In this chapter, the design, fabrication and performance of thermo-responsive adsorption/desorption membranes for affinity separation are introduced. Firstly, the design of fabrication of thermo-responsive affinity membranes with nano-structured pores and grafted PNIPAM surface layer for hydrophobic adsorption are described. The membrane shows efficient “adsorbing at a temperature above the LCST–desorbing at a temperature below the LCST” performance for bovine serum albumin molecules. Then a temperature-dependent molecular-recognizable membrane with both grafted PNIPAM chains and immobilized β-CD moieties for affinity separation is introduced. Contrariwise to the first kind of membrane, this membrane demonstrates effective “adsorbing at a temperature below the LCST–desorbing at a temperature above the LCST” performance for guest molecules.

### 6.1 Introduction

As mentioned in Section 1.3.1, poly(N-isopropylacrylamide) (PNIPAM) is a popular thermo-responsive polymer. It shows a distinct and reversible phase transition at the lower critical solution temperature (LCST) around 32 °C. When the environmental temperature is lower than the LCST, the PNIPAM can bind plenty of water molecules on its amide groups through hydrogen-bonding interaction, and thus it is in a swollen and hydrophilic state; however, when the temperature is higher than the LCST, the PNIPAM is dehydrated because of the cleavage of the hydrogen-bonding, and thus it is in a shrunken and hydrophobic state. Furthermore, it has been reported that the phase transition of PNIPAM responding to temperature change could affect the association constant between β-CD and guest molecules in a PNIPAM-modified β-CD system (Chapter 5). Such
dramatic phase transition characteristics make PNIPAM extremely attractive for developing thermo-responsive smart membranes for affinity separation. In this chapter, two kinds of PNIPAM-based thermo-responsive membranes for affinity separation, which are thermo-responsive membranes with nano-structured pores and grafted PNIPAM surface layer for hydrophobic adsorption, and thermo-responsive molecular-recognizable membranes for affinity separation, will be introduced.

6.2 Thermo-Responsive Affinity Membrane with Nano-Structured Pores and Grafted PNIPAM Surface Layer for Hydrophobic Adsorption

Affinity membranes are membranes that can identify and separate specific molecules. In the fields of separation and purification of protein, enzyme, chiral substance, hydrophobic solutes and so on, affinity membranes have been widely studied. It has been reported that thermo-responsive affinity membranes with PNIPAM functional surface layers can be used for hydrophobic adsorption and separation of hydrophobic solutes, because the surfaces of PNIPAM-grafted membranes can change from a hydrophilic to hydrophobic state when the environmental temperature increases across the LCST of PNIPAM and vice versa. It has been verified that the micro- and nano-structures on the surfaces of some natural plants such as lotus leaves contribute significantly to their surface superhydrophobicity. Inspired by such natural phenomena, micro- and nano-structures have been applied to achieve artificial superhydrophobic surfaces. For PNIPAM-modified functional surfaces, it has been found that micro- and/or nano-structured surfaces could enhance the thermo-responsive wettability change between hydrophobicity and hydrophilicity, i.e., micro- and/or nano-structured surface architectures could make the PNIPAM-modified surfaces more hydrophilic at temperatures below the LCST but more hydrophobic above the LCST. For example, surface-initiated atom-transfer radical polymerization was used to fabricate thermo-responsive PNIPAM thin film on both flat and nano-structured silicon substrates, and the results showed that the water contact angle of the flat surface increased from 63° to 93° when the temperature changed from 25 °C to 40 °C, while the water contact angle value of the nano-structured surface was about 0° below 29 °C and about 150° above 40 °C. Such results show a promising approach for improving the hydrophobic adsorption performance of PNIPAM-grafted thermo-responsive membranes. It means that if we introduce nano-structures onto the membrane surfaces and membrane pore surfaces before grafting the PNIPAM surface layer, the reversible hydrophobic-adsorption/ hydrophilic-desorption performance could be improved.