

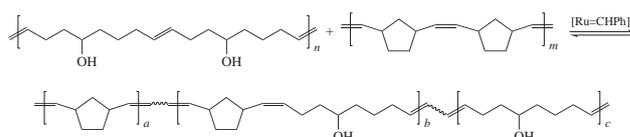
New multiblock copolymers of norbornene and 5-hydroxycyclooctene

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Cross-metathesis of 5-hydroxycyclooctene and norbornene homopolymers affords the multiblock copolymer possessing a broad range in the degree of blockiness (from 0.03 to 1).



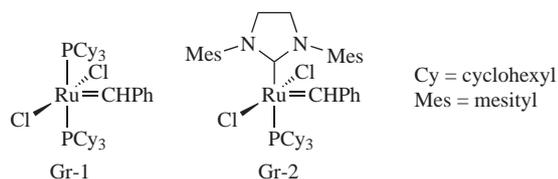
The metathesis reaction between unsaturated compounds is nowadays a versatile and effective tool in organic and polymer chemistry, which makes it possible to create new double C=C bonds in almost any substrate due to achievements in catalyst design.^{1,2} Several types of this reaction are distinguished, namely olefin cross-metathesis, ring-closing metathesis (RCM), ring-opening metathesis polymerization (ROMP), *etc.*¹ However, this list still does not include the cross-metathesis between macromolecules, whereas polymer–monomer and polymer–catalyst interactions are generally considered. The possible reason is that the polymer cross-metathesis (PCM) was historically classified as a side reaction in the course of ROMP and the studies were mostly focused on its suppression. Recently, several publications emerged that systematically addressed this reaction,^{3–7} which can be considered as an example of interchain exchange well-known for condensation⁸ and dynamic covalent⁹ polymers. PCM was shown to be practically important, for instance, in making polybutadiene networks malleable and capable of self-healing upon adding thereto a metathesis catalyst^{10,11} or in the reactive compatibilization of polymer blends.¹²

In this study, PCM is first used for the synthesis of multiblock copolymers containing hydroxyl substituents. New copolymers of norbornene (NB) and 5-hydroxycyclooctene (HCO) are obtained. The main problem in their synthesis directly from monomers *via* co-metathesis reaction stems from a substantial difference in the polymerization activity. The latter is, in turn, bound to different strain energy of NB and HCO cyclic molecules to be opened in the course of metathesis.¹³ Earlier, HCO was involved in the metathesis copolymerization with cyclooctene¹⁴ and ROMP in the presence of 1,4-diacetoxybut-2-ene¹⁵ and acryloyl glycerol carbonate derivatives¹⁶ as chain transfer agents. In the presence of the 1st generation Grubbs' catalyst (Gr-1), norbornene is polymerized first, then a low-strained cycloolefin like cyclooctene undergoes polymerization.¹⁷ As a result, a mixture of homopolymers is formed. The difference in the strain energy of

norbornene and *cis*-cyclooctene or its derivatives is especially high. *trans*-Cyclooctene ring is more strained and so *trans*-isomer is more active as compared with *cis*-cyclooctene, however, only a diblock copolymer polynorbornene–polyoctenamer can be synthesized by ROMP.¹⁸ Moreover, the hydroxyl substituent in cyclooctene can coordinate with the metathesis catalyst thus reducing its activity. Carrying out the cross-metathesis between the corresponding homopolymers, polynorbornene [poly(1,3-cyclopentylenevinylene), PNB] and polyhydroxyoctenamer [poly(5-hydroxycyclooctenylene), PHCO], allows one to eliminate the influence of the ring strain difference. Note that hydroxyl-containing macromolecules are of practical interest as potentially amphiphilic compounds. The obtained copolymers contain blocks of norbornene and hydroxyoctenylene units, the latter ones representing an unsaturated analogue of widely used commercial copolymer of ethylene and vinyl alcohol.

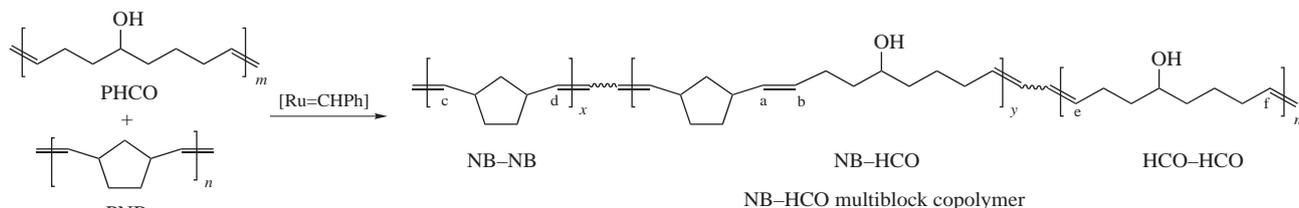
New multiblock NB–HCO copolymers were synthesized by an interchain exchange reaction between PNB and PHCO homopolymers *via* the cross-metathesis mechanism (Scheme 1).[†]

The initial PNB was synthesized *via* the metathesis polymerization of norbornene as described⁶ (polymer yield 98%, $M_w = 360\,000$, $D = 2.9$, $T_g = 37^\circ\text{C}$). The HCO monomer was obtained by the epoxydation of *cis,cis*-1,5-cyclooctadiene followed by the reduction of 5,6-epoxycyclooctene with LiAlH_4 .¹⁹ HCO was homopolymerized in bulk using the metathesis reaction mediated by Gr-1, ([HCO]:[Gr-1] = 150:1, 25 °C, 24 h, see Online Supplementary Materials) (Scheme 2, yield 50–55%, $M_w = 141\,000$,



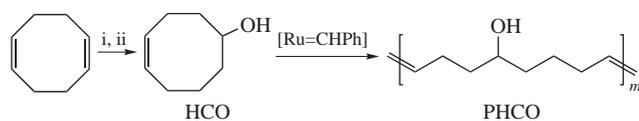
[†] A mixture of PNB (27 mg, 0.3 mmol) and PHCO (36 mg, 0.3 mmol) homopolymers was placed into the reactor, then dry chloroform (0.8 ml) and dry methanol (0.05 ml) were added under argon and the system was left overnight. Before the reaction, the polymer solution was degassed and the Gr-2 catalyst (23 mg, 0.027 mmol) in chloroform (0.24 ml) was added. The reaction was carried out under argon and stopped after a required time by adding ethyl vinyl ether (13.5 mmol) to the reaction mixture and stirring for 30 min. Then an oxidation inhibitor 2,2'-methylenebis(6-*tert*-butyl-4-methylphenol) was added and the solution was concentrated *in vacuo*.

For NB–HCO copolymer: ¹H NMR (500 MHz, CDCl₃) δ: 6.05–4.95 (m, 2H), 3.73–3.54 (br. m, CHOH), 1.92–1.33 (CH₂ PHCO), 2.8–1.06 (CH₂, CH PNB). ¹³C NMR (126 MHz, CDCl₃) δ: 134.84–134.51 (m, C=C heterodyad NB–HCO), 133.91–132.49 (m, dyad NB–NB), 130.49–129.24 (m, dyad HCO–HCO), 128.74–128.28 (m, C=C heterodyad HCO–NB), 72.33–70.02 (m, CHOH), 43.9–22.6 (region of CH and CH₂ PNB+PHCO).



Scheme 1

$\bar{D} = 2.4$, $T_g = 11^\circ\text{C}$). The ROMP of HCO in the presence of Grubbs' catalysts, analogous to 1st and 2nd generation ones, to give PHCO in 65 and 55% yields, respectively, was reported.^{19,20} Moderate yields of PHCO were explained by low polymer solubility in the reaction media, which caused its precipitation together with a part of the catalyst.²⁰ In our case, the polymerization of HCO led to the formation of a very viscous solution, which presumably hindered monomer diffusion and, therefore, consumption. NMR and IR spectra of PHCO were in agreement with the published data (see Online Supplementary Materials).¹⁹



Scheme 2 Reagents and conditions: i, *m*-CPBA, CHCl_3 , $\sim 20^\circ\text{C}$, 12 h; ii, LiAlH_4 , THF, $65\text{--}70^\circ\text{C}$, 4 h.

Efficient interchain cross-metathesis of PNB and PHCO requires a specific solvent providing maximum homopolymer concentration in the solution. This is necessary for diminishing the role of intrachain cross-metathesis that leads to the formation of cyclo-oligomers and a decrease in the molar mass of polymers. A mixture of chloroform and methanol was chosen as the common solvent for PNB and PHCO. Note that PHCO is insoluble in chloroform in the absence of alcohol, whereas high content of the latter leads to the precipitation of PNB. An optimal composition of the chloroform–methanol mixture was found to be of 10 : 1 (v/v).

The NB–HCO multiblock copolymers were analyzed by the ^1H and ^{13}C NMR spectroscopy, GPC, and DSC. NMR signals were assigned according to our previous studies and the literature data.^{6,19} The copolymer formation manifested itself by the appearance of NB–HCO dyad peaks in the 134.77–134.44 ppm range of the ^{13}C NMR spectrum (Figure S1, Online Supplementary Materials). Since HCO–NB and HCO–HCO peaks in the 127–129 ppm range are partially overlapped with the catalyst ones (see Figure S1), the mean block length was evaluated using the PNB range as $L_{\text{NB}} = [I(\text{C}^{\text{c,d}}) + I(\text{C}^{\text{a}})]/I(\text{C}^{\text{a}})$, where $I(\text{C}^{\text{a}})$ is the intensity of the peaks from carbon atoms in NB–HCO heterodyads (134.77–134.44 ppm) and $I(\text{C}^{\text{c,d}})$ is that in NB–NB dyads (132.88–133.67 ppm).

Interchain cross-metathesis of PNB and PHCO was carried out in the presence of Gr-1 and Gr-2 at the total polymer concentration [PNB + PHCO] of 4.5 wt% (Table 1). Previously we have demonstrated that at the first stage (~ 30 min) of the PCM reaction the catalyst moieties are incorporated into macromolecules *via*

cleavage of C=C bonds in their backbones, which leads to lowering an average molar mass of the system.⁶ A similar effect was observed in the present study (see Table 1).

When mediated by Gr-1 (PNB : PHCO : Gr-1 molar ratio of 10 : 10 : 1, see Table 1, run 1), the cross-metathesis proceeded only upon heating up to 45°C (^{13}C NMR monitoring). The glass-transition temperature of the product was 17°C less than that of the initial PHCO, which can be explained by decreasing the fraction of hydroxyl-containing blocks in the copolymer. An inflection point at the DSC curve corresponding to the glass-transition temperature of NB blocks is poorly defined, which can be related to a low molar mass of the copolymer. Note that the copolymer, contrary to the initial PHCO, is soluble in chloroform without adding alcohol.

The Gr-2 catalyst was found to be more active in the cross-metathesis of PNB with PHCO (Table 1, runs 2–4). In this case, a completely random copolymer with the mean block length of 2.1 units and the degree of blockiness close to unity was obtained. The values of glass transition temperature T_g for the copolymers obtained with different catalysts and possessing considerably different degrees of blockiness are close, therefore being determined mostly by the same composition of copolymers. Note that the T_g values measured by DSC during the heating runs 1 and 2 are considerably different, which emphasizes importance of the thermal history of the copolymers obtained. We observed a similar effect in the non-substituted PCO.²¹ If the amount of catalyst is lowered, the copolymer mean block length is decreased, its solubility in chloroform is improved, and the thermal properties are changed.

An interesting result was obtained for the long-lasting (2 days) cross-metathesis of PNB with PHCO in the chloroform–methanol mixture (see Table 1, run 4). NMR data indicate lowering the double-bond content in the copolymer products. In the ^{13}C NMR spectrum the NB double bonds are practically absent, while in the ^1H NMR spectrum the fraction of double bond signals in the range of 5.0–6.4 ppm is decreased by 25–28% for 24 h. A slow decrease in the double bond integral intensity is noticeable when one compares the spectra obtained during ^1H NMR *in situ* monitoring of the PCM (Figure S2).

According to reported data,²² the interaction of primary alcohols with the Gr-2 catalyst leads to the formation of hydride ruthenium complexes. It is also known that alcohols can serve as hydrogen donors for the hydrogenation of double bonds, which proceeds nearly quantitatively in the presence of 2–5 mol% of the Ru-hydride complex at $50\text{--}70^\circ\text{C}$ in 10–15 h.²³ The conditions of our experiments are similar to those described in ref. 23, so that

Table 1 Synthesis of NB–HCO multiblock copolymers.

Run	Catalyst	Catalyst-to-polymers molar ratio	$T/^\circ\text{C}$	t/h	M_w	\bar{D}	Block length, L_{NB}	Degree of blockiness	$T_g/^\circ\text{C}$	$T_m/^\circ\text{C}$
1	Gr-1	1 : 20	45	24	18 400	2.4	55	0.04	–8; 41	–
2	Gr-2	1 : 20	24	24	13 000	1.8	2.1	0.95	–8; 44	–
3	Gr-2	1 : 100	25	24	32 700	1.9	19	0.11	–8; 41	–
4	Gr-2	1 : 20	20	48	6 600	1.8	–	–	–20 ^a	105

^a Only one glass transition was detected.

the partial hydrogenation of C=C double bonds is not unusual. Note that a melting peak appears on the DSC curve of the reaction product at 105 °C, which is close to the T_m of hydrogenated PNB.

In a few studies reported on using Grubbs' catalysts for implementing metathesis and hydrogenation as tandem reactions,^{24,25} the metathesis was carried out first and then hydrogen was fed into the reactor. This resulted in the transformation of a metathesis catalyst into a hydride complex which promoted hydrogenation of double C=C bonds in the metathesis product. In the future, we plan to study such processes in our system in more detail.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2017.07.034.

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