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Characterization of the combined molecular weight and composition distribution of industrial ethylene/α-olefin copolymers

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Abstract

The composition–molecular weight distribution, CD × MWD, of ethylene/α-olefin copolymers was measured quantitatively using two methods: (1) temperature rising elution fractionation (TREF) followed by size-exclusion chromatography (SEC) of each fraction and (2) SEC followed by Fourier-transform infrared spectroscopy (FTIR) of each fraction. TREF-SEC provides a rather complete, accurate, and quantitative representation of the CD × MWD. On the other hand, SEC-FTIR leads to loss of information on some details of the CD × MWD. The extent of the loss depends on the material examined. The main advantage of SEC-FTIR is the much shorter analysis time compared to TREF-SEC.

We briefly discuss another method, TREF followed by measurements of the molecular weight of the fractions by light scattering, LS — either off-line or on-line. We point out that this technique also leads to some loss of information on the CD × MWD. However, for linear low density polyethylene-type materials, TREF-LS may be a more useful technique than SEC-FTIR while less time-consuming than TREF-SEC.

Finally, we use deconvolution of the SEC-FTIR data into Flory–Stockmayer distributions in an attempt to recover all or part of the information loss inherent in the SEC-FTIR method. The attempt was not successful when applied to the data presented in this work. We discuss several reasons for this failure including limited instrumental resolution and intrinsic limitations of the SEC-FTIR technique. © 2001 Published by Elsevier Science Ltd.

Keywords: Ethylene copolymers; Molecular distributions; Chromatography

1. Introduction

Many polyolefins of commercial interest are copolymers of ethylene and a higher α-olefin such as hexene. The comonomer is used to impart to the final material some desired property that would not be achievable by the homopolymer. For example, copolymerization of ethylene with a few mole percent of butene, hexene, or octene produces linear low-density polyethylene (LLDPE) a material with much better impact and film tear properties than high-density polyethylene (HDPE), which has little or no comonomer.

When conventional Ziegler–Natta catalysts are used, the incorporation of comonomer is not uniform. Instead, a broad distribution of polymer chains with different comonomer contents is present in the final product [1]. The shape of this distribution has a profound effect on the end-use properties of the material, such as puncture resistance and FDA extractable limits. It should also be noted that the composition distribution (CD) is superposed to the usual broad molecular weight distribution (MWD) provided by these catalysts.

Metallocene catalysts are capable of producing olefin copolymers with narrow MWD and uniform CD [2,3]. However, the CD of metallocene-produced polymers can still be manipulated — and the properties modified accordingly — by the choice of the polymerization process and the use of mixed catalysts with different abilities to incorporate comonomer in the final product.

In summary, in an ethylene/α-olefin copolymer with no long-chain branching there are essentially two molecular parameters of interest: the MWD and the CD, which are manipulated to impart desired properties to the final product. The MWD tells how much material of a certain molecular weight is present. The CD tells how much material of a certain composition, or comonomer content, is present. Intra-chain structural distributions, such as “blockiness”, may also be present but will be neglected in

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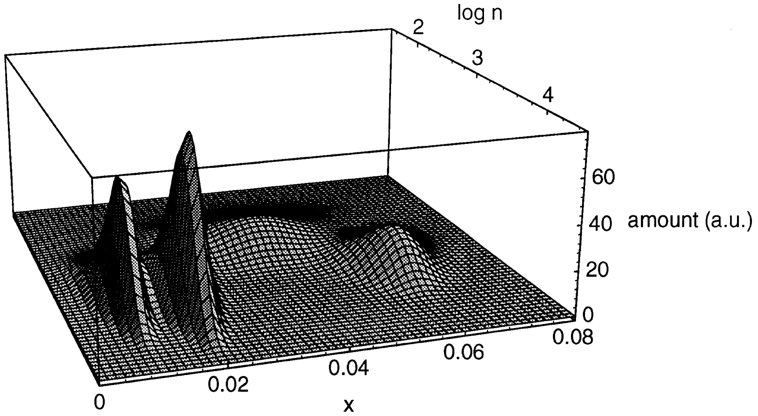

Fig. 1. CD × MWD surface generated by the superposition of four Flory–Stockmayer distributions [13], where n is the degree of polymerization and x is the comonomer mole fraction.

this work. We will assume that the average comonomer content of each chain is the only compositional parameter required for a full characterization of the CD.

There are two convenient ways of acquiring information on these distributions. One is size-exclusion or gel-permeation chromatography (SEC or GPC), which gives the MWD, and the other one is temperature-rising elution fractionation (TREF), which measures the CD. TREF takes advantage of the progressive depression in melting point caused by increasing comonomer content [4]. Crystallization analysis fractionation (CRYSTAF) is a recently developed technique that can also be used to determine the CD of semicrystalline copolymers [5,6]. Separate information on MWD and CD, however, is not sufficient for a full characterization of ethylene/α-olefin copolymers. One would not generally know, for instance, whether it is the low- or the high-molecular weight portion of the material that contains the most comonomer. It is really the combination of the two distributions, the MWD and the CD, that determines the physical, mechanical, and end-use properties of ethylene/α-olefin copolymers. Since there are two molecular variables of interest, molecular weight and composition, the graphical rendition of the CD × MWD will take the form of a 3D surface; a hypothetical example is shown in Fig. 1. The same information can be displayed in a more compact form by using a contour plot representation, as illustrated in Fig. 2. In this work, we will use both means of displaying the CD × MWD.

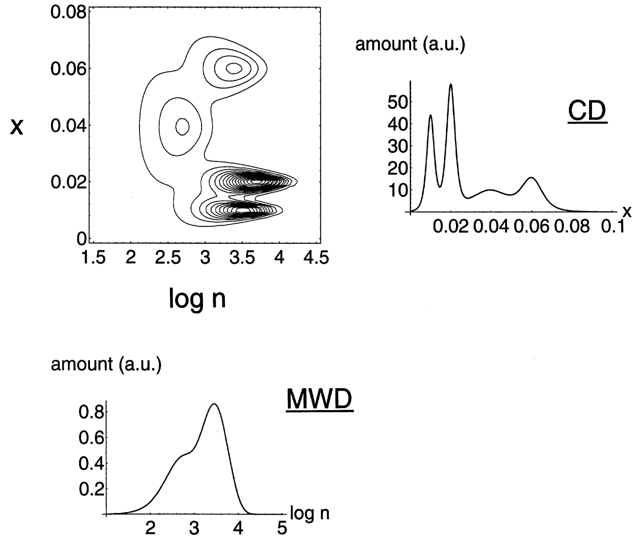

Fig. 2. Contour plot of the surface in Fig. 1. The corresponding CD and MWD are also displayed.

The CD × MWD surface contains all the information on the molecular make-up of ethylene/α-olefin copolymers (with the restrictions discussed above). Each region on the surface gives the relative amount of the species with a given molecular weight and composition. The projection of the surface on the amount-composition plane gives the CD curve that would be obtained by TREF. The projection on the amount-molecular weight plane gives the MWD as would be obtained by SEC. For the reasons discussed above, the reverse construction is not possible, however. The independent acquisition of TREF and SEC curves is not sufficient to reconstruct the CD × MWD surface, cross-fractionation of the material is required for that.

Experimental methods that probe the CD × MWD do not usually reconstruct the surface in every detail; some information is lost. There are various reasons for this situation. We already mentioned neglecting the intra-chain distribution. Lack of perfect resolution is another source of loss. Certain methods only measure some average value of either the CD or the MWD whereas the remaining distribution is measured in full. Methods in this last category will always suffer from information loss; its extent will depend on the shape of the CD × MWD and therefore on the particular resin, the type of catalyst used, and the polymerization process employed.

In this paper, we will describe and compare some of the methods we have developed to advance the simultaneous characterization of MWD and CD of ethylene copolymers. We will discuss cross-fractionation by TREF and SEC and

Table 1
Characteristics of the samples used in this work

Sample	Comonomer (mol%)[a]	Catalyst	Process
ZN-1	Butene, 4.1	Ziegler–Natta	Gas phase
ZN-2	Hexene, 3.7	Ziegler–Natta	Gas phase
Met-1	Hexene, 4.6	Metallocene	Homogeneous
Met-2	Hexene, 3.9	Metallocene	Homogeneous
Met-3	Hexene, 7.0	Metallocene	Homogeneous

[a] The comonomer amounts reported here are average values by ^{1}H NMR.

compare it to the data obtained by SEC fractionation followed by FTIR analysis of the fractions and to the results provided by TREF fractionation coupled with the determination of the molecular weight of the fractions. We will also point out the limitations inherent in each method.

2. Experimental

Table 1 shows the ethylene/α-olefin copolymer samples used in this work; the list includes different comonomers, catalysts, and processes.

For SEC-FTIR analyses, the samples were dissolved in 1,2,4-trichlorobenzene (TCB) at 160°C. Dissolution times were 2–4 h, during which the samples were occasionally shaken. To prevent oxidation, approximately 6 g of 2,6-di-*tert*-butyl-4-methyl-phenol (commonly known as Butylated Hydroxy Toluene, BHT) were added to 4 l of TCB. Sample concentrations were typically 3 mg/ml for the metallocene samples and 5.0 mg/ml for the Ziegler–Natta ones.

The SEC-FTIR method implemented in this work is described elsewhere [7]. Briefly, the SEC eluent is split in two portions one of which is nebulized in a nozzle and sprayed onto a Ge disk rotating at fixed speed. As the spray exits the nozzle, it is confined by a heated sheath gas to a 3–5 mm spot. The sheath gas and the surrounding heated oven environment cause the evaporation of the solvent, thus allowing the polymer to be deposited onto the disk. Since the disk rotates during the SEC elution, the final result is a track of solid polymer along the disk. Each track position corresponds to a certain SEC retention volume. The composition at each position along the track is determined by FTIR spectroscopy. The other portion of the SEC eluent is directed to a differential refractive index (DRI) detector.

Each SEC retention volume element may contain polymer chains with different compositions, but FTIR analysis of the corresponding position along the track determines only the average composition of that volume element. No information is given on the distribution of compositions contained in each volume element. For these reasons, SEC-FTIR is not a true cross-fractionation method.

The FTIR spectra are acquired by placing the disk on a 3 × beam condenser (Lab Connections) housed within an IR spectrometer. The IR beam passes through the sample, is reflected by an Al coating at the back of the disk, and travels through the sample again. Although it is possible to acquire FTIR spectra continuously along the track by automatically rotating the disk in the condenser, in this work the disk is rotated to a set angle and the spectra are acquired at that position. (The only exception is the determination of the volume lag between the DRI trace and the deposit, see below.) This method, although less efficient than continuous rotation, allows the use of arbitrary IR acquisition parameters. Generally, a spectrum is acquired every 5° along the polymer track. Typical IR acquisition parameters are: 4 or 8 cm^{-1} resolution, 256 scans averaged, 600–4500 cm^{-1} spectral region. The following absorbances were used in this work: 1377 cm^{-1} CH_3 symmetrical bending, 770 cm^{-1} CH_2 side-branch rocking (butene comonomer only), and 4325 cm^{-1} for thickness normalization. We used no peak deconvolution procedure and no attempt was made to correct for CH_3 groups at the chain ends. The latter approximation is justified in light of the molecular weight and compositions measured in this work. First we will consider the FTIR calibration. Given the molecular weights of the standards, the maximum error resulting from neglecting the chain ends of the standards (see below) is 8% and occurs for the standard with the lowest comonomer content (1.6 mol%) under the assumption that both ends carry a CH_3 group. In reality, these standards contain some end unsaturation that will reduce the error somewhat. As the comonomer content increases, the error decreases: it is at most 4% for the next higher composition (2.1 mol%) and only 1% for the highest one (12 mol%). Next we consider the error in the composition measurements of the samples examined in this paper, if the chain-end correction is neglected. One would expect the largest error at the lowest molecular weight we could measure with SEC-FTIR, which was about 10,000. The structure of the samples is such that the comonomer content at that molecular weight is about 4 mol%. The composition error for these types of data is estimated to be at most 14%, again considering the worst case of two CH_3 groups per chain. We estimate that our FTIR measurements have an average variability of 0.7 mol%. In conclusion, for standards and samples the experimental error is much larger than the error introduced by neglecting the effect of chain ends except for very few datapoints.

The SEC-FTIR instrument coupled a Waters 150C chromatograph to an LC-Transform solvent evaporation interface (Lab Connections). The operating conditions were as follows: 140°C SEC oven temperature, TCB as carrier solvent (with BHT), three mixed-bed columns (either PLgel Mixed-B from Polymer Laboratories or AT-806MS from Shodex), 0.5 ml/min flowrate, 0.45 ml injection volume, 8.7 ml/min nebulizer flowrate, 7.2 l/min sheath gas flowrate, 145°C transfer line temperature, 160°C LC-Transform oven temperature, 165°C sheath gas temperature, nitrogen as sheath gas, 10° per minute disk speed. The

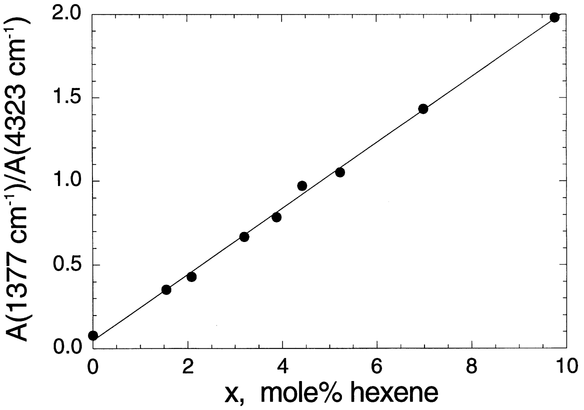

Fig. 3. FTIR calibration for ethylene–hexene copolymers. The absorbance ratio is the absorbance at 1377 cm^{-1} divided by the absorbance at 4323 cm^{-1}, measured after the appropriate baseline subtractions.

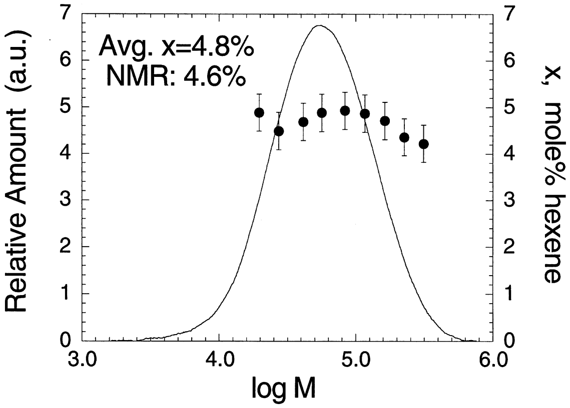

Fig. 5. MWD and distribution of average compositions for Met-1, as obtained by SEC-FTIR. The value labeled as NMR was obtained from ^{1}H NMR on the unfractionated sample.

nozzle flowrate was adjusted to provide a 3–5 mm wide track. The previous settings of the LC-Transform gave the best compromise between the quality of the deposition and the quantity of material deposited.

The SEC columns were calibrated using polystyrene, PS, standards from Polymer Laboratories. The standards covered the 680–9.88 × 10^6 range of molecular weight and their concentrations were approximately 10 times below the overlap concentration, C^*. ($C^* = 15.5/[\eta]$, where C^* is expressed in mg/ml and the intrinsic viscosity, $[\eta]$, is expressed in dl/g.) The molecular weight distribution was obtained from the DRI output and known Mark–Houwink coefficients for PS and polyethylene (PE) [8–10] assuming that the universal calibration concept applies. No attempt was made to correct the MWD for comonomer content.

The retention volume lag between the DRI signal and the IR deposit was determined by comparing the peaks of the DRI trace and the IR chromatogram obtained by Gram–Schmidt reconstruction; a PS standard was injected for this purpose under the same conditions as the samples. (Gram–Schmidt reconstruction requires using continuous disk rotation in the condenser.)

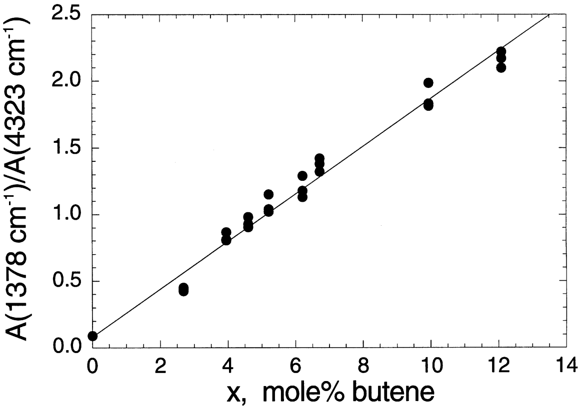

Fig. 4. FTIR calibration for ethylene–butene copolymers. The absorbance ratio is calculated as in Fig. 3.

The FTIR calibration was established using narrow-CD copolymers of known comonomer content. These materials were run in the SEC-FTIR apparatus under the same conditions as the samples, but with no disk rotation. All the deposit was therefore concentrated in one spot on the Ge disk. Figs. 3 and 4 show the calibrations for hexene and butene copolymers based on the 1378 cm^{-1} absorbance. Good linearity is observed in both cases.

The principles of TREF has been extensively reviewed elsewhere [1] and will not be discussed further here. The apparatus used in this work has also been described in the literature [11]. The TREF instrument was calibrated using narrow-CD polymers of known comonomer content. As mentioned in the introduction, we neglect the intra-chain structure of these standards on the calibration curve. We also neglect any difference in the intra-chain structure of the standards and the other measured samples. Taking these intra-chain distributions into account is a difficult and unresolved problem for the TREF method. The TREF fractions from the samples were poured into methanol and filtered to isolate the solid polymer, which was then dried under vacuum and weighed to determine the relative amount of each fraction. The compositions of the fractions were determined by NMR and the MWDs by SEC. A calibration based on NBS 1475 — a linear PE with broad MWD — was used for these SEC analyses.

Fast, automated TREF-SEC analyses were also carried out using the Mitsubishi T-150A cross-fractionation chromatograph, CFC. A description of the design, procedure, and data analysis features of the CFC has been presented [12].

3. Results and discussion

Fig. 5 shows the results of SEC-FTIR for Met-1. The

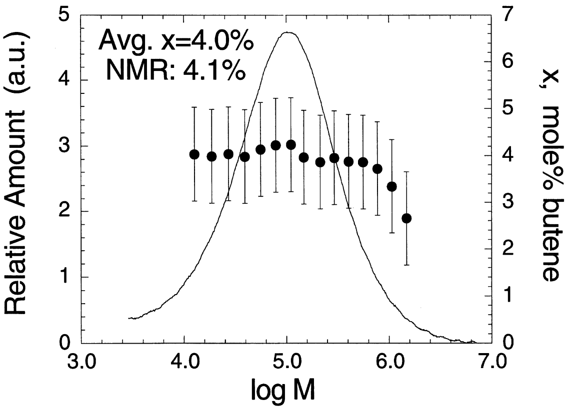

Fig. 6. MWD and distribution of average compositions for ZN-1, as obtained by SEC-FTIR.

smooth curve gives the MWD whereas the full circles represent the molar composition at a given MW. The copolymer composition is rather uniform across the MWD, as expected. Some variation is evident, especially at the higher MWs, but it is hard to separate it from experimental error. The average molar composition computed from the SEC-FTIR data, 4.8% hexene compares very well with the value obtained from NMR, 4.6%. TREF data — not shown here — confirm that this metallocene copolymer has a narrow composition distribution: a plot of the detector response as a function of temperature shows a narrow peak.

The SEC-FTIR results for ZN-1 are displayed in Fig. 6 in the same manner as discussed before: a graph of the MWD with composition values superposed at selected MWs. As revealed by SEC-FTIR, the composition distribution is quite narrow. (The distribution in Fig. 6 is one of average compositions since, as we discussed in the Experimental section, each composition value measured in SEC-FTIR is an average over all the chains with similar retention volumes). The comonomer content of ZN-1 is somewhat lower at higher MWs, but the decrease is rather small, especially when compared to the uncertainty of the data. Moreover, according to these data, there is no component anywhere in the MWD that contains little or no comonomer. Such a component might be present in the outermost high-MW portion of the MWD — beyond the range shown in Fig. 6 — but the amount of material in such region is so small as to prevent accurate FTIR analysis. The average butene content calculated from the SEC-FTIR data compares very well with the NMR value, a fact that supports the accuracy of the SEC-FTIR data. However, the SEC-FTIR results for ZN-1 seem to be at variance with some well-established experimental evidence accumulated on ZN-LLDPEs [1]: (1) these materials have a broad, often bimodal, composition distributions with a sharp-peaked component that contains little or no comonomer; (2) the low-comonomer species contain chains of higher molecular weight. TREF characterization of ZN-1 — see Fig. 8 — confirms that point (1) applies to this material. It will be shown later that so does point (2). The experimental CD × MWD surface of ZN-1 is shown in Fig. 7; it was obtained by collecting TREF fractions and characterizing each fraction via SEC and NMR. This surface contains very detailed information on the molecular constitution of ZN-1. One can see immediately that the peaks of the various MWDs shown in Fig. 7 are roughly aligned perpendicularly to the MW axis. Another way to express the same idea is that there is not much change in the weight-average molecular weight, M_w, of the TREF fractions. This result is showed more clearly in Fig. 8, where M_w is plotted vs. the molar composition of the TREF fractions. To give a visual idea about the location of the fractions, the CD of ZN-1 is also shown in the figure. The decrease in M_w with increasing comonomer content is appreciable, but not large: about 70% from the first TREF fraction to the last. If the CD × MWD data are analyzed further, one realizes that the fractions with lower comonomer content have a progressively narrower MWD. In particular, the MWD of the amorphous fraction shows a noticeable low-molecular weight tail. The behavior of the polydispersity index, M_w/M_n, is displayed in Fig. 9. It should be noted that the fractions lowest in comonomer have polydispersities close to the values typical of the Flory–Schulz most probable distribution.

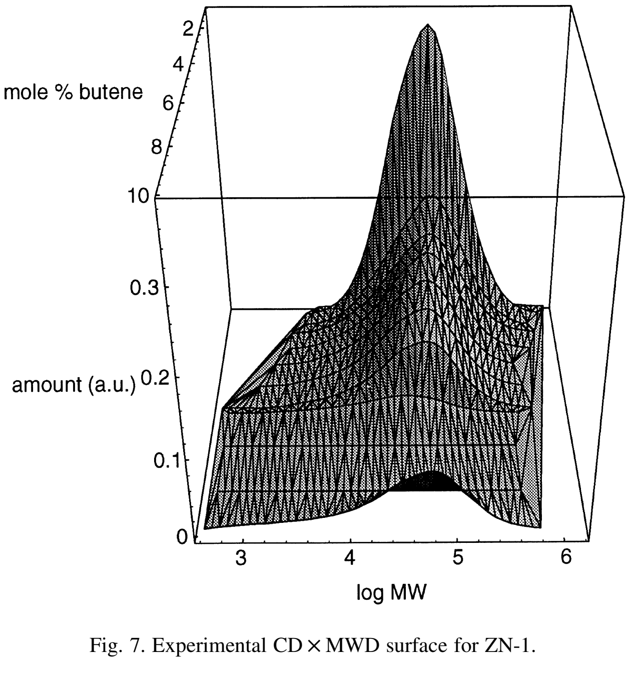

Fig. 7. Experimental CD × MWD surface for ZN-1.

The type of information just presented is extremely important for understanding the molecular origin of the physical properties of ethylene/α-olefin copolymers. It should also prove significant for reaching a better understanding of the mechanisms and kinetics of the catalysts — Ziegler–Natta, metallocene, or any other — used to produce the materials.

The CD × MWD surface of ZN-1 can also be used to show that the disagreement between the SEC-FTIR results and the experimental evidence on LLDPEs is only

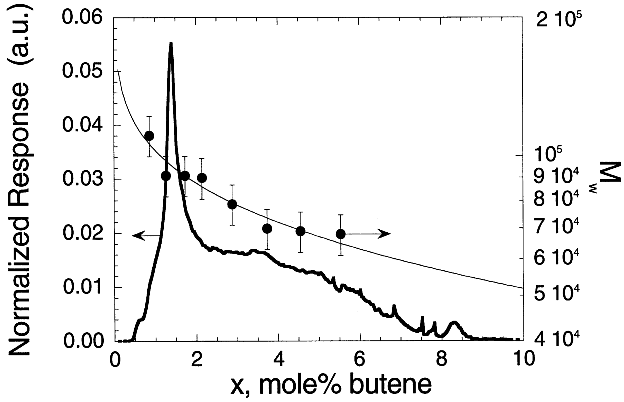

Fig. 8. Weight-average molecular weight of ZN-1 (●) as a function of composition. The CD of ZN-1 measured by TREF is also shown (—).

superficial and is readily resolved. One can use the experimental CD × MWD surface to reproduce the SEC-FTIR results of ZN-1. This is done simply by finding all the points with a given MW — equivalent to taking an SEC slice — and reading their compositions. Finally, all the compositions are averaged using the relative amounts as weights, a step that corresponds to measuring the composition at a specific position along the SEC-FTIR track. For $MW = 350,000$ the above procedure gives an average composition of 2.7 mol% whereas at $MW = 15,000$ the average composition is 3.5%. The difference between these two compositions is rather small and not very different from the experimental error. Clearly, for ZN-1, the CD × MWD data are consistent with the uniform composition across the MWD revealed by SEC-FTIR. There is no contradiction between the SEC-FTIR results on ZN-1 presented here and previous data on LLDPEs; the superficial difference is a result of the composition averaging inherent in the SEC-FTIR method, which causes a loss of information about the details of the CD. For ZN-1 the loss is substantial.

An even clearer example of the loss of information intrinsic in SEC-FTIR is offered by a 50–50 blend of two copolymers with almost identical MWDs and narrow CDs, but two rather different comonomer contents. The CD × MWD of such blend contains two peaks whose separation depends on the difference in the comonomer contents of the two components. Fig. 10 shows such a CD × MWD generated by superposition of two Flory–Stockmayer's distributions [13]. The projection of the CD × MWD on the MW plane — which gives the overall MWD — is a unimodal curve very close to the MWDs of the two components. The projection on the composition plane — which gives the overall CD — is a bimodal curve indicating the presence of two distinct comonomer contents in the blend. (Again, the degree of separation between the two populations depends on the difference in the comonomer contents of the blend components.) Since SEC-FTIR corresponds to taking successive slices perpendicular to the MW axis and measuring their average composition, the shape of the CD × MWD surface guarantees that such composition will be the same for each MW slice. By SEC-FTIR, the blend will appear uniform in composition whereas the true CD is bimodal.

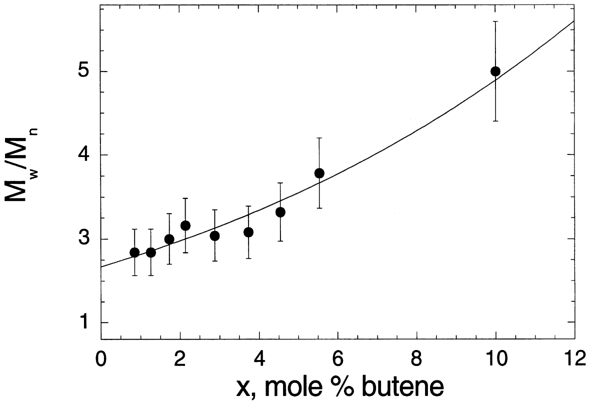

Fig. 9. Polydispersity index, M_w/M_n, of ZN-1 as a function of composition. The solid line is only a guide to the eye.

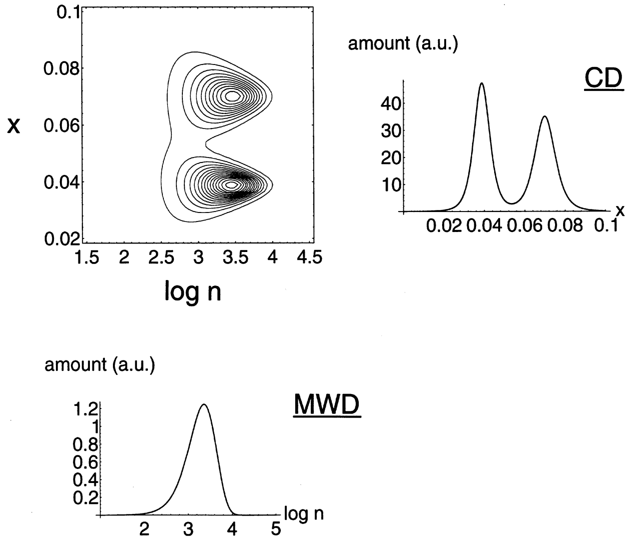

Fig. 10. CD × MWD (contour plot), CD, and MWD obtained from the superposition of two Flory–Stockmayer distributions having different average compositions but identical MWDs.

Using metallocene polymers, one can experimentally verify the above predictions. Fig. 11 shows the TREF trace of a nearly 50–50 blends of Met-2 and Met-3; as expected, the trace of the blend is bimodal. Since the two copolymers have very similar MWDs, each SEC elution volume — and therefore each small element of the deposit on the disk — will be made of a 50–50 blend of the two copolymers. Each position along the track will have the average composition of the two components and, since the components have narrow CDs, such average will remain the same across the MWD of the blend. Thus, one predicts that in this case SEC-FTIR will measure a uniform composition across the MWD of the blend. The measured

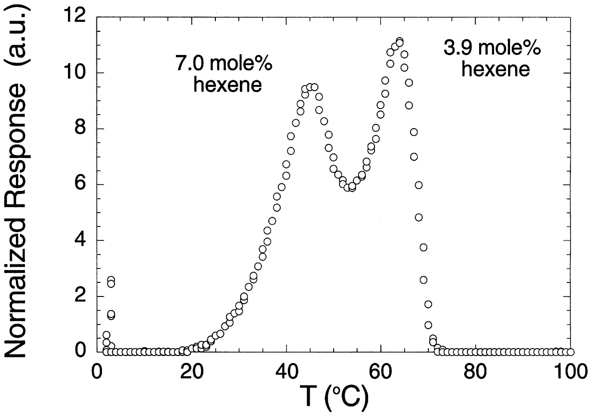

Fig. 11. TREF data for a 51/49 wt.% blend of Met-2 and Met-3.

comonomer content will be the average of the values for the components, 5.5 mol%.

The SEC-FTIR data for the blend conforms to these expectations. The data in Fig. 12 are again presented as a graph of the MWD with composition values superposed at selected MWs. The graph indeed shows a uniform composition across the MWD and an average value of 5.4 mol%, very close to the expected value. In this case, all the features of the CD evident from the TREF data are lost; there is no evidence of either a broad or a bimodal CD.

Not all cases are as pathological as the blend just examined. The amount of information loss in SEC-FTIR depends on the details of the CD × MWD surface of each material. Fig. 13 shows for ZN-2 the expected decreasing average comonomer content with increasing molecular weight. The average hexene content agrees well with the NMR value. Unlike for ZN-1, SEC-FTIR is capable of producing at least a qualitative indication that ZN-2 is not compositionally homogeneous. As before, however, the data contain no hint that this LLDPE mostly contains polymer with little or no comonomer. There is also no indication that the material contains a fair amount of amorphous, high-hexene copolymer. Again, many details of the CD × MWD of ZN-2 are lost when this material is characterized using SEC-FTIR, but the extent of information loss is not as pronounced as for ZN-1. It should be pointed out that if it were possible to measure compositions near the high- and low-MW tails, more information could be gathered about this polymer sample, which would lead to an improved resolution of SEC-FTIR.

TREF-SEC cross-fractionation was also carried out on ZN-2; the results are presented Fig. 14 in the form of a contour plot. The resolution is somewhat poor because only eight TREF fractions were taken. The main features of the CD × MWD surface are nevertheless evident. The most prominent population is the low-comonomer component. Similar to the ZN-1 case, the surface has one of its main axis nearly perpendicular to the MW axis. The weight-average molecular weight nearly doubles from 50,000 to 110,000 as the hexene amount changes from 6.8 to 0.74 mol%. The polydispersity decreases from 3.5 to 2.1 as the comonomer content decreases.

SEC-FTIR is not the only method for obtaining information on the molecular weight-composition inter-relation without carrying out the experimental search for the full CD × MWD. Another possibility is to measure some average molecular weight of the TREF fractions using a suitable molecular weight-sensitive detector, such as light scattering, LS. The appeal of this method rests on the possibility of interfacing directly the TREF instrument to the MW-detector in an automated fashion. Jeansonne and Yau [14] have demonstrated the feasibility of this approach. The type of data accessible with a TREF-LS combination is similar to those presented in Fig. 8 for ZN-1. In general, TREF-LS also suffers from a potential loss of information due to the MW-averaging over each TREF fraction, which results in no data on the shape of the MWD of the fraction. The extreme case will occur for a material that has a superposition of populations with very similar CDs but very different M_ws. In this instance, TREF-LS will measure a single,

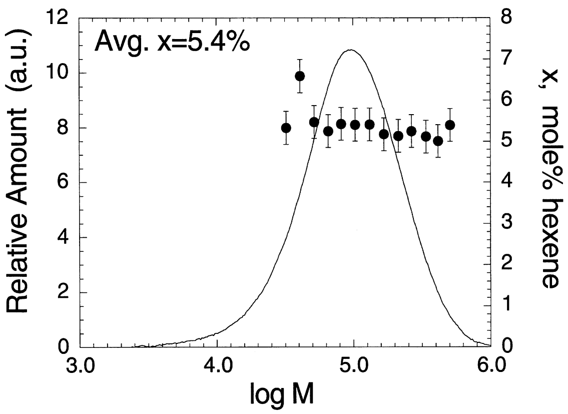

Fig. 12. MWD and distribution of average compositions for a 51/49 wt.% blend of Met-2 and Met-3; by SEC-FTIR.

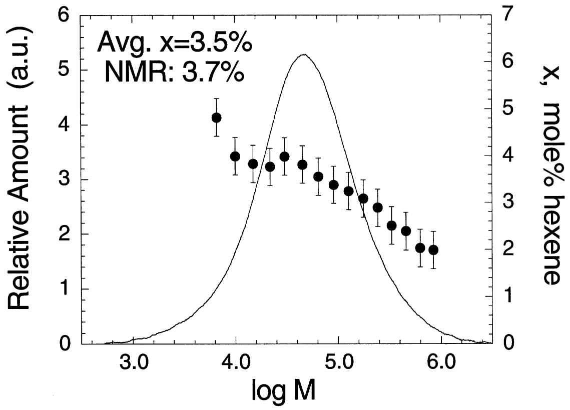

Fig. 13. MWD and distribution of average compositions for ZN-2; by SEC-FTIR. The value labeled as NMR was obtained from ^1H NMR on the unfractionated sample.

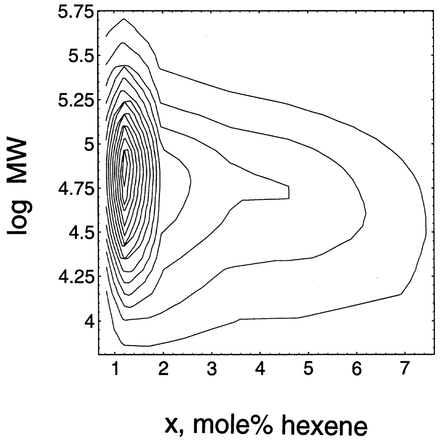

Fig. 14. Experimental CD × MWD (contour plot) of ZN-2 obtained by SEC analysis of TREF fractions.

intermediate value of M_w across the overall CD and completely miss that the real MWD may be distinctly bimodal or multimodal. Usually, ZN catalysts produce populations with distinct CDs, thus making TREF-LS somewhat more useful and less misleading, at least in this case, than SEC-FTIR.

Yet another way of obtaining the CD × MWD is to carry out a fractionation based on MW with subsequent TREF analysis of each fraction. We have not explored this sequence in the present work; for an LLDPE, Aust et al. found it superior to the more common TREF-SEC sequence [15].

The above discussion demonstrates that for a comprehensive characterization of the CD × MWD of ethylene/α-olefin copolymers one needs a complete cross-fractionation of the material. Methods, such as SEC-FTIR and TREF-LS that carry out the fractionation only along one molecular axis and determine some average of the other result in some information loss. The extent of the loss depends on the method employed and on the shape of the CD × MWD surfaces of the materials of interest. Thus, it is generally preferable to access the full CD × MWD; we showed how it is possible to do so by collecting TREF fractions that are then analyzed by SEC. However, the procedure, although effective, is rather expensive and time-consuming whereas SEC-FTIR and TREF-LS are much faster and might find applications when many analyses are required in a relatively short time. The Mitsubishi T-150A CFC allows the TREF-SEC cross-fractionation to be carried out efficiently and on a small scale in an integrated instrument. Fig. 15 shows an example of the data that can be obtained with the CFC; the material is ZN-2. In the figure, the horizontal axis gives the molecular weight whereas the left ordinate indicates the temperature. The composition on the right ordinate can be easily found from the temperature by calibration, although such calibration was not carried out in this work. The relative amounts are shown here as a contour plot. The qualitative features of the CD × MWD surface obtained with the Mitsubishi instrument are very similar to the ones displayed in Fig. 14, which was obtained by isolation of TREF fractions and subsequent SEC analyses. The main difference is resolution; the CFC contour plot was obtained from 25 fractions rather than only eight in Fig. 14. Data collection and analysis take 1–2 days on the CFC instead of about one week for the collection of TREF fractions followed by SEC analyses.

Another way to carry out TREF-SEC, with efficiency intermediate between the manual isolation of the TREF fractions and the full automation of the Mitsubishi CFC, is to use a commercially available instrument — CRYSTAF by Polymer Char [5,6] — that fully automates both fractionation by composition and the isolation of dry fractions. In this way the labor-intensive manual collection of the TREF fractions is eliminated with a great gain in the overall speed of the analyses.

In the remainder of the paper, we return to a discussion of the SEC-FTIR method. We have already shown that SEC-FTIR gives intrinsically less information on the CD × MWD than available from a full cross-fractionation method. In the following, we want to explore whether some important and not directly accessible details of the CD × MWD are "hidden" in the SEC-FTIR data rather than being irretrievably lost. If the former is the case, we

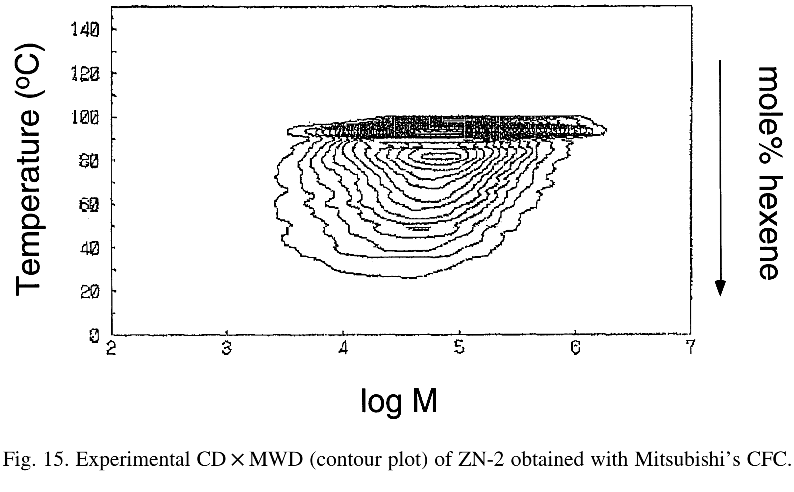

Fig. 15. Experimental CD × MWD (contour plot) of ZN-2 obtained with Mitsubishi's CFC.

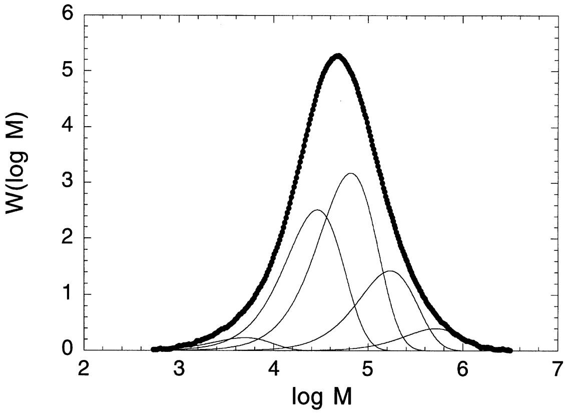

Fig. 16. MWD of ZN-2 and associated fit by a linear superposition of five Flory–Stockmayer distributions.

want to probe whether these details can be recovered. To this end, the MWD of the material is decomposed in a series of Flory–Stockmayer bivariate distributions. The parameters are fixed by fitting the overall experimental MWD and the composition curve provided by SEC-FTIR. The details of this procedure are discussed elsewhere [16]. Fig. 16 shows that the MWD of ZN-2 can be accurately fit by five Flory–Stockmayer distributions. The composition data from SEC-FTIR can also be fit rather well by adjusting the appropriate parameters of the five Flory–Stockmayer distributions, as shown in Fig. 17.

Through the fit to the SEC-FTIR data — MWD and average compositions along it — all the parameters of the Flory–Stockmayer distributions are determined. In this work, it was assumed that the reactivity ratios, r_1 and r_2, are such that $r_1r_2 = 1.0$ for all site types. Although this assumption is probably incorrect for heterogeneous Ziegler–Natta catalysts it was made since: (1) there is no unequivocal way of determining r_1r_2 per site type for heterogeneous Ziegler–Natta catalysts; (2) peak broadening due to non-idealities in TREF will likely be of much more importance than the r_1r_2 parameter [17]. If the information on the CD × MWD contained in the five distributions is complete, it should be possible to simulate accurately the experimental CD curve with no additional parameter fitting. Fig. 18 shows a comparison of the CD curves obtained experimentally for ZN-2 and as a sum of the five Flory–Stockmayer distributions discussed above. The agreement is manifestly poor. There is only a faint qualitative similarity between the two CD curves. The lack of agreement may be due to several factors discussed below in inverse order of importance.

No TREF instrumental broadening was included in the predicted CD curve whereas the experimental curve includes this effect. We do not believe that including band broadening would completely explain the observed differences.

The accuracy of the TREF calibration curve must be ensured before the experimental data are compared to the predicted curve. Errors in the calibration curve lead to incorrect shifts, compression, and stretching of the measured CD curve along the composition axis, which would clearly result in a poor fit of the predicted and experimental CD curves. The calibration curve used to produce the measured CD in Fig. 18 was based on the elution temperatures and the NMR-measured compositions of fractions obtained from the parent material. We believe that any errors contained in the TREF calibration are too small to explain the lack of fit observed in Fig. 18.

It is interesting to notice how the range of the predicted CD is nearly the same as the composition range measured in SEC-FTIR, see Fig. 17. This behavior indicates that the deconvolution procedure described above is incapable of providing more information on the composition distribution than originally contained in the data. This last observation and the failure of the comparison between predicted and observed CD curves, lead to the following conclusion: for the materials examined herein and using the currently available instruments, the information loss on the CD × MWD as determined by SEC-FTIR is too great to be recovered by deconvolution of the data into Flory–Stockmayer distributions.

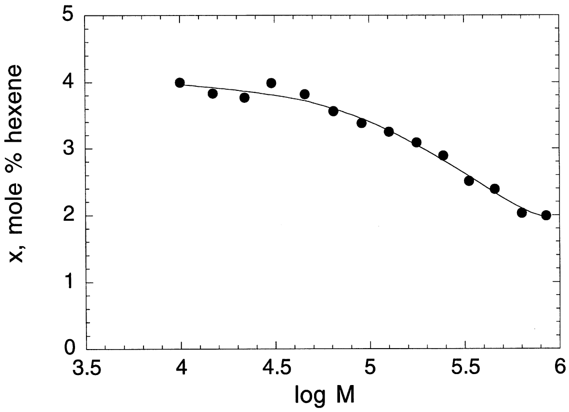

Fig. 17. SEC-FTIR composition data of ZN-2 and associated fit by a linear superposition of five Flory–Stockmayer distributions.

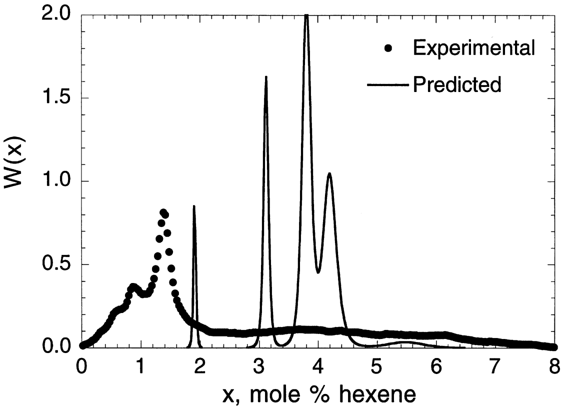

Fig. 18. Experimental and calculated CDs of ZN-2. The calculated values were obtained from a linear superposition of five Flory–Stockmayer distributions and the parameters determined by fitting the data in Figs. 16 and 17.

4. Conclusions

In this work we exhaustively discuss two methods used to quantify the composition–molecular weight distribution, CD × MWD, of ethylene/α-olefin copolymers. One, called TREF-SEC, involves first fractionation by composition and then fractionation of each fraction by molecular weight. This method is implemented using temperature rising elution fractionation, TREF, and size-exclusion chromatography, SEC. Another method, SEC-FTIR, uses first fractionation by molecular weight followed by a measurement of the average composition of each fraction. The technique is implemented using SEC coupled to a solvent evaporation interface and Fourier transform infrared spectroscopy, FTIR. A third method, not discussed in detail here, involves first fractionation by composition followed by the determination of the weight-average molecular weight of each fraction. This technique is implemented using TREF coupled with a molecular weight-sensitive detector such as light scattering, LS.

We show how TREF-SEC gives a detailed, accurate, and quantitative representation of the CD × MWD. On the other hand, both SEC-FTIR and TREF-LS lead to some loss of information about the features of the CD × WD. The amount of the loss depends on the specific material examined; it is almost complete for a commercial ethylene–butene linear low density polyethylene, LLDPE, produced in a gas-phase process; it is partial for a commercial ethylene–hexene LLDPE produced with the same process; and it is again complete for a blend of metallocene copolymers with different average compositions but with the same molecular weight distributions. For conventional ZN-LLDPE resins — a CD similar to Fig. 8 and unimodal MWD — and the currently available instrumentation, TREF-LS provides more information than SEC-FTIR about the CD × MWD of these materials.

Since the complete characterization of the CD × MWD by the implementation of TREF-SEC described here involves a labor-intensive procedure and the collection of a rather large amount of data, we briefly discuss various ways of implementing this method in the laboratory. They include a fully automated TREF-SEC instrument and an automated TREF apparatus.

We sought to recover part of or all the information loss in SEC-FTIR by deconvolution of the data into individual Flory–Stockmayer distributions. The attempt was not successful for the data presented in this work, but the deconvolution method described here may be useful in the development of structure–property relationships and the elucidation of the behavior of catalyst systems.

Finally, although the materials used in this work were conventional LLDPE and metallocene copolymers, the concepts developed herein apply to the characterization of the CD × MWD of all copolymers.

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