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Chemoselectivity and Stereospecificity of Chromium(II) Catalysts for 1,3-Diene Polymerization

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ABSTRACT: 1,3-Butadiene, isoprene, (*E*)- and (*Z*)-1,3-pentadiene were polymerized with catalyst systems based on $CrCl_2(dmpe)_2$ and $Cr(CH_3)_2(dmpe)_2$ (dmpe = 1,2-bis(dimethylphosphino)ethane) and $Al(C_2H_5)_3$ or methylaluminoxane (MAO). The chemo- and stereoselectivity of these systems are strongly influenced by monomer structure. They give 1,2-syndiotactic polybutadiene, 3,4-amorphous polyisoprene, *cis*-1,4-isotactic poly[(*E*)-pentadiene] and *cis*-1,4-atactic poly[(*Z*)-pentadiene]. The factors influencing chemo- and stereoselectivity are discussed.

Introduction

Various types of chromium catalysts have been used for the polymerization of butadiene, eg. $AlEt_3-Cr(acac)_3$, $AlEt_3-Cr(CO)_3py_3$, $Cr(allyl)_3$, $Cr(allyl)_2Cl$, $Cr(acac)_3-$MAO.[1−6] Some of these systems give polybutadiene with a predominantly 1,2-structure; others give predominantly *cis*-polybutadiene. Isoprene has been polymerized with some Cr−allyl derivatives,[3−5] but nothing has been reported on the polymerization of other dienes.

We now have examined the polymerization of some 1,3-dienes using catalysts derived from $CrCl_2(dmpe)_2$ and $Cr(CH_3)_2(dmpe)_2$ [dmpe = 1,2-bis(dimethylphosphino)ethane] in combination with $AlEt_3$ or methylaluminoxane (MAO). These systems are active not only for the polymerization of butadiene but also for that of isoprene and (*E*)- and (*Z*)-1,3-pentadiene.

The main interest of these systems lies in the fact that they give polymers with different structure from the various monomers. The results obtained allow one to have additional information on the factors determining or influencing chemo- and stereoselectivity in diene polymerization. In addition, the catalysts of this note are highly active for the preparation of 1,2-syndiotactic polybutadiene, a polymer of some practical interest.

This note reports on the polymerization of butadiene, isoprene, and (*E*)- and (*Z*)-1,3-pentadiene with catalysts derived from $CrCl_2(dmpe)_2$ and $Cr(CH_3)_2(dmpe)_2$.

Experimental Section

Materials. $CrCl_2(THF)$,[7] $CrCl_2(dmpe)_2$,[8] and $Cr(CH_3)_2(dmpe)_2$[8] were prepared as reported in the literature. Triethylaluminum [$Al(C_2H_5)_3$] (Aldrich, 93% pure) and methylaluminoxane (MAO) (Witco, 10 wt % solution in toluene) were used without further purification. Toluene (Fluka, > 99.5% pure) was refluxed over Na for ca. 8 h and then distilled and stored over molecular sieves under dry nitrogen. 1,3-Butadiene (Air Liquide, > 99.5% pure) 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 (Aldrich, 99% pure), (*E*)-1,3-pentadiene (Aldrich, 98% pure), and (*Z*)-1,3-pentadiene (Fluka, > 98% pure) were refluxed over CaH_2 for ca. 2 h and then distilled trap-to-trap and stored under dry nitrogen.

Polymerization. All operations were carried out under an atmosphere of dry dinitrogen. A standard procedure is reported. Monomer and toluene, in the amount indicated in Tables 1 and 2, were introduced into a 25 mL dried glass reactor, and the solution so obtained was brought to the desired temperature. The aluminum alkyl and the chromium compound were then added as toluene solutions in that order. The polymerization was terminated with methanol containing a small amount of hydrochloric acid; the polymer was coagulated and repeatedly washed with methanol and then dried in vacuo at room temperature.

Polymer Characterization. Intrinsic viscosities were determined in toluene at 25 °C or in *o*-dichlorobenzene at 135 °C, using a Desreux-Bischof viscometer. ^{13}C NMR measurements were performed with a Bruker AM 270 instrument. The spectra were obtained in $CDCl_3$ at room temperature (tetramethylsilane, TMS, as internal standard) or $C_2D_2Cl_4$ at 103 °C (hexamethyldisiloxane, HMDS, as internal standard). The concentration of polymer solutions was about 10 wt %. Differential scanning calorimetry (DSC) scans were carried out on a Perkin-Elmer Pyris 1 instrument. Typically, ca. 10 mg of polymer were analyzed in each run, while the scan speed was ca. 20 K/min under a dinitrogen atmosphere. X-ray diffraction powder spectra of the polymers were recorded on an Italstructure θ/θ diffractometer. The infrared spectra were performed with a Bruker IFS 48 instrument, using polymer films on KBr disks. The films were obtained by deposition from solutions in benzene or hot (ca. 100 °C) solutions in 1,2,4-trichlorobenzene. Polymer microstructure was determined as reported in the literature.[9−16]

Results

Table 1 reports some data on the polymerization of 1,3-butadiene and isoprene.

The results can be summarized as follows:

(1) $CrCl_2(dmpe)_2-Al(C_2H_5)_3$ gives at room temperature a 1,2-syndiotactic polybutadiene (mp ca. 120 °C). A more stereoregular polymer (mp 160 °C) has been obtained using MAO instead of $AlEt_3$ as cocatalyst, as indicated by the higher intensity of the peak at 112.30 ppm (*rrrr* pentads) in the ^{13}C NMR spectrum[9−11] (Figure 1, parts a and b).

In these sytems, one bidentate phosphine is likely displaced from the metal. If we consider that the

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Table 1. Polymerization of Butadiene and Isoprene with Cr(II) Catalysts[a]

		Cr compound		Al compound					polymer microstructure,[b] %			
run	mon	type	mol × 10^5	type	Al/Cr	temp, °C	time, min	convn, %	1,2[e]	[rrrr][f]	mp,[c] °C	$[\eta]$,[d] dL g^{-1}
1	B	$CrCl_2(dmpe)_2$	2	$AlEt_3$	10	+20	22	18	95	54.4	121	
2	B	$CrCl_2(dmpe)_2$	2	$AlEt_3$	100	+20	61	21.0	95			
3	B	$CrCl_2(dmpe)_2$	1	MAO	1000	+20	22	11.7	95	59.2	151	
4	B	$CrCl_2(dmpe)_2$	1	MAO	100	+20	15	15.3	95	64.9	152	2.6
5	B	$CrMe_2(dmpe)_2$	1	MAO	100	+20	15	14.5	95			
6	B	$CrCl_2(dmpe)_2$	1	MAO	10	+20	70	11.3	95	62.1	148	
7	B	$CrCl_2(dmpe)_2$	2	MAO	100	−30	1340	9.2	97	90	198	2.8
8	B	$CrMe_2(dmpe)_2$	2	MAO	100	−30	240	49	97		196	
9	B	$CrCl_2(THF)$	3	MAO	100	+20	4020	34.7	[g]			
10	I	$CrCl_2(dmpe)_2$	3	MAO	100	+20	6000	69	90[h]			
11	I	$CrCl_2(dmpe)_2$	3	MAO	100	−30	6000	traces				

[a] Polymerization conditions: monomer, 2 mL; toluene, 16 mL. [b] Determined by NMR and IR analysis. [c] Determined by DSC. [d] Intrinsic viscosity determined in *o*-dichlorobenzene at 135 °C. [e] The remaining units are *cis*-1,4. [f] Syndiotactic pentads percentage. [g] Remaining units: 73.5%, 1,4-*cis*; 19.5%, 1,4-*trans*. [h] 3,4-units.

Table 2. Polymerization (*E*)-1,3-Pentadiene and (*Z*)-1,3-pentadiene with Cr(II) Catalysts[a]

							polymer microstructure, %	
run	monomer[b]	Cr compound	temp, °C	time, h	convn,%	$[\eta]$, [c] dL g^{-1}	*cis*-1,4	1,2
1	EP	$CrCl_2(dmpe)_2$	+20	1.5	75.6	1.1	84	16
2	EP	$CrCl_2(dmpe)_2$	−30	120	6.4	2.1	90	10
3	EP	$Cr(CH_3)_2(dmpe)_2$	−30	24	43.5	2.0	93	7
4	ZP	$CrCl_2(dmpe)_2$	+20	0.5	84.5	1.2	99	
5	ZP	$CrCl_2(dmpe)_2$	−30	122	14.3	2.0	99	
6	ZP	$Cr(CH_3)_2(dmpe)_2$	−30	24	50	1.9	99	

[a] Polymerization conditions: monomer, 1 mL; toluene, 8 mL; Cr-compound, 3 × 10^{-5} mol; MAO/Cr = 100. [b] EP, (*E*)-1,3-pentadiene; ZP, (*Z*)-1,3-pentadiene. [c] Intrinsic viscosity, determined in toluene at 25 °C.

growing chain is η^3-bonded to the Cr atom and the monomer is η^4-coordinated, only one bidentate phosphine can remain coordinated to Cr.

(2) In a polymerization run carried out at −30 °C with $CrCl_2(dmpe)_2$−MAO, a polybutadiene with a melting point of 198 °C has been obtained. This polymer is more stereoregular than those obtained at higher temperature, as indicated by the ^{13}C NMR spectrum (Figure 1c; practically only the peak at 112.30 ppm due to the *rrrr* pentads is observed) and the X-ray powder spectrum (Figure 2). The $[\eta]$ value of this polymer, determined in *o*-dichlorobenzene at 135 °C, is about 2.8 $dL\cdot g^{-1}$, close to that of the polybutadiene obtained at room temperature (2.6 $dL\cdot g^{-1}$).

(3) $CrCl_2(dmpe)_2$−MAO and $Cr(CH_3)_2(dmpe)_2$−MAO have almost the same activity in polymerizations carried out at room temperature, but the $Cr(CH_3)_2(dmpe)_2$ catalyst is more active at −30 °C. This seems to indicate that the alkylation of $CrCl_2$ is rather rapid at room temperature, while it is slower at −30 °C.

(4) The maximum activity was observed for Al/Cr molar ratio in the range 100−1000, although even catalysts obtained at a molar ratio of about 10 exhibit some activity.

(5) Isoprene polymerizes more slowly than butadiene, to give an essentially 3,4-polymer (≥90%), which was found to be amorphous by X-ray. The low stereoregularity of this polymer is indicated by the multiplicity of each carbon resonance in the ^{13}C NMR spectrum (Figure 3).

The system $CrCl_2(dmpe)_2$−MAO was also used for the polymerization of (*E*)-1,3-pentadiene and (*Z*)-1,3-pentadiene. The results, Table 2, can be summarized as follows:

(1) (*E*)-1,3-pentadiene gives polymers with a predominantly *cis*-1,4-structure (85% ca.), the remaining units being *trans*-1,2; the cis content increases with decreasing polymerization temperature (Table 2, runs 1−2). The polymers have an isotactic structure, as indicated by the ^{13}C NMR spectra[14−16] (Figure 4a).

(2) (*Z*)-1,3-pentadiene gives polymers with a very high cis content (99% ca.) either at room temperature or at −30 °C. The polymers are not crystalline and have an atactic structure as indicated by the multiplicity of each carbon resonance in the ^{13}C NMR spectra[13−15] (Figure 4b).

(3) The higher activity of $Cr(CH_3)_2(dmpe)_2$−MAO with respect to $CrCl_2(dmpe)_2$−MAO at low temperature is also observed for the polymerization of 1,3-pentadiene.

Discussion

Three of the above results are worth examining:

(1) Butadiene gives a 1,2-syndiotactic polybutadiene; (*E*)-1,3-pentadiene gives a *cis*-1,4-isotactic polymer.

(2) Isoprene gives, under the same conditions, a 3,4-polymer which is amorphous by X-ray because of insufficient stereoregularity.

(3) (*Z*)-1,3-Pentadiene gives a *cis*-1,4-atactic polymer.

With regard to point 1, analogous results have been reported for the polymerization of butadiene and (*E*)-1,3-pentadiene with $AlEt_3$−$Ti(OnBu)_4$.[17−19]

This system too, at room temperature, gives a 1,2-syndiotactic polybutadiene and a *cis*-1,4-isotactic polypentadiene. The results were interpreted assuming a *cis*-η^4-coordination for the monomer and an anti-η^3 bond between the growing polymer chain and the transition metal.[20−24] Small variations in the geometry of the catalytic complex, due to the presence of the methyls in the monomer and the allyl group, may cause reaction of the incoming monomer at C1 of the allyl group, with formation of a *cis*-1,4-unit, or at C3, with formation of a 1,2-unit. We believe that the schemes previously reported are also valid for the Cr catalysts of this work.

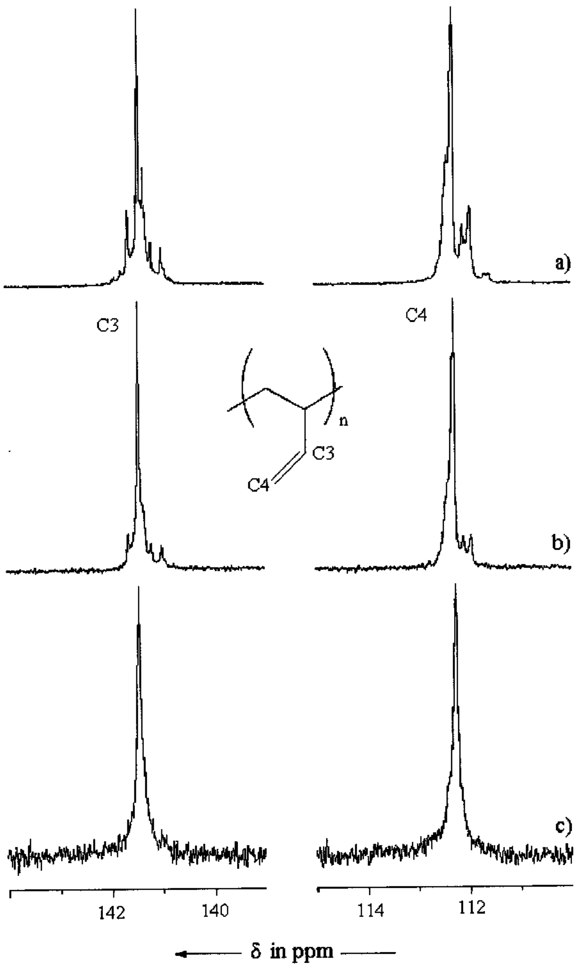

Figure 1. 67 MHz ^{13}C NMR spectra (olefinic region): (a) polybutadiene obtained with $CrCl_2(dmpe)_2/Al(C_2H_5)_3$ (Table 1, run 1); (b) polybutadiene obtained with $CrCl_2(dmpe)_2$/MAO at +20 °C (Table 1, run 4); (c) polybutadiene obtained with $CrCl_2(dmpe)_2$/ MAO at −30 °C (Table 1, run 7) [$C_2D_2Cl_4$, 103 °C, HMDS as internal standard].

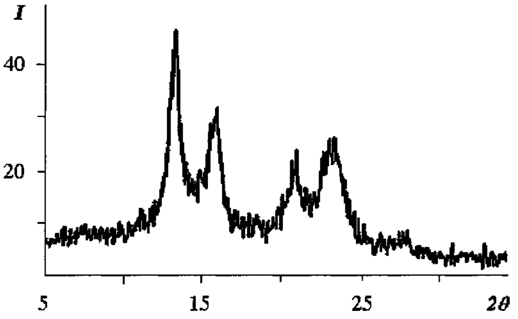

Figure 2. X-ray powder spectra of polybutadiene obtained with $CrCl_2(dmpe)_2$/ MAO at −30 °C (Table 1, run 7).

3,4-Polyisoprene is formed in the same way as 1,2-polybutadiene, that is by reaction of the new monomer to C3 of the last-inserted unit. The lack of stereoregularity of polyisoprene is likely due to the stronger steric interaction between the new monomer and the allylic group, because of the methyl group. The steric interaction may favor the formation of an *exo*−*endo* situation, in addition to the *exo*−*exo* one.

While the *exo*−*exo* arrangement leads to a 3,4-syndiotactic diad, the *endo*−*exo* one leads to an isotactic diad (Figure 5).

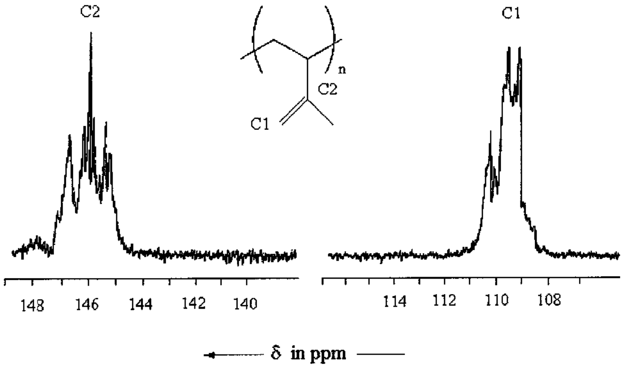

Figure 3. 67 MHz ^{13}C NMR spectrum (olefinic region) of the polyisoprene obtained with $CrCl_2(dmpe)_2$/MAO system (Table 1, run 10) [$C_2D_2Cl_4$, 103 °C, HMDS as internal standard]

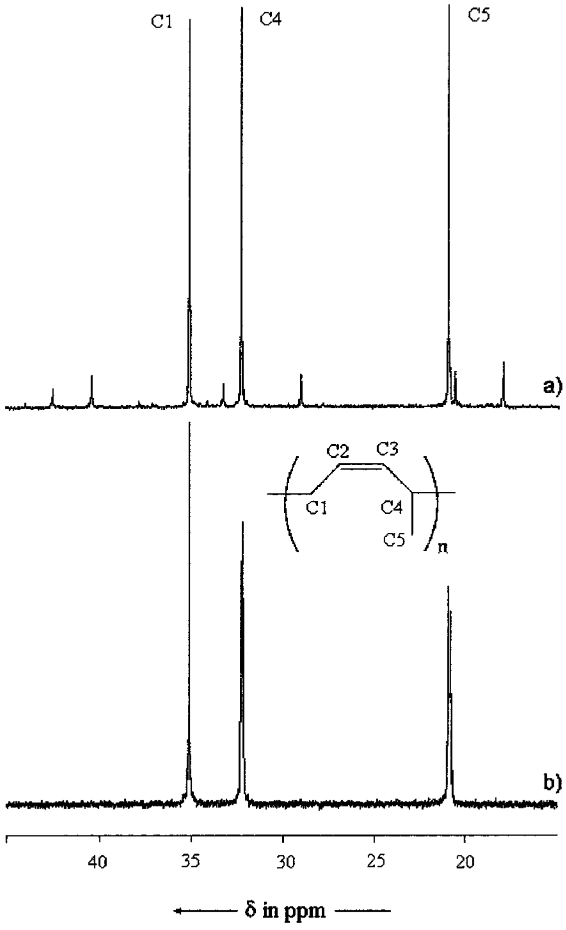

Figure 4. 67 MHz ^{13}C NMR spectra (aliphatic region) of (a) poly[(*E*)-1,3-pentadiene] (Table 2, run 2) and (b) poly[(*Z*)-1,3-pentadiene] (Table 2, run 5) obtained with $CrCl_2(dmpe)_2$/MAO system at −30 °C.

This interpretation is in agreement with the ^{13}C NMR spectrum of polyisoprene, which shows a high multiplicity for each carbon resonance (Figure 3).

The case of (*Z*)-1,3-pentadiene is rather intriguing. Poly[(*Z*)-1,3-pentadiene]) consists essentially of *cis*-1,4-units (ca. 99%). However, according to the ^{13}C NMR spectrum (Figure 4b), it has a rather irregular structure. Our interpretation is that also in this case, for steric reasons, an *exo*−*endo* situation may occasionally form during polymerization, causing steric errors along the chain.

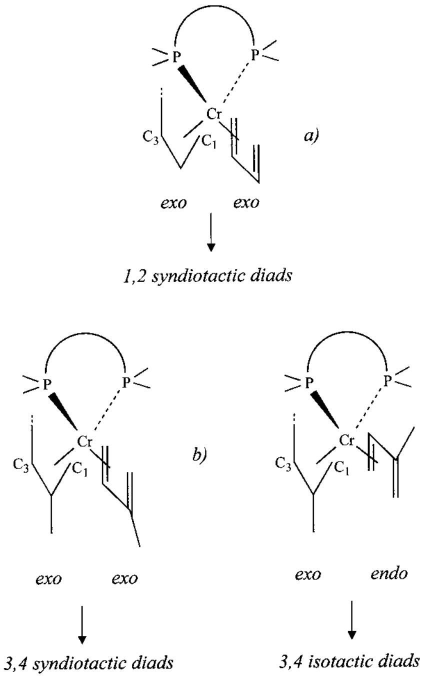

Figure 5. Scheme for formation of syndiotactic and isotactic diads in the polymerization of (a) butadiene and (b) isoprene.

Conclusions

$CrCl_2(dmpe)_2$/MAO and $Cr(CH_3)_2(dmpe)_2$−MAO give a crystalline 1,2-syndiotactic polybutadiene. The stereoregularity seems to be slightly dependent on the polymerization temperature, being higher at low temperature. The polyisoprene obtained under the same conditions, although predominantly 3,4, is not stereoregular and hence is not crystalline.

(*E*)-1,3-Pentadiene and (*Z*)-1,3-pentadiene give predominantly *cis*-1,4-polymers. The formation of 1,2-syndiotactic polybutadiene and a *cis*-1,4-isopoly(*E*)-pentadiene had already been observed with the system $Ti(OnBu)_4$−$AlEt_3$.

A case worth of attention is that of (*Z*)-1,3-pentadiene. With $CpTiCl_3$−MAO, (*Z*)-1,3-pentadiene gives a predominanatly cis polymer at +20 °C, and a 1,2-syndiotactic polymer at −20 °C.[25] The Cr(II) catalyst of this note gives cis polymers either at +20 or at −30 °C. It is difficult to give an interpretation of this different behavior, which is likely related to the different coordination geometry and steric situation around the Ti and Cr catalytic species. The results with the catalysts of this note confirm that chemo- and stereoselectivity in diene polymerization is influenced or affected by factors that have not been yet fully clarified. More experimental data are necessary to arrive at a better understanding of these phenomena.

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