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Highly efficient synthesis of cylindrical polymer brushes with various side chains via click grafting-onto approach

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ABSTRACT

Though much attention has been paid to synthesis of cylindrical polymer brushes, it is still not easy to prepare well-defined brushes by a general approach. Herein, well-defined cylindrical polymer brushes with various side chains were synthesized via grafting-onto approach by CuAAC click chemistry. Narrowly dispersed polymer backbones functionalized with azide groups were obtained by post-modification of poly(glycidyl methacrylate) (PGMA) which was prepared by reversible addition-fragmentation chain transfer (RAFT) mediated radical polymerization. The alkyne-terminated side chains, polystyrene, polyacrylates, polymethacrylates and poly(*N*-alkyl acrylamide)s, were synthesized by RAFT mediated radical polymerization with alkyne-containing chain transfer agents (CTAs). The CuAAC reactions between the backbone and side chain polymers were conducted with an equivalent feed of alkyne-terminated side chains and azide groups under mild conditions. Influences of reaction conditions and chemical composition of polymer side chains on grafting efficiency and molecular weight distribution of the polymer brushes were investigated. It is demonstrated that the side chains of polystyrene, polyacrylates and poly(*N*-alkyl acylamide)s were grafted at a density above 85% while that of polymethacrylates decreased to ca. 50%. The polymer brushes synthesized under the optimized reaction conditions had well-defined chemical composition and narrow distribution of molecular weight, and their wormlike morphology was visualized by atomic force microscopy (AFM).

1. Introduction

Cylindrical polymer brush is a kind of graft polymers which possess a linear polymer backbone and densely grafted polymer side chains [1,2]. The molecules may adopt a wormlike conformation due to the steric repulsion between bulky side chains. In view of their unique physical properties [3–9] and potential applications in fields of nanomaterials [10–17] and drug delivery [18–22], cylindrical polymer brushes have received significant attention. There are three strategies for preparing cylindrical polymer brushes: grafting-through [23–26], grafting-from [27–31], and grafting-onto [32–35]. Combinations of two of them have also been applied to prepare polymer brushes with hybrid side chains [36,37]. The grafting-through method involves polymerization of macromonomers. This method guarantees complete grafting, but the length of the backbone is often poorly controlled. In recent years, ring-opening metathesis polymerization (ROMP) of macromonomers has been applied to prepare narrowly dispersed polymer brushes with long backbone [38,39]. In the approach of grafting-from, a polymer backbone with initiation sites (macroinitiator) along the repeating units is prepared first and side chains are formed by grafting polymerization from the backbone. This approach enables preparation of polymer brushes with long backbone, but the conversion of the side-chain monomers is limited in order to suppress intra- and interbrush radical–radical coupling. Recently grafting-from polymerization conducted in miniemulsion using activator generated by electron transfer for atom transfer radical polymerization has been applied to avoid the interbrush coupling [40].

The grafting-onto approach involves coupling pre-fabricated terminal reactive polymers onto a polymer backbone. As the backbone and side chains are prepared separately, the chemical structure and the size of the obtained polymer brushes can be well defined. However, the grafting density of this approach is often limited due to the steric congestion of grafted side chains. To overcome this drawback, efficient coupling reactions, for example, copper-catalyzed azide-alkyne cycloaddition (CuAAC) [41], have been used. Owing to its high reaction efficiency, high tolerance of functional groups and low solvent sensitivity, CuAAC has been

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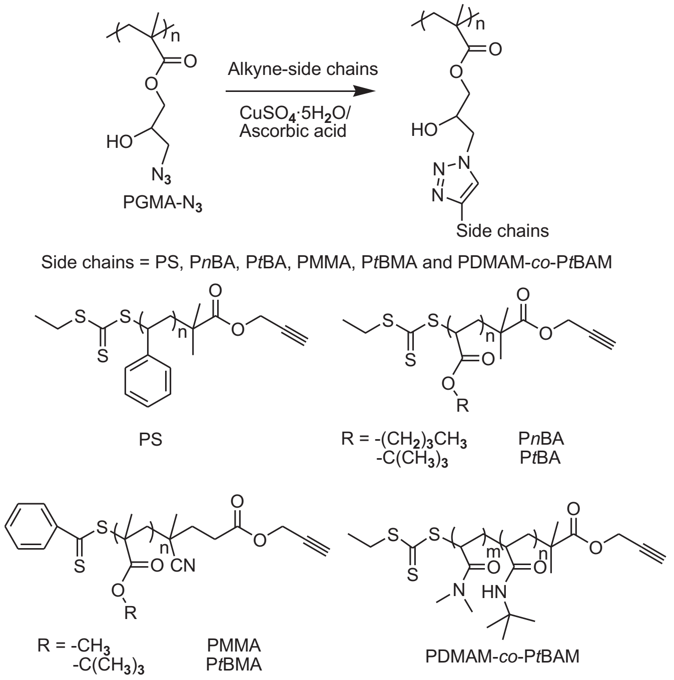
widely used for preparing polymers with intricate structures or specific properties [42,43]. By conducting grafting-onto strategy via CuAAC click reaction, several groups have synthesized polymer brushes. For example, Gao et al. have synthesized polymer brushes using alkyne modified poly(2-hydroxyethyl methacrylate) backbone and different azido-terminated linear polymer side chains by combination of ATRP and CuAAC reaction [32]. It was concluded that the grafting density of the polymer brushes was affected by the molecular weights and chemical structures of the linear polymer side chains, as well as the initial molar ratio of azido units and alkyne groups. It was found that thinner PEO was grafted relatively easier than bulkier polymers like polystyrene (PS) and poly(*n*-butyl acrylate) (P*n*BA). Zhang et al. prepared a series of core/shell polymer brushes with helical polypeptide backbone and polylactide-*b*-poly(ethylene glycol) block copolymers side chains via grafting-onto strategy and CuAAC reaction. The high grafting density (82–93%) was inferred to result from the helical conformation of the polypeptide backbone which could alleviate the steric repulsions between copolymer side chains [44]. Hu et al. prepared amphiphilic polymer brushes via grafting-onto method by conducting CuAAC reaction on the interface of two immiscible solvents in order to reduce the steric hindrance of the crowded side chains. With this method, they obtained polymer brushes with molecular weight polydispersity index (M_w/M_n) less than 1.12 and the overall grafting density higher than 95% [45]. Recently, they prepared ternary graft copolymers by quantitatively grafting alkyne-end polymer side chains onto azido polymer backbone using CuAAC reaction and then produced nanocapsules with the graft copolymers [46]. They also synthesized a family of binary graft copolymers by the similar method and the grafted side chains can segregate into alternating lamellae by bulk self-assembly [47]. Relatively to other two approaches, the grafting-onto approach is much less applied due to the concern of low grafting efficiency and tedious removal of unreacted side chains.

Although various chemistries on polymer brush synthesis have been reported, it is still not easy to prepare polymer brushes with both controlled backbones and side chains in a large amount. Moreover, it is particularly challenging for efficient preparation of the brushes with long backbones, which endow the wormlike morphology. Cylindrical polymer brushes with a large aspect ratio are wormlike molecular nanoobjects, which is the most amazing character of polymer brushes. It is noteworthy that preparation of long polymer brushes by grafting-from and grafting-onto approaches is not simply to extend backbones. This is because the brushes may become poorly controlled even if slightly unclear side reactions occur. Therefore, it is still necessarily to develop a facile approach to prepare cylindrical polymer brushes with controlled chemistry, which becomes a bottleneck of the research and application of polymer brushes.

Previously this group has prepared cylindrical polymer brushes with poly(glycidyl methacrylate) (PGMA) as backbone and poly(ethylene oxide) (PEO) as side chains via grafting-onto strategy and CuAAC reaction. It is surprisingly that the grafting PEO chains of 5 kg/mol proceeded nearly quantitatively under the optimized reaction conditions despite that the molar feed ratio of alkyne-terminated side chains to azido units on the backbone was 1:1 [48]. Herein, we expand this chemistry to the side chains of polystyrene, polyacrylates, polymethacrylates, and poly(*N*-alkyl acrylamide)s of different molecular weights. As illustrated in Scheme 1, azido-pendent polymer backbones PGMA-N_3 were grafted by alkyne-terminated polymer side chains. The influences of structures and length of polymer side chains as well as reaction conditions including reaction time and reactant concentration were discussed. Well-defined cylindrical polymer brushes with PS, polyacrylates and poly(*N*-alkyl acrylamide)s side chains with M_w/M_n less than 1.2 and grafting density more than 85% were prepared under the optimized reaction conditions and their wormlike morphology was observed by atomic force microscopy (AFM).



Scheme 1. Outline for the synthesis of cylindrical polymer brushes via grafting-onto strategy and CuAAC reaction.

2. Experimental section

2.1. Materials

Glycidyl methacrylate (GMA, 99%, Aldrich), styrene (S, CP, Beijing Chemical Reagent Co.), *N,N'*-dimethylacrylamide (DMAM, 98%, TCI) and *tertial*-butyl methacrylate (*t*BMA, >98%, TCI) were distilled under reduced pressure. *Tertial*-butyl acrylate (*t*BA, 99%, Alfa Aesar) was passed through a column filled with basic alumina to remove the inhibitor. *N-tertial*-butyl acrylamide (*t*BAM, >98%, TCI) was recrystallized from acetone. 2,2′-Azobisisobutyronitrile (AIBN) was purified by recrystallization from ethanol and stored at 4 °C. Dichloromethane (DCM, AR, Beijing Chemical Reagent Co.) was refluxed over CaH_2. 1,4-Dioxane (AR, Beijing Chemical Reagent Co.) was refluxed over sodium. CTAs, cumyl dithiobenzoate (CDB) [49], 4-cyanopentanoic acid dithiobenzoate (CTP) [50] and *S*-ethyl-*S'*-(α,α'-dimethyl-α''-acetic acid) trithiocarbonate (EDMAT) [51] were synthesized according to literature. Other reagents and solvents were purchased and used as received unless otherwise noted.

2.2. Measurements

^{1}H NMR and ^{13}C NMR spectra were recorded with a Bruker 400 MHz spectrometer with $CDCl_3$ or acetone-d_6 as solvents and tetramethylsilane as an internal standard. The molecular weight and distribution of molecular weight were measured on size exclusion chromatography (SEC) equipped with a Waters 515 HPLC pump, three Waters Styragel columns (HT2, HT4, and HT5) and a Waters 2414 refractive-index (RI) detector. PS standards were used to calibrate the SEC system. DMF with LiBr (0.01 mol/L) was used as eluent at a flow rate of 1.0 mL/min at 50 °C. Fourier transform infrared absorption spectra (FT-IR) were obtained on a Thermo