Are all Growing Active Chain-Ends Located at the Surface of the Dispersed Particle in the Living Dispersion Polymerization System?

Hyo Jin Kim, Hyeonsoo Ryu, Keon Hyeong Kim, Soonjong Kwak, Seung Sang Hwang, Kwang Ung Kim and Jungahn Kim*

Polymer Hybrids Center, Korea Institute of Science and Technology, P.O. Box 131 Cheongryang, Seoul, Korea

Seung Soon Ihm

The Department of Textile Engineering, Hanyang University, Seoul, Korea

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Abstract: Synthesis of functionalized disperse polystyrenes was successfully performed through living dispersion polymerization (LDP) following surface-functionalization. The dispersed polymers were characterized by a combination of 1H NMR, FT-IR, scanning electron microscopic (SEM) analysis, and titration. The LDP methodology led to the production of not only the quantitative surface-carboxylated but also the surface-hydroxylated dispersed polystyrenes. It was found that 70-90 mol% of the active and growing chain-ends in the LDP were located at the surface of the dispersed polymer particle on the basis of the functionalization yields.

Introduction

Disperse polymeric particles have been used in a variety of application fields. In addition, surface-functionalized polymer particles play presumably an important role as the polymeric matrix in the combinatorial chemistry field.4-5 With these regards, the subject for understanding and synthesizing polymeric particles carrying surface-functional groups must be a current interest. The particulate polymerization such as emulsion, dispersion, or suspension polymerization implements presumably the production of polymeric particles. The size-selectivity depends mostly upon a choice of the polymerization methodologies. Dispersion polymerization leading to the production of a medium range (0.01-50 µm), i.e., 'nanosphere'/microparticle', of polymeric particle size usually differs from suspension or emulsion polymerization with regard to solubility related to the formed polymer and the initial state of materials used in the polymerization system.6

Functional microspheres are usually synthesized via two methods: one is a copolymerization of functionalized monomers, the other is a post-reaction leading to functionalization of preformed microspheres.10 From a mechanistic point of view, the growing chain-ends on its surface of disperso polystyrene prepared in aliphatic hydrocarbon via anionic dispersion polymerization, called as 'living dispersion polymerization' (LDP), will exhibit the living nature as shown in Scheme I.11 Furthermore, it has been well known that alkylolithium-initiated anionic polymerization implements a quantitative yield in chain-end functionalization using a proper electrophile as a deliberately terminating agent.12-14 Specifically, chain-end hydroxylation of poly(styryllithium) using ethylene oxide and 1,1′-bis(4-t-butyldimethylsiloxyphényl)ethylene in hydrocarbon or the mixture of benzene/tetrahydrofurane are almost the quantitative yields.15-16 With this regard, the surface-functionalizations of dispersed polymers

*e-mail: jakim@kistmail.kist.re.kr
by the LDP presumably give rise to the quantitative yields assuming that all growing polymeric chain-ends generating dispersed particle in the living dispersion system exist at the surface of particle. In this communication, we report not only the results for the particle size control of the gel type (crosslinked) of dispersed poly(styrene-co-divinylbenzene) prepared through the LDP but also a prediction of the fraction of the active chain-ends located at the surface of particle based on the results for the surface-functionalizations of non-crosslinked disperse polystyrenes.

**Experimental**

**Materials.** Styrene (Junsei Chem. Co., reagent grade), tert-butylstyrene (Daicel, 95%), and n-hexane (Oriental Chem. Co., reagent grade) were purified by following the procedures described in the literature. Toluene (Oriental Chem. Co., reagent grade) was purified by the similar procedures to those for benzene except for stirring time over concentrated sulfuric acid. Pyridine (Aldrich Chem. Co., 98%) for making a titrant was doubly distilled from freshly ground calcium hydride. 100 g of commercial divinylbenzene (Aldrich Chem. Co., technical grade, 55% mixture of isomer) was first cooled to 0-5 °C, followed by addition of 30 g cuprous chloride, anhydrous with vigorously stirring. After 30 min a yellow solid complex was separated from the mixture, followed by washing twice with excess toluene and decomposing the complex in fresh toluene by heating to 80 °C. Toluene and cuprous chloride were then removed by vacuum distillation and filtration, respectively. Finally, pure para-divinylbenzene was obtained by recrystallization from methanol, followed by distillation to make an ampoule from freshly ground calcium hydride (Aldrich Chem. Co., 98%) and storing it below -18 °C prior to use. The yield was 45 wt% based on the amount commercial divinylbenzene used initially. n-Hexane and benzene (Oriental Chem. Co., reagent grade) were purified by following the procedures described in the literature. sec-Butyllithium (sec-BuLi; FMC Corp. 1.6 M in cyclohexane) was used as the anionic initiator without further purification. N,N,N',N'-Tetramethyleneetetraamine (TMEDA; Aldrich Chem. Co., 98%) was purified by the double distillation after stirring over freshly ground CaH₂ in a high vacuum line, followed by making ampoule containing a required amount. Ethylene oxide (Dae-Han Gas Co., 99%) was purified by following the procedures described in the literature and carbon dioxide (CO₂; Shinyang Gas Products, 99.99%) was used without further purification. 1,1-Bis(4-t-butyldimethylsilyloxyphenyl)ethylene was prepared and purified by following the reaction procedures in the literature. Acetic anhydride (Aldrich Chem. Co., 98%) was used as purchased.

Synthesis of gel-type-dispersed poly(styrene-co-p-divinylbenzene). The living dispersion copolymerizations of purified p-divinylbenzene and styrene (DVB: 5-15 wt%) were performed by following the same procedures as those explained in the literature except for using the mixture of monomers. The particle sizes were controlled in the 0.65-8 μm range by changing the mole ratio of sec-BuLi to a preformed poly(t-butyldiphenyl) lithium as the steric stabilizing moiety having over 1.8×10⁴ g/mol of the molecular weight.

**Surface-Functionalization of Dispersed Polystyrene.** Surface-active dispersed polystyrene was prepared by polymerization of styrene using the mixture of sec-BuLi and a preformed poly(t-butyldiphenyl) lithium as the anionic initiator as already described in the previous publication. Surface-hydroxylated dispersed polystyrene was synthesized by both a delivery of ethylene oxide
and 1,1-bis(4-t-butyldimethylsiloxyphenylethyl)-ene via a breakseal technique into the dispersed polymer system in the mixture of n-hexane and THF (95/5, v/v). The reaction mixture was stirred at room temperature for 24 h, followed by addition of 0.1 N HCl methanol solution to produce hydroxyl-functionalized dispersed polystyrene. Similarly, surface-carboxylated dispersed polystyrene dissolved in toluene was titrated using 0.01 M KOH in methanol and phenolphthalein indicator solution following the similar procedures explained in the literature.26

Results and Discussion

Synthesis of Gel-Type Dispersion Polymer by LDP. As already described in the previous section, the authors have reported that anionic dispersion polymerization of styrene using the mixture of poly(t-butylstyryl)lithium and n-butyllithium or sec-butyl lithium in situ forms poly(t-butyldivinyl-styrene) as the steric stabilizer as well as produces the sterically stable disperse polystyrene.11 It has been reported that the gel type of dispersion poly(divinylbenzene) and poly(styrene-co-divinylbenzene) was also prepared by an anionic mechanism.22 Especially, as shown in Scheme II, anionic dispersion copolymerization of styrene with divinylbenzene presumably produces the gel type of polymer particle containing vinyl units. Unreacted vinyl units in the formed polymer particle were able to be qualitatively identified by 'H-NMR spectroscopic analysis.22 As shown in Figure 1, the chemical shift at δ=5.75 ppm is clearly assigned as the protons of the unreacted vinyl group (CH=CH-Ph) on the

Scheme II
divinylbenzene. The experimental conditions and the results for the living dispersion copolymerizations of styrene with divinylbenzene are shown in Table I. As expected, a broadening of the particle size distribution was observed as shown in Table I except for the case of LDP 5. This arises from the increase of the heterogeneity of the system with increasing the particle size. The major variable to control the particle size is also found to be the mole ratio of simple alkyl lithium to poly 
(r-butylstyryl)lithium as the steric stabilizing moiety as shown in Figure 2 and Table I. Even though a positive effect of the theoretical molecular weight of the anchoring moiety on the increase of the particle size is presumably expected, the small molecular weight of the anchoring moiety rather produces the bigger size of the dispersed polymer as in the cases of LDP 2 and LDP 3 (also see LDP 4 and LDP 5). The ratio dependency on the particle growth may not be derived quantitatively because of a complicated association behavior of organolithium compounds in hydrocarbon. Based on the mechanism for the particle formation in the LDP described in the previous publication, the increase of the A/S balance, i.e., the increase of molecular weight of the anchoring moiety, is expected to effect a linear increase of the particle size even considering the Daoud-Cotton model for star-branched polymers. It has been reported that the ratio \([\text{RLi}] / [\text{PlLi}]\) governs the concentration as well as the in-situ formation of the steric stabilizer which plays a very important role to control the size of dispersed polymer. A different cross-association state depending upon the ratio \([\text{RLi}] / [\text{PlLi}]\) is expected as proposed in the literature. The important observation is simply that the formed particles are relatively uniform. This seems to arise from a uniform association number of the mixture of organolithium compounds acting as micelle in the common dispersion polymerization system using a preformed stabilizer under the LDP conditions. Its exact association number could not be predicted. Simply, the increase of the concentration of low molar mass organolithium in the ratio \([\text{RLi}] / [\text{PlLi}]\) gives rise to the decreasing effect of the steric stabilizer concentration as in the dispersion polymerization system using a preformed steric stabilizer. Thus, the gel-type of dispersed polymer carrying some

| Sample | \(M^*_{a} \times 10^{3}\) | A/S | DVB\(^b\) | [RLi]\(^d\) | Particle Size [\(\mu\text{m}\)]
|--------|-----------------|------|--------|--------|-----------------
| LDP 1  | 20              | 3/1  | 10/90  | 1/1    | 0.6 ± 0.001   
| LDP 2  | 20              | 3/1  | 10/90  | 2.3/1  | 1.2 ± 0.003   
| LDP 3  | 20              | 2/1  | 15/85  | 3.5/1  | 2.7 ± 0.025   
| LDP 4  | 20              | 2/1  | 15/85  | 5/1    | 4.7 ± 1.075   
| LDP 5  | 20              | 1/1  | 15/85  | 7/1    | 6.3 ± 0.500   
| LDP 6  | 20              | 0.5/1| 15/85  | 10/1   | 8.0 ± 1.500   

\(^{a}\) The number average molecular weight of the poly(r-butylstyrll) as the stabilizing moiety.

\(^{b}\) The theoretical ratio of the molecular weights of the anchoring moiety to the stabilizing moiety.

\(^{c}\) The volume ratio of divinylbenzene to styrene used in dispersion polymerization.

\(^{d}\) The molar ratio of sec-butyllithium (RLi) to poly(r-butylstyryll)lithium (PlLi).

The quantitative functionalization yields inform presumably us that the mole fraction of the active chain-ends located at the surface, consisting of one dispersed particle. Experimentally, the same particle sizes were first obtained by a combination of the A/S balance and the mole ratio of simple to polymeric organolithium compounds, i.e., the ratio [RLi]/[PLi], as shown in Table II. The typical scanning electron microscopic photographs of a few dispersed polymers in Table II are compared in Figure 3. With a mechanistic point of view for stabilization of polymeric particle, it is expected that the stabilization of the polymer particles may be governed by both steric and electrostatic stabilization as shown in Figure 3(b) and (c). The incipient flocculation of dispersed particles seems to be vanished in this LDP and the functionalization systems. The surface-hydroxylations of the dispersed polymers were readily performed using ethylene oxide or diphenylethylene derivative carrying para-silyloxy group as shown in Scheme III. Furthermore, the direct delivery of carbon dioxide into the reactor containing the living dispersed polymer in the absence or presence of excess TMEDA forms the surface-carboxylated dispersed polymer in a high vacuum line. The titration and the 'H-NMR spectroscopic analysis of the products for characterization of the functionalization yields were carefully carried out. The functionalization yields of the products are also shown in Table II. Specifically, the surface-hydroxylations of the formed dispersed polystyrene using ethylene oxide/THF solution (n-hexane/THF=95/1, v/v) were not quantitative but maximum 92 mol% as shown in Table II even considering the quantitative yield even in benzene. In addition, the diphenylethylene chemistry has been utilized for the synthesis of the efficient chain-end functionalizations of polymeric organolithium compounds because of the quantitative addition of diphenylethylene derivatives at polymeric organolithium chain-end without any homopolymerization in hydrocarbon. In order to prepare the aromatic hydroxyl-functionalized disperse polystyrene, 1,1-bis(4-t-butyldimethylsiloxyphenylethyl)ethene as the diphenylethylene de-

![Figure 2. SEM photographs of the gel-type of polystyrene-co-p-divinylbenzene. LDP 2, LDP 3, and LDP 5 in Table 1 prepared by the LDPs.](image)
Table II. Surface-Functionalizations of the Dispersed Polystyrenes Prepared by the Living Dispersion Polymerization in n-Hexane and Their Characterization Results

<table>
<thead>
<tr>
<th>Sample</th>
<th>$M_n$ ($\times 10^3$)</th>
<th>$A^s$</th>
<th>[RLI]'/[PLI]</th>
<th>Particle Size (µm)</th>
<th>Functionalization Yield (%)</th>
<th>$\text{Y}^1$</th>
<th>$\text{Y}^2$</th>
</tr>
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<tr>
<td>LDP 7</td>
<td>1.85</td>
<td>1/1</td>
<td>1/1</td>
<td>1.5±0.12</td>
<td>92</td>
<td>185</td>
<td>40</td>
</tr>
<tr>
<td>LDP 8</td>
<td>1.85</td>
<td>2/1</td>
<td>1/3.2</td>
<td>1.5±1.16</td>
<td>89</td>
<td>173</td>
<td>38</td>
</tr>
<tr>
<td>LDP 9</td>
<td>1.85</td>
<td>3/1</td>
<td>1/6.6</td>
<td>1.6±0.51</td>
<td>90</td>
<td>173</td>
<td>43</td>
</tr>
</tbody>
</table>

$^*$The number average molecular weight of poly(t-butylstyrene) as the stabilizing moiety.

$^1$The ratio of the molecular weights of polystyrene as the anchoring moiety to poly(t-butylstyrene) as the steric stabilizing moiety.

$^2$The mole ratio of sec-BuLi (RLI) to poly(t-butylstyryllithium (PLI) used in the living dispersion polymerization.

$^4$The yield from functionalization using ethylene oxide.

$^6$The yield from the reaction with 4,4-bis(t-butyldimethylsilyloxyphenyl)ethyleneglycol.

$^7$The yield from carboxylation using CO$_2$ gas in the absence of N,N,N',N'-tetramethyleneethylenediamine (TMEDA).

$^8$The yield from carboxylation using CO$_2$ gas in the presence of TMEDA with 50 times molar concentration compared to that of organolithium compound.

Figure 3. SEM photographs of unfunctionalized dispersed polystyrene, LDP 7, hydroxylated dispersed polystyrene, LDP 8 (OH), and carboxylated dispersed polystyrene, LDP 9 (Y), in Table II.

Rivietive was first synthesized by following the procedures in the literatures and its THF solution was then delivered for functionalization (n-hexane/THF=95/5, v/v). From the p-silyloxyphen-yl-functionalization yields, about 15 mol% of the active chain-ends seemed to be still embedded inside the particle irrespective of the number of polymeric chains consisting of one particle.

On the other hand, while the carboxylation yields were relatively low in the absence of TMEDA (nearly 40 mol% shown in the X row of Table II), minimum 74 mol% of carboxylation was observed in the presence of a large excess TMEDA ([TMEDA]/[Li] = 50/1, mol/mol) in spite
of the quantitative carboxylation of polymeric organolithium compounds (see the Y row in Table II). The difference between the hydroxylation and the carboxylation yields may arise from the different diffusion rate of the terminating agents in the different solution state. Practically, considering the diffusion-controlled reaction, the diffusion of the carbon dioxide is limited in the non-swollen state of dispersed particle even in the presence of TMEDA. On the other hand, in the cases of both hydroxylations, the small THF fraction renders the dispersed particle swollen and the termination by ethylene oxide diffused near the surface of the swollen particle leads to the production of relatively high yields. With these regards, it can be deduced that 74 mol\% of the active chains are located at the surface of non-swollen dispersed particle in the LDPE.

Conclusion

The living dispersion copolymerizations of styrene with $p$-divinylbenzene using a mixture of sec-BuLi and poly(1-butylstyryllithium) as the steric stabilizing moiety in $n$-hexane produce successfully a surface-active dispersed polymer including a few vinyl units depending on the reaction time. This indicated that $p$-divinylbenzene was not completely reacted during 24 h reaction period under our reaction conditions. The particle size of the dispersed copolymers could be controlled by the mole ratio of simple to polymeric organolithium. Surface-hydroxylated yields using ethylene oxide or 1,1-bis(1-butylidimethylsiloxy)ethylen in the mixture of $n$-hexane and THF (95/5, v/v) informed us that ca. 89 mol\% of the active growing chain ends consisting of one particle are located at the surface of the particle. However, without any polar solvent, surface-carboxylation results indicated that about 74 mol\% of the active chain-ends are located at the surface of particle. The difference between the hydroxylation and the carboxylation yields arises from a polar solvent leading to a swollen state of dispersed particle giving rise to an easy diffusion of the terminating agent into the particle. From these results, it can be concluded that about 70–90 mol\% of the growing chain-ends even in the heterogeneous state must be located at the surface of dispersed polystyrene and the remaining chain-ends will be embedded inside the particle depending upon the terminating conditions in the living dispersion polymerization.

References


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(22) The sample preparation for a 1H-NMR analysis was performed by crushing the dried dispers particle in a jar and dissolving in CDCl₃ followed by filtration.