Synthesis of New Glycerol-Based Hyperbranched Polycarbonates

Paweł G. Parzuchowski,* Michał Jaroch, Mariusz Tryznowski, and Gabriel Rokicki

Faculty of Chemistry, Warsaw University of Technology, Noakowskiego 3, 00-664 Warszawa, Poland

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ABSTRACT: This paper describes the synthesis of a new cyclic carbonate AB_2 type monomer, 5-{3-[(2-hydroxyethyl)thio]propoxy}-1,3-dioxan-2-one (**5**), and its application for preparation of hyperbranched polymers. In addition, a linear analogue of poly(**5**) was prepared, and the structures were compared by means of ^{13}C NMR. Ring-opening polymerization of **5** leads to a polymer containing solely primary hydroxyl groups. The influence of the catalyst and reaction conditions used for the polymerization on the structure of the polymer is discussed. Moreover, the presence of glycerol and carbonate residues in the repeating unit makes the polymer potentially biodegradable and biocompatible—promising material for drug delivery. The application of free-radical addition of mercaptoethanol to allyl bonds simplified the synthetic route and allowed the use of hyperbranched polymer (HBP) with thioether groups as potential host molecules for transition metal cations (Cr, Rh) complexation.

Introduction

Hyperbranched polymers (HBPs), highly branched, three-dimensional molecules, have gained widespread attention in the past decades.[1−4] HBPs possess several unique features such as high number of reactive sites, low viscosity, and high solubility which are characteristic for dendrimers. However, dendrimers demand tedious multistep synthetic procedures. In contrary, HBPs are usually produced in simple one-step procedures. This makes hyperbranched polymers a good alternative to dendrimers for chemists, biochemists, biologists, and biomedical experts.[5]

So far, there is still a relatively low number of monomers used for the preparation of hyperbranched polymers described in the literature. Among them, the most popular and well investigated are polyglycidol[6] and polymers based on 2,2-bis-(hydroxymethyl)propionic acid.[7] In this group of HBPs the main interest is placed in finding new applications and properties of the products obtained by copolymerization with other monomers. Sunder et al. obtained hyperbranched block copolymers of glycidol and propylene oxide of controlled hydrophilicity and low molecular weight distributions.[8] Polyglycidol−poly-(ethylene glycol) nanoparticles were used as RNA carriers, protecting it from enzymatic degradation.[9] Glycidol was also copolymerized with lactide leading to linear and hyperbranched architectures.[10] Other glycidol-based hyperbranched polymers (epoxy[11] or cyclic carbonate[12] functionalized) were successfully applied as liquid rubbers for epoxy resin toughening. The polyglycidol structure was also obtained from a more environmentally friendly monomer: glycerol carbonate.[13] A 2,2-bis(hydroxymethyl)propionic acid structure has been incorporated into a variety of new monomers which were then used for the preparation of hyperbranched polymers[14,15] or used as a branching point in a HB polylactide structure.[16]

Aromatic hyperbranched polymers are mainly polyesters,[17] including polycarbonates,[18] but there were also polyethers,[19] polystyrenes,[20] poly(phenylene sulfide), poly(phenylene sulfone),[21] and poly(hydroxy ether)[22] reported.

Recently, two 1,4-dioxan-2-one derivatives were also used for the preparation of water-soluble hyperbranched polyesters via ring-opening polymerization.[23,24]

The role of biodiesel as an alternative, ecologically more friendly fuel has increased considerably within the past years. During the fuel production glycerol is formed in large quantities. It becomes a nonexpensive and easily available starting material for the synthesis of new monomers and polymers.

* Corresponding author. E-mail: pparzuch@ch.pw.edu.pl.

The aim of this work was the synthesis of a new glycerol-based heterocyclic AB_2 monomer and its application for the preparation of a new carbonate-based hyperbranched polymer.

Experimental Section

Materials. Allyl chloride, benzaldehyde, ethyl chloroformate, 2-mercaptoethanol, 1-hydroxycyclohexylphenyl ketone (Irgacure 184), and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) were purchased from Aldrich Chemical and used as received. Solvents were purchased from POCh (Gliwice, Poland) and dried prior to use, except for ethyl ether, which was used as received. Glycerol (POCh) was pretreated by azeotropic water removal with toluene. Stannous octoate was a gift from LPT (Warsaw, Poland) and was purified as described in ref 25. Compounds **1**[26] and **2**−**3**[24] were synthesized according to the literature procedures.

Instrumentation. IR spectra were recorded on a Biorad FTS 165 FTIR spectrometer as KBr pellets. UV−vis spectra were registered using a Cary 5000 (Varian) spectrometer. ^1H NMR and ^{13}C NMR spectra were recorded on a Varian VXR 400 MHz spectrometer using tetramethylsilane as an internal standard and deuterated solvents ($CDCl_3$, DMSO-d_6). FD-mass spectra were recorded on a Finnigan MAT 8230; MALDI-TOF spectra were recorded on a Bruker-Biflex III (Leipzig, Germany) apparatus. Molecular weight measurements were performed with GPC LabAlliance apparatus using chloroform as an eluent at 35 °C and using polystyrene for the calibration. The light-induced reactions were performed with medium-pressure mercury lamp PLK type 5 (80 W) supplied by the Electrotechnical Institute (Warsaw, Poland) over the following frequency ranges: 100−280 nm (maximum 10% absorption), 280−314 nm (minimum 30% absorption), 315−380 nm (minimum 50% absorption).

Synthesis of 5-Allyloxy-1,3-dioxan-2-one (4). In a 500 mL three-neck flask equipped with a magnetic stirrer, nitrogen inlet, and a thermometer 5.95 g (45 mmol) of a diol **3** was dissolved in 300 mL of freshly distilled THF. The solution was cooled to −20 °C, and then 8.6 mL (90 mmol) of ethyl chloroformate was added. The mixture was stirred for 20 min at −20 °C. Then 12.6 mL (90 mmol) of triethylamine was added dropwise, maintaining the temperature below −15 °C. The reaction mixture was allowed to warm to room temperature and then stirred for an additional 1 h. The precipitate of triethylamine hydrochloride was filtrated off and washed with THF. Combined filtrates were evaporated to dryness. The product was purified by column chromatography (silica gel, ethyl acetate, $R_f = 0.3$). 5.09 g (71%) of **4** was obtained as a colorless oil. ^1H NMR ($CDCl_3$, 400 MHz): δ (ppm) = 5.95−5.83 (m, 1H, −C*H*=), 5.35−5.27 (m, 1H, =CH_2), 5.26−5.21 (m, 1H, =CH_2), 4.47−4.45 (d, 4H, CH_2O, $J = 2.5$ Hz), 4.12−4.08 (m, 2H, CH_2), 3.90−3.86 (m, 1H, C*H*O). FT-IR (cm^{-1}) = 3068 (CH_2=),

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3036 (CH_2=), 1736 (C=O), 1117 (C−O−C). UV−vis (film) (nm) = 230, 200. MS (FD) *m*/*z* 158.3 (M^+).

Synthesis of 5-{3-[(2-Hydroxyethyl)thio]propoxy}-1,3-dioxan-2-one (5). 3.43 g (22 mmol) of **4** was placed in a glass reactor covered with a PMMA cover equipped with a nitrogen inlet and magnetic stirrer. 0.0686 g (0.34 mmol) of Irgacure 184 was added, followed by 8.57 g (0.1084 mol, 7.7 mL) of 2-mercaptoethanol. The reaction mixture was stirred under nitrogen for 2 h under a UV lamp at 0 °C. The reaction progress was monitored by FT-IR spectroscopy at 3068 and 3036 cm^{-1} (disappearance of the bands). The product was isolated by column chromatography (silica gel, ethyl acetate, $R_f = 0.2$). 2.67 g (52%) of **5** was obtained as a pale yellow liquid. ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) = 4.54−4.41 (m, 4H, OCH_{2cycl}), 3.84−3.80 (m, 1H, CHO_{cycl}), 3.73 (t, 2H, OCH_2, J = 6.0 Hz), 3.66 (t, 2H, OCH_2, J = 5.9 Hz), 2.73 (t, 2H, SCH_2, J = 6.0 Hz), 2.65 (t, 2H, SCH_2, J = 6.9 Hz), 1.95−1.85 (m, 2H, $CH_2CH_2CH_2$), 1.89 (s, 1H, O*H*). ^{13}C NMR ($CDCl_3$, 400 MHz): δ (ppm) = 148.2 (C=O), 70.0 ($CH_{2\,cycl}$), 67.4 (CHO_{cycl}), 67.0 (OCH_2), 60.8 ($HOCH_2$), 35.4 (SCH_2CH_2OH), 29.7 (CH_2), 28.3 (SCH_2). FT-IR (cm^{-1}) = 3407 (OH), 2922 (CH), 2874 (CH), 1736 (C=O), 1115 (COC). UV−vis (methanol) (nm) = 225, 195. MS (FD) *m*/*z* 236.1 (M^+).

Polymerization of 5-{3-[(2-Hydroxyethyl)thio]propoxy}-1,3-dioxan-2-one (5). *Bulk polymerization:* 0.18 g (0.76 mmol) of **5** was placed in a vial equipped with a magnetic stirrer and a Teflon seal followed by the addition of the catalyst: $Sn(Oct)_2$or DBU (1.9 μmol) in toluene solution. The solvent was removed under reduced pressure. Samples were flushed with nitrogen for 5 min, and the vial was closed and heated in an oil bath at 75−110 °C. The reaction mixture was stirred at this temperature for 72 h. The resulting polymer (**P1**−**P3**) was analyzed without further purification.

Solution polymerization: 0.13 g (0.55 mmol) of **5** was placed in a vial equipped with a magnetic stirrer and a Teflon seal followed by the addition of the catalyst: $Sn(Oct)_2$ (1.4 μmol) or DBU (2.8 μmol) or DMAP (2.8 μmol) in toluene solution addition. The solvent was removed under reduced pressure, and 0.5 mL of toluene or chloroform was added. The solution was flushed with nitrogen for 5 min, and the vial was closed and heated in an oil bath at 80 °C for toluene or 60 °C for chloroform. The reaction mixture was stirred at this temperature for 18−20 h. The resulting polymer (**P4**−**P11**) was analyzed without further purification.

Polymerization of 5-Allyloxy-1,3-dioxan-2-one (4). 0.131 g (0.83 mmol) of 5-allyloxy-1,3-dioxan-2-one (**4**) was placed in a round-bottom flask, followed by 1.1 mg (1.4 μmol) of 1,3-propanediol and 1.9 mg (1.4 μmol) of DMAP as 0.3 M ethyl acetate solutions. The solvent was removed under reduced pressure. The reaction mixture was flushed with nitrogen and closed with a Teflon sealed cap. Polymerization was carried out at 65 °C for 24 h. The polymer (**Poly(4)**) was used without further purification.

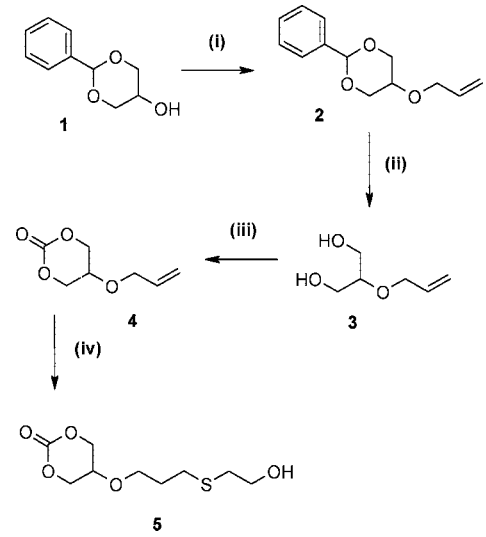
Reaction of 2-Mercaptoethanol with Poly(4). To the flask containing 0.12 g of poly(**4**), 2.7 mg of Irgacure 184 was added followed by 1.5 mL of mercaptoethanol. The reaction mixture was placed under UV lamp irradiation for 1.5 h and kept under nitrogen. The excess of mercaptoethanol was removed under vacuum. The remains of mercaptoethanol were removed by multiple addition and evaporation of chloroform.

Hydrolysis/Degradation. Polymer samples were placed in an oven in open vessels at 120 °C for 24 h, and the resultant liquid product was analyzed.

Results and Discussion

Monomer Synthesis. Because of the growing biodiesel production, large amounts of glycerol are expected to be available at the market. This work presents one of the possible applications of glycerol for the synthesis of degradable, hyperbranched polymers. These polymers, due to the advantages mentioned in the Introduction, could be a good material for drug delivery as well as host molecules for complexation of transition metal and silver ions.[27] Scheme 1 shows the synthetic pathway toward the new monomer: 5-{3-[(2-hydroxyetyl)thio]propoxy}-1,3-dioxan-2-one (**5**). Starting acetal **1** was synthesized according to the literature procedures from glycerol and benzaldehyde.[26] In this process a mixture of products is formed, from which only **1** in the *cis* conformation crystallizes from cold ethyl ether. **1** was then treated with allyl chloride in the presence of sodium hydride at room temperature to give allyl derivative **2** with 74% yield. Subsequently, the acetal protective group was removed with methanol diluted hydrochloric acid and the product purified by vacuum distillation to give 1,3-diol **3**. The reaction of **3** with ethyl chloroformate yielded cyclic carbonate **4**. Because of high reactivity of carbonate bonds in the cyclic monomer, the last synthetic step should be carried out under mild reaction conditions. The addition of mercaptoethanol to allyl group of **4** was performed in an ice bath according to the mechanism of free-radical-induced addition of thiols to double bonds. Taking into account that the hydroxyl group can react with cyclic carbonate in an uncontrolled manner, monomer **5** was stored in diluted solutions in a freezer and the solvent was evaporated prior to use. Figure 1 shows the ^{1}H NMR spectrum of cyclic carbonate monomer **5**.

Scheme 1. Synthesis of 5-{3-[(2-Hydroxyetyl)thio]propoxy}-1,3-dioxan-2-one (5)[a]



[a] Conditions: (i) NaH, $ClCH_2CH=CH_2$, THF, rt, 74%; (ii) 5% HCl, ethanol, rt 97%; (iii) ClCOOEt, TEA, THF, −15 °C, 71% (IV) $HSCH_2CH_2OH$, Irgacure 184, rt, 52%.

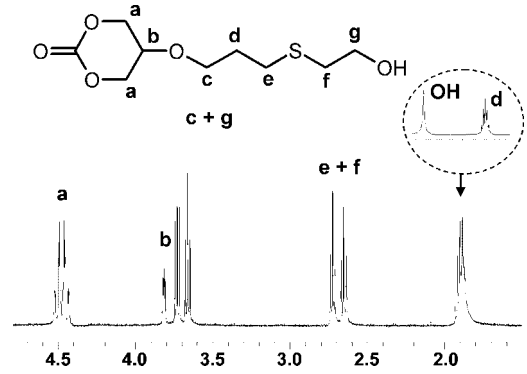


Figure 1. ^{1}H NMR ($CDCl_3$, 400 MHz) spectrum of **5**.

There are characteristic signals **a** and **b** of the CH_2 protons of the cyclic carbonate moiety present in the range of 4.55−3.70 ppm. Two conformers are possible for the cyclic structure, where the O-alkyl substituent can take the axial or equatorial position; therefore, signals **a** of the CH_2 groups appear as a complicated multiplet. The rest of the signals belong to the side chain of the

Table 1. Composition and Conditions of the Polymerization Reactions of the Synthesized Poly(5)

sample	catalyst	temp [°C]	solvent	time [h]	yield [%]
P1		110		72	96
P2	$Sn(Oct)_2$ (1:400)	110		72	98
P3	DBU (1:400)	110		72	97
P4		80	toluene	18	99
P5	$Sn(Oct)_2$ (1:400)	80	toluene	18	96
P6	DBU (1:200)	80	toluene	18	95
P7	DMAP (1:200)	80	toluene	18	98
P8		60	chloroform	20	98
P9	$Sn(Oct)_2$ (1:400)	60	chloroform	20	97
P10	DBU (1:200)	60	chloroform	20	97
P11	DMAP (1:200)	60	chloroform	20	98

molecule. The signals **c**, **g**, **e**, and **f** of CH_2 protons appear as triplets. The signal **d** of CH_2 protons appears as a multiplet at around 1.9 pmm which overlaps the signal of the OH group. The ^{13}C NMR and FT-IR spectroscopies confirmed the number of carbon atoms and the presence of carbonyl group in the molecule, respectively.

Polymerization. The ring-opening polymerization (ROP) of **5** was carried out in bulk or in solution in the presence of a catalytic amount of $Sn(Oct)_2$(coordination polymerization and transesterification catalyst[28,29]), DBU (anionic polymerization initiator[30]), and 4-(dimethylamino)pyridine (DMAP).

In the ring-opening polymerization of monomer **5** the molar concentration of initiating alcohol groups relative to that of $Sn(Oct)_2$ ([M]/[Cat]) was kept high (ratio 400:1). Table 1 presents the reaction conditions for the polymer synthesis. Details are given in Experimental Section. The products of each experiment were characterized by means of ^1H NMR, ^{13}C APT NMR, FT-IR spectroscopies, MALDI TOF spectrometry, and GPC chromatography.

The theoretical chemical structures of the obtained products are shown in Figure 2. There are five main subunits characteristic for the hyperbranched polymer. The polymerization starts at the core unit A. The completely substituted subunit B represents the branching points. There are two different linear subunits C, depending on which hydroxyl group reacted with a monomer. The outer sphere D consists of subunits with two hydroxyl groups. All hydroxyl groups in the molecule are primary groups of equal reactivity. This is an advantage over structures like polyglycidol[6] or poly(6-HDON),[23] in which there are also secondary OH groups present of lower reactivity.

It was found that polymers obtained by polymerization carried out at higher temperature (**P1**−**P7**) were insoluble in typical

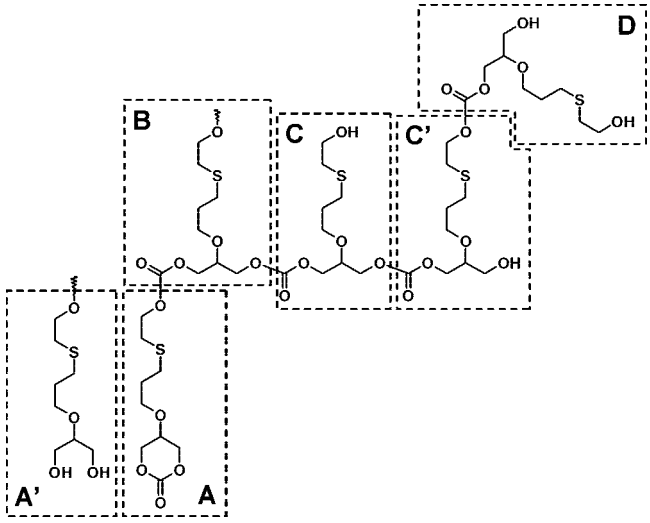


Figure 2. Theoretical chemical structure of poly(**5**).

Scheme 2. Transesterification Leading to Cross-Linked Polymers at Higher Conversion Rates

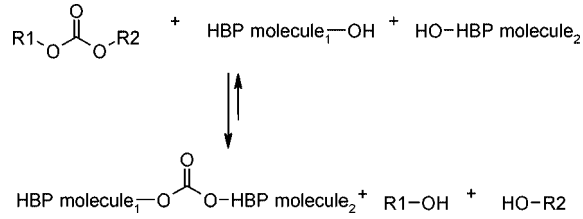


Table 2. GPC Characteristics of the Synthesized Poly(5)

sample	M_n	M_w	D
P8	1120	1915	1.71
P9	743	951	1.28
P10	2369	6677	2.82
P11	2656	5225	1.97

organic solvents. This can be explained by the cross-linking reactions. The cross-linking occurs according to the transesterification mechanism (Scheme 2). Polycarbonates are "carbonic acid" derivatives, which is difunctional. At higher conversion rates this difunctional moiety can chemically bind macromolecules leading to cross-linking. However, even the insoluble samples are easily hydrolyzable in ethanolic NaOH. The only product of hydrolysis is triol **6** (Scheme 6).

The GPC analysis was performed for the soluble samples prepared in chloroform. Table 2 gives the GPC characteristics of the resulting polycarbonates. All the samples showed rather low molecular weights of up to 10 monomer units per molecule and dispersities in the range of 1.71−2.82.

The progress of the polymerization can be monitored by means of ^1H NMR spectroscopy. Figure 3 shows the progress of polymerization carried out in deuterated chloroform in presence of DBU in a NMR tube at 60 °C.

Besides the conversion of cyclic carbonate CH_2 groups into "linear" ones, which is marked with arrows (Figure 3), there can be observed a significant shift of the OH signals toward the lower field values, from 1.89 to 3.83 ppm. It can be explained by the intramolecular hydrogen bonds formation in the branched structures. The ^1H NMR spectrum measured in d_6-DMSO gives a more detailed look into the structure.

Figure 4 shows the signals assignment for the HBP structure (**P10**). The signals of the starting subunit (Figure 2A) could not be distinguished in the spectrum. An interesting finding were the G signals of the 1,3-diol units (Figure 2A′). They were indentified on the basis of the compound **3** ^1H NMR spectrum and further confirmed by ^{13}C NMR and MALDI-TOF spectra. The 1,3-diol units could be produced in two ways. One is the

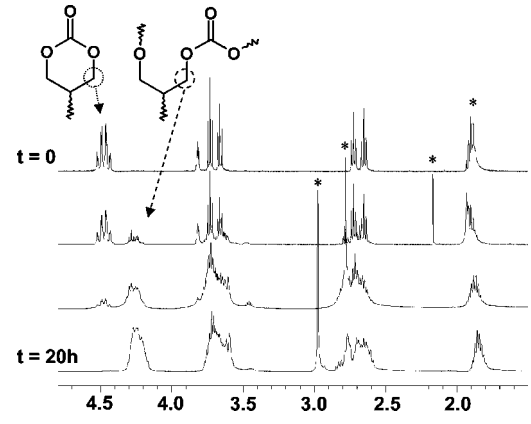


Figure 3. Progress of the polymerization of **5** monitored by ^1H NMR ($CDCl_3$, 400 MHz) (**P10**).

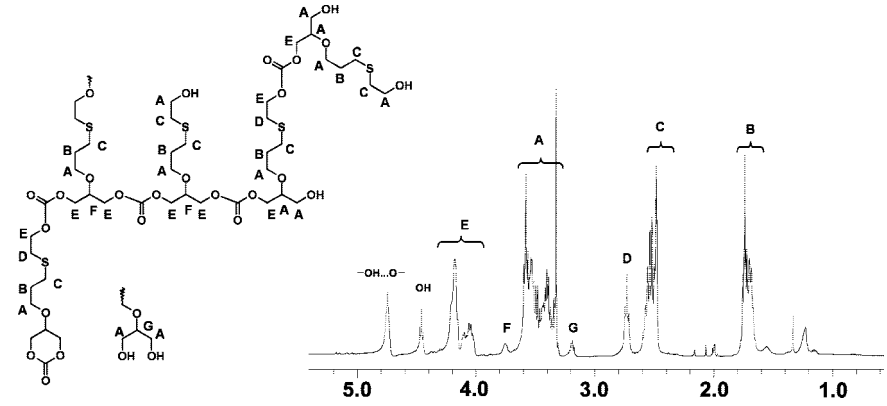


Figure 4. ^{1}H NMR (400 MHz, d_6-DMSO) spectrum of poly(**5**) polymerized in presence of DBU (**P10**).

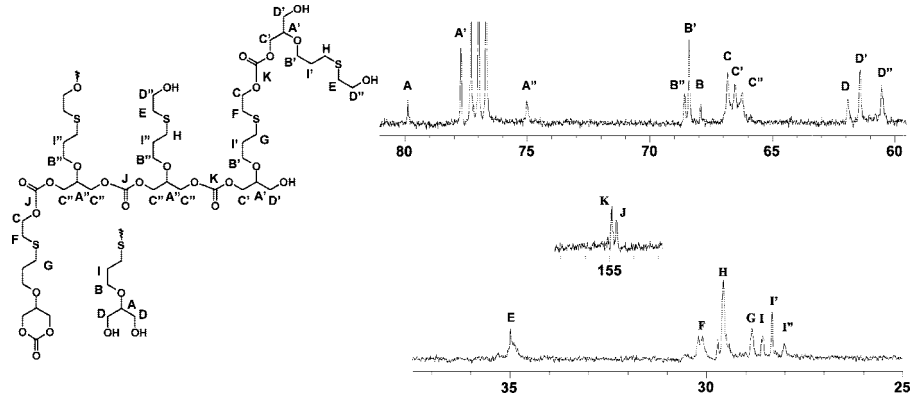


Figure 5. ^{13}C NMR (400 MHz, $CDCl_3$) spectrum of poly(**5**) obtained in the presence of DBU.

hydrolysis of the starting subunit A (Figure 2) or more likely by an inter- or intramolecular attack of the free OH group on the carbonyl group of the hyperbranched structure.

Figure 5 shows signals assignment in the ^{13}C NMR spectrum of poly(**5**). The glycerol units appear as mono-, di-, and trisubstituted structures. The six-membered cyclic carbonate structure is not observed. The OH end groups coming from mercaptoethanol appear as free or substituted structures.

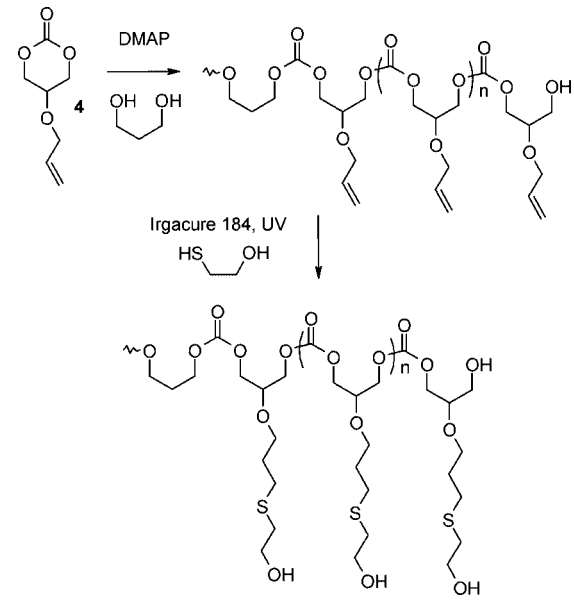
From the ^{13}C NMR spectrum one could expect to calculate the degree of branching for the HBP structure.[31] However, in this case it is not possible. The fully substituted glycerol substructures (signals C″A″C″ in Figure 5) are present both in branching structure B (Figure 2) and linear structure C (Figure 2). The same situation is for the disubstituted glycerol substructures. The C′A′C′ signals are present for both terminal unit D and linear unit C′ (Figure 2).

On the basis of the A signal (Figure 5), it is possible to a certain extent to investigate the structure of the obtained polymer. The A signal (Figure 5) is assigned to a secondary carbon atom of the glycerol structure linked by an ether bond to an alkyl chain. Next to this carbon there are two CH_2OR groups, where R can be a proton or a carbonate bond. This gives three possible combinations which can be seen in the spectrum as separate signals. To prove the signals assignment, a linear polymer has been synthesized (Scheme 3).

The linear product with pendant SCH_2CH_2OH groups was obtained by the polymerization of compound **4** followed by free radical addition of mercaptoethanol to the pendent allyl groups. In this structure glycerol units are linked in the 1,3-positions by carbonate bonds. Similar polycarbonates were synthesized from 5-benzyloxy-1,3-dioxan-2-one and further functionalized by Grinstaff et al.[32]

Figure 6 shows the differences between polymers synthesized using two types of catalysts. As can be seen, line **c** does not

Scheme 3. Synthesis of a Linear Polycarbonate



show the 79.2 ppm signal which can be assigned to the glycerol unit with one CH_2OH group (structure C′ in Figure 2). Line **a** (polymer obtained with $Sn(Oct)_2$) shows the majority of glycerol units substituted with carbonate groups in the 1,3-positions. This proves the coordination−insertion mechanism (Scheme 4) proposed by Libiszowski et al. for the polymerization of cyclic carbonates and lactides.[33] A similar mechanism was proposed by us for cyclic lactone.[24] It is worth mentioning that stannous octoate can also act as a transesterification catalyst. It explains

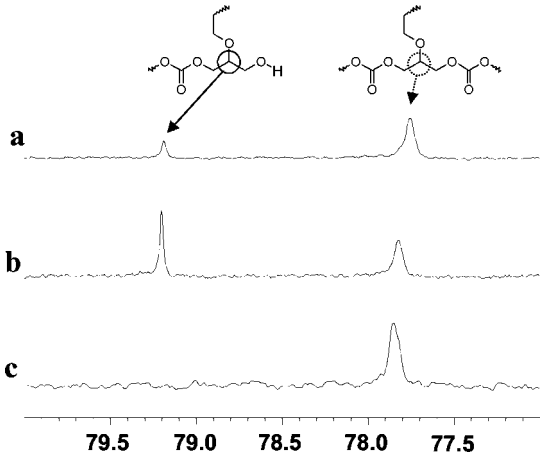


Figure 6. Influence of the catalyst on the structure of the polymer observed in the ^{13}C NMR spectrum (400 MHz, DMSO-d_6): (a) the polymer obtained in the presence of DBU; (b) in the presence of $Sn(Oct)_2$; (c) linear polymer.

the presence of methine carbon next to CH_2OH group signal in the spectrum (Figure 6a).

The polymer synthesized in presence of DBU (Figure 6, line **b**) showed a majority of linkages where the glycerol unit has one free primary hydroxyl group.

In the presence of DBU, migration of the propagation center is possible. Therefore, in the ^{13}C NMR spectra of the products there are the signals which can be assigned to two types of linear subunits, with CH_2OH and SCH_2CH_2OH groups (Figure 6).

Additional information on the structure of poly(**5**) is provided by the MALDI-TOF mass spectrum. In the mass spectrum there are several series of signals corresponding to polycarbonate macromolecules. The peaks of each series are characterized by a mass increment of 236 Da and appear as proton and sodium cation adducts. This mass increment equals the mass of the repeating unit (monomer) in polycarbonate. The most intensive series of signals (**B** in Figure 7) can be assigned to the sodium cation adduct of the macromolecules containing hydrolyzed **5** as the core (residual mass 210 Da). The hydrolyzed monomer core series are also present in molecules where one decarboxylation took place both for proton and sodium cation adducts. A decarboxylation is an effect of the MALDI-TOF measurement conditions, not the polymerization conditions, as no other method showed a decarboxylated structure. The less intensive series of signals (**A**) corresponds to the macromolecules containing monomer as the core unit (236 Da). This series appears only as a proton adduct. The third series of peaks (**C**) of the smallest intensity corresponds to the macromolecules containing a decarboxylated monomer molecule (192 Da) and again appear as sodium and proton adducts. Similar mass spectra were registered for other obtained polymers.

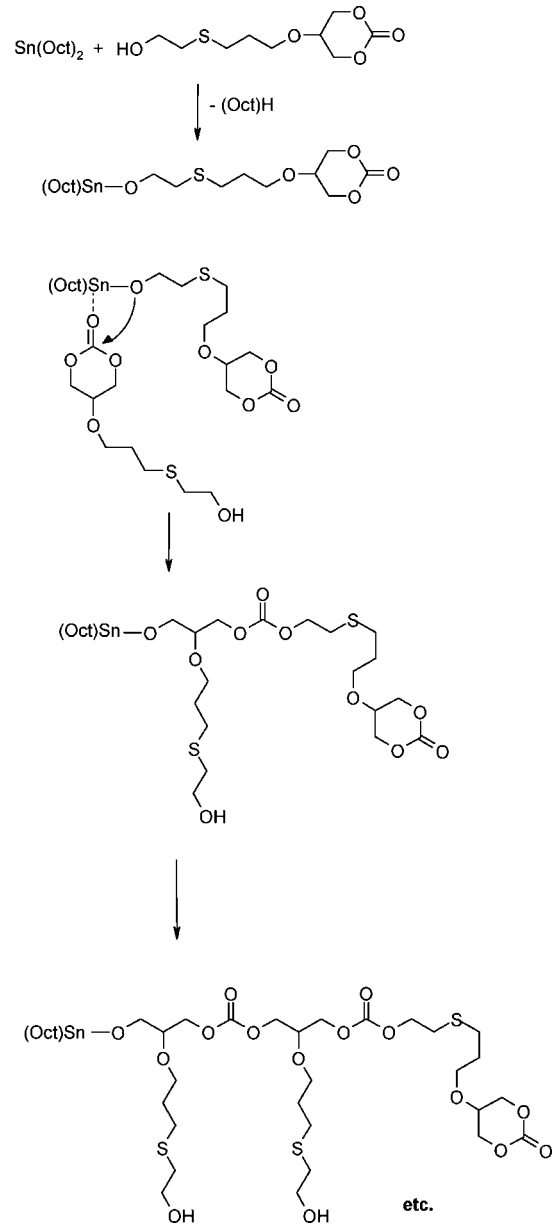
The GPC analysis was performed for the soluble samples prepared in chloroform. All the samples showed rather low molecular weights of up to 10 monomer units per molecule and dispersities in the range of 1.71−2.82.

It is interesting that all the polymer samples **P1**−**P11**—cross-linked and hyperbranched— are easily degradable. Heating of the samples at 120 °C at ambient moisture atmosphere after 24 h yields exclusively 2-{3-[(2-hydroxyethyl)thio]propoxy}propane-1,3-diol (**6**) as a product (Scheme 6).

Conclusions

The monomer 5-{3-[(2-hydroxyethyl)thio]propoxy}-1,3-dioxan-2-one (**5**) was synthesized and used for the ring-opening polymerization, yielding hyperbranched polycarbonates. The chemical structures of the monomer and the polymer were

Scheme 4. Mechanism of Coordination−Insertion Polymerization of 5 in the Presence of $Sn(Oct)_2$



analyzed by means of ^1H and ^{13}C NMR spectroscopies as well as MALDI-TOF spectrometry and GPC chromatography. In

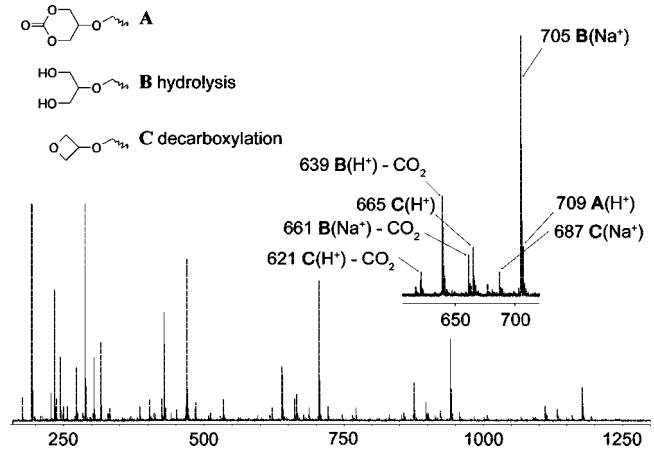
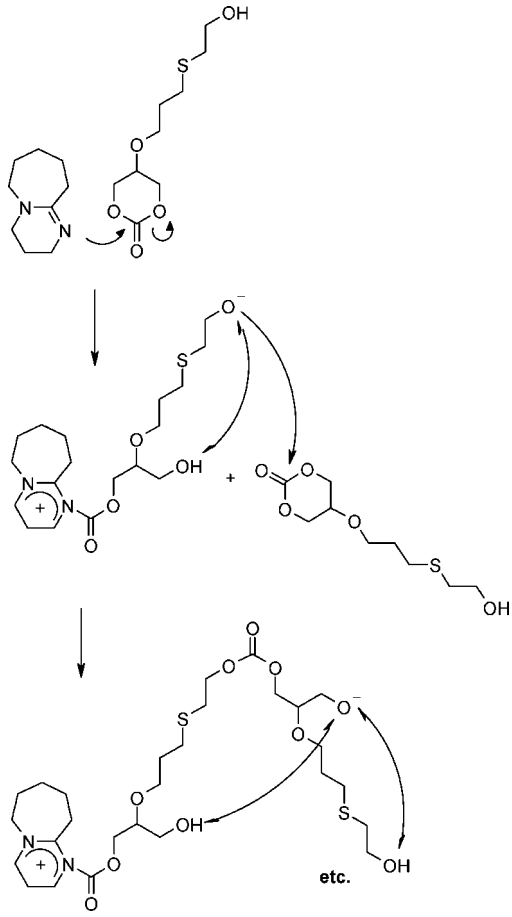
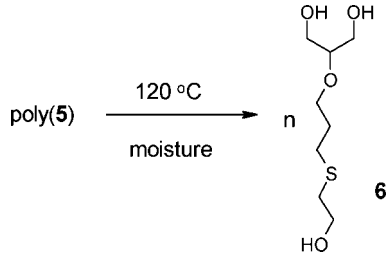


Figure 7. MALDI-TOF mass spectrum of the poly(**5**) (**P10**).

Scheme 5. Mechanism of an Anionic Polymerization of 5 in the Presence of DBU



Scheme 6. Degradation of Polymers P1−P11 in the Presence of Moisture at 120 °C



addition, linear analogues of poly(**5**) were prepared and their structures compared by means of ^{13}C NMR. Ring-opening polymerization of **5** leads to a polymer containing solely primary hydroxyl groups. The influence of the catalyst and reaction conditions used for the polymerization on the polymer structure was discussed. The presence of glycerol and carbonate residues in the repeating unit makes the polymer potentially biodegradable and biocompatible—promising material for drug delivery. High molecular weight polymers may find use as biocompatible and easily removable coatings. The application of free-radical addition of mercaptoethanol to allyl bonds simplified the synthetic route and allowed the potential use of a polymer with thioether groups for transition metal cations complexations.

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