Hybrid Photo-induced Copolymerization of Ring-Strained and Vinyl Monomers Utilizing Metal-Free Ring-Opening Metathesis **Polymerization Conditions**

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Supporting Information

ABSTRACT: We introduce the hybrid copolymerization of two disparate monomer classes (vinyl monomers and ring-strained cyclic olefins) via living photopolymerization. The living character of the polymerization technique (metal-free photo-ROMP) is demonstrated by consecutive chain-extensions. Further, we propose a mechanism for the copolymerization and analyze the copolymer structure in detail by high-resolution mass spectrometry.

opolymerization within the same class of monomers, / following the same polymerization mechanism, can be conducted for almost every polymerization technique. Hybrid copolymerization and interconversion between different polymerization mechanisms is rarely reported and mostly confined to block copolymer formation. Zhang et al. recently established an interconverting polymerization system using heat and light as triggers for the interconversion of anionic ring-opening polymerization (AROP) and photoinduced electron transfer reversible addition-fragmentation chain transfer polymerization (PET-RAFT), affording multiblock copolymers.¹ Despite the few reports on hybrid copolymerizations, some innovative approaches, such as tandem catalysis, afford block, 2^{2-6} brush, 7-9 graft comb¹⁰ or bridge-like¹¹ polymer structures. Buchmeiser and co-workers demonstrated a sophisticated tandem copolymerization of cyclic olefins with ethylene via a reversible interconversion of the catalyst to catalyze either ring-opening metathesis polymerization (ROMP) or vinyl-insertion polymerization (VIP) to construct the lateral chain.¹²⁻¹⁶ The interconversion of two addition polymerizations, e.g. cationic- and radical polymerization of vinyl monomers was recently reported by Fors and coworkers.^{17,18}

Metal-free ROMP (MF-ROMP) was demonstrated by Boydston and co-workers and follows a step-growth mechanism where the ω -chain end can be reversibly activated or deactivated by oxidizing the double bond or reducing the cationic radical.¹⁹ Those authors presented random copolymerizations with different ring-strained monomers, the majority constituted of norbornene derivatives and dicyclopentadiene. Furthermore, copolymerization using a bifunctional initiator was shown, affording block copolymers.²⁰

Our approach merges the rich variety of vinyl monomers in a hybrid copolymerization with ring-strained monomers utilizing MF-ROMP conditions and paves the way for new copolymer structures not accessible by other means. The unsaturated backbone and side chains of these copolymers are synthetically readily accessible for functionalization.

Photoinduced homo- and copolymerization of norbornene with vinyl monomers under MF-ROMP conditions were performed utilizing ethyl-1-propenyl ether as well as (2methoxyvinyl)cyclohexane as initiators and 2,4,6-tris(4methoxyphenyl)pyrylium tetrafluoroborate (MeOTPP $^{+}BF_{4}^{-}$) as the oxidizing photocatalyst.

The two structurally distinct monomer classes usually follow different polymerization mechanisms, involving radical cations or radicals as the reactive intermediates. Whereas in hybrid copolymerization one reactive species is generated that can add both ring-strained andvinyl monomers to the growing chain (Scheme 1).

A selection of the obtained polymers and the corresponding characteristics are summarized in Table 1. Methyl methacrylate and methyl acrylate were utilized as the main representative vinyl monomers and norbornene as the ring strained monomer. Styrenes as well as vinyl ethers are readily oxidized and cannot be polymerized using the same reaction conditions.²¹ No quenching agents were required as the polymerization ceases in the dark due to reduction of the active chain end and regeneration of the catalyst.¹⁹ Prior to the herein presented in-depth analysis, mass spectrometric studies have previously not been conducted on polymers obtained via MF-ROMP. For the norbornene homopolymer (entries 1 and 2, Table 1), solely consisting of the highly apolar norbornene repeating unit and the respective end groups originating from

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Scheme 1. Hybrid Copolymerization of Ring-Opening Cyclic Olefins with Vinyl Monomers via MF-ROMP Conditions



the utilized initiator, proton nuclear magnetic resonance (¹H NMR) spectroscopy clearly shows the anticipated α - and ω chain ends as highlighted by Boydston and co-workers (Figure S5).¹⁹

A corresponding ionized species was not identified in the recorded electrospray ionization (ESI) mass spectra, most likely due to low ionization efficiencies, however, the correct repeating unit spacing of 94.08 Da was observed (refer to Figure S16). A possible explanation for the species in the mass spectrum could be the [2+2]-cycloaddition of the charged ω chain end with a neutral initiator molecule, as is often observed in radical cation chemistry.²² However, the corresponding species would inhibit the polymerization and would be in conflict with the ¹H NMR spectrum, therefore, the presence of the observed end group species may result from preferential ionization. After successful homopolymerization using MF-ROMP conditions, the possibility of orthogonal reactivities between MF-ROMP and radical polymerizations of vinyl monomers was investigated. Thus, a polymerization of norbornene via MF-ROMP in the presence of methyl methacrylate (MMA) was performed. The presence of MMA did not inhibit the ROMP, nor was it orthogonal to MF-ROMP, as can be seen in the ¹H NMR spectrum in Figure 1. The proton resonances of the methoxy group at 3.60 ppm, and for the methyl group at 0.84 ppm, are suitable signals for the identification of MMA units in the copolymer. The norbornene repeating unit can be readily identified via the resonances at 5.34 and 5.20 ppm, associated with the backbone double bonds formed during ROMP, as well as the

100:1:0.03

100:1:0.03

100:1:0.03

101:1:0.03

112:1:0.03

97:1:0.03

97:1:0.03

50

50

0

50

45

51

51

4

5

6

7

8

9

10

MMA

MA

MMA

MMA

TFEMA

BA

IBA



Figure 1. ¹H NMR spectrum of poly(norbornene-co-MMA), synthesized under MF-ROMP conditions with a 50/50 mixture of the two monomers in dichloromethane and (2-methoxyvinyl)cyclohexane as initiator.

CH resonances of the five-membered ring at 2.78 and 2.43 ppm.

The polymer sample contained 90% norbornene and 10% methyl methacrylate using (2-methoxyvinyl)cyclohexane as initiator. It is important to note that the same ω -chain end identified for a norbornene homopolymer was also identified via ¹H NMR (trans, 6.28 and 4.71 ppm; cis, 5.81 and 4.30 ppm). Critically, size exclusion chromatography (SEC) showed a monomodal shape with $M_n = 3700 \text{ g} \cdot \text{mol}^{-1}$ and $M_w = 6300 \text{ g} \cdot \text{mol}^{-1}$ mol⁻¹, underpinning the copolymerization between norbornene and MMA. Experiments performed under the same conditions, yet without norbornene, did not result in the formation of poly(methyl methacrylate), indicating that norbornene has to generate cationic radicals to incorporate MMA units (entry 6, Table 1). The same observation applies in the absence of initiator (entry 7, Table 1).

While improved conversion in MF-ROMP using nondeoxygenated reaction mixtures was observed for the homopolymerization of norbornene,²³ the copolymerization with vinyl monomers requires inert reaction conditions. The incorporation of MMA in a copolymerization with norbornene completely ceased in the presence of oxygen (entry 3, Table 1). Any attempted copolymerization of norbornene with vinyl

60

60

60

60

60

60

60

3

5

/

/

n.d.

5

3

3600

1700

/

/

2100

3400

2200

entry	M1 (%)	$M2^d$	M _{total} :I:PC	$[M]_0 \; (\text{mol}{\cdot}L^{-1})$	conversion M1 (%)	conversion M2 (%)	time (min)	$M_{\rm n} \left({\rm g \cdot mol^{-1}} \right)$
$1^{b,c}$	100	/	108:1:0.05	2.3	44	/	100	17600
2 ^b	100	/	102:1:0.05	2.0	35	/	90	9900
3 ^b	50	MMA	100:1:0.05	2.6	36	0	90	/

Table 1	. Different	(Co)po	lymers O	btained	Utilizing	MF-ROMP	Conditions ⁴
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2.3

2.0

2.3

2.3

2.2

1.9

1.9

"All reactions were performed in dry dichloromethane at 445 nm LED @ 10 W (0.7 A, 8.85 V input) for the stated period of time. (2methoxyvinyl)cyclohexane was utilized as initiator. The conversions were determined using ¹H NMR in CDCl₃. ^bNon-deoxygenated. ^cEthyl-1propenyl ether. ^dAbbreviations: methyl methacrylate (MMA); methyl acrylate (MA); 2,2,2-trifluoroethyl methacrylate (TFEMA); n-butyl acrylate (BA); isobutyl acrylate (IBA).

14

7

/

/

n.d.

13

24

 $M_{\rm w} (\rm g \cdot \rm mol^{-1})$

25900

15500

1

6000

4700

/

/

4400

2200

5600

Đ

1.5

1.6

/

1.7

2.7

/

1

2.1

2.2

2.6

monomers (Table 1 and Figure S15) exhibited a higher conversion of norbornene compared to the vinyl monomer conversion, likely as a result of the high ring-strain of norbornene and the known fast polymerization kinetics in $\rm ROMP.^{24}$

Unambiguous evidence for the hybrid copolymerization between the two monomer classes was provided by SEC/ESI-MS analysis of the polymer samples (Figure 2).



Figure 2. High-resolution mass spectrum of poly(norbornene-*co*-MMA) with spacings of the isotopic patterns corresponding to the exact masses of the repeating unit and the associated mass-to-charge difference between the repeat units. The mass spectra were analyzed using pyMacroMS.²⁶

This hyphenated technique enables separation of the polymer by chain length (SEC) and consecutive online recording of the mass spectrum by ESI-MS, facilitating the separation of the polymer fractions by different charge states aiding an unambiguous identification of the macromolecular species according to their sum formula.²⁵ Contrary to the apolar norbornene homopolymer, species with multiple charges were observed indicating a copolymer consisting of MMA and norbornene. The copolymer exhibits a far better ionization due to the rather polar MMA repeating units.

The singly charged region (z = 1) was used for further analysis, whereas higher charged regions (e.g., z = 2) also exhibit the characteristic copolymer pattern. The mass spectrum contains repetitive signal patterns characteristic for copolymers, such as isotopic patterns with an m/z spacing corresponding to both monomers (norbornene, $\Delta = 94.08$ Da; MMA, $\Delta = 100.05$ Da) and the spacing of $\Delta = 5.97$ Da between neighboring isotopic patterns, corresponding to the difference in mass between norbornene and MMA repeating units (Figure 2 inset). Comparison of the high-resolution mass spectra of poly(norbornene-*co*-MMA) obtained using either ethyl-1-propenyl ether or (2-methoxyvinyl)cyclohexane as initiators provided insight into the end group functionalities of the copolymers (Figures S17 and S18).

Matching sum formulas for the copolymer mass spectra were found if the α -chain end remains intact, while the ω -chain end is converted to an aldehyde under cleavage of the alkoxy group during ionization. The degradation yielding an aldehyde can also be observed for a norbornene homopolymer and the initiator under MF-ROMP conditions in acid containing solvents such as CDCl₃ (Figures S6 and S7).

A proposed mechanism for the copolymerization of norbornene and MMA is shown in Scheme 2. Similar to the mechanism proposed for the previously reported procedure for MF-ROMP, the copolymerization commences with the initiation of norbornene.¹⁹ A subsequent metathesis of MMA with the active chain end, and release of an α -vinyl ether, results in an intermediate that can initiate the radical polymerization of MMA. The released α -vinyl ether does not initiate new chains as previously observed.¹⁹

The nucleophilic addition of the prior released α -vinyl ether to the radical-cation of the active chain end will lead to the regeneration of the vinyl ether end group allowing for further norbornene addition. This assumption is in agreement with a recent publication of Huang and co-workers reporting the nucleophilic addition of a vinyl ether to a radical cation.²⁷ Importantly, the kinetics for a 50/50 mixture of MMA and

Scheme 2. Proposed Mechanism for the Hybrid Copolymerization of Norbornene (M1) and MMA (M2)





Figure 3. Conversions of norbornene and MMA at different times (A) and relative progress of the conversions (B). SEC traces at the corresponding times (C) showing a gradual increase in molecular weight M_p (D), while maintaining a monomodal distribution.

norbornene reveal an increase of the conversion over time for both monomers, with norbornene being the predominantly incorporated monomer, especially during the early stages of the polymerization (Figure 3A,B).

The conversion after 3 h reaches 15% of norbornene and 5% of MMA in the case of the experiment shown in Figure 3. The conversions and molecular weights obtained with the general procedure for hybrid copolymerization utilizing MF-ROMP conditions can be increased by sequential addition of the pyrylium salt (Table S1). The initially added pyrylium salt does not fully recover and thus the polymerization stops. Our kinetic data support a gradient copolymerization rather than a block copolymerization as MMA is incorporated into the polymer from the beginning and the entire molecular weight distribution-including the oligomer region-shifts toward higher molecular weights (Figure 3C,D). Furthermore, in the case of a polymer blend, a bimodal distribution would be expected at a certain stage of the polymerization, which was not observed. Nonetheless, analysis via ¹³C NMR spectroscopy points toward a high degree of blockiness, as no distinct resonances corresponding to the diad of norbornene adjacent to MMA were identified (Figures S8-S10). Caused by the relatively low percentage of incorporated vinyl monomer, the fraction of interconverting points in the polymer was too low to be detected via ¹³C NMR.

In order to gain further information on the copolymerization mechanism, we attempted a chain extension of a copolymer consisting of MMA and norbornene. After purification of the copolymer the chain growth was successfully re-initiated by addition of a fresh norbornene feed and catalyst (Figure 4), proving the living character of the hybrid copolymerization. Critically, the complete molar mass distribution is shifted toward higher masses, starting from $M_p = 4800 \text{ g}\cdot\text{mol}^{-1}$ and shifting to $M_p = 58\ 600 \text{ g}\cdot\text{mol}^{-1}$ after chain extension. The possibility of a chain extension further supports the hybrid copolymerization proposed in Scheme 2. The ¹H NMR spectra before and after chain extension also support hybrid copolymerization, showing an increase in the content of norbornene of the chain extended polymer, while the MMA



Figure 4. Chain extension of poly(norbornene-*co*-MMA) with norbornene (black and red lines) or a mixture of norbornene and 2,2,2-trifluoroethyl methacrylate (blue and purple dashed lines).

content remains the same as prior to the chain extension (Figure S11).

To demonstrate the living character and the end group fidelity of the developed technique, poly(norbornene-*co*-MMA) was chain extended with a mixture of 2,2,2-trifluoroethyl methacrylate and norbornene to obtain a terpolymer consisting of two blocks of different gradient copolymers—a microstructure unprecedented in literature (Figure 4, dashed lines, and Figure S12). A shift of the full mass distribution from $M_p = 7500 \text{ g}\cdot\text{mol}^{-1}$ to 55 700 g $\cdot\text{mol}^{-1}$ was observed.

In conclusion, we introduce the hybrid copolymerization of ring-strained monomers with vinyl monomers utilizing MF-ROMP conditions. The final copolymers contain a high proportion of the norbornene repeating unit. Monomers suitable for MF-ROMP but exhibiting less ring-strain compared to norbornene may enable a shift of the equilibrium further to the side of the vinyl monomer. The resulting copolymers are promising candidates for future applications, as the backbone, as well as the side chains, can be readily altered. For example, introducing a cleavable group into the lateral chain via the ring-strained monomer will open a promising avenue for materials with novel features, especially in the field of biodegradable polymers.²⁸

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.9b09025.

Experimental details; analytical data including NMR, SEC, MS, and UV/vis (PDF)

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Notes

The authors declare no competing financial interest.

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