Polyiodides represent one of a few classes of compounds that can form extensive inorganic homoatomic polymeric networks. Furthermore, polyiodide compounds exhibit useful redox properties, as well as electrical conductivity uncommon for nonmetals. Therefore, they have found technical applications in electronic and electrochemical devices such as batteries, fuel cells, dye-sensitized solar cells, optical devices, etc. We investigated the response of tetraethylammonium di-iodine triiodide (TEAI) for compression, using powder and single-crystal X-ray diffraction, electrical conductivity, and first principle calculations. We report the high-pressure structural characterization of TEAI in which a progressive addition of iodine to triiodide groups occurs. Compression leads to the initial formation of discrete heptaiodide units, followed by polymerization to a 3D anionic network. Although the structural changes appear to be continuous, the insulating salt becomes a semiconducting polymer just above 10 GPa. The features of the pre-reactive state and the polymerized state are revealed by analysis of the computed electron and energy densities. The unusually high electrical conductivity can be explained with the formation of new bonds. These features make TEAI a tunable pressure-sensitive electric switch. Structural studies at high pressure can rationalize the synthesis and search for the future organic and hybrid semiconductors based on polyiodides and other iodine-rich compounds. This includes structures with the soft I···I contacts, which are the most prone for charge transport across the crystal under increased pressure.