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# Ring-Opening Metathesis Polymerization (ROMP) in Ionic Liquids: Scope and Limitations

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ABSTRACT: The ring-opening metathesis polymerization (ROMP) of functional norbornenes, i.e., *exo,endo*-5-norbornene-2-carbonitrile (**3**), methyl (*exo,endo*-5-norbornene-2-carboxylate) (**4**), norborn-5-ene-2-yl acetate (**5**), 2-propyl *exo,endo*-5-norbornene-2-carboxylate (**6**), norborn-5-ene-2-carboxylic acid (**7**), *exo,endo*-5-norbornene-2-methanol (**8**), *exo,endo*-5-norbornene-2-ylmethyl bromide (**9**), *exo,endo*-5-norbornene-2-ylmethylamine (**10**), *exo,endo*-5-norbornene-2-triethoxysilane (**11**), dimethyl *exo,endo*-5-norbornene-2-yl phosphonate (**12**), *exo,endo*-5-norbornene-2-ylcarboxyethyl-3-ethylimidazolium bis(trifluoromethylsulfonyl)imide (**13**), *exo,endo*-5-norbornene-2-ylcarboxyethyl-3-ethylimidazolium tetrafluoroborate (**14**), 7-oxanorborn-5-ene-2,3-dicarboxylic anhydride (**15**), was performed in a variety of pure ionic liquids (ILs) in the absence of any cosolvent. Both imidazolium, i.e., [1-butyl-3-methylIM]$^+$X$^-$ and [1-butyl-2,3-dimethylIM]$^+$X$^-$ (IM$^+$ = imidazolium, X$^-$ = PF$_6{}^-$, CF$_3$SO$_3{}^-$, (CF$_3$SO$_2$)$_2$N$^-$, CF$_3$COO$^-$, NO$_3{}^-$, BF$_4{}^-$, Br$^-$), and phosphonium-based ILs, i.e., [P$^+$(C$_6$H$_{13}$)$_3$(C$_{14}$H$_{29}$)]X$^-$ (X$^-$ = PF$_6{}^-$, BF$_4{}^-$, Cl$^-$), were used. In this context, the principal compatibility of an IL with a series of ruthenium-based catalysts, i.e. RuCl$_2$Py$_2$(IMesH$_2$)(CHPh) (**1**) and RuCl$_2$(IMesH$_2$)(2-(2-PrO−C$_6$H$_4$) (**2**) (Py = pyridine, IMesH$_2$ = 1,3-bis(2,4,6-trimethylphenyl)-4,5-dihydroimidazolin-2-ylidene) was shown. The influence of temperature, concentration of both the initiator and the monomer and nature of the IL on ROMP was investigated. ROMP of norbornene derivatives in ionic solvents proceeded with high speed and offered access to high molecular weight polymers ($M_w$ up to 1 500 000 g/mol) in high yields. Most important, ILs allowed for the synthesis of polymers from monomers that are hardly polymerizable in organic solvents, e.g. of **15**. The use of **3** in [1-methyl-3-butylIM]$^+$PF$_6{}^-$ as the reaction medium along with 2-(2-propoxy)styrene allowed for the recycling of the ruthenium catalyst. The interaction of catalyst **2** with different ILs, which allowed for an explanation of the influence of the IL's nature upon the polymerization process, was investigated by IR- and UV−vis spectroscopy. These investigations will facilitate the choice of the optimum IL in future investigations.

## Introduction

Functional poly(norbornene)s are of particular interest because of their unique physical and optoelectronic properties, such as high glass transition temperature, optical transparency and low birefringence.[1] Ring-opening metathesis polymerization (ROMP) is nowadays a well-established polymerization technique.[2−5] Both well-defined Schrock[6−8] and Grubbs[3,9] type initiators are suited for these purposes and allow for polymerizations in a truly living manner. In Ru-catalyzed ROMP, N-heterocyclic carbene (NHC)-based ruthenium benzylidenes[9−11] are in most cases the preferred initiators.[12,13] The increasing demand for clean chemical synthesis is becoming more striking from both an economical and environmental point of view. As a consequence, there is a strong need for new chemical technologies using novel types of environmentally benign media. In this context, water, supercritical fluids (such as carbon dioxide), and ionic liquids (ILs)[14−18] are nowadays considered as such reaction media and have become a part of the intensively developing branch of chemical science termed "green chemistry".[19]

The term "ionic liquids" identifies a class of organic compounds, composed entirely of ions, which are liquid at or near room temperature (mp <100 °C) and, as consequence of their nature, show some intriguing features such as extremely low vapor pressure, high thermal stability, the ability to retain the liquid state over a wide temperature range and the ability to solvate many organic, inorganic, and polymeric materials.[20−22] In addition, ILs are noncorrosive and nonflammable. Numerous reactions have already been carried out in ILs including metathesis,[23−28] polymerization and polycondensation reactions.[20,29−33] Surprisingly, there exists only one successful publication so far[34] describing the ROMP of nonfunctionalized, pure norborn-2-ene using a cationic catalyst and a *binary solvent system* consisting of an IL and toluene. Thus, the scope of this contribution was to accomplish ROMP in neat ILs *in the absence of any cosolvent* with well-defined Grubbs and Grubbs−Hoveyda catalysts, respectively, to investigate the influence of the IL's and catalyst's nature on polymerization and, finally, to recycle the catalyst.

## Results and Discussion

**Preliminary Experiments.** Several considerations were taken into account for the catalysts to be used for ROMP in IL. Because of their high reactivity, their tolerance to most functional groups and their ability to produce well-defined polymers with controlled architectures, the ruthenium-based catalysts **1**-**2** were chosen. While RuCl$_2$(PCy$_3$)(1,3-dimesityl-4,5-dihydroimidazolin-2-ylidene)(=CHPh) displays comparably high reactivity, initiation efficiencies with various norborn-2-
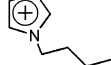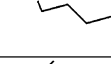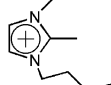
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**Table 1. Polymerization of 3 in Different ILs by Use of 1[a]**

| No | Ionic Liquid | | [Monomer] | [Cat] | N[b] | Yield [%] |
|---|---|---|---|---|---|---|
| | Cation | Anion | mmol/g of IL | mg/g of IL | | |
| 1[c] | | $PF_6^-$ | 0.48 | 1.76 | 200 | no polymer |
| 2 | | | 0.48 | 1.76 | 200 | no polymer |
| 3 | | | 0.48 | 1.76 | 200 | 8 |
| 4 | | $PF_6^-$ | 0.48 | 3.52 | 100 | 22 |
| 5 | $P^+(C_6H_{13})_3(C_{14}H_{29})$ | $PF_6^-$ | 0.48 | 1.76 | 200 | 57 |
| 6 | | | 0.24 | 1.76 | 100 | 25 |
| 7 | | | 0.18 | 1.76 | 70 | 30 |
| 8[d] | | | 0.96 | 3.52 | 200 | 4 |
| 9 | | | 0.48 | 3.52 | 100 | 85 |
| 10 | | | 0.24 | 3.52 | 50 | 31 |
| 11[e] | $CHCl_3$ | | 0.48 | 1.76 | 200 | 72 |

[a] Conditions: $T = 55$ °C; reaction time, 4 h. [b] Number of monomer equivalents. [c] $T = 40$ °C. [d] Onset temperature of mass loss is 305 °C. [e] For comparison, the onset temperature of mass loss is 320 °C.

ene-based monomers are typically in the range of 3−5%.[11] Therefore, to increase initiation efficiency, the pyridine-containing Ru-based catalyst $RuCl_2Py_2(IMesH_2)(CHPh)$ (**1**) was used.[35] Finally, the Grubbs−Hoveyda initiator[36] $RuCl_2(IMesH_2)(2-(2-PrO−C_6H_4)$ (**2**) was taken into consideration.

On the basis of work by Shaplov et al.[31,37] which revealed superior solubility of acrylonitrile in ILs, *exo,endo*-5-norbornene-2-carbonitrile (**3**) was chosen for preliminary investigations. Various ILs were tested in order to retrieve information on the solubility of this monomer. These revealed that this monomer can in fact be dissolved in ionic solvents based on 1,3-dialkylimidazolium or tetraalkylphosphonium cations in combination with anions such as $BF_4^-$, $PF_6^-$ or $Cl^-$. For our initial investigations, we chose one of the most frequently used ILs—1-methyl-3-butylimidazolium hexafluorophosphate ($[1-Me-3-BuIM]^+PF_6^-$) and initiator **1**. The latter was prepared according to a protocol published by Grubbs et al. via reaction of $RuCl_2-(PCy_3)(1,3-Mes_2-imidazolin-2-ylidene)(CHC_6H_5)$ with excess pyridine[35] and is a fast initiating derivative of the second generation Grubbs catalyst.

Disappointingly, practically no polymer was formed in this IL even after heating to 55 °C over a period of 4 h, as can be deduced from Table 1, entries 1−3. This might be explained by the degradation of this particular IL via proton abstraction at the C-2 position followed by the formation of a carbene species.[17,34] Alternatively, an oxidative addition of Ru to the imidazolium cation might be considered.[38] For a detailed discussion of this issue vide infra. To avoid these problems, the hydrogen at the C-2 position of the imidazolium based IL was replaced by a methyl group by using $[1,2-Me_2-3-BuIM]^+-PF_6^-$. Polymerizations carried out in this IL resulted in polymer yields around 20% (Table 1, entry 4). These low polymer yields are attributed to polymer precipitation from the solution at very early stages of the reaction. In an effort to further increase polymerization yields, several phosphonium based ILs were utilized as alternatives (Table 1, entries 5−10). Indeed, replacement of $[1-Me-3-BuIM]^+PF_6^-$ by trihexyltetradecyl phosphonium hexafluoroborate resulted in the formation of a viscous

solution and the isolation of the desired polymer in yields around 85% (Table 1, entry 9), which at least rival yields obtained in a standard organic solvent such as $CHCl_3$.

At this point it was not possible to extensively vary the reaction temperature since the melting point of trihexyltetradecyl phosphonium hexafluoroborate is 50 °C and Ru-based catalysts are prone to decomposition at temperatures above 60 °C.[39] Therefore, the search for optimal parameters was reduced to variations in monomer and catalyst concentration. The decrease of monomer concentration at a constant volume of the IL and quantity of catalyst led to reduced polymer yields (Table 1, entries 5−7). Similarly, an increase in monomer concentration with preservation of monomer/catalyst ratio decreased product yields (Table 1, entries 5 and 8). Thus, the optimum polymer yield was achieved by increasing the catalyst concentration to 4.8 $\mu$mol/g and setting the monomer concentration to 0.48 mmol/g. (Table 1, entry 9). To characterize the structures of poly-**3** derived polymers, we carried out IR-, NMR- and DSC measurements on the polymers obtained both in ILs and chloroform. These investigations revealed that the structure of poly-**3** obtained in ILs was identical to that of poly-**3** synthesized in chloroform (approximately 80% trans, 20% cis).

**Influence of the IL's Structure on ROMP.** It is well-known[21,22] that the properties of ILs depend on the structure of the cation (the symmetry and the length of alkyl substituents, the presence of hydrophobic groups, etc.) as well as on the degree of anion charge delocalization. The general problem in the use of ILs is the choice of the best IL for a concrete process out of so far roughly $10^8$ possible structural variations in the combination of different cations and anions.[21] To elucidate the influence of the IL's nature on the yield and molecular weight of polymers, the ROMP of methyl (*exo,endo*-5-norbornene-2-carboxylate) (**4**) in different ILs was studied (Table 2). This monomer was chosen due to the good solubility of the resulting polymer in organic solvents, thus allowing for the investigation of its molecular weight. On the basis of our previous investigations[29−31,37,40] along with those reported by other groups,[20,41] it is possible to divide commonly used ionic solvents into several groups according to their influence upon the polymerization and polycondensation reactions. The representatives of the first group are ILs with counteranions such as $PF_6^-$, $BF_4^-$, bis(trifluoromethylsulfonyl)imide, bis(pentafluoroethyl-sulfonyl)imide, tri(pentafluoroethyl)trifluorophosphate and others, whose distinguishing feature is their weak coordination ability. Frequently, such ionic liquids are capable to dissolve polymers like polyacrylates, while fully aromatic polyhet-eroarylenes precipitate from their solutions on early stages of the polycondensation process. The second group represents ionic solvents with $CF_3COO^-$, $CH_3COO^-$, and fluorobutyl acetate anions. These ILs in many cases can even not dissolve the starting monomers. Somewhere between the first and second group are ILs based on trifluoromethanesulfonate, tosylate and methanesulfonate anions. The fourth group is formed by ILs containing anions like $NO_3^-$, $SO_4^{2-}$, hydrogen sulfate, etc. Finally, a separate group is comprised by bromide- and chloride-based ionic solvents. They differ from the others by excellent solubilizing properties for both the starting monomeric compounds and resulting polymers. Thus, for polymerization of **4**, we chose one representative from each group and applied the optimum conditions elaborated above ([initiator] = 4.8 $\mu$mol/g; [**4**] = 0.48 mmol/g).

First, it is noticeable that the use of ILs based on strongly coordinating counteranions such as halogens and $NO_3^-$ did not give rise to the formation of any polymer (Table 2, entries 4

**Table 2. Polymerization of 4 Prepared by the Action of 1 in Different ILs[a]**

| No | Ionic Liquid | | Time | Yield, | $\overline{M}_{n\,(LS)}$ | $\overline{M}_{w\,(LS)}$ | PDI$_{(LS)}$ |
|---|---|---|---|---|---|---|---|
| | Cation | Anion | min | % | b | | |
| 1 | | CF$_3$SO$_3^-$ | 240 | 99 | 71200 | 265000 | 3.70 |
| 2 | | (CF$_3$SO$_2$)$_2$N$^-$ | 240 | 81 | 182000 | 748000 | 4.10 |
| 3 | | CF$_3$COO$^-$ | 240 | 76 | 14600 | 30600 | 2.09 |
| 4 | | NO$_3^-$ | 240 | - | - | - | no polymer |
| 5 | | BF$_4^-$ | 240 | 75 | 14300 | 59400 | 4.11 |
| 6 | | Br$^-$/ PF$_6^-$ (1:1) | 240 | 90 | 220000 | 760000 | 3.44 |
| 7 | | PF$_6^-$ | 240 | 91 | 800000 | 1500000 | 1.90 |
| 8 | | PF$_6^-$ | 4 | 54 | 290000 | 653000 | 2.24 |
| 9[c] | | PF$_6^-$ | 4 | 99 | 26600 | 74800 | 2.81 |
| 10 | P$^+$(C$_6$H$_{13}$)$_3$(C$_{14}$H$_{29}$) | PF$_6^-$ | 240 | 94 | 177000 | 525000 | 2.96 |
| 11[d] | | PF$_6^-$ | 4 | 82 | 116000 | 244000 | 2.10 |
| 12[c] | | PF$_6^-$ | 4 | 84 | 107000 | 242000 | 2.25 |
| 13[e] | | PF$_6^-$ | 4 | 59 | 234000 | 440000 | 1.87 |
| 14[f] | | PF$_6^-$ | 4 | 58 | 88500 | 214000 | 2.41 |
| 15 | | BF$_4^-$ | 240 | 92 | 392000 | 898000 | 2.29 |
| 16 | | BF$_4^-$ | 4 | 68 | 538000 | 741000 | 1.38 |
| 17 | | Cl$^-$ | 240 | - | - | - | no polymer |
| 18[g] | CHCl$_3$ | | 240 | 57 | 14000 | 18100 | 1.29 |

[a] Conditions: 55 °C; catalyst:monomer = 1:100; i.e., $\overline{M}_{n(theor)}$ = 15300 g/mol; [cat] = 3.5 mg/g of solvent; [monomer] = 0.48 mmol/g of solvent. [b] GPC data measured in THF. [c] Prepared by the action of catalyst **2**. [d] Onset temperature of mass loss is 375 °C. [e] [cat] = 1.7 mg/g of solvent; [monomer] = 0.24 mmol/g of Solvent. [f] [cat] = 1.2 mg/g of solvent; [monomer] = 0.16 mmol/g of Solvent. [g] For comparison, the onset temperature of mass loss is 395 °C.

**Table 3. Polymerization of Monomers 5−15 Prepared by the Action of 1 in Various ILs[a]**

| No | Ionic Liquid | | Monomer | Yield,% | $\overline{M}_{n\,(LS)}$[b] | $\overline{M}_{w\,(LS)}$ | PDI$_{(LS)}$ |
|---|---|---|---|---|---|---|---|
| 1 | P$^+$(C$_6$H$_{13}$)$_3$(C$_{14}$H$_{29}$) | PF$_6^-$ | 5 | 81 | 177400 | 322600 | 1.81 |
| 2 | | | 6 | 94 | 166500 | 368700 | 2.21 |
| 3[c] | | | 6 | 76 | 33000 | 78600 | 2.37 |
| 4[d] | | | 7 | 13 | - | - | - |
| 5[d] | | | 7 | 11 | - | - | - |
| 6[d] | | | 9 | - | - | - | no polymer |
| 7 | | | 10 | - | - | - | no polymer |
| 8 | | | 11 | 95 | - | - | - |
| 9[d] | | | 13 | 12 | - | - | - |
| 10[d] | | | 15 | - | - | - | no polymer |
| 11 | | PF$_6^-$ | 5 | 83 | 80900 | 250500 | 3.09 |
| 12 | | | 6 | 92 | 71500 | 165700 | 2.31 |
| 13[d] | | | 7 | 52 | - | - | - |
| 14[d] | | | 8 | 89 | - | - | - |
| 15 | | | 9 | - | - | - | no polymer |
| 16 | | | 10 | - | - | - | no polymer |
| 17[d,g] | | | 13 | 99 | - | - | - |
| 18[d,g] | | | 14 | 99 | 23900 | 29800 | 1.25 |
| 19[c,d,g] | | | 14 | 99 | 21000 | 26000 | 1.24 |
| 20[d,e,f] | | | 15 | 75 | 29000 | 56800 | 1.95 |
| 21[d,f] | | BF$_4^-$ | 12 | 59 | 32200 | 52900 | 1.64 |
| 22[c,d,g] | | | 14 | 80 | - | - | - |

[a] Conditions: 55 °C; catalyst:monomer = 1:100; [cat] = 3.5 mg/g of solvent; [monomer] = 0.48 mmol/g of solvent; reaction time, 4 min. [b] GPC data measured in THF. [c] Prepared by action of catalyst **2**. [d] Reaction time, 4 h. [e] The polymer was converted into the soluble diester by boiling in dry methanol for 5 h. [f] Using RI detection. [g] $\overline{M}_w$ by static light scattering; $\overline{M}_n$, $\overline{M}_w$ by sedimentation analysis by means of ultracentrifuge in acetone.

and 17). However, changing to fluorinated, weakly coordinating anions resulted in the formation of high molecular weight poly-**4**. Among the ILs bearing large sized anions the highest molecular weight was achieved in a bis(trifluoromethylsulfonyl)-imide derived ionic liquid, unfortunately along with the highest PDI (Table 2, entries 1−3). Values for $\overline{M}_n$ close to the theoretical one ($\overline{M}_n$ = 15300 g/mol) were obtained in 2-methylimidazolium based ILs containing trifluoroacetate and tetrafluoroborate anions (Table 2, entries 3 and 5). On the other hand, the use of a phosphonium tetrafluoroborate IL allowed for the synthesis of low PDI polymers (Table 2, entry 16), however, with poor control over molecular weight. The utilization of a mixture of two ILs with bromide and hexafluorophosphate anions reduced molecular weights and increased PDIs in comparison to the data of polymers obtained in pure [1,2-Me$_2$-3-BuIM]$^+$PF$_6^-$ (Table 2, entries 6 and 7).

**Precipitation Polymerization in ILs.** It is worth mentioning that in all ILs used, polymers derived from monomer **4,** readily precipitated from the reaction mixture within a few minutes after the beginning of the process. This allows running such polymerizations in the form of precipitation polymerizations. This approach is of particular attractiveness, since the polymer formed may easily be removed from the reaction mixture by filtration. By such an approach, polymers of high purity are accessible. Such precipitation is also observed for lower concentrations of both the monomer and the catalyst (Table 2, entries 11, 13, and 14). Moreover, as observed for **4**, this decrease in monomer and catalyst concentrations gave again rise to low polymer yields and molecular weights and should therefore be avoided. Since we anticipated that PDIs increased after polymer precipitation, it was of particular interest to isolate the polymer right at the moment of its precipitation. Not

unexpected, this gave raise to decreased polymer yields (Table 2, entries 7, 8, 10, and 11) and molecular weights. Interestingly, isolation of polymers short after initiation (approximately 4 min) from the phosphonium based IL led to a decrease in PDI (Table 2, entries 10, 11, 15, and 16), while in the case of an imidazolium based IL higher PDIs were observed (Table 2, entries 7−8). Switching from catalyst **1** to catalyst **2** resulted in an increase in PDI and decrease in molecular weights (Table 2, entries 8, 9, 11, and 12). Thus, it seemed rather important to overcome the problem of polymers precipitation. For this purpose, *exo,endo*-5-norbornen-2-yl acetate (**5**), which is quite similar to **4**, was investigated. Results identical to polymerization of **4** were obtained (Table 3, entries 1 and 11) with the exception that in [1,2-Me$_2$-3-BuIM]$^+$PF$_6^-$ the PDI was quite high (3.09). It is well-known, that polymer solubility can be increased through the introduction of either long side chains or bulky groups. We therefore synthesized 2-propyl *exo,endo*-5-nor-bornene-2-carboxylate (**6**), expecting the resultant polymer to be soluble in ILs. Unfortunately, poly-**6** was also precipitating during the polymerization in a form of swelled gel from all ILs tested (Table 3, entries 2, 3 and 12).

**Other Monomers.** These findings so far demonstrated the principal applicability of ILs to ROMP; however, we sought to check for the general applicability of ILs to ROMP and, most important, to identify particular advantages of their utilization. As shown previously,[32] some dicarboxylic acids possess good solubility in ionic solvents. Thus, we attempted to polymerize norborn-5-ene-2-carboxylic acid (**7**) (Table 3, entries 4 and 13). Interestingly, poly-**7** was formed in very low yield (11%) in the phosphonium based IL while the use of [1,2-Me$_2$-3-BuIM]$^+$-PF$_6^-$ allowed for its formation in 52% yield. The same was observed for *exo,endo*-5-norbornene-2-methanol (**8**). Its polym-erization could only be accomplished in an imidazolium derived

**Table 4. Recycling of Catalyst 2 in the Polymerization of 14 in [1,2-Me$_2$-3-BuIM]$^+$PF$_6^{-a}$**

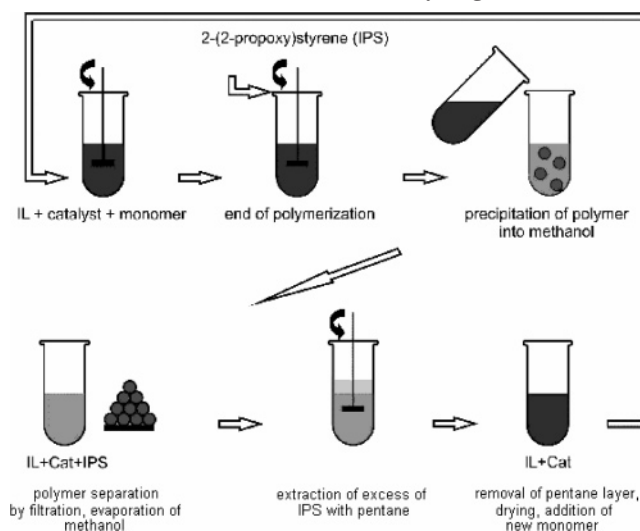| no. | recycling | yield,% | $\bar{M}_n^b$ | $\bar{M}_w$ | PDI |
|-----|-----------|---------|---------------|-------------|-----|
| 1 | 0 | 99 | 21 000$^c$ | 26 000 | 1.24 |
| 2 | 1 | 91 | | 12 800$^b$ | |
| 3 | 2 | 14 | | | |

$^a$ Conditions: 55 °C; catalyst:monomer = 1100; [cat] = 3.5 mg/g of solvent; [monomer] = 0.48 mmol/g of solvent; reaction time, 4 h. $^b$ $\bar{M}_w$ by static light scattering. $^c$ $\bar{M}_n$ by sedimentation analysis using ultracentrifuge in acetone.

IL (Table 3, entries 5 and 14). This can be explained by the different dissolving ability of phosphonium and imidazolium ionic solvents. Having identical anions, these ILs vary both in the cation's nature and the length of alkyl chains. As a result, poly-**7** and poly-**8** precipitated from imidazolium hexafluorophosphate, while they were found to be soluble until the end of the reaction in the phosphonium-based ionic liquid.

Disappointingly, no polymer was formed from monomers **9** and **10**. The polymerization of *exo,endo*-5-norbornene-2-triethoxysilane (**11**) resulted in the precipitation of white fibers, which were insoluble in any organic solvent after their isolation (Table 3, entry 8). To prepare a monomer, that is fully compatible with ILs, we synthesized monomer **12** containing a phosphorus group similar to a phosphonium derived IL. In fact, **12** was successfully polymerized in trihexyltetradecyl phosphonium hexafluorophosphate and the polymer that formed was soluble during the entire polymerization process. Disappointingly, it was not possible to isolate the product from the ionic solvent due to its high solubility in common organic solvents. However, a quite elegant solution to this problem was found taking advantages of ILs as a design solvents. Thus, polymerization of **12** was carried out in [1,2-Me$_2$-3-BuIM]$^+$BF$_4^-$, which is soluble in water. Poly-**12** was simply isolated by washing the reaction mixture with water (Table 3, entry 21). Similarly, two ionic monomers, **13** and **14**, structurally similar to the IL were developed. While the polymerization of **14** in a phosphonium derived ionic solvent did not result in the formation of any polymer (Table 3, entry 9), ROMP of **13** and **14** proceeded smoothly in all imidazolium derived ILs tested (Table 3, entries 17−19 and 22) and gave rise to virtually quantitative yields (99%) and low PDIs.

Despite these encouraging results for ionic monomers, the probably most striking advantage of ILs in ROMP is that they offer the possibility to polymerize monomers that are either hardly polymerizable in traditional organic solvents or cannot be polymerized at all. To demonstrate that, we chose 7-oxanorborn-5-ene-2,3-dicarboxylic anhydride (**15**), which forms insoluble polymers (at degrees of polymerization > 10) in standard organic solvents.[42,43] To our pleasure, **15** was readily polymerized in 75% yield in an imidazolium-derived IL. (Table 3, entry 20). Poly-**15** was then converted into a soluble form via reaction with methanol and studied. GPC measurements revealed that poly-**15** was obtained with high molecular weight and acceptable PDI (1.95).

**Catalyst Recycling.** In the next step, we investigated the possibility of catalyst recycling. To remove the Ru−alkylidene from the polymer, compounds such as ethyl vinyl ether are usually added. For recycling experiments, we decided to use initiator **2** and 2-(2-propoxy)styrene.[36] A first run with monomer **14** was performed as described above with the exception that, after 4 h, 2-(2-propoxy)styrene was added to the solution in order to cleave off the catalyst from the polymer chain and regenerate **2** (Table 4, entry 1). Addition of methanol resulted in the precipitation of poly-**14** that had formed, which was

**Scheme 1. Illustration of the Recycling Process**



separated by filtration. The methanol was removed in vacuo, excess of 2-(2-propoxy)styrene was extracted with pentane, new portion of monomer was added and the polymerization was allowed to resume. Scheme 1 illustrates these experiments.

Using this protocol, the second run in the restored system allowed for obtaining the polymer in 91% yield (Table 4, entry 2), however, with decreased values for $M_w$. The third run resulted in comparably low polymer yields up to 14%. Nevertheless, these experiments clearly demonstrate the principal possibility of initiator recycling by use of ILs.

**Interaction Between Catalyst and ILs. General Information.** In the absence of a protective methyl substituent at C$_2$ of the imidazolium ring the acidic proton can be removed to form carbene complexes with metals. Thus, palladium complexes of the general type PdX$_2$(1,3-R$_2$IM)$_2$ were isolated from solutions of Pd(CH$_3$COO)$_2$ and PdCl$_2$, respectively, in [1,3-Bu$_2$IM]$^+$Br$^-$ as well as [1,3-Bu$_2$IM]$^+$BF$_4^-$.[44] Phosphine ligands, ammonium and phosphonium halides as well as quarternary ammonium salts have been found to stabilize the Pd-catalysts probably via formation of a zerovalent Pd species and accelerate olefination reactions.[45−48] It was also found that the presence of halide ions is necessary for the formation of carbene complexes in ILs. Thus, Xu et al.[49] reported that during the dissolution of palladium(II) acetate in [1-Me-3-BuIM]$^+$BF$_4^-$ and [1-Me-3-BuIM]$^+$Br$^-$, respectively, the corresponding carbene complexes were formed only with the latter IL. Palladium carbene complexes were also detected in ILs based on the (CF$_3$SO$_2$)$_2$N$^-$ anion.[50] However, the authors also demonstrated that utilization of ILs based on [N-butylpyridinium]$^+$PF$_6^-$, [1,2-Me$_2$-3-BuIM]$^+$-BF$_4^-$ or 1,2-Me$_2$-3-BuIM]$^+$(CF$_3$SO$_2$)$_2$N$^-$ did *not* result in any carbene formation. While studying the Suzuki coupling,[51] the authors discovered that the Pd(0) complex Pd(PPh$_3$)$_4$ dissolved in [1-Me-3-BuIM]$^+$BF$_4^-$ in the presence of a small quantity of sodium chloride generated the Pd(II) complex [(PPh$_3$)$_2$Pd-(bmimy)X]$^+$BF$_4^-$, (bmimy = 1-methyl-3-butylimidazole-2-ylidene, X = Cl, Br). Other examples of metal-containing ILs and their reactions with metals can be found in a recent review.[52]

The use of ruthenium catalysts in ILs for ring-closing metathesis (RCM),[23−25,53−56] olefin cross-metathesis,[57] and Aldol- and Mannich-type reactions[58] is known. Although a wide range of ruthenium catalysts have been examined, very little information concerning transformations of the catalyst is available, in part because in situ $^1$H and $^{13}$C NMR analysis requires the use of deuterated ionic liquids, which are extremely expensive. Furthermore, extraction of the catalyst after reaction

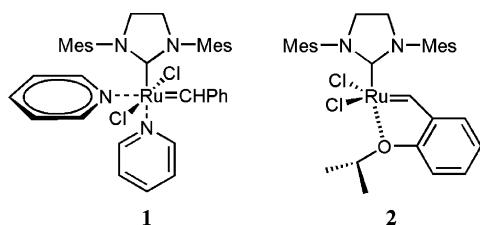**Figure 1.** Structure of catalysts **1** and **2** used in ROMP (Mes = 2,4,6-Me$_3$C$_6$H$_2$).

is often not possible (at least for catalysts that do not easily leach), which prevents postreaction analysis by spectroscopic techniques. Thus, discussions are speculative so far. In this context it was argued that the decrease in catalyst's activity can be connected with its partial decomposition in ILs at elevated temperatures as well as with its extraction to the organic phase. Dyson et al.[59] suggested electrospray ionization—ion trap mass spectrometry for the study of ionic [Ru($\eta^6$-*p*-cymene)($\eta^2$-triphos)Cl][PF$_6$], [Rh($\eta^5$-C$_2$Me$_5$)(dppe)ClBF$_4$], and ([Ru($\eta^6$-*p*-cymene)(pta)Cl$_2$]) catalysts dissolved in [1-Me-3-BuIM]$^+$PF$_6^-$. While the first two catalysts did not form any aggregates, signals for [M + MeBuIM]$^+$ were observed in the solution of the latter in the IL. Daguenet et al.[60] demonstrated the inhibition of catalytic activity in ILs. It was shown that due to the ionic dissociation in [1-Me-3-BuIM]$^+$Cl$^-$, substitution of Cl by hydride in ruthenium(II) $\eta^6$-*p*-cymene(dppm) derivatives occurred. Nevertheless, the interaction of **1** or **2** with different ILs has not yet been investigated.

**IR Spectroscopy.** For obvious reasons, the recyclable Grubbs—Hoveyda catalyst **2** appears much more attractive in terms of the recycling aspect based on a "release and return" olefin metathesis mechanism[53,61] and was thus chosen for our studies (vide supra). Coordination of the 2-Pr—O-ligand to the Ru-core is comparably weak.[61] In addition, one might think of replacement of one or two chlorines by other ligands[62,63] and finally, replacement of the N-heterocyclic carbene by a solvent derived one. To shed some light on this issue, we dissolved catalyst **2** in three different ILs, heated the solutions to polymerization temperature, extracted the resultant compounds and investigated them by IR spectroscopy.

The IR spectrum of the *parent catalyst* **2** shows two $\nu_{Ru-Cl}$ bands at 345 and 371 cm$^{-1}$, weak CH bands of the NHC ligand at 3086, 3070 cm$^{-1}$ as well as strong bands of the 2-(2-propoxy)-styrene ligand (749, 1111, 1259, 1481, and 1452 cm$^{-1}$). For pure [1-Me-3-BuIM]$^+$PF$_6^-$, there were two strong CH bands at 3171 and 3125 cm$^{-1}$ and PF$_6^-$ anion bands at 850 and 566 cm$^{-1}$. Pure [1,2-Me$_2$-3-BuIM]$^+$PF$_6^-$ showed a strong $\nu_{CH}$ band at 3158 cm$^{-1}$ with a shoulder at 3188 cm$^{-1}$ as well as PF$_6^-$ bands at 850 and 566 cm$^{-1}$. Along with this [1,2-Me$_2$-3-BuIM]$^+$-CF$_3$COO$^-$ had a strong $\nu_{CH}$ band at 3106 cm$^{-1}$ with a shoulder at 3180 cm$^{-1}$ and bands for the CF$_3$COO$^-$ anion at 517 (CF$_3$ group), 801 and 825 (COO−), and finally 1693 cm$^{-1}$. After heating a solution of **2** in [1-Me-3-BuIM]$^+$PF$_6^-$ and re-extraction of **2** there from the characteristic bands for the PF$_6^-$ anion at 850 and 566 cm$^{-1}$ were observed. At the same time, $\nu_{CH}$ bands at 3171 and 3125 cm$^{-1}$ attributable to the parent IL had disappeared. These findings are indicative rather for the formation of a new compound than for a simple co-extraction of **2** together with the IL. New $\nu_{CH}$ bands appeared at 3148 and 3096 cm$^{-1}$, shifted relative to the $\nu_{CH}$ of [1-Me-3-BuIM]$^+$ cation, which can be assigned to the new complex (Figure 3a).

Simultaneously, one of the $\nu_{Ru-Cl}$ band (371 cm$^{-1}$) completely disappeared while another still remained. This is indicative for the substitution of one chloride ligand by the imidazolium
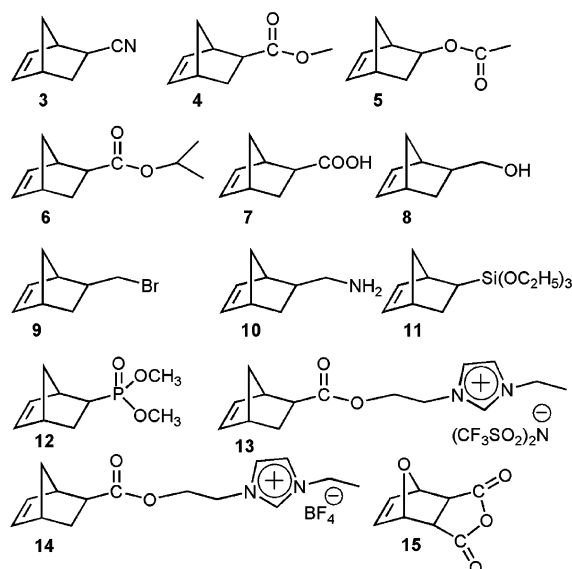


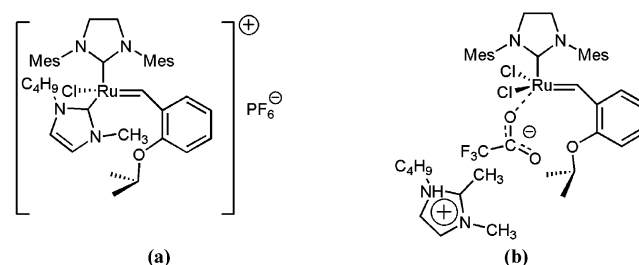**Figure 2.** Structures of monomers **5**−**15** used for ROMP in ionic liquids.



**Figure 3.** Proposed interaction of **2** with different ILs: [1,2-Me$_2$-3-Bu-IM]$^+$PF$_6^-$ (a) and [1-Me-3-Bu-IM]$^+$CF$_3$COO$^-$ (b).

carbene derived from the IL. According to the positions of the corresponding bands, the 2-(2-propoxy)styrene ligand remained unchanged. Because of the high similarity of the N-heterocycling carbene in **2** with the IL's cation, no other changes could be traced unambiguously.

In contrast to that, catalyst **2** was extracted unaffected after dissolution and heating in [1,2-Me$_2$-3-BuIM]$^+$PF$_6^-$. Thus, no traces of PF$_6^-$ were observed in its IR spectrum. $^{19}$F NMR studies supported these findings. Moreover, the IR spectrum of **2**, extracted from [1,2-Me$_2$-3-BuIM]$^+$PF$_6^-$, was fully identical to that of freshly prepared **2**. Finally, reextraction of **2** from its solution in [1,2-Me$_2$-3-BuIM]$^+$CF$_3$COO$^-$ showed a $\nu_{CO}$ band at 1692 cm$^{-1}$ as well as signals for the CF$_3$ group at 517 cm$^{-1}$. This is indicative for the presence of at least one coordinated CF$_3$COO$^-$ anion. Simultaneously, both of the two Ru—Cl bonds were present, demonstrating intact signals at 371 cm$^{-1}$ together with a small shift of the parent signal at 345 to 340 cm$^{-1}$. This can be explained by the coordination of the CF$_3$COO$^-$ anion to the ruthenium center with synchronous cleavage of the Ru···O bond of the 2-(2-propoxy)styrene ligand (Figure 3b). Transformation of the OCO signal of CF$_3$COO$^-$ at 825 cm$^{-1}$ complementary confirms its coordination to the catalyst.

**UV—Vis Spectroscopy.** To confirm these results, we additionally studied solutions of identical concentration (1.6 × 10$^{-6}$ mol/g of solvent) of **2** in various ILs and organic solvents by UV spectroscopy. Most of the solutions showed bands in the yellow-green region. A (weak) hypsochromic effect was observed when changing from noncoordinating to coordinating anions. Thus, the absorption maximum of **2** shifted in the order [1,2-Me$_2$BuIM]$^+$PF$_6^-$ (381 nm) $\cong$ [1,2-Me$_2$BuIM]$^+$(CF$_3$-

$SO_2)_2N^-$ (380 nm) > dichloromethane (378 nm) > cyclohexanone (375 nm) $\cong$ methanol (375 nm) > $[1,2\text{-Me}_2\text{-}3\text{-BuIM}]^+\text{-}$ $CF_3COO^-$ (319 and 368 nm), respectively. Finally, reaction of **2** with $[1\text{-Me-}3\text{-BuIM}]^+PF_6^-$ (substitution of at least one chlorine atom, vide supra) led to a brown color and formation of several bands at 315, 390, and 495 nm. All this is indicative for a different extent of solvent coordination to **2** at room temperature.

In summary, these spectroscopic investigations provide substantial information on the specific interaction between **2** and various ILs. Thus, the finding that $[1\text{-Me-}3\text{-BuIM}]^+PF_6^-$ does not allow for the formation of any polymer (Table 1, entries 1−3) can be traced back to the coordination of an IL-derived N-heterocyclic carbene to the catalyst and loss of a chlorine ligand. In contrast, such coordination is impossible in case phosphonium-based ILs or imidazolium-based ILs with a protective methyl group are used, giving rise to polymer yields up to 85% (Table 1). The influence of the different counterions (Table 2, entries 1−7) on polymerization activity can be explained by the formation of more complex structures in the case of coordinating anions such as $CF_3COO^-$ and $CF_3SO_3^-$ or, vice versa, by the absence of any interaction, e.g., in the case of $PF_6^-$ and $(CF_3SO_2)_2N^-$. Spectroscopic data are in accordance with polymerization data (Table 2, entries 1 and 3). Thus, it becomes evident that the $CF_3COO^-$ anion is, at least among those anions investigated, the strongest coordinating one, thus lowering the activity of ruthenium catalyst. In contrast, the different influence of the $PF_6^-$ and the $(CF_3SO_2)_2N^-$ anion, respectively, on ROMP (Table 2, entries 2 and 7) is believed to stem rather from the differences in the solubility behavior and viscosities of the discussed ILs[21] than from different coordination behavior.

## Conclusions

The principal suitability of a *pure* ionic liquid system in combination with ruthenium-based catalysts for ROMP was shown. It was demonstrated that the use of bromide-, chloride-, or nitrate-based ILs does *not* lead to the desired polymers whereas application of ILs consisting of low coordinating anions such as $BF_4^-$ and $PF_6^-$ allows for a high yield synthesis of polymers with high molecular weights. Another important finding in this context is that for the achievement of high molecular weight polymers via ROMP only ILs based on weakly coordinating anions and cations without the ability to form carbene species should be employed. Furthermore, it was found that the nature of the IL strongly influences the molecular weight and PDI of resulting polymers. Because of their special solubility parameters, monomers, which form polymers insoluble in standard organic solvents may in fact be polymerized in certain ILs. However, there is no "general" ionic liquid that allows ROMP of any monomer. Thus, ROMP of a certain monomer to be carried out in ILs requires the careful choice of the corresponding IL. Structural similarities between the IL and the monomer enhance the solubility and facilitate polymerization.

The most striking advantages of ILs in ROMP are (1) the high reaction speed that may be achieved, resulting in the formation of polymer within a few minutes, (2) the high polymer yields in comparison to regular organic solvents, (3) the high molecular weights up to $M_w = 1\,500\,000$, and (4) the possibility of catalyst recycling. By use of certain monomers that formed polymers soluble in ILs it is possible to obtain quite low satisfactory PDIs. On the contrary, the utilization of ILs does not lead to well-controlled polymerizations so far. This issue is currently under investigation.

## Experimental Section

**General Data.** All manipulations were performed under an argon atmosphere. *exo,endo*-5-Norbornene-2-methanol (98%, Greyhound Chromatography and Allied Chemicals, UK), *exo,endo*-5-norbornene-2-carbonitrile (98%, Aldrich, Germany), *exo,endo*-5-norbornen-2-carboxylic acid (98%, Aldrich, Germany), *exo,endo*-5-norbornene-2-carbonyl chloride (99%, Chemos GmBH, Germany) and *exo,endo*-5-norbornen-2-yl acetate (98%, Acros Organics, Belgium) were distilled under reduced pressure and checked by GC-MS and NMR prior to use. *exo,endo*-5-Norbornene-2-yltriethoxysilane (97%, ABCR GmbH &Co. KG, Germany) was used as received. 1,3-Bis(1,3,5-trimethylphenyl)-4,5-dihydroimidazolin-2-ylidene ($PCy_3 = $ tricyclohexylphosphine) and $[RuCl_2(IMesH_2)_2\text{-}(=CH\text{-}2\text{-}(2\text{-PrO})\text{-}C_6H_4)]$ (**2**) were purchased from Aldrich Chemical Co. (Germany) and used without further purification. Alkyl halides (Acros Organics, Belgium), 1-methylimidazole (99%, Acros Organics, Belgium) and 1,2-dimethylimidazole (98%, Aldrich, Germany) were distilled under inert atmosphere from $CaH_2$. Silver trifluoromethanesulfonate (99+%, Aldrich), ammonium tetrafluoroborate (99%, Aldrich), potassium hexafluorophosphate (98%, Aldrich), lithium bis(trifluoromethylsulfonyl)imide (99%, Fluka), silver trifluoroacetate (99%, Fluka), silver nitrate (99%, Fluka), triphenylphosphinodibromide (98%, Aldrich), lithiumaluminumhydride (LAH, Aldrich), anhydrous $Na_2SO_4$ (>98,5%, KMF Laborchemie Hadels GmbH), sodium bicarbonate (99%, Fluka), sodium chloride (98%, Fluka), $CaH_2$ (98%, Aldrich), ethyl vinyl ether (>99%, Fluka), phosphorus pentoxide (>98%, Fluka), dimethyl vinylphosphonate (98%, ABCR GmbH & Co. KG, Germany), and dicyclopentadiene (95%, Fluka) were used as received. Triethylamine (99%, Fluka) was distilled over sodium hydroxide prior to use. Reagent grade diethyl ether, methylene chloride, tetrahydrofuran, and pentane were obtained from KMF Laborchemie Handels GmbH (Germany) and dried by means of an MBraun (Germany) SPS drying system. Chloroform (99.5%) and acetonitrile (99%) were purchased from KMF Laborchemie Hadels GmbH (Germany) and distilled from $CaH_2$ prior to use. Dry methanol (99.5%, KMF Laborchemie Handels GmbH) was prepared by distillation from Mg pellets. Molecular weights and polydispersity indexes (PDIs) of the polymers were determined by gel permeation chromatography (GPC) on Polymer Laboratories columns (PLgel 10 mm MIXED-B, 7.5 × 300 mm) in tetrahydrofuran (THF) at 25 °C using a Waters Autosampler, a Waters 484 UV detector (254 nm), an Optilab Rex refractive index (RI) detector (685 nm, Wyatt), and a mini-dawn light scattering (LS) detector (Wyatt, $\lambda = 690$ nm). The flow rate was set to 0.7 mL·min$^{-1}$. Narrow polystyrene standards were purchased from Waters Corporation. The $dn/dc$ values for poly-**4**, poly-**5**, and poly-**6** were 0.161, 0.131, and 0.146. Weight-average molecular weights ($\bar{M}_w$) of poly-**14** were determined via static light scattering on a Fica-50 photogoniodiffusometer (France) in vertically polarized light at $\lambda = 546$ nm in the angular range from 30 to 150° at 25 °C. Prior to measurements, polymer solutions were filtered through Millipore 0.45 $\mu$m filters. $\bar{M}_n$ as well as $\bar{M}_w$ of poly-**14** were also determined in acetone at 25 ± 0.1 °C by sedimentation analysis using a MOM3180 ultracentrifuge (Hungary). NMR data were obtained at 250.13 MHz for proton and 62.90 MHz for carbon in the indicated solvent at 25 °C on a Bruker Spectrospin 250 and are listed in parts per million downfield from tetramethylsilane for proton and carbon. $^{31}$P NMR and $^{19}$F NMR spectra were measured on a Gemini 2000 at 200 MHz. IR spectra were recorded on a Bruker Vector 22 using ATR technology. GC-MS investigations were carried out on a Shimadzu GCMS-QP5050, using a SPB-5 fused silica column (30m × 0.25 $\mu$m film thickness). Dynamic thermogravimetric analysis (TGA) was performed in air on a Perkin Elma TGA7 or Netzsch Jupiter STA449C applying a heating rate of 10 °C/min. High-resolution mass spectra (HRMS) measured by means of electron spray ionization (ESI) were recorded on a FT-ICR-MS Bruker Daltonics APEX II, mass spectra (FAB mode) were recorded on a VG ZAB HSQ using 3-nitrobenzylic alcohol as matrix.

**Spectroscopic Measurements for the Estimation of the Interaction between Catalyst and Ionic Liquids.** Catalyst **2** was

dissolved under an inert atmosphere in the ionic liquid of choice and was treated at 55 °C for 20−30 min. The resulting solution was extracted with dry, freshly distilled benzene and dried at 40−45 °C under high vacuum. IR spectra of the compounds obtained were measured on a Specord M-82 (Carl Zeiss Jena) spectrometer with 2 cm$^{-1}$ resolution and on an Infralum FT-801 (Lumex) FTIR spectrometer. IR spectra of the solid samples in Nujol mulls and liquid films were recorded over the range of 200−4000 cm$^{-1}$. Solutions of catalyst **2** in organic solvents and ionic liquids were prepared under inert atmosphere with a concentration of $1.6 \times 10^{-6}$ mol of **2**/g of solvent. UV measurements were performed on UVIKON 922 (Kontron Instruments) spectrophotometer in 2 mm cells.

**Ionic Liquids (ILs).** Ionic liquids used in this study were prepared in accordance with described procedures[29,30,64−67] and characterized by elemental analysis, NMR and IR spectroscopy. Alkylphosphonium-based ILs were granted by Cytec Inc.

**2-(2-Propoxy)styrene.** The compound was synthesized according to published procedures,[62] however with some minor changes. Salicylaldeyde (10.3 g, 88.0 mmol), tetrabutylammonium bromide (25.1 g, 78.0 mmol), and 2-propyl iodide (20 mL, 0.20 mol) were dissolved in methylene chloride (300 mL). NaOH (3.5 g, 88 mmol), dissolved in water (150 mL), was slowly added to the stirred solution. After the reaction was stirred for 3 days, the organic phase was separated and the aqueous phase was washed with methylene chloride (3 × 50 mL). The combined organic phases were dried in vacuo, redissolved in ethyl acetate, and filtered. The filtrate was dried over Na$_2$SO$_4$ and evaporated to dryness, yielding a yellow oil, which was distilled under reduced pressure resulting in a colorless liquid. Yield: 6.68 g (48%). Spectroscopic data of intermediary *O*-(2-propoxy)salicylaldehyde were in accordance with the data reported in the literature.[62] Methyltriphenylphosphonium bromide (14.1 g, 39.6 mmol) was dried in a Schlenk tube at 55 °C. Dry THF (55 mL) was added, followed by *n*-butyllithium (2 N in pentane, 20.4 mL, 39.6 mmol) at 0 °C. The mixture was stirred for 30 min at 0 °C and for another 30 min at room temperature. *O*-(2-Propoxy)salicylaldehyde (6.68 g, 39.6 mmol) was slowly added at room temperature and stirring was continued for 12 h. Water (5 mL) was added to the yellow suspension, which was then dried in vacuo. The product was extracted with diethyl ether (3 × 25 mL), then the combined organic phases were dried over Na$_2$SO$_4$. Removal of all volatiles gave a liquid which was distilled from copper wire under reduced pressure yielding a colorless clear liquid in 3.9 g (61%). Spectroscopic data of the target compound were in accordance with those reported in the literature.[62]

**Synthesis of Methyl *exo,endo*-5-Norbornene-2-carboxylate (4).** This monomer was prepared according to a procedure described in the literature.[68,69] *exo,endo*-5-Norbornene-2-carboxylic chloride (9.05 g, 60.6 mmol) was placed inside a Schlenk flask and cooled to 0 °C. Dry methanol (10.0 mL, 246 mmol) was slowly added under vigorous stirring. After 1 h at 0 °C, the reaction mixture was allowed to warm to room temperature, and stirring was continued for another 4 h. Methanol was evaporated, and the residue was dissolved in 30 mL of methylene chloride. The organic layer was washed consecutively with 2 × 30 mL of water, then with 2 × 40 mL of concentrated sodium bicarbonate solution and finally with 2 × 40 mL of concentrated brine solution. Then it was dried over Na$_2$SO$_4$, and evaporated to dryness. The resulting liquid was distilled under reduced pressure (bp = 78 °C/10 mmHg) yielding a colorless oil. Yield: 7.5 g (90%). IR (ATR mode): 3066 (s), 2983 (m), 2948 (m), 2869 (s), 1731 (vs, $\nu_{CO}$), 1567 (s), 1434 (m), 1335 (vs), 1271 (vs), 1195 (vs), 1173 (vs), 1110 (m), 1066 (m), 1031 (vs), 899 (m), 839 (s), 712 (vs), 621 (m) cm$^{-1}$. $^1$H NMR (CDCl$_3$): $\delta$ 6.16−6.13 (q, 1H, CH=CH), 5.90−5.87 (q, 1H, CH=CH), 3.58 (s, 3H, −O−*CH$_3$*), 3.16 (s, 1H), 2.89 (m, 2H), 1.90−1.82 (m, 1H), 1.47−1.22 (m, 3H). $^{13}$C NMR (CDCl$_3$): $\delta$ 175.3 (C=O), 138.1, 137.8 (C=C), 135.8, 132.4, 51.8, 51.5, 49.7, 46.6, 46.4, 45.7, 43.2, 43.0, 42.6, 41.65, 30.4, 29.3. GC−MS (EI, 70 eV): calculated for C$_9$H$_{12}$O$_2$, $m/z$ = 152.19; found, $m/z$ = 152 (M$^{\bullet+}$).

**(2-Propyl) *exo,endo*-5-Norbornene-2-carboxylate (6).** The same synthetic procedures as describe for the synthesis of **4** were used. The product was obtained by distillation under reduced pressure in form of a colorless liquid (bp = 92−93 °C/10 mmHg) in 58% yield (4.6 g). IR (ATR mode): 3063 (s), 2977 (vs), 2941 (m), 2873 (s), 1729 (vs, $\nu_{CO}$), 1467 (m), 1373 (m), 1336 (m), 1271 (m), 1193 (vs), 1106 (vs), 1022 (m), 993 (s), 903 (s), 839 (s), 822 (s), 712 (m) cm$^{-1}$. $^1$H NMR (CDCl$_3$): $\delta$ 6.15−6.12 (q, 1H, CH= CH), 5.89−5.85 (q, 1H, CH=CH), 4.99−4.85 (m, 1H, −*CH*− (CH$_3$)$_2$), 3.16 (s, 1H), 2.89−2.83 (m, 2H), 1.88−1.78 (m, 3H), 1.23−1.14 (m, 6H, −CH−(*CH$_3$*)$_2$). $^{13}$C NMR (CDCl$_3$): $\delta$ 174.2 (C=O), 138.1, 137.7 (C=C), 135.8, 132.3, 67.4, 67.2, 49.6, 46.7, 46.3, 45.8, 43.6, 43.4, 42.6, 41.7, 30.3, 29.1, 21.9, 21.9. GC−MS (EI, 70 eV): calculated for C$_{11}$H$_{16}$O$_2$, $m/z$ = 180.24; found, $m/z$ = 180 (M$^{\bullet+}$).

***exo,endo*-5-Norbornene-2-ylmethyl Bromide (9).** Triphenylphosphinodibromide (9.358 g, 22.17 mmol) was suspended in 80 mL of acetonitrile and cooled to 0 °C. Consecutively, triethylamine (5.60 mL, 40.3 mmol) and a solution of 5-norbornene-2-methanol (2.50 g, 20.1 mmol) in 40 mL of acetonitrile was added. The reaction mixture was stirred at room temperature for 24 h. Then all volatiles were evaporated and the residue was dissolved in *n*-pentane. The product was purified by chromatography (silica/ *n*-pentane). Yield: 2.50 g (67.5%). IR (ATR mode): 3058 (m, CH stretch), 2957 (vs), 2866 (s), 1633 (s), 1569 (s), 1446 (m), 1432 (m), 1349 (s), 1328 (s), 1272 (m), 1255 (vs), 1217 (vs), 1150 (m), 1121 (s), 1085 (s), 1038 (s), 989 (m), 918 (m), 831 (m), 785 (s), 720 (vs), 668 (vs), 652 (vs, $\nu_{Br}$), 633 (vs) cm$^{-1}$. $^1$H NMR (CDCl$_3$): $\delta$ 6.0−6.2 (m, 2H, C=C), 3.2−3.4 (m, 2H, CH$_2$Br), 3.0−2.8 (m, 2H, CH), 2.52, 1.93 (m, 2H, CH$_2$), 1.2−1.4 (m, 3H, CH, CH$_2$). $^{13}$C NMR (CDCl$_3$): $\delta$ 138.4, 137,2, 136.5, 131.7 (CH), 49.8 (CH$_2$), 46.5, 45.9 (CH), 45.1, 43.2 (CH), 42.5, 42.2 (CH), 39.4, 38.5 (CH$_2$-Br), 33.5, 29.8 (CH$_2$). GC−MS (EI, 70 eV): calculated for C$_8$H$_{11}$-Br, $m/z$ = 187.07; found, $m/z$ = 186 (M−H$^{\bullet+}$).

***exo,endo*-5-Norbornene-2-ylmethylamine (10).** A solution of 5-norbornene-2-carbonitrile (3.00 g, 25.2 mmol) in 10 mL of diethyl ether was added to a suspension of LiAlH$_4$ (1.885 g, 55.46 mmol) in 20 mL of diethyl ether at 0 °C. The reaction mixture was stirred for 1 h at room temperature and then refluxed for 0.5 h. After that, 15 mL of water were slowly added, and the ether layer was washed consecutively with 30 mL of water, 30 mL of 10% NaOH solution, and 30 mL of brine solution. Finally, the organic layer was dried over anhydrous Na$_2$SO$_4$ and concentrated. Yield: 2.8 g (90%). IR (ATR mode): 3369 (s, $\nu_{NH2}$), 3294 (s, $\nu_{NH2}$), 3056 (m, CH stretch), 2959 (vs), 2863 (vs, CH stretch), 1612 (m, NH$_2$), 1446 (s), 1384 (s), 1337 (m), 1252 (s), 1149 (s), 1073 (m), 1018 (s), 903 (vs), 819 (vs), 718 (s), 625 (vs) cm$^{-1}$. $^1$H NMR (CDCl$_3$): $\delta$ 6.10, 5.92 (m, 2H, =CH), 2.79 (m, 3H, −CH$_2$N, CH), 2.36, 1.81 (m, 1H, CH), 1.4 (m, 5H, CH$_2$, CH). $^{13}$C NMR (CDCl$_3$): $\delta$ 137.3, 136.5, 131.9 (CH), 49.4 (CH$_2$), 49.5, 47.8 (CH), 46.2, 44.9, 43.9, 43.8 (CH), 42.5, 42.2 (CH), 41.5 (CH$_2$NH$_2$), 31.8, 29.6 (CH$_2$). GC−MS (EI, 70 eV): calculated for C$_8$H$_{13}$N, $m/z$ = 123.19; found, $m/z$ = 123 (M$^{\bullet+}$).

**Dimethyl *exo,endo*-5-Norbornene-2-yl Phosphonate (12).** Cyclopentadiene (5.8 g, 88.2 mmol, freshly cracked from dicyclopentadiene), dimethyl vinylphosphonate (10 g, 73.5 mmol) and hydroquinone (200 mg) were heated to 170 °C in a Teflon valve sealed glass reactor for 20 h. After the reaction mixture was cooled to room temperature, 200 mL of diethyl ether was added and the insoluble solid that formed was separated by filtration. The ether was removed under reduced pressure. Pure product was obtained by distillation at (70 °C/10 mmHg). Yield: 12 g (80%). IR (ATR mode): 3469 (m), 3058 (s), 2950 (m), 2873 (m), 2849 (m), 1461 (s), 1447 (s), 1234 (s, $\nu_{P=O}$), 1183 (s), 1132 (s), 1054 (s, $\nu_{P−O−C}$), 1023 (s), 973 (s), 856 (s), 763 (m), 653 (s) cm$^{-1}$. $^1$H NMR (CDCl$_3$): $\delta$ 6.04−6.13 (m, 2H), 3.62−3.76 (m, 6H), 2.94 (m, 2H), 1.58 (m, 1H), 1.19−1.30 (m, 4H). $^{13}$C NMR (CDCl$_3$): $\delta$ 136.9, 136.7, 133.0, 133.0, 52.6, 52.3, 50.5, 50.2, 44.4, 43.6, 42.5, 42.4, 36.0, 35.3, 33.6, 33.1, 27.9, 27.1. $^{31}$P NMR (CDCl$_3$, 200 MHz): $\delta$ 37.99, 36.92 (*exo:endo*: 55:45). GC−MS (EI, 70 eV): calculated for C$_9$H$_{15}$O$_3$P, $m/z$ = 202.18; found, $m/z$ = 202 (M$^{\bullet+}$).

***exo,endo*-5-Norbornene-2-yl Carboxyethyl-3-ethylimidazolium Bromide.** *exo,endo*-5-Norbornene-2-carbonyl chloride (6.98 g, 44.6 mmol) was placed inside a Schlenk flask and cooled to 0 °C. Separately, a solution of 1-(2-hydroxyethyl)-imidazole (5 g, 44.6 mmol) and freshly distilled triethylamine (7.5 mL, 53.5 mmol) in 25 mL of dry methylene chloride was prepared. This solution was placed in a funnel and then added dropwise to the acid chloride at 0 °C. The reaction mixture was stirred for 1 h at 0 °C and then allowed to warm to room temperature. After 4 h stirring at room temperature, 25 mL of water were added to the reaction mixture, resulting in the formation of two layers. Water was decanted off and the methylene chloride layer was washed consecutively with 2 × 30 mL of water, 2 × 40 mL of concentrated sodium bicarbonate solution and finally with 2 × 40 mL of concentrated brine solution. Then it was dried over $Na_2SO_4$, and evaporated to dryness. The resulting liquid was distilled under reduced pressure (bp = 158−162 °C/1 mmHg) yielding a colorless oil. Yield: 3.73 g (36%). IR (ATR mode): 3116 (s), 3058 (s), 2971 (vs), 2873 (s), 1726 (vs, $\nu_{CO}$), 1505 (m), 1444 (m), 1366 (s), 1334 (m), 1270 (m), 1230 (m), 1170 (vs), 1108 (vs), 1076 (m), 1039 (vs), 906 (m), 816 (m), 713 (m), 665 (vs), 613 (m) cm$^{-1}$. $^1$H NMR (CDCl$_3$): $\delta$ 7.41 (s, 1H, C$_2$im), 6.97 (s, 1H, C$_4$im), 6.87 (s, 1H, C$_5$im), 6.05−6.04 (m, 1H, CH=CH), 5.68−5.65 (m, 1H, CH=CH), 4.16−4.10 (m, 4H, −O−CH$_2$−CH$_2$−), 3.05 (s, 1H), 2.85−2.80 (m, 2H), 1.79 (m, 1H), 1.31 (m, 3H). $^{13}$C NMR (CDCl$_3$): $\delta$ 175.6 (C=O), 174.1 (C=O), 138.0, 137.9 (C=C), 137.3, 135.4, 132.0, 131.8, 130.0, 127.4, 118.9, 63.2, 63.1, 62.9, 49.5, 46.4, 46.2, 45.6, 45.6, 43.0, 42.8, 42.3, 41.4, 30.2, 29.0, 23.2, 19.6, 15.4, 8.4, 7.5. GC−MS (EI, 70 eV): calculated for C$_{13}$N$_2$H$_{16}$O$_2$, *m/z* = 232.28; found, *m/z* = 166 (M + H$^+$-imidazole).

*exo,endo*-5-Norbornene-2-yl carboxyethyl-1-imidazole (3.73 g, 16 mmol) was placed into a round-bottom flask equipped with a magnetic stirrer, a condenser, and a CaCl$_2$ tube, and 35 mL of dry chloroform were added. The solution was cooled to 0 °C, and an excess of 1-bromoethane (5 mL, 64 mmol) was slowly added to the vigorously stirred reaction mixture. The reaction mixture was stirred at 0 °C for 24 h. After that, stirring was continued at 20 °C for another 24 h, then at 35 °C for another 24 h and finally at 45 °C for a final 24 h. After completion of the alkylation process, the chloroform and excess C$_2$H$_5$Br were removed by distillation under reduced pressure at 55 °C. The remaining slightly yellow viscous liquid was kept at 55 °C in high vacuum for 5 h. Yield: 5.44 g (99%). IR (ATR mode): 3438 (vs), 3138 (m), 3063 (vs), 2976 (vs), 2873 (s), 2056 (s), 1729 (vs, $\nu_{CO}$), 1633 (m), 1564 (vs), 1449 (m), 1410 (s), 1386 (m), 1360 (s), 1335 (vs), 1295 (s), 1273 (m), 1252 (s), 1233 (s), 1166 (vs), 1110 (m), 1067 (s) cm$^{-1}$. $^1$H NMR (DMSO-$d_6$): $\delta$ 9.37 (s, 1H, C$_2$im), 7.88 (s, 1H, C$_4$im), 7.84 (s, 1H, C$_5$im), 6.13−6.10 (q, 1H, CH=CH), 5.70−5.66 (q, 1H, CH=CH), 4.50−4.35 (m, 2H, N−CH$_2$−CH$_3$), 4.34−4.21 (m, 4H, −O−CH$_2$−CH$_2$−), 3.05 (m, 2H), 2.83 (m, 1H), 1.84 (m, 1H), 1.42 (m, 3H, N−CH$_2$−CH$_3$), 1.26 (m, 3H). $^{13}$C NMR (DMSO-$d_6$): $\delta$ 174.1 (C=O), 173.2 (C=O), 137.8, 137.7 (C=C), 136.2, 135.5, 132.1, 122.8, 122.2, 62.0, 61.8, 49.0, 48.5, 48.0, 45.9, 45.8, 45.0, 44.2, 42.4, 42.2, 41.8, 41.0, 23.0, 28.6, 15.1.

***exo,endo*-5-Norbornene-2-yl carboxyethyl-3-ethylimidazolium Bis(trifluoromethyl-sulfonyl)imide (13).** To a solution of *exo,endo*-5-norbornene-2-yl carboxy-1,3-diethylimidazolium bromide (5.44 g, 16.0 mmol) in 20 mL of deionized water was slowly added an aqueous solution of lithium bis(trifluoromethylsulfonyl)imide (4.18 g, 14.5 mmol). The resulting suspension was stirred at 55 °C for 2 h, and then the upper layer was removed by decantation and the residuary oily product was washed several times with water. The product was dried in vacuo at 55 °C over P$_2$O$_5$. Yield: 6.5 g (75%). IR (ATR mode): 3151 (s), 3117 (s), 2977 (s), 2874 (s), 1732 (vs, $\nu_{CO}$), 1565 (m, $\nu_{SO2}$), 1449 (m), 1348 (vs, $\nu_{CF}$), 1331 (vs), 1270 (s), 1225 (m), 1179 (vs, $\nu_{CF}$), 1134 (vs), 1110 (m), 1053 (vs), 956 (s), 908 (s), 838 (m), 790 (m), 740 (m), 714 (m), 652 (m), 616 (vs), 566 (vs), 499 (vs) cm$^{-1}$. $^1$H NMR (CDCl$_3$): $\delta$ 8.80 (s, 1H, C$_2$im), 7.41 (s, 1H, C$_4$im), 7.39 (s, 1H, C$_5$im), 6.17−6.14 (q, 1H, CH=CH), 5.77−5.74 (q, 1H, CH=CH), 4.44−4.24 (m, 6H), 3.13 (s, 1H), 2.98−2.90 (m, 2H), 1.90 (m, 2H), 1.54 (m, 3H, N−CH$_2$−

CH$_3$), 1.28 (m, 3H). $^{13}$C NMR (CDCl$_3$): $\delta$ 175.8 (C=O), 174.2 (C=O), 138.4, 138.3 (C=C), 135.7, 135.6, 135.1, 132.0, 127.5, 123.2, 122.4, 122.2, 120.8, 117.3, 112.2, 62.1, 62.0, 49.8, 49.1, 48.9, 46.6, 46.3, 45.8, 45.6, 43.1, 42.8, 42.6, 41.7, 30.6, 29.4, 15.2. $^{19}$F NMR (CDCl$_3$): $\delta$ −79.46. HRMS: calculated for C$_{17}$H$_{21}$N$_3$O$_6$S$_2$F$_6$, *m/z* = 541.49; found, 543.2 (M$^+$ + H), 261.2 (M$^+$ − (CF$_3$SO$_2$)$_2$N).

***exo,endo*-5-Norbornene-2-yl carboxyethyl-3-ethylimidazolium Tetrafluoroborate (14).** A solution of *exo,endo*-5-norbornene-2-yl carboxy-1,3-diethylimidazolium bromide (4.81 g, 14 mmol) in 20 mL of deionized water was mixed with an aqueous solution of silver tetrafluoroborate (2.74 g, 14.50 mmol) at room temperature. After 1 h of stirring at 55 °C, the silver bromide was filtered off and the solution was concentrated under reduced pressure. The product was dried in vacuo over P$_2$O$_5$ at 55 °C. Yield: 4.81 g (99%). IR (ATR mode): 3162 (m), 3116 (s), 2975 (m), 2876 (s), 1727 (vs, $\nu_{CO}$), 1634 (s), 1566 (vs), 1449 (m), 1410 (s), 1388 (s), 1335 (m), 1271 (m), 1165 (vs), 1049 (vs, $\nu_{BF4}$), 916 (s), 851 (m), 812 (s), 752 (m), 715 (s) 628 (vs) cm$^{-1}$. $^1$H NMR (CDCl$_3$): $\delta$ 8.86 (s, 1H, C$_2$im), 7.46 (s, 1H, C$_4$im), 7.44 (s, 1H, C$_5$im), 6.11 (m, 1H, CH=CH), 5.75 (m, 1H, CH=CH), 4.47−4.24 (m, 6H), 3.11 (s, 1H), 2.94−2.86 (m, 2H), 1.88 (m, 1H), 1.52 (m, 3H, N−CH$_2$−CH$_3$), 1.35 (m, 3H). $^{13}$C NMR (CDCl$_3$): $\delta$ 175.8 (C=O), 174.3 (C=O), 165.52, 138.22, 138.16 (C=C), 135.94, 135.65, 132.44, 132.12, 127.43, 123.10, 122.19, 62.48, 62.35, 62.17, 49.75, 48.95, 48.80, 46.56, 46.33, 45.75, 45.40, 43.06, 42.82, 42.52, 41.64, 30.50, 29.31, 15.24. $^{19}$F NMR (CDCl$_3$): $\delta$ −151.22 and −151.27. HRMS: calculated for C$_{15}$H$_{21}$N$_2$O$_2$, *m/z* = 261; found, *m/z* = 261.2 (M$^+$).

**Typical Polymerization Procedure.** The catalyst (**1**, 4.4 mg, 6 × 10$^{-6}$ mol) was dissolved in 1,2-dimethyl-3-butyl imidazolium hexafluorophosphate ([1,2-Me$_2$-3-BuIM]$^+$PF$_6^-$, 1.2 g) at 55 °C. Methyl *exo,endo*-5-norbornene-2-carboxylate (91 mg, 6 × 10$^{-4}$ mol) was added to the green solution. The mixture was stirred for 4 h, then ethyl vinyl ether (0.8 mL) was added via a syringe. After being stirred for 0.5 h at 55 °C, the reaction mixture was poured into the methanol. The resulting polymer was filtered off, thoroughly washed with fresh methanol, and dried in vacuo at elevated temperature. Yield: 0.083 g (91%).

**Poly-3:** IR (KBr): 2926 (vs), 2856 (m), 2360 (m), 2334 (m), 2239 (vs, $\nu_{CN}$), 1443 (m), 1417 (s), 1260 (m), 1152 (s), 1056 (vs), 1026 (vs), 1013 (vs), 960 (m), 843 (m), 765 (m), 665 (s). $^1$H NMR (DMSO-$d_6$): $\delta$ 5.57−5.26 (br m, 2H, CH=CH), 3.23 (m, 1H), 2.84 (m, 1H), 2.24 (m, 1H), 2.06−1.94 (br m, 2H), 1.61 (m, 1H), 1.24 (m, 1H). $^{13}$C NMR (DMSO-$d_6$): $\delta$ 135.6 (C=C), 132.7 (C=C), 131.9 (C=C), 129.7 (C=C), 123.1 (CN), 121.9 (CN), 49.2, 44.4, 44.1, 37.7−35.9 (br m), 33.6.

**Poly-4:** IR (ATR mode): 3012 (m), 2948 (s), 2864 (m), 1725 (vs, $\nu_{CO}$), 1434 (s), 1364 (s), 1249 (m), 1194 (s), 1167 (vs), 1098 (m), 1025 (m), 965 (s), 867 (m), 809 (m), 748 (vs), 666 (s) cm$^{-1}$. $^1$H NMR (CDCl$_3$): $\delta$ (6.15, m, C=C$_{trans}$), 6.05 (m, C=C$_{cis}$), 5.89 (m, C=C$_{trans}$), 3.65 (OCH$_{3-cis}$), 3.58 (OCH$_{3-trans}$), 3.16 (b, 1H), 3.02−2.80 (m), 2.18 (m), 1.91 (m), 1.50−1.20 (br m). $^{13}$C NMR (CDCl$_3$): $\delta$ 170.4 (C=O), 135.8 (C=C), 129.2 (C=C), 126.9, 70.2, 64.9, 47.0, 41.8, 39.4, 35.3, 21.1.

**Poly-5:** IR (ATR mode): 2985 (s), 2882 (m), 1745 (vs), 1460 (m), 1392 (vs), 1270 (vs), 1057 (vs), 988 (m), 952 (m), 828 (m), 780 (vs) cm$^{-1}$. $^1$H NMR (CDCl$_3$): $\delta$ 5.34−5.24 (br m, 2H, CH=CH), 5.07 (s, 1H), 2.85 (s, 1H), 2.54 (s, 1H), 2.25 (s, 1H), 2.02 (s, 3H, OOC−CH$_3$), 1.86−1.24 (br m, 3H). $^{13}$C NMR (CDCl$_3$): $\delta$ 170.4 (C=O), 135.8 (C=C), 126.9 (C=C), 64.9, 47.1, 41.8, 39.42 (CH$_2$), 39.3 (CH$_2$), 35.3, 21.1.

**Poly-6:** IR (KBr pellet): 3005 (vs), 2890 (m), 1742 (vs), 1482 (m), 1391 (vs), 1279 (s), 1205 (vs), 1165 (s), 1126 (vs), 992 (m), 938 (s), 843 (m), 780 (s) cm$^{-1}$. $^1$H NMR (CDCl$_3$): $\delta$ 5.40−5.20 (br m, 2H, CH=CH), 4.92 (m, 1H, −CH−(CH$_3$)$_2$), 3.08−2.44 (br m, 3H), 1.95−1.71 (br m, 3H), 1.32 (m, 1H), 1.23 (br s, 6H, −CH−(CH$_3$)$_2$). $^{13}$C NMR (CDCl$_3$): $\delta$ 174.2 (C=O), 134.5−129.5 (br m, C=C), 67.5 (s, C−CH−(CH$_3$)$_2$), 48.2, 45.9, 42.7, 40.7, 39.7, 36.3, 35.8, 29.6, 29.4, 22.1 ((CH$_3$)$_2$).

**Poly-7:** IR (KBr): 3443 (m, $\nu_{OH}$), 3008 (m), 2943 (m), 2865 (m), 1726 (m), 1734 (vs, $\nu_{COOH}$), 1695 (vs), 1630 (m), 1539 (vs),

1504 (m), 1421 (m), 1395 (s), 1204 (m), 1056 (m), 1030 (m), 1008 (m), 973 (s), 839 (vs), 765 (s), 739 (s), 669 (s). $^1$H NMR (DMSO-$d_6$): $\delta$ 11.96 (br s, −COO*H*), 5.41−5.21 (br m, 2H, CH=CH), 3.18 (m, 1H), 2.81−2.51 (m, 2H), 1.91−1.59 (br m, 3H), 1.24−1.08 (m, 1H). $^{13}$C NMR (DMSO-$d_6$): $\delta$ 176.1 and 175.8 (HO−C=O), 144.6−129.7 (br m, C=C), 122.7, 121.3, 48.3, 47.7, 36.5, 35.1, 31.6, 19.3, 13.9, 9.5.

**Poly-12:** IR (KBr): 3510 (vs), 3008 (vs), 2987 (vs), 2885 (m), 1670 (m), 1479 (vs), 1433 (s), 1395 (s), 1265 (vs), 1204 (vs), 1087 (vs), 995 (m), 943 (m), 848 (vs), 780 (vs), 680 (s), 575 (vs) cm$^{-1}$. $^1$H NMR (CDCl$_3$): $\delta$ 5.68−5.17 (br m, 2H, CH=CH), 3.70−3.64 (m, 6H, O−(*CH$_3$*)$_2$), 3.13−2.63 (br m, 1H), 2.32−1.91 (br m, 4H), 1.67 (m, 1H), 1.29−1.17 (br m, 1H); $^{31}$P NMR (CDCl$_3$): $\delta$ = 36.8, 34.4 (65:35).$^{13}$C NMR (CDCl$_3$): $\delta$ 133.1−132.2 (br m, C=C), 52.5 (s, −(OCH$_3$)$_2$), 52.2 (s, −(OCH$_3$)$_2$), 43.9 (br m, C$^5$), 43.5 (s, C$^4$), 43.4 (d, C,$^5$ $^2J_{PC}$ = 17.5 Hz), 43.1 (s, C$^4$), 39.9 (s, C$^3$), 38.8 (d, C$^1$P, $^1J_{PC}$ = 216.7 Hz), 37.7 (s, C$^3$), 34.2 (br s, C$^2$), 34.1 (d, C$^1$P, $^1J_{PC}$ = 202.4 Hz).

**Poly-14:** IR (ATR mode): 3195 (m), 2990 (m), 2888 (m), 1748 (vs), 1582 (m), 1470 (m), 1411 (s), 1371 (s), 1275 (s), 1186 (vs), 1070 (m), 865 (vs), 773 (s) cm$^{-1}$. $^1$H NMR (DMSO-$d_6$): $\delta$ 9.18 (br s, 1H), 7.81−7.76 (m, 2H, CH=CH), 5.36−4.98 (br m, 2H), 4.43−4.20 (br m, 6H), 3.10−2.83 (br m, 2H), 2.58−2.51 (br m, 1H), 1.85−1.69 (br m, 2H), 1.44−1.28 (br s, 4H), 1.15−0.91 (br m, 1H) cm$^{-1}$. $^{13}$C NMR (DMSO-$d_6$): $\delta$ 205.2 (C=O), 172.7(C=C), 171.8 (C=C), 134.9 (C$^2$ im), 133.8 (−OCH$_2$CH$_2$), 121.6−120.2 (br m, C$^4$ and C$^5$ im), 119.9 (OCH$_2$CH$_2$), 60.7−59.4 (m), 47.0−45.4 (m), 43.5−42.2 (m), 42.0, 34.07, 14.6−12.2 (br m, CH$_2$CH$_3$). $^{19}$F NMR (DMSO-$d_6$): $\delta$ 148.27.

**Poly-15 (Transformed into the Diester):** IR (ATR mode): 3480 (m), 2953 (vs), 2926 (vs), 2599 (m), 2294 (s), 1981 (s), 1721 (vs, $\nu_{CO}$), 1439 (m), 1394 (vs), 1367 (vs), 1296 (m), 1254 (vs), 1209 (vs), 1149 (m), 1032 (vs), 964 (m), 844 (m), 799 (m), 750 (s), 723 (m), 697 (m). $^1$H NMR (DMSO-$d_6$): $\delta$ 5.79 (s, 1H, CH=CH), 5.55 (s, 1H, CH=CH), 4.89 (br s, 1H), 4.52 (br s, 1H), 3.59−3.57 (m, 6H, (OC*H$_3$*)$_2$), 3.17−3.12 (m, 2H). $^{13}$C NMR (DMSO-$d_6$): $\delta$ 172.5 (C=O), 171.4 (C=O), 132.7−131.6 (br m, C=C), 80.9 (C$_5$), 77.4 (C$_2$), 53.5 (C$_3$), 53.1 (C$_4$), 52.2 (O−CH$_3$).

**Recycling.** A typical polymerization procedure based on catalyst **2** as described above was used. Ethyl vinyl ether was replaced by 2-(2-propoxy)styrene (100 mg, 6 × 10$^{-4}$ mol) at the end of reaction. After being stirred for 4 h at 55 °C, the reaction mixture was poured into dry methanol. The precipitated polymer was filtered off and washed several times with dry methanol. All methanol solutions were combined and all volatiles were evaporated under reduced pressure. The resultant yellow-green solution was extracted with 3 × 30 mL of dry pentane in order to remove excess 2-(2-propoxy)-styrene and dried in vacuo at 55 °C for 2 h. Finally, a new portion of monomer was added and polymerization was started again.

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