Equilibrium molecular dynamics simulations were conducted to analyze the rotational decorrelation rates of different molecules in unmodified and polymer-modified asphalts. The motivation is to relate chemical characteristics of the asphalt to mechanical properties, such as viscosity and complex modulus. Model asphalts were devised based on solubility and polarity, using one or more compounds to represent each of the typical classifications found in real asphalts (asphaltene, polar aromatic, naphthene aromatic, saturate). Relaxation dynamics were calculated using extrapolations of Legendre polynomial regressions to rotational correlation functions, based on aromatic ring normal vectors and chain molecule end-to-end vectors. Relaxation behaviors were then described using modified KWW fits of the simulation results. Temperature dependences of relaxation rates and viscosity were related via Debye-Stokes-Einstein relationships and showed good correspondence with experimental results. The mechanism of how polymer chains modify asphalt viscosity was also analyzed. The long-term results can supply guidance for designing new functional polymers for use in road pavements.