Colloid particles with dipolar interactions that self-assemble into pre-defined microstructures have the potential to serve as the foundation for a new generation of micro- and nano-structures of remarkable complexity and precision. Dipolar colloidal particles self-assemble into a rich variety of microstructures ranging from co-crystals of novel symmetry, to open networks (gels) of cross-linked chains of particles. We use discontinuous molecular dynamics computer simulation to explore the self assembly, structure, crystallization and/or gelation of single-component and binary mixtures of colloid particles with permanent dipole moments. Many different types of phases are found, including ordered phases (FCC, HCP and BCT) at high packing fractions and fluid, string-fluid and gel phases at low packing fractions. The very low volume fraction gel phases and the well ordered crystal phases are promising for materials applications. The results of this study should help guide our experimental colleagues in their quest to design and engineer “smart” gels and materials.