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Copolymerization of Isobutene with trans-1,3,5-Hexatriene

A. Priola, C. Corno, M. Bruzzone and S. Cesca

ASSORENI, Polymer Research Laboratories, 20097 San Donato Milanese, Italy

SUMMARY

The cationic copolymerization of isobutene (I) and trans-1,3,5-hexatriene (HT) at low temperature occurs randomly (r_I= 0.59, r_{HT}= 1.57). The prevalent 1,6-opening of the triconjugated system of HT was ascertained mainly by ^{1}H- and ^{13}C-NMR analysis. The formation of gelled products was avoided by working in a homogeneous medium and the cyclization of the triene units by copolymerizing I and HT in bulk.

INTRODUCTION

Recently we projected to synthesize isobutene (I) based copolymers containing a system of conjugated double bonds, analogous to previous investigations carried out on unsaturated ethylene-propylene based terpolymers (1), and we succeeded in obtaining them with cationic catalysts. A general picture of this work was published previously (2) and now we present in this paper the detailed results on the synthesis and structural characterization of I-trans-1,3,5-hexatriene (HT) copolymers. The homopolymerization of HT by means of typical coordination catalysts was studied by BELL (3) who found the conditions for obtaining the prevalent formation of 1,6-, 1,4- or 1,2-units. In some experiments BELL found that also cationic initiators are able to polymerize HT. Copolymers based on I and containing a system of conjugated double bonds were prepared by BALDWIN et al. (4) through an indirect procedure, i.e. by chlorination of I-isoprene copolymer and subsequent dehydrochlorination of the obtained product. However, the final copolymers contained different types of conjugated double bond systems since both the chlorination and dehydrochlorination reactions do not follow a unique path.

EXPERIMENTAL

HT was prepared according to BELL (3). The raw product was purified from the main impurity (1,3-cyclohexadiene) by crystallization (twice) from n-pentane at -78°C and distillation (b.p.=30-

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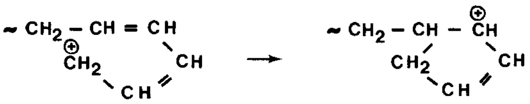
÷35°C/130 torr). The final product was 98% pure and consisted of the trans-isomer the remainder being n-pentane (VPC analysis; column EAS, 20%, 5 m, 100°C). The yield with respect to sorbyl alcohol was 54%. Isobutene, solvents and catalysts were commercial pure grade products purified and used as reported previously (5). The polymerization equipment and procedure were essentially the same as described in previous works (5,6). The hydrogenation of the copolymers was carried out as described elsewhere (6). Also VPC analyses, viscometric and $\bar{M}_n$ determinations were performed as reported previously (6). UV spectra were recorded with a Perkin-Elmer 402 instrument. Cyclohexane solutions of copolymers and 2,4-hexadiene (a 30/70 mixture of cis-trans and trans-trans isomers; ε = 22,200 l/mole.cm), used as a model compound, were employed. IR spectra were obtained with a Perkin--Elmer 125 instrument from copolymer films resulting from evaporation of CS_2 solutions. Both ^{1}H- and ^{13}C-NMR spectra were obtained as described previously (6).

RESULTS AND DISCUSSION

The cationic homopolymerization of trans-HT was formerly accomplished under the experimental conditions adopted for the copolymerization runs (Table I). The spectroscopic analyses (IR and NMR) of poly-HT (s. below) indicate that the polymer contains mainly 1,6-unit, but in the ^{1}H-NMR spectrum the ratio of the bands due to unsaturated (H_u) and saturated protons (H_s) shows that more than one double bond disappeared during the copolymerization step. Most likely, cyclization reactions are responsible for this result as can be inferred from the broadness of the band due to H_s (7). A possible reaction scheme is as follows:



However, we have not collected evidence for the presence of five or higher membered rings. We found that the samples reported in Tab. I were cyclized to an extent of about 50%. Table I shows the results obtained in copolymerization runs with low amounts of HT and adopting different experimental conditions. When the separation of the copolymer occurred, e.g. by working in CH_3Cl, it appeared insoluble and highly crosslinked. A similar result was observed during the synthesis of I copolymers with cyclopentadiene or isoprene containing a relatively high concentration of unsaturation (8). Evidently, the diffusion of the monomers and their reactivity encounter some difficulty under heterogeneous conditions and hence interchain reactions are favored. Analogous to the behavior of conjugated dienes

TAB. I - COPOLYMERIZATION OF I WITH LOW AMOUNTS OF HT

[I] + [HT] (mol/l)	HT in the feed (mol %)	$[EtAlCl_2]$ (mmol/l)	Conv. (%)	$[\eta]$ (dl/g)	$\bar{M}_v \cdot 10^{-5}$ (a)	C.D.B.(b) content (mol %)
4	0.68	1.67	52	2.57	6.00	0.32
4	1.24	1.67	34	2.39	5.50	0.41
4	1.74	2.50	26	2.01	4.20	0.89
4	2.00	2.50	35	1.90	3.90	1.10
4	2.50	2.91	38	1.86	3.75	1.29
4	2.60	3.33	31	2.23	4.80	1.80
4	4.50	4.17	31	1.98	4.15	2.51
4(c)	0.68	1.50	22	insol.	-	-
4(c)	1.74	1.80	33	insol.	-	-
4(e)	2.4	1.4	30	1.43	2.60	1.18(f)
4(e)	2.4	1.8	51	1.17	1.90	1.20(f)
0.6	100	6.0	11	n.d.	-	-
0.2	100	40(d)	20	n.d.	-	-

Conditions: T = -70°C; solvent = n-heptane + CH_3Cl (1/1 by vol.); time = 20 min.; 50% of HT was introduced continuously during the polymerization time.

(a) Calculated according to $[\eta] = 2.65 \cdot 10^{-4} \bar{M}_v^{0.69}$, in cyclohexane at 30°C (12)

(b) C.D.B.= Conjugated Double Bonds, determined by UV analysis of the copolymer.

(c) Carried out heterogeneously, in CH_3Cl only.

(d) $BF_3 \cdot OEt_2$

(e) Isoprene was used instead of HT

(f) By iodometric titration (5).

TAB. II - COPOLYMERIZATION OF I WITH HT AND WITH HIGH MONOMERS CONCENTRATION.

$[EtAlCl_2]$ (mmol/l)	HT in the feed (mol %)	Conv. (%)	$[\eta]$ (dl/g)	$\bar{M}_v \cdot 10^{-5}$	C.D.B. content (mol %)
2.0	0.70	8	1.98	4.15	0.90
2.0	1.34	6	1.84	3.70	2.02
2.4	1.80	5	1.70	3.30	2.30
2.6	1.80	9	2.05	4.30	2.10

Conditions: as in Tab. I, except solvent = n-heptane only, and [I] + [HT] = 10 mol/l.

TAB. III - COPOLYMERIZATION OF I WITH HIGH AMOUNTS OF HT.

HT in the feed (mol %)	Conv. (%)	HT in the copolymer (mol %)		Percentage of triads by ^{1}H-NMR		
		VPC	NMR	III	HII+IIH	HIH
10.5$^{(a)}$	29	15.5	7.5	68.0	23.0	9.0
16.5$^{(a)}$	29	25.0	11.5	56.0	31.0	13.0
26.0$^{(a)}$	33	30.0	17.0	55.5	32.0	12.5
26.0$^{(a)}$	5	n.d.	14.0	52.0	29.0	19.0
32.0$^{(a)}$	31	50.0	32.0	39.0	32.0	29.0
40.0$^{(a)}$	27	63.0	35.0	n.d.	n.d.	n.d.
6.0$^{(b)}$	3	n.d.	8.0	75.0	17.0	8.0
13.5$^{(b)}$	11	18	15.5	68.0	26.0	6.0
20.0$^{(b)}$	5	n.d.	26.0	39.5	35.0	25.0
22.0$^{(b)}$	12	37	34.0	45.5	38.5	16.0

Conditions: as in Tab. I, except T = -60°C and all HT is added to the feed at the beginning of the run; $[EtAlCl_2]$ = 2-12 mmol/l; (a): [I] + [HT] = 1.0 mol/l, (b) [I] + [HT] = 10 mol/l.

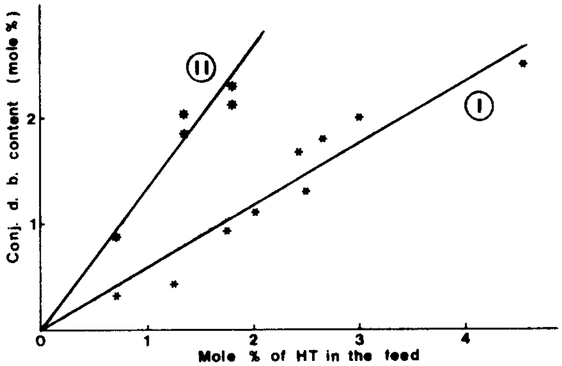


Fig. 1

COPOLYMERIZATION OF I WITH HT

① [I] + [HT] = 4 mol/l

⑪ [I] + [HT] = 10 mol/l

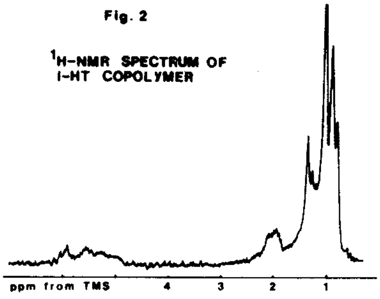


Fig. 2

^{1}H-NMR SPECTRUM OF I-HT COPOLYMER

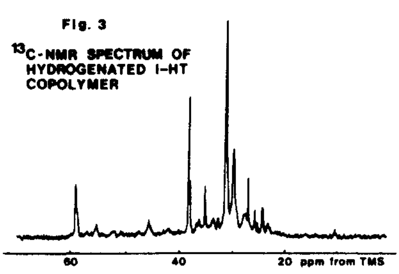


Fig. 3

^{13}C-NMR SPECTRUM OF HYDROGENATED I-HT COPOLYMER also HT progressively reduces the $\overline{M}_v$ of the copolymer when its level in the feed increases (at least up to 2,5 mol %). Comparable copolymerization experiments carried out with I and isoprene (s. the last runs in Tab. I) indicate that HT possesses a chain transfer coefficient lower than that of isoprene.

The relationship of the content of HT in the feed vs. the content of conjugated double bonds (UV determination) in the copolymer is plotted in Fig. 1 for two different overall monomer concentrations. It is evident in Fig. 1 that the content of conjugated double bonds in the copolymer increases markedly for each composition when the overall concentration of monomers increases. This behavior is typical of a copolymerization occurring with cyclization of at least one monomer since the cyclization reaction is monomolecular and favored by the monomer dilution (9). Therefore, in order to achieve a high content of conjugated double bonds, a high monomer concentration is necessary. The most favorable situation implies bulk copolymerization conditions, but in this case a low conversion is necessary to avoid the high viscosity of the reaction mixture and the occurrence of intermolecular side reactions which yield gel.

By working in bulk (Tab.II and line II in Fig.1) the cyclization of HT units is practically negligible as confirmed by the fact that the copolymer composition data determined by ^{1}H-NMR analysis or by the monomer conversion (VPC analysis of the unreacted monomer) are coincidental (s. Tab.III, second part) within the experimental errors. Conversely, when diluted concentrations of the feed are used, the content of HT in the copolymer determined by VPC is always higher than that obtained spectroscopically. However, according to Tab. III, a relatively high concentration of conjugated unsaturation can be introduced in polyisobutene chains. The copolymer composition, obtained from samples prepared at low conversion and in bulk, can be correlated with the feed composition for calculating the reactivity ratios of I and HT. However, because of the difficulty encountered in synthesizing copolymer samples in a broad range of compositions, we have preferred to obtain the reactivity ratios from the values of the sequence fractions obtained by NMR spectroscopy. In fact, the signals of the methyl groups in the ^{1}H-NMR spectra of I-HT copolymers allow the determination of the fractions of triads centered on I (s. below and Tab. III). These values were used for calculating the reactivity ratios according to the method proposed in a previous work (10). The HARWOOD program (11) is the basis of the computation. This program, in its original version enables the calculation of the copolymer composition and of dyad, triad, tetrad and pentad distributions from the feed composition, the conversion and the reactivity ratios. We used this program as a subroutine in an optimization procedure introducing the feed and conversion data and going on to determine the values of the reactivity ratios which minimize the sum of the squares of the differences between the calculated and the experimental values of the sequence fractions (in this case the fractions of triads centered on I). The calculation was carried out by considering only the terminal reactivity ratios. The "simplex" method (13) was used as a minimization algorithm, the initial values from which to carry out the regression being both the arbitrary values $r_{IH} = r_{HI} = 1$ and other pairs of values. The results obtained from the different regressions were identical in all the cases and the following values were obtained:

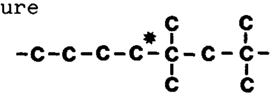
$$r_{IH} = 0.59 \qquad r_{HI} = 1.57$$

These values indicate that the introduction of a vinyl group in the butadiene frame enhances markedly the nucleophilicity of the conjugated system and hence its reactivity during cationic copolymerization processes. In fact, the reactivity of butadiene (BD) in the cationic copolymerization with I is lower by about 2 orders of magnitude than that of HT, as can be shown by using previous data (14) obtained at -100°C ($r_{IB} = 43$) and ours in the following ratio: $r_{IB}/r_{IH} = k_{IH}/k_{IB} = 73$. Our investigations on I-BD copolymer (6) agree with this conclusion, although we were not able to obtain meaningful values of r_{IB} and r_{BI}. The evaluation of the reactivity ratios of I and HT according to the approach described above has the advantage of utilizing copolymer samples obtained also at high conversion (11). Furthermore, the values of the triad fractions obtained by ^{1}H-NMR analysis are comprehensive also of the small quantities of HT yielding structural units different from 1,6 and in this way all the content of triene is taken into account. In fact, the upfield shift of signals of different triads occurs when the lateral I unit is substituted by whatever unit is not crowded by methyls of the gem-dimethyl group (6) and hence by every unit arising from HT.

Finally, the product of the obtained reactivity ratios is nearly one, indicating a random distribution of the monomeric units in the copolymer.

STRUCTURAL INVESTIGATION ON I-HT COPOLYMER

Mainly ^{1}H- and ^{13}C-NMR analyses were carried out on the polymers described above in order to ascertain: (i) the copolymer composition, (ii) the triene structure and (iii) the distribution of the monomeric units. However point (i) was tackled also by UV and (ii) by IR spectroscopy. The band evident at 226 nm in the UV spectra of both HT homopolymer and copolymer confirmed the presence of conjugated unsaturations. Strong absorption bands were present at 990-2 and 972 cm^{-1} in the IR spectra. They can be attributed to trans-trans and trans-cis conjugated double bonds, respectively (3). A weak band is present in the IR spectra of poly-HT at 909 cm^{-1} which can be assigned to vinyl unsaturation (less than 10%) arising from 1,2- or 1,4-units. The copolymer composition can be easily determined from the ratio of the areas of signals (between 4.5 and 6 ppm) of H_u and H_s, present in ^{1}H-NMR spectra (Fig. 2). In the presence of cyclized units the content of HT is underestimated since the spectroscopic methods give only the actual amount of double bonds instead of the copolymer composition. However, the NMR analysis allowed to identify the type of structural units and their distribution when samples of copolymer rich in HT were studied. As mentioned above, the ^{1}H-NMR spectrum gives the values of the triad fractions centered on I unit. In fact, as it was observed in the case of other isobutene copolymers (6,15), the methyl groups give rise to 3 signals in the aliphatic region of the spectrum (Fig. 2). The first, observed at 1.1 ppm, is attributable to triad III, the second occurring at 1.0 ppm is due to triads IIH+ +HII and the third, evident at 0.85 ppm, to triad HIH. The upfield shift of methyl signals observed in copolymers of I with different monomers, lacking in gem-dimethyl groups, was discussed previously (6,15). The three peaks of methyls mentioned above allow a rather satisfactory calculation of the values of the triad fractions (Table III). Conversely, it is difficult to determine from the ^{1}H-NMR spectra the type of structure of HT. Three units can arise from HT, i.e. the 1,6-, 1,4- and 1,2-unit. Their identification is possible by ^{13}C-NMR analysis, in particular in the hydrogenated copolymer (Fig. 3). The possible presence of methyl signals, arising from 1,2- and 1,4- units are expected at ca. 14 and 11 ppm respectively (16), in a region of the spectrum free from other signals. Fig. 3 shows only the existence of a very weak peak at 11.8 ppm due to the methyl of the hydrogenated 1,4-unit. Therefore, the 1,6-unit is largely prevalent and is accompanied by a trace of 1,4- unit. Besides the identification of the type of units arising from HT, the ^{13}C-NMR spectrum gives information on the distribution of the monomeric units. In principle, the interpretation of the spectrum is easy, since it is rather similar to the work made with hydrogenated I-BD copolymer (6). The unique difference in the presence of (1+6n) methylenes between two isopropylidene groups instead of (1+4n) methylene groups and the difference does not imply changes in the assignments. The problem in this case is the scarce number of signals clearly identifiable, because of the low content of the triene. In practice there is evidence of the peaks of the I methyls in the triad III (at 31.3 ppm) and of the quaternary carbon in the triad III (38.2 ppm) and in the triad IIH (HII) (35.3 ppm). Furthermore, four signals due to methylene carbons are identified, i.e. the signals of I methylene in the IIII tetrad (59.6 ppm) and in the IIIH (HIII) tetrad (55.8 ppm), the signal at 45.8 of the methylene marked out by an asterisk in the following structure



$$-C-C-C-C\overset{*}{-}\underset{C}{\overset{C}{C}}-C-\underset{C}{\overset{C}{C}}-$$

and the peak of HT methylenes more than four bonds away from the isopropylidene group (at 29.9 ppm) that partly overlaps the I methyls peak in the triad IIH (HII).Hence, some information about the monomer distribution can be obtained on the basis of these assignments, but the lack of a complete set of values for the tetrad sequences (obtained in a previous work (17) on other I copolymers) has not allowed the utilization of these data for thecalculation of the reactivity ratios.

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