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Modeling the Chain-Length Differentiated Polymer Microstructure of α-Olefins

This work is dedicated to the occasion of the 70th birthday of Prof. Dr. Ing. G. Luft

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Summary: Due to a complex polymerization scheme, incorporating besides propagation, termination and transfer to monomer and chain transfer agents in addition intra- and inter-molecular transfer to polymer as well as β-scission, α-olefin (co)polymers feature a quite complex polymeric microstructure. It is demanding to design a kinetic model that describes these in a predictive manner in order to have a tool for computer-aided product design. The molecular weight distribution and branching indices together with the composition are the subjects of interest in this case. The latter quantities are often provided as being averaged over the molecular weight distribution. Modern coupled analytical techniques of size exclusion chromatography provide even more insight. The combination of size exclusion chromatography with fractionation techniques provide under adequate processing of the data branching indices and co-polymer composition differentiated with respect to chain-lengths. This contribution will inspect how good a model for predicting the chain-length differentiated co-polymer composition in high-pressure high-temperature ethene – vinyl acetate-*co*-polymerizations will coincide with analytical results of technical products.

Keywords: α-olefins; modeling; polymeric microstructure; polymerization

Introduction

Controlling the polymeric microstructure during synthesis is one of the most demanding goals in macromolecular science. To achieve this as two polar approaches there exist the chemical design of the macromolecules via multi-step synthesis opposed by control by process conditions via the kinetics. The first approach may be closest to the mind of a macromolecular scientist and very distinct structures can be realized. However, the other side of this medal is that the quantity of product is limited in most cases. Therefore, the application of such a strategy may be limited to small scale high value specialized products. The second approach is even applicable to products of world scale production, classifying a plant capacity of about 400 kt/a. Here modeling is an extremely valuable tool. A physico-chemical reasonable kinetic model incorporates the information about a complex network of elementary polymerization reactions. In combination with the dependence of rate coefficients on the process conditions (temperature, pressure and viscosity of the reaction environment), it bridges the reaction conditions with the microscopic polymeric structure that determines the applicational properties of the polymer. Acquiring the necessary information demands often extensive experimental work. Therefore, this approach is applied more frequently for polymers in large-scale

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production. Here, the investment and the return of benefit balance in a maximum. For all these reasons, the high-pressure high-temperature ethene polymerization was an attractive subject of investigation. Luft[1] designed in the late 80s a process model for the ethene homo- and ethene – vinyl acetate – *co*-polymerization based on the method of moments. Later, with the *h-p*-Galerkin technique numerical tools (PREDICI) became available that allow for the deterministic and rigorous computation of molecular weight distributions (MWD). Busch[2] demonstrated how to couple this tool with engineering models. The core idea for this was born by Marquardt.[3] He coined the approach of horizontal modeling integration. Models that behave in an essential core similar are developed further into differing directions to treat specialized problems. By this, the numerical efforts limited for each case itself. Here this means the engineering model based on momentum equations and that one describing rigorously the MWD and the polymeric micro-structure (using PREDICI) behave absolute identical with respect to species conversions and thermodynamic properties. Both, conversion and system viscosity control the heat exchange and pressure drop. Therefore, the engineering model is used to describe the behavior of the technical tube reactor and generates the temperature and pressure profiles. The detailed kinetic model within PREDICI is then used to calculate the polymeric micro-structure along these profiles. The success in this field of planning processes and products was encouraging. For that reason, such strategies were developed further when in the calculus of boundary density functions was introduced into PREDICI. This technology allows for computing the MWD rigorously. Further the momentum approach is used to calculate free definable events chain-length differentiated. These event counters are hosted by (pseudo) distributions being approximated by the *h-p*-Galerkin method. This limits the computational efforts significantly. Hutchinson[4] and Iedema[5] applied this to ethene polymerizations inspecting the MWD and chain-length differentiated long-chain branching densities (I_{LCB}). Busch[6,7] applied it to short-chain branching densities (I_{SCB}) in technical ethene polymerizations. Using for the event counter higher moments together with a Wesslau distribution, bi-variate MWDs were computed and their surfaces compared to experimental data from temperature rising elution fractionation – size exclusion chromatographic experiments (TREF-SEC). The embedding of this into the interests of product development has been shown by Schmidt et al.[8] The further potential, e.g. to calculate chain-length differentiated values for average side-branch length, is demonstrated by Busch[9] in addition. In both cases, the work on chain-length differentiated values of I_{LCB} as well as on I_{SCB}, results have been encouraging and demonstrate the potential of the combination of the *h-p*-Galerkin method with the calculus of boundary density functions. From this perspective, it is only consequent to inspect whether this can be adapted to other systems. Having investigated the high-pressure high-temperature ethene homo-polymerization so far, it is close to move to co-polymerizations of this monomer. Besides the branching structure, which would mean a simple adaptation of the homo-polymerization implementations to one of the co-monomers, the co-monomer incorporation itself is of interest. For this reason we developed a model describing chain-length differentiated the incorporation of the co-monomer and compared the simulations to experimental results of FT-IR-SEC-coupling. A good sensor in this procedure is the carbonyl bond of co-monomers commonly used in ethene-*co*-polymerizations. As a matter of interest, we choose here vinyl acetate as co-monomer. With reactivity ratios close to one, the composition of the monomer mixture and the co-polymer can be tuned in wide ranges. The properties of the co-polymer change significantly with composition and vinyl acetate has a strong effect as inner co-solvent. For this reason and as long chains are short enough, ethene-*co*-vinyl acetate – polymers should be soluble in contrast to other ethene-polymers even under standard SEC conditions.

Analytics

To analyze the ethene-*co*-vinyl acetate – waxes different analytical setups come into action. The main interest is directed to a coupling of a high-temperature size exclusion chromatograph (HT-SEC) where after separation the solution is sprayed on a rotating Germanium disk. The different sectors are analyzed later on by Fourier-Transform Infrared Spectroscopy (FT-IR) and having monitored the angel these results can be correlated with the retention time on the HT-SEC setup. By this, chain-length differentiated values of co-polymer composition become accessible. The HT-SEC setup is a Waters 150C coupled with an LC-Transform module of LabConnections. The rotation speed is 10° min^{-1}. For the FT-IR spectroscopy a Nicolet PROTÉGÉ 460 is used. For reasons of resolution and detection sensitivity calibration of the HT-SEC under this configuration is a difficult task.

To have more accuracy here in parallel the samples are investigated on a HT-SEC PL 220 with RI-detector using a mixed bed column set (4 mixed A columns, at 150 °C with tri-chloro-benzene stabilized by 3,5-bis(1,1-dimethylethyl)-4-hydroxytoluene). Fortunately, the co-polymers are soluble also under ambient conditions in THF. To have an estimate how the measured MWD correlate under different chromatographic conditions, the polymers are investigated in addition on a Waters RI 410 at ambient conditions with THF as eluent using three SDV columns. In any case, calibration is

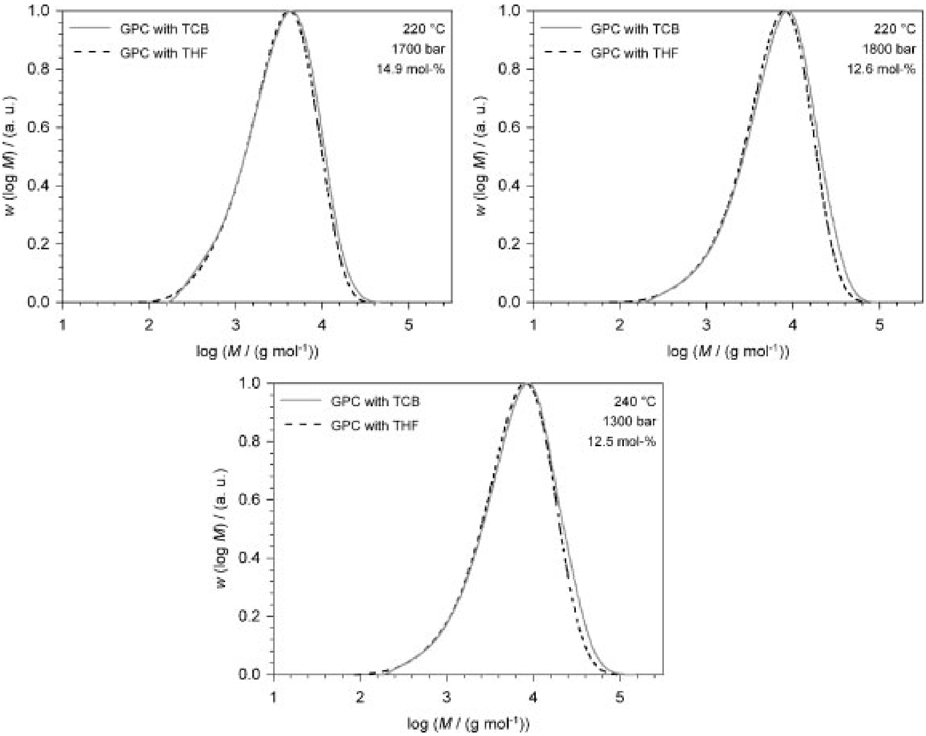

Figure 1.

Comparison of MWDs measured at high-temperature and ambient SEC conditions for three ethene-*co*-vinyl acetate – polymers. Reaction pressure und temperature as well as vinyl acetate co-polymer content in mol-% are given in the legend.

done against polystyrene standards using universal calibration to compute polyethylene equivalents.

Figure 1 compares the MWDs that were measured at high-temperature (full grey line) and ambient SEC (broken black line) condition. The excellent agreement is obvious and it can be concluded with some justification that, although the signal quality on the coupled SEC setup will be significantly worse the calibration and separation will be of similar level.

The samples were chosen in that way that at comparable reaction pressure and temperature two samples exist with a differing ratio of co-monomer vs. chain-transfer agent (CTA). These samples will be used in the next section to adapt two kinetic parameters that are unknown from literature. A third sample at differing reaction conditions is used to test the model especially with respect to its predictive potential. If they are display together in one figure, the organization will be as follows: The two samples used for adaptation are displayed on top the one used for verification in the bottom of the graph. At this point, it is important to realize that analysis went well for all three samples on the same level of quality.

Simulation Model

The simulation model is based on a generalized implementation of Busch and van Boxtel for ethene – acrylate-*co*-polymerization.[10] It features propagation, termination, transfer to monomer, backbiting, inter-molecular transfer to polymer and β-scission for any of the co-monomers and the respective cross-reactions in-between macro-species being terminated at the reactive chain end by differing monomer types. To keep this presentation brief it is omitted to describe the full model here. The reader is kindly asked to refer to the cited work for a full description. In essence, it is an implementation of the implicit penultimate- unit model for co-polymerizations. The radical reactivities are estimated on the base that both are with equal and their product is equal to the product of reactivity ratios. Also for the transfer to monomer an implicit penultimate approach has been chosen. As an adjustable parameter to absolute level of the cross-transfer reactions is left and has to be fitted by some experimental data, while the ratio of cross- transfer of the monomers is estimated based on the chain-transfer constants of the homo-polymerizations and the reactivity ratios. Intra- and inter-molecular transfer is implemented explicitly considering the formed transient secondary or tertiary macro-radical species. This provides the potential to formulate the full reaction sequence considering any cross-reaction steps on the base of homo-reactions and relative reactivities similar as in the concept of propagation.[10]

New to be introduced are the reactions with the CTA agent propionic aldehyde. Assuming a similarity in-between methyl acrylate as the object of model development and vinyl acetate as the monomer of interest here, the species may be replaced by each other and the developed framework of the model may be accepted to be of some general character.

For the rate coefficients of ethene the data summarized by Busch[11] are used. The situation for vinyl acetate (VA) and the co-polymerization is a bit more complex. For propagation a joined fit of the data of Buback[12] and Hutchinson[13] is used. To describe the termination, data from Yokava and Ogo[14,15] together with Pernecker and Foldes-Berezsnich[16] are jointly fitted. The rate coefficients for the transfer to monomer are also derived from a combined data fit. The sources in this case are: Parnell und Russell,[17] Clarke et al.,[18] Moze et al.[19] and Potnis und Deshpande.[20] For intra-molecular transfer there are no literature data and there are some indications that this reaction indeed is not very relevant for this monomer. For inter-molecular transfer again data from Wheeler et al.,[21] Clarke,[22] Schulz and Stein,[23] Stein[24] and Kwart et al.[25] are interpreted together. The reactivity ratios are used as provided by Rhode[26] for r_{VA} and Rätzsch et al.[27]

For the conversion dependence of this co-polymerization it is assumed that it is dominated by the ethene species. This is quite justifiable as the co-polymers are ethene rich and therefore in supercritical solution of ethene the properties of the ethene species should dominate. The complete set of equations describing the conversion dependence of the ethene homo-polymerization can be found at Busch.[7,11]

Besides this intensive literature study two quantities are remaining to be adjusted: One is the absolute level of cross-transfer to monomer, the other the transfer of vinyl acetate terminated macro-radical chains to propionic aldehyde (PA). However, if the concept formulating such quantities in terms of relative reactivities holds, with two parameters (Fac_{M} scaling the cross-transfer, Fac_{PA} scaling transfer of VA terminated macro-radicals to PA relative to the respective ethylene terminated species) an adaptation should be possible. What is needed are two experiments were the level of PA and VA is significantly different. This is the case for the upper two samples displayed in Figure 1. The left experiment has significantly shorter chains (significantly more PA) and higher VA content (moderately more VA) compared to that one displayed on the right. Figure 2 shows the sensitivity with respect to the average molecular weight of the co-polymer when screening these to scaling factors for these experiments. It is clearly seen, that the differing reaction conditions pose a twist in the sensitivities. From this point of view, a unique solution can be found and now it is interesting to see, how the explorative potential of the model is.

Figure 3 displays the consequences of the adaptation procedure. The top two graphs display the MWDs for the experiments being used to adapt, the bottom one is a MWD from another independent experiment. The full lines indicate simulation results, the broken lines indicate experimental MWDs being measured on the HT-SEC setup and transformed to polyethylene equivalents in molecular weight, respectively. The grey lines indicate situation of the simulation results before the two factors have been adapted. In this case, no cross-transfer to monomer was assumed and the transfer of VA to PA was estimated on rather scarce literature data. It can be seen that any simulation was off to higher molecular weight in this case. The offset was significant.

Inspecting the two experiments being displayed at the top it is seen that after the adaptation of the two factors there exists a good match in-between the simulation results and the experiments. This is not unexpected, as these two experiments have been used for the procedure. However, it may be worth to mention that the excellent overlap of the MWD over the complete course of the distribution is not found for every simulation of technical products. More information about the quality of the model may be derived from the bottom part of Figure 3.

Here the simulation result for the MWD of an independent experiment at differing reaction temperature and pressure is displayed. It can be taken as an indication for the good predictive potential of the model that under these circumstances still the MWDs of experiment and simulation match extremely well. Of course, conversion and co-polymer composition are matched well within the experimental accuracies for all of these experiments. However, this is not as surprising as conversion is controlled by the initiator efficiency that is, bottom of the line, adjusted, and co-polymer composition is controlled by the reactivity ratios that can be determined in quite good quality. Moreover, co-polymer composition is more or less not being affected by reactions that control the polymeric structure such as I_{SCB}, I_{LCB} and the MWD. From this point of view, the situation is very much encouraging to go into more detail in modeling the polymeric micro-structure.

The implementation of the boundary density function approach cannot be replicated here for the sake of compactness. The mathematical background of the principle can be found at Gerstlauer[28]

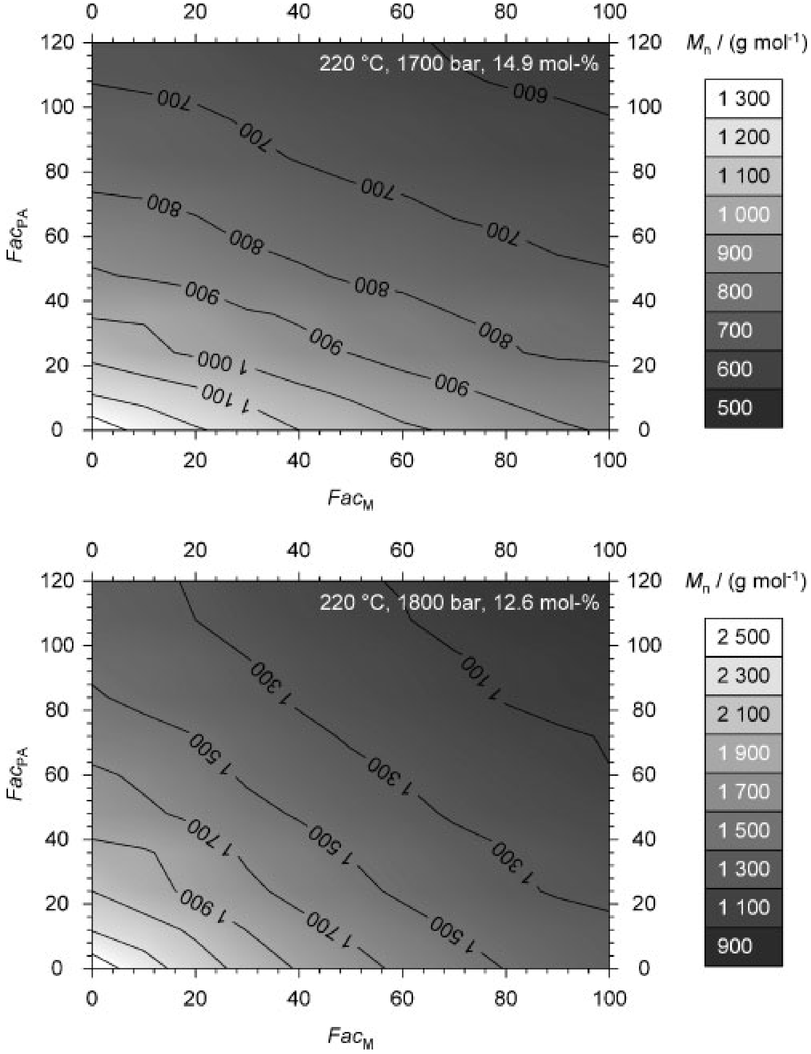

Figure 2.
Sensitivity analysis for transfer from vinyl acetate terminated macro-radicals to propionic aldehyde and cross-transfer activity in-between ethylene and vinyl acetate terminated radicals with respect to average molecular weight of the co-polymer.

and Hutchinson[4] and Iedema[5] pinned down the equations for an implementation to describe chain-length differentiated values of I_{LCB} for the ethene homopolymerization. Busch[9] demonstrated how the implementation in PREDICI is made using a concept of (pseudo) reaction steps. In principle, two types of these (pseudo) reaction steps have to be considered: One that increment a counter at a given chain-length if an event takes place that shall be observed (here the incorporation of one co-monomer). The others that shift these counters in a (pseudo) distribution, which is used to host them, synchronously to the polymerization events that take place. This has to be adapted to counting the incorporation of co-monomer by propagation and shifting the balances in the (pseudo) distributions synchronously to propagation of the other co-monomer, transfer to monomer, transfer to CTA,

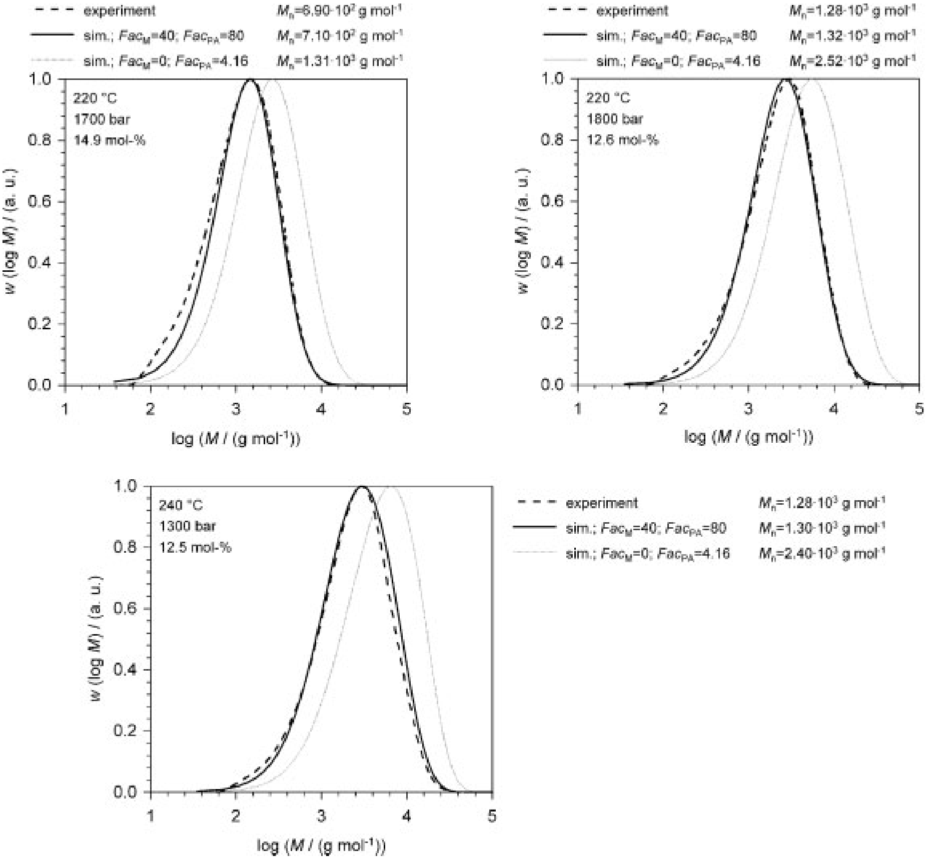

Figure 3.

Comparison of experimental and simulated MWDs. Dotted grey lines for simulations indicate the result with the starting set of parameters, full black lines indicate the results after adaptation of transfer from vinyl acetate terminated macro-radicals to propionic aldehyde and cross-transfer activity in-between ethylene and vinyl acetate terminated radicals. Broken black lines indicate experimental data. The top two samples were used to adapt these parameters, the bottom as an independent control at varied conditions.

intra- und inter-molecular transfer and β-scission. There are no more rate coefficients required, just the set of differential equations growths to account for the additional demands.

Comparison of Results on Chain-Length Differentiated co-Polymer Composition

From this point on the model is more or less invariant. There are no parameters that can be adjusted just in case the data of the chain-length differentiated quantities would not fit to experimental results.

Figure 4 compares the results of chain-length differentiated co-polymer composition and molecular weight distribution as acquired by coupled HT-SEC – FT-IR spectroscopy with simulation data. The MWD is derived from the integral of C–H stretching vibrations from saturated carbons (Int(C–H)). The co-monomer content is accessed by the ratio of absorption bonds from the carbonyl stretching vibration (Int(C=O)) and Int(C–H). Due to the detection method a direct calibration is not accessible. The shapes of the accessed MWD data indicate already that the signal to noise ratio is dramatically worse than using a RI detector. However, as the

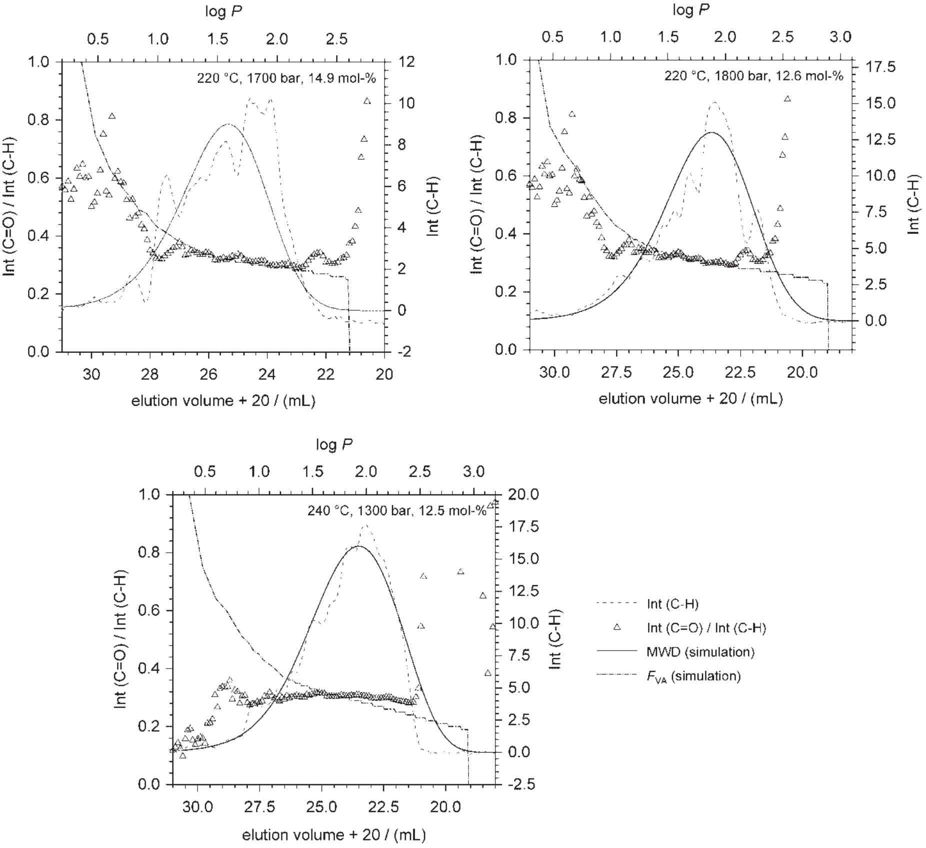

Figure 4.

Comparison of experimental and simulation results for MWDs and values of chain-length differentiated co-polymer composition regarding all three chosen co-polymer samples.

samples are measured in parallel on a HT-SEC with RI detector featuring the same column configuration for separation still there exists a way to correlate the analytical with the simulation data. As the simulation results are in good coincidence with the signals from the RI detector and both SEC setups have similar separation units also the MWD data should coincide with the simulated data. This justifies transforming the MWDs from FT-IR detection in a manner to match the simulation results for MWDs. If now the composition data from FT-IR detection is transformed in the same way, it becomes directly comparable to the simulation results. This kind of procedure has been applied to the data being presented in Figure 4.

Again, the result is surprisingly good. With no further adaptation and without any presumption or prior knowledge the data agree well. In the range where there is a sufficient signal to noise ratio for the two samples displayed in the upper part the agreement is perfect. In contrast to Figure 3 here this is not a matter of course because no further adaptation has been made and the MWD is not necessarily correlated with chain-length dependent co-polymer composition. For the third sample being displayed at the bottom of the figure the agreement is less perfect. However, still the level of the data is good and their course with the chain-length shows the right trend. For a pilot study in a field with quite complicated analysis still this is well acceptable.

Conclusions

It could be shown in this study that the co-polymerization model being designed for general application in ethene – acrylate-*co*-polymerizations does a quite acceptable job also for ethene – vinyl acetate-*co*-polymerizations. The major part of the rate coefficients were taken from the literature. Especially for vinyl acetate, some sources were quite a bit older and it was necessary to combine some sources to derive the required rate coefficients. However, the overall quality of these combined data is apparently high as the good agreement of simulation and experimental results demonstrate. This may be taken for encouragement to anyone who questions the sense of such detailed kinetic measurements because of the efforts and workload that come with such experimental work. Apparently, it worth doing it.

Furthermore, it could be demonstrated that the approach of computing chain-length differentiated (co-)polymer properties can be extended reasonably from branching indices (I_{LCB}, I_{SCB}) to co-polymer composition. Good agreement can be found in-between simulation results and experimental data for products from technical ethene-*co* – vinyl acetate – polymer production. This may be taken as an encouragement for both sides. For the part of simulations it is shown that it is worth going deeper in detail for the polymeric micro-structure and more micro-structural characteristics may come into the focus. Further, it is demonstrated that such simulation results can be experimentally verified. On the analytical side, these results can be taken as a proof that it is worth to develop such complex combined chromatographic techniques. They are not only useful for analyzing trends on a relative scale. Accompanied by simulations now the question after calibrated separation coordinates arises, to have more facilities for comparison with theoretical calculations.

Overall, the simulation bridges from the reaction conditions under which the polymer is produced to micro-structural properties of the product. All this can be verified by analysis. Proceeding further along this lines and developing the techniques further will bring polymer science closer to the vision of computer aided product design. Being successful in this area, this would speed up the development process for polymeric product significantly. In addition, retro-design seems possible or (retro-) analysis for material science. However, on both sides, model design and chromatographic analysis, still there is a way to go. The message for today is that strategies seem to be right, following this path is worth doing it and goals seem to be in reach.

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