Characterization of Ethylene Copolymers with Liquid Chromatography and Melt Rheology Methods

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Summary: Melt rheology and polymer chromatography methods were applied to characterize molecular heterogeneities in products of free radical copolymerization of ethylene with methyl acrylate and vinyl acetate comonomers performed in continuously stirred tank and tubular reactors. We found that the ethylene–vinyl acetate copolymers made in both reactors had similar linear viscoelastic properties typical to branched products of the high pressure process. But the ethylene–methyl acrylate copolymers obtained in the tubular reactor had unusually high melt viscosity at low shear rate and much lower onset of shear thinning despite the narrower molecular weight distribution and the lower overall amount of long-chain branches compare to their autoclave counterparts with similar average molecular weight and chemical composition. Using interaction polymer chromatography method called gradient elution at critical point of adsorption we found that ethylene-acrylate copolymers from the tubular reactor had very broad chemical composition distribution, which was consistent with a significant difference in reactivity ratios between ethylene and acrylate comonomers. Such chemical composition heterogeneity can be a reason for the observed unusual rheological properties of these copolymers.

Keywords: chemical heterogeneity; ethylene copolymer; liquid chromatography; melt rheology; tubular reactor

Introduction

Traditional high-pressure, free radical polymerization incorporating a polar monomer in a polyolefin chain, remains a valuable approach to produce low density polymers with high flexibility/low crystallinity in combination with a low melting point.[1] Such process can be performed in two different types of reactors, a continuously stirred tank reactor (CSTR, or autoclave) and a tubular reactor. In case of commercial polyethylene, it is well known that the products of these two processes differ in molecular weight distribution (MWD) and degree, structure and distribution of long-chain branches (LCB).[2] Differences in the mechanism of mixing and residence time distribution is believed to lead to the differences in molecular structure. While in a continuously stirred autoclave the polymer is usually produced at constant pressure, temperature and monomer conversion, in a tubular reactor, the temperature and the conversion usually increase between the beginning and the end of the reaction zone along the tube. This may produce a noticeable difference in molecular structure between polymer chains, i.e., introduce a chemical heterogeneity of the polymer.[3] A well-known example is a distribution of LCB in the products of autoclave and tubular reactors. In the autoclave process, branching points are usually evenly distributed along the polymer chain irrespective of its molecular weight, resulting in tree-like random LCB structure. In the tubular reactor, the higher molecular weight macromolecules produced in the

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reactor zone with higher temperature and conversion have a higher degree of long-chain branching, often with comb-like structure, compared with their tree-like lower molecular weight counterparts produced in the beginning of the reaction zone.[4–6] An extensive analysis of tubular LDPE with multidetector size exclusion chromatography (SEC) revealed that the highest ($>10^6$) molecular weight chains may even have a intramolecular branching heterogeneity, when the periphery of the molecule have much higher degree of LCB than its center part shielded against abstraction of hydrogen by a radical.[6]

The inclusion of a polar monomer into polyethylene chains in free radical copolymerization may introduce additional types of molecular heterogeneity related to the distributions of different monomer units within the same macromolecule or between different macromolecules. Thus, depending on the reactivity ratios of the comonomers, a higher conversion and a noticeable difference in the reaction conditions in different parts of the reaction zone in the tubular reactor can produce heterogeneity in the chemical composition of the copolymer. This involves a variance in chemical composition either between different polymer chains, resulting in a broad chemical composition distribution (CCD), or within the same macromolecule, e.g., an ethylene-rich backbone with comonomer-rich branches.[7]

Molecular heterogeneities can significantly affect the end-use properties of the polymer. The introduction of acrylate comonomer in the polyethylene chains makes polymer softer and more polar, which improves its flexibility, adhesion and compatibility with other, especially polar, polymers. In case of compositionally homogeneous autoclave products, the melting point decreases linearly with the acrylate content, which makes the resin stickier and somewhat more dificult to process. In contrast, in the tubular reactor, the combination of higher monomer conversion and difference in the reactivity ratios of the comonomers may lead to a broader chemical composition distribution such that the melting point of the resin remains practically unchanged despite the high content of acrylate. The higher melting point makes the tubular resins easier to handle and process. Other benefits of a broad CCD may include improved stress crack resistance, higher melt strength and extensional thickening.[1,3] But the same properties can also be attributed to the effect of long chain branching, as tubular products are known to have very high-MW fractions with a significant amount of LCB.[8–10] A possible way to clarify which molecular heterogeneity in the ethylene copolymers is responsible for the aforementioned polymer properties is to combine rheological measurements with polymer chromatography methods. Rheological measurements are very sensitive to even subtle differences in molecular structure. However, when several different types of structural variations occur simultaneously, it can be difficult to determine the nature of the structure variations based solely on rheological data. The combination of rheological measurements with direct measurement of the molecular heterogeneities using chromatography methods provides a powerful tool for probing molecular structure.[7,11–13]

In this study, the rheological and chromatographic properties of resins prepared using high-pressure free radical ethylene copolymerization performed in both stirred tank and tubular reactors are investigated. Two different types of copolymers were selected for comparison: ethylene-vinyl acetate (EVA) and ethylene-methyl acrylate (EMA) resins. In the first case, close reactivity ratios[14] of the comonomers suggest that the chemical composition distribution of the EVA copolymers should be similar for autoclave and tubular products with the same average composition, so that any differences in rheological behavior are caused by molecular weight and/or branching distributions. In case of ethylene-methyl acrylate copolymers, a significant difference in reactivity ratios[14] allows for the possibility of a broad chemical composition distribution of the tubular products, which may produce an additional effect on the rheological properties.

We used oscillatory rheometry to analyze the linear viscoelastic properties of the copolymers. Size exclusion chromatography was used to measure molecular weight and branching distributions, while interaction polymer chromatography (IPC) was utilized to analyze a possible chemical composition heterogeneity. On-line FTIR spectroscopy was also applied in both chromatographic modes to analyse chemical composition of the seaparted fractions.

Experimental Part

Materials

The ethylene-methyl acrylate copolymers investigated in this study are listed in Table 1, and the ethylene-vinyl acetate copolymers are listed in Table 2. Several additional copolymers with different compositions have been made for the chromatographic experiments using tubular and autoclave processes.

Melt Rheology

The linear viscoelastic properties were measured in accordance with ASTM D 4440[15] using a ARES L32 controlled-stress rheometer from TA Instruments (New Castle, DE) equipped with a forced convection oven (FCO) and 25 mm parallel plates with smooth surfaces. Plate temperature was calibrated using a disk made of nylon with a thermocouple embedded in the middle. Discs with a diameter of 25 mm and a thickness of 1 mm were prepared from pellets by compression molding under vacuum and a temperature of 180 °C using a Dake Model 944605 laboratory press.

The linear viscoelastic properties were measured at 190 °C. A molded disc was inserted between the parallel plates at room temperature and conditioned at the test temperature for 4 minutes before starting the test. After 2 minutes of conditioning, the FCO was opened, the edges of the sample were carefully trimmed, and the gap adjusted to 1 mm. A frequency sweep was performed between 0.05 and 100 rad/s using a strain of 1%. The measurement was performed in duplicate with a fresh sample loading each time.

Size Exclusion Chromatography

All SEC experiments were performed on integrated triple detection system Alliance GPCV 2000™ from Waters Corporation (Milford, MA) equipped with on-line differential refractometer, differential capillary viscometer and additionally installed two-angle light scattering photometer PD 2040™ from Precision Detectors (now Varian Inc, Walnut Creek, CA), at 135 °C. Three mix-bed styrene-divinyl benzene columns HT806™ from Shodex (Japan) were used for separation in 1,2,4-trichlorobenzene (J.T. Baker, Phillipsburg, NJ) stabilized with 0.025% 2,6-di-tert-butyl-4-methylphenol from Aldrich (Milwaukee, WI). Data reduction including MWD and branching calculation was performed without any standards for column calibration using Empower™ version 2 chromatography manager from Waters. The furher details regarding the triple detector SEC data processing including the incorporated customized algorithms are described elsewhere.[16]

Table 1.
Average chemical composition and melt flow index (MI) of EMA copolymers.

Resin	Abbreviation	Reactor	MA (% w/w)	MI @190 °C (g/10 min)
Elvaloy® AC1125	T-EMA-1	Tube	25	0.6
Elvaloy® AC1224	T-EMA-2	Tube	24	2
Elvaloy® AC1330	T-EMA-3	Tube	30	3
Elvaloy® AC1335	T-EMA-4	Tube	35	3
Optema™ TC113	A-EMA-1	CSTR	23.5	1
Optema™ TC221	A-EMA-2	CSTR	27	5

Table 2.
Average chemical composition and melt flow index (MI) of EVA copolymers.

Resin	Abbreviation	Reactor	VA (% w/w)	MI @190 °C (g/10 min)
Elvax® 670A	T-EVA-1	Tube	12	0.3
Elvax® 360A	T-EVA-2	Tube	25	2
Elvax® 265A	T-EVA-3	Tube	28	3
Elvax® 670	A-EVA-1	CSTR	12	0.3
Elvax® 360	A-EVA-2	CSTR	25	2
Elvax® 265	A-EVA-3	CSTR	28	3

Interaction Polymer Chromatography

Gradient separations of ethylene copolymers were performed on two different chromatography systems. System 1 is comprised of Alliance 2695™ Separation Module (Waters) with column and sample heaters and on-line evaporative light scattering detector (ELSD) PL-ELS 1000™ (Polymer Laboratories, Varian Inc, Church Stretton, England). The module provides a low-pressure quaternary gradient pumping system with lag volume 0.6 mL to the column inlet, on-line solvent degassing and automated sample injection. Nova-Pak™ Silica or C_{18} chromatographic columns (150×3.9 mm i.d.) from Waters were used for separations at system 1. Added LC-Transform™ interface model 600 from Lab Connections (now Leap Technologies, Carrboro, NC) allowed one to continuously deposit the separated fractions on germanium XY plate for the on-line FTIR analyses. The collected fractions were placed into transmission part of the FTIR spectrometer (Spectrum GX™ from Perkin Elmer, Shelton, CT), which provided the IR spectra with resolution 4 cm^{-1}, 16–32 scans per fraction. System 2 is a custom built integrated high temperature PL-GPEC system (Polymer Laboratories) equipped with high pressure binary gradient valve and capable to operate in both isocratic (SEC) and gradient (IPC) modes at temperature up to 130 °C. Special modification was made to minimize the lag volume of the system (<1 mL). This system containes two built-in detectors, ELSD 1000 and Knauer UV photometer, and has been also coupled with LC- Transform™ interface model 303 (Lab Connections) for on-line analyses of ethylene copolymers in high boiling solvents. Diamond Bond™ C_{18} 150×4.6 mm i.d. zirconia-based column from ZirChorm Separations (Anoka, MN) was used in system 2 at temperature 130 °C. All HPLC-grade solvents used in the IPC experiments (tetrahydrofurane, n-hexane, toluene, ethyl acetate, methanol, dimethylacetamide and cyclohexanone) were obtained from J. T. Baker and used without further purification.

Results and Discussion

Figure 1 shows plots of complex viscosity versus frequency for each material listed in Table 1 and Table 2. The plot on the left compares EVA copolymers of the same VA content and melt flow rate prepared in tubular and autoclave reactors. In general, the complex viscosities of the tubular and autoclave resins are very similar. At the same VA content, the viscosities of the tubular resin might be slightly lower than the complex viscosities of the corresponding autoclave resin, possibly due to small differences in molecular weight. The plot on the right compares the EMA copolymers. For these resins, the complex viscosities of the tubular and autoclave resins are very different. At comparable MA levels, the viscosities of the autoclave resins are much lower than those for the tubular resins. In addition, the tubular resins exhibit power-law like behavior over the entire range of measured frequencies whereas at the lower frequencies the autoclave resins are at or approaching the Newtonian plateau (terminal zone).

When comparing resins of different molecular weights, it can be difficult to separate the effects of molecular weight, molecular weight distribution (MWD), and

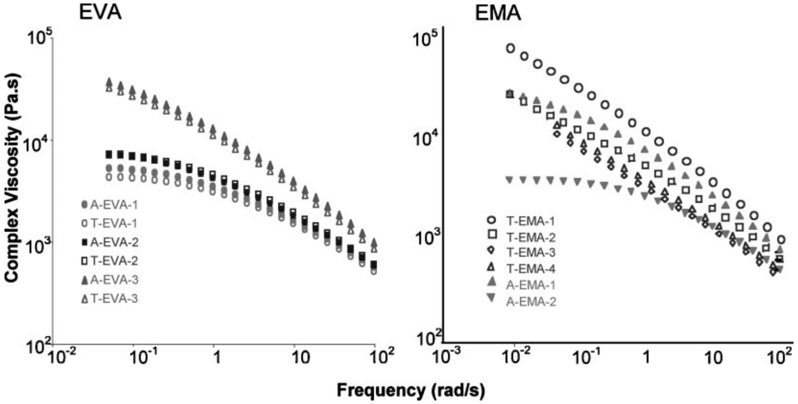

Figure 1.
Complex viscosity at 190 °C of EVA (left) and EMA (right) copolymers.

LCB using only plots of either G′ and G″ or complex viscosity versus frequency. Another way to use this data to compare the resins is a modified Cole-Cole plot, which is a plot of G′ versus G″.[17] Since G′ and G″ have similar dependency on temperature and molecular weight, a plot of G′ versus G″ is both temperature and molecular weight invariant. At low values of G″ (in the terminal zone), chemically similar materials should overlay irrespective of the molecular weight if there are no marked differences in MWD or LCB.[18] Cole-Cole plots for the EVA and EMA copolymers are shown in Figure 2. For the EVA resins, there does not appear to be any major differences between the autoclave and tubular resins. In contrast, for the EMA resins, there are large differences between the tubular and autoclave products. At a given value of G″, the elasticity (G′) of the autoclave resins is much lower than of the tubular resins. This suggests that when the reactivity ratios of the comonomers are comparable, as is the case for the EVA copolymers, the type of the reactor does not noticeably affect the microstructure of the polymer chains. However, when the reactivity ratios of the monomers are different, the higher monomer conversion in the tubular reactor gives rise to some additional structural heterogeneities, observed for the EMA copolymers.

A triple detector SEC method was used to determine if the differences between the tubular and the autoclave EMA

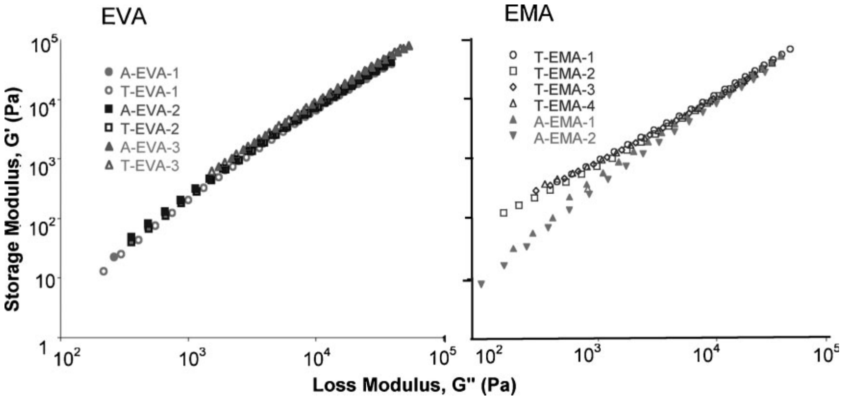

Figure 2.
Cole-Cole plots at 190 °C for EVA (left) and EMA (right) copolymers.

copolymers could be explained by a broader MWD or higher degree of LCB for the tubular resins. In this method, molecular weight and intrinsic viscosity for each data point (slice) are obtained directly using ratios of responses from respectively a light scattering photometer (measures excess Raleigh ratio, ΔR_θ, at scattering angle θ) or a capillary viscometer (specific viscosity, η_{sp}) to the response from a differential refractometer (refractive index change due to polymer in solution, Δn), and mass distribution of these properties – from the refractometer trace, without column calibration.[16]

An estimation of degree of branching is possible in the SEC experiments through its effect on the size of a macromolecule in dilute solution. A macromolecule's hydrodynamic volume (also known as viscometric volume) is proportional to the product of intrinsic viscosity by molecular weight, so that the ratio of intrinsic viscosity of branched and linear macromolecules with identical chemistry and the same molecular weight, called branching index g', can be used to estimate the reduction in size caused by branching.

Figure 3 shows SEC traces from two EMA copolymers with similar values of chemical composition and melt index. A significant response at lower retention time (high molecular weight shoulder) from all three detectors clearly points to a broader MWD, seen in Figure 4 for these two copolymers, and higher averall degree of LCB for the product of the autoclave process. This fact is also confirmed by the values of polydispersity and weight-average branching index calculated with the triple detection SEC and presented in Table 3. Hence, the unusual rheological behavior of tubular EMA copolymers cannot be explained by neither a broader polydispersity nor higher average degree of branching.

Previous studies have shown that polymers from tubular reactor may posses a noticeable amount of highly branched extremely high molecular weight fractions usually absent in the autoclave products.[6,11] These fractions can be seen as a small low retention time "bump" at a molecular weight elution profile obtained from the multidetector SEC for the EMA and even to a higher extent, for the EVA copolymers.[19] While the quantitation of such a structural heterogeneity from the SEC data is quite a challenging problem due to a significant local polydispersity and usually a very low refractometer response in the region of interest,[16] it can affect the rheological properties.[8,9,11] We can speculate that in the case of the tubular EVA copolymers, the effect of these highest molecular weight branched molecules can counterbalance the effects of higher polydispersity and higher amount of more moderate LCB in the autocalve products,

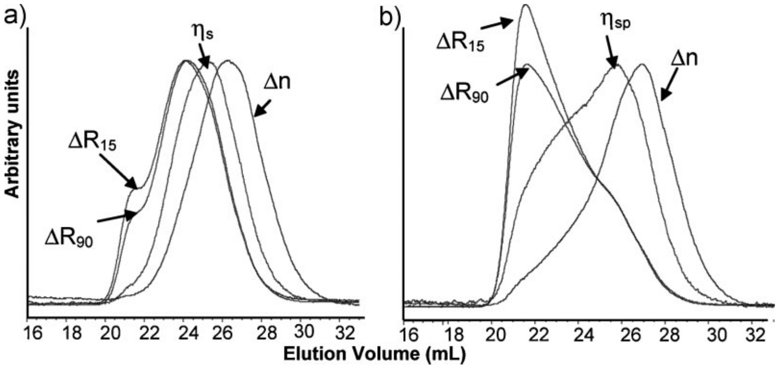

Figure 3.
Traces from refractometer (solid line), viscometer (dotted line) and light scattering photometer from two scattering angles (dashed line) for T-EMA-1 (a) and A-EMA-1 (b).

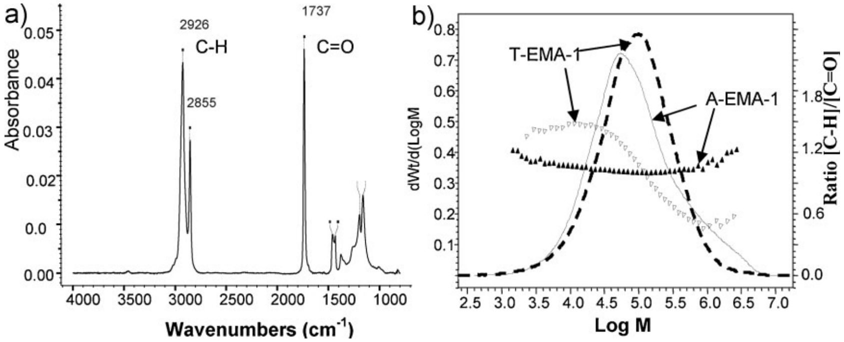

Figure 4.
SEC-IR spectrum taken at the apex of the polymer peak (a) and molecular weight distribution and compositional drift measured for A-EMA-1 (solid line, ▲) and T-EMA-1 (dashed line, ▽) resins using peak area ratio for two characteristic bands C−H and C=O (b).

so that the tubular and the autoclave EVA copolymers have similar viscoelastic properties. But in case of the EMA copolymers, the effect of the high molecular weight branched fractions should be much stronger to explain the unusual behavior of the tubular products depicted in Figure 1 and Figure 2, and there is no indication from the SEC data that the tubular EMA materials have more such fractions compare with the tubular EVA copolymers.

Another explanation for the difference in the rheological behavior of the tubular and autoclave EMA copolymers may be a difference in chemical composition distribution of the tubular EMA copolymers caused by a difference in the reactivity ratios of the comonomers and the nature of mixing in the tubular reactor. Using the FTIR spectra of the EMA copolymers generated across the entire polymer distribution by coupling LC-Transform interface to the multidetector SEC system (example of a such spectrum taken at the apex of the distribution is shown in Figure 4a), a significant composition drift in the tubular copolymer is observed as shown in Figure 4b. The drift can be estimated using the ratio of two peaks, the aliphatic C−H stretch at 2926 cm^{-1} and the ester C=O group at 1737 cm^{-1}. Of course, the accurate calculation of the chemical composition drift across the polymer distribution requires the calibration of the detector response at different compositions, but even the ratio of the areas of the corresponding peaks demonstrates a significant excess of acrylate comonomer in the higher molecular weight portion of the tubular copolymers, while the autoclave products do not show any noticeable difference in the composition across the polymer distribution.

In general, SEC separates macromolecules by size and does not offer a direct way to measure chemical composition heterogeneity of a copolymer. Thus, the absence of the compositional drift in the SEC separation of a copolymer does not necessarily prove that such a heterogeneity does not exit. A variety of liquid chromatography techniques with different mobile phase (eluent) gradients have been tried to solve this problem, including adsorption polymer chromatography, precipitation-redissolution chromatography, gradient polymer elution chromatography, and

Table 3.
Weight-average molecular weight (M_w), polydispersity (PD = M_w/M_n, M_n-number-average molecular weight), z-average molecular weight (M_z) and weight-average branching index (g'_w) of EMA copolymers listed in Table 1.

Resin	Denote	Mw	PD	Mz	g'_w
ElvaloyAC1125	T-EMA-1	113,000	3.82	386,000	0.71
ElavaloyAC1224	T-EMA-2	104,000	4.64	441,000	0.73
ElvaloyAC1330	T-EMA-3	100,000	4.46	402,000	0.73
ElvaloyAC1335	T-EMA-4	103,000	4.5	438,000	0.73
OptemaTC113	A-EMA-1	199,000	8.73	1,380,000	0.54
OptimaTC221	A-EMA-2	106,000	5.82	543,000	0.61

others.[20–22] These techniques are usually referred to as interaction polymer chromatography (IPC) methods to distinguish them from the SEC approach, where any enthalpic interaction with a stationary phase (the internal surface of porous particles inside a chromatographic column) is suppressed, so that the separation by size through the steric (size-exclusion) interaction of the entropic nature could be achieved. But the application of IPC techniques for polymer characterization is usually limited by a requirement of full suppression of the effect of molecular weight (or size) of macromolecules on retention, which is necessary if the differences in chemical composition, microstructure or topology of individual macromolecules are to be revealed.

Such suppression of the molecular weight effect is possible at a specific mobile phase composition called critical point of adsorption (CPA) or critical eluent composition.[21] This composition depends on chemical structure of both stationary phase and polymer chains, but not on the polymer molecular weight. At CPA, steric and enthalpic (usually, adsorption) interactions between repeating monomer units of the macromolecules and the stationary phase in the presence of solvent completely compensate each other. As the result, all molecules with the same CPA (e.g., homologous polymer series) elute with the same liquid volume independent on their molecular weight or size. It has been demonstrated that at certain conditions even in a gradient mode macromolecules elute near their respective CPA in a molecular weight-independent order (gradient elution at CPA).[23,24] Consequently, in such a mode, a mixture of polymer chains with distinct CPA values will be separated by fractions with specific critical points of adsorption independent of their molecular weight. It was shown[25] that individual macromolecules of statistical copolymers may also possess a CPA similar to one for homopolymers, with the critical eluent composition depending on their chemical composition and microstructure, but not molecular weight. As the result, gradient elution at CPA can provide an ideal way to separate such copolymers by chemical composition and elucidate their chemical composition heterogeneity.

This approach was used to analyze the EVA and EMA copolymers obtained in the tubular and autoclave processes. Several acceptable solvents-column combinations with suitable region of critical eluent compositions were found for these copolymers. One such combination is normal phase n-hexane-tetrahydrofuran (THF) gradient on a silica column. The evaporative light scattering detector (ELSD) chromatograms of several autoclave-produced EMA copolymers with similar molecular weight distributions are shown at Figure 5. The chromatogram of poly (methyl acrylate) homopolymer is added for comparison.

Despite similar molecular weights, the copolymers are easily separated from each other according to average content of acrylate shown at the top of each peak. Each copolymer elutes at the corresponding CPA, and the difference in retention between different polymers is determined by the dependence of this point on the copolymer chemical composition. A chemical composition calibration curve can be constructed by plotting the corresponding value as a function of peak apex retention time, similar to the molecular weight calibration curve in SEC. Each fraction from the same copolymer also elutes at the corresponding CPA, so that the width of each peak is directly related to the width of the chemical composition distribution of the copolymer, i.e., its compositional heterogeneity. The CCD of each copolymer can be calculated by applying the chemical composition calibration curve to the corresponding elution profile. The finite width of the homopolymer peak in Figure 5 is caused by a band broadening phenomenon and is not related to any compositional or structural heterogeneity within the sample. All other peaks in Figure 5 are only slightly broader, suggesting a very modest compositional heterogeneity of the EMA

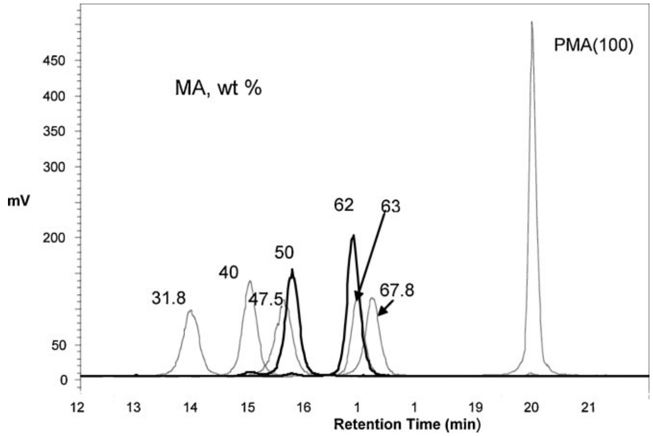

Figure 5.
ELSD traces of EMA copolymers made in CSTR. Dashed line – poly (methyl acrylate). IPC conditions: system 1 with hexane-THF (0–100%) linear gradient over 10 min after 10 min conditioning in 100% hexane, column - NovaPak^{TM} silica, temperature – 40 °C, flow rate - 1 ml/min

copolymers produced in the autoclave process. Notice that the instrument band broadening (or axial dispersion), which broadens the apparent polymer peak, as well as a non-linearity of the ELSD response, which makes this peak slightly narrower, should be taken into account if accurate quantitative results in calculating the CCD of copolymers are required.

The n-hexane-THF separation is limited by solubility of the ethylene copolymers in THF at 40 °C, which requires at least 30 wt% comonomer even in the compositionally homogeneous copolymers, like those shown at Figure 5. Another chromatographic system, shown at Figure 6 and 7, extends the applicability of the method to the polymers soluble in hot toluene. This system allowed for the characterization of all EMA copolymers listed in Table 1. Figure 6 and 7 demonstrate a dramatic difference between the EVA and EMA copolymers. There is practically no difference in elution profiles of the EVA copolymers produced in the autoclave and tubular reactors respectively (Figure 6), while the EMA copolymer T-EMA-1 made in the tubular process has a significantly broader IPC peak than the corresponding autoclave product A-EMA-1 with practically the same average composition. Interestingly, this is the opposite to the result of the SEC separation, where the elution profile of A-EMA-1 is much broader (Figure 3). There is no contradiction in this observation: the autoclave copolymer has broader MWD, which is reflected in the size-exclusion separation, while the tubular product has a much broader CCD as revealed by the gradient elution at CPA. The chemical composition distributions shown at Figure 7b are calculated using the chemical composition calibration curve obtained from a series of the autoclave-made EMA copolymers with methyl acrylate content from 18 through 68 wt%. Note that no correction has been made for the axial dispersion or non-linearity of the ELSD response, which would probably just slightly change the shape of the distributions shown in Figure 7b.

A more serious limitation of the described method is related to the poor solubility of the copolymers with low amount of the comonomer in toluene at 80 °C. Even the EMA copolymers made in the autoclave reactor did not dissolve in this temperature if average MA content is less 22 wt%. The solubility of the EVA copolymers is only lightly better. The solubility of the tubular EMA products is even worse as they contain a significant amount of

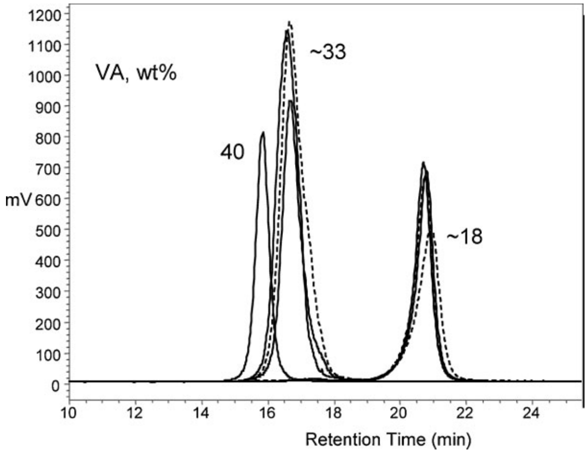

Figure 6.
ELSD traces of EVA copolymers made in autoclave (solid line) and tubular (dashed line) reactors. IPC conditions: system 1 with ethyl acetate/methanol (50/50) - toluene (50–100%) linear gradient over 10 minutes after 10 min conditioning in the initial eluent, column - NovaPak™ C_{18}, temperature – 80 °C, flow rate - 1 ml/min

fractions with the acrylate content lower than the average value. The data presented at Figure 7 suggests that T-EMA-1 resin contains fractions with as low as 15 wt% acrylate. It is possible a noticeable amount of those and especially lower acrylate-containing fractions is lost in the sample preparation and/or gradient elution steps, so that the actual CCD of these copolymers may be even broader than it appears in Figure 7.

To overcome the aforementioned solubility limitations, a high temperature integrated system 2, similar to the system described previously,[26] was used to develop an IPC method applicable to the ethylene copolymers with all possible chemical compositions, including polyethylene. The required temperature (at least, 130 °C) has a significant effect on column efficiency, selectivity and especially stability.[27] We found that among silica-based chromatographic columns only bare silica was thermally stable enough to "survive" over a week at 130 °C. Unfortunately, all silica columns tried (including those recommended in[28,29]) demonstrated very poor resolution in normal phase separations of

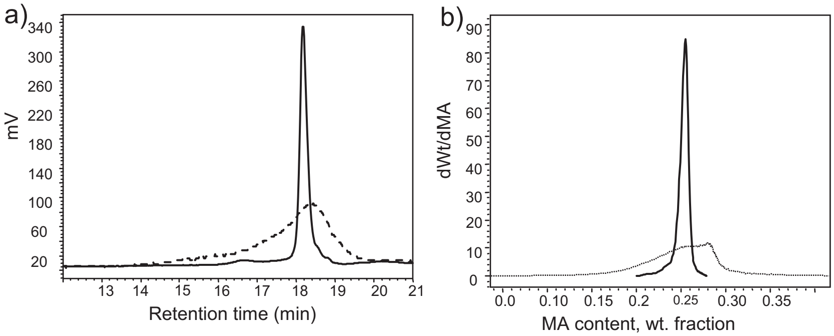

Figure 7.
Chemical composition heterogeneity of EMA copolymers: A-EMA-1(solid line) and T-EMA-1 (dashed line). ELSD traces obtained at gradient elution described in Figure 6 (a) and the calculated chemical composition distribution of the copolymers (b).

the copolymers with low amount of acrylate, i.e., in the most important region where the low-temperature chromatographic approaches did not work due to the poor solubility of the copolymers.

Unlike silica-based columns, zirconia-based columns demonstrated exceptional thermal stability and selectivity in high temperature gradient separations of ethylene copolymers with broad range of chemical compositions. The use of a zirconia-based column for the reversed-phase gradient separation of the EMA copolymers with average compositions from 16 to 68 wt% acrylate is shown in Figure 8. All four copolymers produced in the autoclave reactor demonstrate relatively narrow symmetrical peaks, while their tubular counterparts have very broad multimodal distributions indicating a significant chemical composition heterogeneity.

Conclusion

Different types of molecular heterogeneities in synthetic polymers, described by the related distribution functions, such as MWD, CCD, branching distribution, functional group distribution, etc., may have dramatic effect on the properties of these polymers and should be taken into account in developing and optimization of the chemical reactors. The challenge is to differentiate the effects from different type of heterogeneities on the specific polymer property of interest so that the reproducible structure – property correlations can be established. To achieve this goal polymer characterization techniques capable of directly measuring these heterogeneities are needed, such as liquid chromatography methods. Multidetector SEC can be used to analyze molecular weight and branching distributions, while the gradient elution at specific conditions (critical point of adsorption) reveals the CCD of the ethylene copolymers. Using these techniques, it was shown that the EMA and EVA copolymers made in the tubular reactor, have lower polydispersity but broader long chain branching distribution compared to the chemically identical copolymers made in the autoclave. All of the EVA and the autoclave-produced EMA copolymers have very homogeneous chemical composition distributions, while the EMA copolymers from the tubular reactor are extremely heterogeneous in chemical composition with high molecular weight fractions noticeably enriched with acrylate comonomer. These peculiarities of the molecular structure of the tubular EMA copolymers, with chemical composition heterogeneity as a dominant factor, are

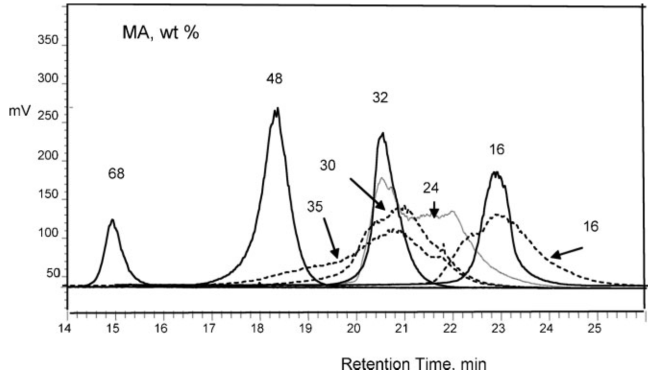

Figure 8.
ELSD traces of EMA copolymers made in autoclave (solid line) and tubular (dashed line) reactors. IPC conditions: system 2 with dimethylacetamide/water (90/10) - cyclohexanone (0–100%) 10 min linear gradient after 10 min conditioning in the initial eluent, column – Diamond Bond^{TM} C_{18}, temperature – 130 °C, flow rate - 1 ml/min.

belived to be responsible for the unusually high melt elasticity of these copolymers observed in the melt rheology experiments.

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