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One-pot synthesis of poly(triazole-*graft*-caprolactone) via ring-opening polymerization combined with click chemistry as a novel strategy for graft copolymers

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The one-pot construction of polytriazole grafted with poly(ε-caprolactone) via the polymerization of 4-azido-1-(prop-2-yn-1-yloxy)butan-2-ol (N_3hydroxypropargyl) and ε-caprolactone monomers is reported. For this purpose, a click reaction and ring-opening polymerization (ROP) were combined and carried out simultaneously. N_3hydroxypropargyl served as both the ROP initiator and a monomer for the click polymerization. Thus, an in situ “grafting-through and from” strategy was established in one pot. CuBr and $Sn(Oct)_2$ were utilized as dual catalysts, and the polymerization reactions were carried out at 120 °C under a N_2 atmosphere.

1. Introduction

Interest in graft copolymers, a decades-old area of polymer research, has recently increased due to their synthetic challenges and potential applications as impact-resistant materials, nanomedicine carriers, organic–inorganic hybrid nano-materials, etc. Cylindrical, spherical, or worm-like morphologies can be generated with graft copolymers made of various monomers by altering the chain length of either the side chains or backbone. Three strategies are typically used to synthesize graft copolymers: “grafting from” (polymerization of monomers from pre-synthesized linear polymers containing initiating functionalities), “grafting through” (end-group polymerization of macromonomers) and “grafting onto” (combination of separately prepared backbones and side chains with suitable functionalities) [1]. Despite the wide use of all three methods, the synthesis of graft copolymers remains challenging due to the number of required steps and the complicated synthetic procedures. A one-step approach capable of simplifying the process is desirable and has gained the attention of polymer scientists [2,3]. To date, numerous graft copolymers with different structures have been synthesized via one-pot techniques that combine certain chemistry methods including the following examples: the one-pot formation of polymers with reactive anion sites [4], the synthesis of chitosan-containing graft copolymers by combining “click” chemistry and nitroxide-mediated radical coupling [5], the one-pot synthesis of graft copolymers based on a metathesis skeleton with poly(methyl methacrylate) [6], the synthesis of block copolymers bearing reactive isocyanate functional groups [7], the preparation of ABA-type block-graft copolymers using Cu-catalyzed “click” chemistry and atom transfer nitroxide radical coupling (ATNRC) reactions [8], the synthesis of graft copolymers by combining free-radical polymerization and polyadditions [9], and the synthesis of well-defined brush copolymers via tandem RAFT and ROMP [10] were reported. A one-pot strategy requires the judicious selection of multiple chemistries to maintain harmony and to improve the efficiency of the chemical reactions. Hence, non-interfering reactions are necessary to improve results. For example, combining the ring-opening polymerization (ROP) of lactones and “click” chemistry meets the requirements of a one-pot strategy largely due to the character of click reactions [11–13] that renders these reactions tolerant to a variety of functional groups. Moreover, click reactions feature high yields, high atom economy, and regioselectivity. To date, the “click” reactions most widely applied in polymer and materials science are the copper-catalyzed Huisgen reaction [14–16], Diels–Alder cycloaddition [17,18] and thiol-ene (or thiol-yne) reactions [19–26]. Of these, the copper-catalyzed Huisgen 1,3-dipolar cycloaddition, which unites two unsaturated azide- and alkyne-containing reactants, is used most often. Accordingly, the use of Huisgen-type click reactions has yielded many reports within the field of polymer science. Various block, star-shaped, and graft copolymers, and telechelics have been

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successfully constructed using this strategy [27–36]. However, the most convenient route to obtain poly(ε-caprolactone) (PCL) is an ROP of ε-caprolactone (CL) [37]. Different initiators, including tin and aluminum alkoxides [38], zinc chloride [39], zeolites [40], ytrium derivatives [41], tetrabutyl tin [42] and tin octoates, have been used to polymerize CL. The compatibility of tin octoate in a reaction that combines click and ROP in one pot was tested and found successful for synthesizing miktoarm star polymers [43]. By utilizing the compatibility of ROP with a copper-catalyzed Huisgen 1,3-dipolar cycloaddition, we developed a one-pot synthesis of graft copolymers based on a polytriazole skeleton grafted with poly(ε-caprolactone) using a tin octoate, copper (I) bromide catalyst system. The graft copolymer was grown from small molecules using one-step approach by avoiding the preparation of pre-synthesized polymers, etc. This strategy established an in situ "grafting through and from" system, utilizing two tandem polymerizations for the backbone and side-chain formations.

2. Experimental

2.1. Materials

Glycidyl propargyl ether (Aldrich, ⩾90%), sodium azide (Aldrich, ⩾99.5%), *N*,*N*,*N*′,*N*″,*N*″-pentamethyldiethylenetriamine (PMDETA) (Aldrich, 99%), copper (I) bromide, (Acros, 98%), tin octoate (Aldrich, ∼95%), ethanol (Acros, 96%), dichloromethane (Acros, ⩾99 + %), magnesium sulfate (Sigma–Aldrich, ⩾97%), *N*,*N*-dimethylformamide (DMF) (Sigma, ⩾99.8%), diethyl ether (Sigma–Aldrich, ⩾99.8%), and tetrahydrofuran (THF) (Sigma–Aldrich, ⩾99.9%) were used as received. The ε-caprolactone (Aldrich, 97%) was distilled prior to use.

2.2. Characterization

The ^{1}H NMR spectra were recorded in $CDCl_3$ on a Bruker AC250 and an Agilent VNMRS instrument with $Si(CH_3)_4$ as an internal standard at proton frequencies of 250 and 500 MHz, respectively. The FTIR spectra were recorded on a Perkin Elmer Spectrum One instrument with an ATR accessory (ZnSe, Pike MIRacle accessory) and a cadmium telluride (MCT) detector at a resolution of 4 cm^{-1} and 24 scans at 0.2 cm/s. The molecular weights were determined via gel permeation chromatography (GPC) using a Viscotek GPCmax autosampler system consisting of a pump, three ViscoGEL GPC columns (G2000H HR, G3000H HR and G4000H HR), and a Viscotek differential refractive index (RI) detector with a THF flow rate of 1.0 mL min^{-1} at 30 °C. The RI detector was calibrated using PS standards with a narrow molecular weight distribution. The data were analyzed using Viscotek OmniSEC Omni-01 software. Differential scanning calorimetry (DSC) was performed on a PerkinElmer Diamond DSC with a heating rate of 2.5–20 °C/min under a nitrogen flow (20 mL/min). Thermogravimetric analysis (TGA) was performed on a PerkinElmer Diamond TA/TGA with a heating rate of 10 °C/min under a nitrogen flow (200 mL/min).

2.3. Synthesis

2.3.1. Synthesis of 4-azido-1-(prop-2-yn-1-yloxy)butan-2-ol (N_3hydroxypropargyl)

The following modified procedure was used [44]: A solution of sodium azide (4.1 g, 63.21 mmol) in H_2O (60 mL) was added to a solution of glycidyl propargyl ether (2.5 mL, 21.07 mmol) in ethanol (75 mL) at room temperature. Then, the mixture was stirred for 36 h. The ethanol was evaporated, and the residue was extracted with 200 mL CH_2Cl_2. The organic layer was washed with H_2O and dried ($MgSO_4$). The solvent was removed under reduced pressure leaving a yellow oil. For further purification, column chromatography was performed using neutral alumina (2/1 EtAc/hexane, v/v) (yield = 76%).

2.3.2. Synthesis of poly(hyrdoxytriazole) (PHT)

4-Azidozido-1-(prop-2-yn-1-yloxy)butan-2-ol (2 mmol), CuBr (0.2 mmol), and PMDETA (0.2 mmol), were dissolved in 5 mL dry DMF in a dry Schlenk tube and stirred at ambient temperature in a N_2 atmosphere for 24 h. The reaction mixture was filtered through a short alumina column with 50 mL THF. This solution was concentrated under vacuum and precipitated in 2–3 drops HCl (35%) containing 200 mL cold diethyl ether. The oily polymer was decanted, washed with cold diethyl ether and dried under vacuum for 2 days for a yield of 59%.

2.3.3. Synthesis of poly(triazole-graft-caprolactone) (PT-g-PCL) through a "grafting from" approach

PHT (210 mg), ε-caprolactone (15.4 mmol), and $Sn(Oct)_2$ (0.154 mmol) were dissolved in 2 mL dry DMF in a dry Schlenk tube and stirred at 120 °C in a N_2 atmosphere for 72 h. The reaction mixture was cooled to room temperature and filtered through a short alumina column with 50 mL CH_2Cl_2. The CH_2Cl_2 solution was concentrated under vacuum and precipitated in 150 mL cold diethyl ether. The sticky product was filtered and washed with cold diethyl ether. The product was then dried under vacuum for 2 days for a yield of 37%.

2.3.4. One-pot synthesis of poly(triazole-graft-caprolactone) (PT-g-PCL)

The following provides a representative procedure: 4-azido-1-(prop-2-yn-1-yloxy)butan-2-ol (1.93 mmol, 1 eq.), CuBr (0.193 mmol, 0.1 eq.), PMDETA (0.193 mmol, 0.1 eq.), ε-caprolactone (15.4 mmol, 8 eq.), and $Sn(Oct)_2$ (0.154 mmol, 0.08 eq.) were dissolved in 2 mL dry DMF in a dry Schlenk tube and stirred at 120 °C in a N_2 atmosphere for 72 h. The reaction mixture was cooled to room temperature and filtered through a short alumina column with 50 mL CH_2Cl_2. The CH_2Cl_2 solution was concentrated under vacuum and the solution was precipitated in 150 mL cold diethyl ether. The sticky product was filtered and washed with cold diethyl ether. The product was then dried under vacuum for 2 days for a yield of 32%.

3. Results and discussions

Ring-opening polymerizations and Huisgen-type click reactions have been used extensively for post-polymerization modifications of homopolymers, random copolymers, and block copolymers [45,46]. Therefore, the present study attempts to extend this post-polymerization modification approach to the one-pot construction of linear polymer chains grafted by poly(ε-caprolactone) via the polymerization of 4-azido-1-(prop-2-yn-1-yloxy)butan-2-ol (N_3hydroxypropargyl) and ε-caprolactone monomers. This work demonstrates a new approach for graft copolymer synthesis, an "in situ grafting through and from strategy." This strategy can be considered as a combination of the "grafting through" and "grafting from" approaches following the formation of oligomers during polymerization. This approach requires a suitable monomer similar to an inimer with the ability to construct a backbone using the initiating functional groups as side chains. A comparison of the in situ grafting through and from strategy with other well-known grafting strategies is provided in Scheme 1.

Using this strategy, N_3hydroxypropargyl was initially synthesized as the monomer to satisfy the in situ grafting through and from requirement that this monomer be able to construct both a triazole-containing backbone and poly(ε-caprolactone) side chains (Scheme 2).