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Hyper-cross-linked polyacetylene type microporous networks decorated with terminal ethynyl groups as heterogeneous acid catalysts for acetalization and esterification reactions

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Abstract: Heterogeneous catalysts based on materials with permanent porosity are of great interest owing to high specific surface area and easy separation, recovery and recycling. Additionally, Porous Polymer Catalysts (PPCs) allow us to tune catalytic activity by introducing various functional centres. This study reports the preparation of PPCs with a permanent micro/mesoporous texture and a specific surface area S_{BET} of up to 1000 m² g⁻¹ active in acid catalysed reactions, namely aldehyde and ketone acetalization and carboxylic acids esterification. These PPCtype conjugated hyper-cross-linked polyarylacetylene networks were prepared by chain-growth homopolymerization of 1,4diethynylbenzene, 1,3,5-triethynylbenzene and tetrakis(4ethynylphenyl)methane. However, only some ethynyl groups of the monomers (from 58 to 80%) were polymerized into the polyacetylene network segments while the other ethynyl groups remained unreacted. Depending on the number of ethynyl groups per monomer molecule and covalent structure of the monomer, PPCs were decorated with unreacted ethynyl groups from 3.2 to 6.7 mmol g⁻¹. The hydrogen atoms of the unreacted ethynyl groups served as acid catalytic centres of the aforementioned organic reactions. To our best knowledge, this is first study describing the high activity of hydrogen atoms of ethynyl groups in acid catalysed reactions.

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Introduction

Porous Polymer Catalysts (PPCs) are a promising new subclass of heterogeneous catalysts based on materials with permanent porosity.^[1-8] In contrast to conventional polymer-supported catalysts based on solvent-swellable polymers,^[9-12] PPCs show permanent porosity with sizes ranging from micropores to mesopores and with high specific surface area. Most PPCs possess the architecture of polymer networks whose porosity results from the rigidity of the segments forming the networks and from extensive cross-linking. PPCs can be prepared to have a wide spectrum of chemical functionalities that differ them from most heterogeneous catalysts based on inorganic porous supports.

Synthesis of PPCs using both step-growth and chain-growth polymerization has been described in the literature. Step-growth polymerization using Sonogashira coupling was efficient for copolymerization of 1,3,5-triethynylbenzene with Tröger's base derivative containing two iodo substituents into porous organocatalysts, with a Brunauer-Emmett-Teller surface area S_{BET} of up to 750 m² g⁻¹, which were active in benzaldehyde alkylation with diethylzinc.^[13] The same synthetic path was used to prepare a PPC organocatalyst with boron-dipyrromethene units active in selective thioanisole oxidation.^[14] Organometallic PPCs active in sulphide oxidation with O_2 ($S_{BET} \sim 1300 \text{ m}^2 \text{ g}^{-1}$) were prepared by Suzuki-Miyaura coupling of 1,4phenvldiboronic acid and [tetrakis(4'bromophenyl)porphyrin](Fe^{III}).^[15] Ru and Ir complexes with ethynylated 2,2'-bipyridine ligands were copolycyclotrimerized with tetrakis(4-ethynylphenyl)methane into organometallic photocatalysts (S_{BET} up to 1500 m² g⁻¹) active in aza-Henry reactions and in aldehyde oxyamination.[16] Knitting polymerization of 2,4,6-tris(carbazolo)-1,3,5-triazine was used to prepare base PPC organocatalysts ($S_{BET} \sim 840 \text{ m}^2 \text{ g}^{-1}$) for the Knoevenagel reaction.^[17] The same synthetic path provided organometallic PPCs with Ru active centres complexed with 2,2'-bis(diphenylphosphino)-1,1'-binaphthyl segments active in asymmetric hydrogenation.[18] Knitting polymerization of carbazole with 1,4-bis(bromomethyl)benzene followed by sulfonation of the parent network provided PPC efficient in esterification and transesterification reactions.^[19]

Chain-growth copolymerization of divinylbenzene (DVB) with sodium *p*-styrene sulfonate followed by ion exchange with sulfuric acid provided acid PPCs of the hyper-cross-linked polymer network type (S_{BET} up to 535 m² g⁻¹) active in acetic acid esterification.^[20] The organometallic PPC active in Huisgen 1,3-dipolar cycloadition and in Glaser homocoupling of alkynes was

prepared using the same type of copolymerization of DVB with N-(1,10-phenanthroline-5-yl)acrylamide followed by metalation of the 1,10-phenanthroline segments of the porous networks with Cu2+.[21] The hyper-cross-linked PPCs prepared by chaingrowth homopolymerization (referred to as self-polymerization) have also been described in a review.^[7] In these reactions, the monomers containing both (i) catalytic active centres or their precursors and (ii) vinyl groups were radically polymerized into PPCs. For example, bis-1,2-(diphenylphospino)ethan with one vinyl group on each phenyl ring was polymerized into a hypercross-linked porous polymer of S_{BET} ~ 950 m² g¹1, which was subsequently metalated into an organometallic PPC active in alkene hydroformylation.^[22] Tetrastyrylporphyrin was another multi-vinylic monomer efficiently polymerized into a hyper-crosslinked polymer network. Poly(tetrastyrylporphyrin) metalation with Co provided an organometallic PPC active in the transformation of epoxides to carbonates in reaction with CO2.^[23] The above survey shows that PPCs are mostly prepared by polymerization of (co)monomers already decorated with catalytically active centres or their precursors. Preparing extensively cross-linked PPCs with permanent micro/mesoporous texture requires using (co)monomers with catalytically active centres and with a sufficient number of polymerizable groups per monomer molecule. When preparing PPCs by step-growth polymerization, (co)monomers with an average number of polymerizable groups per molecule ≥ 2.5 were used, and the conditions were optimized to achieve a nearly quantitative conversion of these groups. When preparing hyper-cross-linked PPCs by chain-growth polymerization, fewer polymerized groups per monomer molecule are required for polymer network formation. For example, the aforementioned chain-growth copolymerization of DVB with functionalized styrenes provided PPCs, although the average number of polymerized (vinyl) groups per (co)monomer molecule was only 1.5.^[7] However, even when synthesising PPCs by chain-growth polymerization of vinylic monomers, polymerization feeds with a higher number of vinyl groups per monomer molecule were often used to obtain more extensively cross-linked products. Crosslinking was extended to offset the partly flexible saturated main chains of polyvinylic networks that do not sufficiently contribute to the formation of a permanent microporous texture, which is a key drawback of polyvinylic PPCs.

We have recently published the preparation of highly rigid hypercross-linked porous polymers by chain-growth (coordination) polymerization diethynylarenes of (specifically diethynylbenzenes)[24-26] or by copolymerization of these monomers with monoethynylarenes.^[27] This polymerization provides micro/mesoporous polymer networks (S_{BET} up to 1400 $m^2 g^{-1}$) with rigid conjugated main chains of the polyacetylene type in which double and single bonds alternate between carbon atoms. These chains are cross-linked by arylene (most commonly phenylene) links in the same way as in poly(divinylbenzene), P(DVB) networks. Thus, the architecture of polyacetylene networks resembles that of cross-linked P(DVB), although the conjugated unsaturated main chains of polyacetylene networks are significantly more rigid than the saturated main chains of P(DVB). Due to the higher rigidity of

the main chains, polyacetylene networks achieve microporous texture, even when cross-linking is less extent.^[27] Therefore, we hypothesised that chain-growth polymerization of ethynylarenes

into polyacetylene networks could be used to prepare hypercross-linked PPCs because fewer ethynyl groups are required for polymerization, thereby allowing the introduction of a higher number of catalytically active groups (centres) into PPCs. Accordingly, this study reports the preparation of acid PPC organocatalysts via chain-growth homopolymerization of ethynylarenes with two, three or four ethynyl groups per molecule as the only type of functional group. Only some ethynyl groups of the monomers were consumed in the polymerization while the other ethynyl groups remained unreacted and served as the acid catalytic centres of acetalization and esterification reactions. To our best knowledge, this is first study describing the high activity of hydrogen atoms of ethynyl groups in acid catalysed reactions.

Results and Discussion

Preparation of microporous polymer networks decorated with terminal ethynyl groups

To prepare hyper-cross-linked microporous polymer networks extensively decorated with terminal ethynyl groups, we used chain-growth polymerization catalysed by the [Rh(nbd)acac] complex and monomers with two, three and four terminal ethynyl namely 1,4-diethynylbenzene (DEB), aroups. 1.3.5triethynylbenzene (TEB) and tetrakis(4-ethynylphenyl)methane (TEPM) (Scheme 1). Chain-growth polymerization of alkynes with one ethynyl group per monomer molecule catalysed by Rh-, W- or Mo-based catalysts yielding the linear substituted polyacetylenes has been used for several decades.^[28,29] The ethynyl groups of the monomer molecules are transformed into polyene (polyacetylene)-type conjugated main chains in this polymerization [see Scheme 1 depicting the polymerization of phenylacetylene to linear poly(phenylacetylene)]. Recently, we found that Rh(I) catalysts also polymerized diethynylarenes (diethynylbenzenes and 4,4'-diethynylbiphenyl),^[24-26] and mixtures of diethynylarenes with monoethynylarenes.^[27] In this case, the polymerization provided non-swellable polyacetylene networks with permanent microporosity in which the polyene chains were cross-linked with arylene links.

Chain-growth polymerization of DEB, TEB and TEPM (see Scheme 1) was performed under conditions given in ref.^[30] (see Experimental part). Quantitative yields of the respective polymer networks, P(DEB), P(TEB) and P(TEPM), were assessed in all polymerizations. The prepared polymer networks were totally insoluble in the solvents tested (DCM, methanol, THF and benzene). The dark red colour of P(DEB), P(TEB) and P(TEPM) indicated their conjugated character (see Figure S1 for the DR UV/vis spectra in ESI). Thermogravimetric analysis (TGA) confirmed the high thermal stability of the polymer networks prepared (see Figure S2 for the TGA curves in ESI). A mass loss of 5 wt.% was observed by TGA ($t_{95\%}$) at the following values of temperature: 419°C [P(DEB)], 529°C [P(TEB)] and

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Scheme 1. Structure of the monomers PhA, DEB, TEB and TEPM. A to D represent possible types of monomeric units in polymer networks P(DEB), P(TEB) and P(TEPM).

505°C [P(TEPM)]. Figure 1 shows ¹³C CP/MAS spectra of P(DEB), P(TEB) and P(TEPM). The ¹³C CP/MAS NMR spectra of all polymer networks contained (i) a broad, partly resolved signal in the region from 115 to 150 ppm that corresponds to the resonance of aromatic carbons and carbons of the polyene main-chains and (ii) signals around δ = 82 ppm and δ = 75 ppm



Figure 1. $^{13}\mbox{CP/MAS}$ NMR spectra of polymer networks P(DEB), P(TEB) and P(TEPM).

that correspond to carbons of non-transformed (unreacted) terminal ethynyl groups. The central sp³ carbon of the TEPM monomeric units was manifested in the ¹³C CP/MAS NMR spectrum of P(TEPM) by a signal at 64 ppm. The presence of unreacted terminal ethynyl groups in all polymer networks prepared was also confirmed by IR spectroscopy [see bands at 2110 cm⁻¹ ($v_{C=C}$) and 3300 cm⁻¹ ($v_{=C-H}$) in Figure S3 in ESI]. The quantification of ¹³C CP/MAS spectra of P(DEB), P(TEB) and P(TEPM) provided values of the number of terminal ethynyl groups (per monomeric unit) that were transformed during the formation of the polymer networks from individual monomers $(n_{\rm TE})$ and the values of the respective degree of conversion of ethynyl groups (ξ_E) (see Table 1). The values of n_{UE} in Table 1 express the number of terminal ethynyl groups (per monomeric unit) remaining in the polymer networks. Because the monomeric units of P(DEB), P(TEB) and P(TEPM) differ in molar mass, we also report the content of unreacted ethynyl groups in the polymer network in mmol g^{-1} (c_E) (Table 1). The values of n_{TE} of the polymer networks increased with the number of ethynyl groups in the parent monomers (n_{E0}) . However, this increase was not proportional to $n_{\rm E0}$. While the DEB monomer with two ethynyl groups provided P(DEB) in which 1.6 ethynyl groups per monomeric units were converted, the monomer TEPM with four ethynyl groups provided P(TEPM) with only partly enhanced n_{TE} = 2.3 (see Table 1). Therefore, the value of $\xi_{\rm E}$ decreased in the series P(DEB) > P(TEB) > P(TEPM), ranging from 0.80 in the case of P(DEB) to only 0.58 in the case of P(TEPM). The decrease in $\xi_{\rm E}$ with increasing $n_{\rm E0}$ most likely resulted from steric hindrance in transforming a higher number of ethynyl groups per monomeric unit. All polymer networks contained a significant amount of unreacted ethynyl groups [n_{UE} from 0.4 for P(DEB) to

P(TEB)

P(TEPM)

3

4

0.2

0.3

ethynyl groups (p ethynyl groups in area, S_{BET} , specifi	er monomeric u the polymer net c surface area of	nit) transformed in works (per monom micropores, S _{micro}	polymerization, r_{UE} , co neric unit), n_{UE} , co , volume of microp	σ_{TE} , degree of content of ethynyl gores, V_{micro} .	proups in the polyme	groups in polyme er networks in mr	erization, $\xi_{\rm E}$, numl nol g ⁻¹ , $c_{\rm E}$, overall	specific surface
Polymer network	n _{E0}	n _{TE}	ξ _E	n _{ue}	c _E (mmol g⁻¹)	S_{BET} (m ² g ⁻¹)	S_{micro} (m ² g ⁻¹)	$V_{\rm micro}$ (cm ³ g ⁻¹)
P(DEB)	2	1.6	0.80	0.4	3.2	1007	832	0.4

1.0

1.7

6.7

4.1

Table 1. Covalent and textural characteristics of the polyacetylene polymer networks; number of ethypyl groups per molecule of monomer

1.7 for P(TEPM)].The values of c_E ranged from 3.2 to 6.7 mmol g^{-1} and increased in the series P(DEB) < P(TEPM) < P(TEB). The results of ¹³C CP/MAS NMR spectroscopy partly allowed us to specify the covalent structure of the polymer networks. P(DEB) most likely consists of two types of monomeric units: (i) linear units (40 mol % content) in which only one ethynyl group of DEB was transformed into a segment of the polyacetylene main chain while the second ethynyl remained unreacted (Scheme 1, units A_{P(DEB)}) and (ii) cross-linking units (60 mol % content) in which both ethynyl groups of DEB were transformed into the segments of the polyacetylene main chains and interconnected two main chains via 1,4-phenylene links (Scheme 1, units B_{P(DEB)}). P(TEB) may contain linear units with

2.0

2.3

0.67

0.58



Figure 2. N₂ adsorption (full symbols) and desorption (open symbols) isotherms at 77 K on the polymer networks P(DEB), P(TEB) and P(TEPM).

only one transformed ethynyl group (Scheme 1, units A_{P(TEB)}) and two types of cross-linking monomeric units in which either two or three ethynyl groups were transformed (Scheme 1, units B_{P(TEB)} and C_{P(TEB)}, respectively). Four types of monomeric units can be contained in P(TEPM): a linear monomeric unit (Scheme 1, units A_{P(TEPM)}) and three types of cross-linking units with two, three or four transformed ethynyl groups (Scheme 1, units B_{P(TEPM)}, C_{P(TEPM)} and D_{P(TEPM)}, respectively). Unfortunately, the content of the individual unit types in P(TEB) and P(TEPM) could not be determined from ¹³C CP/MAS NMR spectra.

914

711

741

699

Nitrogen adsorption isotherms (77 K) on P(DEB), P(TEB) and P(TEPM) (see Figure 2) showed a steep increase in the quantity of N₂ adsorbed in the relative pressure (p/p_0) region from 0 to 0.1 (p_0 = 101325 Pa), thus confirming the presence of micropores in the polymer networks. P(TEB) and P(DEB) also contained mesopores (in addition to micropores) as shown by the steep increase in adsorbed N₂ at $p/p_0 > 0.6$ and by significant hystereses on adsorption/desorption isotherms. The Brunauer-Emmett-Teller specific surface area of the polymer networks (S_{BET}) ranged from 711 to 1007 m² g⁻¹, slightly decreasing in the order P(DEB) > P(TEB) > P(TEPM), although the extent of cross-linking of the polymer networks (roughly proportional to $n_{\rm TF}$) increased in the same order. In polymer networks with a higher extent of cross-linking, the tight packing of some links and chain segments may have restricted the formation of micropores in the polymer networks. Nevertheless, the difference in S_{BFT} of the P(DEB), P(TEB) and P(TEPM) may also be affected by the geometry of the DEB, TEB and TEPM monomers used to prepare the polymer networks. The evaluation of the desorption branches of N₂ isotherms by the Barrett-Joyner-Halenda (BJH) method confirmed the presence of mesopores in P(DEB) and P(TEB). The mesopore diameter distributions of both networks were broad (see Figure S4 in ESI) with maxima at about 9 nm [P(DEB)] and 6 nm [P(TEB)]. The micropore diameter of P(DEB), P(TEB) and P(TEPM) was around 0.7 nm. Figure S5 in ESI shows Scanning Electron Microscopy (SEM) images of P(DEB), P(TEB) and P(TEPM). The networks consisted of approximately spherical particles 20 - 100 nm in diameter.

DEB, TEB and TEPM and other aromatics with ethynyl groups have often been described as the starting materials for the synthesis of structurally diverse microporous polymers by

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various step-growth polymerizations. Based on the pioneering studies by Cooper et al., [31] step-growth polymerization through Sonogashira coupling yielding conjugated microporous poly(aryleneethynylene)s is arguably the most commonly used technique in this field. The poly(aryleneethynylene)s prepared from DEB and TEB have a S_{BET} of up to 1000 $\text{m}^2~\text{g}^{\text{-1},[31,32]}$ and poly(aryleneethynylene)s prepared from TEPM have a value of S_{BET} = 1917 m² g⁻¹.^[33] However, a nearly quantitative conversion of ethynyl groups of the monomers by step-growth polymerization is required to prepare microporous poly(aryleneethynylene)s with high S_{BET} values. In this respect, the chain-growth technique used by us for the polymerization of DEB, TEB and TEPM differs: for obtaining microporosity and satisfactory S_{BET} values of polyacetylene-type P(DEB), P(TEB) and P(TEPM) partial conversion of ethynyl groups of the monomers was sufficient that allowed preparing conjugated microporous polymer networks extensively decorated with (unreacted) terminal ethynyl groups (Table 1). Moreover, the content of the unreacted terminal ethynyl groups of polymer networks can be partly controlled by selecting monomer molecules with a different number of terminal ethynyl groups.

Catalytic activity of polymer networks P(DEB), P(TEB) and P(TEPM)

The acetylenic hydrogen of terminal ethynyl groups is known to have Brønsted acid character. This property is used in chemical reactions with terminal alkynes as substrates. However, the acid character of the acetylenic hydrogen may also make it possible to use terminal alkynes as acid organocatalysts. Although phenylacetylene has been described as a cocatalyst in the transformation of some transition metal complexes into homogenous catalysts,^[34] no systematic study on the use of terminal alkynes as acid catalysts has been published in the literature thus far. This may be due to difficulties in separating the product from the alkyne that would be used as a homogeneous catalyst.

The acidity of acetylenic hydrogen should be not only maintained in the terminal ethynyl groups of P(DEB), P(TEB) and P(TEPM), but also increased upon conjugation of triple bonds of ethynyl groups with conjugated segments of the polymer networks. We confirmed the Brønsted acidity of P(DEB), P(TEB) and P(TEPM) by an indirect method based on measuring the decrease of basicity of dimethyl sulfoxide (DMSO) caused by the presence of dispersed acid solid.^[35] Due to the presence of dispersed terminal ethynyl groups containing P(DEB), P(TEB) or P(TEPM), pH of DMSO dropped from 13 to 9 (see Experimental part for details). Conversely, pH of DMSO decreased only marginally (from 13 to 12) due to adding reference linear poly(phenylacetylene) P(PhA), which did not contain the terminal ethynyl groups (see Scheme 1). It should be noted that the sensitivity of the method used was not sufficient to determine any differences in acidity between P(DEB). P(TEB) and P(TEPM). Based on the above finding, we decided to study the activity of P(DEB), P(TEB) and P(TEPM) as heterogeneous acid organocatalysts. Two typical acid-catalysed reactions have been chosen for this purpose: acetalization of carbonyl compounds and esterification of carboxylic acids by methanol. In the initial stage of the catalytic study, we confirmed

 Table 2. Yield of acetals achieved in the acetalization of various aldehydes or ketones with methanol catalysed with the polymer networks P(DEB), P(TEB) and P(TEPM) (100 mg aldehyde or ketone, 10 mg polymer network, 3 mL methanol, 60°C, reaction time 0.25 h and 7 h).

	R_{1} R_{2})c=o	+ 2 <mark>C</mark>	Н₃ОН — ►		СН ₃ СН ₃	- H ₂ O			
	P(D	EB)		Р(TEB)			P(TE	EPM)	
Aldehyde	Yield (%) at			Yield	Yield (%) at			Yield (%) at		
or Ketone	reaction time:			reaction	reaction time:			reaction time:		
	0.25 h	7 h	l	0.25 h	7 h			0.25 h	7 h	
Pentanal	1.8	49	(18) ^a	15	80	(14) ^a		11	84	(24) ^a
Hexanal	1.4	38	(12) ^a	12	98	(15) ^a		13	89	(22) ^a
Heptanal	3.3	22	(6) ^a	19	91	(12) ^a		8.6	81	(17) ^a
Isobutanal	0.5	18	(8) ^a	5.4	50	(10) ^a		1.5	28	(9) ^a
Isopentanal	1.3	32	(12) ^a	14	88	(15) ^a		10	76	(22) ^a
Acetone	3.5	31	(17) ^a	16	36	(9) ^a		12	40	(17) ^a
Butanone	4.8	14	(6) ^a	12	13	(3) ^a		9.8	15	(5) ^a

^a Turn over number (TON) in mol of converted substrate per mol of ethynyl groups of the catalyst.

Table 3. Yield of methyl esters achieved in the esterification of various carboxylic acid with methanol catalysed with either the polymer network P(TEB) or phenylacetylene applied as a homogeneous catalyst (100 mg carboxylic acid, 10 mg catalyst, 5 mL methanol, 65°C).

	R-C O-H	+ CH	₃OH>	$R - C + H_2$	C			
Carboxylic Acid	P(TEB) Yield (%) at reaction time:			Phenylacetylene Yield (%) at reaction time:				
	1 h	7 h	24 h	1 h	7 h	24 h		
Acetic	2.4	13	39 (10) ^a	0.9	5.2	12 (2) ^a		
Propionic	1.9	14	30 (6) ^a	0.5	5.8	8.2 (1) ^a		
cis-Hex-3-enoic	5.5	21	31 (4) ^a	1.0	4.6	12 (1) ^a		

^a Turn over number (TON) in mol of converted substrate per mol of ethynyl groups of the catalyst.

the positive catalytic effect of P(DEB) on the isopentanal acetalization by methanol (see Experimental part for conditions): 32% conversion of isopentanal to isopentanal dimethyl acetal was achieved with P(DEB) within 7 h while only 3% conversion was assessed in the same reaction performed without the catalyst. Because P(DEB) may contain residua of the [Rh(nbd)acac] complex (applied as polymerization initiator), we tested [Rh(nbd)acac] (dissolved in methanol) for its eventual activity in isopentanal acetalization. The result was negative, thus confirming that acetalization was not catalysed by [Rh(nbd)acac]. Isopentanal acetalization by methanol was also performed with dispersed linear P(PhA) polymer (Scheme 1), which contained polyene main chains substituted with phenyl groups similarly to P(DEB), albeit without terminal ethynyl groups. The result was also negative: poly(phenylacetylene) did not catalyse isopentanal acetalization. The above finding strongly indicates that the catalytic activity of P(DEB) in acetalization resulted from the acidity of acetylenic hydrogens of the terminal ethynyl groups present in P(DEB), which corroborates the certain ability of phenylacetylene to catalyse acetalization: 8% conversion of isopentanal was achieved when applying phenylacetylene as a homogeneous catalyst. However, the catalytic activity of phenylacetylene was lower than that of P(DEB), which may reflect the lower acidity of acetylenic hydrogen of phenylacetylene than that of acetylenic hydrogens of the more conjugated P(DEB).Table 2 summarizes the results of the P(DEB)-, P(TEB)- and P(TEPM)-catalysed acetalization of various carbonyl compounds by methanol. The only products formed in these reactions were the expected dimethyl acetals (no hemiacetals or any side products were detected). The catalytic activity of the networks in aldehyde acetalization (expressed by aldehyde conversion) increased approximately in the same order in which the content of terminal ethynyl groups in the networks (c_E) increased, that is, [P(DEB) < P(TEPM) \leq P(TEB)] (see Table 1 and 2). This finding further confirms that the terminal ethynyl groups of the networks served as the acid catalytic centres. Based on the comparison of TON values listed in Table 2, which quantify the ability of ethynyl groups of the individual networks to catalyze acetalization of aldehydes, P(TEPM) appeared to be slightly more efficient than P(TEB) and P(DEB). This may be related to the fact that ethynyl groups in P(TEPM) are relatively distant from knots of the networks and can therefore be better sterically accessible for substrate molecules (see Scheme 1). The catalytic activity of the networks in acetalization depended on the character of the substrates. Pentanal, hexanal and heptanal acetalization generated the expected acetals in yields \geq 80% when P(TEPM) and P(TEB) were used as the catalyst. Conversely, isobutanal acetalization was less efficient: with P(TEB) catalyst, an acetal yield of only 50% was achieved, most likely because the branching of the butane chain near the HC=O group sterically complicated the isobutanal acetalization. In turn, an acetal yield of 88% was achieved in the P(TEB)-catalysed acetalization of isopentanal in which the branching of substrate alkane chain apparently caused no sterical hindrance because it was farther from the aldehyde group.

P(DEB), P(TEB) and P(TEPM) also catalysed the acetalization of acetone and butanone with methanol to acetone dimethyl acetale and butanone dimethyl acetale, respectively. The yield achieved after 0.25 h was similar to that assessed after the acetalization of most aldehydes in the same period. However, the final yield of acetals (after 7 h of reaction) was lower than that of aldehyde acetalization. Lengthening the reaction time failed to increase the yield. Notwithstanding, we believe that further optimizing the reaction conditions may increase the efficiency of P(DEB), P(TEB) and P(TEPM) in ketone acetalization. It should be noted that no traces of product were detected (by GC) in the acetalization of acetone and butanone performed under the same conditions without adding P(DEB), P(TEB) or P(TEPM). No products were detected when acetone and butanone acetalization was attempted in the presence of phenylacetylene.[36]

The most catalytically active network, P(TEB), was tested for reusability in isopentanal acetalization [200 mg of isopentanal, 20 mg of P(TEB), 4 mL of methanol, 60° C, 4 h]. After each reaction cycle, P(TEB) was separated, washed four times with

DCM and dried (always at room temperature) prior to repeated use. Isopentanal conversion was as follows, in consecutive cycles: 95% (1-st cycle), 84% (2-nd cycle), 68% (3-rd cycle), 68% (4-th cycle). Thus, even at the third and fourth use, P(TEB) showed satisfactory catalytic activity. The decrease in catalytic activity between the first and third reaction cycles may reflect deterioration of the access to the smallest pores of P(TEB) as a result of possible reaction components trapping in these pores.

P(TEB) network was also active in esterification reactions, namely the esterification of acetic, propionic and *cis*-hex-3-enoic acids with methanol at 65°C (see Table 3). The yields of the respective methyl esters achieved after 24 h were, however, only moderate (ranging from 30 to 39%). Nevertheless, P(TEB) was significantly more active in the studied esterifications than phenylacetylene applied as a homogeneous catalyst in the same reactions (see Table 3). The studied esterifications provided no esters when performed without adding a catalytically active component. The P(TEB) network is a less efficient esterification catalyst than conventional mineral acids. However, easy separation of P(TEB) from the liquid part of the reaction system is a clear advantage of this catalyst.

Conclusions

Hyper-cross-linked conjugated polymer networks of the polyacetylene-type extensively decorated with terminal ethynyl groups were prepared by chain-growth homopolymerization of 1,4-diethynylbenzene, 1,3,5-triethynylbenzene and tetrakis(4ethynylphenyl)methane. In the polymerization, only some ethynyl groups of the monomers (from 58 to 80%) were converted into polyacetylene-type segments of the main chains of the networks while the other ethynyl groups remained unreacted in the prepared networks. Depending on the number of ethynyl groups per monomer molecule and covalent structure of the monomer, the prepared networks were decorated with unreacted ethynyl groups from 3.2 to 6.7 mmol g⁻¹. Conversely, the networks prepared showed permanent micro or micro/mesoporous texture (S_{BET} from 700 to 1000 m² g⁻¹) although the polymerizations proceeded only under partial transformation of the polymerizable (ethynyl) groups of the monomers

The prepared networks were active as heterogeneous organocatalysts in reactions known to require acid catalysis, such as aldehyde and ketone acetalization by methanol. The respective dimethyl acetals were the only products from the acetalizations catalysed by these networks. The catalytic activity of the networks in acetalization correlated well with the content of the ethynyl groups in the networks. The network prepared from 1,3,5-triethynylbenzene was shown to also catalyse the esterification of carboxylic acid with methanol although the yields of the respective methyl esters were only moderate. We attributed the catalytic activity of the networks to the acidity of the acetylenic hydrogen atoms of the ethynyl groups abundantly present in the networks. Surprisingly, the networks prepared showed higher catalytic activity than the phenylacetylene that we tested as a homogeneous ethynyl-group containing catalytic

analogue to the networks. The acidity of the acetylenic hydrogen atoms may be increased in the networks prepared due to the conjugation of ethynyl groups with conjugated network segments. To our best knowledge, this is first study describing the high activity of hydrogen atoms of ethynyl groups in acid catalysed reactions.

Experimental Section

Materials

1,4-Diethynylbenzene (DEB), 1,3,5-triethynylbenzene (TEB), tetrakis(4ethynylphenyl)methane (TEPM), acetylacetonato(norborna-2,5diene)rhodium(I), [Rh(nbd)acac] (all by TCI Europe), acetic acid, butanone, propionic acid (all by Lach-Ner, Czech Republic), acetone, methanol (both by Penta, Czech Republic), heptanal, hexanal, *cis*-hex-3enoic acid, isobutanal, isopentanal, pentanal, propanal, phenylacetylene and tetrahydrofuran (THF) (all by Sigma-Aldrich) were used as obtained. Dichloromethane (DCM) (Lach-Ner, Czech Republic) was distilled from P₂O₅. Linear poly(phenylacetylene) was prepared by polymerization of phenylacetylene with [Rh(nbd)acac] polymerization catalyst in DCM according to ref.^[37]

DEB, TEB and TEPM polymerization

All polymerizations were performed in DCM at 70°C in sealed thick-wall ampoules under argon atmosphere. The complex [Rh(nbd)acac] was used as a polymerization catalyst. The reaction time was 72 h. The initial concentrations in the reaction mixtures were: [[Rh(nbd)acac]]₀ = 18 mmol dm^{-3} , [monomer]₀ = 0.6 mol dm^{-3} (in the case of DEB and TEB monomers), [monomer] $_0$ = 0.25 mol dm⁻³ (a lower concentration was used due to worse solubility of TEPM in DCM). Polymerizations provided quantitative yields of the respective polymer networks, P(DEB), P(TEB) and P(TEPM). Typical example of polymerization reaction (polymerization of DEB): 1 g (7.9 mmol) of DEB was placed into an ampoule, dissolved in 10 mL of DCM and subsequently mixed (under stirring with a magnetic stirrer bar) with a solution of 70 mg (0.24 mmol) of [Rh(nbd)acac] in 3 mL of DCM. Within two to three minutes, the gelation point was reached, preventing further stirring. The ampoule was then sealed and placed in the oven preheated to 70°C. After 3 days of reaction at 70°C, the solid polymer network was separated and washed repeatedly with DCM until the colourless filtrate was obtained. Polymer network was subsequently dried in vacuum at room temperature for 7 days, and the yield of the polymer network was determined gravimetrically.

Application of the polymer networks P(DEB), P(TEB) and P(TEPM) as heterogeneous catalysts

The prepared polymer networks were applied as heterogenous catalysts of (i) acetalization of aldehydes and ketones with methanol (reaction temperature 60°C) and (ii) esterification of carboxylic acids with methanol (reaction temperature – boiling point of methanol, ~ 65°C, oil bath 90°C). Acetalization and esterification were performed in a stirred batch reactor (400 rpm). Most often, 10 mg of the polymer network was dispersed in methanol (from 3 to 5 ml). The dispersion was stirred for 20 min to solvate the surface of the polymer network. Then, 100 mg of substrate was added under stirring, and the course of the reaction was monitored by Gas Chromatography (GC). The samples were centrifuged using rotation centrifuge (Hettich Zentrifuge EBA 20), and the liquid part was analyzed by GC.

Techniques

All $^{\rm 13}\text{C}$ CP/MAS NMR spectra were measured at 11.7 T using a Bruker Avance 500 WB/US NMR spectrometer in a double-resonance 3.2-mm probehead at 20 kHz spinning frequency. The 90° (¹H) pulse length was 2.5 $\mu s,$ the strength of the spin-locking field $B_1(^1H,\ ^{13}C)$ expressed in frequency units $\omega_1/2 \pi = \gamma B_1$ was 64 kHz, the recycle delay was 6 s, and the cross-polarization contact time to reach quantitative results was 3 ms. Active cooling was used to offset the frictional heating of rotating samples.^[38] Diffuse reflectance (DR) UV/vis spectra of polymer networks were recorded using a PerkinElmer Lambda 950 spectrometer. Samples were diluted with BaSO₄. Fourier transform IR spectra were measured on a Nicolet Magna IR 760 using the diffuse reflection mode. Samples were diluted with KBr. Thermogravimetric analysis (TGA) was performed on a TA Q500 apparatus under nitrogen atmosphere with a heating rate of 10°C min⁻¹ from 40 to 800°C. The samples were treated at 100°C for 60 min under nitrogen flow prior to analysis to remove trapped moisture. Nitrogen adsorption/desorption isotherms on the polymer network samples were measured at 77 K using a static volumetric adsorption system TriFlex analyzer, Micromeritics, Norcross, USA. The samples were degassed at 373 K (12 h) prior to N₂ adsorption analysis. The adsorption isotherms were fitted using the (i) Brunauer-Emmett-Teller (BET) method, to assess the specific surface area (S_{\text{BET}}), and the (ii) tplot method to determine the external specific surface area (Sext). The specific surface area of the micropores (S_{micro}) was assessed using the following equation: $S_{micro} = S_{BET} - S_{ext}$. Horvath-Kawazoe method was used to estimate the diameter of micropores. To determine the mesopore diameter distribution the desorption branches of the N₂ isotherms were evaluated by the Barrett-Joyner-Halenda (BJH) method. GC analysis of reaction mixtures was performed on (i) a Shimadzu GC-17A chromatograph equipped with a flame ionisation detector and a non-polar ZB-5 column and on (ii) a Shimadzu GC-2010 Plus chromatograph equipped with a mass spectrometer Shimadzu GC-MS QP 2010 Ultra and a non-polar ZB-1 column. Scanning Electron Microscopy (SEM) was performed using Tescan Lyra3 apparatus (TESCAN Brno, Itd., Czech Republic) at accelerating voltage of 10 kV. The values of DMSO pH were determined using automatic pH meter (Hanna Instruments HI 3220 pH/ORP Meter). The dispersions of polymer (10 mg in 15 mL of DMSO) were prepared and placed to the magnetic stirrer (450 rpm). The values of pH were measured for a period of 30 s at 23 °C.

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Entry for the Table of Contents FULL PAPER

Arenes substituted only with ethynyl groups were used for polymerization construction of new hyper-cross-linked Porous Polymer Catalysts. In the polymerization, only some ethynyl groups of the monomers were converted into polymer segments while the other ethynyl groups remained unreacted and served as acid catalytic centres of acetalization and esterification reactions.



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Hyper-cross-linked polyacetylene type microporous networks decorated with terminal ethynyl groups as heterogeneous acid catalysts for acetalization and esterification reactions