

ABSTRACT

The synthesis has been described yielding a new type of rigid conjugated polymer networks which possess a high content of permanent micropores and macropores and exhibit high surface areas up to 1469 m²/g. The networks have been prepared via chain-growth coordination polymerization catalysed with insertion catalysts based on Rh complexes. This polymerization has been newly applied to bifunctional acetylenic monomers of diethynylarene type (1,4-diethynylbenzene, 1,3-diethynylbenzene and 4,4'-diethynylbiphenyl). The covalent structure of the networks consists of the polyacetylene main chains densely connected by arylene struts. The W and Mo metathesis catalysts have been revealed as inefficient for the synthesis of these networks. The increase in the polymerization temperature and time has been shown to affect positively the content and the diameter (up to 22 nm) of the mesopores in the networks. A mechanism has been proposed that explains the mesopores formation as a result of mutual knitting of small particles of the microporous polymer. The application of emulsion polymerization technique allowed to prepare texturally hierarchical polyacetylene networks possessing interconnected open macropores (diameter up to 4,8 μm) the walls of which exhibited micro/mesoporous texture. It was demonstrated that cross-linking of the networks can be enhanced by postpolymerization thermally induced reaction of free terminal ethynyl groups present in the networks.

Using newly the catalyst system TaCl₅/Ph₄Sn the diethynylarenes (1,4-diethynylbenzene and 2,6-diethynyl-naphthalene) were efficiently polycyclotrimerized to micro/mesoporous hyper-branched and partly cross-linked polycyclotrimers in which the arene cores of the monomer are linked by benzenetriyl linkers. The polycyclotrimers exhibit an unusual mode of trapping of gases (N₂ and CO₂) that is mainly manifested by significant hystereses on the adsorption/desorption isotherms. An explanation has been proposed for this behaviour based on the dual mechanism of the gas trapping according to which the trapping of a gas is contributed by adsorption on the surface of the permanent pores and by penetration of the gas into the nonporous segments of the adsorbent under formation of temporary pores. The formation of the temporary pores is discussed in connection to conformational flexibility of the segments of polycyclotrimers.