A New Route for Preparation of High-density Organic Phase to High Selective HPLC for Polycyclic Aromatic Hydrocarbons by Atom-transfer Radical Polymerization of Octadecyl Acrylate on Silica

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(Received September 6, 2007; CL-070972; E-mail: ihara@kumamoto-u.ac.jp)

We have previously reported that poly(octadecyl acrylate) as an organic stationary phase in HPLC shows high molecular-shape selectivity through carbonyl–π interaction on highly ordered structures of long alkyl chains. In this communication, a new "grafting-from" strategy based on surface-initiated atom-transfer radical polymerization is applied for ordering of poly(octadecyl acrylate) on silica to lead to remarkable selectivity increase.

There are two principal techniques for the surface modification of inorganic particles by polymeric organic phases: (1) "grafting-to" method, where end-functionalized polymers react with the functional groups on the inorganic particle surface,[1] and (2) "grafting-from" method, where polymer chains grow from the initiator-modified inorganic particle surface.[2] In "grafting-to" technique well-characterized polymers can be immobilized onto the surface but the method has some disadvantages: e.g., limitation of the graft density on silica caused by the increase of sterical hindrance as the polymerization degree is increasing.[3] To circumvent these problems, we have shifted our focus to the surface-initiated "living"/controlled processes that are advantageous in all the aspects of grafting density, polymer architecture, and end functionalities.[4] Among the controlled radical polymerization techniques, atom-transfer radical polymerization (ATRP) has attracted a lot of attention in the past few years.[5] In the surface-initiated ATRP process the polymer chains grow from the initiators that have been previously anchored on to the inorganic particle surface and the grafted chains do not hinder the diffusion of the small monomers to the reaction sites, consequently well-defined polymer chains with higher graft density can be obtained.[6,7]

In this study, poly(octadecyl acrylate) was chosen as a polymeric organic stationary phase because of its high potential selectivity through carbonyl–π interaction assisted by ordering of octadecyl side chains.[8–10] At low temperature, long alkyl chains and carbonyl groups remain ordered states, those facilitate carbonyl–π interaction between the stationary phase and the solute molecules. At high temperature, long alkyl chains become disordered and cover the carbonyl groups which hinder the interaction between carbonyl–π and the guest molecules. We demonstrate the first example of surface-initiated ATRP of octadecyl acrylate on silica and its successful application in the reversed phase-HPLC (RP-HPLC).

The ATRP initiator was synthesized from 2-bromo-2-methylpropionic acid undecyl ester by hydrosilation with trichlorosilane according to a previously reported method.[6] This initiator involves a trichlorosilane reacting group which is able to bound to silica surface and an α-halo ester moiety that acts as radical initiator after the reversible halogen atom transfer reaction with the Cu^{I} complex. The attachment of the initiator onto porous silica[11] surface was carried out in dry toluene in the presence of dry triethylamine under inert conditions giving initiator-modified silica (Sil-initiator). The reaction between a trichlorosilane anchoring group and a surface OH-group of silica resulted in the formation of self-assembled monolayer (SAM) of the initiator (Figure 1). The surface-initiated polymerization of octadecyl acrylate (ODA) was carried out at 90 °C from initiator-grafted silica using copper(I) bromide and *N*,*N*,*N*′,*N*′,*N*″-pentamethyldiethylenetriamine (PMDETA) as catalyst precursors giving poly(octadecyl acrylate)-grafted silica (ATRP-Sil-ODA$_n$) (Figure 1). Spectroscopic analysis (e.g. DRIFT) and elemental analysis results revealed that ATRP initiator has been successfully grafted on silica particles and surface-initiated polymerization took place providing highly dense ATRP-Sil-ODA$_n$. The elemental analysis indicated that in the case of ATRP-Sil-ODA$_n$, the amount of immobilized polymer (24.95 wt %) and surface coverage (3.75 µmol m^{-2}) were much higher than that we measured in the case of Sil-ODA$_n$ prepared by the "grafting-to" method (15.7 wt % and 2.63 µmol m^{-2} respectively).[12] The polymer content of ATRP-based Sil-ODA$_n$ was also measured by weight loss of thermogravimetric analysis (TGA). It showed the weight loss of 23.0% at 800 °C indicating that the polymer content of the grafted silica was fairly high.

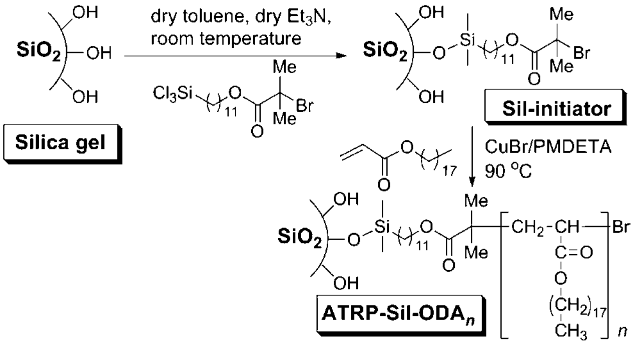

Figure 1. Preparation of poly(octadecyl acrylate)-grafted silica by ATRP technique.

Differential scanning calorimetry (DSC) indicates that the phase transition between ordered and disordered states takes place in ODA$_n$ grafted on silica. The peak-top temperature (T_c) of ATRP-Sil-ODA$_n$ (Figure 2) increased to 43 °C compared to those of previous Sil-ODA$_n$ and Sil-co-ODA$_n$ (38 and 33 °C, respectively).[9,10] This indicates that ODA$_n$ prepared by ATRP method can retain ordered state upto a higher temperature. Suspension-state ^{1}H NMR of ATRP-Sil-ODA$_n$ was measured in a temperature from 25 to 50 °C in order to evaluate the orientation of the side-chain alkyl groups of ODA$_n$. The intensity of the molecular mobility of the C3–C17 methylene groups increased dra-

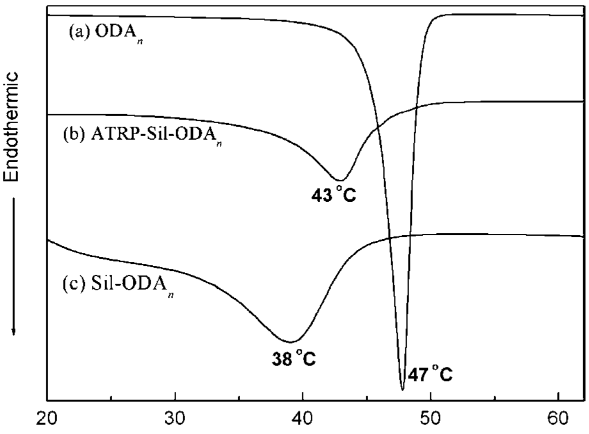

Figure 2. DSC thermogram of ODA$_n$, Sil-ODA$_n$, and ATRP-Sil-ODA$_n$.

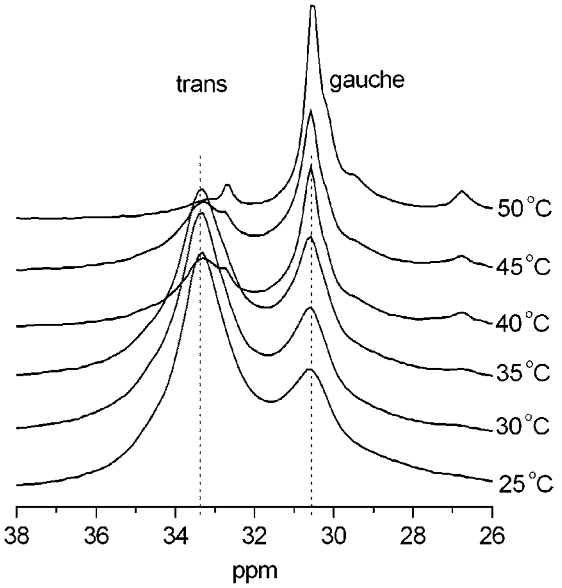

Figure 3. Variation of trans to gauche ratio with temperature in ^{13}C CP/MAS NMR spectroscopy for ATRP-Sil-ODA$_n$.

matically towards liquid scale at around 43 °C, which is very close to the endothermic peak in the DSC thermogram confirming the phase transition of the polymer from order-to-disorder states. Solid-state ^{13}C CP/MAS NMR measurements were also carried out at different temperatures from 25 to 50 °C to investigate the conformations of the methylene chains in the grafted organic phase. The NMR signal for the methylene groups occurs at 33.3 ppm due to trans conformation, indicating crystalline and rigid state, and at 30.6 ppm attributed to gauche conformation, indicating disordered and mobile state as shown in Figure 3. Comparison of the trans to gauche ratio of Sil-ODA$_n$ and ATRP-Sil-ODA$_n$ confirms the domination of ordered state of alkyl chains for ATRP-Sil-ODA$_n$ than for previous Sil-ODA$_n$. For example, trans to gauche ratio at 25 °C for ATRP-Sil-ODA$_n$ and Sil-ODA$_n$ are 2.76 and 1.24 respectively.

ATRP-Sil-ODA$_n$ was packed into a stainless-steel column (4.6 mm i.d. × 150 mm) and retention behavior for various polycyclic aromatic hydrocarbons (PAHs) using a methanol–water mixture as a mobile phase was investigated and compared with previous columns such as Sil-ODA$_n$ and octadecylated silica (ODS). The results showed that ATRP-Sil-ODA$_n$ yielded extremely higher retention as well as selectivity for all PAHs than Sil-ODA$_n$ and ODS. The retention and separation factors (k and α) of PAHs for the three columns are given in Table 1. In general, in RP-HPLC, higher alkyl chain density increases the shape selectivity for PAHs as it was demonstrated in a previous report for ODS namely high-density ODS showed better selectivity than low-density ODS.[13]

Table 1. Typical retention and separation factors of PAHs for ATRP-Sil-ODA$_n$, Sil-ODA$_n$, and ODS stationary phases[a]

Solute	ATRP-Sil-ODA$_n$		Sil-ODA$_n$		ODS	
	k	α	k	α	k	α
Triphenylene	9.761	**1.41**	3.153	**1.35**	5.43	**1.07**
Benzo[*a*]anthracene	13.751	**1.60**	4.240	**1.47**	5.84	**1.07**
Chrysene	15.631	**3.32**	4.625	**2.73**	5.84	**1.27**
Naphthacene	32.365		8.624		6.90	
o-Terphenyl	1.187	**3.78**	0.710	**1.86**	3.46	**1.47**
m-Terphenyl	4.485	**6.87**	1.320	**3.52**	5.11	**1.53**
p-Terphenyl	8.815		2.500		5.29	

[a] Mobile phase: methanol–water (9/1). Column temperature: 20 °C. Flow rate: 1.00 mL min.$^{-1}$

Suspension-state ^{1}H NMR, solid-state ^{13}C CP/MAS NMR, and DSC analyses suggest that ATRP-Sil-ODA$_n$ can remain ordered or rigid state up to higher temperature than Sil-ODA$_n$. This molecular ordering was found to be important because molecular-shape selectivity largely depends on the molecular ordering of organic phase on the silica surface.[14] Previously, we have reported about the enhanced molecular-shape selectivity mechanism of Sil-ODA$_n$ for PAHs.[8]

In summary, we have demonstrated the first synthesis of high-density poly(octadecyl acrylate)-grafted silica by surface-initiated atom-transfer radical polymerization. Solid-state ^{13}C CP/MAS NMR measurements revealed that ATRP technique provided surface-attached polymers with higher trans to gauche ratio. These results are in good agreement with suspension-state ^{1}H NMR measurements that indicated the lower mobility of the polymer main chain in ATRP-Sil-ODA$_n$. Increasing long-chain density, rigidity, and molecular ordering increases the retention time as well as selectivity therefore much shorter HPLC column can be employed for ATRP-Sil-ODA$_n$ than that used for Sil-ODA$_n$ or ODS to reduce the separation time.

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Published on the web (Advance View) November 10, 2007; doi:10.1246/cl.2007.1460