



# PNIPAm-P123-PNIPAm五嵌段共聚物的溶液行为和微观结构研究

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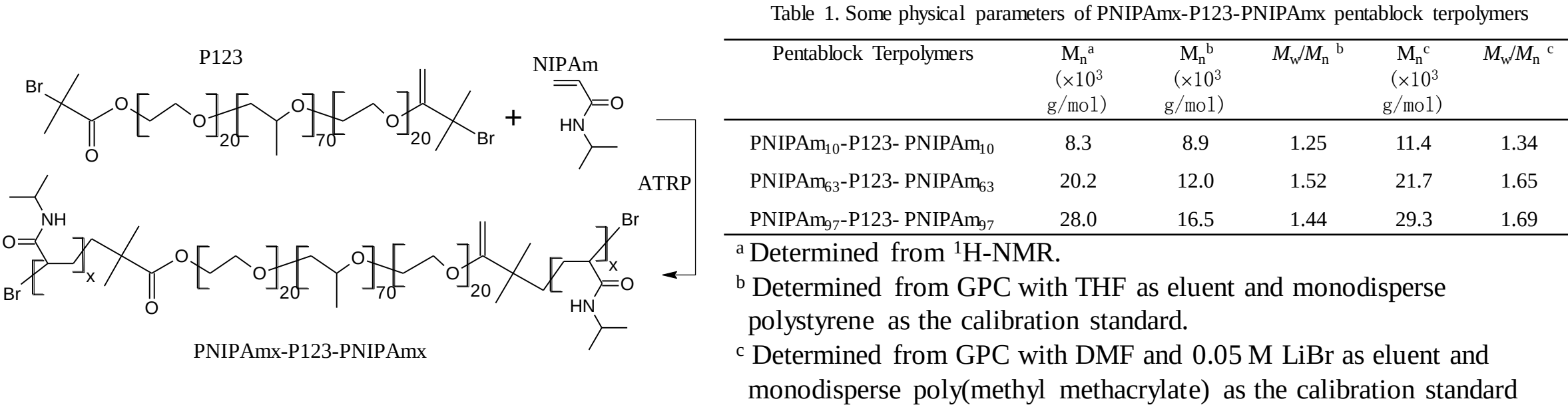
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## 背景介绍

近年来, 对嵌段数大于三的多嵌段共聚物的合成方法、链构象、溶液特性、吸附行为等的研究已引起越来越多的兴趣和关注。多嵌段共聚物的结构被认为与生物大分子接近, 因此对其链构象和溶液行为的研究将有助于我们理解生物大分子的溶液行为。归因于其科学的重要性和潜在的应用价值, 对多嵌段共聚物的合成、链构象、溶液行为和对应的物理特性的研究已成为高分子科学领域的重要研究课题。

## 实验部分



在这里, 我们采用 ATRP 的方法, 以 NIPAm 为单体, 末端改性的 P123 (PEO<sub>20</sub>-PPO<sub>70</sub>-PEO<sub>20</sub>) 为大分子引发剂成功合成了一系列具有不同 PNIPAm 链段长度 x 的温敏性五嵌段三元共聚物, PNIPAm<sub>x</sub>-P123-PNIPAm<sub>x</sub>。通过采用了差示扫描微量热法 (micro-DSC)、静态和动态激光光散射 (SLS&DLS) 以及小角 X 射线散射 (SAXS) 等手段系统地研究了 PNIPAm<sub>x</sub>-P123-PNIPAm<sub>x</sub> 在水溶液中的链行为和微观结构。

## 结果与讨论

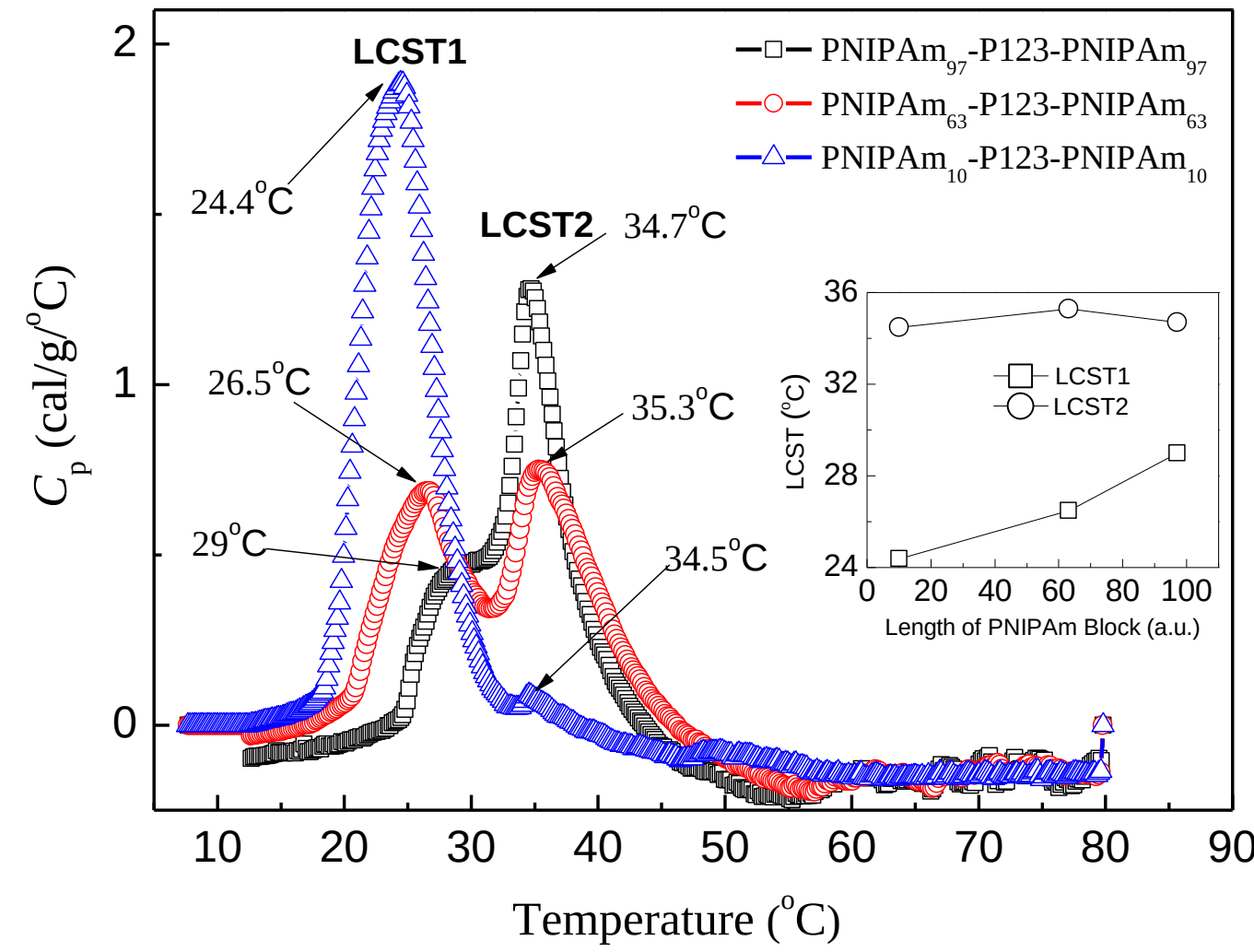


Figure 1. Temperature dependence of the specific heat capacity ( $C_p$ ) for the PNIPAm<sub>x</sub>-P123-PNIPAm<sub>x</sub> pentablock terpolymers in aqueous solutions with concentration of 5 mg/mL. The inset shows the change of the two LCSTs as a function of length of PNIPAm block.

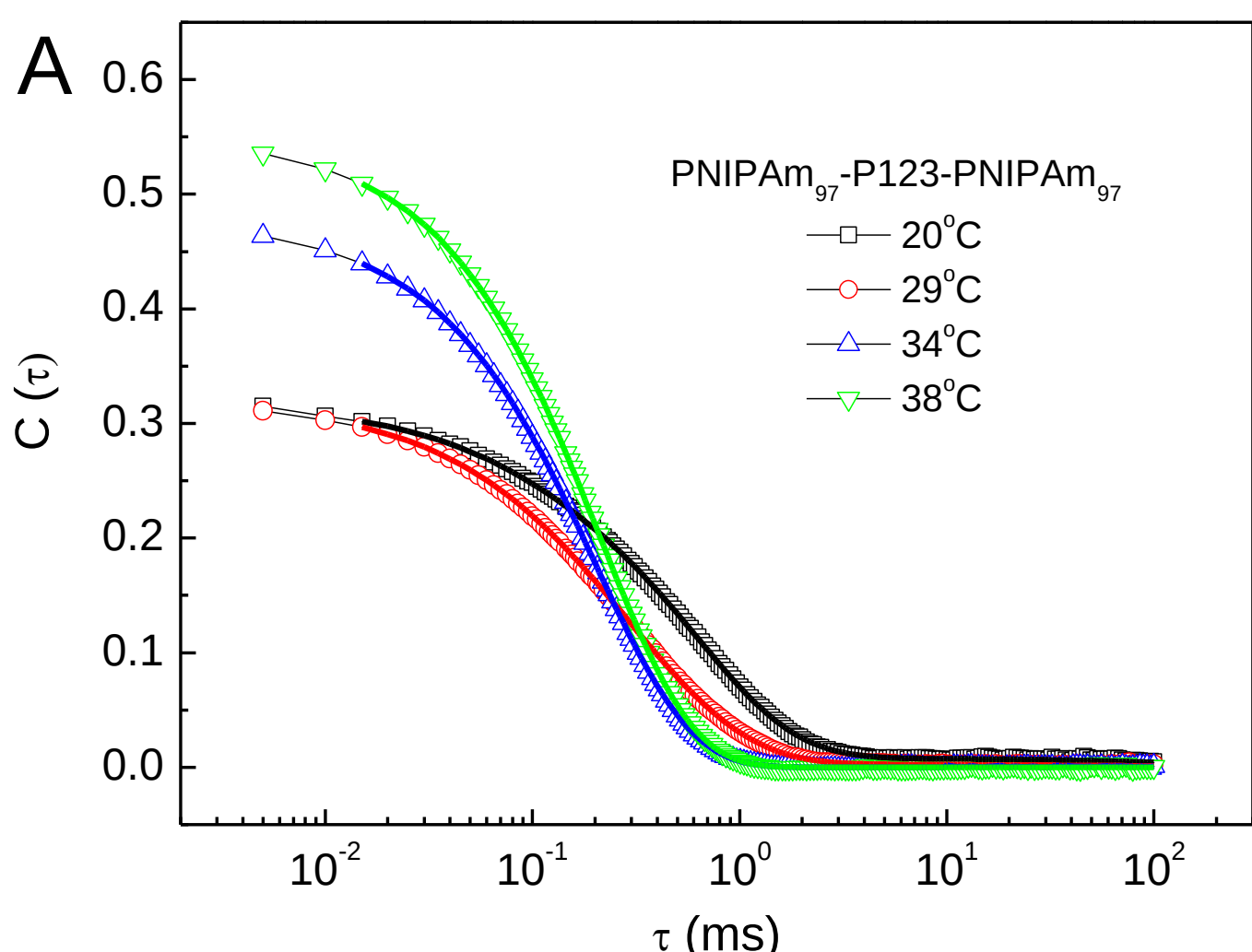


Figure 2. (A) The autocorrelation function  $C(t)$  measured by DLS for PNIPAm<sub>97</sub>-P123-PNIPAm<sub>97</sub> aqueous solution with the concentration of 0.5 mg/mL at different temperatures, i.e. 20 °C, 29 °C, 34 °C and 38 °C. The solid lines are CONTIN fits. (B) The corresponding distribution of hydrodynamic radius ( $R_h$ ) calculated by using CONTIN routine

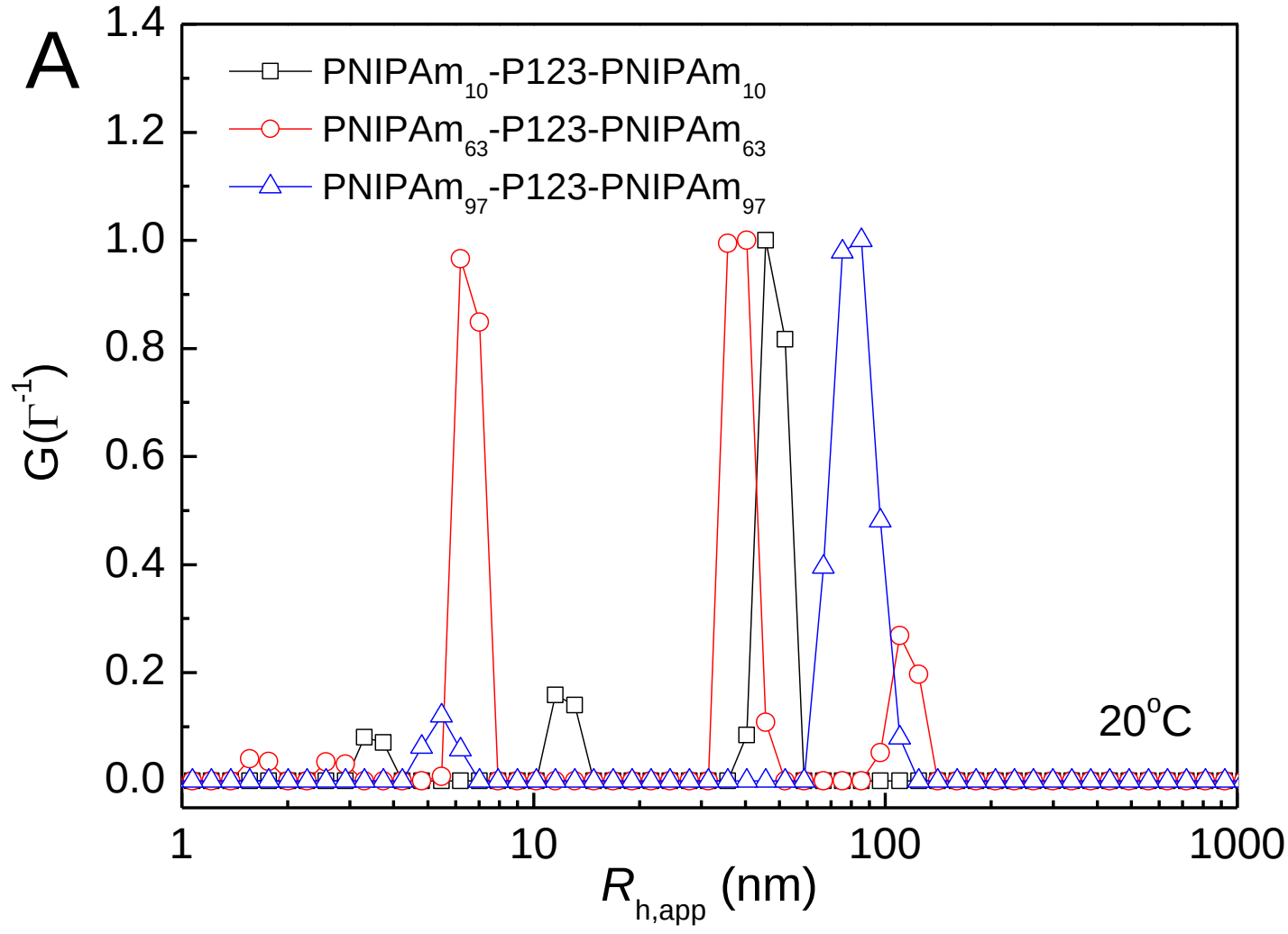
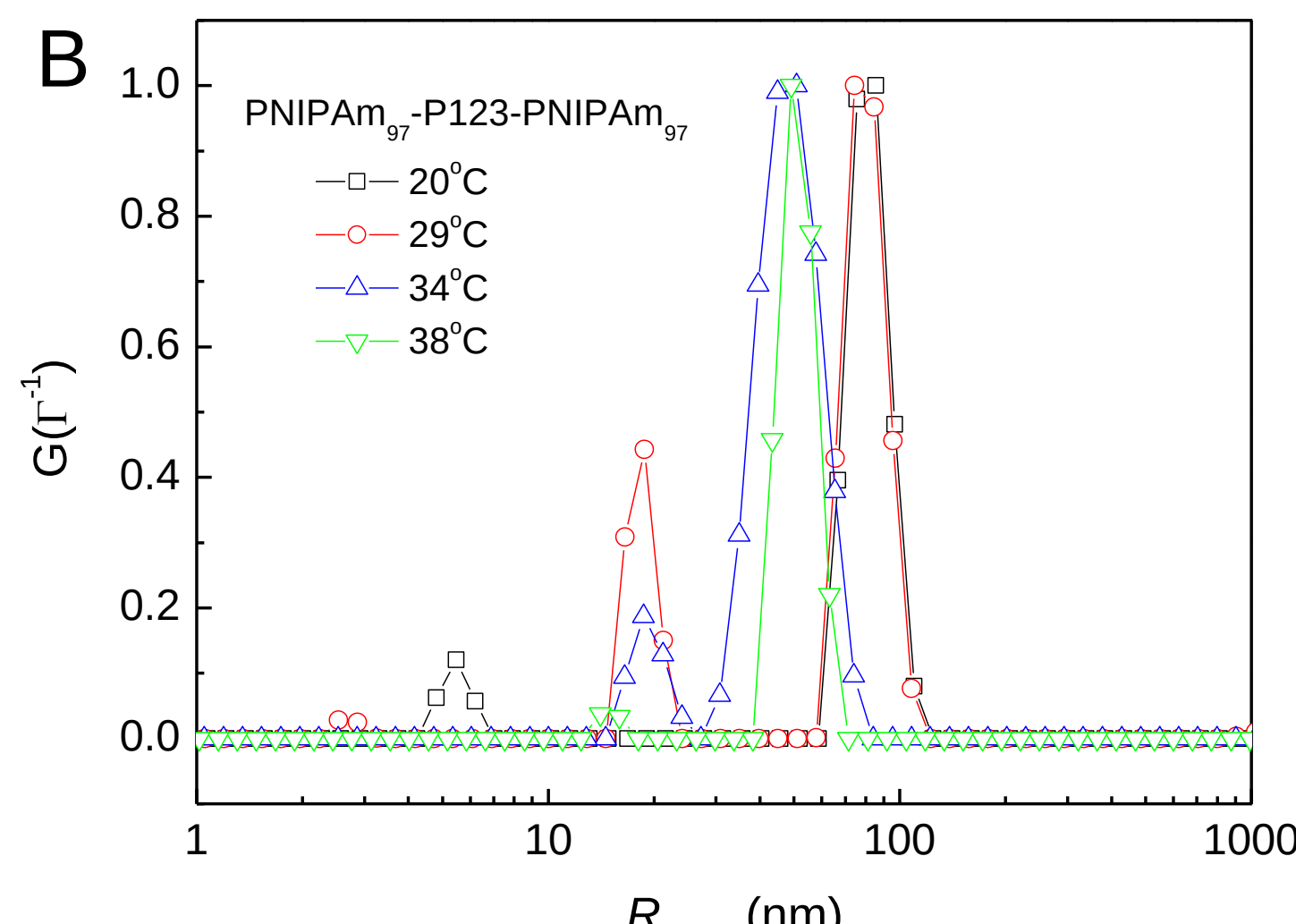


Figure 3. The distribution of hydrodynamic radius ( $R_h$ ) measured by DLS at scattering angle of 90 ° for PNIPAm<sub>x</sub>-P123-PNIPAm<sub>x</sub> pentablock terpolymers in aqueous solutions with the concentration of 0.5 mg/mL at various temperatures. (A) 20 °C, and (B) 45 °C.

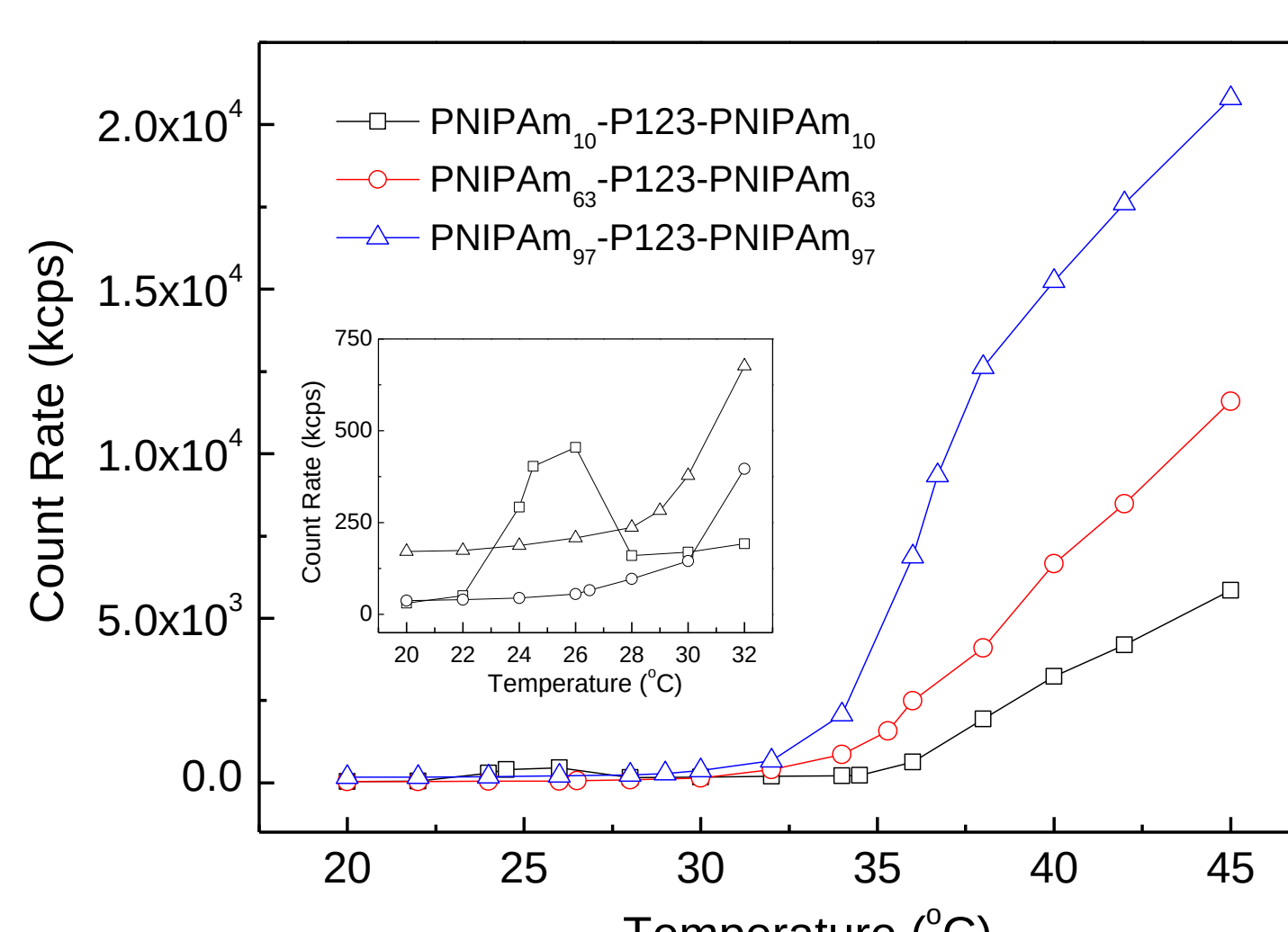
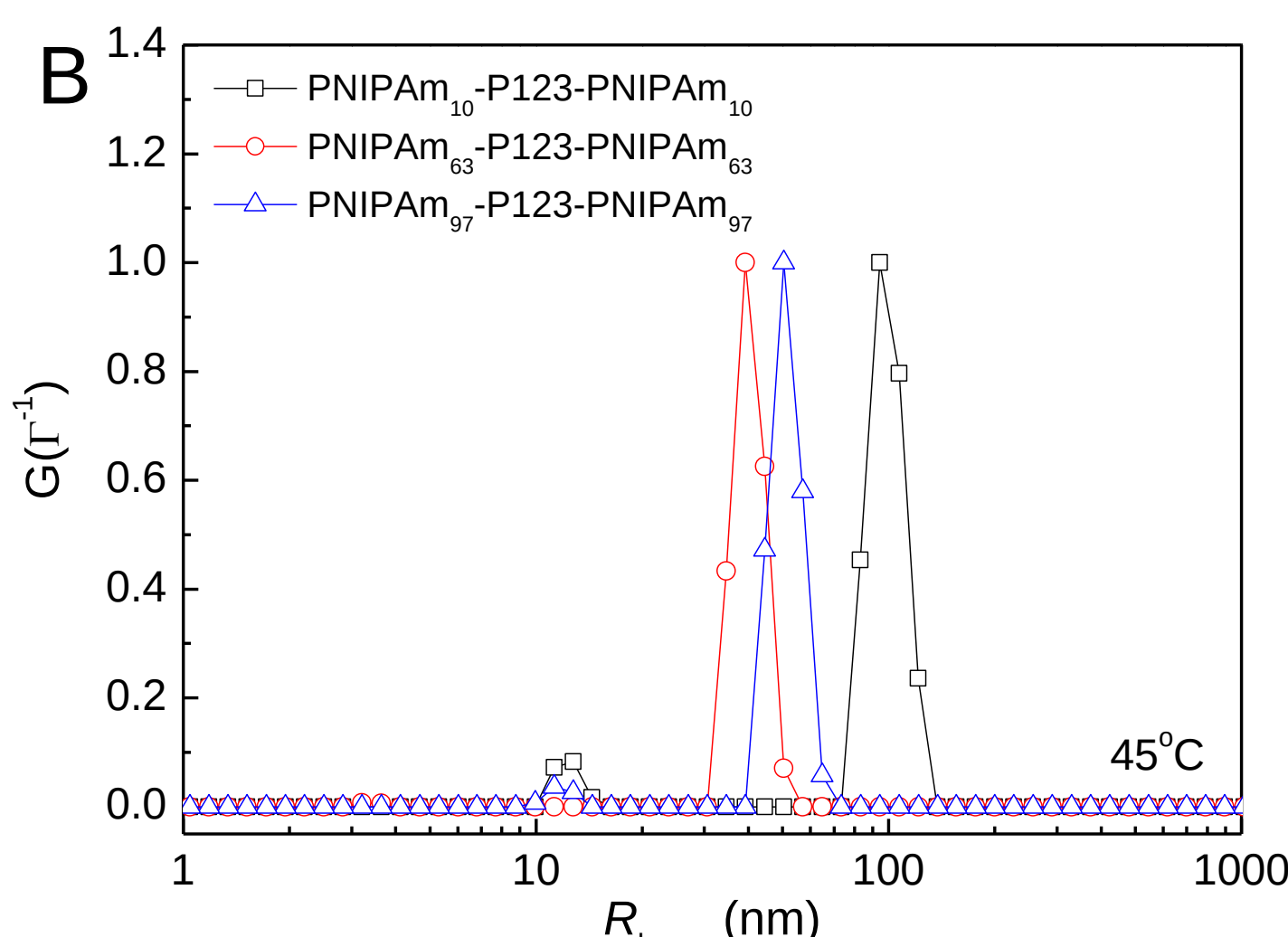


Figure 4. Scattering intensity (count rate) measured by DLS at scattering angle of 90 ° for PNIPAm<sub>x</sub>-P123-PNIPAm<sub>x</sub> pentablock terpolymers in dilute aqueous solutions with concentration of 0.5 mg/mL as a function of temperature. The inset was the enlarged count rate at low temperature range of 20-32 °C.

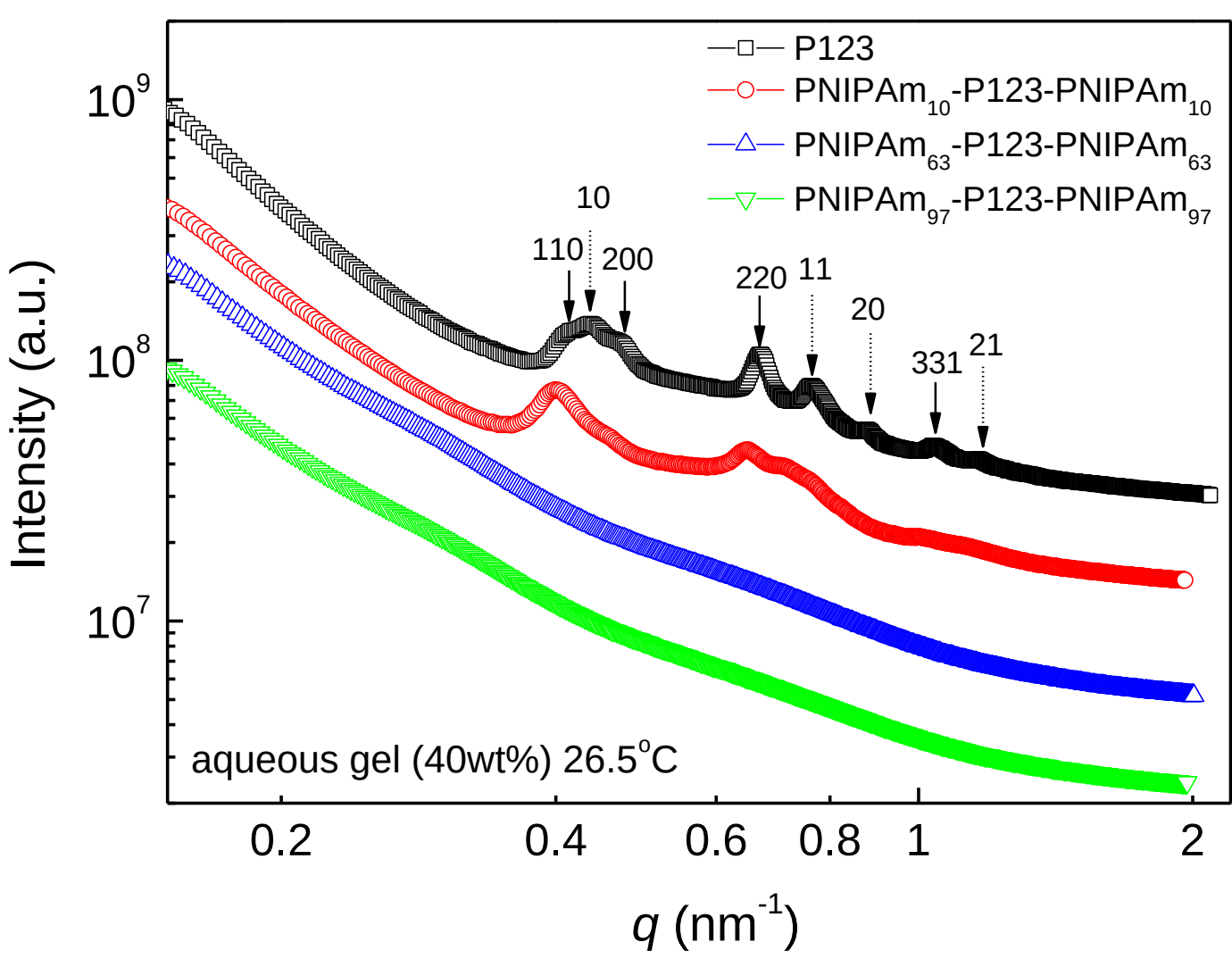


Figure 5. SAXS profiles for 40 wt% aqueous gels of P123 and PNIPAm<sub>x</sub>-P123-PNIPAm<sub>x</sub> pentablock terpolymers at room temperature, i.e. 26.5 °C at SSRF.

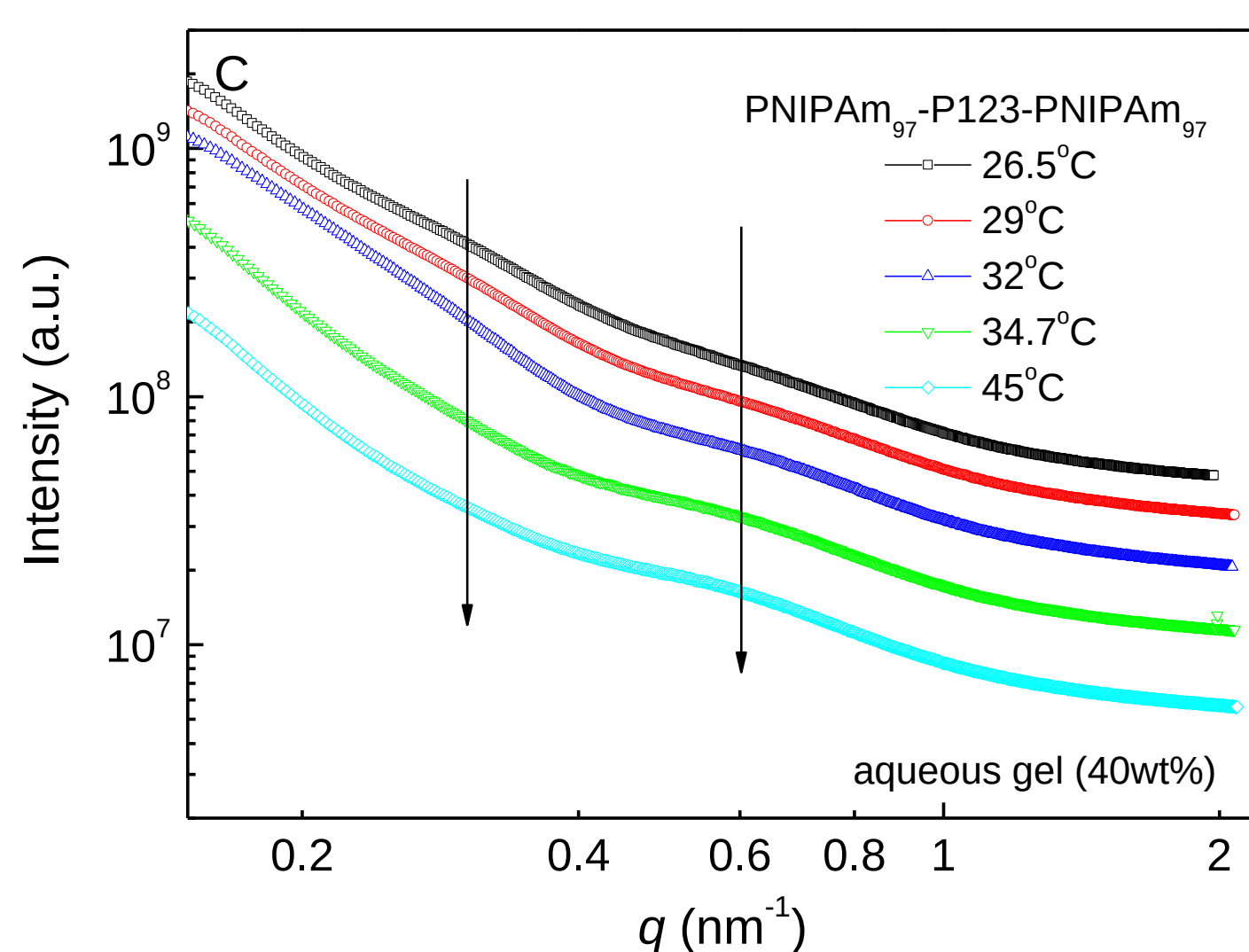
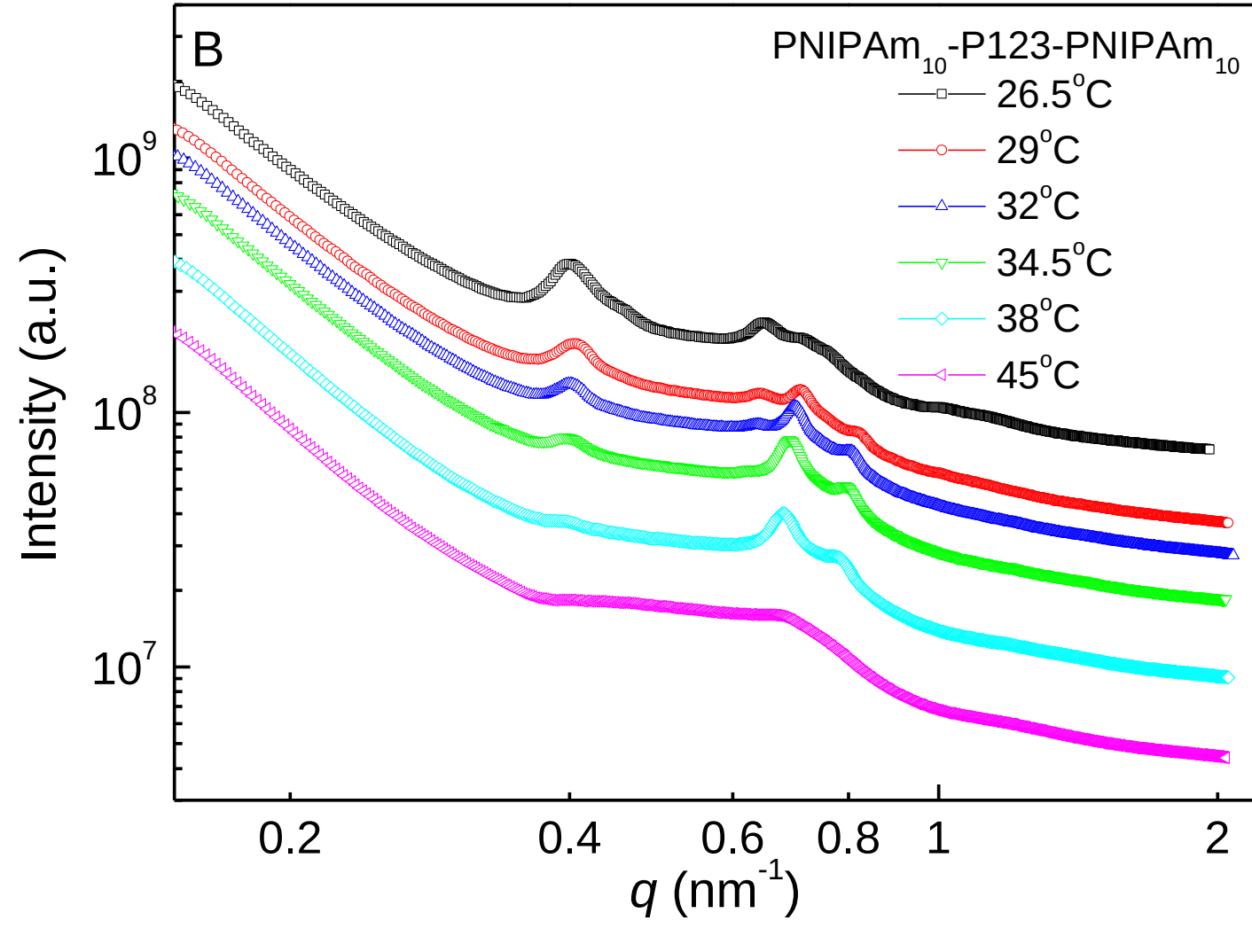
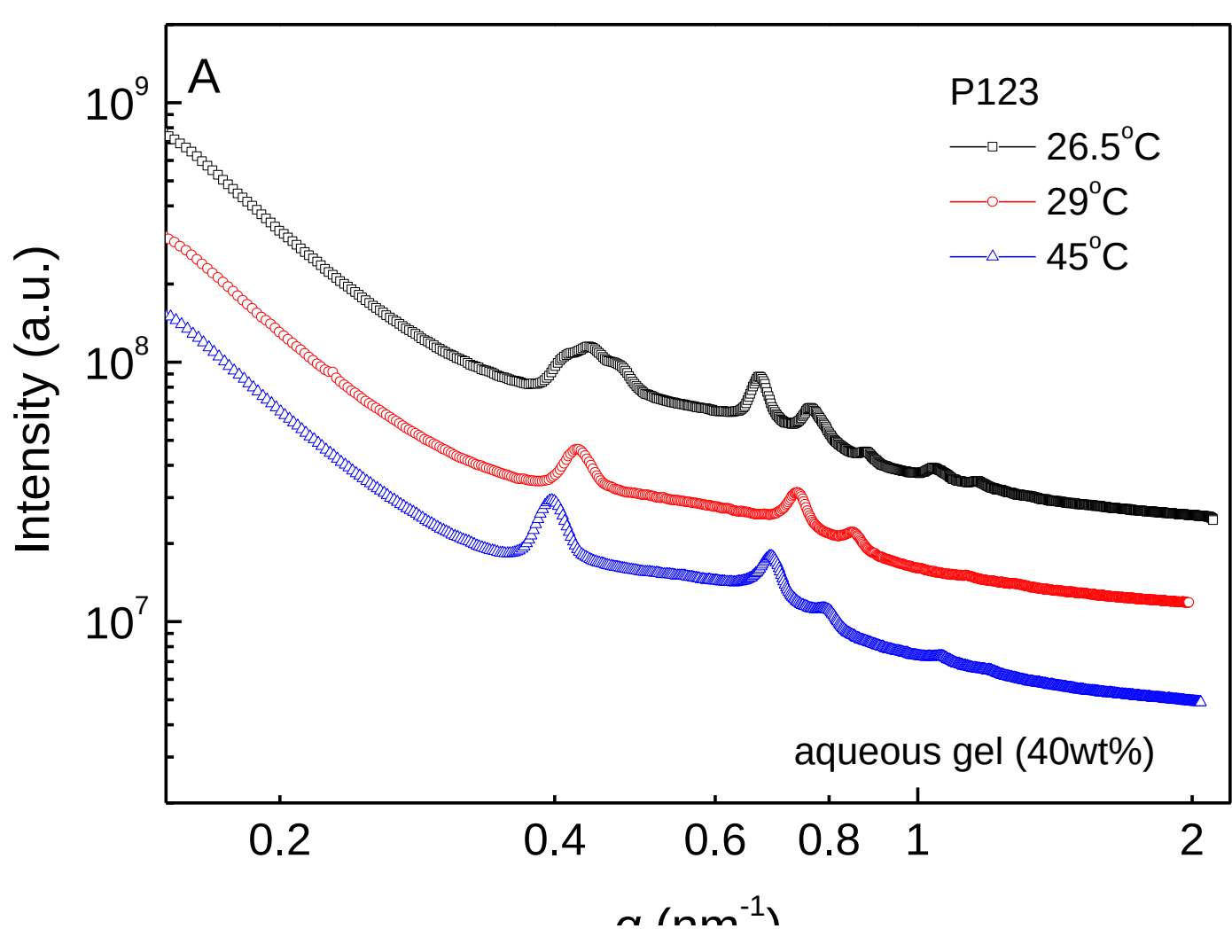


Figure 6. SAXS profiles for 40 wt% aqueous gels of (A) P123, (B) PNIPAm<sub>10</sub>-P123-PNIPAm<sub>10</sub> and (C) PNIPAm<sub>97</sub>-P123-PNIPAm<sub>97</sub> at various temperatures.

## 结论

- ◆ 相应PNIPAm、PPO、PEO嵌段的长度对于五嵌段聚合物在稀水溶液和浓水溶液中的溶液行为和微观结构都有显著影响;
- ◆ micro-DSC结果表明, 在稀溶液中, PNIPAm<sub>x</sub>-P123-PNIPAm<sub>x</sub>存在两个低临界溶解温度 (LCST), 分别对应于PPO和PNIPAm链段;
- ◆ 激光光散射数据表明, 在低温所有链段均可溶的条件下 (20°C), 五嵌段共聚物形成了松散的聚集结构, 其与单分子链构象共存, 而且其尺寸随着PNIPAm链段长度的增加而增加;
- ◆ 在高温下, 即PNIPAm的LCST以上, 五嵌段共聚物则形成了以疏水PNIPAm和PPO链段为核、亲水链段PEO为壳的胶束;
- ◆ 该五嵌段共聚物在高浓度下形成了水凝胶, SAXS结果表明, 其水凝胶的微观结构强烈地依赖于环境温度和链段的相对长度。