Letter

Synthesis of two novel thermally stable classes of polynorbornene with pendant aryl ether or ester chains

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Reactions of 5-norbornene-2-methanol with arene cyclopentadienyliron complexes led to the synthesis of two new classes of norbornene monomers with ether or ester bridges; ring-opening metathesis polymerization of these monomers using ruthenium-based catalysts gave rise to high molecular weight polymers displaying exceptional thermal stability.

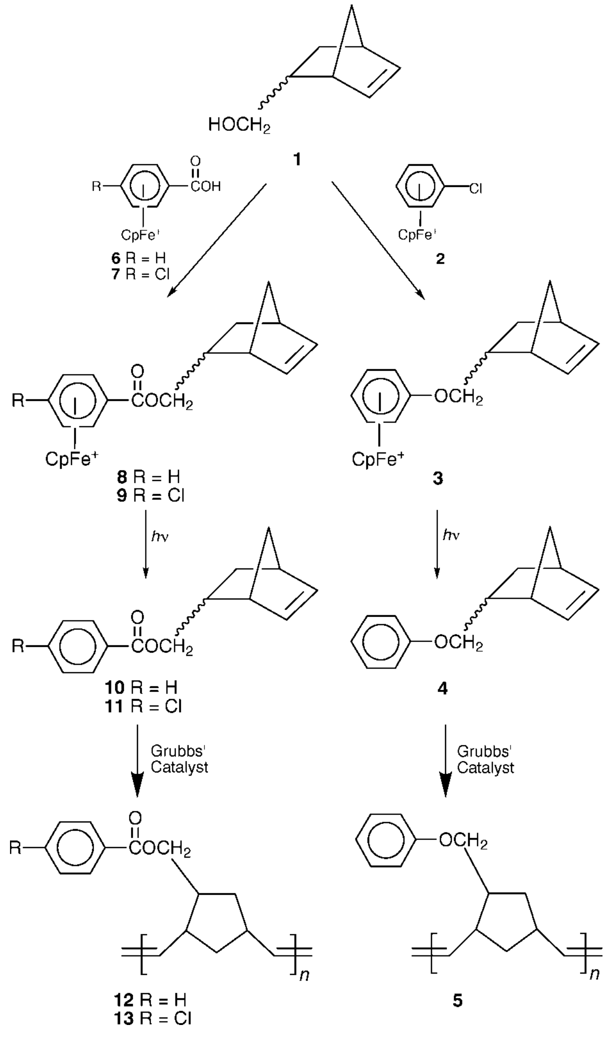
Polynorbornene (Norsorex) has been manufactured industrially since 1976 for a wide variety of applications, including engine mountings, shock-proof bumpers and flexible couplings.[1,2] In recent years, attention has focused on improving the thermal properties of these materials.[3,4] These studies have also shown that a marked increase in the thermal stability of the resulting polymeric material can be achieved upon functionalization of the norbornene monomer. In particular, the incorporation of an ester functionality into polynorbornene is of interest and warrants further investigation due to its potential as a thermoplastic resin.[2]

Since the first report detailing its general synthesis appeared four decades ago,[1] significant strides have been made in the area of ring-opening metathesis polymerization (ROMP) of functionalized polynorbornenes.[5–11] To date, a large variety of transition-metal-based catalysts have been shown to be suitable for ROMP. Ruthenium carbene complexes as well as molybdenum and tungsten alkylidene complexes have surfaced as the two predominant catalytic systems routinely used in ROMP. Ruthenium-based catalysts have greater application industrially due to their lack of sensitivity towards both protic environments and air, as well as their ability to polymerize a wider variety of functionalized monomers.[5,6,9]

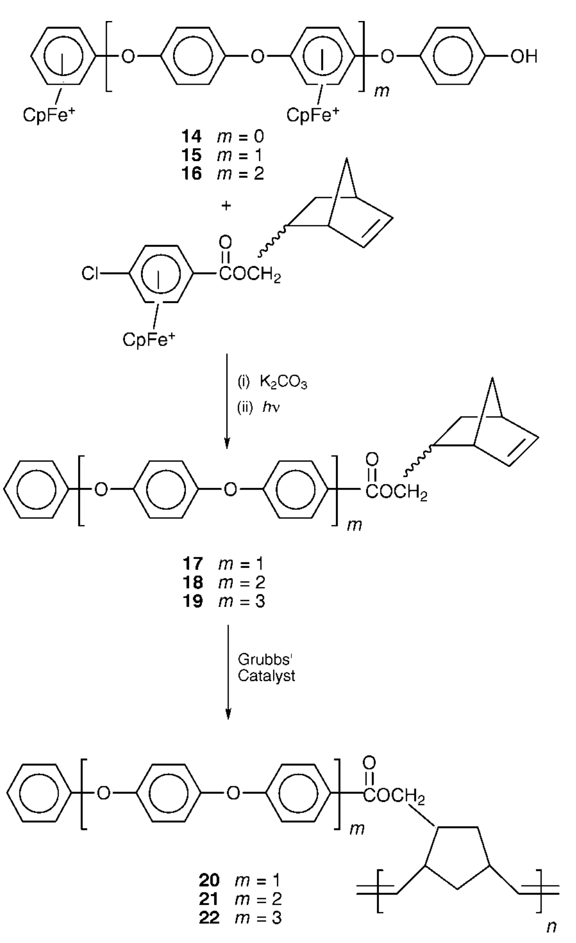
Our recent success in the synthesis of poly(aromatic ethers) has prompted our investigation into the controlled molecular design of norbornene monomers with pendant ether or ester chains.[12] Interest in these classes of materials originates from their thermooxidative stability, resistance to high-energy radiation and good mechanical properties. In this communication, two classes of substituted norbornene were synthesized. The first class involved metal-mediated nucleophilic aromatic substitution of η^6-chlorobenzene-η^5-cyclopentadienyliron hexafluorophosphate (**2**, 1.0 mmol) with the commercially available *exo,endo*-5-norbornene-2-methanol (**1**, 2.1 mmol) in the presence of potassium *tert*-butoxide (2.5 mmol) in a 6 : 1 ratio of THF–DMF under a N_2 atmosphere. This methodology involving metal activation of the chlorobenzene complex allowed for the efficient formation of an etheric bridged complex (**3**) as is described in Scheme 1. The second class of monomers were prepared *via* the condensation of benzoic acid complexes (**6**, **7**, 0.5 mmol) with **1** (0.8 mmol) in the presence of dicyclohexylcarbodiimide (DCC, 0.5 mmol), pyridine (4 drops) and dichloromethane (10 mL). Photolytic demetallation of both classes of complexes was accomplished by dissolving the metallated species in a 4 : 1 mixture of dichloromethane–acetonitrile, followed by irradiation with a xenon lamp for 4 h. This allowed for the liberation of the modified norbornene monomers (**4**, **10**, **11**) from their $CpFe^+$ moieties in yields ranging from 75–83%.

This methodology was also extended to include side chains consisting of two, three and four pendant cyclopentadienyliron moieties. Nucleophilic aromatic substitution reactions of complex **9** with oligomeric ethers **14**–**16** in a 1 : 1 ratio, followed by photolytic demetallation, gave the norbornene building blocks with pendant aryl ether or ester chains (**17**–**19**) in 68-75% yields, as described in Scheme 2.

Structural characterization of these functionalized norbornene monomers was accomplished using one- and two-dimensional NMR, MS, IR, and elemental analysis. The monomeric materials, **4**, **10**, **11** and **17**–**19**, were isolated as a mixture of *exo*, *endo* isomers. Assignment of the chemical shifts of the two isomers was accomplished primarily by the use of HH and CH COSY NMR. Protons H-1, H-2 and H-3x



Scheme 1



Scheme 2

(see Fig. 1) proved essential in the identification of these isomers.

Examination of the HH COSY spectrum in Fig. 2 showed a strong cross-peak for the *exo* H-2 proton (2.59 ppm) and the bridgehead H-1 proton (3.07 ppm), which is characteristic of the *endo* isomer, as has been observed from the coupling constants in a series of substituted norbornenes.[13] In contrast, the *exo* isomer does not exhibit a cross-peak for the *endo* H-2 proton and H-1 proton, which is consistent with previous findings.[13] The magnitude of the *exo-exo* coupling (H-2 and H-3x), $J_{(2,3x)} = 9.4$ Hz, is also in agreement with previous values for the *endo* isomer.[13] Upon identification of the chemical shifts of the individual isomers using HH COSY connectivities, it was observed that monomers **10**, **11** and **17**–**19** were synthesized with preferential formation of the *endo* isomer (60 : 40) , whereas a 50 : 50 ratio existed for the etheric-bridged monomer (**4**).

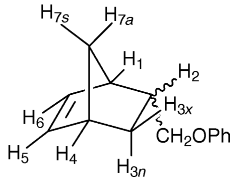


Fig. 1 Proton numbering scheme for monomer **4**.

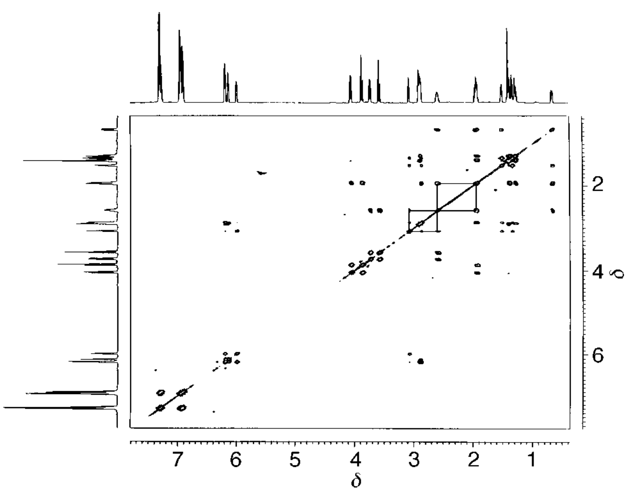


Fig. 2 HH Cosy NMR spectrum of monomer **4**.

Ring-opening polymerization of monomer **4** was accomplished using ruthenium-based catalysts. Initially, we investigated the polymerization of **4** with ruthenium chloride. Activation of the $RuCl_3 \cdot H_2O$ catalyst was accomplished *via* stirring in the presence of ethanol for 2 h. Polymerization was then initiated by the addition of the catalyst solution to the monomer, which was subsequently allowed to react at 60 °C for 24 h, resulting in the isolation of a fibrous solid (**5**). Previous studies involving ruthenium chloride catalysts note that an increase in molecular weight is obtained upon increasing the percentage of water in the solvent.[5] In keeping with these observations, polymerizations were carried out with varying ratios of ethanol to water. The molecular weights of the resulting polymers were calculated using gel permeation chromatography (GPC) *vs.* polystyrene standards giving weight average molecular weights ranging from 290 000 (EtOH 100%) to 535 000 (EtOH–H_2O 50 : 50) with narrow polydispersities (2.1 to 2.6). However, although polymerizations in 100% water were successful, lower molecular weight polymers (397 000) were prepared, which was attributed to the lack of solubility of the monomer in water.

Ruthenium benzylidene catalysts have recently demonstrated remarkable advantages over ruthenium chloride catalysts.[14] Recently, Grubbs and his co-workers introduced the highly reactive bis(tricyclohexylphosphine)benzylidene ruthenium(IV) dichloride catalyst (Grubbs' catalyst), which allows milder reaction conditions to be used and leads to greater conversion of the monomer.[8,14] In an attempt to compare the effectiveness of the two ruthenium catalysts, we polymerized monomer **4** with $(Cy_3P)_2Cl_2Ru{=}CHPh$. Upon addition of ruthenium benzylidene to the monomer in dichloromethane, polymerization was accomplished within minutes. This showed a marked improvement in reaction time as compared to the 24 h period required for polymerization in the presence of ruthenium chloride. As monomer **10** did not undergo polymerization with ruthenium chloride, monomers **10**, **11** and **17**–**19** were also subjected to polymerization with Grubbs' catalyst with ratios of monomer to catalyst of 100 : 1. The polymers obtained by this method were white solids (**12**, **13**, **20**–**22**) with weight average molecular weights ranging from 156 000 to 542 000 and polydispersities of 1.6 to 2.4.

Thermal analysis of these polymeric materials using DSC and TGA techniques demonstrated that increasing the length of the pendant aryl ether and ester chains resulted in an increase in thermal stability. While the glass transition temperature (T_g) of commercially available polynorbornene is 35 °C, incorporation of the pendant chains into the polymer backbone resulted in a noteable increase of T_g. When the polymer contained a single aromatic moiety (**12**), T_g was found to be 55 °C and increased to 74 °C when the number of aromatic moieties pendant to the polynorbornene backbone was five (**21**). The extent of polymer degradation was determined using TGA analysis. It was found that as the number of aromatic ether groups pendant to the polymeric backbone increased the midpoint of polymer degradation also increased, showing signs of decomposition at 417 °C for **12** and at 460 °C for **21**. In comparison to unsubstituted polynorbornene, which has a reported decomposition at 400 °C, aryl ether and ester functionalized polymers offer the advantage of preparing polynorbornenes with enhanced thermal stability.[15] In each of the analyses, single-step weight losses in the range of 90 to 100% were consistently observed.

In conclusion, metal-mediated nucleophilic aromatic substitution and condensation under mild reaction conditions allowed for the preparation of novel substituted norbornene monomers in good yields. ROMP of these monomers in the presence of Grubbs' or ruthenium chloride catalysts was investigated. Grubbs' catalyst demonstrated remarkable success in the ROMP of both the ether and ester norbornene monomers, giving high molecular weight polymers with narrow polydispersities. In comparison, ruthenium chloride was only successful in the polymerization of the ether monomer, with longer reaction times being required. Thermal analysis of these polymers demonstrated increased T_g and higher degradation temperatures upon increasing the length of the pendant chain.

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