비닐기로 기능화된 실리카로부터 메틸메타크릴레이트의 2-(2-cyanopropyl) Dithiobenzoate에 의한 그래프트 중합

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2-(2-Cyanopropyl) Dithiobenzoate-mediated Grafting Polymerization of Methyl Methacrylate from Vinyl Modified Silica

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Abstract: Grafting polymerization of methyl methacrylate (MMA) from vinyl modified silica mediated by 2-(2-cyano-propyl) dithiobenzoate was first conducted. Surface radicals generated by the addition reaction of "free" polymeric radicals with surface vinyl could initiate reversible addition-fragmentation chain transfer (RAFT) grafting polymerization of MMA from silica. The RAFT grafting polymerization of MMA from silica exhibited a living character, evident from the linear relationship of grafting ratio with monomer conversion. Grafting polymerization rate appeared dependent on target molecular weight and initiator concentration because of diffusion-controlled RAFT process on silica. The PMMA-grafted silica allowed for a second-step grafting polymerization due to the existence of dithioester group on the chain ends of grafted PMMA. In this case, surface radicals were generated by the reaction of "free" polymeric radicals with the surface RAFT agents, which differed from the RAFT process of grafting polymerization from vinyl modified silica. This method could be extended to prepare a variety of block copolymers from silica.

Keywords: grafting, radical polymerization, reversible addition-fragmentation chain transfer, surface modification, diffusion.

Introduction

Considerable attentions have been paid to reversible addition-fragmentation chain transfer (RAFT) polymerization since its invention by CSIRO group. RAFT polymerization has been effectively employed to construct complex macromolecular architectures ranging from block, star and comb copolymers due to its mild reaction condition and tolerance to a broad range of monomers.[1-4]

More recently, grafting polymerization from surface using RAFT technique has been reported. Functional surface with RAFT agent through Z-group allows for the immobilization of designed macromolecules onto surface.[5-8] "Free" polymeric radicals formed in solution would diffuse and attach to surface by the reversible addition-fragmentation reaction with surface RAFT agent. R-group as a leaving radical would diffuse into solution, and consequently no surface radicals are formed. This process is similar to that of "grafting to" approach. In "grafting to" approach, the later incoming chains are severely limited to diffuse onto the surface because of the steric hindrance from the early grafted chains. This leads to low grafting density and grafting ratio. While, the grafting polymerization form functional surface with RAFT agent through R group resembles "grafting from" approach.[9-15] In general, surface radicals are generated by the transfer reaction of "free" radicals with surface RAFT agent and subsequently initiate grafting polymerization from surface in a living/controlled manner. Monomer molecules are small and could thus easily diffuse onto propagating sites on the surface, yielding high grafting density and grafting ratio. In addition, surface radicals could be introduced through the immobilization of azo initiator on surface. Baum and Brittain[16] reported the immobilization of azo initiator and

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grafting polymerization of styrene, methyl methacrylate and *N*, *N*-dimethylacrylamide from silica in the presence of 2-phenylprop-2-yl dithiobenzoate. Of these reports, the immobilization of RAFT agent (through R-group) or azo initiator on surface is conducted either by the reaction of silane agents bearing dithioester or azo group with surface or by an indirect method via several reaction steps. The synthesis of siliane agents bearing dithioester or azo group involves several steps of reactions and purifications, which lead to a low yield. Also, for the stepwise immobilization of RAFT or initiator onto surface, the surface structure could be undefinite due to the non-quantitative reactions on surface.

Compared with silane agents bearing dithioester or azo group, 3-methacryloxypropyl trimethoxy silane (MPS), as a cheap commercial product, was more applicable in industrial practice. In this paper, vinyl modified silica were prepared through hydrolyzing alkoxysilane moiety of MPS and then condensation-reacting with hydroxide group on silica. Grafting polymerization of methyl methacrylate (MMA) from vinyl modified silica mediated by 2-(2-cyanopropyl) dithiobenzoate was first investigated. The effect of target molecular weight and AIBN concentration on grafting ratio of PMMA from silica was discussed. Poly(MMA-*b*-St)-grafted silica was also prepared based on PMMA-grafted silica.

Experimental

Materials. 2-(2-cyanopropyl) dithiobenzoate (CDB) was prepared and purified according to the literature.[17] ^{1}H NMR (CDCl$_3$) δ (ppm): 1.95 (s, 6H), 8.01~7.88 (d, 2H), 7.51~7.66 (t, 1H), 7.47~7.35 (t, 2H).

Silica used was Aerosil 200 (Degussa) with a specific surface area of 200 ± 25 m^2 g^{-1}. Methyl methacrylate (MMA) and styrene (St) were dried over CaH$_2$ and then distilled under vacuum before use. Azobis(isobutyronitrile) (AIBN) was recrystallized from ethanol and dried under vacuum. All the other chemicals were analytical grade and used without further purification.

RAFT Grafting Polymerization of MMA from Vinyl Modified Silica. Before polymerization, vinyl was immobilized onto silica. The mixture of toluene (150 mL), MPS (1.36 g) and silica (5 g) was ultrasonically dispersed at 0 ℃ until getting a suspension. The suspension was immediately transferred to a 250 mL three-neck flask and was stirred for 8 h at 70 ℃. Then, the reaction mixture was centrifuged at 8000 rpm for 30 min. The remaining white solids, namely vinyl modified silica, were further washed for five times by the procedure of centrifugation-dispersion in toluene.

Grafting polymerization of MMA from vinyl modified silica mediated by CDB was conducted as follows: the mixture of toluene, vinyl modified silica, CDB and MMA was ultrasonically dispersed at 0 ℃ until getting a suspension. The suspension was immediately transferred to a 250 mL four-neck flask, followed by adding AIBN under continuous agitation. After flushing with N$_2$ for 2 h at 0 ℃, the flask was bathed in water at 70 ℃. After a preset period of time, a certain amount of reaction mixture was sampled. The mixture was centrifuged at 8000 rpm for 30 min. The solid was further dissolved in toluene, ultrasonicated for 30 min at room temperature and centrifuged. In order to obtain PMMA-grafted silica perfectly free of "free" PMMA, this cycle of dispersion-centrifugation in toluene was conducted until no precipitate formed when the supernatant liquid was added dropwise to the methanol. The recipes for grafting polymerization were listed in Table 1.

Table 1. Recipes for Grafting Polymerization of MMA from Vinyl Modified Silica Mediated by CDB

Exp	MMA (g)	Toluene (g)	Vinyl modified silica[a] (g)	RAFT[a] (g)	AIBN[a] (g)	[RAFT]$_o$/[AIBN]$_o$ (molar ratio)
1	80	40	1.6	0.3536	0.0656	4.00
2	80	40	1.6	0.8845	0.1646	3.99
3	80	40	1.6	1.7683	0.3280	4.00
4	80	40	1.6	3.5360	0.6576	3.99
5	80	40	1.6	0.8845	0.6562	1.00
6	80	40	1.6	0.8845	0.3218	2.04
7	80	40	1.6	0.8845	0.1102	5.96
8	80	40	1.6	0.8845	0.0820	8.00

[a]Based on monomer.

Preparation of Poly(MMA-*b*-St) Grafted Silica. The mixture of toluene, PMMA-grafted silica, CDB and St was ultrasonically dispersed at 0 °C until getting a suspension. The suspension was immediately transferred to a 250 mL four-neck flask, followed by adding AIBN under continuous agitation. After flushing with N_2 for 2 h at 0 °C, the flask was bathed in water for 24 h at 70 °C. The mixture was centrifuged at 8000 rpm for 30 min. The solid was further dissolved in toluene, ultrasonicated for 30 min at room temperature and centrifuged. In order to obtain poly(MMA-*b*-St) grafted silica perfectly free of "free" PSt, this cycle of dispersion-centrifugation in toluene was conducted until no precipitate formed when the supernatant liquid was added dropwise to the methanol.

Characterization. All tested samples were dried under vacuum at 30 °C for 24 h before use.

The fourier transform absorption spectra were recorded on a Brucker Tensor 37 FTIR spectrometer using KBr pellet method.

Thermal gravimetric analysis (TGA) was conducted on Perkin-Elmer Pyris 1 thermal gravimetric analyzer. Samples were heated from 30 to 800 °C at a heating rate of 20 °C·min⁻¹. The air flow rate was kept at 60 mL·min⁻¹.

Results and Discussion

Grafting Polymerization of MMA from Vinyl Modified Silica Mediated by CDB. In this study, vinyl was directly immobilized onto silica via hydrolyzing alkoxysilane of MPS and then condensation-reacting with hydroxide group on silica. Grafting polymerization of MMA from vinyl modified silica was mediated by CDB. The polymerization proceeded simultaneously in solution and on silica. The radicals generated in solution could initiate RAFT polymerization in solution. At the same time, the addition reaction of "free" radicals with surface vinyl could form surface radicals, which could initiate RAFT grafting polymerization from silica. Surface radicals could react with "free" RAFT agents and consequently dithioester groups were introduced onto silica. The RAFT process on silica was shown in Scheme 1. In equilibrium, surface RAFT grafting polymerization involved the reversible addition-fragmentation transfer reaction of surface radicals with neighboring RAFT agent on surface and "free" RAFT agent in solution. Surface radicals were decided by the three reaction modes: the addition of "free" polymeric radicals with surface vinyl, "free" polymeric radicals transfer from solution onto surface and surface radicals transfer from surface into solution. "Free" polymeric radicals and "free" RAFT agent must diffuse
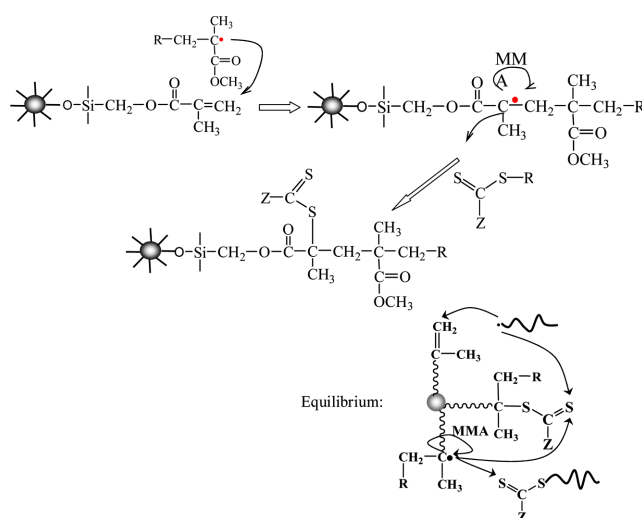
Scheme 1. RAFT process of grafting polymerization of MMA from vinyl modified silica mediated by CDB.

onto silica, which might be influenced by viscosity of polymer solution. After RAFT grafting polymerization, grafted PMMA chains would bear dithioester groups.

Characterization of PMMA-grafted Silica by FTIR. The cycle of dispersion-centrifugation in toluene was conducted until no precipitate formed when the supernatant liquid was added dropwise to the methanol, which indicated that PMMA-grafted silica was perfectly free of "free" PMMA. FTIR spectra of PMMA-grafted silica and "free" PMMA obtained from polymerization in solution were shown in Figure 1. The spectrum of PMMA-grafted silica exhibited carbonyl group absorption band at 1726 cm⁻¹ and C-H stretching vibrations at 2939 and 2987 cm⁻¹, which was in good agreement with the
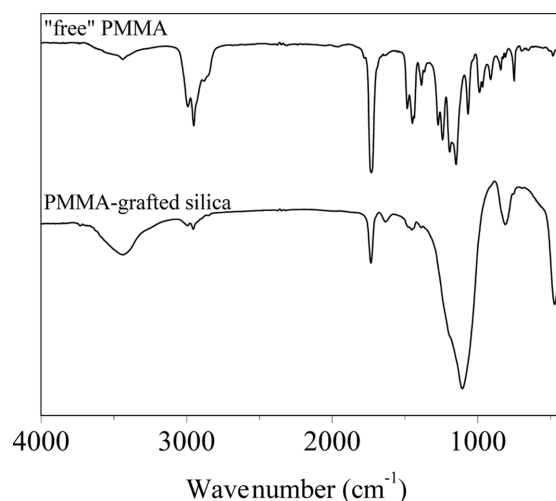
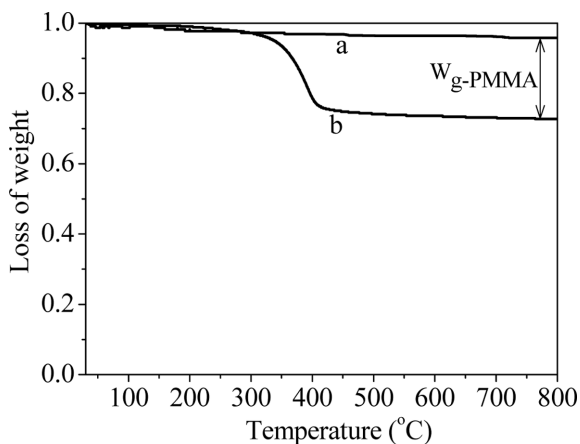**Figure 1.** FTIR spectra of "free" PMMA and PMMA-grafted silica.

spectrum of "free" PMMA. The results revealed that PMMA had been covalently grafted onto silica.

Effect of Target Molecular Weight on RAFT Grafting Polymerization of MMA from Vinyl Modified Silica.

TGA analysis could be efficiently used to quantify grafting ratio.[18] In the present study, surface coverage of grafted PMMA per gram of silica was estimated by TGA experiments. The mass of bare silica kept stable up to 800 °C except that 3% of mass loss due to the dehydroxylation of the silica surface. Grafting ratio of MPS from silica was 0.014, which was calculated by the mass loss of vinyl modified silica using the following eq. (1). The mass loss of PMMA-grafted silica nanoparticles included the dehydroxylation of the silica surface, the decomposition of MPS and grafted PMMA when the temperature was up to 800 °C. W_{g-PMMA}, the mass of grafted PMMA, was obtained from TGA data of and PMMA-grafted silica, as shown in Figure 2. Then, grafting ratio (G_r) of PMMA from silica was defined as the percentage of grafted PMMA per gram of vinyl modified silica and could be calculated by the following eq. (2).

$$G_{r,MPS} = \frac{W_{g-MPS}}{W_{SiO_2}} \tag{1}$$

$$G_{r,PMMA} = \frac{W_{g-PMMA}}{W_{g-MPS}} \tag{2}$$

In controlled/living polymerization, grafting ratio was dependent on the molecular weight of grafted PMMA. The linear relationship of grafting ratio with monomer conversion could provide the information about living character for surface grafting polymerization.
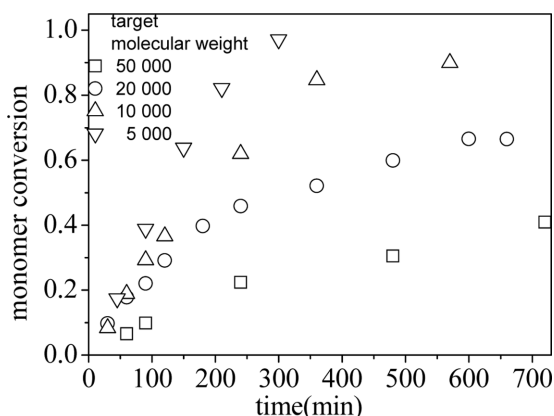
The content of vinyl modified silica was the same for all polymerization system. In order to evaluate the effect of target molecular weight on RAFT grafting polymerization of MMA from vinyl modified silica, we kept $[CDB]_0/[AIBN]_0$ constant and varied target molecular weight from 5000 to 50000. From Figure 3, it was clear that in all the cases, grafting ratio increased linearly with monomer conversion, which hinted the living character in RAFT grafting polymerization of MMA from silica. The slopes of the plots of grafting ratio *versus* monomer conversion in Figure 3 reflected grafting polymerization rate. Grafting polymerization rate appeared dependent on target molecular weight due to its increasing with target molecular weight. This hinted that surface radical concentration increased with target molecular weight. However,
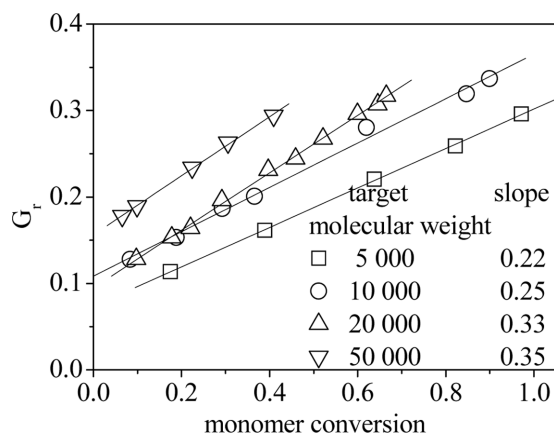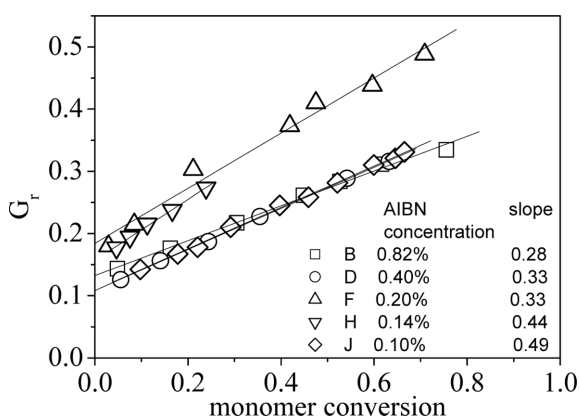
Figure 3. Grafting ratio *versus* monomer conversion for polymerization systems with different target molecular weights but the same molar ratios of RAFT agent to AIBN.

Figure 2. TGA curves of (a) vinyl modified silica; (b) PMMA-grafted silica of eq. (1), in which MMA conversion was 0.259.

Figure 4. Monomer conversion *versus* time (min) in solution polymerization of MMA mediated by CDB for polymerization systems with different target molecular weights but the same molar ratios of RAFT agent to AIBN.

RAFT polymerization rate in solution decreased with the increasing targeted molecular weight, as shown in Figure 4, which was in sharp contrast to the results of grafting polymerization. This discrepancy might be ascribed primarily to the viscosity change. The higher RAFT polymerization rate in solution would lead to a rapid increase in viscosity of polymer solution. The highly viscous polymer solution largely suppressed the diffusion of "free" polymeric radicals or polymeric RAFT agents onto silica. Surface radicals were much lower in the system with lower target molecular weight than that with higher target molecular weight. Consequently, the system with higher target molecular weight exhibited a higher grafting polymerization rate. Especially, at a given monomer conversion, grafting ratio for target molecular weight of 50000 was much higher than that for target molecular weight of 5000. So, it was concluded that RAFT grafting polymerization from vinyl modified silica was a diffusion-controlled process.

Effect of Initiator Concentration on RAFT Grafting Polymerization from Vinyl Modified Silica. To further confirm the effect of diffusion on RAFT grafting polymerization from vinyl modified silica, AIBN concentration (based on MMA) varied from 0.1% to 0.82% while maintaining target molecular weight of 20000. In general, polymerization rate would increase with the increasing initiator concentration. While, the system with lower AIBN concentration exhibited higher RAFT grafting polymerization rate than that with higher AIBN concentration, just as seen from the slopes of plots in Figure 5. Also, from Figure 5, it was clear that grafting ratio in the system with lower AIBN concentration was higher than that system with higher AIBN concentration at a given monomer conversion. These observations also suggested that
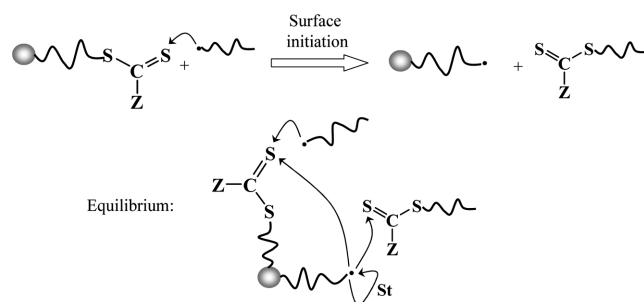
Scheme 2. RAFT process of grafting polymerization of St from PMMA-grafted silica mediated by CDB.

the diffusion of "free" polymeric radicals and polymeric RAFT agents onto silica was suppressed due to higher viscosity in the system with higher AIBN concentration.

Block Copolymerization from Silica. After RAFT grafting polymerization of MMA from silica, the chain ends of grafted PMMA should be terminated by dithioester groups. RAFT grafting polymerization of St should continuously proceed from PMMA-grafted silica. Considering this, a second-step grafting polymerization from PMMA-grafted silica (34.0% of grafting ratio) of eq. (1) was performed in the presence of CDB. Grafting ratio of grafted PSt was 26.1%. This stepwise growth of PMMA and PSt could be used as a qualitative indication of the living nature for grafting polymerization from vinyl modified silica. RAFT process of grafting polymerization from RAFT modified surface (R group) had been reported[11] and differed from RAFT grafting polymerization of MMA from vinyl modified silica. In this case, surface radicals were generated from the reaction of "free" polymeric radicals with surface RAFT agent, just as shown in Scheme 2. In equilibrium, surface radicals could experience RAFT grafting polymerization mediated by surface RAFT agents and "free" RAFT agents in solution.

Conclusions

RAFT grafting polymerization of MMA from vinyl modified silica was successfully performed using CDB as a RAFT agent and exhibited a living characteristic RAFT process. Grafting polymerization rate appeared dependent on target molecular weight and initiator concentration because of diffusion-controlled RAFT process on silica. PMMA-grafted PMMA allowed for RAFT grafting polymerization of St due to the existence of dithioester groups on the chain ends of grafted PMMA. This method could enable the preparation of a variety of block copolymers from silica.

Figure 5. Grafting ratio *versus* monomer conversion for polymerization systems with different AIBN concentrations but the same target molecular weights.

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