On the Dimension of a Hyperbranched Polymer

Synthesized from a Styrene Derivative

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SUPPORTING INFORMATION

Characterization of the HBP aggregates

We can estimate the apparent hydrodynamic radius $R_{H,app,2}$ and the excess Rayleigh ratio $R_{\theta,2}$ of the slow relaxation component 2 from eqs 2 and 3 where $A_1(\tau,q)$ is replaced by $A_2(\tau,q)$. Figure S1 shows concentration dependences of $R_{H,app,2}^{-1}$ and $\ln(R_{0,2}/Kc)$ where $R_{0,2}$ is $R_{\theta,2}$ extrapolated to $\theta=0$ and K is the optical constant. The positive slope of $\ln(R_{0,2}/Kc)$ for THF (a good solvent for component 1) and MEK (a theta solvent) solutions suggests that the HBP aggregates formed in THF and MEK were dissociated by the dilution of the solutions.
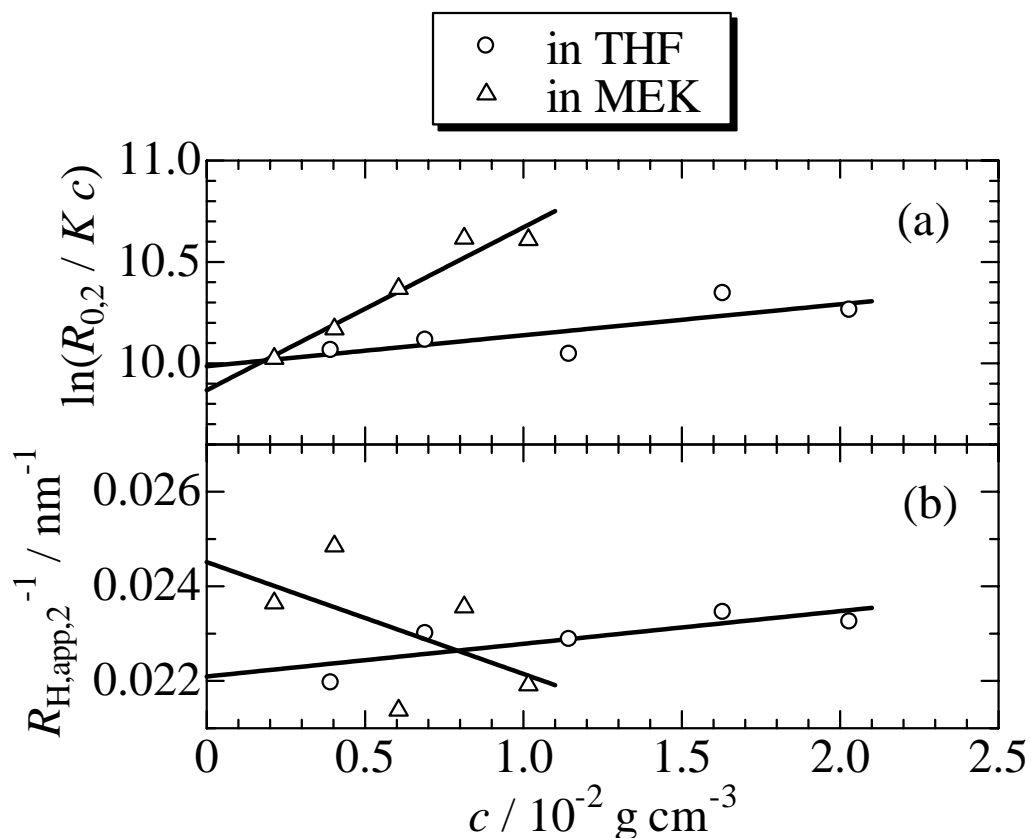
Figure S-1. The concentration dependence of the excess Rayleigh ration (a), and apparent hydrodynamic radius (b) of HBP aggregates.

As the second virial terms can be neglected in a theta solvent, we first discuss on the HBP aggregates in MEK. The (true) hydrodynamic radius of aggregates, $R_{H,2}$ can be estimated in MEK by $R_{H,2} = R_{H,app,2}(R_{H,1}/R_{H,app,1})$ with $R_{H,1} = 5.6$ nm (cf. Table I). When the second virial terms can be neglected, $\ln(R_{0,2}/Kc)$ gives $\ln(w_2 M_{w,2})$ where w_2 stands for the weight fraction of aggregates. If the aggregating component is spherical where the HBP are closely packed, the aggregation number m may be estimate by

$$m \approx \left(R_{H,2}/R_{H,1}\right)^3 \tag{S-1}$$

From the results shown in Tables 1 and S-1 and eq. S1, m is estimated to be in the order of 400 in MEK. Furthermore, using this m and the result of $w_2 M_{w,2}$ in Table S1, it turns out that w_2 is as small as 6×10^{-4}.

Table S-1. Dimension and molar mass of HBP aggregates in MEK.

c / 10^{-2}gcm^{-3}	$w_2 M_2$ / 10^4	$R_{H,2}$ / nm
0.213	2.26	42
0.403	2.61	39
0.605	3.18	45
0.812	4.08	40
1.015	4.05	42

On the other hand, if the component 2 is like random aggregates comprising monomers with functionality f, the weight-average aggregation number m_w is written in the form[1]

$$m_w = \left(\frac{C'}{2} \frac{R_{H,2}}{R_{H,1}} \right)^2 \tag{S-3}$$

where the constant C' slightly depends on f. When we choose $f = 4$, C' equals 2.8[1] and m_w equals ca. 100. This m_w along with the experimental $w_2 M_{w,2}$ gives us $w_2 \sim 2 \times 10^{-3}$.

In both cases of the spherical and random aggregates, the amount of the aggregates estimated was quite small. This is consistent with the result shown in Figure 3 in the text where the intercept of $\ln(R_{0,1}/Kc)$ obtained by the batch measurement agrees with the result of the SEC-MALS performed for a very dilute solution.

In THF, $R_{H,2}$ was not estimated due to the unknown second virial terms but $R_{H,1}$ and $R_{H,2,app}$ in THF are the same order as in MEK, so that we expect the same order of the aggregation number and weight fraction in THF.

REFERENCES

1.   K. Kajiwara, *J. Chem. Phys.*, **54**, 296 (1971).