SYNTHESIS OF DIBLOCK COPOLYMERS
FOR OBTAINING FUNCTIONALIZED NANOPISTICLES

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ABSTRACT

A first step to synthesize polymer-based nanocomposites with functionalized metallic nanoparticles has been made. A novel dibloc copolymer characterized with one block such as trimethoxysilyl and another block such as a typical phosphonate is attractive for a nanocomposites base. In this work a monobloc copolymer only has been synthesized by a Controlled Radical Polymerization (CRP) consisting of two stages: firstly the monobloc copolymer has been synthesized by Atom Transfer Radical Polymerization with a Br-end group (ATRP) and secondly the Br-end group has been transformed in a I-group by Iodine Transfer Polymerization (ITP). This monobloc copolymer is characterized with well-defined complex architecture, composition and functionality. The molecular mass and the index of polydispersity ($1 < I_p < 4$) have been calculated using Nuclear Magnetic Resonance (NMR) and Gel Permeation Chromatography (GPC).

Keywords: dibloc copolymers, monobloc copolymers, functionalized metallic nanoparticles, polymer-particle nanocomposites, Controlled Radical Polymerization (CRP), Atom Transfer Radical Polymerization (ATRP), Iodine Transfer Polymerization (ITP).

INTRODUCTION

The nanotechnologies are a promising direction of the technological progress during the 21\textsuperscript{st} century, while the development of polymer-based nanocomposites is exclusively actual in the area of materials. The polymer-based nanocomposites with low content of nanoparticles ($< 5\%$) are an important class of strengthened polymers.

The present investigation is intend in the area of nanotechnologies and nanomaterials, and more specific is referred to the obtaining of hybrid functionalized nanoparticles of the type metal core/polymer shell which should be important part for preparing of nanocomposites.

Among the different polymer architectures, the amphiphilic dibloc copolymers with well-defined composition and chemical structure have been investigated intensively because of their capability to self-organize and to form nanoparticles representing interesting nanomaterials for varied applications.

Recently the interest in metallic functionalized nanoparticles obtained within diblock copolymers containing poly (3-trimethoxysilyl) propyl methacrylate (TMSPMA) as first block and polyphosphonate in neutral form as second block, has increased because of their potential applications as biocompatible and bio-degradable nanocomposites in important areas such as biotechnology and biochemistry, as well as for biomedical use.
The aim of this work is to synthesize a monoblock copolymer as a first step for preparing functionalized metallic nanoparticles for nanocomposites. One new base for nanocomposites such as a diblock copolymer characterized with one block of type poly (3-trimethoxysilyl) propyl methacrylate (TMSPMA) and another block of type polyphosphonate in neutral form (dialkyl(2-methacryloyloxyethyl)phosphonate (DMOEP)) is very interesting and attractive. The synthesis method used in this work is a Controlled Radical Polymerisation (CRP) by a transfer of atom (ATRP) which will allow obtaining diblock copolymer characterized with a well defined complex architecture, composition and functionality. This method is easy to realize for polymers with a complex architecture.

The functionalized metallic nanoparticles of the core/shell type should act within the copolymers as a nanoreactor via the polyphosphonate bloc having ligand properties capable to complex the metal cations in metal salts solutions (Co, Ni, Cu). The poly (3-trimethoxysilyl) propyl methacrylate (TMSPMA) block should be reticulate by hydrolysis and capuslate the metal/phosphonate core with a shell of type Si-O-Si. Similar nanoparticles have been described in the case of gold Au [1] acting as initiators for the polymerization (CRP).

In our future work we will use for the second block a monomer of the type DMOEP having properties of a ligand. There are few literature data about using DMOEP monomer for this application.

The CRP method for synthesis of copolymers has to be carried out in two stages: the first block will be synthesized by Atom Transfer Radical Polymerization (ATRP) with Br-end group and the second block will be attached by Iodine Transfer Polymerization.

**EXPERIMENTAL**

The copolymers molecular mass and the index of polydispersity (1, 2<IP<1, 4) are calculated using Nuclear Magnetic Resonance (NMR) and Gel Permeation Chromatography (GPC).

Controlled Radical Polymerization (CRP) as a typical Radical Polymerization by Transfer of Atom (ATRP) has been used for the synthesis of a monoblock copolymer with one block of type (3-trimethoxysilyl) with Br-end group. This method allows good controlling the chemical structure of the copolymer combining the flexibility of the radical processes and the advantages of the living systems which is a guarantee for the forming of nanoparticles.

The Controlled Radical Polymerisation (CRP) as an advanced method is used in this work for the synthesis of the monoblock copolymer in two variations – Radical Polymerisation by a Transfer of Atom (ATRP) and Polymerisation by Iodine Transfer (ITP) which determines the originality of our investigation.

In principle the synthesis of diblock copolymers should be realized by the following stages:

1) Synthesis of the first block of poly (3-trimethoxysilyl) propyl methacrylate (TMSPMA) by ATRP [2];

2) Transforming of the end of the first block chain (Br-end group) by ITP for adapting to the synthesis of the second block [3, 4];

3) Grafting of the second polyphosphonate block by ITP.

Generally the scheme of a copolymer synthesis with diblock architecture could be presented as follows (Fig. 1).

The CRP method of the type ATRP allows controlling the molecule - mass characteristics and chemical structure of the polymer combining the flexibility of the radical processes and the advantages of living systems which is a guarantee for a successful synthesis of the diblock copolymer and for obtaining of nanoparticles.

The synthesized by ATRP first block in which the Br-end group is transformed in I-group plays the role of a macro initiator (an agent of chain transfer) in
the synthesis of the second block. The choice of the monomer for the synthesis of the second block carrying the phosphonate group (2-methacryloloxoethyle)phosphonate (DMOEP) is due to its exceptional properties of a ligand which allow the polymer to complex metal oxides on its surface [5,6]. The agent of chain transfer is a macro initiator of type poly (methacryloxypropyl trimethoxisilanol) (MOPS) [7], synthesized by ATRP with Br-end group transformed by I-atom [8,9].

By the methods of Nuclear Magnetic Resonance (NMR) and Gel Permeate Chromatography (GPC) the controlled character of the radical polymerization is verified. Different characteristics of the process are determined such as the change of the molecular mass (Mₙ) during the conversion, the index of polydispersity (1, 2 < M_p < 1, 4, i.e. M_p < 1, 5 at ATRP). It has been found that the change of ln([M]₀/[M]) as a function of the time is linear (where [M]₀ and [M] are concentrations of the monomer respectively at time t=0 and t=t).

RESULTS AND DISCUSSION

The first stage of the synthesis of the copolymer is realized and a monomer with one block of the type poly (3-trimethoxysilyl) propyl methacrylate (TMSPMA) is obtained by PRC-ATRP.

The scheme of ATRP synthesis of PTMSPMA realized in the present work in toluene in the presence of an initiator brommethylbensen, C₃H₇Br, a catalyst Cu (I) Br and a ligand of pentamethyldiethylentriamine (PMDETA) C₅H₁₂N₃ is shown in Fig. 2. It is established that the nature of the solvent influences essentially the process of the polymerization.

The synthesized monomer PTMSPMA representing a tellehelic polymer is characterized with a benzyl group at the one side of the chain and a Br-end group allows to rafting of the second block by ITP. The monomer TMSPMA is very sensitive to humidity and the surrounding environment and that is why all stages of the synthesis have been carried out in an inert and dry medium [9]. By ATRP of methylmethacrylate (MMA) at the same conditions (as in the case of PTMSPMA) polymethylmethacrylate (PMMA) with a low molecular mass and Br-end group is also synthesized. The obtained PMMA with end groups identical with those of PTMSPMA will be used as a model in the case of the investigations to realize ITP for grafting of the second block to the copolymer.

The scheme of the MMA model via the ATRP method is shown in Fig. 3.

Fig. 4 presents a 3D image of the synthesized monobloc copolymer PTMSPMA with a benzyl group in the beginning and a Br-end group.

The polymerization of dialkyd(2-methacryloloyloxyethyl)phosphonate with 3-(trimethoxysilyl)propyle methacrylate in Fig. 5 is realized for the obtaining of the diblock structure.

First of all the Br group is replaced from the iodine group then the copolymerization is completed by the Iodine Transfer Polymerization method (ITP) in Fig. 6.
Fig. 4. 3D image of PTMSPMA.

Fig. 5. Preparation of PTMSPMA-co-DMOEP.

Fig. 6. 3D image of PTMSPMA-co-DMOEP.

Fig. 7. Dependence of the monomer conversion on the reaction time at temperatures of 50°C and 60°C.

In Figs. 7 and 8 are shown, respectively, the monomer conversion and the linear dependence of \( \ln [M/M_0] \) on the time, while in Fig. 9 presents the change of the molecular mass in connection of the conversion of the initial monomer at two reaction temperatures (50°C and 60°C).

CONCLUSIONS

A Controlled Radical Polymerization (CRP) of TMSPMA at 50°C and 60°C is realized and a monoblock copolymer PTMSPMA with Br-end group is synthesized. By analogy is obtained PMMA with a low molecular mass by CRP of MMA as a model for the transformation.
of Br-end group. A good control of the molecule-mass characteristics and the chemical structure of the monoblock copolymers is carried out which is a guaranty for the successful synthesis of a diblock copolymer in the next stage.

We expect the diblock copolymer to complex by the phosphonate group from the second block with metal cations in polymer solution of metal salts (Co, Ni, Cu, Pt) while by a hydrolysis in the first block to create Si-O-Si bonds (a reaction of a reticulation). This would allow forming of nanoparticles, carrying a polyphosphinate/metal core and a shell from polysiloxane with a potential application in medicine and the biotechnologies. The novelty and the originality of this investigation work is the applying of a Controlled Radical Polymerization via ATRP for a synthesis of a new attractive diblock copolymer with well-defined complex architecture, composition and functionality to be prepared by functionalized metallic nanoparticles.

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