



Peculiarities of crystallization in the multiblock copolymers of norbornene and cyclooctene

Georgiy A. Shandryuk, Yulia I. Denisova, Maria L. Gringolts, Liya B. Krentsel, Arkadiy D. Litmanovich, Eugene Sh. Finkelshtein, Yaroslav V. Kudryavtsev*

Tpchiev Institute of Petrochemical Synthesis, Russian Academy of Sciences, Leninsky prosp. 29, 119991 Moscow, Russia

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ABSTRACT

Crystallinity of statistical multiblock copolymers of norbornene and cyclooctene with nearly equimolar composition and different degrees of blockiness is studied by differential scanning calorimetry including thermal fractionation by successive self-nucleation and annealing and by X-ray diffraction. The copolymers are synthesized via recently invented reaction of polymer cross-metathesis, as a result of interchain exchange between polynorbornene and polyoctenamer in the presence of Grubbs' catalyst of the first generation. This catalyst raises the fraction of *trans*-octenylene units up to more than 80% promoting formation of triclinic crystals. The copolymer degree of crystallinity and melting peak temperature decrease with the cross-metathesis conversion. At the same time the equilibrium melting temperature predicted by the Flory theory of copolymer crystallization is not much affected by the interchange reaction. Compared with the pure polyoctenamer or its equimolar blend with polynorbornene, the norbornene-cyclooctene copolymers form considerably smaller crystallites. Thermal fractionation makes it possible to find their size distribution, which correlates with the average length of *trans*-octenylene blocks. Short annealing the multiblock copolymers above their melting points gives rise to a small but persistent endotherm 5–10 degrees above the annealing temperature, which is absent in polyoctenamer and, therefore, may indicate mixing of segregated norbornene and cyclooctene blocks.

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1. Introduction

Statistical multiblock copolymers represent a compromise between the need to retain the properties of individual comonomers in one material and the desire to avoid complex synthetic procedures developed for regular multiblocks. Controlled chain-growth polymerization techniques [1–3] and modification of homopolymers by low-molecular substances or via intermacromolecular reactions [4–7] help to obtain multiblock copolymers of diverse chemical nature. Their application in chemical engineering based on the self-assembly of similar blocks is a fast growing field [8] encompassing smart structural (shape memory, self-healing) and advanced functional (drug delivery, ionic transport) materials.

Polymer cross-metathesis, a novel interchange reaction between unsaturated macromolecules [9], was recently implemented by us [10–12] as a route to practically promising multiblock copolymers of norbornene (NB) and cyclooctene (COE). Whereas these monomers cannot be copolymerized by ring-opening metathesis polymerization (ROMP) in the pres-

* Corresponding author.

E-mail address: yar@ips.ac.ru (Y.V. Kudryavtsev).

ence of the 1st generation Grubbs' catalyst $\text{Cl}_2(\text{PCy}_3)_2\text{Ru} = \text{CHPh}$ [13,14], their copolymer can be easily obtained on the same catalyst by the cross-metathesis of polynorbornene (PNB) and polyoctenamer (PCOE) homopolymers (Scheme 1). As interchange reactions do not affect the type of monomer units, the copolymer properties are determined by its degree of blockiness, which can be effectively regulated by the reaction time, catalyst amount, and initial blend composition [12].

In this study we make a step forward and seek for the structure-property relationships by comparing the crystallinity of NB-COE copolymers of nearly equimolar composition and different degree of blockiness. A similar approach was previously implemented for the vinyl acetate – vinyl alcohol statistical multiblock copolymers in Refs. [15,16], where we demonstrated that a subtle difference in the average block length (2 and 5 units) can lead to a pronounced shift in the thermodynamic, rheological, and relaxation behavior in solution and bulk.

Conclusions regarding polymer crystallinity can be made basing on standard DSC scans but more detailed information becomes available by employing thermal fractionation techniques, in particular, successive self-nucleation and annealing (SSA) [17]. This method was originally developed to investigate structural characteristics in branched polyethylene and copolymers of ethylene and α -olefins but later it was widely used for various copolymers containing at least one type of crystallizable monomer units. By applying several heating-annealing-cooling steps with gradually decreasing temperature of annealing, it is possible to form a set of crystallites with different melting temperatures as a footprint of the block length distribution in the studied copolymer. Correct interpretation of a toothed final melting thermogram requires careful design of the SSA experimental protocol [18].

NB-COE copolymers demonstrate more complex behavior than previously studied monomer pairs because their crystallinity depends on the chain microstructure, namely on the amount and distribution of *cis* and *trans* double bonds in COE units. It was shown in the literature that both *cis* [19,20] and *trans* [21,22] configurations can crystallize but a typical commercial PCOE obtained by ROMP (Vestenamer) and characterized by a 55–85% *trans* content reveals crystallinity typical of *trans*-COE units only [23]. It means that even a PCOE homopolymer could be considered as a pseudo-copolymer with a certain fraction of crystallizable monomer units depending on the polymerization conditions and catalyst type.

Another feature of NB-COE copolymers is related to the glass transition of NB units taking place within the crystallization/melting range of COE units. The potential effect can be studied by comparing the DSC behavior of the copolymers and of PCOE/PNB blends at a fixed composition.

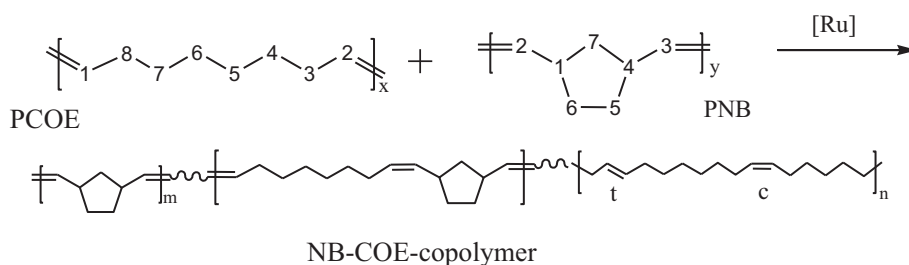
The paper is organized as follows. We start with describing the synthesis and characterization of PCOE and PNB homopolymers, PCOE/PNB blend, and three NB-COE copolymers of different degree of blockiness, including the detailed investigation of chain microstructure by NMR. Then we continue with presenting the results of DSC and XRD measurements on all mentioned systems with and without SSA thermal fractionation. Finally, we discuss correlations between the chain structure and crystallinity and end the paper with a summary of our findings.

2. Experimental section

2.1. Synthesis

Polyoctenamer (poly(1-octenylene), PCOE) and polynorbornene (poly(1,3-cyclopentylenevinylene), PNB) were synthesized by ring-opening metathesis polymerization (ROMP) in the presence of the 1st generation Grubbs' catalyst $\text{Cl}_2(\text{PCy}_3)_2\text{Ru} = \text{CHPh}$ (Gr-1, Aldrich) as described in Ref. [11]. The initial catalyst to monomer molar ratio of 1/700 was used in the both cases. In order to remove the catalyst residues, 0.9 M polymer solutions of PCOE in methylene chloride and PNB in toluene were passed through a column with SiO_2 (SiO_2 :polymer = 8:1, wt/wt) and precipitated in ethanol, decanted, washed with several portions of the ethanol, and dried under reduced pressure at room temperature until constant mass. The reaction yield was 58% for PCOE and 96% for PNB.

The cross-metathesis of PCOE and PNB in the presence of the same Gr-1 catalyst ($[\text{Pm}]:[\text{cat}] = 300:1$ mol/mol) was carried out in CHCl_3 as described in Ref. [11]. PNB (60 mg, 0.64 mmol) and PCOE (70 mg, 0.60 mmol) were dissolved in CHCl_3 (1.62 mL) in a round-bottom glass flask (5 mL) under inert atmosphere at 20 °C. Then 0.008 M solution of Gr-1 (0.62 mL, 4 mg, 0.005 mmol) in CHCl_3 was added. The mixture was continuously stirred for the required time. The reaction was ter-



Scheme 1. Cross-metathesis of PNB and PCOE.

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