Synthesis and functionalization of novel star-shaped copolymers

Ph.D. Thesis

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I. Introduction and Aims

Nowadays, dental filling materials are produced via radical photopolymerization of methacrylates. The volumetric shrinkage occurring during this process has a disadvantageous effect on the properties of the filler. Therefore, one of the main goals of the current research and developments is the elimination of polymerization shrinkage. Previously, novel low molecular weight monomers with potential low shrinkage were synthesized and tested, and then it was realized that macromolecules with appropriate functionality and structure can affect the polymerization behavior favorably. Macromolecules with special structure and functionality can be synthesized via quasiliving atom transfer radical polymerization (ATRP), which was developed in the mid 1990s. Although, several types of branched polymers can be created, only dendrimers, which are special types of hyperbranched polymers, has been investigated as multifunctional monomers in dental composites.

In the course of my research, synthesis of novel branched multifunctional polymers, which can affect the properties of dental filling materials advantageously, has been carried out via ATRP. A method of synthesizing star-shaped and grafted star-shaped copolymers consisting of methyl methacrylate and 2-hydroxyethyl methacrylate has been developed. Macroinitiator and macromonomer have been prepared via modification of functional groups of the copolymers. The polymerization shrinkage that occurred during the photopolymerization of macromonomers has been investigated. Polyurethane networks have been synthesized from the new hydroxyl group containing copolymers. The structure and the composition of the synthesized materials have been analyzed with $^1$H NMR spectroscopy. The molecular weight distribution of polymers was determined by gel permeation chromatography (GPC).
II. Applied Methods

The monomers and the solvents used during the polymerization were purified by vacuum distillation. The tetrafunctional initiator was synthesized by esterification reaction. For the copolymerization, 2-hydroxyethyl methacrylate was protected by trimethylsilyl group to avoid side reaction. The poly(2-hydroxyethyl methacrylate) sequence was obtained by deprotection of the trimethylsilyl group with acidic ion exchange resin. A copolymerization of methyl methacrylate and 2-hydroxyethyl methacrylate was carried out at 60 °C in bulk with CuBr/N,N,N’,N’’,N’’’-pentamethyldiethylenetriamine catalyst.

Copolymerizations of methyl methacrylate and 2-hydroxyethyl methacrylate (2-(trimethylsilyloxy)ethyl methacrylate) were conducted at 10 °C in methanol and isopropanol with CuCl/2,2’-bipyridine catalyst. Macromonomer and macromonomer were synthesized by esterification reaction of the hydroxyl groups of star-shaped copolymers. The macroinitiator was used for the copolymerization of methyl methacrylate and 2-hydroxyethyl methacrylate. The ATRP catalyst was copper(I)-chloride with 2,2’-bipyridine ligand. The monomer conversion and polymer composition were analyzed by $^1$H NMR spectrometry. The molecular weight of the copolymers was determined by gel permeation chromatography (GPC) equipped with a dual detector system.

Polymer networks were prepared by the photopolymerization of the macromonomers and methyl methacrylate with 2,2-dimethoxy-acetophenone photoinitiator. The polymerization shrinkage and extraction ratio were measured.

Hydroxyl functional star-shaped copolymers were cross-linked by a diisocyanate. The curing reactions of polymeric films were carried out at 70 °C for 41 h. The extraction ratio was measured by gravimetry.
III. New Scientific Results

1. A method was developed to synthesize poly(methyl methacrylate–r–2-hydroxyethyl methacrylate) star-shaped copolymers by using quasiliving atom transfer radical polymerization. In the course of the copolymerizations of methyl methacrylate and 2-hydroxyethyl methacrylate, I proved that well-defined star copolymers can be obtained with narrow molecular weight distribution by convenient selection of solvents (methanol and isopropanol), catalyst (CuCl/2,2’-bipyridine) and reaction conditions (at 10 °C for 2 h). It was found that there are no significant differences in the macromolecular properties of poly(methyl methacrylate–r–2-hydroxyethyl methacrylate) star copolymers by using different synthetic routes, that is by applying either the trimethylsilyl protected or the nonprotected 2-hydroxyethyl methacrylate as comonomers.

2. Multifunctional macromonomers containing initiating and vinyl groups have been synthesized via esterification reaction between hydroxyl groups of star-shaped poly(methyl methacrylate–r–2-hydroxyethyl methacrylate) and methacryloyl chloride. Networks have been synthesized via photopolymerization of multifunctional macromonomers derived from the star-shaped poly(methyl methacrylate–r–2-hydroxyethyl methacrylate) and methyl methacrylate. The polymerization shrinkage occurred during the synthesis of networks was significantly lower in the case of the multifunctional macromonomers than in the case of methyl methacrylate and 1,4-butanediol dimethacrylate, which are currently applied dental filling materials. The extraction ratio of formed networks
proved that no unreacted monomers are present after the photocuring of the star-shaped macromonomers.

3. It was proved that the star-shaped poly(methyl methacrylate-r-2-hydroxyethyl methacrylate) copolymers can form networks with diisocyanates. The extraction ratios of synthesized polyurethane networks were between 0-10%. It was concluded that this process is an effective method to synthesize poly(methyl methacrylate) networks, which can be the basis of new utilization fields of this polymer.

4. Macroinitiators were synthesized via esterification reaction of hydroxyl groups of star-shaped poly(methyl methacrylate-r-2-hydroxyethyl methacrylate) copolymers with α-bromoisobutyryl bromide. Methyl methacrylate and 2-hydroxyethyl methacrylate have been copolymerized using the resulting new macroinitiator and CuCl/2,2′-bipyridine as catalyst complex in methanol at 10 °C. Gel permeation chromatography (GPC) proved that the macroinitiator is an effective initiator under ATRP conditions, and novel grafted copolymers can be obtained from the star-shaped copolymer.

IV. Significance of the New Results

In the course of my investigations, new multifunctional star-shaped copolymers with well-defined structure were synthesized form methyl methacrylate and 2-hydroxyethyl methacrylate via quasiliving atom transfer radical polymerization.
Multifunctional macromolecules derived from these star-shaped copolymers have advantageous photopolymerization behavior, therefore these macromolecules can serve as advantageous macromonomers in dental filling materials with low shrinkage. The hydroxyl group containing star-shaped copolymers can be also utilized as starting materials to prepare special coatings.

Grafted star-shaped macromolecules have compact structure and large number of functional groups. These copolymers can have numerous application possibilities because of the easy transformation of hydroxyl groups.

V. Publications and Presentation

Publications


Proceedings

1. A. Soltész, T. Fónagy, M. Szesztay, B. Iván: Hyperbranched Polymers with Polymerizable Groups from Dental Filling Monomers


Presentations

   Centenáriumi Vegyészkonferencia, Sopron, 2007. május 29.-június 1. (poster)

2. A. Soltész, T. Fónagy, M. Szesztay, B. Iván: Functional hyperbranched poly(methyl methacrylate) as a potential new dental filling precursor
   European Polymer Congress, Portoroz, 2-6 July 2007 (poster)

   American Chemical Society Meeting, Boston, 2007. augusztus 19-23. (poster)

5. Soltész Amália, Fónagy Tamás, Szanka István, Szesztay Andrásné, Iván Béla
Egy új fogtömőanyag prekurzor: hiperelágazásos poli(metil-metakrilát)
(postér)

6. Erdődi Gábor, Fodor Csaba, Groh Werner Péter, Haraszti Márton, Hellner
Ákos, Iván Béla, Kali Gergely, Kasza György, Mezey Péter, Pálfi Viktória,
Soltész Amália, Szabó L.Sándor, Szanka István, Szarka Györgyi, Verebélyi
Klára:
Nanoszerkezetű polimereken alapuló új nanohibrid anyagok
ELTE Innovációs Nap, Budapest, 2008. február 05. (postér)

7. Soltész Amália, Kasza György, Kali Gergely, Szanka István, Szesztay
Andrásné, Iván Béla:
Hiperelágazásos multifunkciós polimerek mint fogtömő és módosító
alapanyagok
VIII. Téli iskola, Balatonfüred, 2008. február 06-08.

8. Béla Iván, Gábor Erdődi, Ákos Hellner, Péter Werner Groh, Gergely Kali,
György Kasza, Amália Soltész, István Szanka, Márta Szesztay:
New ways for the synthesis of hyperbranched polymers
Makromolekulares Kolloquium, Freiburg (Németország), 2008. február 28-
március 1.

9. Soltész A., Szanka I., Szesztay A., Iván B.:
Multifunkciós hiperelágazásos polimerek fogtömő anyagokként használt
monomerekből, mint kis zsugorodást eredményező potenciálisan új fogtömő
anyagok prekurzorai
Magyar Tudományos Akadémia, Műanyag és Természetes Polimerek

Hiperelágazásos polimerek szintézise láncvégi és láncmenti reakciókkal - új
potenciális energiatakarékos adalékoktól új fogtömőanyagokig

Szesztay, Á. Szabó, K. Verebélyi, B. Iván:
New Functional Polymers with Linear and Hyperbranched Topologies
Frontiers in Polymer Science, Mainz, Germany, 7-9 June, 2009 (poster)


