# Synthesis and Properties of Comb Polymers with Semirigid Mesogen-Jacketed Polymers as Side Chains

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**ABSTRACT:** A series of novel comb polymers, poly{2,5-bis[(4methoxyphenyl)oxycarbonyl]styrene}-*g*-polystyrene (PMPCS-*g*-PS), with mesogen-jacketed rigid side chains were synthesized by the "grafting onto" method from  $\alpha$ -yne-terminated PMPCS (side chain) and poly(vinylbenzyl azide) (backbone) by Cu(l)catalyzed 1,3-dipolar cycloaddition click reaction. The  $\alpha$ -yne-terminated PMPCS was synthesized by Cu(l)-catalyzed atom transfer radical polymerization initiated by a yne-functional initiator. Poly(vinylbenzyl azide) was prepared by polymerizing vinylbenzyl chloride using nitroxide mediated radical polymerization to obtain poly(vinylbenzyl chloride) as the precursor which was then converted to the azide derivative. The chemical structure and architectures of PMPCS comb polymers were confirmed by <sup>1</sup>H NMR, gel permeation chromatography, and multiangle

**INTRODUCTION** Polymer brushes with well-defined structures have attracted much attention in recent years.<sup>1</sup> Comb polymers, which are densely grafted polymer brushes, have distinct properties compared with sparsely grafted polymer brushes and linear homologues.<sup>2-4</sup> Comb polymers have wide applicability by tailoring their chemical components and structural parameters, which endow them potential functionalities in various fields. In a comb polymer, side chains are densely packed around the backbone, resulting in a fully stretched backbone. Even a soft backbone, for example, polystyrene, in a comb polymer exhibits a rigid or worm-like conformation rather than random-coil.<sup>5,6</sup> The persistence length of polymethacrylate-g-polymethylmethacrylate combs can reach 120 nm,<sup>7</sup> and the backbone stiffness is strongly affected by solvent quality.<sup>8</sup> Thus, a comb polymer usually acts like a rigid or worm-like semirigid cylinder, which is also called a "cylindrical polymer" or "bottle brush." Comb polymers have been well-characterized by a variety of physical techniques. More importantly, because of its high molecular weight (MW) and large diameter, an individual comb polymer can be visualized by scanning probe microscopy (SPM).<sup>9</sup> A poly(2-vinylpyridine)-*co*-polymethylmethacrylate-g-polymethacrylate comb shows completely different laser light scattering. Both surface morphologies and solution behaviors were investigated. Surface morphologies of PMPCS combs on different surfaces were investigated by scanning probe microscopy. PMPCS combs showed different aggregation morphologies when depositing on silicon wafers with/ without chemical modification. The PMPCS comb polymers transferred to polymer-modified silicon wafers using the Langmuir-Blodgett technique showed a worm-like chain conformation. © 2011 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 50: 918–926, 2012

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morphologies in neutral and charged states.<sup>10</sup> Moreover, the dynamic processes, for example, the collapse/decollapse of polymethacrylate-*g*-polybutylacrylate comb polymers, have also been visually observed.<sup>11,12</sup> The molecular weights and MW distributions of comb polymers can be determined by multiangle laser light scattering (MALLS).<sup>13</sup> Besides the experimental studies, theoretical simulation and modeling on comb polymers have also been established recently.<sup>14,15</sup>

Controllable methods, such as atom transfer radical polymerization (ATRP),<sup>16</sup> ring-opening polymerization (ROP),<sup>17</sup> and ionic polymerization,<sup>18</sup> have been widely applied in the synthesis of comb polymers, while click reaction<sup>19</sup> and singleelectron-transfer LRP<sup>20-22</sup> have also been introduced in recent years. Different strategies, classified as "grafting through," "grafting from," and "grafting onto," have been well developed for synthesizing comb polymers. In the grafting through strategy, comb polymers are obtained from radical<sup>16</sup> or ionic<sup>18</sup> polymerization of vinyl-terminated macromonomers, or from ring-opening polymerization of norbornenylterminated macromonomers.<sup>17</sup> In the grafting from strategy,<sup>23,24</sup> the polymer backbone is first synthesized, followed by the polymerization of side chains. In the grafting onto

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strategy,<sup>25,26</sup> the polymer backbone and side chains are separately polymerized and then coupled, and the parameters of both the backbone and side chains can be individually tailored. To attach side chains onto the backbone efficiently, highly efficient, quantitative reactions, such as nucleophilic reaction,<sup>26,27</sup> click reaction,<sup>25,28</sup> and atom transfer nitroxide radical coupling (ATNRC),<sup>29</sup> have been widely used in the grafting onto strategy. So far, most of the reported works on comb polymers use flexible, coil-like polymers, such as polystyrene (PS),<sup>27</sup> polybutylacrylate,<sup>30</sup> poly(ethylene oxide),<sup>31</sup> as the side chains, either linear or multibranched self-assembly dendrons.<sup>32–39</sup> However, comb polymers with rod-like side chains are rarely reported<sup>40</sup> due to the difficulty in synthesis caused by the immense steric hindrance of such crowded side chains.

Mesogen-jacketed liquid crystalline polymers (MJLCPs), which usually contain bulky mesogenic side groups, have been extensively studied by our group.<sup>41,42</sup> In this kind of polymers, mesogenic side groups are considered to be densely packed around the backbone; therefore, the MJLCP molecules may act as semirigid rod-like objects and form ordered phases in certain conditions. The rigidity of MJLCP rods can be easily tailored by varying the length, shape, rigidity, and tails of side groups. Therefore, MJLCP is an excellent rod-like candidate to build block copolymers with various architectures. Researches on rod-coil,<sup>43</sup> rod-rod,<sup>44</sup> triblock,<sup>45</sup> and multiarmed<sup>46</sup> polymers containing MJLCPs as the rod component have been investigated. However, comb polymers containing MJLCPs as rigid side chains have never been reported.

Herein, we report a new kind of comb polymers with polystyrene (PS) as the backbone and an MJLCP, poly{2,5-bis[(4methoxyphenyl)oxycarbonyl]styrene} (PMPCS), as the rodlike side chain. By combining ATRP, nitroxide mediated radical polymerization (NMRP), and Cu(I)-catalyzed classic click reaction, we successfully synthesized a series of MJLCPcontaining comb polymers (PMPCS-*g*-PS) with different backbone length via the grafting onto strategy. The surface morphologies of comb polymers on different substrates were investigated by SPM, respectively.

#### **EXPERIMENTAL**

# **Characterization Methods**

# **SPM Measurements**

SPM Images were obtained at ambient conditions with a Seiko SPI3800/SPA400 instrument (Seiko Instrument, Japan) operating in DFM mode. SI-DF3 cantilever was used as a probe with a resonance frequency of about 24 kHz and a spring constant of 1.4 N/m. Both height and phase images were recorded.

#### Light Scattering Measurements

A commercial laser light scattering spectrometer (Brookhaven, Holtsville, NY) equipped with a BI-200SM goniometer and a BI-TurboCorr digital correlator was used to perform both static light scattering (SLS) and dynamic light scattering (DLS) over scattering angles ranging from 20 to 150°. A



## **Other Experimental Methods**

Gel permeation chromatographic (GPC) experiments were conducted on a Waters 2410 instrument equipped with a Waters 2410 refractive index (RI) detector and two Waters  $\mu$ -Styragel columns (103 and 104 Å). THF with a flow rate of 1.0 mL/min was used as the eluent. The calibration curve was obtained with linear polystyrenes as standards. <sup>1</sup>H NMR spectra were obtained with a Varian 300 MHz spectrometer. Thermogravimetric analysis (TGA) was performed on a TA Q600 SDT instrument in a nitrogen atmosphere. Differential scanning calorimetric (DSC) examination was carried out on a TA Q100 calorimeter in a nitrogen atmosphere.

#### Materials

2-Bromo-2-methylpropionyl bromide (98%, Acros), ethyl 2bromoisopropionyl (98%, Acros), 2,2,6,6-tetramethylpiperidinyloxy (TEMPO, 98%, Acros), propargyl alcohol (99%, Aldrich), sodium azide (99%), and *N,N,N',N'',N''*-pentamethyl diethylenetriamine (PMDETA, 98%, TCI) were used as received. *N,N*-Dimethylformamide (DMF), tetrahydrofuran (THF), and triethylamine (98%, Beijing Chemical Reagents, A.R.) were used after distillation. Chlorobenzene was successively washed with concentrated sulfuric acid to remove residual thiophenes, 5% sodium carbonate solution, and deionized water, and then dried with anhydrous calcium chloride before finally distilled for use. All other reagents were purchased from Beijing Chemical Reagents and used as received.

# Synthesis of MJLCP Comb

# Synthesis of Monomer {2,5-bis[(4-Methoxyphenyl) oxycarbonyl]Styrene} (MPCS)

MPCS was synthesized from 2,5-dimethylbenzonic acid and p-methyloxy phenol by the method described in literature.<sup>47</sup>

## Synthesis of Propargyl 2-Bromoisobutyrate

Propargyl alcohol (1.1 g, 19.6 mmol) and triethylamine (3.5 g, 23.5 mmol) were dissolved in anhydrous THF (30 mL), and the solution was cooled down to 0 °C. THF (30 mL) containing 2-bromo-2-methylpropionyl bromide (3.0 g, 23.5 mmol) was added dropwise. The reaction mixture was stirred at 0 °C for 30 min and at ambient temperature overnight. An equal amount of water was then added, and the mixture was extracted with 100 mL dichloromethane for three times. After the removal of solvents, the raw product was purified by silica column chromatography. The product was a yellowish liquid with a yield of 73%.

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz,  $\delta$ ): 4.78 (d, 2H, CH<sub>2</sub>O), 2.53 (t, 1H,C=CH), and 1.96 (s, 6H, (CH<sub>3</sub>)<sub>2</sub>C).

# Polymerization of MPCS Initiated by Yne-Functional ATRP Initiator

In a typical experiment for polymerization, MPCS (0.5 g, 1.2 mmol), propargyl 2-bromoisobutyrate (4.2 mg, 20  $\mu$ mol), CuBr (2.9 mg, 20  $\mu$ mol), PMDETA (3.5 mg, 20  $\mu$ mol), and chlorobenzene (2.8 g) were added into a polymerization tube. The concentration of MPCS was 15 wt %. After degassed by three freeze-pump-thaw cycles, the tube was



sealed under vacuum. Subsequently, the tube was immerged into an oil bath thermostated at 90 °C for 12 h. At the end of polymerization, the tube was quenched in liquid nitrogen. The polymer solution was diluted by an equal amount of cold THF and passed through a neutral alumina column to remove the Cu(I) catalyst, and then the polymer was precipitated out from methanol to obtain a white solid. The conversion was about 90%, and the polydispersity index (PDI) was determined to be about 1.1 by GPC.

## Synthesis of TEMPO-Cl

TEMPO-Cl was prepared by following the reported method.<sup>48</sup> [*N*,*N'*-Bis(3,5-di-*tert*-butylsalicylidene)-1,2-cyclohexanediaminato]manganese(III) chloride (1.9 g), followed by di-*tert*-butyl peroxide (2.94 g) and sodium borohydride (1.5 g), was added to a solution of *p*-chloromethylstyrene (3.0 g, 19.7 mmol) and TEMPO (3.0 g, 19.2 mmol) in 1:1 toluene/ ethanol (v/v, 90 mL). The suspension obtained was stirred at ambient temperature for 24 h and then poured into 200 mL of deionized water. The mixture was extracted with dichloromethane (200 mL) three times. The combined organic layers were then dried, and the crude product was purified by flash chromatography, eluted with a mixed solvent of dichloromethane/petroleum ether (1:9 gradually increased to 1:1, v/v). The product (TEMPO-Cl) was obtained as a light yellowish solid (4.20 g, 52.5% yield).

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz,  $\delta$ ): 0.66, 1.02, 1.16, 1.28 (s,12H, CH<sub>3</sub>), 1.25-1.54 (m, 6H, CH<sub>2</sub>), 1.45 (d, 3H, CH<sub>3</sub>), 4.59 (s, 2H, CH<sub>2</sub>Cl), 4.80 (q,1H, CH), 7.26-7.34 (m, 4H, ArH). ELEM. ANAL. Calcd. for C<sub>18</sub>H<sub>28</sub>ClNO: C, 69.8%; H, 9.11%; N, 4.52%. Found: C, 69.24%; H, 9.10%; N, 4.23%.

# Polymerization of Vinylbenzylchloride

In a typical experiment for polymerization, vinylbenzylchloride (VBC) (1.0 g, 6.5 mmol), TEMPO-Cl (6.8 mg, 23  $\mu$ mol), and chlorobenzene (2.3 g) were added into a polymerization tube. The concentration of VBC was 30 wt %. After degassed by three freeze-pump-thaw cycles, the tube was sealed under vacuum. Subsequently, the tube was immerged into an oil bath thermostated at 120 °C for 48 h. At the end of polymerization, the tube was quenched in liquid nitrogen. The polymer solution was diluted by an equal amount of cold THF, and the polymer was precipitated out from methanol to obtain poly(vinylbenzyl chloride) (PVBC) as a white solid. The conversion was about 70%, and the PDI was around 1.3 determined by GPC.

# Azide Substitution of PVBC

PVBC (500 mg) was dissolved in 20 mL of anhydrous DMF, and NaN<sub>3</sub> (1.0 g) was added to the solution. The suspension was stirred at ambient temperature for 24 h. When the reaction was completed, 100 mL of water was added. Pure poly (vinylbenzyl azide) (PVBA) was collected by filtration as a white solid and dried overnight.

## Click Reaction of PVBA and *α*-Yne PMPCS

A typical procedure is described as follows.  $\alpha$ -Yne-terminated PMPCS (400 mg,  $M_{\rm n} = 18,000$  g/mol, 22  $\mu$ mol yne moiety), PVBA (2.3 mg, 14.8  $\mu$ mol azide moiety), and CuBr (3.1 mg,

22  $\mu$ mol) were introduced into a Schlenk flask and dissolved in DMF (4.0 g). The ratio of yne moiety and azide moiety was 1.5:1 (mol/mol). The Schlenk flask was degassed by the freeze-pump-thaw sequence for three cycles, sealed under vacuum, stirred at ambient temperature for 4 h, and then immerged into an oil bath thermostated at 80 °C for 24 h. The solution was diluted by an equal amount of cold THF and passed through a neutral alumina column to remove Cu(I) catalyst. The comb polymer was precipitated out from methanol. The raw product of the comb polymer was then reprecipitated.

## Reprecipitation

In a general procedure, 400 mg of the raw comb polymer was dissolved in 20 mL of THF. An equal amount of methanol was added dropwise to the solution until it was turbid. The suspension was centrifuged at 4000 rpm for 15 min, and the supernatant was carefully removed. The gel-like solid was washed with THF quickly, dissolved in fresh THF, and then precipitated in methanol. This procedure was repeated for several times until no signal of unreacted PMPCS was detected by GPC measurements.

# Surface Modification of Silicon Wafer

# Initiator Grafting

Silicon disks were cut into 1 cm  $\times$  1 cm pieces, cleaned according to a four-step RCA method,<sup>49</sup> and dried at 90 °C for 2 h (Marked as Si—OH). The Si—OH wafers were put in a beaker and immerged into 100 mL of anhydrous THF containing 1 mL Et<sub>3</sub>N. An additional 20 mL of THF solution containing 1 mL of 2-bromo-2-methylpropanoyl bromide was added dropwise under stirring. The mixture was stirred for another 4 h and then poured into 100 mL of deionized water to remove excess 2-bromo-2-methylpropanoyl bromide. The silicon wafers were washed with deionized water and acetone and dried at ambient temperature in a nitrogen atmosphere (Marked as Si—Br).

## **PMPCS Grafting**

MPCS (0.2 g, 0.48 mmol) and a Si-Br wafer were put in a polymerization tube, which was then added with predetermined amounts of ethyl 2-bromopropionate free initiator, PMDETA, and CuBr. Chlorobenzene (0.46 g) was added as a solvent, and the final concentration of MPCS was 30 wt %. The tube was treated by freeze-pump-thaw for three cycles, sealed under vacuum, and then put into an oil bath thermostated at 90  $^{\circ}$ C. After 24 h, the tube was quenched by liquid nitrogen, and the solution was dissolved in THF. The polymer solution was passed through a neutral alumina column, and the polymer was precipitated out from methanol, and characterized by GPC. The silicon wafer was successively washed thoroughly with DMF to remove adsorbed Cu(I) catalyst and then with deionized water and acetone, and it was dried at ambient temperature in a nitrogen atmosphere (Marked as Si-Polymer).

## Langmuir-Blodgett Film Preparation

Samples were dissolved in chloroform to obtain a 1 mg/mL solution. The injected volume was 50  $\mu$ L. Each sample had 20 min to reach equilibrium before compression. The



**FIGURE 1** GPC traces of methacryl-terminated PMPCS before (blue line) and after (red line) polymerization. Peaks on the red line refer to monomer, dimer, and trimer.

compression speed was 20  $\text{cm}^2/\text{min}$ . The monolayer film was transferred onto a silicon wafer (dipping up) at the selected pressure. During the transfer process the pressure remained constant. All sample wafers were kept dry for 24 h before the SPM measurement was conducted.

# **RESULTS AND DISCUSSION**

#### **Comb Synthesis**

To obtain a comb polymer there are three strategies classified as grafting through, grafting from, and grafting onto. We first attempted to use the grafting through method and synthesized two kinds of PMPCS macromonomers with methacryl and vinylbenzyl terminal groups. Polymerizations of both kinds of macromonomers with different molecular weights were subsequently attempted under various condiARTICLE

tions. However, only methacryl-terminated PMPCS macromonomer could be polymerized to afford oligomers (Fig. 1). This might be caused by the bulkiness of the PMPCS side chain and the relatively low concentration of the terminal group.

Alternatively, we chose the grafting onto strategy taking its advantages over control of backbone length, side-chain length, and polydispersity. The key step for this strategy is to choose an effective reaction that ensures maximum grafting efficiency. Click reaction<sup>50</sup> has been widely used in the synthesis of brush polymers and proven to be quantitative. Herein we designed a synthetic scenario shown in Scheme 1.

Because vinylbenzyl azide was unstable in the polymerization process, the PVBC backbone was polymerized from VBC as a precursor and then converted to PVBA by azide substitution with high efficiency (Supporting Information Fig. S4). Polymerization of MPCS was initiated by an ATRP initiator containing yne group. The polymerization was carried out in a dilute solution to prevent yne-yne coupling. In the <sup>1</sup>H NMR spectrum the signal of the hydrogen on terminal  $-C \equiv CH$  appeared at  $\delta = 2.20$  ppm (Fig. 2, curve 1). Finally, the backbone and the side chains were linked by the classic click reaction, and PMPCS combs were obtained. After click reaction and reprecipitation, the resonance of yne at  $\delta =$ 2.20 ppm disappeared (Fig. 2, curve 2), indicating that no residual side chains remained in the PMPCS combs.

The CuBr catalyst worked so well in our experiment that no ligand (e.g., PMDETA) was needed for this reaction. Parameters for the click reaction were carefully chosen. Higher temperature, higher concentration, or longer reaction time led to inevitable gelation. Figure 3 shows the influence of molar feeding ratio of yne to azide. Sufficient feeding of side chains (yne moiety) resulted in a broad and asymmetric peak, which might be due to side reactions such as



SCHEME 1 Synthesis routine of comb polymers with a semirigid MJLCP as side chains.



FIGURE 2 <sup>1</sup>H NMR spectra of yne-PMPCS (curve 1), and PMPCS comb after click reaction (curve 2).

intermolecular coupling or degradation induced by unreacted azide groups. Therefore, we added excess amount of yne moiety to eliminate side reactions and to obtain a maximum grafting density. The eluent peak became monomodal as the concentration of the side chain increased. However, the removal of unreacted side chains became a challenge (Fig. 3, black curve). The optimal yne to azide ratio was determined to be 1.5:1. After careful reprecipitation in a selective solvent of 1:1 THF/methanol (v/v), a series of PMPCS combs with different lengths of side chains and backbone were obtained. The results are shown in Table 1.

GPC equipped with an RI detector was used to monitor the reprecipitation process. Typical GPC eluent curves for a PMPCS comb before and after reprecipitation are shown in Figure 4. However, for comb polymers molecular weights measured by GPC are not accurate. Side chains in PMPCS combs were densely packed, and their molecular weights, calibrated by linear polystyrenes, were strongly underestimated. In addition, anomalous elusive behavior of high MW combs in GPC measurements<sup>7</sup> also makes molecular weight deviate from the true value. GPC traces showed monomodal peaks, and hydrodynamic radius ( $R_h$ ) of each sample presented a single narrow peak from DLS measurements; therefore, unreacted PMPCS side chains had been completely removed.



FIGURE 3 GPC traces of click reaction with different yne:azide ratios.

The absolute molecular weights were obtained from SLS results, and according to which the grafting densities were calculated.<sup>24,28</sup> The  $M_{\rm w, LS}$  of combs were in accordance with the theoretical molecular weights (see Table 1) calculated from the DPs of the backbone and the side chain. For Comb 1 and Comb 2, grafting densities were 100% and 92%, respectively. Thus, almost each site had a PMPCS grafted. For Comb 3 with the longest backbone, because its precursor PVBA with a large molecular weight ( $M_{\rm n} = 150,000$  g/mol) had relatively poor solubility during the click reaction,  $M_{\rm w, LS}$  measured by SLS was lower than the theoretical value, indicating a lower grafting density of about 75%.

All samples had glass transition temperatures of about 130 °C, and the temperatures at which 5% weight loss occurred were all over 300 °C. Compared with linear PMPCS which is soluble in common organic solvents, PMPCS combs were only soluble in DMF, THF, dichloromethane, and chloroform because of their large molecular weights.

#### Surface Modification of Silicon Wafers

SPM technique is widely used in probing comb polymers. However, the imaging of PMPCS combs was rather challenging. Because PMPCS combs contained fewer ester groups

	<i>M</i> <sub>n,backbone</sub> (g/mol) <sup>a</sup>	<i>M</i> <sub>n,side chain</sub> (g/mol) <sup>b</sup>	DP <sub>backbone</sub>	$DP_{side chain}$	<i>M</i> n, <sub>comb</sub> (10 <sup>6</sup> g/mol) <sup>a</sup>	PDI <sup>c</sup>	<i>M</i> <sub>w,LS</sub> (10 <sup>6</sup> g/mol) <sup>d</sup>	Y <sub>graft</sub> (%) <sup>e</sup>	T <sub>g</sub> (°C) <sup>f</sup>	7 <sub>d, 5%</sub> (°C) <sup>g</sup>
Comb 1	8,500	20,000	54	50	0.18	1.4	1.50	$\sim\!100$	128	342
Comb 2	4,5000	20,000	283	50	0.21	1.4	7.15	92	132	360
Comb 3	150,000	19,000	943	47	0.37	1.3	16.8	75	132	364
Comb 4	8,500	30,000	54	74	0.24	1.3	2.91	_	130	_

**TABLE 1** Structural Parameters and Characterizations of PMPCS Combs

<sup>a</sup> Determined by the GPC (calibrated with polystyrene standards).

<sup>b</sup> Obtained by the GPC value (calibrated with polystyrene standards) multiplied by 1.52. In previous work<sup>44</sup> we have proven that the absolute molecular weight of linear PMPCS is approximately 1.52 times of the GPC  $M_n$  value.

<sup>c</sup> PDI =  $M_w/M_n$  from GPC results.

<sup>d</sup> Determined by SLS in DMF (for details see Supporting Information).

<sup>e</sup> Calculated according to  $M_{\rm w, LS}$  measured by SLS.

<sup>f</sup> Determined from DSC measurements in a nitrogen atmosphere.

<sup>g</sup> Determined by TGA measurements in a nitrogen atmosphere.



**FIGURE 4** GPC traces of PMPCS side chain (blue curve), crude comb (red curve), and reprecipitated comb (black curve).

than polybutylacrylate combs, they could not stick on mica or silica surface firmly. Moreover, neither silica nor silicon wafer is PMPCS-philic, PMPCS combs tended to form clusters on these wafers. Therefore, surface modification was first performed to improve compatibility.

An ATRP initiator based on 2-bromo-2-methylpropanoyl was introduced onto silica surface. Because surface-initiated ATRP has the same controllable features as in solution,<sup>51</sup> free initiator ethyl 2-bromopropionate was added for the easy characterization of free polymers by conventional methods. The  $M_{n, GPC}$  of the surface-grafted polymer was regulated to be 20,000 g/mol. After polymerization, free PMPCS was precipitated out from methanol and analyzed by GPC. Si—Polymer wafer was immersed into pure DMF and washed thoroughly to remove Cu(I) residues adsorbed on surface. XPS spectra (Fig. 5) showed that the surface C composition increased from 14.5% on the Si—OH to 35.5% on the Si—Polymer, and Si composition decreased from 54.3% to 35.7%, confirming that PMPCS polymers were successfully grafted onto the silicon wafer.

# **Surface Morphologies**

Because Comb 3 had the largest aspect ratio with a DP of 943 in the backbone and a DP of 44 in each PMPCS side chain, it was chosen for SPM measurements. The physical shape of the probe will affect the SPM imaging process. The height measurement in SPM is relatively reliable. However, the diameter of an object is, to a certain degree, larger than its real value depending upon the tip radius of the SPM probe and the shape of the object. Therefore, we used the following equations to correct the diameters:

$$W_{\rm real}/2 = \frac{(W_{\rm exp}^2 + 4h^2)}{8h}$$
 (1)

$$W_{\text{real}} = W_{\text{exp}} - 2\delta = W_{\text{exp}} - 2\sqrt{R_t^2 - (R_t - h)^2}$$
 (2)



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where  $W_{\text{real}}$  and  $W_{\text{exp}}$  are the real and apparent diameters of the object,  $R_{\text{t}}$  is tip radius of the probe (10 nm for SI-DF3 probe used in our case), *h* is the height of the sample (particles or plateaus), and  $\delta$  is the illusional length which should be subtracted. Equation 1 applies to large spherical particles,<sup>52</sup> while eq 2 to flat plateau samples.<sup>53</sup> All diameters given below were calibrated using these equations.

In the first attempt to deposit PMPCS combs on wafers, 30  $\mu$ L of a dilute DMF solution with a concentration of 0.1 mg/ mL (DLS results indicated that PMPCS combs existed as single polymer chains under such conditions) was added dropwise onto different wafers. Imaging results showed that PMPCS combs aggregated into uniform nanospheres with an average diameter of 350 nm on unmodified Si-OH wafer. These nanospheres further assembled into crowded "necklace" pattern [Fig. 6(a,b)]. In contrast, the spherical nanospheres were mostly individually distributed on the Si-Polymer wafers, and no further aggregation was observed [Fig. 6(c,d)]. This phenomenon indicated a "twostep aggregation" mechanism. During solvent evaporation, PMPCS combs aggregated and formed free-standing nanospherical aggregates (first step) in the remaining solution. This step of aggregation occurred on both types of wafers. When the solvent continued to evaporate, on Si-OH wafers, further aggregation occurred due to the incompatibility between PMPCS nanospheres and the silica surface, and different patterns of spherical aggregation were formed (second step). However, we could not explain the formation of the necklace pattern observed in various locations. On the other hand, the situation was different on the PMPCS-modified surface. The modified surface was more PMPCS-philic than silica; therefore, primary nanospheres were "stuck" onto the surface that prohibited the second-step aggregation, resulting in the formation of well distributed nanospheres. Correlated to the results from light scattering measurements, the aggregation number was estimated to be 60 ( $N_{agg} = R_{SPM}^3 / R_{gLS}^3$ ).



FIGURE 5 XPS spectra of Si—OH (Curve 1, Si 54.3%, C 14.5%), Si—Br (Curve 2, Si 48.1%, C 22.3%), and Si—polymer (Curve 3, Si 35.7%, C 35.5%).



FIGURE 6 PMPCS comb aggregations of Comb 3 on different types of surfaces: Si-OH wafer (a,b); Si-polymer wafer (c,d).

To obtain the unimolecular image, we employed the Langmuir-Blodgett technique to avoid the aggregation of PMPCS combs. From the  $\pi$ -A curve (Supporting Information Fig. S5), the zero-pressure area was  $\sim 20$  Å per MPCS unit which equals to 10,000 nm<sup>2</sup> per comb. The compression process was irreversible. Owing to the relatively slow conformational transition for such a rigid comb, combs were fixed on the water surface after solvent evaporation. Because the film was not quite stable at high pressures, the transfer pressures were chosen as 1 and 5 mN/m.

From the SPM images in Figure 7, unimolecules were clearly visualized. The height of the PMPCS comb was 3.8 nm, indicating that the combs lied flat on the surface. The average diameter (*a*) of PMPCS comb cylinders was 21.3 nm. This diameter gave the length per PMPCS monomer  $l_{\text{DP,PMPCS}} = a/2\text{DP}_{\text{side chain}} = 2.3$  Å, suggesting that the side chains of the PMPCS comb were fully extended and rod-like. The average length of the comb,  $L_{\text{SPM}}$ , was 200 nm after calibration. Thus, the length per DP was calculated as  $l_{\text{DP,backbone}} = L_{\text{SPM}}/DP_{\text{backbone}} = 2.1$  Å, which indicated that the comb backbone

behaved as a semirigid chain with the *gauche/trans* conformation. The aspect ratio of combs obtained from SPM was 9.4 ( $L_{\rm SPM}/L_{\rm diameter}$ ), which was close to 10.0, the theoretical value calculated from DP<sub>backbone</sub>/2DP<sub>side chain</sub>.

In common situations the repulsion between neighboring groups becomes a minimum when the backbone takes alltrans conformation. In PMPCS combs, however, it was not the optimal conformation. In all-trans conformation the neighboring groups point to the same direction. Considering that the diameter of bulky PMPCS side chains (15.9 Å) was overwhelmingly larger than the maximum value of  $l_{\text{DP,backbone}}$ (2.5 Å), there was not enough space for PMPCS side chains to pack around an all-trans backbone. According to the high grafting density obtained from light scattering measurements and diameters measured by SPM, we propose that the backbones in PMPCS combs took a partially coiled conformation to stagger side chains to decrease hindrance. On the other hand, in PMPCS side chain the mesogenic groups was not so bulky that in side chains the vinyl backbone took a conformation which was closer to all-trans conformation, which



**FIGURE 7** SPM images of PMPCS Comb 3 on Si—Polymer wafers. The dipping speed was 2 mm/min with a transfer pressure of 1  $N/m^2$ : (a) height image, vertical scale 10 nm; (b) height image, vertical scale 9 nm; (c) phase image of b; (d) 3D view of b; (e) altitude measurement, vertical scale 10 nm; (f) cross-sectional analysis of (e), vertical scale 5 nm. The apparent distance between triangles is 37.1 nm. After calibration using eq 2, the real distance is 21.3 nm.

was why in PMPCS comb  $l_{\rm DP,side\ chain}$  was slightly larger than  $l_{\rm DP,backbone}$  in our measurements.

Samples prepared under different conditions were all analyzed. Although the transfer pressure and the dipping speed were varied, the shape and average length of the single molecules remained almost the same (Supporting Information Fig. S6). This observation was in accordance with the irreversible compression behavior in the Langmuir-Blodgett technique. Because there was no significant selectivity on dipping speed or transfer pressure, the comb molecules could be totally fixed on water surface after solvent evaporation before transfer. Moreover, the attempts to transfer PMPCS Langmuir-Blodgett film onto silicon wafers without modification were failed, which might be due to the incompatibility between PMPCS combs and silicon wafer.

### CONCLUSIONS

A series of new comb polymers containing rod-like side chains, poly{2,5-bis[(4-methoxyphenyl)oxycarbonyl]styrene}*g*-polystyrene (PMPCS-*g*-PS), with different lengths of the backbone and side chains were successfully synthesized by the grafting onto method. By combining ATRP, NMRP, and click reaction, lengths of both the backbone and side chains could be well tailored. This strategy was proven to be an effective way to prepare rod-grafted comb polymers. PMPCS combs exhibited a two-step aggregation behavior when depositing on different types of silicon surfaces. By using the Langmuir-Blodgett technique, we found that PMPCS comb polymers showed a worm-like chain conformation on PMPCS-modified silicon wafers.

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