# SURFACE AND BULK NANOSTRUCTURING OF POLYMERS USING IONIZING RADIATION

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## 1. INTRODUCTION

Ionizing radiation has long been known to be a powerful tool in modifying and controlling the properties, forms and eventually end-uses of polymeric materials for a variety of applications. Industrial applications are full of successful examples of macro scale, bulk property modifications by radiation. Extremely short wavelength of ionizing radiation however, makes it an important and useful tool in creating very small size structures in polymers. One of the the most successful such industrial applications has been known as microlithography which is based on the development submicron size features as a result of positive or negative resist character of the polymer irradiated under a mask. Lithography is not the only way of introducing nanoscale forms in polymers. Polymer surfaces or the bulk can also be structured in nanoscale by proper use of ionizing radiation. In fact very well know effects of radiation in terms of chain scission, crosslinking and grafting and even curing have been utilized for surface and/or bulk modification of polymers at nanoscale. A very interesting and promising application of radiation-induced grafting is radiation-initiated nanosurface modification for tissue engineering. By optimizing electron beam grafted responsive polymer thickness down to 100 nm, cells grown on a polystyrene substrate grafted with nanometer thick poly(N-isopropyl acrylamide) were harvested by controlling the external stimuli such as temperature. Electron beams are uniquely useful to prepare large amount of stimuli-responsive culture surfaces required for tissue engineering in a very simple way. The cell sheets thus obtained have already been clinically applied in plastic constructive surgery and ophthalmology.

The use of ionizing radiation for the preparation of nano-sized gels has been proven to be very efficient way of synthesizing these materials. Since no externally added substances are required for the crosslinking of individual polymer chains in aqueous solutions, the gels obtained by this technique are free from impurities or foreign materials. They have the potential to be used as drug, enzyme carrying agents.
Radiation-curable polymeric nanocomposites with enhanced surface-mechanical properties have been developed. Adequate electron beam curing activity was imparted on inorganic nanoparticles, e.g. silica and alumina, by grafting onto them functionalized trialkoxysilanes, yielding covalent-bonded hydrolysis-stable surface compounds. Transparent, scratch and abrasion resistant coatings were obtained by radiation curing of acrylate formulations containing high amount of nanosized modified silica and alumina fillers. Radiation curing has shown its great potential particularly in fabricating protective polymeric composite coatings. This list can be extended to include preparation of ion track membranes for use in filtration, separation of liquids and gases biological species, production of nanowires, nanotubes, sensors etc. Radiation –induced reduction of metal ions in aqueous solutions for the synthesis of nanoparticles, nanoclusters has been shown to be a simple direct method for their prepation. Preparation of microfluidic devices, lab-on-a-chips, monoliths and molecularly imprinted polymeric matrices can be achieved by using ionixing radiation.

Three directions of research on radiation formation of nanostructures have been envisaged in this project, all related to the final application of developed systems for health-care. The first part concerns the preparation of well defined nanoscale polymeric grafts (also called brushes) on cell culture devices that would allow easy detachment of cell sheets. The monomers to be grafted from the surfaces would have temperature responsive behavior to cause them undergo large volume changes upon small temperature differences for the non-invasive, non-destructive release of surface grown cell sheets. The second part of the project deals with the radiation synthesis of nanogels from aqueous solutions of hydrophilic polymers. Dilute solutions of hydrophilic polymers when irradiated with ionizing radiation acquire intramolecular crosslinks leading the formation of nanoscale insoluble polymer coils, namely nanogels. They will be further tested for drug loading and eventual release. The sizes of pristine polymer coils will be controlled by carefully monitoring the denaturing effect of some agents. The third part of the project is related to the synthesis of molecularly imprinted polymeric matrices with the ultimate aim of using them as recognitive systems, drug delivery systems. The nanoscale cavities to be produced during radiation-induced crosslinking of functional polymers around the template will be the key factor in controlling the performance of these systems in molecular imprinting.

## 2. EXPERIMENTAL

### I. Synthesis of Polymeric Brushes

**Materials.** NIPAAm (97%, Aldrich) was recrystallized twice from hexane and dried under vacuum prior to use. AA was distilled under vacuum and used immediately. The synthesis of the RAFT agent, 3-benzylsulfanylthiocarbonylsulfanyl propionic acid (BPATT), has been described elsewhere. All other chemicals and solvents where purchased from Sigma-Aldrich, Acros, and Fluka at the highest available purity and were used as received. Whatman No. 1 filter paper was used as cellulose substrate due to its high cellulose content (98% α-cellulose), lesser amount of impurities, and ease of chemical modification.

**Polymerization.** The monomers, NIPAAm and AA, were dissolved separately with BPATT in deionized water-ethanol mixture (9:1 v/v). After complete dissolution of the reactants, the stock solution was divided into 10 mL aliquots and transferred to glass sample vials. BPATT-immobilized cellulose, i.e. macro-CTA, (≈0.01 g) was also added to vials as the substrate to be grafted (the synthesis of BPATT-immobilized cellulose and the reason of using a RAFT agent immobilized surface was explained elsewhere. The vials were capped with rubber septa and deoxygenated by purging with nitrogen gas for 20 min each. The samples were placed in a shielded irradiation room with a $^{60}$Co source at ambient temperature, and then removed periodically to investigate the reaction kinetics. Monomer to polymer conversions were evaluated using $^{1}$H NMR spectroscopy. Synthesized cellulosic copolymers were purified with sufficient rinsing. Details of this purification and calculation method for graft ratio (*G.R.*, wt.%) and graft frequency (*G.F.*) were described elsewhere.

**Characterization.** $^{1}$H NMR spectra were recorded on a Bruker spectrometer (300 MHz) in $D_2O$. GPC was performed in DMAc (0.03% w/v LiBr, 0.05% BHT) at 40 $^{o}$C (flow rate 1mL min$^{-1}$) (more details on the GPC system can be found elsewhere). Contact angle (CA) measurements were achieved using a Krüss DSA100 model CA goniometer. Drop volumes were 10 μL and the average CA value was obtained by measuring the same sample in four different positions. XPS measurements were carried out on a VG ESCALAB220i-XL surface

analysis instrument with a mono-chromatized Al Kα X-ray source (more details on XPS can be found elsewhere).

**II. Preparation of Molecularly Imprinted Matrices**

**Materials**

The crosslinking agents; diethyleneglycol diacrylate (DEGDA) and polypropylene glycol dimethacrylate (PPGDMA with Mn= 560) were purchased from Aldrich (Milwaukee, USA), triethyleneglycol dimethacrylate (TEGDMA) was purchased from Aldrich (Steinheim, Germany). The template molecule, D-glucose and functional monomer, 2- hydroxyethyl methacrylate (HEMA) were obtained from Fluka (Buchs, Switzerland). The solvents; dimethyl sulfoxide (DMSO) and ethanol (EtOH) were purchased from Merck (Darmstadt, Germany). All chemicals were analytical grade and used as received.

**Synthesis of D-Glucose imprinted network**

All MIP systems with different compositions of template, crosslinking agent and functional monomer were synthesized in the presence of a solvent via radiation polymerization. In order to achieve pre-polymerization complex formation; template molecule, D-glucose was first mixed with the monomer, then with the crosslinking agent and the solvent. The crosslinking agents used were DEGDA, TEGDMA, PPGDMA; in order of increasing chain length. Crosslinking agent concentration in the polymerization mixture (monomer, crosslinking agent and template) covered a range of 10, 20, 30, and 70 % by mole. The mole ratio of D-glucose to functional monomer, HEMA, was kept as 1:3. Control matrices called non-imprinted polymers (NIPs) were synthesized with exactly the same compositions as MIPs in the absence of D-glucose. To investigate the crosslinking effect of radiation, HEMA networks were also prepared without crosslinking agent in the same manner. All MIP systems were prepared in appropriate amount of DMSO:EtOH (3:1 volume:volume) solvent mixture. Irradiations were carried out in air at ambient temperature in a Gammacell 220, $^{60}$Co-γ irradiator (Nordion, Canada) with absorbed doses changing from 1 to 15 kGy. The MIP matrices in disc forms were then placed in 200 mL of deionized water. The rinsing solutions were changed three times a day to remove the template and unpolymerized material if any. The resulting discs were then dried in air at room temperature and then placed in a vacuum oven (T=40 ºC, 100 mbar vacuum), until complete dryness.

**PAL Experiments and Data Analysis**

For positron annihilation lifetime (PAL) experiments a positron source was prepared by depositing ca. 1.8 MBq of aqueous $^{22}$NaCl on a 7 μm-thick Kapton foil having a 10x10 mm$^2$ area. After drying, the $^{22}$NaCl deposited foil was covered with foil of the same size, and the foil edges were glued with epoxy resin. A sandwich arrangement (sample-source-sample) was used. PAL experiments were carried out using a conventional fast-fast coincidence system having a time resolution (FWHM) of about 280 ps. The measurements were carried out in air at room temperature. The spectra were recorded at every 2 hours with total counts in each spectrum being of ~ $1.8\times10^6$. Then, for each type of sample, the first 5 spectra were summed together resulting in statistics of ~ $9\times10^6$ counts.

## 3. RESULTS AND DISCUSSION

The results related to characterization of nanoscale grafted poly(NIPAAm) and PAA on cellulose have been reported in detail in our papers already submitted for publication. Their responsive behaviours are outlined briefly below.

**Smart attitudes of cellulosic graft copolymers**

PNIPAAm is one of the most studied synthetic responsive polymers and it undergoes a sharp coil-to-globule transition in water around its lower critical solution temperature (LCST) of 32 $^{o}$C, changing from a hydrophilic state below this temperature to a hydrophobic state above it. PAA responds to changes in pH and ionic strength by changing coil dimensions and solubility. In general, PAA displays a broad pKa value of 4–5 and thus a proportion of its side chain carboxyls are ionized around pH 5–6. Below this pH value, a PAA-grafted surface is hydrophobic with collapsed polymer brushes whereas it becomes hydrophilic in neutral and alkaline aqueous media.

The effect of temperature on the wettability of the PNIPAAm-grafted cellulose surfaces was characterized by static contact angle (CA) measurements. At temperatures below LCST (i.e. 25 $^{o}$C), a water droplet applied to the surface had a CA of 101.4° (±2.8); however, it was gradually adsorbed into the surface and disappeared within 60 seconds. When the temperature increased to 35 $^{o}$C (i.e. above LCST) the CA was 111.0° (±3.1) with an increased stability; it was around 38° and 22° after 60 and 90 seconds, respectively, and became totally absent at the end of the second minute. The increased durability of CA above the LCST is attributed to the hydrophobicity of the surface induced by PNIPAAm grafts. However, results also indicate that the surface of cellulose was not totally covered with PNIPAAm, and the exposed areas lead to the adsorption of water due to their hydrophilicity.

The response of PAA-grafted cellulosic copolymer to change in pH was characterized by static CA measurements at pH 3 and 11. The collapse of the brushes in acid media (i.e. pH 3) was reflected by changes in the wettability of the surface: At pH 11, the ionized PAA-modified cellulose surface is hydrophilic, and the applied water droplet is rapidly adsorbed into the surface within a couple of seconds (the CA measured at the third second was 28.6° ±2.4). At pH 3, well below the pKa for PAA, the cellulose surface presents an increased hydrophobic character with a CA of 68.7° ±4.5 due to the collapse of the polymer brushes.

**HPLC Studies Using MIPs**

In order to investigate the efficiency of imprinting process on the selective separation of D-Glucose; dilute solutions of D-Galactose, D-Fructose and D-Glucose were prepared and injected into columns filled with NIPs and MIPs. Since the non-imprinted networks do not have cavities produced to selectively retain the glucose molecules, retention time of glucose in the column filled with NIPs was found to be the same for the other two monosaccharide molecules. No separation among these three saccharides was observed for NIP filled columns.

Among various MIPs prepared, DEGDA containing MIPs showed the best performance for the separation of D-Glucose as seen from Figure 3. D-glucose was retained in the column longer than the two other monosaccharides owing to the better match between the sizes of D-Glucose imprinted cavities and D-Glucose itself. Smallest cavity size obtained in the presence of this crosslinking agent and flexibility of acrylate groups compared to more rigid methacrylate groups present in the other two crosslinking agents seem to have brought a better selectivity toward D-glucose, otherwise the chemical affinity of base polymers for the

three monosaccharide samples would not be expected to be too different. This work has demonstrated the succesful formation of radiation induced molecularly imprinted matrices of D-(+)-Glucose by using appropriate crosslinking agents. For the optimization of free-volume-holes in imprinted network; crosslinkers with different chain lengths and amounts, template-functional monomer ratio, radiation dose effects were investigated via PAL and swelling experiments. The results obtained show the feasibility of controlling cavity size based on the template molecule in the imprinting system. The successful formation of MIP matrices based on hydroxyethyl methacrylate polymer and their binding/separation efficiency were checked by HPLC studies.

## REFERENCES

[1] BARSBAY, M., GUVEN, O., DAVIS, T. P., BARNER-KOWOLLIK, C. BARNER, L. "RAFT-mediated polymerization and grafting of 4-styrenesulfonate form cellulose initiated via gamma-radiation", Polymer **50** (2009) 973-982.

[2] BARSBAY, M., GUVEN, O., DAVIS, T. P., BARNER-KOWOLLIK, C. BARNER, L. STENZEL, M. H., "Verification of Controlled Grafting of Styrene from Cellulose via Radiation-Induced RAFT Polymerization", Macromolecules **40** (2007) 7140-7147.

[3] DJOURELOV, N. ATES, Z., GUVEN, O., MISHEVA, M., SUZUKI, T., "Positron annihilation lifetime spectroscopy of molecularly printed hydroxyethyl methacrylate based polymers", Polymer **48** (2007) 2692-2699

[4] ATES, Z. GUVEN, O. "Radiation induced molecular imprinting od d-glucose onto poly(2-hydroxyethyl methacrylate) matrices using various crosslinking agents", Rad. Phys. Chem. in print (2009).