Macromolecules 1981, *14*, 475–478

Acknowledgment. This work was supported by the National Institutes of Health under Grant GM 18595, for which the authors are grateful.

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Cationic Copolymers of Isobutylene. 5. Copolymerization of Isobutylene and *cis*-1,3-Pentadiene

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ABSTRACT: The structure of cationic isobutylene (I)–*cis*-1,3-pentadiene (cP) copolymer was investigated by means of ^{13}C NMR spectroscopy. The diene was present in the copolymer chains mainly as trans-1,4 units, but cis-1,2, trans-1,2, trans-4,1, and trans-4,3 units were also observed. The attack at position 4 of cP occurred by sterically unhindered carbenium ions arising from cP and not from I. The isomerization of cP to *trans*-1,3-pentadiene was ascertained to occur under mild conditions in the presence of $BF_3{\cdot}OEt_2$. The evaluation of the fractions of triads centered on I was found to be in fair agreement with the calculated random distribution of the monomer units.

Introduction

In previous work we studied the structure and the monomer distribution in isobutylene–*trans*-1,3-pentadiene (I–tP) copolymers by means of ^{13}C NMR spectroscopy.[1] *cis*-1,3-Pentadiene (cP) is less reactive than the trans isomer in both the cationic homopolymerization and copolymerization with isobutylene.[2,3] This minor reactivity is accompanied by a major complexity of the copolymerization and of the structural features of the resulting copolymer. These aspects are investigated in the present paper.

Experimental Section

Materials. Reagents and solvents, i.e., isobutylene, $C_2H_5AlCl_2$, *n*-pentane, and CH_2Cl_2, were obtained and handled as described previously.[1a,3] $BF_3{\cdot}OEt_2$ (Fluka AG) was distilled under vacuum before use and stored under a dry nitrogen atmosphere. *cis*-1,3-Pentadiene (Fluka AG) was purified by distillation under an inert atmosphere and stored at 0 °C (VPC purity >99%, the remaining main components being cyclopentene (0.5%) and *trans*-1,3-pentadiene (0.3%)).

Procedure. The copolymerization procedure previously described for I–tP copolymer[1a] was adopted. Typical copolymerizations were carried out under the following conditions: -70 °C, $[I] = 1.5$ mol/L, $[cP]/[I] = 1.14$ mole ratio, $[C_2H_5AlCl_2] = 0.050$ mol/L, solvent 1:1 *n*-pentane–CH_2Cl_2 mixture (by volume), time 30 min, conversion 21%. The cP content of the resulting copolymer was 29 mol%; $[\eta] = 0.13$ dL/g (in cyclohexane, 30 °C).

Some GPC experiments carried out as previously reported[4] yielded broad, symmetric monomodal distribution curves. Homopolymerizations and cis–trans isomerization experiments with cP were performed under conditions similar to those of the copolymerizations. The diene, dissolved in the *n*-pentane–CH_2Cl_2 mixture and kept at -70 °C, was contacted with catalyst for different time periods. Samples withdrawn from the reactor were treated with CH_3OH and analyzed by VPC (column: 20% β,β'-oxobis(propionitrile), 5 m, $T = 50$ °C, carrier He, 60 cm^3/min) for the relative concentration of cis and trans isomer. At the end of each experiment, the solution was poured into methanol to precipitate any formed polymer.

Analyses. ^{1}H and ^{13}C NMR spectra were obtained at 25 °C in $CDCl_3$ with a Varian XL-100 spectrometer as described previously.[1a] Selective-decoupling experiments were carried out as reported elsewhere.[1a] The copolymer composition was evaluated by ^{1}H NMR measurements. IR spectra were obtained with a Perkin-Elmer Model 225 instrument.

Results and Discussion

I–cP Copolymer and cP Homopolymer. Figure 1 shows the ^{13}C NMR spectrum of I–cP copolymer containing 29 mol % cP. All the signals observed previously in the spectrum of I–tP copolymer are also present in Figure 1. They were assigned in previous work[1a] and comprise almost all the signals having stronger intensity.

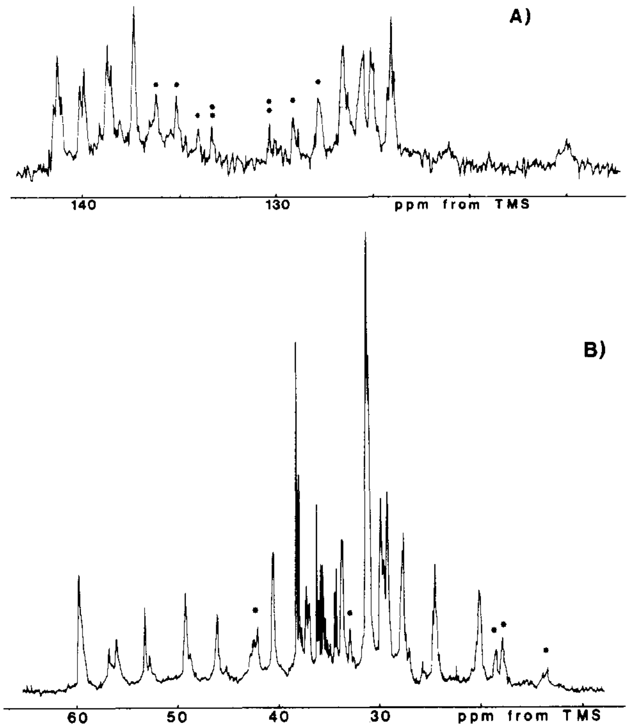


Figure 1. ^{13}C NMR spectrum of a typical cationic I–cP copolymer: (A) olefinic region; (B) aliphatic region.

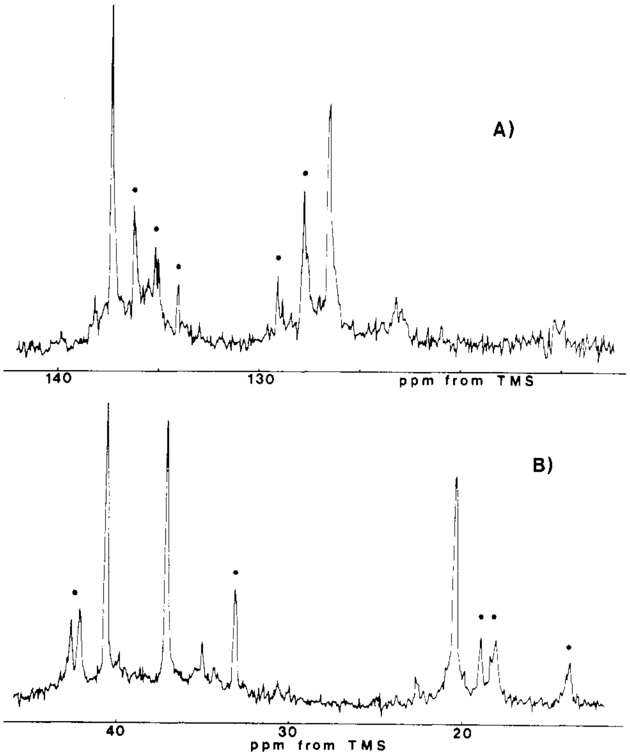


Figure 2. ^{13}C NMR spectrum of a cationic poly-cP: (A) olefinic region; (B) aliphatic region.

This fact suggests that the main arrangement of cP in I–cP copolymers is trans-1,4. However, other signals clearly indicate the presence of structural units different from those identified in I–tP copolymers. These signals are denoted by one or two asterisks in Figure 1.

We consider first the peaks marked with one asterisk. They are also present, even though they are not the main signals, in the spectrum of the cationic homopolymer of cP (Figure 2; corresponding peaks also indicated by an asterisk), prepared under the same conditions as the I–cP copolymer.

Table I lists the assignments of the peaks present in Figure 2. These assignments are based on reported chemical shifts of alkenes[5] and poly(1,3-pentadienes) obtained with *n*-butyllithium catalyst.[6] According to the assignments, poly-cP contains irregular head-to-head and tail-to-tail arrangements of the monomer, i.e., trans-4,1 units ($\overleftarrow{\mathrm{P}}$), besides the "normal" trans-1,4 unit ($\overrightarrow{\mathrm{P}}$). The signals due to the irregular arrangements are those marked by just one asterisk in the spectra of Figures 1 and 2. That means that I–cP copolymer contains a pentadiene sequence where the diene has the trans-4,1 configuration. Furthermore, the spectrum of Figure 2 shows two peaks at 13.35 and 17.96 ppm attributable to methyls belonging to cis-1,2 and trans-1,2 units, respectively. The origin of the trans-1,2 unit in both poly-cP and I–cP will be discussed in the next section. Finally, a weak signal present in the region of unsaturated carbons at 115.90 ppm is assigned to a vinyl CH_2═, which indicates the presence of a small quantity of 4,3 or 3,4 units.[7] The presence of vinyl groups in poly-cP was previously established by means of IR investigations.[3]

The signals marked by two asterisks in the spectrum of I-cP copolymer, which are absent in the spectrum of poly-cP, indicate that trans-4,1 P units are joined to isobutylene units. Two dyads are to be considered, i.e., I$\overleftarrow{\mathrm{P}}$ and $\overleftarrow{\mathrm{P}}$I. Actually, appreciable amounts of I$\overleftarrow{\mathrm{P}}$ dyad are not present, because no peak is observed in the region around 15 ppm where the signal of methyl belonging to pentadiene of this dyad is expected. Conversely, the analysis of the olefinic region of the spectrum indicates the presence of the dyad $\overleftarrow{\mathrm{P}}$I. In fact, the two peaks of the

Table I
^{13}C NMR Chemical Shifts in Cationic Poly-cP

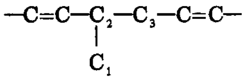
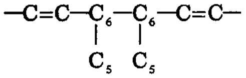
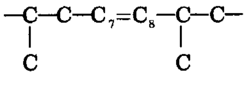
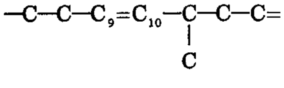
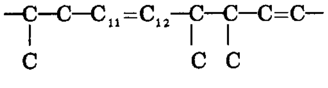
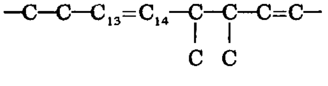
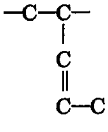
structural unit	atom	sequence	chemical shift
 $-C{=}C{-}\underset{\substack{\vert\\ C_1}}{C_2}{-}C_3{-}C{=}C-$	C_1 C_2 C_3	$\overrightarrow{\mathrm{P}}\,\overrightarrow{\mathrm{P}}$	20.04 36.89 40.28
$-C{=}C{-}C_4{-}C_4{-}C{=}C-$	C_4	$\overleftarrow{\mathrm{P}}\,\overrightarrow{\mathrm{P}}$	32.91
 $-C{=}C{-}\underset{\substack{\vert\\ C_5}}{C_6}{-}\underset{\substack{\vert\\ C_5}}{C_6}{-}C{=}C-$	C_5 m C_5 r C_6 m C_6 r	$\overrightarrow{\mathrm{P}}\,\overleftarrow{\mathrm{P}}$	17.69 18.42 41.96 42.47
 $-\underset{\substack{\vert\\ C}}{C}{-}C{-}C_7{=}C_8{-}\underset{\substack{\vert\\ C}}{C}{-}C-$	C_7 C_8	$\overrightarrow{\mathrm{P}}\,\overrightarrow{\mathrm{P}}\,\overrightarrow{\mathrm{P}}$	126.58 137.34
 $-C{-}C{-}C_9{=}C_{10}{-}\underset{\substack{\vert\\ C}}{C}{-}C{-}C{=}$	C_9 C_{10}	$\overleftarrow{\mathrm{P}}\,\overrightarrow{\mathrm{P}}\,\overrightarrow{\mathrm{P}}$	127.93 136.33
 $-\underset{\substack{\vert\\ C}}{C}{-}C{-}C_{11}{=}C_{12}{-}\underset{\substack{\vert\\ C}}{C}{-}\underset{\substack{\vert\\ C}}{C}{-}C{=}C-$	C_{11} C_{12}	$\overrightarrow{\mathrm{P}}\,\overrightarrow{\mathrm{P}}\,\overleftarrow{\mathrm{P}}$	127.93 135.29
 $-C{-}C{-}C_{13}{=}C_{14}{-}\underset{\substack{\vert\\ C}}{C}{-}\underset{\substack{\vert\\ C}}{C}{-}C{=}C-$	C_{13} C_{14}	$\overleftarrow{\mathrm{P}}\,\overrightarrow{\mathrm{P}}\,\overleftarrow{\mathrm{P}}$	129.23 134.17
 $-C{-}\underset{\substack{\vert\\ C\\ \Vert\\ C-C_{15}}}{C}-$	C_{15} cis C_{15} trans		13.35 17.96

Table II
Cis–Trans Isomerization Studies on cP and Poly-cP[a]

substrate	catalyst type	catalyst mmol	% tP[b]
cP	$EtAlCl_2$	0.1	*c*
cP	Et_2AlCl	1.0	*c*
cP	Et_2AlCl	0.2	0[d]
cP	$BF_3 \cdot OEt_2$	1.0	11[e]
cP	$BF_3 \cdot OEt_2$	2.5	21[e]
cP	$BF_3 \cdot OEt_2$	5.0	42[e]
poly-cP	$EtAlCl_2$	1.0	*f*
poly-cP	$BF_3 \cdot OEt_2$	2.5	*g*

[a] Conditions: 0.68 g of cP or 1.0 g of poly-cP in 10 mL of solvent (1:1 *n*-pentane + CH_2Cl_2 (v/v)), $T = -70$ °C, time 2 h. [b] Percent area of tP with respect to cP + tP by VPC analysis. [c] Complete polymerization. [d] Partial polymerization (about 20% conversion). [e] Mean value of two experiments. No polymer could be coagulated in methanol. [f] Insoluble product. Cis-1,2 units are still present (IR analysis). [g] No polymer modification (^{13}C NMR analysis).

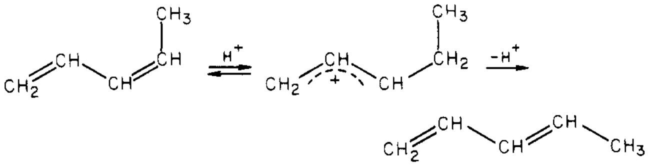
olefinic region denoted by two asterisks occur between the two resonances of the triad $\vec{P}\vec{P}\vec{P}$ and this fact agrees with their assignment to the unsaturated carbons of the irregular $\overleftarrow{P}$I dyad. This conclusion can be derived by calculating the chemical shifts of the two unsaturated carbons influenced by the *gem*-dimethyl group (γ and δ' are negative and γ' and δ are positive[1]). Due to the 4,1-addition the resonance of the unsaturated carbon linked to the methylene group is hence shifted downfield and the resonance of the second unsaturated carbon is shifted upfield.

Finally, the spectrum of I–cP copolymer shows the peaks at 13.35 and 115.90 ppm already observed in poly-cP, assigned to the methyl of the cis-1,2 unit and to the vinyl of CH_2= of the 4,3 units, respectively. These peaks are weak but clearly identifiable because they occur in regions not crowded by other signals. The peak of the methyl belonging to the trans-1,2 unit, which is partly overlapped by other signals and which is already very weak in poly-cP, can be observed only in I–cP copolymer samples containing a high amount of diene, e.g., 50 mol %.

Cis–Trans Isomerization of cP. The spectra of both the cationic I–cP copolymer (containing a very high level of diene) and the cP homopolymer show between 17 and 19 ppm the methyl resonance arising from the trans-1,2 unit (see previous section). The assignments of the peak occurring at 17.96 ppm to the methyl of the trans-1,2 units and the other two peaks to the methyls of the $\vec{P}\overleftarrow{P}$ dyad are based on selective-decoupling experiments. Irradiation at 89 and 162 Hz from Me_4Si confirms that the peak at 17.96 ppm is due to a methyl present in the α position to a double bond and hence belongs to the 1,2 unit, whereas the other two signals are due to the methyls of the dyad $\vec{P}\overleftarrow{P}$.

The presence of the trans-1,2 unit must be the result of cis–trans isomerization. However, it would be of interest to learn whether the isomerization takes place (1) before the polymerization step (monomer isomerization), (2) during the polymerization, as a rearrangement of the last monomeric unit entering the growing chain, or (3) after polymerization (polymer isomerization).

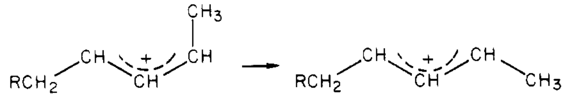
In order to find out experimentally at what stage the isomerization takes place, we have carried out a series of experiments by contacting cP and poly-cP with different cationic catalysts. The results are shown in Table II. In the presence of low concentrations of Et_2AlCl or $EtAlCl_2$ and under conditions similar to those adopted in copolymerization experiments, only cP polymerization was evident. Conversely, $BF_3 \cdot OEt_2$ partially converts cP to tP at −70 °C without polymerization. Thus, monomer isomerization has been verified when the initiator is a weak Lewis acid, unable to initiate the polymerization of both cP and tP under the conditions adopted. This result can be explained by assuming that H^+ attacks position 4 of cP and a protonation–deprotonation reaction takes place as follows:



The second step of the reaction scheme is not reversible since tP is not protonated in position 4.[1] Since the possibility of monomer isomerization exists, the I–cP copolymerization should be considered to be an I–cP–tP terpolymerization.

As far as the true cP cationic polymerization is concerned, the results described in the previous section clearly indicate that cP, in contrast to tP, can be attacked in both positions 1 and 4 when the electrophilic species does not arise from isobutylene because cis-1,2, trans-1,2, and trans-4,3 units are present in the I–cP copolymer besides 1,4 and 4,1 units.

No experimental evidence was found relating to the possibility of isomerization during polymerization. However, evidence was found that when an electrophilic species R^+ reacts with position 1 of cP, the resulting intermediate (1) rearranges to the more stable conformation (2), from



1 **2**

which the trans-1,2 unit arises, as postulated in the case of coordinated polymerization of cP[8] and in the case of solvolytic reactions involving allyl cations.[9]

Finally, in the presence of $EtAlCl_2$, poly-cP becomes an insoluble, cross-linked material, but IR analysis shows that the cis-1,2 unit is still present. On the other hand, $BF_3 \cdot OEt_2$ is unable to modify at −70 °C the structure of poly-cP, as indicated by the absence of changes in the ^{13}C NMR spectra obtained before and after the treatment. Thus, cis–trans isomerization in the polymer appears unlikely under our experimental conditions.

Quantitative Analysis. On the basis of the assignments reported in Table I, it is possible to estimate the percentage of structural units in the cP homopolymer. We

Table III
Fraction of Triads Centered on I in Cationic I–cP Copolymer

copolymer composition I/P mole ratio	copolymer % conversion	III exptl	III calcd	IIP + PII exptl	IIP + PII calcd	PIP exptl	PIP calcd
71/29	21	0.571	0.504	0.312	0.412	0.117	0.084
67/33	25	0.475	0.449	0.363	0.442	0.162	0.109

obtain the following values: 1,4- and 4,1-trans, 75%; 1,2-cis, 12%; 4,3, 8%; 1,2-trans, 5%. The ratio of the dyads $\overrightarrow{P}\overrightarrow{P}$ + $\overleftarrow{P}\overleftarrow{P}$ vs. $\overrightarrow{P}\overleftarrow{P}$ + $\overleftarrow{P}\overrightarrow{P}$ is ca. 3/1. However, these values are obtained by neglecting the cyclic structures which are present in a very high concentration, up to 30–40%, depending on the experimental homopolymerization conditions. The presence of cyclic structures is evidenced by a broad band in the aliphatic region of the ^{13}C NMR spectrum. Their amount can be evaluated, as shown in other cases,[10] by the ratio of the areas of unsaturated and saturated protons obtainable from ^{1}H NMR spectra. The study of the monomer distribution in I–cP copolymer is more complicated than in the case of the corresponding I–tP copolymer[1] because of possible 4,1-addition of the diene and its cis–trans isomerization.

In the copolymer the percentages of 1,2 and 4,3 units are difficult to estimate because of their low content. Furthermore, the extent of the 4,1-addition, which depends on the copolymer composition (dyad $I\overleftarrow{P}$ is hindered), cannot be calculated because of overlapping of same resonances of the terpolymeric system ($I\overrightarrow{P}\overleftarrow{P}$).

As far as the sequence fractions are concerned, the calculation of the triad and pentad fractions centered on P from the signals due to unsaturated carbons is rather complicated and gave inaccurate results. However, the signals of the quaternary carbons and the methyls of the *gem*-dimethyl groups allow the calculation of the triad and pentad fractions centered on I.

The experimental values of the triad fractions are compared in Table III with the values calculated for a random distribution. The agreement between the two series of data is fair. An analogous result was obtained for I–tP copolymer (a slight tendency toward alternation was, however, observed[1]), and hence it can be concluded that, within the limits discussed above and due to the complexity of I–cP copolymer, the monomer distribution in both the copolymers is similar even though the reactivity of cP is lower than that of tP.

Conclusions

The study of the structure of cationic I–cP copolymers permits the following conclusions to be drawn.

(1) The diene is mainly present as trans-1,4 unit, but minor amounts of cis-1,2, trans-1,2, trans-4,1, and trans-4,3 units have also been observed. The attack on the diene at position 4 is due, excluding the initiation, only to the carbenium ion arising from another diene unit and not from isobutylene. This fact can be accounted for by the steric hindrance existing on $R^+C(CH_3)_2$ carbenium ions and is supported by the block character of I copolymers with 2,4,6-octatriene.[11]

(2) The isomerization of cP to tP occurs in the presence of a weak cationic initiator (e.g., $BF_3{\cdot}OEt_2$) under the copolymerization conditions adopted. This result can explain the presence of trans-1,2 units in I–cP copolymers. Accordingly, the copolymerization of I and cP is actually a terpolymerization involving both geometrical isomers of 1,3-pentadiene. Therefore, the reactivity of cP in cationic copolymerizations can hardly be evaluated since the results obtained concern also the highly reactive trans isomer. The method of predicting the relative reactivity of the two isomers and the possible positions of attack by electrophilic species on the basis of electron density data[12] is probably on oversimplified approach. More adequate calculations should also involve steric effects and solvation phenomena of the active species. Some work along these lines is in progress.

(3) The formation of trans-1,2 units through a cis–trans isomerization occurring on the ultimate unit of the growing chain cannot be ruled out. However, no evidence of this possibility was found or of possible postisomerization of cis-1,2 units present in copolymer chains.

(4) Despite the difficulty encountered in evaluating the monomer distribution, the calculation of the monomer sequence fractions by assuming a Bernoullian copolymerization of I and cP is in fair agreement with the experimental data concerning the triad fractions centered on I.

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