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Synthesis and characterization of syndiotactic 3,4-polyisoprene prepared with diethylbis(2,2′-bipyridine)iron–MAO

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Abstract

The soluble system diethylbis(2,2′-bipyridine)Fe–MAO is very active for the polymerization of isoprene to predominantly 3,4 polymers (ca. 80%). The polymers obtained at 25 °C are amorphous by X-ray examination, while those obtained below 10 °C are crystalline. The identity period determined from the X-ray fiber spectrum, ca. 5.2 Å, and the NMR analysis show that the polymer contains stereoregular sequences of 3,4 syndiotactic structure. An interpretation is given of the effect of polymerization temperature on stereospecificity. Some differences between the 1,2 polymerization of butadiene and the 3,4 polymerization of isoprene are examined.

Keywords: Isoprene; Iron-based catalysts; 3,4 Syndiotactic polyisoprene

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1. Introduction

Polymers of isoprene consisting predominantly of 3,4 units have been obtained with various catalysts, e.g. $AlEt_3$–$Ti(OR)_4$ (R = alkyl group) [1,2], $(dmpe)_2CrCl_2$–MAO (dmpe = 1,2-bis(dimethyl-phosphino)ethane) [3] and some iron-based catalysts containing chelate nitrogen ligands [4,5]. The 3,4 content of these polymers is in general not very high, maximum ca. 80%, the other units being almost exclusively *cis*-1,4. The polymers obtained with the Ti and Cr catalysts are amorphous by X-ray examination, but those obtained with some Fe-based systems were found to be crystalline.

The first synthesis of a crystalline 3,4-polyisoprene was reported by Chinese authors, who obtained a polymer consisting of about 70% 3,4 and 30% *cis*-1,4 units using as catalyst $Fe(acac)_3$–$AlEt_3$-D (D = nitrogen donor) at 10 °C [4]. Recently, using as catalyst $(Bipy)_2FeEt_2$–MAO (Bipy = 2,2′-bipyridine), we have obtained [5] a crystalline 3,4-polyisoprene exhibiting an X-ray powder spectrum analogous to that reported in Ref. [4]. Nothing is known about the type of stereoregularity of the crystalline 3,4-polyisoprene obtained with these iron-based catalysts.

We have now investigated the structure of the polymer obtained with $(Bipy)_2FeEt_2$–MAO using X-ray and NMR methods and have found that the polymer crystallinity is due to sequences having a 3,4 syndiotactic structure. This type of stereoregularity had never been observed before in a 3,4-polyisoprene. This note reports on a preliminary characterization of this polymer, and reports new data on the synthesis with $(Bipy)_2FeEt_2$, which show that this catalyst is one of the most active so far identified for the polymerization of 1,3-dienes.

2. Experimental

2.1. Materials

Diethylbis(2,2′-bipyridine)Fe was prepared according to the literature [4]. MAO (Witco, 10 wt% solution in toluene) was used as received. Toluene (Baker, >99.5%) was dried by refluxing for 10 h over K-diphenylketyl, then distilled

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and stored over molecular sieves under dry argon. Isoprene (Aldrich, 98%) was refluxed over CaH_2 for ca. 2 h, then distilled trap-to-trap and stored at −20 °C under dry argon.

2.2. Polymerization

All operations were carried out in an atmosphere of dry argon. Polymerizations were carried out in 250 ml dried glass reactors. Monomer, toluene and MAO (amounts given in Table 1) were introduced into the reactor, equipped with a magnetic stirrer, and the solution was heated to the desired temperature, under stirring. Diethylbis(2,2′-bipyridine)Fe was then added as a toluene solution (ca. 0.2 mg of compound/100 ml of toluene). The polymerization was terminated with methanol containing a small amount of aqueous hydrochloric acid. The polymer was coagulated, repeatedly washed with methanol and then dried in vacuo at room temperature.

2.3. Polymer characterization

Infrared spectra were taken with a Nicolet MAGNA -IR 560 spectrometer, using polymer films on KBr disks. The films were obtained by deposition from solution in methylene chloride.

^1H and ^{13}C NMR spectra have been run in a $C_2D_2Cl_4$ solution (10 mg/ml) at 360 K, on a Bruker Avance 600 spectrometer operating, respectively, at 600.13 and 150.90 MHz.

Molecular weights were determined on a Water Alliance GPC 2000 instrument using polymer solutions in toluene at 50 °C and polystyrene standards.

X-ray analysis was carried out using the Ni-filtered Cu K_α radiation. Powder spectra were collected with a Philips PW3710 automated diffractometer operating in the conventional $\theta/2\theta$ Bragg–Brentano geometry. Fibers of the polymer were obtained by the following procedure: samples of the as prepared polymer were heated under pressure at 50 °C for 20 min, quenched in a mixture of ice and water and stretched (450%) at room temperature.

3. Results and discussion

The polymerization of isoprene with $(Bipy)_2FeEt_2$–MAO is very rapid at room temperature. Under the conditions of Table 1, the polymerization medium becomes very viscous and difficult to stir after 1–2 min. The data of Table 1 indicate that a full conversion is reached after 5 min in polymerizations at room temperature, but presumably less time is sufficient. A comparison of the data of Table 1 with those reported in Ref. [4] indicate that $(Bipy)_2FeEt_2$–MAO is much more active than the ternary system $Fe(acac)_3/AlEt_3/Bipy$, for which a full monomer conversion is reached in 2 h at 10 °C. The higher activity likely is attributable to a higher number of active centers in the $(Bipy)_2FeEt_2$–MAO system, which contains preformed Fe-C bonds. The data of Table 1 also show that the activity of $(Bipy)_2FeEt_2$–MAO is comparable with that of the most active systems so far known for 1,3-diene polymerization, for instance some soluble cobalt-based catalysts [6].

The freshly prepared polymer is for the most part (ca. 95%) soluble in toluene at room temperature. IR analysis indicates that the polymer consists predominantly of 3,4 units (intense band at 889 cm^{-1}, typical of $-CH_2-CH(CMe{=}CH_2)-$). According to the ^1H NMR spectra the polymer (either that obtained at +25 °C or that obtained at −20 °C) has a 3,4 content of about 80%, the other units being predominantly *cis*-1,4.

As we have reported in a previous paper [5], the polymer obtained at +25 °C is practically amorphous, while that obtained at −20 °C is partially crystalline. Information on the type of stereoregularity of the polymer has been obtained by X-ray investigation. Fig. 1 shows the X-ray powder spectrum of the as prepared polymer. The estimated value of the crystallinity is about 50%. Fig. 2 shows the fiber spectrum obtained by the cylinder camera. The fiber sample appears well oriented and its spectrum exhibits several equatorial reflections but a low number of layer reflections. However, the analysis of the fiber spectrum has allowed the determination of the value of the *c* axis (5.25 ± 0.10 Å).

It is well known that the chains of constitutionally and configurationally regular polymers assume in the crystal

Table 1
Polymerization of isoprene with $(Bipy)_2FeEt_2$–MAO

Monomer (ml)	$(Bipy)_2FeEt_2$ (M)	Polymerization		Polymer yield (g)	Molecular weight (10^{-3})
		Temperature (°C)	Time		
2	1.1×10^{-6}	+25	5 min	1.32	M_n 148 M_w 349
2	1.3×10^{-6}	0	5 min	1.32	M_n 174 M_w 610
2	1.22×10^{-6}	−20	5 min	1.03	M_n 192 M_w 392
3	1×10^{-4}	−90	18 h	2	M_n 132 M_w 251

Solvent, toluene; MAO 10 wt% solution in toluene, 5 ml; total volume, 200 ml.

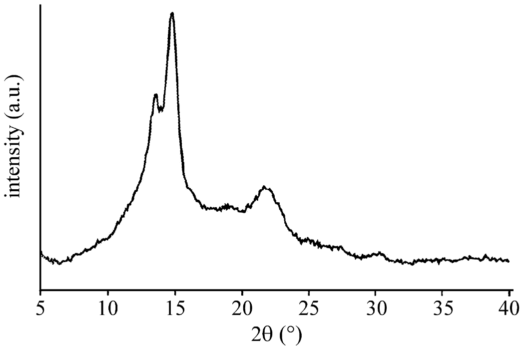

Fig. 1. X-ray powder spectrum of the 3,4 syndiotactic polyisoprene obtained with $\mathrm{(Bipy)_2FeEt_2}$–MAO.

state regular conformations. The conformations of vinyl polymers having formula $(-\mathrm{CH_2}-\mathrm{CHR}-)_n$, with R being an aryl or alkyl group, depend on their configuration. Isotactic vinyl polymers assume helical conformation because highly extended conformations are hindered by the repulsive interactions between lateral groups. In this case the minimum number of monomer units contained in the chain axis is 3 and the value of the *c* axis is greater than 6 Å [7]. On the contrary, syndiotactic vinyl polymers can assume both highly extended and helical conformations because also in the first case lateral groups are sufficiently far to avoid highly repulsive interactions [8]. In the highly extended chains the minimum number of monomer units contained in the chain axis is 2 and the value of the *c* axis is about 5.1 Å. In the helical conformations the minimum number of monomer units contained in the chain axis is 4 and the value of the *c* axis is greater than 7 Å [7]. Hence, the value of the *c* axis found for the 3,4-polyisoprene is compatible only with a syndiotactic polymer having a highly extended conformation. This conclusion is strengthened by the complete crystal structure determination reported in a parallel paper [9].

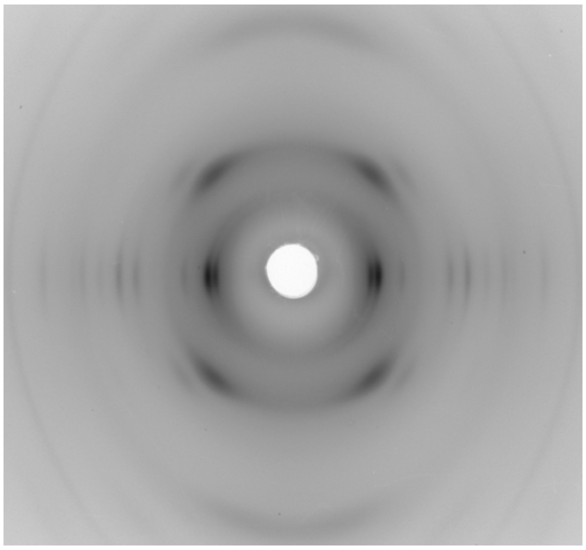

Fig. 2. X-ray fiber spectrum of the 3,4 syndiotactic polyisoprene obtained with $\mathrm{(Bipy)_2FeEt_2}$–MAO.

^{1}H and ^{13}C NMR spectra (Fig. 3) show a large number of resonances from which few sharp lines emerge. The spectra are of difficult interpretation and are indicative of a non-highly regular structure, that is of the presence of constitutional and configurational defects in the chain. However, on the basis of X-ray analysis, the sharp lines in the NMR spectra seem to be attributable to stereoregular 3,4 syndiotactic sequences.

The defects present in a real polymer are generally segregated in the amorphous phase, but they can be included, if tolerated, in the crystal. We have verified that for this polymer the chain conformation in the crystal phase remains highly extended also in the presence of some amount of configurational defects consisting in the presence of some isotactic placements.

As mentioned before, $\mathrm{(Bipy)_2FeEt_2}$–MAO gives a partially crystalline polymer only below 10 °C. The formation of 3,4 syndiotactic sequences can be interpreted on the basis of the schemes we have proposed in previous papers [10–14]. According to our interpretation, a 1,2- or 3,4 syndiotactic sequence derives from a situation as that in Fig. 4(a), in which the allyl group (the last-inserted monomer) and the new monomer adopt a *supine/supine* orientation (we are using the terms defined in Ref. [15]). Reaction of the new monomer at C3 of the allyl group causes the formation of a 1,2 (3,4) unit and of a new allyl group having an opposite chirality with respect to previous one. Hence this mechanism leads to the formation of a 1,2 (3,4) syndiotactic sequence. A *prone/supine* or a *supine/prone* orientation as in Fig. 4(b) and (b′) produce instead an isotactic placement [10–14].

This interpretation is supported by the fact that in the allylic complex (5-methyl-hepta-2,6-dien-1-yl)(butadiene) Co, $(\eta^3\text{-}\mathrm{C_8H_{13}})(\mathrm{C_4H_6})\mathrm{Co}$, which is active for butadiene polymerization to 1,2 syndiotactic polymer, the allyl group and the coordinated butadiene have a *supine/supine* orientation [16,17].

However, some authors have proposed [18], on the basis of molecular mechanics analysis, that, at least with some catalysts and in particular with $\mathrm{CpTiCl_3}$–MAO, stereoregular polydienes derive from a *prone/prone* orientation of the allyl group and the new monomer (Fig. 4(c)). Also in this case reaction of the new monomer at C3 of the allyl group gives rise to a 1,2 or 3,4 syndiotactic sequence.

Several (allyl)(diene) complexes of transition metals have been reported and in these complexes the allyl group and the η^4-coordinated diene adopt different relative orientations depending on steric and electronic factors [15]. It is possible, therefore, that the situation may vary from one catalyst to another. A detailed discussion on whether 1,2 (3,4) syndiotactic polydienes derive from a *supine/supine* or *prone/prone* orientation is out of the scope of this note. Specific cases will be discussed in forthcoming papers.

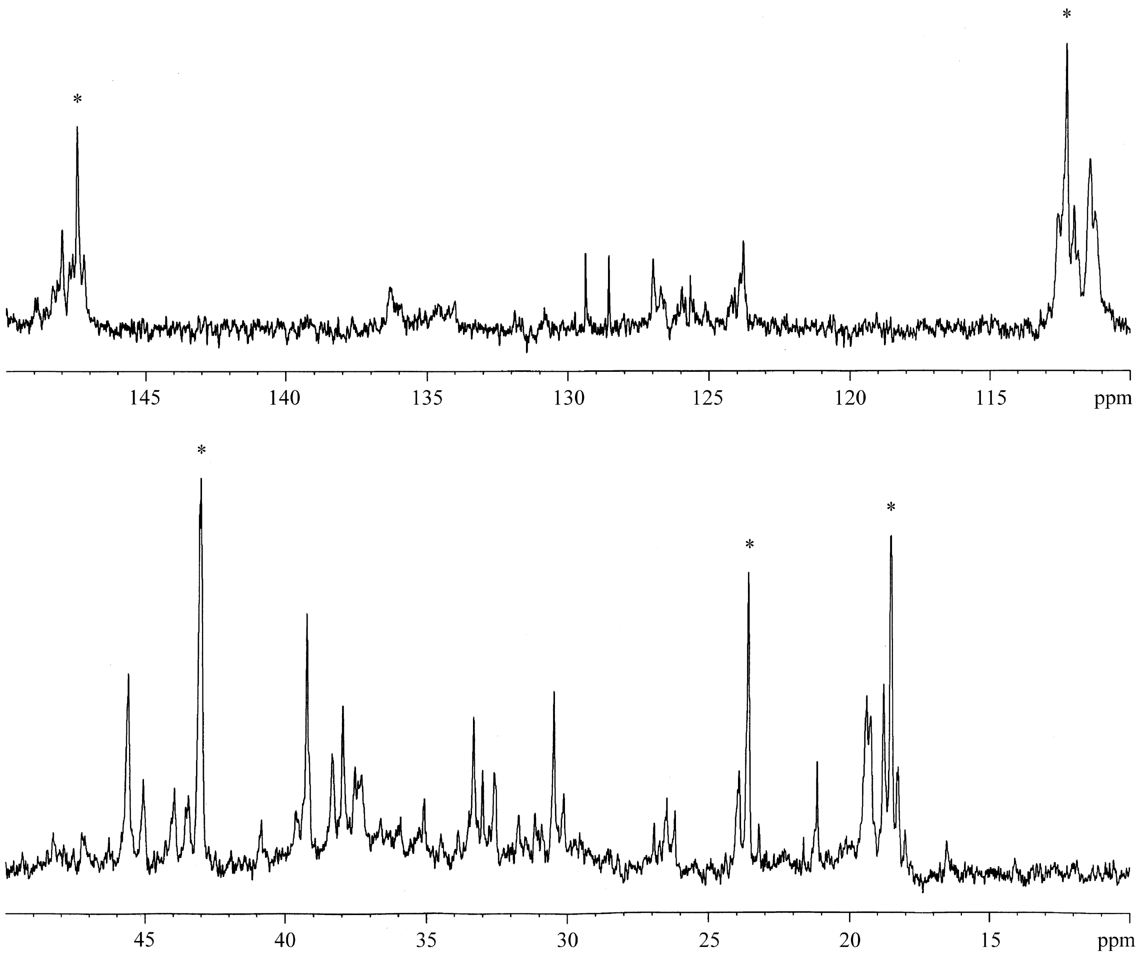

Fig. 3. ^{13}C-NMR spectrum of the 3,4-polyisoprene obtained with $(Bipy)_2FeEt_2$–MAO ($C_2D_2Cl_4$; 363 K). $*$: Resonances attributable to 3,4 syndiotactic sequences.

In the case of isoprene polymerization with $(Bipy)_2FeEt_2$–MAO the stereospecificity increases with decreasing the polymerization temperature. Since steric errors in a 1,2 (3,4) syndiotactic polymerization derive from a *supine/prone* or *prone/supine* orientation, monomer insertion from these two forms becomes less frequent at low temperature, presumably because these forms are present in lower amount.

It is interesting that so far crystalline syndiotactic 3,4-polyisoprene has been obtained only with Fe-based systems containing chelate nitrogen ligands. It is well known, on the other hand, that several systems have been identified for the 1,2 syndiotactic polymerization of butadiene [19]. These systems, some of which give highly stereoregular 1,2 polybutadiene, give in general atactic 3,4 polyisoprene. A case recently studied is reported in Ref. [3]. In our opinion the different stereospecificity in butadiene and isoprene polymerization with the same catalyst can be attributed to the fact that in isoprene polymerization the *supine/supine* orientation is less favored than in butadiene polymerization because of the interaction between the methyl group of the last-inserted unit and the methyl group of the new monomer. This interaction may favor occasionally a *supine/prone* or *prone/supine* orientation, with consequent formation of 3,4 sterically irregular sequences.

4. Conclusions

$(Bipy)_2FeEt_2$–MAO is a very active system for the polymerization of isoprene to crystalline polymers

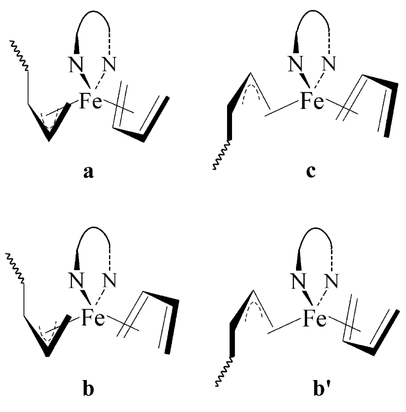

Fig. 4. Possible orientations of the incoming monomer with respect to the last-inserted unit.

consisting of ca. 80% 3,4 units. The value of the identity period determined from the X-ray fiber spectrum, ca. 5.2 Å, indicates that the crystallinity is attributable to the presence of stereoregular sequences having a 3,4 syndiotactic structure. It is to be noted that most of the catalysts identified for the 1,2 syndiotactic polymerization of butadiene give amorphous 3,4 polymers from isoprene. Only by using iron-based catalysts it has been possible to obtain a crystalline 3,4 syndiotactic polyisoprene, whose stereoregularity, however, is not high according to the NMR and X-ray investigation. The difficulty in obtaining a highly stereoregular 3,4 syndiotactic polyisoprene is likely attributable to the fact that in isoprene polymerization the steric interaction between the new monomer and the last-inserted unit is higher than in butadiene polymerization, due to the methyl group. This makes the *supine/prone* geometry more probable, with consequent formation of steric errors.

Acknowledgements

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