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Solution Behavior of Temperature-Responsive Molecular Brushes Prepared by ATRP

Joanna Pietrasik, Brent S. Sumerlin, Robert Y. Lee, Krzysztof Matyjaszewski*

Molecular brushes, with side chains consisting of two copolymers: 2-(dimethylamino)ethyl methacrylate with methyl methacrylate, and *N,N*-dimethylacrylamide with butyl acrylate were prepared by grafting-from via atom transfer radical polymerization (ATRP). Poly(2-(2-bromo-isobutyryloxy)ethyl methacrylate) and poly(2-(2-bromopropionyloxy)ethyl methacrylate) were used as macroinitiators. Dynamic light scattering (DLS) studies were performed for aqueous solutions of molecular brushes below and above the lower critical solution temperature (LCST), and an unusual concentration-dependent LCST was observed. Due to the compact structure of molecular brushes, intramolecular collapse can occur when the average distance between molecules is much larger than the hydrodynamic dimensions of the individual macromolecules. However, if the concentration of the solution of molecular brushes is increased to the level in which the separation distance is comparable with the brush hydrodynamic dimensions, intermolecular aggregation occurs, as typically observed for solutions of linear polymers.
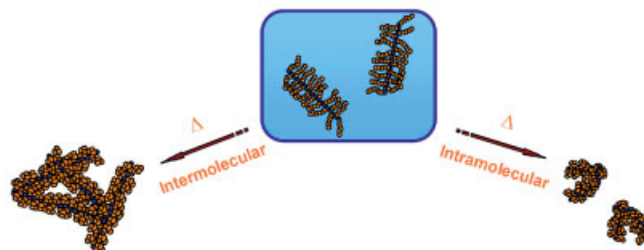
Introduction

Densely-grafted copolymers, also known as molecular bottle brushes,[1,2] are the subject of continuing interest

J. Pietrasik, B. S. Sumerlin, R. Y. Lee, K. Matyjaszewski
Center for Macromolecular Engineering, Department of Chemistry, Carnegie Mellon University, 4400 Fifth Avenue, Pittsburgh, Pennsylvania 15213, USA
E-mail: km3b@andrew.cmu.edu
J. Pietrasik
Current Address: Institute of Polymer & Dye Technology, Department of Chemistry, Stefanowskiego 12/16, 90-924 Lodz, Poland
B. S. Sumerlin
Current Address: Department of Chemistry, Southern Methodist University, 3215 Daniel Avenue, Dallas, TX 75275-0314, USA

mainly due to their unusual architecture and properties. A molecular bottle brush consists of a flexible backbone with a high density of side chains separated by a distance much smaller than their unperturbed dimensions. This leads to significant congestion and entropically unfavorable extension of the backbone and side chains, which prevents the polymer from adopting a random coil conformation. Conformational behavior of molecular brushes in solution and at interfaces has been studied theoretically and experimentally. Polymer conformation can be influenced by external factors, such as solvent,[3] light,[4] and temperature.[5] Conformational changes of single molecules were observed, and the mechanism and driving forces for the conformational variation can be unique for a specific brush molecule.[6–8] Recently, we reported the synthesis of copolymer brushes containing azobenzene

methacrylate and 2-(dimethylamino)ethyl methacrylate monomer units in the side chains, which allowed the molecule to respond to both light and temperature.[4] A temperature-induced coil collapse of single molecular brush macromolecules with poly(N-isopropylacrylamide) side chains was also reported.[5]

Within the context of the current study, we were primarily interested in how water-soluble molecular brushes respond to changes in solution temperature. Polymers that undergo a transition from hydrophilic to hydrophobic upon heating demonstrate lower critical solution temperature (LCST) behavior. Changes in hydrophilic/hydrophobic composition of a molecule influence the LCST.[9,10] A two-stage mechanism is responsible for the thermoreversible phase transition: (i) individual chains are dehydrated and collapse intramolecularly, which eventually leads to (ii) intermolecular aggregation of the globules.[11]

Atom transfer radical polymerization (ATRP)[12–14] and other controlled radical polymerization (CRP) mechanisms are suitable for the synthesis of multifunctional macromolecules, since the low radical concentrations present during the polymerizations reduce the contribution of inter- and intramolecularly terminated chains. This is especially important for the preparation of brush macromolecules, due to the high concentration of chains that exist in the vicinity of the backbone polymer and to the propensity for crosslinking when intermolecular termination occurs between multifunctional (co)polymers. Due to the wide range of monomers that can be polymerized by ATRP, molecular brushes with interesting solution properties can be envisioned. The synthesis of molecular brushes by grafting from via ATRP have involved the polymerization of acrylate,[15–17] methacrylate,[18] and styrenic[15–17] monomers.

Poly(2-(dimethylamino)ethyl methacrylate) (PDMAEMA) and poly(N,N-dimethylacrylamide) (PDMA) display an LCST at approximately 40 °C and above 100 °C, respectively. Copolymerization of hydrophilic and hydrophobic monomers allow fine tuning of the LCST.[19] In this study temperature-responsive brushes with tunable LCST were prepared by statistical copolymerization of DMAEMA with methyl methacrylate (MMA) and DMA with butyl acrylate (BA) from a macroinitiator backbone. The solution behavior of these responsive brushes was studied by dynamic light scattering (DLS) at higher (1 wt.-%) and lower (0.1 wt.-%) concentrations.

Experimental

Materials

All chemicals were purchased from Aldrich or Acros and used as received unless otherwise stated. MMA (Acros, 99%), BA (Acros, 99%), DMAEMA (Aldrich, 99%), DMA (Aldrich, 99%) and 2-(trimethylsilyloxy)ethyl methacrylate (HEMA-TMS) (Polysciences) were purified by vacuum distillation before use. Copper (I) chloride and copper (I) bromide (Aldrich, 98+%) were purified by stirring with glacial acetic acid followed by filtering and washing the resulting solids with ethanol (3 times) and diethyl ether (2 times). Tris(2-(dimethylamino)ethyl)amine (Me$_6$TREN) was synthesized following previously reported procedure.[20]

Analysis

Apparent molecular weights and molecular weight distributions were measured by gel permeation chromatography (GPC) (Eluent: DMF; Flow rate = 1.0 mL·min^{-1}; Temperature = 55 °C) with a Waters 510 HPLC pump, three Waters UltraStyragel columns (102, 103, and 105 Å), and a Waters 410 differential refractive index detector. Poly(methyl methacrylate) standards were used to construct a conventional calibration employing WinGPC software from Polymer Standards Service. ^{1}H NMR spectra of copolymers were examined in CDCl$_3$ at 30 °C using a Bruker Avance 300 MHz spectrometer. Monomer conversion was determined by ^{1}H NMR spectroscopy or by gravimetry. Average hydrodynamic diameters (D_H) were determined by dynamic light scattering (DLS) in water at various temperatures (20–55 °C) with a Malvern HPP5001 High Performance Particle Sizer. Three measurements were taken for each temperature. Temperature was changed every 7–9 min in order to reach an equilibrium state.

Syntheses

Poly(2-(trimethylsilyloxy)ethyl methacrylate) (PHEMA-TMS), poly(2-(2-bromoisobutyryloxy)ethyl methacrylate)) (PBIBM) and poly(2-(2-bromopropriontyloxy)ethyl methacrylate (PBPEM) were synthesized as previously reported.[16]

Poly((2-(2-bromoisobutyryloxy)ethyl methacrylate)-*graft*-2-(dimethylamino)ethyl methacrylate)), poly(BIBM-*graft*-DMAEMA) (*B1*), was prepared as follows: CuCl$_2$ (0.0037 g, 0.027 mmol), HMTETA (44.5 μL, 0.160 mmol) and PBIBM (0.0380 g, 0.136 mmol–Br, $\overline{M}_n$ = 69 200, $\overline{M}_w/\overline{M}_n$ = 1.18) were dissolved in acetone (2.9 mL) in a 25 mL Schlenk flask equipped with a magnetic stir bar. DMAEMA (11.5 mL, 68.0 mmol) was added, and oxygen was removed by three freeze-pump-thaw cycles. Next, CuCl (0.0135 g, 0.136 mmol) was added under nitrogen flow. After placing in a 30 °C oil bath, samples were withdrawn periodically to monitor conversion (^{1}H NMR spectroscopy) and molecular weight (GPC). The polymerization was stopped by opening the flask and exposing the contents to air. The reaction mixture was diluted with acetone and passed through a neutral alumina column to remove the catalyst. The polymer was precipitated by addition to hexane, filtered, and dried under high vacuum for 24 h at room temperature.

Poly((2-(2-bromoisobutyryloxy)ethyl methacrylate)-*graft*-(2-(dimethylamino)ethyl methacrylate)-*stat*-methyl methacrylate)), poly(BIBM-*graft*-(DMAEMA-*stat*-MMA)) brushes were

prepared at two comonomer feed ratios (**B3** and **B4**) under conditions similar to those employed for the synthesis of brushes with DMAEMA side chains.

Poly(2-(2-bromopronionyloxy)ethyl methacrylate-*graft*-(*N*, *N*-dimethylacrylamide-*stat*-butyl acrylate), poly(BPEM-*graft*-(DMA-*stat*-BA), (B4), was prepared by ATRP according to the following general procedure. PBPEM (0.10 g, 0.38 mmol −Br), DMA (11.5 mL, 113 mmol), BA (5.3 mL, 38 mmol), tris[2-(dimethylamino)ethyl]amine (Me$_6$TREN) (0.10 mL, 0.38 mmol), and toluene (16.9 mL) were added to a 50 mL Schlenk flask equipped with a magnetic stir bar. Oxygen was removed by freeze-pump-thaw technique (3 times), and CuCl (38 mg, 0.38 mmol) was added under nitrogen flow. The copolymerization was conducted at 25 °C for 24 h. The reaction was stopped by opening the flask to air, and the catalyst was removed by passing through alumina.

Figure 1 demonstrates the evolution of molecular weight distribution during the polymerization of DMAEMA from a PBIBM backbone.

Results and Discussion

Synthesis of Brush Copolymers

The syntheses of molecular brushes with DMAEMA or DMA homopolymer side chains and their copolymers with MMA or BA, respectively, are illustrated in Scheme 1. A poly(2-(2-bromoisobutyryloxy)ethyl methacrylate) (PBIBM) macroinitiator served as the backbone for the grafting from polymerization for the methacrylates and poly(2-(2-bromopropionyloxy)ethyl methacrylate) (PBPEM) for the acrylate/acrylamides. Monomer conversion during side chain synthesis was limited to less than 20% in order to avoid intermolecular termination reactions that could lead

Figure 1. GPC traces as a function of polymerization time from the ATRP of DMAEMA from a PBIBM backbone (PBIBM $\overline{M}_n = 69\,200$ g · mol^{-1}, $\overline{M}_w/\overline{M}_n = 1.18$, poly(BIBM-*graft*-DMAEMA) $\overline{M}_n = 534\,900$ g · mol^{-1}, $\overline{M}_w/\overline{M}_n = 1.26$).

to loss of molecular weight control and macroscopic gelation. Halogen exchange was employed by using a CuCl catalyst along with the bromine-containing macroinitiator to facilitate well-controlled polymerizations and reduce the rate of propagation with respect to initiation.[21]

Molecular weight distributions remained relatively narrow throughout the polymerizations (Table 1). The true molecular weights of these highly-branched polymers are significantly higher than those measured from gel permeation chromatography (GPC) calibrated with linear standards. Previous MALLS and AFM analyses indicate the experimental values should correlate well with the theoretical values calculated from monomer conversion and macroinitiator concentration.[22,23]

Brush Copolymer Solution Properties

Molecular bottle brushes can be considered as molecularly pre-organized systems due to the high local concentration of uniform side chains. Thus, their solution behavior can be significantly different from that observed for linear polymers. Therefore, the factors which typically determine solution phase transitions for linear polymers could have a different impact on solutions of molecular brushes. Within the current study, we evaluated the importance of solution concentration and hydrophilic/hydrophobic balance on the LCST behavior for the brush copolymers.

PDMAEMA and PDMA have LCST values of approximately 40 and above 100 °C, respectively, and brushes with side chains composed of these polymers are expected to have similar values. The LCST transition of the poly(BIBM-*graft*-(DMAEMA-*stat*-MMA)) and poly(BPEM-*graft*-(DMA-*stat*-BA)) copolymer brushes depends on the relative ratios of the two comonomers. Increased incorporation of the hydrophobic MMA or BA should lower the LCST of the resulting copolymers.

Figure 2 shows the relative dependence of apparent hydrodynamic diameter as a function of temperature for the poly(BIBM-*graft*-DMAEMA) molecular brush together with two brushes containing different amounts of hydrophobic MMA incorporated into side chains of poly(BIBM-*graft*-(DMAEMA-*stat*-MMA)). The apparent diameter of the poly(BIBM-*graft*-DMAEMA) molecules was about 40 nm at room temperature. The fully-extended cylindrical brush with DP$_{backbone} = 232$ is expected to have a length of 62 nm. The incorporation of MMA as a comonomer resulted in a noticeable decrease in apparent size as measured by DLS. The presence of the hydrophobic MMA units leads to a more compact structure of the brushes due to reduced hydration.

The apparent hydrodynamic diameter of brushes with PDMAEMA side chains increased from 40 to 60 nm near the expected LCST of 40 °C. The increase in size was much smaller for a brush with 8 mol-% MMA (≈ 33 nm to 45 nm)
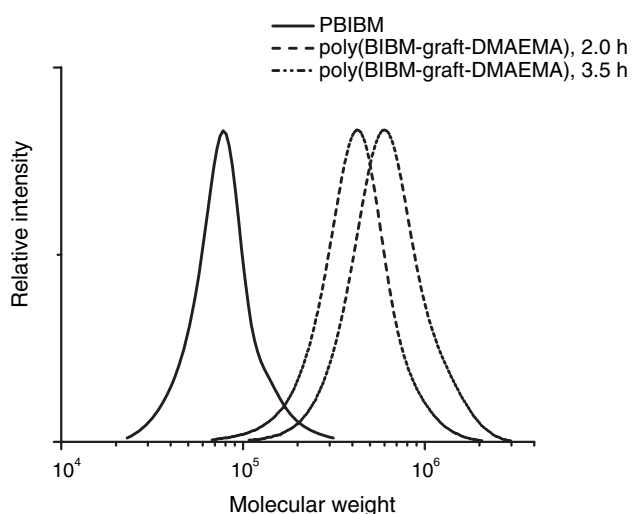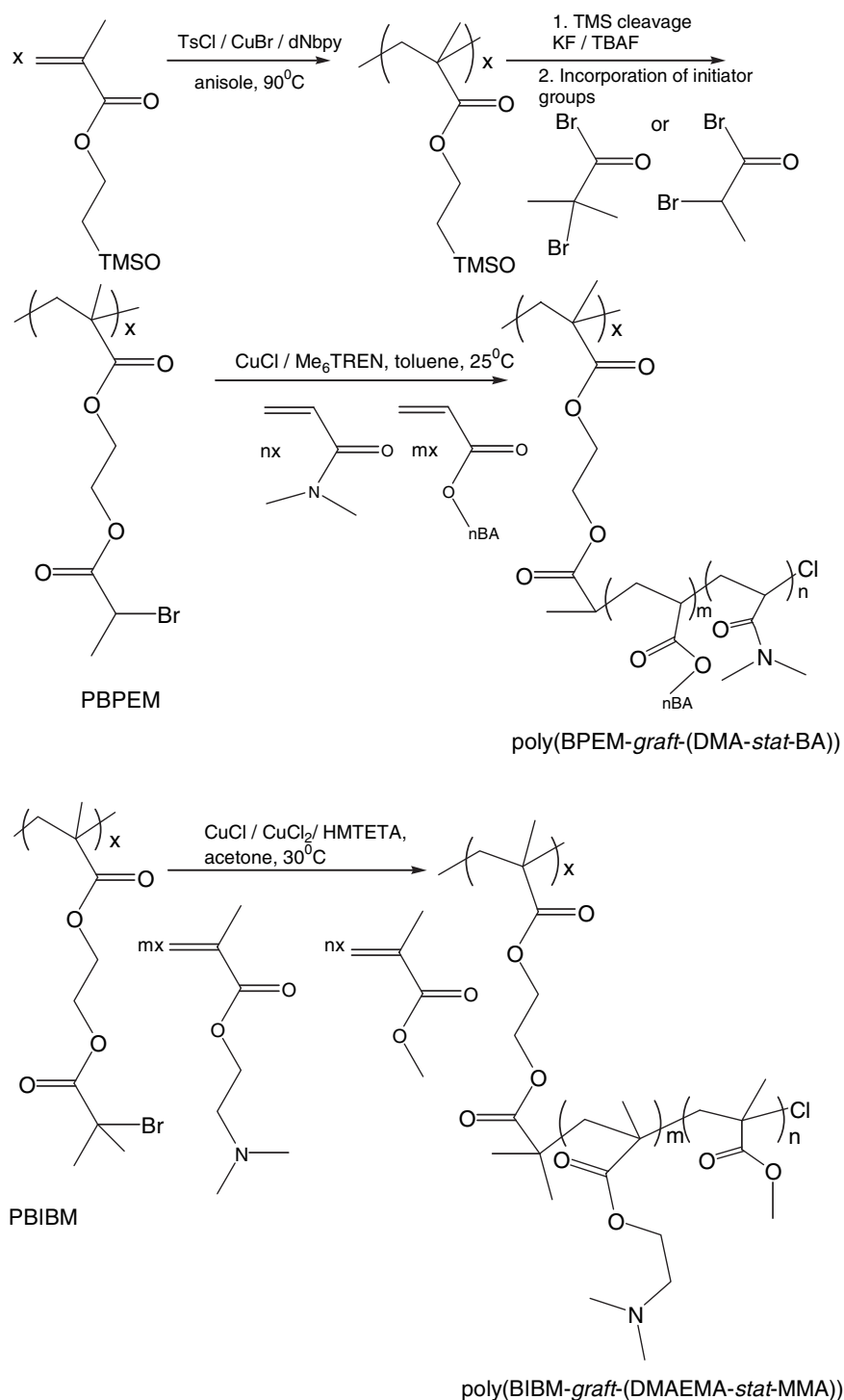
Scheme 1. . Synthesis of the PBIBM and PBEM macroinitiators backbones and the subsequent grafting from polymerizations to yield poly(BIBM-graft-DMAEMA) and poly(BIBM-graft-(DMAEMA-stat-MMA)) and poly(BPEM-graft-(DMA-stat-BA)) molecular brushes.

and was essentially invisible for a brush with 15 mol-% of MMA, as will be explained later. It should be noted that globulization of single molecules leads to changes in geometry and subsequent changes in the hydrodynamic

form factor. Consequently, the actual dimensional changes of the molecular brushes can be to some extent different than those measured by DLS. Nevertheless, to elucidate the LCST phenomena it is interesting to compare the size of the brushes with respect to the average intermolecular distance in the 1 wt.-% solution. This concentration corresponds to 3.4×10^{-6} mol · dm^{-3}, or 2.04×10^{18} molecules · dm^{-3} for **B1**. The latter value indicates that one brush molecule occupies on average 490 000 nm^3, i.e. (79 nm)^3. For the brushes **B2** and **B3** this volume is approximately (75 nm)^3 and (76 nm)^3. The distance between the mass centers of the brushes is below 80 nm and is comparable to the length of an extended brush ($\approx$60 nm) and the apparent hydrodynamic diameter values determined by DLS. Although the apparent hydrodynamic diameter we obtained by DLS can be different from the absolute value due to the geometry of the brushes, the decrease in decay rate observed by DLS suggests the possibility of multimolecular aggregation due to intermolecular interactions. Apparently, the brush with the highest content of MMA exhibits the smallest degree of the agglomeration due to its compact size.

DLS studies were also carried out with a solution concentration of 0.1 wt.-% (3.4×10^{-7} mol · dm^{-3}, 2.04×10^{17} molecules · dm^{-3}, **B1**). At this concentration, the volume occupied by one brush molecule is 4 900 000 nm^3 which corresponds to an intermolecular average distance of $\approx$170 nm. Under such dilution the aggregation of brushes above the LCST were suppressed. Additionally, the time of diffusion-limited aggregation calculated from the equation $\tau_{aggreg} = 3$ $\eta/2$ c $k_B\theta$, for concentration c $= 2.04 \times 10^{14}$ chains · cm^{-3}, water viscosity $\eta = 8.9 \times 10^{-4}$ P, the Boltzmann constant $k_B = 1.38 \times 10^{-23}$ J · K^{-1}, and temperature $\theta = 308$ K equals $\tau_{aggreg} = 26$ min and is quite long. In fact, no significant changes in apparent size was observed even at very long equilibration times, as will be discussed

Table 1. Properties of synthesized poly(BIBM-*graft*-DMAEMA), poly(BIBM-*graft*-(DMAEMA-*stat*-MMA)) and poly(BPEM-*graft*-(DMA-*stat*-BA)) brush copolymers with varying Copolymers composition.

Sample	DMAEMA[a]/DMA[b] Conv.	DP $_{SC\ theory}$[c]	$\overline{M}_{n,app}$[d]	$\overline{M}_w/\overline{M}_n$[d]	$\overline{M}_{n,th}$	Mol Fraction MMA[a]/BA[a]
	%		$g \cdot mol^{-1}$		$g \cdot mol^{-1}$	
B1	15[a]	73	694 000	1.35	2 950 000	0
B2	13[a]	66	669 000	1.33	2 520 000	0.08
B3	14[a]	71	679 000	1.25	2 630 000	0.15
B4	9[b]	35	691 000	1.40	1 600 000	0.26

[a]Determined from ^{1}H NMR spectroscopy; [b]Determined gravimetrically; [c]Degree of polymerization for side chains of molecular brush calculated from $DP_{SC\ theory} = ([M]/[-Br]) \times$ conversion; [d]Apparent values determined by GPC with a PMMA calibration. **B1**: [DMAEMA]:[PBIBM-Br]:[CuCl]:[CuCl$_2$]:[HMTETA] = 500:1:1:0.15:1.15, **B2**: [DMAEMA]:[MMA]: [PBIBM-Br]:[CuCl]:[CuCl$_2$]:[HMTETA] = 465:35:1:1:0.2:1.2, **B3**: [DMAEMA]:[MMA]:[PBIBM-Br]:[CuCl]:[CuCl$_2$]:[HMTETA] = 425:75:1:1:0.2:1.2, at 30 °C, 25 vol.-% of acetone, **B4** [DMA]:[BA]:[PBPEM-Br]:[CuCl]:[Me$_6$TREN] = 300:100:1:1:1, at 25 °C, 100 vol.-% of toluene.
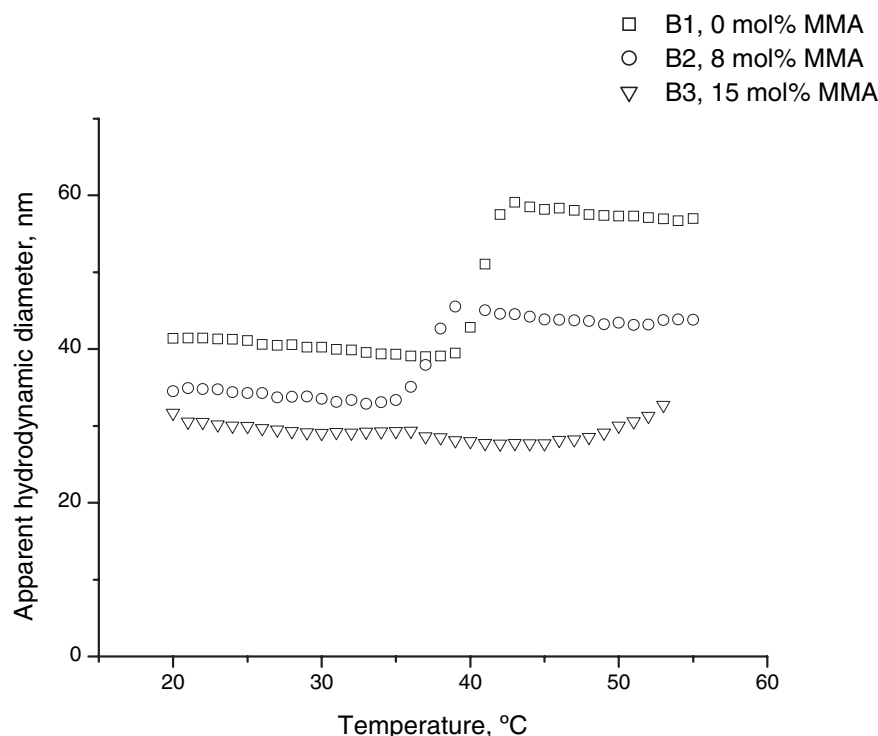

☐ B1, 0 mol% MMA
○ B2, 8 mol% MMA
▽ B3, 15 mol% MMA

Figure 2. Apparent hydrodynamic average diameters as a function of temperature for poly(BIBM-graft-DMAEMA), (**B1**, $\overline{M}_{n,th} = 2\,950\,000$ g·mol^{-1}, DP$_{SC} = 73$), and poly(BIBM-*graft*-(DMAEMA-*stat*-MMA)), (**B2**, $\overline{M}_{n,th} = 2\,520\,000$ g·mol^{-1}, DP$_{SC} = 66$, **B3**, $\overline{M}_{n,th} = 2\,630\,000$ g·mol^{-1}, DP$_{SC} = 71$) molecular brushes, 1 wt.-% solution concentration.

extent of simultaneous intermolecular aggregation cannot be excluded.

As opposed to the phenomena observed at 1 wt.-% concentration, the behavior of the poly-(BIBM-*graft*- DMAEMA) and both poly(BIBM-*graft*-(DMAEMA-*stat*-MMA)) brushes are very similar in more dilute solutions.

Analogous behavior was observed for the brushes with poly(DMA-*stat*- BA) side chains (Figure 4). The 1.0 wt.-% solution of brush **B4**, which contained 26 mol-% BA, demonstrated a broad phase transition with an onset near 25 °C. This broad transition most likely results from the chain-chain heterogeneity in copolymer composition.[25] When the solution concentration was decreased from 1.0 wt.-% to 0.1 wt.-%, the decay rate observed by DLS increased as a function of temperature ($D_H = 47$ nm at 55 °C), suggesting intramolecular collapse as the operative size-determining phenomenon.

Solutions of these individually collapsed chains were stable for at least 24 h at 55 °C, with no significant change in size being observed during this period. Such a unimolecular response is particularly interesting and is similar to what was reported for brushes with PNIPAM side
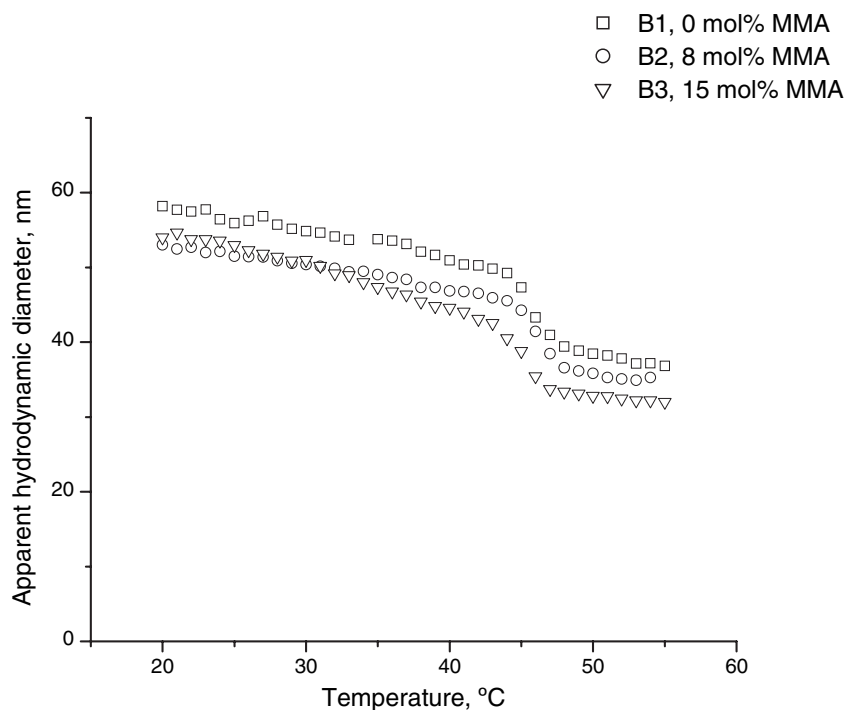
later. Therefore, intramolecular collapse of single brush molecules is suggested (Figure 3). However, as proposed by Chu et al.,[24] the aggregates of the collapse chains have very compact structure, and overall their size can be smaller than the singles molecules. Therefore, the possibility of a small

Figure 3. Apparent hydrodynamic average diameters as a function of temperature for poly(BIBM-*graft*-DMAEMA), (**B1**, $\overline{M}_{n,th} = 2\,950\,000$ g·mol^{-1}, DP$_{SC}$ = 73), and poly(BIBM-*graft*-(DMAEMA-*stat*-MMA)), (**B2**, $\overline{M}_{n,th} = 2\,520\,000$ g·mol^{-1}, DP$_{SC}$ = 66, **B3**, $\overline{M}_{n,th} = 2\,630\,000$ g·mol^{-1}, DP$_{SC}$ = 71) molecular brushes, 0.1 wt.-% solution concentration.

Figure 4. Apparent hydrodynamic average diameters as a function of temperature for poly(BPEM-*graft*-DMA-*stat*-BA), (**B4**, $\overline{M}_{n,th} = 1\,600\,000$ g·mol^{-1}), molecular brush, 0.1 wt.-% and 1.0 wt.-% solutions concentrations.

chains.[26] These observations indicate that the unique nature and compact structure of molecular brushes facilitate intramolecular collapse above the LCST when the average distance between molecules is much larger than their hydrodynamic dimensions. Therefore, the brushes undergo a transition from extended cylinders to more compact morphologies with increasing temperature. However, when the concentration of the molecular brush solution was increased to 1 wt.-%, intermolecular separation distance was comparable to the individual molecular dimensions, and intermolecular aggregation is suggested. The latter behavior is similar to that of most temperature-responsive linear polymers in solution. In order to better understand the LSCT phenomena of those unique objects, more detailed scattering studies that consider angular dependence are being considered.

Conclusion

While analysis of the rod-like objects presents many challenges, the reported observations suggest intriguing inter/intramolecular aggregation phenomena of molecular brushes. An unusual concentration-dependent LCST behavior was observed for molecular brush with PDMAEMA-*co*-PMMA and PDMAA-*co*-PBA side chains. Intramolecular collapse occurs for diluted brush solutions when the average distance between molecules is much larger than the hydrodynamic dimensions of the individual brushes. On the other hand, if the concentration was increased such that the separation distance was comparable to the dimensions of individual brushes, intermolecular aggregation appeared.

The phase transition of copolymer brushes can be tuned by changing the content of the hydrophobic units. LCST values are lower for the side chains with more hydrophobic copolymers. Both intra- and intermolecu-
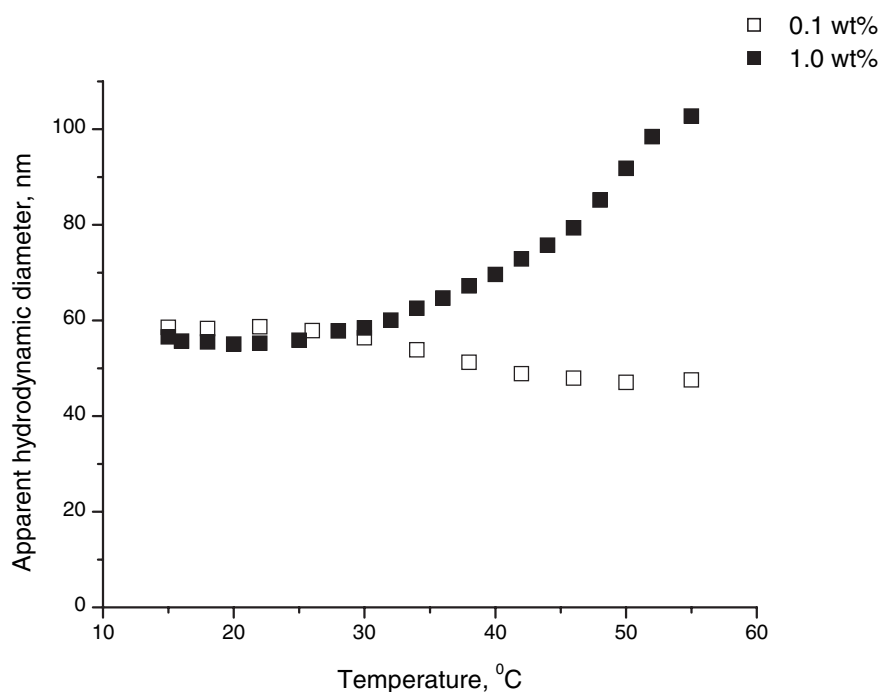
lar aggregation can be induced through appropriate selection of solution concentration.

[1] A. Bhattacharya, B. N. Misra, Prog. Polym. Sci. **2004**, *29,* 767.
[2] M. Zhang, A. H. E. Mueller, J. Polym. Sci., Polym. Chem. **2005**, *43,* 3461.
[3] K. Fischer, M. Schmidt, Macromol. Rapid Comm. **2001**, *22,* 787.
[4] H.-I. Lee, J. Pietrasik, K. Matyjaszewski, Macromolecules **2006**, *39,* 3914.
[5] C. Li, N. Gunari, K. Fischer, A. Janshoff, M. Schmidt, Angew. Chem. Int. Ed. **2004**, *43,* 1101.
[6] I. I. Potemkin, A. R. Khokhlov, S. Prokhorova, S. S. Sheiko, M. Moeller, K. L. Beers, K. Matyjaszewski, Macromolecules **2004**, *37,* 3918.
[7] S. J. Lord, S. S. Sheiko, I. LaRue, H.-I. Lee, K. Matyjaszewski, Macromolecules **2004**, *37,* 4235.
[8] M. O. Gallyamov, B. Tartsch, A. R. Khokhlov, S. S. Sheiko, H. G. Boerner, K. Matyjaszewski, M. Moeller, Chem.-Europ. J. **2004**, *10,* 4599.
[9] L. D. Taylor, L. D. Cerankowski, J. Polym. Sci., Polym. Chem. **1975**, *13,* 2551.
[10] Y. Xia, X. Yin, N. A. D. Burke, H. D. H. Stoever, Macromolecules **2005**, *38,* 5937.
[11] I. Yamamoto, K. Iwasaki, S. Hirotsu, J. Phys. Soc. Japan **1989**, *58,* 210.
[12] J.-S. Wang, K. Matyjaszewski, J. Am. Chem. Soc. **1995**, *117,* 5614.
[13] K. Matyjaszewski, J. Xia, Chem. Rev. **2001**, *101,* 2921.
[14] J. Pyun, T. Kowalewski, K. Matyjaszewski, Polymer Brushes **2004,** 51.
[15] G. Cheng, A. Boeker, M. Zhang, G. Krausch, A. H. E. Mueller, Macromolecules **2001**, *34,* 6883.
[16] K. L. Beers, S. G. Gaynor, K. Matyjaszewski, S. S. Sheiko, M. Moeller, Macromolecules **1998**, *31,* 9413.
[17] H. G. Boerner, K. Beers, K. Matyjaszewski, S. S. Sheiko, M. Moeller, Macromolecules **2001**, *34,* 4375.
[18] D. Neugebauer, Y. Zhang, T. Pakula, K. Matyjaszewski, Polymer **2003**, *44,* 6863.
[19] K. F. Mueller, Polymer **1992**, *33,* 3470.
[20] J. Xia, S. G. Gaynor, K. Matyjaszewski, Macromolecules **1998**, *31,* 5958.
[21] D. A. Shipp, J.-L. Wang, K. Matyjaszewski, Macromolecules **1998**, *31,* 8005.
[22] S. S. Sheiko, M. da Silva, D. Shirvaniants, I. LaRue, S. Prokhorova, M. Moeller, K. Beers, K. Matyjaszewski, J. Am. Chem. Soc. **2003**, *125,* 6725.
[23] B. S. Sumerlin, D. Neugebauer, K. Matyjaszewski, Macromolecules **2005**, *38,* 702.
[24] G. Raos, G. Allegra, Macromolecules **1996**, *29,* 8565.
[25] T. Mori, Y. Fakuda, H. Okamura, K. Minagawa, S. Masuda, M. Tanaka, J. Polym. Sci., Polym. Chem. **2004**, *42,* 2651.
[26] C. Li, N. Gunari, K. Fischer, A. Janshoff, M. Schmidt, Angew. Chem. Int. Ed. **2004**, *43,* 1101.