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Synthesis of hyperbranched polymers and hyperbranched block copolymers through “$A_2 + B_3$” click reaction

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ABSTRACT

Long-chain hyperbranched and hyperbranched block polymers were synthesized through Cu catalyzed azide-alkyne cycloaddition (CuAAC) of A_2 macromonomers with two alkyne groups and B_3 coupling reagent with three azide groups. Polystyrene (PSt) homopolymers and block copolymers of styrene and butyl acrylate (P(St-*b*-BA-*b*-St)) with two alkyne groups were obtained via reversible addition-fragmentation chain transfer (RAFT) polymerization using a RAFT agent with two alkyne groups, S, S′-bis(α, α′-dimethyl – α″-propargyl acetate) trithio carbonate (BPTTC). Besides, the hyperbranched block copolymers were also prepared through the successive RAFT polymerization of BA with the hyperbranched PSt as RAFT agents. The evidence of ^{1}H NMR, IR and GPC-Viscosity-MALLS measurements conformed the structure of the polymers. Dp_ws, the ratio of the weight average molecular weights of the hyperbranched polymers to those of the macromonomers, reached above 60 at most, calculated from MALLS measurement, which showed a high degree of the coupling reaction. The degree of branched of the hyperbranched polymers kept on increasing with the reaction time, according to the branching factor, g'.

1. Introduction

The unique multi-branched molecular structure of hyperbranched polymers supplies some special fluid properties, spatial characteristics and functional features, which bring them a wide range of applications in adjusting the viscosity of the polymer melt or solution, drug loading, catalysis and other functional materials [1–3]. Hyperbranched polymers may be prepared through both step polymerization of multifunctional monomers and chain polymerization of diene monomers or inimers. In recent years, HyperMacs, a kind of hyperbranched polymer with long chain branched structure gradually attracted interest, which was first proposed by Hutchings et al. [4–6]. The polymers have long subchains with uniform length between any two neighboring branching points, and this structure makes their hydrodynamic properties different from those ordinary hyperbranched polymers [7], and lead to more functionality [8–10].

Long-chain hyperbranched polymers are typically prepared by macroinitiators [11–13] or macromonomers, especially AB_n ($n \geqslant 2$) type, due to no gel conditions [4–8,14–32]. To obtain AB_n ($n \geqslant 2$) macromonomers, the initiators with different functional groups are usually used to initiate the living or controlled polymerization. Then the terminal groups perhaps need be further transformed for the following coupling reaction. There were some reports of $A_2 + B_f$ ($f \geqslant 3$) type polymerization [33–36], the soluble hyperbranched polymers could be obtained by controlling the reaction conditions such as the

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monomers' ratio. Generally, A_2 and B_f monomers were more readily available than AB_n monomers. Click chemistry, a simple and efficient coupling reaction, was widely used in the preparation of HyperMacs polymers [23–31], but $A_2 + B_3$ type polymerization process has still seldom been reported [37,38].

Furthermore, a novel class of block copolymer, hyperbranched block copolymer or HyperBlock, has been developed based on the researches of the long-chain hyperbranched polymers [39,40]. The hyperbranched topology may affect the interaction between the different blocks, giving some new properties and applications. In this paper, we explored the synthesis of hyperbranched polystyrene and hyperbranched block copolymers of styrene and butyl acrylate with long branched chains through $A_2 + B_3$ type polymerization process, combining the reversible addition – fragmentation chain transfer (RAFT) polymerization with azide – alkyne click reaction. Comparing with other methods, a large number of propagating chain active centers, trithio carbonate groups, are kept in the middle of every subchain in the hyperbranched polymers, which make the polymers can be successively copolymerized with other monomers. Using this strategy, it will be easy to synthesize the hyperbranched block polymers with different block lengths but fixed degree of polymerization.

2. Experimental

2.1. Materials

Propargyl α-bromoisobutyrate was synthesized according to the procedure described in ref [41]. CS_2 (AR, Shanghai No. 4 Reagent & H.v Chemical Co., Ltd.), tetrahydrofuran (THF, CP, Sinopharm Chemical Reagent Co., Ltd., refluxed with Na, then distilled), styrene and butyl acrylate (CP, Shanghai Chemical Reagent Co., dried with anhydrous $MgSO_4$, then distilled under reduce pressure), azobisisobutyronitrile (AIBN, AR, Shanghai Chemical Reagent Co., recrystallized in acetone), other reagents were of analytical grade purchased from Shanghai Chemical Reagent Co., and used as received.

2.2. Synthesis of trithiocarbonate BPTTC

Propargyl α-bromoisobutyrate (5.12 g, 25 mmol), CS_2 (2.00 g, 26.25 mmol) and 25 mL N,N-dimethylformamide (DMF) were added into a 50 mL flask with a magnetic stirrer, 3.5 g K_2CO_3 was added after 10 min, the reaction was carried out 24 h at 40 °C. The reaction solution was extracted three times with 30 mL ethyl acetate each, and then washed three times with saturated brine and distilled water respectively, the organic phase was dried with anhydrous $MgSO_4$ overnight. After filtration, the solvent was removed by rotary evaporation. The crude product was purified by column chromatography, petroleum ether/ethyl acetate (V:V, 8:1) as eluent. The yellow solid was obtained after the solvent was evaporated under reduced pressure, dried to constant weight in a vacuum oven at 25 °C, weighed 3.125 g (69.8% yield). ^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ (ppm): 1.65 (s, 6H, $—CH_3$), 2.48 (s, 1H, $\equiv CH$), 4.68 (s, 2H, $—CH_2—$).

2.3. RAFT polymerization of styrene

Styrene (2.50 g, 24 mmol), BPTTC (0.14 g, 4 mmol) and AIBN (0.007 g, 0.04 mmol) were added into a 10 mL glass tube with a magnetic stirrer, and then the polymerization system was degassed by three vacuum-N_2 cycles. The tube was sealed and immersed into an oil bath at 80 °C. After the polymerization was finished, the polymer solution was diluted by THF, and precipitated in ethanol. The yellow polymer powder was collected by filtration and then dried in a vacuum oven at 35 °C. ^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ (ppm): 0.95 ($—CH_3$ of isobutyrate segments), 1.43 and 2.10 ($—CH_2—$ and $—CH—$ of PSt backbone), 2.50 ($\equiv CH$ at the end of PSt), 4.10 ($—CH_2—$ close to ester groups), 6.3–7.5 (aromatic H).

2.4. Synthesis of tribolck copolymer P(St-b-BA-b-St)

PSt (M_n = 3800 g/mol, 0.50 g, 0.133 mmol), BA (1.70 g, 13.3 mmol), AIBN (0.001 g, 6.67 μmol) and 4.0 mL anisole were added into a 10 mL glass tube with a magnetic stirrer, and then the polymerization system was degassed by three vaccum-N_2 cycles. The tube was sealed and immersed into an oil bath at 80 °C. After the polymerization was finished, the polymer solution was diluted with THF, and precipitated in methanol. The product was collected by filtration and then dried in a vacuum oven at 35 °C. ^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ (ppm): 0.8–2.2 ($CH_3—$ and $—CH_2—$ of BA, except that close to ester groups, $—CH_2—$ and $—CH—$ of backbone), 2.50 ($\equiv CH$ at the end of the copolymer), 4.16 ($—CH_2—$ close to ester groups), 6.3–7.5 (aromatic H).

2.5. Synthesis of the coupling reagent with three azide groups (B_3)

α-Bromoisobutyric acid (41.75 g, 0.25 mol), 1,1,1-tris(hydroxy methyl) propane (6.76 g, 0.05 mol) and *p*-toluene sulfonic acid (0.5 g) were dissolved in 80 mL benzene, refluxed in a 250 mL flask equipped with a Dean–Stark trap and a condenser connected to an anhydrous $CaCl_2$ tube at 90 °C. After 24 h the reaction was stopped. Excess benzene was distilled off, 20 mL CH_2Cl_2 was added, and then the solution was washed 3 times with 5% NaOH solution and distilled water respectively. The organic layer was dried with anhydrous $MgSO_4$, CH_2Cl_2 was removed by distillation to give the product as a white powder in