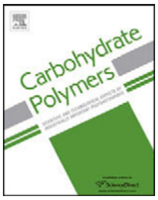
Carbohydrate Polymers 87 (2012) 2237–2245

Contents lists available at SciVerse ScienceDirect

Carbohydrate Polymers

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



Comb-shaped graft copolymers with cellulose side-chains prepared *via* click chemistry

Yukiko Enomoto-Rogers, Hiroshi Kamitakahara*, Arata Yoshinaga, Toshiyuki Takano

Division of Forest and Biomaterials Science, Graduate School of Agriculture, Kyoto University, Kitashirakawa-Oiwake-cho, Sakyo-ku, Kyoto 606-8502, Japan

ARTICLE INFO

Article history:
Received 3 September 2011
Received in revised form 20 October 2011
Accepted 20 October 2011
Available online 28 October 2011

Keywords:
Cellulose
Reducing-end
Comb-shaped graft copolymer
Cellulose side-chain
Click-chemistry

ABSTRACT

Comb-shaped copolymers with cellobiose acetate or cellulose triacetate (CTA) side-chains, PPMA-*g*-(CTA2-C15) and PPMA-*g*-(CTA13-C15), were prepared by grafting *N*-(15-azidopentadecanoyl)-2,3,6-tri-*O*-acetyl-4-*O*-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)-β-D-glucopyranosylamine (CTA2-C15-N_3) and *N*-(15-azidopentadecanoyl)-tri-*O*-acetyl-β-cellulosylamine (CTA13-C15-N_3, number average degree of polymerization (DP_n) = 13) onto poly(2-propyn-1-yl methacrylate) (PPMA, weight average degree of polymerization (DP_w, $X + Y = 5.59 \times 10^2$)) *via* “click chemistry”. The copolymers were characterized by ^{1}H, ^{13}C and two-dimensional NMR and size exclusion chromatography–multi-angle laser light scattering (SEC–MALS) measurements. The numbers of CTA side-chains (*X*) of PPMA-*g*-(CTA2-C15) and PPMA-*g*-(CTA13-C15) were calculated as 4.03×10^2 and 2.45×10^2, respectively. Copolymers with cellulosic side-chains, PPMA-*g*-(CELL2-C15) and PPMA-*g*-(CELL13-C15), were successfully obtained after deacetylation of PPMA-*g*-(CTA2-C15) and PPMA-*g*-(CTA13-C15), respectively. X-ray diffraction measurements revealed that PPMA-*g*-(CELL13-C15) showed crystalline pattern of cellulose II, which is believed to have anti-parallel orientation.

1. Introduction

Cellulose is a linear (1→4)-β-glucopyranan having three hydroxyl groups per anhydroglucose unit. There have been several studies on cellulose graft copolymers, and a variety of polymers have been grafted onto the cellulose main-chain through its hydroxyl groups at C2, C3, and C6 positions to alter properties of cellulose or cellulosic materials (Dou & Jiang, 2007; Kang et al., 2006; Nishio, 2006). On the other hand, there have been many reports on glycopolymers with mono-, di-, or oligo-saccharides as pendent groups binding at the reducing-end on a main-chain (Kamitakahara et al., 1998; Ladmiral et al., 2006; Narumi, Miura, et al., 2006; Narumi, Otsuka, et al., 2006; Ohno, Fukuda, & Kitano, 1998; Ohno, Tsujii, & Fukuda, 1998). However, to our knowledge, there has been no report on a graft copolymer having cellulose side-chains. A comb-shaped copolymer with cellulose side-chains could achieve parallel orientation of cellulose molecules, and might have unique unknown properties such as crystallinity.

We have therefore prepared a novel graft copolymer with cellulose side-chains *via* free radical copolymerization of a cellulose macromonomer with methyl methacrylate, based on “graft through” (homo- or co-polymerization of macromonomers) strategy (Enomoto-Rogers, Kamitakahara, Nakayama, Takano, & Nakatsubo, 2009; Enomoto-Rogers, Kamitakahara, Takano, & Nakatsubo, 2009). The number of cellulose graft chains per main-chain was, however, only 3.86, because of low reactivity of a cellulose macromonomer, while the weight average degree of polymerization of poly(methyl methacrylate) main-chain was 4.14×10^2. It has been reported that the semi-flexible or rigid macromonomers such as methacrylate-end capped poly(n-hexyl isocyanate) (Kawaguchi, Mihara, Kikuchi, Lien, & Nagai, 2007; Se & Aoyama, 2004) are hard to polymerize, whereas other flexible macromonomers such as poly(ethylene oxide) (Ito, Tomi, & Kawaguchi, 1992) or poly(dimethylsiloxane) (Shinoda, Miller, & Matyjaszewski, 2001) are not.

On the other hand, “grafting onto” (attachment of side-chains to the backbone) strategy is known as another way to synthesize graft copolymers (Hourdet, L’AIloret, & Audebert, 1997; Kamitakahara et al., 1998; Poe, Jarrett, Scales, & McCormick, 2004). Thus, the “grafting onto” strategy was investigated to introduce more cellulose molecules as side-chains compared to our former study, and to control the orientation of cellulose chains.

Recently, the concept of “click chemistry” invented by Sharpless and coworkers (Kolb, Finn, & Sharpless, 2001; Wu et al., 2004) has been introduced into the synthesis of polymeric materials with well-defined and complex chain architectures. Specifically, Cu(I)-catalyzed Huisgen 1,3-dipolar cycloaddition between organic azides and terminal alkynes for the transformation of 1,2,3-triazoles has been received much attention as a highly efficient

---

* Corresponding author. Tel.: +81 75 753 6255; fax: +81 75 753 6300.
E-mail address: hkamitan@kais.kyoto-u.ac.jp (H. Kamitakahara).

0144-8617/$ – see front matter © 2011 Elsevier Ltd. All rights reserved.
doi:10.1016/j.carbpol.2011.10.055

and stereoselective reaction coupled with an excellent compatibility for functional groups. Ladmiral et al. (2006) have reported the preparation of glycopolymers by attaching azide containing mono-saccharides onto the alkyne containing polymer main-chain *via* "click chemistry".

In the present study, based on "grafting onto" strategy and "click chemistry", we prepared comb-shaped copolymers with cellulose side-chains, by grafting cellulose derivatives carrying a single azide group onto the alkyne containing polymer main-chain. Chemical structures of the synthesized graft copolymers and their crystalline patterns were investigated.

2. Experimental

2.1. Materials

N-(15-Azidopentadecanoyl)-2,3,6-tri-*O*-acetyl-4-*O*-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)-β-D-glucopyranosylamine (CTA2-C15-N_3) ($M = 874.97$) and *N*-(15-azidopentadecanoyl)-tri-*O*-acetyl-β-cellulosylamine (CTA13-C15-N_3, $DP_n = 13$) ($M_n = 4.12 \times 10^3$, $M_w = 5.33 \times 10^3$) were prepared as described in our previous articles (Kamitakahara, Enomoto, Hasegawa, & Nakatsubo, 2005; Kamitakahara & Nakatsubo, 2005). The cellulose and cellulose triacetate derivatives were abbreviated as CELL or CTA with the number of the degree of polymerization (DP_n) of the cellulosic chain (2 or 13), followed by the abbreviation of the pentadecanoyl group (C15), and the end group (N_3). MALDI-TOF MS measurements revealed that the molecular weights of CTA13-C15-N_3 with each DP value agreed well with theoretical values, and quantitative substitution of the reducing-end was confirmed. 2,2′-Azobis(isobutyronitrile) (AIBN) was crystallized from ethanol before use. 3-(Trimethyl silyl)-2-propyn-1-ol, methacryloyl chloride, triethylamine (Et_3N), *N*,*N*,*N*′,*N*′,*N*″-pentamethyldiethylenetriamine (PMDETA), copper(I)bromide (Cu(I)Br), tetrabutyl ammonium fluoride trihydrate (TBAF·$3H_2O$), and all other reagents were commercially obtained and used without further purification.

2.2. 3-(Trimethylsilyl)-2-propyn-1-yl methacrylate (TMS-PMA)

3-(Trimethylsilyl)-2-propyn-1-yl methacrylate (TMS-PMA) was prepared according to the previous article (Ladmiral et al., 2006; Scarpaci et al., 2009). To a solution of 3-(trimethylsilyl)-2-propyn-1-ol (1.0 ml, 1 eq.) and Et_3N (1.5 ml, 1.5 eq.) in dichloromethane (2.0 ml), methacryloyl chloride (1.0 ml, 1.5 eq.) was added. The mixture was stirred at room temperature for 0.5 h under nitrogen. After completion of the reaction, the mixture was extracted with ethyl acetate, washed with water and brine, dried with Na_2SO_4, and concentrated to dryness. Crude product was purified by open preparative column chromatography (eluent:ethyl acetate/*n*-hexane (1:19, v/v)) to give colorless syrup (1.12 g, 81.1% yield). ^1H NMR ($CDCl_3$): δ 0.20 (CH_3 (TMS)), 1.98 (CH_3), 4.78 (–O–CH_2–), 5.64, 6.20 (C=CH_2). ^{13}C NMR ($CDCl_3$): δ −0.35 (CH_3 (TMS)), 18.3 (CH_3), 52.9 (–O–CH_2–), 91.9 (–C≡*C*-TMS), 99.1 (–*C*≡C-TMS), 126.4 (CH_2=C–CH_3), 135.7 (CH_2=*C*–CH_3), 166.5 (*C*=O).

2.3. Poly (3-(trimethylsilyl)-2-propyn-1-yl methacrylate) (TMS-PPMA)

TMS-PMA (0.3 ml, 1 eq.) and AIBN (2.5 mg, 0.01 eq.) in benzene (0.3 ml) were loaded into a glass tube, and degassed by three freeze–pump–thaw cycles. The tube was sealed under vacuum, and placed in an oil bath at 75 °C for 1 day. The tube was cooled to room temperature, and opened. The reaction mixture was poured into methanol, filtered, and dried *in vacuo* to give an amorphous solid (158.6 mg, 58.7% yield). ^1H NMR ($CDCl_3$): δ 0.20 (CH_3 (TMS)), 0.95, 1.20 (CH_3), 1.85, 1.95 (CH_2), 4.60 (–O–CH_2–). ^{13}C NMR ($CDCl_3$): δ −0.24 (CH_3 (TMS)), 17.4, 19.0 (CH_3), 44.8, 45.1 (–CH_2–*C* (CH_3)–), 53.0 (–O–CH_2–), 54.3 (–CH_2–C (CH_3)–), 92.3 (–C≡*C*-TMS), 98.4, 98.7 (–*C*≡C-TMS), 176.1, 176.5 (*C*=O).

2.4. Poly(2-propyn-1-yl methacrylate) (PPMA)

To a solution of TMS-PPMA (128 mg) and acetic acid (50 μl. 1.5 eq. to PMA monomer unit) in tetrahydrofuran (THF) (10 ml), TBAF·$3H_2O$ was added dropwise at −20 °C. The mixture was stirred at room temperature for 3 h under nitrogen. The reaction mixture was poured into methanol. The precipitate was collected by centrifugation at 1000 rpm for 3 min, and dried *in vacuo* to give an amorphous solid (78.1 mg, 96.4% yield). The number and weight average molecular weights ($M_{n,PS}$, $M_{w,PS}$) estimated by polystyrene standards were $M_{n,PS} = 1.92 \times 10^4$ and $M_{w,PS} = 3.54 \times 10^4$, respectively. The absolute molecular weight (M_w) was calculated as 6.94×10^4 by MALS measurements. The weight average degree of polymerization (DP_w) was calculated as 5.59×10^2 from $M_w(\mathrm{PPMA})/M(\mathrm{PMA}) = 6.94 \times 10^4/124.21$. The DP_w of PPMA is described as $DP_w = X + Y$: X and Y are the numbers of cellulosic graft chains and PMA units of the graft copolymer (see Fig. 1). ^1H NMR ($CDCl_3$): δ 0.94, 1.09 (CH_3), 1.90, 1.98 (CH_2), 2.51 (–C≡*C*H), 4.62 (–O–CH_2–). ^{13}C NMR ($CDCl_3$): δ 16.9, 18.9 (CH_3), 44.8, 44.9 (–CH_2–*C* (CH_3)–), 52.2 (–O–CH_2–), 53.9 (–CH_2–C (CH_3)–), 75.5 (–*C*≡CH), 77.2 (–C≡*C*H), 175.5, 176.7 (*C*=O).

2.5. PPMA-g-(CTA2-C15)

CTA2-C15-N_3 (17.6 mg, 1 eq. to PMA monomer), PPMA (2.5 mg), and PMDETA (7 μl, 2 eq. to PMA monomer) in *N*,*N*-dimethylformamide (DMF) (0.3 ml) were loaded into a glass flask, and degassed by three freeze-pump-thaw cycles. The flask was purged with nitrogen, Cu(I)Br (5.7 mg, 2 eq. to PMA monomer) was added, and the flask was degassed again and sealed. The mixture was stirred at room temperature for 24 h. After completion of the reaction, the mixture was extracted with chloroform, washed with water and brine, dried with Na_2SO_4, and concentrated to dryness. The crude product was analyzed by SEC–MALS measurements. The compound was dried *in vacuo* to give an amorphous solid PPMA-g-(CTA2-C15) (17.8 mg, 88.6% yield). The number and weight average molecular weights ($M_{n,PS}$, $M_{w,PS}$) estimated by polystyrene standards were $M_{n,PS} = 7.58 \times 10^4$ and $M_{w,PS} = 2.24 \times 10^5$, respectively. The absolute molecular weight (M_w) was determined to be 4.22×10^5 by MALS measurements. Number of graft chains (X) was calculated as $X = 4.03 \times 10^2$ from $X = (M_w(\text{PPMA-}g\text{-(CTA2-C15)}) - M_w(\mathrm{PPMA}))/M(\text{CTA2-C15-}N_3) = (4.22 \times 10^5 - 6.94 \times 10^4)/874.97$. Number of PMA units ($Y$) was calculated as $Y = 1.56 \times 10^2$ from $Y = DP_w(\mathrm{PPMA}) - X = 5.59 \times 10^2 - 4.03 \times 10^2$. ^1H NMR ($CDCl_3$): δ 1.24 (br. s, aliphatic-H), 1.99, 2.01, 2.03, 2.04, 2.09, 2.11 (CH_3–CO), 3.72 (C5′-H, C5-H), 3.78 (C4-H), 4.01–4.17 (C6′-H_b, C6-H_b), 4.04, 4.16, 4.40, 4.44, 4.46 (C6′-H_a, C6-H_a), 4.57 (C1′-H), 4.84 (C2-H), 4.93 (C2′-H), 5.09 (C4′-H), 5.17 (C3′-H), 5.23 (C1-H), 5.27 (C3-H), 6.67 (NH), 7.93 (triazole). ^{13}C NMR ($CDCl_3$): δ 18.3 (CH_3), 20.4, 20.6, 20.8 (CH_3–CO–), 25.1 (C1–NH–CO–CH_2–*C*H_2–), 26.5, 29.2, 29.6, 30.3 (aliphatic-C), 36.4 (C1–NH–CO–*C*H_2–), 44.7 (CH_2–*C*), 50.4 (CH_2–O), 58.3 (*C*H_2–C), 61.5 (C6′), 61.9 (C6), 67.8 (C4′), 70.8 (C2), 71.5 (C2′), 71.8 (C5′), 72.5 (C3), 72.9 (C3′), 74.6 (C5), 77.9 (C1), 100.6 (C1′), 124.4 (CH (triazole)), 141.6 (C (triazole)), 169.1, 169.3, 169.5, 170.2, 170.3, 170.5, 171.0 (CH_3–*C*O–), 173.7 (C1–NH–*C*O–), 176.1, 177.1 (CO).