Journal of Organometallic Chemistry, 451 (1993) 67–72

JOM 23597

Polymerization of 1,3-dienes with the soluble catalyst system methylaluminoxanes–[CpTiCl$_3$]. Influence of monomer structure on polymerization stereospecificity *

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(Received October 22, 1992)

Abstract

In combination with methylaluminoxanes, [CpTiCl$_3$] gives a soluble catalyst that has remarkable activity for the polymerization of conjugated dialkenes. Polymers with a *cis*-1,4 structure (> 98%) have been obtained from 2,3-dimethylbutadiene, 2-methylpentadiene and (*Z*)-pentadiene. Crystalline polymers with a 1,2 syndiotactic structure have been obtained from 4-methylpentadiene. Other monomers give amorphous polymers with a mixed 1,4/1,2 structure. An interpretation of the mechanism of formation of the polymers is proposed. The mode of orientation of the incoming monomer with respect to the last polymerized unit and the different reactivity of the butenyl groups derived from the various monomers are believed to be the main factors that determine polymer structure.

1. Introduction

Much attention has been given during recent years to polymerization catalysts derived from methylaluminoxanes (MAO) and some soluble titanium compounds, such as [Ti(OR)$_4$] (R = alkyl group), [CpTiCl$_3$] (Cp = C_5H_5), and [Ti(benzyl)$_4$]. The main reason is the fact that they are highly stereospecific for the polymerization of styrene to syndiotactic polymer [1]. However these systems are also of great interest for the polymerization of conjugated dialkenes. Not only do they exhibit remarkable activity for this class of monomer, but they are also able to polymerize some dialkenes, such as (*Z*)-1,3-pentadiene and 4-methyl-1,3-pentadiene, which are not polymerized by other catalysts [2–4].

We have investigated the polymerization of various conjugated dienes with MAO–[CpTiCl$_3$]. This system polymerizes several types of diene and gives polymers of different structures from the different monomers some of which highly stereoregular. For example, it gives a *cis*-1,4 isotactic polymer from (*E*)-2-methyl-1,3-pentadiene, a 1,2 syndiotactic polymer from 4-methyl-1,3-pentadiene, and polymers of mixed 1,4/1,2 structure from other monomers. The work with MAO–[CpTiCl$_3$] has permitted us to gather information on the influence of monomer structure on polymerization stereospecificity. Furthermore, it has provided data useful to check the validity of the interpretation already proposed for some aspects of the catalysis of diene polymerization [5].

2. Results and discussion

The following monomers have been polymerized: 1,3-butadiene, isoprene, 2-ethyl-1,3-butadiene, 2,3-dimethyl-1,3-butadiene, (*E*)- and (*Z*)-1,3-pentadiene, (*E*)-2-methyl-1,3-pentadiene, 3-methyl-1,3-pentadiene, 4-methyl-1,3-pentadiene, 1,3-hexadiene, and (*E*,*E*)-2,4-hexadiene. Some data on the polymerization of these monomers are reported in Table 1. The results are summarized as follows.

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* Dedicated to Professor G.P. Chiusoli on the occasion of his 70th birthday and in recognition of his important contributions to organometallic chemistry and its application in organic synthesis.

0022-328X/93/$6.00

(1) At room temperature, (*Z*)-pentadiene, 2-methylpentadiene, and 2,3-dimethylbutadiene gave polymers with an almost exclusive *cis*-1,4 structure (> 98%). The polymers of 2,3-dimethylbutadiene were highly crystalline and were found to be identical by X-ray and NMR analysis to those obtained with $AlEt_2Cl-Nd(OCOR)_3-Al(^iBu)_3$ [6]. However, their molecular weight was lower than that of the Nd polymers, which explains their lower melting point (120°C *vs.* 193°C). The polymers of 2-methylpentadiene had an isotactic structure according to NMR analysis and were found to be identical by X-ray analysis to the toluene-insoluble fraction isolated from the product obtained with the Nd catalyst [7]. The difference between the Ti and Nd catalysts in the polymerization of 2-methylpentadiene is that the Ti system gives a product of higher stereoregularity, as can be seen by a comparison of the NMR spectrum of the Ti polymer and that of the most stereoregular fraction of the Nd product (Fig. 1). The latter shows resonances that are not attributable to stereoregular *cis*-1,4 isotactic sequences. However, the Ti polymers had a lower molecular weight, which explains their lower melting point (147°C *vs.* 165°C).

The polymer of (*Z*)-pentadiene was a waxy product of rather low molecular weight. The NMR spectrum (Fig. 2) indicates that isotactic triads, mm, prevail in the polymer, but rm triads are also present [8]. The low degree of isotacticity may be a consequence of an *anti–syn* isomerization of the monomer in polymerization under our conditions.

(2) Butadiene and (*E*)-pentadiene gave amorphous polymers consisting essentially of *cis*-1,4 and 1,2 units,

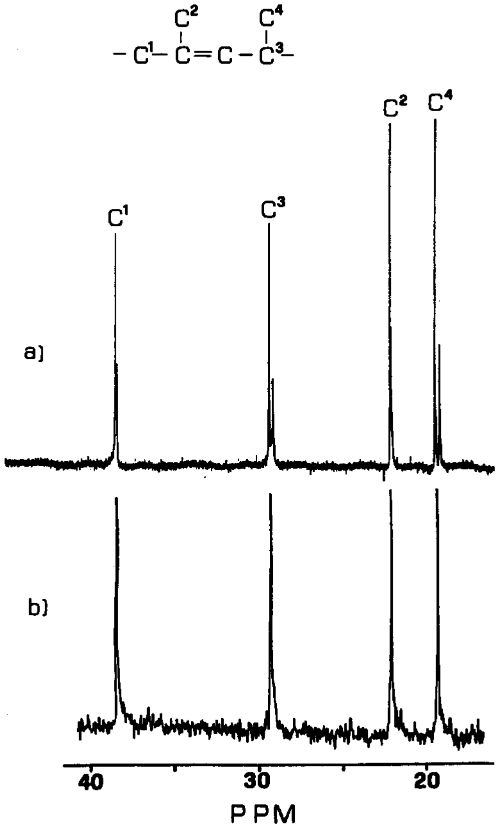


Fig. 1. ^{13}C NMR spectra (aliphatic region) of the poly(2-methylpentadiene) obtained with $AlEt_2Cl-Nd(OCOR)_3-Al(^iBu)_3$ (toluene insoluble fraction), (a), and with $[CpTiCl_3]/MAO$ (crude polymerization product), (b). ($C_2D_2Cl_4$, 90°C, HMDS as internal standard). Peaks attribution as in [7].

TABLE 1. Polymerization of 1,3-dienes with $[CpTiCl_3]$–MAO

Monomer	Temp. (°C)	Time (h)	Conv. (%)	*cis*	*trans*	1,2	Polymer	
					(%)		M.p (°C)	[η] (dl g^{-1})
1,3-Butadiene	15	0.5	51.7	79		21		4.1
Isoprene	−18	96	traces					
2-Ethyl-1,3-Butadiene	−18	20	traces					
2,3-Dimethyl-1,3-Butadiene	20	70	85.3	≥ 98			120 [a]	0.25
(*E*)-1,3-Pentadiene	20	0.5	65.1	43		57		2.6
(*E*)-1,3-Pentadiene	−18	22.5	46	40		60		–
(*Z*)-1,3-Pentadiene	20	95	100	≥ 98				–
(*E*)-2-Methyl-1,3-Pentadiene	20	18.5	14.7	≥ 95			136 [b]	–
(*E*)-2-Methyl-1,3-Pentadiene	−18	71.5	89.6	≥ 95			147 [b]	0.4
3-Methyl-1,3-Pentadiene	−18	6	55.9	50		50		2.5
4-Methyl-1,3-Pentadiene	20	70	100			≥ 98		0.1
4-Methyl-1,3-Pentadiene	−18	6	68.8			≥ 98	95 [c]	0.4
1,3-Hexadiene	−18	20	47.2	55		45		1.9
(*E*,*E*)-2,4-Hexadiene	−18	115	37.3		30	70		–

Polymerization conditions: monomer, 2ml; toluene, 8ml; $[CpTiCl_3]$, $1 \cdot 10^{-5}$ moles; MAO, $1 \cdot 10^{-2}$ moles. For butadiene polymerization, see Experimental section. [a] Melting point of the ether insoluble fraction. [b] Isotactic structure by RX analysis. [c] Syndiotactic structure by NMR analysis.

the *cis* content being *ca.* 79% for the polybutadiene, *ca.* 40% for the polypentadiene.

1,3-Hexadiene and 3-methylpentadiene also gave polymers of mixed *cis*-1,4/1,2 structure. Isoprene and 2-ethylbutadiene gave only oils, which were not analyzed.

(3) The polymers obtained from 4-methylpentadiene consisted essentially of only 1,2 units; NMR analysis showed them to have a syndiotactic structure [2]. The polymers obtained at −18°C were found to be crystalline by X-ray analysis (Fig. 3), whereas those obtained at room temperature were amorphous, although no significant difference was noticed in the NMR spectra of the two products. We are now examining the effect of annealing on the crystallinity to clarify this problem.

(4) 2,4-Hexadiene gave polymers amorphous by X-ray analysis, consisting of 1,2 units together with a minor amount of *trans*-1,4 units.

We shall first discuss the results obtained from 2-methylpentadiene and 4-methylpentadiene. In diene polymerization, the formation of 1,4 or 1,2 units depends on whether the incoming monomer reacts at C1 or at C3 of the last polymerized unit, which is η^3-bonded to the transition metal of the catalyst [5a]. The structure of the catalytic complex is one of the factors that determine reaction at C1 or C3. There are several pieces of evidence showing that in soluble catalytic complexes the incoming monomer coordinates as a *cis*-η^4 ligand [5]. In some complexes one terminal C atom of the coordinated monomer is at bonding distance from C1 leading to a *cis*-1,4 unit, in others it is at bonding distance from C3 and a 1,2 unit will result.

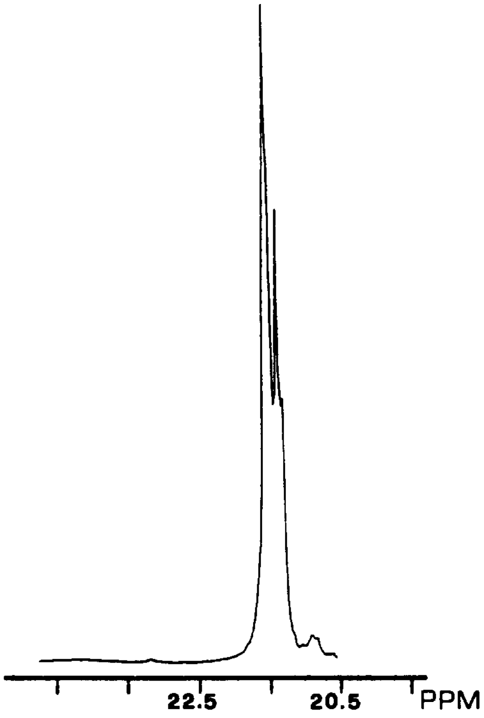


Fig. 2. Methyl resonances in the ^{13}C NMR spectrum of poly((*Z*)-pentadiene) obtained with [$CpTiCl_3$]-MAO. The peak at 21.632 ppm is attributable to mm triads, that at 21.490 ppm to mr triads [8]. (C_6D_6; room temperature; TMS as internal standard.)

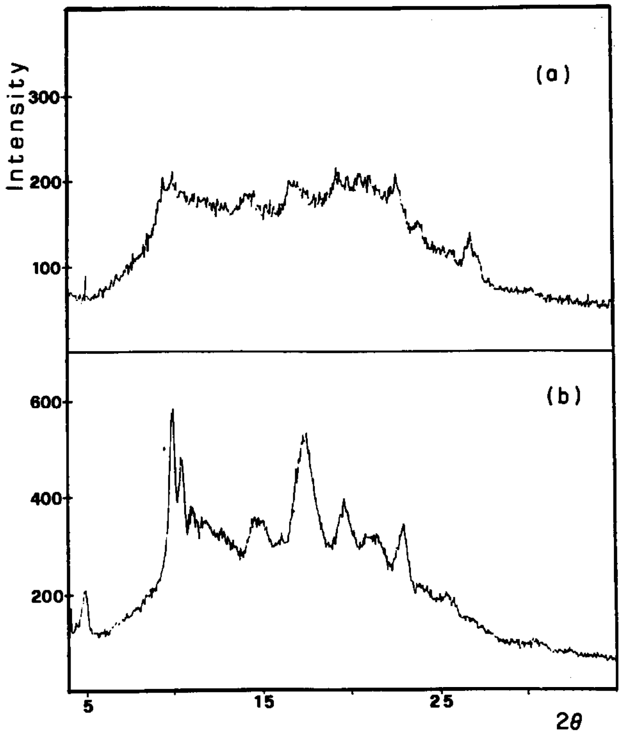


Fig. 3. X-ray spectra of poly(4-methylpentadiene) obtained with [$CpTiCl_3$]-MAO at −18°C: (a) crude polymerization product; (b) MEK insoluble fraction.

Another factor that determines whether reaction occurs at C1 or C3 is the presence of substituents on these carbon atoms. 2-Methylpentadiene and 4-methylpentadiene can each give two different types of η^3-butenyl group (Fig. 4). However, in the case of 4-methylpentadiene, only **Ia** is formed, since only this group can give a monomeric unit of structure $-CH_2-CH(CH{=}CMe_2)-$. The reason **Ia** gives only 1,2 units is that due to the steric hindrance of the two methyl groups C1 is much less reactive than C3.

In the case of 2-methylpentadiene, either **IIa** or **IIb** can give a *cis*-1,4 unit. However, the complete absence in the polymer of units $-CH(CMe{=}CH_2)-CMe-$ seems to indicate that only **IIa** is formed. In this group C1 is less substituted and hence more reactive than C3; the incoming monomer will thus react at C1, giving *cis*-1,4 units.

In conclusion, the different reactivities of C1 and C3 in the η^3-butenyl groups account for the formation of a 1,2 polymer from 4-methylpentadiene and a 1,4 polymer from 2-methylpentadiene.

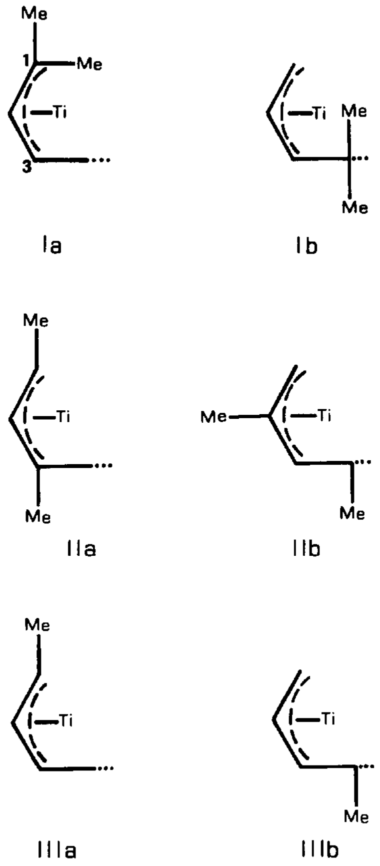


Fig. 4. η^3-Butenyl groups that can be obtained from 4-methylpentadiene (**Ia**, **Ib**), 2-methylpentadiene (**IIa**, **IIb**) and (*E*)-pentadiene (**IIIa**, **IIIb**) on insertion into the growing polymer chain (only the *anti* form is shown).

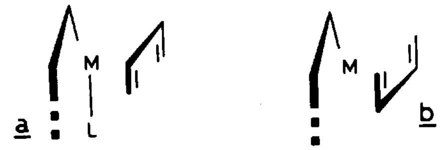


Fig. 5. Possible orientations of the incoming monomer with respect to the last polymerized unit. L is a generic anionic ligand.

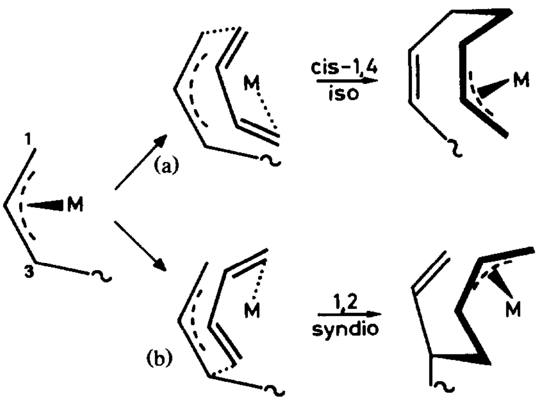
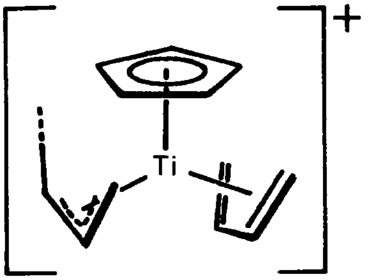


Fig. 6. Scheme for the formation of a *cis*-1,4 isotactic and a 1,2 syndiotactic polymer from a generic diene. In (a) and (b) the last polymerized unit is below the plane of the figure, the incoming monomer is above and the transition metal, M, is on the plane.

The different type of stereoregularity of poly(2-methylpentadiene) and poly(4-methylpentadiene) (iso- and syn-diotactic, respectively) can be interpreted on the basis of the schemes previously proposed for the formation of stereoregular diolefin polymers [5]. The fact that the $[CpTiCl_3]$ catalyst gives a *cis*-1,4 polymer from 2-methylpentadiene indicates that the last polymerized unit has an *anti* configuration and that the incoming monomer is coördinated as a *cis*-η^4-ligand. With this type of coordination a diene monomer can take two orientations with respect to the last polymerized unit, depending on the presence or absence of anionic ligands (L) bonded to M of the catalyst as shown in Fig. 5(a) and (b). It can easily be seen that only the orientation in Fig. 5(a) can give rise to a *cis*-1,4 isotactic polymer. Figure 6 represents the same situation as that of Fig. 5(a), in a different form (L is not shown for simplicity): if the incoming monomer reacts at C1 of the butenyl group, a *cis*-1,4 unit is obtained and the new butenyl group has the same chirality as its predecessor; hence, a *cis*-1,4 isotactic diad will result. Various catalysts are known to give *cis*-1,4 isotactic polymers from substituted butadienes [5]. There are several pieces of evidence showing that these polymers are all formed according to the scheme of Fig. 5(a). In these systems the orientation of the new monomer probably depends on the fact that anionic ligands (such as chlorine atoms, alkoxy groups, and Cp groups) are bonded to M [5].

There are various examples in the literature of allyl-butadiene complexes in which the allyl group and the diene are in the arrangement shown in Fig. 5(a). One of these is the complex $Zr(\eta^3\text{-}C_3H_5)(C_4H_6)$ [9], which has analogies with the active species in the $[CpTiCl_3]$ catalyst.

The reaction of $[CpTiCl_3]$ with MAO produces $CpTiCl_2$ [1e,10]. The active species derives from the alkylation of $CpTiCl_2$ by MAO and subsequent formation of an ionic complex. During the polymerization this generates the cation shown.



(*Z*)-Pentadiene gave a *cis*-1,4 polymer with $[CpTiCl_3]$/MAO. It is reasonable that in this case also the last polymerized unit has an *anti* configuration and that the incoming monomer coordinates *cis*-η^4. A coordination of this type is not common for the (*Z*)-isomer of a diene, but some examples are known [11].

Presumably the 1,2-syndiotactic poly(4-methylpentadiene) also derives from the arrangement of Fig. 5(a). If (*Z*)-pentadiene coordinates to Ti as *cis*-η^4 it is reasonable that 4-methylpentadiene coordinates in the same way. According to the scheme of Fig. 6, reaction of the incoming monomer at C3 of the butenyl group produces a 1,2 unit and the new butenyl group has an opposite chirality with respect to the preceding one. A syndiotactic diad will result. An alternative mechanism for the formation of 1,2-syndiotactic poly(4-methylpentadiene) has been proposed [5d] based on coordination of the monomer *trans*-η^2. However, in the case of the [CpTiCl$_3$] catalyst, the mechanism based on a *cis*-η^4-coordination is supported by the results obtained from (*Z*)-pentadiene.

In the butenyl groups derived from butadiene and (*E*)-pentadiene, the difference of reactivity between C1 and C3 is not so great as to direct the reaction in one sense alone. The incoming monomer can react either at C1 or C3, giving a polymer of mixed 1,2/*cis*-1,4 structure. In the case of (*E*)-pentadiene, some structural features of the polymer give an indication of its mode of formation. Vinyl groups are completely absent in the polymer, which means that (*E*)-pentadiene gives only the butenyl group **IIIa** (Fig. 4) on insertion into the growing chain. The formation of a 1,2/*cis*-1,4 polymer probably occurs according to the scheme of Fig. 7(a) and (b). Reaction of the monomer as in (a) gives rise to a *cis*-1,4 unit, since formation of the new C–C bond between C1 and C1′ is favoured for steric reasons over that between C3 and C4′. In contrast, reaction as in (b) gives a 1,2-unit. The 1,2/*cis*-1,4 ratio depends on the relative concentrations of the species (a) and (b) and on the relative rates of incorporation of the incoming monomer into the two species. A mechanism of this type should result in a polymer without inversions such as $-CH_2CH{=}CHCH(Me)-CH(Me)CH{=}CHCH_2$ and $-CH_2CH{=}CHCH(Me)CH(CH{=}CHMe)CH_2-$. Inversions of this type have not been observed by NMR analysis, which supports the validity of the schemes of Fig. 7.

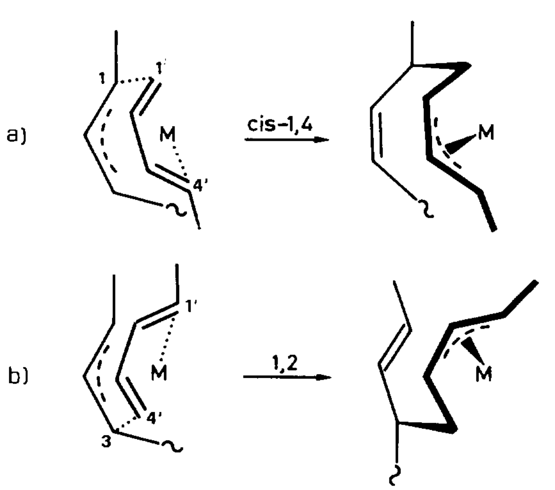


Fig. 7. Scheme for the formation of a polymer of (*E*)-pentadiene with a mixed 1,2/*cis*-1,4 structure.

The formation of a polymer with 1,2/*trans*-1,4 structure from 2,4-hexadiene is not surprising. It is well known [12] that this monomer gives predominantly *trans* polymers, even with catalysts that give *cis* polymers from common monomers such as butadiene, isoprene, (*E*)-pentadiene. It has been shown that the formation of *trans* units is because this monomer polymerizes much more slowly than butadiene or isoprene, due to the steric hindrance of the methyl groups. The last polymerized unit, which is *anti*-η^3-bonded to M, has time to isomerize to the more stable *syn* form prior to monomer incorporation. Reaction of the new monomer at C1 of a *syn* butenyl group gives rise to a *trans*-1,4 unit, while reaction at C3 will give a 1,2-unit [5]. Therefore, 2,4-hexadiene behaves like butadiene and (*E*)-pentadiene, except that the butenyl group has a *syn* structure, as a result of the *anti*–*syn* isomerization.

3. Conclusions

(1) [CpTiCl$_3$]–MAO is a catalyst for the polymerization of several types of conjugated dialkene. Its activity is comparable to that of the most common systems used for the polymerization of this class of monomer. In contrast, [Cp$_2$TiCl$_2$]–MAO is practically inactive in the polymerization of butadiene, probably because the monomer cannot coordinate η^4 with this system.

(2) The polymerization with the [CpTiCl$_3$] catalyst has shown that substituents at C1 and C3 of the last polymerized unit (the η^3-butenyl group) is one of the factors that determines the formation of 1,4 or 1,2 units.

(3) With the same catalyst and under the same conditions, the formation of a *cis*-1,4-isotactic poly-(2-methyl-1,3-pentadiene) and of a 1,2-syndiotactic poly(4-methyl-1,3-pentadiene) is consistent with the interpretation already proposed for the formation of iso- and syndiotactic polymers of conjugated dialkenes.

4. Experimental details

4.1. Materials

[CpTiCl$_3$] (Strem Chemicals) and MAO (Schering, 30 wt% solution in toluene) were used as received.

Toluene (Baker, > 99% pure) was refluxed over Na for *ca.* 8 h, then distilled and stored over molecular sieves under dry dinitrogen. Butadiene (> 99.5% pure) was received from Enichem Elastomeri (Milan). It was evaporated from the container prior to each run, dried by passing through a column packed with molecular sieves and condensed into the reactor, which had been precooled to −20°C.

Isoprene (Enichem Elastomeri, > 99.5% pure), (*E*)-1,3-pentadiene (Aldrich, 98% pure), (*Z*)-1,3-pentadiene (Fluka, > 98% pure), (*E*)-2-methyl-1,3-pentadiene (Fluka, > 98% pure), 2,3-dimethyl-1,3-butadiene (Fluka, > 97% pure), 1,3-hexadiene (Aldrich, 99% pure, prevalently the (*E*)-isomer), 3-methyl-1,3-pentadiene (Aldrich, 99% pure, mixture of (*E*)- and (*Z*)-isomers), 4-methyl-1,3-pentadiene (Fluka, > 98% pure), (*E*,*E*)-2,4-hexadiene (Fluka, > 98%) were refluxed for ca. 1 h over CaH_2, then distilled trap-to-trap and stored under dry dinitrogen.

4.2. Polymerization

The polymerization of butadiene is a standard procedure. The monomer (17.5 g) was condensed in a 250 ml glass cylindrical reactor kept at −20°C. Toluene (100 ml) was then added and the solution was brought to +15°C, with magnetic stirring.

MAO (5.75 ml of the toluene solution, 2.5×10^{-2} mol) and [$CpTiCl_3$] (2.5×10^{-5} mol) were added in that order. The polymerization was terminated with methanol, the polymer was coagulated and repeatedly washed with a large excess of methanol, then dried *in vacuo* at room temperature. The other polymerization runs were carried out in a similar way, under the conditions indicated in Table 1.

4.3. Polymer characterization

Intrinsic viscosities were determined in toluene at 25°C using a Desreux–Bishof viscometer. ^{13}C NMR examination was performed with a Bruker AM 270 instrument. The spectra were obtained in 1,1,2,2-tetrachloroethane-d_2 at 90°C (HMDS as internal standard) or in $CDCl_3$ or C_6D_6 at room temperature (TMS as internal standard). The concentrations of the polymer solutions were about 10%. IR spectra were taken on a Perkin-Elmer 457 grating spectrophotometer using films on KBr discs. Polymer microstructure was determined as indicated in the literature [13]. Differential scanning calorimetric (DSC) measurements were made with a Mettler TA 3000 instrument and a scan speed ranging from 2 to 5 K/min. X-ray diffraction spectra were taken with a Siemens D500 diffractometer for unoriented samples.

Acknowledgements

This work has been carried out with the financial support of Consiglio Nazionale delle Ricerche, "Programma Finalizzato Chimica Fine II", and of Ministero Università e Ricerca Scientifica e Tecnologica, Rome, Italy. We thank Mr. Giulio Zannoni, Mr. Francesco Provasoli and Mr. Cesare Comitani for technical assistance.

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