

[1.1.1]Propellane and Maleic Anhydride: Face-Specific Copolymerization with Formation of an Alternating 1:1 Copolymer

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The spontaneous and face-specific copolymerization of [1.1.1]propellane and maleic anhydride to give the strictly alternating 1:1 copolymer **2** is described. The molecular weight

of **2** after transformation into the corresponding diester **5c** was determined to be 80.000 (M_n) and 220.000 (M_w), respectively.

[1.1.1]Propellanes upon addition of acrylonitrile¹⁾ and other acceptor-substituted olefins²⁾ form strictly alternating copolymers which contain the bicyclo[1.1.1]pentane moiety as a hitherto unknown repeating unit. Maleic anhydride (MA) is an important comonomer for the synthesis of alternating copolymers, the structures of which as well as the mechanisms of formation of which have been studied in detail³⁾. Here we report on the spontaneous copolymerization of parent [1.1.1]propellane (**1**) with MA emphasizing on both a precise elucidation of the molecular structure of the

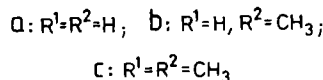
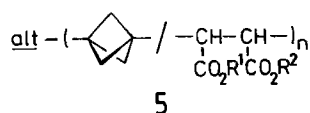
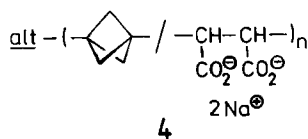
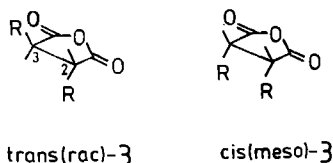
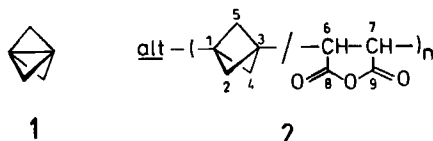
copolymer obtained, including stereochemical aspects, and the accurate determination of the achieved molecular weight.

Copolymerization and Molecular Structure

Large quantities of propellane **1** may be prepared according to two different procedures furnishing this reactive monomer either as a 3% solution in diethyl ether or as neat material of moderate purity⁴⁾. We chose the first procedure since it is more practical⁵⁾. To achieve copolymerization, the propellane solution was transferred in vacuo into a cooled flask containing the equivalent amount of neat MA. As soon as the temperature was raised to about -30°C , the stirred mixture became homogenous for a short time before polymeric material started to precipitate. Usual workup furnished a polymer, to which we ascribe structure **2**, in a yield of ca. 95% based on monomer **1**.

Elemental analysis established that the product was a 1:1 copolymer, and detailed examination of the highly resolved ^1H - and ^{13}C -NMR spectra leads to the conclusion that it is a perfectly alternating copolymer (Figure 1 a). All signals are easily assigned by analogy to known shifts and on the basis of a DEPT pulse sequence⁶⁾. Both spectra show a surprisingly low number of signals considering the fact that most of the known MA copolymers contain the succinic anhydride moiety in both possible stereoisomeric forms, *cis* (*meso*) and *trans* (*rac*), in ratios depending upon the reaction conditions⁷⁾. The ^1H -NMR spectrum of copolymer **2** is of specific interest in this regard. It shows only one singlet at $\delta = 3.33$ (in $[\text{D}_6]\text{DMSO}$) for the methine protons of the succinic anhydride moiety. The chemical shifts of the methine protons in succinic anhydrides **3**, substituted in positions C-2 and -3, are sensitive towards the respective stereochemical configuration. They differ by at least 0.28 ppm for the *cis*-(*meso*)-**3** compared with the *trans*-(*rac*)-**3** derivatives ($\text{R} = \text{alkyl, aryl}$), whereby the methine proton signals of *cis*-(*meso*)-**3** always appear at lower field, for alkyl substituents typically between $\delta = 3.01 - 3.23$ (in CDCl_3)⁸⁾. Thus, it seems unlikely that the signal of copolymer **2** at $\delta = 3.33$ is a superposition of accidentally isochronous methine protons of different stereoisomers. To further rule out this possibility, a spectrum of **2** was recorded in $[\text{D}_8]\text{DMF}$. The signal under consideration is shifted to $\delta = 3.49$, but it remains one sharp line.

In order to assign the stereochemistry, a 2:1 mixture of *rac*- and *meso*-2,3-dimethylsuccinic anhydride **3** ($\text{R} = \text{CH}_3$) was



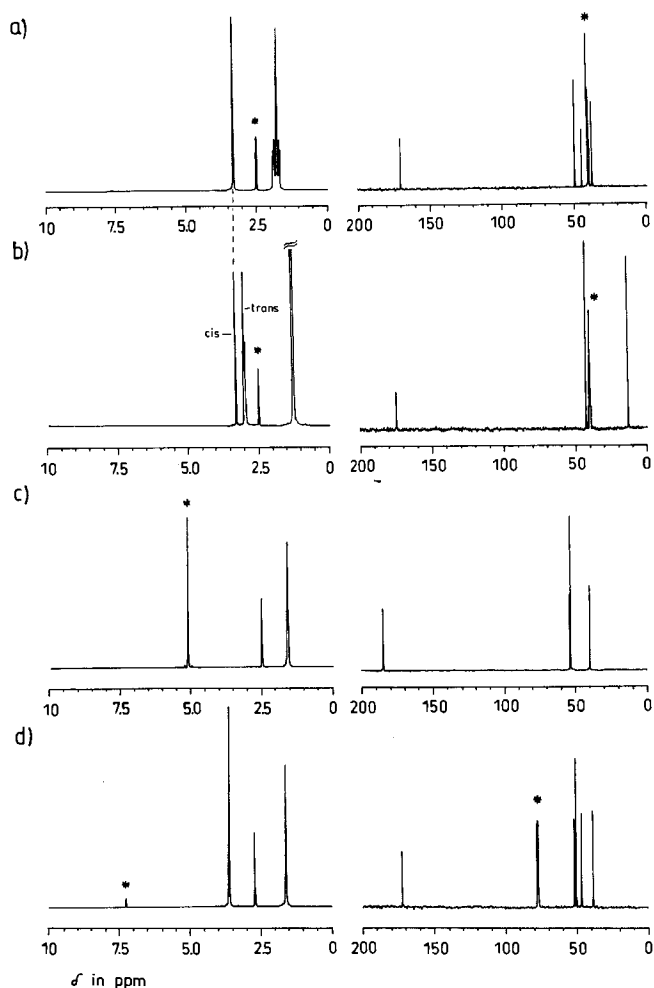
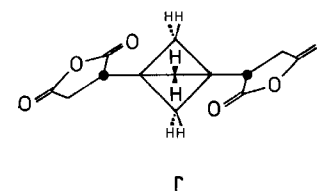
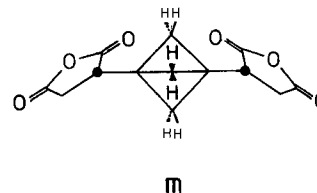


Figure 1. ^1H - and ^{13}C -NMR spectra of the copolymer **2** (a), a 1:2 mixture of the model compounds *cis*-(*meso*)-**3** and *trans*-(*rac*)-**3** (b), the polyelectrolyte **4** (c), and the diester **5c** (d), respectively. The spectra were taken in $[\text{D}_6]\text{DMSO}$ (a, b), $\text{NaOD}/\text{D}_2\text{O}$ (c), and CDCl_3 (d), respectively, at room temperature. Solvent signals are marked (*)

prepared⁸), and its ^1H -NMR spectrum was taken in $[\text{D}_6]\text{DMSO}$, the same solvent as used for the copolymer **2** (Figure 1a). The two signals for the isomeric methine protons at $\delta = 3.32$ and 2.98 were assigned to *cis*-(*meso*)-**3** ($\text{R} = \text{CH}_3$) and *trans*-(*rac*)-**3** ($\text{R} = \text{CH}_3$), respectively, in analogy to the literature⁸). The comparison of the proton spectra of Figure 1a and 1b reveals an excellent match of the methine proton signal of model *cis*-(*meso*)-**3** ($\text{R} = \text{CH}_3$) at $\delta = 3.32$ with the corresponding signal of copolymer **2** at $\delta = 3.33$ suggesting an *all-cis* (*meso*) configuration of the succinic anhydride functions of copolymer **2**⁹. This finding is somewhat unexpected since the *trans* (*rac*) arrangement should be thermodynamically favored.

The proton spectrum of copolymer **2** contains another important structural information which may be obtained from an analysis of the signal group centered at $\delta = 1.77$. This group is assigned to the protons of the bicyclo[1.1.1]pentane repeating unit. The relatively complex signal pattern (generally such protons absorb isochronously¹⁰) can be explained assuming two diades, *r* (*rac*) and *m* (*meso*), which have a different effect on the protons of the bicyclopentane repeating unit. In the *r* diade the stereocenters adjacent to the cage have the same configuration [(*RR*) or (*SS*)], in the *m* diade these stereocenters have the opposite configuration [(*RS*) or (*SR*)]. In the *r* diade all protons of the freely rotating

bicyclic cage are equivalent, and their signal appears as a singlet ($\delta = 1.77$), whereas in the *m* diade the two protons of each methylene group are different. Consequently, the two sets of three protons each absorb at different chemical shifts ($\delta = 1.86$ and 1.69). In addition, these signals are split into doublets due to a 4J coupling of 9.3 Hz which is typical for bicyclopentanes. Based on this interpretation the ratio of both diades is easily obtained from the integration as $r:m \approx 1.0$.



Polymer-Analogous Reactions and Molecular Weight of Copolymer **2**

The determination of the molecular weight of copolymer **2** using size-exclusion chromatography (SEC) was not possible¹¹. We therefore tried to convert this copolymer into the corresponding diester **5c**. For that purpose, copolymer **2** was hydrolyzed under basic conditions furnishing the polyelectrolyte **4**¹². Upon addition of acid the corresponding free acid **5a** is formed which, unfortunately, turned out to be insoluble. Attempts to esterify at this stage failed. Very clean conversion into the diester **5c** was achieved, however, when copolymer **2** was methanolyzed with methanolic HCl to give the half ester **5b**¹³, followed by an exhaustive methylation of this intermediate with diazomethane^{7b}. The structures of the copolymers **4** and **5c** were proven by their ^1H - and ^{13}C -NMR spectra (Figures 1c, d). These highly resolved spectra show, how clean the sequence hydrolysis, partial esterification, and exhaustive esterification proceeds.

Typical samples of the diester **5c** obtained according to this sequence have molecular weights of the order of 80.000 (M_n) and 220.000 (M_w) by SEC (THF; standard: polystyrene). From a fraction of this copolymer the molecular weight obtained by SEC (M_n : 49.000; M_w : 50.000; $D = 1.2$) was compared with that obtained from a membrane-osmotic measurement in toluene (M_n : 55.000). The fair agreement between these data suggests that SEC gives a relatively realistic picture of the actual molecular weight.

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Experimental

General: Apparatuses used were as described elsewhere¹⁴. Tetracyclo[1.1.1.0^{1,3}]pentane (**1**) was prepared according to the literature in diethyl ether⁴ (3% according to ^1H -NMR analysis). The accuracy of this method is estimated to be $\pm 10\%$. Therefore all yields given in the following may vary in the same range. The NMR spectra taken in $\text{NaOD}/\text{D}_2\text{O}$ are referenced to internal 3-trimethylsilyl-1-propanesulfonic acid, sodium salt.

[1.1.1]Propellane and Maleic Anhydride

Poly(tetracyclo[1.1.1.0^{1,3}]pentane-alt-maleic anhydride) (2): In a typical experiment the ethereal solution of **1** containing 2.0 g (30 mmol) of this monomer was vacuum-transferred (1 mbar) into a cooled (-78°C) glass tube (equipped with a Rotaflo[®] tap), which had been charged with maleic anhydride [3.18 g (32 mmol)]. The tube was let down to nitrogen, sealed, removed from the vacuum line and allowed to warm to room temperature where it was kept for 8 h. For the following workup procedure Schlenk equipment was used in order to avoid hydrolysis of the anhydride repeating units. The precipitated material was recovered, washed with dry ether followed by dry acetone and then dried, to give colorless copolymer **2**; yield 5.06 g (98%). Alternatively, the copolymer may be purified by precipitation from DMSO with acetone. — $^1\text{H NMR}$ ($[\text{D}_6]\text{DMSO}$): $\delta = 1.69$ [d, $^2J_{\text{HH}} = 9.3$ Hz, 3H, 2-, 4-, 5-H (*meso* diad)], 1.77 [s, 6H, 2-, 4-, 5-H₂ (*rac* diad)], 1.86 [d, $^4J_{\text{HH}} = 9.3$ Hz, 3H, 2-, 4-, 5-H (*meso* diad)], 3.33 (s, 2H, 6-, 7-H). — $^{13}\text{C NMR}$ ($[\text{D}_6]\text{DMSO}$): $\delta = 37.5$ (s, C-1, -3), 44.8 (d, C-6, -7), 48.9 (t, C-2, -4, -5), 170.7 (s, 2 CO).

$$(\text{C}_9\text{H}_8\text{O}_3)_n (164.2)_n \quad \text{Calcd. C 65.83 H 4.91} \\ \text{Found C 64.54 H 5.05}$$

Poly(tetracyclo[1.1.1.0^{1,3}]pentane-alt-maleic acid monomethyl ester) (5b): To a suspension of **2** (500 mg) in methanol (250 ml) was added concentrated HCl (25 ml) whereupon the mixture warmed to 45°C . After 24 h at room temperature, the mixture had turned into a clear solution. After solvent removal, the polymer was dissolved in methanol and precipitated from this solution with chloroform, to give 550 mg (100%) of colorless copolymer **5b**. — $^1\text{H NMR}$ ($[\text{D}_4]\text{Methanol}$): $\delta = 1.0$ (br. s, 6H, 2-, 4-, 5-H₂), 2.72 (s, 2H, 6-, 7-H), 3.68 (s, 3H, OCH₃). The carboxylic proton could not be detected. — $^{13}\text{C NMR}$ ($[\text{D}_4]\text{Methanol}$): $\delta = 39.1$ (br. s, C-1, -3); 51.6 (t, C-2, -4, -5); 52.1 (q, OCH₃); 174.0, 174.6, 175.8, 176.4 (q, 2 CO). The carbon atoms C-6 and -7 absorb at $\delta \approx 46$. The signals are partially hidden by the solvent signal.

Poly(tetracyclo[1.1.1.0^{1,3}]pentane-alt-maleic acid dimethyl ester) (5c): To a suspension of **5b** (600 mg) in THF (100 ml) was added diazomethane (560 mg) dissolved in ether (50 ml). After 24 h at room temperature, acetic acid (10 ml) was added until the yellow color had disappeared. The polymer was obtained by precipitation from THF with low-boiling petroleum ether; yield 630 mg

(100%). — $^1\text{H NMR}$ (CDCl_3): $\delta = 1.59$ (s, 6H, CH₂), 2.68 (s, 2H, CH), 3.61 (s, 6H, OCH₃). — $^{13}\text{C NMR}$ (CDCl_3): $\delta = 38.4$ (s, C-1, -3), 46.7 (d, C-6, -7), 50.4 (t, C-2, -4, -5), 51.6 (q, 2 OCH₃), 172.5 (s, 2 CO).

$$(\text{C}_{11}\text{H}_{14}\text{O}_2)_n (210.2)_n \quad \text{Calcd. C 62.87 H 6.71} \\ \text{Found C 62.21 H 6.68}$$

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- ⁵⁾ Even in dilute solution propellane **1** forms high-molecular-weight copolymers, as long as acceptor-substituted olefins are used as comonomers (ref.²⁾).
- ⁶⁾ For example, see: R. K. Harris, "Nuclear Magnetic Resonance Spectroscopy", Pitman Books Ltd., London 1983. For a specific example, see: P. F. Barron, D. J. T. Hill, J. H. O'Donnell, P. W. O'Sullivan, *Macromolecules* **17** (1984) 1967.
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- ⁸⁾ J. Bode, H. Brockmann jr., *Chem. Ber.* **105** (1972) 34.
- ⁹⁾ Unfortunately, the $^{13}\text{C-NMR}$ spectra of *rac*- and *meso*-**3** (R = CH₃) do not provide additional stereochemical information since the methine carbon atoms of both compounds absorb isochronously in $[\text{D}_6]\text{DMSO}$.
- ¹⁰⁾ Such a signal pattern has never been observed in all of about 15 investigated cases (ref.²⁾).
- ¹¹⁾ Solutions of copolymer **2** in DMF led to a pressure increase on the SEC column rendering the results obtained unreliable and irreproducible.
- ¹²⁾ **4**: $^1\text{H NMR}$ (NaOD): $\delta = 1.54$ (s, 6H, 2-, 4-, 5-H₂), 2.50 (s, 2H, 6-, 7-H).
- ¹³⁾ Besides the two dominant signals at $\delta = 174.6$ and $\delta = 175.8$, the carbonyl region of the $^{13}\text{C-NMR}$ spectrum of the half ester **5b** shows two signals of low intensity at $\delta = 174.0$ and 176.4 which presumably are due to moieties with two acid and two ester functions, respectively.
- ¹⁴⁾ K. Blatter, A.-D. Schlüter, *Chem. Ber.* **122** (1989) 1351.

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