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Copolymerization of Isobutene with 2,4,6-Octatriene and Other Triconjugated Trienes

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SUMMARY

The cationic homogeneous copolymerization at low temperature of 2,4,6-octatriene (OT), 1,3,5-heptatriene (HPT), 2,5-dimethyl-1,3,5-hexatriene (DMH) and alloocimene (AO) with isobutene (I) was performed and the structure of the resulting copolymers examined spectroscopically. OT reacted mainly by 2,7-opening of the triene system yielding soluble copolymers with block character and containing a low amount of cyclized units. Soluble I-HPT copolymers containing 2-4 mol % of conjugated double bonds were obtained. DMH alway gave insoluble copolymers and only traces of conjugated unsaturations were found in I-AO copolymer.

INTRODUCTION

The cationic copolymerization of isobutene (I) with the simplest triconjugated triene, i.e. 1,3,5-hexatriene (HT) was described in a previous paper (1). Pursuing our work we have investigated the copolymerization of I with some superior homologues of HT, i.e. 2,4,6-octatriene (OT), 1,3,5-heptatriene (HPT), 2,5-dimethyl-1,3,5-hexatriene (DMH) and alloocimene (2,6-dimethyl-2,4,6-octatriene; AO).

EXPERIMENTAL

The synthesis of OT was performed by dimerization of butadiene in the presence of $Pd(0)\cdot(PEt_3)_4$ complex (2). The procedure in the presence of $RhCl_3$ (3) gave poor selectivity and low yield The selectivity of $Pd(PEt_3)_4$ is controlled by working in the presence of CO_2 (28 g of butadiene in 50 cm^3 of anhydrous benzene; 1% of Pd complex; 8 atm of CO_2. T = 105°C; t = 5 h). We obtained 63% of OT (b.p. = 51°C/15 torr) with VPC purity = 96%, the remainder being 1,3,7-octatriene (prevalent) and 4-vinyl-cyclohexene-1. The obtained product contained 4 main geometrical isomers as revealed by VPC-MS and ^1H-NMR analyses.
HPT was prepared as described previously (4) and was mainly

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constituted by trans-trans isomer.The product after distillation (b.p. = 61-64°C/120 torr) was 92% pure (VPC), the remainder being a mixture of 6-methyl-1,3-cyclohexadiene and 6 methyl-1,4--cyclohexadiene (VPC-MS and ^{1}H-NMR).

DMH was obtained by following the procedure described elsewhere (5,6). After distillation of the raw product, a main fraction (60%; b.p. = 50-52°C/50 torr) was collected. ^{1}H-NMR analysis showed that DMH contained dimethyl-cyclohexadiene isomers. By crystallization from n-pentane at -78°C the final product (VPC purity = 96%) was obtained. AO was a commercial product (Fluka) having purity = 99%. Other reagents, solvents and catalysts were the same as described in the previous paper (1); the polymerization, hydrogenation and analytical procedures were also reported previously (1).

RESULTS AND DISCUSSION.

OT is an interesting triene since it can be obtained with good yield from butadiene in the presence of a Pd based catalyst (s. Experimental) as a mixture of geometrical isomers which was used as obtained. OT can be homopolymerized with cationic initiators to a high molecular weight and soluble product (Tab.I the last runs). From its IR and ^{1}H-NMR spectra which will be discussed below, it can be concluded that: 1) 2,7-unit is largely prevalent; 2) the content of cyclized units is rather low. Therefore, the behavior of OT in cationic polymerization is different from that of HT, i.e. 1,3,5-hexatriene (1). The presence of two terminal methyl groups in the triconjugated system hinders, probably for steric reasons, cyclization reactions. Tab. I shows the results of I-OT copolymerization carried out under different experimental conditions. No gel was formed when homogeneous systems were used. The continuous introduction of OT in the feed was necessary to obtain a regular distribution of the unsaturations (Fig. 1). Conversely, when all the triene is introduced in the reaction mixture before the copolymerization starts, the content of OT in the copolymer markedly depends on the conversion (Fig. 2). This behavior can be attributed to the great difference of reactivity exhibited by the two monomers towards the electrophilic species. OT appears more reactive than I and, very likely, initiates the copolymerization process yielding long sequences of triene. Actually, the block character of I-OT copolymer has been confirmed by the spectroscopic analysis (s. below). Copolymerization experiments carried out at very low conversion (the last runs in Tab. I) yielded still a block copolymer and hence blockiness appears as an intrinsic characteristic of the I-OT system. Therefore, under these circum

TABLE I - COPOLYMERIZATION OF I WITH OT

I+OT (mol/l)	OT in the feed (mol %)	$EtAlCl_2$ (mmoli/l)	Conv. (%)	$[\eta]$ (dl/g)	$M_v.10^5$ (a)	C.D.B.(b) content (mol %)
4.0	1.0	2.3	31	3.40	9.20	0.83
4.0	1.6	2.7	35	2.96	7.20	1.10
4.0	2.5	2.3	33	2.16	4.78	1.44
4.0	3.3	3.1	30	2.20	4.80	1.90
4.0(c)	4.1	2.7	31	1.80	3.60	3.10
4.0(d)	1.6	3.3	53	Part.Ins.	-	-
4.0	2.5	2.0(e)	24	Part.Ins.	-	-
4.0	2.5	8.3(f)	22	0.60	0.75	1.84
4.0	2.0	8.3(g)	7	1.29	2.20	1.60
1.1(h)	12.0	4.0	13	0.51	-	25(k)
1.1(h)	31.0	4.0	43	1.08	-	48(k)
2.2(h)	17	0.9	2.5	-	-	40(k)
2.2(h)	7	1.0	3.5	-	-	13(k)
0.6(h)	100	61(j)	41	0.62(m)	-	(i)
0.6(h)	100	20(j,n)	25	n.d.	-	-

Conditions: T = -70°C; solvent = n-heptane + CH_3Cl (1/1 by vol.) time = 20 min.; OT was added continuously during the copolymerization time (1/3 at the beginning of each run).

(a) Calculated according to $[\eta] = 2.65.10^{-4} M_v^{0.69}$, in cyclohexane at 30; (b) C.D.B. = Conjugated Double Bonds, by UV analysis; (c) T = -75°C; (d) Carried out heterogeneously, in CH_3Cl only; (e) $AlCl_3$ in EtCl solution; (f) $Et_2AlCl + (CH_3)_3CCl$(0.33 mmol/l) (g) $(Et_3Al_2Cl_3)_{1/2}$; (h) n-Pentane + CH_2Cl_2 (1/1 by vol.); (k) mol. % of OT by NMR analysis; (j) $BF_E.OEt_2$; (i) 80% of 2.7-unit and 20% of 2.5-unit (by NMR); (m) in toluene at 30°C; (n) T = -20°C.

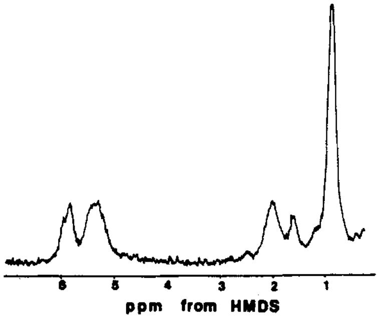


Fig. 1 - ^{1}H-NMR spectrum of poly-OT.

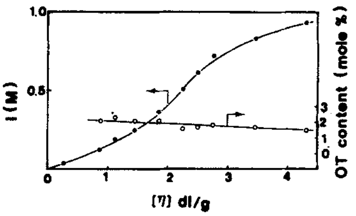


Fig. 2 - Fractionation data and integral MWD curve of I-OT copolymer (OT = 1,60 mol %, [η] = 1,83 dl/g in the unfractionated sample).

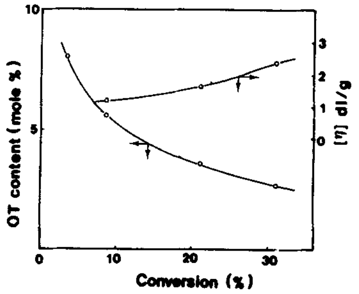


Fig. 3 - OT content and vs. conversion in I-OT copolymerization (T = 70°C; I+OT = 4 mol/l; OT = 2,5 mol %; $EtAlCl_2$ = 1,2 mmol/l).

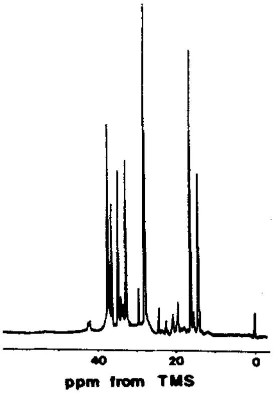


Fig. 4 - ^{13}C-NMR spectrum of hydrogenated poly-OT.

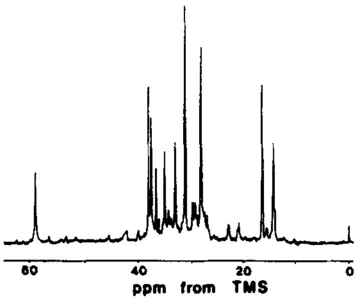


Fig. 5 - ^{13}C-NMR spectrum of hydrogenated I-OT copolymer (OT = 40 mol %).

stances, the determination of the reactivity ratios of I and OT is meaningless and also practically impossible.

By adopting a continuous feeding of OT it is possible to reduce the length of the OT blocks as shown in Fig. 1 and by crosslinking investigations (8). However, the efficiency of OT as a functionalizing agent of the poly-I chains (1) is lower than that of HT which randomly distributes the conjugated unsaturations in the copolymer. Fig. 1 shows also a symmetrical distribution of MW, similar to that observed in the case of I-isoprene copolymers prepared under similar conditions (9). The value of the polydispersity index (M_w/M_n) of I-OT and I-isoprene copolymers was found to be in the same range, i.e. between 2.5 and 3.3.

Tab. II shows the results of some preliminary copolymerizations of I with HPT, DMH and AO. As expected, the behavior of HPT is intermediate between that of HT and OT. Soluble I-HPT copolymers, displaying high M_v and containing 2-4 mol % of HPT were obtained. However, in some experiments, even though carried out under homogeneous conditions, gel formation was observed. This finding suggests that branching and cross-linking reactions occurred to some extent. DMH always yielded crosslinked material when the copolymerization with I was attempted in the presence of $EtAlCl_2$. Probably the nucleophilicity of the triconjugated system is markedly increased by the presence of two electron donor methyl groups. In fact, the homopolymerization of DMH in the presence of a weak Lewis acid, such as BF_3OEt_2, yielded a product which contained 50% of cyclized units, the remaining ones having 1,6- (75%), 1,4- and probably 1,2- structure (^{1}H-NMR analysis). AO can be homopolymerized cationically, as shown previously by MARVEL and KIENER (10) who found that the polymer structure incorporated prevailingly the 4,7-unit (35% of the 6,7-unit was also present). However, only traces of conjugated unsaturation were observed in I-AO copolymers (UV analysis) while a block distribution of the triene seemed to occur according to preliminary spectroscopic investigations. Efficient chain transfer reactions are promoted by AO, because the M_v of the obtained copolymers was relatively low.

SPECTROSCOPIC INVESTIGATIONS ON CATIONIC POLY-OT AND I-OT COPOLYMER.

The spectroscopic techniques employed in the study of I-HT copolymer (1) were also used in the case of cationic poly-OT and I-OT copolymer.

The IR spectrum of poly-OT shows the strong absorption bands at 990-2 and 972 cm^{-1} discussed previously (1) which suggest

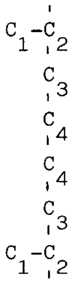
TABLE II - COPOLYMERIZATION OF I WITH DIFFERENT TRICONJUGATED TRIENES.

Triene (Type)	Triene (mol.%) (a)	$EtAlCl_2$ (mmol/T)	Conv. (%)	$[\eta]$ (dl/g)	$M_v.10^{-5}$ (b)	C.D.B.(c) (mol.%)
HPT	2.0	2.5	17	2.53	5.8	3.85
HPT	2.0	2.8	24	3.20	8.2	1.81
HPT	2.8	2.9	19	2.78	6.8	3.90
HPT	3.2	5.0	15	ins.	-	-
DMH	2.4	6.5	10	ins.	-	-
DMH	1.6	8.3	12	ins.	-	-
AO	1.6	8.3	77	0.95	1.45	trace
AO	2.0	5.0	65	1.22	2.00	trace
AO	2.8	8.3	56	1.30	2.20	trace
AO(d)	2.0	3.6	35	1.46	2.60	trace

Conditions: as in Table I; [I] + [Triene] = 4.0 mol/l; 50% of triene was introduced continuously in the feed during the copolymerization

(a) In the feed; (b) s. foot note (a) of Tab. I; (c) as in Tab. I; (d) T = - 75°C.

TABLE III - CHEMICAL SHIFTS OF HYDROGENATED I-OT COPOLYMER(a)

Structure	Atom	Experimental	Calculated(b)
	C_1	16.54-14.47	16.64
	C_2	36.69-37.66	37.06
	C_3	33.05-35.05	34.32
	C_4	28.19	27.77

(a) Containing OT as 2.7-unit; (b) According to ref. (13).

the presence of only 2,7- and 2,3- units. In the UV spectra of poly-OT there is an absorption band at 235 nm ($\epsilon = 15{,}650$ l/mol cm) typical of an 1,4-dialkyl conjugated system. By referring to the UV spectrum of 2,4-hexadiene ($\epsilon = 22{,}200$ l/mol cm) assumed as a model compound, poly-OT contains ca. 70% of 2,7- and/or 2,3- units, the remainder being cyclized or 2,5-units. An analogous result was obtained from the ^{1}H-NMR spectrum (Fig.3) since the ratio of the area of signals of H_s and H_u (1) is 2.2, while the calculated value for the 2,7-unit is 2.0.

The signals due to H_u occur in the ^{1}H-NMR spectrum between 5 and 6 ppm, while at ca. 2 ppm the peak of the methine in α position to the double bond is evident. At ca. 0.8 ppm there is the signal of methyls which, although linked to tertiary carbons, does not appear as a doublet because the overall structure $-CH(CH_3)CH(CH_3)-$ implies the further splitting due to the existence of the two meso and racemic dyads. In practice, the fine structure is lost and the peak appears as a broad singlet. The weak signal occurring at 1.6 ppm and assigned to the methyl in α position to the double bond, suggests the presence of low amounts of 2,5- and 2,3-units. However, the position of the signal does not allow deciding whether both the units or which of them is present.

The essential features evident in the IR, UV and ^{1}H-NMR spectra of poly-OT, were also present in the spectra of I-OT copolymers whose composition is easily obtainable from the ratio of the areas of signals of H_u and H_s. However, the ^{1}H-NMR spectra of the copolymer do not give accurate data on the monomer distribution because of the overlapping, in the region between 1.1 and 0.8 ppm, of the signals of OT methyls with those of methyls due to I in different triads (11). Therefore, the study of the monomer distribution was carried out by ^{13}C-NMR spectroscopy. By employing this technique, we first examined hydrogenated poly-OT, whose ^{13}C-NMR spectrum is shown in Fig. 4. Seven main peaks appear at 14.47, 16.54, 28.19, 33.05, 35.05, 36.69 and 37.66 ppm from TMS. The first two signals can be attributed surely to CH_3 groups and arise from the reciprocal orientation (meso and racemic) of two gem-dimethyl groups, as observed in hydrogenated 2,5-poly(2,4-hexadiene) (12). Other assignments can be made (Tab. III) by comparing the experimental values with those calculated according to the addition rules (13).

As expected C_4 of Tab. III is the unique carbon whose signal is practically not split because of its distance from the methyl groups. The agreement between calculated and observed values is good and it becomes excellent for the two methyls when the literature values $\gamma_m = -3.05$ and $\gamma_r = 4.83$ ppm (14), concerning a γ substitution which takes into account the relative

orientation, are adopted. In this case the calculated values of C_1 are: C_{1m} = 16.58 and C_{1r} = 14.80 ppm.
If we consider now the ^{13}C-NMR spectrum of a hydrogenated I-OT copolymer (Fig. 5), the almost negligible presence of alternate sequences is evident. In fact, the spectrum appears as the superimposition of the spectra of the two homopolymers. The unique peaks revealing alternate dyads occur upfield relative to the signal of CH_2 present in the tetrad IIII, i.e. between 50 and 58 ppm. These signals are attributable to the methylene group of I in tetrads different from IIII (15). However, they are very weak despite the almost equimolar composition of the sample examined, thus confirming the blocky structure of I-OT copolymer. Because of the low intensity, these signals cannot be used for calculating sequence fractions and hence the reactivity ratios whose product has to be, evidently, much higher than one.

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