

ABSTRACT

The preparation of a new group of functionalized conjugated polymer networks has been described based on spontaneous quaternization polymerization of ethynylpyridines with bis(bromomethyl)arenes. The networks consisted of polyacetylene chains with pyridyl and pyridiniumyl pendants cross-linked with $-\text{CH}_2(\text{arylene})\text{CH}_2-$ links. The variation of the ratio of monomer and quaternization agent in the feed modified the ratio of pyridyl and pyridiniumyl groups in the networks (pyridyl/pyridiniumyl ratios from 0 to 1.32). The networks did not exhibit a permanent microporosity that could be confirmed by nitrogen adsorption at 77 K. Nevertheless, all networks were active in capture of CO_2 at 293 K (up to 0.73 mmol CO_2/g , 750 Torr). It has been hypothesized that CO_2 capture reflected formation of a temporary porous texture of the networks through conformational changes of the network segments enabled by the segments mobility at room temperature.

The preparation of functionalized conjugated polymer networks with permanent micro/mesoporosity (S_{BET} up to 667 m^2/g) has been described that was based on chain coordination copolymerization of acetylenic monomers. The copolymerization of 1,4-diethynylbenzene or 4,4'-diethynylbiphenyl with mono or diethynylbenzenes bearing NO_2 or CH_2OH groups has been demonstrated as particularly efficient. The networks consisted of polyacetylene chains interconnected by arylene links while linear units of the networks possessed pendants substituted with heteroatomic groups in the amount up to 3.9 mmol/g. The networks functionalized with NO_2 or CH_2OH groups exhibited up to 58 % higher adsorption capacity for CO_2 than the non-functionalized networks. Most probably, this was owing to an enhancement of the energy of interaction of CO_2 with the surface of the functionalized networks.

A series of mostly new monomers has been prepared and characterized. The monomers were of aromatic Schiff base type and contained two or three ethynylated benzene rings connected by methanimine groups. Diethynylated monomers were efficiently polymerized in a chain manner to highly functionalized micro/mesoporous (S_{BET} up to 803 m^2/g) conjugated polyacetylene networks with the main chains interconnected with 1,4-phenylene-methanimine links of various length. The relative contents of micro- and mesopores in the networks were partly controlled by the structure of the monomer used for the polymerization.