Oligomeric Branched Polyethers with Multiple Hydroxyl Groups by Cationic Ring-Opening Polymerization for Inorganic Surface Modification

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Summary: Cationic ring-opening polymerization of cyclic ethers (also esters and acetals) substituted with hydroxyl groups leads to branched multihydroxyl polymers. When 4-membered hydroxysubstituted oxetanes or 5-membered hydroxysubstuituted oxolanes (or lactone and 1,3-dioxolane) are used as monomers the polymerization products have limited molecular weights (about 1000). Polymerization of these monomers leading *in situ* to oligomeric products was used for inorganic surface modification. Successful polymerizations of oxetane as well as considered as difficult to polymerize 5-membered hydroxysubstituted cyclic monomers initiated from montmorillonite clay and silica nanoparticles surfaces were performed.

Keywords: branched polyethers; ring-opening polymerization; surface modification

Introduction

During the last two decades multifunctional branched polymers has gained much attention because of their physical properties originating from the compact, globular structure and multiplicity of end groups. Different methods of the synthesis were developed, most of them were based on the polycondensation of AB_x type monomers but large group of branched products were also obtained by chain polymerizations, that is self condensing vinyl polymerization (SCVP)[1] or ring-opening polymerization of the ‘‘latent AB_x’’ monomers.[2] The application of ring-opening polymerization of cyclic monomers allows for the synthesis of branched polymers which couldn't be obtained using another method as e.g. branched, multihydroxyl polyethers.

Presented work concerns the synthesis of branched multihydroxyl polyethers on the inorganic surfaces by using cationic ring-opening polymerization of cyclic ethers substituted with hydroxyl groups. Cationic homo- and copolymerization of this group of cyclic compounds was investigated by us in recent years. Cationic polymerization of cyclic ethers in the presence of hydroxyl groups proceeds by activated monomer mechanism (AM)[3] of propagation, which is competitive to known active chain end mechanism (ACE). According to AM mechanism at acidic conditions monomer molecule undergoes protonation and the protonated monomer reacts with hydroxyl group at the end of growing macromolecule.

When growing macromolecule contains many hydroxyl groups, all these groups are involved in propagation process, leading to branched product.

The situation presented in the scheme above occurs in the case of using cyclic monomers which contain –OH group in their own molecule, that is monomers of ‘‘latent AB_2’’ type (generally AB_x type). As it was already stated, polymerization of such monomers leads to branched products and is often named ring-opening multibranching polymerization (ROMBP).[4]

The simplest cyclic ether of AB_2 type is 3-membered glycidol (2-hydroxymethylox-

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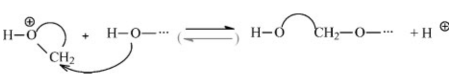


Scheme 1.

irane). This monomer containing strained, reactive 3- membered ring may be polymerized by cationic as well as by anionic mechanisms. Both types of polymerizations, leading to similar branched products were investigated, but this is an anionic process which was explored deeply and described in more detail.

In the present work we applied the ring-opening multibranching polymerization to the monomers containing larger 4- and 5-membered rings, that is monomers which can be polymerized only cationically, for the modification of surfaces of inorganic materials for example montmorillonite and silica nanoparticles.

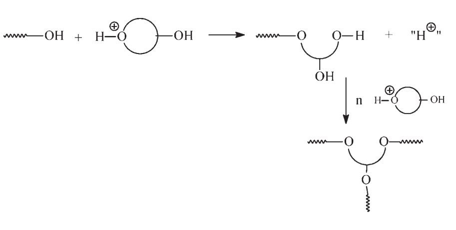
Experimental Part

Materials

Monomers

Hydroxysubstituted oxetanes (EHMOX, BHMOX, diHO-diOX) were synthesized according to the procedures described in Ref. [5a, 5c, 5d], hydroxysubstituted 5-membered monomers (2-$HOCH_2$-THF, 4-$HOCH_2$-DXL, 3-HO-THF, 3,4-diHO-THF, BL-OH) were purchased from Aldrich and used after vacuum distillation.[8,9] Polymerization catalysts (CF_3SO_3H, $BF_3 \cdot Et_2O$, $HBF_4 \cdot Et_2O$, $SnCl_4$ and $(CF_3SO_3)_3Sc$, Aldrich) were used as supplied. Solvents were distilled before use.

CLOISITE-Na (being a montmorillonite clay with sodium cations in the interlayer spaces) was obtained from Southern Clay Products (Gonzales, TX).



Scheme 2.

Polymerization of Oxetanes

Polymerizations of EHMOX were performed in bulk or in solvent in the presence of acidic catalysts under argon atmosphere. Solid, brittle product of bulk polymerization was purified by extraction (Soxhlet apparatus) with CH_2Cl_2. Powdered product of solution polymerization was washed with methanol. Polymerization of BHMOX and its copolymerization with EHMOX were performed in bulk, products were purified by extraction of low molecular compounds with hot methanol. Copolymerization of diOH-diOX with EHMOX was performed in CH_2Cl_2, product which precipitated from reaction mixture was washed with methanol. Detailed descriptions of polymerization processes are given in the Ref.[5b-5d].

Polymerization of 5-membered Cyclic Ethers, Ester and Acetal

Polymerizations of 2-$HOCH_2$-THF, 3-HO-THF, 3,4-diHO-THF, BL-OH and 4-$HOCH_2$-DXL were performed according to the procedures described in the Ref. [8,9]. Bulk polymerizations were performed in the presence of about 5–10 mol% of catalyst (CF_3SO_3H or $BF_3 \cdot Et_2O$; BL-OH was additionally polymerized in the presence of $HBF_4 \cdot Et_2O$, $SnCl_4$ and $(CF_3SO_3)_3Sc$). After the time from 24 h to 240 h, polymerizations were finished by neutralization of polymerizing mixtures with about 10 wt.% of CaO. Polymers were separated after diluting with CH_2Cl_2, filtering and evaporating of solvent.

Polymerization in the Presence of Montmorillonite

In order to generate acidic sites inside interlayer spaces, montmorillonite clay was activated by stirring in 0.25 M aqueous solution of sulfuric acid for two days (5 g of clay in 40 ml of solution). Next the clay was washed four times with distilled water (each time, a clay was separated on a centrifuge). Polymerizations were performed by vigorous stirring of about 1 g of clay with about

4 g of monomer at 60 °C during 4 days under nitrogen. Modified clay was separated after washing 4 times with THF with the subsequent centrifugation and was dried for 8 hours on vacuum line.

Measurements

^{1}H and ^{13}C NMR spectra were recorded with a Bruker 200-MHz spectrometer.

SEC analysis was carried out according to the conditions described in Ref. [4b-5d] using CH_2Cl_2 or THF as eluent and polystyrene standards for calibration.

MALDI-TOF spectra were recorded with a Voyager Elite apparatus with dihydroxybenzoic acid as a matrix and NaI as a cationating agent. Nitrogen laser desorption at a wavelength equal to 337 nm was applied.

TGA analysis was performed using THA Perkin-Elmer instrument at a heating rate 20 °/min, from 0 to 800 °C in air.

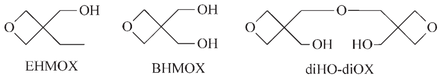
XRD measurements were performed in the transmission mode in the 1.2° to 10° range of 2θ, with wide-angle goniometer coupled with source of CuK_α radiation, operating at 50kV and 30mA (Philips PW3830).

Results and Discussion

Oligoethers Obtained by Polymerization of 4-membered Hydroxyoxetanes

3-Ethyl-3-hydroxymethyloxetane (EHMOX) containing strained 4-membered ring, as well as its analogues such as BHMOX or diHO-diOX, polymerize easily in bulk or in solution in the presence of protonic (CF_3SO_3H) and Lewis acids ($BF_3 \cdot Et_2O$).[5,6]

^{13}C NMR spectra of the obtained products allowed the confirmation that branched polymers were indeed formed. In the ^{13}C NMR spectra signals coming from linear, branched, and terminal units were well separated (after esterification with $(CF_3CO)_2O$). Determined DB (degree of branching) values were about 0.25.



Scheme 3.

Unfortunately the molecular weights of the obtained products were limited to about 1000–1500 independently on the conditions used for the polymerization, and the polymerization time. In the Table 1 some results of the polymerization of EHMOX are presented.

In order to explain the reasons of the limitation of the macromolecules growth during polymerization an attempts to explain the mechanism of the process were undertaken. Investigation of the nature of the active centers present in the polymerizing system by the phosphorus ion trapping method[7] allowed for the identification of secondary and tertiary oxonium ions which are characteristic for propagation by AM and ACE mechanisms respectively indicating that polymerization proceeds with the participation of both mechanisms.

MALDI TOF mass spectrometry together with ^{1}H NMR analysis allowed for the determination of the structure of the individual macromolecules. In MALDI TOF spectra only the signals corresponding to the macromolecules being multiplicity of monomeric units (i.e. without additional ends from the initiation and termination) were present. From ^{1}H NMR spectra it was evident that the macromolecules didn't contained oxetane ring. The reasonable conclusion was that the macromolecules must be cyclic (or contain cyclic fragment). The ring closure proceeds as a result of intramolecular chain transfer reaction with participation of any of hydroxyl groups present in the growing macromolecule with terminal oxetane ring from initiation by AM mechanism or oxonium ion of the macromolecule propagating by ACE mechanism (Scheme 4).

After reaching certain size (DP_n ~12) due to increasing number of hydroxyl groups in the macromolecule chain transfer to polymer is becoming dominant and the macromolecule stops to grow. This ring closure is facilitated by strong

Table 1.
Dependence of molecular weight of polyEHMOX on polymerization conditions.[5b]

Polymerization conditions	Monomer conversion, %	Mn (GPC, polystyrene)
Bulk, 25 °C, $[BF_3 \cdot Et_2O]_0 = 3.2 \cdot 10^{-3}$ mol · L^{-1}		
15 min.	11	1390
5 h	25	1480
48 h	80	1470
Bulk, 25 °C, $[CF_3SO_3H]_0 = 5 \cdot 10^{-3}$ mol · L^{-1}		
48 h	68	1250
Chloroform, 25 °C*	90	900
Chloroform, 60 °C*	98	950
o-dichlorobenzene, 60 °C*	~90	1120

*$[M]_0 = 2.15$ mol · L^{-1}, $[BF_3 \cdot Et_2O]_0 = 2 \cdot 10^{-2}$ mol · L^{-1}, 48 h

intramolecular hydrogen bonding (detected by IR) between multiple hydroxyl groups.[5e]

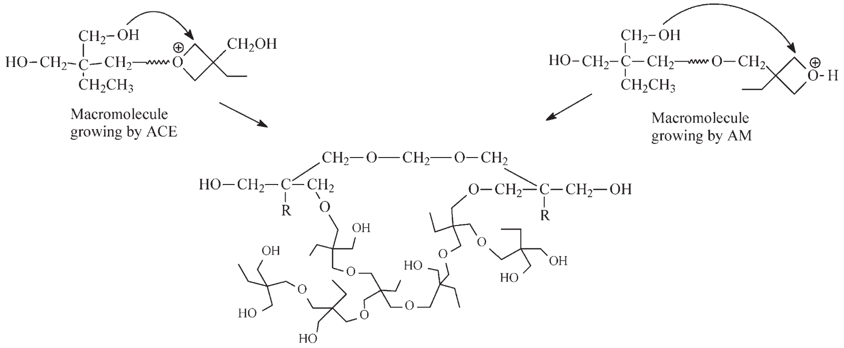
The limitations with reaching higher molecular weights and higher degree of branching of the polyethers based on the oxetane monomer could be to some extent overcome by copolymerization of EHMOX with dihydroxysubstituted oxetane (BHMOX)[5c] or with dihydroxysubstituted dioxetane (diHO-diOX) respectively.[5d]

Oligoethers Obtained by Polymerization of 5-membered Hydroxysubstituted Cyclic Ethers (Esters, Acetals)

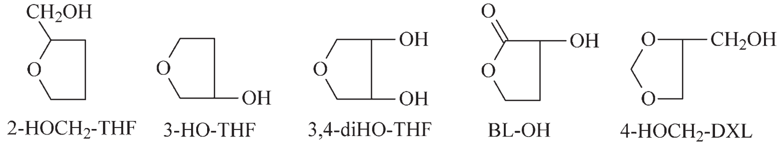
Polymerization of 5-membered cyclic compounds may be difficult because of low ring strain and consequently reversible character of the propagation. The presence of substituents additionally reduces thermodynamic polymerizability. In spite of these limitations the choice of 5-membered cyclic ethers, (or esters and acetals) containing hydroxyl groups as monomers for polymerization seemed to be attractive because some of those compounds are derived from renewable resources. In Scheme 5 the compounds which were chosen for the polymerization are presented.

Bulk polymerizations of those monomers performed in the presence of protonic acid (CF_3SO_3H) and Lewis acid ($BF_3 \cdot Et_2O$) as catalysts at the temperature range 25–90 °C resulted in low molecular weight products with M_n of about few hundreds to 1000.[8–10] The general feature of the polymerization of the whole group of investigated 5-membered cyclic monomers appeared to be the dehydration reaction occurring with participation of hydroxyl groups.

This dehydration leads to the formation of unsaturated groups from one side and, unfortunately, to the reduction of the total number of hydroxyl groups from the other side. The determination of the number of



Scheme 4.



Scheme 5.

hydroxyl groups in respect to the theoretical value indicated the loss of about 40% of −OH groups.

The dehydrated macromolecules were detected in the polymerization products using MALDI TOF MS analysis. Figure 1 presents MALDI TOF spectrum of poly-(2-HOCH$_2$-THF).

Possible Applications of Multihydroxyl Branched Oligoethers as Inorganic Surface Modifiers

The formation of a stable dispersion of inorganic filler in polymer matrix is important for the final properties of nanocomposites. To improve the compatibility of inorganic and polymeric materials, surface modification by *in situ* polymerization initiated by the groups connected to the inorganic surface is often used (''grafting from'' method).

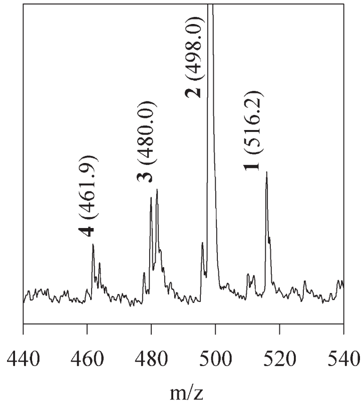


Figure 1.
MALDI TOF spectrum of poly(2-HOCH$_2$–THF)[8]; polymerization conditions: [monomer]/[catalyst] =10, temperature = 60 °C, time = 240 h. The region corresponding to pentamers is presented:
1: $m/z = 5 \times M - 18 + 23 = 515.65$
2: $m/z = 5 \times M - 2 \times 18 + 23 = 497.65$
3: $m/z = 5 \times M - 3 \times 18 + 23 = 479.65$
4: $m/z = 5 \times M - 4 \times 18 + 23 = 461.65$
M = mass of 2-HOCH$_2$-THF = 102.13
23 – mass of Na$^+$
18 – mass of H$_2$O.

Oligoethers with limited molecular weights produced in the present work may be useful as thin polymeric layers changing the inorganic surface properties. The ''inside'' of branched polyether macromolecule is rather hydrophobic while terminal hydroxyl groups are hydrophilic. Depending on the type of monomer used (4- or 5-members hydroxysubstituted cyclic ether) polymerization may proceed without or with dehydration thus branched polyethers containing different fractions of terminal hydroxyl groups may be obtained.

Terminal hydroxyl groups may be further transformed into another groups or may be used as initiating groups for subsequent polymerization leading to additional modification. The multiplicity of functional groups in branched polymers applied for the surface modification may thus offer significant advantage in comparison with the modification with linear polymers. By changing functionality of the surface of inorganic material, one may achieve desired interaction with different polymer matrices (hydrophilic or hydrophobic).

Organophilization of Montmorillonite

Layered silicates such a montmorillonite are commonly used as fillers to improve mechanical and barrier properties of different polymeric materials. The hydrophilic nature of silicates makes difficult their homogeneous dispersion in the organic polymer matrix. To make silicates more organophilic, cationic surfactants being long chain alkyl ammonium or alkyl phosphonium salts, are introduced into the interlayer space (galleries) of silicates.[11] This modification should facilitate intercalation and exfoliation processes.

We decided to use hydroxyl groups naturally present in the galleries of montmorillonite to initiate polymerization of hydroxysubstituted cyclic ethers (acetals). We used for this purpose 4-membered 3-ethyl-3-hydroxymethyloxetane (EHMOX) as well as 5-membered 2-hydroxymethyltetrahydrofuran - cyclic ether (2-HOCH$_2$-THF) and 4-hydroxymethyl-1,3-dioxolane - cyclic acetal (4-HOCH$_2$-DXL). Because polymerization of those monomers gives only low molecular weight oligomers, a formation of thin layers of polymeric material within interlayer space could be achieved and premature exfoliation should be avoided. It may be expected that when modified montmorillonite was used as filler for e.g. polylactide, polyether layer should have better affinity to polylactide which should facilitate the exfoliation. From the other side, the application of 5-membered monomers for polymerization which give oligomers with reduced number of hydroxyl groups may appear advantageous for hydrophobic matrix.

Figure 2 presents the idea of the *in situ* polymerization. Hydroxyl groups present on the surfaces of silica platelets could act as initiating groups for *in situ* polymerization of low molecular weight monomer (easy to insert into interlayer spaces). The presence of oligomeric molecules should increase the basal plane spacing from one side, and should facilitate introducing of the polyester macromolecules of polymer matrix of target hybrid nanocomposite.

The bulk polymerizations of 5-membered cyclic ether 2-HOCH$_2$-THF and cyclic acetal 4-HOCH$_2$-DXL as well as 4-membered EHMOX in the presence of montmorillonite clay CLOISITE-Na activated earlier with sulfuric acid were performed. The double modification – first by 2-HOCH$_2$-THF polymerization followed by subsequent cationic polymerization of lactide was also performed. The activation of the silica layers causes that they act not only as support for initiating groups but also contain catalytic (acidic) sites. Montmorillonite clay was analyzed before and after modification using TGA and XRD analysis. In the Table 2 the results of the montmorillonite modification are presented. The last position in the Table concerns typical organophilization by ammonium salt which is presented for comparison.

The increase of the distances between galleries was clearly observed. That should facilitate the intercalation and next the exfoliation processes during the preparation of polylactide/montmorillonite composites. The investigation of the morphologies of the composites as well as their physical properties is in progress.

Organophilization of Silica Nanoparticles

The possibility of modification of the surface of inorganic materials by ROMBP involving 5-membered cyclic ethers containing hydroxyl groups was further confirmed by modification of silica nanoparticles.

Silica-polymer hybrid materials are the most often reported in the literature among the different inorganic-organic hybrids. Silica nanoparticles may be used as fillers in the paints and rubber products. Then the improvement of the compatibility of the polymer matrix with particle surface is very

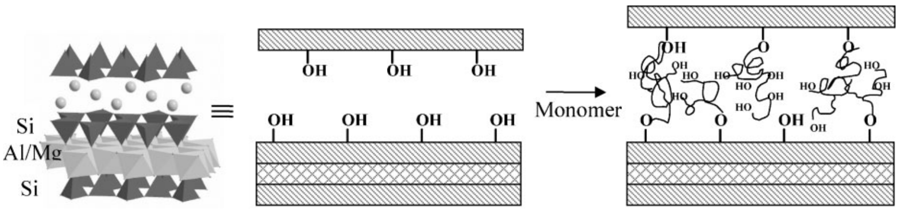


Figure 2.

Schematic representation of the ROMBP from the montmorillonite surfaces.

Table 2.
The results of CLOISITE-Na modification.

No	Modification with	Increase in mass, mass %; TGA	Interlayer distance Å; XRD
1	Oryginal clay with Na^+ cations		11.95
2	Poly(THF-CH_2OH)	10	14.15
3	Poly(DXL-CH_2OH)	10	14.78
4	Poly(EHMOX)	14	14.72
5	Poly(THF-CH_2OH) + polyLA	24	18.40
6	Typically used ammonium salt		18.40

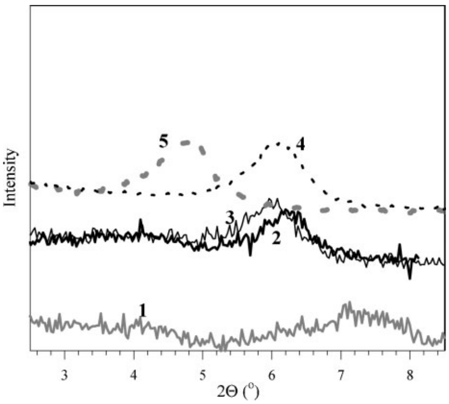
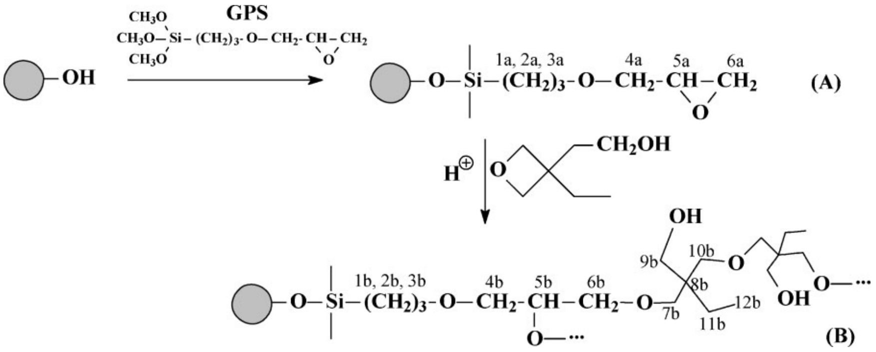


Figure 3.
XRD spectra of CLOISITE-Na before and after modification by polymerization of different monomers. Numbers on the plots correspond to the numbers in the Table 2.

important and may be achieved by grafting polymer chains modifying hydrophobic/hydrophilic properties. Another possible applications of organically modified silica nanoparticles are stationary chromatography phases or heterogeneous supported catalysts. Surface initiated polymerization from silica nanoparticles may be accomplished by different methods (free radical, ionic, ring-opening, controlled radical techniques). In most cases the first step of the modification involves formation of an initiator layer on the silica surface followed by polymerization.

There were only few attempts of ring opening polymerization of AB_x type monomers leading to branched polymer layer on the silica nanoparticles.[12] In the present work, we polymerized hydroxysubstituted oxetane (EHMOX) after functionalization of nanoparticles with 3-glycidoxypropyl trimethoxysilane (GPS).[13] The applied procedure is depicted in the Scheme 6.

The increase of the mass of the sample by about 20 mass% of the used SiO_2-GPS (A) was observed after polymerization of EHMOX performed in CH_2Cl_2 in the presence of SiO_2-GPS and trifluoromethanesulfonic acid as catalyst. To ensure the total removing of poly(EHMOX) not chemically bound to the silica surface, the modified nanoparticles were 5 times washed with THF and centrifuged. The



Scheme 6.

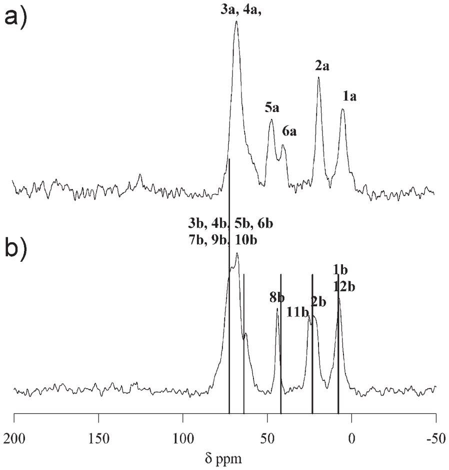


Figure 4.
^{13}C CP MAS spectrum of SiO_2 nanoparticles after functionalization with GPS (a) and after subsequent polymerization of EHMOX (b) (Vertical lines represent simulated ^{13}C NMR spectrum of poly(EHMOX)).

presence of GPS fragments and poly(EHMOX) macromolecules on the silica surface was confirmed by the ^{13}C CP MAS analysis. Figure 4 presents corresponding spectra.

Conclusions

Cationic ring-opening multibranching polymerization (ROMBP) of 5-membered cyclic ethers and acetals containing hydroxyl group as substituent may be applied for the modification of surfaces of inorganic materials including clay minerals or silica. For such applications, the limited molecular weights of corresponding branched polymers may be an advantage as in the case of montmorillonite modification when polymerization within interlayer galleries leads to increase of interlayer distances without premature exfoliation.

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