{quantile}$ is calculated as −4.8 wt % P from online composition of E/P-Broad. $\Delta P_{quantile}$ is calculated to be −1.7 wt % P for E/P-87. The absolute values of the metric are lower in SEC than those in SGIC (Table 2). SEC with composition-sensitive detectors is

only good at detecting compositional hetereogeneity when the compositional distribution is broad, and composition varies with molecular weight. However, SGIC is sorting chains mainly by chemical composition, and it is thus more sensitive to chemical composition heterogeneities. In summary, chemical composition distribution can only be obtained from chemical composition-sensitive separation but not from size separation.

MW as a Function of Elution Volume. The weight-average molecular weights of the fractions after SGIC separation are shown in Figure 7 for sample E/P-Broad.
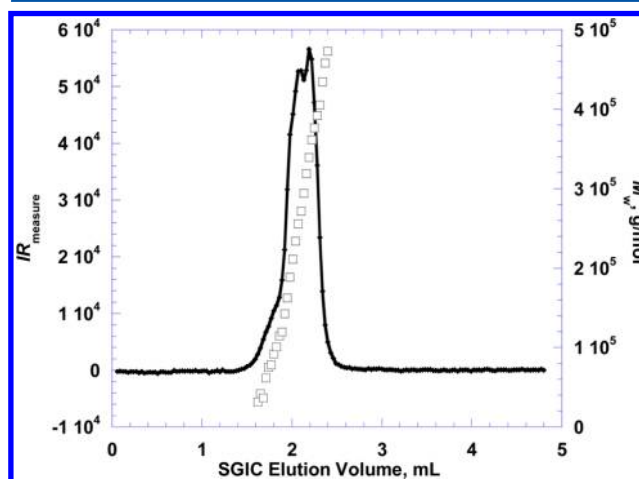
Figure 7. SGIC chromatogram of E/P-Broad shown with online M_w (open squares). The SGIC × SEC 2D chromatogram can be seen in the Supporting Information.

Early-eluting polymer chains have lower M_w compared to those eluting later. Figure 4 and 5 indicate that the propylene content of polymer chains decreases as elution volume increases. Combing online composition and M_w data, SGIC data suggest that the higher M_w polymer chains in E/P-Broad have lower propylene content. This conclusion is consistent with the SEC result shown in Figure 6, where the early eluting polymer chains have higher M_w but lower propylene contents.

Polymer chains are separated by hydrodynamic volume in SEC, giving rise to the semilog relationship between MW and elution volume.[2] The SEC chromatogram of E/P-Broad is shown in Figure 8 together with the online measured MW. The MW in logarithmic scale decreases linearly as elution volume increases. In SGIC separation, the MW shows a linear correlation to elution volume with the MW plotted on the linear scale (Figure 7). Note that the linear correlation is specific to the sample. Other kinds of correlations would be possible for polymers prepared under different conditions. In summary, SEC with online composition data measures the chemical composition as a function of logMW, whereas SGIC with online composition and MW data measures the MW as a function of chemical composition. Because separation in SEC is by logMW, its ability to discriminate polymer chains of different compositions is limited to the situation when there is correlation between MW and chemical composition. Even when there is a molecular weight–composition correlation, the detection of chemical composition heterogeneities is less sensitive in SEC compared to that in SGIC. This is why the absolute $\Delta P_{quantile}$ values are higher in SGIC experiment than those in SEC experiments.
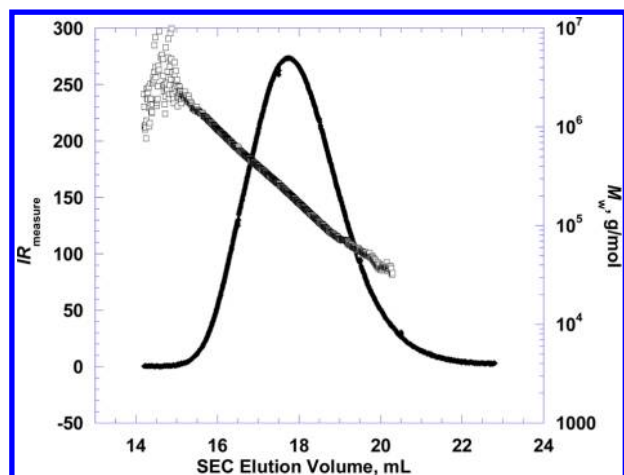
Figure 8. SEC chromatogram of E/P-Broad shown with the online MW.

CONCLUSIONS

This report documents the online chemical composition and MW analysis of ethylene−propylene copolymers after SGIC separation. A metric, $\Delta P_{quantile}$, was derived from online concentration and chemical composition. This metric was shown to be independent of gradient conditions used in separations, serving as the evidence to obtain absolute CCD from simultaneous measurement of composition and concentration after polymer separation.

Simultaneous measurement of MW and chemical composition after SGIC separation allows studying the relationship between MW and chemical composition. For the studied samples, the relationship is qualitatively consistent with that measured by SEC with online composition data, which gives chemical composition as a function of logMW. It is, however, important to know that the separation mechanism plays a critical role in studying MW and chemical composition heterogeneities in copolymer. A separation only based on chemical composition should be used to obtain CCD. Unfortunately, current separation methods for chemical composition, such as SGIC and TGIC, not only separate copolymers by chemical composition but are also affected by MW and chain architecture. The ability to measure MW online after SGIC separation would allow us to study the impact of MW in the separations and give us the opportunity to obtain information about architecture of polymer chains.

ASSOCIATED CONTENT

Ⓢ Supporting Information

SGIC × SEC 2D chromatogram of E/P-Broad. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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REFERENCES

(1) Calhoun, A.; Peakcock, A. J. *Polymer Chemistry: Properties and Applications*; Hanser Gardner: Munich, 2006.

(2) Striegel, A.; Yau, W. W.; Kirkland, J. J.; Bly, D. D. *Modern Size-Exclusion Liquid Chromatography: Practice of Gel Permeation and Gel Filtration Chromatography*, 2nd ed.; John Wiley & Sons: Hoboken, NJ, 2009.

(3) *Handbook of Size Exclusion Chromatography and Related Techniques*, 2nd ed.; Wu, C. S., Ed.; Marcel Dekker: New York, 2004.

(4) Brun, Y. *J. Liq. Chromatogr. Relat. Technol.* **1999**, *22*, 3027.

(5) Brun, Y. *J. Liq. Chromatogr. Relat. Technol.* **1999**, *22*, 3067.

(6) Pasch, H.; Trathnigg, B. *HPLC of Polymers*; Springer: New York, 1999.

(7) Ryu, J.; Chang, T. Y. *Anal. Chem.* **2005**, *77*, 6347.

(8) Cong, R. J.; deGroot, W.; Parrott, A.; Yau, W.; Hazlitt, L.; Brown, R.; Miller, M.; Zhou, Z. *Macromolecules* **2011**, *44*, 3062.

(9) Brun, Y.; Foster, P. *J. Sep. Sci.* **2010**, *33*, 3501.

(10) Park, I.; Park, S.; Cho, D. Y.; Chang, T. Y.; Kim, E.; Lee, K. Y.; Kim, Y. J. *Macromolecules* **2003**, *36*, 8539.

(11) Pasch, H.; Hiller, W. *Macromolecules* **1996**, *29*, 6556.

(12) Hiller, W.; Hehn, M.; Hofe, T.; Oleschko, K.; Montag, P. *J. Chromatogr. A* **2012**, *1240*, 77.

(13) Hiller, W.; Pasch, H.; Macko, T.; Hofmann, M.; Ganz, J.; Spraul, M.; Braumann, U.; Streck, R.; Mason, J.; Van Damme, F. *J. Magn. Reson.* **2006**, *183*, 290.

(14) Kramer, I.; Hiller, W.; Pasch, H. *Macromol. Chem. Phys.* **2000**, *201*, 1662.

(15) Hiller, W.; Hehn, M.; Sinha, P.; Raust, J. A.; Pasch, H. *Macromolecules* **2012**, *45*, 7740.

(16) Kok, S. J.; Wold, C. A.; Hankemeier, T.; Schoenmakers, P. J. *J. Chromatogr. A* **2003**, *1017*, 83.

(17) Tribe, K.; Saunders, G.; Meissner, R. *Macromol. Symp.* **2006**, *236*, 228.

(18) Kok, S. J.; Arentsen, N. C.; Cools, P.; Hankemeier, T.; Schoenmakers, P. J. *J. Chromatogr. A* **2002**, *948*, 257.

(19) Adrian, J.; Esser, E.; Hellmann, G.; Pasch, H. *Polymer* **2000**, *41*, 2439.

(20) Kuligowski, J.; Quintas, G.; Tauler, R.; Lendl, B.; de la Guardia, M. *Anal. Chem.* **2011**, *83*, 4855.

(21) Kuligowski, J.; Carrion, D.; Quintas, G.; Garrigues, S.; de la Guardia, M. *J. Chromatogr. A* **2010**, *1217*, 6733.

(22) Cheng, G. L.; Cullen, J.; Wu, C. S. *J. Chromatogr. A* **2011**, *1218*, 237.

(23) Albrecht, A.; Brull, R.; Macko, T.; Pasch, H. *Macromolecules* **2007**, *40*, 5545.

(24) Macko, T.; Brull, R.; Wang, Y. M.; Coto, B.; Suarez, I. *J. Appl. Polym. Sci.* **2011**, *122*, 3211.

(25) Cheruthazhekatt, S.; Harding, G. W.; Pasch, H. *J. Chromatogr. A* **2013**, *1286*, 69.

(26) Lee, D.; Miller, M. D.; Meunier, D. M.; Lyons, J. W.; Bonner, J. M.; Pell, R. J.; Shan, C. L. P.; Huang, T. *J. Chromatogr. A* **2011**, *1218*, 7173.

(27) Ortin, A.; Lopez, E.; Monrabal, B.; Torres-Lapasio, J. R.; Garcia-Alvarez-Coque, M. C. *J. Chromatogr. A* **2012**, *1257*, 66.

(28) Ortin, A.; Monrabal, B.; Montesinos, J.; del Hierro, P. *Macromol. Symp.* **2009**, *282*, 65.

(29) Qiu, X. H.; Zhou, Z.; Gobbi, G.; Redwine, O. D. *Anal. Chem.* **2009**, *81*, 8585.

(30) Roy, A.; Miller, M. D.; Meunier, D. M.; Degroot, A. W.; Winniford, W. L.; Van Damme, F. A.; Pell, R. J.; Lyons, J. W. *Macromolecules* **2010**, *43*, 3710.

(31) van der Horst, A.; Schoenmakers, P. J. *J. Chromatogr. A* **2003**, *1000*, 693.

(32) Li Pi Shan, C.; Miller, M.; Lee, D.; Zhou, Z. *Macromol. Symp.* **2012**, *312*, 1.

(33) Mekap, D.; Macko, T.; Brull, R.; Cong, R. J.; deGroot, W.; Parrott, A.; Yau, W. *Macromol. Chem. Phys.* **2014**, *215*, 314.

(34) *Polymer Handbook*, 4th ed.; Brandrup, J., Immergut, E. H., Grulke, E. A., Eds.; Wiley-Interscience: New York, 1999.

(35) Medrano, R.; Laguna, M. T. R.; Saiz, E.; Tarazona, M. P. *Phys. Chem. Chem. Phys.* **2003**, *5*, 151.