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Synthesis and characterization of amphiphilic comb-polymers via ring-opening metathesis polymerization of *exo,exo*-5,6-bis(alkoxymethyl)-7-oxabicyclo[2.2.1]hept-2-enes

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Summary

A number of *exo,exo*-5,6-bis(alkoxymethyl)-7-oxabicyclo[2.2.1]hept-2-enes (*exo,exo*-5,6-bis(alkoxymethyl)-7-oxanorbornenes) with long alkyl chains were prepared by reduction of the Diels-Alder adduct of furan and maleic anhydride, followed by alkylation with a series of different n-alkylbromides. These monomers were polymerized via ring-opening metathesis polymerization (ROMP) catalyzed by ruthenium trichloride in ethanolic solution. Contrary to a helical conformation as it was predicted by a previous molecular model study the poly(7-oxanorbornenes) adopt a coil conformation in solution. In bulk the materials show side chain crystallization.

Introduction

Recent publications by Novak and Grubbs [1,2] as well as from Feast and Harrison [3,5] have described the ring-opening metathesis polymerization (ROMP) of *exo,exo*-5,6-bis(methoxymethyl)-7-oxabicyclo[2.2.1]hept-2-ene using ruthenium trichloride as an effective catalyst in aqueous solution (reaction scheme1:1a). The resulting ROMP-polymer was found to have a high molecular weight ($M_n = 1.5 \times 10^5$; $M_w / M_n = 2.5$) and contains predominantly double bonds in E-configuration (trans).

Molecular model studies indicated that such poly(7-oxanorbornenes) could have the ability to form helical structures with all the ring-oxygen atoms facing into the interior of the helix (Figure1).

It was speculated that as a result of this macroconformation these polymers could act as acyclic ionophores or ion permeable membranes [1]. The introduction of long alkyl chains (1b-g) into the positions 5 and 6 of the 7-oxabicyclo[2.2.1]hept-2-ene system may stabilize the proposed helical structure of the resulting ROMP-polymer.

This paper describes the synthesis of a series of 7-oxanorbornenes with long alkyl chains (1b-g) and their polymerization via ring-opening metathesis polymerization catalyzed by ruthenium trichloride to the corresponding amphiphilic comb-like polymers. The poly(7-oxanorbornenes) (2b-g) are characterized by viscosity and

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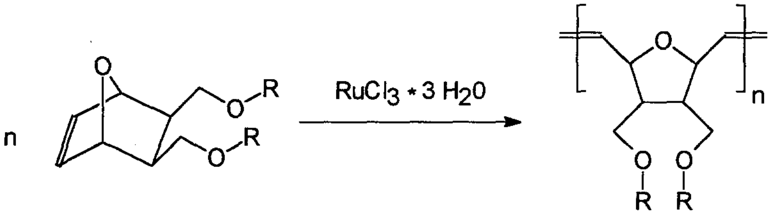
light scattering measurements to get an insight into their structure in solution. From DSC-experiments first indications on the bulk structure will be derived.



1

2

$R = -(CH_2)_m-CH_3$

m:
a) 0
b) 9
c) 13
d) 15
e) 17
f) 19
g) 21

Reaction scheme 1

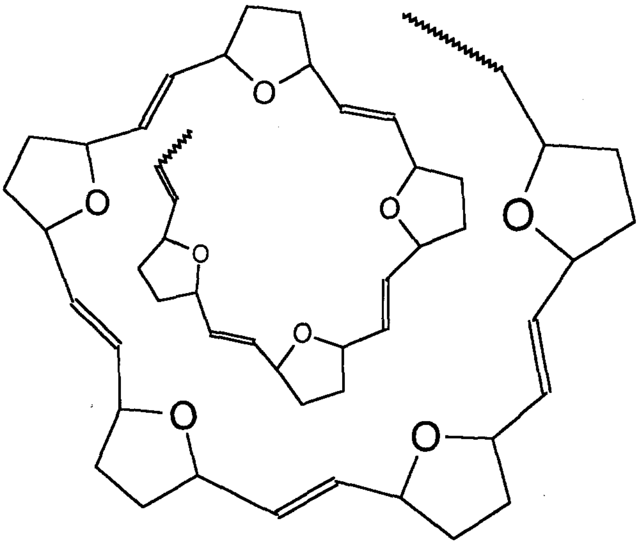


Figure 1: *Helical structure of poly(7-oxanorbornene) as suggested from molecular modelling calculations (according to [1]).*

Experimental

Materials:

Laboratory grade reagents, solvents and ruthenium trichloride were used as supplied. In order to calculate concentrations, the catalyst was assumed to be $RuCl_3 \times 3H_2O$.

Monomer synthesis:

Exo,exo-5,6-bis(hydroxymethyl)7-oxabicyclo[2.2.1]hept-2-ene was prepared via reduction of the Diels-Alder adduct of furan and maleic anhydride using $LiAlH_4$ as reducing agent and tetrahydrofuran as solvent (see reaction scheme 2) [1,5]. For the alkylation of the resulting diol 10 mmol *exo,exo*-5,6-bis(hydroxymethyl)7-oxabicyclo[2.2.1]hept-2-ene were dissolved in 100 ml dry dimethylformamide. For alkylation with long alkylbromides ($C_nH_{2n+1}Br$; n = 18, 20, 22) a mixture of dimethylformamide / tetrahydrofuran (3/1) was used as solvent to get better solubility of the alkylbromide. The reaction mixture is cooled to 0°C followed by addition of 22 mmol sodium hydride (80% suspension in paraffine). After stirring for 3 hours at room temperature 80 mmol of alkylbromide in 100 ml solvent is added. The reaction is stopped after 24 hours by the addition of a small amount of water. After evaporation of the solvent the product is purrified by chromatography through silica gel with a mixture of ethyl acetate and petroleum ether. The overall yield of *exo,exo*-5,6-bis(alkoxymethyl)7-oxabicyclo[2.2.1]hept-2-ene based on the Diels-Alder adduct of furan and maleic anhydride was about 50%.

Polymer synthesis:

Ring-opening metathesis polymerization (reaction scheme 1) was carried out at 55°C under a normal laboratory atmosphere and run for 3 days during which time the polymer precipitates from the reaction mixture. In general the polymerization was performed by adding an ethanolic solution of ruthenium trichloride to a stirred emulsion of the monomer in ethanol. Typical concentrations of the reactants were about 1.5 mmol monomer / ml ethanol and the molar ratio of monomer to ruthenium was 12/1. The solid polymeric products of each reaction were recovered by filtration, and purified by three succesive reprecipitations of a tetrahydrofuran solution into methanol. The resulting polymers were dried in vacuo for two days.The yields were between 60 and 70%.

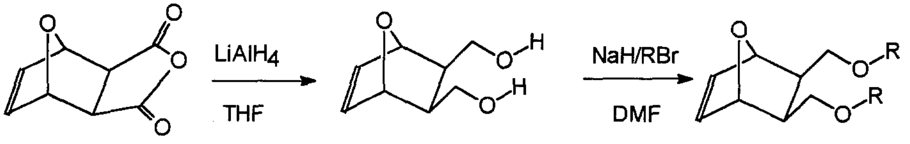
Analysis:

NMR-spectra were recorded using a Bruker AC 200 NMR-spectrometer (200MHz; $CDCl_3$). Gel permeation chromatography (GPC) was performed in tetrahydrofuran with a set of 10μm PL-Gel-columns (10^5, 10^4, 10^3 and 10^2 Å) with refractive index and UV detection at 254nm (calibration with PS-standards). Measurements of differential scanning calorimetry were recorded with a Perkin Elmer DSC-7. The static light scattering measurements were carried out using a SOFICA 42000 photogonio-diffusometer equipped with a 4 mW helium-neon-laser and computerized data accumulation (SLS-Systemtechnik). The experiments were performed in THF at 25°C (λ_0 = 632.8nm, angular range from 30° to 130° in steps of 5 degrees). The refractive index dn/dc was determined using a Brice-Phoenix differential refractometer. Viscosity measurements were carried out using a Schott AVS/G viscosimeter system.

Results and discussion

Monomer synthesis and characterization:

The synthesis of a series of *exo,exo*-5,6-bis(alkoxymethyl)7-oxanorbornenes was accomplished via reduction of the Diels-Alder adduct of furan and maleic anhydride followed by alkylation with a number of different n-alkylbromides as shown in reaction scheme 2. The monomers were characterized by ^1H- and ^{13}C-NMR-spectroscopy as well as by infrared-spectroscopy and elemental analysis. Figure 2a) gives a typical ^1H-NMR-spectrum of one of the monomers (R = $-(CH_2)_{13}-CH_3$).



Reaction scheme 2

The ^1H-NMR-spectra of the other di-n-alkyl substituted 7-oxanorbornenes show the same chemical shifts, only the intensity of the signal at 1.24 ppm, which is assigned to the long alkyl chains, varies with the length of these side chains.

Synthesis of ROMP-polymers and their characterization:

The schematic representation of the ring-opening metathesis polymerization of these monomers is outlined in reaction scheme 1. Polymerizations were carried out at 55°C in ethanolic solutions using $RuCl_3 \times 3H_2O$ as catalyst [1,2]. The ^1H-NMR-spectra of the ROMP-polymers differ from those of the corresponding monomers in the chemical shifts of the methine and vinylic protons of the bicyclo-ring system. The double bond of the polymers may have cis or trans configuration resulting in two resonances of the vinylic (trans: 5.72 ppm; cis: 5.52 ppm) and allylic protons (trans: 4.20 ppm; cis: 4.54 ppm) [3,4,5]. Integration of this region demonstrates that all polymers have predominantly trans double bonds (> 70%). The NMR-spectrum of the di-tetradecyl substituted poly(7-oxanorbornene) and the assignment of the observed resonances is outlined for demonstration (Figure 2b)). Molecular weights of the polymers as determined by gel permeation chromatography are summarized in Table 1.

The di-hexadecyl substituted 7-oxanorbornene (R = $-(CH_2)_{15}-CH_3$) was further analyzed by static light scattering. The absolute molecular weight was determined to 2×10^6 g/mol ($dn/dc = 0.081$; $\langle s^2 \rangle^{1/2} = 85$nm; $A_2 = 1.1 \times 10^{-4}$molxml/g^2)).

Viscosity measurements were carried out in different solvents to get further information about the solution structure. No significant differences in [η] were observed in toluene and tetrahydrofuran. This indicates that the polymers have an identical hydrodynamic behaviour in both solvents. This finding points for the same macroconformation in toluene and tetrahydrofuran, which is most probably a coil-conformation. We thus conclude that the two n-alkyl groups are not able to stabilize the proposed helical structure of poly(7-oxanorbornenes) in tetrahydrofuran or toluene.

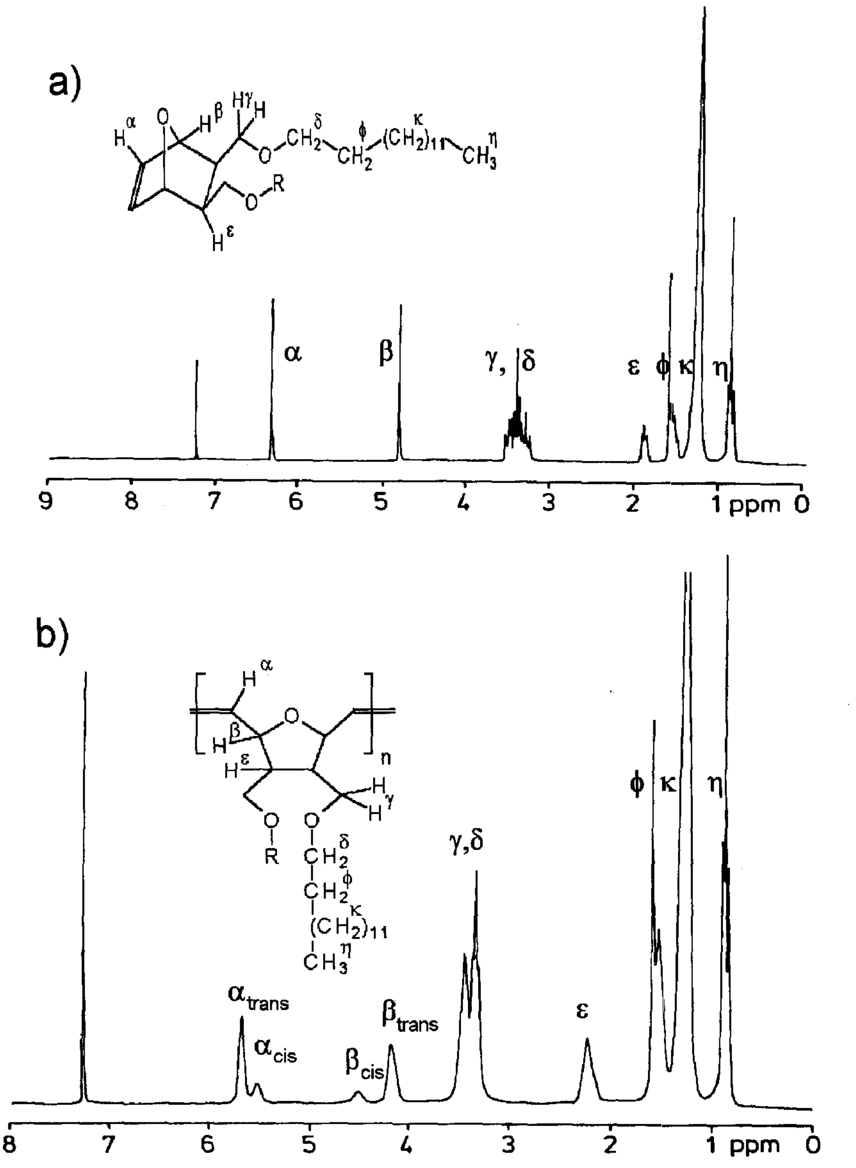
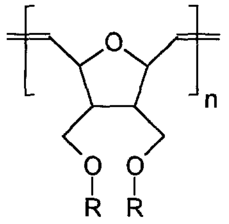


Figure 2: *200MHz-^{1}H-NMR-spectrum of exo,exo-5,6-bis(tetradecyloxymethyl)7-oxabicyclo[2.2.1]hept-2-ene (a) and the corresponding ROMP-polymer (b) in CDCl$_3$*

Table 1: *Molecular weights of poly(di-n-alkoxymethyl-7-oxanorbornenes) as determined by GPC (THF) using standard polystyrene calibration.*



R	M_n	M_w	M_w/M_n
$-(CH_2)_9-CH_3$	1.4×10^5	3.0×10^5	2.1
$-(CH_2)_{13}-CH_3$	2.8×10^5	6.1×10^5	2.2
$-(CH_2)_{15}-CH_3$	3.4×10^5	6.3×10^5	1.9
$-(CH_2)_{17}-CH_3$	4.2×10^5	9.3×10^5	2.2
$-(CH_2)_{19}-CH_3$	2.6×10^5	4.4×10^5	1.7
$-(CH_2)_{21}-CH_3$	2.8×10^5	5.3×10^5	1.9

First studies of the bulk behaviour were performed by differential scanning calorimetry (DSC). Figure 3 shows a typical DSC trace of the polymer with hexadecyl side chains. All polymers with alkyl chains (m>9) show narrow melting peaks in the DSC-measurements. The data are summarized in Table 2.

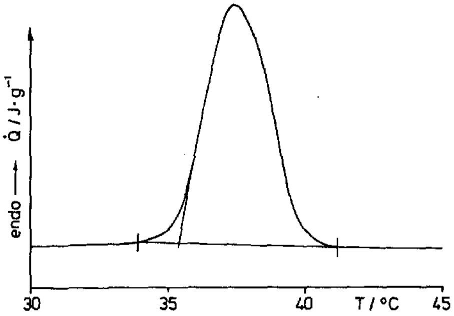


Figure 3: *DSC-trace of the hexadecyl substituted poly(7-oxanorbornene); heating rate 10K/min.*

Table 2: *Melting behavior of poly(di-n-alkoxymethyl-7-oxanorbornenes) in comparison to corresponding n-alkanes.*

R	T_m(onset)$^{1)}$	ΔH/alkyl chain kJ/mol	corresponding alkane	m.p. of corr. alkane
$-(CH_2)_9-CH_3$	-	-	$C_{10}H_{22}$	-29.7°C
$-(CH_2)_{13}-CH_3$	8.3°C	11.4	$C_{14}H_{30}$	5.86°C
$-(CH_2)_{15}-CH_3$	31.7°C	24.8	$C_{16}H_{34}$	18.17°C
$-(CH_2)_{17}-CH_3$	42.6°C	35.1	$C_{18}H_{38}$	28.18°C
$-(CH_2)_{19}-CH_3$	49.2°C	28.8	$C_{20}H_{42}$	36.80°C
$-(CH_2)_{21}-CH_3$	57.7°C	44.7	$C_{22}H_{46}$	44.40°C

1) extrapolated to heating rate 0°C/min

Figure 4 shows the melting points of the various polymers in comparison to the melting point of the corresponding n-alkanes as a function of the number of C-atoms per alkyl chain. The n-alkyl substituted poly(7-oxanorbornenes) show higher T_m than the corresponding n-alkanes.

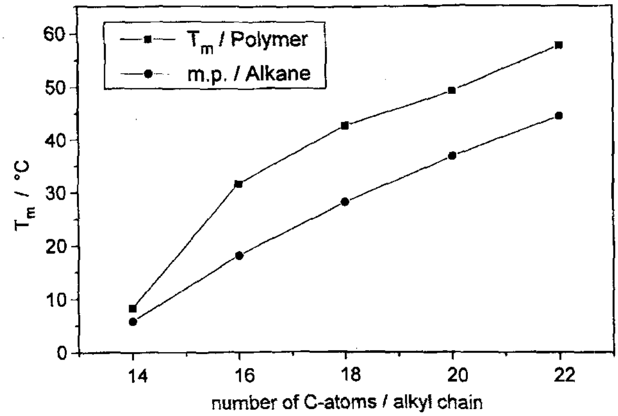


Figure 4: *Plot of T_m of n-alkyl substituted poly(7-oxanorbornenes) and m.p. of corresponding n-alkanes versus the number of C-atoms per alkyl chain.*

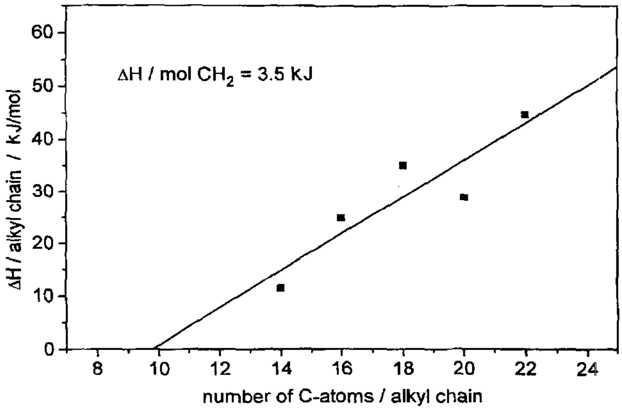


Figure 5: *Plot of ΔH as a function of the number of C-atoms per alkylchain.*

This behaviour is analogous to other comb polymers with long alkyl chains indicating that the observed melting of the poly(7-oxanorbornenes) corresponds to the crystallizing of the side chains [6]. This conclusion is supported by the analysis of the melting enthalpies. The melting enthalpies (in kJ/mol) are plotted in figure 5 as a function of the number of methylene units.

Within experimental uncertainity, the melting enthalpy increases linearly with m(CH_2). From the slope of this plot the contribution of each methylene unit to the melting enthalpy can be obtained. The value of 3.5 kJ/mol CH_2 is only slightly lower than the corresponding value reported for polyethylene (4.11 kJ/mol CH_2) [7]. These DSC data demonstrate that the incorporated n-alkyl chains cause not the organization of the main chain into the proposed helical structure (figure1). From the crystallization behaviour of the side chains a layer-like structure seems more plausible [8].

Conclusions

The di-n-alkyl derivatives of 7-oxanorbornene can be directly polymerized via ring-opening metathesis polymerization in ethanolic solutions using ruthenium trichloride as catalyst. The introduction of long alkyl chains into the poly(7-oxanorbornene) system shows no significant effect in stabilizing the previously proposed helical structure [1] in solution. Moreover the result of the viscosity measurements in toluene and tetrahydrofuran indicates a coil-conformation.

Differential scanning calorimetry shows that n-alkyl groups cause side chain crystallisation. The melting point of the synthesized poly(7-oxanorbornenes) can be controlled by the length of the n-alkyl side chains.

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