Macromol. Symp. **2009**, 282, 167–174 DOI: 10.1002/masy.200950817

Simultaneous Deconvolution of Molecular Weight Distribution and Chemical Composition Distribution of Ethylene/1-Olefin Copolymers Synthesized with Multiple-Site-Type Catalytic Systems

Siripon Anantawaraskul,[*1] *Warawut Bongsontia,*[1] *João B.P. Soares*[2]

Summary: Ethylene/1-olefin copolymers synthesized with multiple-site-type catalytic systems typically exhibit broad molecular weight distribution (MWD) and chemical composition distribution (CCD). These microstrucral characteristics can be described by the presence of several active site types, each of which produces chains with distinct chain microstructures. In this work, a new approach to identify the number of active site types and chain microstructures produced on each active site type was developed based on simultaneous deconvolution of the bivariate MWD/CCD information. Chain microstructures produced on each active site type are assumed to follow Stockmayer's bivariate distribution. The proposed approach was validated with simulated data of model ethylene/1-butene and ethylene/1-octene copolymers.

Keywords: chemical composition distribution; modeling; molecular weight distribution; polyethylene

Introduction

Ethylene/1-olefin copolymers synthesized with multiple-site-type catalytic systems (*i.e.*, systems with multiple-site-type catalysts, mixed catalysts, or hybrid catalysts) typically exhibit broad molecular weight distribution (MWD) and chemical composition distribution (CCD). These microstrucral characteristics can be described by the presence of several active site types, each with a different set of polymerization kinetic parameters, producing chains with distinct microstructures. Ethylene/1-olefin copolymers made with these systems can be considered a mixture, at the molecular level, of chains with various molecular weights (MW) and comonomer contents (CC) produced from all active site types.

To identify the number of active site types and chain microstructures produced on them, deconvolution of MWD obtained from gel permeation chromatography (GPC)[1–5] and deconvolution of CCD obtained from temperature rising elusion fractionation (TREF) or crystallization analysis fractionation (Crystaf)[6,7] have been investigated. The deconvolution of CCD was often performed implicitly by deconvolution of TREF or Crystaf profiles without calibration. Moreover, differences in the estimated number of active site types and mass fractions of polymers produced on each active site type may result when MWD and CCD of the same sample are deconvoluted separately.[6] Therefore, a new strategy is required to yield consistent results.

Recent advances in polyolefin characterization can help provide a great wealth of information on chain microstructures. The new developments include automated full cross-fractionation techniques (cross-fractionation by GPC/TREF or TREF/GPC which describe the interrelationship

---

[1] Department of Chemical Engineering, Kasetsart University 50 Phaholyothin Rd, Jatujak, Bangkok, Thailand 10900
Fax: 00662 561-4621; E-mail: fengsia@ku.ac.th

[2] Department of Chemical Engineering, University of Waterloo, Waterloo, Ontario, Canada N2L 3G1, USA

between MW and CC, known as the bivariate MWD/CCD).[8,9] The simultaneous deconvolution of such detailed information may lead to more accurate and consistent results compared to the ones obtained from separated deconvolution.[10,11]

The objective of this work is to develop a new approach for the simultaneous deconvolution of the bivariate MWD/CCD in order to determine a consistent number of active site types and chain microstructures produced on each active site type. Chain microstructures produced on each site type are assumed to follow Stockmayer's bivariate distribution. The proposed approach was validated with simulated data of ethylene/1-octene and ethylene/1-butene copolymers.

Mathematical Modeling

Microstructures of Polymer Chains Produced on Each Active Site Type

The bivariate MWD/CCD of copolymers produced on each active site type is assumed to follow Stockmayer's bivariate distribution, which is an analytical expression describing the weight distribution of kinetic chain lengths (r) and chemical compositions (F_1) for linear binary copolymers.[12,13] This distribution efficiently quantifies the distributions of molecular weight and comonomer composition due to the statistical nature of copolymerization. Stockmayer's distribution for linear binary copolymers made on each active site type is expressed as follows,

$$w(r,F_1) = r\cdot\tau^2\cdot\exp(-r\cdot\tau)\cdot\frac{1}{\sqrt{2\pi\beta/r}}\cdot\exp\left[-\frac{(F_1-\overline{F_1})^2}{2\beta/r}\right] \qquad (1)$$

$$\beta = \overline{F_1}\cdot(1-\overline{F_1})\cdot\sqrt{1+4\cdot\overline{F_1}\cdot(1-\overline{F_1})\cdot(r_1\cdot r_2-1)} \qquad (2)$$

where $\overline{F_1}$ is the average mole fraction of monomer type 1 in the copolymer (as calculated by the Mayo-Lewis equation), r is the kinetic chain length, r_1 and r_2 are the reactivity ratios for copolymerization ($r_1\cdot r_2=1$ for random copolymers), and (is the ratio of the sum of all transfer rates to the propagation rate. Note that the number average chain length is given by $1/\tau$ and, therefore, the number average molecular weight (M_n) can be calculated as $M_n = M_{repeating\ unit}/\tau$., where $M_{repeating\ unit}$ is the average molar mass of the repeating unit in the copolymer chains.

The MWD component of Stockmayer's distribution (Flory's most probable distribution), can be obtained by integrating Stockmayer's distribution over all chemical compositions:

$$w(r) = r\cdot\tau^2\cdot\exp(-r\cdot\tau) \qquad (3)$$

Similarly, the CCD component of Stockmayer's distribution can be obtained by integrating Stockmayer's distribution over all chain lengths:

$$w(F_1) = \frac{3}{4\sqrt{2\beta\tau}\left[1+\frac{(F_1-\overline{F_1})^2}{2\beta\tau}\right]^{5/2}} \qquad (4)$$

Microstructures of Polymer Chains Produced with Multiple-Site-Type Catalytic Systems

Polymer chain microstructures produced with multiple-site-type catalytic systems can be considered a mixture of polymer chain microstructures produced on each active site type. Therefore, the bivariate MWD/CCD can be calculated from a superposition of Stockmayer's distributions,

$$w(r,F_1) = \sum_{i=1}^{n} m_i w_i(r,F_1) \qquad (5)$$

where n is the number of active site types, m_i is the mass fraction of polymers produced on site type i, and $w_i(r, F_1)$ is the weight distribution function of polymers produced on site type i.

Similarly, the MWD and CCD of polymers produced with multiple-site-type catalytic systems can be obtained with the expressions:

$$w(r) = \sum_{i=1}^{n} m_i w_i(r) \tag{6}$$

$$w(F_1) = \sum_{i=1}^{n} m_i w_i(F_1) \tag{7}$$

where $w_i(r)$ and $w_i(F_1)$ are the MWD and CCD of copolymers produced on site type i, respectively.

Deconvolution Procedure

Theoretically, deconvolution of any weight distribution functions (Equations (5), (6), or (7)) should yield the same set of mass fractions and kinetic parameters. However, separated deconvolutions of MWD and CCD were reported to lead to slightly different results, which is not surprising given that the analytical errors in GPC, TREF and Crystaf are not the same.[6] In this work, a simultaneous deconvolution approach is proposed to obtain a more consistent set of model parameters that can describe the MWD and CCD of polyolefins. This approach should be easily applicable as the bivariate MWD/CCD information required can be obtained experimentally using automated full cross-fractionation (cross-fractionation by GPC/TREF or TREF/GPC)

To perform the deconvolution, the following procedure was used. The calculation was started by assuming that the number of active site types was 2. Simultaneous deconvolution of the bivariate MWD/CCD was performed by matching the experimental data with a superposition of Stockmayer's distribution from all active site type. The objective function (*i.e.*, the sum of the squares of differences between experimental profiles and model predictions) to be minimized is,

$$\text{Objective function} = \sum_{F} \sum_{r} \left[w_{\exp}(r, F_1) - w_{sim}(r, F_1) \right]^2 \tag{8}$$

where $w_{sim}(r, F_1)$ can be calculated with Equation (5). The mass fraction and kinetic parameters for each active site type is estimated and the value of the objective function was recorded. For n active site types, $4n$-1 parameters must be estimated (4 parameters per site, m, $\overline{F_1}$, β, and τ and $\sum_{i=1}^{n} m_i = 1$).

The number of active site types is then gradually increased and the calculation repeated until the value of the objective function stops decreasing with increasing the number of site types.

Validation of Proposed Simultaneous Deconvolution Approach

In order to validate the proposed simultaneous deconvolution approach, simulated data of a model ethylene/1-butene copolymers with five active site types and a model ethylene/1-octene copolymers with four active site types were used. The mass fractions of polymers produced on each site type and the kinetic parameters of each site type for both copolymers are summarized in Table 1 and 2. Note that, in this study, F_1 represents the mole fraction of ethylene in the copolymer. The simulated chain microstructures of both model copolymer samples are shown in Figure 1 and 2.

Table 1.
Model parameters for the model ethylene/1-butene copolymer.

Model parameters	Active site type				
	1	2	3	4	5
m	0.0160	0.2300	0.4000	0.2000	0.1540
$\overline{F_1}$	0.8838	0.9208	0.9500	0.9795	0.9841
β	0.0087	0.1427	0.3461	0.1177	0.1397
M_n	3,960	12,700	32,000	72,800	181,000

Table 2.
Model parameters for the model ethylene/1-octene copolymer.

Model parameters	Active site type			
	1	2	3	4
m	0.2790	0.3730	0.2290	0.1190
$\overline{F_1}$	0.9701	0.9907	0.9931	0.9959
β	0.2324	0.0447	0.0398	0.0437
M_n	56,561	122,322	302,387	735,595

Results and Discussion

Simultaneous deconvolution results of both model ethylene/1-butene and ethylene/1-octene copolymers are shown in Figure 3 and 4. By comparing Figure 3 with Figure 1a and Figure 4 with Figure 2a, it can be observed that two active site types cannot describe the bivariate MWD/CCD of model samples adequately. As the number of site types increases, the agreement between predictions and the "experimental" bivariate MWD/CCD increases. The parameters estimated for both model samples using a different number of active site types are summarized in Table 3 and 4.

The "optimum" number of active site types needed to describe the bivariate MWD/CCD can be determined by observing how the value of the objective function varies when the number of active site types is increased, as shown in Table 5 and 6. The sum of squares of the deviation between predictions and the model "experimental" value decreases significantly with the addition

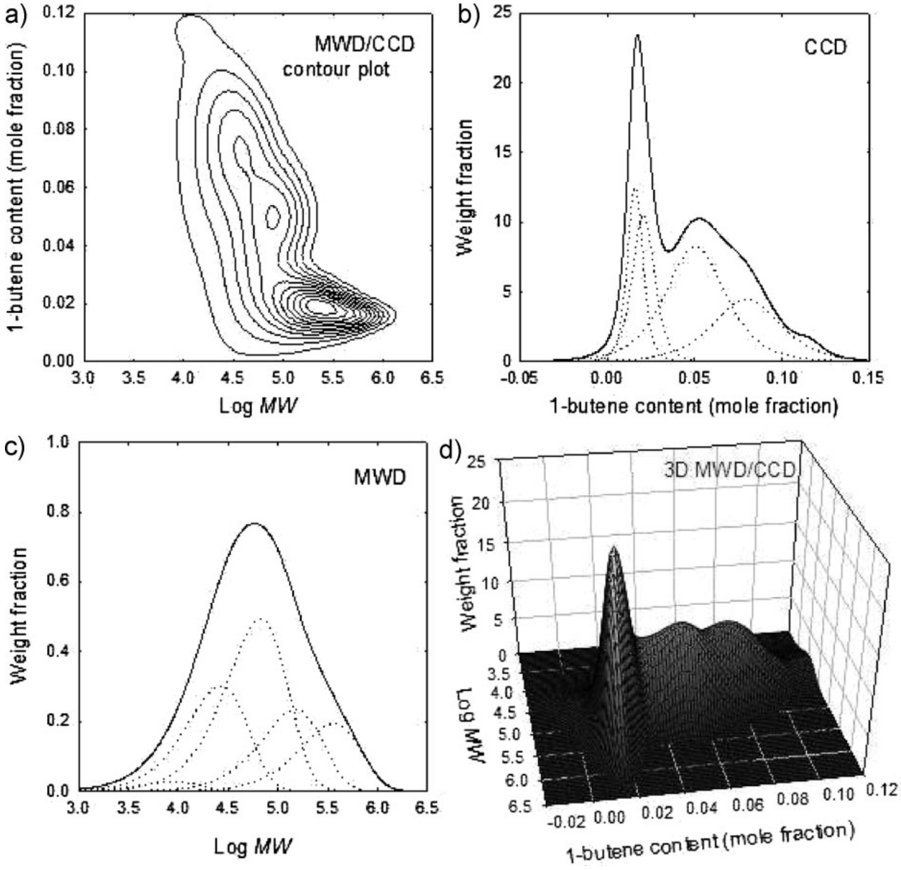

Figure 1.
Chain microstructures of a model ethylene/1-butene copolymer: (a) MWD/CCD contour plot, (b) CCD, (c) MWD, and (d) MWD/CCD.

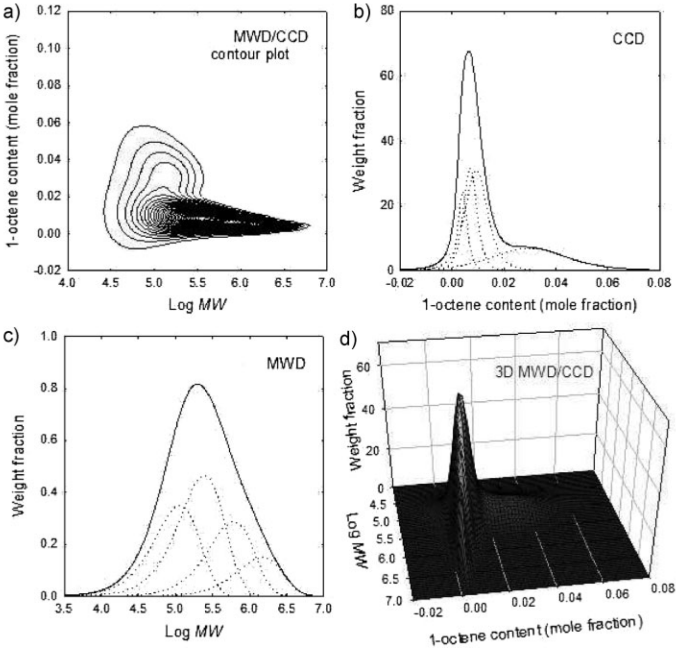

Figure 2.
Chain microstructures of a model ethylene/1-octene copolymer: (a) MWD/CCD contour plot, (b) CCD, (c) MWD, and (d) MWD/CCD.

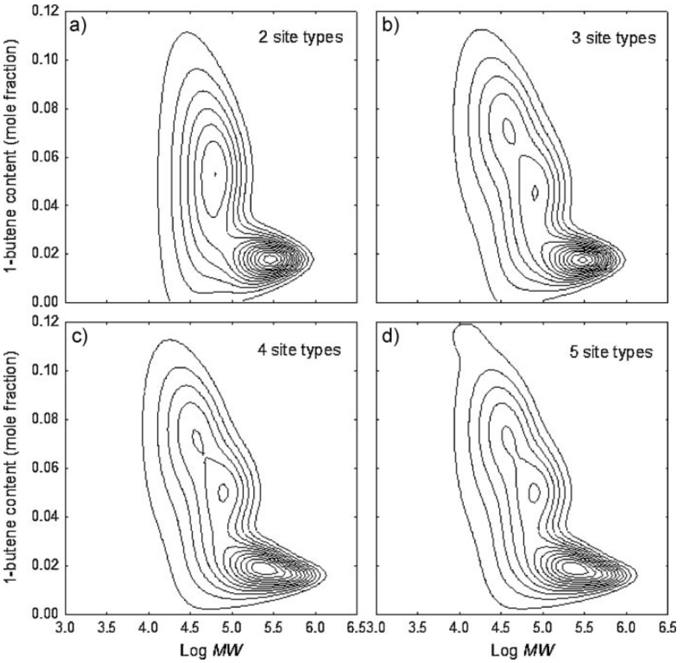

Figure 3.
Deconvolution of a model ethylene/1-butene copolymer using a different number of site types: (a) 2, (b) 3, (c) 4, and (d) 5.

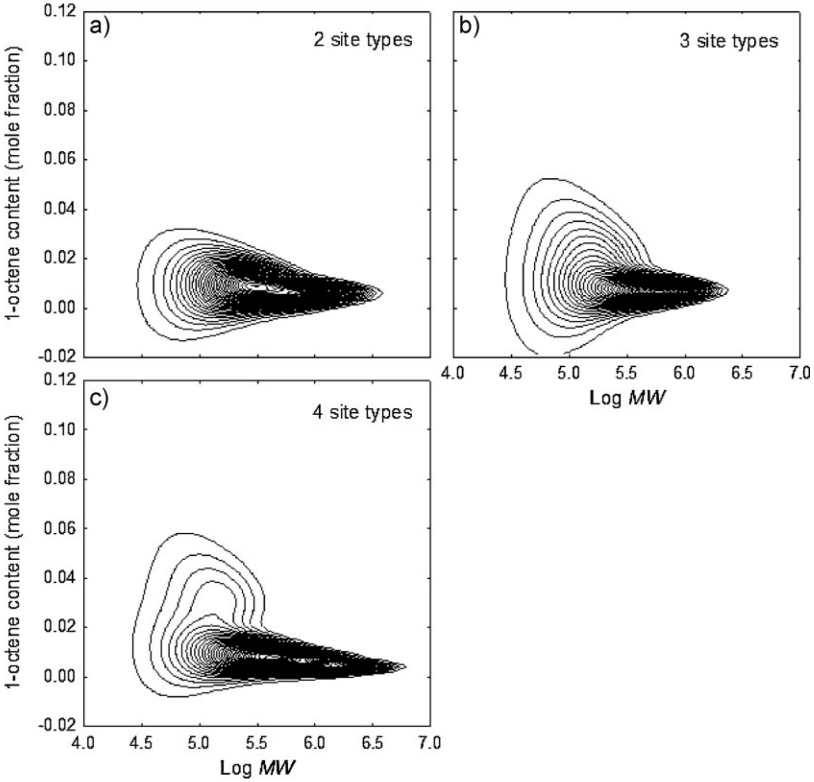

Figure 4.
Deconvolution of a model ethylene/1-octene copolymer using a different number of site types: (a) 2, (b) 3, and (c) 4.

Table 3.
Summary of model parameters for the simultaneous deconvolution of the bivariate MWD/CCD of a model ethylene/1-butene copolymer.

Parameters	Active site type				
	1	2	3	4	5
2 site types					
m	0.683000	0.317000			
$\overline{F_1}$	0.946655	0.982165			
β	1.152648	0.321425			
M_n	24,946	116,378			
3 site types					
m	0.238562	0.473654	0.287784		
$\overline{F_1}$	0.922503	0.953653	0.982364		
β	0.284059	0.972162	0.279254		
M_n	12,112	32,666	120,341		
4 site types					
m	0.239864	0.406473	0.200236	0.153427	
$\overline{F_1}$	0.920499	0.949916	0.979517	0.984092	
β	0.275411	0.666501	0.229042	0.274423	
M_n	12,281	32,042	73,290	181,671	
5 site types					
m	0.016000	0.230000	0.400000	0.200000	0.154000
$\overline{F_1}$	0.883796	0.920827	0.950019	0.979482	0.984077
β	0.014626	0.254063	0.642755	0.228368	0.272882
M_n	3,960	12,700	32,000	72,800	181,000

Table 4.
Summary of model parameters for the simultaneous deconvolution of the bivariate MWD/CCD of a model ethylene/1-octene copolymer.

Parameters	Active site type			
	1	2	3	4
2 site types				
m	0.636000	0.364000		
$\overline{F}_1$	0.990233	0.994167		
β	0.341577	0.282844		
M_n	103,190	413,244		
3 site types				
m	0.341205	0.329025	0.329771	
$\overline{F}_1$	0.983455	0.992978	0.913425	
β	1.041264	0.202136	0.000185	
M_n	66,889	248,082	452,153	
4 site types				
m	0.279000	0.373000	0.229000	0.119000
$\overline{F}_1$	0.970050	0.990690	0.993060	0.995940
β	0.833835	0.172853	0.154990	0.172088
M_n	56,561	122,322	302,387	735,595

of active site type when additional site types are necessary to improve the fitting; however, it will change little or even increase when redundant active site types are added, which lead to redundant parameters and over fit model. For the two cases investigated herein, the number of active site types could be easily and correctly determined, i.e., 5 active site types for an ethylene/1-butene copolymer and 4 active site types for an ethylene/1-octene copolymer.

Table 5.
Value of the objective function as a function of the number of active site types for a model ethylene/1-butene copolymer.

Number of active site types	Objective Function Equation (8)
2	7.61×10^{-1}
3	2.19×10^{-1}
4	9.61×10^{-3}
5	2.90×10^{-6}
6	2.75×10^{-5}

Table 6.
Value of the objective function as a function of the number of active site types for a model ethylene/1-octene copolymer.

Number of active site types	Objective Function Equation (8)
2	4.43×10^{-3}
3	2.09×10^{-3}
4	1.26×10^{-13}
5	3.53×10^{-4}

From both case studies, it is clear that the proposed simultaneous deconvolution approach is very effective for identifying the number of active site types and chain microstructural parameters for each site used to produce the model copolymer. This approach can be extended to experimental resins to investigate the influence of operation parameters on chain microstructures produced on each active site type, help better quantify the main characteristics of multiple-site catalysts, and led to a better control of polymer properties made by these systems.

Conclusion

A new approach for identifying the number of active site types and polymer chain microstructural parameters produced on each active site type for ethylene/1-olefin copolymers synthesized with multiple-site-type catalytic systems was proposed. This approach is based on the simultaneous deconvolution of the bivariate MWD/CCD, which can be obtained experimentally using GPC/TREF or TREF/GPC cross-fractionation techniques. The proposed approach was validated with model ethylene/1-butene and ethylene/1-octene copolymers, and showed to correctly recover the parameters used in the construction of the bivariate MWD/CCD of the model polymers.

Acknowledgements: Siripon Anantawaraskul thanks financial supports from the Thailand Research Fund (TRF) and Center of Excellence for Petroleum, Petrochemicals and Advanced Materials (PPAM).

[1] J. B. P. Soares, A. E. Hamielec, *Polymer* **1995**, *36*, 2257.
[2] J. B. P. Soares, *Polym React Eng.* **1998**, *6*, 225.
[3] J. B. P. Soares, R. F. Abbott, J. N. Willis, X. Liu, *Macromol Chem Phys.* **1996**, *197*, 3383.
[4] D. E. Thompson, K. B. McAuley, P. J. McLellan, *Macromol React Eng.* **2007**, *1*, 523.
[5] D. E. Thompson, K. B. McAuley, P. J. McLellan, *Macromol React Eng.* **2007**, *1*, 264.
[6] A. A. Da Silva Filho, J. B. P. Soares, G. B. de Galland, *Macromol Chem Phys.* **2000**, *201*, 1226.
[7] A. Faldi, J. B. P. Soares, *Polymer* **2001**, *42*, 3057.
[8] A. Ortin, B. Monrabal, J. Sancho-Tello, *Macromol Symp.* **2007**, *257*, 13.
[9] W. W. Yau, *Macromol Symp.* **2007**, *257*, 29.
[10] A. A. Alghyamah, J. B. P. Soares, *Macromol. Rapid Commun.*, submitted.
[11] A. A. Alghyamah, J. B. P. Soares, *Macromol. Symp.*, submitted.
[12] W. H. Stockmayer, *J Chem Phys.* **1945**, *13*, 199.
[13] R. Simha, H. Branson, *J Chem Phys.* **1944**, *12*, 253.