Synthesis of multifunctional star and hyperbranched polymers by quasiliving atom transfer radical polymerization

Ph.D. Theses

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I. Introduction and Aims

In the last decade, polymer chemistry, the related material science, and especially the macromolecular engineering have witnessed explosive development. Quasiliving radical polymerizations processes, including atom transfer radical polymerization (ATRP) have enabled synthesis of many well-defined polymers.

Since the mid 1990s, the ATRP has allowed the synthesis of various types of polymeric materials with unique physical and chemical properties. The outstanding advantageous properties of the resulting polymers may open the way for the utilization of these materials in the high added value market.

We have developed a novel one-pot synthesis to produce hyperbranched polystyrene with pendant vinyl groups and chain-end functionality from commercially available inexpensive styrene and divinyl monomers. The effect of reaction parameters on the branched structure formation and gelation was studied.

In addition, two other polymerization techniques (inimer and „core-first” methods) have been used for the preparation of multifunctional star-shape and hyperbranched polyacrylate copolymers. The copolymers with diverse composition allowed the investigation on the correlation between composition and thermal properties. The polyurethane film formation capability of these functional polymers was also demonstrated.

The structure and composition of hyperbranched polymers was analyzed by \(^1\)H NMR spectrometer. Molecular weights of branched copolymers were determined by gel permeation chromatography (GPC) equipped with triple detector system. The glass transition temperatures were measured by differential scanning calorimetry (DSC).
II. Applied Methods

The monomers used during the polymerization were purified by vacuum distillation. The (co)polymerizations were carried out under inert atmosphere at 80 °C and aliquots were periodically withdrawn for $^1$H NMR and GPC (Wyatt MiniDawn®) characterization of monomer conversions and polymer molecular weights. In ATRP, the initiator was 1-phenylethyl bromide and the catalyst was copper(I)-bromide with N,N,N',N'',N''-pentamethyldiethylenetriamine (PMDETA) ligands. We varied the concentration of divinyl benzene and the monomer/initiator ratio. The 2-(2-bromoisobutyryloxy)ethyl acrylate (inimer) and the tetrafunctional initiator were synthesized by esterification reaction. A copolymerizations of inimer, butyl acrylate, isobornyl acrylate and 2-(trimethylsilyloxy)ethyl acrylate were conducted at 80 °C in toluene with CuBr/2,2-bipyridine catalyst. The poly(2-hydroxyethyl acrylate) sequence was obtained by deprotection of trimethylsilyl group with acidic ion exchange resin. The curing reactions of polymeric films were carried out at 80 °C for 24 h. The thickness and extraction ratio were measured.

III. New Scientific Results

1. Controlled propagation in ATRP processes enables the synthesis of multifunctional hyperbranched copolymers from commercially available inexpensive mono- and divinyl monomers in one-pot. In copolymerization of styrene and divinyl benzene we proved that gelation can be avoided by convenient selection of reaction conditions.

2. The formation of the compact hyperbranched structure of poly(styrene-co-divinyl benzene) copolymers was characterized by gel permeation chromatography.
3. The purified poly(styrene-co-divinyl benzene) copolymers were analyzed by $^1$H NMR spectroscopy, and the investigations showed that a multifunctional hyperbranched polymer was obtained which contains alkyl halides at the chain-end and pendant vinyl groups.

4. In addition it was found that in contrast to the conventional radical polymerization, there are opportunities for the preparation of hydroxy functional hyperbranched polyacrylates by quasiliving atom transfer radical copolymerizations of inimer (initiator+monomer) and 2-(trimethylsilyloxy)ethyl acrylate with Cu(I)Br/2,2'-bipyridine catalyst.

5. The composition of the hyperbranched and star polyacrylates depends on the techniques of monomer addition (in single reaction or sequential monomer addition) during the ATRP process. The structure and composition of hydroxy functional hyperbranched polymers synthesized by ATRP of 2-(2-bromoisobutyryloxy)ethyl acrylate, butyl acrylate, isobornyl acrylate and 2-(trimethylsilyloxy)ethyl acrylate were investigated in details with GPC and $^1$H NMR analyses.

6. The glass transition temperature of polymers was determined by differential scanning calorimetry. The copolymers with diverse composition allowed the investigation on the correlation between composition and thermal properties. During this study, it was concluded that ATRP is an appropriate method for fine tuning of glass transition temperature of these novel hyperbranched polymers.

7. Tetrafunctional initiator was used to synthesize well-defined star polymers with arms consisting of random or block polymer sequences. The composition and structure of the star copolymers were confirmed by $^1$H NMR spectroscopy.
8. The effect the ratio between butyl acrylate and isobornyl acrylate on the glass transition temperature (Tg) of the star polymers was studied in details. The relation between Tg and the HEA content and sequence distribution (random or block) was also investigated. It was found that the Tg of random copolymers is higher than that of the star block polyacrylates with the same composition. This finding provides an opportunity to fine tuning of Tg of these polymers by selecting the required structural sequence order.

9. Film formation was successfully demonstrated by reacting star polymers with hydroxy groups synthesized via ATRP and hyperbranched polyacrylates with diizocyanates. Thickness and extraction ratio of the synthesized polyurethane films were determined. It was found that these branched polymers lead to homogeneous and intact coatings.

IV. Publications and Presentation

Publications

1. O. Kovács, I. Szanka, B. Iván
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   On the Dynamics of the Cholestane Spin Probe in a Nematic Azobenzene Side Group Oligomer

   New Ways for the Synthesis of Hyperbranched Polymers


Proceedings


Presentations


5. I. Szanka, S. Caricato, G. Galli
   Recent Advances In Liquid Crystals With Different Molecular Architectures

6. I. Szanka, O. Kovács, B. Iván
   Synthesis of Poly(Methacrylate)S by Quasiliving Atom Transfer Free Radical
   Polymerization With Slow Initiation
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7. I. Szanka, M. Szesztay, B. Iván
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   Polymerization, 4th European Polymer Congress 2007 (EPF 2007) - 2007. július 2-6.,
   Portorož, Szlovénia

   Soltész A., Szabó S., Szanka I., Szarka Gy., Verebélyi K.
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    Transfer Radical Polymerization
    NATO Advanced Study Institute (ASI), 2008. szeptember 1-12., Antalya, Törökország

    New and Easy Preparations of Branched Polymeric Structures Based on Different Vinyl
    Monomers
    Interfaces ’08, Sopron, September 24-26, 2008.

    Szesztay, K. Verebélyi
    New Functional Polymers with Linear wnd Hyperbranched Topologies
    Int. Symp. on Frontiers in Polymer Science, Mainz, June 7-9, 2009
New routes to novel hyperbranched polymers
European Polymer Congress, Graz, July 12-16, 2009

15. Illés G., Iván B., Szanka I.
Amifil polimer kotérhálók szintézise "click" kémiai kapcsolási reakcióval
Magyar Kémikusok Egyesülete 2010. évi Vegyészkonferenciája, Hajdúszoboszló