Chain Microstructure, Crystallization and Morphology of Olefinic Blocky Copolymers (OBCs)

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Introduction: Recent developments in polyolefin synthesis by The Dow Chemical Company enable to synthesize olefinic blocky copolymers (OBCs) in a continuous process with two catalysts and chain shuttling agent.[1] The OBCs have a statistical multi-block chain structure with a distribution both in block length and in the number of block per chain. The OBCs consist of crystallizable ethylene-octene blocks (hard blocks) with very low comonomer content, alternating with amorphous ethylene-octene blocks (soft bocks) with high comonomer content. Due to the dispersity in both the block length and composition, the chain structure and its effect on morphology of OBCs are difficult to characterize.

Method

1. The chain microstructure of three OBCs was analyzed by ^{13}C-NMR with two-site first-order Markovian model, shown in Table 1.
2. The presence of partially ordered phases was measured by DSC and WAXD.
3. Crystalline morphology was examined by SAXS and POM and TEM.

Table 1. Molecular characteristics of three OBCs

Sample	M_n (kg/mol)	M_w/M_n	C_8 in hard blocks (mol %)	C_8 in soft blocks (mol %)	ΔC_8 (mol %)	Net C_8 content (mol %)	Wt % of hard blocks
OBC-A	29	3.1	1.4	23.7	22.3	13.2	35
OBC-B	40	2.3	1.0	21.9	20.9	15.9	20
OBC-C	30	2.1	0.9	25.0	24.1	13.2	36

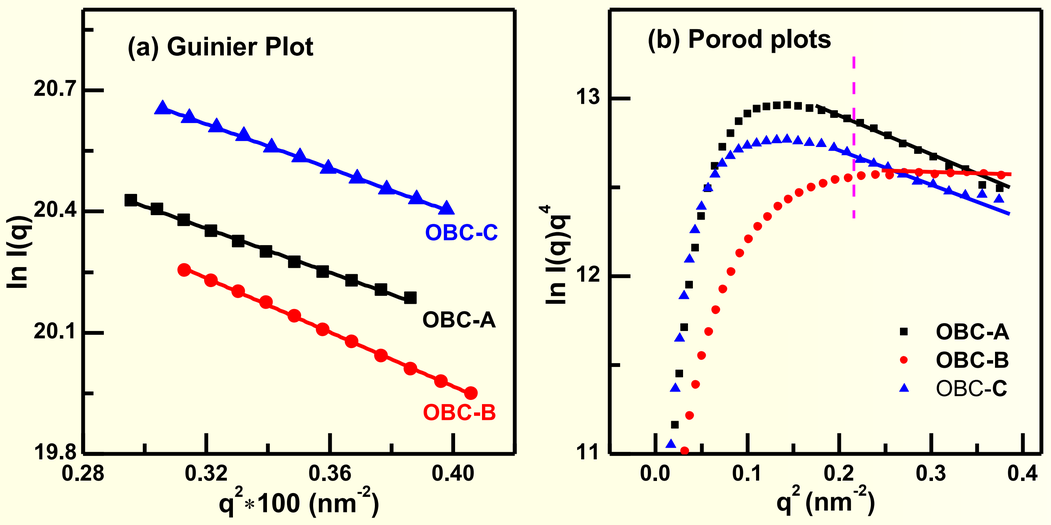


Figure 3. The Guinier plots (a) at low q and Porod plots (b) at large q for three OBCs at room temperature.

Result

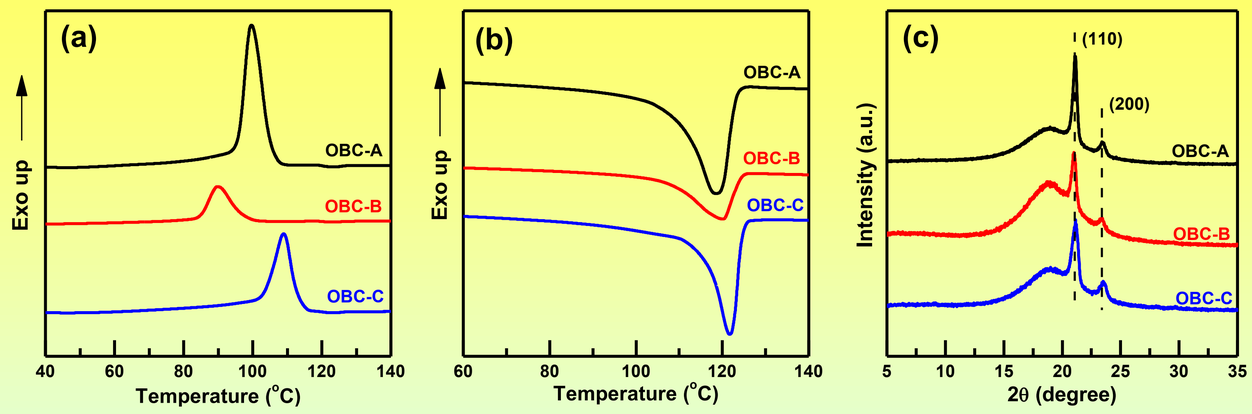
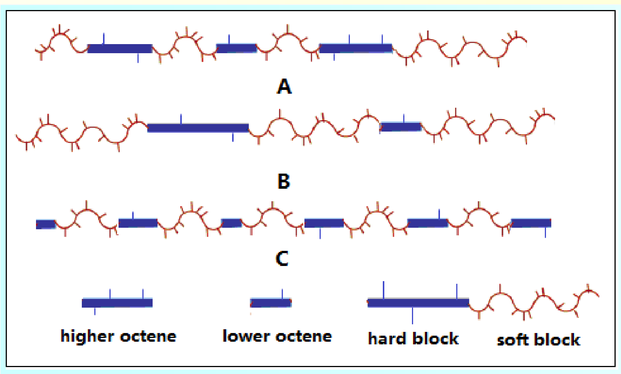


Figure 1. Non-isothermal crystallization curves (a), subsequent melting curves (b) and WAXD patterns (c) of three OBC samples.

Table 2. Thermal properties and crystallinity of the three OBC samples

Samples	T_m [°C]	T_c [°C]	ΔH_m [J g^{-1}]	ΔH_c [J g^{-1}]	X_c^{DSC}	X_c^{WAXD}	X_{vol}
OBC-A	119	103	45.5	44.6	15.7%	25.5%	22.6%
OBC-B	120	90	20.1	19.8	7.0%	13.4%	11.7%
OBC-C	122	106	35.8	36.7	12.3%	26.4%	23.5%



Scheme 1. Schematic chain structures for three OBC samples.

The chain architecture of three OBCs is established based on ^{13}C-NMR and the combination of DSC and WAXD

Porod plots show that the partially ordered phases in OBC-A and OBC-C are mainly located at the interface between the crystalline and amorphous phases, but exist as separated microdomains and there is no interphase between the crystalline and amorphous layers in OBC-B.[2-3]

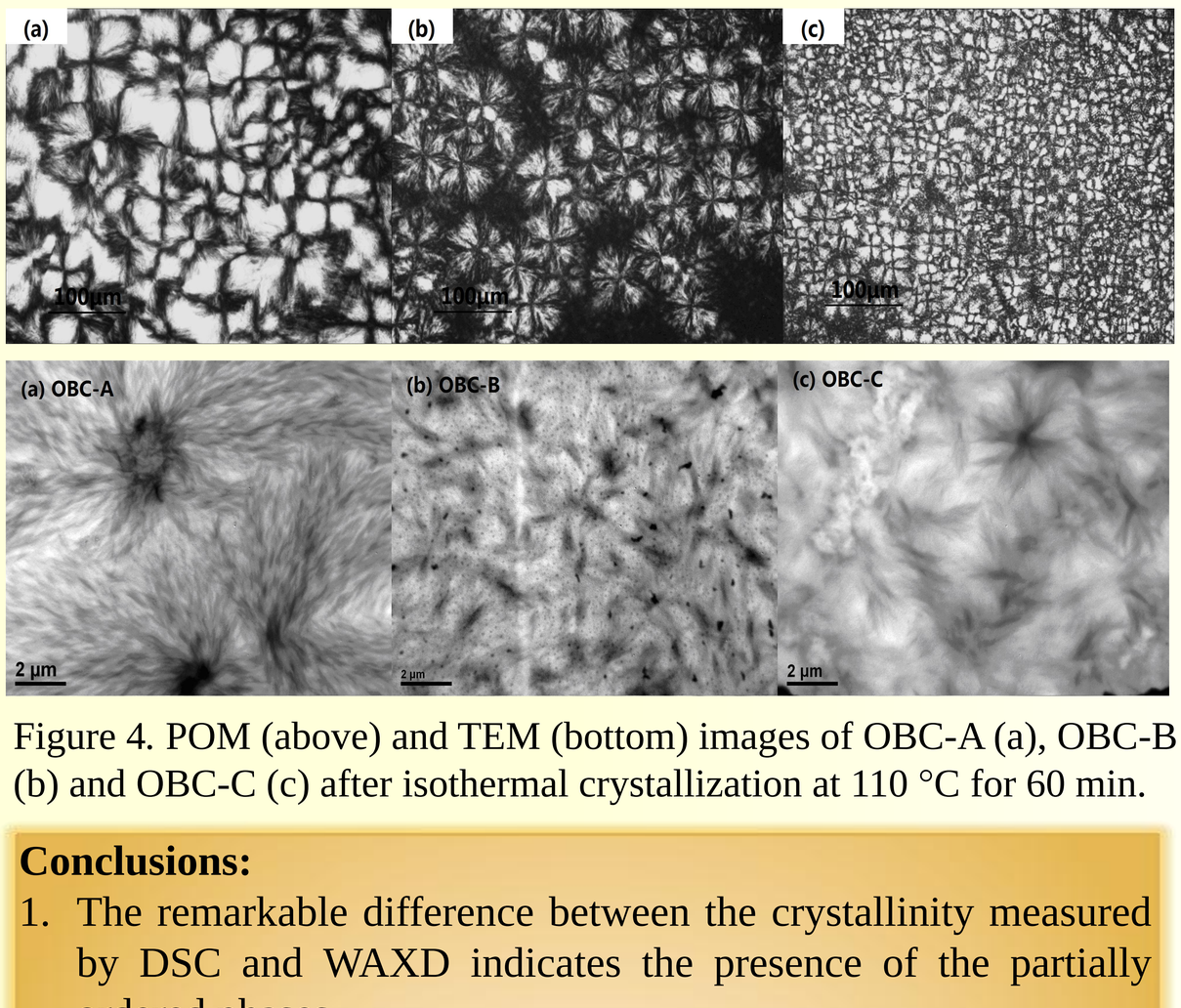


Figure 4. POM (above) and TEM (bottom) images of OBC-A (a), OBC-B (b) and OBC-C (c) after isothermal crystallization at 110 °C for 60 min.

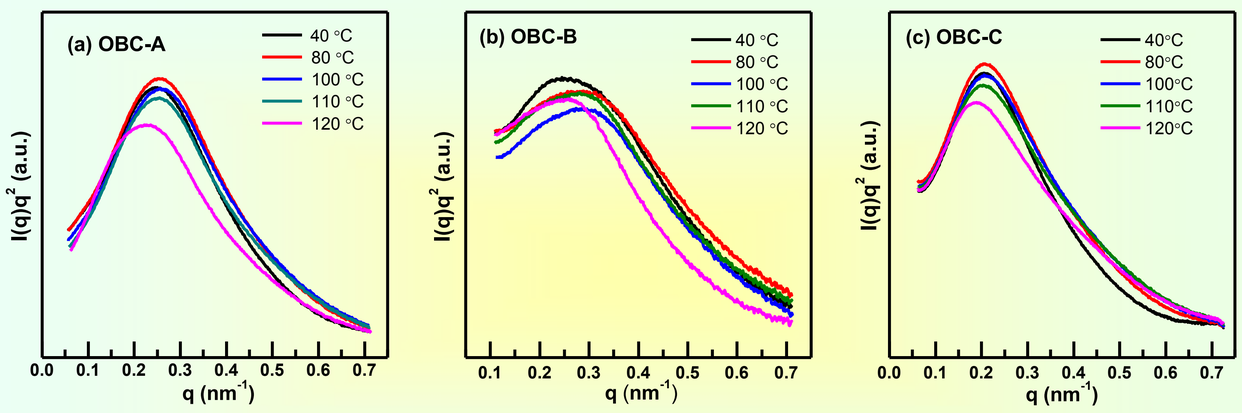


Figure 2. Lorentz-corrected SAXS profiles of OBC-A (a), OBC-B (b) and OBC-C (c) at various temperatures.

Conclusions:

1. The remarkable difference between the crystallinity measured by DSC and WAXD indicates the presence of the partially ordered phases.
2. The partially ordered phases are mainly located at the interface between crystalline and amorphous phases in OBC-A and OBC-C, but exist as separated microdomains in OBC-B.

Reference:

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2. Z. Z. Tong, J. T. Xu, S. J. Xia, Z. Q. Fan, *Polym. Int.* **2013**, 228-237.
3. Z. Z. Tong, J. Huang, B. Zhou, J. T. Xu, Z. Q. Fan, *Macromol. Chem. Phys*. **2013**, 605-616.

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