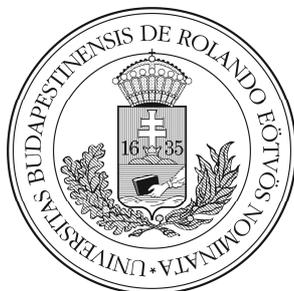


Carbocationic and Atom Transfer Radical Polymerization in Benzotrifluoride Solvent

Ph. D. Theses

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Budapest

2012

I. Introduction and Objectives

Quasiliving polymerization techniques are considered as main tools for macromolecular engineering by which macromolecules can be synthesized with predetermined average molecular weight, low polydispersity, designed structure and terminal groups. In the carbocationic polymerization of vinyl monomers, low polymerization temperature (even $-80\text{ }^{\circ}\text{C}$ or lower) and huge amounts of polar solvents, especially chlorinated hydrocarbons are generally used in order to suppress side reactions and to ensure the desirable ionization state of the carbocations. Solvents play an important role in the widely spread and frequently studied atom transfer radical polymerization as well, primarily because providing homogeneous reaction conditions in the favor of controllability is an important but often not easily manageable requirement.

During my PhD work, carbocationic and atom transfer radical polymerization reactions were investigated in order to explore and optimize reaction conditions which can decrease the environmental impact of the processes while maintaining their effectiveness. First, the replacement of the most common solvents of carbocationic polymerizations, namely dichloromethane and chloroform were aimed at. These compounds are considered as highly harmful materials due to their remarkable health and environment polluting effects combining with low volatility which is responsible for the million tons range of annual emission of these solvents. Based on previous reports from the field of organic and fluorine chemistry, I started to study benzotrifluoride (BTF) as a chlorine free, less volatile alternative solvent. Besides carbocationic polymerization, the application of BTF was investigated also in atom transfer radical polymerization in order to investigate the applicability of this solvent to replace compounds, such as benzene and toluene, with toxic and harmful labels. Interestingly, in polymerization reactions BTF has been mainly applied for the polymerization of fluorine containing monomers so far.

In the course of my research, systematic experiments were carried out in order to answer three main questions: (1) is BTF a suitable solvent in the polymerization of non-fluorine monomers, (2) can any significant solvent effect be observed by the replacement of the classic solvents, (3) how can these results be utilized for the synthesis of functional polymers.

II. Applied Methods

The syntheses of the polymers were carried out by carbocationic and atom transfer radical polymerization. The carbocationic polymerization of styrene was performed in the presence of an organic halide initiator, transition metal containing Lewis acid coininitiator (TiCl_4 or SnCl_4) and polymerization additive (nucleophile or tetrabutyl ammonium salt) in dichloromethane and in benzotrifluoride solvents. The effects of reaction conditions, like temperature and coininitiator concentration, were studied on the outcome and kinetics of the polymerization process. The atom transfer radical polymerization of styrene, methyl metacrylate and *n*-butyl acrylate were also performed. The applied initiator system consisted of alkyl halide initiator, copper bromide catalyst and amine type ligand. During these polymerizations BTF was used instead of the mostly applied toluene, benzene or anisole. The kinetics of the processes were followed by sample withdrawal.

The application of BTF was also demonstrated in the random carbocationic and atom transfer radical copolymerization of styrene and *p*-divinyl benzene.

The determination of the average molecular weight and the molecular weight distribution of the resulting polymers and the identification of hyperbranched structure were carried out by gel permeation chromatography. The structural analysis of the polymers was accomplished by ^1H NMR spectroscopy.

III. Major Scientific Results

1.

Comparative carbocationic polymerization investigations of styrene were carried out in benzotrifluoride and dichloromethane solvents using 1-phenylethyl chloride initiator and TiCl_4 coininitiator at $-20\text{ }^\circ\text{C}$. The nucleophilic additive, 1,1,4,4-tetramethylethylenediamine (TMEDA) was applied for the first time in this reaction. I have concluded that the polymerization reaction produces polymers with remarkable conversion after only 5 minutes reaction time, which is outstanding compared to most of the published cases where the reaction time is often measured in days. These results prove that this initiator system can be successfully applied for the carbocationic polymerization of styrene.

2.

The synthesis of polystyrene by carbocationic polymerization was performed for the first time in benzotrifluoride solvent. As a comparison, the reaction was carried out also in dichloromethane which is the most commonly applied solvent for this reaction. On the basis of the results, it can be stated that DCM can be successfully replaced by the environmentally more favored BTF without significant changes in the conversion or in the basic properties of the resulting polymers.

3.

The carbocationic polymerization of styrene was studied without cooling the reaction system, i.e. at room temperature. The experiments revealed that the polymerization in BTF led to slightly lower conversion data but the resulting polymers possess theoretical number average molecular weight (M_n) values. Increasing the reaction temperature led to the decrease of the polydispersity values can be observed. From all of these results, I have concluded that using the above mentioned initiator system at room temperature, polystyrene with higher conversion, theoretical M_n values and narrower molecular weight distributions can be synthesized in BTF than in DCM.

4.

The effect of the $TiCl_4$ coininitiator concentration was investigated on the outcome and kinetics of the polymerization of styrene. It was proved that beside the expected decrease of the conversion, the carbocationic polymerization of styrene can be carried out with only twofold excess of $TiCl_4$ over initiator in contrast to the published examples where the $TiCl_4$ /initiator ratio is in the range of 10-16. The presence of side reactions was determined at every coininitiator/initiator ratio within the studied range. The appearance of side reactions showed correlation with the $TiCl_4$ extent, which can be related through the conversion data to the free monomer concentration. The major side reaction was identified as terminal indanyl ring formation, which is one of the specific side reactions of carbocationic polymerization of styrene, by assigning the characteristic chemical shifts in the 1H NMR spectra of the formed polystyrenes. Furthermore, I have found that the proton eliminated in the ring formation does not participate in chain transfer reactions because of the proton binding ability of the TMEDA nucleophile. This conclusion was supported by the obtained number average molecular weights. From these results, it can be stated that a successful method was developed for the

elimination or suppression of the frequent chain transfer to monomer side reaction. On the basis of these findings, the presumable reaction mechanism of the carbocationic polymerization of styrene under the investigated reaction conditions was described, which involves initiation, chain propagation, reversible chain termination and terminal indanyl ring formation.

5.

The application of BTF as a solvent was also investigated in the SnCl₄ catalyzed carbocationic polymerization of styrene in the presence of *n*-tetrabutyl ammonium bromide salt at -15 °C. Unexpected induction period was observed in this polymerization reaction, on the one hand. On the other hand, the polymerization showed quasiliving nature. From the observed low initiation efficiency data it can be concluded that the polymerization is accompanied with slow initiation. According to my results, quasiliving nature cannot be observed at room temperature. However, by decreasing the high initial coinitiator/initiator ratio, the results indicate the improvement of the controllability and the initiating efficiency at this temperature. Applying fourfold SnCl₄ extent over the initiator, the absence of irreversible chain termination, chain transfer or slow initiation was observed, which proves the quasiliving mechanism of the carbocationic polymerization of styrene under these conditions.

6.

On the basis of the above mentioned results, hyperbranched, multifunctional copolymers were synthesized by the random carbocationic copolymerization of styrene and *p*-divinyl benzene in BTF. I have found that by selecting the proper comonomer/initiator ratio, the copolymerization reaction results in the desired copolymers quantitatively within five minutes reaction time at room temperature without gelation. The hyperbranched structure was determined by multi angle light scattering gel permeation chromatography, and the multifunctionality was proved by ¹H NMR spectroscopy.

7.

BTF was also investigated in atom transfer radical polymerization as an alternative solvent of toluene, benzene, xylene, anisole, which are widely applied in spite of their toxic or harmful labeling. I have found that during the ATRP of styrene, quasiliving polymerization with slow initiation occurs as proved by kinetic experiments. The ATRP of methyl methacrylate was

also conducted in BTF. The results showed that the polymerization was not quasiliving due to side reactions in this process. In the case of the *n*-butyl acrylate monomer, the investigated polymerization system proceeded by quasiliving manner and led to linear polymers effectively with predetermined molecular weights and extremely narrow molecular weight distributions.

8.

The random atom transfer radical copolymerization of styrene and *p*-divinyl benzene was also carried out in BTF. According to my results, this method is also suitable for the gelation free synthesis of hyperbranched, multifunctional copolymers. The hyperbranched structure was determined by multi angle light scattering gel permeation chromatography, while the multifunctionality was proved by ¹H NMR spectroscopy.

IV. Significance of the New Results

In the course of my PhD work, I have studied the application possibilities of benzotrifluoride (BTF) as a reaction medium in carbocationic and atom transfer radical polymerizations. I demonstrated the advantages and limits of benzotrifluoride (BTF) with the example of a widely used non-fluorous monomer, styrene, which can be polymerized by ionic and radical mechanisms and can be applied for mass and for specific polymer syntheses as well.

My investigations on the carbocationic polymerization of styrene have proved that BTF is an outstanding alternative for the environmentally more disadvantageous dichloromethane (DCM). The TiCl₄ catalyzed reaction was successful even at room temperature. The polymers obtained in this process possess low polydispersities and M_ns close to the theoretical values. Terminal, intermolecular ring formation was found to take place as side reaction during the polymerization, which is promoted by the decrease of the actual monomer concentration. By applying SnCl₄ as coinitiator, the polymerization was observed to become slower in BTF than in DCM. Although the polymerization was accompanied by an induction period and slow initiation as well, quasiliving polymerization takes place with this coinitiator at low temperatures. At room temperature, only the reduction of the SnCl₄ concentration results in the suppression of side reactions, which allows quasiliving polymerization to occur. As a conclusion, in contrast to the widely applied

conditions in both academia and industry, which involve the application of DCM as solvent, low reaction temperature and high Lewis acid concentration, my new results clearly indicate that efficient synthesis of polystyrene can be carried out in a chlorine free, low volatility solvent, i. e. BTF, with low coinitiator concentrations and at room temperature. This can substitute the actual industrial processes for polystyrene production which apply high excess of Lewis acid (AlCl_3 or BF_3), low reaction temperatures and long reaction times.

In the case of the atom transfer radical polymerization, BTF was investigated as an alternative solvent for benzene, toluene, anisole, xylene etc. By this technique, styrene polymerized with slow initiation, but chain breaking steps were not present according to the results of kinetic experiments. The ATRP of MMA was accompanied by chain termination and chain transfer as well, while *n*-butyl acrylate polymerized without any side reactions, and resulted in polymers with predetermined molecular weights and uniquely low polydispersities.

By both methods, BTF was successfully applied as a solvent for the preparation of hyperbranched, multifunctional copolymers without gelation. The resulting copolymers can be widely applicable by the transformation and polymerization possibilities of the terminal chloride and vinyl groups.

V. Publications and Presentations

Publications

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