FUNCTIONALIZATION OF POLYMER COATED SURFACES BY RADICAL-EXCHANGE REACTIONS

by

Gizem Yeter Baş

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To my family

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ABSTRACT

The synthesis of functional polymeric coatings has gained great interest for various research area especially biosensor applications. In this thesis, novel method to make end group modifications of polymer brushes on silicon surfaces is disclosed. As an application, the aim is to design polymeric coatings with dendritic structures as a multivalent ligand display to increase binding affinity of protein during biomolecular recognition. This thesis explores the initial step of end group modification using a radical exchange reaction. In particular, di(ethylene glycol) methyl ether methacrylate based hydrophilic polymer brushes were synthesized via reversible addition-fragmentation chain transfer polymerization (RAFT) with ‘grafting from’ approach. Removal of dithio benzoate group of RAFT chain transfer agent and functionalization of polymer brush end groups were achieved via radical cross coupling reaction. Polymer brushes were treated with diazo-based derivatives containing clickable azide groups. These were modified using an alkyne containing fluorescent dye. First and second generation of polyester dendrons containing diazo groups at the core were synthesized and used for polymer chain end functionalization.

ÖZET

Fonksiyonel polimer fırçaların sentezi, özellikle biyosensör uygulamaları için büyük ilgi kazandı. Bu tezde, silikon yüzey üzerindeki polimer fırçaların uç grup modifikasyonu için özgün yöntem ortaya koyuldu. Uygulama olarak amaç, biomolekülerin tanınması sırasında proteinlerin bağlanmalarını arttırmak için çoklu etkileşim yapabilen dendritik yapılar bulunduran polimerik yüzey kaplamalar tasarlamaktır. Bu tez radikalik yer değiştirme reaksiyonu kullanarak uç grup modifikasyonunun ilk adımını araştırır. Özellikle dietilen glikol metil eter metakrilat tabanlı hidrofilik polimer fırçalar katılma-ayrışma zincir transfer polimerleşmesi kullanılarak yüzeyden sentezlendi. RAFT ajanının ditiyo benzoat grubunun uzaklaştırılması ve polimer fırçaların uç gruplarının fonksiyonelleştirilmesi radikalik çapraz eşleşme reaksiyonu kullanılarak gerçekleştirildi. Polimer fırça kaplı yüzeyler click edilebilen azit gruplarını içeren diazo temelli benzeri dendronlara maruz bırakıldı. Bu yüzeyler alkin içeren floresan boyalar kullanılarak modifiye edildi. Korunda diazo grup bulunduran birinci ve ikinci nesil poliester dendronlar sentezlendi ve polimer zinciri uç grup işlevselleştirilmesi için kullanıldı.

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AIBN	Azobisisobutyronitrile
Bis-MPA	2,2-bis(hydıorxymethyl)propionic acid
BODIPY	Boron-dipyrromethene
$CDCl_3$	Deuterated Chloroform
CH_2Cl_2	Dichloromethane
CTA	Chain Transfer Agent
DCC	Dicyclohexylcarbodiimide
DEGMA	Di(ethylene glycol) methyl ether methacrylate
DMAP	N,N-Dimethylpyridin-4-amine
DMF	N,N-Dimethylformamide
EDC	N-(3-Dimethylaminopropyl)-N'-ethylcabodiimide
FT-IR	Fourier Transform Infrared
G1	Generation 1 dendron
G2	Generation 2 dendron
MeOH	Methanol
NMR	Nuclear Magnetic Resonance
PMDETA	N,N,N',N',N"-Pentamethyldiethylenetriamine
pTSA	p-Toluenesulfonic acid monohydrate
RAFT	Reversible Addition-Fragmentation Chain Transfer
Si/SiO_2	Silicon/Silicon Dioxide
THF	Tetrahydrofuran
UV	Ultraviolet
V-501	4,4'-Azobis(4-cyanovaleric acid)

1. INTRODUCTION

1.1. Polymer Brush

Features of materials can be tailored by using thin polymer coatings onto their surface. This enables control of the interaction between the material and its environment [1]. Modification of surfaces with thin polymer films make it possible to tune surface properties such as wettability, biocompatibility, corrosion resistance and friction [2]. Such thin coatings are very attractive for variable applications, for instance protection layers in devices [3], biosensors and implants surfaces [4,5], chromatographic separation [6], lithium batteries [7], nonfouling surfaces [8], drug delivery [9], protein immobilization [10] and stimuli responsive surfaces [11].

All these above mentioned applications require display of particular functional groups on the surface of polymer films. In this regard, polymer brushes serve as suitable designs for obtaining functional and tunable surfaces since they allow control of architectural features. Furthermore, they can be applied to various surfaces such as gold, silica, and magnetic nanoparticles [12].

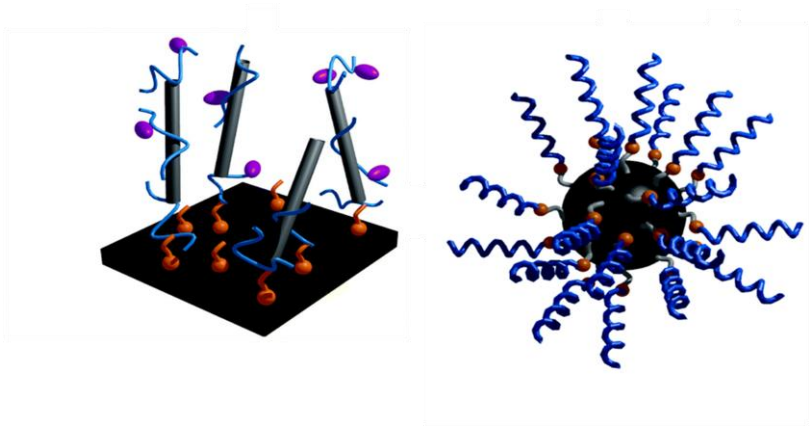

Figure 1.1. Polymer brushes on flat and spherical surface. Reprinted with permission from [13].

Polymer brushes are thin coatings where one end of the polymer chains are tethered onto the solid substrate through covalent attachment or physical adsorption (Figure 1.1) [14,15]. Compared to other surface modification techniques, polymer brushes are more advantageous in terms of mechanical (e.g. good long term stability) and chemical robustness (since the polymer chains are irreversibly attached to the substrate), and synthetic feasibility in order to introduce various functional groups [1,2].

1.1.1. Polymer Brush Properties and Applications

As mentioned before, the control of functionalization of polymer brushes enables to create a wide variety of functional surfaces that can find applications as responsive coatings [16], protein immobilization [17], non-biofouling surface [18], antibacterial coatings [19] etc. Functional responsive coatings alter surface properties according to external stimuli such as temperature, solvent polarity, pH value, light, or electric current which are very favorable for obtaining materials whose properties can be changes either on demand or as a response to the environment (Figure 1.2) [20].

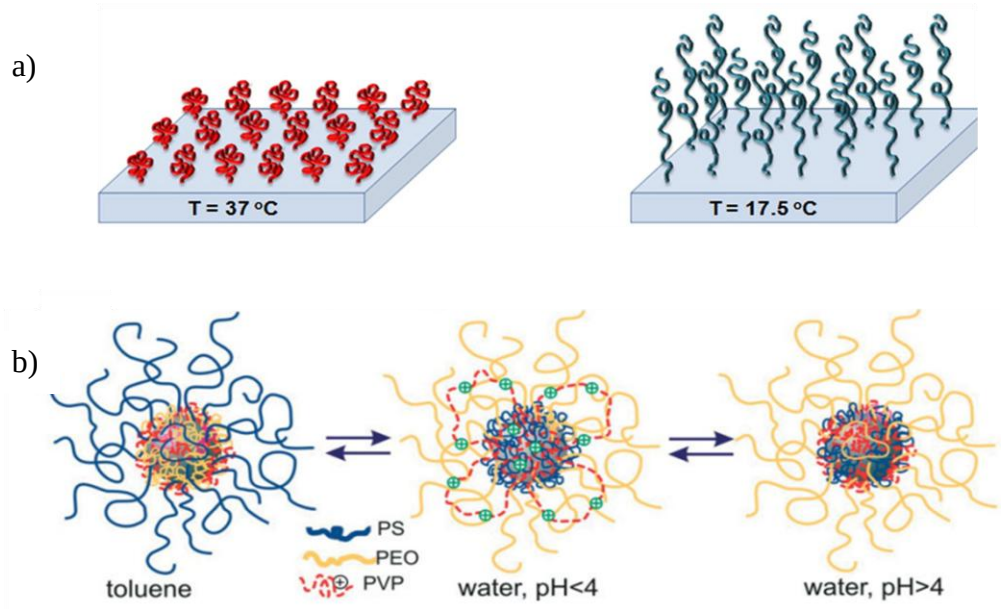

Figure 1.2. Schematic representation of responsive polymer brushes
a) Thermoresponsive polymer brush. Reprinted with permission from [21]. b) Solvent and pH responsive polymer brush. Reprinted with permission from [22].

Non-biofouling and antibacterial coatings are unavoidably necessary to protect surfaces from bacterial contamination and nonspecific adsorption of proteins for medical devices, food package and industrial pipes [19,23]. Polymer films allows one to develop such non-biofouling coatings [15]. Polymer brushes prepared from 2-hydroxyethyl methacrylate (HEMA) and poly(ethyleneglycol) methacrylate (PEGMA) are example for non-biofouling brushes that resist nonspecific adsorption of protein and cell [18,24]. These monomers have similar properties with PEG which is known to be protein and cell resistant [23]. As illustrated in Figure 1.3, bacteria is either repelled or killed by properly functionalized surface, while on the other hand bacterial cells are attached to the unmodified surface that results in formation of biofilm [25].

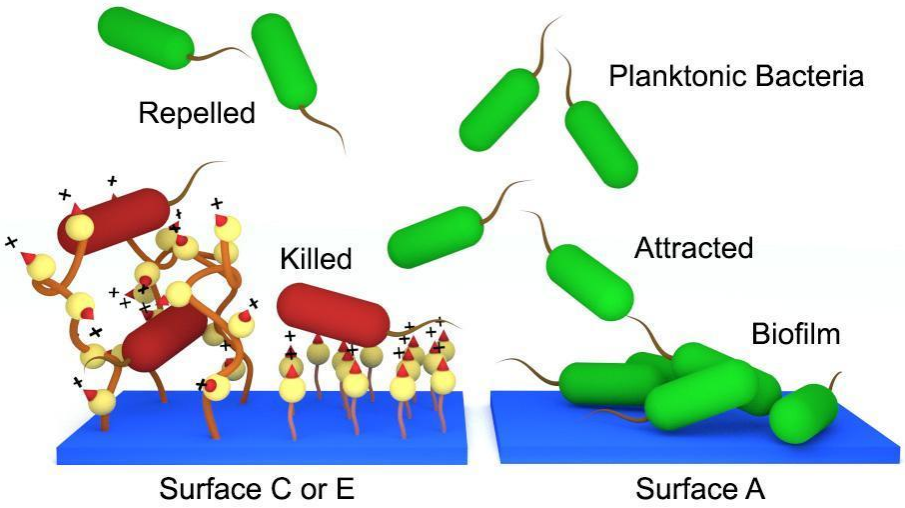

Figure 1.3. Bactericidal and bacterial repelling coated surface (left) Biofilm formation on unmodified surface (right). Reprinted with permission from [25].

In the area of biomolecular recognition, polymer brushes are very attractive platforms in terms of the ability to increase binding and immobilizations of biomolecules such as protein, enzyme, antibodies and so on. Furthermore, compared to other materials, since polymers are anchored to the solid surface, they have great mechanical stability and high surface concentration of functional groups that are controllable by monomer type and brush length [10,15]. In order to immobilize biomolecules, a variety of methods can be used for example covalent attachment, adsorption, or physical entrapment [26].

1.1.2. Polymer Brush Fabrication Strategies

The distance between polymer chains have an effect on architecture of the brush. At high grafting density, small distance between neighboring grafting polymers, steric repulsion results in chain stretching and leading to brush type conformation, whereas at low grafting density, polymer chains interact with themselves creating mushroom like structure (Figure 1.4) [15,27].

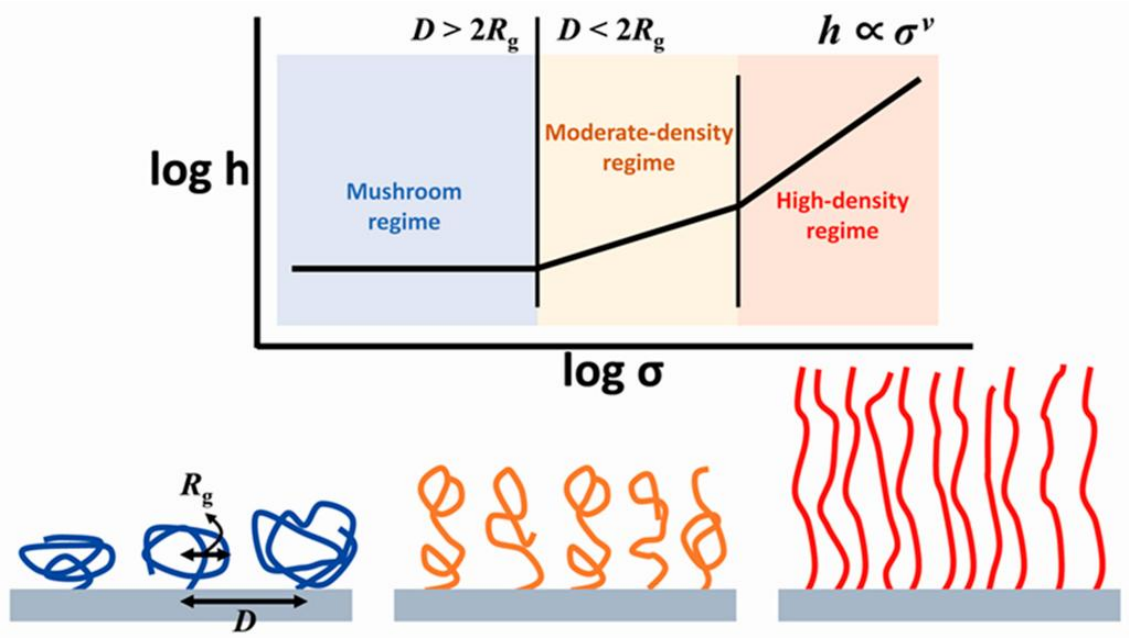

Figure 1.4. Schematic representation of relation between grafting density and brush thickness. Reprinted with permission from [24].

Commonly, polymer brushes are prepared by following two approaches: *grafting to* or *grafting from* (Figure 1.5) [28]. The *grafting to* strategy requires the attachment of preformed polymer chains either via physisorption [29] or chemisorption [30]. The *grafting to* method is experimentally simple but has some drawbacks. Although the polymer chains are thermally stable and are not released into the solvent, grafting density and film thickness are quite low resulting in inhomogeneous polymeric layer [31,32] due to slow diffusion and steric repulsion between already grafted polymer chains and incoming units from solution [27].

In the *grafting from* approach, so called surface-initiated polymerization, the polymerization is directly started from initiator-modified surfaces [33]. Various types of surface initiated polymerization, particularly controlled/"living" polymerization techniques are available [34] to fabricate polymers on the solid substrate i.e. ring-opening polymerization (ROP) [35], ring-opening metathesis polymerization (ROMP) [36], reversible addition fragmentation transfer radical polymerization (RAFT) [37], nitroxide-mediated polymerization (NMP) [38], atom transfer radical polymerization (ATRP) [32].

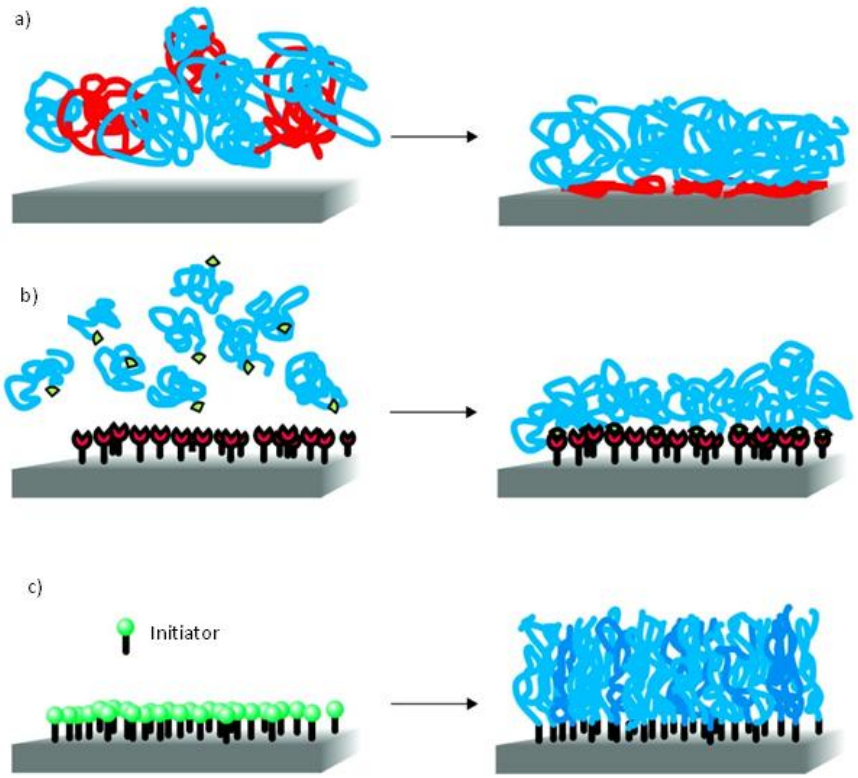

Figure 1.5. Polymer brush preparation approaches: *grafting to* via; a) physisorption b) chemisorption *grafting from* via c) surface-initiated polymerization. Reprinted with permission from [15].

In contrast to *grafting to* method, all of these methods allow polymerization of wide range of monomers as well as control over grafting density, brush thickness and functionality [2] and enable to generate high density polymer brushes due to densely immobilized initiators and the high initiator efficiency [31].

1.1.3. Post-polymerization Modification of Polymer Brush

Surface-initiated controlled/“living” polymerization techniques enable to use various functional groups however, polymer brushes with particular functional groups might not be obtained by using direct surface-initiated polymerization [15]. In order to adjust surface properties of polymer brush or to introduce diverse functional groups, polymer brushes can be functionalized by using post-polymerization modification methods. As illustrated in Figure 1.6, these methods can be applied to only side chain, or only chain end or both side chain and chain end of polymers.

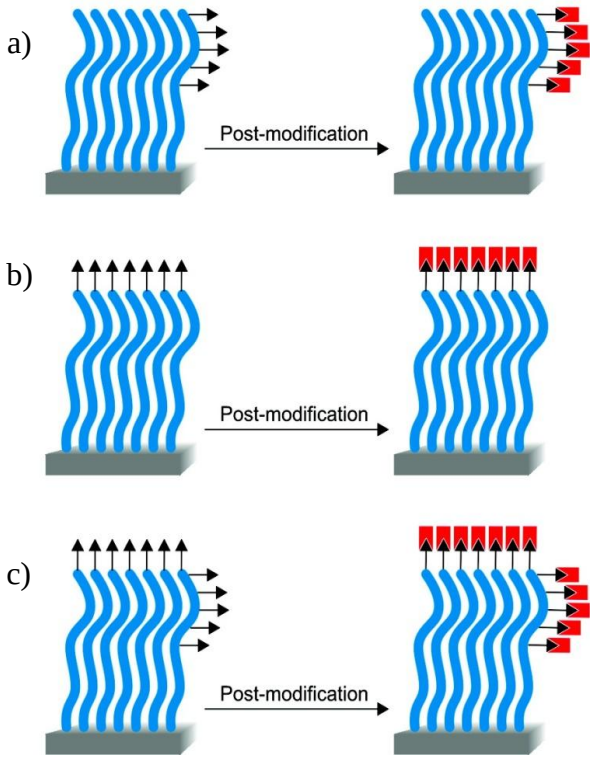

Figure 1.6. Post-polymerization modification of polymer brush: a) side chain modification b) chain end modification c) side chain-chain end modification. Reprinted with permission from [15].

For example, Klok and Desseaux designed a surface with thermoresponsive polymers to allow reversible cell adhesion and detachment. Polymer brushes are generated with copolymers of HEMA, $PEGMA_6$, and MEO_2MA monomers by ATRP method, followed by functionalization with RGD peptide in three steps (Figure1.7) [39].

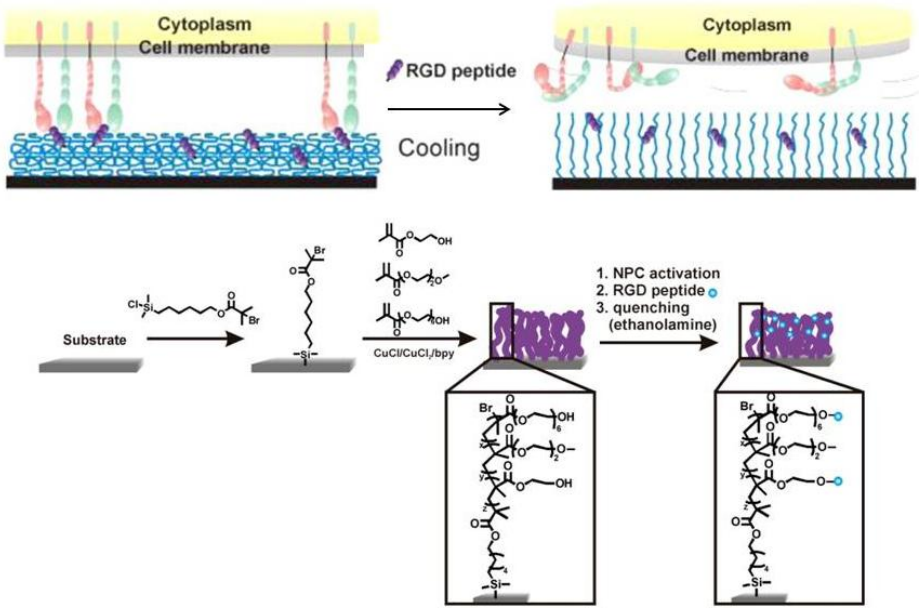

Figure 1.7. Schematic illustration of polymer brush side group modification. Reprinted with permission from [39].

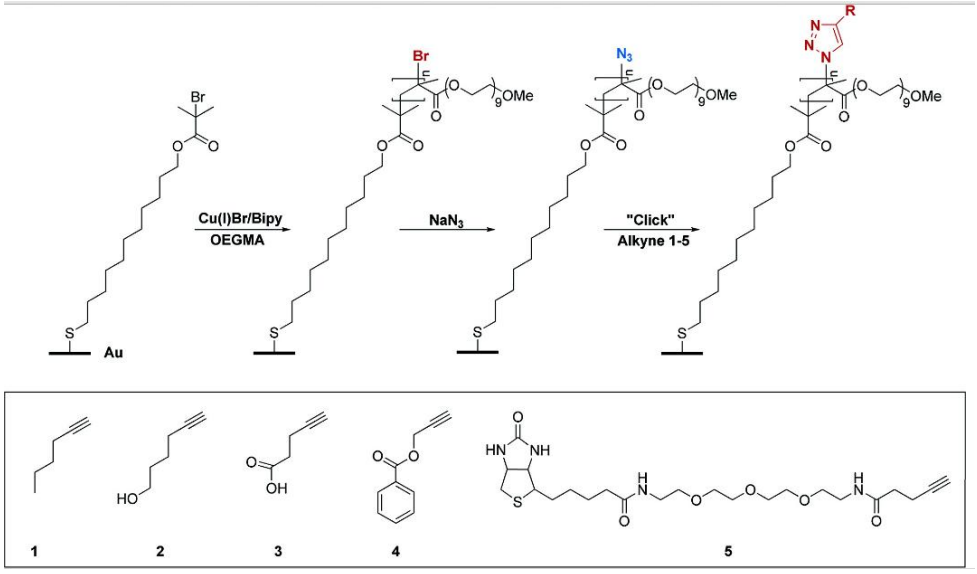

Figure 1.8. Schematic illustration of polymer brush chain end modification. Reprinted with permission from [40].

As an example for end group modification, Choi and coworkers developed a surface which is resistant to nonspecific adhesion of biomolecules. As shown in Figure 1.8, non-biofouling POEGMA brushes were fabricated by ATRP. Polymers chain ends which were converted to azido groups were conjugated with alkyne unit bearing

compounds via click reaction [40]. The efficiency of such modification on chain-end of methacrylate group can be challenging.

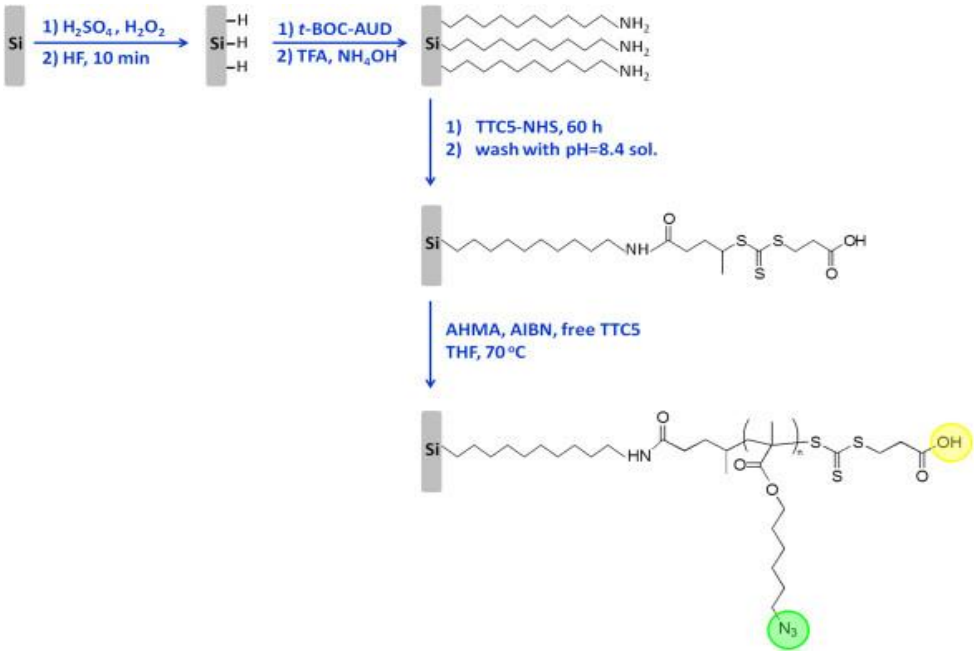

Figure 1.9. Schematic representation of side chain and chain end modification of polymer brushes. Reprinted with permission from [40].

Post-polymerization modification methods enables functionalization of side chains and end groups of polymer brushes in order to design dual functional surfaces. As illustrated in Figure 1.9, side chains of polymers which were prepared by RAFT polymerization of AHMA can be modified with alkyne groups via click reaction. Likewise, end groups of polymers can be modified by amide reaction [41].

1.2. Cluster Effect

In recent years, multivalent ligands are gaining increased interest for enhancing molecular recognition. Multivalent ligands have ability to increase binding affinity of weak ligands of biomolecules because multivalent systems enhance the relative affinity of a ligand in other words ligand can become more effective in a cluster than alone, *cluster effect* [42]. Furthermore, mmultivalent interactions are stronger and also provide higher selectivity than monovalent interactions [43].

Synthetic organic chemistry allows designing a wide variety of multivalent ligand platforms that might have various size, shape, orientation, and density of binding sides for instance; liposome, linear polymer, dendrimer and so on (Figure 1.11) [44].

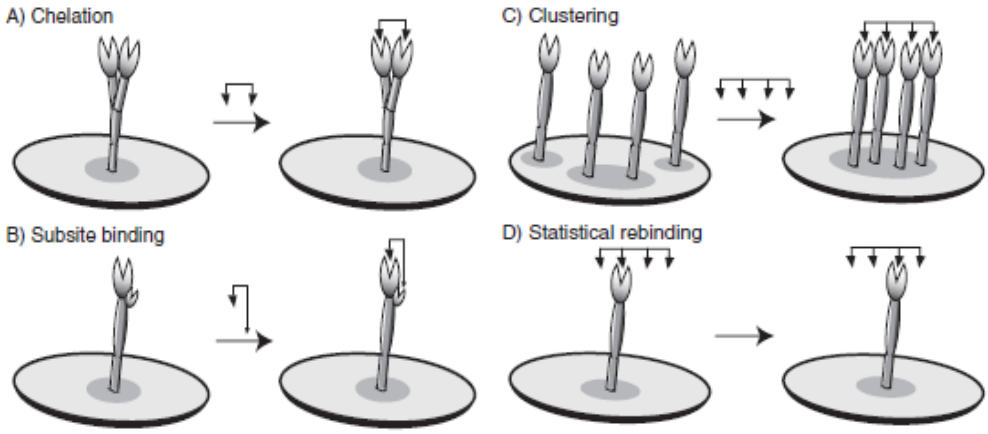

Figure 1.10. Schematic depicting multivalent binding mechanisms. Reprinted with permission from [44].

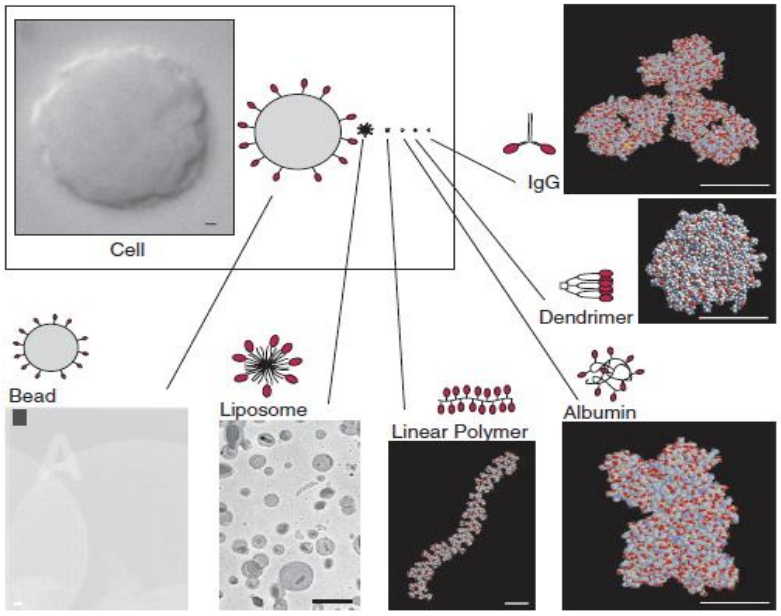

Figure 1.11. Examples of multivalent architectures. Reprinted with permission from [44].

Peptide, carbohydrate, protein which binds to a receptor can be used as recognition element for biosensor applications (Figure 1.12) [44]. The problem with molecular recognition is weak binding affinity of biomolecules. For instance, Zeng reported that the drawback of carbohydrate-protein detection is week affinity of carbohydrate-protein interaction because proteins such as lectins bind to carbohydrate through multivalent interactions, instead of monovalent interactions [45].

Moreover, Noble *et al*. showed that as glycosylphosphatidylinositol (GPI) structures in lipid raft are concentrated, multivalent recognition with bacterial toxins or antibodies via cluster glycoside effect increased and the cluster effect significantly affected binding of concanavalin A (Con A) to mannose ligands [46].

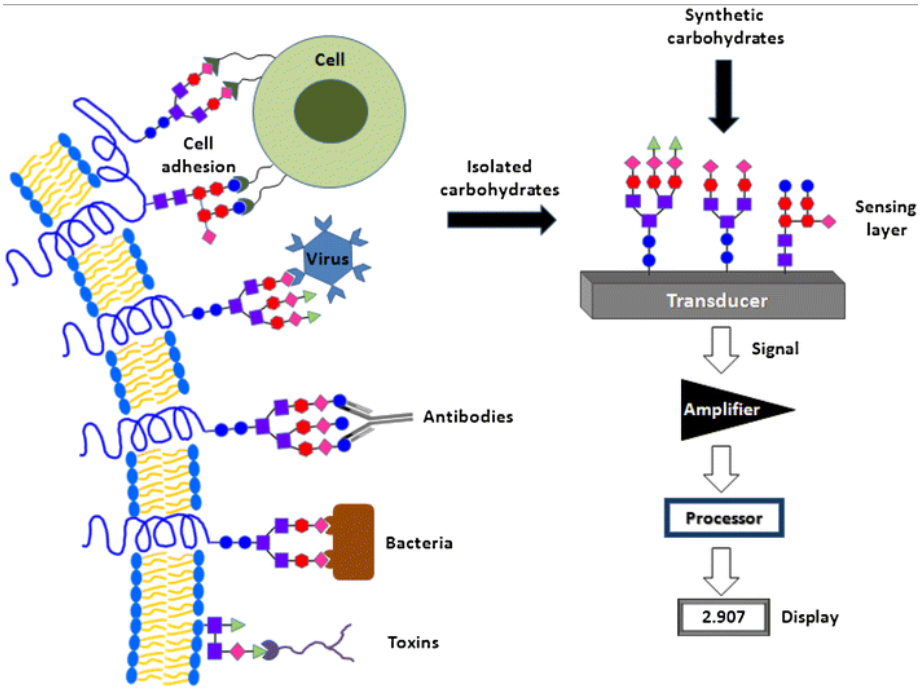

Figure 1.12. Multivalent protein-carbohydrate interactions at cell (left). Developed biosensor (right). Reprinted with permission from [47].

As mentioned before, multivalent ligands provide higher selectivity towards target. To overcome problem of undesired delivery of toxins to normal cells, Carlson et al. undertook a research to figure out if multivalent interactions have an effect on highly specific cell targeting [48]. Previously they had showed that multivalent ligands

increase not only the affinity but also the specificity of ligand-receptor interactions [44]. The result of their study showed that multivalent interactions can be used to distinguish between normal and unwanted target cells (Figure 1.13) [48].

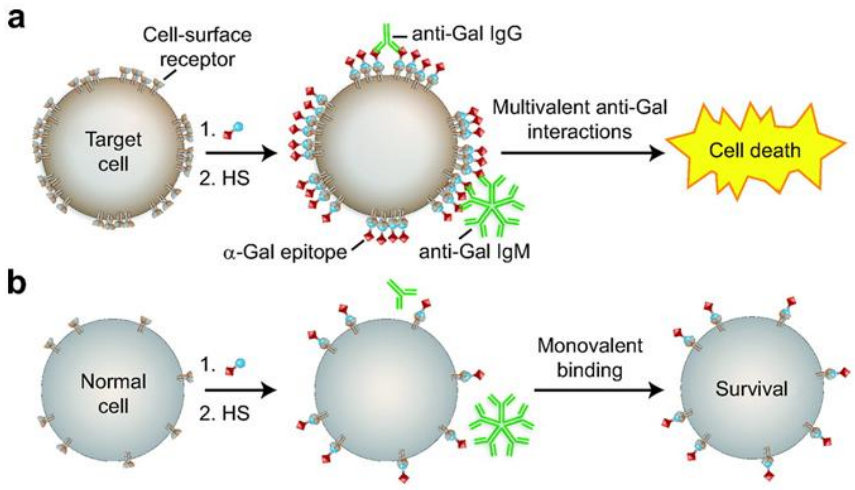

Figure 1.13. Cell targeting strategy. Reprinted with permission from [46].

Dendrimers are commonly used as multivalent ligand since they have comparatively homogenous structures [49]. Cloninger et al. used first through six generation PAMAM dendrimers functionalized with mannose to show different binding affinities for different generations (Figure 1.14). They have concluded that as the generations of dendrimers increased, dendrimers showed increase in binding affinity towards Con A due to multivalent interaction [50].

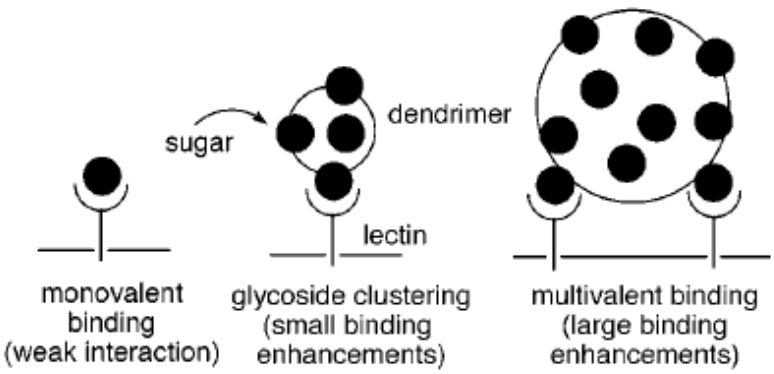

Figure 1.14. Schematic representation of interactions between dendrimer and Con (A). Reprinted with permission from [50].

Along these lines, Wang et al. designed a HIV vaccine based on multivalent carbohydrate-protein interaction [51]. They reported that structures in Figure 1.15a and 15b that have monovalent carbohydrate-protein interaction were not suitable for vaccine purposes whereas the dendrimeric scaffold and dendron modified surfaces enhanced carbohydrate-protein interactions via multivalent display.

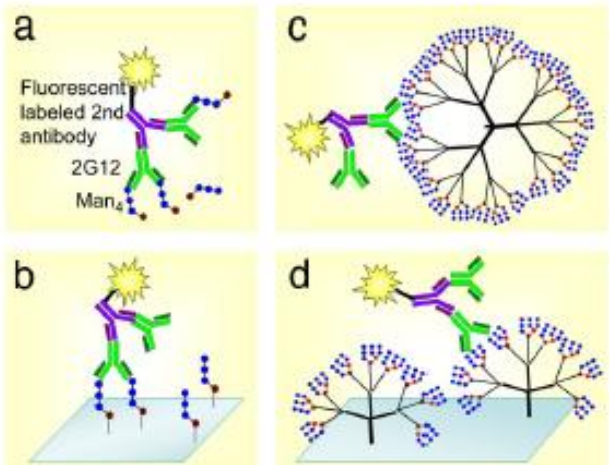

Figure 1.15. a,b) Monovalent binding of antibody c,d) Multivalent binding of antibody. Reprinted with permission from [51].

1.3. Reversible Addition-Fragmentation Chain Transfer (RAFT) Polymerization

Controlled/"living" polymerization techniques are very favorable for preparation of polymer brushes because these techniques allows one to graft uniform and homogenous polymers in different thickness and to functionalize polymer brushes which is difficult to obtain directly from surface-initiated polymerization. As mentioned previously, *grafting from* approach enable to use controlled/"living" polymerization methods such as ROP, ROMP, NMP, RAFT and ATRP.

Compared to other controlled/"living" polymerization techniques, RAFT polymerization is considerably advantageous because this method allows polymerization of a wide range of monomers including functional monomers such as acid (i.e. acrylic acid), acid salt (i.e. styrenesulfonic acid sodium salt), hydroxyl (i.e.

hydroxyethyl methacrylate) or tertiary amino (i.e. dimethylaminoethyl methacrylate) groups [52]. In addition, RAFT polymerization can be used to perform polymerization at different temperatures, and also to fabricate polymer brushes with functional end or side groups leading synthesis of block polymers or more complex structures [52,53].

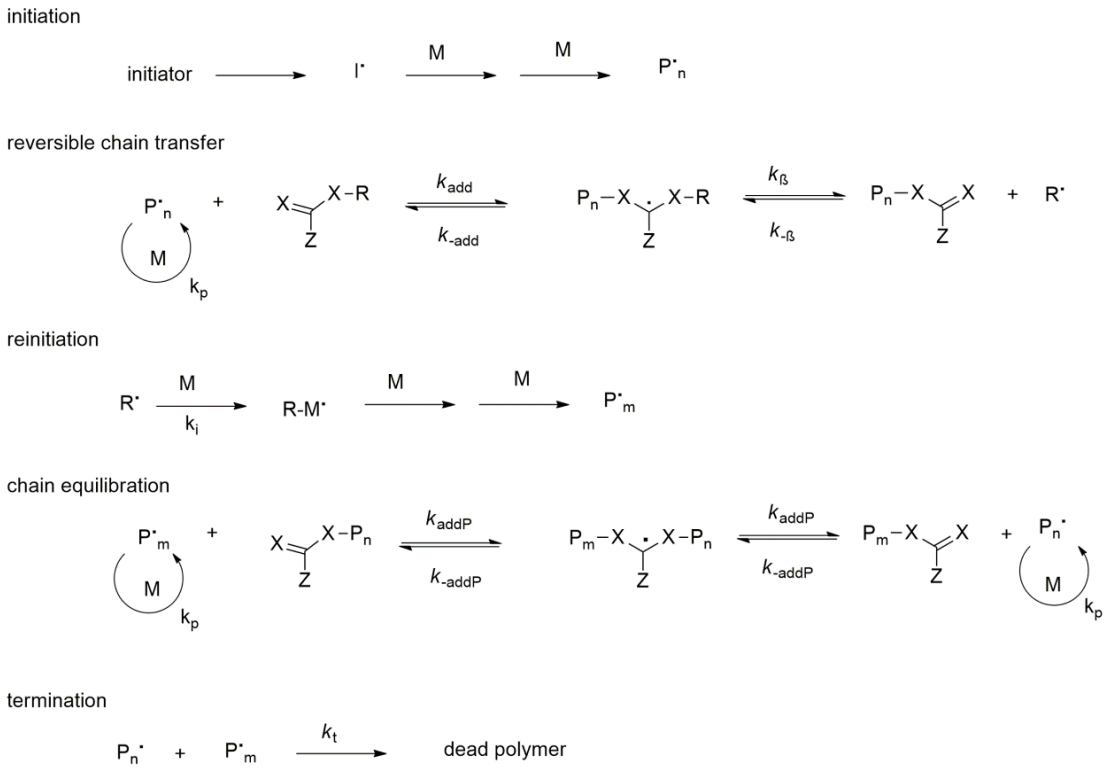

Figure 1.16. General mechanism of RAFT polymerization.

As shown in Figure 1.16, RAFT polymerization is starts with decomposition of a free radical initiator and then it forms propagating polymer radical ($P_n^{\cdot}$) which reacts with thiocarbonlythio compound. R group leaves yielding new radical ($R^{\cdot}$) then it reacts with monomer to reinitiate another polymerization leading new propagating radical ($P_m^{\cdot}$). Eventually, rapid equilibrium between propagating (P_n and P_m) and dormant chains can be reached and narrow polydispersity polymers can be obtained [54]. Different thiocarbonythio compounds called as chain transfer agent (CTA) are available for instance aromatic and aliphatic dithioesters, trithiocarbonates, xanthates [52].

Moad et al. showed that dithioester or trithiocarbonates are more effective for polymerization of more-activated monomers such as MMA, MA, AM. On the other hand, xanthates are good candidates for less-activated monomers [55]. Thus it is very important to choose appropriate R and Z groups of CTA and monomer for the effectives of RAFT agent [54,56]. In other words, Z groups should be sufficiently reactive towards propagating radicals and stable to the intermediate radicals whereas R should be homolytic leaving group which should be efficiently reinitiate polymerization.

As shown in Figure 1.17, chain transfer agent can be attached to the surface through either "R" or "Z" groups [57]. R group approach requires the attachment of RAFT agent to the substrate via R group resulting *grafting from* procedure [41]. On the other hand, Z group approach, Z group of RAFT agent is immobilized to the surface, comparable to grafting to method [15,52]. The main difference is also in the final position of the chain transfer agent in the newly formed polymer brush.

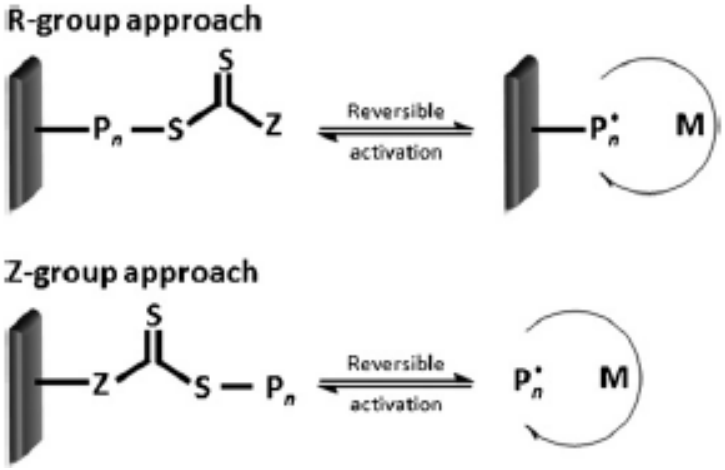

Figure 1.17. R-group and Z-group approaches. Reprinted with permission from [52].

1.3.1. End Modification of RAFT Polymers

It might be necessary to remove or transform thiocarbonlythio group in order to obtain end-functional polymers, for instance to alter the color of the polymer caused by the thiocarbonlythio groups [55] or to overcome the instability of thiocarbonylthio group [58].

End group modification of polymers can be achieved through either α-end group of RAFT polymers by introducing functional R group of RAFT agent which is similarly obtained by other controlled/living polymerization methods (ATRP, NMP etc.) [59] or ω-end group of polymers via reactions such as thermolysis [60], radical addition-fragmentation coupling [61], oxidation [62], hetero-Diels-Alder reactions [63] and so on. Rizzardo and coworkers showed that radical addition-fragmentation coupling can be achieved by heating polymer with excess of azo initiator such as AIBN [64]. However, this method is successful for dithiobenzoates and trithiocarbonates whereas it is less effective with xanthate chain ends [65].

This radical exchange reaction based modification was used by Hawker *et al.* to prepare polystyrene-coated Au nanoparticles [66]. Au nanoparticles are coated by following two methods: secondary thiol end group containing RAFT polymer and primary thiol end group containing RAFT polymer modified by radical coupling method after synthesis of macro RAFT agent (Figure 1.18). Finally, they obtained particles as localized and densely coated by following second approach.

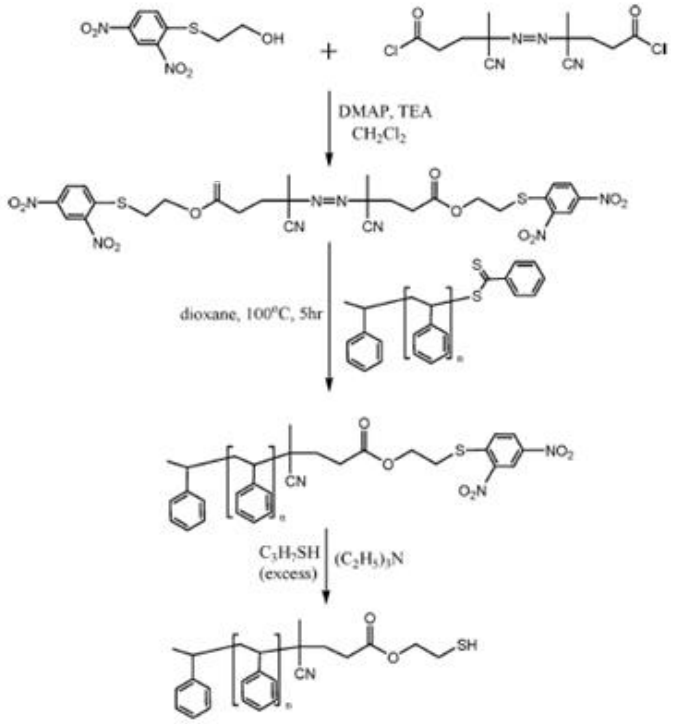

Figure 1.18. Modification of RAFT polymer via radical cross coupling reaction. Reprinted with permission from [66].

1.4. Click Chemistry

Click chemistry based reactions continue to gain increasing attention because of their specificity and high reaction yields under mild conditions. Thiol-ene, thiol-yne, alkyne-azide are example for click type reactions (Figure 1.19). Particularly, the copper (I) catalyzed azide-alkyne cycloaddition (CuAAC) is the most commonly used click reaction because it allows reactions with wide variety of solvents and functional groups at moderate temperatures (25-70 °C) [67,68]. Also its high reaction yields, no byproduct formation and functional group orthogonality makes this a popular reaction [69,70]. Since CuAAC reactions are highly efficient, very specific, and compatible with water, it can find many material applications such as functionalization of polymers and dendrimers [71], bulk surfaces such as silica [72], as well as obtaining biosensors by immobilization of biomolecules on gold [73] or iron oxide magnetic nanoparticle [74].

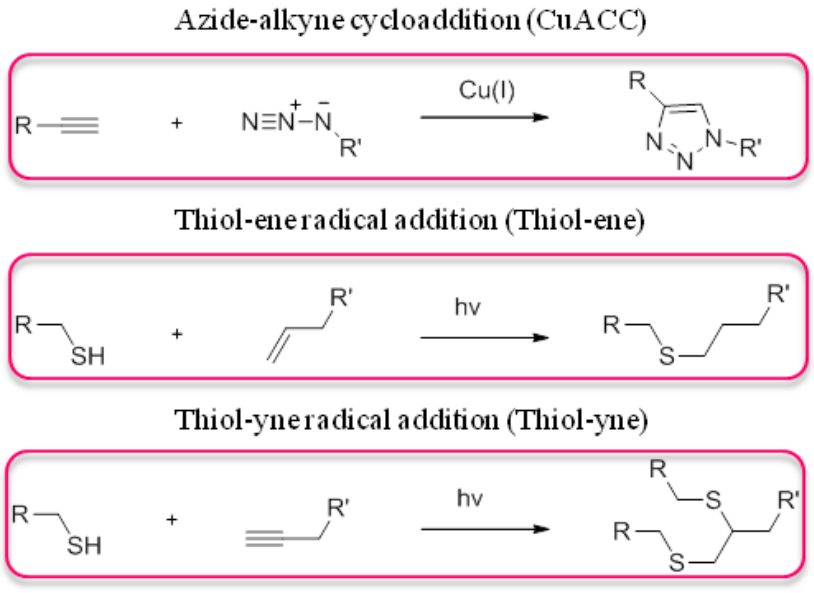

Figure 1.19. Common types of click reactions.

As an example for functional orthogonality, Yang and Weck were conjugated poly(norbornene)-based random copolymer having azide-ketone functional groups by following one-pot strategy (Figure 1.20). The orthogonal functionalization of the

copolymers were achieved through 1,3-dipolar cycloaddition and hydrazone formation of phenylacetylene and phenylhydrazine [70].

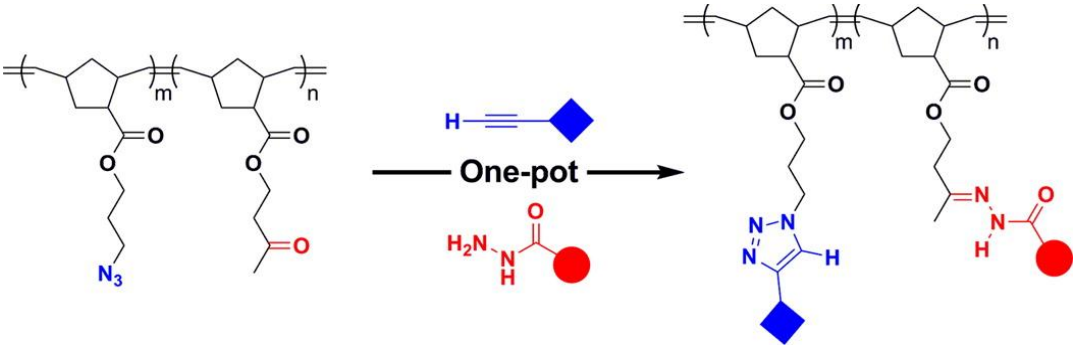

Figure 1.20. Schematic representation of the one-pot functionalization of random copolymers. Reprinted with permission from [70].

2. AIM OF THE STUDY

The aim of this study is to design a polymer brush coated surface that can be easily modified using radical exchange reactions. After development of such exchange reaction protocol, the methodology will be used to obtain surfaces with dendritic ligands for multivalent binding of biomolecules such as protein. This will be done by modification of silicon surfaces with chain transfer agents to enable polymerization. Polymers will be grafted from surface by using hydrophilic monomer via RAFT polymerization. Post-polymerization modification via radical cross coupling reaction will be evaluated. Consequently, polymer brush will modified with diazo-based reagents containing azide, and first and second generation dendrons as functional groups.

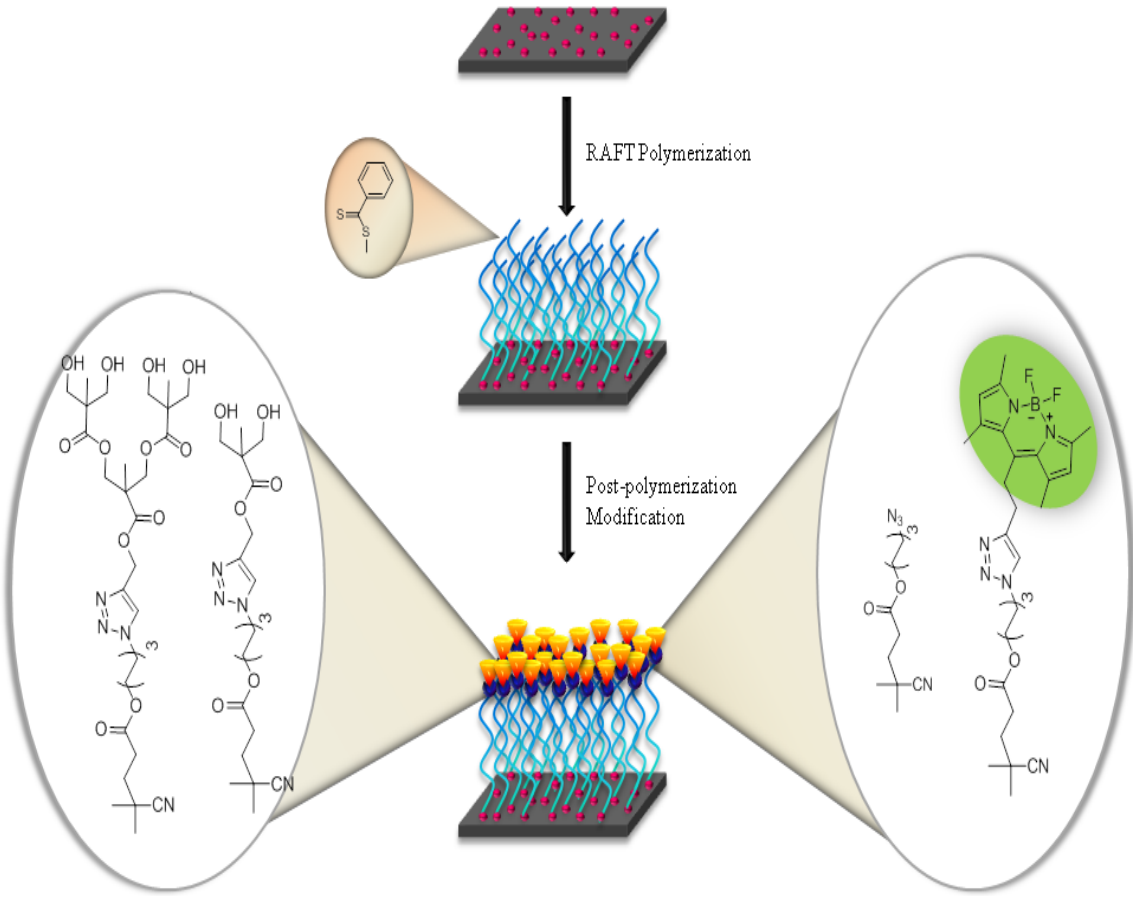

Figure 2.1. General scheme of the project.

3. RESULTS AND DISCUSSION

3.1. Grafting of Polymer Brushes via RAFT Polymerization

As mentioned previously, *grafting from* method enables to use controlled/"living" polymerization techniques to obtain well-defined polymer brushes. In this study, polymer brush was generated via RAFT polymerization**.** To be able to use this method, firstly, silicon surfaces were coated with surface attachable RAFT agent and followed by surface initiated polymerization.

3.1.1. Modification of Surface with RAFT Agent

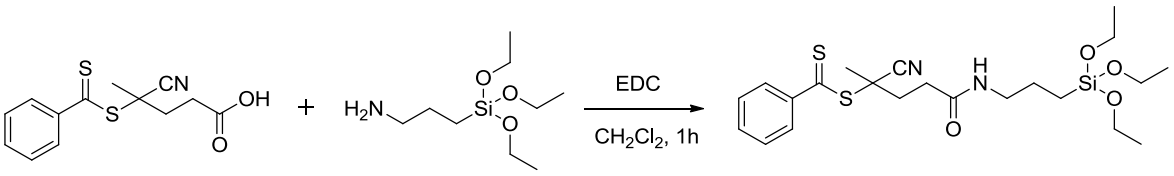

Figure 3.1. Synthesis of surface active RAFT agent.

In order to graft polymers from Si/SiO_2 surface, RAFT agent was modified with (3-aminopropyl)-triethoxysilane as a surface anchoring unit. The silane group is able to form a strong bond between organic and inorganic materials [75]. Surface RAFT agent was synthesized by reacting 4-cyanopentanoic acid dithiobenzoate and (3-aminopropyl)-triethoxysilane at room temperature in the presence of EDC (Figure 3.1) [76].

Chemical structure of the modified RAFT agent was confirmed by using ^{1}H-NMR spectroscopy (Figure 3.2). Aromatic ring protons appear at 7.3-7.9 ppm, also presence of amide peak at 5.9 ppm confirms successful conjugation of chain transfer agent and silane surface anchoring group.

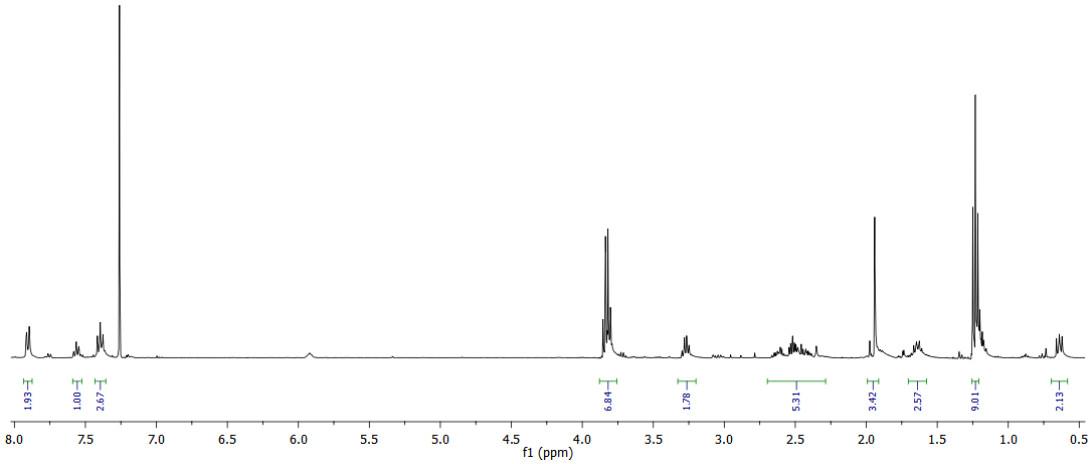

Figure 3.2. ^{1}H-NMR spectrum of surface active RAFT agent

The first step in the synthesis of polymer brushes is immobilization of RAFT agent. After synthesis of surface RAFT agent, Si/SiO_2 wafers were cleaned with ethanol and acetone then exposed to UV/ozone chamber to activate Si-OH groups. Activated silicon wafers were immersed 2 mM solution of surface RAFT agent in anhydrous toluene for 24h so that OH groups of the surface react with ethoxysilane groups of modified CTA (Figure 3.3).

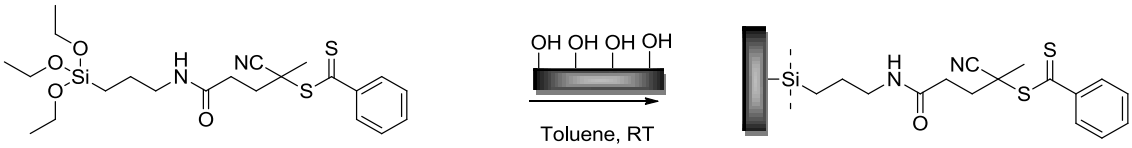

Figure 3.3. The immobilization of RAFT agent onto silicon surface.

Water contact angle of Si/SiO_2 substrates was increased from 2-3° to 71° (Figure 3.4). In addition, immobilization of RAFT agent was confirmed by FT-IR (Figure 3.5). Amide peak (1651 cm^{-1}) shows that surface was successfully coated with RAFT agent.

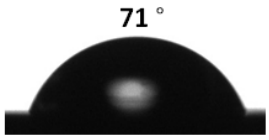

Figure 3.4. Contact angle of RAFT agent coated silicon surface

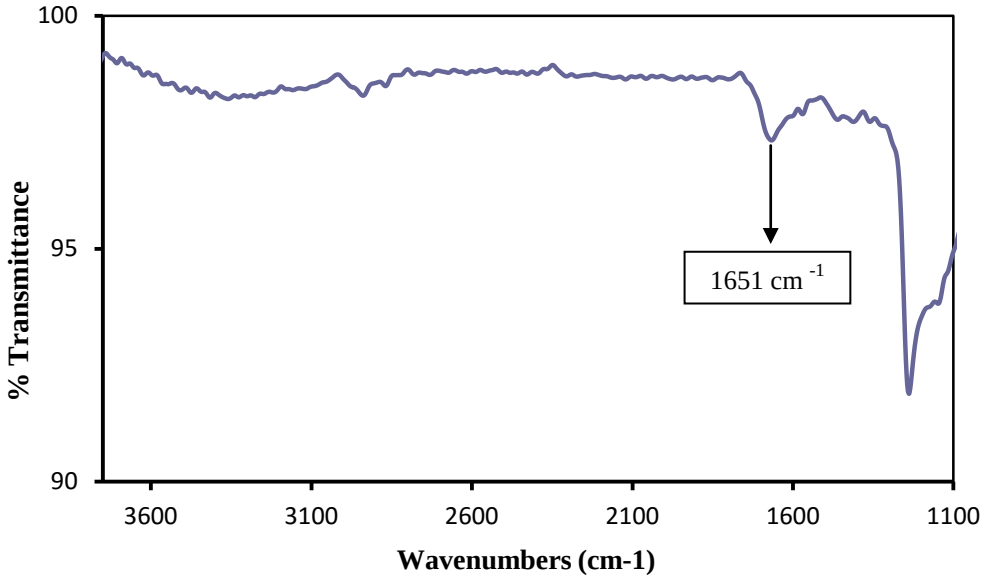

Figure 3.5. FT-IR spectra of RAFT agent coated surface.

3.1.2. Grafting Polymers from Surface

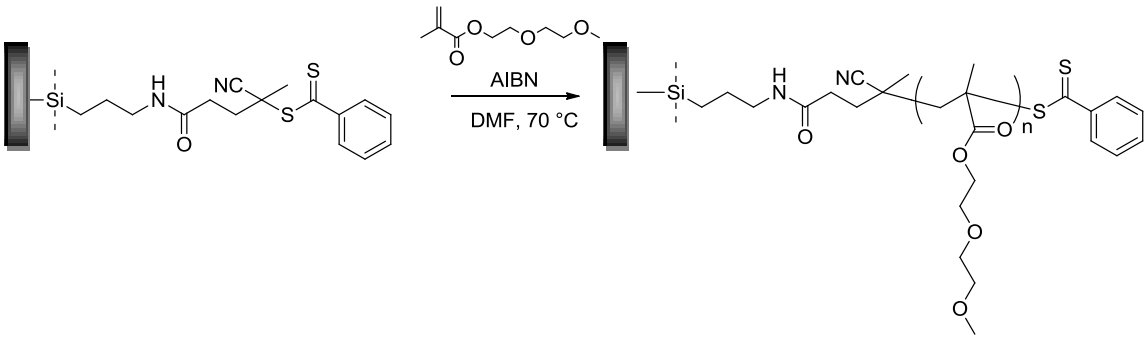

Figure 3.6. Schematic representation of DEGMA polymer brushes.

Polymer brushes were prepared with DEGMA monomer which has antibiofouling character and hydrophilic nature. As illustrated Figure 3.6, surface RAFT polymerization was carried out in the presence of DEGMA monomer and AIBN as an initiator. RAFT agent coated silicon surfaces were immersed in DMF solution containing DEGMA and AIBN at 70 °C for predetermined period of time. After that, the surfaces were washed with methanol and water to remove physically attached monomer, and then dried over N_2 stream. The height of the polymer brush was obtained as 32±3 nm under these conditions as analyzed using atomic force

microscopy. Furthermore, silicon surfaces were characterized by FT-IR and contact angle measurement.

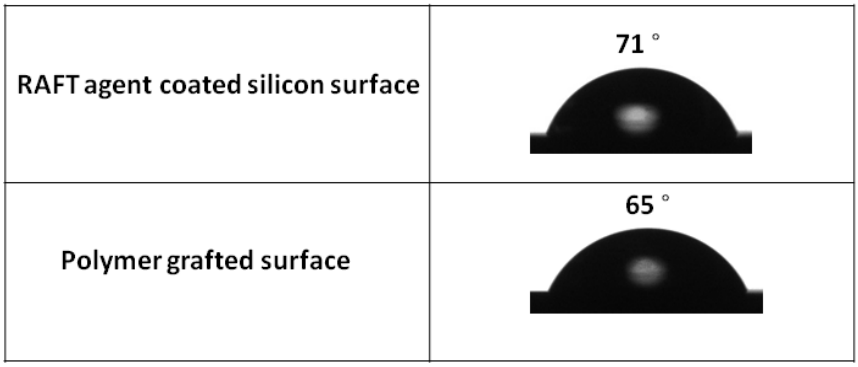

Figure 3.7. Contact angle of DEGMA polymer brushes.

Water contact angle on polymer brushes decreased from 71° to 65° due to hydrophilic character of DEGMA (Figure 3.7).

In addition, FT-IR spectrum shows carbonyl (C=O) stretch of ester group at 1728 cm^{-1}, the band at 3100-2750 cm^{-1} belongs to the C-H bond stretching (Figure 3.8.).

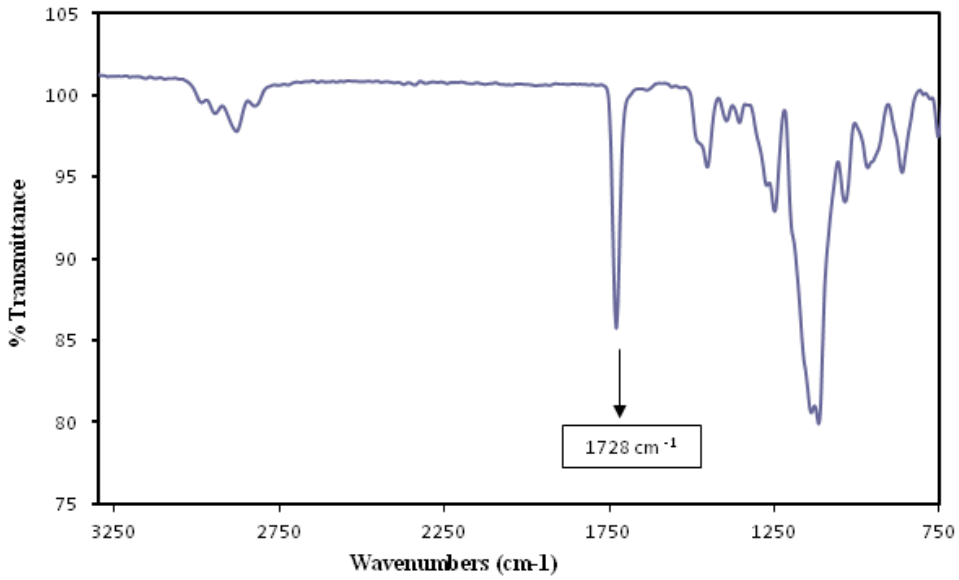

Figure 3.8.FT-IR spectra of DEGMA polymer brushes.

3.2. Synthesis of V-401 Derivative Dendron via “Click” Reaction

For the post-polymerization modification, before conjugation of alkyne unit bearing dendron and diazido V-501, compound 2 was synthesized to divergently grow dendron directly from azo initiator end groups. Firstly, compound 1 was synthesized in the presence of 2,2 dimethoxypropane, acetone and pTSA (Figure 3.9).

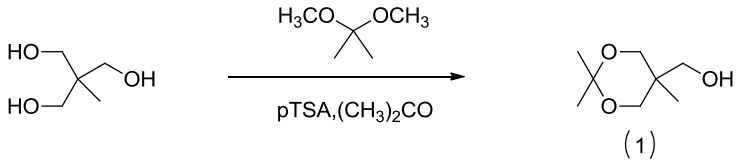

Figure 3.9. Synthesis of acetal protected alcohol.

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^{1}H-NMR of compound 1 shows acetal protecting group protons appear at 3.61-3.68 ppm (Figure 3.10).

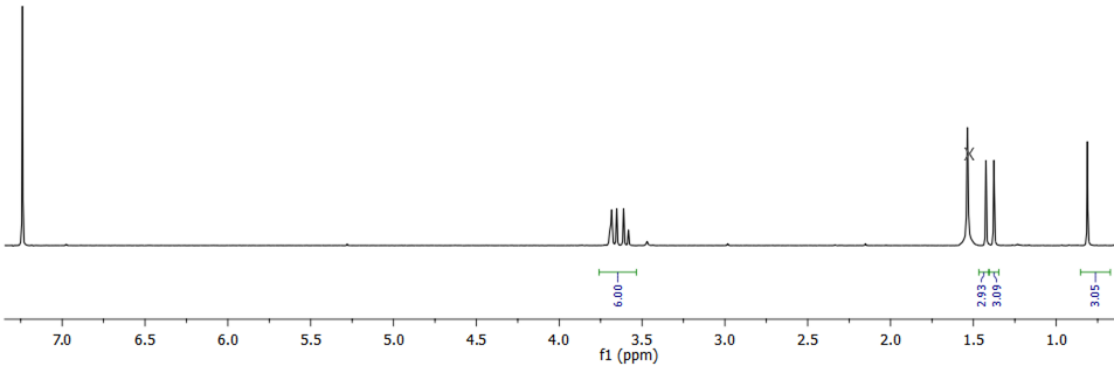


Figure 3.10. ^{1}H-NMR spectra of compound 1.

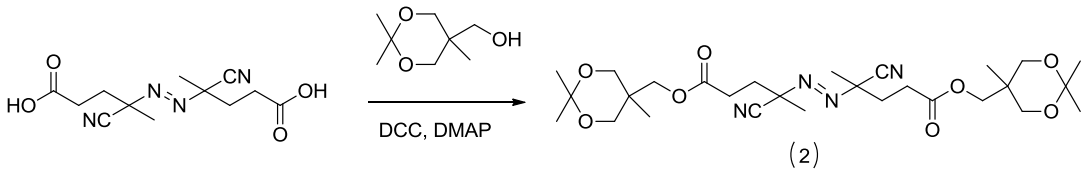


Figure 3.11. Synthesis of acetal protected azo initiator

The second step in the synthesis was coupling of alcohol and 4,4'-azobis(azidohexanoyl 4-cyanopentanoate) via Steglich Esterification reaction (Figure 3.11). However, successful purification was not achieved so new strategy was developed for the synthesis of conjugated dendron.

Azo initiator was synthesized via click reaction between diazo V-501 and polyester dendron. Firstly, diazido compound was synthesized and then, alkyne unit containing at the focal point G1 and G2 generation dendrons were synthesized. Finally, diazido V-501 and G1 and G2 generation dendrons were combined to obtain hydroxyl terminated different generation dendrons.

3.2.1. Synthesis of Diazido V-501 Compound

Diazido V-501 compound was synthesized by following two steps (Figure 3.12). The first step is conversion of 6-chlorohexanol to 6-azidohexanol via sodium azide in water. Afterwards, diazido V-501 compound was synthesized according to previous literature example [77]. 4,4'-azobis(azidohexanoyl 4-cyanopentanoate), 6-azidohexanol and DMAP were dissolved in anhydrous dichloromethane at 4°C under N_2 atmosphere. DCC was dissolved in anhydrous dichloromethane and then added to reaction mixture dropwise. The reaction was stirred at room temperature for 24h. After purification via column chromatography, pure product was obtained with 45% yield.

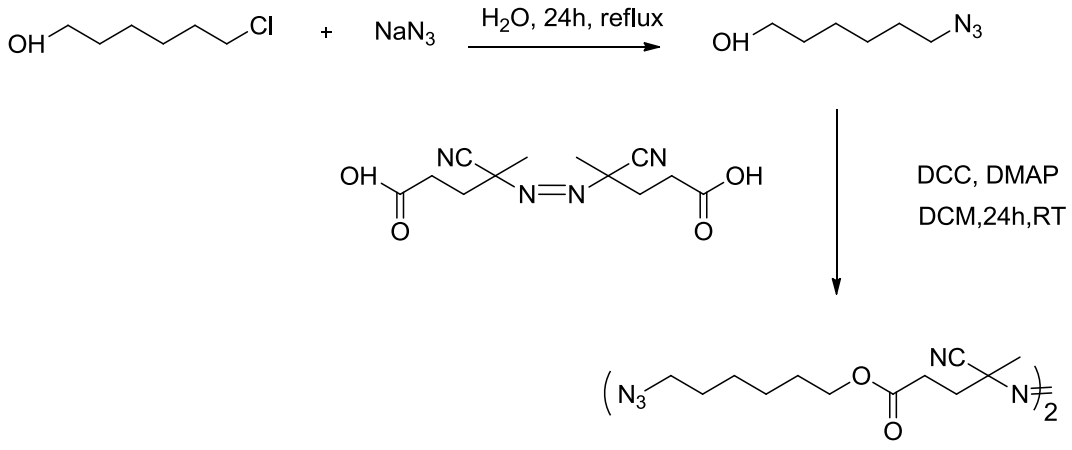


Figure 3.12. Synthesis of diazido V-501.

3.2.2. Synthesis of Dendrons

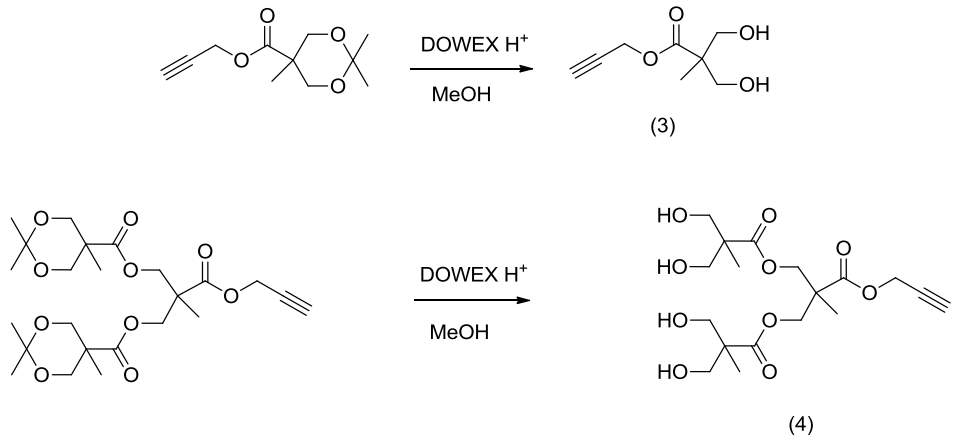


Figure 3.13. Synthesis of hydrophilic dendrons with alkyne unit at focal point.

Synthetic pathway for synthesis of dendrons is illustrated at Figure 3.13. Alkyne containing at the focal point compound G1 and G2 are synthesized by following previously reported procedure [78]. Afterwards, acetonide protecting groups were removed by treatment with DOWEX, H^+ in methanol, resulting hydroxyl groups.

3.2.3. Modification of Diazido Compound with Dendron via Click Reaction

As mentioned before, end groups of polymer brushes was functionalized via V-501 derivative dendron which was synthesized by using Huisgen type [3+2] cycloaddition reaction between alkyne unit bearing dendrons and diazo-V-501 compound [79]. As shown in Figure 3.14 and 3.17, click reaction was achieved in the presence of CuBr and PMDETA. Briefly, diazo compound and dendron was dissolved in anhydrous THF and CuBr/PMDETA was also dissolved in anhydrous THF. After purging both solutions, CuBr/PMDETA solution was added onto reaction mixture under N_2 atmosphere and stirred at 40 °C for 24 h.

G1 dendron-diazido-V501 conjugation was confirmed by ^{1}H-NMR and ^{13}C-NMR, shown in Figure 3.15 and Figure 3.16. ^{1}H-NMR of the compound 5 shows that the new aromatic proton of triazole ring appears at 7.58 ppm.

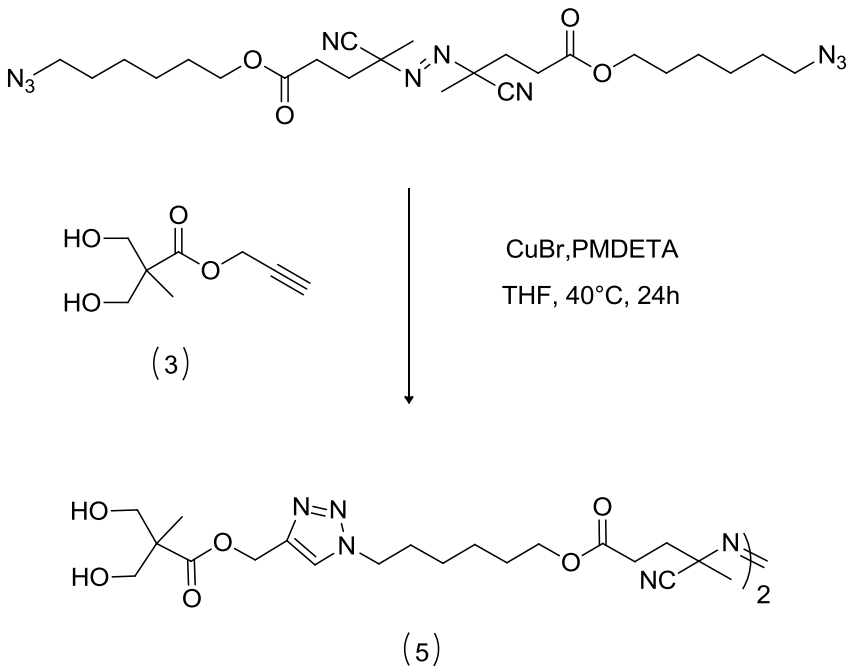


Figure 3.14. Synthesis of Click reaction between G1 dendron and Diazo-V-501.

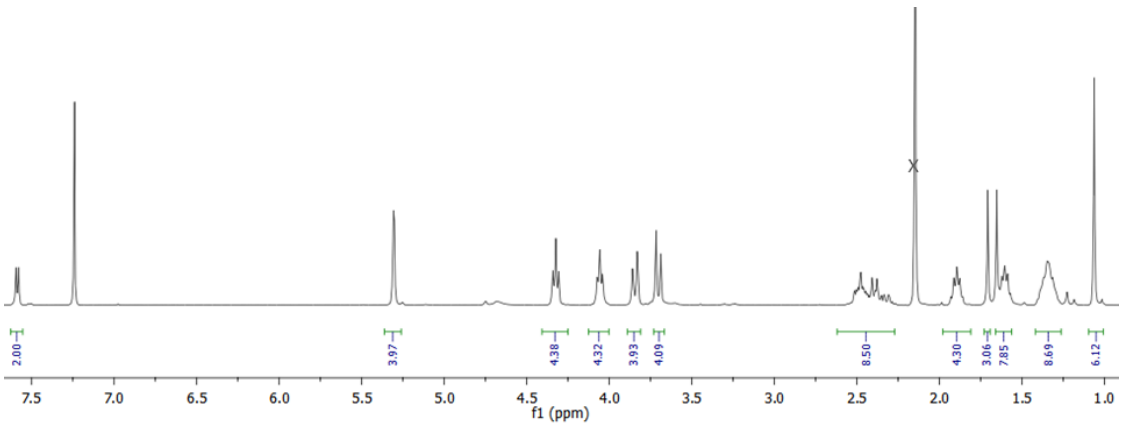


Figure 3.15. ^{1}H-NMR spectrum of compound 5.

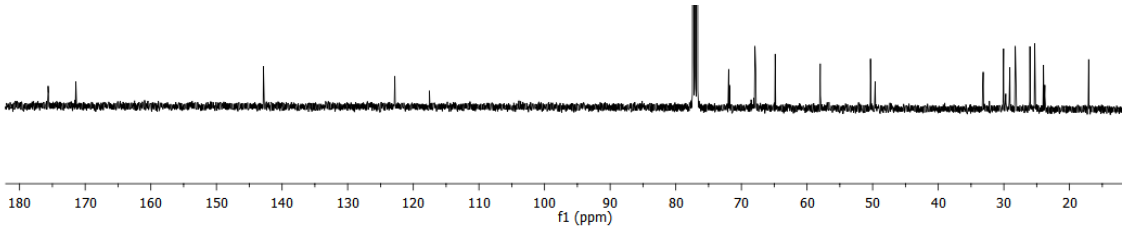


Figure 3.16. ^{13}C-NMR of compound 5.

For the synthesis of compound 6, diazido V-501 and compound 4 was conjugated via click reaction by following same procedure written in the beginning of this section (Figure 3.17).

Conjugation of compound 6 and diazido-V-501 was confirmed by ^{1}H-NMR. As shown in Figure 3.18, triazole aromatic proton coming from cycloaddition of alkyne and azide appears at 7.64 ppm.

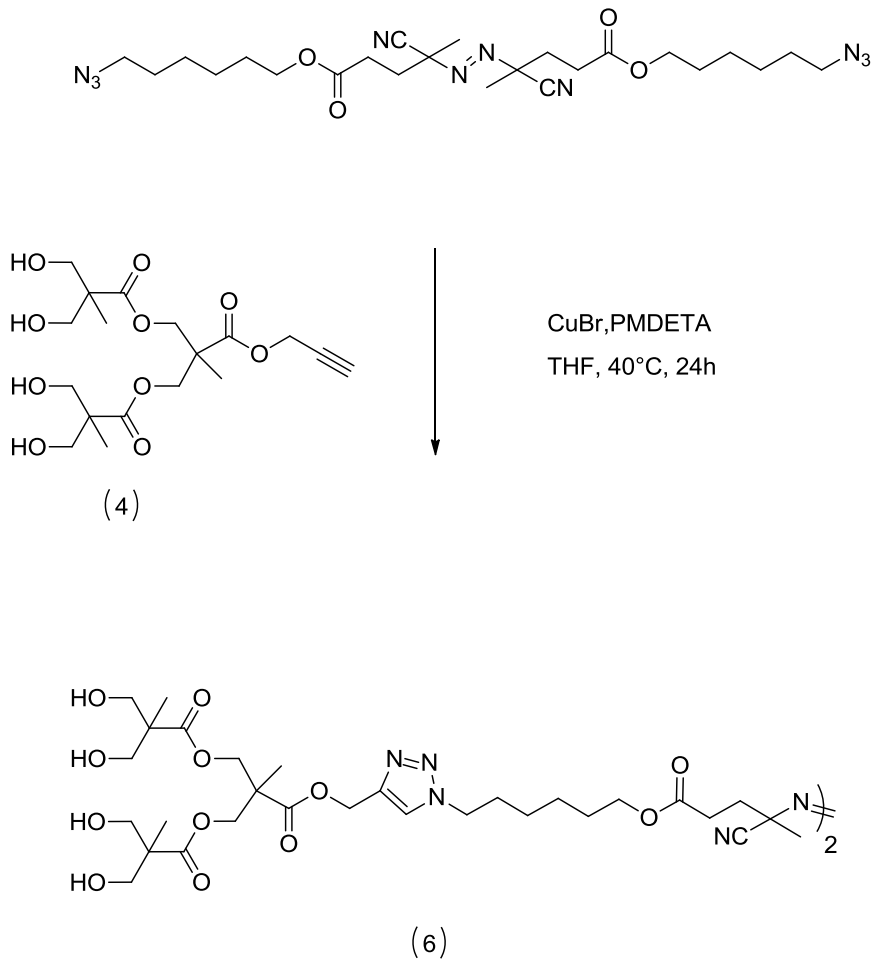


Figure 3.17. Synthesis of G2 dendron and diazido V-501 conjugate.

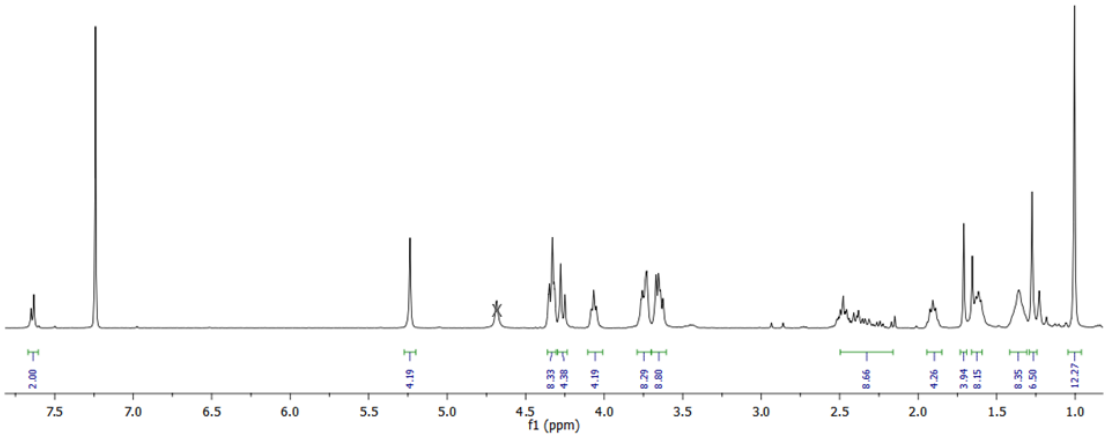


Figure 3.18. ^{1}H-NMR spectrum of compound 6.

3.3. Post-polymerization Modification of Polymer Brush via Radical Cross Coupling Reaction

3.3.1. Surface Modification with Azide Functional Group

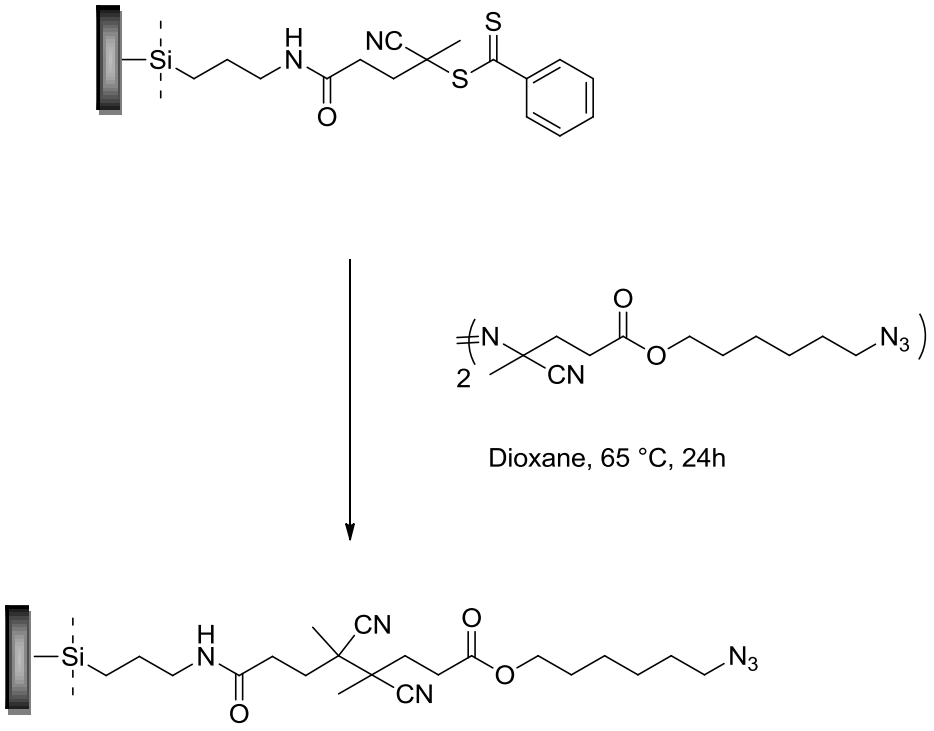


Figure 3.19. Schematic illustration of end group modification of RAFT coated silicon surface.

Although there are examples for end group modification of soluble polymers via radical cross coupling reaction [80,81], this study is unique for surface bound polymer end group modification. In other words, we investigate if it is possible to functionalize polymer films with dendritic structures or various ligands using radical exchange reactions. Before trying modification of end groups of polymer brush, we first tried modification of the monolayer i.e. the RAFT agent immobilized Si/SiO_2 surface (Figure 3.19). At the end, successful modification was confirmed by FT-IR spectra. Figure 3.20 shows azide peak at around 2100 cm^{-1} appears after modification.

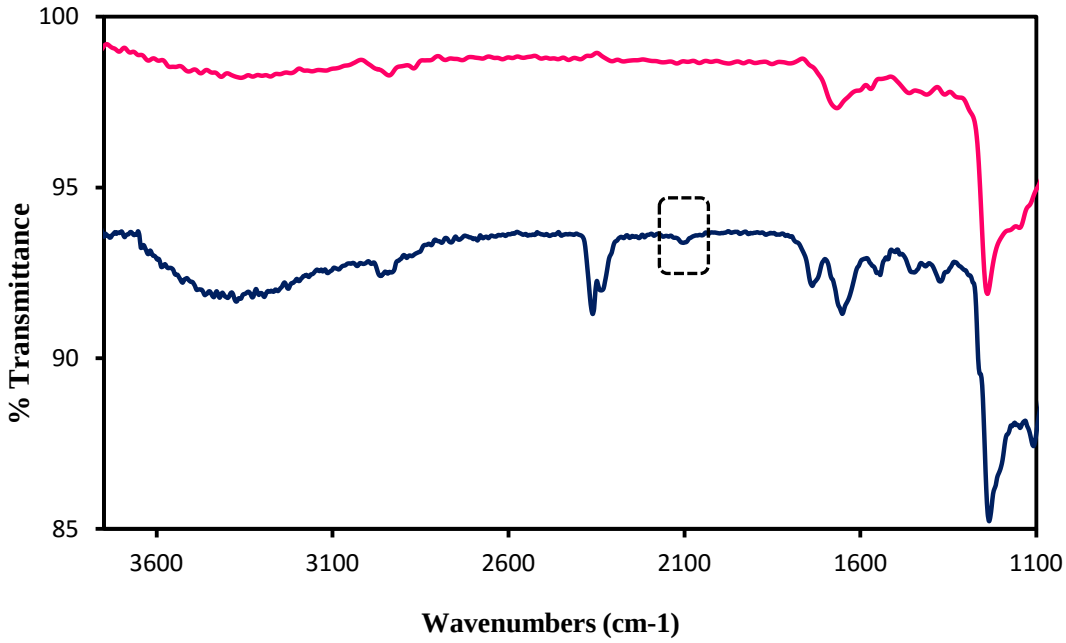


Figure 3.20. FT-IR spectra of azide terminated silicon surface.

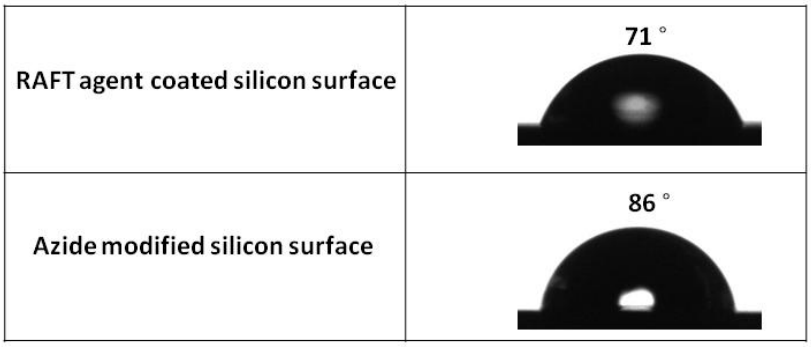


Figure 3.21. Contact angle of silicon surface after modification.

In addition, contact angle of azide modified silicon surface was increased dramatically from 71° to 86° (Figure 3.21).

After that, DEGMA polymer brushes were modified with diazido-V-501 (Figure 3.22). Shortly, dizo-V-501 compound dissolved in dioxane under N_2 stream and transferred to degassed reaction vessel. The vessel was sealed and kept at 65°C oil bath for 24h.

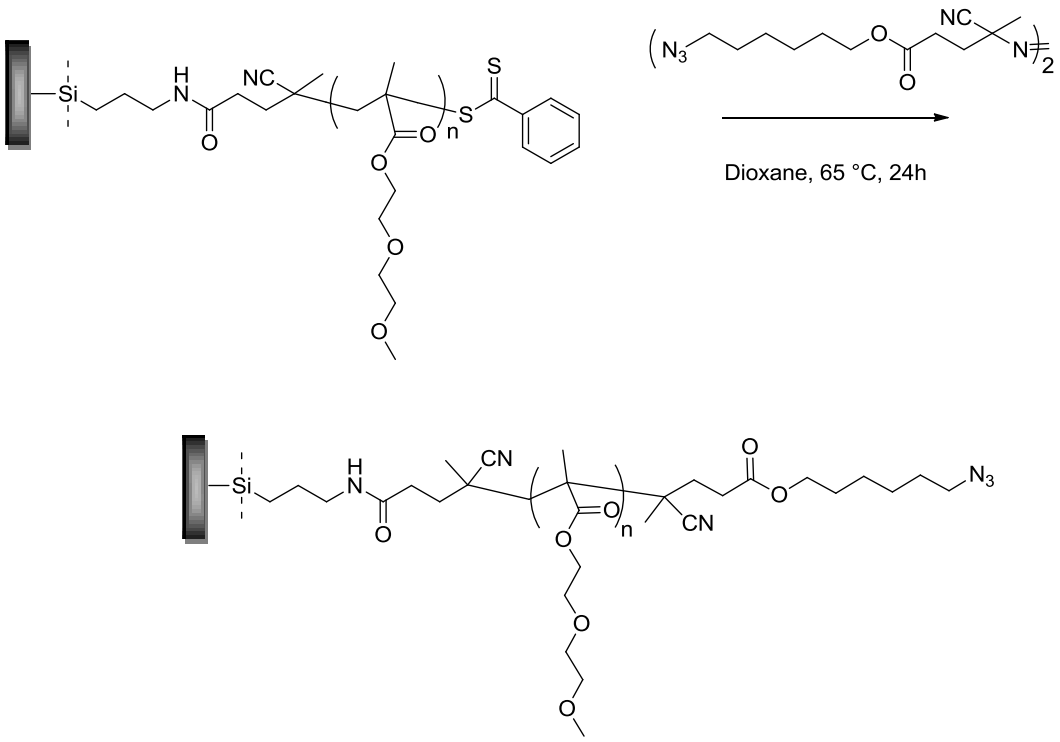


Figure 3.22. Schematic representation of end group modification of DEGMA polymer brush with diazide-V501.

As shown in Figure 3.23b, azide modification of DEGMA brush end groups was confirmed via FT-IR spectra. The amount of carbonyl coming from DEGMA chains are much more larger than azide groups because only end groups of brushes contain azide whereas all surface coated with bunch of carbonyl functional groups of polymer chains. Moreover, it is only a thin film. These are the reasons for azide peak on polymer brushes appears very small.

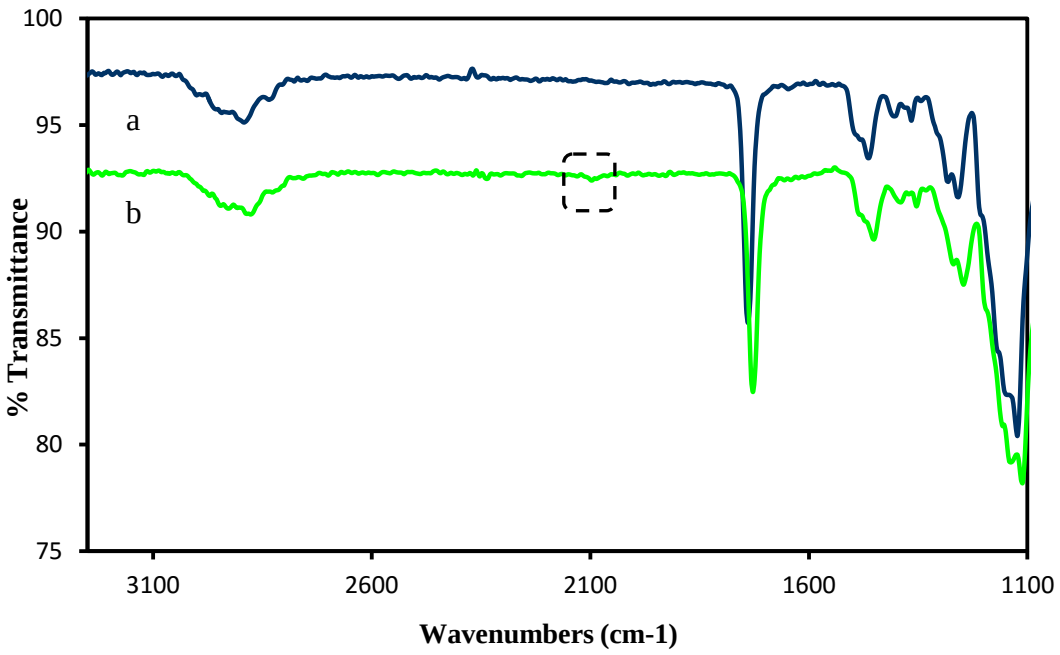


Figure 3.23. FT-IT spectra of a) DEGMA polymer brushes b) post-polymerization modification of DEGMA brushes with diazido-V-501

3.3.2. Surface Modification with BODIPY-alkyne

Next step was conjugation azide end groups with alkyne BODIPY dye which is a fluorescent dye so that successful modification can be tracked via fluorescence microscopy (Figure 3.24) [82].

After IR spectrum confirmed that dithio benzoate unit of RAFT agent was removed, azide containing silicon surfaces were treated with alkyne BODIPY dye in the presence of $CuSO_4$ and sodium ascorbate. Silicon surfaces were immersed in MeOH:H_2O solution. $CuSO_4$ and sodium ascorbate were added to reaction mixture and left overnight at room temperature. Silicon surfaces were washed with methanol to remove unreacted compound residues.

BODIPY dye conjugated silicon surfaces were examined by fluorescence microscopy as shown in Figure 3.25. It can be concluded that BODIPY conjugation with azide terminated polymer brush was successfully achieved (Figure 3.25b)

whereas attachment of BODIPY dye was not observed for the control group (Figure 3.25a).

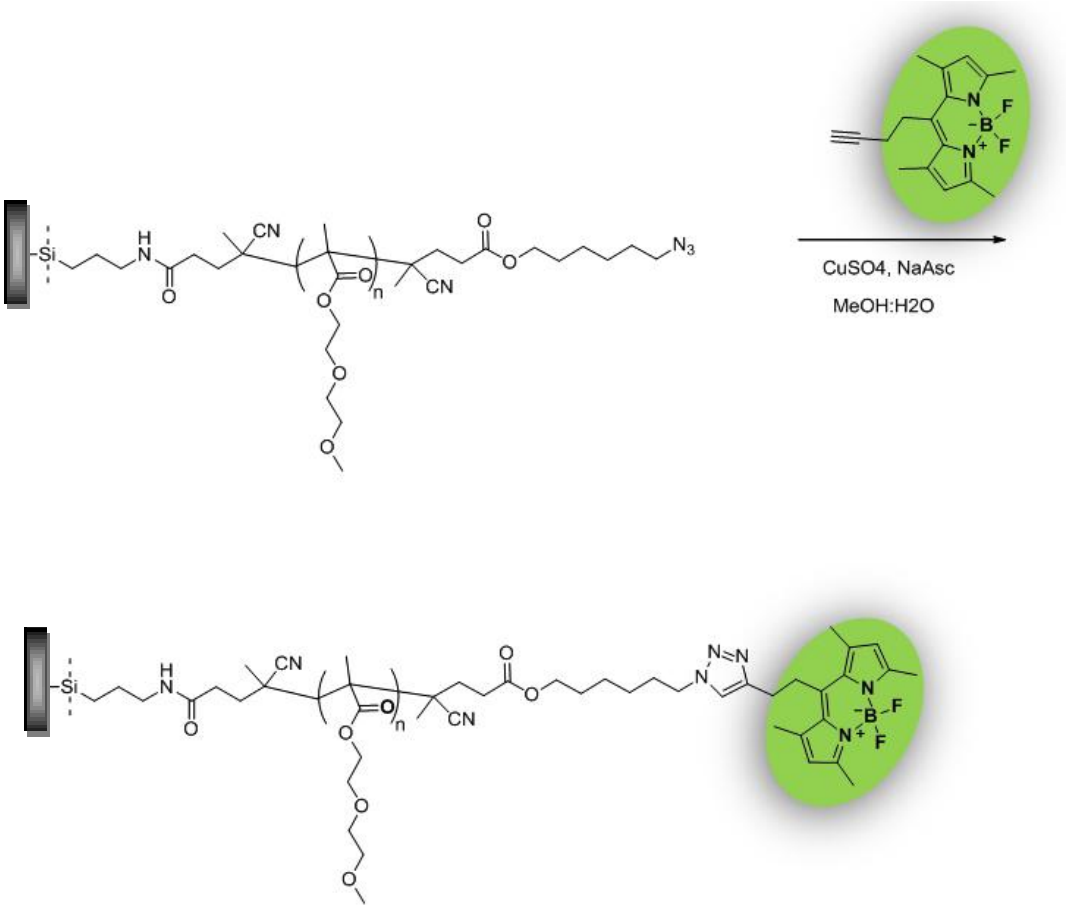


Figure 3.24. BODIPY dye conjugation on polymer brushes.

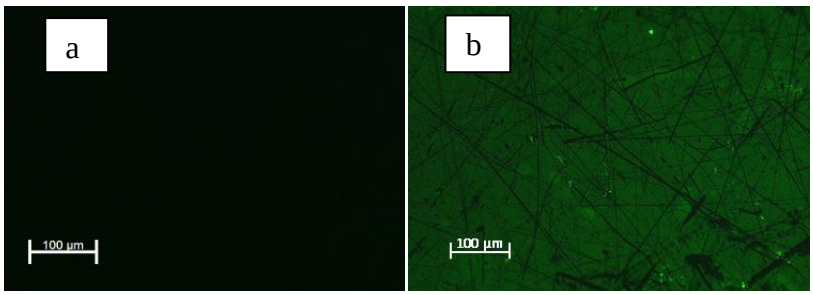


Figure 3.25. Fluorescence image of (a) control group (b) BODIPY conjugated surface

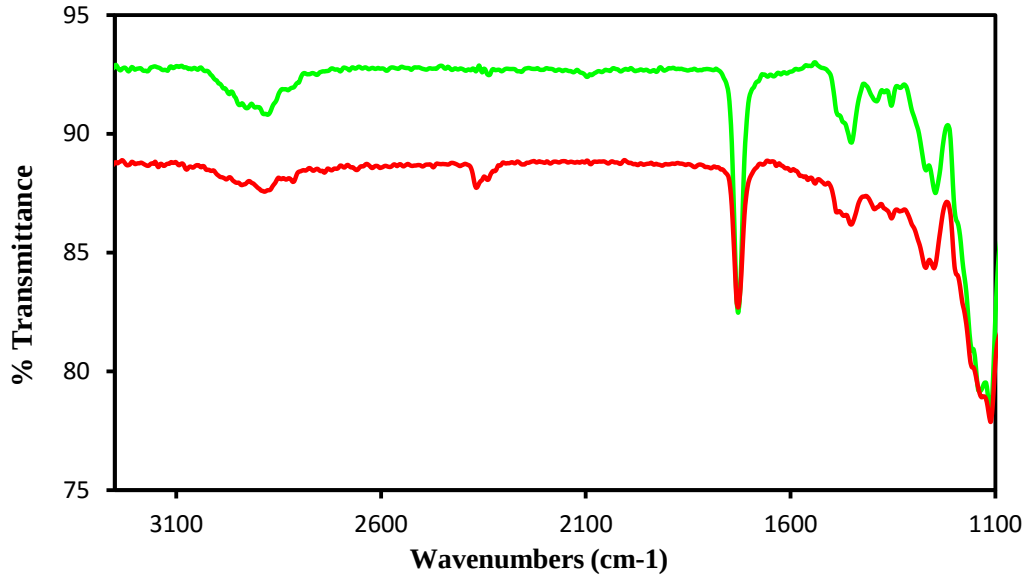


Figure 3.26. FT-IR spectra of polymer brush after click reaction with BODIPY dye

In addition, DEGMA polymer brush which was not modified with diazido V-501was used as control group and azide modified polymer brush were treated with alkyne containing BODIPY dye. As shown in FT-IR spectra of polymer brushes, azide peak disappeared after click reaction with BODIPY dye (Figure3.26).

3.3.3. Surface Modification with V-501 Dendron derivative

After synthesis of V-501 derivative various generations of dendrons, post-polymerization modification step was carried by following similar procedure for previously done azide functionalization (Figure 3.27). Briefly, G1 and G2 generation dendron terminated azo initiators were dissolved in separate reaction vessels containing dioxane under N_2 stream. After 15 minutes purging, reaction mixtures were transferred onto degassed Si/SiO_2 surfaces and heated at 65 °C oil bath for 24 h. As shown previously, contact angle of polymer brush coated surface was measured as 65° (Figure 3.8.). After modification with compound 5, contact angle was measured as 60° due to hydrophilic character of –OH groups (Figure 3.28).

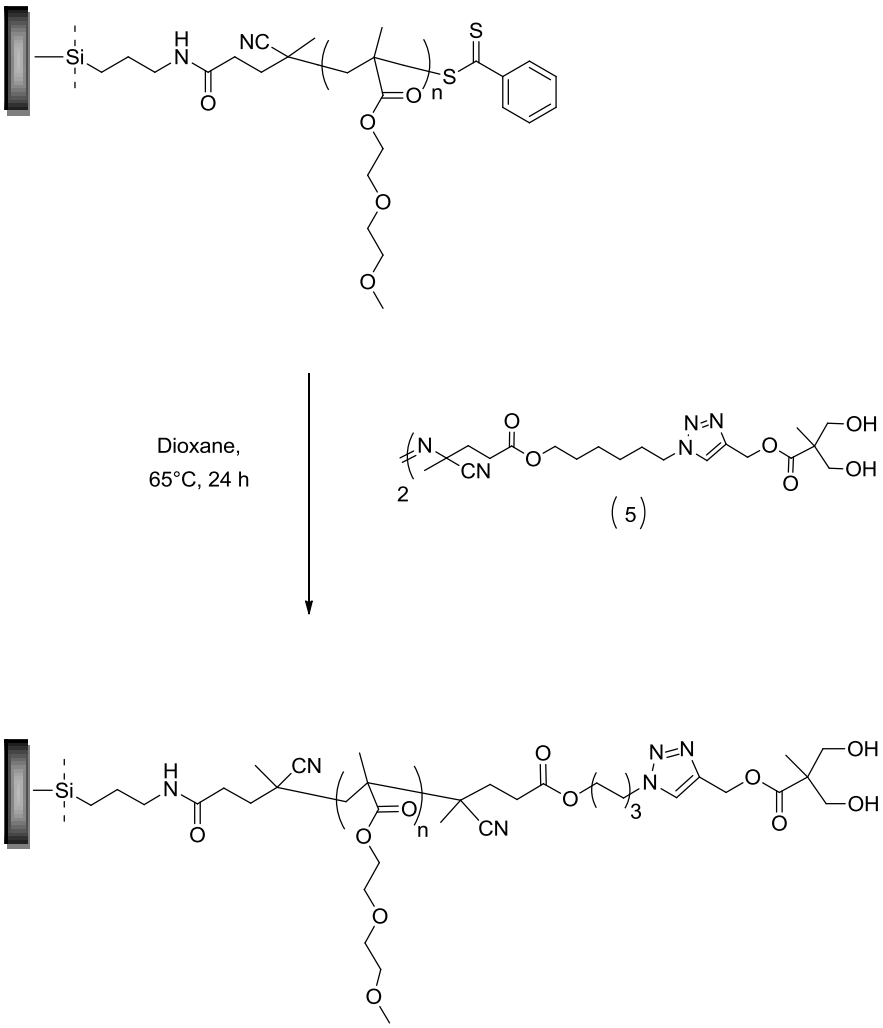


Figure 3.27. Post-polymerization modification with compound 5.

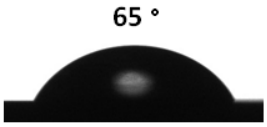
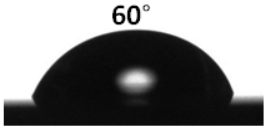
Polymer grafted surface	
End group modified surface with compound 5	

Figure 3.28. Contact angle results of DEGMA brush.

Figure 3.29 shows polymer brush spectra (top) and modified spectra (bottom). After modification of brushes –OH stretching around 3200-3500 cm-^{1} appears slightly.

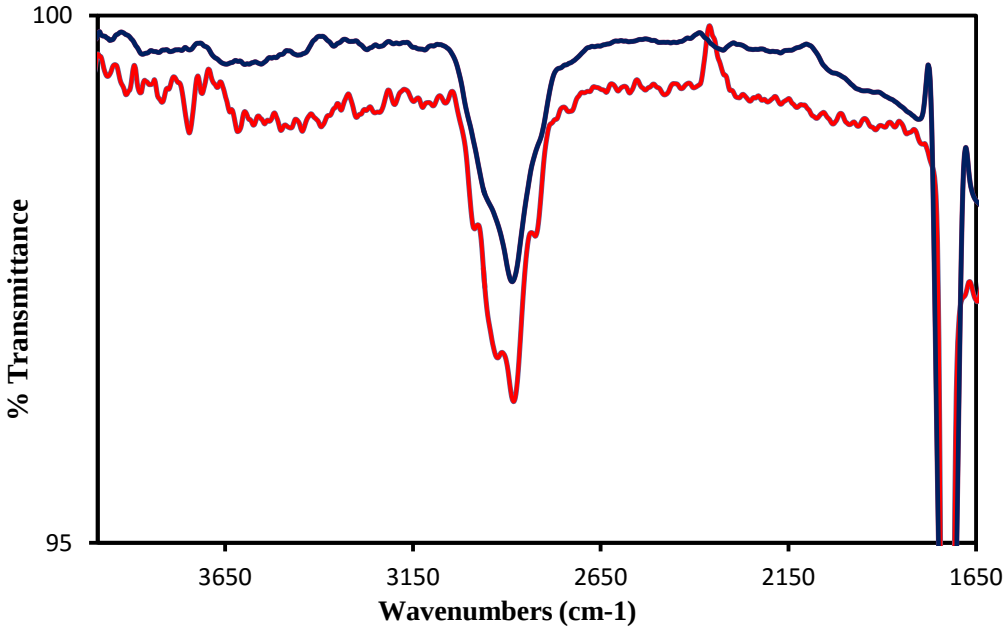


Figure 3.29. FT-IT spectra of polymer brush before and after modification.

By following similar procedure, end groups of polymer brushes were functionalized via radical exchange reaction (Figure 3.30).

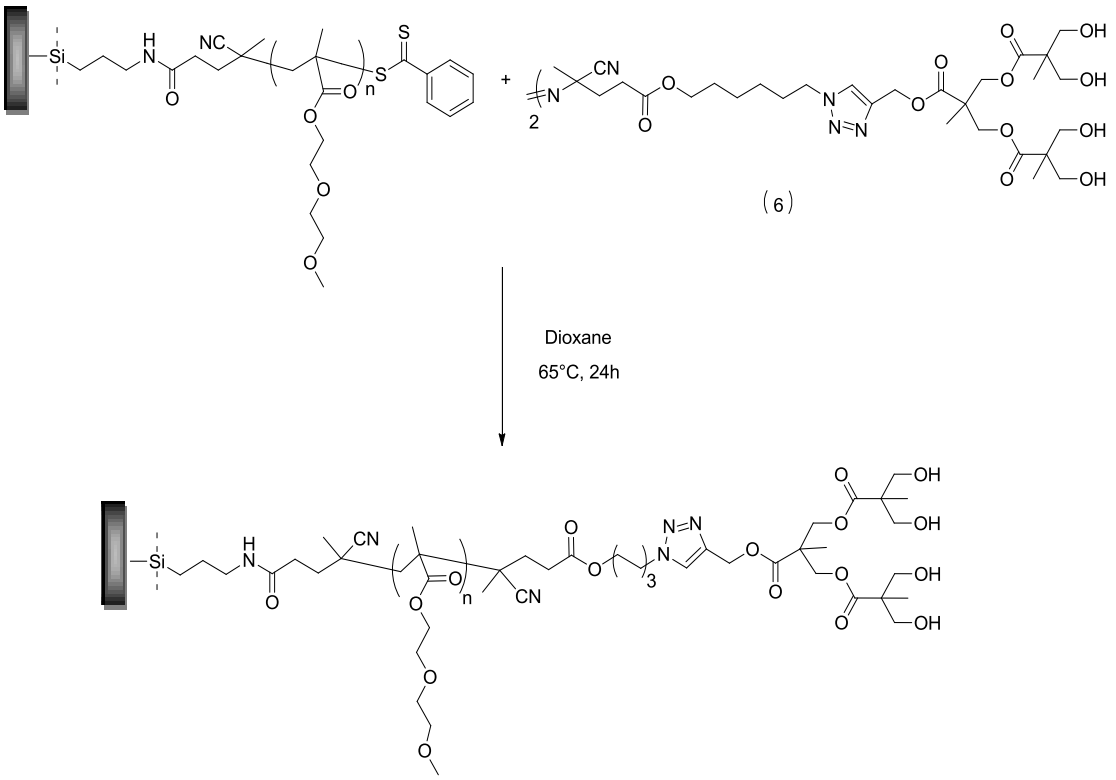


Figure 3.30. Post-polymerization modification with compound 6.

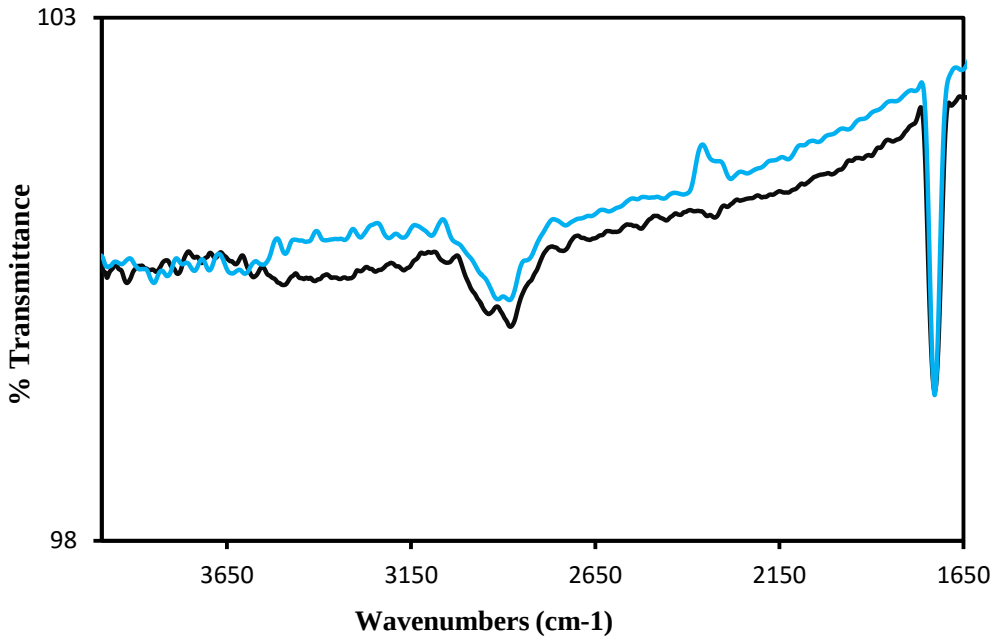


Figure 3.31. FT-IR spectra of polymer brushes modified with compound 6.

After modification of brushes with compound 6, –OH stretching around 3200-3500 cm^{-1} was observed as shown in Figure 3.31. In addition, contact angle degreased from 65 ° to 59 ° after modification of surface (Figure 3.32).

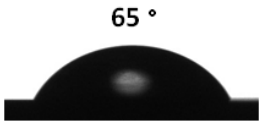
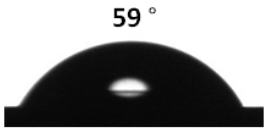
Polymer grafted surface	
End group modified surface with compound 6	

Figure 3.32. Contact angle results of DEGMA brush.

The dendron attachment to polymer chain ends needs to be investigated more rigorously in future by doing X-ray photoelectron spectroscopy analysis, as well as derivatization of newly formed hydroxyl groups on the surface.

4. EXPERIMENTAL

4.1. Measurements

Si/SiO_2 surfaces were cleaned by using Novascan PSD Series UV/Digital Ozone System. Water contact angle measurements were carried with KSV's CAM 101. Attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectroscopy was performed by Thermo Scientific Nicolet 380 FT-IR spectrophotometer equipped with ATR accessory with Ge crystal. ^{1}H-NMR and ^{13}C-NMR spectra were obtained on Varian 400 MHz.

4.2. Preparation of Polymer Brushes via RAFT Polymerization

4.2.1. Synthesis of Surface Attachable RAFT Agent

The surface RAFT agent was synthesized according to the literature procedure [76]. 4-cyanopentanoic acid dithiobenzoate (25 mg, 89.6 μmol) and (3-aminopropyl)-triethoxysilane (21 μl, 89.6 μmol) were dissolved in 5 ml anhydrous dichloromethane. After addition of 17 mg EDC, the mixture was stirred for one hour at room temperature. The mixture was extracted with brine and the organic phase was dried with Na_2SO_4. The solvent was evaporated and the product was obtained as a pink oil form. The product was used without further purification (21.6 mg, 51% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (dd, *J* = 8.4, 1.1 Hz, 2H), 7.59 – 7.52 (m, 1H), 7.39 (dd, *J* = 13.8, 6.2 Hz, 2H), 3.88 – 3.76 (m, 6H), 3.33 – 3.20 (m, 2H), 2.70 – 2.29 (m, 5H), 1.99 – 1.91 (m, 5H), 1.70 – 1.57 (m, 3H), 1.26 – 1.21 (m, 8H), 0.65 (dd, *J* = 19.0, 10.9 Hz, 2H).

4.2.2. Immobilization of RAFT Agent on Silicon Surfaces

Silicon wafers were cut into rectangular pieces and cleaned before immobilization of surface RAFT agent. Initially, silicon surfaces were sonicated in

ethanol, acetone and water for 5 min. After drying surfaces with nitrogen stream, they were exposed to UV/ozone chamber for 30 min for the activation of silicon surfaces. The surface RAFT agent immobilization was carried out as described in previous report [76]. The activated silicon wafers were immersed in 1 mM solution of surface RAFT agent in anhydrous toluene. The surfaces were left in solution at room temperature. After 24 hours, silicon surfaces were washed with dichloromethane, methanol and water a few times and dried under nitrogen stream.

4.2.3. RAFT Polymerization of Di(ethylene glycol) Methyl Ether Methacrylate (DEGMA)

DEGMA (2.26 mg, 12 mmol), AIBN (3.25 mg, 0.02 mmol) was dissolved in DMF (9 ml). After passing a N_2 gas for 20 min, the solution mixture was transferred into the previously prepared vessels containing silicon wafers under N_2 atmosphere. The reaction vessels were sealed and kept at 70 °C oil bath for a predetermined period of time. After silicon wafers were rinsed with dichloromethane, methanol and water, they were dried via N_2 stream.

4.3. Synthesis of V-501 derivative polyester Dendron

4.3.1. Synthesis of First and Second Generation Dendron

Alkyne containing compound 3 and compound 4 were synthesized according to previous report [78].

4.3.2. Synthesis of 4,4’-azobis(azidohexanoyl 4-cyanopentanoate)

6-chlorohexanol and 4,4’-azobis(azidohexanoyl 4-cyanopentanoate) were synthesized according to previous report [77,83].

4.3.3. Synthesis of V-501 Derivative G1-OH Dendron.

Diazido-V-501 (142.18 mg, 0.27 mmol) and G1-OH-alkyne (101.6 mg, 0.59 mmol) were dissolved in anhydrous THF (2 ml) under N_2 atmosphere. CuBr (7.75 mg, 0.054 mmol) and PMDETA (9.36 mg, 0.054 mmol) were dissolved in anhydrous THF (1 ml) under N_2 purge. CuBr/PMDETA solution was added onto reaction mixture and stirred at 40 °C for 24 h. After solvent was evaporated, product was dissolved in DCM (100 ml) and then extracted with water (10 ml) two times. Crude was dried over Na_2SO_4 and concentrated via rotary evaporation. The crude was purified via column chromatography with MeOH:EtOAc (10:80) (146.5 mg, 62% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (s, 1H), 7.58 (s, 1H), 5.31 (s, 2H), 5.30 (s, 2H), 4.32 (t, *J* = 7.0 Hz, 4H), 4.06 (t, *J* = 6.5 Hz, 4H), 3.84 (d, *J* = 11.3 Hz, 4H), 3.70 (d, *J* = 11.3 Hz, 4H), 2.51 – 2.30 (m, 8H), 1.93 – 1.86 (m, 4H), 1.71 (s, 3H), 1.65 (s, 3H), 1.64 - 1.57 (m, 4H), 1.37 - 1.31 (m, 8H), 1.06 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.6, 171.43, 171.38, 142.8, 122.83, 122.77, 117.6, 117.5, 71.9, 71.8, 67.9, 67.8, 64.8, 57.9, 50.3, 49.60, 49.58, 33.2, 33.1, 30.0, 29.7, 29.1, 28.2, 26.0, 25.3, 23.9, 23.7, 17.0.

4.3.4. Synthesis of V-501 derivative G2-OH Dendron.

Compound diazido-V-501 (60 mg,0.113 mmol) and G2-OH-alkyne (100 mg, 0.249 mmol) were dissolved in anhydrous THF (2 ml) under N2 atmosphere. CuBr (6.48 mg, 0.045 mmol) and PMDETA (9.4 mg, 0.054 mmol) were dissolved in anhydrous THF (1 ml) under N2 purge. CuBr/PMDETA solution was added onto reaction mixture and stirred at 40 °C for 24 h. After solvent was evaporated, product was dissolved in DCM (100 ml) and then extracted with distilled water (10 ml) two times. Crude was dried over Na_2SO_4 and concentrated via rotary evaporation. The crude was obtained with 73% yield as was used as it is for next step. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (s, 1H), 7.63 (s, 1H), 5.24 (s, 4H), 4.36 – 4.31 (m, 8H), 4.26 (d, *J* = 11.2 Hz, 4H), 4.07 (t, *J* = 6.4 Hz, 4H), 3.77 – 3.73 (m, 8H), 3.67 – 3.63 (m, 8H), 2.52 – 2.17 (m, 8H), 1.94 – 1.87 (m, 4H), 1.71 (s, 3H), 1.66 (s, 3H), 1.63 – 1.57 (m, 4H), 1.41 – 1.32 (m, 8H), 1.27 (s, 6H), 1.00 (s, 12H).

4.3.5. Synthesis of V-501 Derivative Dendrons via “Click” Reaction

Diazido-V-501 and G1-OH-alkyne/G2-OH-alkyne dendron click reaction was carried out according to literature example [79].

4.4. Post-polymerization modification of polymer brush

4.4.1. Surface Modification with Azide Functional Group

Diazido V-501 compound was dissolved in dioxane under N_2 atmosphere for 15 min. Polymer brush was placed into a vial and purged with N_2 for a few min. 0.026 mM diazido V-501 compound solution was transferred to previously prepared vials containing polymer brush. The reaction vials were incubated in 65 °C oil bath for 24h. After reaction was completed, modified surfaces were sonicated in methanol and water.

4.4.2. Surface Modification with BODIPY Dye

$CuSO_4$ (0.056 mg) was dissolved in distilled water (6 µl). After BODIPY was dissolved in methanol (1.5 ml), $CuSO_4.H_2O$ solution was added onto dye containing mixture. NaAsc (0.39 mg) was dissolved in distilled water (1 ml). Subsequently, NaAsc mixture was added onto BODIPY dye mixture. Then, azide terminated polymer brushes were immersed in alkyne BODIPY dye solution and left overnight. Surface was washed with methanol and distilled water to remove unreactant BODIPY dye.

4.4.3. Modification with V-501 derivative dendrons

Surface modification was done as same as procedure mentioned at 4.4.1. section.

5. CONCLUSION

In this study, poly(ethylene glycol) based polymer brushes were modified using radical exchange reaction. The aim is to develop a new strategy for attaching containing dendritic end groups on polymer chain ends via *grafting from* approach. Initially, surface anchoring group and CTA were conjugated in order to immobilize them onto silicon surfaces. Polymer brushes were generated directly from surfaces via RAFT polymerization method obtaining brushes with thickness around 35 nm. Post-polymerization modification of polymer brushes was achieved via radical cross coupling reaction in the presence of azo-initiator which was modified with various functionalities such as azides and hydroxyl end groups bearing generation 1 and generation 2 dendrons. Radical exchange procedure requires heating polymer brushes that results in replacement of dithiobenzoate unit of RAFT agent with radicals generated from azo initiator. Azide terminated polymer brushes thus obtained were treated with alkyne unit containing BODIPY dye. Successful attachment of dye was confirmed via fluorescence microscopy. Similarly, end group modification of polymers was carried with dendron bearing azo initiators and characterized via FT-IR and contact angle measurement.

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FT-IR spectra of compound 5 and compound 6 are as shown in Figure A.1 and Figure A.2.

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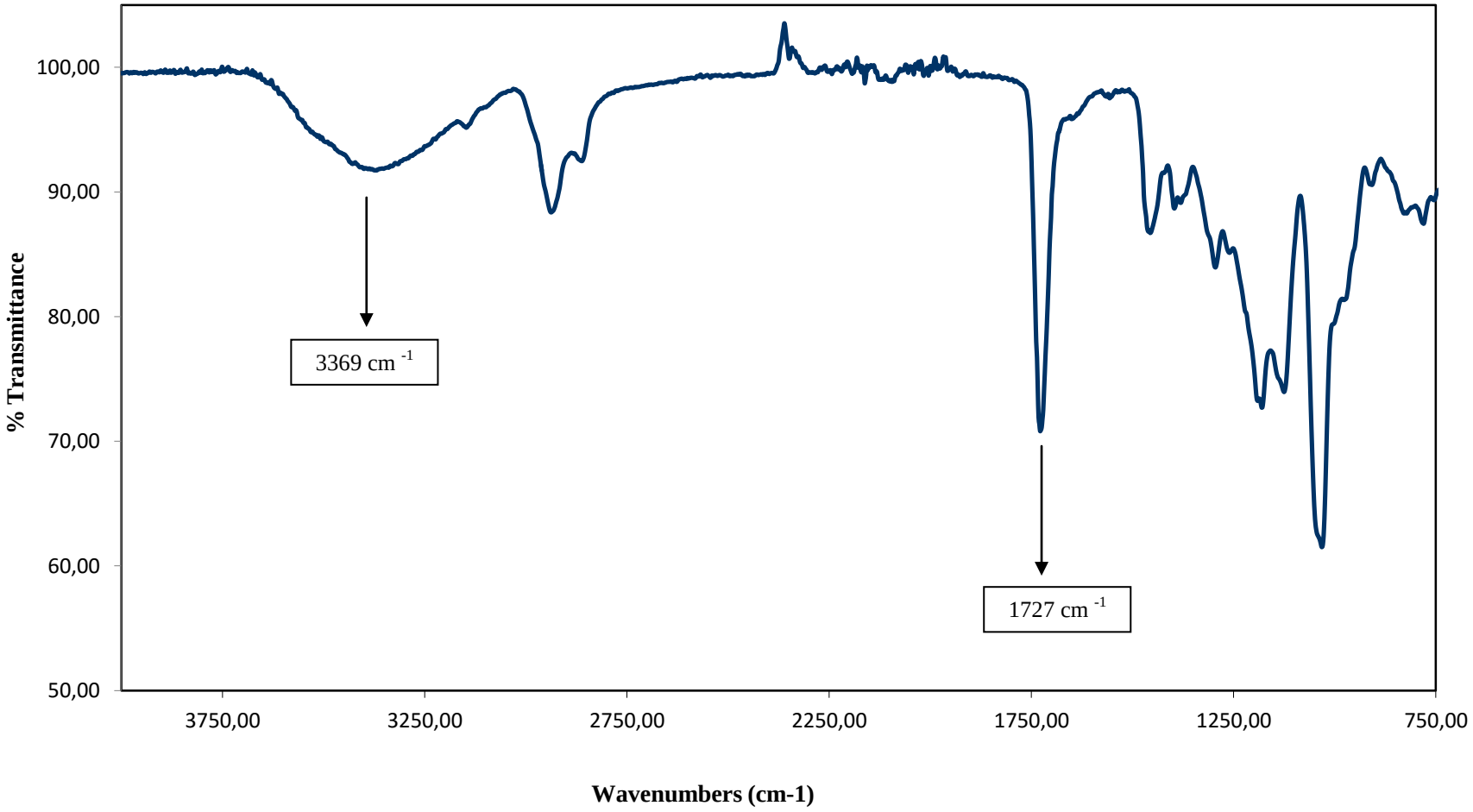
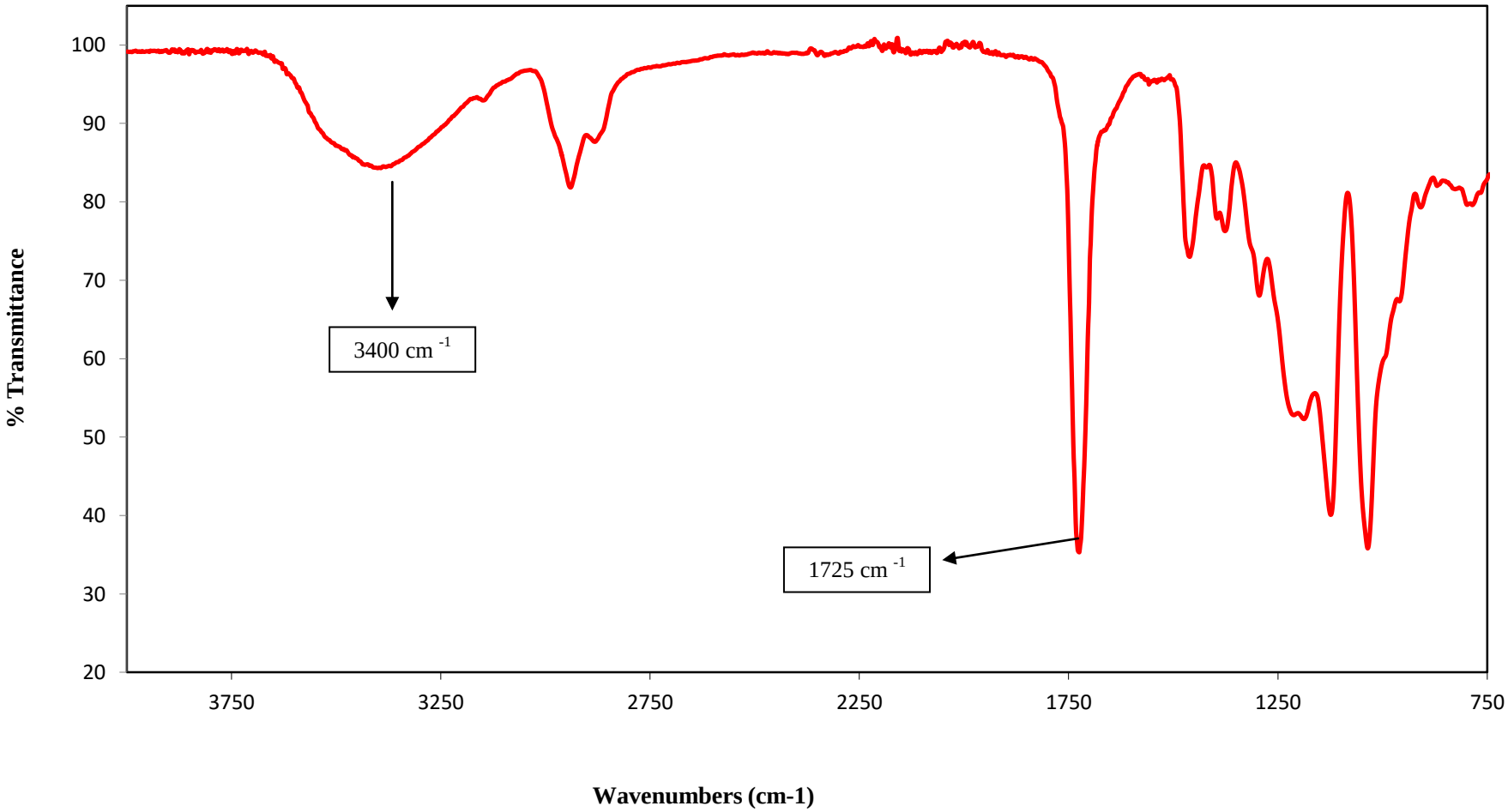


Figure A.1. FT-IR spectrum of compound 5.



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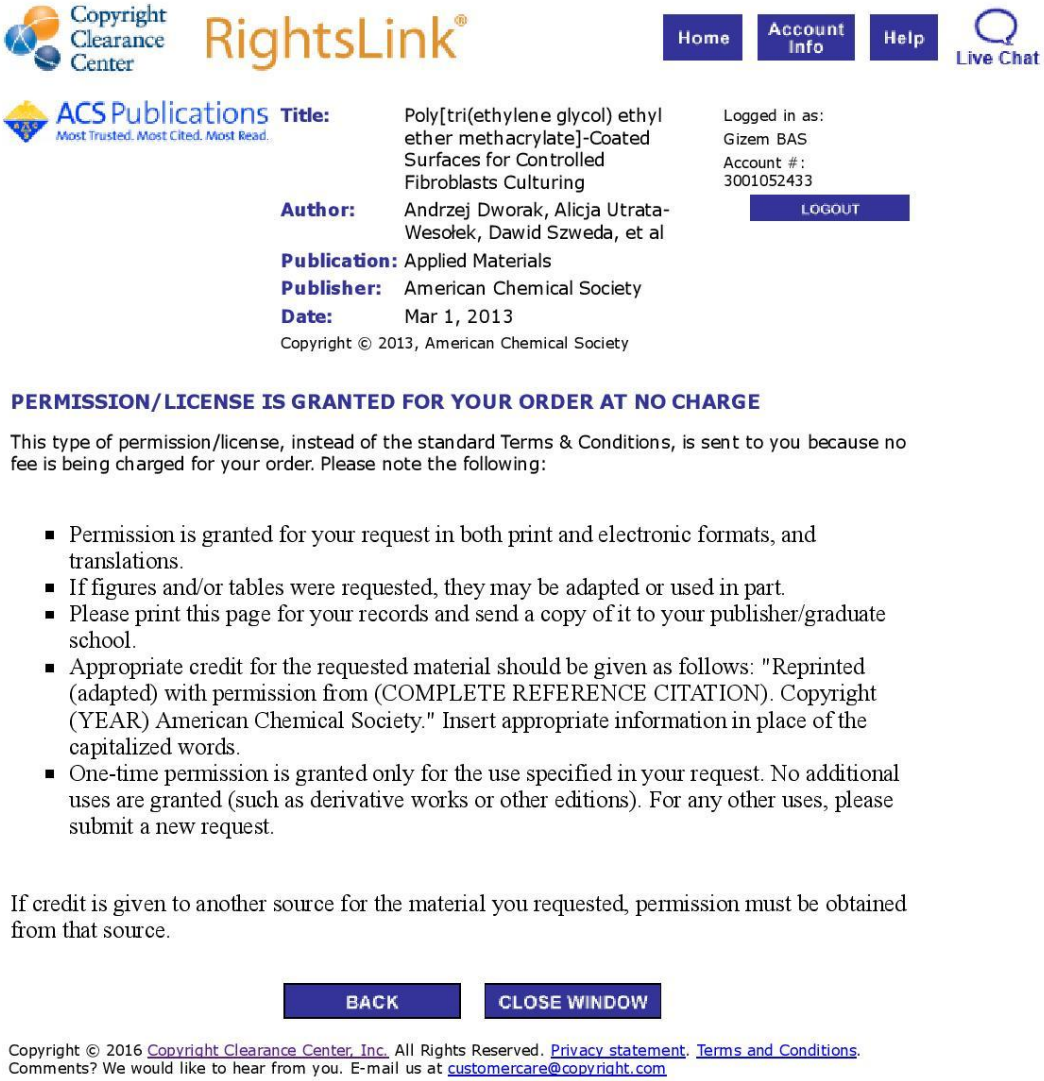

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Publication: Applied Materials

Publisher: American Chemical Society

Date: Mar 1, 2013

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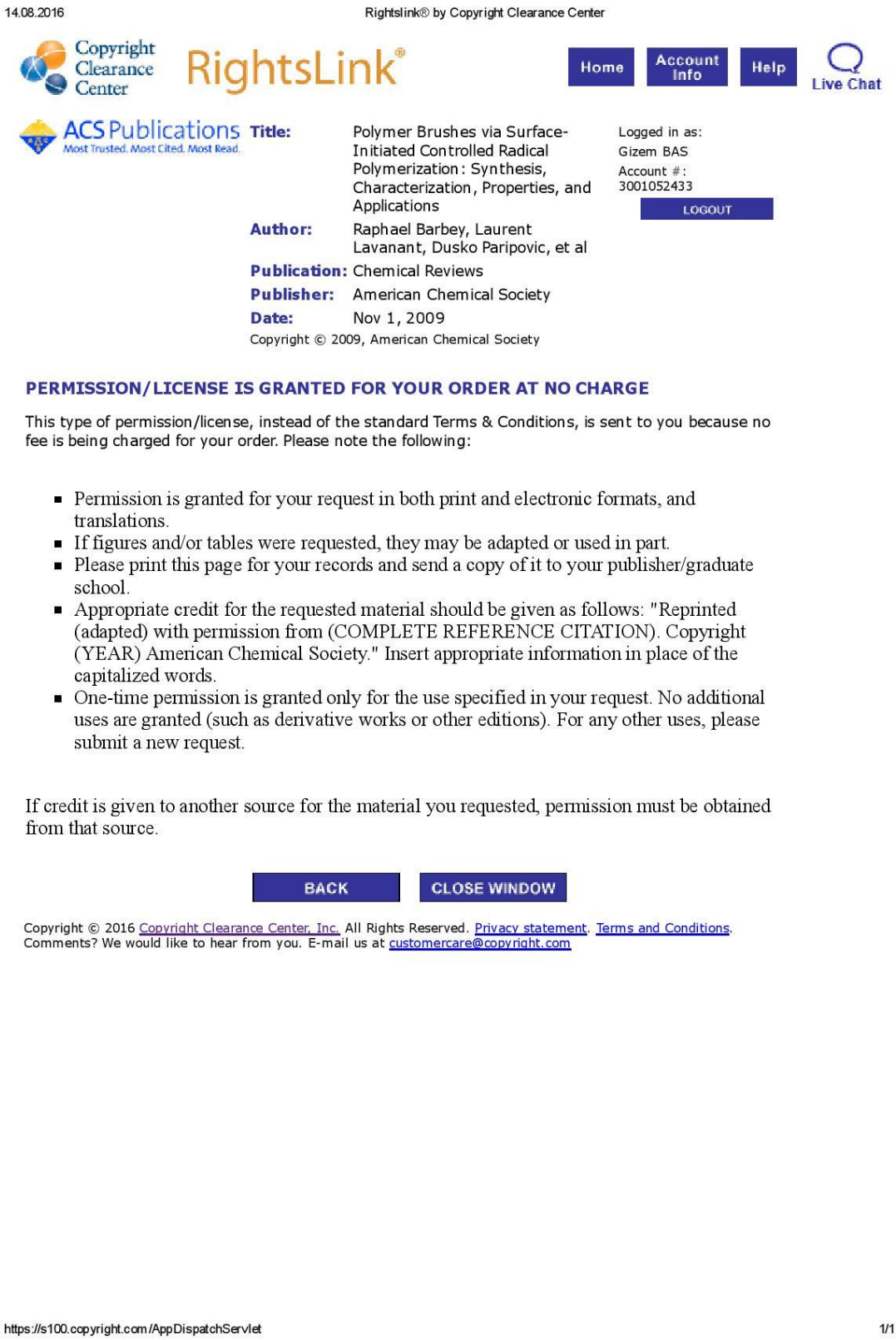

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Publisher: American Chemical Society

Date: Nov 1, 2009

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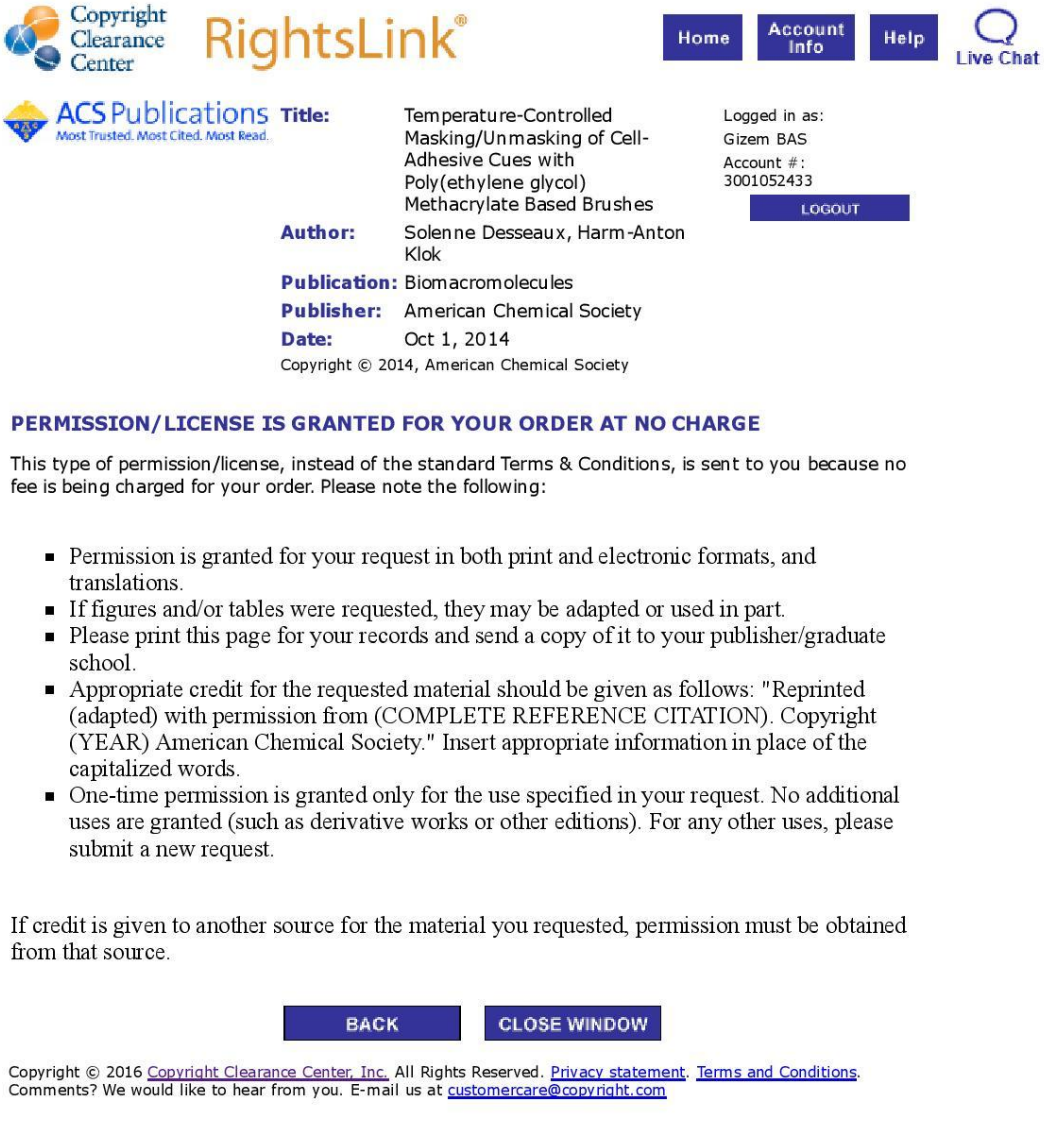

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Publication: Biomacromolecules

Publisher: American Chemical Society

Date: Oct 1, 2014

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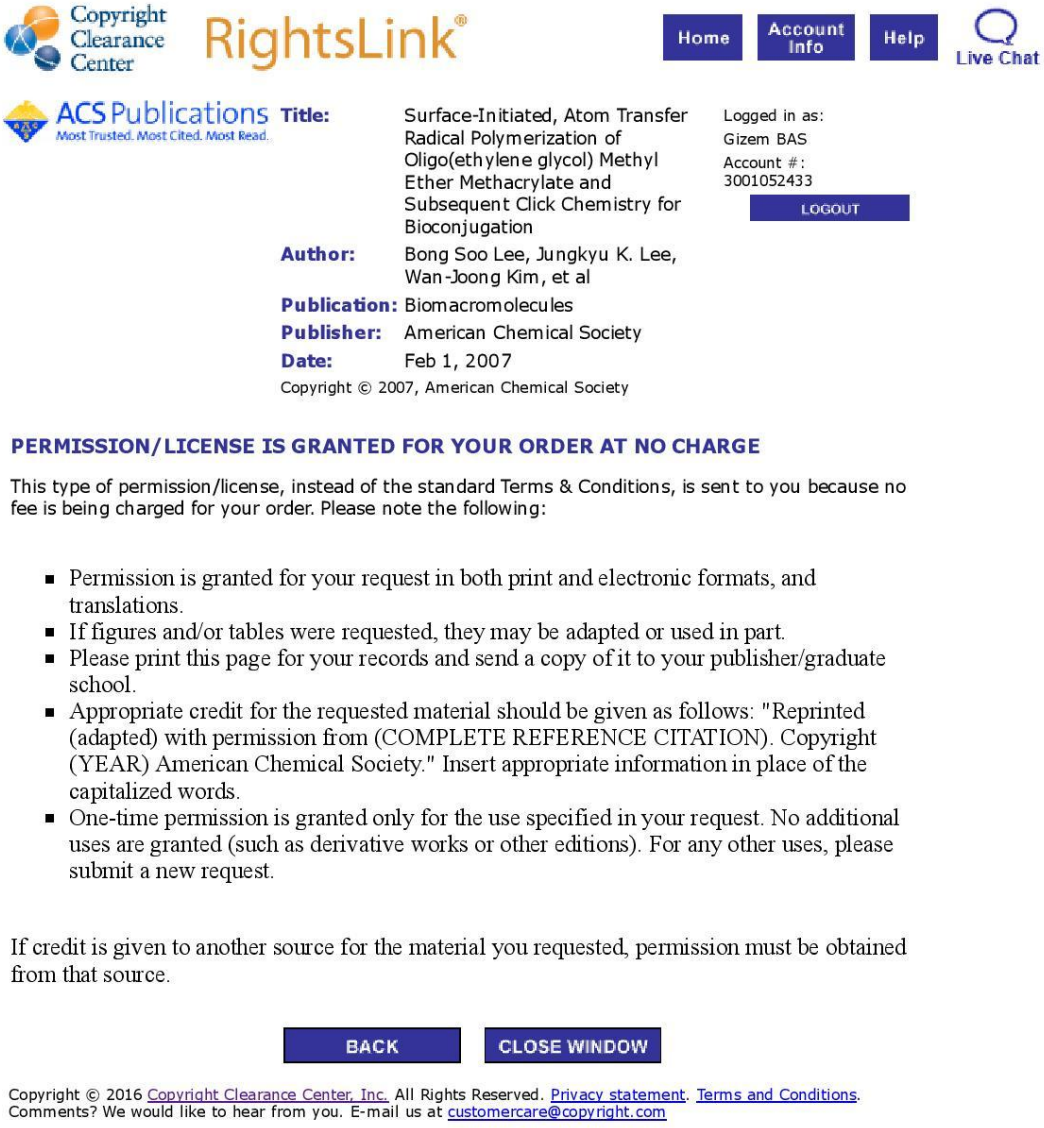

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Author: Bong Soo Lee, Jungkyu K. Lee, Wan-Joong Kim, et al

Publication: Biomacromolecules

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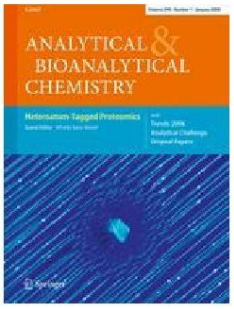

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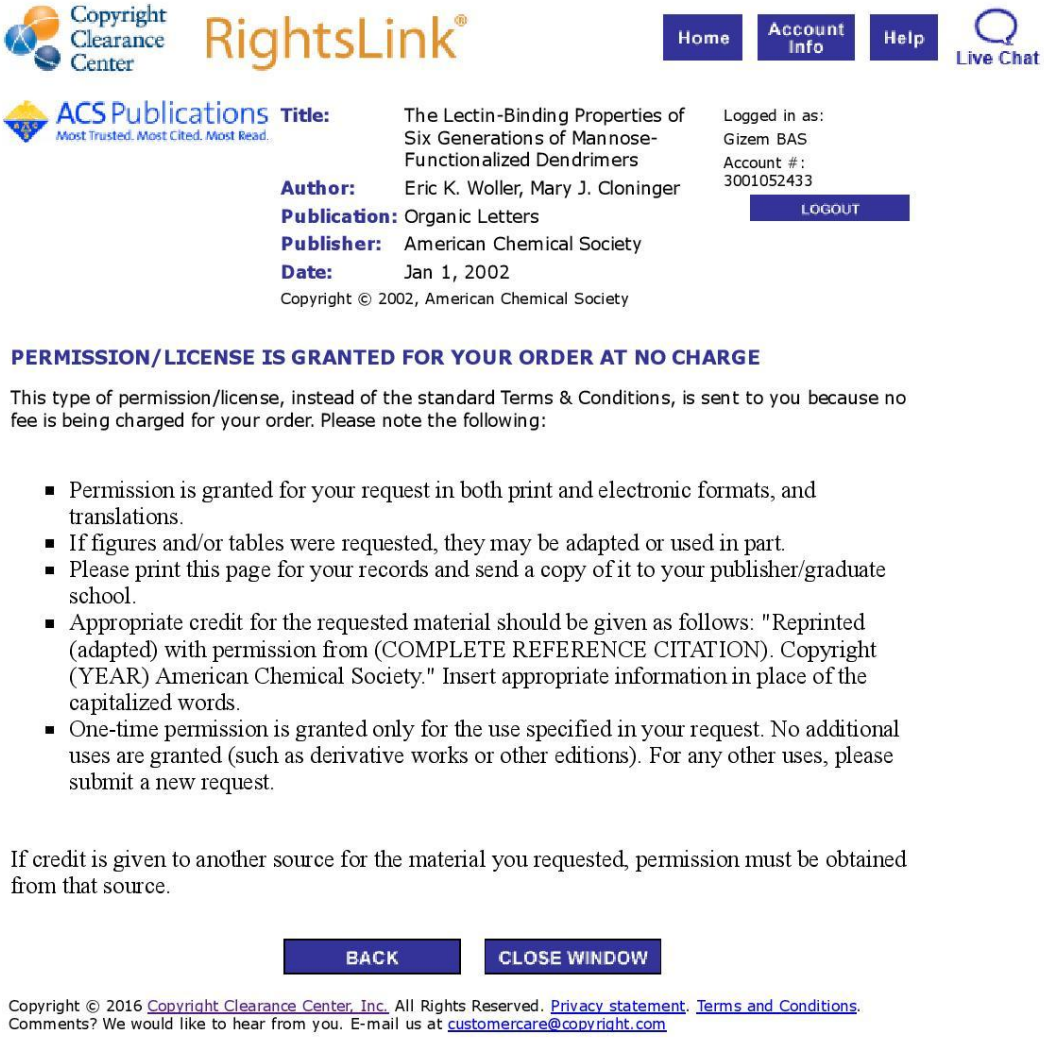

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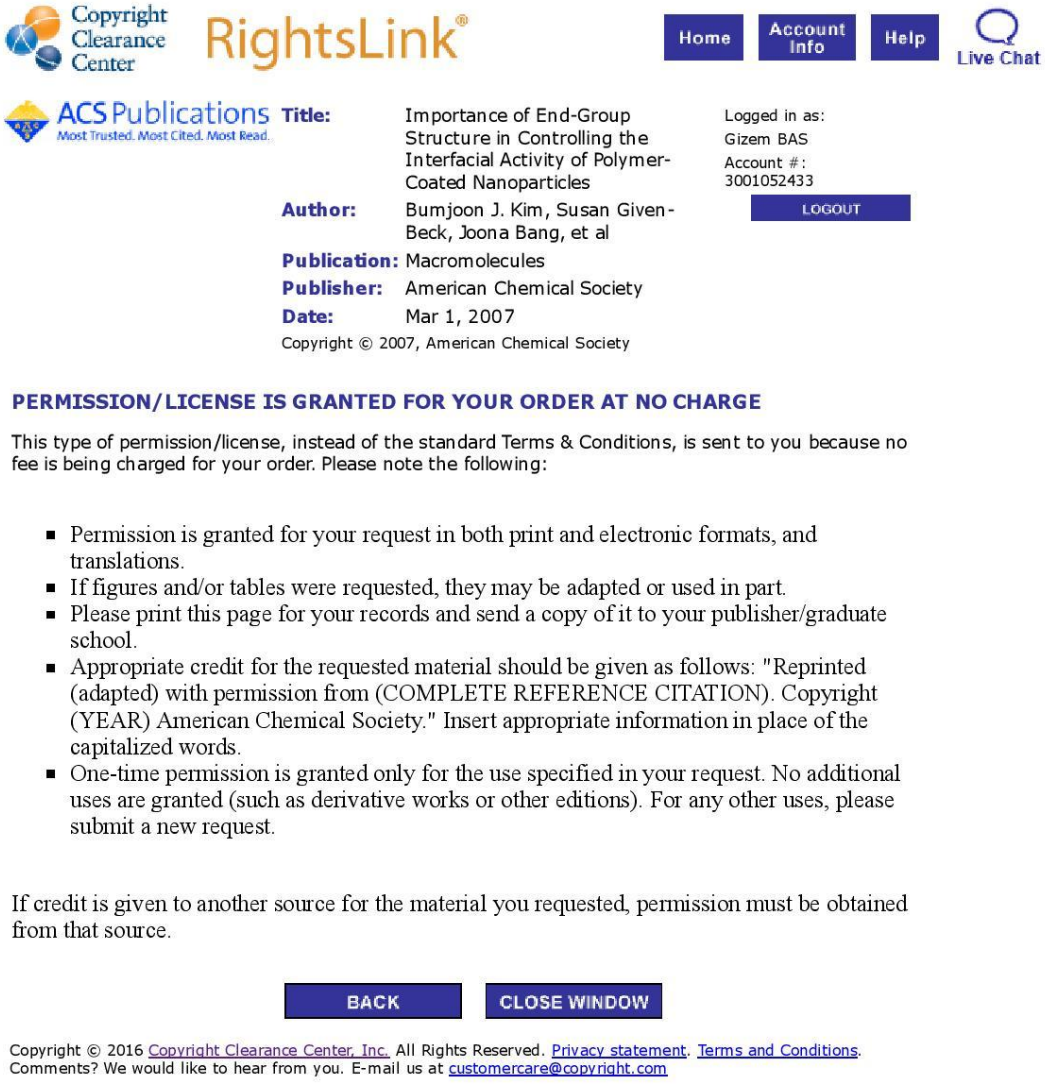

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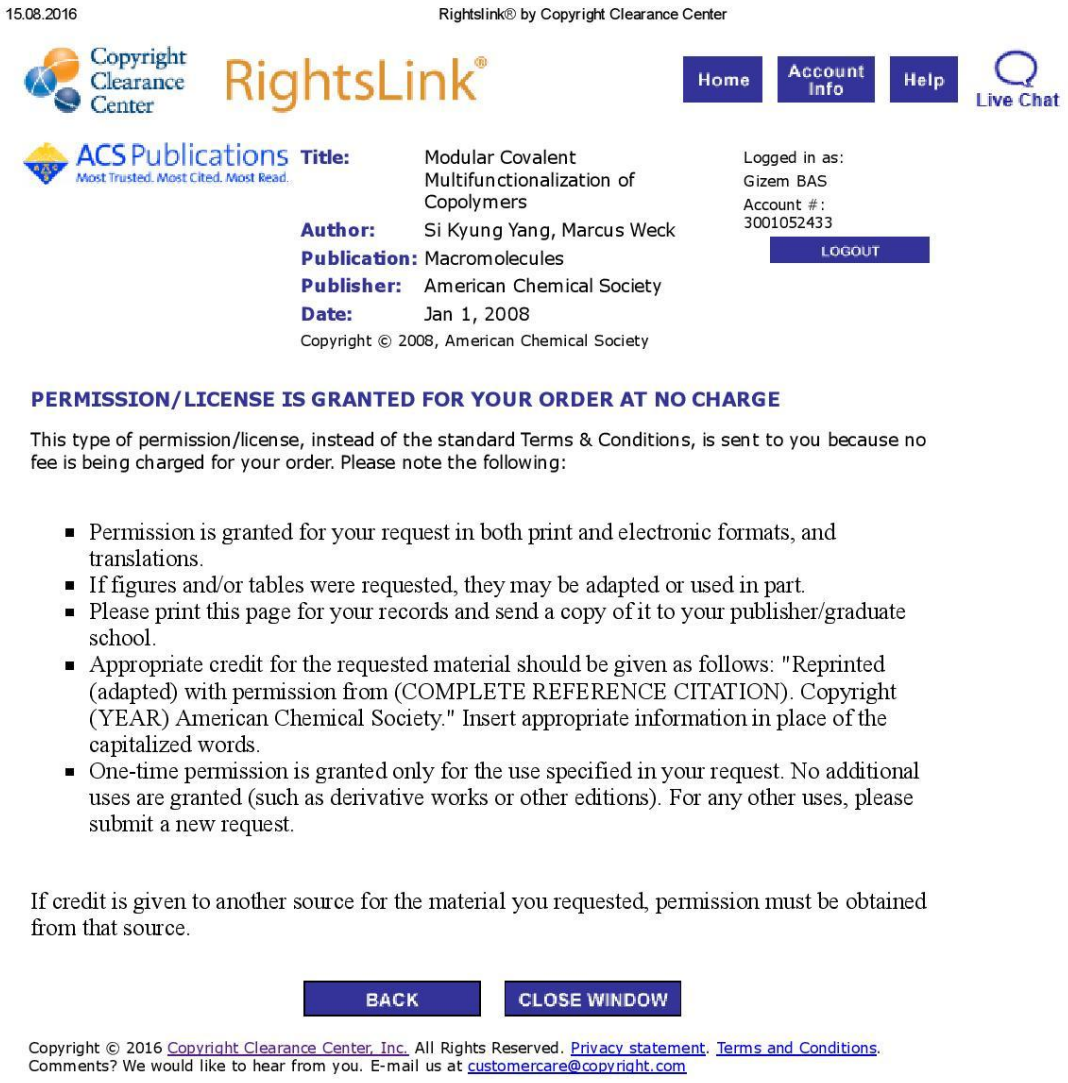

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