Surface-Graft Hyperbranched Polymer via Self-Condensing Atom Transfer Radical Polymerization From Zinc Oxide Nanoparticles

Peng Liu, Tingmei Wang
1 State Key Laboratory of Applied Organic Chemistry, Institute of Polymer Science and Engineering, College of Chemistry and Chemical Engineering, Lanzhou University, Gansu 730000, People’s Republic of China

2 State Key Laboratory of Solid Lubrication, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, Lanzhou 730000, China

We present the synthesis of hyperbranched polymer grafted zinc oxide (ZnO) hybrid nanoparticles by self-condensing vinyl polymerization (SCVP) via surface-initiated atom transfer radical polymerizations (SI-ATRP) from ZnO surfaces. ATRP initiators were covalently linked to the surfaces of ZnO particles, followed by SCVP of an initiator-monomer (“inimer”) which has both a polymerizable group and an initiating group in the same molecule. Well-defined polymer chains were grown from the surfaces to yield hybrid nanoparticles comprised of ZnO cores and hyperbranched polymer shells having multifunctional chlorobenzyl functional end groups. The percentage of grafting (PG%) achieved 429% in 6 h, calculated from the elemental analysis results. The hybrid nanoparticles were also characterized using Fourier transform infrared spectroscopy, UV–vis absorption spectroscopy, thermogravimetric analysis, X-ray photoelectron spectroscopy, and transmission electron microscopy.

INTRODUCTION

In recent years, much attention has been paid to the use of controlled/“living” polymerizations from flat [1] and nano [2] surfaces, because this allows better control over the target molecular weight and molecular weight distribution of the target polymer [3]. By using the techniques, a high grafting density and a controlled film thickness can be obtained, such as brushes consisting of end-grafted, strictly linear chains of the same length with the chains forced to stretch away from the surfaces [4–8].

Highly branched polymers play an increasingly important role in interface and surface science, since their distinctive chemical and physical properties can be used advantageously as functional surfaces and as interfacial materials [9–12]. Because of the highly compact and globular shape as well as the monodispersity, for example, dendrimers attached to flat and nano [13, 14] surfaces are useful for many applications. The self-condensing atom transfer radical polymerization techniques had been successfully applied for the graft hyperbranched polymers from various surfaces, such as silica [15], silicon [16], and carbon nanotubes [17]. These reactions are based on an initiator-monomer (“inimer”) of the general structure AB*, where the double bonds are designated A and B* are groups capable of initiating the polymerization of vinyl groups.

Zinc oxide (ZnO), a wide bandgap (3.4 eV) II–VI compound semiconductor, has a stable wurtzite structure with lattice spacing \( a = 0.325 \text{ nm} \) and \( c = 0.521 \text{ nm} \). It has attracted intensive research effort for its unique properties and versatile applications [18–22]. Based on these remarkable physical properties and the motivation of device miniaturization, large effort has been focused on the synthesis, characterization, and device application of ZnO nanomaterials [23–25] and the polymer modified ZnO nanomaterials [22, 26–28].

The self-condensing vinyl polymerization (SCVP) of \( p \)-chloromethyl styrene (CMS) using metal-catalyzed living radical polymerization catalyzed by the complex CuCl/2,2’-bipyridyl has been attempted [29]. In the present work, hyperbranched polymer was grafted from the surfaces of ZnO nanoparticles via the surface-initiated self-condensing atom transfer radical polymerization technique using CMS as inimer and 1,10-phenanthroline/Cu(I)Br as catalyst (Scheme 1). Differing with the works...
reported, the polymerization was conducted only with the inimer without any other comonomer.

**EXPERIMENTAL SECTION**

**Raw Materials**

The ZnO nanoparticles used were MN6Z, with average particle size and surface area of $25 \pm 5$ nm and $50 \pm 10$ $\text{m}^2/\text{g}$, obtained from Zhoushan Mingri Nano-materials Co., Zhejiang, China.

$\gamma$-Aminopropyltriethoxysilane (APTES) (Gaizhou Chemical Industrial Co. Ltd., Liaoning, China) was used as received. Both bromoacetyl bromide and $p$-chloromethyl styrene (CMS) are analytical reagent grade from ACROS ORGANICS. Both 1,10-phenanthroline and Cu(I)Br are analytical reagent grade and re-crystallization from ethanol before using. Distilled water was used in all experiments. Other solvents used are all analytical reagent grade.

**Immobilization of Initiator on the Surface**

As shown in Scheme 2, the preparation procedure comprised the two steps: Firstly, the initiating compound was prepared by the quantificational reaction of APTES and bromoacetyl bromide: 0.02 mol bromoacetyl bromide was added dropwise into 20 ml chloroform solution containing 0.02 mol APTES with a small quantity of pyridine as catalyst at room temperature in 30 min. Then the solution was stirred for further 12 h at room temperature and refluxed for another 3 h.

Secondly, the ZnO nanoparticles (5.0 g), and the initiating compound solution prepared (5.0 ml) were added into 50 ml chloroform and the mixture was irradiated ultrasonically for 30 min and refluxed 8 h with electromagnetic stirring. Then the bromo-acetamide modified ZnO nanoparticles (BrA-ZnO) were filtered and thereafter thoroughly washed with dichloromethane and ethanol. The BrA-ZnO was dried in vacuum at 40°C.

**Self-Condensing ATRP**

The self-condensing ATRP of CMS from the BrA-ZnO macriniitators was accomplished by the followed procedure (Scheme 2): 2.0 g BrA-ZnO, 0.06 mol inimer (CMS), 6.0 mmol Cu(I)Br, 12.0 mmol 1,10-phenanthroline, and 100 ml toluene were mixed into a 250 ml flask. The mixture was irradiated with ultrasonic vibrations for 5 h.

\[ \text{SCHEMA 1. SCVP of an AB$^*$ inimer (CMS) from a functional ZnO (I$^*$).} \]

\[ \text{SCHEMA 2. The preparation procedure to the HP-ZnO nanoparticles.} \]
30 min, bubbling with Nitrogen (N₂). Then the mixture was refluxed with electromagnetic stirring for 6 h. N₂ was bubbled throughout the polymerizing period. The products, hyperbranched polymer grafted ZnO nanoparticles (HP-ZnO), were separated by centrifugation and extracted with toluene subsequently to remove completely the possible non-grafted polymer [30]. To remove the copper contaminants from the celadon raw product, the product was extracted with acetylacetone-ethanol solution (100 ml, vol. ratio of 1:5) for 24 h [31].

The hyperbranched polymer grafted ZnO hybrid nanoparticles (HP-ZnO) were dispersed into toluene and superfluous hydrochloric acid was added into the dispersion. Then the mixture was stirred violently overnight to remove the ZnO nanoparticle cores. Then the mixture was distilled and the residual, the hyperbranched polymer, was dried in vacuum overnight for the 1H NMR analysis.

Analytical Methods

Elemental analysis (EA) of C, N and H was performed on Elementar vario EL instrument. Bruker IFS 66 v/s infrared spectrometer was used for the Fourier transform infrared (FTIR) spectroscopy analysis. The UV–vis absorption spectra of HP-ZnO nanoparticles were measured using a UV–vis spectrophotometer (Lambda 35, Perkin-Elmer Corporation, USA), by the diffuse reflection method. Thermogravimetric analysis (TGA) was performed with a Perkin-Elmer TGA-7 system (Perkin-Elmer Corporation, USA) at a scan rate of 10°C min⁻¹ to 800°C in N₂ atmosphere. X-ray photoelectron spectroscopy (XPS) was accomplished using a PHI-5702 multi-functional X-ray photoelectron spectrometer with pass energy of 29.35 eV and an Mg Kα line excitation source. The binding energy of C 1s (284.6 eV) was used as a reference. The morphologies of the bare ZnO and HP-ZnO nanoparticles were characterized with a JEM-1200 EX/S transmission electron microscope (TEM). The powders were dispersed in toluene in an ultrasonic bath for 5 min, and then deposited on a copper grid covered with a perforated carbon film.

RESULTS AND DISCUSSION

The functional silanes have been widely used for the surface-modification of metal oxides including iron oxides. In our previous work [32], the HBr created in the reaction of APTES and bromoacetyl bromide was found to be reacted with the Fe₂O₃ nanocrystallines during the reaction of the γ-aminopropyltriethoxysilane modified Fe₂O₃ nanocrystallines and bromoacetylbromide. So the bromoacetylated silane was synthesized and then chemical bonded onto ZnO nanoparticles after complete removal of HBr to avoid the reaction of HBr with ZnO by heating.

The amide groups characteristic of BrA-ZnO at 1628 cm⁻¹ (C=O stretching), 1549 cm⁻¹ (N—H bending), and 1221 cm⁻¹ (C—Br of bromo-acetamide) were found in the FTIR spectrum of the bromo-acetamide modified ZnO nanoparticles (BrA-ZnO) (Fig. 1). It was also found that the absorbance band at 3444 cm⁻¹ of hydroxyl groups of moisture was weakened. It indicated that the most used initiating groups for ATRP, bromo-acetamide groups had been successfully introduced onto the surfaces of ZnO nanoparticles. And the elemental analysis results showed that the macro-initiator had a functional group content of about 1.0 mmol/g.

As for the hyperbranched polymer grafted ZnO nanoparticles (HP-ZnO), the alkyl C—H vibration bands of CH₂ stretch modes increased and the polystyrene characteristic at 3020–3100 cm⁻¹ and the benzene ring characteristic at 700 cm⁻¹ appeared in the FTIR spectrum of HP-ZnO nanoparticles (HP-ZnO) (see Fig. 2). BrA-ZnO was used as a polyfunctional initiator (I*) in the SCVP via ATRP to produce hyperbranched macromolecule functionalized ZnO nanoparticles, as illustrated in Scheme 2. During the SCVP of CMS (AB*) via the ATRP process, because both the AB* inimer and the

FIG. 1. FTIR spectrum of the macro-initiator (BrA-ZnO).

FIG. 2. FTIR spectrum of the hyperbranched polymer grafted ZnO (HP-ZnO).
BrA-ZnO have initiating groups capable of initiating the polymerization of vinyl groups, the chain growth can be started from both I* in the BrA-ZnO and B* group in the inimer. Both the activated B* can add to the double bond, A, to form the ungrafted or grafted dimer with a new propagating center, A*. Further addition of AB* inimer or dimer to A* and B* centers lead to the hyperbranched polymers. From the structures of I* of BrA-ZnO and B* in AB* inimer, it is clear that I* of BrA-ZnO has a higher activity of adding to the double bond than that of AB*; thus, most of the B* immobilized on the surface of ZnO nanoparticles has participated in initiating SCVP via slow addition of AB* inimer, as reported previously [15–17]. Of course, some free ungrafted hyperbranched polymers were still produced during the polymerization. After the polymerization, the reaction mixture was diluted with toluene, and the nanoparticles were extracted thoroughly with toluene and then filtered to remove soluble ungrafted hyperbranched polymers. Washing was done until no polymer was found in the filtrate. And the percentage of grafting (PG, mass ratio of the grafted polymer to ZnO) was found to be 429%, according to the elemental analysis. This is in good consistent with the result of about 440% from the TGA analysis. The experiment also showed that almost all the polymers generated were covalently bonded onto the ZnO surfaces at the conversion of monomer (inimer) of about 94%.

The mechanism given in Schemes 1 and 2 was also testified by the surface composition of the bare ZnO nanoparticles (ZnO), the bromo-acetamide modified ZnO nanoparticles (BrA-ZnO), and the hyperbranched polymers grafted ZnO nanoparticles (HP-ZnO) with XPS analysis (Table 1). After the assembly of the initiating groups, the presence of Si, C, N, and Br elements and the decrease of the surface Zn and O elemental contents were demonstrated in the surface analyses of the macro-initiators indicating that the surfaces of the ZnO nanoparticles were successfully modified with bromo-acetamide groups with the mechanism shown in Scheme 2. And the increase in the intensity of the carbon and chlorine signals compared to the BrA-ZnO indicates the addition of the hyperbranched polymer to the surfaces. And the disappearance of the zinc, oxide, and silicon signals shows that the thickness of the polymer layer is thicker than the photoelectron escape depth. The relative atomic compositions of Cl and C element were 24.63 and 74.47%, respectively, which agrees with the expected value based on the chemical composition of CMS (about 25% Cl). The presence of the surface Br element may be due to the formation of the C—Br bond in the polymerization in presence of Cu(I)Br although the carbon-halogen bond of C—Cl was stronger than that of C—Br [31, 32].

The 1H NMR spectrum was used for the structural analysis of the well-defined hyperbranched polymer grafted (Fig. 3). It showed each characteristic signal of the monomer unit, chlorobenzyl (b) at 11.4–12.0 ppm, phenyl (a) at 13.4–14.8 ppm and main-chain methylene (c) at 8.4–9.2 ppm and methine (d) at 9.2–9.6 ppm. The peak intensity ratio of the phenyl to the benzyl groups was 5.29/2.00, higher than the calculated values (4/2) assuming that the benzyl chloride moiety was kept intact [33]. It indicated that the chlorobenzyl groups had acted as the initiating groups in the polymerization as described in Scheme 1.

The UV–vis adsorption (see Fig. 4) analysis showed the adsorption of the HP-ZnO nanoparticles extended the whole UV–vis region compared with that of the bare ZnO nanoparticles in only UV region (<400 nm), because of the grafted hyperbranched polymers. Figure 5 shows the representative TEM micrographs of the hyperbranched polymers grafted ZnO nanoparticles obtained from the dilute toluene suspension. The resulting particles are seen to form clusters of micrometer size. Such aggregation morphologies were also observed in the previous works.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Zn</th>
<th>O</th>
<th>Si</th>
<th>N</th>
<th>C</th>
<th>Br</th>
<th>Cl</th>
</tr>
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<tr>
<td>ZnO</td>
<td>53.47</td>
<td>46.53</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>BrA-ZnO</td>
<td>21.90</td>
<td>29.96</td>
<td>0.90</td>
<td>1.20</td>
<td>44.26</td>
<td>1.79</td>
<td>—</td>
</tr>
<tr>
<td>HP-ZnO</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0.12</td>
<td>74.47</td>
<td>0.78</td>
<td>24.63</td>
</tr>
</tbody>
</table>

FIG. 3. 1H NMR spectrum of the hyperbranched polymer cut from the HP-ZnO.

FIG. 4. The UV–vis adsorption curves of the ZnO and HP-ZnO nanoparticles.
A possible reason is the fact the aggregation of the primary particles via van de Waals interparticle attraction and the aggregation is kept somehow during the preparation of the functional ZnO particles as well as the following polymerization and purification process.

CONCLUSION

The hyperbranched polymer grafted ZnO nanoparticles (HP-ZnO) were synthesized by surface-initiated self-condensing vinyl polymerization (SI-SCVP) of a styrene AB* inimer from ZnO nanoparticles functionalized with monolayer of ATRP initiators. Elemental analysis and FTIR measurements of the resulting products indicate the formation of nanoparticles composed of an inorganic ZnO core and an outer layer of covalently attached hyperbranched polymer with a high density of chlorobenzyl groups. The products are expected to be used in the functional devices directly or after further surface modifications based on the chlorobenzyl functional groups.

REFERENCES

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