

# Separation of Polyolefins Based on Comonomer Content Using High-Temperature Gradient Adsorption Liquid Chromatography with a Graphitic Carbon Column

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**ABSTRACT:** This report describes the application of a recently developed polyolefin characterization tool based upon gradient adsorption high-temperature liquid chromatography (HT-LC) using a graphitic carbon stationary phase to polyolefin homopolymer and previously unreported copolymer systems. Polyolefin-based materials find utility in a broad range of applications and are differentiated by parameters such as molecular weight and comonomer content. Polymer comonomer distribution is commonly determined by crystallinity-based separations (ATREF, CRYSTAF). These techniques, however, are time consuming. In addition, some semicrystalline polymers undergo cocrystallization, impacting the techniques' universal utility. Adsorption-based HT-LC can ideally overcome the limitations of crystallinity-based separations,

shedding new light on the composition of randomly-polymerized polyolefins. In this report the basic separation capability of the adsorption HT-LC technique, using a graphitic carbon column, is demonstrated for poly(ethylene-co-octene) and poly(ethylene-co-propylene) systems and compared with select precipitation/redissolution HT-LC and ATREF results. Select results in this paper are also compared and contrasted to other recent publications on similar separations of polyolefins. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 123: 1238–1244, 2012

**Key words:** polyolefins; chromatography; copolymers; high performance liquid chromatography; separation of polymers

## INTRODUCTION AND BACKGROUND

Polyolefin polymers, i.e., polyethylenes (PE) and polypropylenes (PP), are commercially important materials considering their wide range of application as well as the sheer volume of their global production. Use of  $\alpha$ -olefins as comonomers with ethylene results in the presence of short-chain branches and the way they are arranged within the polyolefin backbone is known as the short-chain branching distribution (SCBD). The combination of the length, amount, and distribution of these branches among the polymer chains strongly influences the performance properties of the materials and all three are of utmost interest. As a very basic example, consider linear low density PE (LLDPE). LLDPE can be made from ethylene and 1-octene using either a Ziegler-Natta (Z-N) catalyst system or a more recently developed metallocene catalyst system. In these

cases, the  $\alpha$ -olefin species and octene content could be identical, but the overall chain-to-chain distribution of comonomer could be very different.

One of the most common ways to investigate the comonomer content of polyolefins is to apply a dilute solution crystallinity-based method such as analytical temperature rising elution fractionation (ATREF)<sup>1,2</sup> or crystallization analysis fractionation (CRYSTAF).<sup>3</sup> The basic theory behind crystallinity-based techniques has been reported elsewhere,<sup>4–6</sup> but put simply the dissolution temperature of semicrystalline polymer chains is related to the molar fraction of the crystallizing repeat unit as well as the comonomer distribution. For example, higher amounts of octene in a randomly polymerized poly(ethylene-co-octene) (EO) polymer chain results in lower dissolution temperatures.

Crystallization-based techniques present several challenges. The first and foremost difficulty has to do with the innate mechanism of the separation. Crystallinity-based techniques can only obtain chemical composition information if the polymer actually crystallizes. Amorphous material is not easily characterized. In some applications, the entire polyolefin polymer is amorphous and crystallization-based techniques have severely limited applicability.

Additional Supporting Information may be found in the online version of this article.

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Another drawback of this technique is the time involved to execute the experiment. There are steps in which the system is cooled and then subsequently heated. Ideally, the rate of temperature change is slow to maximize the onion-peel-like layering of polymer as it deposits onto the packing material (ATREF) or onto suspended crystallized nuclei (CRYSTAF). Otherwise, the quality of the separation markedly decreases. An ATREF experiment conducted in an optimal manner can take several hours - nonideal when throughput is concerned. However, the recently developed crystallization elution fractionation (CEF) technique,<sup>7</sup> combining some of the attributes of ATREF and CRYSTAF, has drastically reduced run times down to under an hour while obtaining the same chemical composition distribution information. CEF does not overcome the need for a crystallization step to take place, however, as it is still a crystallization-based technique.

Cocrystallization also hampers applications of ATREF to some polyolefin systems.<sup>8</sup> This phenomenon occurs when polymer chains of similar crystallizability are chemically compatible and can crystallize together. This is generally observed as lower crystallinity material eluting with higher crystallinity material, giving a potentially false impression of the composition of a polymer. The occurrence of cocrystallization would clearly impact the quantitative ability of techniques like ATREF, CRYSTAF, and CEF. Retaining the powerful chemical composition distribution information provided by the crystallization techniques, but without the influence of cocrystallization, would be a marked improvement in polyolefin characterization.

One potential way to overcome the issues of lack of crystallinity, long analysis time, and cocrystallization is to employ high temperature liquid chromatography (HT-LC). HT-LC offers several advantages over the traditional crystallization-based techniques. By using micron-sized particles packed into small columns, both high efficiencies and short analysis times can be realized. Separations are realized by selective interactions of the solute with a stationary phase, where interactions are transient - there is no slow kinetic solubilization of crystallized polymer. This enables the possibility of very rapid separations.

HT-LC separations of nonpolyolefin polymers have also been performed in an adsorption (or interaction) mode using a gradient. Striegel demonstrates this concept in his report on the use of solvent gradient normal phase liquid chromatography to determine the vinyl alcohol functionality in poly(vinyl butyral).<sup>9</sup> Interestingly, Striegel takes advantage of a combination of sorption as well as precipitation/redissolution of the polymer during the gradient to affect a separation. Striegel also uses reference com-

position standards to build a calibration curve and then generate composition distribution moments.

Thermal gradient interaction chromatography (TGIC) is a form of adsorption chromatography where polymer separations are affected by a temperature gradient as opposed to the previously described solvent gradient.<sup>10-12</sup> Several examples of this technique exist in the literature for nonpolyolefin polymers, including separations of star-polystyrene (PS) by number of arms<sup>13</sup> as well as linear PS,<sup>13</sup> poly(2-vinylpyridine),<sup>14</sup> and polydisperse poly(vinyl chloride) by molecular weight.<sup>15</sup> Thermal gradients are of high potential value as they can occur under isocratic conditions, allowing the employment of universal or molecular weight-sensitive detection techniques such as refractive index, light scattering, or viscometry that are easily perturbed by changes in solvent properties.

Current explorations into the liquid chromatography of polyolefins have focused on the separation of blends of PE and PP using isothermal conditions both with and without solvent gradients. Macko et al. published the first isocratic chromatographic system that selectively removed PE or PP from a blend of both by employing zeolites as packing materials.<sup>16,17</sup> Perhaps most importantly, these systems elute random poly(ethylene-co-propylene) (EP) copolymers while retaining long-chain-branched and linear PE, affecting separation between homopolymer and copolymer. Heinz and Pasch reported a gradient separation of PE and PP using a precipitation/redissolution mechanism with a silica column.<sup>18</sup> This mechanism is likely pure precipitation/redissolution with limited interaction between the polymer analytes and the column. Finding a stationary phase that was capable of selective interactions with polyolefins would be a significant advance. With the inclusion of adsorptive effects, a host of interactions can drive retention, including: interactions between the stationary phase and the polymer chain segments, interactions between the mobile phase and the polymer chain segments, interactions between the mobile phase and the stationary phase, and the graft density of the stationary phase.

Such an advance was recently reported by Macko et al. in a pair of publications. They found that a liquid chromatography column made of graphitic carbon, the Hypercarb column, was capable of tacticity based separations of PP as well as compositional separations of poly(ethylene-co-hexene) (EH) as well as propene copolymerized with various alkenes.<sup>19,20</sup> However, when demonstrating the separation of EH copolymers, different tacticities of PP, and some of the poly(propylene-co-alkene) polymers, a nonretained break-through peak is observed. This is especially notable with isotactic polypropylene as well a 62 mol % hexane EH polymer. When polymer elutes

in a break-through peak, there is no way to determine any chemical composition distribution information, so this is nonideal.

This report presents composition-based separations of EO and EP by adsorption LC using a graphitic carbon column. This represents a fundamentally new advance in the field of polymer characterization of EO and EP, demonstrating high resolution architecture-based separations of randomly polymerized polyolefins in less than 30 min per analysis. Specifically, by employing graphitic carbon as a stationary phase, EO and EP polymers are both separated by comonomer content over the entire composition range, from 0 to 100 mol % comonomer. This is possible as the mechanism is not pure precipitation/redissolution, but in fact heavily influenced by selective adsorption with the stationary phase. Notably, this technique has also been leveraged to a 2D HT-LC/SEC technique by some of the same authors of this report.<sup>21</sup> To highlight this new advance, results using the silica column system designed by Heinz et al. are compared against new data generated using the graphitic carbon column.<sup>18</sup> Previous results with a graphitic carbon column from Macko et al. are also compared to the current work.<sup>19,20</sup>

## EXPERIMENTAL

### Materials

Ethylene Glycol Monobutyl Ether (EGMBE, spectrophotometric grade, >99.0%), 1-decanol (>99%), and 1,2,4-trichlorobenzene (TCB, ReagentPlus, >99%) were all used as received from  $\zeta$ -Aldrich (St. Louis, MO). Homopolymer polyethylene, isotactic polypropylene (iPP,  $M_w$  of 277,000 g/mol), and randomly polymerized EO and EP polymers were produced internally by the Dow Chemical Company and were characterized by <sup>13</sup>C NMR to obtain their average comonomer content where applicable. The melt flow rate of the EP copolymers was 2 g/10 min following ASTM D 1238 and weight-average molecular weights as well as polydispersity data for the EO copolymers are provided in Table I. Polymer molecular weight data was measured by size exclusion chromatography.

### Columns

The silica column discussed in this report is from Macherey-Nagel (Bethlehem, PA) and is described as a Nucleosil column with 300 Å pores, 5- $\mu$ m particles, and dimensions of 4.6  $\times$  250 mm<sup>2</sup>. The graphitic carbon column discussed in this report is from Thermo (Bethlehem, PA) and is described as a Hypercarb column with 250-Å pores, 5- $\mu$ m particles,

**TABLE I**  
Weight-Average Molecular Weight ( $M_w$ ) and Polydispersity of Ethylene Octene Random Copolymers

Mol% Octene	$M_w$ (g/mol)	Polydispersity
0	104,200	1.9
2.6	103,800	2.0
8.5	111,200	2.0
14.8	123,400	3.3
15.9	129,300	2.1
19.0	Not Available	Not Available
21.7	170,000	2.6
24.3	182,000	2.7
100	631700	3.8

and dimensions of 4.6  $\times$  100 mm<sup>2</sup>. Note that the both columns must be equipped with fittings capable of withstanding the high temperatures required for polyolefin separations.

### Instrumentation

The HT-LC system in this report consists of: a Waters GPCV 2000 acting as a column oven and heated autosampler, an Agilent 1200 binary pump as a gradient pump, a Waters In-Line Degasser AF to degas solvents, and a Polymer Labs ELS 1000 evaporative light scattering detector (ELSD) as a detector. EZChrom version 3.2.1 with an SS420x A/D converter is used to control the pump and collect data from the ELSD.

### Separation conditions

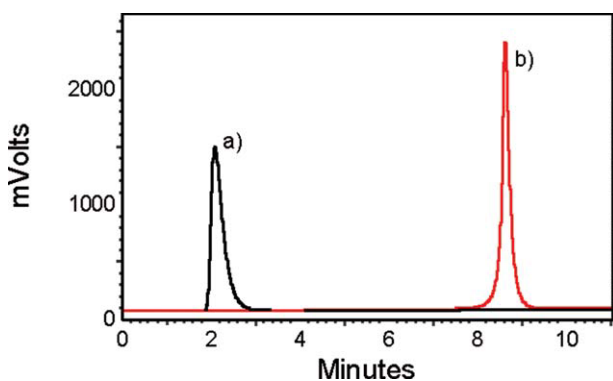
The HT-LC separation conditions for this report are as follows unless stated otherwise. The polymer was dissolved in 1-decanol at a concentration of 2 mg/mL. The autosampler and injector temperatures on the Waters GPCV 2000 were 160°C while the column oven temperature was 140°C. The injection size was 10  $\mu$ L and the LC pump flow rate is a constant 1 mL/min. The ELSD conditions were 1.4 L/min for N<sub>2</sub> gas flow, 200°C for the detector nebulizer and 250°C for the detector evaporator.

The solvent gradient begins with a 3 min hold of 100% EGMBE, followed by a 15-min linear gradient to 100% TCB, followed by a 6 min hold of 100% TCB. This is sufficient to elute homopolymer PE, the most retained polymer in these experiments. Following the TCB hold a 3-min gradient back to 100% EGMBE is used and the column is re-equilibrated for the next injection. The entire cycle takes less than 30 min.

## RESULTS AND DISCUSSION

### Initial investigation of adsorptive phenomenon

Initial testing with the graphitic carbon column focused purely on iPP, as previously conducted



**Figure 1** Overlay of iPP eluted on an (a) silica column and a (b) graphitic carbon column using conditions from the experimental section. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

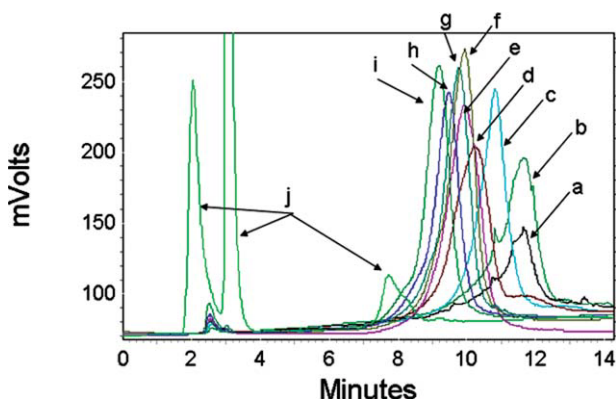
precipitation/redissolution HT-LC experiments eluted this material in SEC mode with no retention from precipitation or adsorption. Employing the instrument and gradient conditions from the experimental section of the paper and a graphitic carbon column, an injection of iPP resulted in a strong retentive interaction of the polymer with the stationary phase where it eluted after eight minutes instead of in the break-through. An overlay of iPP separated using a silica column and a graphitic carbon column under the same gradient conditions is given below in Figure 1. As an approximation, with the silica column iPP eluted when the mobile phase was 100% EGMBE/0% TCB at the detector while with the graphitic carbon column iPP eluted when the mobile phase was about 68% EGMBE/32% TCB at the detector. This behavior is different from what was observed by Macko et al., where they report that iPP is unretained.<sup>19,20</sup> The use of EGMBE (instead of 1-

decanol used by Macko) as the weak eluent in these experiments coupled with the lower experiment temperature (140°C compared to 160°C used by Macko) may contribute to additional retention in the current experiments.

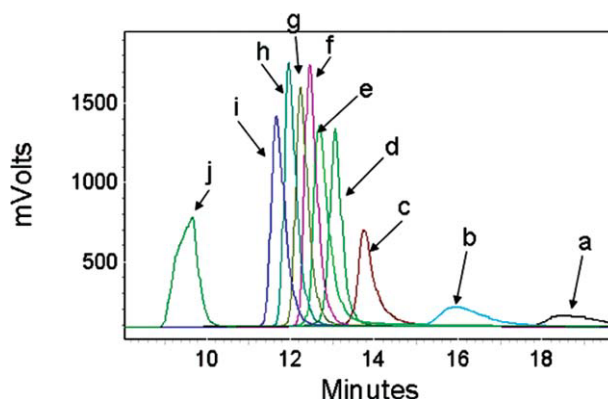
### Separations of poly(ethylene-co-octene) copolymers

To further probe the adsorptive properties of the graphitic carbon columns with respect to polyolefins, an extended range of randomly polymerized EO materials containing 0–27.7 mol % octene were acquired and tested on both the silica and graphitic carbon columns. A polyoctene polymer was also tested. Figures 2 and 3 illustrate the improved ability of the graphitic carbon column to separate random EO copolymers. The overlaid chromatograms in Figure 2 were obtained using a silica column for separation while the overlaid chromatograms in Figure 3 were obtained using a graphitic carbon column. The experimental conditions, except for the choice of columns, are the same for the data displayed in both Figures. The individual peaks are identified according to their mole percent octene with the remainder being ethylene.

Illustrated in Figure 2, the 0 to 27.7 mol % octene EO samples separated using a silica column elute over a range of about 5 min. There is also significant overlap between many of the polymers. For example, consider the 14.8 and 27.7 mol % octene samples. The 14.8 mol % octene material elutes between retention times of about 7.5 min to 11 min while the 27.7 mol % octene sample elutes over nearly the same range. There is notable overlap. The polyoctene sample elutes at the break-through in SEC mode (between 2 and 3.5 min) and in a later peak at



**Figure 2** Overlay of chromatograms of EO copolymers composed of: (a) 0, (b) 2.6, (c) 8.5, (d) 14.8, (e) 15.9, (f) 19.0, (g) 21.7, (h) 24.3, (i) 27.7, (j) 100 mol % octene separated on a silica column using conditions from the experimental section. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]



**Figure 3** Overlay of chromatograms of EO copolymers composed of: (a) 0, (b) 2.6, (c) 8.5, (d) 14.8, (e) 15.9, (f) 19.0, (g) 21.7, (h) 24.3, (i) 27.7, (j) 100 mol % octene separated on a graphitic carbon column using conditions from the experimental section. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

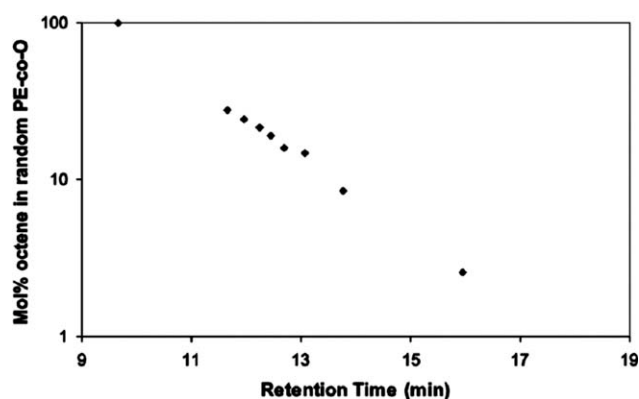


about 8 min. This suggests that the portion of the polyoctene sample eluting as break-through was soluble in the nonsolvent, EGMBE, while another portion elutes at 8 min as the fraction of solvent, TCB, increases. This behavior complicates interpretation and limits the applicability of the pure precipitation/redissolution technique as all material that coelutes unretained in SEC mode will be structurally indistinguishable.

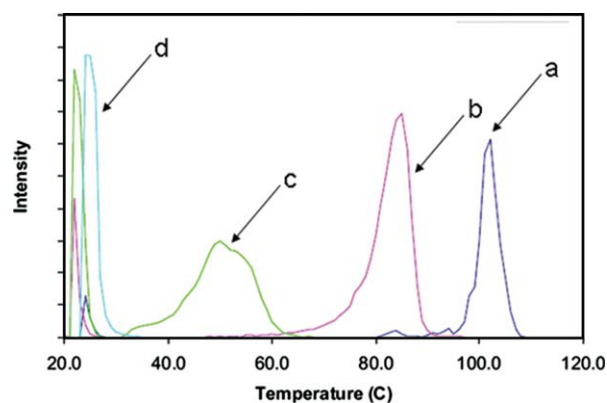
In Figure 3, the separation is performed with the same samples and conditions on a graphitic carbon column. Employing the graphitic stationary phase leads to a significantly enhanced separation as the polymers elute as single peaks that are much narrower than the ones shown in Figure 2. Again, consider the 14.8 and 27.7 mol % octene samples. The 14.8 mol % octene sample elutes over a range of about 12.5 to about 14 min while the 27.7 mol % octene sample elutes from about 11 to 12.75 min. There is nearly baseline separation between these two samples, indicative of the novel, improved separation using a graphitic stationary phase. Additionally, the polyoctene sample is adsorptively retained and now elutes as a single, although non-Gaussian-shaped, peak.

Another advantage of the graphitic carbon system is that no polymer elutes in the break-through region. This allows compositional information to be extracted from the entire range of polymer compositions, from polyoctene to PE. This is a benefit of this currently reported system compared to the system reported previously where EH polymers with high mol % H eluted partially in the break-through region.<sup>20</sup>

Building on the concept of extracting compositional information from the entire range of copolymer compositions, a calibration curve can be constructed using the known composition of the randomly polymerized EO materials and their retention times at maximum peak height. Such a calibration curve is shown in Figure 4. Note that the func-



**Figure 4** Calibration curve based upon the data in Figure 3. The  $y$ -axis is plotted in logarithmic scale.



**Figure 5** Overlay of IR data from TREF separations of a series of random EO polymers: (a) 0, (b) 2.6, (c) 8.5, (d) 14.8 mol % octene showing the lack of separation above a certain comonomer content. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

tional relationship between octene content and retention time appears to be log-linear. Further studies will explore the full range of octene in EO polymers, covering the region between 30 and 100 mol % octene, as well as investigating the effect of molecular weight on retention.

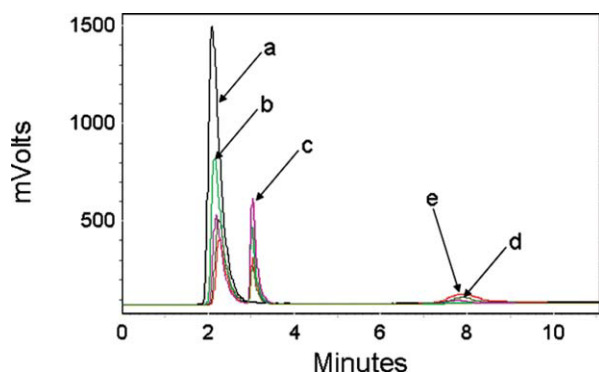
Using the same basic mathematical and statistical calculations employed in SEC, this calibration curve can be employed to facilitate an area normalized comonomer distribution plot (an apparent composition distribution) of a polymer as well as calculate statistical averages. This practice enables a high degree of differentiation among polymers of interest.

#### ATREF data of EO copolymers

Figure 5 shows how gradient HT-LC using a graphitic stationary phase can provide a significant and exceptional advantage over crystallinity-based techniques such as ATREF. Figure 5 is an overlay of the IR signal from the ATREF separations of 0, 2.6, 8.5, and 14.8 mol % octene EO samples. Though there is ample differentiation between the 0, 2.6, and 8.5 mol % octene samples by the ATREF technique, the 14.8 mol % octene copolymer has no crystallinity and therefore elutes in a single purge peak. This same phenomenon would hold true for higher fractions of octene in the polymer as well. HT-LC with a graphitic stationary phase possesses the capability to easily separate and differentiate these noncrystalline EO polymers. Doing so with ATREF or CRYSTAF would be more challenging.

#### Separations of poly(ethylene-co-propylene) copolymers

Figures 6 and 7 illustrate that the graphitic carbon stationary phase enables a HT-LC-based characterization methodology for another copolymer of

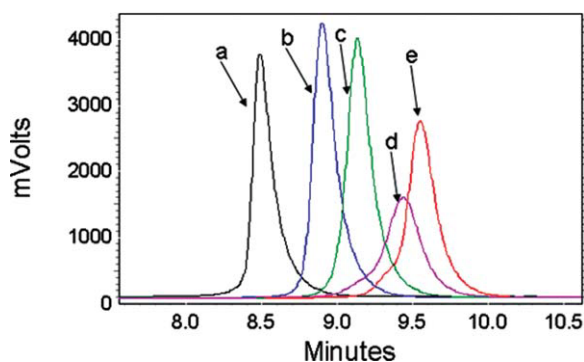


**Figure 6** Overlay of chromatograms of EP copolymers: (a) 0, (b) 6.2, (c) 11.5, (d) 16.0, and (e) 18.8 mol % C2 separated on a silica column using conditions from the experimental section. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

industrial interest, randomly polymerized EP. The conditions for these separations are given in the experimental section of this paper.

Figure 6 shows an overlay of chromatograms of randomly polymerized EP polymers ranging from 0 to about 19 mol % C2 (or ethylene) separated on a silica column. With this column, there are two main regions of interest. The first region is between 2 and 3 min where material soluble in EGMBE elutes as break-through in SEC mode with two peaks representing excluded polymer at about 2 min and polymer eluted by the slug of injection solvent (1-decanol) at about 3 min. In this domain, there is no resolution among any of the polymers despite a subtle trend where the peak at about 2 min elutes at slightly longer retention times with higher C2 mol %.

The second region of interest in Figure 6 is the broad peak at about 8 min. This peak represents ma-



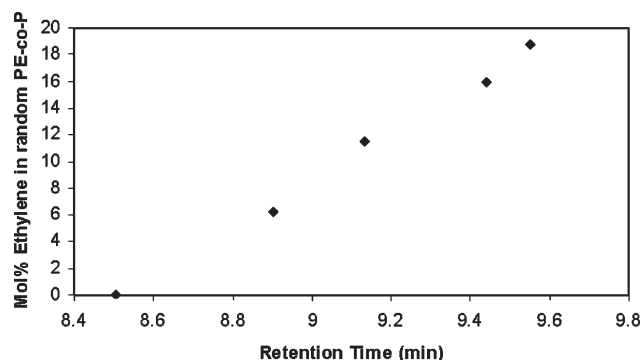
**Figure 7** Overlay of chromatograms of EP copolymers: (a) 0, (b) 6.2, (c) 11.5, (d) 16.0, and (e) 18.8 mol % C2 separated on a graphitic carbon column using conditions from the experimental section. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

terial that precipitates in EGMBE but then elutes as the TCB fraction of the mobile phase is increased. Again, there is no resolution among any of the polymers as a function of C2 mol %, but the peak tends to grow larger with increasing C2 mol %. This is reasonable as greater amounts of ethylene in the polymers will raise their UCST (Upper Critical Solution Temperature), making them less soluble in EGMBE, increasing the amount of material that precipitates and must then be redissolved by increasing the concentration of TCB in the mobile phase. As the materials increase in C2 mol % to 100%, this peak will likely elute at about 11–12 min, as shown by the pure PE sample in Figure 2.

The overlay in Figure 7 shows that the graphitic stationary phase enables differentiation as a function of mol % C2 that did not exist with the silica column. Now, the EP copolymers are uniquely separated as a function of mol % C2 with no breakthrough. There is near-baseline resolution between 0 and 11.5 mol % C2 and even the 11.5 and 18.8 mol % C2 samples are significantly resolved. Again, a calibration curve can be constructed from these data to obtain a composition distribution of C2 in EP. This is shown below in Figure 8. Note that with these EP polymers the relationship between ethylene content and retention time is qualitatively linear. This linearity may not hold when the full range of ethylene content in the polymers is evaluated.

#### Hypothesis on the separation mechanism of the graphitic stationary phase

There are select literature reports that may lend insight into what may be driving the adsorptive separation. In a book chapter by Knox and Ross (it should be noted that Knox was part of the group that initially developed the graphitic carbon columns),<sup>22</sup> they discuss numerous aspects of graphitic stationary phases. Topics covered include: performance, structure, retention studies, and retention



**Figure 8** Calibration curve based upon the data in Figure 7.

mechanism. Knox and Ross state that there are four drivers that affect retention by graphite in LC:

1. Eluant-analyte interactions that lower retention.
2. Hydrophobic eluant-analyte repulsions that encourage retention.
3. London-type dispersive interactions between the graphite surface and the analyte that promote retention.
4. Charge induced interactions of the analyte which encourage retention of polar compounds.

Of these four factors, the first and second will certainly apply. "Eluant-analyte interactions that lower retention" are exactly what happen as the solvent quality increases to the point that the polymer elutes. "Hydrophobic eluant-analyte repulsions" may not be explicitly hydrophobic in the separation system described in this report, but the solvent quality is poor enough at the beginning of the separation that the polymer chains prefer association with the graphitic carbon stationary phase. The "charge induced interactions" described in the fourth item are likely not a contributor considering the polymer chains are principally carbon and hydrogen and thus bonds among them are nonpolar. The interaction that most likely drives retention in this system is the third item: "London-type dispersive interactions between the graphite surface and the analyte."

The proposed mechanism of this separation involves assuming that the polymer is interacting with the molecularly flat planes of graphite. Continuous ethylene chains are better capable of interacting with the graphite surface. Each  $\alpha$ -olefin monomer unit creates a branch that would sterically hinder this interaction. Considering randomly polymerized EO and EP polymers, lower amounts of comonomer suggests that there are longer continuous ethylene segments. This would make homopolymer PE the most retained while poly( $\alpha$ -olefin) would be the least retained. However, even polyoctene and polypropylene adsorb to the graphite, suggesting that the carbon-carbon bond backbone of the polymer chains itself significantly contributes to retention. This mechanistic description is in line with Macko et al.<sup>20</sup>

## CONCLUSIONS

This article documents the gradient adsorption HT-LC separation of randomly polymerized EO and EP polymers as a function of comonomer content. This new method exhibits improved separation resolution compared with pure precipitation/redissolution separations using silica columns. These new separations enable studies of noncrystalline polyolefins that are

difficult to execute with crystallization-based techniques such as ATREF. In addition, this improved separation range allows for the construction of composition calibration curves for both EO and EP polymers. The range of compositions that can be analyzed via an adsorption mechanism spans from 0 to 100 mol percent octene for EO copolymers, and it spans from 0 to 100 mol percent propylene for EP copolymers. Being able to elute all of these polymers via an adsorption mechanism, without breakthrough issues, avoids problems of ambiguous composition assignment for components that elute in the break-through region, and quantitation problems for later eluting components than may have partially eluted in the break-through region. The mechanism of separation is speculated to be based on dispersive forces and interactions are driven by how the polymer chains (specifically continuous segments of PE) interface with the molecularly planar sheets of graphite.

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