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ARTICLE

Conjugated Microporous Polymer Networks via Yamamoto Polymerization

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ABSTRACT: The Yamamoto polymerization has been used for the synthesis of conjugated, microporous polymer networks. The polymerization is advantageous as only a single, halogen-functionalized monomer can be used to form polymer networks. Polymer networks are presented based on spirobifluorene and benzene units, which reveal high surface areas of up to 1275 m^2/g. Furthermore, copolymerization can be carried out using additionally linear linkers during the polymerization. The nearly regular incorporation of such units into the networks enables to tailor the luminescence properties of the materials.

Introduction

Lately, increasing research activities have been focused on the generation of microporous, covalent, purely organic materials, which promise to complement the classical microporous materials such as zeoliths and zeotypes, activated carbons, and metal organic frameworks (MOF) in a variety of applications.[1] While the covalent bonds in such networks or frameworks provide increasing thermal and chemical stability especially compared to MOFs, the organic structure allows incorporation of multiple chemical functionalities into the networks, not possible for zeolites or activated carbons. Also, some physical properties, such as ductility and light weight, add to the superior properties of such materials. Some different types of microporous polymers can be already distinguished, regarding their structure or synthesis procedures.

Hyper-cross-linked polymers (HCP),[2] covalent organic frameworks (COF),[3−7] and polymers of intrinsic microporosity (PIM)[8−10] are such different types of microporous covalent organic materials, while the latter two examples rely on the same type of scaffolding concept for the generation of microporosity. In both cases, a structure directing unit is covalently bonded to linear linkers, thus opening up a 2- or 3-dimensional polymer network, with the difference that for COFs network formation is carried out under thermodynamic and for PIMs under kinetic control generating periodic and amorphous networks, respectively. Regarding their structural features, element organic frameworks (EOF)[11,12] and conjugated microporous polymers (CMPs)[13−18] are further distinguishable classes of microporous organic materials, even though amorphous networks are observed as well.

Conjugated microporous polymers (CMPs) feature interesting optoelectronic properties combined with a stable, very high surface area, which make them attractive as hosts for chromophores, hole or electron conductors, which might cause interesting synergism effects for applications in organic devices.[17] Indeed, the lately described CMPs are chemical relatives to hyperbranched, dendritic, or star-shaped conjugated polymers, which have been largely described as suitable compounds for such devices as aggregation and excimer formation, found for their linear counterparts, can be successfully suppressed.[19−22] Indeed, the only difference is the higher amount of cross-linking in CMPs making them insoluble in any solvent but providing the high accessible surface areas and porosities.

CMPs can be obtained via different reaction routes employing C−C coupling reactions, similar to the coupling reactions described for other conjugated polymers. Thus, Sonogashira−Hagihara coupling has been used to synthesize microporous poly(arylene ethynylene) and poly(phenylene butadiynylene) networks based on 1,3,5-substituted benzenes[13,14] or tetraphenylmethane and -silane compounds[12] and Suzuki couplings for microporous poly(*p*-phenylene) and poly(phenyleneethynylene) networks based on a spirobifluorene.[15] Thiophene-containing networks have been synthesized via oxidative polymerization.[16]

In this article we introduce a new reaction route to CMP networks, namely the Yamamoto polymerization.[23−27] The Yamamoto reaction in general is a C−C coupling of aryl−halogenide compounds mediated by a transition metal complex, mostly bis(1,5-cyclooctadiene)nickel(0) (Ni(COD)). The polymerization is advantageous as only one type of functionality is required and just a single, halogen-functionalized monomer can be used to form polymers, while on the other hand, stoichiometric quantities of the nickel complex are required. Nevertheless, the simplicity of the reaction procedure and the already shown synthesis of high molecular weight polyaromatics make it an interesting reaction for network formation.[28−36]

Results and Discussion

We first attempted to use the main advantage of the Yamamoto protocol, that is, that a direct coupling of one single type of halogen-functionalized, structure-directing monomer can be accomplished. In our recent studies on spirobifluorene-based microporous polymers tetrabrominated spirobifluorenes have been used as structure directing agent and combined with diboronic acids or diacetylens via Suzuki or Sonogashira couplings.[15] We and others further used 1,3,5-trisubstituted benzene as structure directing motif for the generation of CMPs.[13,15] In contrast to the so far described C−C couplings for the generation of CMPs, the Yamamoto coupling now allows for the direct

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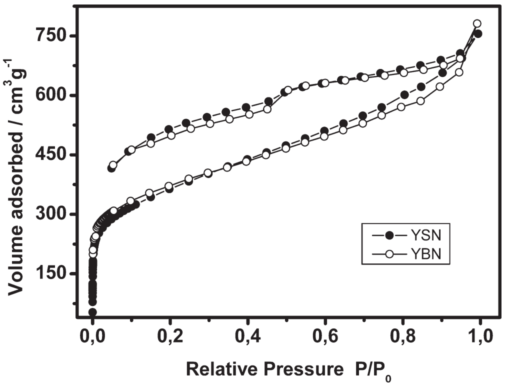
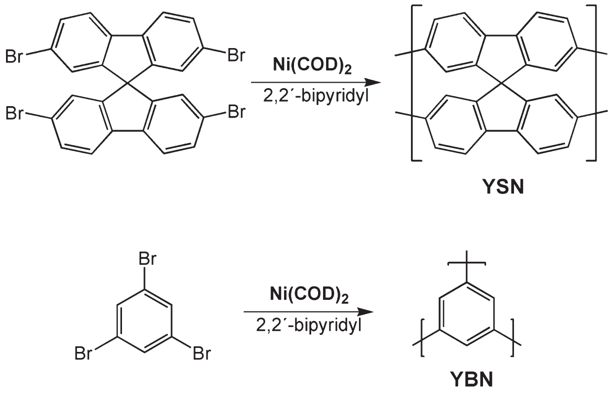


Figure 1. Nitrogen sorption isotherms of microporous polymer networks YSN and YBN.

Scheme 1. Polymerization of 2,2′,7,7′-Tetrabromo-9,9′-spirobifluorene (YSN) and 1,3,5-Tribromobenzene (YBN) via Yamamoto Polymerization



coupling of such monomers for the generation of dense networks (Scheme 1). Indeed, the microwave-assisted polymerization of 2,2′,7,7′-tetrabromo-9,9′-spirobifluorene together with Ni(COD)$_2$ in THF leads to a conjugated polymer network that precipitates during the reaction (Yamamoto derived spirobifluorene network, YSN). Even though any measure of molecular weight or the degree of polymerization is hindered by the insolubility of the network, after 3 h reaction in the microwave no bromine end groups can be detected by EDX and FTIR spectroscopy, proving that nearly all possible functional groups have been reacted (Supporting Information). The same experimental conditions were applied for the coupling of 1,3,5-tribromobenzene, yielding as well insoluble networks and no traceable end groups by EDX measurements (Yamamoto derived benzene network, YBN) (Supporting Information).

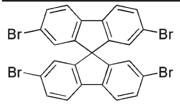
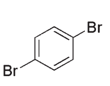
The nitrogen sorption isotherms for networks YSN and YBN reveal nearly identical, high surface areas of 1275 and 1255 m^2/g associated with a high pore volume of 0.997 and 0.971 cm^3/g at $p/p_0 = 0.9$, respectively (Figure 1).

It can be assumed that the porosity of the polymer scaffold is created by the monomer architecture as no porogen was added to the reaction mixture. Average pore diameters can be calculated from the nitrogen isotherm and are both in the range of 1.5 nm, intriguingly a typical value derived from NLDFT pore size distributions for several, even though structurally different microporous polymer networks. This shows again that this data should be carefully judged as porous polymers can for example show pressure-dependent structural changes.[37] Neither method like nonlinear density functional theory (NLDFT) or Horvarth−Kawazoe (HK) considers for instance these swelling effects and thus cannot be uncritically applied for such networks.

Table 1. Surface Area, Total Pore Volume, and Micropore Volume of Networks YSN and YBN

network	S_{BET} (m^2/g)	V_{total} (cm^3/g)	V_{micro} (cm^3/g)
YSN	1275	0.997	0.749
YBN	1255	0.971	0.737

Table 2. Ratio, Surface Area, and Pore Volume of Polymerized Networks

		S_{BET} m^2/g	V_{total} cm^3/g	V_{micro} cm^3/g
1	0	1275	0.997	0.749
1	1	887	0.686	0.504
1	2	580	0.415	0.335
1	3	457	0.305	0.240
1	4	156	0.159	0.097

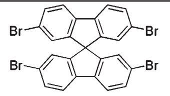
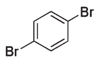
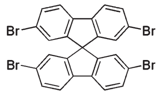
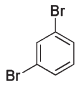
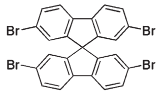
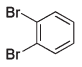
CMP networks have been so far always fabricated using alternating copolymerization. The Yamamoto route principally yield statistical copolymers when a second functionalized monomer, in our case 1,4-dibromobenzene, is added to the reaction mixture. Of course, the second monomer has not necessarily been connected to the structure directing, namely the spirobifluorene monomer, and products from alternating copolymers to two distinct homopolymers can be imagined.

While the ratio of 2,2′,7,7′-tetrabromo-9,9′-spirobifluorene and 1,4-dibromobenzene was varied, networks featuring different surface areas were obtained. The increase of the amount of 1,4-dibromobenzene in the network leads to a constant decrease of the resulting surface area. From 1275 m^2/g for the pure poly(9,9′-spirobifluorene), the surface area decreases to 887 m^2/g for a ratio of 1:1. Monomer ratios of 1:2, 1:3, and 1:4 result in surface areas of 580, 457, and 156 m^2/g, respectively (Table 2 and Supporting Information).

Pore volumes of the networks show the same tendency to decrease with increasing amount of 1,4-dibromobenzene.

This decrease in surface area and pore volume can be explained by the integration of the second monomer into the network structure of poly(9,9′-spirobifluorene). Indeed, a similar trend was observed for CMPs synthesized via Sonogashira−Hagihara coupling, that is, for alternating copolymers, with increasing linker length.[18] While for periodic frameworks increase in the linker size yield bigger pores and thus overall higher pore volumes,[4] for amorphous frameworks the opposite is true, probably due to the higher flexibility and thus higher packing ability of such networks. Also, interpenetration of the polymers cannot be excluded when longer linkers are introduced in the networks. The network with a 1:2 and 1:4 monomer ratio can be compared to networks formed by alternating polymerization via Suzuki coupling with 1,4-benzenediboronic acid and 4,4′-biphenyldiboronic acid.[15] Surface areas of these networks are comparable to the here shown approach (450 to 580 m^2/g and 200 to 156 m^2/g for the Suzuki and Yamamoto derived polymer networks, respectively), pointing indeed to a regular incorporation of the linkers at least to some extent, that is, to an alternating polymerization. A regular incorporation of the phenyl groups into the spirobifluorene units can be furthermore proven by

Table 3. Angle Dependence of Surface Area and Pore Volume (Ratio 1:1)

monomers		S_{BET} (m^2/g)	V_{tot} (cm^3/g)	V_{micro} (cm^3/g)
		887	0.686	0.504
		361	0.248	0.179
		5	-	-

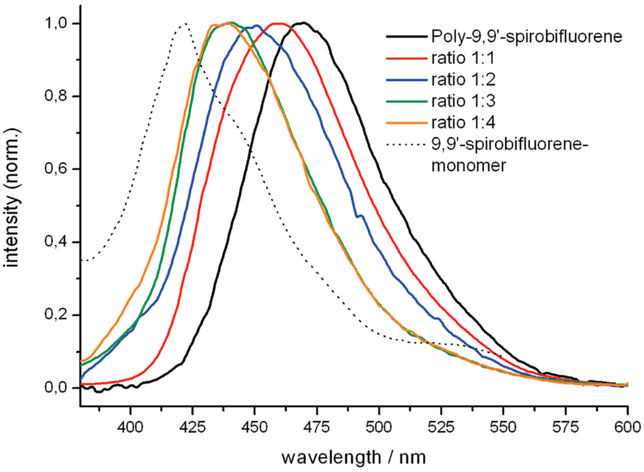
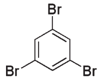
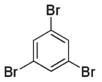
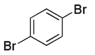
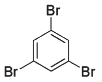
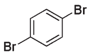
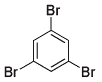
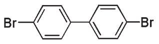
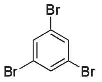
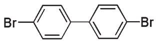


Figure 2. Fluorescence spectra of poly(9,9′-spirobifluorene) (YSN) and copolymers derived therefrom ($\lambda_{excitation}$: 350 nm).

optical measurements. The fluorescence spectra of the pure and the copolymers are shown in Figure 2. The spirobifluorene monomer shows a fluorescence with an emission maximum of 415 nm, while the fluorescence of the homopolymer, poly(9,9′-spirobifluorene) (YSN), shows a bathochromic shift to ~472 nm due to its extended conjugated system with 2,2′-bifluorenyl as the most extended conjugated segment. With increasing incorporation of 1,4-dibrombenzene the emission maximum shifts again to shorter wavelengths, so it can be assumed that the conjugated system gets more and more disturbed, probably because the benzene ring is flexible enough to turn out of the conjugation plane. Polymers synthesized with a spirobifluorene:linker ratio of 1:2 show comparable fluorescence to the equivalent networks prepared via Suzuki coupling[15] (455 and 460 nm, respectively).

Beside their length, it can be expected that also the angle of the linkers should have an influence on the porosity of the networks. Indeed, changing the angle from 180° in case of para-substituted dibromobenzene to 120° and 60° for the meta- and ortho-position, respectively, the surface area decreases to 361 and 5 m^2/g; that is, no porosity accessible for nitrogen can be observed for the latter. Moreover, using the ortho-substituted monomer, a soluble network is obtained, showing that the reaction is impeded by introducing narrow angles into the networks, thus sterically preventing further reaction on these functionalities.[38] FTIR measurements on such networks show some considerable amounts of unreacted bromo functionalities, thus supporting that a high polymerization degree cannot be achieved using linkers with narrow angles (Supporting Information).

Table 4. Surface Area and Pore Volume of 1,3,5-Tribromobenzene-Based Polymer Networks

monomers		ratio	S_{BET} m^2/g	V_{tot} cm^3/g
		-	1255	0.971
		1:1	292	0.195
		1:3	48	0.061
		1:1	475	0.352
		1:3	46	0.052

Several CMPs are accessible using 1,3,5-trisubstituted benzene as structure directing motif. In principle, such a tecton should yield in 2D polymer networks; however, contortion of the linkers out of plane yield in amorphous 3D networks. As seen, the resulting poly(*p*-phenylene) network (YBN) from direct coupling of 1,3,5-tribromobenzene shows a remarkably high surface area of 1255 m^2/g. Also in this case an amorphous network is formed (confirmed by XRD measurements), not surprisingly, as sterical hindrance of hydrogens in the phenyl−phenyl bridges should yield a slight contortion of the rings, opening up the 3D structure. Copolymerizations were carried out using 1,4-dibromobenzene and 4,4′-dibromobiphenyl as linker. For the copolymers a similar behavior as for the 9,9′-spirobifluorene-based networks can be obtained; thus, surface area and pore volume decrease with raising amount of second monomer.

Conclusion

In summary, Yamamoto polymerization was used as a novel route to synthesize microporous polymer networks. Because only one type of functionality is required, the polymerization can be performed with a single monomer only, yielding porous networks with high surface areas up to 1275 and 1255 m^2/g. Copolymerization has been carried out adding dibromo compounds. With increasing amount of the second monomer, surface areas and pore volumes decreases, while the fluorescent properties of networks derived from tetrabromospirobifluorene point to a rather alternating incorporation of the linear linkers. The surface area also decreases with reducing angle between the two bromo functionalities of the second monomer. The here shown approach shows that Yamamoto polymerization is indeed an easy to perform reaction with high yields, leading to microporous polymer networks.

Experimental Section

Materials. 2,2′,7,7′-Tetrabromo-9,9′-spirobifluorene was synthesized according to the literature.[39] 1,3,5-Tribromobenzene, 1,4-dibromobenzene, 1,3-dibromobenzene, 1,2-dibromobenzene, 4,4′-dibromobiphenyl, Ni(COD)$_2$, 2,2′-bipyridyl, 1,5-cyclooctadiene, and anhydrous THF were purchased from Sigma-Aldrich and used without further purification.

Methods. Nitrogen sorption experiments and micropore analysis were conducted at 77 K using an Autosorb-1 from Quantachrome Instruments. Before sorption measurements, the samples were degassed in vacuum overnight at 100 °C. The surface area was calculated from multipoint BET plot, and the pore volume was determined by NLDFT.

The fluorescence measurements were carried out with a Perkin-Elmer luminescence spectrometer (LS 50 D).

Synthesis. All reactions were performed under a nitrogen atmosphere. Sealed glass tubes were used in microwave at 150 W and 110 °C. Typically 1.2 equiv of 2,2′-bipyridyl, Ni(COD)$_2$, and 1,5-cyclooctadiene were used per resulting bond. For homopolymerization 2,2′,7,7′-tetrabromo-9,9′-spirobifluorene (1 equiv), 2,2′-bipyridyl (4.8 equiv), Ni(COD)$_2$ (4.8 equiv), and 1,5-cyclooctadiene (4.8 equiv) were mixed with 10 mL of THF and homogenized for 5 min in an ultrasonic bath. For copolymerization the according amount of second monomer was added also.

The resulting precipitate was filtered, washed intensively with THF, HCl$_{(aq)}$, and saturated EDTA solution and dried in vacuum afterward. Yields between 60% and 85% were achieved.

Acknowledgment. The authors thank Prof. Ullrich Scherf for motivating us to use the Yamamoto protocol for the synthesis of porous networks. This work was supported by the Max Planck Society within in the framework of the project house ENERCHEM.

Supporting Information Available: Nitrogen sorption isotherms and FT-IR spectra of spirobifluorene networks; EDX measurements and elemental analysis of YSN and YBN. This material is available free of charge via the Internet at http://pubs.acs.org.

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