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Microporous polyphenylenes based on diacetylaromatic compounds

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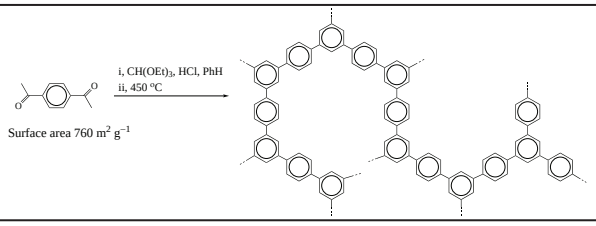
A series of porous polyphenylenes has been synthesized from diacetyl aromatic compounds *via* two step trimerization–cyclocondensation. The monomer structure influences the value of the polymer porosity. The polyphenylene networks have BET surface up to 760 m^2 g^{-1}.



Keywords: microporous polyphenylenes, intrinsic microporosity, trimerization–cyclocondensation, diacetyl aromatic compounds, BET surface, cross-linking.

Solids that contain interconnected pores less than 2 nm are defined as microporous materials. They typically have an accessible surface area of 300–1300 m^2 g^{-1} measured by gas adsorption[1] and are used in various physical and industrial processes like heterogeneous catalysis, hydrogen storage, gas and oil sorption[1–7] as well as membrane-based gases separation.[7,8]

Formerly only the crystalline inorganic substances like zeolites or amorphous network structures like silica or activated carbon were considered as microporous materials. However, microporous polymer-based mesh materials have been extensively investigated in the last decade[5] due to a need for compounds with controlled microporous structure and various functional groups necessary for chemisorption and heterogeneous catalysis.

In this regard, polyphenylenes[9] are most suitable, because virtually any functional groups can be introduced into their structure either during the polymerization or through polymer-analogous transformation. At the same time, polyphenylenes are highly heat-resistant polymers and, unlike the majority of poly-heteroarylenes, have a backbone with high chemical resistance to both acidic and alkaline media, which allows these compounds to be employed for a long time in aggressive environment and/or at elevated temperature.

For the synthesis of microporous polyphenylenes, several methods have been developed. In particular, a sample of three-dimensional polyphenylene structure obtained by the Yamamoto reaction from tetra(4-bromophenyl)methane, with the highest BET surface area among all porous materials, namely 5600 m^2 g^{-1},[10] deserves special note. As well, the Yamamoto homocondensation of 1,3,5-tribromobenzene resulted in polyphenylene with a surface area of 1255 m^2 g^{-1}, whereas its copolycondensation with bi-functional monomers like *p*-dibromobenzene or 4,4′-dibromobiphenyl in the 1 : 1 ratio led to a sharp decrease in the surface area up to 292 or 475 m^2 g^{-1}, respectively.[11] The polymer from 2,2′,7,7′-tetrabromo-9,9′-spirobifluorene, obtained by the same reaction type, had a surface area of 1275 m^2 g^{-1}, whereas for its copolymer with 1,3,5-tribromobenzene, this value was 580 m^2 g^{-1}.[11]

By the Suzuki reaction of 2,2′,7,7′-tetrabromo-9,9′-spirobifluorene with *p*-phenylene- and *p*-diphenylenediboronic acids, the polymers with BET surface areas of 450 and 210 m^2 g^{-1}, respectively, were obtained.[12] Other reported syntheses of porous polyphenylene-based materials include acetylenic trimerization[13] and oxidative coupling.[13,14]

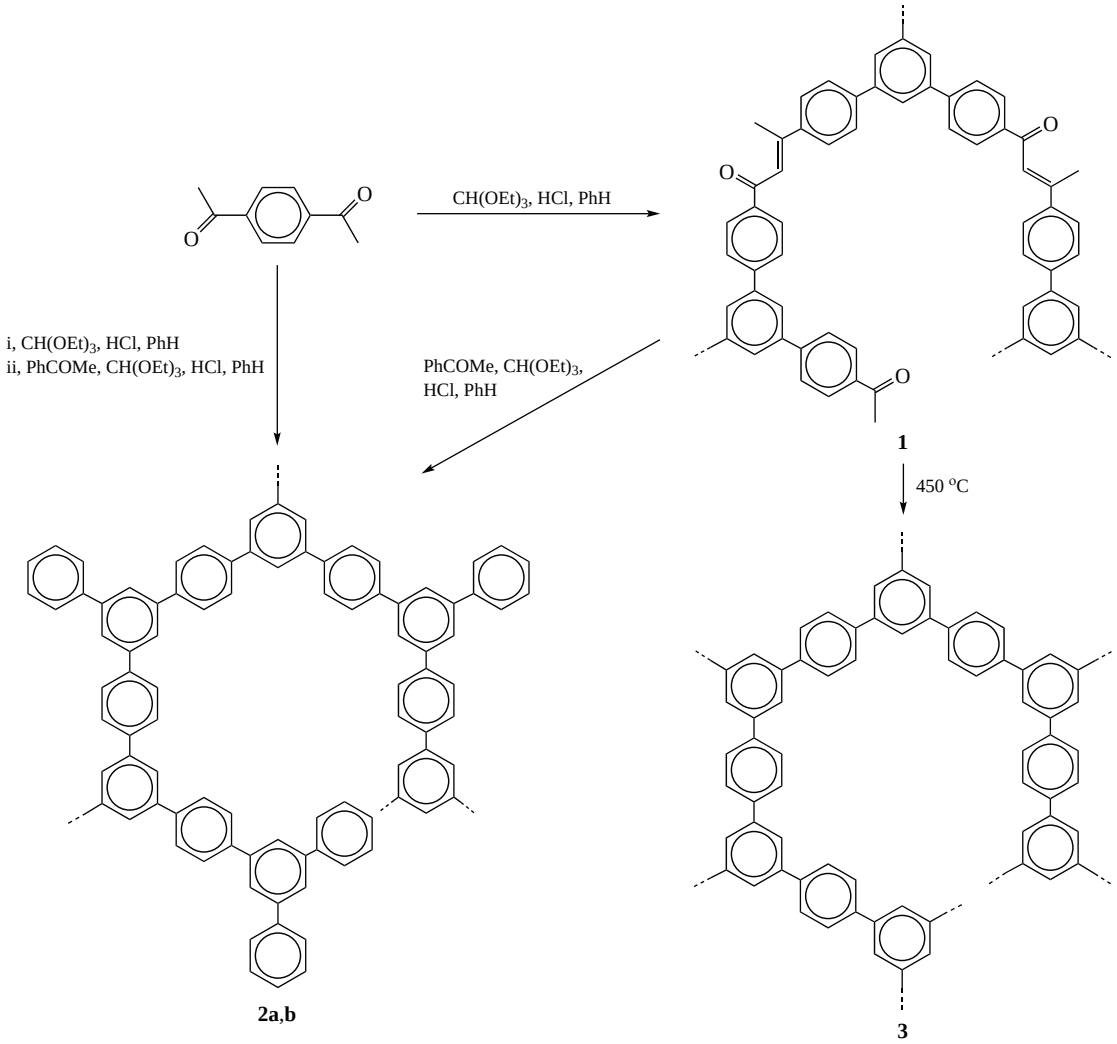
As an alternative to the methods described for the synthesis of polyphenylenes, a simple way to obtain heat- and chemically-resistant microporous three-dimensional polyphenylenes has been developed via trimerization–polycyclocondensation of diacetyl aromatic compounds.[15] This reaction does not require ultrapure conditions or expensive catalysts. In its course, 1,3,5-phentriyl moieties are formed as the branching points and finally a three-dimensional polymer is generated with a continuous network of interconnected intramolecular voids.

In this work, polyphenylene **1** was synthesized *via* trimerization–polycyclocondensation of *p*-diacetylbenzene (Scheme 1) as a product insoluble in organic solvents (for details, see Online Supplementary Materials).

The IR spectrum of compound **1** (Figure 1, spectrum *1*) contains the absorption bands at 1680, 1600, 1270 and 825 cm^{-1}, typical of C=O bond in the acetyl group, phenylene moiety, arylalkyl ketone and CH groups of the 1,4-disubstituted benzene ring, respectively. There is also an absorption band at 1660 cm^{-1} related to C=O groups of diphenylpropenone fragment formed as a result of acetyl groups dimerization, *i.e.*, the dimers are intermediates in the trimerization process. Weak absorption bands at 880, 760 and 700 cm^{-1} correspond to CH groups of 1,3,5-trisubstituted benzene ring.

Since the network polymers synthesized contained residual acetyl groups and diphenylpropenone moieties, to increase the conversion of these reactive groups, an attempt was made to block them by acetophenone. The corresponding polymers were prepared in two different ways. The first one consisted in the above standard procedure with the addition of acetophenone at the final stage of the synthesis and resulted in polymer **2a**. The second method involved the interaction of isolated polyphenylene with acetophenone and led to polymer **2b**.

IR spectra of compounds **2a** and **2b** practically do not differ from each other. In comparison with polymer **1**, the intensity of bands related to 1,3,5-trisubstituted benzene ring is noticeably increased. However, polymers **2** still contain definite amount of residual acetyl groups and diphenylpropenone moieties (Figure 1, spectrum *2*).



Scheme 1

Therefore, to increase further the conversion of reactive groups and the degree of cyclocondensation, heat treatment of polymer **1** in argon at 450 °C was carried out, resulting in polymer **3**.

As evidenced from IR data (Figure 1, spectrum *3*), acetyl groups and diphenylpropenone moieties are absent in polymer **3**, though the aromatic structure is preserved, as the intensity of the absorption bands at 880, 760 and 700 cm^{-1} corresponding to the vibrations of 1,3,5-trisubstituted benzene ring increases significantly, which indicates more complete cyclocondensation under these conditions and confirms indirectly the existence of more ordered macromolecular structure. The disappearance of bands at 1680 and 1660 cm^{-1} in the spectrum of polymer **3**, which are related to the terminal acetyl groups and diphenylpropenone moieties, respectively, indicates a greater degree of crosslinking. This is evidenced also by the fact that the surface area of polymer **3**, namely 760 $m^2\ g^{-1}$, is notably higher than that for the original network polymer **1** (290 $m^2\ g^{-1}$).

Based on these results, a number of polyphenylenes were obtained from monomers of different structure to control the degree of crosslinking, namely from 4,4′-diacetylbiphenyl with a rigid rod chain structure, 2,8-diacetyldibenzofuran with a rigid-chain sickle-

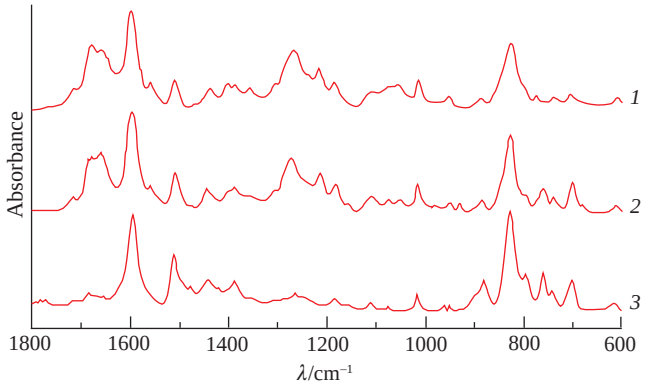
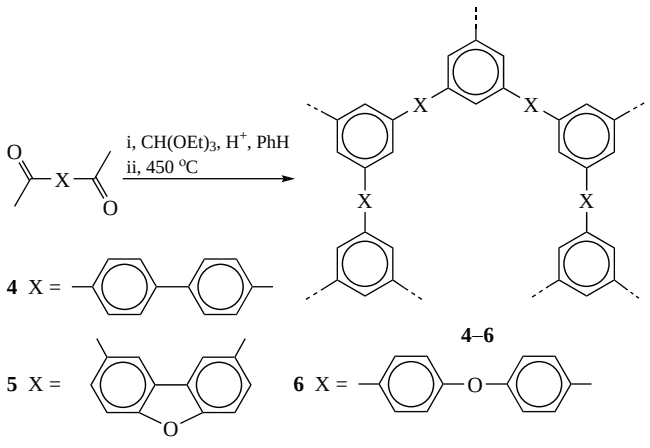


Figure 1 IR spectra of polymers: (*1*) **1**, (*2*) **2a** and (*3*) **3**.



Scheme 2

shaped moiety and 4,4′-diacetyldiphenyloxide bearing a hinged oxygen link (Scheme 2).

Polyphenylene **4** obtained from 4,4′-diacetylbiphenyl, similarly to polymer **3**, had a high surface area value of 640 $m^2 g^{-1}$, in contrast to polymer **5** prepared from 2,8-diacetyldibenzofuran with surface area of 47 $m^2 g^{-1}$ and polymer **6** from 4,4′-diacetyldiphenyloxide with the 38 $m^2 g^{-1}$ value. The low surface area values of polymers **5** and **6** bearing a crescent internodal group and a hinge fragment, respectively, can be explained by the fact that their macromolecules are easier to pack due to cohesive interaction of fragments in the polymeric chain, which minimizes the residual empty space. Contrary to that, the structures of polymers **3** and **4** have a significant amount of free space due to the stiffness of all the polymer units, as well as due to the rod-like interstitial fragments and symmetrically branched nodes of the polymer networks.

In summary, for the synthesis of microporous polyphenylenes with a large surface area *via* trimerization–polycyclocondensation of acetyl aromatic compounds, it is preferable to use monomers having a rigid chain rod structure. The optimal structures are the ones based on rigid phenylene and biphenylene linking groups.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2020.05.035.

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