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Microporous polymers based on triacetylarenes

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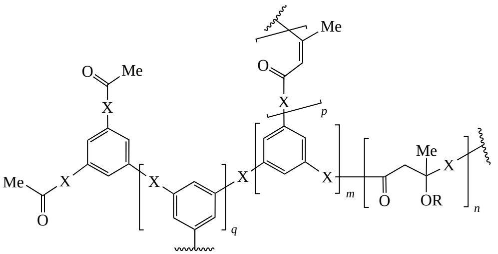
Three-dimensional polymers are synthesized by polycondensation of triacetylarenes with the formation of 1,3,5-phentriyl and dimeric diphenylpropenone fragments. Microporous polyphenylenes with an intrinsic surface area of 650–690 m^2 g^{-1} were obtained by additional heating at 450 °C. The values of the intrinsic surface area of polyphenylenes with rigid-chain rod-shaped inter-nodal fragments significantly exceed those of polyphenylenes with a flexible-chain inter-nodal fragments.


R = H or Et

Keywords: triacetylarenes, diacetylarenes, trimerization, polycyclocondensation, phentriyl fragments, dimer fragments, microporous polyphenylenes, infrared spectra, intrinsic surface area.

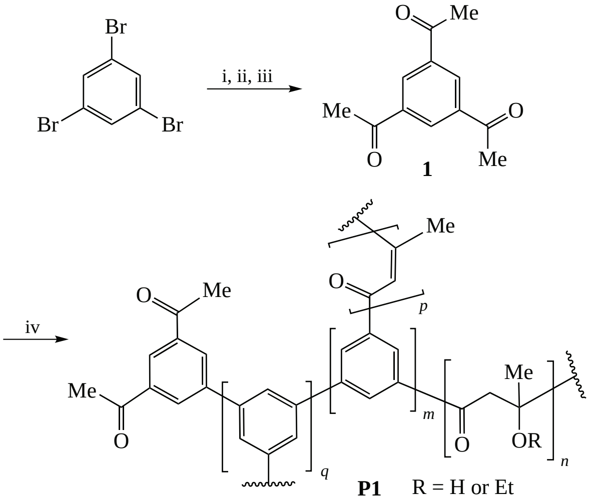
In recent years, there has been significant progress in research of microporous network materials based on polymers,[1] since there is a need for materials with a controlled microporous structure. These materials found application in adsorption, heterogeneous catalysis, gas storage, and can also be used as membranes.[2–7] Among polymers, polyphenylenes are of special interest for the high heat resistance. In addition, unlike most polyheteroarylenes, they have a high chemical resistance of the polymer skeleton both in acidic and alkaline media. This allows the long-term use of materials based on polyphenylenes in aggressive environments at elevated temperatures. Polyphenylenes can be transformed into fused aromatic structures or can form carbon nanostructures with remarkable physical properties.[8]

Microporous polyphenylenes were previously synthesized by the metal-catalyzed Yamamoto[9,10] and Suzuki[11] reactions as well as by the trimerization homocondensation of tri- or tetraethynylarenes.[12] An alternative way for their synthesis is based on trimerization polycyclocondensation of diacetylarenes.[13–16] This polymer-forming reaction does not require ultrapure conditions and the use of expensive catalysts. Homopolycondensation of the diacetylarenes is carried out in the presence of triethyl orthoformate and gaseous hydrogen chloride as a catalyst and leads to the gel formation.

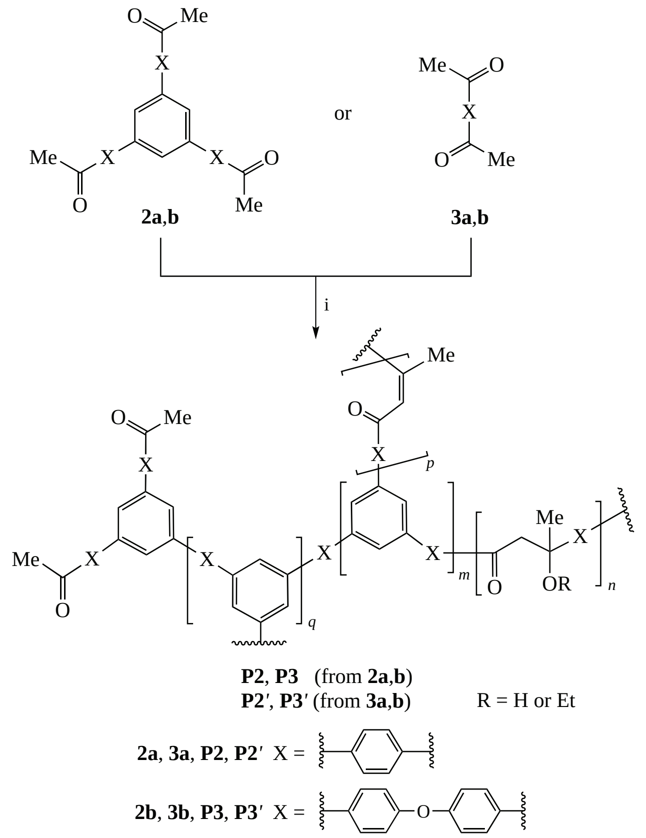
It should be noted that the reaction of three molecules of monoacetylarenes under the same conditions leads to products containing mainly a new 1,3,5-triarylbenzene moiety. The yield of such cyclotrimers is usually higher than 70%.[17] On the contrary, in the course of condensation of diacetyl aromatic compounds the amount of phentriyl fragments in polymer gels is significantly lower as the formation of polymer structure stops at the stage of dimerization condensation of acetyl groups.[16] It should be due to low mobility of the forming polymer chains. In this work, in order to improve the fraction of phentriyl fragments in polymer gels in the synthesis of microporous polyphenylenes, we propose to use triacetyl aromatic compounds, which, in turn, are the products of primary trimerization cyclocondensation of diacetylarenes.

Triacetylarene monomers were selected so that the inter-node fragments would be a simple ordinary bond, a rigid-chain rod-like fragment and flexible-chain, hinged fragments. 1,3,5-Triacetylbenzene (monomer **1**) was synthesized according to Scheme 1.

1,3,5-Tris(4-acetylphenyl)benzene (monomer **2a**) was obtained by the Friedel–Crafts acetylation of 1,3,5-triphenylbenzene. 1,3,5-Tris[4-(4-acetylphenoxy)phenyl]benzene (monomer **2b**) was prepared by sequential monoacylation of diphenyl oxide, cyclotrimerization of the obtained 4-phenoxyacetophenone and triacetylation of the resulting diphenyl oxide-containing cyclotrimer (Scheme 2). The polymer-forming reactions based on monomers **1**, **2a**,**b** were carried out in the presence of triethyl orthoformate and hydrogen chloride (see Schemes 1, 2). For comparison, polymers based on diacetylarenes were also synthesized (*p*-diacetylbenzene was monomer **3a**, and 4,4′-diacetyldiphenyl oxide was monomer **3b**). The thus obtained polymers **P1**, **P2**, **P3**, **P2′**, **P3′** were insoluble in organic solvents.


1 **P1** R = H or Et

Scheme 1 *Reagents and conditions*: i, HC≡CSiMe$_3$, Pd(PPh$_3$)$_4$, CuI, NEt$_3$; ii, KOH, MeOH, THF; iii, TsOH·H$_2$O, AcOH, 80 °C; iv, HC(OEt)$_3$, HCl gas, toluene, room temperature.


2a,**b** or **3a**,**b**

P2, **P3** (from **2a**,**b**)
P2′, **P3′** (from **3a**,**b**) R = H or Et

2a, **3a**, **P2**, **P2′** X =

2b, **3b**, **P3**, **P3′** X =

Scheme 2 *Reagents and conditions*: i, $HC(OEt)_3$, HCl gas, toluene, room temperature.

In the IR spectrum of polymer **P1** (Table 1), in comparison with the spectrum of monomer **1**, the intensity of the absorption band at 1680 cm^{-1}, characteristic of stretching vibrations of the C=O bond in the acetyl group, decreases. In this case, absorption bands appear at 1180 cm^{-1}, related to the products of aldol homocondensation of acetyl groups (shown in Scheme 1 with the polymerization coefficient ‘*n*’), at 1660 cm^{-1}, characteristic of carbonyl groups of the dimer products forming during crotonic homocondensation of acetyl groups (diphenylpropenone or dipnon fragments, the polymerization coefficient ‘*p*’), as well as at 870, 760 and 700 cm^{-1}, related to vibrations in 1,3,5-trisubstituted benzenes (the polymerization coefficient ‘*q*’), connected to other aromatic moieties. In addition, the intensity of the absorption band at 1600 cm^{-1} increases and an absorption band appears at 1500 cm^{-1}, which are characteristic of the stretching in-plane C=C vibrations in the aromatic system.

Table 1 Absorbance wavenumber and intrinsic surface area (I_{SA}) of monomers and polymers.[a]

Sub-stance	Intensity for absorbance at specified wavenumber/cm^{-1}								Intrinsic surface area (I_{SA})/$m^2\ g^{-1}$
	1680	1660	1600	1500	1180	870	760	700	
1	s	–	w	–	–	–	–	–	–
P1	s	s	s	w	s	m	vw	w	35
Q1	m	–	s	w	–	m	w	m	480
2a	s	–	m	–	vw	–	–	–	–
P2	m	m	s	w	w	vw	vw	vw	67
Q2	w	–	s	m	vw	w	w	w	650
2b	m	–	m	s	–	w	–	–	–
P3	w	–	m	s	–	w	vw	vw	19
Q3	vw	–	m	s	–	w	vw	vw	61
3a	s	–	–	w	–	–	–	–	–
P2′	m	m	s	w	w	vw	0	w	38
Q2′	w	–	s	m	vw	w	w	w	690
3b	s	–	m	w	–	vw	–	–	–
P3′	vw	vw	m	s	–	w	–	–	10
Q3'	–	–	m	s	–	w	vw	vw	36

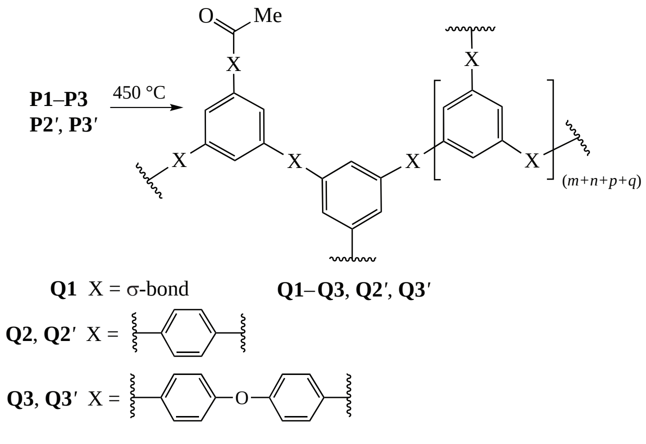
[a] Absorption bands: – is absent; vw is very weak; w is weak; m is medium; s is strong.

In the IR spectrum of the polymer **P2** based on monomer **2a**, in comparison with the spectrum of **P1**, the absorption bands intensity of ‘*p*’ and especially ‘*n*’ fragments are much lower. In the IR spectrum of the polymer **P3** based on **2b**, the absorption bands related to fragments ‘*p*’ and ‘*n*’ are completely absent. The latter can be explained by the better mobility of functional groups and fragments due to the flexibility of the chains containing the hinged oxygen atom, as well as the larger dimensions of the free space in **P3** compared to **P1** and **P2**.

IR spectra of **P2′** and **P2** differ only in higher intensity in the spectrum of **P2′** band at 1660 cm^{-1}, *i.e*. a large number of dipnon fragments. A similar trend is observed for oxygen-containing polymers. The IR spectrum of **P3′**, in contrast to the spectrum of **P3**, contains an absorption band of dipnon fragments (1660 cm^{-1}).

The presence of fragments of incomplete cyclocondensation in polymers, *i.e*. defect fragments, significantly affects the porosity of polymers.[16] So, the intrinsic surface areas (I_{SA}) of **P1** and **P2** are 35 and 67 $m^2\ g^{-1}$, respectively. Polymer **P2′** containing a greater number of defect fragments in comparison with **P2**, has a lower I_{SA} of 38 $m^2\ g^{-1}$. A similar phenomenon is observed when comparing **P3′** and **P3**. In addition, due to the conformational flexibility of the chains, these polymers are ‘packed’ more tightly, resulting in lower intrinsic surface areas compared to rigid-chain polymers. To improve the degree of conversion of reactive acetyl groups and to increase the degree of cyclocondensation, polymers **P1**, **P2**, **P3**, **P2′**, **P3′** were heated in argon at 450 °C giving new products **Q1**, **Q2**, **Q3**, **Q2′**, **Q3′**, respectively (Scheme 3).

In the IR spectrum of **Q1**, in comparison with the spectrum of **P1** (see Table 1), there is a significant decrease in the intensity of the acetyl absorption band at 1680 cm^{-1}; however, this band still remains in the spectrum, which indicates the presence of residual acetyl groups. In the polymer spectrum, the bands for the products of dimerization condensation of acetyl groups are practically absent. In this case, the intensity of signals from the 1,3,5-trisubstituted benzene moiety increases significantly. A similar picture is observed in the spectra of **Q2** and **Q2′**. In the IR spectra of **Q3** and **Q3′**, the intensity of the bands for the phentriyl fragments also increases due to the complete conversion of acetyl groups in the course of trimerization cyclocondensation reaction. However, the conformational flexibility of chains of heated polymers


P1–**P3**
P2′, **P3′**

Q1 X = σ-bond **Q1**–**Q3**, **Q2′**, **Q3′**

Q2, **Q2′** X =

Q3, **Q3′** X =

Scheme 3 *Reagents and conditions*: 450 °C, argon, 3 h.

containing an oxygen bridge negatively affects the I_{SA} of these polymers: these values for **Q3** and **Q3′** are 61 and 36 m^2 g^{-1}, respectively. In the case of rigid-chain polymers, the heating of the synthesized polymers leads to a significant increase in the I_{SA}, which for **Q1**, **Q2**, and **Q2′** gives the values of 480, 650, and 690 m^2 g^{-1}, respectively.

In conclusion, the value of the I_{SA} of polyphenylenes with rigid-chain rod-like inter-nodal fragments **Q2** and **Q2′** is higher than this value for polyphenylene without inter-nodal fragments **Q1** and 10 times higher than this value for polyphenylenes **Q3** and **Q3′** with flexible-chain inter-nodal fragments. At the same time, although the synthesized polymers based on three-functional monomers **P2** and **P3** contained less defective fragments than similar polymers based on difunctional monomers **P2′** and **P3′**, after heating the structure as well as intrinsic surface area of new polyphenylenes **Q2**, **Q3**, **Q2′**, **Q3′** did not change significantly.

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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.2022.03.030.

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