Novel semirigid water-soluble thermoresponsive polymers based on mesogen-jacketed liquid crystal polymers[†]

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Two novel semirigid smart polymers based on mesogen-jacketed liquid crystal polymers were successfully synthesized *via* free radical polymerization, which showed both characteristic liquid crystal properties of mesogen-jacketed liquid crystal polymers and remarkably reversible thermoresponsive phase transition behaviors.

Stimuli-responsive polymers, often referred to as "smart or intelligent" polymer systems, which exhibit reversible property changes in response to changes in environmental factors such as temperature or pH, have attracted considerable research interest due to their promising potential.¹ As a good candidate, thermoresponsive polymers have been widely investigated because of various applications such as rheological control additives, thermal affinity separation,² controlled drug release³ and gene therapy.⁴ In general, this kind of polymer is soluble in aqueous solution at low temperature but can be rapidly phase-separated from solution when the temperature is raised above the lower critical solution temperature (LCST).

One of the most widely studied synthetic thermo-responsive polymers is poly(N-isopropylacrylamide) (PNIPAM). The repeat unit of PNIPAM consists of hydrophilic (amide) and hydrophobic (isopropyl) groups, and the LCST is about 32 °C.⁵ Besides PNIPAM (a typical example of N-alkyl-substituted polyacrylamides), there are many non-acrylamide-containing thermoresponsive polymers, which have also attracted considerable interest, such as poly[(2-dimethylamino)ethyl methacrylate],⁶ poly[N-(2-methacryloyloxyethyl) pyrrolidone],⁷ poly(vinyl methyl ether),⁸ poly(N-vinylcaprolactam),⁹ poly-(proprylene oxide),¹⁰ and poly(2-isopropyl-2-oxazoline),¹¹ etc. However, the remarkable character of these thermo-responsive polymers is that their main chains are mostly flexible. Of course, there is another class of interesting and important thermo-responsive polymer, polypeptide¹² and alkyl-substituted celluloses, which have semirigid main chains. For example, hydroxypropylcellulose (HPC),⁵ methylcellulose (MC),⁸ and

ethyl(hydroxyethyl)cellulose (EHEC),⁸ have LCSTs at 42 °C, 50 °C and 65 °C, respectively. But it is impossible to control the molecular weight of these natural polymer derivatives and copolymerize with other special functional comonomers. Therefore, it is a challenge to see if we can design and synthesize a water-soluble thermo-responsive polymer possessed semirigid main chain. Clearly, the different topological architectures of polymers will have an immense impact on their properties. So, developing this new type of thermo-responsive polymer will be meaningful in both academic research and practical applications.

It is well-known that mesogen-jacketed liquid crystal polymers (MJLCPs) have a typical semirigid chain structure.13 This is because MJLCPs are constructed by laterally attaching the bulky side groups to the main chain through a short linkage, forming a dense "jacket" around each chain backbone due to their high population.¹⁴ The main chains of MJLCPs are forced to take the extended conformation by the surrounding jacket.¹⁵ So MJLCPs exhibit semirigid properties similar to those of main-chain liquid crystal polymers (MCLCPs). So far, the synthesized mesogen-jacketed liquid crystal polymers are hardly water-soluble and much less thermo-responsive. Here we design a novel polymer in the light of the idea of combining mesogen-jacketed liquid crystal polymer with thermosensitive polymer. The chemical structure model is shown in Fig. 1. Like other MJLCPs, this polymer has a semirigid main chain due to the presence of bulky side groups. What is more, it has not only hydrophobic groups but also hydrophilic groups in side chains. Accordingly, it is reasonable to expect that adjusting the hydrophobic/ hydrophilic balance of the macromolecule might trigger a thermoresponsive behavior. The novelty of our work lies in successfully designing and synthesizing new thermoresponsive polymers having both liquid crystal properties and thermoresponsive properties, which will enrich their species and broaden their applications.

Two new mesogen-jacketed liquid crystal monomers bis-(*N*-hydroxyethyl pyrrolidone) 2-vinylterephthalate (M1) and bis(*N*-hydroxypropyl pyrrolidone) 2-vinylterephthalate (M2) were synthesized *via* direct esterification reactions between 2-vinylterephthaloyl chloride and *N*-hydroxyethyl pyrrolidone and *N*-hydroxypropyl pyrrolidone, respectively. Corresponding polymers named P1 and P2 were successfully synthesized *via* free radical polymerization. The synthetic route is shown in Scheme 1.

GPC, TGA, and DSC results of two polymers are listed in Table 1. From P1 to P2, the glass transition temperatures (T_g)

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Fig. 1 The molecular model of novel semirigid thermoresponsive polymers based on MJLCPs.



Scheme 1 Synthetic route of the monomers and polymers.

decreased with the increasing number of flexible alkyl groups. Birefringences of these two polymers were observed by POM and the images are provided in the ESI.[†] Similar to previous MJLCPs, the liquid crystal textures did not appear until the temperature reached 180 °C and still retained before the decomposition temperature. Furthermore, the textures could be maintained during the cooling process. To study their supermolecular structures, we performed the wide angle X-ray diffraction. Firstly, we used the one-dimensional wide angle X-ray diffraction (1D WAXD) under variational temperatures to investigate the structural evolution, as shown in the ESI.[†] When the temperature reached 170 °C, the samples exhibited sharp and intense diffractions at low 2θ angles, indicating the existence of ordered structures. And then, two-dimensional wide angle X-ray diffraction (2D WAXD) experiments on the oriented samples were carried out by aligning the X-ray incident beam along different directions. Fig. 2 shows 2D WAXD patterns of P2 obtained with the X-ray beam perpendicular (a) and parallel (b) to the fiber direction. 2D WAXD patterns of P1 are shown in the ESI.[†] Like other MJLCPs, P1 exhibited a columnar nematic (Φ_N) phase and P2 exhibited a hexatic columnar nematic $(\Phi_{\rm HN})$ phase.¹⁶ In addition, we took P2 as a typical example and confirmed the polymers we synthesized were semirigid by solid-state NMR experiments.¹⁷ Details are provided in the ESL[†]

Interestingly, when P1 was dissolved in pure deionized water, it was always transparent even when the temperature rose to 100 °C, indicating that P1 was completely water-soluble and non-thermoresponsive in aqueous media; however, when P1 was dissolved in D_2O , it was turbid at 88.0 °C, meaning the occurrence of phase separation. Accordingly, we thought the lower critical solution temperature (LCST) of P1 in water was too high to measure at 1 atm. This



Fig. 2 2D WAXD patterns of P2 obtained with the X-ray beam perpendicular (a) and parallel (b) to the fiber direction.

phenomenon had also been reported in poly[N-(2-hydroxyisopropyl)acrylamidel, the LCST of which exceeded the temperatures that could be measured.¹⁸ Subsequently, in order to decrease the cloud point, we designed and synthesized another new polymer P2 by introducing a more hydrophobic alkyl group. Just as expected, P2 polymer aqueous solution at the concentration of 2.0 mg ml⁻¹ exhibited a sharp and rapid phase transition around 65.0 °C. When the concentration of P2 was 20.0 mg ml⁻¹, the LCSTs of P2 were 52.0 $^{\circ}$ C in H₂O and 47.5 °C in D₂O. Therefore, the concentration and the deuterium isotope have a great effect on the cloud point. The cloud point decreased with the increasing concentration of the polymer solution. At the same concentration, the cloud point in D₂O was lower than that in H₂O. This cloud point difference was attributed to the polar difference between D₂O and H₂O. Apparently, the more hydrophobic propyl group decreased the cloud point. To the best of our knowledge, this is the first report on synthetic thermo-responsive polymers which have both thermoresponsive properties and liquid crystal properties. The LCSTs of P1 and P2 in D2O were measured by visual method. Fig. 3 illustrates the appearance changes of 20.0 mg ml⁻¹ P1 and P2 in D₂O during phase separation. The LCST of P2 in H2O was obtained by Laser Light Scattering. Fig. 4f shows the temperature dependence of light scattering intensity of 2.0 mg ml⁻¹ P2 polymer aqueous solution during a heating and cooling cycle. Clearly, polymer P2 exhibited a remarkably reversible thermoresponsive phase transition behavior in aqueous solution. Moreover, no hysteresis phenomenon was observed in P2 aqueous solution during a heating and cooling cycle. Fig. S10[†] in the ESI shows a light scattering intensity of 20.0 mg ml⁻¹ in P2 polymer aqueous solution as a function of solution temperature on heating.

In conclusion, we have successfully designed and synthesized a new family of semirigid smart polymers based on mesogen-jacketed liquid crystal polymers, which show both liquid crystal properties and thermoresponsive behaviors. This new thermosensitive polymeric material undoubtedly provides new opportunities in the field of thermoresponsive systems. Further studies on these new smart polymers are in progress, such as determining the thermoresponsive mechanism, solution properties and so on.

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Table 1	Molecular characteristics and properties of two polymers							
Sample	$Mn(\times 10^4)^a$	PDI ^a	$T_g/^{\circ}C^b$	$T_d/^{\circ}C^{c}$	$\mathrm{LCST}_1/^{\circ}\mathrm{C}^d$	$LCST_2/^{\circ}C^e$	$LCST_3/^{\circ}C^f$	Liquid crystallinity ^g
P1	8.40	2.26	53.8	388.3			88.0	Yes
P2	7.75	2.63	23.8	386.9	65.0	52.0	47.5	Yes

^{*a*} The Mn and PDI of polymers were measured by GPC using PS standards and DMF as solvent. ^{*b*} The glass transition temperatures were obtained by DSC at a heating rate of 20 °C min⁻¹ under N₂ during the second heating process. ^{*c*} The decomposition temperatures at 5% weight loss of the samples measured by TGA heating experiments at a rate of 20 °C min⁻¹ under N₂. ^{*d*} The polymers were dissolved in the highly pure deionized water and then the aqueous solutions of polymers (2.0 mg ml⁻¹) were measured by Laser Light Scattering. ^{*e*} The aqueous solutions of polymers (20.0 mg ml⁻¹) were measured by Laser Light Scattering. ^{*f*} The polymers P1 and P2 were dissolved in D₂O, respectively, and then the polymer solutions (20.0 mg ml⁻¹) were measured by visual method. ^{*g*} Liquid crystallinity was observed by polarized optical microscopy.



Fig. 3 Appearance changes of 20.0 mg ml⁻¹ P1 (a) and P2 (b) in D₂O during phase separation.



Fig. 4 Temperature dependence of light scattering intensity of 2.0 mg ml^{-1} P2 polymer aqueous solution during a heating and cooling cycle.

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Notes and references

E. S. Gil and S. M. Hudson, *Prog. Polym. Sci.*, 2004, **29**, 1173;
 R. X. Liu, M. Fraylich and B. R. Saunders, *Colloid Polym. Sci.*, 2009, **287**, 627;
 S. Wan, M. Jiang and G. Z. Zhang, *Macromolecules*,

2007, **40**, 5552; J. Zou, B. Guan, X. J Liao, M. Jiang and F. G. Tao, *Macromolecules*, 2009, **42**, 7465; O. Ihata, Y. Kayaki and T. Ikariya, *Chem. Commun.*, 2005, 2268; D. Roy, J. N. Cambre and B. S. Sumerlin, *Chem. Commun.*, 2009, 2106.

- S. Anastase-Ravion, Z. Ding, A. Pellé, A. S. Hoffman and D. Letourneur, J. Chromatogr., B: Biomed. Sci. Appl., 2001, 761, 247; A. Kondo, T. Kaneko and K. Higashitani, Biotechnol. Bioeng., 1994, 44, 1.
- 3 A. S. Dilgimen, Z. Mustafaeva, M. Demchenko, T. Kaneko, Y. Osada and M. Mustafaev, *Biomaterials*, 2001, **22**, 2383.
- 4 W. L. J. Hinrichs, N. M. E. Schuurmans-Nieuwenbroek, P. van de Wetering and W. E. Hennink, J. Controlled Release, 1999, 60, 249;
 V. Bulmuş, S. Patır, S. A. Tuncel and E. Pişkin, J. Controlled Release, 2001, 76, 265; S. Dinçer, A. Tuncel and E. Pişkin, Macromol. Chem. Phys., 2002, 203, 1460.
- 5 H. G. Schild and D. A. Tirrel, J. Phys. Chem., 1990, 94, 4352.
- 6 S. H. Yuk, S. H. Cho and S. H. Lee, *Macromolecules*, 1997, 30, 6856.
- 7 J. J. Deng, Y. Shi, W. D. Jiang, Y. F. Peng, L. C. Lu and Y. L. Cai, *Macromolecules*, 2008, 41, 3007.
- 8 J. Persson, H. Johansson, I. Galaev, B. Mattiasson and F. Tjerneld, *Bioseparation*, 2000, **9**, 105.
- 9 A. Laukkanen, L. Valtola, F. M. Winnik and H. Tenhu, *Macro-molecules*, 2004, 37, 2268.
- 10 S. Y. Liu and S. P. Armes, J. Am. Chem. Soc., 2001, 123, 9910.
- 11 H. Uyama and S. Kobayashi, Chem. Lett., 1992, 21, 1643.
- 12 C. H. Luan and D. W. Urry, J. Phys. Chem., 1991, 95, 7896.
- 13 F. Hardouin, S. Mery, M. F. Achard and L. Noirez, J. Phys. II, 1991, 1, 511; F. Hardouin, N. Leroux, S. Mery and L. Noirez, J. Phys. II, 1992, 2, 271; Q. F. Zhou, X. H. Wan, X. L. Zhu, F. Zhang and X. Feng, Mol. Cryst. Liq. Cryst., 1993, 231, 107; G. Z. Xu, W. Wu, D. Y. Shen, J. A. Hou, S. F Zhang, M. Xu and Q. F. Zhou, Polymer, 1993, 34, 1818; X. H. Wan, F. Zhang, P. Q. Wu, D. Zhang, X. D. Feng and Q. F. Zhou, Macromol. Symp., 1995, 96, 207; Y. F. Tu, X. H. Wan, D. Zhang, Q. F. Zhou and C. Wu, J. Am. Chem. Soc., 2000, 122, 10201.
- 14 Q. F. Zhou, H. M. Li and X. D. Feng, *Macromolecules*, 1987, 20, 233; Q. F. Zhou, X. L. Zhu and Z. Q. Wen, *Macromolecules*, 1989, 22, 491.
- 15 V. Percec, C. H. Ahn, G. Ungar, D. J. P. Yeardley, M. Moller and S. S. Sheiko, *Nature*, 1998, **391**, 161.
- 16 X. Y. Yin, C. Ye, X. Ma, E. Q. Chen, X. Y. Qi, X. F. Duan, X. H. Wan, S. Z. D. Cheng and Q. F. Zhou, *J. Am. Chem. Soc.*, 2003, **125**, 6854; C. Ye, H. L. Zhang, Y. Huang, E. Q. Chen, Y. L. Lu, D. Y. Shen, X. H. Wan, Z. H. Shen, S. Z. D. Cheng and Q. F. Zhou, *Macromolecules*, 2004, **37**, 7188.
- 17 J. J. Ge, M. M. Guo, Z. H. Zhang, P. S. Honigfort, I. K. Mann, S. Y. Wang, F. W. Harris and S. Z. D. Cheng, *Macromolecules*, 2000, **33**, 3983; J. L. Cheng, Y. Yoon, R. M. Ho, M. Leland, M. M. Guo, S. Z. D. Cheng, P. Chu and V. Percec, *Macromolecules*, 1997, **30**, 4688.
- 18 T. Maeda, T. Kanda, Y. Yonekura, K. Yamamoto and T. Aoyagi, *Biomacromolecules*, 2006, 7, 545.