Monte Carlo light transport simulation has become a de-facto standard tool for photorealistic rendering. However, the algorithms used by the current rendering systems are often ineffective, especially in scenes featuring light transport due to multiple highly glossy or specular interactions and complex visibility between the camera and light sources. It is therefore desirable to adopt more robust algorithms in practice. Light transport algorithms based on Markov chain Monte Carlo (MCMC) are known to be effective at sampling many different kinds of light transport paths even in the presence of complex visibility. However, the current MCMC algorithms often over-sample some of the paths while under-sampling or completely missing other paths. We attribute this behavior to insufficient global exploration of path space which leads to their unpredictable convergence and causes the occurrence of image artifacts. This in turn prohibits adoption of MCMC algorithms in practice. In this thesis we therefore focus on improving global exploration in MCMC algorithms for light transport simulation. First, we present a new MCMC algorithm that utilizes replica exchange to improve global exploration. To maximize efficiency of replica exchange we introduce tempering of the path space, which allows easier discovery of important parts of the path space by the Markov chain. We further enhance replica exchange by designing novel replica exchange moves. Second, we present a different MCMC algorithm that is built upon the vertex connection and merging (VCM), a.k.a. unified path space sampling (UPS) algorithm. The path sampling techniques and subpath reuse from VCM/UPS leads to easier global exploration of the path space in the presence of glossy or specular transport. Besides the new algorithms that aim at improving global exploration, this thesis also contains a comprehensive survey of the Markov chain Monte Carlo methods used in light transport simulation.