Graft Polymerization Initiated by Photosensitizer Segregated at Surface of Polymer Film upon Ultraviolet Irradiation

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A novel approach to surface modification of polymer films is proposed on the basis of graft polymerization initiated from photosensitizers attached to hyperbranched polymers which are localized at the film surface.

Surface modification of polymer materials without changing the bulk has prompted extensive studies based on a wide variety of chemical and physical methods due to scientific interests as well as industrial applications.[1] Graft polymerization is one of promising techniques for the purpose and possesses a unique feature that the surface chemistry can be voluntarily controlled if the system is adequately chosen.[2,3]

The graft polymerization of vinyl monomers is mainly categorized into two ways such as "grafting from" and "grafting onto" methods.[4–9] In the former case, the polymerization reaction is initiated from activated species at the surface to be modified. To realize this, the polymer is generally treated with γ-ray radiation, ozone, plasma, light, etc. The alternative "grafting onto" method is that polymer chains with activated species react with the surface. Thus, there should exist functional groups, which terminate the activated species in the polymer chains so as to attain a high grafting yield. Although both methods have advantages and disadvantages, from the practical point of view, the former seems to be better in terms of applicability to monomers as well as polymers, controllability for thickness, grafting yield, etc. Especially, a "grafting from" method, which does not need large facilities, is desired in industry.

In this letter, we propose an easy and practical method to localize a photosensitive initiator at the surface of a polymer film and present the performance of a successive graft polymerization using the initiator. Our strategy is to use a hyperbranched polymer with a photosensitive initiator at the end portions. The hyperbranched polymer is mixed into a polymer, which possesses the surface to be modified, with a dilute concentration, and is selectively partitioned to the surface mainly owing to an entropic factor. Then, polymerization is initiated from the surface upon light irradiation. Our method basically accepts any kinds of monomers, matrix polymers and hyperbranched polymers.

Hyperbranched polystyrene (HBPS) with dithiocarbamate (DC) end groups, as schematically shown in Figure 1a, was synthesized.[10] A styrene unit basically possesses one DC group in a molecule. As a linear component, monodisperse polystyrene (PS, Aldrich Chem. Co.) was used. Number-average molecular weights (M_n) of HBPS-DC and PS were 4.9 k and 1.55 M, respectively. Blends of HBPS-DC and PS (5/95 wt %) were prepared by mixing each toluene solution. Blend films with the thickness of about 200 nm were spin-coated from toluene solutions onto silicon wafers. These films were annealed in water under Ar bubbling for 15 h at 358 K so that HBPS-DC was segregated at the surface.

Graft polymerization of *N*-isopropylacrylamide (NIPAAm, Kanto Chemical Inc.) was carried out in a setup shown in Figure 1b. The HBPS-DC/PS film, in which HBPS-DC was segregated at the surface, was placed at the bottom in a tube, and then, 10 wt % solution of NIPAAm was gently poured in it. After Ar bubbling in the solution to degas for 1 h, the tube was sealed under vacuum. UV light generated from a mercury-xenon lamp (Hamamatsu L8251) was shed onto the film for 3 h at 323 K through a color filter (UV-33, Toshiba Glass Co.), which can pass UV light with the wavelength larger than 330 nm. The absorption edge of NIPAAm was approximately 325 nm, whereas that of the DC groups was 365 nm. Thus, only the DC groups were cleaved by UV light, leading to the graft polymerization of NIPAAm from the surface of the HBPS-DC/PS film. If the filter was not used, the polymerization reaction proceeded much faster. However, the bulk polymerization of NIPAAm simultaneously occurred because the double bonds of NIPAAm were also cleaved by the UV light with shorter wavelength. The intensity of illumination was 15 mW·cm^{-2}. After the graft polymerization, the film was well washed in ethanol and was dried under vacuum at room temperature. The grafting layer grown from the HBPS-DC/PS surface was characterized by X-ray photoelectron spectroscopy (XPS, PHI 5800 ESCA system, Physical Electronics, Co., Ltd.), dynamic mode atomic force microscopy (AFM, SPA 300HV, SII Nanotechnology, Inc.) and water contact angle measurement (Kyowa Interface Science Co., Ltd., DM500).

Figure 2 shows XPS (a) nitrogen 1s (N_{1s}) and (b) carbon 1s (C_{1s}) spectra for the HBPS-DC/PS films. Take-off-angle of photoelectrons was set to be 15°, meaning that the current analytical depth of the measurement was approximately 2.7 nm. When the HBPS-DC/PS film was annealed under vacuum, the N_{1s} peak was not observed at all, indicating that HBPS-DC with the surface free energy higher than that of PS

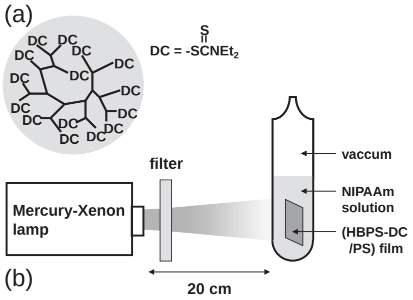

Figure 1. Schematic representations of (a) HBPS-DC and (b) setup for surface graft polymerization.

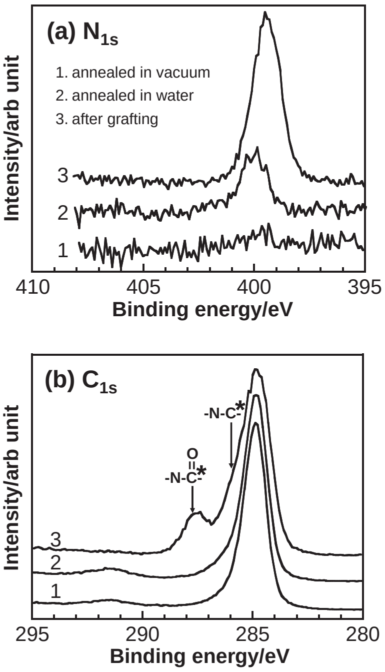

Figure 2. XPS spectra for HBPS-DC/PS film before and after graft polymerization of NIPAAm: (a) N_{1s} and (b) C_{1s}.

was depleted at the film surface. This is simply because the aggregation state is stable under vacuum. Hence, using the HBPS-DC/PS film annealed under vacuum, the graft polymerization of NIPAAm from the film surface was not attained. On the other hand, if the HBPS-DC/PS film is annealed in water, the DC groups should be preferentially segregated at the outermost region of the film to minimize the interfacial energy with water. Actually, the observation of N_{1s} peak for the HBPS-DC/PS film, shown in the panel (a) of Figure 2, is a clear signature for this. Interestingly, as the film was exposed to the air for a long time, HBPS-DC migrated into the bulk even at room temperature (not shown), because the surface covered with HBPS-DC was unstable under air. However, as long as the surface, at which HBPS-DC was enriched, was consumed for the graft polymerization within 2 days, a well-defined PNIPAAm layer was formed from the film surface, as later discussed. This is a key to our surface graft polymerization.

Once the surface, at which the DC groups were segregated, was exposed to the UV light in the NIPAAm solution, the surface was chemically modified. On the C_{1s} spectrum, a peak assigned to carbonyl carbons was observed at the binding energy of ca. 288 eV, as shown by the curve 3. Also, a shoulder corresponding to carbons bonded to nitrogen was seen at the binding energy of 286 eV. In addition, the intensity of the N_{1s} peak increased and the peak binding energy was slightly shifted toward a lower side. These are essentially the same as those of the PNIPAAm film and thus make it clear that the PNIPAAm layer was formed on the surface of the HBPS-DC/PS film. Although the depth profiling of the PNIPAAm layer is not shown for a reason of space, the layer thickness was approximately 8.5 nm. Of course, it was definitely possible to regulate the layer thickness by changing power of illumination, temperature, solution concentration, etc. Surface morphology of the HBPS-DC/PS film before and after the graft polymerization was observed. The root-mean-square roughness of the HBPS-DC/PS film before and after the graft polymerization was 0.48 ± 0.10 and 0.74 ± 0.13 nm, respectively, implying that the PNIPPAm layer was uniformly formed at the surface of the HBPS-DC/PS film.

We now turn to surface wettability of the HBPS-DC/PS film. The water contact angle (θ_w) of PS and PNIPAAm films at room temperature was 90.3 ± 0.5 and $62.6 \pm 3.4^\circ$, respectively. Since PNIPAAm was soluble in water at room temperature, the contact angle was defined as a value 1 s after placing a water droplet on the surface. Besides, the θ_w value of the HBPS-DC/PS film before and after the water annealing was 88.4 ± 0.6 and $87.3 \pm 0.3^\circ$. The difference in the two was whether HBPS-DC was existed at the surface. This indicates that the presence of HBPS-DC does not so alter the wettability of PS. On the other hand, the θ_w value decreased to be $71.1 \pm 1.5^\circ$ after the graft polymerization of NIPAAm. Therefore, it can be claimed that the surface modification of PS was successfully achieved. A point should be addressed is why the θ_w value of the PNIPAAm/HBPS-DC/PS film was larger than that of the homo PNIPAAm film. PNIPAAm chains would be dissolved into water right after a droplet was placed on the surface. Thus, the θ_w value might result from the contribution of the hydrophobic HBPS-DC/PS surface.

In conclusion, the ultrathin graft layer could be successfully formed on polymer surfaces based on a newly proposed "grafting from" method via the surface localization of a photosensitive initiator. If a cross-linking agent is mixed into monomers, an ultrathin gel layer can be formed on the polymer film. We believe that if an initiator connected directly to hyperbranched polymers is adequately chosen, surface graft polymerization even with a living manner will be realized on the basis of the method proposed here.

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References

1 C. M. Chan, *Polymer Surface Modification and Characterization*, Hanser Publishers, New York, **1993**.
2 B. Zhao, W. J. Brittain, *Prog. Polym. Sci.* **2000**, *25*, 677.
3 A. Bhattacharya, B. N. Misra, *Prog. Polym. Sci.* **2004**, *29*, 767.
4 A. Halperin, M. Tirrell, T. P. Lodge, *Adv. Polym. Sci.* **1992**, *100*, 31.
5 P. Mansky, Y. Liu, E. Huang, T. P. Russell, C. Hawker, *Science* **1997**, *275*, 1458.
6 T. Otsu, *J. Polym. Sci., Part A: Polym. Chem.* **2000**, *38*, 2121.
7 Y. Tsujii, K. Ohno, S. Yamamoto, A. Goto, T. Fukuda, *Adv. Polym. Sci.* **2006**, *197*, 1.
8 T. Matsuda, *Adv. Polym. Sci.* **2006**, *197*, 67.
9 M. Kobayashi, R. Matsuno, H. Otsuka, A. Takahara, *Sci. Tech. Adv. Mater.* **2006**, *7*, 617.
10 K. Ishizu, A. Mori, *Macromol. Rapid Commun.* **2000**, *21*, 665.