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Conformational Change of Trifunctional Poly(oxypropylene)amines Intercalated within a Layered Silicate Confinement

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ABSTRACT: Smectic montmorillonite clay was modified via cation exchange with ammonium salts of poly(oxypropylene)−polyamines (400, 3000, and 5000 M_w). Unusually wide silicate basal spacing (up to 80 Å) and high organic contents (up to 75 wt %) were observed when a 5000 M_w amine was used as the intercalating agent. Moreover, intercalation of the amines not only contributes to the widening of the silicate interlayer but also alters its organophilic nature. After intercalation of appropriate amine, the modified clays were highly dispersible in organic solvents and capable of lowering the interfacial surface tension of a toluene/water mixture. These properties were correlated to the amine conformational changes within the silicate gallery.

Introduction

The literature contains a great body of research involving intercalation of organic alkylammonium cations into montmorillonite clay (MMT).[1−3] Most of these intercalating agents are low-molecular-weight alkylammonium salts, amino acids, diamine salts, etc.[4−6] Typically, intercalation results in a widening of the clay basal spacing in the range 19−40 Å, which correlates linearly to the molecular size of the intercalating agents.[3,4,7] These intercalated smectic clays may be exfoliated with a polymer to form nanocomposites.[8] The naturally occurring montmorillonite is commonly used as the silicate source because of its high surface-to-weight ratio.[9] The resultant polymer/clay nanocomposites demonstrate a host of improved properties such as material toughness,[1,2,10,11] barrier property enhancement,[5,12] and resistance to heat.[13,14]

Previously, we reported the use of high-molecular-weight poly(oxypropylene)diamine as intercalating agents.[15−17] This work demonstrated that the molecular weight and number of amine functionalities affected not only the enlargement of the basal spacing but also the organophilicity of the modified silicates. The resulting wide interlayer spacing and high organic content facilitated subsequent exfoliation of the modified silicates into a polymer matrix.

In this study we further investigate the role of intercalated organics with respect to their effects on the hydrophilic/hydrophobic properties of modified silicates. Moreover, the intercalation of different trifunctional poly(oxypropylene)amines allows us to explore conformational changes at the molecular level within the interlayer confinement and how the conformational changes affect the amphiphilic properties[18] of the modified clay.

Experimental Section

Materials. Sodium montmorillonite (Na^+-MMT), supplied by Kunimine Ind. Co., is a Na^+ type montmorillonite with a cationic exchange capacity (CEC) of 1.15 mequiv/g. Poly(oxyalkylene)diamines including the poly(oxyethylene) (POE)- and poly(oxypropylene) (POP)-backboned amines, which are commercially available under the Jeffamine trade name, were purchased from Huntsman Chemical Co. or Aldrich Chemical Co. The POE-amines are α,ω-diamines containing a poly(oxypropylene)-*block*-poly(oxyethylene)-*block*-poly(oxypropylene) backbone of 2000 g/mol M_w (POE-D2000). The POP-amines are diamines containing a poly(oxypropylene) backbone of 2000 M_w (POP-D2000) and triamines containing poly(oxypropylene) backbones of 400, 3000, and 5000 M_w (POP-T400, POP-T3000, and POP-T5000, respectively). The chemical structures are illustrated in Figure 1.

Preparation of the Amine Intercalated MMT. An example of a preparative procedure for preparing wide *d* spacing silicates follows. Na^+-MMT (10 g, 1.15 mequiv/g) was placed in a 2 L beaker and dispersed vigorously into 1 L of deionized water at 80 °C. In a separate vessel the precursor intercalating agent (POP-T5000; 57.5 g, 11.5 mmol) was acidified with hydrochloric acid (37% in water, 1.2 g, 11.5 mmol; acidification ratio of $H^+/NH_2 = 1/3$) in 30 mL of ethanol. The solution was then poured into the vessel containing the swelled Na^+-MMT slurry. The mixture was stirred vigorously at 80 °C for 5 h and then allowed to cool to room temperature. The resulting agglomerated precipitate was collected and washed thoroughly with toluene/ethanol to remove free amines. The POP-T5000/MMT was dried in a vacuum oven at 80 °C for 24 h before the analysis.

Measurements. X-ray powder diffraction (XRD) analysis was performed by using a Schimadzu SD-D1 diffractometer with Cu target ($k = 1.5605$ Å) at a generator voltage of 35 kV, current of 30 mA, and a scanning rate of 2° min^{-1}. The *d* spacing of the intercalated MMT was analyzed by using Bragg's equation ($n\lambda = 2d \sin \theta$). The value for $n = 1$ was calculated from the observed values of $n = 2, 3$, etc. Thermal gravimetric analysis (TGA) was performed using a Perkin-Elmer at a heating rate of 10 °C/min up to 900 °C. Interfacial tension was measured by using a Kruss-K10 digital tensiometer equipped with a spherical ring. The average particle diameters were estimated by using a Brookhaven 90 Plus particle sizer.

Results and Discussion

Organophilicity of POP-Amine Intercalated MMTs. Sodium montmorillonite, which consists of negatively charged silicate surfaces and positively charged sodium counterions ($\equiv Si-O^-Na^+$), may be modified by cation exchange with organic ammonium salts ($-NH_3^+Cl^-$). Trifunctional poly(oxypropylene)amines (POP-amines) of 400, 3000, and 5000 g/mol

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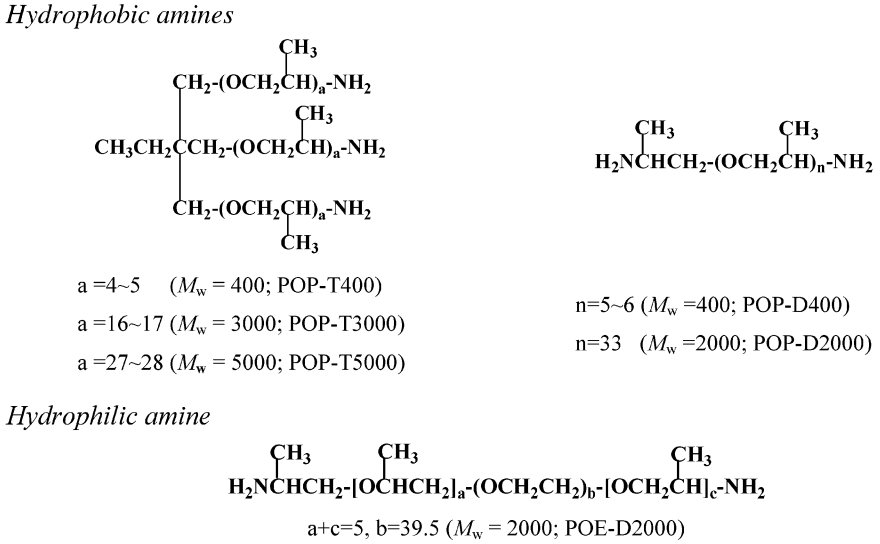

Figure 1. Chemical structures of poly(oxypropylene)− and poly(oxyethylene)−polyamine intercalation agents.

Table 1. Basal Spacing, Composition, and Solvophilicity of MMT Intercalated by Polyoxyalkylene Amines

intercalation agent	H^+/NH_2[a]	d (n = 1) (Å)[b]	weight fraction (w/w)[c] CEC[d]	 TGA[e]	solvophilicity[f,19] H_2O	 toluene
none (Na^+-MMT)		12	0/100		+	−
		Hydrophilic Diamine				
POE-D2000	1/2	20	70/30	43/57	+	−
	2/2	19	53/47	44/56	+	−
		Hydrophobic Diamine				
POP-D2000	1/2	58	70/30	63/37	−	+
	2/2	47	53/47	55/45	−	+
		Hydrophobic Triamine				
POP-T400	1/3	16	32/68	18/82	+	−
	2/3	16	19/81	18/82	+	−
	3/3	16	13/87	15/85	+	−
POP-T3000	1/3	63	78/22	69/31	−	+
	2/3	52	63/37	60/40	−	+
	3/3	31	53/47	46/56	−	+
POP-T5000	1/3	80	85/15	75/25	−	+
	2/3	75	74/26	72/28	−	+
	3/3	61	66/34	67/33	−	+

[a] Acidification ratio (H^+ to NH_2). [b] X-ray d spacing calculated on the basis of Bragg equation ($n\lambda = 2d \sin \theta$). [c] Weight fraction of intercalated organics/silicates. [d] Calculated by CEC (1.15 mequiv/g) × equivalent weight. [e] Measured by TGA. [f] + = dispersible and − = aggregate.

molecular weight (M_w) were acidified to the corresponding ammonium salts, which were then used for the MMT intercalation (Table 1).

The low-molecular-weight POP-T400 is hydrophilic and water-soluble. Consequently, intercalation of the POP-T400 ammonium salt does not significantly alter the hydrophilic property of the MMT. Higher-molecular-weight POP-amines (e.g., POP-T3000 and POP-T5000) are hydrophobic and water-insoluble. Consequently, intercalation of POP-T3000 and POP-T5000 affords hydrophobic MMT particles that are readily dispersible in toluene. A dynamic laser particle size analyzer further provided the measurements of the secondary aggregation of these modified MMT particles. For example, the hydrophobic POP-T5000/MMT was dispersed in toluene (1.0 wt %) and measured to have an average particle size of 2.6−3.2 μm in diameter. By comparison, Na^+-MMT and the POP-T400/MMT hybrids are not dispersible in toluene. However, they were dispersed well in water and measured to have particle sizes of 0.35−1.5 and 1.4−1.6 μm, respectively.

Effect of Polyammonium Ions on Intercalation. The amount of incorporated POP-amines in the organoclays is estimated on the basis of the stoichiometric ionic exchange reaction between the sodium cations and the organic ammonium ions. The theoretical organic fraction is calculated on the basis of the POP-amine molecular weight. Thermal gravimetric analysis (TGA) indicates the actual organic/silicate weight fraction of 75/25 (w/w) for POP-T5000, 69/31 (w/w) for POP-T3000, and 18/82 (w/w) for POP-T400. By controlling the degree of hydrochloric acid neutralization (i.e., the acidification ratio), the amount of intercalated POP-amine can be controlled in a precise manner. For example, by varying the acidification ratio for POP-T5000, the organic/silicate fractions of 85/15, 74/26, and 66/34 (w/w) are obtained. As summarized in Table 1, the TGA measurements are generally consistent with calculations based on the CEC and the ammonium equivalent weights. However, in some cases the measured organic contents are lower than the calculated values. For example, using an acidification ratio of 1/3 for POP-T500, the calculated organic/silicate ratio is 85/15 (w/w), whereas the mea-

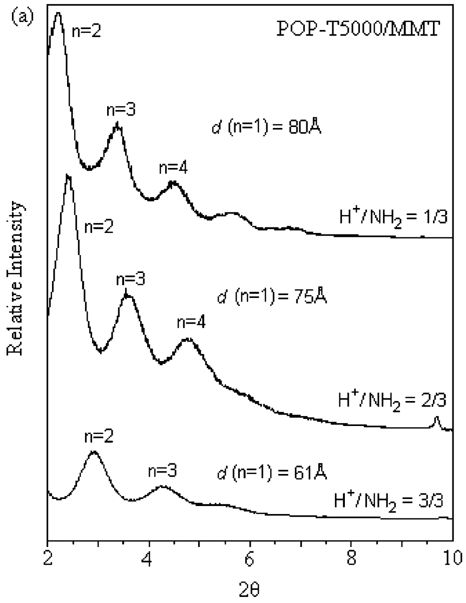

Figure 2. X-ray diffraction patterns of (a) POP-T5000/MMT and (b) POP-T3000/MMT with various H^+/NH_2 ratios.

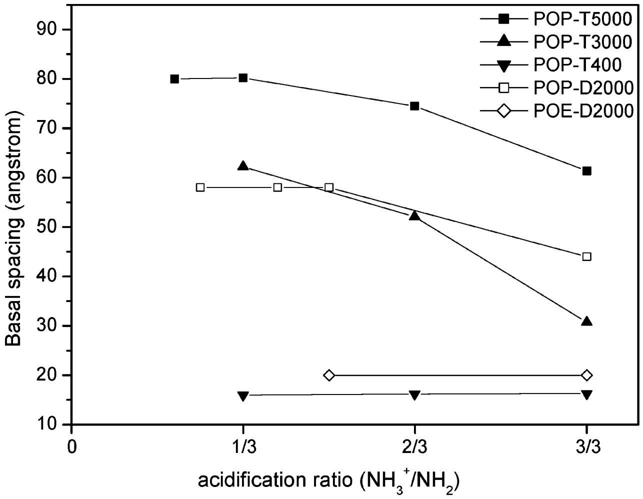

Figure 3. Trend of basal spacing changes for amine-intercalated MMTs at various acidification ratios.

sured organic/silicate fraction is 75/25 (w/w) by TGA. This indicates incomplete Na$^+$-MMT exchange reaction with the POP-amine, perhaps due to space-filling limitations.

Conformational Change of POP-Amines at Different Acidification Ratios. Since the POP-triamine has three amine functionalities, three different ammonium ionic sites tethering with the silicate surface are possible. With a 1/3 acidification ratio, the POP-triamines (POP-T5000, POP-T3000, and POP-T400) form the intercalated MMTs exhibiting X-ray *d* spacing of 80, 63, and 16 Å, respectively (Table 1). The enlargement of the *d* spacing corresponds to the increasing M_w of the intercalating agents. This implies that the POP backbone is responsible for the observed silicate interlayer spacing. Furthermore, the POP backbone expands the silicate interlayer space in a uniformed manner. For example, the POP-T5000/MMT with a 1/3 acidification ratio exhibits Bragg's peaks for $n = 2$, 3, and 4 (Figure 2), indicating a high regularity of the interlayer gallery. The appearance of more than two peaks in the wide-angle XRD pattern allows calculation of the hidden $n = 1$ peak. According to the Bragg equation, $n\lambda = 2d \sin \theta$, the relationship for the *d* spacing for $n = 1$, 2, 3, and 4 corresponds to $(1/1) \times d$, $(1/2) \times d$, $(1/3) \times d$, and $(1/4) \times d$, respectively. Hence, there is a characteristic "constant" relationship for each pair of neighboring peaks. In Figure 2 the actual $n = 1$ basal spacing is therefore assignable according to Bragg's relationship. For the pattern having multiple diffraction peaks, the third reading can be used to confirm the previous pair of neighboring peaks. For the POP-T3000 intercalated clay at acidification ratio of 3/3, the $n = 1$ peak is not easily assignable. However, on the basis of the observed *d* spacing trend for acidification ratios of 1/3, 2/3, and 3/3 for the POP-T5000 MMT, the basal spacing for POP-T3000 at acidification ratio of 3/3 is estimated to be $n = 1$ ($d = 31$ Å).

By increasing the acidification ratio from 1/3 to 2/3 or 3/3, the XRD *d* spacing of the POP-T5000/MMT decreases from 80 to 75 or 61 Å, accordingly. A similar trend of *d* spacing decreasing is observed for POP-T3000/MMT (Figure 3, ■ and ▲). These observations reveal a conformation change in the T-series amine quaternary ammonium salts. It is hypothesized that the backbone of the intercalated POP-amine adopts a twisted polymer coil shape, as illustrated in Figure 4. With a 3/3 acidification ratio, each POP-amine has three ammonium ionic sites per molecule and binds strongly with three silicate surface sites, and a lower *d* spacing results. In contrast, the 1/3 acidified POP-triamine, which has only one ammonium site per molecule, binds with only one silicate surface site. The other two weakly binding amine functionalities have a high degree of entropic freedom and should occupy a larger molecular volume. Consequently, the 1/3 acidified POP-triamine has a larger conformation and the *d* spacing is greater. The observed trends in the XRD data support this hypothesis.

In contrast to the high-M_w POPs, the low-M_w POP-T400 intercalated MMTs exhibit similar interlayer spaces regardless of the acidification ratio (Figure 3, ▼). This result is attributed to the short POP backbone, which is less hydrophobic and less apt to self-aggregation.

The fundamentally different intercalating mode[17] between the hydrophobic and the hydrophilic amines

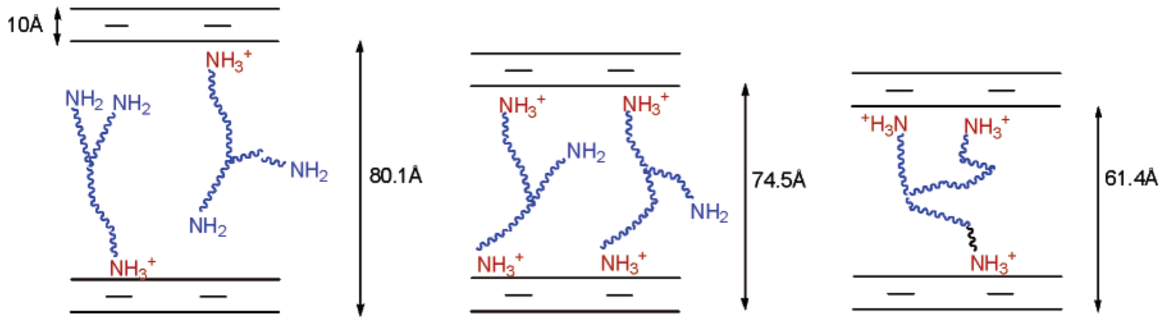

Figure 4. Conceptual representation of conformations for POP-T5000 intercalation at H^+/NH_2 = 1/3, 2/3, and 3/3.

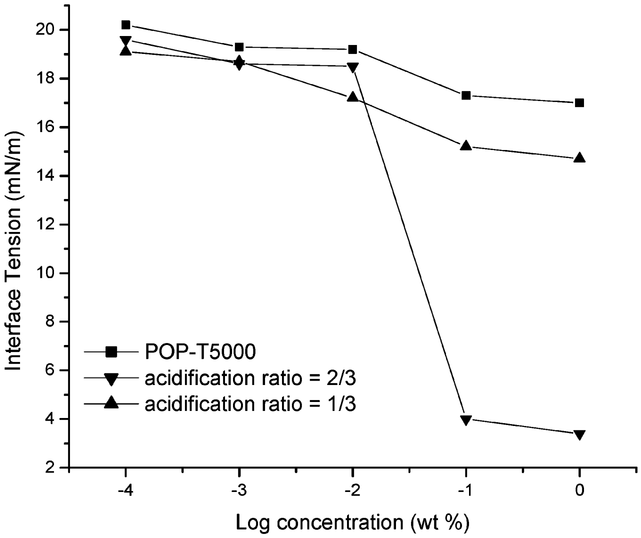

Figure 5. Comparison of interfacial tension reductions of POP-T5000 and its intercalated MMTs at different acidification ratios.

is further demonstrated with the high-M_w poly(oxyethylene)diamine (POE-amines). Intercalation of the hydrophilic POE-D2000 afforded the MMT with *d* spacing of 19−20 Å that is invariant with the acidification ratio (Figure 3, ◇). Because the POE backbone has a high affinity for ionic silicate surfaces, hydrophobic self-assembly within the interlayer does not occur, and the *d* spacing does not expand. By comparison, the hydrophobic POP-D2000 diamine exhibited high *d* spacing 58 and 47 Å at acidification ratios of 1/2 and 2/2, respectively.

Self-Associating Properties of the POP-Amine/MMT Hybrids. The POP-amine intercalated MMTs are composed of alternating layers of self-assembled organic POP-amines and inorganic silicates. Moreover, these modified MMTs are dimensionally stable. Not surprisingly, the POP-T5000/MMT hybrid readily disperses in toluene and significantly reduces interfacial tension at the toluene/water interface. The critical association concentration in toluene was determined by plotting the interfacial tension vs the hybrid concentration in toluene. The final interfacial tension at 4−5 mN/m implies significant self-aggregation at the interface. However, the interfacial tension reduction trends are significantly different for POP-T5000/MMT at different acidification ratios. For example, as indicated in Figure 5, the 2/3 acidification ratio hybrid has dramatically lower surface tension than the 1/3 acidification ratio hybrid. The specific balance between the hydrophobic POP-amine and the hydrophilic silicate plates may explain the observation. The different POP conformations affect the layered silicate in two ways: the interlayer *d* spacing and the amount of intercalated POP organics. When the organic fraction is high, the hydrophilic/hydrophobic balance[18] is overwhelmed, and the hybrid is similar to the pure POP-T5000, which is ineffective at reducing interfacial surface tension.

Table 2. Particle Sizes of POP-T5000/MMT (1.0 wt %) in Toluene at Different Temperatures

	average diameter (μm)	
H^+/NH_2 (acidification ratio)	25 °C	75 °C
1/3	3.2	1.6
2/3	2.8	1.9
3/3	2.6	2.0

Novel Templates for Thermally Stable Micelles. The POP-T5000/MMT structure contains hydrophilic portions consisting of silicate/ammonium ion pairs and hydrophobic portions consisting of free pending amine functionalities. These hybrids readily disperse in toluene and afford particle sizes of 2.6−3.2 μm in diameter for POP-T5000/MMT. It is noteworthy that the particle size (2.6 μm vs 2.0 μm) is relatively insensitive to the temperature change in the range 25−75 °C, particularly for the hybrid intercalated by the fully acidified amine (Table 2). These thermally stable hybrids are significantly different from typical surfactants or amphiphilic copolymers. In general, micelles are thermally unstable and sensitive to temperature or medium environment. The layered silicate structure, which serves as a rigid binding template for the POP ammonium salts, enforces the self-assembly of the POP backbones within the interlayer. As a result, the hybrid structure is amphiphilic, thermally stable, and capable of lowering surface tension in the toluene/water interface.

Conclusions

The intercalation of Na^+-MMT by high-molecular-weight POP-triamines generated organoclays with *d* spacing that ranged from 16 to 80 Å. The molecular weight and the polyfunctionality of the ammonium cationic sites are two important factors which influence the silicate *d* spacing and the conformations of the confined organics. These organoclays are dispersible in organic solvents. By judiciously varying the acidification ratio, amphiphilic organoclays can be prepared and exhibit a property of critical association concentration at the toluene/water interface. Microdispersibility in toluene and interfacial tension reduction in the toluene/water mixture are explained by the conformations of the amine confined within the layered silicates.

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References and Notes

(1) Pinnavaia, T. J. *Science* **1983**, *220*, 365−371.

(2) Zanetti, M.; Lomakin, S.; Camino, G. *Macromol. Mater. Eng.* **2000**, *279*, 1−9.

(3) Giannelis, E. P. *Appl. Organomet. Chem.* **1998**, *12*, 675−680.

(4) Theng, B. K. G. *Formation and Properties of Clay-Polymer Complexes;* Elsevier: New York, 1979.

(5) Alexandre, M.; Dubois, P. *Mater. Sci. Eng.* **2000**, *28*, 1−63.

(6) LeBaron, P. C.; Wang, Z.; Pinnavaia, T. J. *Appl. Clay Sci.* **1999**, *15*, 11−29.

(7) Vaia, R. A.; Ishii, H.; Giannelis, E. P. *Chem. Mater.* **1993**, *5*, 1694−1696.

(8) Usuki, A.; Kojima, Y.; Kawasumi, M.; Okada, A.; Fukushima, Y.; Kurauchi, T.; Kamigaito, O. *J. Mater. Res.* **1993**, *8*, 1179−1184.

(9) Usuki, A.; Hasegawa, N.; Kadoura, H.; Okamoto, T. *Nano Lett.* **2001**, *1*, 271−272.

(10) Beall, G. W.; Tsipursky, S. T. In *Chemistry and Technology of Polymer Additives*; Malaika, S. A., Golovoy, A., Wilkie, C. A., Eds.; Blackwell Science: Cambridge, MA, 1999; Chapter 16.

(11) Yao, K. J.; Song, M.; Hourston, D. J.; Luo, D. Z. *Polymer* **2002**, *43*, 1017−1020.

(12) Matayabas, J. C.; Turner, S. R. In *Polymer-Clay Nanocomposites;* Pinnavaia, T. J., Beall, G. W., Eds.; John Wiley & Son: New York, 2001; pp 207−266.

(13) Zhu, J.; Morgan, B. A.; Wilkie, C. A. *Chem. Mater.* **2001**, *13*, 3774−3780.

(14) Porter, D.; Metcalfe, E.; Thomas, M. J. K. *Fire Mater.* **2000**, *24*, 45−52.

(15) Lin, J. J.; Cheng, I. J.; Wang. R. C.; Lee, R. J. *Macromolecules* **2001**, *34*, 8832−8834.

(16) Chou, C. C.; Shieu, F. S.; Lin, J. J. *Macromolecules* **2003**, *36*, 2187−2189.

(17) Lin, J. J.; Cheng, I. J.; Chou, C. C. *Macromol. Rapid Commun.* **2003**, *24*, 492−495.

(18) Lin, J. J.; Hsu, Y. C.; Chou, C. C. *Langmuir* **2003**, *19*, 5184−5187.

(19) Marmur, A. *J. Am. Chem. Soc.* **2000**, *122*, 2120−2121.

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