The Synthesis of Random Brush for Nanostructure of Block Copolymer

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Summary: Polymer brush has been synthesized via conventional free radical polymerization to use a surface active material on the silicon substrate. The synthesized polymer brushes were successfully grafted onto the silicon oxide substrate and the hydrophilic silicon oxide substrate has been changed into the more hydrophobic one. The synthesized poly(styrene-*ran*-methyl methacrylate) brush grafted silicon substrate could provide poly(styrene-*block*-methyl methacrylate) with neutral surface.

Keywords: block copolymer; nanostructure; polymer brush; self-assembly; thin film

Introduction

Random copolymer brush has attracted significant attention as an useful surface active material due to their precise tunability over surface energy by changing the composition of each repeating unit in the brush chains.[1] As a representative example, the random copolymer brushes with the appropriate compositions of two kinds of monomers can provide a chemically neutral surface for the block copolymers made from those monomers. In order to control the surface property precisely, a random copolymer brush is required to have appropriate composition and random sequence of repeating units, and a proper surface reactive functional group. In particular, the precise synthesis of random brush is important because it can be used to control nanostructure of block copolymer.[2–4]

Practically, the conventional polymerization methods for well-defined molecular structures such as cationic and anionic polymerizations, are not suitable for the synthesis of random copolymer brush because it requires extremely delicate control over reaction condition, it has only a small pool of applicable monomers as well as it is hard to achieve completely random sequence of repeating unit. Conventional free radical polymerization has been excluded also, because it was considered to have a poor control over molecular weight distribution and the functionality at a chain end. Up to now most of random copolymer brushes have been synthesized by living free radical polymerization such as atom transfer radical polymerization (ATRP),reversible addition fragmentation transfer polymerization (RAFT),or nitroxide mediated polymerization (NMP).

Here, we use a simple approach to synthesize poly(styrene-*ran*-methyl methacrylate) (P(S-*r*-MMA)) brushes with relatively narrow molecular weight distribution and functionality at a chain end via conventional free radical polymerization. Our strategy relies on the combined application of a commercially available functionalized free radical initiator and a chain transfer agent. The functionalized initiator provides the surface reactive functionality at a chain end and the chain transfer agent controls the molecular weight as well as molecular weight distribution.

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Experimental Part

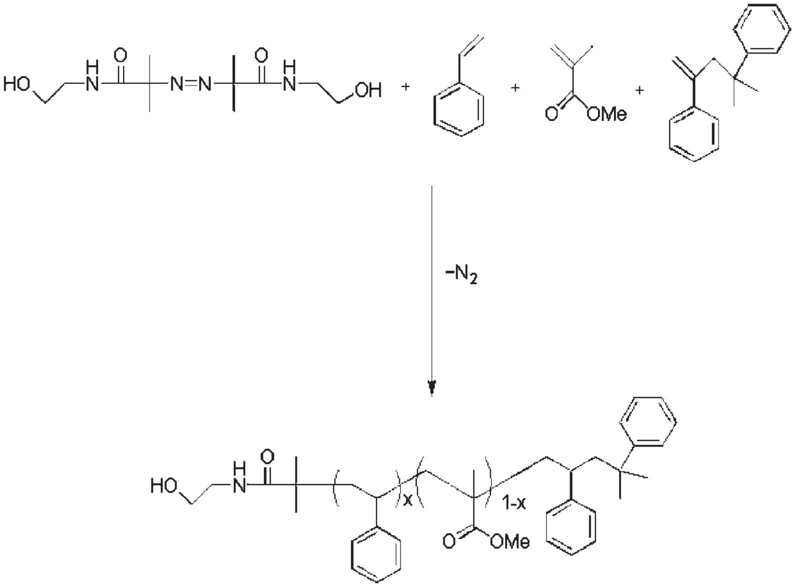
A free radical initiator, V086(trade name), 2,2′-Azobis[2-methyl-N-(2-hydroxyethyl)-pro-pionamide] was purchased from WAKO Pure Chemical Industries, Ltd. 2,4-diphenyl-4-methyl-1-pentene as a chain transfer agent, styrene and methyl methacrylate were purchased from Aldrich.

Hydroxyl terminated poly(styrene-*ran*-methyl methacrylate) copolymer brushes were synthesized as scheme 1: 2,2′-Azobis[2-methyl-N-(2-hydroxyethyl)-propionamide] as a free radical initiator, styrene and methyl methacrylate as monomers, and 2,4-diphenyl-4-methyl-1-pentene as a chain transfer agent were premixed at room temperature for more than 30 min under N_2. After the mixing process, a bulk polymerization was conducted at 70 °C for about 8 hrs. The reaction was terminated by quenching the reaction mixture to room temperature. Reaction products were washed several times by purified water in a separating funnel in order to remove the unreacted initiator and then precipitated into methanol.

The prepared polymer brushes were deposited onto silicon wafers as follows; Silicon wafers were cleaned by piranha treatment at 110 °C for 30 min and washed sufficiently by distilled water. 2.5 wt% solutions of polymer brushes in toluene were spin coated at 2,000 rpm onto the silicon wafer, yielding the thin films with the film thickness around 80 nm. The brushes coated substrates were annealed under vacuum at 160 °C for a sufficient time in order to allow the chemical reaction between the hydroxyl groups of polymer brush and oxide layer of silicon wafer surface. After the annealing, unreacted polymer brushes were removed by rinsing several times with toluene.

Results and Discussion

The molecular composition and the sequence distribution of styrene and methyl methacrylate in the copolymer brushes were characterized by 500 MHz ^{1}H-NMR in Figure 1.



Scheme 1.
The synthesis of hydroxyl terminated poly(styrene-*ran*-methyl methacrylate) copolymer brush.

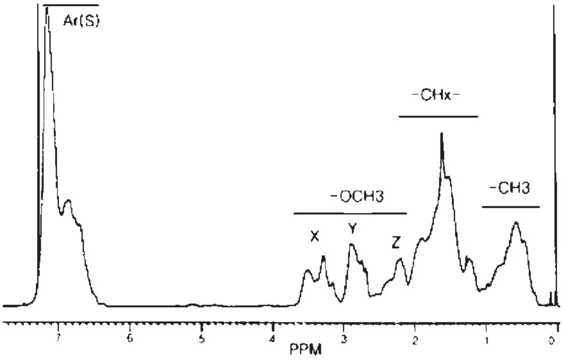


Figure 1.
A 500 MHz ^{1}H-NMR spectrum of a poly(styrene-*ran*-methyl methacrylate) copolymer brush synthesized by run 4 in Table 1.

It was turned out from the –OCH3 peak distribution between 2 ppm and 3.5 ppm that the synthesized copolymer brushes had random sequential distribution. From the comparison between Ar peak of polystyrene and –CH3 peak of polymethyl methacrylate, it was found that final composition ratio of polystyrene to polymethyl methacrylate was the almost same as the feed ratio.

Table 1 shows the characterizations of the prepared polymer brushes. All polymer brushes had unimodal molecular weight distribution. Molecular weight and molecular weight distribution monotonously decrease with the amount of chain transfer agent. Remarkably, the random copolymer brushes synthesized by using excess amounts of chain transfer agents had comparable molecular weight distribution (M_w/M_n) with the literature value, 1.32 of the one synthesized from functionalized nitroxide mediated living radical polymerization.

Figure 2 shows the water droplet images on the bare silicon and brush grafted silicon substrates. In Figure 2a, the bare wafer indicating the piranha treated silicon wafer had 11° of the contact angle of water droplet. And the wafer treated polystyrene brush, synthesized by run 6 in Table 1, had 79 ± 1° of the contact angle of water droplet in Figure 2b. In Figure 2c, polymer brushes synthesized by run 4 in Table 1 were deposited on the substrate. P(S-*r*-MMA) brush grafted silicon wafer showed 76 ± 1° of water contact angles.The results indicate that polymer brushes synthesized by con-

Table 1.
Characterizations of the synthesized poly(styrene-*ran*-methyl methacrylate) copolymer brushes.

Run	Feed ratios of reactants	M_w[g/mol]	M_w/M_n	f_s[d]
	CTA[a]: Initiator[b]: Styrene: MMA[c]			
1	4 : 2 : 60 : 40	51,339	1.85	0.56
2	10 : 2 : 60 : 40	22,861	1.78	0.58
3	15 : 2 : 60 : 40	16,651	1.57	0.56
4	20 : 2 : 60 : 40	12,834	1.43	0.62
5	30 : 2 : 60 : 40	9,684	1.32	0.58
6	20:2:100:0	9,570	1.54	0.99

[a] CTA: Chain transfer agent, 2,4-diphenyl-4-methyl-1-pentene;
[b] Initiator: 2,2′-Azobis[2-methyl-N-(2-hydroxyethyl)-propionamide];
[c] MMA: methyl methacrylate;
[d] f_s: the fraction of polystyrene in the synthesized hydroxyl terminated poly(styrene-*ran*-methyl methacrylate) copolymer brushes.

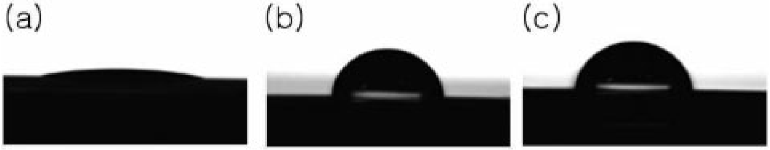


Figure 2.
Water droplets on (a) bare silicon wafer (b) polystyrene brush treated silicon wafer and (c) P(S-*r*-MMA) brush treated silicon wafer.

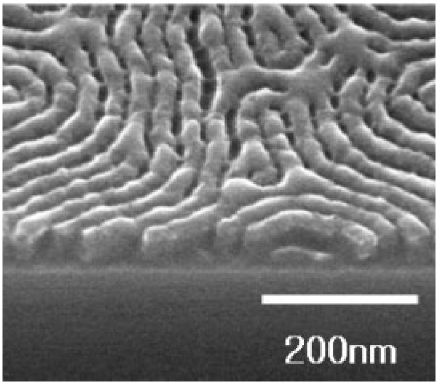


Figure 3.
SEM image of 25k-26k PS-*b*-PMMA with the thickness of 34.7 nm on the random copolymer grafted silicon wafer.

ventional radical polymerization were successfully grafted onto the silicon oxide substrate and the hydrophilic silicon oxide substrate has been changed into the more hydrophobic one.

The P(S-*r*-MMA) brush synthesized by run 4 in Table 1 was acted as neutral surface which has the same surface energy for polystyrene and polymethyl methacrylate. Figure 3 shows SEM image of of 25k-26k poly(styrene-*block*-methyl methacrylate) (PS-*b*-PMMA) on the P(S-*r*-MMA) brushes grafted silicon wafer. The block copolymer was the thickness of 34.7 nm. Every lamellae had the clear perpendicular orientation on the P(S-*r*-MMA) brushes grafted silicon wafer.

Conclusion

Surface reactive P(S-*r*-MMA) brushes were successfully synthesized by conventional free radical polymerization. In the present approach key strategy was the combined applications of a functionalized free radical initiator, 2,2′-Azobis[2-methyl-N-(2-hydroxyethyl)-pro-pionamide] and a chain transfer agent, 2,4-diphenyl-4- methyl-1-pentene. The functionalized free radical initiator provided surface reactive functionality, while the chain transfer agent controlled over the molecular weight and molecular weight distribution. The synthesized random copolymer brushes were successfully applied to control the orientation of lamellar structure of the PS-*b*-PMMA. Our strategy could be simply expended into the polymer brushes with other functional groups by changing the combination of free radical initiators and chain transfer agents.

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