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A Review on Stimuli-responsive grafted membranes Based on Facile Synthesis Process and Extensive Applications

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ABSTRACT: In the past few years, an increasing number of stimuli responsive thin polymer films and intelligent hydrogels have been reported in the literature for various biomedical applications, including drug delivery, tissue engineering and wound healing. The thermo-sensitive approach can be advantageous for some specific applications as it does not require organic solvents, co-polymerization agents, or an externally applied trigger for gelation. The conformation as well as change in physical properties of polymer brushes and polymer hydrogel can be influenced by the environmental stimuli, such as solvent composition, temperature, pH and electric fields. This review focuses on the recent advances of these stimuli responsive molecular thin film and stimuli responsive polymeric gels with unique properties and utilities. We also discuss some conflicting behaviors shown by polymer grafted membrane and polymer gel surfaces, synthesized by using same monomers. Major properties of stimuli responsive thin polymer films, and on their potential application in the field of nano-optics, ultrasensitive spectroscopies and other biomedical applications including drug delivery are also outlined.

KEYWORDS: drug delivery system; molecularly imprinted polymer; nanoparticles; stimuli-responsive.

1 INTRODUCTION

For more than two decades, stimuli-sensitive polymers have been drawn consequential attention for the fabrication of so-called “smart”, “intelligent”, or “environmentally sensitive ” polymers, which can undergo a reversible and yet discontinuous volume phase change in response to various external physicochemical factors [1], [2], [3], [4], [5]. Molecular interactions between polymer chains, or between polymer chain and solutes present in a system will alter by pH, metabolites and ionic factors. On the other hand, for altering molecular interactions of polymer chain, physical stimuli, such as temperature or electrical potential, can also provide various energy sources. Among them, temperature and pH-responsive grafted membrane have been expensively studied due to their physiological significance [6]. Recently a trend has been observed in engineering biomimetic nanostructured thin films that combine a wide range of functional properties found in cell membranes [7]. These materials carry some practically important properties of synthetic materials, such as, mechanical and chemical stability, electrical, optical, magnetic properties, wetting, and adhesion [8], [9], [10], [11].

Fabrication of different types of grafted polymer film have been reported by several deposition techniques. Homopolymer brushes, which can be synthesized in various ways are exist in a large variety of structural geometries with vastly different bonding characteristics between the metal and oxygen. The characteristics of metal oxides are strongly dependent on their exact composition, fabrication temperature, crystal morphology, surface area, and crystallite size [12], [13]. The layer-by-layer deposition technique has been devoted to the development of molecular assemblies of thin film. This technique mainly on based successive deposition of alternate layers of anionic and cationic polyelectrolytes including synthetic polymers, proteins and nucleic acids. The electrostatic force of attraction play as an origin of the strong adhesion between the anionic and cationic layers [14]. The layer-by-layer structure is possible to construct by means of polymers and biomaterials which have biological interactions such as protein–ligand, antibody–antigen and lectin–saccharide bindings. Bimetallic particles have also been of considerable attraction, because the physical and chemical properties of the metal particles can be developed by adding the other component to the monometallic particles [15]. Cross linked film is very important because of its importance in the industrial production of many semiconductors, hard disk drive storage devices, and micro-electromechanical systems. Surface-initiated polymerization method has the advantage of tethering polymers onto the surface with high grafting densities, which is ideal for coating surfaces. This method was also used for surface modification with surface-initiated grafted polymers prepared via physisorption onto the surface or chemisorption by covalent bonding [16]. Binary mixed homopolymer brushes, which represent a new, intriguing class of environmentally responsive materials are composed of two chemically distinct homopolymers randomly or alternately immobilized by one end via a covalent bond on the surface of a solid substrate. The two grafted polymers can undergo spontaneous chain reorganization in response to environmental variations and show different nanostructures and surface properties [17], [19]. These brushes exhibit different nanostructures and surface properties under different conditions. Block copolymer brushes exhibits complicated phase-separation behavior in a thin film, compared with in bulk due to the interfacial interactions of the blocks with the underlying substrate, the surface energies of the blocks and commensurability with the film thickness. According to the the Flory–Huggins interaction parameter $\varkappa$, block copolymer can self assemble into a variety of nanoscale structures (spherical, cylindrical, gyroidal, lamellar) with dimensions from a few nanometres to above 100nm depending on molecular weight, segment size, and the strength of interaction between the blocks. Molecular brushes have drawn progressive attention since its first preparation report by ATRP reported in 1998 [20]. The field of stimuli-responsive molecular brushes has been reported with a large number of papers. In the first part of this article, we review the general aspects of these stimuli responsive polymer thin film, their properties, ability to selectively recognize external signals and polymeric responsive systems. In the second part we discuss the recent developments and future trends dealing with stimuli responsive hydrogels. Rational approaches to induce stimuli-responsiveness of both cases are also highlighted.

2 STIMULI RESPONSIVE GRAFTED POLYMER

2.1 CONVENTIONAL POLYMERIZATION TECHNIQUES

Many methods have been developed for the polymerization of grafted polymer at different temperature by using different types of organic solvent like, 2,2_-azobis(isobutyronitrile) (AIBN) or peroxide initiators, or in water using ammonium persulfate or potassium persulfate initiator in the presence of activators [21]. Polymerization in the presence of various chain transfer agents has been examined in order to control molecular weight and structure, especially for the functionalization of end groups. But in many cases inappropriate methods were selected for making the high-density polymer brushes. It has only recently been seriously considered that an appropriate surface conditions have to choose for attaching monomer to one end and the preparatory method to form grafted polymer for making a real high density polymer film.

Atom transfer radical polymerization (ATRP) [22], reversible addition fragmentation chain transfer (RAFT) [23], nitroxide-mediated polymerization (NMP) [24], are attractive living radical polymerization technique. A variety of monomers can be used and a variety of block copolymers were synthesized. Polymerization could be done at relatively low temperature and polymers having a narrow molecular weight distribution were successively investigated. Ring-opening metathesis polymerization (ROMP) using fast-initiating ruthenium catalysts (Figure 1) have allowed the preparation of new materials with unprecedented functional and structural diversity and blurred the line between small-molecule and polymer synthesis. This development in catalysis is particularly suited for the synthesis of diverse side-chain functional polymers with controllable molecular weights (Mn) and low polydispersities (PDI) [25], [26].

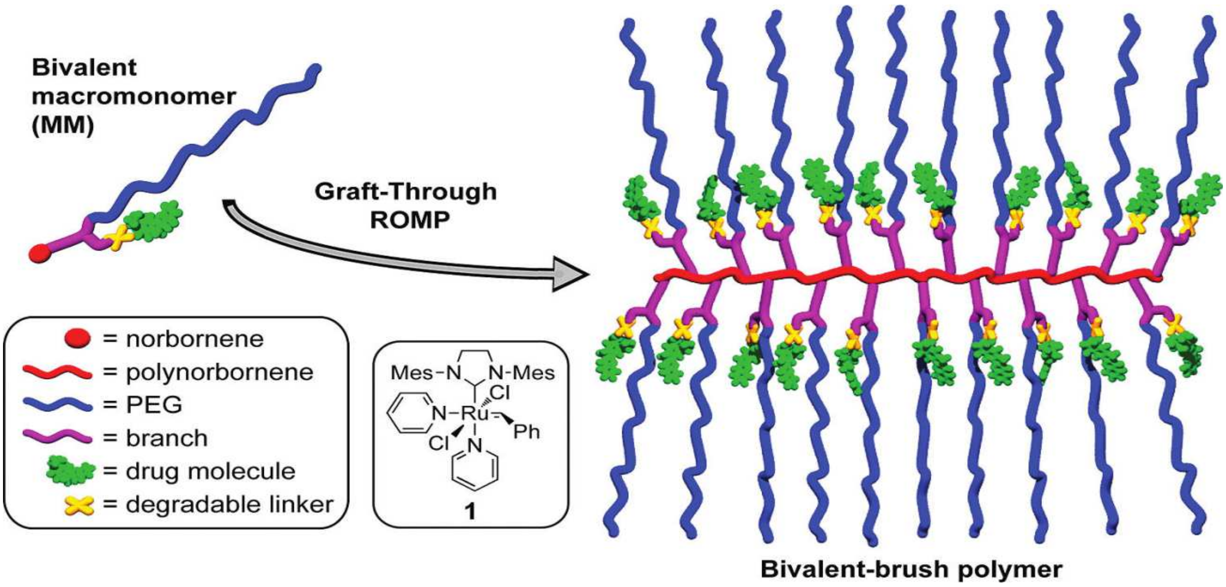


Figure 1. Schematic depiction of bivalent macromonomer (MM) and bivalent-brush polymer.

Numerous reports describing the successful synthesis of stimuli responsive polymer grafted film have appeared. For example, Guoqing et al. described a unique approach to obtain molecularly imprinted polymers (MIPs) with both pure water compatible (i.e., applicable in the pure aqueous environments) and stimuli-responsive binding properties. MIPs brushes were synthesized by poly(NIPAAm) (PNIPAAm) via surface-initiated reversible addition–fragmentation chain transfer (RAFT) polymerization [27]. Edwards et al. have recently demonstrated that capping gold nanoparticles (NPs) with thermoresponsive copolymers of di(ethylene glycol) methyl ether methacrylate (MEO_2MA) and poly (ethylene glycol) (OEGMA) methyl ether methacrylate, which results in a composite material and is capable of crossing the water-oil interface in response to the salt concentration of the aqueous phase [28]. Further investigation of this work was gold NPs capped with copolymers of MEO2MA and OEGMA were prepared to investigate how surface chemistry, particle size, and salt chemistry affect the transfer of these particles across the water-oil interface [29]. Stimuli-responsive polymer brushes are excellent materials for active plasmonic devices because the conformation of polymeric chains can be controlled by pH, ionic strength, and temperature. In case of the polymer, which is bound to noble-metal nanostructures, the stimuli-sensitive conformational changes of the polymer can modify drastically the refractive index of the NPs' surrounding medium and consequently, their optical properties [30], [31]. There is a drawback of gold colloidal NPs or island films attached to polymer brushes. The optical response of these substrates prevent any improvement in analytical applications such as chemical sensoring or surface-enhanced spectroscopies due to broad localized surface plasmon resonance (LSPR) bands. To improve pasmonic system performences, fabrication of perfectly calibrated systems and control of the polymer grafting steps for optimization of the stimuli-induced response of the polymer with high grafted density of polymer brushes have to be considered. Helene et al. demonstrate thermally induced modifications of the plasmonic response of lithographic gold nanoparticles functionalized by thermosensitive polymer brushes of (poly(N-isopropylacrylamide) (Fig:2) to emphasize the idea that such structures may act as efficient real-time nanosensors [32]. A new bivalent-brush polymer structure was introduced by Jeremiah et al. for use in chemotherapy delivery. A water-soluble PEG side chain and a drug molecule were attached to a polynorbornene backbone via a branch point. In response to an appropriate stimulus, the drug is released in a controlled way after it attached via a degradable linker. The power of this approach for the preparation of water-soluble polynorborneneg-PEG brush polymers and copolymers that have anticancer drug, doxorubicin (DOX) and camptothecin (CT) covalently bound near the core through a photocleavable linker was also demonstrated [33].This process ensures that the weight percentage of drug loaded onto the brush polymers is the same as the weight percentage of drug on the macromonomers.

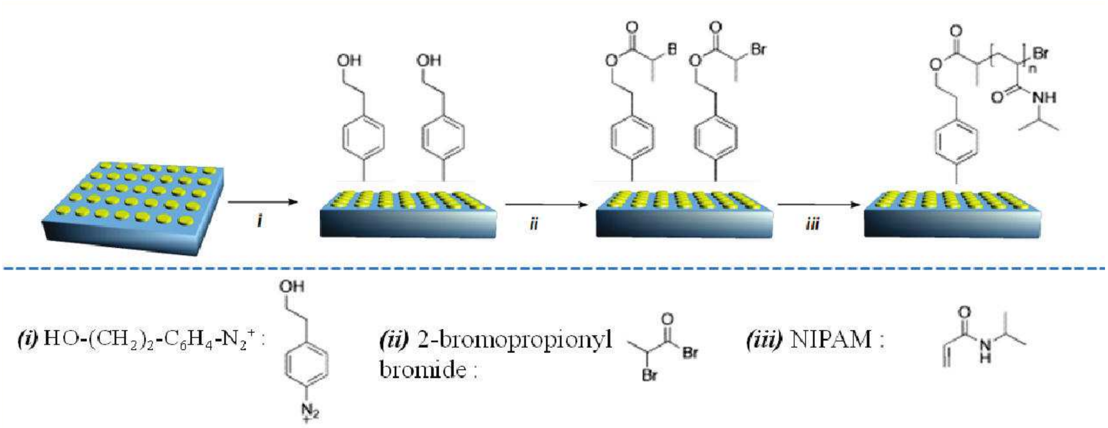


Figure 2 Fabrication of PNIPAM-grafted brushes on lithographic gold nanodot arrays. (i) Electroreduction of HO-$(CH_2)_2$-C_6H_4-N_2^+ salts on the substrate, (ii) esterification by 2-bromopropionyl bromide, and (iii) ATRP of NIPAM on the initiator-modified gold substrates.

Solution-based processing techniques of high performance organic semiconductor (OSC) materials have emerged as the most promising in terms of fulfilling the requirements of low cost, high functionality electronics, such as, thin film transistor circuits for flexible active matrix backplanes [34].

High mobility is one of the important production requirements for OSC materials. There was an approach to improve self-assembly of the functional molecules, which have a better control diffusion in the drying film by reducing the evaporation rate [35]. A higher boiling point solvent, such as toluene, xylene, etc. is used in this system. In this way mobilities close to but not much higher than 1 $cm^2 V^{-1} s^{-1}$ could be achieved. Later, Maria et al. reported another approach for further increasing mobilities of OSC transistors based on a dual solvent system [36]. In the case of the single solvent film, large elevations on the surface consisting of needle-shaped crystals are clearly visible, whereas a platelet-shaped crystallites was observed for double-solvent film. Platelet-shaped growth allows for better bridging of the electrodes and provides charge carrier pathways along two more directions, which maximize the charge transport across the channel. In this way, a very high device mobilities was achieved.

2.2 MAGNETICALLY MODALIZED THIN FILM

Magnetite nanoparticles are biocompatible and slowly degradable under biological conditions, which have different protein forms viz; ferritin and hemosiderin as major degradation products [37]. Magnetic nanoparticles have potential uses in magnetic field guided drug delivery, magnetic hyperthermia treatment of cancer and as contrast enhancement agents in magnetic resonance imaging [38]. If magnetic nanoparticles are encapsulated with poly(NIPAAm) based copolymers, it have been found to be a good drug carrier with controlled release behavior and magnetic field guided targetibility. To release drug above LCST, Poly(NIPAAm) based magnetic nanohydrogels containing particle sizes in the nano range with optimized LCST of above 42 ^{o}C will be a suitable choice for combined hyperthermia and drug delivery system. Temperature optimized biocompatible nanohydrogel and magnetic nanohydrogel was synthesized by the Manish et al. for possible application in hyperthermia for cancer treatment [39]. The average size of magnetic nanoparticles was found to be in the range of 10–12nm. and the presence of Fe_3O_4 encapsulated within polymer hydrogel matrix was supported by electron diffraction analysis. A shift in LCST of poly(NIPAAm) based hydrogels either by grafting chitosan and/or encapsulating magnetic nanoparticles was observed. During reaction, a considerable change in poly(NIPAAm)-chitosan nanohydrogel size was observed when chitosan concentration was exceeded due to crosslinking of chitosan to poly(NIPAAm) and/or partially to the adhesion of free chitosan particles onto growing poly(NIPAAm)-chitosan hydrogel particles. An increase in LCST due to presence of iron oxide magnetic nanoparticles was suggested that dipole–dipole interactions may be responsible which prevent collapsing of crosslinked polymer segments. The magnetic nanohydrogels exhibits a moderate specific absorption rate and excellent cytocompatibility studies and can be considered as a potential appellant for hyperthermia treatment of cancer.

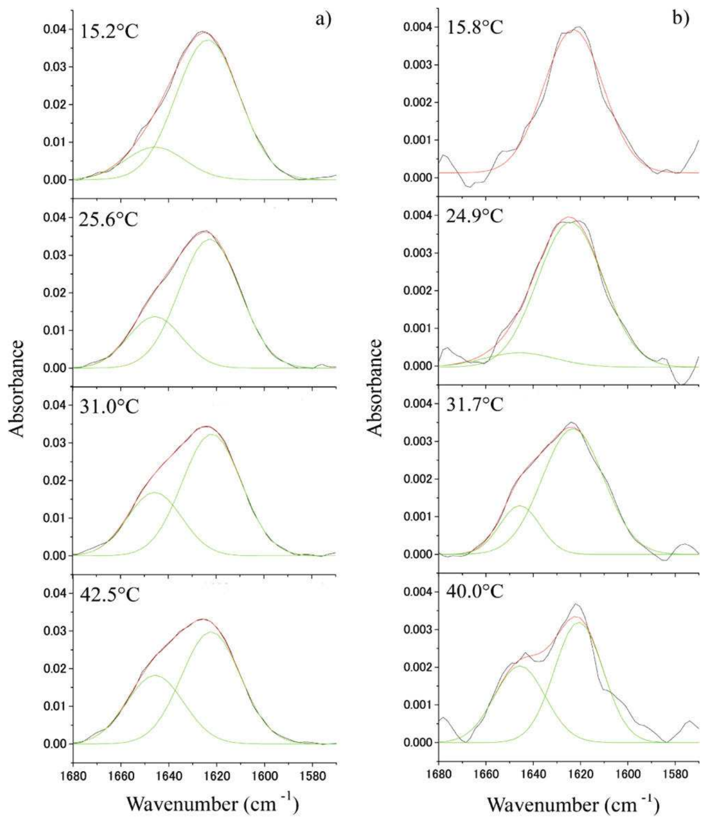


Figure 3. IR absorption spectra in amide I region for PNIPA grafted membranes with different graft densities at several temperatures. Black line: baseline subtracted amide I band, red line: curve fitted peak, green line: best fitted single Gaussian component. (a) high density brush; (b) low density brush.

2.3 INTERACTION INFORMATION OF PNIPA GRAFTED FILM

FT-IR is a powerful means to explain the interaction information of grafted membrane at the molecular level. Molecular behavior of PNIPA has been studied by several research group and brought out some interesting report. The vibration of amide group in PNIPA are highly sensitive during the change in temperature across the LCST. During changing the temperature across LCST, there exist two absorption peak at 1637 cm^{-1} for the PNIPA linear polymer in a solution state. But the intensity of these peaks are different. Maeda et al. interpret that intensity peak observed at 1625 cm^{-1} is assigned for C=O group that is bound to water molecules, and the intensity peak appeared at 1650 cm^{-1} is the peak of C=O group that is interact with neighboring N-H group [40]. However Katsumoto et al. reported dissimilar views regarding these peaks. According to them, the peak at 1625 cm^{-1} is refers the peak of C=O group forming a strong hydrogen bonding with the neighboring N-H group, and the peak at 1650 cm^{-1} is because of free C=O group [41]. H-NMR and UV spectra indicate that formation of hydrogen bonding with water depends on temperature [42], [43]. Change of the absorption peaks around the vibrations of amide groups in high and low density PNIPA brushes from 15.2 ^{o}C to 42.5 ^{o}C was observed [44]. In case of high density PNIPA brush, the amide I band was fitted at 1625 cm^{-1} and 1650 cm^{-1} at all temperature. The intensity peak at 1625 cm^{-1} decreased with the temperature increase, while the one at 1650-1 cm increased (Fig: 3a). On the other hand, the amide I band of low density PNIPA brush consist only a single Gaussian component at 15.2 ^{o}C centered at 1625 cm^{-1} (Fig: 3b). The component centered at 1650 cm^{-1} appeared at only higher temperature. PNIPA chains in the high-density brush are in a physically constrained state and the thickness of the membrane changed continuously over a much broader range with changes in temperature.

2.4 BIMETALLIC NANOPARTICLES DISPERSION IN POLYMER THIN FILMS

Metal and semiconductor nanoparticles dispersed in polymeric matrices exhibit unusual physical and chemical properties based on size-quantization effects of the noparticles. Bimetallic particles have also significant interest in surface chemistry, because the physical and chemical properties of the metal particles can be improved by adding the other component to the monometallic particles [45], [46]. Polymer thin films containing metal nanoparticles can be synthesized by successive vacuum vapor deposition of a polymer and a metal followed by thermal annealing [47], [48]. If the films are annealed at a temperature above the glass transition temperature (Tg) of the polymer, the dispersion of the deposited metals can be achieved. But it has been shown that upon annealing in an inert atmosphere, Au particles can penetrate into nylon 11 films but Cu particles cannot [49]. To find out the reason behind this property, a further investigation was carried out which studied the effect of the composition and atmosphere on the dispersion of Au/Cu bimetallic nanoparticles, as well as their monometallic particles, induced by annealing in an N2 atmosphere [50]. Deposition of Au and Cu on nylon 11 sample was confirmed by TEM image (Fig: 4). Although the formation of small particles on the nylon 11 surface at room temperature indicates a significant surface mobility of Au (and Cu) atoms, the changes in particle size with composition can be caused by the different surface diffusion coefficients of the Au and Cu atoms, depending on the interaction between the deposited metal atoms and the nylon 11 molecules. Remarkable composition dependence was observed in the particle distribution. The photoelectron intensity of the Au and Cu samples as a function of film depth shows that no indication of oxidation state for Cu was observed in the Cu Auger electron spectrum. According to the surface stress coefficient and critical composition results, it can be said that there is a strong correlation between the structure and dispersibility of particles in a polymer matrix, providing insight into the formation, structure and stability of metal/polymer composite systems.

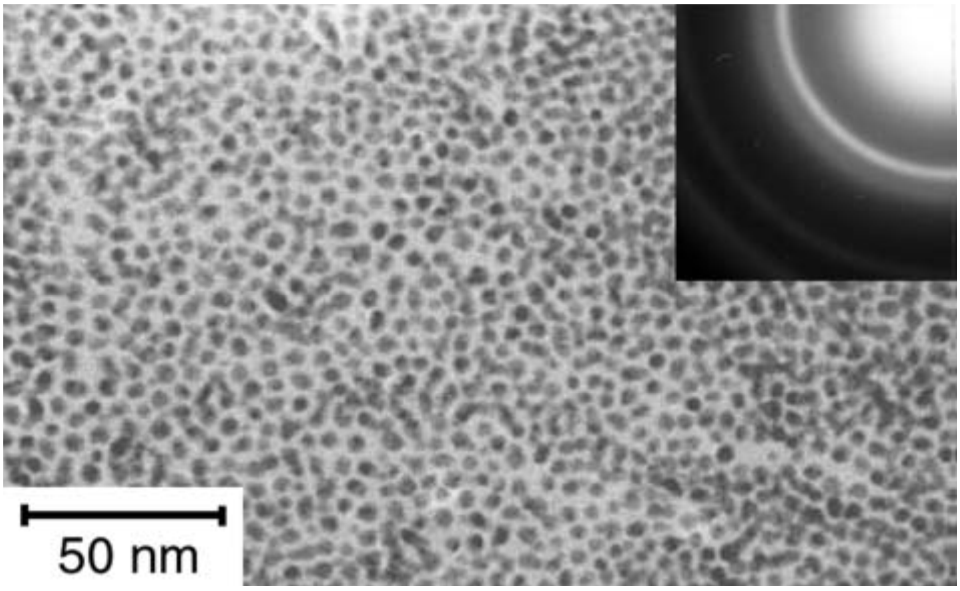
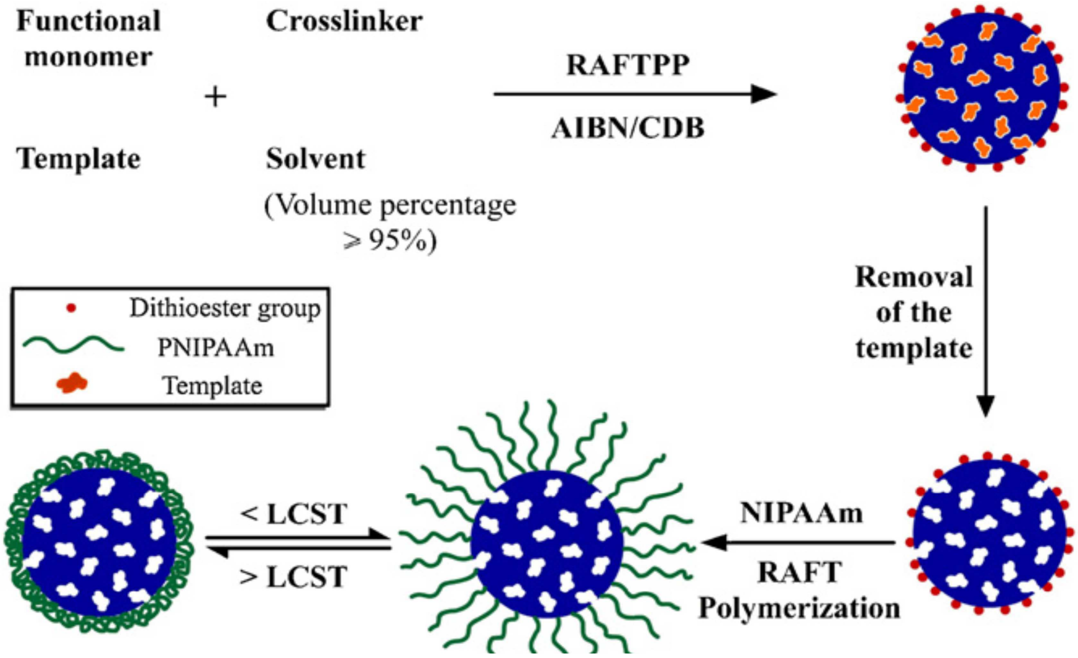


Figure 4. TEM image and SAED pattern of as-deposited Au0.70Cu0.30 nanoparticles deposited on the nylon 11 surface.

2.5 MOLECULARLY IMPRINTED POLYMER BRUSH

In nature, biological processes like immuno-responses between the antibody and antigen, the ligand–receptor interaction, and enzyme catalysis are governed by molecular recognition mechanisms. Molecularly imprinted polymer (MIP) has proven to develop synthetic receptors with an affinity and specificity approaching that achieved in nature. MIP has also a lot of stimuli responsive properties, such as outstanding molecular recognition ability in the aqueous environments. Designing of advanced MIP is a matter of big challenge for the biological reporters [51]. MIP developed by Komiyama et al. are only organic solvent-compatible and fails to show specific binding significantly. This MIP has a limitation to their practical applications in the fiend of biotechnology [52]. Meng et al. also successfully prepared pure water-compatible MIPs by adding certain amounts of hydrophilic monomers (e.g., 2-hydroxyethyl methacrylate and acrylamide) [53], [54]. Later an efficient approach has been reported by Guoqing et al. to obtain MIP brushes of poly(NIPAAm) via surface-initiated (RAFT) polymerization (Scheme: I). Aim of this experiment was to obtaining both pure water-compatible and stimuli-responsive onto the preformed MIP particles [55]. Their result shows that the MIPs exhibit significantly lower binding capacities towards phenoxyacetic acid and high molecular recognition selectivity of the ungrafted and grafted MIPs. Equilibrium binding experiments established that polymer brushes-grafting approach is highly efficient for the preparation of water-compatible MIPs. In comparison with the organic solvent-compatible MIPs and pure water-compatible MIPs, Guoqing`s et al approach should be more efficient in improving the surface hydrophilicity of the MIPs because it allows all the hydrophilic monomers to be grafted on the surfaces of the MIP particles.



Scheme I. Protocol for the preparation of water-compatible and stimuli-responsive MIP microspheres with surface-grafted functional polymer brushes.

2.6 ATTACHMENT AND DETACHMENT OF BACTERIA ON POLYMER THIN FILM

Biofilms are ubiquitous and its basic biological outline has been established and elaborated [56], [57]. The interfacial interactions between the cells and the supporting base are less well understood. Removal of unwanted biofilms, or biofouling, requires a better understanding of the substratum properties that are important in the maintenance of a biofilm. Hydrophobicity play an imoportant role in maintaining cellular attachment. If some cells attach initially to hydrophobic surface, these cells can easily be removed upon application of low shear forces [58]. The ability of the temperature responsive polymer (PNIPAAm) has been shown to release not only newly attached bacteria but also fully developed biofilms. The composition of the underlying SAM influences grafting efficiency may provide a means of controlling the polymerization process and the subsequent properties of the grafted surface. According to Cunliffe et al., the expected phase transitions of the polymers in solution were partly reflected by changing surface hydrophobicity. But there is a topographic differences in the polymer surfaces over the same temperature ranges [59]. Bacterial adsorption of surfaces also depend on the temperature, it increased with increasing the temperatures where the polymers were above the LCST but didn`t change significantly to control surfaces or to a polymer surface. To release some bacteria like Cobeitia marina and Staphylococcus epidermidis, the surface transition must be from one favored for attachment to one disfavored. For example, C. marina attaches well to PNIPA above 32 ^{o}C, released from the surface when rinsed with solutions below 32 ^{o}C. But in the case of S. epidermidis, it attaches larger numbers to surfaces with low water contact angle [60]. PNIPAAm from SAMs of ω-substituted alkanethiolates on gold surfaces were used to investigate the effect of water contact angles and the change in contact angle over the transition on the attachment and release of C. marina and S. epidermidis [61]. In the case of C. marina, tunable PNIPAAm provides a means by which cells can be removed at different points in biofilm development in order to assay physiological changes in attached (or attaching) cells. This system will only work for those strains of bacteria that can be attached with hydrophobic surfaces. For the attachment of S. epidermidis to SAMs, there is no strong dependence of C. marina as a function of water contact angle to the tunable PNIPAm surface. In addition, the model of this two bacteria are not alike. Liu at al. proposed that the attachment of bacteria to surfaces can be accurately patterned by also considering the contributions of Lewis-acid/base interactions to the surface energy of the attachment substratum [62]. The thermodynamic analysis underestimated bacterial retention when specific interactions between bacteria and serum proteins were considered for S. epidermidis. A combination of PNIPAAm and serum proteins and bacteria for biomaterial surfaces, as well as bacteria/bacteria and protein/protein interactions might well be the best means for similar studies with hydrophilic organisms.

2.7 POLYMER COATED PLASMONIC NANOSTRUCTURE

Noble-metal nanoparticles (NPs) have a wide range of applications in nano-optics and ultrasensitive spectroscopies include guiding light on the submicrometer scale, light sources, filters, surface-enhanced Raman scattering or fluorescence. Many groups have considered the importance of achieving stimuli responsive plasmonic systems using active materials as a surrounding medium, applying a continuous and reversible modulation of the plasmonic response. Wurtz et al. observed a strong coupling between a plasmon supported by an assembly of oriented gold nanorods (ANR) and a molecular exciton. Their observation showed that both spatial and spectral overlap between the plasmonic structure and molecular aggregates are controlled [63]. Zheng et al. fabricated Au nanodisk arrays on glass substrates using nanosphere lithography combined reactive ion etching. Their analysis suggested that the nanoscale movements within surface-bound “molecular machines” can be used as the active components in plasmonic devices [64]. Leroux et al. fabricated a square array of oblate gold particles, the minor axis of which is oriented normally to the indium-tin oxide surface, and built an array of gold particles, which exhibits different localized surface plasmons (LSP) under X- and Y-polarizations due to some anisotropy. A short conclusion of their result reveals that conducting polymer electrochemical switching is a suitable way for adjusting the highest wavelength of nanoparticle surface plasmon resonance in a reversible way as well as combining conducting polymers and gold nanoparticle arrays allows one to develop switches and modulators [65]. Leroux et al. again used indium-tin oxide substrate as plasmonic devices to show that the quenching of the LSPR of gold NPs, induced by polyaniline switch, is stronger at higher wavelengths. According to their assessment, conducting polymer can be tailored at will supposed to change their switching potential or the transformation of their dielectric function upon switching which will yield to electrochemically driven plasmonic devices with adjusted optical characteristics [66]. A good control of the LSPR wavelength through the modification of the external stimulus can make gold nanoparticles polymer brushes. This system could be a very good candidate for real-time nanosensors. Thermosensitive properties of a hybrid plasmonic device based on stimuli responsive brushes grafted to lithographically designed gold nanostructures was analyzed to have a narrow LSPR band display [60]. The LSPR maximum position is mostly affected by the refractive index of water, because the NPs are deposited and not embedded in the indium-tin oxide substrate. This type of polymer structure has a fine tuning of their optical response through the change of temperature. This strategy can be applied to attach other stimuli-responsive polymer brushes on the lithographic system giving an efficient nanosensor lab-on-chip.

2.8 SELF-CLEANING POLYMER BRUSH

Segmented polyurethane type of polymer, which have both fluorocarbon and poly ethylene glycol segments and exhibits an enormous change of hydrophilicity have been reported several times [67], [70]. This type of polymer could be useful in the ability of the polymer to resist and release soils, combating fouling, and selective adsorption–desorption of proteins. Ability of stimuli-responsive polymer brushes to elicit a change in wettability upon solvent exposure is a continual development of polymer thin film. For a given surface, wettability depends on the surface tension of the fluids. If a homogeneous polymer grafted substrates has a lower surface energy than water, then the grafted membrane will always have a lower contact angle than water. To overcome the limitation of thermodynamics surface energetics, solvent-sensitive stimuli-responsive surfaces could be a good alternate. John et al. synthesized such type of polymer brush surfaces using oligomeric amphiphiles of polyethylene glycol and created a short perfluorinated end caps (f-PEG) [71]. According to their report, receding contact angle of a low surface energy fluid (hexadecane) is greater than the advancing contact angle of water. Because f-PEG surfaces displayed an increase in hexadecane contact angle and a decrease in the water contact angle. Polymer brush surfaces can be both truly oleophobic and hydrophilic and preferentially de-wet oil in favor of water producing self-cleaning surfaces where oil is removed by immersion of the surfaces. It was also exhibited that two droplets of different fluids (water and oil) on the same surfaceat the same time showed different constituents of the surface dominating interfacial energy. This type of surface behavior has potential application as self-cleaning coatings and oil-resistant anti-fog coatings.

2.9 RE-ASSEMBLY OF POLYMER THIN FILM

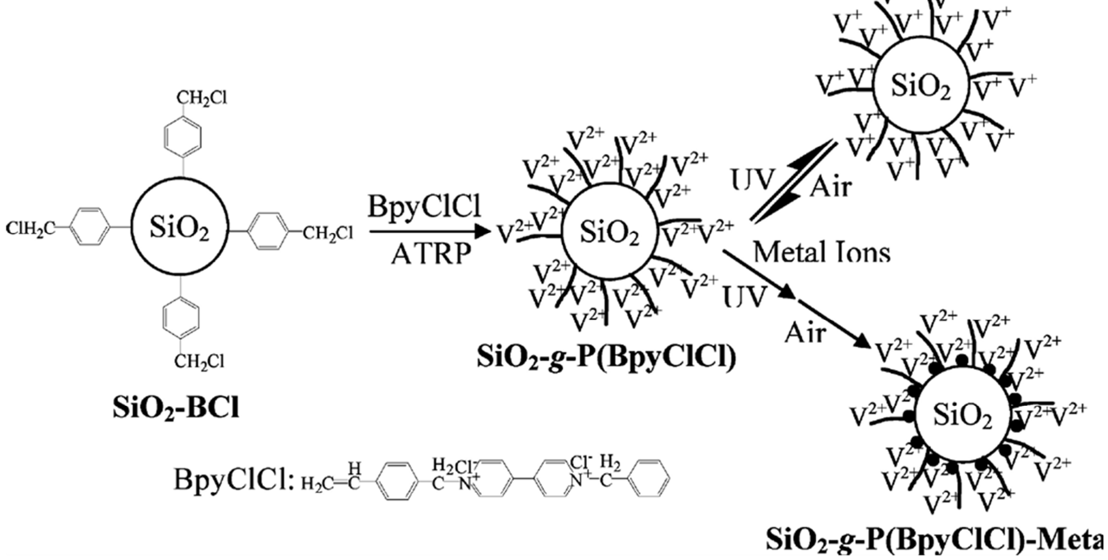
Patterned nanomaterials such as wires, rods, tubes, particles, flowers made from polymeric, metals, ceramics, composites, etc. have unique properties and wide applications. Patterned nanorings with different size, shape and interfacial spacing have been used to develop the performances of photocatalytic, optoelectronic, sensing, and data storage devices. Sun et al. synthesize hierarchical nanoporous TiO_2 mesoscopic ring arrays on solid substrates by using the annealed template-induced sol-soaking strategy. The ring size was controlled by changing the sol concentration and varying the annealing time of the polystyrene sphere colloidal monolayer. TiO2 metal loaded ring arrays might be used in optoelectronic devices, photocatalytic systems, and gas sensors [72]. Elin et al. demonstrated a linear relationship between sensitivity and spectral position for LSPR's situated in the near-infrared by exploring the LSPR resonance sensitivity of nanorings to bulk refractive index change. The sensing characteristics were expected to be influenced by the bulk sensitivity and the profile and homogeneity of the decay of the optical field away from the particle surface [73]. Guo et al. prepared a triblock copolymer by sequential anionic polymerization, end capping with ethylene oxide and subsequent aluminum catalyzed polymerization. A polyisoprene-b-polystyrene-b-polylactide triblock copolymer thin film was used as a template. They formed a core polyisoprene - shell polystrene cylinders in a polyactide matrix with the cylinder axis oriented normal to the modified SiO_2 substrate. These nanoporous thin films should be able to perform as a good templates for the generation of metal anti-ring arrays upon deposition and template lift-off [32]. However, those methods can only be used to obtain special polymeric or pseudopolymeric rings, but it cannot be used flexibly and simply to fabricate different kinds of polymeric and organic–inorganic composite nanoring arrays. Xihong et al. demonstrated a technique of selective and sequential re-assembly of two blocks of a block copolymer thin film, patterned polymer arrays, including nanoislands, nanorings, etc., can be fabricated [74]. This is a facile approach to fabricate different types of functional polymeric nanoislands, polymeric nanoring and organic–inorganic composite nanoring arrays. This report demonstrated a technique to ordered Au-polymer composite nanoring arrays by pre-loading randomly distributed Au nanoparticles inside or on a diblock polymer thin film. During re-assembly process, Au or other nanoparticles are mixed in side or placed on the surface of the block copolymer thin film that can also be moved along with the polymer blocks. So disordered Au nanoparticles inside or on the surface of the thin film will be assembled again to form similar nanopatterns as the pure polymer.

2.10 MIXED METAL COMPLEXES THIN FILM

Inorganic oxides exist in a large variety of structural geometries have found a wide range of applications in electronics, photocatalysis, solar hydrogen generation, and sensors [75], [76]. The characteristics of metal oxides are strongly dependent on their exact composition, fabrication temperature, crystal morphology, surface area, and crystallite size. Preparation of mixed metal oxides in various forms have approached by many soft chemistry methods, such as sol–gel, hydrothermal syntheses, and single-source precursor routes as well as chemical procedure such as chemical vapour deposition and aerosol assisted chemical vapour deposition method (AACVD). Liu et al. reported a synthesis procedure of free-standing 10-30 nm Lead zirconate titanate (PZT) nanoparticles with a modified sol-gel method [77]. This is the first report to synthesis free-standing PZT nanoparticles. The studies on PZT nanoparticles in a free-standing form elucidate the mechanism of ferroelectric properties in reduced dimensions as well as facilitate the applications of ferroelectric nanoparticles in advanced technologies. Muthar et al. described a high-pressure monoclinic and rhombohedral perovskite phases of PbTiO3, in which more widespread use of this promising materials could greatly advance the field [78]. The results were consistent with Wu`s principles theoretical predictions [79], but has a higher phase diagram than anticipated; moreover, the predicted electromechanical coupling at the transition is larger. This result also showed that at ambient pressure, the high electromechanical coupling in solid solutions with lead titanate is due to tuning of the high-pressure morphotropic phase boundary in pure lead titanate. It was also reveals that complex microstructures or compositions are not necessary to obtain strong piezoelectricity. Using this process, High-performance and pure electromechanical materials is possible to discovery, which could greatly decrease costs and expand the utility of piezoelectric materials. Qing et al. used sol-gel method by using a seed-mediated monodisperse spinel cobalt ferrite, $CoFe_2O_4$, nanocrystals can grow into a nearly spherical shape or an almost perfect cube in a highly controllable manner [80]. By adjusting the crystal growth rate, the shape of the nanocrystals was remarkably controlled. The shape of the nanocrystals can also be reversibly interchanged between spherical and cubic shape. Size of nanocrystal is depends on the blocking temperature, saturation, and remanent magnetization regardless of the spherical or cubic shape. But AACVD is easy to conduct, relatively simple and very versatile method among the alternative thin film deposition techniques. Using AACVD method, a single solution source can be used to fabricate multi component. This process also ensure both reproducibility and the presence of all the components in the deposited layer. Sultan et al. used Cu/ZnO mixed-metal oxide system to design and synthesis of discrete single source precursors for mixed-metal oxide composites and their subsequent use for the deposition of thin films by AACVD [81]. The microstructure, size and shape of the crystallites of films has changed by changing with substrate temperature. The crystallinity and the particle sizes are also depend on deposition temperatures. This system thus opens a new approaches towards the synthesis of nanostructured thin films of mixed metal oxide composite such as Cu/ZnO on a range of substrates and control of their microstructures.

2.11 NOVEL POLYELECTROLYTE FILM

Electronically charged polymer are very important for their relevance and importance to nanotechnology, surface engineering, and biotechnology. Polyelectrolyte brushes, which have ionic strength, pH, and solvent responsive behavior are often been used to design smart surfaces and to achieve control over surface properties, such as wettability. Well-defined metal nanoparticles (NPs) can be prepared by the confinement of metal ions (such as $AuCl_4$- and PtCl6-2) within certain polyelectrolyte films. Boyes et al. synthesized polyelectrolyte grafted membrane of either styrene or methyl acrylate and poly-(acrylic acid) modified by treatment with an aqueous solution of metal cations [82]. Zerovalent metal within the polymer brush was formed since the metal cations were reduced during treatment with H_2. Furthermore, if the brush surface is treated with H_2, it changes from smooth and featureless to having definite surface features. This was attributed to the formation of metal nanoparticles with in the polymer brush. Mei et al. present a systematic study of the catalytic activity of platinum nanoparticles immobilized on spherical polyelectrolyte brushes that act as carriers [83]. As a model reaction, they use the reduction of p-nitrophenol by sodium borohydride that can be easily monitored by UV/vis spectroscopy. The average size of divalent PtCl6-2 ions were 2 nm, which was bound as counterions within the brush layer and reduced to yield nearly monodisperse nanoparticles of metallic platinum. The reaction was pseudo-first-order with regard to p-nitrophenol and high catalytic activity was found when photometrically monitoring the reduction of p-nitrophenol by$NaBH_4$ in the presence of the nanoparticles. But it is well known that NPs show different characteristics as compared with their bulk counterparts and are of importance to application in emerging areas of nanoscience and nanotechnology. Xu et al. prepared a novel stimuli-responsive polyelectrolyte brushes of poly(N-benzyl-N0-(4-vinylbenzyl)-4,40-bipyridium dichloride) or



Scheme II. Schematic Diagram Illustrating the Preparation of P(BpyClCl) Brushes via Surface-Initiated ATRP of BpyClCl from the SiO_2-BCl NPs and of Metal Nanodots on the SiO_2-g-P(BpyClCl) Surface.

P(BpyClCl) via surface-initiated ATRP of N-benzyl-N0-(4-vinylbenzyl)- 4,40-bipyridiumdichloride P(BpyClCl) from the benzyl chloride - immobilized SiO_2 (SiO_2-BCl) NPs [84]. The exchange rate between BV2+ and BV + states of the P(BpyClCl) brushes on the SiO2 nanaoparticles can be utilized directly, instead of metal reducing agents, to decorate the NPs with metal nanodots (<5 nm) (Scheme II). The P(BpyClCl) brushes on the SiO_2 nanospheres were used as the reduction process of the metal ions was actuated by activating the P(BpyClCl) brushes with BV2+ via UV irradiation in degassed metal salt solutions. The reduction process was terminated through the introduction of air to produce the metal nanodots (SiO_2-g-P(BpyClCl)-metal NPs) after a predetermined period. These smart P(BpyClCl) brushes offer a facile route and added flexibility in the construction and preparation of high-surface-area substrates with well-dispersed metal or bimetal species.

2.12 ULTRATHIN FILM

Electropolymerization have been investigated to fabricate polymeric ultrathin films with respect to their synthesis properties, and characterization. The study of electropolymerizable monomers such as thiophene, aniline, pyrrole, and carbazole can yield unique polymerization mechanisms and electro-optical applications. Electropolymerization of 2,2`:5`,2``-

terthiophene (3T) at the interface between two immiscible electrolyte solutions (ITIES) where the interfacial potential is controlled by partitioning ions was reported by Evans-Kennedy et al. [85]. It was demonstrated that with low concentrations of 3T in the organic phase the hexamer of thiophene, sexithiophene (6T), can be synthesized at the liquid/liquid interface. Electropolymerization of terthiophene leads to the formation of highly electrochromic and conducting polythiophenes. Different thiophene oligomers species were identified spectroelectrochemically depending on the interfacial potential and the concentration of 3T present in the organic phase. Sexithiophene and its bipolaron were found as main products at low concentrations. But at higher concentrations, an insoluble black polymer was precipitated at the interface and sexithiophene radical cations and radical cation dimers were found to be present in solution. Modification of controlled living radical polymerization techniques such as surface-initiated RAFT or SI-RAFT permits the synthesis of tethered polymers with different functionalities. It provides a powerful tool for tailoring functionality and thickness of nanostructured coatings. It also exhibiting good control over molecular weight (MW), polydispersity index (PDI), composition, and macromolecular architectures. Carlos et al. focused for the first time a new route to forming surface-grafted polymers through the electropolymerization of electro-active chain transfer agent moieties followed by the homo- and diblock RAFT polymerization of different monomers from the surface [86]. In order to control molecular weight growth from the surface and maintain active “living” end groups, addition of free CTA and AIBN was performed in each case. The MW and PDI for these reaction was controlled by using the free polymer chains obtained from the solution. It should be possible to analyze various combinations of electroactive polymers and polymer compositions together with site directed electropatterning. This newly presented method opens a new favorable circumstance for further investigation and establishment of the “polymer brush” behavior under different conditions.

3 GRAFT COPOLYMERIZED HYDROGEL

3.1 RADIATION-INDUCED GRAFT POLYMERIZATION

If hydrogels are crosslinked structures and contact with water, it exhibit very low mechanical strength. To have a free movement of the hydrogels in polymer chains, it is therefore, appropriate to attach these hydrogels to another water insoluble surface by graft polymerization so that a comb like structure is produced. The grafting can be initiated by high energy radiation or a chemical means and materials with sutures, wound dressings, implants and tissue engineering may be produced [87]. The lower critical solution temperature (LCST) of the grafted polymer stays at 32 ^{o}C, but it should be above 37 ^{o}C to achieve the required task of drug delivery. S. Ikram et al. developed a smart polypropylene(PP) non- woven fabric where the drug release takes place above 37 ^{o}C in contact with the human body [88]. According to their result, the grafting parameters play a key role in the graft management within the fabric matrix. Due to the higher peroxidation at higher doses,

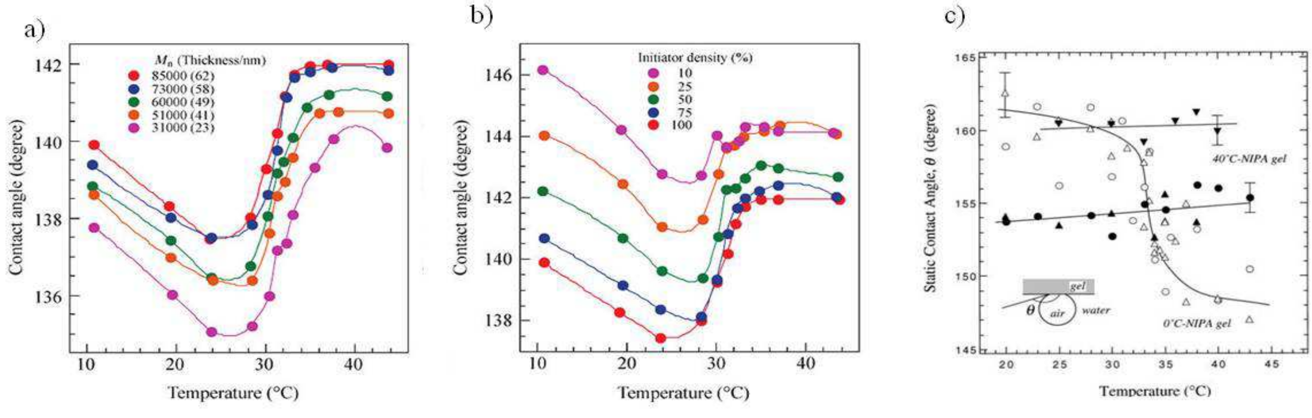


Figure 5. Contact angle of air bubble underneath PNIPA grafted membranes in water, (a) for the same high density PNIPA brushes with different molecular weight (b) for the almost same molecular weight PNIPA grafted membranes with different grafted densities, and (c) PNIPA gel surface in water as a function of temperature.

3.2 CONFLICTING BEHAVIOR BETWEEN GRAFTED MEMBRANE AND HYDROGEL

Recent progress in controlled or living radical polymerizations, which has extensive properties of the component polymer in the diluted solution can be applied in various smart soft materials with ordered architectures [89], [90], [91], [92]. As a result highly ordered soft materials can be fabricated, and their physicochemical properties are strongly influenced by molecular interactions. Synthesis and characterization of semi dilute, medium density and high density polymer brushes has been reported in many studies [93], [94], [95]. Inappropriate methods were selected for making the high-density brushes of PNIPA. Appropriate surface conditions is most important factor for attaching PNIPA to one end and the preparatory method to form grafted PNIPA for making a real high density brush of PNIPA. A high-density PNIPA brush is necessary to obtained more precise properties due to the presence of intermolecular interactions. Suzuki et al. reported the precise preparation of a high density brush of poly(N-isopropylacrylamide) (PNIPA) brush on silicon substrate by ATRP and performed a systematic study of the physicochemical properties of the brushes [44]. Sessile drop method was used to measure contact angle and examine the hydrophilicity of water-soluble polymer grafted membranes. According to their result, The contact angle decreased with an increase in temperature up to 24 ^{o}C but the value of contact angle increasing when temperature passes LCST (Fig: 5a). A similar change was observed for the PNIPA brushes, composed of different molecular weights but with nearly identical graft density (Fig: 5b). This temperature dependent contact angle result is conflicting with previously reported PNIPA hydrogel surface [96]. Atsushi et al. conducted similar experiment on PNIPA gel and found that the absolute value of contact angle at different locations decrease with increasing the temperature, where the decrement of contact angle at temperature around 32 ^{o}C become large in accordance with increment with temperature (Fig: 5c). The static contact angle versus temperature was found to be quite different between two reports. But contact angle of both PNIPA grafted membrane and PNIPA gel decrease up to around 25 ^{o}C in water, indicating that the hydrophilicity of the surface decreases gradually.

3.3 FUNCTIONALIZED POLYMER GEL

Environmental stimuli-responsive gating membranes exhibit permeability changes in response to external stimuli such as temperature, pH, ionic strength, electric field, and substance species. It can be prepared by grafting of functional polymers or graft copolymerization of functional monomers directly onto the existing porous membranes [97], [98], [99]. A functional membrane consisting of a thermo-sensitive polymer gel, PNIPAAM, on the surface and inside the pores of track-etched polycarbonate (PC) membranes, which have straight cylindrical pores with a sharp pore-size distribution was developed by Wencai et al. [100]. Their report demonstrated a fast and reversible valve switching mechanism in a small temperature range. The surface morphology data of PC membrane reveal that the pristine PC membranes has cylindrical and straight pores, having uniform pore geometry with a pore size of 0.7-0.9 µm, which was consistent with the reported 0.8 µm nominal pore size. Water contact angle result of pristine PC membrane and the PC-g-PNIPAAM membranes at 25 and 40 ^{o}C showed a reverse properties of hydrophobicity and hydrophilicity. When the temperature increased above LCST, the hydrophilic/hydrophobic transition of the grafted PNIPAAM layer on the PC-g-PNIPAAM membrane surface made the PC-g-PNIPAAM hydrophobic. A hydrophilic membrane surface is better to increase the water flux of membrane rather than a hydrophobic membrane surface. Similarly a hydrophilic pore surface should be helpful to increase the water flux of membrane than a hydrophobic pore surface.

Natural amphoteric polyelectrolyte derived from chitosan, has a wide range of biomedical applications especially in its biocompatibility such as wound dressings, artificial bone and skin, bacteriostatic agents and blood anticoagulants etc. The graft copolymerization of N-isopropylacrylamide (NIPAAm) with carboxymethylchitosan (CMCS) was carried out by Hou-feng et al. and compared with PNIPAAm gel [101]. The poly(NIPAAm-g-CMCS) hydrogel has numerous open and porous structure in swelling state to reduce the flow resistance of water molecules in or out of the hydrogel to improve temperature sensitivities. This thermosensitive and biodegradable hydrogel have been used to separate and purify some biological materials such as proteins, enzymes and amylase as well as in the drug delivery system.

4 CONCLUSIONS

The recent decade was fruitful in the development of number of stimuli-responsive polymer grafted membranes and nanoparticle-polymer composites that open a wide research area in the field of polymer. Development of polymer grafted film was approached in the understanding of intrinsic properties and envisaged therapeutic use. Some extensively unique properties of polymer grafted films, like flexibility and biomedical application associated with the in situ method of fabricating, grafted membrane have considerably enhanced their visibility in recent years. It triggered a quantum jump in research efforts leading to the optimization of new synthesis protocols, establishment of novel systems and investigation of special features and applications. The grafted film prepared by graft copolymerization of PNIMAm onto various types substrate have shown a LCST in the range of 25-33 oC. The stimuli responsive polymer films have shown an improved drug loading capacity, and a sustained release behavior. It was developed that a smart polypropylene(PP) non- woven fabric where the drug release takes place above 37 oC in contact with the human body. The grafting parameters play a key role in the graft management within the fabric matrix. Still some limitation is of grafted film in seen especially for biomedical applications. A range of materials capable of recognizing important signaling molecules with a high level of selectivity must be developed. We do believe that his review could help to develop new stimuli responsive polymer grafted film which could be utilized in various field.

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