Heterotelechelic Poly(oxazolidine-acetals) and Their Functionalization

Jolanta Maślińska-Solich, Edyta Gibas*

Department of Physical Chemistry and Technology of Polymers, Silesian University of Technology, ul. M. Strzody 9, 44-100 Gliwice, Poland
E-mail: jms1acet@zeus.polsl.gliwice.pl

Summary: Telechelic poly(1,3-oxazolidine-acetal)s with $-CH_2OH$ and –CHO groups were synthesized by polycondensation of the 2-amino-2-hydroxy-1,3-propanediol (**1**) (TRIS) with terephthaldehyde (**2**). The degree of polymerization (DP) was controlled by the ratio of **1** to **2** at the given reaction time. Characterization was achieved by ^1H and ^{13}C NMR and IR spectroscopy. The distribution of oxazolidine-acetal units in the polymer chain has been performed using ESI-MS. The activities of telechelic poly(oxazolidine-acetal) were determined in reaction oxidation (4-chloroperbenzoic acid), reduction (CH_3MgCl) and nucleophilic substitution (acylation, alkylation).

Keywords: nucleophilic substitution; oxazolidine; oxidation; polycondensation; reduction

Introduction

The introduction of a particular functional group, reagent or catalyst to a polymer supported by chemical modification of the latter is by far the most commonly used method. This approach has the advantage of not requiring the synthesis of an elaborate comonomer.

In this context, some attempts have been made to use functionalized macromolecules with N,O- and O,O-acetal moicties for facile preparation of grafting and branched structures.

Experimental

Measurements

The NMR spectra were recorded using a UNITY INOVA 300 MHz (Varian Associates Inc.) multinuclear spectrometer. The ^1H and ^{13}C NMR spectra were run in DMSO-D_6 and in deuterated chloroform using TMS as an internal standard.

ESI-MS experiments were performed using a Finnigan MAT TSQ 700 triple stage quadrupole mass spectrometer equipped with an electrospray ionization (ESI) source (Finnigan, San Jose, CA, US).

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EPR spectrum was recorded at room temperature on a RADIOPAN type SE/X – 2543 spectrometer with compatible computer acted as the control center of this system, operating at 9.3 GHz microwave frequency. The modulation amplitude was 0.1 mT, the attenuation 10 dB, the time constant was 0.3 s, the receiver gain $1*10^4$ (50% diode current) and the scan range was 20 mT.

Polycondensation

Poly(oxazolidine-acetals) **3** were obtained by polycondensation of **1** with **2** (at molar ratio 1:1) at 80 – 110 °C in solution (benzene, toluene, benzene DMSO, benzene DMF) at 80-110 °C in the presence of an acidic catalyst (p-toluenesulfonic acid (TsOH) or its complex with poly(4-vinylpyridine-divinylbenzene) PVP TsOH).

Chemical modification

*N-Alkylation of polycondensation products (**4**)*

Polymer samples **3** (0.5-1.0g) were alkylated with an excess of alkyl iodide (methyl, ethyl, butyl and decyl) at 30 to 40 °C in a sealed tube (5-14 hr) under ultrasonication. The semi-solid product was washed with water, acidified with a diluted solution of acetic acid and extracted with chloroform. The organic layer was first washed with a 10 % solution of NaOH, then with water, finally it was dried over anhydrous $MgSO_4$. Chloroform was evaporated and the residue was dried under reduced pressure. The N-alkylated polymer **4** was purified by precipitation from tetrahydrofurane (THF) solution with methanol. The degree of N-alkylation (60-89 %) was determined from ^{1}H NMR spectra.

*N-Acetyl derivative of poly(oxazolidine-acetal) (**5**)*

The polymer sample **3**, 1.5g in 10 ml of pyridine and 2.5 ml of acetic anhydride was stirred at room temperature for 14 day. The reaction mixture was then suspended in water ice. The resulting solid polymer was neutralized with sodium hydrocarbonate and then washed with a sufficient amount of water. Finally the polymer was dissolved in THF and after precipitating using ethanol, it was dried under vacuum at 80 °C for several hours. The amount of N-acyloxazolidine units calculated from the ^{1}H NMR spectrum of **5** corresponds closely to the almost of oxazolidine units in polymer **3** (calc. CH_3CO 20.0%; found 23.5%).

*Reduction with Grignagd reagent (**6**)*

A sample of 1.16g (5.3 mmol) of polymer **3** dissolved in 10 ml of THF was added dropwise to a stirred 2M solution of CH_3MgCl (53 mmol) in THF at 0 °C under argon atmosphere. The reaction mixture was left to warm to ambient temperature during 8 hours and than quenched with saturated aqueous ammonium chloride solution (10 ml). The aqueous phase was separated and extracted with chloroform (4x10 ml). The combined organic extracts were dried ($MgSO_4$) and evaporated. The degree of reduction (57 %) was determined from ^1H NMR spectrum.

*Oxidation (**7**)*

The polymer sample **3**, 1g and 2g of 4-chloroperbenzoic acid in 20 ml of dry chloroform were stirred at room temperature for 12 hrs. The chloroform layer was washed with cold 5 % sodium bicarbonate solution and dried over anhydrous $MgSO_4$. The solvent was removed under vacuum and the product **7** was analyzed by EPR (Figure 4).

Results and discussion

Synthesis and characterization

The polycondensation of **1** with **2** was performed in solution (benzene, toluene, benzene DMSO, benzene DMF) at 80-110 °C in the presence of an acidic catalyst.[1] The examination of condensation products allows to follow the influence of several parameters on the formation of macromolecules. It was found that the stepwise reaction between the functional groups of reactants **1** and **2** with the molar ratio 1:2 proceeds almost immediately after the start of reaction to form the bis-oxazolidine compound. The O,N acetal units exist predominately in solution as oxazolidine-imine tautomers according the appropriate resonances in their ^1H and ^{13}C NMR spectra, as demonstrated in Table 1.

Table 1. The dynamic equilibrium of oxazolidine-imine system in DMSO-D_6.

time	% imine	% oxazolidine
0	-	100
3 h	6.7	93.3
4 days	11.86	88.13
5 days	12.56	87.44

The condensation of **1** with **2** at a molar ratio 1:1 conducted in the presence of an acidic catalyst (TsOH or PVP TsOH) leads to the formation of products with M_w~9600 g · mol^{-1}. An excess of one of the reagents (TRIS) lead to a mixture of oligomers or a crosslinked structure.[1]

The IR and NMR spectra indicate the presence of O-C-O and O-C-N units and also aldehyde groups in the polymers. The IR spectrum of the polymer shows typical absorption peaks at 1080 - 1180 cm^{-1} assigned to -O-C-O and O-C-N groups as well as distinct absorption due to -OH groups at 3340-3450 cm^{-1}. The absorption band at 1645 cm^{-1}(with weak intensity) may be assigned to the CH=N group in the polymer. The ^{1}H NMR spectrum of the polymer showed broad peaks centered at 3.3, 3.65, 3.88. 3.81 ($C\underline{H}_2O$), 5.02, 5.54 (N-C$\underline{H}$-O and O-C$\underline{H}$-O), 6.8-7.9 (aromatic protons) and a weak peak at 10 ppm. By monitoring the intensities of the peaks due to Ar-$\underline{H}$, OC$\underline{H}$O, OC$\underline{H}$N, and $C\underline{H}_2O$ protons, it was possible to show that the polymers exist in solution as oxazolidine-acetal macromolecules. The determination of differences in the chemical structure of the end groups was possible only by ESI-MS investigation.[2]

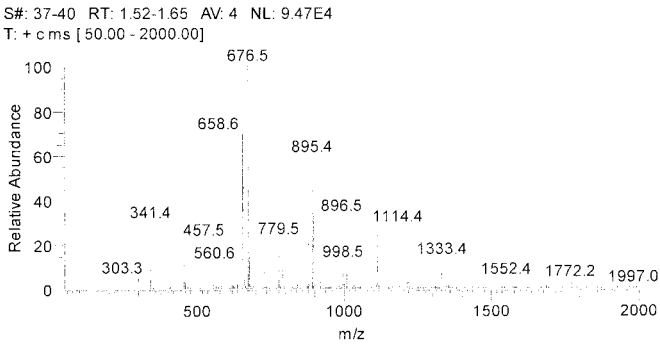
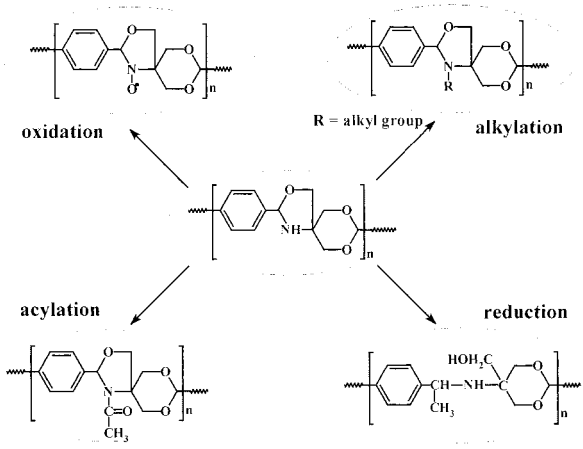


Figure 1. The ESI-MS spectrum of polymer **3**.

The ESI mass spectrum (in positive-ion mode) of the sample **3** (Mn = 2300 g · mol^{-1}) is presented in Figure 1. Analysis of this ESI mass spectrum revealed the presence of protonated molecules with m/z values corresponding to three kinds of macromolecular chains containing different end groups, i.e., CHO and OH groups (A), only OH groups (B), and oligomers with no end-groups, i.e., macrocyclic compounds (C). The number of repeating units in the MH^+ ions varied from A_n = 3-8, B_n = 2-3, C_n = 3-5. The signals in the spectrum show a peak-to-peak mass increment of 219 Da, which is equal to the molecular weight of mono-oxazolidine as the repeating unit in polymer **3**.

Chemical modifications of polymer **3**

The telechelic poly(1,3-oxazolidine-acetal)s were tested in oxidation, reduction and nucleophilic substitution (alkylation, acylation) reactions, as depicted on Scheme 1.



Scheme 1. Chemical modification of new heterotelechelic poly(oxazolidine-acetal).

The presence of CHO groups in the polymer **4** after alkylation was observed in IR and NMR spectra. The signal at 191.2 ppm increased in their intensity when compared to the polymer before alkylation (Figure 2). During alkylation the oxazolidine end groups of macromolecules are

isomerized to the imine form, which then is partially hydrolyzed into secondary amino-triol and macromolecules with aldehyde groups at the chain end.[1, 3]

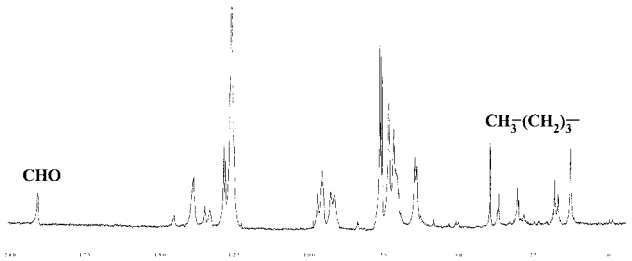


Figure 2. ^{13}C NMR (75 MHz) ($CDCl_3$) spectrum of N-alkylated polymer **4** with buthyl iodide.

Acylation of the polymer **3** with acetic anhydride occurs with an effective N-substitution of O,N-acetal units. Figure 3b presents the spectrum of N-acetylated polymer **5**. The observed difference in the chemical shifts of CH_3CO- protons (1.89 and 2.06 ppm) may be accounted for the existence of both, the envelope and twist conformations of oxazolidine rings in the polymer chain.

The Grignard reagents (RMgX) are known to react with 1,3-oxazolidines.[4] The addition of methylmagnesium chloride (MeMgCl) was carried out in THF at room temperature. Reduction of O,N-acetal units of polymer **3** occurs with forming poly(amine-acetal). The ^1H NMR spectrum of polymer **6** shows the appearance of a new band centered at 1.25 ppm (-NH-), 1.8 ppm (CH_3-CH) and 4.18-4.23 ppm (-CH-N). Based on the ^1H NMR spectrum it was found that 57 % oxazolidine units were converted into the amine groups. This reaction is presented in Scheme 1 and Figure 3c.

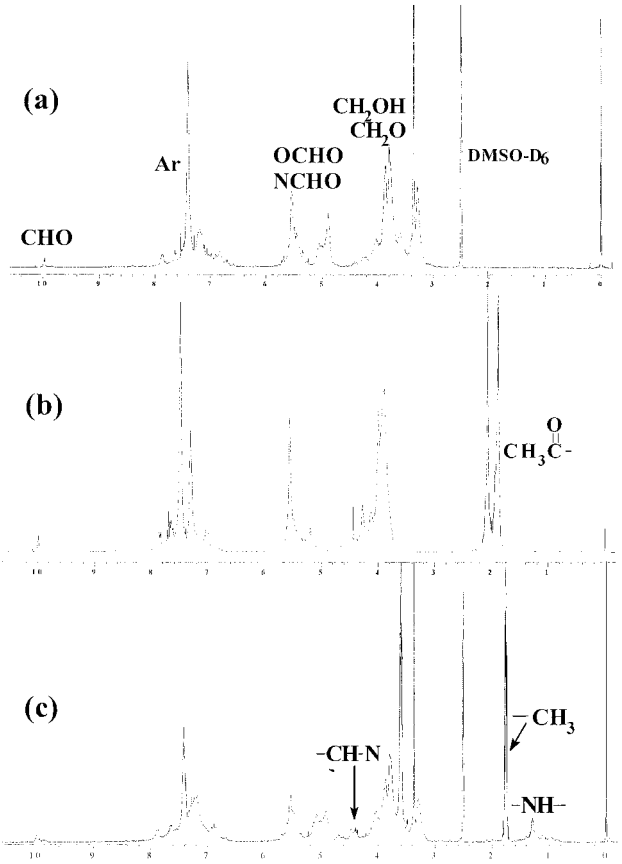


Figure 3. ^{1}H NMR (300 MHz) (dmso-d_6) spectra of: a) polymer **3**; b) ($CDCl_3$) N-acylated polymer **5**; c) and after reduction with CH_3MgCl **6**.

The spectroscopic data of all new compounds are in accordance with their structural assignments.

New stable nitroxide free radicals were generated in the oxidation reaction of oxazolidine units of polymer **3** with m-chloroperbenzoic acid. The radicals gave EPR spectrum, similar to TEMPO, with a triplet hyperfine splitting due to the nitrogen nucleus (see Figure 4). Studies on polymerization of model graft polymers with the nitroxide free radicals are in progress.

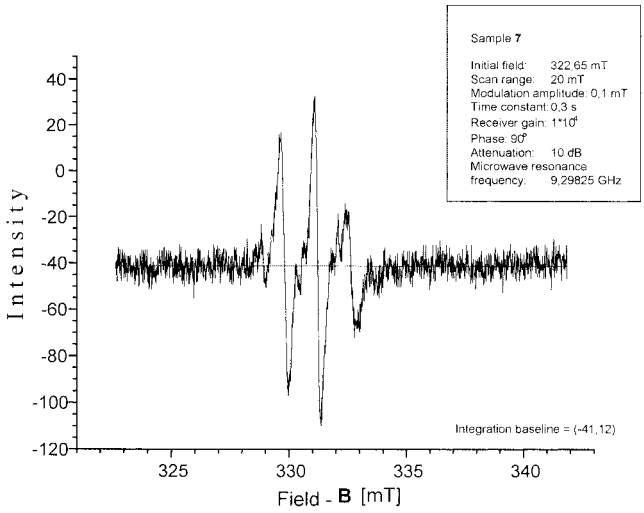


Figure 4. The EPR spectrum of the nitroxide free radicals in polymer chain.

Conclusion

The polycondensation of terephthalaldehyde with 2-amino-2-hydroxymethyl-1,3-propanediol under acidic catalysis leads to the formation of linear polymers containing different end groups, i.e., CHO and OH.

The activities of poly(oxazolidine-acetal)s were investigated in oxidation, reduction and nucleophilic substitution (acylation, alkylation) reaction. It was demonstrated that new nitroxide radicals were easily prepared in the reaction polymer **3** with 4-chloroperbenzoic acid.

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