Chain Dimension of Polystyrene-like Hyperbranched Polymers with Various Chain End Groups in THF

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Abstract. A hyperbranched polymer (HPS-DC) synthesized using $N,N$-diethylamino-dithiocarbamoylstyrene as an inimer and a hyperbranched poly(4-methylstyrene) (HPS-H) prepared by hydrogenation of the HPS-DC are characterized in tetrahydrofuran (THF) solutions by static and dynamic light scattering measurements. The experimental values of z-averaged mean-square radius of gyration ($<S^2>_z^{1/2}$) and hydrodynamic radius ($R_H$) of the HPS-H have smaller dimensions than those of the linear polystyrene (PS) at the same degree of polymerization ($N_w$), whereas the $R_H$ of the HPS-DC in the region of $N_w < 700$ is larger than that of the linear PS at the same $N_w$. The $N_w$-dependence of $<S^2>_z^{1/2}$ and $R_H$ for the HPS-H are described by a randomly trifunctional branched polymer model with the molecular weight per a branch point (4.55 $\times$ 10$^3$ g/mol) and the chain dimensions of the linear PS in THF at 25 °C.

1. Introduction

Hyperbranched polymers are usually prepared by condensation reactions between the A and B groups using AB$_f$ monomers ($f \geq 2$). The resulting product is a highly polydisperse mixture of randomly branched molecules. The hyperbranched polymers generally have smaller dimensions and higher density of terminal functional groups on their surfaces than those of corresponding linear polymers with the same degree of polymerization. Moreover, the hyperbranched polymers have unique physical and chemical properties such as low viscosity both in the solution and in the melt state in comparison with their linear analogues [1-3], and thus potential in variety of commercial applications.

Ishizu et al. reported synthesis of polystyrene-like hyperbranched polymer (HPS-DC) by one-pot photopolymerization of $N,N$-diethylaminodithiocarbamoylmethylstyrene, which can also work as an initiator for polymerization to afford branching point, so-called “inimer” [4]. They estimated the degree of branching (DB) by kinetic approach [5] and NMR [6] to be as high as ca. 0.3 $\sim$ 0.4.

We have recently reported the chain dimension of the same HPS-DC in tetrahydrofuran (THF) and methyl ethyl ketone by dynamic light scattering measurement, and obtained the hydrodynamic radius ($R_H$) being larger than that of the linear PS with the same degree of polymerization because of the different local structure of polymer chain [7].
In this study, the chain dimension of polystyrene-like hyperbranched polymers (HPS-DC and hydrogenated HPS-H) in THF were measured by static and dynamic light scattering measurements. Especially, relationship between a chain dimension and the molecular size of chain end groups were discussed.

2. Experimental

2.1. Polystyrene-like Hyperbranched Polymers

The polystyrene-like hyperbranched polystyrene (HPS-DC) was synthesized by photopolymerization of \(N,N\)-diethylamidionidothiocarbamoylmethylstyrene as an inimer according to a previous procedure reported by Ishizu and Mori [1]. The hyperbranched poly(4-methylstyrene) (HPS-H) was prepared by hydrogenation of HPS-DC in the presence of tri-n-butyltin hydride. The obtained HPS-DC and HPS-H were fractionated to 11 parts with different size by a recycling preparative HPLC system (Japan Analytical Industry Co. Ltd. LC-9104) equipped with a RI detector (JAI RI-7s) and a UV-vis detector (JAI 310) using two columns (JAI GEL 3H-40 and 4H-40) in series with chloroform as the eluent at a flow rate of 14 mL/min at room temperature. The composition of styrene unit (\(x\)) of each HPS-DC fraction was determined by \(^1\)H NMR to be 0.77 ± 0.02, which was independent on the weight-averaged degree of polymerization (\(N_w\)). The degree of branching (DB) of the HPS-DC in the region of 38 < \(N_w < 720\) evaluated from value of \(x\) was 0.48 ± 0.02, and larger than that of reported by Ishizu et al. [5, 6].

Size exclusion chromatography (SEC) was carried out using a RI detector (SHIMADZU RID-10A) and a UV-vis detector (SHIMADZU SPD-10AV vp) equipped with three columns (TOSOH TSKgel G4000HXL, G5000HXL, and G6000HXL) in THF as the eluent at a flow rate of 0.5 mL/min at 40 °C. Weight-averaged molecular weight (\(M_w\)), z-averaged mean-square radius of gyration (\(<S^2>_z\)), and \(R_H\) of the fractionated HPS-DC and HPS-H were determined by the SEC equipped with a multilength light scattering detector (MALS; Wyatt Technology DAWN-EOS, wavelength: \(\lambda = 690\) nm) and a quasi-elastic light scattering detector (QELS; Wyatt Technology WYATT-QELS, scattered angle: 99.8 °) (SEC-MALS-QELS) at room temperature. The Rayleigh ratio \(R(90)\) at a scattered angle of 90 ° was based on that of a pure toluene. The corrections for sensitivity of 16 detectors at angles of other than 90 ° and dead volume for each detector were performed using the scattering intensities of 0.30 wt% THF solution of a PS standard with \(M_w = 2.23 \times 10^4\) g/mol and \(M_w/M_n = 1.04\). Polymer sample solutions with mass concentration (\(C_p\)) of about 1 × 10^{-3} g/mL were injected using a sample loop of 100 µL to SEC columns.

The specific refractive index increment (\(dn/dc\)) of the HPS-DC and HPS-H in THF at 25 °C was measured using a differential refractometer (Otsuka Electrics DRM-1020, wavelength: \(\lambda = 633\) nm). The measured \(dn/dc\) of the HPS-DC and HPS-H in THF were 0.225 \(s\) mL/g and 0.178 \(s\) mL/g, respectively. Cauchy dispersion formula shows that there is linear relationship between \(dn/dc\) and \(\lambda^2\) to reveal independence of wavelength at longer region. Thus, \(dn/dc\) at \(\lambda = 633\) nm was also used for the analysis of SEC-MALS-QELS.

3. Results and Discussion

Figure 1 shows a typical SEC curve of a fractionated HPS-DC (\(M_w = 3.91 \times 10^4\) g/mol, \(M_w/M_n = 1.14\)), together with the absolute calibration curves of the HPS-DC (circles), HPS-H (squares), and PS (triangles) determined by SEC-MALS. It should be noted in this figure that the \(M_w\) of HPS-DC and
HPS-H in the region of all retention volume (RV) were larger than that of the linear PS at the same RV. The \( M_w \) of HPS-DC was smaller than those of the corresponding the HPS-H in the smaller RV region than 23 mL, whereas the \( M_w \) of HPS-DC was larger than those of the corresponding the HPS-H in the larger RV region than 23 mL. These results clearly demonstrate that the \( M_w \) and polydispersity index of the HPS-DC and HPS-H chains determined with a conventional PS calibration curve were significantly underestimated than those of actual HPS calculated from the corresponding absolute calibration curve determined by SEC-MALS. We supposed that the effect of branching structure of polymer chain and molecular size of chain end group appeared in the calibration curves.

Figure 1. SEC curve of a fractionated HPS-DC (\( M_w = 3.91 \times 10^4 \) g/mol, \( M_w/M_n = 1.14 \)) in THF, together with the absolute calibration curves of the HPS-DC (circles), HPS-H (squares), and PS (triangles) determined by SEC-MALS.

Figure 2. (a) \( N_w \)-dependence of the measured \( <S^2>_{1/2} \) for the HPS-DC (circles) and HPS-H (squares) in THF, together with that of the linear PS in THF at 25 °C [8]. (b) \( N_w \)-dependence of the measured \( R_{H1} \) for the HPS-DC (circles) and HPS-H (square) in THF, together with that of the linear PS in THF at 25 °C [9]. The bold lines show the calculated values of a randomly trifunctional branched polymer model calculated form equations 1 and 2 with \( \gamma_M^{-1} = 4.55 \times 10^3 \) g/mol and the chain dimensions of linear PS in THF at 25 °C.

Figure 2 (a) and (b) show the double-logarithmic plots of the \( <S^2>_{1/2} \) and \( R_{H1} \) versus \( N_w \) for the HPS-DC (circles) and HPS-H (squares) in THF, together with that of the linear PS in THF at 25 °C [8, 9], respectively. It should be noted in their figures that both the \( <S^2>_{1/2} \) and \( R_{H1} \) of the HPS-H were much smaller than those of the linear PS and HPS-DC with the corresponding \( N_w \). Another interesting point in Figure 2 (b) is that the \( R_{H1} \) of the HPS-DC in the region of \( N_w < 700 \) was larger than that of the linear PS with the corresponding \( N_w \), consistent with previous report [7]. Whereas, both the \( <S^2>_{1/2} \) and \( R_{H1} \) of the HPS-DC in the region of \( N_w > 700 \) have smaller dimension than those of the linear PS at the same \( N_w \). Although the both the \( <S^2>_{1/2} \) and \( R_{H1} \) of the HPS-DC were larger than those of the HPS-H at
the same $N_w$ range, the power law exponent ($ca.$ 0.47) of $N_w$-dependence of $R_{1l}$ of the HPS-DC was close to that ($ca.$ 0.46) of the HPS-H. This was simply caused by difference in the size of functional group between DC-group and H-group. In general, power law relationships of the chain dimension and molecular size is mainly depending on the degree of branching, not on chemical structure. Therefore, polymer with bulky DC-groups afforded larger $<S>_{z}^{1/2}$ and $R_{1l}$ compared with HPS-H, but showed the same value of the power law relationships.

The dependence of $<S>_{z}^{1/2}$ and $R_{1l}$ on $N_w$ for the HPS-H are precisely analyzed by the trifunctional randomly branched polymer model. We proposed the HPS-H as a randomly branched poly(4-methyl styrene) with trifunctional branching units, from composition of styrene unit ($ca.$ 0.77) evaluated by $^1$H NMR. The structure sensitive size parameters $g_S$ [10] and $g_{1l}$ [11] for the randomly branched polymer chain with trifunctional branching units are expressed by

$$g_S = \frac{\langle S^2 \rangle_b}{\langle S^2 \rangle_l} = \left[ \left(1 + \frac{\gamma_M M}{7} \right)^{\frac{1}{2}} + \frac{4\gamma_M M}{9\pi} \right]^{\frac{1}{2}}$$

$$g_{1l}^{-1} = \frac{R_{1l,b}}{R_{1l,l}} = \frac{1}{2} \left( \frac{7}{4} \right)^{1/2} \left( \gamma_M M + \frac{1}{2} \right)^{1/2} + \frac{3}{4} \Gamma \left( \frac{5}{4} \right) \left( \gamma_M M + \frac{1}{2} \right)^{1/4}$$

where the subscripts $b$ and $l$ indicate branched and linear molecules of the same degree of polymerization, $\gamma_M^{-1}$, $M$, and $\Gamma$ are the molecular weight per a branch point, the molecular weight, and a gamma function, respectively. Figure 2 (a) and (b) show the comparison of the experimental data of the HPS-H with calculated values (bold lines) form equations 1 and 2 with the fitting parameter $\gamma_M^{-1} = 4.55 \times 10^3$ g/mol and the chain dimensions of linear PS in THF at 25 °C. Their theoretical curves in their figures were close to the experimental points. Thus, the HPS-H can be categorized as a randomly trifunctional branched poly(4-methyl styrene).

4. Conclusion

The $M_w$ and polydispersity index of the HPSs determined with a conventional PS calibration curve are significantly underestimated than those of actual HPS calculated from the corresponding absolute calibration curve determined by SEC-MALS. The chain dimensions of the HPS-H have smaller dimensions than those of the linear PS and HPS-DC at the same $N_w$, whereas the $R_{1l}$ of the HPS-DC in the region of $N_w < 700$ is larger than that of the linear PS at the same $N_w$. We supposed that bulky chain end group has a strong effect on chain dimension of hyperbranched polymer with decreasing $N_w$. The experimental $N_w$-dependence of $<S>_{z}^{1/2}$ and $R_{1l}$ for the HPS-H in THF are described by a randomly trifunctional branched polymer model with $\gamma_M^{-1} = 4.55 \times 10^3$ g/mol and the chain dimensions of linear PS in THF at 25 °C.

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