Self-Assembly Kinetics of Amphiphilic Dendritic Copolymers

Cuiyun Zhang,‡§⊥ You Fan,‡ Yunyi Zhang,‡§⊥ Cong Yu,§⊥ Hongfei Li,⊥∥ Yu Chen,⊥∥ Ian W. Hamley,*∥ and Shichun Jiang*‡§⊥

1School of Materials Science and Engineering, Tianjin University, Tianjin 300072, P. R. China
2State Key Laboratory of Electroanalytical Chemistry, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, P. R. China
3University of Chinese Academy of Science, Beijing 100049, P. R. China
4State Key Laboratory of Polymer Physics and Chemistry, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, P. R. China
5Department of Chemistry, School of Sciences, Tianjin University, Tianjin 300072, P. R. China
*School of Chemistry, Pharmacy and Food Biosciences, University of Reading, Whiteknights, Reading RG6 6AD, United Kingdom

ABSTRACT: The self-assembly process of amphiphilic dendritic copolymers (ADPs) with a hydrophilic core and a hydrophobic shell was investigated via laser light scattering. The self-assembly occurs via a fast step and a slow step with different relaxation times. At the critical micelle concentration (CMC), the fusion of small micelles results in the rapid increase of the micelle size in the fast step. The slow step is associated with equilibrium through the fission and fusion of the micelles. The micelle size increases with the unimer concentration, which leads to a lower micelle concentration. The lower micelle concentration makes the relaxation time of the fast step increase with increasing unimer concentration. However, the fusion of larger micelles at higher concentration is more efficient to increase micelle size. The fusion of small micelles with large micelles at higher concentration accelerates the approaching equilibrium of the micelles except for the fission and fusion of micelles. With the increasing degree of amidation (DA), the relaxation time in the fast step increases and in the slow step it decreases.

1. INTRODUCTION

Following development of the linear, branched, and cross-linking polymers, dendritic polymers including hyperbranched polymers and dendrimers are the fourth generation of polymer architectures.1,2 Hyperbranched polymers consisting of dendritic, linear, and terminal units have an irregular structure compared with dendrimers. Dendritic polymers are highly branched with a three-dimensional architecture and have low viscosity and better solubility than their linear analogues. Great efforts have been devoted to understand and control the self-assembly of amphiphilic dendritic polymers. Multiple morphologies of self-assembled dendritic polymers such as micelles, vesicles, macroscopic tubes, and fibers have been reported,3–6 and the self-assembly has been exploited in areas of drug delivery, sensing and cell imaging, etc.7–9

The self-assembled morphology of polymers is influenced by their topology, the solvent quality, and the solvophobic/solvent/solvophilic ratio. For amphiphilic polymers containing a hyperbranched core, they can self-assemble into spherical micelles, wormlike micelles, and vesicles with an increase in the degree of branching of the core.10 The self-assembled structure of a gradient copolymer was observed to change from spherical micelles to cylindrical micelles and then to vesicles with decreasing solvent quality.11 The size of the spherical micelles formed by amphiphilic hyperbranched polymers in aqueous solution decreases with increasing hydrophilic volume fraction.2,11 In 2005, Yan suggested a multimicelle aggregate mechanism (MMA), which included two steps; i.e., the hyperbranched copolymers first self-assemble into small micelles, and then the small micelles aggregate to form large micelles.12 In 2007, Yan and Haag observed small spherical building units inside the micelles by TEM and cryo-TEM,13,14 which proved the MMA mechanism. Based on dissipative particle dynamics simulations, the dynamic self-assembly processes and the detailed self-assembly mechanism were analyzed,15 which demonstrated the unimolecular micelle aggregation mechanism and the small micelle aggregation mechanism. In the former mechanism, the unimolecular micelles directly aggregate to form large micelles without microphase separation. In the small micelle aggregate mechanism, the amphiphilic hyperbranched copolymers first rearrange the hydrophilic and hydrophobic parts to form...
microphase-separated small micelles. Then the small micelles assemble into large multimolecular micelles. Also, the increase of the radius of gyration ($R_g$) with time reflects the dynamic process. However, except for computer simulations, the dynamic self-assembly process of the ADPs is rarely reported. The fusion process of polymer vesicles was observed by optical microscopy.\textsuperscript{16,17} However, the formation process of the vesicles before the size is large enough for observation by optical microscopy is unclear.

The micellization kinetics of surfactants and block copolymers has been studied both theoretically and experimentally.\textsuperscript{18–22} The Aniansson–Wall theory provides a widely accepted kinetic description of the self-assembly process of small surfactant molecules, which divides the micellization process into a fast and a slow step.\textsuperscript{18,21} In the fast step, the aggregation number ($N_{agg}$) of each micelle increases with no change in the total number of micelles. In the slow step, the self-assembly process approaches equilibrium accompanied by the formation and fusion of the micelles with a variation in the number of micelles. The micellization process of block polymers is similar to that of surfactants. The unimers quickly associate to form quasi-equilibrium micelles, and the increasing micelle number dominates over the growth of the micelles in the first process. In the second process the micellization approaches equilibrium with an increase in micelle size combined with a decrease in the number of micelles.\textsuperscript{22} The self-assembly kinetics of the ADPs is expected to be similar.

To date, studies of the self-assembly of dendritic polymers have mainly focused on the final equilibrium structure which is observed by TEM.\textsuperscript{3–6} During the sample preparation, the solvent evaporation leads to shrinkage, collapse and even deformation of the micelles.\textsuperscript{23} The increasing concentration resulting from the solvent evaporation may induce the fusion of micelles, which creates artifacts in TEM images. In contrast, it is possible to measure $R_g$ and hydrodynamic radius ($R_h$) in situ using laser light scattering. Furthermore, the time dependence of scattering intensity, $R_g$ and $R_h$ provides information on the dynamic processes of self-assembly. In order to observe the dynamic process, the self-assembly process should be slow enough for the detection by laser light scattering.\textsuperscript{24} A relatively narrow distribution of the micelles is desirable for the calculation of $R_g$.

In this paper, first, the critical self-assembly conditions of the ADPs were explored. Second, the dynamic self-assembly process was studied. Then the influence of concentration and solvophobic/solvophilic ratio on the self-assembly process was discussed. We believe that this represents the first report on the self-assembly kinetics of the ADPs using the laser light scattering method.

### 2. EXPERIMENTAL SECTION

#### 2.1. Materials

Hyperbranched polyethylenimine (HPEI, $M_w = 10^4$ g mol$^{-1}$, $M_w/M_n = 2.5$) was purchased from Aldrich. 2,2-Bis(hydroxy-methyl)propionic acid (BHP, 99%) was purchased from Beijing Ouhe Technology Company. Palmitic acid (A.R.) was purchased from Tianjin University Kewei Chemical Company. The ADPs were synthesized according to the reported approach, and the synthesis process is shown in Scheme S1.\textsuperscript{25} Detailed information on molar mass and $R_h$ of the studied ADPs,\textsuperscript{26} as well as CMC and critical solvent volume fraction (CSV) values at which methanol volume fraction the ADPs starts to self-assemble are listed in Table 1. The influence of polydispersity on the self-assembly is discussed in the Supporting Information. Chloroform and methanol used in the self-assembly experiment were purchased from the Beijing Chemical Works. Chloroform was refluxed with calcium hydride before distillation.

#### 2.2. Measurements

The light scattering experiments were performed using an ALV CGS-3 light scattering spectrometer equipped with an ALV-5000 multilat digital time correlator and a He–Ne laser ($\lambda = 632$ nm) as light source. The $R_g$ values of the micelles were calculated from the angular dependence of the natural logarithm of the scattered intensity according to the Guinier plot.\textsuperscript{27} The decay rate distribution ($G(\Gamma)$) was obtained from the CONTIN Laplace inversion of the intensity–intensity time correlation function $g(q,\tau)$. The relation between the decay rate and the apparent diffusion coefficient is $\Gamma = q^2D$, where the scattering vector $q = (4\pi/\lambda)\sin(\theta/2)$, $n$ is the refractive index of the solvent, $\lambda$ is the wavelength of the light in vacuum, and $\theta$ is the scattering angle.\textsuperscript{28} From the Stokes–Einstein equation $R_g = k_BT/6\pi n\eta$, the average hydrodynamic radius was calculated, where $k_BT$ and $\eta$ are the Boltzmann constant, the absolute temperature, and the solvent viscosity, respectively. All the solutions were filtered through 0.45 μm Millipore polytetrafluoroethylene filters before measurements.

### 3. RESULTS AND DISCUSSION

#### 3.1. Critical Self-Assembly Conditions for the ADPs

In a mixed solvent system, if the solvent–polymer interaction is stronger than the solvent–non solvent interaction, the preferential solvation will happen and the polymer will be selectively solvated by the solvent.\textsuperscript{30} Because of the preferential adsorption of the solvent to the polymer, the size of the linear polymer is dependent on the solvent quality.\textsuperscript{31} In this work, we choose chloroform as a common solvent and methanol as a nonsolvent for the nonpolar shell. No special interactions, such as hydrogen bonding, exist among chloroform, methanol, and the nonpolar shell of the ADPs. So the solvents will not concentrate around the nonpolar shell. The methanol may form hydrogen bonds with HPEI and concentrate in the inner polar core. Below 10% volume fraction of the methanol, the hydrodynamic radius of P-1 is not influenced by the methanol (Figure S1). Because of the weak response of the hyperbranched structure to the solvent quality,\textsuperscript{25} this phenomenon cannot prove the preferential solvation effects exist or not. With increasing volume fraction of methanol the solvent quality becomes gradually worse for the ADPs, and the preferential solvation effect of the core has no influence on the self-assembly process. The ADPs were first dissolved in chloroform, and then methanol was added dropwise to change the solvent quality slowly. The values of CSV were obtained from the change of the scattering intensity with the methanol volume fraction. The final concentration of the ADPs was 0.5 mg/mL, and before measurement the solutions were kept at 25 °C for 12 h. As shown in Figure 1, at the CSV, the scattering intensity increases sharply upon the formation of micelles. The solvophobic/solvophilic ratio increases with DA, which leads to decreasing polarity of the ADPs. The CSV decreases slightly with DA (Table 1). In terms of the CSV of P-1, P-2, P-3, and

<table>
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<tr>
<th>polymer</th>
<th>DA (°)</th>
<th>$f_{shell/core}$</th>
<th>$M_w/10^4$</th>
<th>$R_h$ (nm)</th>
<th>CSV (%)</th>
<th>CMC (mg mL$^{-1}$)</th>
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<tr>
<td>P-1</td>
<td>38</td>
<td>5.2</td>
<td>6.2</td>
<td>5.2</td>
<td>49</td>
<td>0.57</td>
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<tr>
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<td>6.7</td>
<td>5.5</td>
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<tr>
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<td>7.0</td>
<td>8.0</td>
<td>6.1</td>
<td>44</td>
<td>0.26</td>
</tr>
<tr>
<td>P-4</td>
<td>60</td>
<td>8.3</td>
<td>9.3</td>
<td>7.3</td>
<td>44</td>
<td>0.20</td>
</tr>
</tbody>
</table>

*DA is the degree of amidation, and $f_{shell/core}$ is the weight ratio of the nonpolar shell to the polar core.*
P-4, the solvent containing 50% methanol is a relatively poor solvent, and the ADPs self-assemble in the solvent mixture containing this volume fraction of methanol.

The CMC for the four ADPs was measured in solutions that contained 50% methanol. At the CMC, the scattering intensity of the solution increases due to the formation of micelles. In Figure 2, the scattering intensity of P-1 increases at a concentration of 0.57 mg/mL, suggesting that the CMC for P-1 is 0.57 mg/mL. As shown in Table 1, the CMC for the ADPs decreases with increasing DA because of the increasing solvophobic/solvophilic ratio with DA.

3.2. Self-Assembly Kinetics of ADPs. To date, to our knowledge, there are no reported experimental studies on the self-assembly kinetics of ADPs. For the amphiphilic hyperbranched copolymers with a hydrophobic core and many hydrophilic arms, the hydrophobic groups in the hydrophilic arms are essential for the interchain overlapping and entangling, which drive the micellization of the polymers. In enlarged TEM images, the unimers are observed, indicating that the large micelles are built up from the unimers. The reported unimolecular micelle aggregation mechanism based on the dissipative particle dynamics simulations supports the MMA mechanism. In this work, the real-time self-assembly process was monitored and discussed. The time dependence of the scattering intensity and $R_h$ was measured. The increasing trends of the scattering intensity (Figure 3a) and $R_h$ (Figure 3b) are almost the same, with a rapid initial increase followed by a slower increase. Figure 4a represents the scattering vector dependent decay rate and scattered intensity. Based on the Stokes–Einstein equation and the Guinier plot, the values of $R_g$ and $R_h$ were calculated. The ratio of $R_g$ and $R_h$ reflects the...
the fitting and the precision of the kinetic parameters. As shown in Table 2, the two relaxation times correspond to the two different self-assembly steps. The high DA of the hyperbranched polymers leads to great steric hindrance, which hinders the microphase separation of the unimer. Because of the compact structure and the great steric hindrance, the self-assembly is assumed to follow the unimolecular micelle aggregation mechanism. Vmicelle and Vunimer are the volume of the micelle and the unimer, which are obtained from eq 2. Based on eq 3, the Nagg of the micelle was estimated. The rapid increase of Nagg corresponds to the first step, and the slow increase of Nagg occurs in the second step (Figure 5). The necessary condition for the self-assembly is that the chemical potential of the unimers in the micelles is smaller than that in the solution, and when the chemical potential of the unimers in the micelle holds a minimum value, the process reaches equilibrium. 

\[ V = \frac{4}{3} \pi R^3 \]  

\[ N_{agg} = \frac{V_{micelle}}{V_{unimer}} \]  

The kinetics of the self-assembly is reflected by the increase of Rg. After addition of methanol, the ADPs self-assemble into small micelles, and with time the small micelles grow into larger ones. The distribution of Rg at the CMC is shown in Figure 6. Unfortunately, because of the quick association of the unimers, only for P-1 and P-2 can the self-assembly process of the unimers to micelles transition be monitored owing to the relatively lower solvophobic/solvophilic ratio. The variation of the distribution of Rg from 0 to 100 min is shown in Figure S3. Because of the lack of data on the unimers to micelles transition, we mainly focus on the fusion of the micelles. There are two ways for micelle size to increase. One is the fusion of micelles with comparable size. The other is the fusion of large micelles with small micelles. In order to illustrate the self-assembly kinetics more obviously, the increased hydrodynamic radius (Rg,i) was calculated based on eq 4

\[ V_{i+1} = V_i + V_I \]  

where Vi and V+i are the volumes of the micelles at the times i and i + 1. V_I is the increased volume. Through the values of V_I, the values of Rg,i were calculated. The evolution of Rg,i and the smallest hydrodynamic radius of the micelles in the distribution (Rg,min) are shown in Figure 7. The dotted line in Figure 7 is the cutoff line between the first and the second step. The first step is dominated by the fusion of micelles of comparable size. In the second step, Rg,i is smaller than Rg,min and this suggests that the micelles formed in the first step undergo fusion and a smaller micelle fuses with another larger micelle, which cause the slow increase of the micelle size. This phenomenon is similar to the micellization of block copolymers. Before 80 min the polydispersity index (PDI) obtained from the ratio of \( \mu_i/V^2 \) (\( \mu_i \) is the second cumulant) decreases with time and increases after 80 min (Figure 8). Based on the evolution of Rg,i, PDI, and PDI, the self-assembly process of the ADPs at the CMC is summarized (Scheme 1). In the first step, the unimers aggregate quickly to form small micelles, and then the small micelles fuse into relatively larger and monodisperse micelles. In the second step, through the fusion of the micelles the distribution becomes broader and the self-assembly approaches dynamic equilibrium.

3.3. Influence of Concentration on the Self-Assembly

The phase diagram of block polymers is influenced by the concentration. The size of the nanoparticles formed by the self-assembly of the hyperbranched polymers is larger at higher concentration. As shown in Figure 9, the scattering intensity and hydrodynamic radius increase with concentration. The relaxation times associated with the self-assembly processes at different concentration are shown in Table 2. With increasing concentration, \( \tau_1 \) increases and \( \tau_2 \) decreases. Honda et al. reported that the relaxation time \( \tau_1 \) of block copolymers in the
first process decreased with increasing concentration, and $\tau_2$ was almost independent of the concentration. However, the relaxation times of block copolymers in the rod to vesicle transition increase with increasing concentration. The first step of the micellization of surfactants and block copolymers is mainly the quick association of the unimers, and the relaxation time is on the time scale of seconds. Whereas, in this study, the first step of the ADPs is mainly the fusion of small micelles and the relaxation time is on the time scale of hours. The energy barrier for the fusion of micelles is larger than that for the aggregation of unimers, which suggests that different mechanisms lead to the different time scales. The fusion of micelles through collision mechanism is concentration dependent, and at higher micelle concentration the collision probability increases. The increase of size with concentration may result in the decrease of the small micelle concentration in the first step. The self-assembly rate will slow down with decreasing small micelle concentration. The concentration ratio of two solutions is expressed as high concentration to low concentration. For the two solutions of a given ADP, if the $N_{agg}$ ratio is larger than the corresponding unimer concentration ratio, the micelle concentration of the solution with a higher unimer concentration is lower, and vice versa. As shown in Figure 10a, the $N_{agg}$ ratio is larger than the concentration ratio, indicating the decrease of micelle
concentration with increasing unimer concentration. The increasing value of \( \tau_1 \) with concentration in the first step results from the decreasing micelle concentration. The derivative of the change of scattering intensity with time is shown in Figure 10b. The Y-axis value of the derivative reflects the rate of change of the scattering intensity. The scattering intensity is related to the micelle size and number. With time the micelle number decreases. Therefore, the increasing rate of the scattering intensity change at higher concentration is due to the efficient fusion of the larger micelles. Though the fusion of large micelles takes a longer time (larger \( \tau_1 \)), the rate is higher.

The polydispersity index and \( R_{hI} \) increase with the concentration (Figure S4). For P-4 with a concentration of 0.57 mg/mL, the distribution of the hydrodynamic radius even shows a bimodal distribution after 100 min (Figure S5). With the increasing concentration, the self-assembly kinetics in the second step becomes complex. The increased hydrodynamic radius is larger than the minimum hydrodynamic radius in the distribution (Figure 11). Except for the fission and fusion of the micelles, the self-assembly in the second step includes the fusion of the small micelles with the large micelles. The size of the small micelles increases at higher concentration (Figure S6). As shown in Figure 10b, the faster increasing rate of the micelles at higher concentration contributes to the decrease of \( \tau_2 \) with increasing concentration.

### 3.4. Influence of the DA on the Self-Assembly

Liu et al.\(^ {41} \) reported that the size and \( N_{agg} \) of spherical micelles increased with the solvophobic chain length of the linear block polymer studied. Because of the decreasing apparent activation energy with the increasing solvophobic chain length, the micellization mechanism of the slow process changes from unimer insertion/expulsion to micelle fusion/fission. The self-assembly of the hyperbranched copolymers is also influenced by the solvophilic/solvophobic ratio and the degree of branching of the core.\(^ {4,10} \) For the ADPs, the absence of the microphase separation resulting from the great steric hindrance of the nonpolar shell is conjectured to make the micellization kinetics different. As shown in Figure 12, the scattering intensity and the hydrodynamic radius increase with DA. The ratio of the radius of gyration and hydrodynamic is around 0.74 (Figure S7), indicating that the structure is not influenced by DA.

A study of the aggregation kinetics of block polymers found that the driving force for the micellization increased with the solvophobic chain length, giving rise to decreasing relaxation times.\(^ {40} \) Similar to block polymers, the self-assembly driving force of the ADPs is assumed to increase with increasing DA. As shown in Table 2, with the increasing DA, \( \tau_1 \) increases and \( \tau_2 \) decreases at the same concentration. The molecular weight increases with DA, which induces the decrease of the unimer concentration with increasing unimer concentration. The increasing value of \( \tau_1 \) with concentration in the first step results from the decreasing micelle concentration. The derivative of the change of scattering intensity with time is shown in Figure 10b. The Y-axis value of the derivative reflects the rate of change of the scattering intensity. The scattering intensity is related to the micelle size and number. With time the micelle number decreases. Therefore, the increasing rate of the scattering intensity change at higher concentration is due to the efficient fusion of the larger micelles. Though the fusion of large micelles takes a longer time (larger \( \tau_1 \)), the rate is higher.

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molar concentration. This phenomenon may cause the increase of $\tau_1$. However, as discussed above, with increasing unimer concentration, the micelle concentration decreases and the relaxation time in the first step increases, which suggests that the increase of the unimer molar concentration will not lead to the decrease of $\tau_1$. The $N_{agg}$ of the four ADPs is almost the same in the first step, while the $N_{agg}$ of P-1 is much smaller than that of the other three ADPs in the second step (Figure 13a). Despite the larger $R_h$ of the micelle, the $N_{agg}$ of P-4 is slightly smaller than that of the P-2 and P-3 (Figure 13a). In order to analyze the micelle concentration of the four ADPs in the micellization process, the comparison of the $N_{agg}$ ratio and the unimer molar concentration ratio for different ADPs is shown in Figure 13b–d. If the $N_{agg}$ ratio is larger than the unimer molar concentration ratio, the micelle concentration will be smaller at higher DA, and vice versa. Before the intersection point of the $N_{agg}$ ratio and the unimer molar concentration ratio ($T_1$), the $N_{agg}$ ratio is smaller than the unimer molar concentration, suggesting that the micelle concentration is larger at higher DA. After $T_1$, the $N_{agg}$ ratio is larger than the unimer molar concentration ratio, indicating that the micelle concentration is smaller at higher DA. $T_1$ is smaller than $\tau_1$ (Table 3), which indicates that the smaller micelle concentration in the later period of the first step has an influence on the self-assembly kinetics. The increasing $\tau_1$ results from the smaller micelle concentration, which is similar to the influence of concentration on the kinetics.

The derivative of the change of scattering intensity with time is shown in Figure 14. The $Y$-axis value of the derivative increases with DA, indicating that the increasing rate of the micelle size change is faster at higher DA. Except for P-1, with the increasing DA, the concentration of the ADPs solution is higher than the CMC, meaning that the kinetics of P-2, P-3, and P-4 in the second step includes the fusion of small micelles with large micelles. The size of the micelles that fuse with the large micelles in the second step increases with increasing DA (Figure S8). The faster increasing rate at higher DA gives rise to the decreasing relaxation time $\tau_2$. In the second step, because of the larger $N_{agg}$ ratio compared with the unimer molar concentration ratio for P-2, P-3, and P-4 with respect to P-1 (Figure 13b), the micelle concentration is much smaller than that of P-1, while $\tau_2$ for P-1 is much larger than that of P-2, P-3, and P-4 (Table 2). This phenomenon results from the weaker driving force for P-1 compared with that of ADPs at higher DA.

Figure 12. Time-dependent scattering intensity (a) and hydrodynamic radius (b) at different DA.

Figure 13. Change of $N_{agg}$ with time for P-1, P-2, P-3, and P-4 at 0.57 mg/mL (a). The comparison of the $N_{agg}$ ratio and unimer molar concentration ratio for different ADPs at 0.57 mg/mL (b–d). The subscripts of the $N_{agg}$ represent the DA. The solid line is the corresponding unimer molar concentration ratio.
**Table 3. Comparison of $T_1$ and the Relaxation Time $\tau_1$**

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<thead>
<tr>
<th>ratio</th>
<th>$N_{agg1}/N_{agg3}$</th>
<th>$N_{agg1}/N_{agg5}$</th>
<th>$N_{agg2}/N_{agg5}$</th>
<th>$N_{agg1}/N_{agg3}$</th>
<th>$N_{agg2}/N_{agg5}$</th>
<th>$N_{agg1}/N_{agg3}$</th>
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<tbody>
<tr>
<td>$T_1$ (min)</td>
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<td>46</td>
<td>30</td>
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<td>49</td>
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<tr>
<td>$\tau_1$ (min)</td>
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<td>129.8</td>
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</tbody>
</table>

*E-mail i.w.hamley@reading.ac.uk; Fax +44 118 378 6331 (I.W.H.).

*E-mail scjiang@tju.edu.cn; Fax +86 22 2740 4724 (S.J.).

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