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**Deb Sarzotti**

**Abstract**

**Presentation**

# ETHYLENE AND PROPYLENE COPOLYMERIZATION WITH NON-CONJUGATED DIENES: SYNTHESIS AND CHARACTERIZATION

D.M. Sarzotti, L.C. Simon and J.B.P. Soares

*Institute for Polymer Research, Department of Chemical Engineering, University of Waterloo*

## Introduction

Copolymerization of non-conjugated  $\alpha,\omega$ -dienes with ethylene or propylene yields functional polyolefins with unreacted vinyl groups that can be used to synthesize polyolefins with unique structures.<sup>[1]</sup> These materials have sparked great interest because the reactive vinyl unsaturations can be used to prepare polyolefins with polar or heteroatomic (e.g., N, O) functionalities. Furthermore, polyolefin copolymerization with dienes can generate structures that act as macromonomers (very long  $\alpha$ -olefin chains) and promote the incorporation of long chain branches (LCB) along the polymer backbone. With several coordination catalyst systems, non-conjugated dienes are also capable of undergoing cyclopolymerization resulting in polymers containing cyclic structures along the main chain.

Three types of propagation reactions are possible in the copolymerization of ethylene or propylene with linear, non-conjugated  $\alpha,\omega$ -dienes: 1,2- or 2,1-addition reactions, leaving pendant vinyl groups in the polymer; addition reactions of diene followed immediately by intramolecular cyclization, resulting in the formation of 1,3-cycloalkane structures along the polymer backbone; and reactions between a pendant double bond in the polymer chain with another propagating chain, forming a LCB or crosslinking point.<sup>[2]</sup>

## Ethylene/1,7-Octadiene Copolymerization

We have studied the copolymerization of ethylene with 1,7-octadiene (OD) using a methylaluminoxane (MAO) activated constrained geometry catalyst (dimethylsilyl(*N*-*tert*-butylamido) (tetramethylcyclopentadienyl)titanium dichloride) at 140°C in toluene. The catalyst activity as well as the molecular weights, chemical composition distributions and the number of vinyl functionalities of the resulting copolymers were determined (Table 1). Over the whole range of OD feed concentration investigated, the weight average molecular weight,  $M_w$ , and polydispersity index,  $M_w/M_n$ , increase with increasing OD in the feed. These increases are the result of the production of chains with long chain branches by the incorporation of pendant

double bonds into separate growing polymer chains. Table 1 also shows that the overall number of vinyl unsaturations increases for higher OD contents. The fact that the number of vinyl groups present in the final product increases with increasing OD content indicates that both vinyl groups have been polymerized for only a fraction of the total OD units incorporated.

**Table 1** Ethylene/OD copolymerization results.

run	OD in feed <sup>a</sup> (mol-%)	activity (kg/mol <sub>Ti</sub> ·h)	$M_n^b$ (kg/mol)	$M_w/M_n^b$	$T_c^c$ (°C)	vinyl groups <sup>d</sup> (/1000 C)	vinyl groups <sup>e</sup> (/1000 C)
1	0	15000	32	3.1	85	0.2	0.4
2	0.16	26000	35	5.6	78	1.3	1.3
3	0.31	25000	31	11	69	2.9	2.6
4	0.37	21000	27	14	64	3.5	3.1
5	0.41	16000	28	17	62	4.0	3.8
6	0.46	8000	20	17	57	3.8	4.4

<sup>a</sup> Polymerization conditions:  $T = 140$  °C;  $V$  (toluene) = 400 mL;  $P$  (C<sub>2</sub>H<sub>4</sub>) = 255 psig; [catalyst] = 9 μmol/L; [MAO] = 19.5 mmol/L; polymerization time = 10 min.

<sup>b</sup> Determined by high-temperature GPC.

<sup>c</sup> Peak crystallization temperature determined with Crystaf in TCB.

<sup>d</sup> Number of double bonds per 1000 carbon atoms calculated from FT-IR spectra.

<sup>e</sup> Number of double bonds per 1000 carbon atoms calculated from <sup>1</sup>H NMR spectra.

The distribution of unsaturated end groups was quantified by <sup>1</sup>H NMR and the amounts of vinylidene, vinyl and vinylene functionalities per chain were determined, revealing the relationships between of chain transfer mechanisms and OD content.

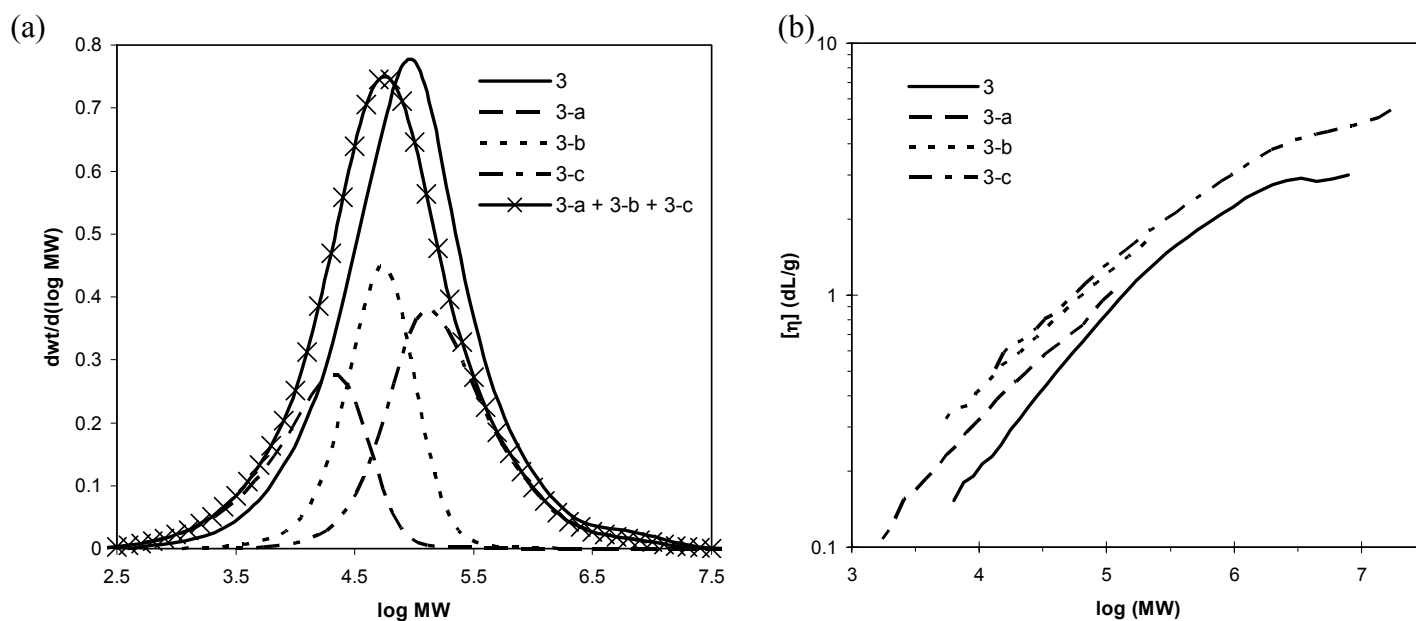
Analysis of ethylene/OD copolymers by <sup>13</sup>C NMR indicates the formation of both 1,3-cycloheptane (CY<sub>7</sub>) and 1,5-cyclononane (CY<sub>9</sub>) structures. The relative amounts of CY<sub>7</sub> and CY<sub>9</sub> units appear to be independent of OD content with approximately 53 % of the total rings being CY<sub>9</sub> units. The ratio of cyclic units to vinyl groups is constant over the range of compositions analyzed, although the number of branches increases relative to both cyclic units and vinyl groups. From the results gathered, it can be concluded that the OD insertion mode is independent of OD content and is kinetically controlled at the polymerization conditions considered in this work.



### **Ethylene/1,7-Octadiene Copolymer Molecular Weight Fractions**

An ethylene homopolymer sample (run 1) and the two ethylene/OD copolymers with the lowest OD contents (runs 2 and 3) were fractionated by molecular weight using a solvent/non-solvent

technique. Figure 1(a) shows the molecular weight distributions of a whole polymer (runs 3) and those of its fractions scaled according to the weight percentage of the total polymer that each represents. Plots of intrinsic viscosity as a function of molecular weight for an ethylene/OD copolymer (run 3) and its fractions (Figure 1(b)) clearly demonstrate that long chain branching increases with increasing molecular weight, as expected.

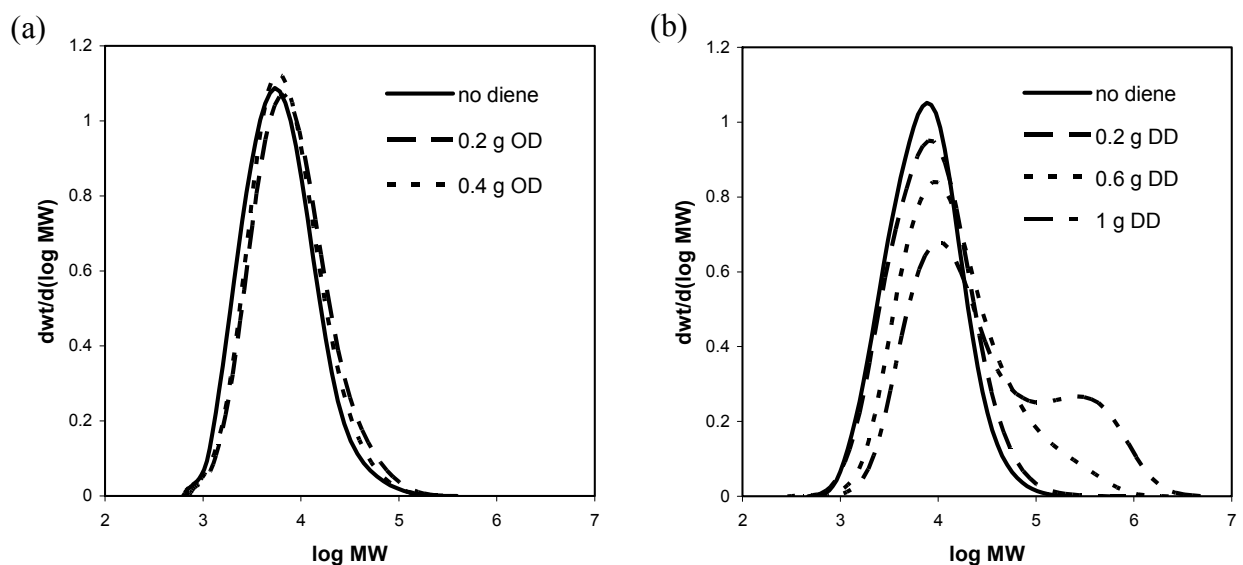


**Figure 1** (a) Molecular weight distributions of ethylene/OD copolymer (run 3) and three fractions. Distributions of the fractions have been scaled by weight percentage and summed for comparison; (b) Intrinsic viscosity,  $[\eta]$ , of an ethylene/OD copolymer (run 3) and its fractions as a function of molecular weight measured by differential viscometry during GPC analysis.

Molecular weight fractions of the copolymer produced in run 3 were further analyzed by  $^1\text{H}$  and  $^{13}\text{C}$  NMR, revealing that the number of cyclic units per 1000 carbon atoms and the relative quantities of  $\text{CY}_7$  and  $\text{CY}_9$  units are independent of molecular weight. As molecular weight increased, the vinyl group content decreased and the number of branches per 1000 carbon atoms increased, confirming that the observed increase in molecular weight with increasing OD content is a result of the incorporation of pendant vinyl groups to form long chain branched or crosslinked structures.

## Propylene/1,7-Octadiene and Propylene/1,9-Decadiene Copolymerization

The copolymerization of propylene with both OD and 1,9-decadiene (DD) using *rac*-dimethylsilanediylbis(2-methyl-4-phenylindenyl)zirconium dichloride/MAO in toluene at temperatures above 100°C has been investigated. The molecular weight distributions of propylene/OD and propylene/DD copolymers synthesized at 120°C with 50 psi monomer pressure are shown in Figure 2. Preliminary results indicate that OD almost exclusively undergoes cyclization following insertion but that DD is incorporated as pendant 1-octenyl branches which are subsequently polymerized, resulting in materials with significant levels of long chain branching.



**Figure 2** (a) Molecular weight distributions of propylene/OD copolymers; (b) Molecular weight distributions of propylene/DD copolymers.

## References

- [1] T. Uozumi, G. Tian, C.-H. Ahn, J. Jin, S. Tsubaki, T. Sano, K. Soga, *J. Polym. Sci., Part A: Polym. Chem.* **2000**, *38*, 1844.
- [2] N. Naga, A. Toyota, *Macromol. Rapid. Commun.* **2004**, *25*, 1623.

# Ethylene and propylene copolymerization with non-conjugated dienes: Synthesis and characterization

Deborah Sarzotti

Department of Chemical Engineering, University of Waterloo

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## Outline

- Introduction
- Propylene copolymerization
  - 1,7-octadiene
  - 1,9-decadiene
- Ethylene copolymerization
  - 1,7-octadiene
  - MW fractionation and compositional analysis
- Conclusions

## Introduction

- Non-conjugated  $\alpha,\omega$ -dienes
- Copolymerization of dienes with ethylene (E) or propylene (P) yields polyolefins with unreacted vinyl groups that can be used to synthesize materials with unique structures
  - incorporate polar or heteroatomic functionalities
  - promote long chain branching
  - cyclic structures along main backbone

## Background

- Three possible propagation reactions:
  - 1,2- or 2,1-addition  $\rightarrow$  pendant vinyl groups
  - addition followed by intramolecular cyclization  $\rightarrow$  1,3-cycloalkane
  - addition of a pendant double bond into another propagating chain  $\rightarrow$  long chain branch or crosslinking point
- 1,5-hexadiene preferentially inserted as cyclopentane
- insertion mode of 1,7-octadiene (OD) dependent on catalyst and polymerization conditions
- little work with 1,9-decadiene (DD)

## P/OD copolymers

Copolymerization of propylene and OD with metallocene/MAO:

run	P (psig)	[OD] (mol/L)	activity <sup>a</sup> (kg·mol <sup>-1</sup> ·atm <sup>-1</sup> ·h <sup>-1</sup> )	$M_n^b$ (kg/mol)	$M_w/M_n^b$	$T_m,final^c$ (°C)	$T_g^c$ (°C)	crystallinity <sup>d</sup> (%)
P/OD-1	50	0	10500	4.8	2.2	132	-	36
P/OD-2	50	0.012	7600	5.4	2.3	129	-12	30
P/OD-3	50	0.024	5200	5.0	2.1	114	-9	21
P/OD-4	70	0	12700	5.3	2.7	139	-	41
P/OD-5	70	0.012	10900	5.9	2.7	133	-12	37
P/OD-6	70	0.024	10100	6.3	2.8	128	-11	35
P/OD-7	70	0.036	10100	6.7	2.7	123	-9	26

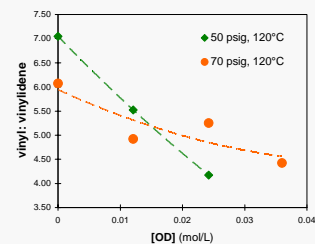
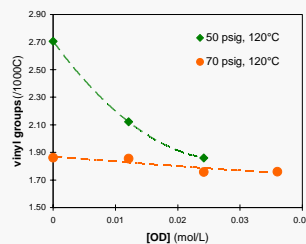
<sup>a</sup> Polymerization conditions:  $T = 120^\circ\text{C}$ ;  $V$  (toluene) = 150 mL; [catalyst] = 3.3  $\mu\text{mol/L}$ ; Al/catalyst = 500; polymerization time = 10 min.

<sup>b</sup> Determined by high-temperature GPC.

<sup>c</sup> Determined by DSC at a heating rate of  $10^\circ\text{C}/\text{min}$  following cooling at the same rate.

<sup>d</sup> Relative to the enthalpy of fusion of 100% crystalline PP, 209 J/g.

## P/OD copolymers – <sup>1</sup>H NMR



## P/DD copolymers

Copolymerization of propylene and DD with metallocene/MAO:

run	T (°C)	[DD] (mol/L)	activity <sup>a</sup> (kg/mol M-atm·h)	M <sub>n</sub> <sup>b</sup> (kg/mol)	M <sub>w</sub> /M <sub>n</sub> <sup>b</sup>	T <sub>m,final</sub> <sup>c</sup> (°C)	T <sub>c</sub> <sup>c</sup> (°C)	crystallinity <sup>d</sup> (%)
P/DD-1	120	0	10500	4.8	2.2	132	-	36
P/DD-2	120	0.010	6300	5.5	2.3	n.m.	n.m.	n.m.
P/DD-3	120	0.029	4500	8.2	4.7	101	-5	- <sup>e</sup>
P/DD-4	120	0.048	2700	11.4	11.5	n.m.	n.m.	n.m.
P/DD-5	105	0	14000	9.9	2.4	148	-	43
P/DD-6	105	0.010	16900	11.1	3.4	n.m.	n.m.	n.m.
P/DD-7	105	0.029	14900	14.9	11.9	121	-4	18
P/DD-8	105	0.048	10400	17.7	21.5	111	-6	- <sup>e</sup>

n.m. - not measured

<sup>a</sup> Polymerization conditions: P(C<sub>3</sub>H<sub>6</sub>) = 50 psi; V (toluene) = 150 mL; [catalyst] = 3.3 μmol/L; Al:catalyst = 500; polymerization time = 10 min.

<sup>b</sup> Determined by high-temperature GPC.

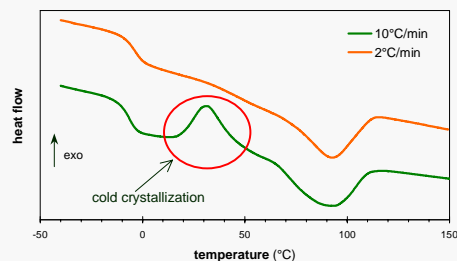
<sup>c</sup> Determined by DSC at a heating rate of 10°C/min following cooling at the same rate.

<sup>d</sup> Relative to the enthalpy of fusion of 100% crystalline PP, 209 J/g.

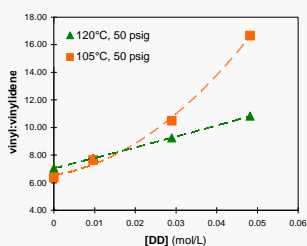
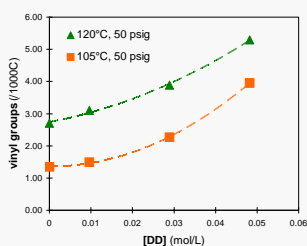
<sup>e</sup> Not calculated due to occurrence of cold crystallization.

## P/DD copolymers – DSC

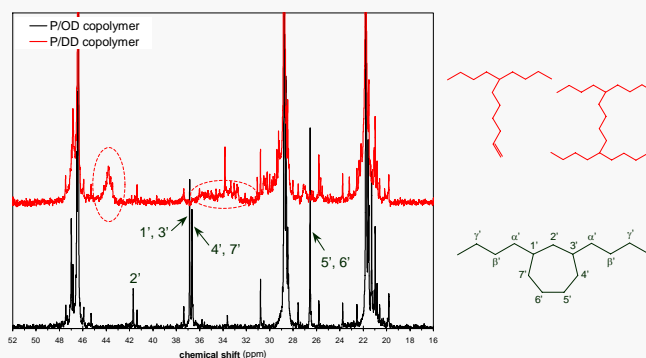
DSC analysis of P/DD-8 at different heating rates



## P/DD copolymers – <sup>1</sup>H NMR

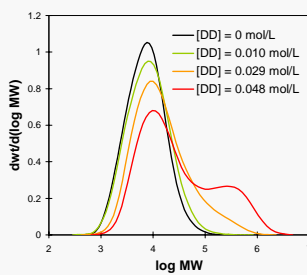
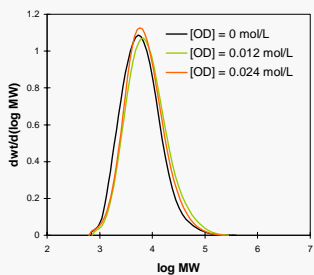


## P/OD and P/DD copolymers – <sup>13</sup>C NMR



## OD & DD copolymers - MWD

Same polymerization conditions (T = 120°C, P(C<sub>3</sub>H<sub>6</sub>) = 50 psig)



## E/OD copolymers

Copolymerization of ethylene and OD with CGC-Ti/MAO [1]:

run	OD in feed <sup>a</sup> (mol-%)	activity (kg/mol <sub>Ti</sub> ·h)	M <sub>n</sub> <sup>b</sup> (kg/mol)	M <sub>w</sub> /M <sub>n</sub> <sup>b</sup>	T <sub>c</sub> <sup>c</sup> (°C)	vinyl groups <sup>d</sup> (/1000 C)	rings <sup>e</sup> (/1000 C)	CY <sub>7</sub> /CY <sub>9</sub> <sup>f,g</sup>
1	0	15000	32	3.1	85	0.4	-	-
2	0.16	26000	35	5.6	78	1.3	2.08	0.95
3	0.31	25000	31	11	69	2.6	4.98	0.96
4	0.37	21000	27	14	64	3.1	-	-
5	0.41	16000	28	17	62	3.8	7.70	0.92
6	0.46	8000	20	17	57	4.4	-	-

<sup>a</sup> Polymerization conditions: T = 140 °C; V (toluene) = 400 mL; P (C<sub>2</sub>H<sub>4</sub>) = 255 psig; [catalyst] = 9 μmol/L; [MAO] = 19.5 mmol/L; polymerization time = 10 min.

<sup>b</sup> Determined by high-temperature GPC.

<sup>c</sup> Peak crystallization temperature determined with Crystaf in TCB.

<sup>d</sup> Number of double bonds per 1000 carbon atoms calculated from <sup>1</sup>H NMR spectra.

<sup>e</sup> Determined by <sup>13</sup>C NMR.

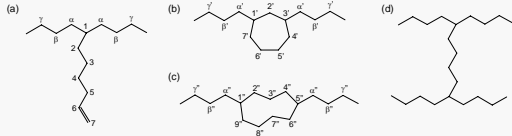
<sup>f,g</sup> Number of cycloheptane units (CY<sub>7</sub>) divided by number of cyclononane units (CY<sub>9</sub>).

[1] D.M. Sarzotti, L.C. Simon, J.B.P. Soares, *Macromol. Mater. Eng.* **2005**, in press.

## E/OD copolymers

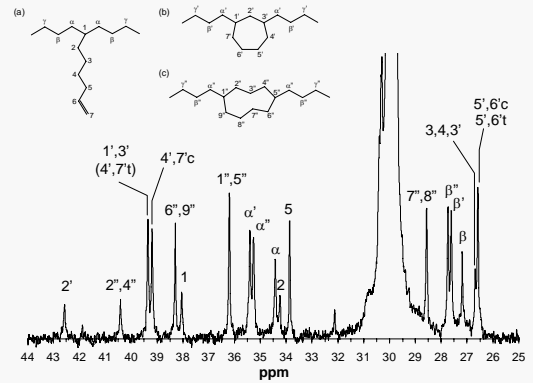
### Four propagation reactions:

- 1,2- or 2,1-addition insertion
- intramolecular cyclization following addition
- intramolecular cyclization in the penultimate position [2]
- addition of pendant double bond (macromonomer)

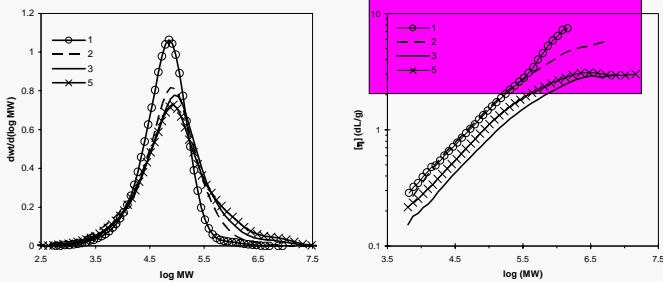


[2] N. Naga, A. Toyota, *Macromol. Rapid. Commun.* **2004**, *25*, 1623.

## E/OD copolymers



## E/OD copolymers -

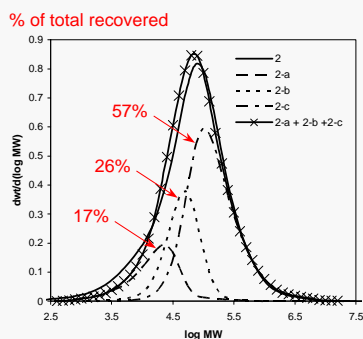


## MW Fractionation

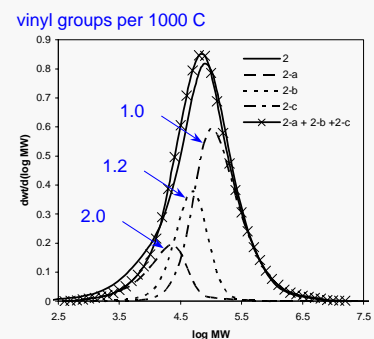
- Investigate compositional uniformity
  - distribution of structures resulting from different modes of diene incorporation
- Pietikäinen *et al.* [3] used thermal analysis and the segregation fractionation technique
  - no physical separation
- Samples fractionated by molecular weight
  - Solvent/non-solvent technique
  - low, medium and high MW fractions with 50, 58 and 100% solvent

[3] P. Pietikäinen, P. Starck, J. V. Seppälä, *J. Polym. Sci., Part A: Polym. Chem.* **1999**, *37*, 2379.

## Fractions of E/OD copolymer

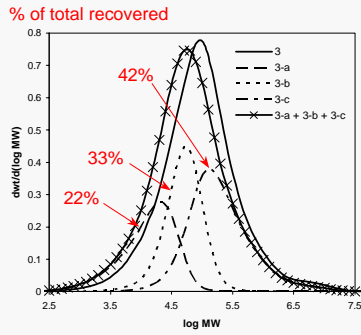


## Fractions of E/OD copolymer

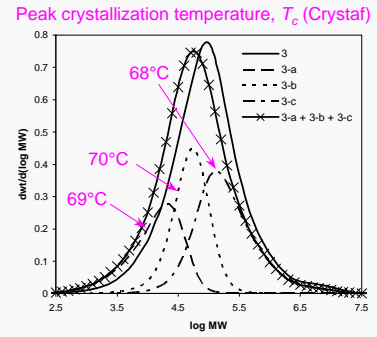




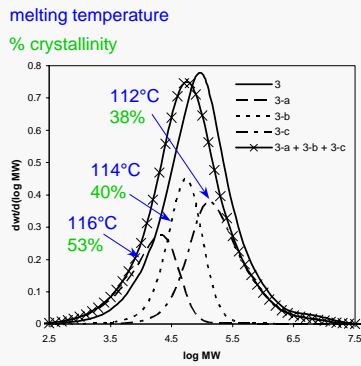
## Fractions of E/OD copolymer



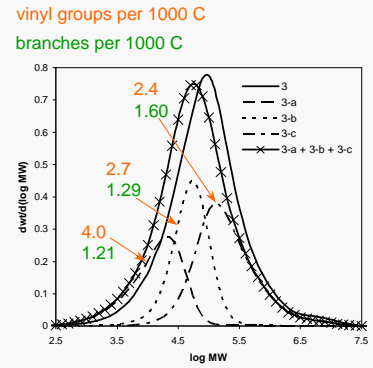
## Fractions of E/OD copolymer



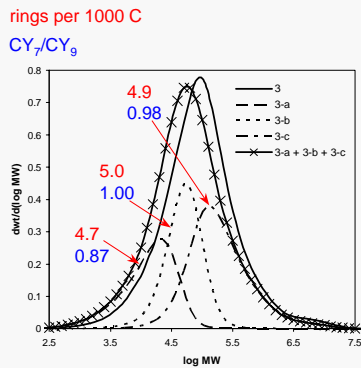
## Fractions of E/OD copolymer



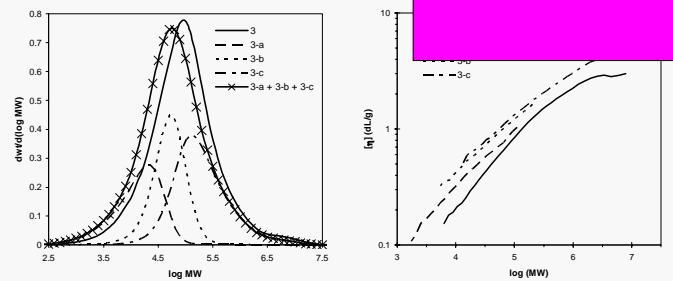
## Fractions of E/OD copolymer



## Fractions of E/OD copolymer



## Fractions of E/OD copolymer



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## Conclusions

- Propylene copolymerization by metallocene/MAO
    - 1,7-octadiene incorporated as cycloheptane units
    - 1,9-decadiene incorporated as 1-octenyl branches and pendant vinyls incorporated to form long chain branches
  - Ethylene copolymerization by CGC-Ti/MAO
    - 1,7-octadiene incorporated as cycloheptane and cyclononane units as well as 1-hexenyl branches
    - fractionation by MW indicates that distribution of structures due to OD incorporation is uniform
-