Polymer 79 (2015) 232–242

Contents lists available at ScienceDirect

Polymer

journal homepage: www.elsevier.com/locate/polymer

Novel graft copolymers with aliphatic polyether and polyester main chains

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ARTICLE INFO

Article history:
Received 24 August 2015
Received in revised form
7 October 2015
Accepted 9 October 2015
Available online 19 October 2015

Keywords:
Graft copolymers
Coupling reactions
Aliphatic polyether

ABSTRACT

A series of new graft copolymers was synthesized by a "grafting to" approach, in the course of which the polymer backbone was build up first by a chain extension reaction of polyether or polycaprolactone diols with bis-N-acyl lactams. During the first reaction step, benzoxazinone groups were introduced into the backbone which served as grafting sites for monoamino-terminated polyamide 12 or polystyrene. Chain extension and grafting could be performed successively and with high selectivity in the melt at 180 −220 °C.

The morphology and the thermo-mechanical behavior of the graft copolymers were strongly influenced by the type of the grafted side chains. Polymers with polyamide grafts exhibited a two phase morphology with a spherulitic superstructure in the micrometer scale. The tensile behavior of these polymers was characterized by a certain elastic component.

In contrast, the phase morphology of a polystyrene grafted polymer was much finer. A strong influence on the glass transitions revealed improved compatibility between the components. Pronounced strain hardening was observed during the tensile test of polystyrene grafted samples.

1. Introduction

Graft copolymers represent a class of branched copolymers with thermodynamically incompatible polymer segments, the properties of which are determined by the properties of their individual segments and their architecture [1]. They are used as adhesives, emulsifiers, compatibilizers, and as plastics with different mechanical performance.

In the recent past, new techniques in the area of controlled living anionic and radical polymerization allowed the synthesis of novel well-defined graft copolymers with low polydispersity, distinct numbers and distances of branch points, and different functionalities in the main and side chains. Whereas the living anionic polymerization is limited to a small number of suitable monomers, controlled living polymerization techniques like RAFT, ATRP and NMP including ROP and ROMP opened a higher chemical diversity of the graft copolymers [2–7].

Generally, graft copolymers can be synthesized by three strategies: "grafting onto", "grafting from", and "grafting through" (macromonomer method) [8]. With respect to our own work the "grafting onto" method is most relevant. It starts from a preformed functionalized polymer, the functional groups of which are converted with the terminal groups of a mono functional oligomer. For example, a common synthetic way is the chloromethylation or chlorosilylation of polystyrene combined with the subsequent grafting of side chains with anionic end groups [4].

In the last years several new coupling approaches have been employed to graft side chains to the polymer backbone [9]. Besides nucleophilic reactions, orthogonal click chemistry such as azide/alkyne cycloaddition reactions, thiol-ene and thiol-yne reactions, Diels–Alder reactions and others were used. The corresponding functional groups are introduced by polymerization of functionalized monomers via controlled/living polymerization, by using functionalized initiators or by post-functionalization. Mild conditions, high selectivities and yields, and little or no byproducts are typical for these reactions [9].

As an example, the synthesis of a polycaprolactone (PCL) grafted polyethylene glycol (PEG) with modulated grafting sites was

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http://dx.doi.org/10.1016/j.polymer.2015.10.023
0032-3861/

described by Ma et al. [10]. Here, the graft copolymer was synthesized by ROP in combination with the Williamson reaction and the thiol-ene addition reaction. On the other hand, graft copolymers with PCL as main chain could be synthesized by copolymerization of ε-caprolactone with functionalized ε-caprolactones. Using α-chloro-ε-caprolactone as comonomer, Zhang et al. synthesized PCL-g-PEG amphiphilic graft copolymers by a combination of ROP and copper(I)-catalyzed cycloaddition. In an intermediate step the chloro groups were converted into azide groups which reacted with alkyne-terminated PEG [11].

Huang et al. described the synthesis of functional PEG and related graft copolymers using 1-ethoxyethyl glycidyl ether or 4-glycidyloxy-TEMPO comonomers resulting in a main chain with hydroxyl or TEMPO groups [12,13].

Solvent free polyaddition or polycondenzation reactions of α,α′-difunctionalized oligomers were also described as an alternative for the synthesis of graft copolymers. Such reactions can be compared with the classical "grafting through" or the macromonomer method.

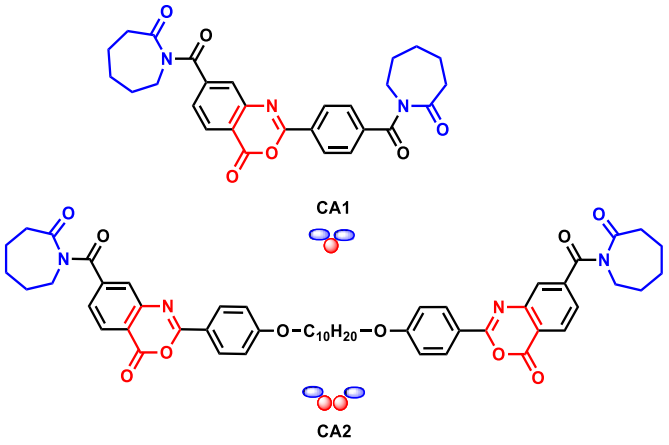
Polystyrenes having a diol end group were synthesized by the reaction of a living PS with a chlorosilane derivative having a trimethylsilyl-protected diol function. After deprotection, the polyaddition reaction with 4,4′-diphenylmethanediisocyanate followed by the chain extension with 1,4-butanediol resulted in polyurethane-PS graft copolymers with controlled graft segment lengths and graft contents [14].

Graft copolymers with a polytetrahydrofuran (PTHF) main chain and molecularly uniform oligourethane grafts were synthesized by polycondensation of a telechelic PTHF with an α,α′-bifunctional oligourethane macromonomer [15]. The polymerization of the α,α′-bifunctional oligourethane macromonomers with α-(chlorocarbonyl)-ω-(chloroformyl) poly(oxytetramethylene) yielded graft copolymers with defined graft distribution and length [16].

The reactions described above were performed in solution or in bulk under mild conditions. An even greater challenge is the solvent-free preparation of defined segmented block and graft copolymers at higher temperatures in the melt. Because of the higher temperatures, more side reactions may occur leading to structural defects or cross-linking. In our previous work we demonstrated that heterobifunctional coupling agents containing oxazoline, benzoxazinone and N-acyl lactam groups in different combinations were able to react highly selective with carboxylic, amino, and hydroxyl groups at elevated temperatures [17,18]. With a coupling agent containing one benzoxazinone and one N-acyl lactam group, segmented multiblock copolymers based on PCL diols and diaminoterminated PA12 oligomers were synthesized [18,19].

Recently, we described the synthesis of novel tri- and tetrafunctional coupling agents (**CA1**–**3**) containing N-acyl lactam and benzoxazinone groups in different combinations (Scheme 1). These coupling agents were designed for solvent free coupling reactions up to 220 °C. By means of model reactions, it was demonstrated that the functional groups of the coupling agents reacted selectively with hydroxyl and amino groups according to reaction Rct1 and Rct2 (Scheme 2), provided the reactants were added in the right sequence, i.e. the hydroxyl group containing reactant had to be added first to react preferably with the N-acyl lactam groups (Rct1). The reaction of the hydroxyl groups with the benzoxazinone groups (Rct4) appeared only as side reaction to a negligible extent. After this, the conversion of the benzoxazinone groups with the amino group containing reactant was performed (Rct2). This sequence had to be complied with since the reaction of amino groups with benzoxazinone and N-acyl lactam groups according to Rct2 and Rct3 was not selective [20].

Based on these results, graft copolymers should be available by a stepwise conversion of the coupling agents **CA1** and **CA2** with hydroxyl and amino group terminated oligomers (Scheme 3a–b). This complies a "grafting to" approach in the course of which the polymer backbone is built up first by chain extension of hydroxy-terminated telechelics followed by grafting of monoamino-terminated oligomers (Scheme 3a and b).



Scheme 1. Tri- and tetrafunctional coupling agents containing N-acyl lactam and benzoxazinone groups in different combinations.

In this article, our focus is on the synthesis of graft copolymers by the "grafting to" approach using **CA1** and **CA2**. Hydroxy-terminated PEG, polypropylene glycol (PPG), polycaprolactone (PCL) and PTHF telechelics were used as building blocks for the polymer backbone. Monoamino-terminated polyamide 12 (PA12) and polystyrene (PS) served as side chains to be grafted to the backbone. Especially, for the combination of a soft polymer backbone and crystallizable side chains a material with pronounced elastic behavior was expected. This approach described here is a continuation of our work to multiblock copolymers based on the same building blocks [19].

2. Experimental

2.1. Materials

PEG diol with a molar mass of M_n = 2000 g/mol was received from Merck. PPG, PTHF, and PCL diols with molar masses of M_n = 2000 g/mol were purchased from Aldrich. Monoamino-terminated PA12 samples with molar masses of M_n = 2000 and 5000 g/mol, respectively, were supplied by the Evonik Industries AG (Germany). The molar masses of the PA12 samples were controlled by adding *n*-dodecylamine to the reaction mixture and determined by ^{1}H NMR end group analysis.

Monoamino-terminated PS was synthesized according to Postma et al. by polymerization of styrene using a phthalimido-functional RAFT agent [21]. The trithiocarbonate functionality in the formed polystyrene was quantitatively transformed into an inert phenylethyl end group by a radical-induced reduction with tributyltin hydride. The deprotection of the primary amino end groups was performed by hydrazinolysis of the phthalimido end groups [21]. Styrene was purified with aluminum oxide.

The molar mass of the monoaminoterminated PS (M_n = 2950 g/mol, M_w/M_n = 1.23) was determined by ^{1}H NMR end group analysis and GPC measurements.

All other chemical and solvents were used as received.

2.2. Coupling agents and model compounds

The coupling agents **CA1** and **CA2** and the model compounds