



α,ω -FUNKCIONALIZÁLT POLIMEREK SZINTÉZISE

Synthesis of α,ω -functionalized polymers

Doktori (PhD) értekezés tézisei

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Introduction

Telechelic polymers especially functionalized polyisobutylene derivatives play an important role both in research and in the industry. Their industrial importance is largely due to their easy processibility. Being low molecular weight ($M_n \approx 500-10000$ g/mole) liquids the process costs can be kept low. Quantitative end functionality is indispensable considering industrial applications. During their reactions we can easily get high molecular weight compounds, namely block copolymers, ionomers and amphiphilic networks, resins and macromonomers.

Their scientific value is represented by the fact that they can be used as starting materials in the synthesis of perfect networks (i. e. networks in which the polymer chains between two link points have the same molecular mass and they do not contain any free chain ends).

Countless methods exist for the preparation of telechelic polymers. Nowadays industrially the free radical polymerization is the most important. Mass production is realized by this method but the significance of anionic and cationic methods are continually increasing. The polymer industry needs more and more low molecular weight, narrow molecular weight distribution and strictly functionalized polymers for example telecheli polyisobutylene.

At the Department of Applied Chemistry of the University of Debrecen extensive studies have been made in the field of functionalized polymer synthesis, but until now the instrumental conditions for the investigation of the functionality were limited. This situation has changed dramatically when a modern Bruker-type MALDI-TOF MS instrument was installed at the Department of Applied Chemistry of the University of Debrecen in 2000. The installation of a new Bruker-type ESI-TOF MS instrument ensured the technical background of further investigations and broadened the scope of polymer characterization. The solution of complex problems i.e. the following of functionalization reactions by mass spectrometric methods became possible. The potential of the MALDI method can be represented by the fact that using this method one can differentiate between polymers having different end groups in a system, moreover the determination of the headgroup and the endgroup in the same polymer

cahin can be achieved, that could be hardly carried out using other characterization methods.

During our research we focused on the preparation of polymers having scientifically and industrially valuable endfunctionality. The research also involved the development of new and effective synthetic routes for the preparation of already existing functionalities. The model polymers as starting materials were selected in a manner that the practical application will cover the most possible fields.

One special kind of cationic polymerizations is the living carbocationic polymerization the history of which began only two decades ago. Its importance resides in that after its discovery the preparation of polymers having controlled molecular weights, exact functionality and never before properties became possible.

The first example in the literature for living carbocationic polymerization was the polymerization of the isobutyl vinyl ether hydrogen iodide/Iodine system. Since the vinyl ethers as monomers have remained in the focus. Due to their structure they are the perfect monomers for the study of cationic polymerization. Recently, great efforts are devoted to develop cheap and efficient initiating systems which would enable a higher control over the properties (molecular weight, stereoregularity and endgroups) of the polymers formed. Lewis acid (AlCl_3 , SnBr_2 , TiCl_4)/protonic acid or organic halide combinations are in the focus of today's butyl vinyl ether polymerizations. Until now initiating systems consisting of an ionic hydride in conjunction with a Lewis acid have not been studied.

Our aim was to develop a new, efficient and cheap initiator for the living polymerization of nbutyl vinyl ether. The discovery of such an initiator would have great significance because it could be extended for the polymerization of other monomers by a little alteration of the reaction conditions. Our aim was also the detailed kinetic investigation of the polymerization reaction because it could provide valuable information for the reaction mechanism. Due to the structure of butyl vinyl ethers stereoregular polymerization can be obtained. Stereoregularity is one of the major factors that largely affect the mechanical properties of a polymer. Great efforts are made to develop new synthetic methods for the preparation of stereoregular polymers, however it may be very difficult especially in homogeneous systems.

In cationic polymerization the control of the propagating chain-end may be the solution. In homogeneous systems Ziegler-Natta type or specially designed complex initiator systems such as alkoxides $\text{Ti}(\text{OR})_n\text{Cl}_{4-n}$ in combination with Lewis acids can be used. Although very high (nearly 90%) isotactic polymer content can be obtained, the preparation of these alkoxides is very expensive and time consuming and in order to reach the maximum isotactic polymer content, very low ($-80\text{ }^{\circ}\text{C}$) temperatures must be applied. The lowering of the costs can be realized in two ways. The first is the development of cheap counter anion for the control of the propagating chain end the other is to carry out the stereoregular polymerization at relatively high temperatures. In our previous experiments using alanes as initiators the isotactic content of the polymers formed was found to be approximately 60 % at $25\text{ }^{\circ}\text{C}$.

Our aim was to optimize the reaction conditions in order to prepare polymers containing the maximum isotactic content reachable

II. Investigation and synthetic methods

II.1. Materials and synthetic methods

The polymerization reactions for the investigation of the kinetics of butyl vinyl ether polymerization were carried out using dry-box techniques. The chloro telechelic polyisobutylenes were also prepared using dry-box techniques. Polyethylene glycol and polypropylene glycol (PPG) was provided by BorsodChem (Hungary) and used as received. During the functionalization reactions of polymer chains the newest semi micro organic synthetic methods were applied.

I.2. Instruments and softwares

MALDI MS and PSD MALDI MS/MS experiments were performed by a Bruker BIFLEX IIITM typed mass spectrometer equipped with a time-of-flight (TOF) mass analyzer and a reflectron. The obtained spectra were evaluated by a Bruker XMASS 5.0 software. The PSD spectra were calibrated by Adrenocorticotrophic Hormone (ACTH).

NMR. The ^1H NMR and ^{13}C NMR measurements were carried out with a *BRUKER AM 360 (360 MHz) spectrometer* at 300K temperature, in CDCl_3 solution and TMS was used as internal standard. The two dimensional experiments were performed on a Bruker DRX-500 spectrometer at 300K temperature, in CDCl_3 solution and TMS was used as internal standard.. Homonuclear correlations were obtained in TOCSY experiments while a gradient enhanced HSQC experiment was run for carbon-proton correlations.

II. New scientific results

II.1. Polymerization of nButyl vinyl ether in the presence of AlH_2Cl

The carbocationic polymerization of n-butyl vinyl ether (BVE) using the new $\text{LiAlH}_4/\text{AlCl}_3$ initiating system was studied. The polymerizations were carried out various solvent mixtures and at different temperatures and the kinetics of the polymerizations was studied. The rate constants, the temperature dependence of the rate constants, and the kinetic order of the reactants were determined. A self-ionization mechanism is proposed to describe the main kinetic features of the polymerization of BVE in the presence of AlHCl_2 . Although the ^{27}Al -NMR spectrum of AlHCl_2 solution did not show the presence of an $\text{AlHCl}^+\text{AlHCl}_3^-$ species, but it can be concluded that this species may exist in low concentration therefore it can initiate the living polymerization of BVE. The endgroups of the polymers were characterized by ^1H -NMR and MALDI-TOF MS methods. The MALDI-TOF MS measurements revealed poly(BVE) with three different, interconvertible endgroups i.e., heteroacetal, homoacetal and aldehyde type. This recognition may be useful for carrying out additional polymer-analog reactions. Based on detailed kinetic and structural investigations a direct initiation mechanism for the polymerization was proposed.

III.2. Investigation of the stereoregularity of the nButyl vinyl ether polymerization

The polymerization proved to be stereoregular. Polymerization reactions were carried out at various temperatures from 25 °C down to –60 °C in various solvent mixtures. The polymers were investigated by ^{13}C NMR, the isotactic content of the chains were determined from the ^{13}C NMR spectra according to the integral ratios of the signals of the chain methylene carbons. The maximum isotactic polymer content can be reached at –40 °C in hexane/diethyl-ether(1:1). It changes inversely with the temperature until – 40 °C but further lowering the temperature results in a reduced isotactic content. The solvent dependence of the reactions was also studied and it was found that the reaction rate increases with increasing solvent polarity.

III.3. New synthetic route to obtain hydroxyl terminated polyisobutylene

A new simple and effective synthetic route to obtain hydroxyl terminated polyisobutylenes was realized. The first step involved the synthesis and characterization of α,ω -di(2-methyl-2,3-epoxypropyl)polyisobutylene. The epoxidation of α,ω -di(isobutenyl)polyisobutylene was achieved at room temperature with dimethyldioxirane, which proved to be a very effective reagent for the epoxidation without formation of side products. A very good agreement was found for the conversion determined by ^1H -NMR and MALDI MS. The kinetics of the reaction and the chain length dependence of the individual composition were also studied by MALDI MS and it was shown that there is no significant dependence on the composition with chain length. It was also shown that the ratio of k_2 and k_1 is close to the theoretical 0.5 value, indicating an equal reactivity for the two olefinic end-groups. The epoxy end-groups were converted quantitatively to aldehyde termini using zinc bromide catalyst. The aldehyde groups were then reduced with LiAlH_4 into primary hydroxyl functions to obtain α,ω -di(2-methyl-3-hydroxypropyl)polyisobutylene with high efficiency.

III.4. Preparation and characterization of aminotelechelic polyisobutylene poly(propylene glycol) and poly(ethylene glycol)

A very simple, convenient synthesis was offered for the preparation of diamino telechelic PPG and PIB from the corresponding dihydroxy derivatives.

The structure of the resulting polymers was unambiguously supported by ^1H -NMR, 2D-NMR HSQC and TOCSY, as well as by MALDI-TOF MS. The synthesis method described can be generalized for the preparation of other types of polymers possessing hydroxyl termini. The synthesis of these amino telechelics were achieved via imidazolylformates by coupling them with ethylene diamine. The corresponding polyethylene glycol (PEG), polypropylene glycol (PPG) and polyisobutylene (PIB) bis(imidazole-1-carboxylate) esters were investigated by MALDI TOF MS. The MS spectra of PPG and PIB bis(imidazole-1-carboxylate) esters recorded in the reflectron mode showed the presence of two additional series of peaks compared to those recorded in the linear mode, while in the case of PEG bis(imidazole-1-carboxylate) only one additional peak series appeared in the reflectron MS spectra. These additional series were attributed to the formation of fragment ions by loss of one and two endgroups in the first field-free region of the instrument. The neutral losses for the three polymers were also supported by using the post-source decay method (PSD MALDI-TOF MS/MS).

The imidazolyl formates were further reacted with ethylene diamine. The structure of the resulting amino functionalized polymers were determined by ^1H -NMR, ^{13}C -NMR and matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF MS). Based on the spectroscopic and spectrometric results completely conversion of dihydroxy termini to diamino endgroups were observed, i.e., the number average functionality was found to be 2.

IV. Tudományos közlemények és konferencia-részvételek / Scientific publications and lectures

IV.1. Az értekezés témájához kapcsolódó közlemények / Publications in the field of the dissertation

1. Sándor Kéki, **Miklós Nagy**, György Deák, Miklós Zsuga: Kinetics and Mechanism of Polymerization of n-Butyl Vinyl Ether Initiated by Dichloro Alane (AlHCl_2): A New Cationic Initiating System. *J. Phys. Chem. B*, **105**, 9896 (2001) IF: 3,38
2. Sándor Kéki, **Miklós Nagy**, György Deák, Albert Lévai, Miklós Zsuga: Dimethyldioxirane: A New Effective Oxidation Agent for the Epoxidation of α,ω -Di(isobutenyl)Polyisobutylene. A Convenient Synthesis of α,ω -di(2-methyl-3-hydroxy-propyl)polyisobutylene. *J. Polym. Sci. Part A, Polym. Chem.* **40**, 3974 (2002) IF: 2,37
3. Sándor Kéki, **Miklós Nagy**, György Deák, Pál Herczegh, Miklós Zsuga: Matrix-Assisted Laser Desorption/Ionization Mass Spectrometric Study of Bis(imidazole-1-carboxylate) Endfunctionalized Polymers, *J. Am. Soc. Mass Spectrom.* **14**, 117 (2003) IF: 3,32
4. **Miklós Nagy**, Sándor Kéki, György Deák, Miklós Zsuga: Stereoregular Polymerization of Butyl Vinyl Ether Using the New $\text{AlCl}_3/\text{LiAlH}_4$ Initiator System, *Polym. Adv. Technol.* **14**, 807 (2003) IF: 1,02
5. Sándor Kéki, **Miklós Nagy**, György Deák, Pál Herczegh, Miklós Zsuga: Aminotelechelic: A Convenient Synthesis and Characterization of Primary Amino Terminated Telechelic Poly(Propylene Glycol) and Poly(Isobutylene), *J. Polym. Sci. Part A, Polym. Chem.* **42**, 587 (2004) IF: 2,37

IF(összes):12,46

IV. 2. Az értekezés témájához kapcsolódó konferencia-részvételek / Lectures in the field of the dissertation

1. **Miklós Nagy**, Sándor Kéki, György Deák, Miklós Zsuga: Stereoregular Polymerization of nButyl Vinyl Ether, *IUPAC International Symposium on Ionic Polymerization*, Boston, MA, June 30-July 04. (poszter)
2. Sándor Kéki, **Miklós Nagy**, György Deák, Lajos Nagy, Pál Herczegh, Albert Lévai, Miklós Zsuga: Novel Synthesis and MALDI-TOF MS Characterization of Dihidroxy Telechelic Polyisobutylene, *IUPAC International Symposium on Ionic Polymerization*, Boston, MA, June 30-July 04. (poszter)
3. Sándor Kéki, **Miklós Nagy**, György Deák, Lajos Nagy, Pál Herczegh, Albert Lévai, Miklós Zsuga: Monitoring the Reactions of Polymers by MALDI-TOF Mass Spectrometry, *28th International Conference on Solution Chemistry*, August 23-28, Debrecen, Hungary. (előadás)
4. György Deák, **Miklós Nagy**, Sándor Kéki, Miklós Zsuga: Stereoregularity of Cationic Polymerization: Cationic Polymerization of nButyl Vinyl Ether by Alanes, *6th Austrian Polymer Meeting, XXIst International H.F. Mark Symposium*, 15-17 September, 2003, Vienna, Austria (előadás)
5. Sándor Kéki, **Miklós Nagy**, György Deák, Lajos Nagy, Pál Herczegh, Albert Lévai, Miklós Zsuga: MALDI-TOF MS Characterization of Telechelic Polyisobutylenes, *6th Austrian Polymer Meeting, XXIst International H.F. Mark Symposium*, 15-17 September, 2003, Vienna, Austria (előadás)
6. **Nagy Miklós**, Deák György, Kéki Sándor, Zsuga Miklós: Vinil-éterek élő kationos és sztereoreguláris polimerizációja alán iniciátorokkal, *VIII. Vegyészkonferencia*, Kolozsvár, Románia (2002. november 15-17.)

7. Deák György., Orosz László., **Nagy Miklós.**, Kéki Sándor., Zsuga Miklós.: Nagy molekulatömegű hidroxil telekelikus poliizobutilének szintézise és karakterizálása, *IX. Vegyészkonferencia*, Kolozsvár, 2003. november 14-16.
8. **Nagy Miklós.**, Kéki Sándor., Deák György., Herczegh Pál., Zsuga Miklós.: Aminotelekelikus poliizobutilén és poli(propilén-glikol) szintézise és karakterizálása, *IX. Vegyészkonferencia*, Kolozsvár, 2003. november 14-16.