

Cationic Copolymerization of Isobutene with *trans*, *trans*-, *trans*, *cis*-, or *cis*, *cis*-2,4-Hexadiene and Structural Characterization of the Product Copolymers

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SUMMARY

The cationic copolymerization of isobutene (I) with the three geometric isomers of 2,4-hexadiene (H) was carried out homogeneously at -70°C with EtAlCl_2 as catalyst. The structure of the copolymers was studied mainly by ^{13}C -NMR and the diene structural units exhibited the *trans*-configuration. From the calculation of some monomer sequence fractions, the following reactivity ratios were obtained: $r_{\text{I}} = 0.74$, $r_{\text{ctH}} = 1.8$; $r_{\text{I}} = 2.3$, $r_{\text{cCH}} = 1.5$; $r_{\text{I}} = 6.0$, $r_{\text{ttH}} = 0.88$.

INTRODUCTION

In the plan of systematic investigations on the cationic copolymerization of isobutene (I) with conjugated dienes, begun upon the system I-butadiene (CORNO et al., 1979), we reported recently on cationic copolymers of I with 2,3-dimethyl-butadiene (CORNO et al., 1982). Pursuing our work, we have studied the cationic copolymerization of I with the three geometric isomers of 2,4-hexadiene (H). They are an interesting example of a conjugated diene system containing two methyl groups in 1,4-position, whose influence on the reactivity of the diene system can be usefully studied.

This interest arose in a previous work concerning the copolymerization of I with 2,4,6-octatriene (OT) (PRIOLA et al.) since a block-type copolymer was obtained. The analogy of H and OT is evident as far as the steric hindrance of substituting methyl groups in the monomeric units is concerned. Therefore, the aim of the present work is the elucidation of the structure of the resulting I-H copolymers, the computation of the monomer sequences in order to calculate, according to a procedure already described (CORNO et al. 1977), the reactivity ratios of I and the three geometric isomers of H, i.e. *trans*, *trans*-, *trans*, *cis*- and *cis*, *cis*-2,4-hexadiene (ttH, tCH, cCH).

The relative reactivity of ttH, tCH and cCH in the presence of cationic catalysts was previously reported (KAMACHI et al.).

EXPERIMENTAL PART

Isobutene, solvents and catalyst were purified and employed as previously reported (CORNO et al., 1979).

The different H isomers were commercial products with the following GC purity: ttH (Fluka) > 98%; tcH (Fluka) > 98%; ccH (K & K) > 95%. They were dried over CaH₂, distilled in vacuo and stored under dry nitrogen at 0°C.

The copolymerization runs were carried out as reported elsewhere (CORNO et al., 1979). Further details concerning the experimental conditions are described in Tab. I. The copolymer solutions were coagulated twice with an excess of methanol and dried in vacuo overnight at room temperature. The copolymer homogeneity was tested by GPC analysis which showed symmetric, monomodal distribution curves. Also the results of DTA analysis were in agreement with this conclusion because a single T_g was observed. Its value varied by changing the copolymer composition (Tab. I).

The analytical methods adopted were described in previous papers (CORNO et al., 1979, 1982). ¹H- and ¹³C-NMR spectra were obtained as reported elsewhere (CORNO et al. 1980).

RESULTS AND DISCUSSION

1. Copolymerization of I with different H isomers

Tab. I shows the difference of reactivity exhibited by ttH, tcH and ccH when they are copolymerized with I under the same conditions. The order of reactivity, deducible from the copolymer composition, is ctH > ccH > ttH in agreement with the results obtained by KAMACHI et al. on the copolymerization of the H isomers only. The data of Tab. I, associated with the monomer sequence fractions, have been used for calculating the reactivity ratios of the monomers involved (cf. par. 3). According to Tab. I the intrinsic viscosity of the copolymers obtained is relatively low, while the T_g value increases when the content of diene in the copolymer increases; this result agrees with a substantially random distribution of the monomeric units, which has been confirmed by the structural characterization of the resulting polymers.

2. Structural characterization of I-H copolymers

The three isomers of H give rise to structural units having the same 2,5-trans enchainment when they are polymerized with cationic catalysts. It has been proposed that the same chain carrier arises from the different geometric isomers of H in the presence of the same catalyst (KAMACHI et al.). Also the copolymers of I with the H isomers exhibit the same spectroscopic features of the homopolymers and hence we will discuss in detail the structure of a typical I-ctH copolymer.

TABLE I: CATIONIC COPOLYMERIZATION OF I WITH DIFFERENT H ISOMERS ^{a)}

Run N°	Isomer [EtAlCl ₂] (mmol/l)	Feed (mole fract. of I)	Convers. (%)	Composit. (mole fract. of I) ^{b)}	c) $[\eta]$ (dl/g)	T _g ^{d)} (°C)
1	tt	12	0.65	22	0.85	-47
2	"	14	0.57	16	0.85	-48
3	ct	10	0.65	22	0.61	-23
4	"	16	0.63	58	0.65	-33
5	"	12	0.50	37	0.40	-12
6	cc	23	0.65	42	0.71	--

a) Experimental conditions: solvent=n-pentane+CH₂Cl₂ (1/1, v/v); I+H =2.0 mol/l; T= -70°C; time=20 min.

b) Determined by ¹H-NMR. c) Determined in cyclohexane at 25°C.

d) Determined by DTA analysis.

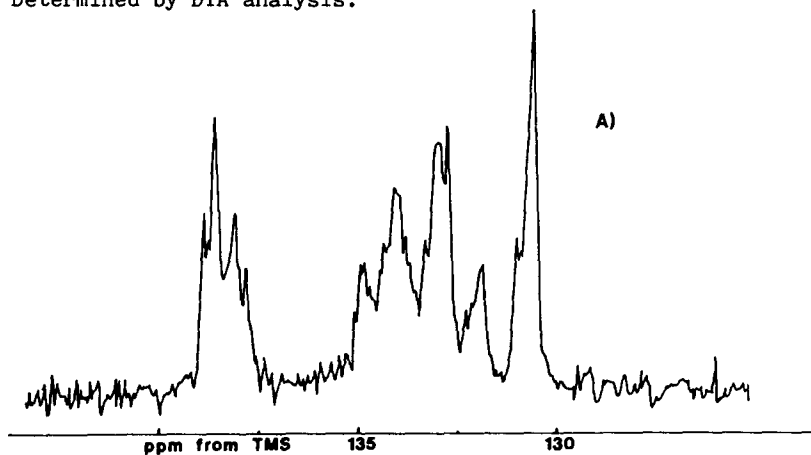
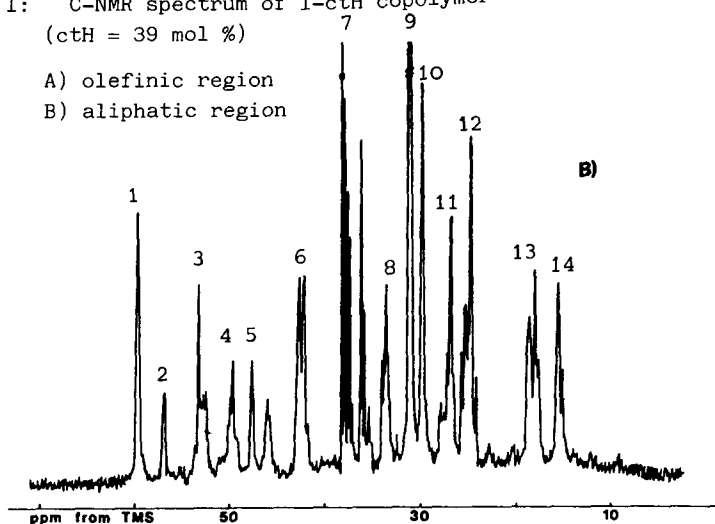


Fig. 1: ¹³C-NMR spectrum of I-ctH copolymer (ctH = 39 mol %)

A) olefinic region

B) aliphatic region



The ^1H -NMR spectrum of the copolymer confirms the 2,5-trans enchainment of the diene. In fact, only a weak signal (at 1.6 ppm from TMS) was observed in samples containing a high amount of H and was assigned to a methyl in α -position to a double bond. It reveals a modest amount of 2,3-units which can be estimated about 10-15% of the total diene content.

Therefore, the ^{13}C -NMR spectrum (Fig. 1) can be interpreted on the basis of the prevalent 2,5-trans structural unit. The presence of a relevant number of signals in Fig. 1 suggests that the monomer distribution is very different from that observed in the I-OT copolymer (PRIOLA et al.).

The interpretation of the spectrum of Fig. 1 was not complete because of the partial overlapping of some signals and the complex situation introduced by the possibility of erythro and threo configuration arising from two vicinal methyls in the H-H dyad. However, useful information on the monomer distribution can be obtained by analysis of the ^{13}C -NMR spectrum.

The olefinic region of the spectrum (Fig. 1A) appears rather complex. In order to carry out its interpretation we denote as $\text{C}_{(1)}$ and $\text{C}_{(2)}$ the unsaturated carbons of the H units, i.e. $-\text{CH}(\text{CH}_3)-\text{C}_{(1)}=\text{C}_{(2)}-\text{H}-\text{CH}(\text{CH}_3)-$, while the I units arise from the head-to-tail addition, i.e. $-\text{CH}_2-\text{C}(\text{CH}_3)=$ (CORNO et al. 1980).

The assignments were carried out following the method adopted for previous copolymers (CORNO et al. 1979, 1980). The resonance of $\text{C}_{(1)}$ and $\text{C}_{(2)}$ in the HHH triad occurs at 134.05 and 132.98 ppm from TMS. The doublet character of the resonance stems from the reciprocal orientation, erythro or threo, of the methyl groups.

The substitution of the neighboring diene units with I units, induces a downfield shift of the $\text{C}_{(2)}$ resonance while that of $\text{C}_{(1)}$ is shifted upfield.

Therefore, the external signals at 138.62 and 130.52 ppm, are certainly attributable to $-\text{C}_{(2)}\text{H}=\text{}$ and $-\text{C}_{(1)}\text{H}=\text{}$, respectively, in the triad IHI. The signal of $-\text{C}_{(2)}\text{H}=\text{}$ in the triad HHI and that of $-\text{C}_{(1)}\text{H}=\text{}$ in the triad IHH will add, respectively, to the resonances mentioned above.

The residual signals of the triads are present in the range between 136 and 131 ppm. However, the fine structure of the entire olefinic region has not been elucidated because of the overlapping of triad signals, long range effects (signals of pentads) observed in previous works (CORNO et al., 1980) and configuration effects arising from the reciprocal orientation of vicinal methyls.

Also the aliphatic region of the ^{13}C -NMR spectrum (Fig. 1B) shows overlapping of signals. However, the assignments of carbons belonging to CH_3 , CH_2 and CH groups are listed in Tab. II.

TABLE II: ^{13}C -NMR CHEMICAL SHIFTS (ppm) OF THE I-H COPOLYMER: ALIPHATIC REGION.

CARBON	STRUCTURE	SEQUENCE	PEAK	CHEMICAL SHIFT
CH_2	$-\text{C}-\underset{ }{\overset{ }{\text{C}}}-\text{C}-\underset{ }{\overset{ }{\text{C}}}-\overset{*}{\underset{ }{\text{C}}}-\underset{ }{\overset{ }{\text{C}}}-\text{C}-\underset{ }{\overset{ }{\text{C}}}-$	IIII	1	59.6
	$=\text{C}-\underset{ }{\overset{ }{\text{C}}}-\text{C}-\underset{ }{\overset{ }{\text{C}}}-\overset{*}{\underset{ }{\text{C}}}-\underset{ }{\overset{ }{\text{C}}}-\text{C}-\underset{ }{\overset{ }{\text{C}}}-$	HIII	2	56.8
	$-\text{C}-\underset{ }{\overset{ }{\text{C}}}-\text{C}-\underset{ }{\overset{ }{\text{C}}}-\overset{*}{\underset{ }{\text{C}}}-\underset{ }{\overset{ }{\text{C}}}-\text{C}=\text{C}-$	IIIH	3	53.2
	$=\text{C}-\underset{ }{\overset{ }{\text{C}}}-\text{C}-\underset{ }{\overset{ }{\text{C}}}-\overset{*}{\underset{ }{\text{C}}}-\underset{ }{\overset{ }{\text{C}}}-\text{C}=\text{C}-$	HIIH	4	49.6
	$-\text{C}-\text{C}=\text{C}-\underset{ }{\overset{ }{\text{C}}}-\overset{*}{\underset{ }{\text{C}}}-\underset{ }{\overset{ }{\text{C}}}-\text{C}-\underset{ }{\overset{ }{\text{C}}}-$	>HII	3	53.2
	$-\text{C}-\text{C}=\text{C}-\underset{ }{\overset{ }{\text{C}}}-\overset{*}{\underset{ }{\text{C}}}-\underset{ }{\overset{ }{\text{C}}}-\text{C}=\text{C}-$	>HIH	5	47.6
CH	$-\text{C}-\underset{ }{\overset{ }{\text{C}}}-\text{C}-\underset{ }{\overset{ }{\text{C}}}-\overset{*}{\underset{ }{\text{C}}}=\text{C}=\text{C}-\underset{ }{\overset{ }{\text{C}}}-$	IIH<	4	49.6
	$=\text{C}-\underset{ }{\overset{ }{\text{C}}}-\text{C}-\underset{ }{\overset{ }{\text{C}}}-\overset{*}{\underset{ }{\text{C}}}=\text{C}=\text{C}-\underset{ }{\overset{ }{\text{C}}}-$	HIH<	6	46.0
	$-\text{C}-\text{C}=\text{C}-\underset{ }{\overset{ }{\text{C}}}-\overset{*}{\underset{ }{\text{C}}}=\text{C}=\text{C}-\underset{ }{\overset{ }{\text{C}}}-$	>HH<	7	42.7-42.1
	$-\text{C}-\text{C}=\text{C}-\underset{ }{\overset{ }{\text{C}}}-\overset{*}{\underset{ }{\text{C}}}-\underset{ }{\overset{ }{\text{C}}}-$	>HI<	8	33.6
CH_3 (I)		III	9	31.3
		HII	10	29.9
		IIH	11	26.8
		HIH	12	24.8
CH_3 (H)		HI	12	24.8
		HH	13	18.6-18.1
		IH	14	15.7

TABLE III: TRIAD AND TETRAD FRACTIONS IN I-H COPOLYMERS

Sample ^{a)}	1	2	3	4	5	6
III	0.791	0.741	0.366	0.462	0.194	0.609
IIH + HII	0.168	0.202	0.432	0.380	0.415	0.290
HIH	0.041	0.057	0.202	0.158	0.391	0.101
IIII	0.636	0.554	0.132	0.225	0.041	0.375
IIIH + HIII	0.106	0.114	0.144	0.142	0.072	0.140
HIIH	0.001	0.001	0.033	0.002	0.051	0.005
IIHI+IHII+	0.130	0.158	0.266	0.292	0.174	0.220
HHII+HHII						
IHHI+HHHI+	0.057	0.087	0.213	0.155	0.392	0.121
IHHH+HHHH						
IHIH+HHIH+	0.070	0.086	0.212	0.184	0.270	0.139

a) The samples are described in Tab. I.

Conversely, the assignments of the quaternary carbon of I have not been attributed, since the observed complex situation has not yet been elucidated.

The principle adopted for the assignments is based on the additive contributions of the gem-dimethyl group.

Furthermore, other assignments have been adopted by comparison with the spectrum of I-trans-1,3-pentadiene (I-tP) copolymer (CORNO et al., 1980) which clearly shows analogies with the copolymer under discussion. In particular, the peaks n° 1,2,8 and part of signals n° 3, relative to the sequence >HII (the symbol > denotes the possibility of unit H or I) have been attributed to the same carbon atoms in the previous work on I-tP. For the peak n° 3 (53.2 ppm), n° 5 (47.6) and for that part of the peak n° 4 relative to the HIIH sequence (49.6), an additional negative γ effect has to be taken into account with respect to the resonance of the analogous carbons of I-tP.

In fact, in that work we observed the corresponding signals at 55.90, 49.42 and 53.44 ppm, and this implies a shift of about 2.5 ppm, typical of a γ effect.

The assignment of the peak n° 7, split for the two possible orientations of the vic-methyls, can be obtained directly by comparison with the spectrum of poly-H prepared by us under the same conditions as I-H copolymers. By referring to this resonance, there is a downfield shift for the signal of the HIH< tetrad (peak n° 6), due to the presence of a second methyl in β position and another shift, along the same direction, for the IIH< tetrad (part of the peak n° 4) due to the presence of a gem-dimethyl group in δ position, occurring after an identical group situated in β position.

The value of this δ_β effect, as observed previously (CORNO et al. 1979, 1980) is about 3-3.5 ppm.

For the assignment of the peaks of methyls, the frequencies of the triad III and HII can be obtained directly by comparison with the spectra of I-tP.

The signal of the triad IIH is shifted upfield about 2.5 ppm with respect to the resonance of the triad IIP in the I-tP copolymer, because of the presence of a γ effect.

A higher upfield shift concerns the signal of the HIH triad which, however, is overlapped by the signal of the methyls belonging to H in the dyad HI. The peaks of the methyl group of the dyad HH occur at 18.7 and 18.0 ppm. The downfield shift for the dyad HI is due to the lack of a γ effect while a δ effect of the gem-dimethyl group is operating. Conversely, the upfield shift for the dyad IH is attributable to the presence of a second methyl in γ position.

3. Determination of the reactivity ratios from monomer sequence distribution

By referring to the signals of different monomer sequences in the ^{13}C -NMR spectra of I-H copolymers discussed in par. 2, it is possible to calculate the fractions of some sequences. Despite the overlapping of some signals, discussed previously, we succeeded in obtaining complete sets of values pertaining to the fractions of triads centered on I and the fractions of the tetrads. These values are listed in Tab. III for the copolymers samples reported in Tab. I, concerning the three geometric isomers of H.

The procedure adopted for the calculation of the reactivity ratios was described in a previous paper (CORNO et al., 1977) and it has been used for the study of other I-conjugated diene copolymers. Further details, not yet published, are described in a forthcoming paper (CORNO et al., 1982b) as far as the confidence interval of the reactivity ratio is concerned. The method of calculation allows to obtain r_1 and r_2 values also when only one copolymer sample is available and whatever the monomer conversion involved may be. This is the case of I-cCH copolymer in the present paper. However, it is evident that the joint confidence interval of the reactivity ratios will be narrower when the type and number of sequence fractions is larger. This is not the case of I-H copolymers since we did not succeed in calculating the fractions of triads centered on H. The following set of values have been obtained:

$$\begin{array}{ll} r_I = 0.74 \pm 0.15 & r_{ctH} = 1.8 \pm 0.59 \\ r_I = 2.3 \pm 0.46 & r_{cCH} = 1.5 \pm 0.89 \\ r_I = 6.0 \pm 1.39 & r_{ttH} = 0.88 \pm 0.78 \end{array}$$

where the joint confidence interval is at 68%, i.e. the standard deviation in the approximation of the normal distribution.

The values of the reactivity ratios obtained in this work agree with the order of reactivity found by KAMACHI et al. and suggest a tendency of the monomers studied to arrange according to a block-type structure since, in every case, $r_1 \cdot r_2 > 1$. However, the situation is distant from that observed for the couple I-OT, because this copolymer showed an enhanced block-type character.

CONCLUSIONS

The ^{13}C -NMR characterization of ttH-, tcH- and cCH-I copolymers has permitted the calculation of the reactivity ratios of the three pairs of monomers. The cationic reactivity of the H isomers, relative to I, was found to be significantly different according to the same order, i.e. $ctH > cCH > ttH$, observed in the copolymerization of only the geometric isomers of the diene (KAMACHI et al.). In particular ctH is more reactive than

2,3-dimethyl-butadiene (CORNO et al., 1982) in the copolymerization with I and this conclusion disagrees with some indications (HASEGAWA et al.) inferred from the behaviour of only tH. Therefore, the influence of the geometric configuration of the different isomer of H is of greater importance in some cases than the influence of the position of the substituting methyl group. Finally, the small tendency of H isomers to give rise to block-type copolymers with I, permits to rule out steric hindrance as the most important factor in determining the blockiness of I-OT copolymer.

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