IV) and trigonal (CBZ II), mentioned by decreasing thermodynamic stability, and orthorhombic form V.[45,46] Interestingly, in membrane crystallization of CBZ at increasing transmembrane flux, the amount of CBZ I in the solid precipitate decreases while the amount of less stable form CBZ IV increases.

8.6.2 Influence of the Chemistry of the Surface

Curcio *et al.* (2014) investigated the effect of polymer–solute interactions on the kinetics of heterogeneous nucleation on membranes; in particular, experimental efforts were focussed on the acetaminophen (ACM) crystallization as a result of specific solute–surface interactions occurring on polydimethylsiloxane (PDMS) with siloxane functional groups Si–O–Si forming the backbone of silicones, partially fluorinated elastomer polyvinylidenedifluoride (PVDF), polystyrene (PS) having weak electron-donor phenyl rings, poly(*n*-butyl methacrylate) (PnBMA) showing ester functionality, polyimide (PI) that includes both hydrogen-bond acceptor imide functionality and carbonyl groups and ethylene/acrylic acid (EAA) copolymer with a carboxyl moiety.[47]

Powder X-ray diffraction (PXRD) analysis demonstrated the occurrence of preferential orientation (PO) as a function of the strength of intermolecular interactions at the polymer–crystal interface taking place at the early stage of nucleation, ranging from non-specific adsorption (PDMS, PnBMA, and PS) to oriented arrangement of molecules in the crystalline lattice (EAA, PI, and PVDF).

All investigated polymeric membranes promoted the formation of the thermodynamically stable monoclinic ACM form I, with the interesting exception of polyimide.

PXRD analysis of ACM crystals nucleating on hydrophobic PVDF shows a main peak at 13.9° (001), and two predominant reflections at 14.1° (001) and 28.1° (002) on the EAA surface (Figure 8.10).

These experimental data indicate a strong orientation of crystals along {001}: hydroxyl groups of the ACM molecules aligned along the plane {001} are perpendicularly oriented with respect to the polymeric surface (interactions through hydrogen-bonding).

Referring to Figure 8.11, the PXRD pattern of ACM crystals nucleated on hydrophobic PDMS surface does not give evidence for a prevalent crystal orientation along a specific crystallographic plane, and four major reflections at 12.1° (110), 15.4° (20$\bar{1}$), 18.9° (020), and 24.4° (220) are observed. Reflections whose linear combinations correspond to vector direction {110} indicate that some ACM molecules are parallel to the membrane surface, while others have hydroxyl and methyl groups alternatively redirected towards the polymeric substrate. The main peak at 15.4°, corresponding to orientation along {20$\bar{1}$}, reveals that methyl groups and the amide portion in some ACM molecules are perpendicularly aligned to the PDMS surface. The PXRD diffractogram of PnBMA shows a similar behavior, although the presence of