Controlled synthesis of reactive polymeric architectures for stimuli-responsive materials

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Introduction

Reactive polymers, such as active ester polymers, have found broad scientific application as synthetic platforms for the versatile preparation of functional polymers.[1] However, mainly active ester polymers based on N-hydroxysuccinimide (NHS) are used in polymer science in the form of NHS-(meth)acrylates.[2]

Controlled radical polymerization techniques gained a lot of interest due to the control of chain length, polydispersity, and microstructure of the respective polymers. The most important processes are nitroxide-mdeiated polymerization (NMP),[3] atom transfer radical polymerization (ATRP)[4] and reversible addition fragmentation chain transfer (RAFT) polymerization.[5]

Up to now, only few of the controlled polymerization techniques have been used to polymerize active ester monomers. NHS-methacrylate was polymerized by ATRP,[6] while the RAFT polymerization of NHS-methacrylate led to rather poor control.[7] Recently, we reported the successful controlled radical polymerization of new active ester monomers, such as endo-N-hydroxy-5-norbornene-2,3-dicarboxyimide acrylate[8] and pentafluorphenyl (meth)acrylate.[9]

Within the present study we investigate new active ester monomers and their RAFT polymerization behavior to synthesize reactive precursor polymers for stimuli-responsive materials.

Experimental

Materials. All chemicals were commercially available, used as received or have been purified according to standard procedures. The transfer agent benzyldithiobenzoate (CTA1) was prepared according to the literature.[10]

Monomers. Active ester monomers have been prepared by reaction from their respective acid chloride with the alcohols in the presence of triethylamine following standard synthetic procedures.

RAFT polymerization. A mixture of 45 eq. monomer, 1 eq. benzyldithiobenzoat (CTA1) and 0.1 eq. AIBN were placed into a Schlenk-flask and dissolved in dry dioxane. Following three freeze-pump-thaw cycles, the flask was immersed in a preheated oil bath of 90°C and kept there for 12 h. After cooling the polymer was isolated by precipitation of the polymer solution into diethylether. The polymer was re-precipitated from dioxane into diethylether, centrifugated and finally dried under vacuum.

Polymer analogous reaction. The reactive polymer was dissolved in dioxane and the respective amount of amine was added. The mixture was stirred at 50°C under nitrogen atmosphere and the resulting polymer was precipitated and dried in vacuum.

Results and discussion

Active ester polymers. Active esters have been well established in organic and peptide chemistry as acylating and coupling reagents, respectively. However, their use in polymer chemistry has so far been limited to N-hydroxysuccinimide acrylate, which cannot be polymerized under controlled radical polymerization conditions. We therefore investigated the controlled radical polymerization behavior of various new active ester monomers, see figure 1.

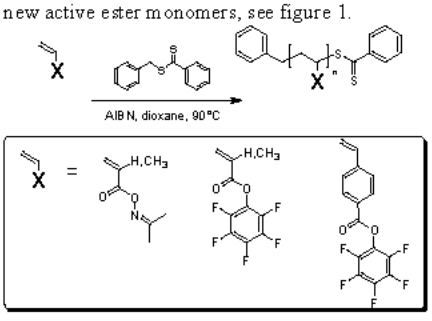

Figure 1. RAFT polymerization of active ester monomers.

RAFT polymerization in solution has successfully been applied to a variety of acrylates using benzyldithiobenzoat (CTA1) as a RAFT agent. Consequently, CTA1 was used as the RAFT agent for the controlled radical polymerization of our active ester monomers, see figure 1. The polymerization was successfully performed in dioxane at 90°C in the presence of CTA1 and AIBN as a thermal initiator, yielding narrow distributed reactive polymers.

The synthetic potential of active ester polymers is based on the possibility to obtain functional polymers by a simple polymer analogous reaction. In this respect, active ester polymers have been reacted with amines to form the respective polyacrylamide derivatives. Considering as example, **P1** was allowed to react with 0.5 eq isopropylamine in dioxane yielding polymer **P1a**, as shown in figure 2. The formation of the isopropylamide was followed by FT-IR. In the IR spectrum of **P1a** the two amide bands at 1647 cm^{-1} and 1539 cm^{-1} can be seen, proving the successful reaction of the acetone oxime ester with isopropyl amine on the polymer backbone. The band at 1750 cm^{-1} shows the existence of remaining acetone oxime groups within the polymer. Afterwards polymer **P1a** was further reacted with ammnonia to yield polymer **P1b**, see figure 2. The IR spectrum of **P1b** shows no trace of active ester band at 1750 cm^{-1}. Only the two amide bands at 1653 cm^{-1} and 1540 cm^{-1} are present. Thus, FT-IR analysis proved the complete conversion to the copolymer poly(N-isopropylacrylamide-co-acrylamide) **P1b**.

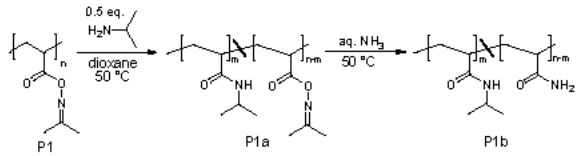

Figure 2. Sequentional polymeranalogous reaction of poly(acetone oxime acrylate) **P1** to poly(*N*-isopropylacrylamide-*co*-acetone oxime acrylate) **P1a**, and to poly(*N*-isopropylacrylamide-*co*-acrylamide) **P1b**.

Active ester polyacrylates offer the advantage to transform them to poly(*N*-isopropylacrylamides) (PNIPAM) by a polymer analogous reaction with isopropylamine. Within this study, we investigated the thermo-responsive behavior of the polymers **P1a** and **P1b**, respectively, in comparison to PNIPAM. To determine the LCST of the polymers, cloud-point measurements were performed. For PNIPAM a LCST of 32°C could be determined, in agreement with the literature.[11] For the copolymer **P1a**, poly(N-isopropylacrylamide-co-acetone oxime acrylate), the solution exhibited a sharp decrease in the optical transmittance at 52°C. Thus, the reactive copolymer **P1a**, features a LCST at 52°C. After full transformation of the acetone oxime acrylate segments to acrylamide units the copolymer **P1b**, poly(N-isopropylacrylamide-co-acrylamide) showed no LCST.

Conclusions

Various new active ester monomers have been successfully investigated under controlled radical polymerization conditions with excellent control, which led to the possibility to prepare reactive block copolymers as precursors for stimuli-responsive polymers.

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