

Multistep Thermosensitivity of Poly(*N*-*n*-propylacrylamide)-*block*-poly(*N*-isopropylacrylamide)-*block*-poly(*N*,*N*-ethylmethacrylamide) Triblock Terpolymers in Aqueous Solutions As Studied by Static and Dynamic Light Scattering

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ABSTRACT: Poly(*N*-*n*-propylacrylamide)-*block*-poly(*N*-isopropylacrylamide)-*block*-poly(*N*,*N*-ethylmethacrylamide) (PnPA-*b*-PiPA-*b*-PEMA) triblock terpolymers of low polydispersity have been synthesized by reversible addition-fragmentation chain transfer (RAFT) polymerization via sequential monomer addition. The temperature-induced formation and dissociation of terpolymer micelles in aqueous solutions in a heating–cooling cycle were investigated by a combination of static and dynamic laser light scattering. In the heating process, the folding of PnPA at ca. 25 °C led to the formation of polymeric micelles with a collapsed hydrophobic PnPA core and a hydrophilic swollen PiPA–PEMA shell. Further increase of the temperature to ca. 32 and 53 °C led to the successive dehydration of PiPA and PEMA on the periphery, respectively. Our results revealed that when PEMA on the periphery of the micelle is too short to stabilize the hydrophobic core, individual micelles tend to aggregate into large micellar clusters, corresponding to the intrachain contraction and interchain association of the PiPA chains. In the cooling process, the complete dissolution temperature was lower than the association temperature in the heating process. At a given temperature, the aggregates in the cooling process had a higher mass than those in the heating process, clearly indicating a hysteresis.

Introduction

Thermosensitive polymers have received much attention because of their potential applications in membranes,¹ drug delivery systems² and isolation of biomolecules.³ The *N*-alkyl substituted polyacrylamides are well-known representatives of the group of thermosensitive polymers with a lower critical solution temperature (LCST) at which a polymer solution undergoes phase transition from a soluble to an insoluble state.^{4–13} Recently, block copolymers whose blocks can be reversibly switched from hydrophilic to hydrophobic by a temperature stimulus have been extensively investigated.^{14–17} Amphiphilic or double-hydrophilic diblock copolymers comprising a thermosensitive block are the most widely studied, which exhibit a single transition.^{18–23} More complex and flexible polymers involving multiple transitions are essential in the understanding of the process and in the design and use of interesting molecular device.¹⁵ Doubly thermosensitive diblock copolymers which exhibit two different LCSTs have been investigated by several groups.^{24–28} In such systems, a transition from a hydrophilic to an amphiphilic and finally to a hydrophobic block copolymer occurs with an increase in temperature.^{24,25,27} Some of the doubly thermosensitive diblock copolymers even present an interesting self-association behavior, which undergo multiple transitions upon heating.^{26,28} Thermosensitive triblock copolymers have attracted considerable

interest because of their complex morphologies.^{29–39} To date, most reports are focused on ABA or BAB triblock copolymers with A representing the hydrophilic block and B the thermosensitive block. The self-assembly behavior of ABA triblock copolymers is very similar to that of the AB diblock copolymers,³⁸ while a BAB architecture tends to yield more complex structure such as flower-like or interconnected micelles and networks.^{32–35,39} The above-mentioned AB, ABA, and BAB block copolymers represent all-or-none systems with respect to temperature-responsive amphiphilicity and associative behavior in aqueous solutions. Under many circumstances, more gradual or more subtle thermosensitivity are desirable. This may be realized by the use of thermosensitive ABC triblock copolymers in which a hydrophilic block is combined with two different thermosensitive blocks.^{31,33,37} Two evident thermal transitions are observed in dilute aqueous solutions of such double thermosensitive ABC triblock copolymers.^{31,33} In addition to block copolymers, doubly thermosensitive unimolecular micelles have been reported and two-stage collapse processes were observed.⁴⁰ Recently, we have synthesized well-defined ABC triblock copolymers by reversible addition-fragmentation chain transfer (RAFT) polymerization via sequential monomer addition.^{41–43} Our ternary block copolymers consist of three different thermosensitive blocks with different cloud points (CP), exhibiting more complex and interesting aggregation behaviors in water. Such polymers exhibited multiple thermosensitivity with accompanying changes in micellar size or shape and solution properties.⁴³ The aggregation mechanism of such multiblock copolymers remains to be explored, and the effect of the length of the final block of the copolymers on their aggregation in solution needs to be elucidated. We use a combination of static and dynamic light scattering (LS), and

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Table 1. Conversion, Molecular Weight, and Polydispersity of the Mono-, Di-, and Triblock Copolymers

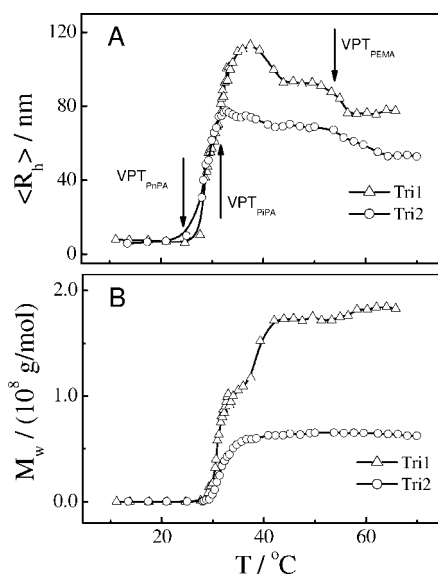
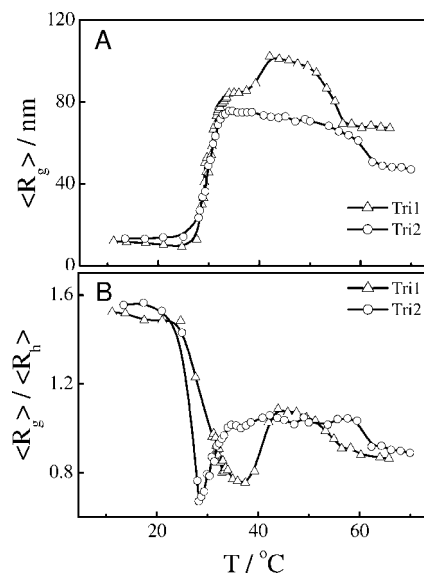
polymer	conversion (%) ^a	M_n^b	M_w/M_n^b
P(nPA) ₁₂₄	69	14 400	1.10
P(nPA) ₁₂₄ - <i>b</i> -iPA ₈₀)	87	23 400	1.10
P(nPA) ₁₂₄ - <i>b</i> -iPA ₈₀ - <i>b</i> -EMA ₄₄) (Tri1)	85	28 400	1.14
P(nPA) ₁₂₄ - <i>b</i> -iPA ₈₀ - <i>b</i> -EMA ₁₆₀) (Tri2)	80	41 500	1.14

^a Measured by ¹H NMR. ^b Measured by SEC.

and modify the phase transition temperatures of the individual blocks from those of the corresponding homopolymers.⁴² In this work, the temperature-induced phase transition behavior of the triblock copolymers in aqueous solutions is systematically investigated at a microscale with a combination of static and dynamic light scattering techniques.

Heating Process. Figure 1A shows the temperature dependence of the hydrodynamic radius (R_h) of the stable aggregates formed by the two different copolymers in the heating process. The temperature dependence of (R_h) of Tri1 is quite different from that of Tri2. When the temperature increases to 25 °C, corresponding to the LCST of PnPA, (R_h) increases abruptly, indicating the aggregation of triblock copolymers. For Tri2 with a longer PEMA block, (R_h) decreases slightly in the range of ~32–38 °C due to the collapse of the PiPA chains on the periphery of the micelles. Further increase in temperature to ~53 °C causes a slight decrease in (R_h), corresponding to the collapse of the PEMA. The volume phase transition (VPT) temperatures of the blocks are shown in Figure 1A. Finally, Tri2 forms a stable mesoglobule after the three-step phase transition. For Tri1, (R_h) continuously increases in the range of ~32–38 °C. Such an increase can be attributed to the aggregation of the micelles. From the results of Tri2, we know that the short PEMA chains on the periphery may have an important effect on the aggregation of the micelles. When the temperature is in the range of 38–45 °C or above ~53 °C, (R_h) decreases as a result of the collapse of PiPA and PEMA chains and even of the likely further contraction of the collapsed PnPA core.

Figure 1B shows the temperature dependence of the apparent molar mass (M_w) of the resultant aggregates in the heating process. Clearly, Tri1 shows a behavior quite different from that of Tri2. At a temperature above 25 °C, the increase in M_w

**Figure 1.** Temperature dependence of (A) the hydrodynamic radius (R_h) and (B) the apparent molar mass (M_w) of the resultant aggregates in the 0.1 mg/mL aqueous solutions of P(nPA)₁₂₄-*b*-iPA₈₀-*b*-EMA₄₄) (Tri1) and P(nPA)₁₂₄-*b*-iPA₈₀-*b*-EMA₁₆₀) (Tri2) in the heating process.**Figure 2.** Temperature dependence of (A) the radius of gyration (R_g) and (B) (R_g)/(R_h) of the resultant P(nPA)₁₂₄-*b*-iPA₈₀-*b*-EMA₄₄) and P(nPA)₁₂₄-*b*-iPA₈₀-*b*-EMA₁₆₀) (Tri1 and Tri2) aggregates in the heating process.

indicates the aggregation of both triblock copolymers. For Tri2, M_w varies very little at ~38 °C and above. For Tri1, however, M_w increases quickly again at ca. 38 °C and a plateau can be observed at ca. 45 °C. The second transition suggests the interchain association of different micelles corresponding to the dehydration of the PiPA blocks. Such micellar clusters have been observed in the self-assembly of the block copolymers.^{50–53} We have demonstrated that a micellar cluster is easily formed when the chains in the shell of the micelles is not long enough to shield the solvophobic core.⁵⁴ In the present case, the PEMA chains on the periphery are too short to shield the hydrophobic core of the micelles when the PiPA chains start to collapse, which makes the clustering of the micelles possible. Note that (R_h) in the range of ~38–45 °C decreases while M_w increases. This is due to the competition between the contraction of the PiPA chains and clustering of the micelles. This can be further viewed in terms of (R_g) in Figure 2.

Figure 2A shows the temperature dependence of (R_g) of the aggregates. At a temperature above 38 °C, (R_g) of Tri1 increases, further indicating the clustering of the micelles due to the association of the PiPA chains in different micelles. (R_g) drops at ~53 °C, indicating the collapse of PEMA chains on the periphery of the micellar clusters or the micelles.

The temperature dependence of the ratio of the radius of gyration to hydrodynamic radius ($\langle R_g \rangle / \langle R_h \rangle$) is shown in Figure 2B. ($\langle R_g \rangle / \langle R_h \rangle$) can describe the structure of a polymer chain or a particle.^{55,56} For uniform nondraining spheres, hyperbranched clusters and random coils, the ($\langle R_g \rangle / \langle R_h \rangle$) values were found to be ~0.774, 1.0–1.2 and 1.5–1.8, respectively.⁵⁶ A spherical micelle generally has a ($\langle R_g \rangle / \langle R_h \rangle$) of 0.7–0.8. For Tri1, as temperature increases from 10 to 35 °C, ($\langle R_g \rangle / \langle R_h \rangle$) decreases from 1.5 to 0.8, clearly indicating the collapse of the chains and the formation of micelles. ($\langle R_g \rangle / \langle R_h \rangle$) increases from 0.8 to 1.0 in the range of 35–45 °C, indicating that the micelles may be forming a cluster. At a temperature above ~53 °C, ($\langle R_g \rangle / \langle R_h \rangle$) decreases and finally levels off, indicating that the clusters become dense after the collapse of the PEMA chains on the periphery. Likewise, for Tri2, ($\langle R_g \rangle / \langle R_h \rangle$) decreases from ~1.5 to 0.7 in the range of ~10–28 °C, indicating the formation of micelles with PnPA as the core and PiPA and PEMA as the shell. The subsequent increase of ($\langle R_g \rangle / \langle R_h \rangle$) starting at ~28 °C can be attributed to the competition between the contraction of the PiPA

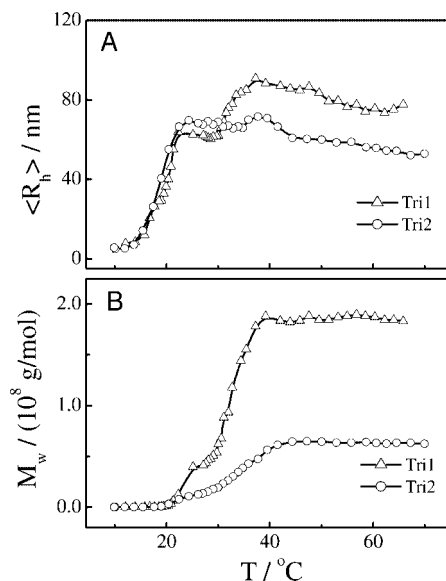


Figure 3. Temperature dependence of (A) the hydrodynamic radius $\langle R_h \rangle$ and (B) apparent molar mass (M_w) of the resultant P(nPA₁₂₄-b-iPA₈₀-b-EMA₄₄) and P(nPA₁₂₄-b-iPA₈₀-b-EMA₁₆₀) (Tri1 and Tri2) aggregates in the cooling process.

chains and the steric repulsion-induced stretching of PEMA chains.⁵⁷ At temperatures above 53 °C, the micelles become denser, so that $\langle R_g \rangle / \langle R_h \rangle$ decreases and levels off.

In short, the PEMA chains in Tri2 are long enough so that the Tri2 micelles exhibit a two-stage collapse in the heating process corresponding to the collapse of the PiPA and PEMA chains, respectively. For Tri1, the shorter PEMA chains on the periphery of the micelles cannot shield the more hydrophobic PnPA and PiPA core completely, so that the PiPA chains in different micelles associate, leading to the formation of micellar clusters.

Cooling Process. The dissolution of the aggregates in the cooling process may provide insight to the origin of the micellar clusters. As shown in Figure 3A, $\langle R_h \rangle$ of Tri2 slightly increases in the range of 60–45 °C and 45–38 °C, corresponding to the swelling of PEMA and PiPA blocks, respectively. The decrease in $\langle R_h \rangle$ in the range of 38–24 °C indicates the dissolution of the micelles. $\langle R_h \rangle$ changes little below ~15 °C, indicating the complete dissolution of the micelles. For Tri1, the change of $\langle R_h \rangle$ is similar to that in the heating process. $\langle R_h \rangle$ increases slightly when the temperature is lowered to ~53 °C due to the swelling of PEMA chains. When the solution is cooled to 38 °C, $\langle R_h \rangle$ decreases sharply probably due to the disassociation of the micellar clusters. When the temperature is decreased to ~24 °C, the micelles begin to dissolve, causing the sharp decrease in $\langle R_h \rangle$. Finally, the micelles completely dissolve into copolymer chains at ~15 °C. Note that the complete dissolution temperature (~15 °C) is lower than the aggregation temperature (~25 °C) in the heating process (Figure 1). The hysteresis is formed probably due to the formation of additional interchain and intrachain hydrogen bonds in the collapsed state of the PiPA and PnPA chains.^{58–60}

The two-stage disintegration of the micellar clusters of Tri1 may also be reflected in the temperature dependence of M_w in Figure 3B. For Tri1, M_w begins to decrease at ~38 °C because of the dissolution of the micellar clusters. Further cooling of the solution to ~28 °C leads to a sudden decrease in M_w due to the dissolution of the micelles. When the temperature is decreased to ~15 °C, M_w becomes much lower and levels off, indicating the complete dissolution of the micelles into individual chains. For Tri2, when temperature decreases from 45

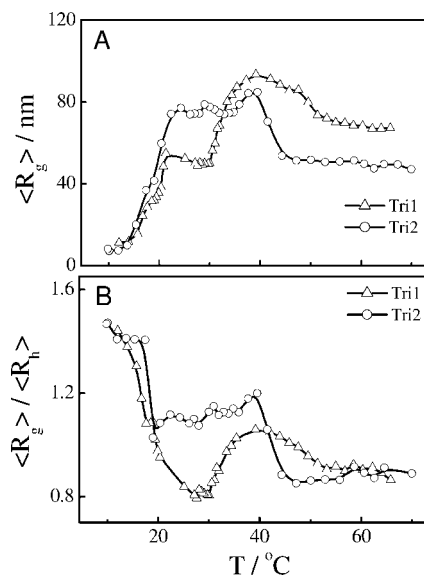


Figure 4. Temperature dependence of (A) the radius of gyration $\langle R_g \rangle$ and (B) $\langle R_g \rangle / \langle R_h \rangle$ of the resultant P(nPA₁₂₄-b-iPA₈₀-b-EMA₄₄) and P(nPA₁₂₄-b-iPA₈₀-b-EMA₁₆₀) (Tri1 and Tri2) aggregates in the cooling process.

to 15 °C, M_w decreases continuously because of the dissolution of the micelles. In comparison with the results in Figure 1B, a clear hysteresis can be observed from the temperature dependence of M_w in Figure 3B. At the same temperature, the aggregates in the cooling process have a higher molar mass than those in the heating process, further revealing that the hysteresis is due to the formation of interchain and intrachain hydrogen bonds between different chain segments of the collapsed PiPA and PnPA chains in the heating process. It takes more time to disrupt these hydrogen bonds and dissolve the aggregates in the cooling process.^{58–60}

Figure 4A shows the temperature dependence of $\langle R_g \rangle$ in the cooling process. For Tri1, the decrease of $\langle R_g \rangle$ in the range of 38–30 °C also indicates that the micellar clusters are swollen and disassociate into micelles. When the temperature is lowered to ~10 °C, the small $\langle R_g \rangle$ indicates that the micelles are dissolved completely. For Tri2, $\langle R_g \rangle$ increases in the range of 45–38 °C, corresponding to the swelling of PEMA. The slight decrease of $\langle R_g \rangle$ in the range of 38–30 °C is due to the dissolution of the micelles. When temperature is below ~15 °C, $\langle R_g \rangle$ decreases abruptly due to the complete dissolution of the micelles.

Figure 4B shows the temperature dependence of $\langle R_g \rangle / \langle R_h \rangle$ in the cooling process. For Tri1, $\langle R_g \rangle / \langle R_h \rangle$ increases from 0.9 to 1.0 and decreases to 0.8 when temperature is decreased from 60 to 30 °C, indicating the micelle clusters are swollen and disassociate into micelles. At a temperature below 15 °C, $\langle R_g \rangle / \langle R_h \rangle$ increases from 0.8 to 1.5, indicating that the micelles disassociate into individual chains. For Tri2, $\langle R_g \rangle / \langle R_h \rangle$ increases from 0.8 to 1.2 in the range of 45–38 °C, corresponding to the swelling of PEMA on the periphery. $\langle R_g \rangle / \langle R_h \rangle$ is ~1.1 in the range of 38–20 °C while M_w continuously decreases, indicating the dissociation of the micelles. The increase in $\langle R_g \rangle / \langle R_h \rangle$ from 1.1 to 1.4 at lower temperatures reveals that the micelles disassociate into individual chains completely.

Microcalorimetry. We also examined the aggregation by microcalorimetry. Figure 5 shows the effect of the block length of PEMA on the specific heat capacity (C_p) of triblock copolymers in one heating–cooling cycle, where the positive and negative C_p values correspond to the endothermic and exothermic processes, respectively. In the heating process, the phase transition temperature (T_p) shifts to a higher temperature

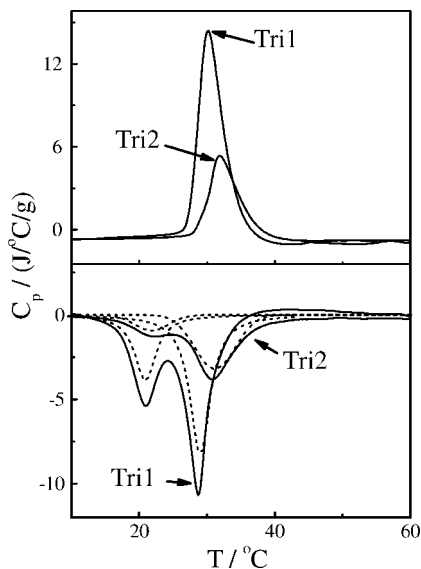


Figure 5. Temperature dependence of the specific heat capacity (C_p) of triblock copolymers in one heating-and-cooling cycle, where the scanning rate is 1.0 °C/min. The dashed lines show the deconvolution of the peaks for Tri1 and Tri2 in the cooling process.

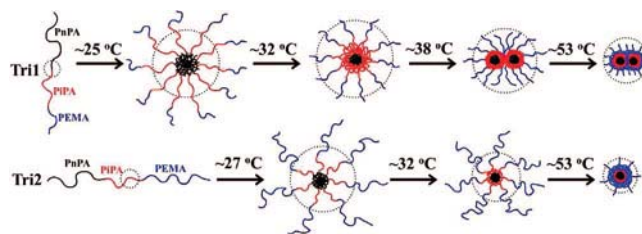
Table 2. Thermodynamic Parameters of the Phase Transition of Triblock Copolymers in the Heating and Cooling Processes

sample	heating		cooling			
	T_p (°C)	ΔH (J/g)	T_{p1} (°C)	ΔH_1 (J/g)	T_{p2} (°C)	ΔH_2 (J/g)
Tri1	30.2	68.0	20.9	-28.4	28.7	-56.0
Tri2	31.9	34.0	21.0	-7.3	30.5	-20.6

as the PEMA length increases, since PEMA is more hydrophilic than PnPA and PiPA. The enthalpy change (ΔH) due to the collapse of the PnPA and PiPA chains during the phase transition of Tri1 is much higher than that of Tri2 (Table 2). This is because the PEMA block in Tri1 is shorter than in Tri2, and the fraction of PnPA and PiPA blocks in the former is higher than in the latter. Note that the collapse of PnPA and PiPA blocks cannot be differentiated from each other in the heating process because their VPTs are close to each other and the collapse is quick. However, the exothermic peaks can be deconvoluted into two peaks in the cooling process (Figure 5, dashed lines). The peak located at ~ 29.0 °C is attributed to the swelling of PiPA blocks and the dissolution of the aggregates. As discussed above, it usually takes time to disrupt the additional hydrogen bonds formed in the heating process.^{58–60} As the temperature decreases, the micelles swell and dissolve gradually PiPA and then PnPA. The hysteresis enlarges the difference in the swelling of the two blocks, so that the peak located at ~ 21 °C associated with the swelling of the PnPA blocks can be observed. On the other hand, since the PiPA block is more hydrophilic than the PnPA block, more energy is needed to swell the chains in the cooling process, so that the peak at ~ 29 °C has a lower intensity than the one at ~ 21 °C. Nevertheless, no endothermic or exothermic peak around ~ 53 °C was observed in either heating or cooling process, due to the very small enthalpy change of the PEMA block.

The micellization of the thermosensitive triblock copolymers is schematically illustrated in Scheme 2. The micellization of Tri1 is quite different from that of Tri2 due to the difference in the length of the PEMA block. For Tri1, the formation of micelles starts at ~ 25 °C and the formed micelles aggregate further into micellar clusters when the temperature reaches above ~ 38 °C. For Tri2, stable micelles are formed at ~ 27 °C and the $\langle R_h \rangle$ of the micelles decreases continuously with the

Scheme 2. Schematic Illustration of the Micellization of Triblock Copolymers^a



^a The dash cycles show only the approximate hydrodynamic size.

continuous increase in temperature due to the consecutive collapse of the PiPA and PEMA chains.

Conclusion

Thermosensitive PnPA-*b*-PiPA-*b*-PEMA triblock terpolymers with different lengths of the final block are shown to form stable micelles. First, the volume phase transition temperature of each of the blocks is influenced by the relative hydrophobicity/hydrophilicity of its neighboring blocks. Second, the micellization process depends on the relative length of the PEMA block. Following the formation of micelles, further increase in temperature leads to the collapse of the PiPA and PEMA chains on the periphery of the micelles. When the PEMA block is short, the PEMA chains cannot shield the hydrophobic PnPA and PiPA core completely, leading to the clustering of the micelles. A longer PEMA block can prevent or delay the formation of micellar clusters. In the cooling process, a hysteresis can be observed due to the formation of additional hydrogen bonds. This finding helps to understand the aggregation of multiblock copolymers in solutions and will help in the design and preparation of useful materials based on the multiple thermosensitivity of this type of polymers.

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Supporting Information Available: Text giving the synthetic details and the characterization of the triblock copolymers, a scheme showing the preparation of the triblock copolymer, a table of polymer characteristics, and figures showing SEC traces, a ¹H NMR spectrum, and UV spectra. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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