

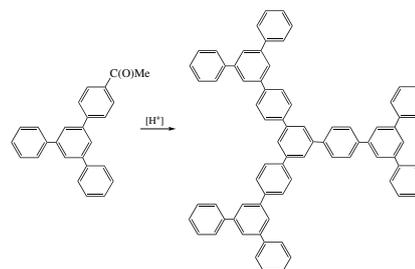
## Second generation phenylene dendrimer, 1,3,5-tris[4-(3,5-diphenylphenyl)phenyl]benzene, as a precursor of a new carbon material

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A second generation phenylene dendrimer, viz. 1,3,5-tris[4-(3,5-diphenylphenyl)phenyl]benzene, was synthesized by cyclocondensation of 4-acetyl-3',5'-diphenyl(biphenyl). This compound on heating to 600 °C is transformed into substance possessing extremely heat-stable secondary structure. It retains the aromatic structure at this temperature and when heated to 1000 °C is converted into material with graphite-like structure.



**Keywords:** 4-acetyl-3',5'-diphenyl(biphenyl), phenylene dendrimers, 1,3,5-tris[4-(3,5-diphenylphenyl)phenyl]benzene, thermal stability.

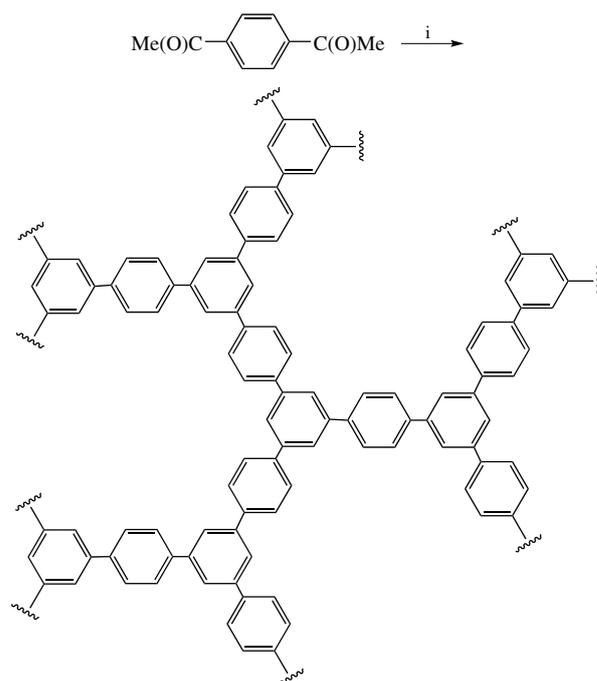
Microporous materials with voids of molecular size (*i.e.*, with pore diameters < 2 nm) are being studied extensively. Polymers are increasingly being considered as such materials.<sup>1–4</sup> The specific surface area of polymeric microporous materials is usually 700–1300 m<sup>2</sup> g<sup>−1</sup>, and sometimes can reach larger values.<sup>5–7</sup> Microporous organic polymers are of growing interest due to their potential applications in gas storage,<sup>8,9</sup> sensors,<sup>10,11</sup> heterogeneous catalysis,<sup>12–14</sup> CO<sub>2</sub> capture,<sup>15,16</sup> and as membranes for gas separation.<sup>17</sup> The advantage of polymeric microporous materials is that their surface can be easily modified<sup>18,19</sup> and, accordingly, various ligands important for sorption can be immobilized to afford some catalytic complexes.

Amorphous organic microporous materials can be obtained by forming a network in hyper-cross-linked polymers.<sup>20</sup> Such materials are formed as a result of irreversible cross-linking reactions, *e.g.*, of chloromethylated styrene.<sup>21,22</sup> Such materials exhibited constant porosity. For example, the BET (Brunauer–Emmett–Teller) method would determine visible surface areas up to 2000 m<sup>2</sup> g<sup>−1</sup> with a wide pore size distribution ranging from micropores through mesopores (2 to 50 nm) to macropores (> 50 nm).<sup>21</sup> Another representative cross-linked polymer obtained by the Friedel–Crafts reaction of tetraphenylmethane and formaldehyde dimethyl acetal belongs to a very attractive family of porous organic networks.<sup>23</sup>

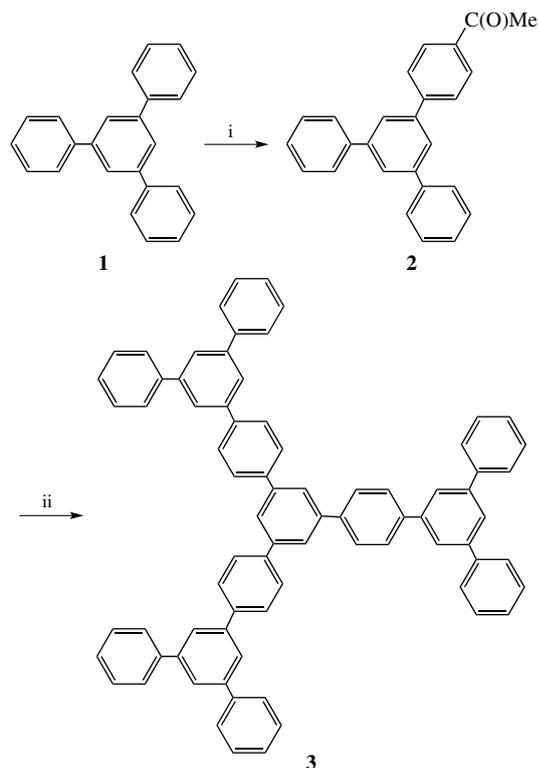
Among the porous polymeric materials, polyphenylenes should be distinguished. They possess high thermal stability being in addition highly resistant to acids and alkalis. These properties allow one to use polyphenylenes in aggressive and high-temperature processes.

Previously, a number of three-dimensional polyphenylenes were obtained by the trimerization polycyclocondensation method starting from various diacetyl aromatic compounds, when a new benzene ring was formed in the course of the polymerization.<sup>24–26</sup> Scheme 1 shows the idealized structure of polyphenylene based on *p*-diacetylbenzene. In reality, in the

course of this polycyclocondensation, in addition to main phenylene fragments, non-cyclized defect reactive fragments are formed, and unconsumed reactive acetyl groups also remain. The heating of this material results in cross-linking to afford three-dimensional porous polymers. Calculations of parameters of their microporous structure have shown that the surface of all pores was ranged from 470 to 980 m<sup>2</sup> g<sup>−1</sup>. Thermogravimetric analysis (TGA) of such polymers revealed their high thermal stability: when heated in an inert atmosphere, the weight loss of the material was about 20% in the range of 200–900 °C.



**Scheme 1** Reagents and conditions: i, HCl (gas), PhH, CH(OEt)<sub>3</sub>.

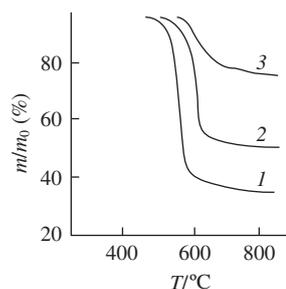


**Scheme 2** Reagents and conditions: i, MeC(O)Cl, AlCl<sub>3</sub>, PhNO<sub>2</sub>, 10–15 °C, 2 h; ii, HCl (gas), PhH, CH(OEt)<sub>3</sub>, 20 °C, 3 h.

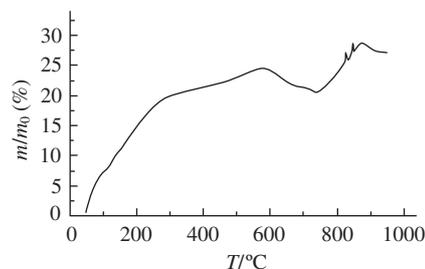
However, the structure of three-dimensional polyphenylene cannot be considered as an ideal aromatic structure since the phenylene fragments are retained in it, which was judged from their IR spectra.<sup>25</sup>

In this study, a more structurally ordered three-dimensional polymer was obtained from the precursor being an individual phenylene dendrimer **1** (Scheme 2). The final compound simulating a fragment of three-dimensional polyphenylene is a dendrimer with thirteen benzene rings, 1,3,5-tris[4-(3,5-diphenylphenyl)phenyl]benzene, or *symm*-terdeciphenyl **3**.<sup>27</sup> The structure of compound **3** was confirmed by IR and NMR spectra, elemental analysis and mass spectrometry (for details, see Online Supplementary Materials).

The cross-linked three-dimensional structure of polyphenylene based on **3** is formed during its pyrolysis. In Figure 1, the TGA curves of compound **3** in argon are shown. Weight loss begins at about 500 °C (curve 1), which is typical for aromatic structures. When the sample is preliminarily heated in an inert atmosphere to 600 °C (curve 2), and when it is kept at this temperature for 30 min (curve 3), the amount of coke residue of the sample significantly increases. In the latter case, it reaches 70% and, thus, long-term heating of compound **3** is required for the formation of a network structure.



**Figure 1** TGA of *symm*-terdeciphenyl **3** samples in argon: (1) compound **3**, (2) compound **3** preheated to 600 °C, (3) compound **3** heated to 600 °C and kept at this temperature for 30 min. Heating rate, 5 K min<sup>-1</sup>.

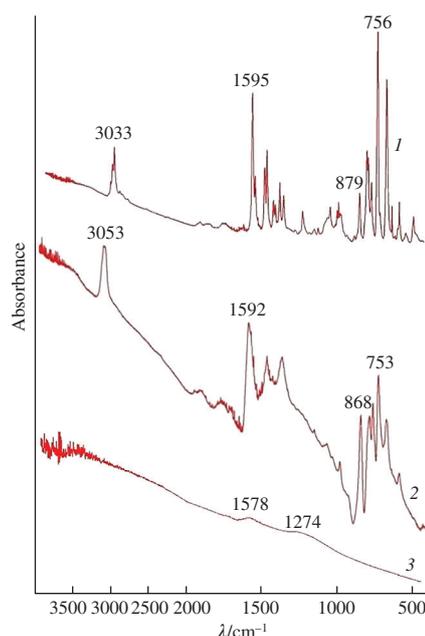


**Figure 2** Differential thermal analysis of compound **3** in argon. Heating rate, 20 K min<sup>-1</sup>.

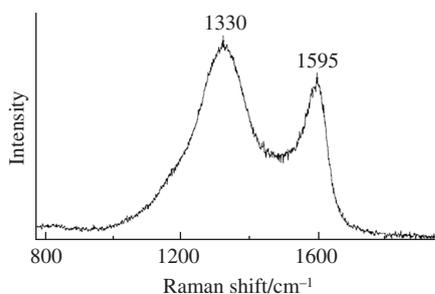
When compound **3** was heated to 1000 °C in an argon atmosphere, in the range from 600 to 800 °C the thermogram (Figure 2) displays a significant endothermic effect. This effect can be associated with a structural rearrangement of the carbon framework and, apparently, with a loss of aromaticity. The preliminary studies have shown that the surface area of material obtained by heating compound **3** to 900 °C was about 500 m<sup>2</sup> g<sup>-1</sup> (determined by the BET method).

The IR spectrum of *symm*-terdeciphenyl **3** contains bands characterizing aromatic compound (Figure 3, curve 1). In the range of 3060–3030 cm<sup>-1</sup>, one can observe bands for stretching vibrations of aromatic =C–H. Planar skeletal vibrations of C=C bonds are manifested in the region of 1600–1440 cm<sup>-1</sup>. The spectrum contains the bands in the region of 1100–1000 cm<sup>-1</sup> associated with planar deformation vibrations of C–H bonds and bands in the region of 900–690 cm<sup>-1</sup> characteristic of out-of-plane deformation vibrations of C–H. The characteristic band at 880 cm<sup>-1</sup> refers to the C–H vibrations in the 1,3,5-trisubstituted benzene ring.

The IR spectrum of material obtained by heating compound **3** at 600 °C for 30 min (see Figure 3, curve 2) shows the presence of characteristic bands of the aromatic compound, which indicates the retention of the aromatic structure. A characteristic band observed at 880 cm<sup>-1</sup> is related to 1,3,5-trisubstituted benzene rings, *i.e.* the structure retains the main aromatic blocks of precursor **3**. The spectrum also contains a band at 3060 cm<sup>-1</sup>, which corresponds to stretching vibrations of aromatic =C–H groups. The IR spectrum of the coke residue (heating **3** to 1000 °C, curve 3) reveals a structural rearrangement of the



**Figure 3** IR spectra of (1) compound **3**, (2) compound **3** heated at 600 °C for 30 min, (3) compound **3** heated to 1000 °C.



**Figure 4** Raman spectrum of compound **3** heated to 1000 °C.

carbon skeleton, since there are no vibrations related to aromatic structures. The spectrum contains an absorption band in the 1578  $\text{cm}^{-1}$  region, which, apparently, can be attributed to stretching vibrations of C=C bonds.

The Raman spectrum of compound **3** upon heating to 1000 °C (Figure 4) contains two broad bands D and G with a frequency of 1330 and 1595  $\text{cm}^{-1}$ , respectively, which characterize the  $\text{sp}^2$  disordered carbon material that is not soot.

In conclusion, *symm*-terdeciphenyl, the second generation phenylene dendrimer **3**, when heated to 600 °C forms a substance possessing secondary three-dimensional structure that retains the elements of the aromatic structure, and when heated to 1000 °C, a graphite-like material is formed.

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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.2021.05.038.

#### References

- 1 L. J. Abbott and C. M. Colina, *Macromolecules*, 2011, **44**, 4511.
- 2 Q. Liu, Z. Tang, M. Wu and Z. Zhou, *Polym. Int.*, 2014, **63**, 381.
- 3 E. S. Trofimchuk, M. A. Moskvina, O. A. Ivanova, V. V. Potselev, V. A. Demina, N. I. Nikonorova, A. V. Bakirov, N. G. Sedush and S. N. Chvalun, *Mendeleev Commun.*, 2020, **30**, 171.
- 4 N. V. Fadeeva, E. I. Knerelman, G. I. Davydova, N. S. Emel'yanova and S. V. Kurmaz, *Mendeleev Commun.*, 2020, **30**, 738.
- 5 G. Bengtson, S. Neumann and V. Filiz, *Membranes*, 2017, **7**, 28.

- 6 K. Müllen, *ACS Nano*, 2014, **8**, 6531.
- 7 N. Chaoui, M. Trunk, R. Dawson, J. Schmidt and A. Thomas, *Chem. Soc. Rev.*, 2017, **46**, 3302.
- 8 C. Shen, Y. Bao and Z. Wang, *Chem. Commun.*, 2013, **49**, 3321.
- 9 Z. Chang, D.-S. Zhang, Q. Chen and X.-H. Bu, *Phys. Chem. Chem. Phys.*, 2013, **15**, 5430.
- 10 Y. Wang, N. B. McKeown, K. J. Msayib, G. A. Turnbull and I. D. W. Samuel, *Sensors*, 2011, **11**, 2478.
- 11 J. C. Thomas, J. E. Trend, N. A. Rakow, M. S. Wendland, R. J. Poirier and D. M. Paolucci, *Sensors*, 2011, **11**, 3267.
- 12 F. Xia, M. Pan, S. Mu, R. Malpass-Evans, M. Carta, N. B. McKeown, G. A. Attard, A. Brew, D. J. Morgan and F. Marken, *Electrochim. Acta*, 2014, **128**, 3.
- 13 M. Carta, M. Croad, K. Bugler, K. J. Msayib and N. B. McKeown, *Polym. Chem.*, 2014, **5**, 5262.
- 14 S. J. Kraft, R. H. Sánchez and A. S. Hock, *ACS Catal.*, 2013, **3**, 826.
- 15 J. Byun, S.-H. Je, H. A. Patel, A. Coskun and C. T. Yavuz, *J. Mater. Chem. A*, 2014, **2**, 12507.
- 16 R. T. Woodward, L. A. Stevens, R. Dawson, M. Vijayaraghavan, T. Hasell, I. P. Silverwood, A. V. Ewing, T. Ratvijitvech, J. D. Exley, S. Y. Chong, F. Blanc, D. J. Adams, S. G. Kazarian, C. E. Snape, T. C. Drage and A. I. Cooper, *J. Am. Chem. Soc.*, 2014, **136**, 9028.
- 17 M. Carta, P. Bernardo, G. Clarizia, J. C. Jansen and N. B. McKeown, *Macromolecules*, 2014, **47**, 8320.
- 18 A. Fuoco, C. Rizzuto, E. Tocci, M. Monteleone, E. Esposito, P. M. Budd, M. Carta, B. Comesaña-Gándara, N. B. McKeown and J. C. Jansen, *J. Mater. Chem. A*, 2019, **7**, 20121.
- 19 D. Ramimoghdam, E. Gray and C. J. Webb, *Int. J. Hydrogen Energy*, 2016, **41**, 16944.
- 20 M. P. Tsyurupa and V. A. Davankov, *React. Funct. Polym.*, 2006, **66**, 768.
- 21 J.-H. Ahn, J.-E. Jang, C.-G. Oh, S.-K. Ihm, J. Cortez and D. C. Sherrington, *Macromolecules*, 2006, **39**, 627.
- 22 K. Haupt and K. Mosbach, *Chem. Rev.*, 2000, **100**, 2495.
- 23 G. Gatti, M. Errahali, L. Tei, M. Cossi and L. Marchese, *Polymers*, 2019, **11**, 588.
- 24 I. A. Khotina, O. A. Filippov and A. I. Kovalev, *Mendeleev Commun.*, 2020, **30**, 366.
- 25 A. I. Kovalev, A. V. Pastukhov, E. S. Tkachenko, Z. S. Klemenkova, I. R. Kuvshinov and I. A. Khotina, *Polym. Sci., Ser. C*, 2020, **62**, 205 (*Vysolomol. Soedin., Ser. C*, 2020, **62**, 210).
- 26 A. I. Kovalev, E. S. Mart'yanova, I. A. Khotina, Z. S. Klemenkova, Z. K. Blinnikova, E. V. Volchkova, T. P. Loginova and I. I. Ponomarev, *Polym. Sci., Ser. B*, 2018, **60**, 675 (*Vysolomol. Soedin., Ser. B*, 2018, **60**, 403).
- 27 I. A. Khotina, V. A. Izumrudov, N. V. Tchebotareva and A. L. Rusanov, *Macromol. Chem. Phys.*, 2001, **202**, 2360.
- 28 I. A. Khotina, O. E. Shmakova, D. Yu. Baranova, N. S. Burenkova, A. A. Gurskaja, P. M. Valetsky and L. M. Bronstein, *Macromolecules*, 2003, **36**, 8353.

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