



**Figure 8.1** Operational principles of a membrane crystallizer. (a) Temperature-driven membrane crystallizer (direct contact configuration), in which a microporous hydrophobic membrane is contacted by the warm crystallizing solution at one side, and by cold pure water on the opposite side; (b) osmotic-driven membrane crystallizer, in which a microporous hydrophobic membrane is contacted by the crystallizing solution at one side, and by a hypersaline solution on the opposite side; (c) antisolvent membrane crystallization: antisolvent is added to the feed solution by diffusion in vapor phase from the opposite side, and the consequent decrease of solubility induces the crystallization.

### 8.3 Membrane Materials and Transport Phenomena

Although, in principle, a large variety of membranes (having different morphology, surface topology, physico-chemical properties, selectivity *etc.*) can be used in membrane-assisted crystallization applications, microporous hydrophobic membranes are the most appropriate when treating aqueous solutions and, so far, are the most utilized.

Among hydrophobic polymers, fluoropolymers represent a unique class of materials with an interesting combination of properties – such as high thermal stability and chemical resistance, and low surface tension as determined by the low polarizability and the strong electronegativity of fluorine atoms – that have attracted significant attention over the past few decades.<sup>13,14</sup>

Fluorinated polymers and copolymers (the most common are listed in Table 8.1) are widely employed to fabricate membranes at industrial level, often manufactured by non-solvent induced phase separation (NIPS) and thermally induced phase separation (TIPS) methods.