The development of new and better sample separation methods depends upon the development of new and better stationary phases. But before those materials can be properly designed and utilized to their full potential, their intrinsic characteristics must be better understood. Organic porous polymer monoliths (PPMs) represent a new type of stationary phase that exhibit many interesting features and characteristics that give them distinctive behavior from, and in many cases improved performance relative to, the more traditional silica based particle stationary phases. Our focus is on elucidating the interactions between analyte, stationary phase, and mobile phase. One of our approaches is to characterize the relationship between retention and diffusion. Our results show that analytes diffuse through the PPM material in a manner more consistent with theory than they do in silica based phases. We attribute this to structural differences between these different stationary phases. These differences are related to surface charge and the relative amounts of stagnant mobile phase zones in the different types of phases. This helps to explain why ideal diffusion-retentions relationships have never been observed with silica based phases.