# Synthesis of New Flame Retardant Polymers via Olefin Metathesis

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# 1. Introduction

Flame retardant polymers belongs to the category of emerging materials as they could have significant impact on transportation, housing, construction, electricity, and packaging using wide scope of polymers. Since 1950, research on the ring opening metathesis polymerization (ROMP) has been also carried out and has led to several industrially relevant polymeric materials[1]. Olefin metathesis polymerization-derived materials exhibit numerous advantageous properties and characteristics.

Polynorbornene-based elastomeric compositions are widely used in various seals, bumpers, insoles, and vibration-damping components, e.g. in vehicles.[2] These polymers feature favourable characteristics for industrial applications, however, their thermal and fire resistance needs to be improved to meet the expectations of additional application areas. The substitution of some widely used halogenated flame retardant is required, since most of the monomers contain halogens that are nowadays used in the synthesis of these flame-retardant polymers. However, there are restrictions in many global markets due to dioxins generation upon their combustion and facilitation of the headway of phosphorus flame retardants[3]. The goal of the research work was to produce new phosphorus-containing norbornene derivatives, polynorbornenes (chapter 3) prepared by metathesis polymerization reactions.

In one hand, olefin metathesis catalysts are reactive enough in ring-opening polymerization and related reactions; however, their reactivity can be optimized. On the other hand, metathesis catalysts are sensitive for air and moisture. For these reasons, new catalyst precursors and ligands were synthetized for less sensitive and more reactive catalyst, which also the important part of the project (see chapter 5). In addition, environmentally more advantageous solvents were also proved to be suitable media for these types of reactions (chapter 6).

# 2. Synthesis and application of new phosphorus containing metathesis monomers

## 2.1. Preparation and copolymerization of phosphorus triamides[4,5]

Phosphoric triamides are one of the most effective flame-retardant additives.[6] Our first attempt was the synthesis of phosphorus triamides with norbornene moieties. We have prepared **4** by reacting phosphorus oxychloride with 5-norbornene-2-ylmethylamine (**3**) prepared previously from acrylonitrile (**1**, Figure 1). The desired pure product **4** was isolated in a high yield in a multigram scale.

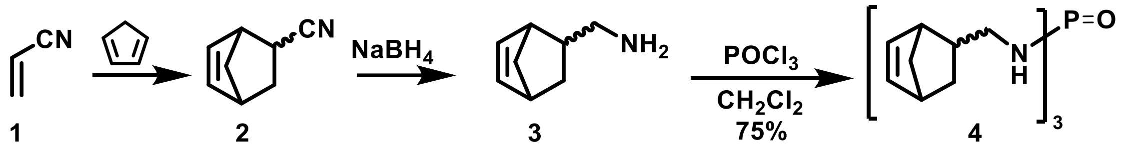


***Figure 1. Preparation of (norbornene-2-ylmethyl) phosphorus triamide 4.***

Using similar reaction pathway, we tried to obtain the phosphoramide from bis-(norbornenemethyl)amine. The secondary amine **7** was prepared by the formation of an imine **5** from 5-norbornene-2-methylamine (**3**) and 5-norbornene- 2-carboxaldehyde followed by reduction using $NaBH_4$. The pure product was reacted with phosphorus oxychloride in DCM at reflux temperature to achieve the desired triamide **7** (Figure 2).

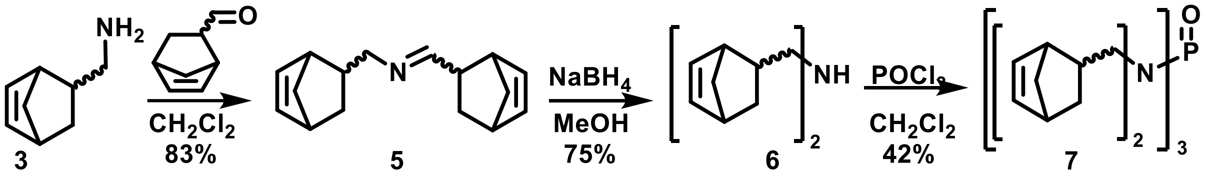
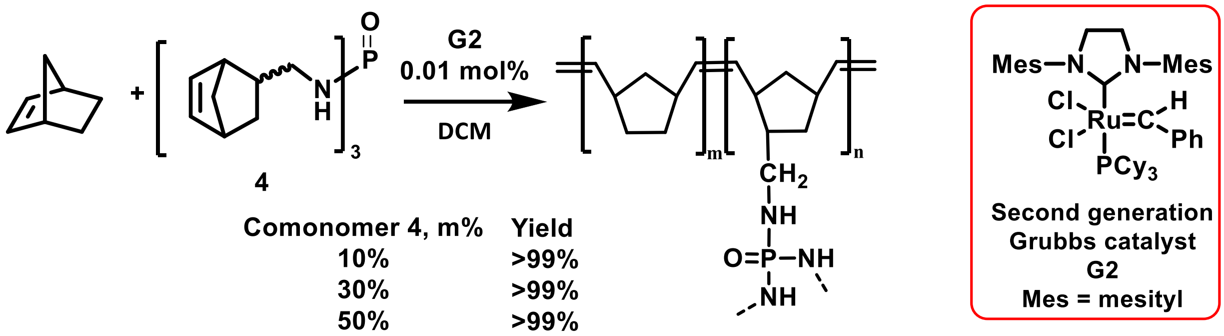


*Figure 2. Synthesis of phosphorus triamide 7 from secondary amine 5.*

The copolymerization of the triamide comonomer **4** and norbornene was carried out with different comonomer mass ratios (1/10; 3/10; 5/10, Figure 3) in the presence of second generation Grubbs catalyst (G2).



| Comonomer 4, m% | Yield |
|---|---|
| 10% | >99% |
| 30% | >99% |
| 50% | >99% |

*Figure 3. Copolymerization of 4 with norbornene in the presence of G2 catalyst.*

The thermal stability of the synthesized copolymers was studied using TGA measurements. As it can be seen from Figure 4, and Table 1, the reference polynorbornene was stable even at 400 °C, while some minor degradation occurred in the case of the 10% P-comonomer-containing sample, and a bigger step was observed in the case of the 30% and 50% comonomer-containing samples. The main degradation step occurred at the same temperature range of 400 - 500 °C for all polymers, with a negligible difference in the onset temperatures. With increasing P-content the rate of degradation ($dTG_{max}$) increased to some extent, and the temperature of the maximum degradation rate shifted to lower values, indicating that the presence of the P-species in the polymer structure improved the char formation at lower temperatures. The height of the step is, however significantly reduced, due to the beneficial effect of the P-species together with the crosslink points appearing in the structure due to the trifunctionality of the comonomer. The highly crosslinked and thus more resistant structure of the synthesized copolymers, led directly to significantly increased amount of charred residues at 600 °C (almost by 700% in the case of the 50% comonomer sample).

***Table 1. TGA data of the synthesized copolymers using 4 and norbornene***

| | $T_{onset}$ (°C) | $T_{-50\%}$ (°C) | $dTG_{max}$ (°C) | $T_{dTGmax}$ (°C) | residue (%) |
|---|---|---|---|---|---|
| polynorbornene | 400.8 | 451.1 | 1.79 | 454.6 | 3.6 |
| 10% comonomer | 400.6 | 452.3 | 1.80 | 461.6 | 2.6 |
| 30% comonomer | 398.9 | 444.6 | 1.88 | 438.9 | 8.1 |
| 50% comonomer | 408.2 | 442.1 | 2.16 | 435.4 | 18.3 |

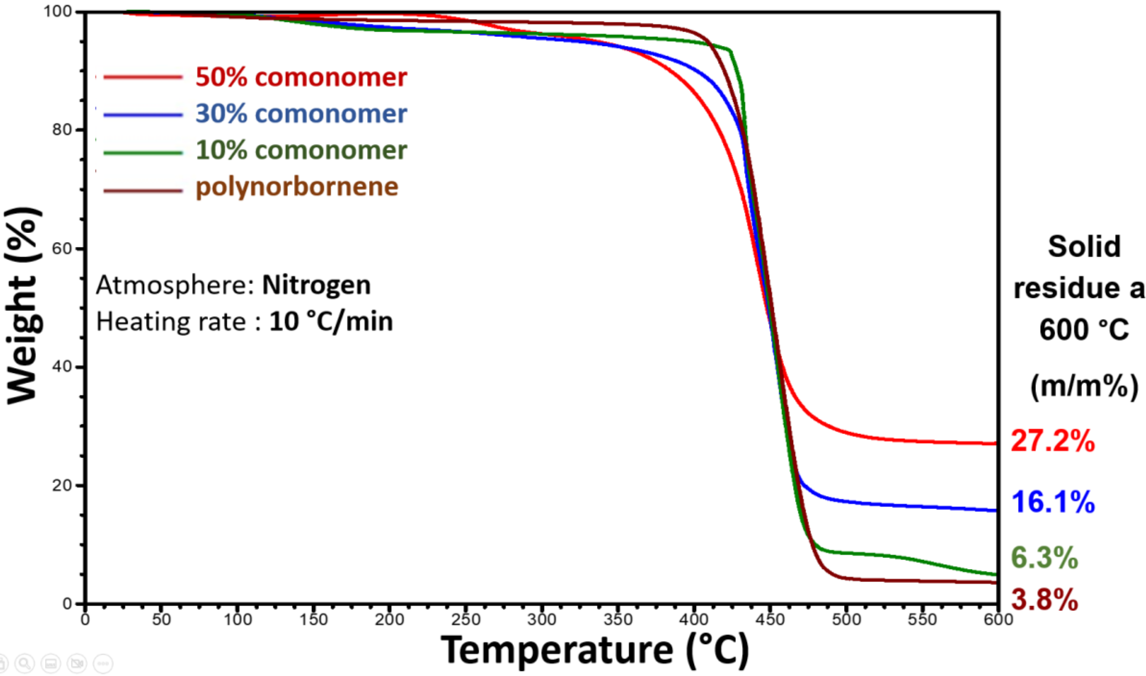
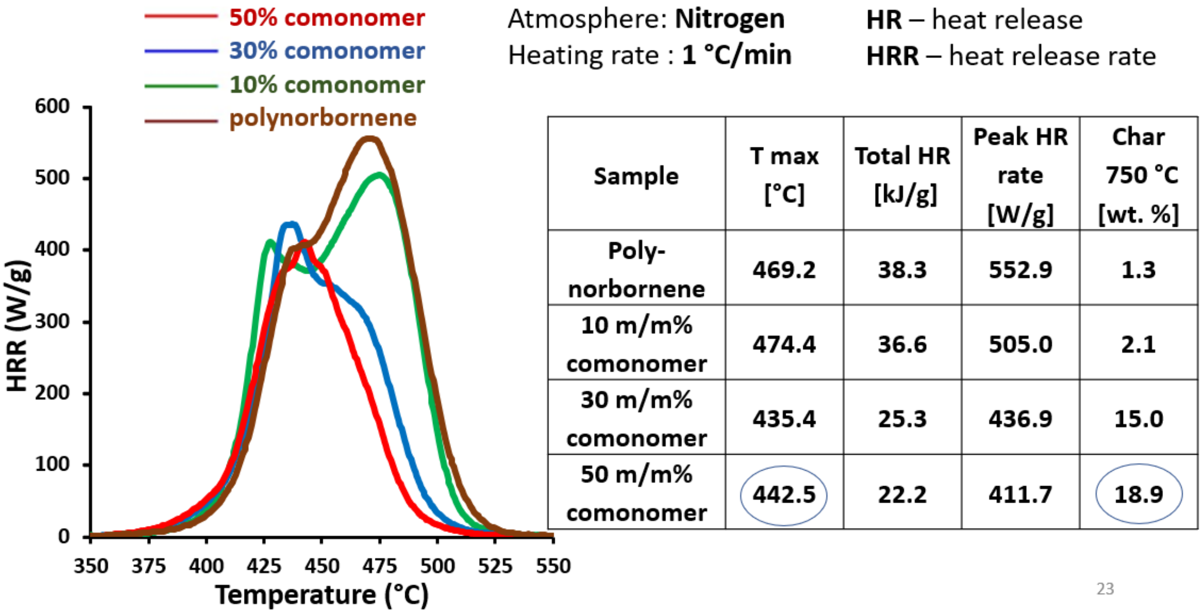


***Figure 4. TGA curves of the synthesized copolymers using triamide 4 and norbornene in the presence of G2 catalyst.***

According to the curves represented in Figure 5, the heat release of the different copolymers decreased with increasing P-containing monomer content. In the case of the reference polynorbornene, the peak appeared at higher temperature than in the case of the P-containing copolymers, but its value was also higher, with the highest total heat release (THR). With increasing P-content, the peak of heat release rate (pHRR) shifted to lower temperatures, and the pHRR and THR decreased gradually. This might be attributed to presence of the less stable P-N bonds in the structure of the copolymers, which lead to earlier degradation, however, the crosslinked structure of the P-containing copolymers is beneficial in terms of the amount of the released combustible pyrolysis products, thus decreased pHRR and THR values. This is in agreement with the TGA results, where decreased degradation rate of the copolymers was detected.

The amount of the charred residue is also increasing with increasing P-content reaching up to 18.9 wt%, similarly to the TGA results, as an evidence of the beneficial effect on the solid-state charring mechanism of the crosslinked structure of the copolymers. Based on these results, this compound can be considered as an additive with beneficial effect on thermal stability and combustion properties in the case of flame retardancy.



Atmosphere: **Nitrogen**
Heating rate : **1 °C/min**

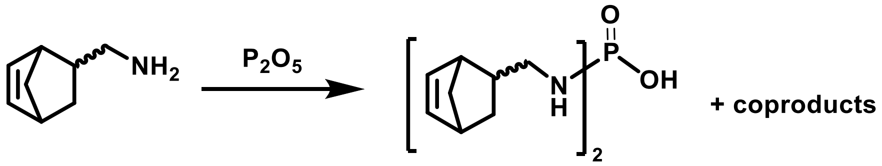
**HR** – heat release
**HRR** – heat release rate

| Sample | T max [°C] | Total HR [kJ/g] | Peak HR rate [W/g] | Char 750 °C [wt. %] |
|---|---|---|---|---|
| Poly-norbornene | 469.2 | 38.3 | 552.9 | 1.3 |
| 10 m/m% comonomer | 474.4 | 36.6 | 505.0 | 2.1 |
| 30 m/m% comonomer | 435.4 | 25.3 | 436.9 | 15.0 |
| 50 m/m% comonomer | 442.5 | 22.2 | 411.7 | 18.9 |

***Figure 5. Microscale combustion calorimetric (MCC) curves and data of the copolymers synthesized from triamide 4 and norbornene.***

## 2.2. Synthesis of norbornene-ylmethyl phosphorus diamide

Our next goals were to synthesize phosphorus amides avoiding the hazardous phosphorus oxychloride. The simple reaction of phosphorus pentoxide and norbornene-2-ylmethyl amine (**4**) resulted dominantly in the substituted phosphorodiamidic acid (**8** in Figure 6) under mild conditions based on GC-MS and NMR measurements, however, the reaction mixture was complex. In the case of the addition of sodium hydroxide solution to the reaction mixture after the reaction was completed, the polyphosphoric residues were hydrolysed, the mixture become less complex, the desired product can be isolated. This novel phosphorylation reaction should have significant relevance in the future for the environmentally friendly synthesis of phosphoramide-type flame retardant additives, however, further investigation is necessary to achieve a simple, chromatography-free isolation method.

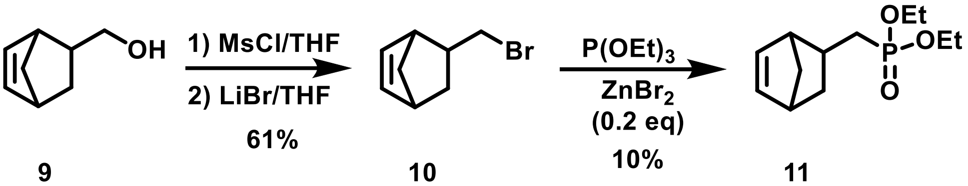


**3** **8**

***Figure 6. Preparation of bis(norbornene-2-ylmethyl) phosphoramide 8 from amine 4 using $P_2O_5$.***

## 2.3. Investigation of phosphonate containing norbornenes

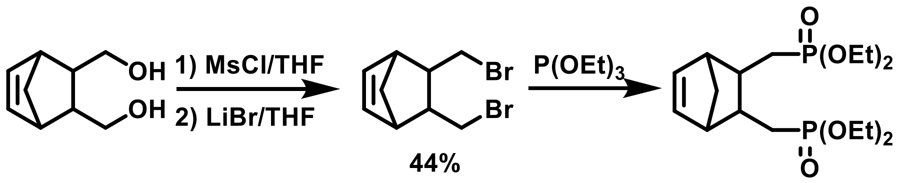
The synthesis of norbornene phosphonate was carried out from norbornene-2-ylmethanol **9**, which was brominated to **10** by a two-step-reaction,[7] then phosphonated **11** was prepared under microwave radiation in the presence of Lewis acid catalyst $ZnBr_2$ (Figure 7). This reaction works even without microwave if the reaction mixture was heated over 24 hours at 170 °C. However, the desired pure product **11** was isolated and fully characterized. The yield was as low as 10%.



**9** **10** **11**

***Figure 7. Preparation of norbornene-2-ylhosphonate 11 from norbornene-methanol 9.***

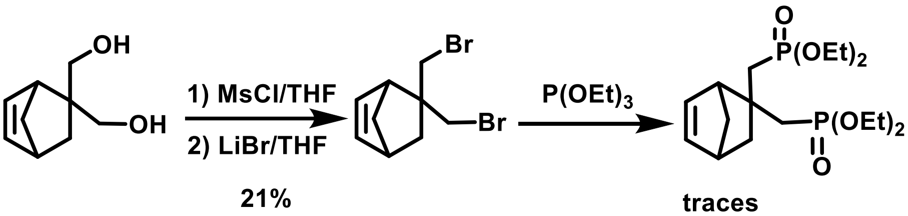
In the next step, the preparation of norbornene-phosphonates with two phosphonate units was the plan. Diol **12** was converted to the dibromide (**13**) in a two-step reaction[7]**.** Arbuzov reaction of **13** gave the bisphosphonate **14** (Figure 8) only in poor yield.



**12** **13** **14**

*Figure 8. Preparation of norbornene-2,3-diylbisphosphonate 14.*

Similar reaction route was attempted to prepare a spiro bis(methyl-diethylphosphonate) norbornene derivative. Dibromination of norbornene diol **15** was carried out in moderate yield, the **16** was reacted with triethyl phosphite, however, based on GC-MS measurement, the product **17** was formed only in traces (Figure 9). In conclusion, further development is necessary for the preparation of phosphonate containing norbornenes in reasonable yields.



**15** **16** **17**

*Figure 9. Synthetic route to bisphosphonate 17.*

## 2.4. Synthesis and application of trinorbornene phosphine oxide

Preparation of a monomer which contains phosphorus atom bonded directly to three norbornene units was successfully carried out. Trivinylphosphine oxide **19** was synthesized by reacting 3 equivalents of vinyl magnesium bromide and phosphoryl chloride[8]. The Diels-Alder reaction of **18** with freshly cracked CPD at high temperature resulted in the desired trinorbornene product **19** (Figure 10) in moderate yield. Thus, a potential flame retardant additive with a very simple synthetic procedure was obtained in this reaction pathway.

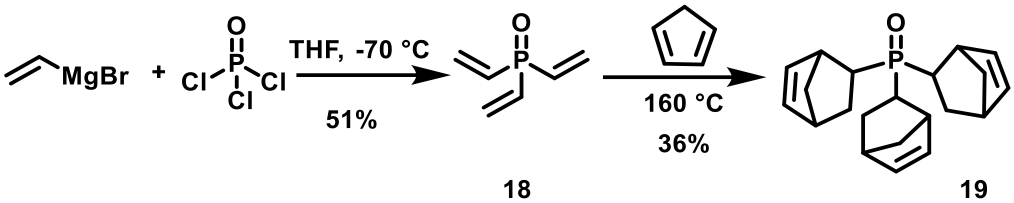
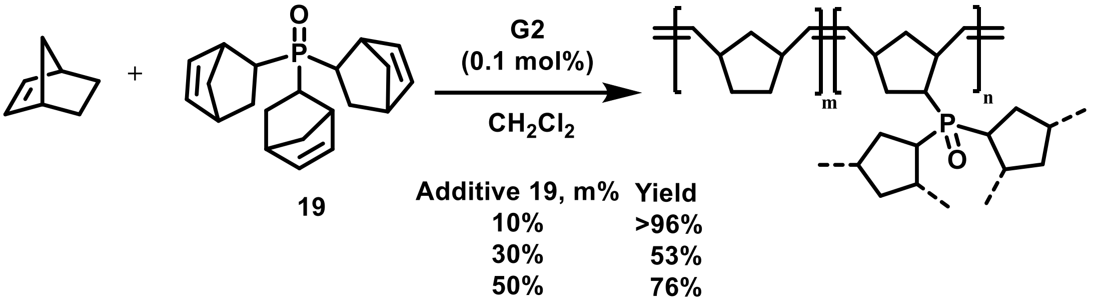


*Figure 10. Synthesis of trinorborene-2-yl phosphine oxide 19 from vinyl magnesium bromide.*

Copolymerization of the comonomer **19** and norbornene was carried out (Figure 11) using G2 catalyst with different monomer ratios (10 m/m%; 30 m/m%; 50 m/m% additive) successfully.



| Additive 19, m% | Yield |
|---|---|
| 10% | >96% |
| 30% | 53% |
| 50% | 76% |

*Figure 11. Copolymerization of the comonomer 19 and norbornene in the presence of G2 catalyst.*

Considering the TGA results of the copolymers prepared using trinorbornene phosphine oxide **19**, the weight ratio of the solid residue of the polymers after the degradation is the highest when using 50 m/m% additive (27.2%) at 600 °C, which is much higher than that of the copolymers with a 30 m/m% (16.1%) and 10 m/m% additive content (6.3%). The less weight loss in the measurement indicates the more char formed which prevents burning (Figure 12). Regarding the MCC results, high additive ratio resulted in the low heat release, which proves a clear flame-retardant effect of the additive (Figure 13). Based on these results, this compound can be considered as an additive with beneficial effect on thermal stability and combustion properties in the case of flame retardancy.

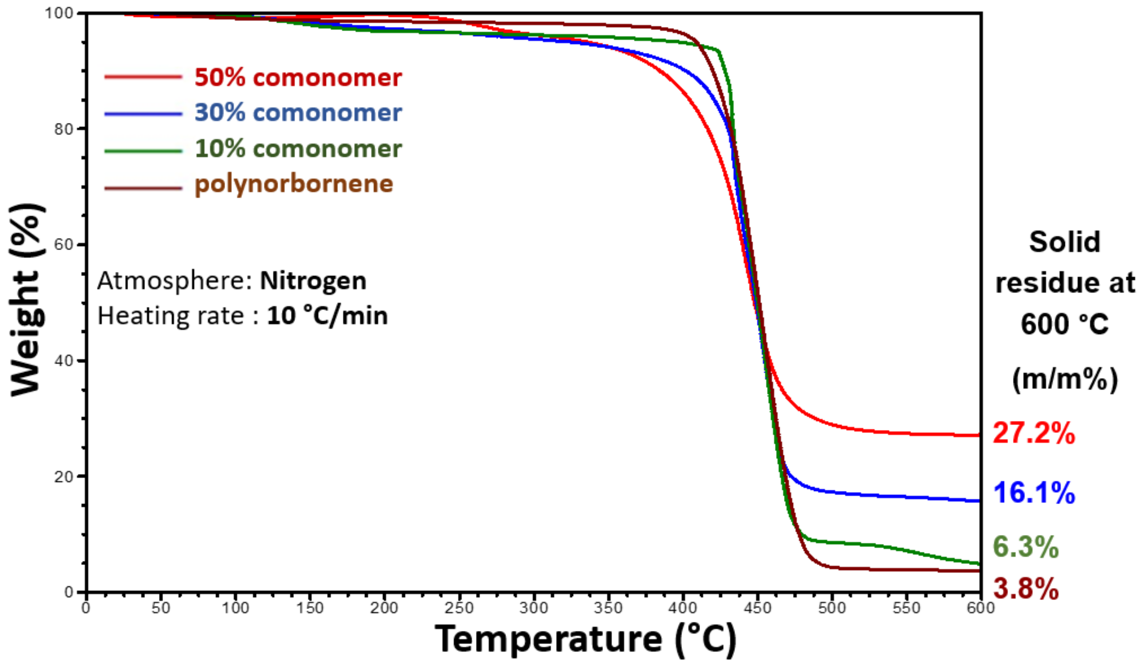
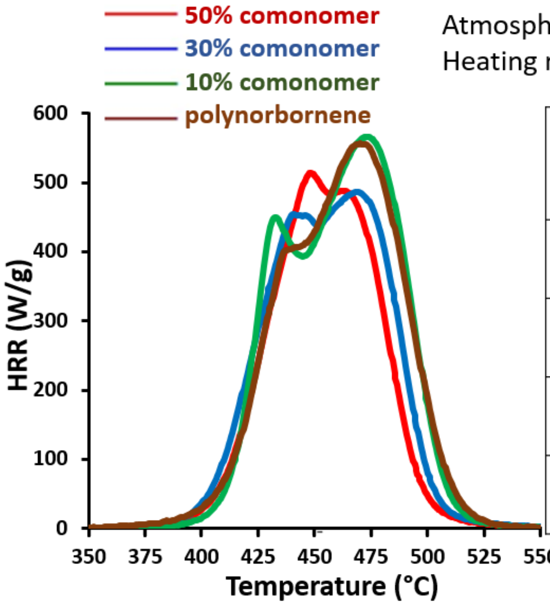


*Figure 12. TGA curves of the synthesized copolymers using trinorborene-2-yl phosphine oxide 19 and norbornene in the presence of G2 catalyst.*



Atmosphere: **Nitrogen**
Heating rate : **1 °C/min**

**HR** – heat release
**HRR** – heat release rate

| Sample | T max [°C] | Total HR [kJ/g] | Peak HRR [W/g] | Char 750 °C [wt %] |
|---|---|---|---|---|
| Poly-norbornene | 469.2 | 38.3 | 552.9 | 1.3 |
| 10 m/m% comonomer | 473.8 | 38.5 | 566.6 | 1.3 |
| 30 m/m% comonomer | 468.9 | 34.3 | 486.6 | 5.6 |
| 50 m/m% comonomer | 448.6 | 31.1 | 513.9 | 8.4 |

*Figure 13. Microscale combustion calorimetric (MCC) curves and data of the copolymers prepared from norbornene and 19 in nitrogen.*

## 2.5. Development of fluorinated polynorbornenes[9]

Polynorbornenes were also synthetized with perfluoroalkyl moieties. Norbornene methyl tosylate (**20**) was treated with the sodium salt of perfluoro-tert-butanol (**21**) in DMF resulted **22** in moderate yield. The diol **15** was converted to bis ether **24** in a different reaction pathway, using Mitsunobu reaction (Figure 14). The monomers **22** and **24** were homopolymerized and copolymerized in the presence of second generation Grubbs (G2) catalyst in high yields. For a different application, copolymers were prepared using these monomers and pyridino crown ether containing norbornene. The thermal stability of the prepared polymers was much lower as the phosphorus containing ones.

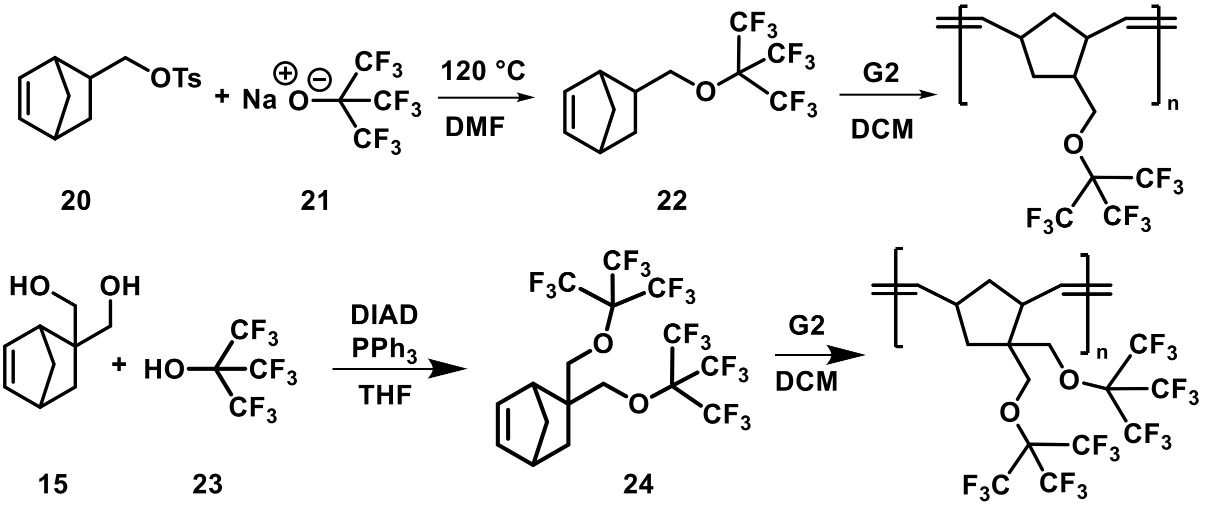


*Figure 14. Synthesis and polymerization of 22 and 24 norbornenes.*[9]

## 3. Synthesis of phosphonate containing polynorbornene by postfunctionalization

In the next step, polynorbornene with phosphonate moieties was prepared from polynorbornene in a simple way. First, the norbornene polymerization was carried out in the presence of second generation Hoveyda-Grubbs catalyst (HG2). In the next step, the polynorbornene was treated with N-bromo succinimide (NBS), the brominated polymer was transferred to phosphorus containing polymer by Arbuzov reaction using triethyl phosphite (Figure 15). The structure of final product was proved by IR and solid-state NMR measurements.

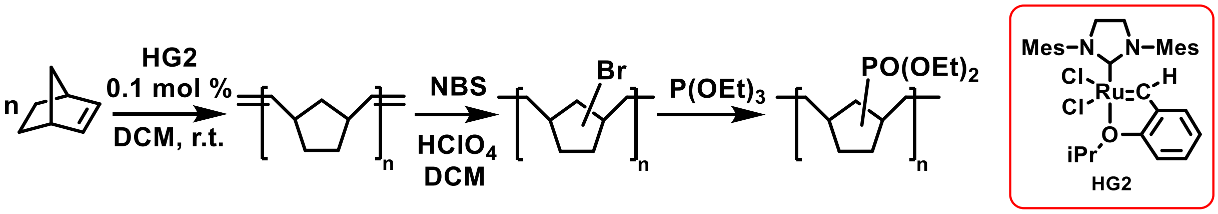


*Figure 15. Synthesis of phosphonate containing polynorbornene by postfunctionalization.*

The thermal characterization of the postfunctionalized polynorbornenes was carried out. For an easy comparison, a similar, well-defined structural polymer was also synthetized by a two-step synthesis[10] (Figure 16).

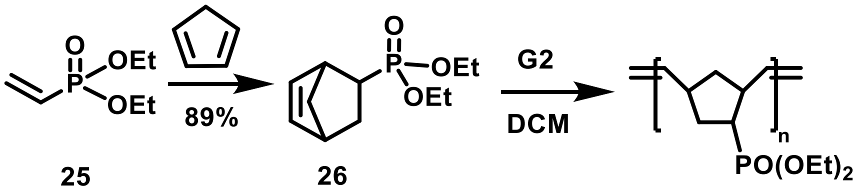


***Figure 16. Synthesis of phosphonate containing polymer by ROMP of 26.***

Considering the TGA analysis of the polymer prepared by postfunctionalization of norbornene, the weight ratio of the solid residue of the polymer (32.2%) after the degradation is much higher than the unsubstituted polynorbornene (3.6%) at 600 °C, as expected, however, somewhat lower, than that in the case of the homopolymer (41.3%) This measurement indicates the relevant amount of char formation which prevents burning (Figure 17). Regarding the MCC results, high P-content resulted in the low heat release, which proves a clear flame-retardant effect (Table 2). Based on these results, this simple postfunctionalization method can be considered as flame retardant material based on its beneficial combustion properties.

***Table 2. MCC results of the postfunctionalized norbornenes and the reference polymers***

| **Polymers** | | **Total HR (kJ/g)** | **$T_{max}$ (°C)** | **Residue (wt%)** |
|---|---|---|---|---|
| **Polynorbornene** | | **29.2** | **465.5** | **1.9** |
| **Phosphonate homopolymer** | | **27.1** | **350.3** | **24.1** |
| **Postfunctionalized polymers** | **Brominated** | **18.4** | **447.6** | **15.7** |
| | **Phosphorylated** | **21.0** | **302.4** | **15.4** |

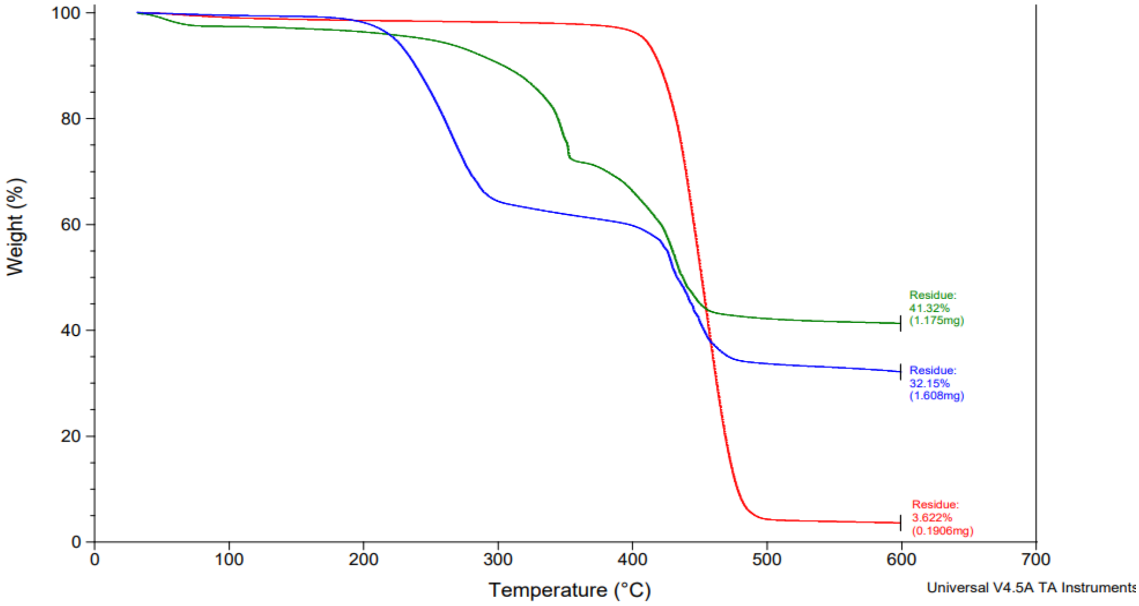
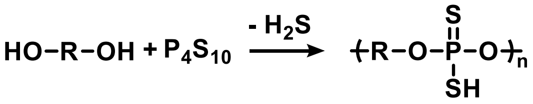


***Figure 17. TG curves of polynorbornene (red), phosphonate containing polynorbornenes prepared by postfunctionalization (blue) or ROMP of 26 (green) (see Table 2).***

# 4. Synthesis of poly(dithiophosphate)s by a catalyst-free reaction[11]

Novel intrinsically flame-retardant polymers have been prepared based on our previous experience in the reaction of amines and phosphorus pentoxide (Chapter 3.2). Experiments to produce phosphorus-containing polymers with phosphorus pentasulfide and various diols were successfully carried out and published recently.[11] The reaction between $P_4S_{10}$ and ethylene glycol, 1,6-hexanediol and poly(ethylene glycol), was investigated for the synthesis of a novel class of functional, phosphorus containing polymers, poly(dithiophosphate)s (PDTPs) under mild conditions. The reactions were carried out without any catalyst in the presence of THF or toluene diluents at a low temperature (60 °C). This simple process successfully results in PDTPs in high yields. The structure of the resulting polymers was revealed by FTIR, $^1$H and $^{31}$P NMR spectroscopies and GPC measurements.



$$HO{-}R{-}OH + P_4S_{10} \xrightarrow{-\,H_2S} \left( R{-}O{-}\overset{S}{\underset{SH}{P}}{-}O \right)_n$$

***Figure 18. Synthesis of poly(dithiophosphate)s from diols and $P_4S_{10}$.***[11]

Interestingly, the formation of branching points were detected in the case of using THF as diluent, which is attributed to the ring-opening of this molecule by the pendant sulfide group in the polymer chain. In contrast, this process is absent when toluene is used. By reacting $P_4S_{10}$ with mixtures of diols, PDTP copolymers were also obtained. The prepared PDTPs possess low glass transition temperatures in the range from -4 °C to -50 °C, indicating the formation of elastic chains. It is important to note that there is no crystalline fraction of PEG in the PDTPs. This can be attributed to preventing the necessary orientation and packing of the PEG chains in PDTPs. The thermogravimetric analyses show that the investigated PDTPs have lower thermal stability than PEG, which is attributed to the lower stability of the P-O-C bonds than the C-O-C ether bonds in PEG. Testing the mechanical properties of the investigated PDTPs by oscillatory rheology measurements indicates that the moduli of these polymers can be varied in a broad range depending on the composition, i.e. on the ratio of the applied diol comonomers. In sum, it can be concluded that the reaction of $P_4S_{10}$ with diols under mild conditions enables the synthesis of a variety of PDTPs with interesting properties. These findings are expected to open new routes for polymer syntheses and various application possibilities, such as flame retardants, pH-responsive polymers etc., with the involvement of the novel poly(dithiophosphate)s.

# 5. Synthesis of N- and S-heterocycles for catalyst ligands[12–15]

Apart from the commercially available Grubbs catalyst systems (NHC ligated ruthenium alkylidenes), development of novel ligands for olefin metathesis catalyst was carried out. Catalyst development was lead to polar (quaternary amino groups) compounds which enable the practical removal of ruthenium via water extraction from the reaction mixtures. 2-Phenylaminoimidazolones (**29**) were prepared in a Knoevenagel condensation of **28** using arylaldehydes (Figure 19)[12].

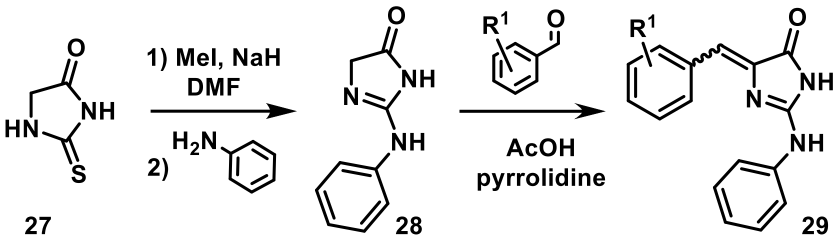
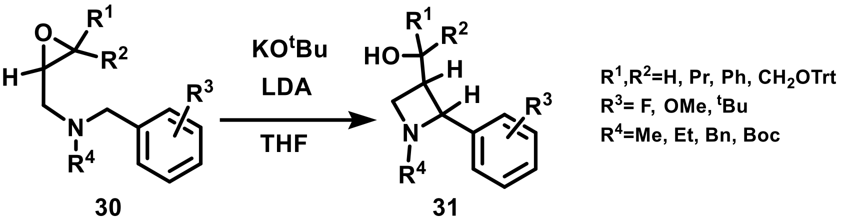


*Figure 19. Synthesis of promising catalyst precursors, 5-benzylidene-2-(phenylamino)-3,5-dihydro-4H-imidazol-4-ones.*[12]

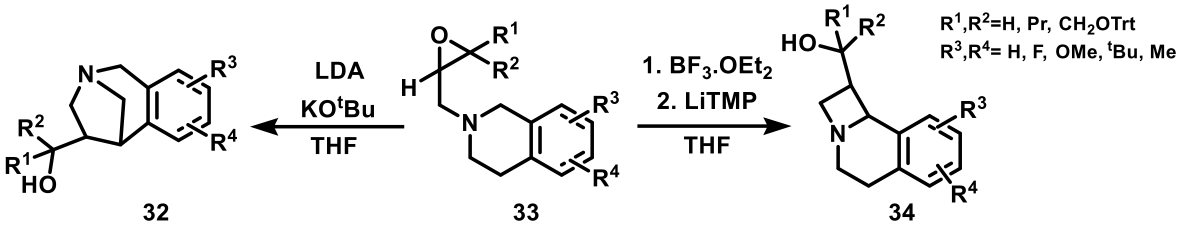
Azetidines (**31**)[13], fused azetidines (**34**) and pyrrolidines (**32**)[14] were prepared previously by a superbase promoted reactions (Figure 20 and 21). In these cases, not only the synthesis but also full interesting theoretical implementation was published successfully in detail recently. In addition, a few of these compounds are proved to be effective organocatalysts.



$R^1$,$R^2$=H, Pr, Ph, $CH_2OTrt$
$R^3$= F, OMe, $^t$Bu
$R^4$=Me, Et, Bn, Boc

*Figure 20. Synthesis of 1,2,3-trisubstituted azetidines organocatalysts in a LDA-KO$^t$Bu superbase promoted rearrangement reaction.*[13]

Fused heterocycles (**39-43**) were prepared by electrocyclization and unexpected reactions of non-stabilised unsaturated azomethine ylides (Figure 22)[15] and published successfully in the last year, part of them was tested as organocatalysts, or they can be useful catalyst ligands and precursors for various transition metal catalysts.



$R^1$,$R^2$=H, Pr, $CH_2OTrt$
$R^3$,$R^4$= H, F, OMe, $^t$Bu, Me

*Figure 21. Preparation novel organocatalysts, bridged (32) and fused (34) N-heterocycles in the presence of lithium organic bases.*[14]

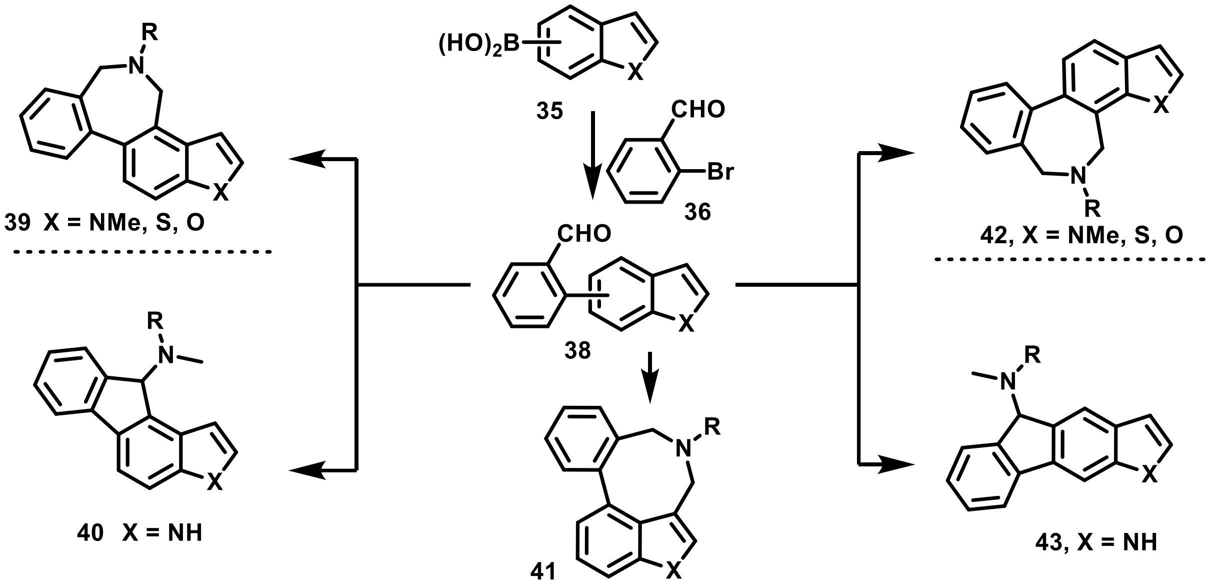


*Figure 22. Synthesis of fused N-heterocycles 39 – 43 from unsaturated azomethine ylides for catalyst ligands.*[15]

1,2-Dithiolium salts (**46**) were formed in a condensation reaction of aryl aldehydes and 1-phenylethane-1-thiones in moderate yields. These compounds with an acidic hydrogen in the heterocycle are promising carbene precursors (like CAAC or NHC precursors) for transition metal-based catalysts (Figure 23), which will be prepared and tested soon as olefin metathesis catalysts.

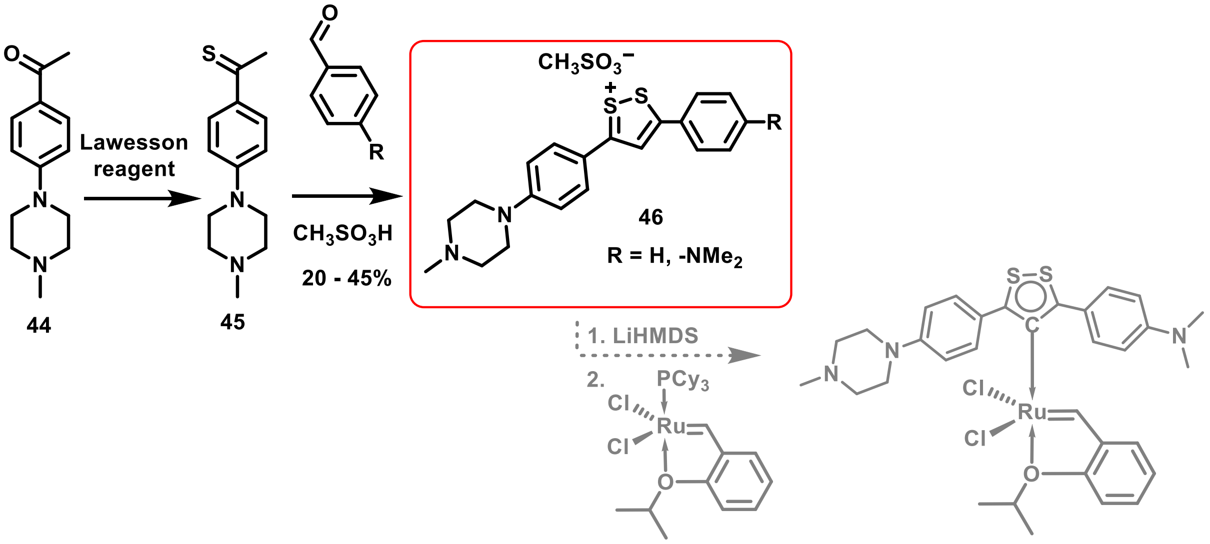


*Figure 23. Synthesis of 1,2-dithiolium salts (46), potential carbene precursors for ruthenium-based catalysts.*

# 6. Green solvents as advantageous media for olefin metathesis reactions[16,17]

Olefin metathesis plays an important role in the field of pharmaceuticals, materials and petroleum refining processes. Due to its success in large scale industries, scientists tried to use more greener solvents to decrease the environmental impacts of this transformation process. Olefin metathesis is typically performed in toxic and volatile solvents such as dichloromethane, toluene, etc.

A systematic study with ruthenium-based catalyst was carried out using benzotrifluoride (BTF), acetone, the environmentally friendly γ-valerolactone and dichloromethane, the commonly used solvent for olefin metathesis reactions. Three well-known metathesis reactions were performed such as ring-opening metathesis polymerization (ROMP), ring-closing metathesis (RCM) and isomerization using typical model substrates and same solvents with the Grubbs G1, G2, and Hoveyda-Grubbs HG2 catalysts (Figure 24). To compare the conditions and catalysts, kinetic measurements have been carried out for all the reactions using $^1$H NMR. Besides, the polymers obtained by ROMP were measured by gel permeation chromatography.

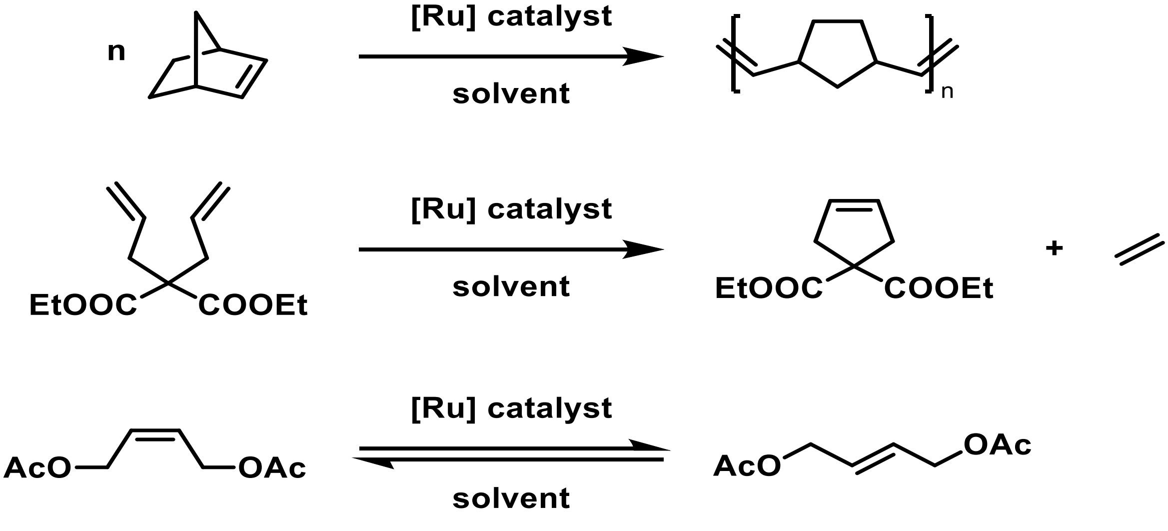


***Figure 24. Ring-opening metathesis polymerization (ROMP) of norbornene (top), ring-closing metathesis (RCM) of diethyl 2,2-diallylmalonate (middle), and the isomerization reaction of (Z)-but-2-ene-1,4-diyl diacetate (bottom) by using ruthenium catalysts.***[16]

Throughout the project, we figured out that benzotrifluoride as an environmentally more advantageous solvent can provide excellent condition for ring-opening metathesis polymerization (ROMP), RCM and isomerisation. In addition, using acetone also provided excellent results in the tested olefin metathesis reactions. We highly suggest using acetone for this reaction type of reaction based on it is environmentally friendly and cost-effective properties. γ-valerolactone also a possible medium for olefin metathesis, however, the reaction kinetic parameters are somewhat less favourable than using acetone or benzotrifluoride (Table 3).

Using technical acetone is also highly recommended to use in ring-opening metathesis polymerization for solving the monomer (i.e., norbornene), its conversion rate is similar to that of ROMP when we use the dry acetone. The technical acetone is cheap, green, and easy to handle.

Significant amount of water has important effect to the polymerization process since they speed up the catalyst decomposition. In another case, air has no obvious effect on ROMP but the prepared polymers can undergo oxidation processes on surface of the polymer. Therefore, the best way is to make the measurements under inert atmosphere like nitrogen or argon to preserve the quality of catalysts and the polymers.

High conversions were achieved in the ring-closing metathesis (RCM) reaction of diethyl 2,2-diallylmalonate in benzotrifluoride and acetone, which proved that this solvent is also a suitable media for the RCM reactions. In addition, in the case of the isomerization reaction of (Z)-but-2-ene-1,4-diyl diacetate, using G2 and HG2 catalysts, much faster initial isomerization occurs in BTF than in DCM, and significantly shorter induction periods are observed in BTF than in DCM.

Based on our results, it can be concluded that benzotrifluoride and acetone can find numerous applications as an alternative, affordable, and sustainable solvent for olefin metathesis processes with high efficiency, not only in academic research but in industrial applications as well, where the use of non-toxic and less volatile solvent is highly recommended. The environmentally friendly γ-valerolactone can also replace the toxic solvents in ROMP and RCM reactions.

***Table 3. The catalyst contents, rate constant ($k_1$) determined by fitting the data in the first 3 minutes, and the number average molecular weight ($M_n$) of the polymers obtained in the ring-opening metathesis polymerization of norbornene in benzotrifluoride (BTF), acetone, γ-valerolactone (GVL) and dichloromethane (DCM) solvents at 25 °C.***

| **Solvent** | **Catalyst (mol%)** | **$k_1$ ($min^{-1}$)** | **$M_n \cdot 10^{-3}$ (g/mol)*** |
|---|---|---|---|
| BTF | G1 (0.050) | 0.82 | 138.7 |
| Acetone | G1 (0.050) | 0.26 | 182.2 |
| GVL | G1 (0.050) | 0.035 | 289.4 |
| DCM | G1 (0.050) | 0.79 | 157.0 |
| BTF | G2 (0.010) | 0.72 | 106.0 |
| Acetone | G2 (0.025) | 1.02 | 220.3 |
| GVL | G2 (0.025) | 0.459 | 108.8 |
| DCM | G2 (0.010) | 0.91 | 245.1 |
| BTF | HG2 (0.003) | 0.66 | 175.8 |
| Acetone | HG2 (0.003) | 1.09 | 251.4 |
| GVL | HG2 (0.003) | 0.087 | 177.9 |
| DCM | HG2 (0.003) | 1.26 | 363.5 |

*Determined by GPC (samples were prepared by using 0.05 mol% catalyst).

# 7. Dissemination of the new scientific results

Four BSc students (Farkas Domahidy, Lan Anh Tran, Akmuhammet Karayev, Nguyen Anh Duc) were involved in the research project. Their contribution has been summarized in BSc thesis works and TDK conference theses, which have defended in the 2019-2022 period. The new scientific results were presented in five international conference presentations, lectures and seven research articles. The PI of the project took part in a summer school as invented lecturer and take a presentation entitled Recent advances in flame retardancy of polymeric materials.

**The new achievements and results have been published in seven manuscripts** [9,11–16] **in leading international journals (D1: 4; Q1: 2; Q2: 1) in chemical sciences.** Due mainly to time consuming and protracted preparative and analytical work, results of additional experiments will be sufficient for other publications in high-quality international journals in the near future. After finishing the experimental and evaluation work, the following manuscripts are planned to be submitted for publication soon.

*Finalization of the manuscripts are in progress*

1. E. Kovács, B. Balterer, N. A. Duc, Gy. Szarka, A Domján, B. Iván: Acetone as a Beneficial Solvent for Olefin Metathesis Polymerization and Related Reactions
2. E. Kovács, B. Balterer, N. A. Duc, Gy. Szarka, A Domján, B. Iván: Gamma-Valerolactone, a Suitable Solvent for Olefin Metathesis Reactions
3. E. Kovács, F. Domahidy, A. Karayev, L. Trif, Zs. Czégény, R. Tuba, B. Iván, B. Szolnoki: Synthesis and characterization of novel norbornene containing phosphorus triamide monomers and its application for flame retardant polymer preparation using metathesis polymerization

*Manuscripts are in preparation*

1. E. Kovács, A. Karayev, Zs. Czégény, B. Iván, B. Szolnoki: Facile synthesis of trinorbornene phosphine oxide monomer for flame retardant polymers.
2. E. Kovács, L. A. Tran, A. Domján, Zs. Czégény, B. Iván, B. Szolnoki: Postfunctionalization of polynorbornene as an effective method for the preparation of flame-retardant polymers.

## 8. Summary

In this highly challenging and collaborative project, intensive investigations have been carried out to synthesize and explore the effect of new phosphorus containing norbornene additives which have not existed before. Development of novel norbornenemethyl phosphorus triamide and trinorborneneyl phoshpine oxide as additives with beneficial effect on thermal characters of the polynorbornene has been successfully achieved by ring-opening metathesis polymerization. The sustainable synthesis of norbornenemethyl phosphorus diamide was accomplished using phosphorus pentoxide as phosphorylating reagent. However, several attempts were made to synthetize norbornenes with phosphonate moieties in high yields in Arbuzov reaction, but these experiments were not as effective as we had expected. Based on its thermal analysis, novel intrinsically flame-retardant polymeric phosphonates were successfully prepared by postfunctionalization of polynorbornenes. In addition, poly(dithiophosphate)s, a new class of intrinsically flame-retardant phosphorus containing polymers were prepared by a simple, catalyst-free synthesis.

New catalyst precursors, ligands were synthetized for the development of less sensitive and more reactive catalyst, as the part of the project. The most promising ones are being tested and will be applied as ruthenium-based catalyst recently under various conditions with promising results.

Benzotrifluoride, γ-valerolactone, in addition to acetone, which was previously said to non-preferred, were identified as suitable solvents for olefin metathesis polymerization and related reactions even in the case of the usage of first-generation Grubbs catalyst.

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