

Addition polymerisation of 5-vinyl-2-norbornene with nickel bis(acetyl acetonate)/methylaluminoxane system

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Abstract

Poly(5-vinyl-2-norbornene) was synthesised using the nickel bis(acetyl acetonate)/methylaluminoxane (Ni(acac)₂/MAO) catalytic system. The polymerisation activity is low and depends strongly on temperature. The low reactivity of 5-vinyl-2-norbornene monomer results from both chelating effects and increased steric hindrance of the bulky monomer and the growing chain, which will account for low complexation and insertion rates. Fourier transform infrared spectroscopy (FTIR) characterisation has shown that polymerisation occurred mainly via addition polymerisation of the more strained endocyclic vinylene bond leaving the less strained exocyclic vinyl bond free. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Nickel bis(acetyl acetonate)/methylaluminoxane; Poly(5-vinyl-2-norbornene); Addition polymerisation; Catalytic activity; Temperature dependence

1. Introduction

Recently a novel group of polymers have been synthesised by the addition polymerisation of norbornene and its derivatives with transition metal catalysts [1–3]. In these polymers, the bicyclic structure of the monomer units are retained and therefore rotation between the neighbouring bulky units is seriously restricted. Though crystalline polymers synthesised with metallocene catalysts have been reported [4], most addition type norbornene polymers are amorphous and assume a rigid random coil conformation [5,6]. In view of their particular structural features, polynorbornenes are expected to show increased optical, ther-

mal and dielectric properties. This makes them good candidates for optical and microelectronic applications [7], but other uses have also been proposed, for example in gas permeation membranes [8,9]. On the other hand, the processability and the mechanical and adhesion properties of unsubstituted polynorbornenes are not the ideal ones. One approach to improve some polymer properties is the introduction of substituents in polynorbornene chains. Dorkenoo et al. [8] have investigated the effect of aliphatic groups on the transport properties of substituted polynorbornenes.

5-Vinyl-2-norbornene is a norbornene derivative with two double bonds in its structure: an endocyclic vinylene double bond and an exocyclic vinyl bond (Fig. 1). Depending on the catalytic system used, polymerisation may proceed either through the exocyclic or the endocyclic vinyl bond. With titanium Ziegler–Natta systems enchainment occurs selectively through the exocyclic double bond [10]. In the presence of soluble metallocene systems [11,12] or

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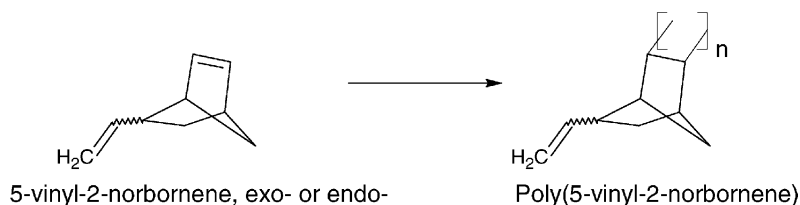


Fig. 1. Scheme for polymerisation of 5-vinyl-2-norbornene.

vanadium catalysts [13], bicyclic olefins are polymerised through the more strained endocyclic double bond. In the latter case the pendant vinyl group is left intact and will impart to the polymer an additional reactivity/functionality. The studies reported so far mainly focus on copolymerisation of ethylene with 5-vinyl-2-norbornene (used as minor comonomer) and little work on the homo and copolymerisation of 5-vinyl-norbornene as main monomer has been done.

Ni-based systems are also able to homo and copolymerise norbornene with good yields [14,15]. It was also recently reported that with the nickel bis(acetyl acetonate)/methylaluminoxane (Ni(acac)₂/MAO) system, polymerisation proceeds through a coordination mechanism and via a 2.3 addition of the endocyclic double bond [14]. The structure and the properties of the polynorbornenes have also been investigated [9].

We report in this paper a preliminary study on the homopolymerisation of 5-vinyl-2-norbornene initiated by the Ni(acac)₂/MAO system and on the structure and the properties of the resultant polymers.

2. Experimental

2.1. Materials

Nickel bis(acetyl acetonate), norbornene and 5-vinyl-2-norbornene were all supplied by Aldrich, with a purity of 99%. Nickel bis(acetyl acetonate) and norbornene were used without further purification. 5-Vinyl-2-norbornene, a mixture of endo- and exo-isomers, was dried over calcium hydride, and then freshly distilled under vacuum prior to polymerisation. Toluene (Petrolgal) was dried over butyl-lithium/styrene and then distilled under reduced pressure. MAO (Witco) was provided as a 10% (w/v) solution in toluene.

2.2. Polymerisation procedure

All the polymerisations were performed in a 0.1 l, 3-necked glass reactor using standard Schlenk technique under a dry nitrogen atmosphere. The calculated amounts of nickel bis(acetylacetonate), toluene and 5-vinyl-2-norbornene were first charged to the reactor and mixed together. The reactor system was preheated to the desired temperature using a temperature controlled oil bath. Then the MAO was added and the polymerisation started. The total reaction volume was kept low, between 10 and 25 ml. For all the polymerisations, the Al/Ni molar ratio used was 500 and the nickel concentration was controlled at [Ni] = 0.001 mol/l.

The polymerisations were terminated by the addition of acidified methanol. The reaction mixture was stirred and then kept still for 30 min. Two phases were formed. The upper phase, the solution of poly(5-vinyl-2-norbornene) and unreacted 5-vinyl-2-norbornene/toluene, was separated and washed repeatedly with acidified methanol and water. Then the resulting polymer/monomer solution was kept still for about 12 h, and a very clear solution was obtained. The polymer was fully precipitated by the addition of methanol to the solution. The resulting polymer was separated by filtration, washed with methanol several times and finally dried under vacuum at 25 °C for more than 18 h.

2.3. Characterisation of the polymers

The Fourier transform infrared (FTIR) spectra of the monomer and the polymer were recorded on a Perkin Elmer 1600 spectrometer. The wide angle X-ray diffraction (WAXD) diagram of the polymer powder was obtained using a Philips diffractometer with monochromatic radiation at a wavelength of 1.54 Å.

3. Results and discussion

The homopolymerisation of 5-vinyl-2-norbornene was carried out at different temperatures and different monomer/Ni molar ratios. In all the experiments, an Al/Ni ratio of 500 was selected, based on earlier results of norbornene homopolymerisation with the Ni(acac)₂/MAO catalytic system. It was seen there that maximal yields were obtained at [Al]/[Ni] = 500 and no significant increase of yield was observed at higher Al/Ni mole ratios [14].

The data reported here shows that the Ni(acac)₂/MAO system is also able to polymerise 5-vinyl-2-norbornene. Fig. 2 illustrates the dependence of the polymerisation activity as a function of temperature. The observed activity is low to moderate and is strongly dependent on temperature. Accordingly, the polymer yield is rather low at room temperature (2%), but increases significantly with polymerisation temperature. The maximal yield (about 20%) is obtained at 80 °C, reflecting the thermal stability of active sites up to this temperature. These are much lower values than those obtained for norbornene homopolymerisation: about 80% yield in the observed temperature range [14].

The dependence of polymerisation activity on the monomer/nickel ratio was also investigated at 60 °C. As shown in Fig. 3, the catalytic activity increased with the monomer/nickel ratio. The same dependence was observed for the homopolymerisation of norbornene initiated by the same Ni system [14]. However the polymerisation activity obtained for

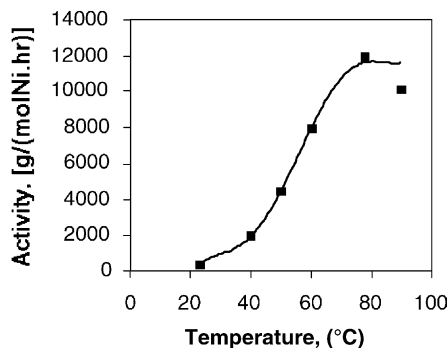


Fig. 2. Dependence of catalyst activity on polymerisation temperature. Initial polymerisation conditions: [Ni] = 0.001 mol/l, [monomer]/[Ni] = 3000, [Al]/[Ni] = 500, time = 6 h.

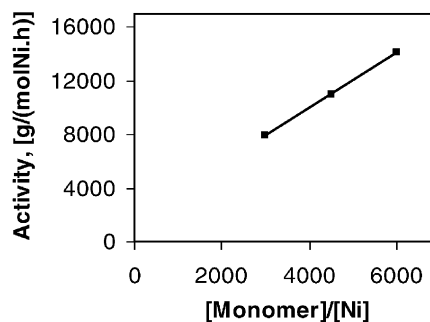


Fig. 3. Dependence of catalyst activity on the monomer/nickel ratio. Initial polymerisation conditions: [Ni] = 0.001 mol/l, [Al]/[Ni] = 500, time = 6 h, temperature = 60 °C.

5-vinyl-2-norbornene is much lower (about seven times) than that reported earlier for norbornene.

The crystallinity of the resultant polymer samples were investigated by WAXD. Fig. 4 shows the WAXD diagram of the as-made poly(5-vinyl-2-norbornene). A broad amorphous halo at $2\theta = 17.5^\circ$ and a small sharp peak at $2\theta = 14^\circ$ are present. This pattern is different from that of polynorbornene [5,9], which displays two halos centred at $2\theta = 10^\circ$ and at $2\theta = 18.8^\circ$, and no sharp peaks are observed. In accordance with polynorbornene data, this halo at $2\theta = 17.5^\circ$ is of predominantly intrachain nature, probably corresponding to a short-range order, or pseudo-periodicity of the arrangement of the bicycle units along the chain. It is interesting to notice that the maximum of this halo is located at a smaller value, $2\theta = 17.5^\circ$, than the corresponding maximum observed for polynorbornene, i.e., $2\theta = 18.8^\circ$. This seems to indicate that along the chain, the monomer units of

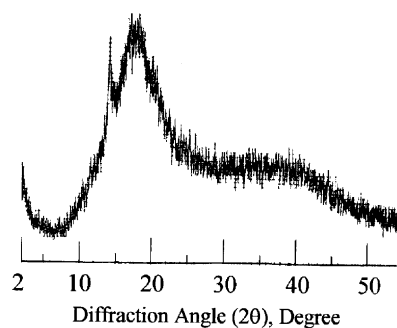


Fig. 4. WAXD diagram of poly(5-vinyl-2-norbornene).

poly(5-vinyl-2-norbornene) are packed a bit loosely than in the case of the unsubstituted polynorbornene.

The characteristic feature of the X-ray diffraction pattern of poly(5-vinyl-2-norbornene) is the sharp peak at 14° . The origin of this peak is not well established. Probably, it may also be attributed to intrachain order, since the possible interchain distance, derived from this peak (7.7 \AA), will be a little bit smaller than the diameter of the polymer chain (about 8 \AA). Some single segments of the polymer may be rather stereo-regular, leading to intrachain Bragg diffraction. However no ordered supermolecular structure is formed in the solid state, and the whole material is still globally amorphous.

The selectivity of enchainment of 5-vinyl-2-norbornene monomer was next investigated by FTIR. Fig. 5 displays the FTIR spectra of 5-vinyl-2-norbornene monomer, of the resulting polyvinylnorbornene and of an addition polynorbornene obtained with the same $\text{Ni}(\text{acac})_2/\text{MAO}$ system.

The spectrum of the 5-vinyl-2-norbornene monomer shows among others absorptions at 1636 , 994 , 906 , 1338 , 832 , and 766 cm^{-1} that can be assigned to carbon double bonds. In accordance with literature, the band around 1636 cm^{-1} is assigned to the stretching of the $\text{C}=\text{C}$ double bond in both ring and pendant group. However, due to the *cis*-configuration, the stretching band of the ring double bond is weak, and on the contrary the stretching band of the pen-

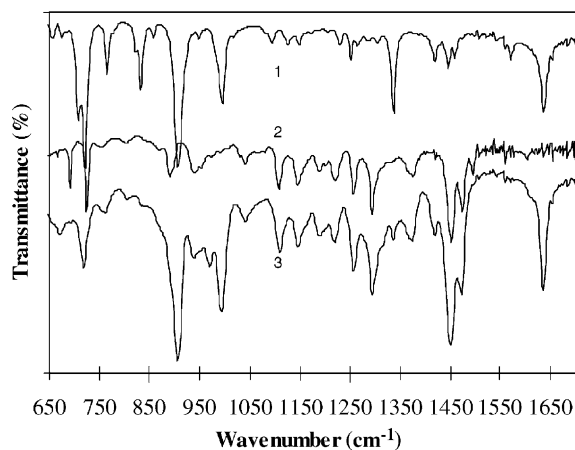


Fig. 5. FTIR spectra of 5-vinyl-2-norbornene (1), addition type polynorbornene (2), and poly(5-vinyl-2-norbornene) (3).

dent vinyl double bond is strong. The bands at 906 and 994 cm^{-1} are characteristic for the out-of-plane bending of olefinic CH bonds in terminal alkenes and therefore can be assigned to the pendant or exocyclic $\text{CH}=\text{CH}_2$ group. The bands at 708 , 766 , 832 and 1338 cm^{-1} are also seen in the spectrum of norbornene monomer and can be attributed to the bending of CH bond in the endocyclic double bond.

If we compare the spectra of the two homopolymers we may see that in the region between 1000 and 1500 cm^{-1} , the spectra are nearly the same and that the bands relative to the endocyclic double bonds are absent or become very weak in both homopolymer spectra. On the other hand, the absorption bands relative to the pendant double bond are absent in addition type polynorbornene spectrum and are still strong in the polyvinylnorbornene spectrum.

These results suggest that the polymerisation of 5-vinyl-2-norbornene, initiated by the $\text{Ni}(\text{acac})_2/\text{MAO}$ system, will proceed mainly through addition polymerisation of the endocyclic vinylene bond, leaving the exocyclic vinyl bond as a pendant group. The higher reactivity of the cyclic double bond towards addition polymerisation is a result of ring strain release. This is in agreement with data reported for the copolymerisation of ethylene and 5-vinyl-2-norbornene with metallocene-based systems. It was found that the 5-vinyl-2-norbornene was incorporated into the chain in a low rate, by addition polymerisation of the ring double bond [11,12].

Although polymerisation mainly proceeds through the endocyclic vinyl double bond, the pendant double bond will also play an active role. Obviously, the increased steric hindrance caused by the pendant vinyl group will make more difficult the complexation and further insertion of the endocyclic double bond. In addition, the possible competition of the pendant vinyl group for the nickel centre followed or not by subsequent insertion cannot be excluded. As a result, high energy barriers for polymerisation will be operating and low polymerisation rates are expected. This is in agreement with the observed experimental results: the polymer yield increases with polymerisation temperature but the maximal yield remains relatively low, about 20% at 80°C .

Another factor that may be limiting the yield is the possible difference in polymerisation reactivity between *exo*- and *endo*-isomers that are present in

5-vinyl-2-norbornene. According to literature data reported for Pd(II) catalysed addition polymerisation, the exo-substituted norbornene derivatives were found to polymerise at higher rates than the corresponding endo-substituted monomers [16,17].

Further work is going on to provide a deeper insight on the poly(5-vinyl-2-norbornene) microstructure and to get quantitative data concerning the selectivity of enchainment of the 5-vinyl-2-norbornene monomer as well as of the relative insertion rate of the two isomers during polymerisation. The influence of polymerisation conditions will also be investigated in more detail.

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