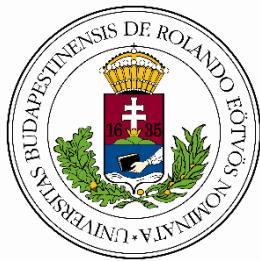


# **Synthesis of linear and branched functional polymers by quasiliving polymerizations and chemical modifications**

Ph.D. Theses



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Budapest  
2017

## I. Introduction and Aims

Nowadays, significant attention is paid to the production of functional polymers with different structures, since functional groups allow wide and special applications of these materials from new structural materials to drug delivery systems. In order to control the structure and functionality of the macromolecules, these polymers can only be synthesized by living polymerization. For this reason, I have tried to develop novel methods via living polymerizations combined with subsequent modifications for producing well-defined linear and hyperbranched macromolecules containing functional groups with predetermined number and location.

Polystyrene (PSt) is produced and used in large quantities worldwide. It is widely applied in many areas, such as from the packaging industry to the production of coronary stents. In spite of its importance, there is not yet a well-developed method for the synthesis of the homottelechelic PSt with allyl, hydroxyl or epoxide functional groups on both terminal chain ends. The previously published techniques are generally based on complex, multi-step, time- and chemical-consuming reactions, and it has been proved, these reactions can not be performed quantitatively in many cases. Therefore, development of a one-pot process of using quasiliving atom transfer radical polymerization (ATRP) of styrene and subsequent carbocationic allylation to obtain allyl-telechelic PSt quantitatively was attempted during my work. It is well known that the allyl group can be further modified by various reactions such as hydroboration or epoxidation to form hydroxyl and epoxide termini, respectively. In my research, I also studied these functionalization reactions to modify the end-groups of allyl-telechelic PSt to obtain novel functional materials.

Hyperbranched polyglycerol (HbPG) is a multifunctional polyether polyol which can be synthesized by the well-controlled living anionic ring-opening multibranching polymerization of glycidol, and its outstanding water solubility and biocompatibility was proved. Because of these advantageous properties and the simple and various functionalization possibilities, HbPG has been in the focus of many fields of polymer chemistry. Nevertheless, numerous applications are conceivable, in which, besides the hydroxyl groups, only one other functional group in the HbPG molecule would be needed to achieve the desired specific aims. Despite of the wide range of possible applications, only few procedures are described in the literature for the synthesis of monofunctional HbPG. Amine monofunctional HbPG is one of the most commonly used functionalities, but obtaining it with the previously developed processes is rather difficult and/or their industrial adaptation is hampered by other factors. Taking all this into account, I have

attempted to apply the phthalimide/phthalimide potassium as an initiating system which has many advantages over previously used initiators. Namely, if it could be achieved that the polymerization has living nature by this initiating system, only one phthalimide group would be incorporated into the polymer, which can be transformed easily to an amine terminus by well-known methods. In addition, by direct mixing of the phthalimide and phthalimide potassium, the activation steps needed for the previous amine-containing initiators are no longer necessary. It should be noted that although in the literature the amine monofunctional HbPG has been successfully applied to increase the solubility and biocompatibility of molecules, the modification reactions to obtain other conjugation relevant functional groups has not been studied yet. Therefore, in my work, I aimed to study the functionalization of the terminal amine group of HbPG, therefore formation of carboxyl, maleimide and chloroacetamide moieties were attempted. These functional groups may be suitable for coupling and conjugation with other (bio)molecules via amide or thioether bond.

There are numerous examples in the literature of HbPG-based block copolymers synthesized by using amine-terminated hydrophobic macromolecules as a macroinitiator. Amphiphilic characteristic and surface active behavior in aqueous solution of these block copolymers have been proved. In the preparation of these macromolecules, the disadvantages of the above-mentioned initiators can be stated, namely the two-step activation of the macroinitiator consisting of the addition of two equivalents of glycidol and the deprotonation of the resulting tetrahydroxy chain end is necessary. Furthermore, it must be emphasized that, to my best knowledge, these materials have not been applied yet for the preparation and surface stabilization of nanoparticles. Therefore, my aim was the development of a method, which is appropriate for the synthesis of well-defined alkyl monofunctional HbPG by the direct application of alkyl alcohols as initiator on the one hand. On the other hand, the determination of the effects of the alkyl chain length on the surface active behavior was also planned to carried out. Hence, I attempted to employ the produced alkyl-HbPGs as a surfactant stabilizer of poly (D, L-lactic acid-*co*-glycolic acid) (PLGA) nanoparticles and to characterize the size and coagulation behavior of the resulting nanoparticles. The main advantage of amphiphilic HbPGs compared with the widely used copolymers (such as Pluronics) is that their hydroxyl groups can be easily modified with targeting or imaging molecules that can be used as drug delivery systems in targeted therapy.

Nowadays, many small molecular additives are used to provide the suitable physical and chemical properties of plastic products over a long period, but numerous environmental concerns have been expressed against them. These problems are particularly important in

packaging and agricultural foils as well as in biomedical devices, as these small molecular additives can migrate easily to the surface and interact with the human body and the environment. The solution would be the application of macromolecular stabilizers, which – due to their higher molecular weights – have lower migration ability. So, these macromolecules are intensively studied in the field of functional polymers. Based on the easy modifiability of the hydroxyl groups of HbPG, my aim was to produce macromolecular antioxidants with different molecular weights, their characterization and study of their thermal stability. My goal was also to determine the effectiveness of the synthesized HbPG-based macrostabilizers in the thermooxidative degradation of PVC, which is widely applied in packaging materials and medical devices. Additionally, I planned to demonstrate by using extraction studies from PVC that the migration of the macromolecular antioxidants is smaller than of the small molecular analogues, which makes them environmentally advantageous materials.

## II. Applied Methods

The bromo-telechelic PSt was prepared by atom transfer radical polymerization (ATRP) of styrene using  $\alpha,\alpha$ -dibromo-toluene initiator and CuBr/pentamethyldiethylenetriamine (PMDETA) catalyst system. Subsequently, the obtained polymer was directly allylated without purification under carbocationic conditions with TiCl<sub>4</sub> and allyl-trimethylsilane reagents in dichloromethane and benzotrifluoride. The hydroboration of the allyl endgroups of PSt with 9-borabicyclo[3.3.1]nonane (9-BBN) followed by oxidation was performed to produce hydroxyl-telechelic PSt. The terminal allyl groups were also modified by epoxidation with *m*-chloroperbenzoic acid. The average molecular weights and molecular weight distributions of the obtained products were analyzed by gel permeation chromatography (GPC) and their structure and functionality were investigated by <sup>1</sup>H, <sup>1</sup>H-<sup>13</sup>C HSQC NMR and ATR-FTIR spectroscopy.

Hyperbranched polyglycerols with various molecular weights were synthesized by living anionic ring-opening multibranching polymerization of glycidol (ROMBP) at 95 °C under inert atmosphere using phthalimide/potassium phthalimide initiating system and slow monomer addition technique. The average molecular weight, molecular weight distribution, the structure of the produced HbPGs and the incorporation of the phthalimide group were investigated by different methods, such as GPC (operated with water and THF eluents), <sup>1</sup>H NMR, <sup>13</sup>C NMR and UV-visible spectroscopies and vapor pressure osmometry. The transformation of the terminal phthalimide functional group of the HbPG to amine functionality

via cleavage of phtaloyl the group was performed by hydrazinolysis. Further modifications of the amine group were studied in three different reactions. Carboxyl-, maleimide- and chloroacetamide-monofunctional HbPGs were prepared by the reactions with succinic anhydride, maleimido-hexanoic acid and chloracetic acid pentachlorophenyl ester, respectively. The functionalization reactions were followed by multidimensional NMR spectroscopy and electrospray ionization mass spectrometry (ESI-MS).

The syntheses of alkyl-monofunctional HbPGs were carried out by direct use of dodecyl- and octadecyl-alcohol initiators, and the glycidol monomer feed rate was changed in three steps to avoid chain transfer to the monomer. The resulting products were characterized by GPC and <sup>1</sup>H NMR, as well as their surface active behavior was investigated. The surface tension of the aqueous solutions of alkyl-HbPGs was measured by drop shape analysis from which critical micelle formation concentrations (*cmc*) were determined as well. The biocompatibility of the produced samples was characterized by the adsorption of bovine serum albumin with quartz crystal microbalance (QCM). Octadecyl-HbPG was functionalized with a carboxyfluorescein dye molecule in the presence of dicyclohexylcarbodiimide and *N,N*-dimethylaminopyridine by the Steglich esterification reaction. The functionality of the obtained product was determined by <sup>1</sup>H NMR spectroscopy. The applicability of the alkyl-HbPGs as a surface active stabilizer was tested, in which poly(D,L-lactic acid-*co*-glycolic acid) (PLGA) nanoparticles were prepared by nanoprecipitation in the presence of the alkyl-HbPGs. The size and dispersity of the produced PLGA-HbPG nanoparticles were measured by dynamic light scattering and atomic force microscopy (AFM), and their surface composition was characterized by electrophoretic mobility measurements. The colloidal stability of the PLGA-HbPG nanoparticles was studied by following the turbidity changes of the solutions due to increasing electrolyte concentration. The PLGA nanoparticle stabilized with carboxyfluorescein-functionalized alkyl-HbPG was examined by fluorescence spectroscopy.

HbPGs were produced by using pentaerythritol initiator and three different monomer/initiator ratios. The resulting products were modified by a carboxyl-functional BHT analogue, namely with 3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionic acid using the above mentioned Steglich esterification reaction. The obtained products were characterized by <sup>1</sup>H NMR and GPC, and the exact antioxidative group contents were measured by UV-Vis spectroscopy, while the thermal properties of the produced samples were investigated by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). The antioxidative efficiency of the obtained HbPG-based macromolecular stabilizers was determined by testing the thermooxidative degradation of PVC with Metrohm PVC Thermomat

763 at 200 °C in trichlorobenzene under oxygen flow with various additive contents. The results were compared with the efficiency of an industrially applied small molecular antioxidant, Irganox1010. During the measurements, the amount of the HCl eliminated from PVC was followed by conductometry, and to determine the extent of chain scission after the treatment, the PVC was precipitated and analyzed by GPC. The migration ability from PVC blends of one selected HbPG-based macrostabilizer and Irganox1010 was compared by hexane and aqueous extraction measurements, and the stabilizer content was followed by  $^1\text{H}$  NMR spectroscopy.

### III. New Scientific Results

1. Bromo-telechelic PSt was prepared under ATRP conditions using a bifunctional initiator. The resulting PSt was directly converted to an allyl-telechelic macromolecule under cationic condition without isolation and purification of the polymeric intermediate. The obtained GPC,  $^1\text{H}$  NMR and HSQC NMR spectroscopy results prove that in the case of appropriate quantities and sequences of reagents, the allylation step is not affected by the reactants of the ATRP. It is also proved that the PSt produced by ATRP can be quantitatively transformed by cationic allylation not only in the generally applied dichloromethane but in the environmentally advantageous benzotrifluoride as well. So, it can be stated that by combining the ATRP of styrene and carbocationic allylation, a simple one-pot method was developed which is suitable for the environmentally advantageous production of allyl-telechelic PSt.
2. The allyl terminal groups of the telechelic PSt were modified by hydroboration and epoxidation. The GPC,  $^1\text{H}$  NMR, HSQC NMR and ATR-FT-IR results prove that the molecular weight and the molecular weight distribution of the synthesized polymers did not change significantly and the desired hydroxyl and epoxide chain ends were formed during the chain end modification. It can be stated that hydroxyl- and epoxide-telechelic PSts were successfully produced quantitatively for the first time. These are supposed to be suitable for producing new macromolecules either by further endgroup modifications or as a base material for polyurethanes and epoxy resins to alter their physical properties.
3. The results proved that the phthalimide/potassium phthalimide as an initiating system can be successfully applied for the living anionic ring-opening multibranching polymerization of glycidol. The used initiator was incorporated quantitatively into the polymer, and each macromolecule contained only one phthalimide functional group, which was confirmed by UV-visible and  $^1\text{H}$  NMR spectroscopies as well as VPO. Proved

directly by  $^{13}\text{C}$ -NMR spectroscopy and indirectly by GPC, polymers with the desired structure and high degree of branching were produced. Furthermore, based on the results, it was found that under the applied conditions the molecular weight of the resulting polymers can be easily controlled by the used monomer/initiator ratio resulting in narrow molecular weight distribution. It can be assumed that the developed initiating system can be used for the polymerization of further epoxides and cyclic monomers, thus producing new phthalimide terminal polymers.

4. The phthalimide monofunctional HbPG was quantitatively converted into an amine functionalized polymer by hydrazinolysis. Three functionalization reactions were performed to confirm the convertibility of this amine group. The results show that well-defined carboxyl, maleimide and chloracetamide monofunctional HbPGs were produced by the amide bond formations. These functional groups can be directly linked to surfaces or bioactive molecules, such as drugs, targeting agents, dyes etc., by conjugation reactions, and the HbPG can potentially increase their water solubility, stability and biocompatibility.
5. Alkyl-monofunctional HbPGs were successfully synthesized by direct application of dodecyl (C12) and octadecyl (C18) alcohols as initiators. The GPC and  $^1\text{H}$  NMR spectroscopy results show that the desired polymers were formed with the predetermined molecular weight and structure by the developed method, i.e., by varying the rate of the monomer addition. It was also demonstrated that these macromolecules have amphiphilic character and exhibit surface active behavior in aqueous solutions, which can be characterized by the critical micelle concentration (*cmc*). The obtained results showed that the surface active behavior (i.e. *cmc*, surface excess concentration, molecular surface area) can be influenced by the length of the alkyl chain and the composition of the macromolecule. By QCM measurements, it was also confirmed that there is not any non-specific protein adsorption with bovine serum albumin (BSA) and the produced alkyl-HbPG, so it is assumed that these HbPGs will also be applicable in biological systems.
6. In my experiments, the applicability of amphiphilic HbPG for the stabilization of poly(lactic acid-*co*-glycolic acid) (PLGA) nanoparticles were also examined. The surface of the PLGA nanoparticles were stabilized due to the orienting interaction of the hydrophobic alkyl segment of the alkyl-HbPG and PLGA surface as proved by the results of zeta-potential experiment. AFM and DLS results demonstrated that average size of the PLGA nanoparticles stabilized by alkyl-HbPG were approximately 100 nm in diameter

with narrow size distribution. It was also confirmed that the alkyl-HbPGs as surface stabilizers greatly increases the aggregation stability of PLGA nanoparticles. It should be highlighted that the C18-HbPG, even at low concentrations, prevented the PLGA nanoparticles from coagulation even at extremely high salt concentrations (2 M). Carboxyfluorescein modified C18-HbPG was also successfully prepared, thereby the easy functionalization of the hydroxyl groups was demonstrated too. The alkyl-HbPG may be modified either with targeting or signaling molecules by which functionalized surface containing drug delivery nanostructures may be obtained.

7. Three different HbPGs with varying molecular weight were synthesized with a pentaerythritol initiator, which were successfully modified by a carboxyl-functional BHT analogue. The high antioxidant content can be achieved by the performed esterification reaction as proved by UV and  $^1\text{H}$  NMR spectroscopies. The TGA analysis showed that the obtained products are thermally stable at the generally applied polymer processing temperatures. It has been found that the HbPG-based macroantioxidants inhibit the thermooxidative elimination of hydrogen chloride in a wide range of compositions and prevent the chain scission of PVC, but the stabilizing efficiency slightly decreases with the increase of the molecular weight. The results show that the antioxidative efficiency of the produced macromolecular stabilizers was slightly lower than that of the generally used small molecular BHT analogue. Migration studies from PVC films showed that the loss of HbPG-based macrostabilizer in both hexane and water is only one third of the loss of the Irganox1010 additive. Hence, it can be concluded that the application of the developed HbPG-based macromolecular antioxidant in PVC is considered as an environmentally advantageous approach.

## IV. Publications and Presentations

### IV. 1. Publications

1. Gy. Kasza, G. Gyulai, Á. Ábrahám, Gy. Szarka, B. Iván, É. Kiss: Amphiphilic hyperbranched polyglycerols in a new role as highly efficient multifunctional surface active stabilizers for poly (lactic/glycolic acid) nanoparticles, *RSC Advances*, **2017**, 7(8), 4348-4352.
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10. **Gy. Kasza** (szerkesztő): Program and Book of Abstracts, International Symposium on Amphiphilic Polymers, Networks, Gels and Membranes (ISBN:978-963-12-3161-8).
11. L. Pethő, **Gy. Kasza**, O. Láng, E. Lajkó, B. Iván, L. Köhidai, G. Mező: Synthesis and in vitro cytotoxic activity of EGF receptor targeting drug-peptide-polymer conjugates, *J. Pept. Sci.*, **2016**, *22*(52S), 190.

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4. Á. Szabó, G. Érsek, A. Domján, Cs. Fodor, G. Kali, **Gy. Kasza**, T. Marek, B. Németh, B. Pásztori, Sz. Pásztor, T. Stumphauser, K. Süvegh, K. Verebélyi, B. Iván: Functional Polymers Obtained by Quasiliving Cationic Polymerizations as Building Blocks of Novel Macromolecular Architectures, IUPAC International Symposium on Ionic Polymerization 2013, Awaji (Japán), 23-28 September 2013. (oral)
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6. **Gy. Kasza**, A. Nádor, Gy. Szarka, B. Iván: Synthesis of bio-friendly hyperbranched polymer based macromolecular antioxidants, International Conference on Bio-Friendly Polymers and Polymer Additives: From Scientific Aspects to Processing and Applications, Budapest (Hungary), 19-21 May 2014. (oral)
7. A. Nádor, **Gy. Kasza**, Zs. Osváth, Gy. Szarka, B. Iván: Syntheses of macromolecular stabilizers based on hyperbranched polymers, New types of phenolic polymeric/oligomeric stabilizer and their testing in PE and PP photo-oxidation, International Conference on Bio-Friendly Polymers and Polymer Additives: From Scientific Aspects to Processing and Applications, Budapest (Hungary), 19-21 May 2014. (poster)
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12. A. Nádor, **Gy. Kasza**, K. Mosnáčková, Zs. Osváth, T. Stumpfhauser, Gy. Szarka, K. Czaniková, J. Rychlý, Š. Chmela, J. Mosnáček, B. Iván: Syntheses and characterization of multicomponent macromolecular stabilizers, International Symposium on Amphiphilic Polymers, Networks, Gels and Membranes, Budapest (Hungary), 30 August - 2 September 2015. (poster)
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20. B. Németh, K. Verebélyi, **Gy. Kasza**, Gy. Szarka, B. Iván: Hiperelágazásos-polisztirol előállítása sztirol és divinil-benzol karbokationos kopolimerizációjával környezetileg előnyös reakciókörülmények között, XVI. Nemzetközi Vegyészkonferencia, Kolozsvár (Romania), 11-14 November 2010. (poster)
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