RADIATION SYNTHESIS OF POLY(N-VINYL PYRROLIDONE) NANOGELS AND NANOSCALE GRAFTING OF POLY(ACRYLIC ACID) FROM CELLULOSE

Olgun Guven, Semiha Duygu Isik, Murat Barsbay, TURKEY

Summary
Ionizing radiation has long been known to be a very useful tool for the preparation of nanogels. Although preparation is straightforward, the control of the sizes of nanogels has been a challenging issue. This report shows the results of our work on using radiation for the synthesis of PVP nanogels in the range of 40-200nm by making use of the principles of solution thermodynamics of aqueous polymer solutions. Nanoscale grafting of responsive polymers however has been of scientific and industrial importance due to fine control of the molecular weight and molecular weight distribution of grafted polymers. The second part of this report deals with the grafting of poly(acrylic acid) onto the surface of cellulose, thus imparting pH response to the substrate. The use of radiation as a constant source of radical generation and Reversible-Addition-Fragmentation-Chain transfer agents for the control of free radical polymerization provided a full control over the molecular weight and distribution of poly(acrylic acid) grafts on cellulose.

1. INTRODUCTION

Irradiation of monomers and polymers with high energy radiation (Gamma rays, X-rays, accelerated electrons and swift heavy ions) leads to the formation of very reactive intermediates in the forms of excited states, ions and free radicals. These intermediates are almost instantaneously used up in several reaction pathways which result in chain reactions, disproportionation, hydrogen abstraction arrangements or formation of new bonds, structures. The ultimate effects of these reactions are the formation of polymers, oxidized products, crosslinking and/or scissioning of main or side chains, curing and grafting. The degree of dominance of these transformations depends on the nature of the polymer and the conditions of treatment before, during and after irradiation. Close control of these factors make the modification of polymers possible by radiation processing. Polymers are generally classified as predominantly undergoing degradation or crosslinking when exposed to ionizing radiation. These two major ultimate effects of ionizing radiation have been effectively used in polymer and plastics industries since the inception of radiation technology in early 1960s. Radiation processing has been exclusively confined to the modification of bulk properties of polymers. As the need to control the properties of materials at nanoscale has moved from laboratory studies into industrial applications and nanotechnology has become an important industrial reality, the ionizing radiation has been considered for nanostructuring of polymers. Radiation can be used both for top-down and bottom-up approaches for the preparation of nanomaterials. In this report two cases of bottom-up syntheses of nanostructures will be discussed, the first one is based on the radiation-induced crosslinking of poly(vinyl pyrrolidone) in its dilute aqueous solutions for the formation of nanosized gels and the other is controlled grafting of poly(acrylic acid) from cellulose surfaces.

The preparation of nanogels using ionizing radiation has been initiated by the classical works of Rosiak and Ulanski almost two decades ago. When predominantly crosslinking type of water soluble polymers are irradiated with gamma rays or accelerated electrons, intramolecularly crosslinked polymer coils are obtained in dilute solutions. Dilute solutions are required to avoid the formation of microgels or wall-to-wall gels. The individual polymer coils thus have been converted
into networks which are termed as nanogels. In similar studies of radiation-synthesis of nanogels the molecular weight of starting polymers is the determining factor for the final size of the nanogels since coil dimensions depend on molecular weights. The control of sizes of nanogels has therefore been a challenging issue and limited with the initial molecular weight of the polymer. In dilute aqueous polymer solutions however the coil sizes of polymer chains can be controlled around the Theta/Flory temperatures. At this particular temperature is approached the coils start to contract with eventual collapse at the Theta temperature resulting with precipitation. Here in this work, for the first time we used this approach and irradiated PVP solutions in acetone/water mixtures around Theta temperature to obtain nanogels of certain size. As for the second part of our work, we combined γ-radiation and Reversible-Addition-Fragmentation-Chain Transfer (RAFT) polymerization for the preparation of graft copolymers with well-defined and smart surface properties. Renewable and natural based intelligent cellulosic surfaces that respond to pH have been prepared via this facile and powerful combination. In first year of this CRP, we reported on the preparation of novel thermo-responsive cellulose surfaces of poly(N-isopropylacrylamide) (PNIPAAm) by using the same approach and in this report we discuss the preparation of pH-responsive cellulose surfaces by grafting of poly(acrylic acid) (PAA) via γ-initiated RAFT graft polymerization technique. The response of PAA grafted surfaces to changing pH values was investigated by following the changes in the contact angle of water.

2. EXPERIMENTAL PART

2.1. Synthesis of poly(N-vinyl pyrrolidone) nanogels

Poly (vinyl pyrrolidone) (BASF, $M_w = (1.278 \pm 0.023) \times 10^6$ g mol$^{-1}$ determined by static light scattering) was used as received without further purification. Acetone (Sigma-Aldrich, Chromasolve® for HPLC, 99.9%) is used without further purification and all the solutions were prepared with deionized water with a max conductivity of 0.01 μS and filtered through 0.2-μm-pore-size Durapore filters (Millipore Corp.) prior to experiments.

Poly(vinyl pyrrolidone) nanogels were synthesized via radiation induced crosslinking method in the presence and absence of acetone in aqueous solutions of PVP. All solutions were prepared freshly and placed in glass vials sealed with rubber septa and saturated with N$_2$O for 10 min prior to irradiation. Dionized water and HPLC grade solvents were used for sample preparation and analysis.

Gamma irradiations were carried out at Sarayköy Nuclear Research and Training Center, Ankara by placing the samples inside the irradiation chamber of a Gamma Cell (Tenex-Issledovatel) at ambient temperature. A $^{60}$Co source with an average dose rate of 1.34 kGy/h was used for the irradiation. Samples were taken from the chamber at different time intervals to adjust the total absorbed dose as 5, 10 and 15 kGy.

The nanogels were characterized by using nanosizer, AFM as well as SEM techniques.

2.2. RAFT-mediated grafting of PAA from cellulose

The monomer, Acrylic Acid (BDH) after standard purification step was dissolved with the RAFT agent BPATT in deionized water-ethanol mixture (9:1 v/v). The monomer concentrations and the monomer/chain transfer agent (CTA) ratios are given in Table 1. 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 vials were capped with rubber septa and deoxygenated by purging with nitrogen.
gas for 20 min each. The samples were gamma irradiated with a $^{60}$Co source at ambient temperature, and then removed periodically to determine conversion and relevant properties of the synthesized polymers. Monomer to polymer conversions was 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[6].

GPC characterization was performed in DMAc (0.03% w/v LiBr, 0.05% BHT) at 40 °C (flow rate 1mL min$^{-1}$). 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 Ka X-ray source.

3. RESULTS AND DISCUSSION

3.1. Synthesis of poly(N-vinyl pyrrolidone) nanogels

Dynamic Light Scattering Analysis

Table 1 shows the peak mean diameters, their standard deviations and polydispersity index values (PDI) for nanogels that were synthesized from 1 mg/mL and 2 mg/mL aqueous PVP solutions by using gamma radiation whereas Table 2 shows the mentioned values for 1 mg/mL and 2 mg/mL aqueous PVP solutions which were synthesized by electron beam irradiation. It can be clearly seen that 2 mg/mL concentration is rather high for this synthesis parameters both for gamma and e-beam irradiations. Especially for gamma, there is a high increase in particle size due to the formation of intermolecular crosslinks. The diameters as high as 248 nm and high PDI values support this approach where the size broadening may be a result of the combination of two processes intra- and intermolecular crosslinking occurring concomitantly. Additionally, the results were found to be very striking that 1 mg/mL gamma irradiated samples show no sensitivity to total absorbed dose which was also the same for the samples prepared in acetone/water mixtures. On the other hand e-beam irradiated samples show a substantial decrease from 59 to 46 nm as the total absorbed dose is increased to 15 kGy. These tabulated results are also collected in Figure 1 and 2 for the samples prepared by gamma radiation.
Figure 1. Effect of total absorbed dose on the peak mean diameter of PVP nanogels that are synthesized from 1 mg/mL aqueous PVP solutions by gamma radiation.

Figure 2. Effect of total absorbed dose on the peak mean diameter of PVP nanogels that are synthesized from 2 mg/mL aqueous PVP solutions by gamma radiation.
Table 1. Peak mean diameters, their standard deviations and PDI values for nanogels that are synthesized from 1 mg/mL and 2 mg/mL aqueous PVP solutions by using gamma radiation.

<table>
<thead>
<tr>
<th>gamma</th>
<th>unirradiated</th>
<th>5 kGy</th>
<th>10 kGy</th>
<th>15 kGy</th>
</tr>
</thead>
<tbody>
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<td>water</td>
<td>d (nm)</td>
<td>std dev.</td>
<td>PDI</td>
<td>d (nm)</td>
</tr>
<tr>
<td>1 mg/mL</td>
<td>58.93</td>
<td>0.75</td>
<td>0.25</td>
<td>76.84</td>
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<tr>
<td>2 mg/mL</td>
<td>63.29</td>
<td>0.37</td>
<td>0.26</td>
<td>206.60</td>
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</tbody>
</table>

Table 2. Peak mean diameters, their standard deviations and PDI values for nanogels that are synthesized from 1 mg/mL and 2 mg/mL aqueous PVP solutions by using e-beam radiation.

<table>
<thead>
<tr>
<th>e-beam</th>
<th>unirradiated</th>
<th>5 kGy</th>
<th>10 kGy</th>
<th>20 kGy</th>
</tr>
</thead>
<tbody>
<tr>
<td>water</td>
<td>d (nm)</td>
<td>std dev.</td>
<td>PDI</td>
<td>d (nm)</td>
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<tr>
<td>1 mg/mL</td>
<td>58.93</td>
<td>0.75</td>
<td>0.25</td>
<td>52.70</td>
</tr>
<tr>
<td>2 mg/mL</td>
<td>63.29</td>
<td>0.37</td>
<td>0.26</td>
<td>151.50</td>
</tr>
</tbody>
</table>

Figure 3 shows the mean particle diameters of PVP nanogels obtained from 2 mg/mL acetone/water mixtures by means of gamma irradiation. As the amount of non-solvent increases polymer-polymer interactions are increased and the contraction of coils help the system prefer intramolecular crosslinking due to shorter inter-radical distances on the same PVP chain. Additionally, Figure 3 also expresses these results in comparison with pristine PVP. A decrease from 236 nm to 44 nm is a clear evidence that this is an efficient and useful approach to control the size of PVP nanogels.

![Figure 3](image_url)

Figure 3. Effect of acetone amount in the acetone/water binary mixture on the peak mean diameter of PVP nanogels that are synthesized from 2 mg/mL PVP solutions by gamma radiation with a total absorbed dose of 15 kGy.
Size distribution of unirradiated PVP coils and PVP nanogels obtained from irradiated Acetone/water solutions are shown in Figure 4. The broad distribution observed for the pristine PVP is seen to become narrower with increasing extent of intramolecular crosslinking upon formation of the nanogels.

![Size Distribution by Intensity](image)

*Figure 4. Size distribution graph based on scattered light intensities of unirradiated PVP (blue) and PVP nanogels prepared in acetone/water mixtures with acetone ratios 0.60 (red), 0.62 (black), 0.64 (pink) and 0.66 (green) from 2 mg/mL PVP solutions using gamma rays with a total absorbed dose of 15 kGy.*

Figure 5 shows the 3D views of the AFM images of mica surface, and soluble PVP and PVP nanogel deposited mica surfaces. The change in the surface profile after the deposition of linear PVP is clearly seen where linear PVP chains coated the surface as a film. However, the background surface of mica in Figure 5-A and PVP deposited mica in Figure 5-C remains to be unchanged which is a proof of the presence of crosslinking. For 5-C small spikes arising from the deposited nanogels are clearly seen. The roughness values are 5.63 nm for mica surface, 4.91 nm for PVP coated mica surface and 12.6 nm for PVP nanogels deposited on mica surface. For better identification of PVP nanogels, cross-sectional views were also taken from previous AFM images. Nanogels deposited on mica surface were found to be of equal size and dimensions, with approximate diameters of 80 nm.
Figure 5. 3D views of AFM images of mica surface (A), PVP coated mica surface (B), PVP nanogels deposited on mica surface (C).

3.2. Synthesis of RAFT-grafted PAA from cellulose

Table 3 and Figure 5 and 6 summarize the results of homo polymers formed during the graft polymerization of AA from cellulose substrate under γ-irradiation at room temperature in aqueous media.

Table 3. Reversible addition fragmentation chain transfer (RAFT) graft polymerization of AA by γ-initiation (0.02 kGy·h⁻¹) with BPATT as the RAFT agent

<table>
<thead>
<tr>
<th>Entry</th>
<th>Monomer</th>
<th>([\frac{[M]_0}{[CTA]}])_b</th>
<th>time (min)</th>
<th>Convn^b (%)</th>
<th>G.R.^c wt.%</th>
<th>G.F.(^c)</th>
<th>(M_{n,\text{theor}})^c (g mol⁻¹)</th>
<th>(M_{n,\text{SEC}})(^d) (g mol⁻¹)</th>
<th>PDF(^d)</th>
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<tbody>
<tr>
<td>1</td>
<td>AA</td>
<td>285</td>
<td>390</td>
<td>21</td>
<td>&lt;2</td>
<td>1.14</td>
<td>4 590</td>
<td>8 800</td>
<td>1.24</td>
</tr>
<tr>
<td>2</td>
<td>AA</td>
<td>285</td>
<td>630</td>
<td>47</td>
<td>5</td>
<td>1.97</td>
<td>9 920</td>
<td>13 300</td>
<td>1.12</td>
</tr>
<tr>
<td>3</td>
<td>AA</td>
<td>285</td>
<td>750</td>
<td>51</td>
<td>6</td>
<td>2.14</td>
<td>10 740</td>
<td>14 100</td>
<td>1.26</td>
</tr>
<tr>
<td>4</td>
<td>AA</td>
<td>285</td>
<td>990</td>
<td>73</td>
<td>9</td>
<td>3.04</td>
<td>15 260</td>
<td>19 500</td>
<td>1.17</td>
</tr>
<tr>
<td>5</td>
<td>AA</td>
<td>285</td>
<td>1440</td>
<td>93</td>
<td>14</td>
<td>3.45</td>
<td>19 360</td>
<td>23 100</td>
<td>1.19</td>
</tr>
<tr>
<td>blank</td>
<td>AA</td>
<td>-</td>
<td>630</td>
<td>&gt;98</td>
<td>8</td>
<td>0.11</td>
<td>-</td>
<td>397 200</td>
<td>2.62</td>
</tr>
</tbody>
</table>

\(^a\)AA content in the graft polymerization was higher than 98%.
RAFT graft-polymerization of [AA]₀ = 2 mol L⁻¹ from BPATT functionalized cellulose (∼0.01 g) initiated via γ-irradiation (0.02 kGy h⁻¹) in water-EtOH (9:1 v/v) at room temperature. Monomer conversion was determined from NMR analysis. See ref. [15] for the details of $G.R$, $G.F.$, and the theoretical number-average molecular weight, $M_n$theor, calculations. Number-average molecular weight, $M_n$, and polydispersity indices, PDI, determined via size-exclusion chromatography, SEC, using DMAc as eluent with polystyrene standards for the non-grafted polymers formed during grafting. The filter paper was not modified with BPATT but subjected to polymerization conditions and no free BPATT was added to the medium.

As can be seen from Table 3, the apparent number-average molecular weights, $M_n$, obtained using polystyrene standards are almost comparable to the theoretical $M_n$ values of PAA. The polydispersity indices (PDI) of the resulting polymers are narrow, i.e., PDI ≤ 1.26, indicating a well-controlled polymerization occurred via the RAFT process. The difference between the theoretical and the experimental molecular weights can be attributed to the calibration of the GPC on the basis of polystyrene equivalents, universal calibration. In addition to the RAFT-mediated graft polymerizations, conventional graft-polymerizations were also achieved (denoted as blank in Table 3) and comparison of the results clearly confirms the controlled fashion and success of the graftings mediated via RAFT (compare the $M_n$, PDI and $G.F.$ values). As can be seen from Figure 5a the GPC traces are unimodal and narrow at all conversions.

Moreover, it is obvious that the molecular weight increases linearly with conversion (see Figure 5b where the number-average molecular weight, $M_n$, and the PDI evolutions with the conversion are depicted) which again demonstrates the well-defined behavior of the grafting for AA under the mentioned reaction conditions.

XPS was used to confirm the grafting of AA from cellulose. The surface chemical compositions calculated using the peak areas of the XPS survey wide scans indicate significant changes following the grafting: the C atom amount increases from 62.8% to 69.0% whereas the O atom amount decreases from 34.1% to 30.7% for the copolymers of PAA, respectively (see the quantification results inserted to the C1s XPS spectra in Figure 5A, C). The C1s XPS spectra show a considerable change in carbon atom amounts in different functional groups: the C1s spectrum of BPATT-immobilized cellulose (Figure 6A) consists of a main peak with a bonding energy (BE) of 286.5 eV attributed to C-O bonds. However after the grafting of AA, the main peaks appear at 285
eV, attributed to non-oxygenated C, i.e. C-C, C-H bonds. These results confirm the successful grafting of PAA from cellulose.

Responsive behavior of graft polymers

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 response of 14% 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. The representative figure for this phenomenon is shown on Figure 6.

Figure 5. C 1s XPS spectra of (A) BPATT-immobilized cellulose; (C) cellulose-g-PAA copolymer with 14% graft ratio. The percentages inserted to C 1s spectra show the surface chemical compositions calculated using the peak areas of the XPS survey wide scans.

Figure 6. Contact angle of PAA grafted cellulose surface at (A) pH=11, (B) pH=3.
Conclusions
We have shown that by considering the fundamental aspects of polymer aqueous solution thermodynamics to control the sizes of polymer coils it is possible to convert these soluble chains into intramolecularly crosslinked network structures by gamma irradiation or EB treatment. PVP nanogels of different sizes with rather low size distributions were thus synthesized in the range of 40-240nm. It has also been shown that by combination of γ-radiation and RAFT polymerization graft copolymers with well-defined and smart surface properties can be easily prepared. Renewable and natural based intelligent cellulosic surfaces that respond to pH have been prepared for the first time via this facile and powerful combination.

REFERENCES