

The diynes of both aliphatic and aromatic types comprising either (i) two internal ethynyl groups or (ii) one internal and one terminal ethynyl group in the molecule were revealed as appropriate monomers for the  $\text{Co}_2(\text{CO})_8$  catalyzed polycyclotrimerization yielding high-molecular-weight products. The polycyclotrimerization of aliphatic diynes with a short  $(\text{CH}_2)_2$  link between ethynyl groups and the polycyclotrimerization of aromatic diynes provided polycyclotrimer networks with tri-, tetra-, penta- and hexasubstituted benzene segments. The polycyclotrimers of aliphatic diynes did not exhibit microporous texture. On the other side, the polycyclotrimers of aromatic monomers were mostly microporous with specific surface area up to  $S_{\text{BET}} = 499 \text{ m}^2/\text{g}$ . The nitrogen desorption isotherms on microporous polycyclotrimers exhibited a significant unclosed hysteresis. This indicated that the penetration of nitrogen into polymers was accompanied by formation of temporary pores or opening permanent pores of worse accessibility.