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SYNTHESIS OF POLYMER BRUSH BY NANOPOROUS
SURFACE-INITIATED POLYMERIZATION



Miss Mayuree Srinunthakul

ศูนย์วิทยทรัพยากร

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Accepted by the Faculty of Science, Chulalongkorn University in Partial
Fulfillment of the Requirements for the Master's Degree


.....Dean of the Faculty of Science
(Professor Piamsak Menasveta, Ph.D.)

Thesis committee


.....Chairman
(Professor Pattarapan Prasassarakich, Ph.D.)


.....Thesis Advisor
(Assistant Professor Vipavee P. Hoven, Ph.D.)


.....Member
(Professor Suda Kiatkamjornwong, Ph.D.)


.....Member
(Assistant Professor Warinthorn Chavasiri, Ph.D.)

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ใช้ซึบสเตรตซิลิกอนออกไซด์กราฟต์ด้วยโมเลกุลชั้นเดียวของทริสโทรมเมทิลไฮดรอกซีไซลิล (ทริสทีเอ็มเอส) เป็นแม่แบบระดับนาโนเมตรในการควบคุมความหนาแน่นการกราฟต์ของพอลิเมอร์บรัช การสังเคราะห์พอลิเมอร์บรัชโดยการริเริ่มปฏิกิริยาพอลิเมอร์ไอโซไซยานูริเริ่มของ 2-เมทอะคริลอิลออกซีเอทิลฟอสโฟริลโคลีน (เอ็มพีซี) และ เทอร์ต-บิวทิลเมทาคริเลต (ที-บีเอ็มเอ) จากหมู่แอลฟาโบรโมเอสเทอร์ซึ่งติดกับหมู่ไฮดรอกซิลที่เคลือบอยู่บนพื้นผิวหลังจากถูกปกคลุมด้วยทริสทีเอ็มเอสปริมาณต่างๆ ด้วยอะตอมทรานส์เฟอร์เรดิคัลพอลิเมอร์ไอโซไซยานูริ โดยใช้คอปเปอร์โบรไมด์/ไบไพรีดีน และคอปเปอร์โบรไมด์/พีเอ็มดีอีทีเอเป็นระบบเร่งปฏิกิริยาในการสังเคราะห์พีเอ็มพีซีและพีทีบีเอ็มเอ ตามลำดับ ร้อยละการปกคลุมของทริสทีเอ็มเอสส่งผลกระทบต่อความหนาแน่นและสัญญาณวิทยาของพอลิเมอร์บรัช ส่วนที่ยื่นนูนซึ่งสังเกตเห็นได้จากภาพเอเอฟเอ็มของพีเอ็มพีซีบรัชเป็นหลักฐานที่แสดงให้เห็นว่า พีเอ็มพีซีบรัชมีการกระจายตัวในระดับนาโนเมตรบนซึบสเตรต ขนาดของส่วนที่ยื่นนูนและความขรุขระของพื้นผิวมีลักษณะสอดคล้องเป็นอย่างดีกับความหนาแน่นการกราฟต์ของพีเอ็มพีซีบรัช การที่พีทีบีเอ็มเอบรัชที่เติบโตจากซึบสเตรตที่มีรูขนาดนาโนเมตรแทบจะไม่ปรากฏลักษณะสำคัญใดๆ แสดงว่าการจับตัวกันเองเป็นกลุ่มก้อนของพีเอ็มพีซีบรัชเกิดจากการเข้ากันไม่ได้ระหว่างเฟสของพีเอ็มพีซีบรัชที่มีสมบัติชอบน้ำและหมู่ทริสทีเอ็มเอสที่มีสมบัติไม่ชอบน้ำ

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Chemically grafted tris(trimethylsiloxy)silyl (tris(TMS)) monolayer on the silicon oxide substrate was used as a nanometer-scale template for controlling the graft density of polymer brushes. Polymer brushes were synthesized by surface-initiated polymerization of 2-methacryloyloxyethyl phosphorylcholine (MPC) and *tert*-butyl methacrylate (*Pt*-BMA) from ∞ -bromoester groups tethered to the residual silanol groups on the surface after creating a range of tris(TMS) coverage *via* atom transfer radical polymerization (ATRP). CuBr/bpy or CuBr/PMDETA was used as a catalytic system for PMPC and *Pt*-BMA synthesis, respectively. The percentage of tris(TMS) coverage significantly influenced the thickness and morphology of polymer brushes. Protrusions representing self-aggregation of PMPC brushes in nanopores as visualized by AFM analysis evidently suggested that PMPC brushes distributed nanoscopically on the surface. The size of protrusion and surface roughness corresponded quite well with the graft density of PMPC brushes. The fact that *Pt*-BMA brushes grown from nanopores were almost featureless implies that self-aggregation of PMPC brushes is truly a consequence of phase incompatibility between hydrophilic PMPC brushes and hydrophobic tris(TMS).

Field of study Petrochemistry and Polymer Science Student's signature Mayuree Srinunthakul
 Academic year 2004 Advisor's signature Vp. Hoven
 Co-advisor's signature -

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LIST OF ABBREVIATIONS

AFM	: Atomic force microscopy
ATRP	: Atom transfer radical polymerization
Å	: Angström
<i>t</i> -BMA	: <i>tert</i> -Butyl methacrylate
bpy	: 2,2'-Bipyridyl
CDCl ₃	: Deuteriochloroform
CuBr	: Copper (I) bromide
CuBr ₂	: Copper (II) bromide
°C	: Degree Celsius
d	: doublet (NMR)
<i>D</i>	: Polydispersity
DEA	: 2-(Diethylamino)ethyl methacrylate
D ₂ O	: Deuterium oxide
<i>dp</i>	: Degree of polymerization
Eq.	: Equation
GPC	: Gel permeation chromatography
<i>k</i> _{act}	: The activation rate parameter
<i>k</i> _{deact}	: The deactivation rate parameter

m	: multiplet (NMR)
MeOH	: Methanol
MEO2PC	: 2-methacryloyloxy ethoxyethyl phosphorylcholine
mg	: miligram
MgSO ₄	: Magnesium sulfate
min	: minute
mL	: mililiter
mm	: milimeter
mM	: milimolar
MMA	: Methyl methacrylate
mmol	: milimole
\bar{M}_n	: Number average molecular weight
MPC	: 2-Methacryloyloxyethyl phosphorylcholine
\bar{M}_w	: Weight average molecular weight
nm	: nano meter
NMR	: Nuclear magnetic resonance spectroscopy
PDI	: Polydispersity Index
PMMA	: Poly(methyl methacrylate)
PMPC	: Poly(2-methacryloyloxyethyl phosphorylcholine)
Pt-BMA	: Poly(<i>tert</i> -butyl methacrylate)

ppm	: part per million
q	: quartet (NMR)
s	: singlet (NMR)
SAM	: Self-assembled monolayer
S.D.	: Standard deviation
SEM	: Scanning electron microscopy
t	: triplet (NMR)
THF	: Tetrahydrofuran
tris(TMS)Cl	: tris (Trimethylsiloxy)chlorosilane
tris(TMS)	: tris (Trimethylsiloxy)silyl
μL	: microliter
wt%	: percentage of weight
XPS	: X-ray photoelectron spectroscopy

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