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Copolymers from [1.1.1]propellanes and acceptor-substituted olefins

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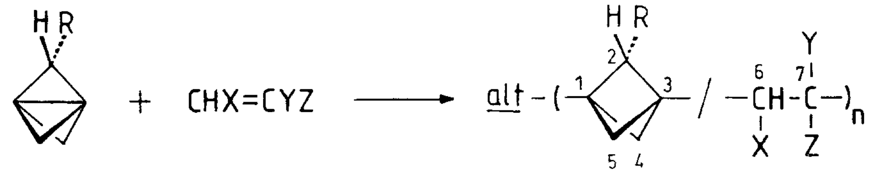
Summary

A variety of substituted olefins which undergo clean copolymerization with [1.1.1]propellanes **1a,b** is presented in this article. For olefins substituted by acceptor groups, strictly alternating 1:1 copolymers are obtained whose structures are proven using high resolution NMR spectroscopy. Evidence for a radical chain mechanism of these copolymerizations is given.

Introduction

We have shown that the [1.1.1]propellanes **1a,b** undergo spontaneous copolymerization with acrylonitrile (1,2), maleic anhydride (3) as well as various other acceptor-substituted olefins (4). Strictly alternating copolymers of high molecular weight are formed (equation 1). Promted by recent work obtaining similar results (5), we wish to give a short report on some of our unpublished but previously presented (4) findings.

(1)



1a,b 2-9 1a2-1b8

a: R=H; b: R=$(CH_2)_4CH_3$

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Results and Discussion

The following olefins were used in copolymerizations with the propellanes **1a,b**: methyl maleimide **2**, dimethyl maleate **3**, methyl acrylate **4**, methyl methacrylate **5**, phenyl vinyl sulfonate **6**, styrene **7**, vinylidene chloride **8** and ethyl vinyl ether **9**. The polymerizations were carried out by reacting the propellane with an excess of the respective olefin (typically 1.5 mol equivalents) for two days in diethyl ether at room temperature under exclusion of oxygen. No initiator was added. The results are summarized in Table 1.

Table I. Some properties of the copolymers prepared

Propellane	olefin	copolymer	yield [%]	M_n x 10^{-3} [α]	T_g [β] [°C]	T_d [β] [°C]	alternating sequence
1a	2	1a2	75	–[γ]	–	>250	yes
1a[δ]	4	1a4	99	200	53	>250	yes
1a	5	1a5	56	10	115	>250	yes
1a	6	1a6	15	11	60	160	yes
1a[δ]	7	1a7	15	40	161	>250	no
1a[δ]	9	–[ε]		–	–	–	–
1b	3	1b3	32	18	–	>250	yes
1b	6	1b6	20	16	21	150	yes
1b	8	1b8	35	16	ca –10	150	no

α) SEC, standard: polystyrene; β) heating rate: 5 K/min; γ) irreproducible results;

δ) 30 % solution in benzene; ε) only very slow homopolymerization of 1a is observed

All copolymers are soluble in at least one of the following solvents at room temperature: chloroform, dimethyl sulfoxide, tetrahydrofuran, and benzene. The molecular weights were determined using size exclusion chromatography (SEC) (standard: polystyrene) except for **1a2** for which SEC data were irreproducible. The obtained data as well as yields, glass temperatures and decomposition temperatures are listed in Table 1. The structures of the copolymers were assigned based on their highly resolved proton and carbon NMR spectra. All chemical shifts are in excellent agreement with those reported in the literature (1,3). Relevant shifts of selected copolymers are given in Table 2. Figure 1 shows the fully assigned carbon NMR spectrum of copolymer **1a6** indicating how clean the copolymerizations proceed.

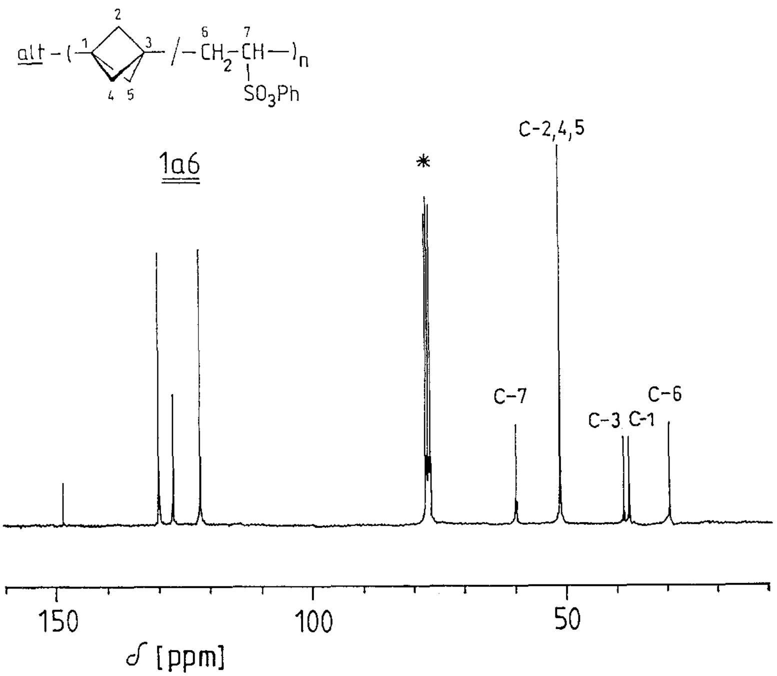
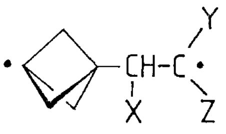


Figure 1: High resolution ^{13}C NMR spectrum of the alternating copolymer 1a6 in deuterio chloroform (*).

Table II. Representative ^{13}C NMR chemicals shifts of selected copolymers in $CDCl_3$ at room temperature.

copolymer	δ [ppm]						
	C–1	C–3	C–2	C–4	C–5	C–6	C–7
1a2	38.9	38.9		48.7$^{\beta}$		44.9	44.9
1a4	37.6	39.7		49.5$^{\beta}$		30.5	45.2
1a5	35.0	45.4$^{\alpha}$		49.0$^{\beta}$		36.7	45.4$^{\alpha}$
1a6	37.4	38.5		51.0$^{\beta}$		29.3	59.7
1b3	41.2	41.2	61.8	46.0	48.7	45.1	45.1
1b6	40.6	41.5	61.8	47.1	50.6	29.1	58.7

α) C–3 and C–7 absorb isochronously in $CDCl_3$. In benzene–d_6 two signals are observed at $\delta = 45.76$ and 45.98 which were not assigned to the respective carbons; β) C–2, C–4 and C–5 are equivalent by symmetry.



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All copolymers have an alternating sequence of repeating units except for the those prepared using styrene or vinylidene chloride. Obviously the acceptor quality of these olefins is not sufficient. If donor substituted olefins like e.g. **9** are used, no copolymerization is observed. We assume that the copolymerizations proceed via a radical chain mechanism. To confirm this assertion, the molecular weight dependence of the conversion was investigated for the monomer system **1a**/**4**. Figure 2 shows a constant molecular weight of about 100 000 g/mol (6) from conversions of less than 10% up to 40-50%, at which point the reaction mixture becomes viscous and the number average values drop significantly. It was also observed that the copolymerizations can be suppressed by the addition of radical inhibitors such as TEMPO or DPPH (7). In addition, the molecular weights of the copolymers are easily reduced by chain transfer reagents like tetrachloromethane (7). We assume that the initiating species is the 1,5-diradical **10** similar to the 1,4-diradical proposed to initiate most of the copolymerizations of donor and acceptor substituted olefins (8). The initiating step of the propellane copolymerizations has also been considered theoretically (9). The results support the existence of a species like **10**.

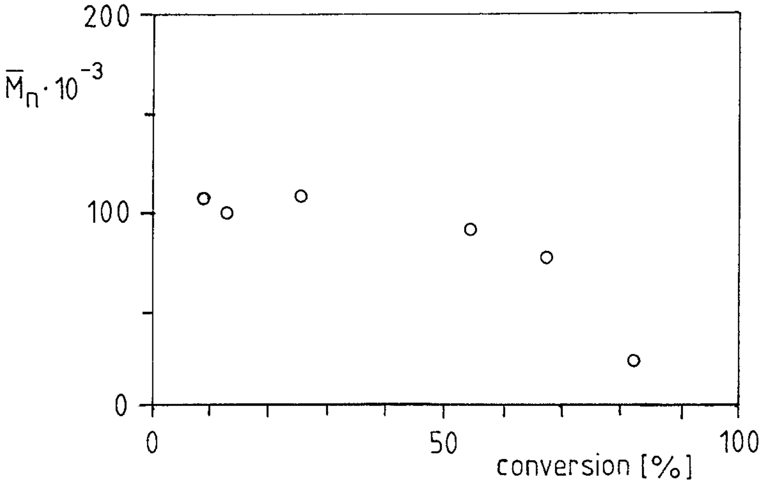

Figure 2: Dependence of molecular weight on conversion for the copolymerization of the [1.1.1]propellane (**1a**) (0.71 mol/l) with ethyl acrylate (**4**) (0.81 mol/l) in benzene at room temperature.

Bromo-, methyl and dichloro maleic anhydride were also used in copolymerizations with propellane **1a**. The copolymers obtained were insoluble. However, they could be brought into solution after hydrolysis of the anhydride ring with aqueous sodium hydroxide (7). Despite opposite claims (10), **1a** also reacts with fumaronitrile and dimethyl maleate to give polymeric material almost quantitatively. The structures of these copolymers as well as their properties are presently under investigation.

Acknowledgement

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(6) Higher molecular weights are easily obtained if the copolymerizations are carried out in more concentrated solutions or neat.

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