Macromolecules **2007,** *40,* 756−759

Direct Construction of Discrete Large Spherical Functional Particles onto Organic Material Surfaces by Photografting Polymerization

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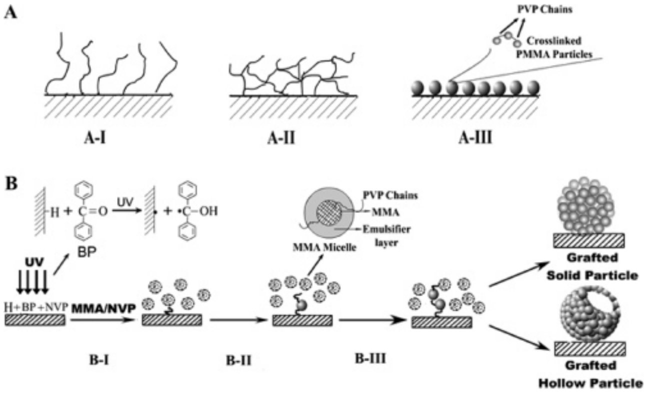
Received September 28, 2006
Revised Manuscript Received November 23, 2006

Photografting polymerization is an effective surface modification method that has been extensively studied during the past decades.[1] Its chemical principle generally involves UV irradiation of the substrate enabling excited photoinitiators (e.g., benzophenone (BP)) to abstract active hydrogen atoms (C−H) from the surface of the polymer substrate. Subsequently, surface free radicals initiate the in-situ polymerization of monomers attached to the substrate. As the polymerization proceeds, surface graft chains or polymer brushes are formed.[2] The advantages of photografting as opposed to other grafting methods consist in the irradiation, initiation, and polymerization being carried out in situ and thus being readily performed. It is also a versatile method for all organic polymeric materials as a result of the abstracting-H chemistry.[3]

In contrast to metals or inorganic materials, organic polymers belong to soft materials,[4] whose surfaces are easily modified by the grafting of polymer brushes (Scheme 1, A-I).[5] Numerous specific properties or functions (e.g., photoelectronic,[6] separating,[7] biological,[8] etc.) can be introduced to the material surfaces.[5b] However, the inherent softness also causes a number of issues in practical applications, for instance (1) surface instability, i.e., the structure of a surface with grafted polymer brushes is readily affected and reconstructed by the surroundings;[9] (2) mechanical instability, i.e., for applications where adhesion or friction resistance is of importance, the thin (generally nanoscale) grafted layer formed by the polymer brushes cannot provide enough mechanical strength; and (3) in applications where reaction agents, catalysts, and bio- and/or optical-electronic functions are required, insufficient surface functional groups are always a concern.[10] One general solution to the above issues is to increase the thickness of graft layers by regrafting or crosslinking the polymer brushes (Scheme 1, A-II),[11] but this always results in the loss of bending properties or flexibility of the organic substrate as well as the loss of transparency.

In order to solve the problems stated above, research in our group has dealt with a series of investigations concerning conventional emulsions or microemulsions to be used as photografting media. Some interesting results were achieved by this method, such as the formation of multilayered or monolayered solid nanoparticles that were immobilized on the surface of biaxially oriented polypropylene (BOPP) films.[12] More recently, we have developed a novel technique called in-situ polymerization stringed assembly (SPSA). This method enables cross-linked poly(methyl methacrylate) (PMMA) nanoparticles (60 nm), used as building blocks, to be covalently linked by poly *N*-vinylpyrrolidone (PVP) chains, subsequently leading to robust microscale solid/hollow spherical particles formed through a microemulsion polymerization.[12d]

Scheme 1. (A) Illustration of Three Kinds of Grafting Topographies with (A-I) Polymer Brushes, (A-II) a Thick Layer of Cross-Linking Polymer Brushes, and (A-III) Discrete Spherical Polymer Particles; (B) Chemical Scheme for the Fabrication of Assembled Microparticles by SPSA with the Formation of (B-I) the Precursors, (B-II) the Primary Particles, and (B-III) the Assembled Solid/Hollow Particles



As a continuation of the work described above, the present study presents the in-situ construction of discrete cross-linked spherical particles on the surfaces of polymer substrates (Scheme 1, A-III). This work combined chemistry with nano-/mesoscale topography modification. Considering the increased surface roughness, the present approach has a number of potentially interesting features,[12b,13] which may deeply improve interfacial properties when used for adhesion, printing, and coating. It increases the surface concentration of functional groups by several orders of magnitude. It is robust and remains almost unaffected by surroundings, so the original bulk properties of the polymer material, including its flexibility, can be maintained.

The present study is based on the principle of SPSA, and the synthetic route is illustrated in Scheme 1B. A BOPP film was selected as the organic substrate. *N*-Vinylpyrrolidone (NVP) was chosen as the linker monomer since its amphiphilic property enabled it to be either dissolved in the water phase or adsorbed onto the BOPP surface and also because of its ability to complex with metal ions, which would fulfill the requirement for "functional particles". The photoinitiator BP that was precoated on the surface of the BOPP film confined the initiation to begin from the substrate's surface under UV light. These in-situ surface free radicals initiated the polymerization of the NVP monomers onto and/or near the surface where they formed PVP chain radicals. These chain radicals then reacted according to SPSA as reported previously[12d] and resulted in the formation of microscale, solid or hollow particles tethered to the surface of the BOPP film. By subsequently introducing nanosized Ag particles on/in these microscale solid particles functionalized by PVP, a facile direct construction of spherical functional particles onto an organic material surface can be developed. This materials design (Scheme 1, A-III) and the bottom-up synthesis strategy (Scheme 1, B) are original and are therefore expected to attract the attention of scientists in the fields of chemistry and materials science.

As reported previously, only nanoparticles (i.e., 60 nm in diameter) were found to be tethered to the surfaces of the BOPP films when a routine MMA microemulsion (20 wt % MMA)

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10.1021/ma062252b CCC: $37.00

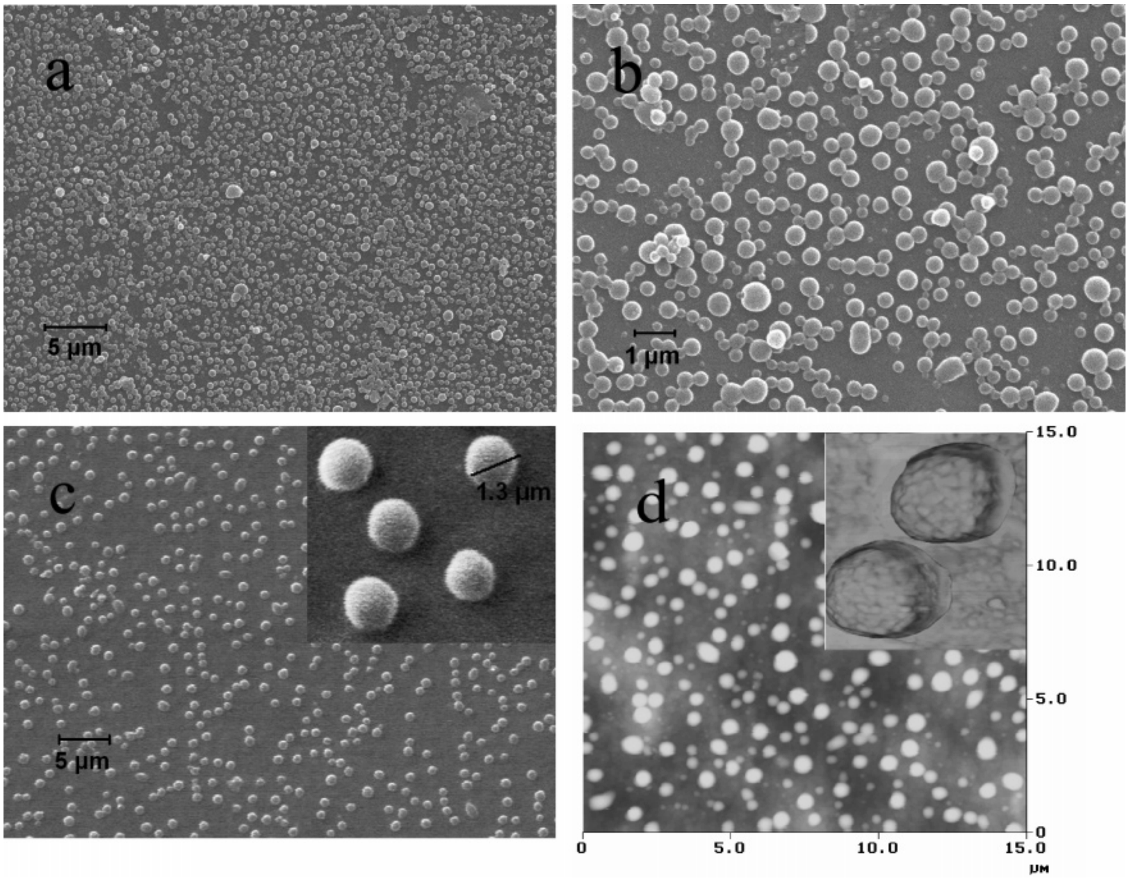

Figure 1. Micrographs displaying the topography of BOPP films grafted with PMMA/PVP particles. The MMA concentration was 20 wt %, the BP concentration 5×10^{-2} wt %, the UV intensity 7 KμW/cm^2, and the irradiation time 10 min at room temperature. (a, b) SEM images where the NVP concentration was 5 wt % and the particle diameter ∼550 nm. (c) SEM image where the NVP concentration was 20 wt % and the particle diameter ∼1.3 μm; the inset displays a side view image. (d) AFM image where the NVP concentration was 5 wt %; the inset displays the AFM phase image showing how the large particles were made up of nanoparticles.

was used.[12b] When a pure NVP aqueous solution was photografted on the BOPP films, a morphology of a cloudlike grafted layer appeared.[12c] However, some remarkable changes were observed when a two-monomer microemulsion of MMA/DVB (divinylbenzene) + NVP was used for the surface photografting (Figure 1a−d). All observed particles could be regarded as tethered to the surface of the BOPP film seeing as the grafted films had been thoroughly cleaned (extracted with methanol/deionized water and oscillated in an ultrasound bath). Most particles appeared to have a completely spherical shape, and the particle sizes were drastically increased, reaching microscale instead of nanoscale. In fact, the size of the spherical particles could be tuned from 0.35 to 1.3 μm by controlling the concentration of NVP (3 to 20 wt %, see Supporting Information) in the microemulsion. It was considered that the NVP was mainly used for the assembly of the PMMA nanoparticles. When the original BP concentration was set, the increase in NVP dosage enabled more PMMA nanoparticles to participate in the formation of the spheres.

Atomic force microscopy (AFM) (Figure 1d, inset) further revealed that the surface grafted particles were closely assembled by a number of primary particles, with mean sizes of ∼60 nm. These similar particles have been obtained in the microemulsion polymerization[12d] and been proved to have an assembled supramolecular structure, where solid cross-linked PMMA nanoparticles served as the building blocks and the PVP chains as linked wires.

In the previous report,[12d] the location of the initiating center was hard to confirm due to the complexity of the microemulsion system. Thus, there was a lack of direct evidence to confirm the SPSA technique. In the case of the surface grafting system, on the other hand, the experiment was designed so that the initiating reaction could start from the BOPP surface, and thus, the assembled particles could be seen as a most direct proof of the SPSA technique. The chemistry and procedure of the SPSA method could thereby be described (according to Scheme 1B) as follows:

(1) Surface initiation (Scheme 1, B-I). Under UV irradiation, the BP that was precoated on the BOPP film abstracted hydrogen atoms from the surface. The numerous surface free radicals[14] that were formed directly initiated the NVP (attached on the surface) to form grafted PVP chains since the amphiphilic NVP had a better affinity for the BOPP surface than MMA.

(2) Formation of primary particles (Scheme 1, B-II). The PVP chains with propagating radicals easily rearranged themselves into micelles (MMA/DVB) due to their good affinity to the used cationic surfactant hexadecyltrimethylammonium bromide (HTAB). The radicals then caused a cross-linked polymerization in the micelles leading to the formation of primary cross-linked PMMA nanoparticles.

(3) Formation of the assembled particles (Scheme 1, B-III). As is well-known, the termination between chain radicals is greatly suppressed in micelles. Therefore, the durable propagating radicals had a chance to move to the interfaces of the micelles and initiate the polymerization of the NVP monomers either there or in the water phase. The formed PVP linking chains could then reenter other micelles to continue the cross-linking polymerization.

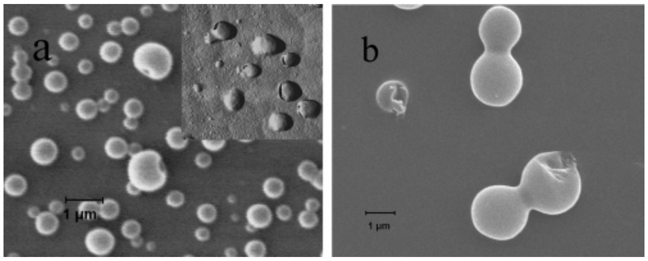

Figure 2. SEM micrographs of the topographies of the films grafted with hollow particles. The NVP concentration was 10 wt %, the BP concentration 5×10^{-2} wt %, the UV intensity 7 KμW/cm^2, and the irradiation time 10 min at room temperature. (a) A microemulsion containing 15 wt % MMA. Inset: an AFM phase image showing the hollow structure of the particles. (b) A microemulsion containing 10 wt % MMA.

By repeating the three above steps, large assembled particles were formed and tethered on the film surface. Furthermore, it should be noted that also this assembled system had an amphiphilic character and preferred to form micelles, thus allowing the self-assembly of spheres.

Self-assembly through noncovalent interactions, such as van der Waals forces,[15] hydrogen bonding,[16] electrostatic forces,[17] $\pi-\pi$ interactions,[18] and capillary force,[19] between the building blocks has been extensively reported to give rise to well-defined two- or three-dimensional superstructures. Compared to these kind of noncovalent assemblies, the covalent bond assembly should provide more stable structures. Consequently, our bottom-up SPSA technique not only is an original method for obtaining a covalent bonding assembly but also provides a novel approach in order to get more robust functional particles.

In order to further reveal the effect of the mass ratio of MMA to NVP on the morphology of the final grafted particles, the MMA concentration was decreased in the original microemulsion. An MMA concentration below 15 wt % resulted in hollow or incomplete particles appearing on the surface (Figure 2). The AFM phase image (Figure 2a, inset) clearly showed the hollow structure of these grafted particles. A slight difference in the SEM image and AFM image may depend on the different observing modes by the two methods (SI Figure S3). Similar results have previously been observed in the polymerization of an MMA/NVP two-monomer microemulsion system.[12d] It was considered that with a fixed amount of NVP in the feed a decreased dosage of MMA would logically cause a decrease in the yield of PMMA nanoparticles. Consequently, the shortage of PMMA nanoparticles would result in the incomplete assembly of particles in the fast photopolymerization.

Moreover, a further utility of being able to assemble discrete functional particles on the flexible BOPP substrate could be demonstrated by a routine silver (Ag) experiment. As is commonly known, PVP has the ability to complex with noble metals.[20] Nanoparticles of noble metal have attracted a great interest in the field of optical devices as a result of their associated strong surface resonance.[21] A generation of diverse Ag nanostuctures in the presence of PVPs has been reported elsewhere.[11a,22,23] In the present study, the primary particles grafted on the BOPP surface were connected by PVP chains, and therefore the films grafted with these PMMA/PVP assembled particles could be further functionalized by preparing polymer/Ag alloy membranes. In experiment, an $AgNO_3$ solution was first infiltrated into the graft particles. The ionic Ag^+ was then reduced in situ to elementary Ag. As shown in Figure 3, the Ag nanoparticles could be clearly recognized, and Figure 3b portrays Ag nanoparticles formed inside a hollow particle. The fact that the samples had experienced oscillation through

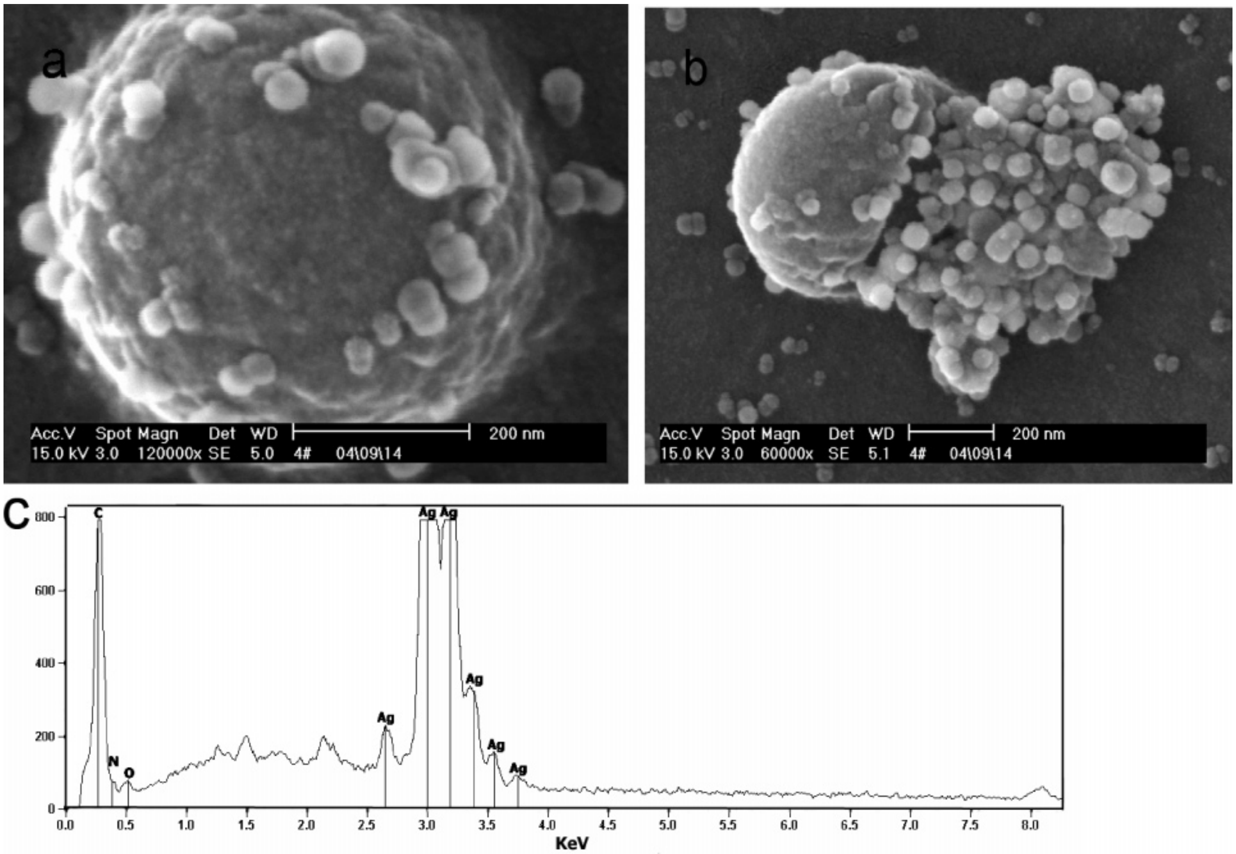

Figure 3. SEM micrographs displaying the morphologies of (a) a solid graft particle complexed with Ag with an original particle diameter of ~550 nm, (b) a hollow graft particle complexed with Ag with an original particle diameter of ~350 nm, and (c) an EDS spectrum of the film corresponding to (b).

an ultrasound treatment proved that there existed a good affinity between the Ag nanoparticles and the matrix. Figure 3c displays a spectrum obtained by energy dispersive spectrometry (EDS), and it is clear from the spectrum that both the elements N (belonging to PVP) and Ag could be recognized.

In summary, a novel method for constructing surface assembled particles was designed. By this surface SPSA method, microscale spherical particles could be directly fabricated on the surfaces of organic substrates. A two-monomer microemulsion of MMA/DVB (hydrophobic phase) and NVP (hydrophilic phase) was employed as the photografting medium. The obtained SEM and AFM images showed that grafted assembled particles (either solid or hollow) with tunable sizes (350 nm−1.3 μm) were tethered on the surface of the substrate. AFM image revealed that the grafted particles were made up of numbers of primary nanoparticles. These particles could be grafted to the films as a result of them containing PVP, and subsequently an in-situ reaction could give rise to the formation of Ag nanoparticles on/in the functional spheres.

Acknowledgment. This work was supported by the Major Project of the National Science Foundation of China (No. 50433040) and the Major Project (XK100100433) for Polymer and Physics Subject Construction from Beijing Municipal Education Commission (BMEC).

Supporting Information Available: Details regarding the surface photografting procedures, the size control of grafting supramolecular particles, and ATR-FTIR characterization and analysis of the surface functional groups. This material is available free of charge via the Internet at http://pubs.acs.org.

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MA062252B