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Biodegradable amphiphilic graft polymer synthesized via the combination of ring-opening polymerization (ROP) and atom transfer radical polymerization (ATRP)

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ABSTRACT

The biodegradability of polyacrylate derivatives is of great importance to their applications in medical and biological science. Here we design a six-membered carbonate monomer 2-(2-bromoisobutyrylamido)trimethylene carbonate (BrTMC) with an atom transfer radical polymerization (ATRP) initiating group 2-bromoisobutyryl. Ring-opening polymerization (ROP) of BrTMC and 2,2-dimethyltrimethylene carbonate (DTC) was carried out to synthesize copolycarbonate P(BrTMC-DTC), which further initiated ATRP of hydroxyethyl methacrylate (HEMA) to prepare biodegradable amphiphilic graft polymer P(BrTMC-DTC)-g-PHEMA. P(BrTMC-DTC)-g-PHEMA was able to form the micelles by self-assembly.

1. Introduction

Atom transfer radical polymerization (ATRP) proposed by Matyjaszewski et al. in 1995 is the most important case of living radical polymerization [1]. Compared with others (e.g., Iniferter, stable free radical polymerization (SFRP), reversible addition-fragmentation chain transfer polymerization (RAFT)), ATRP can effectively control the length of each segment for synthesis of well-defined block copolymers [2]. In addition, the raw materials are various, the operation conditions are relatively mild, the polymerization is not too sensitive to impurities, and the reaction process is easy to be controlled. Using ATRP, functional polymers with site-specific functionalities (such as vinyl, hydroxyl, epoxide, cyano and other groups) and novel architectures (such as star, graft, block and gradient) can be created to explore many high-value applications, especially as biomedical materials [3–6]. The monomers involved in ATRP are very various, for example, styrene, acrylonitrile, acrylate, acrylamide, vinyl acetate, and 4-vinyl pyridine [7]. However, the polymers prepared through ATRP of these monomers are difficult to degrade, which limits their biomedical applications [8].

As a kind of biodegradable polymers, aliphatic polycarbonates have good biocompatibility, biodegradability, and mechanical property [9]. They have been widely studied and applied in the surgical suture, bone fixing material and drug controlled release [10]. The methods for synthesis of aliphatic polycarbonates mainly have transesterification, condensation using phosgene, polyaddition through epoxide and CO_2, and ring-opening polymerization (ROP) of cyclic carbonate monomer [11]. Among them, ROP has become the most important method for synthesis of aliphatic polycarbonates due to its significant advantages of low heating effect in the polymerization, fast rate of polymerization, and high molecular weight of the product [12–16]. By changing the chemical structure of the main chain, polycarbonates have excellent physical, chemical, and biological properties to meet the needs under different application conditions [14]. The introduction of different functional groups, such as carboxyl, amino, hydroxyl, provides further chemical modification of polycarbonates [12]. In the previous studies, we reported some functional polycarbonates via ROP of cyclic carbonate monomers [17–24].

To improve the biodegradability of polyacrylate derivatives, here we describe a facile synthesis of a six-membered carbonate monomer 2-(2-bromoisobutyrylamido)trimethylene carbonate (BrTMC) with an ATRP initiating group 2-bromoisobutyryl. BrTMC and 2,2-dimethyltrimethylene carbonate (DTC) were used to prepare copolycarbonate P(BrTMC-DTC) for further synthesis of biodegradable amphiphilic graft polymer P(BrTMC-DTC)-g-PHEMA via ATRP of hydroxyethyl methacrylate (HEMA). The self-assembly behavior of P(BrTMC-DTC)-g-PHEMA was studied.

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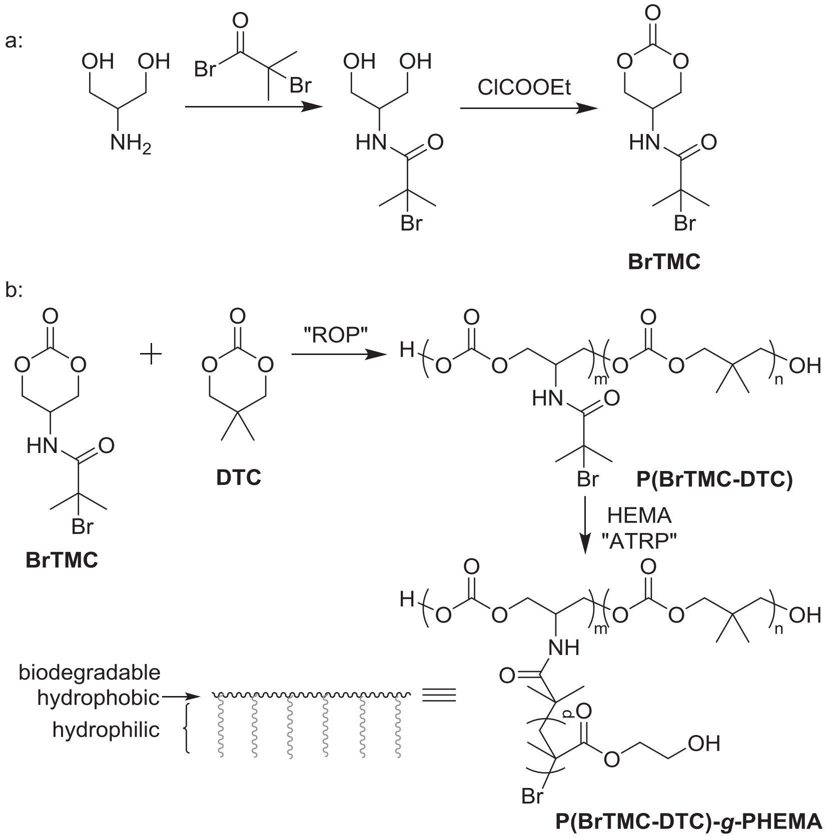

Scheme 1. Synthesis of 2-(2-bromoisobutyrylamido)trimethylene carbonate (BrTMC) (a), biodegradable amphiphilic graft polymer P(BrTMC-DTC)-*g*-PHEMA via the combination of ring-opening polymerization (ROP) and atom transfer radical polymerization (ATRP) (b).

2. Material and methods

The preparation and characterization of 2-(2-bromoisobutyrylamido)trimethylene carbonate (BrTMC), graft polymer P(BrTMC-DTC)-*g*-PHEMA, and the micelles were given in Supplementary Information.

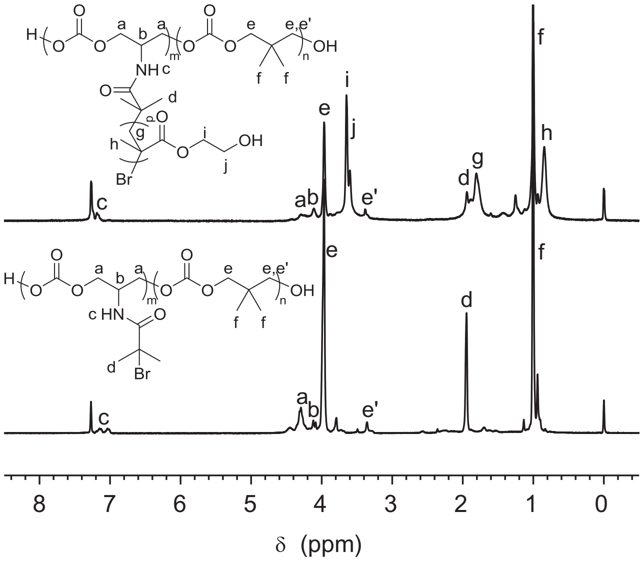

Fig. 1. ^{1}H NMR spectra of P(BrTMC-DTC) and P(BrTMC-DTC)-*g*-PHEMA.

3. Results and discussion

A six-membered carbonate monomer 2-(2-bromoisobutyrylamido)trimethylene carbonate (BrTMC) was synthesized via amidation and cyclization from serinol (Scheme 1a). Serinol was treated with 2-bromoisobutyryl bromide at room temperature in absolute ethanol to prepare 2-(2-bromoisobutyrylamido)propane-1,3-diol. Then 2-(2-bromoisobutyrylamido)propane-1,3-diol was cyclocarbonated using ethyl chloroformate in the presence of triethylamine at room temperature in dry tetrahydrofuran to yield the target

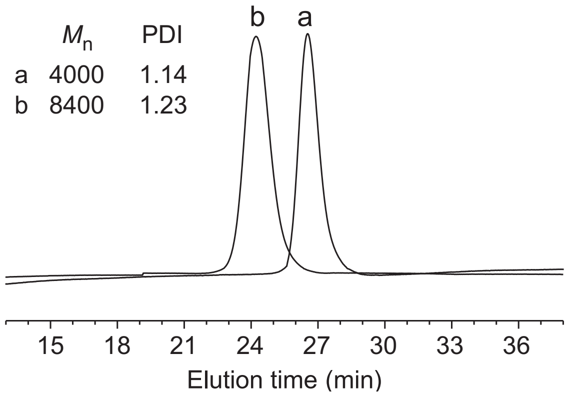

Fig. 2. Normalized GPC curves of P(BrTMC-DTC) (a) and P(BrTMC-DTC)-*g*-PHEMA (b). Since GPC measurements of aliphatic polyesters overestimate the real molecular weights, number-average molecular weights (M_n) in the figure have been corrected by multiplication with a factor of 0.65–0.68.