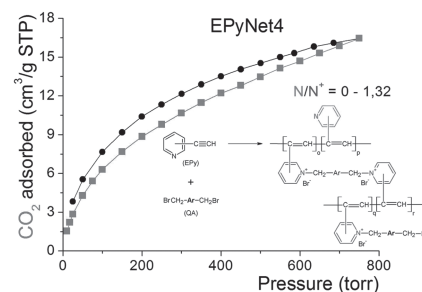


New Hyper-Crosslinked Partly Conjugated Networks with Tunable Composition by Spontaneous Polymerization of Ethynylpyridines with Bis(bromomethyl)arenes: Synthesis, Spectral Properties, and Activity in CO₂ Capture

Sabina Petrášová, Arnošt Zukal, Jiří Brus, Hynek Balcar, Jakub Pastva, Jiří Zedník, Jan Sedláček*

Spontaneous catalyst-free polymerizations of 4-ethynylpyridine (4EPy) and 2-ethynylpyridine with bifunctional quaternizing agents (QAs) of bis(bromomethyl)arenes provide highly crosslinked polymer networks in high yields. ¹³C cross-polarization magic-angle spinning (CP/MAS) NMR, Fourier transform IR (FTIR) and diffuse reflectance vis spectroscopy confirm that these networks consist of polyacetylene main chains substituted with pyridyl and pyridiniumyl groups, the latter interconnected with $-\text{CH}_2(\text{arylene})\text{CH}_2-$ linkers. Variation of the 4EPy/QA ratio in the polymerization feed results in networks with different extents of crosslinking and pyridyl/pyridiniumyl ratio (N/N^+ from 0 to 1.32). Networks exhibit photoluminescence and are also moderately active in CO₂ capture (the highest uptake is 16.4 cm³ (STP) g⁻¹ at 293 K and an equilibrium CO₂ pressure of 750 Torr).



1. Introduction

Ethynyl(s)-containing compounds are versatile building blocks for the preparation of a variety of types of linear

or branched π -conjugated polymers.^[1–10] The step-growth homocoupling and cross-coupling of diethynylarenes provide poly(arylenebutadiynylene)s and poly(aryleneethynylene)s, respectively.^[1,5,6,10] The chain-growth polymerization of mono- or disubstituted acetylenes results in substituted polyacetylenes^[1,2,11–17] and the polycyclotrimerization of mixtures of diethynylarenes and alkylacetylenes provides polyarylene-type polymers.^[1,8,18] In the last half a decade, all of the above synthetic paths have been modified for the preparation of conjugated network-type polymers. Multiethynylarenes have mostly been used as the starting materials. Several series of hyperbranched poly(arylenebutadiynylene) and poly(aryleneethynylene) networks, including those with heteroatoms containing substituents, have been prepared, mainly by Cooper et al.^[19–24] Di-, tri-, and tetraethynylarenes have been polycyclotrimerized into

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polyarylene networks.^[25,26] Recently, we reported that polyacetylene-type networks are prepared by chain-growth polymerization of diethynylarenes.^[27] The conjugated networks mostly exhibited micro- and/or mesoporosity and were studied as materials for gas capture, separation, and storage.^[19,28] The synthesis of the above networks proceeded as transition-metal-catalyzed polymerizations and the prepared networks could be contaminated by catalyst residues. Evidently, the synthesis of conjugated networks proceeding without transition metal catalysts would be beneficial from the point of view of the product purity.

In 1991, Blumstein et al. reported that 2-ethynylpyridine (2EPy), 4-ethynylpyridine (4EPy), 1,2-bis(4-pyridyl) acetylene, and 1,4-bis(4-pyridyl)buta-1,3-diyne polymerize spontaneously in the presence of alkyl bromides and iodides (RX) into soluble conjugated polymers.^[29] Later, the polymerization of 2EPy with RX was studied in detail, and the resulting polymers were described as ionic polymers of the monosubstituted polyacetylene type, in which polyene chains were substituted by *N*-alkylpyridinium-2-yl pendants; the polymers were referred to as poly(*N*-alkyl-2-ethynylpyridinium halogenide)s. The anionic chain growth mechanism was proposed for the polymerization of 2EPy with RX. The incorporation of 2EPy into the growing polymer chain was, however, assumed to be possible only after the 2EPy activation via the quaternization of pyridine nitrogen by RX. Due to this, the 2EPy polymerization with RX is often referred to as quaternization polymerization.^[30] Many poly(*N*-alkyl-2-ethynylpyridinium halogenide)s have been prepared by the variation of the R group in the RX quaternizing agent (QA).^[31–36] Besides RX, also some other QAs have been used for the 2EPy polymerization (e.g., acyl chlorides, bromine, hydrochloric acid^[30,37,38]). Prepared well-soluble polymers of 2EPy have been studied as potential components of photoluminescence (PL) and sensing devices or (nano)composites.^[39–41]

To the best of our knowledge, no systematic study exists in the literature on the quaternization polymerization of ethynylpyridines with QAs of a higher functionality. A mention on this topic has only been made by Zhou and Blumstein.^[42] dealing with 2EPy polymerization with 1-bromobutane. In one experiment, a mixture of 1-bromobutane and 1,4-dibromobutane was applied for the quaternization, and insoluble polymer was obtained. The 2EPy-derived polymers reported in this paper were studied as to their miscibility with urethanes.

Since we considered the polymerization of ethynylpyridines with multifunctional QAs as a promising path to (partly) conjugated polyacetylene-type networks, we performed a systematic study on this topic in which various bis(bromomethyl)arenes were used as QAs. The prepared networks were characterized and their PL and efficiency

in CO₂ capture were investigated. The results of this study are reported in this paper.

2. Experimental Section

2.1. Materials

2-Ethynylpyridine (2EPy), 3-ethynylpyridine (3EPy), 1,4-bis(bromomethyl)benzene (QA1), 2,6-bis(bromomethyl)naphthalene (QA2), 4,4'-bis(bromomethyl)-1,1'-biphenyl (QA3), 2,2'-bis(bromomethyl)-1,1'-biphenyl (QA4), and (*R*)-2,2'-bis(bromomethyl)-1,1'-binaphthyl (QA5), pyridine, 4-vinylpyridine, benzyl bromide, *N,N*-dimethylformamide (DMF) (anhydrous, 99.8%), methanol (all from Sigma–Aldrich), diethyl ether (Lach-ner, Czech Republic), and 4-ethynylpyridine (4EPy) (TCI Europe) were used as obtained. *N*-benzylpyridinium bromide was prepared by quaternization of pyridine with benzyl bromide.^[43] Details on synthesis and characterization are given in the Supporting Information.

2.2. Techniques

All the Fourier transform IR (FTIR) spectra were measured on a Nicolet Magna IR 760 using the diffuse reflection mode (DRIFTS). Samples were diluted with KBr. All the ¹³C cross-polarization magic-angle spinning (CP/MAS) NMR spectra were measured using a Bruker Avance 500 WB/US NMR spectrometer in a double-resonance 4 mm probehead at a spinning frequency of 20 kHz. The ¹H and ¹³C NMR spectra of *N*-benzylpyridinium bromide and 4-vinylpyridine were measured on a Varian Unity Inova 400 spectrometer in CDCl₃. Diffuse reflectance vis spectra of the solid polymers were recorded using a Perkin–Elmer Lambda 950 spectrometer. The polymers were diluted with BaSO₄ (1/10, w/w) before measurements were carried out. Elemental analyses of the products were done at the Institute of Macromolecular Chemistry, Academy of Sciences of the Czech Republic.

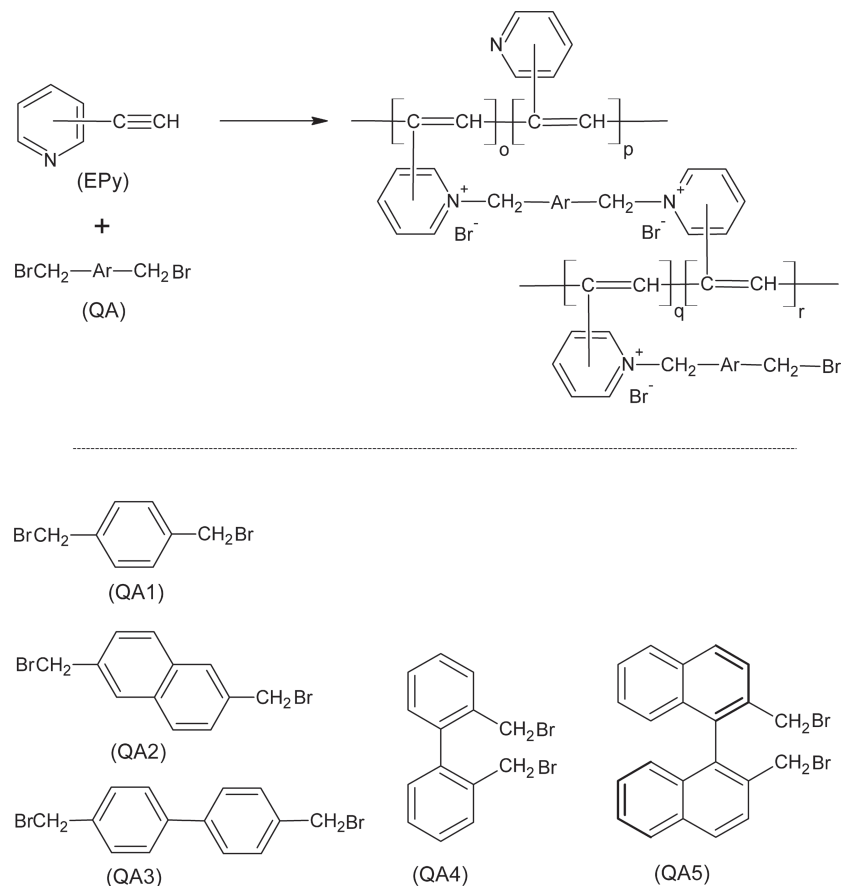
Photoluminescence emission spectra of the solid polymers were measured using a Horiba Jobin Yvon Fluorolog 3 instrument using a solid-state film holder (22.5) and excitation wavelength of 420 nm. Samples for the measurements were prepared as follows. Approximately 10 mg of finely powdered polymer were mixed with three drops of microscope glue (Entellan PB 5265, Euromex Microscopes, Holland). The mixture was transferred to the fresh surface of the slide of pyrolytic graphite (NT-MDT comp.) A slide of the pyrolytic graphite was previously adjusted on a thin glass slide. Thus, the prepared sample was heated at 50 °C for 15 min.

Nitrogen adsorption on the polymers was determined at 77 K using a Gemini II surface area analyzer (Micromeritics). The samples for adsorption analysis were prepared using a FlowPrep 060 degasser. The degassing procedure was performed at 383 K for 8 h in flowing helium. Adsorption/desorption isotherms of carbon dioxide were recorded at 293 K using an ASAP 2020 (Micromeritics) volumetric instrument. The samples were degassed at 383 K for 8 h under a turbomolecular pump vacuum. Since adsorption isotherms of CO₂ on organic polymers can depend on the time allotted to the adsorption measurement,^[26] all of the isotherms

were recorded using the same equilibration time interval of 5 s (the equilibration time interval represents the number of seconds between successive pressure readings during equilibration). The temperature of the sample was maintained with an accuracy of ± 0.01 K using an Iso-Therm thermostat (e-Lab Services, Czech Republic).

2.3. Polymerization

Ethynylpyridines (2EPy, 3EPy, and 4EPy) were polymerized via activation with bifunctional quaternizing agents (QA) of the bis(bromomethylarene) type (QA1, QA2, QA3, QA4, and QA5) under argon atmosphere in DMF at 70 °C (reaction time 72 h). In a typical experiment, an ethynylpyridine isomer (0.5 g, 4.82 mmol) in DMF (1.5 mL) and QA (1.205 mmol) in DMF (1.5 mL) were mixed under argon in a thick-wall glass ampoule. The ampoule was sealed and placed into thermostated bath. The product (obtained in the form of a solid polymer block) was mechanically ground into small pieces and repeatedly washed with methanol until the filtrate was colorless. Finally, the product was separated by filtration, dried in vacuum at room temperature, and the yield was determined gravimetrically.



3. Results and Discussion

3.1. Synthesis of Polymers

Three positional isomers of ethynylpyridine (EPy), 2-ethynylpyridine (2EPy), 3-ethynylpyridine (3EPy), and 4-ethynylpyridine (4EPy) were (separately) polymerized under activation with 1,4-bis(bromomethyl)benzene (QA1). QA1 is a bifunctional quaternizing agent with two equal CH_2Br groups the application of which was believed to transform EPys into hyper-crosslinked polyacetylene-type networks according to Scheme 1. The initial mole ratio of EPy to QA1 in the polymerization mixture was 4:1, which corresponds

Scheme 1. Formation of networks by spontaneous polymerization of ethynylpyridines (EPy) with bifunctional quaternizing agents (QA) of bis(bromomethyl)arene type. Ar stands for arylene core of QA.

to the ratio of EPy nitrogen to Br-groups of QA1, N:Br = 2:1 (the N:Br mole ratio is used in this paper for the characterization of composition of both the polymerization feeds and the prepared polymers). The excess of EPy over Br-groups of QA1 was chosen with the aim to support the conversion of both Br-groups of QA1 molecules incorporated into the polymer. Results of polymerizations are summarized in Table 1. No insoluble polymer was formed in the reaction of 3EPy with QA1. On the other hand, the formation of

Table 1. Polymerization of ethynylpyridines (EPy) with 1,4-bis(bromomethyl)benzene (QA1). N:Br mole ratio in the feed = 2:1, solvent DMF, initial EPy concentration = 1.6 mol L^{-1} , reaction time 72 h, reaction temperature 70 °C. Y is the yield of insoluble polymer, N:Br(polymer) is the N:Br mole ratio in the polymer, $a_{\text{CO}_2, 750 \text{ Torr}}$ is the volume of CO_2 (in cm^3 at standard temperature and pressure (STP)) adsorbed on 1 g of a polymer at 20 °C (CO_2 pressure = 750 Torr).

Polymer code	Monomer	Y [%]	Units ^{a)}	N:Br (polymer)	$a_{\text{CO}_2, 750 \text{ Torr}}$ [$\text{cm}^3(\text{STP})\text{g}^{-1}$]
EPyNet1	2EPy	61	A, B, D	1.52:1	5.0
	3EPy	0	—	—	—
EPyNet4	4EPy	82	A, D	1.61:1	16.4

^{a)}Type of monomeric unit (Scheme 2) prevailing in the polymer.

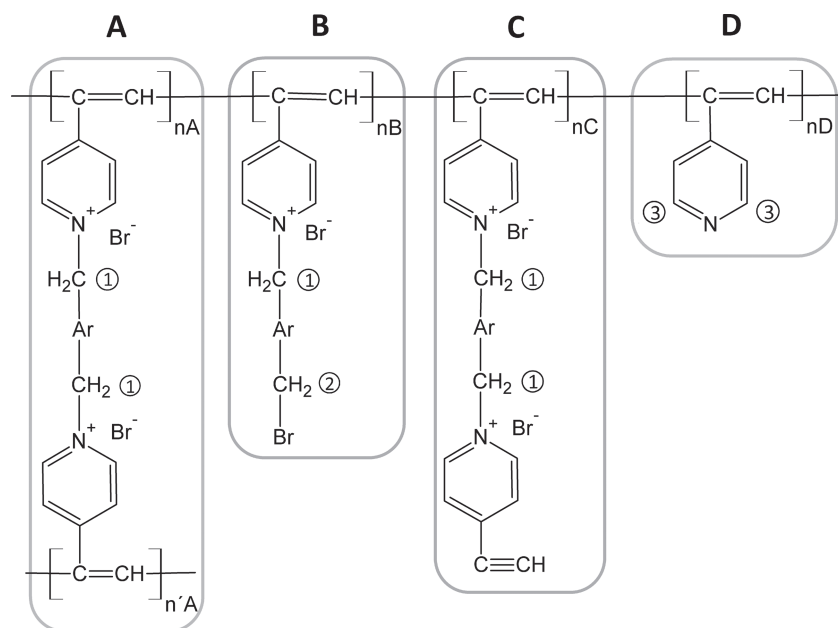
polymers insoluble in the reaction mixture was observed within 1–2 h after mixing either 2EPy or 4EPy with QA1. Polymerizations of both 2EPy or 4EPy resulted in the moderate to high yields of compact blocks of polymers within 72 h. The inactivity of 3EPy in polymerization with QA1 may be connected to the mesomeric effect of the nitrogen group in the pyridine ring. The triple bond of EPy monomers is in conjugation with the pyridine ring. The meta position of nitrogen group in 3EPy should lead to changes in electron density, manifested by a decrease of the acidity of ethynyl group. Polymers derived from 2EPy/QA1 and 4EPy/QA1 were labelled as EPyNet1 and EPyNet4, respectively (see Table 1). The elemental analysis results for EPyNet1 and EPyNet4 are given in Table S1 in the Supporting Information. Table S1 also contains the values of N:Br mole ratios calculated (for each polymer from this paper) independently from: i) Br and N weight contents, and ii) C and Br weight contents. The average of these two values is reported as the N:Br mole ratio of polymers in Table 1.

Blumstein et al.^[30] proposed a mechanism of the spontaneous polymerization of 2EPy with monofunctional QAs of the alkylhalogenide type. Adopting this mechanism for the polymerization of EPys with bifunctional QAs, one can assume several types of monomeric units to be present in the formed polymer networks. The structure and labelling of these units are given in Scheme 2 for the example of the polymer derived from 4EPy. Unit A in Scheme 2 represents the crosslinking unit in which two different pyridyl pendants of the main chains were quaternized by one QA molecule under formation of

bis(methylene)arene crosslink. In the linear unit B, only one CH₂Br group of a QA molecule was involved in the quaternization of the main chain pyridyl pendant while the second CH₂Br group remained unreacted. Unit C is a linear unit in which one CH₂Br group of the QA molecule was connected to the main chain pyridyl pendant while the second CH₂Br group quaternized an EPy molecule that was, however, not incorporated into the polymer main chain. Unit D represents the linear unit in which the pyridyl pendant was not quaternized. Some amount of non-quaternized (pyridyl)vinylene units was admitted to be present in the linear polymers based on 2EPy and monofunctional QAs^[37,40] although their formation was not involved in the mechanism of Blumstein et al. The ¹³C CP/MAS NMR and FTIR spectroscopy and the results of elemental analysis were used for the evaluation of the presence of the above-listed monomeric units in EPyNet1, EPyNet4, and in other polymers reported in this paper.

¹³C CP/MAS NMR spectra of EPyNet1 and EPyNet4 (Figure 1) contain a broad structured signal in the region 100–160 ppm, which corresponds to the resonance of: i) sp² carbons of aromatic rings of EPy and QA1 segments, and ii) sp² carbons of the polyene main chains. The signal at about 62 ppm corresponds to sp³ carbons of CH₂ groups of QA1 involved in the pyridine quaternization (CH₂ groups of N⁺–CH₂–Ar segments, see Scheme 2). Moreover, the ¹³C CP/MAS NMR spectrum of EPyNet1 contains a broad signal in the region 30–45 ppm. We ascribed this signal to sp³ carbons of CH₂ groups uninvolved in quaternization, (CH₂ groups of ArCH₂Br segments, see Scheme 2, units B). The presence of the B-type monomeric units in

EPyNet1 may be due to the difficulties in the reaction of ArCH₂Br pendants of units B with nitrogen of the pyridine ring that is sterically hindered by substitution in the position 2. Either absence, or only a small content (undetectable by ¹³C CP/MAS NMR spectroscopy) of the B-type monomeric units in EPyNet4 reflects the higher smoothness of the reaction of ArCH₂Br pendants of units B with sterically unhindered nitrogen of the 4-substituted pyridine ring. The ¹³C CP/MAS NMR spectra of both EPyNet1 and EPyNet4 do not contain any characteristic signals of carbons of terminal ethynyl groups (expected in the region 75–90 ppm). The absence of ethynyl groups in EPyNet1 and EPyNet4 was confirmed also by FTIR spectroscopy. FTIR spectra of EPyNet1 and EPyNet4 are given in Figure S1 in the Supporting Information. Evidently, both EPyNet1 and EPyNet4



Scheme 2. Possible types of monomeric units in networks derived from 4EPy. Ar stands for arylene core of QA.

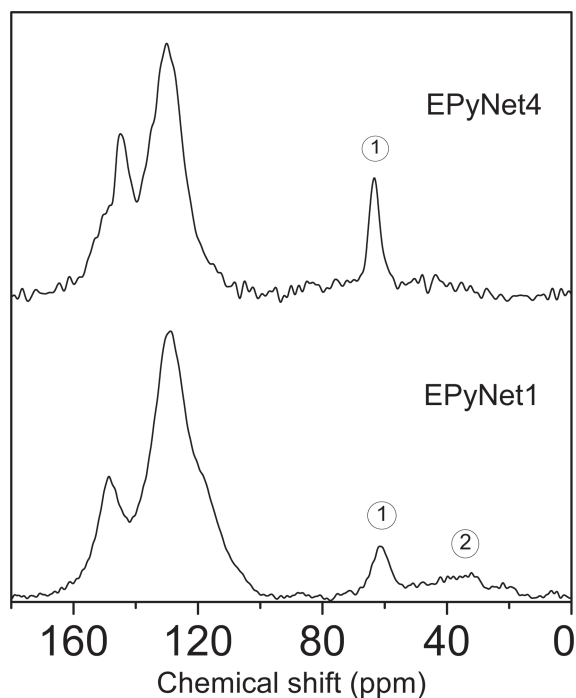


Figure 1. ^{13}C CP/MAS NMR spectra of EPyNet1 and EPyNet4. For sample codes see Table 1, for atoms labelling see Scheme 2.

did not contain the monomeric units of the C type. The EPyNet1 and EPyNet4 polymers exhibited a similar N:Br mole ratio, which was, in both cases, significantly higher than one (see Table 1). This means that non-quaternized units of the type D had to be present in both polymers. The mole ratio of non-quaternized to quaternized pyridine groups, $\text{N:N}^+ = 0.61:1$, resulted for EPyNet4, from the elemental analysis data, under the assumption that polymer did not contain CH_2Br groups (i.e., polymer was free of B-type units). Even higher N:N⁺ ratio for EPyNet1 can be assumed, owing to the B-type units present in the polymer. It can be concluded that the results of elemental analysis and the spectral characterization of newly

prepared polymers were in accord with the composition and structure proposed in Scheme 1: both EPyNet1 and EPyNet4 are polyacetylene-type networks in which the polyene main chains bear pyridiniumyl and pyridyl pendants. The crosslinking is achieved via interconnection of pyridiniumyl pendants by $-\text{CH}_2(\text{phenylene})\text{H}_2\text{C}-$ linkers. Two parameters are important for the evaluation of the extent of EPyNet1 and EPyNet4 crosslinking: i) the N:Br mole ratio in the polymer and ii) the content of B-type monomeric units. Since the N:Br ratio was similar for both polymers, one can state that EPyNet4 (free of B type units) was more crosslinked than EPyNet1 (containing B-type units). Evidently, both higher yield (Table 1) and higher crosslinking extent were achieved in the synthesis of 4EPy-based EPyNet4 than in the synthesis of 2EPy-based EPyNet1. Thus, 4EPy was selected as the monomer for the detailed studies.

Table 2 summarizes the results of polymerizations of 4EPy with QA1 in which the N:Br ratio of the polymerization feed was varied from 1:1 to 4:1. The codes of the prepared polymers are listed in Table 2, the results of elemental analysis of the polymers are available in Table S1 in the Supporting Information. The insoluble polymer yields of about 80% were achieved if the feeds with N:Br ratios of 1:1 and 2:1 were used. An increase of the N:Br ratio in the feed above 2:1 resulted in a lowering of the polymer yield to a value of about 50%. The determined N:Br ratio in the polymers (Table 2) varied from 0.98:1 to 2.31:1 and increased approximately linearly with increasing N:Br ratio in the polymerization feed (in the applied region of feed N:Br ratios).

^{13}C CP/MAS NMR spectra of polymers from Table 2 are given in Figure 2. Signals of terminal ethynyl carbons were not present in the spectra (i.e., none of the analyzed polymers contained C-type monomeric units) (see Scheme 2). The spectra of all the polymers showed a well-evident signal at 62 ppm (sp^3 carbons of $\text{N}^+-\text{CH}_2-\text{Ar}$ segments). On the other hand, a signal ascribable to sp^3 carbons of ArCH_2Br pendants was not unambiguously

Table 2. Polymerization of 4EPy with 1,4-bis(bromomethyl)benzene (QA1) performed at various N:Br mole ratio in the polymerization feed: solvent DMF, initial EPy concentration = 1.6 mol L^{-1} , reaction time 72 h, reaction temperature 70°C . Y is the yield of polymer, N:Br(polymer) is the N:Br mole ratio in the polymer, N:N⁺(polymer) is the mole ratio of non-quaternized and quaternized pyridine pendants in the polymer, c_{N} is the content of non-quaternized pyridine pendants in the polymer, c_{N^+} is the content of quaternized pyridine pendants in the polymer, $a_{\text{CO}_2, 750 \text{ Torr}}$ is the volume of CO_2 (in cm^3 at STP) adsorbed on 1 g of a polymer sample at 20°C (CO_2 pressure = 750 Torr).

Polymer code	N:Br (feed)	Y [%]	Units ^{a)}	N:Br (polymer)	N:N ⁺ (polymer)	c_{N^+} [mmol g ⁻¹]	c_{N} [mmol g ⁻¹]	$a_{\text{CO}_2, 750 \text{ Torr}}$ [cm ³ (STP) g ⁻¹]
EPyNet2	4:1	48	A, D	2.32:1	1.32:1	2.36	3.12	9.6
EPyNet3	3:1	50	A, D	1.85:1	0.85:1	2.76	2.35	11.9
EPyNet4	2:1	82	A, D	1.61:1	0.61:1	2.92	1.80	16.4
EPyNet5	1:1	79	A	0.98:1	0:1	3.11	0	10.2

^{a)}Type of monomeric unit (Scheme 2) prevailing in the polymer.

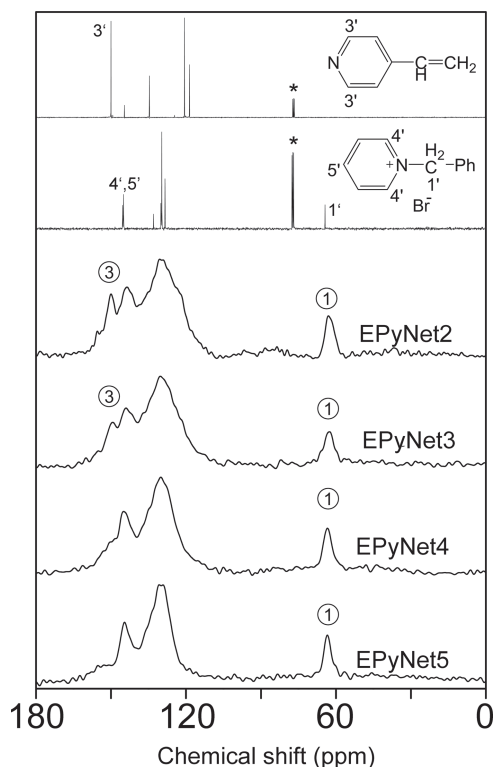


Figure 2. ^{13}C CP/MAS NMR spectra of polymers from Table 2 and ^{13}C NMR spectra (in CDCl_3) of 4-vinylpyridine and *N*-benzylpyridinium bromide. For codes of polymers see Table 2, for atoms labeling of polymers see Scheme 2.

found in the spectra of any of the samples. The character of the broad ^{13}C CP/MAS NMR spectroscopy signal in the sp^2 region (110–160 ppm) varied with the N:Br ratio of the analyzed polymers. The spectrum of EPyNet2 (N:Br = 2.32) contained partially resolved signal at 150 ppm. We believe this signal to be strongly contributed by the resonance of N–C(ring) carbons of the non-quaternized 4-pyridyl pendants. The support for this assignment comes from the ^{13}C NMR spectrum of 4-vinylpyridine (measured in CDCl_3), which is given for comparison in Figure 2. The intensity of the signal at 150 ppm was decreasing in the polymer series from EPyNet2 to EPyNet5. The resonance of ring-carbons in the vicinity to 4-pyridiniumyl nitrogen [^+N –C(ring) carbons] contributed to the signal at 144 ppm, which is well evident in the ^{13}C CP/MAS NMR spectra of all the samples in Figure 2. The support for this assignment comes from ^{13}C NMR spectrum of *N*-benzylpyridinium bromide (measured in CDCl_3 , see Figure 2). It should be noticed that also some other carbons of polymers most probably contributed to the ^{13}C CP/MAS NMR spectroscopy signal at 144 ppm. The results of ^{13}C CP/MAS NMR spectroscopy and elemental analysis allowed us to draw conclusions on the composition of polymers from Table 2: i) the types of monomeric units present in particular polymers are listed in Table 2. Linear units

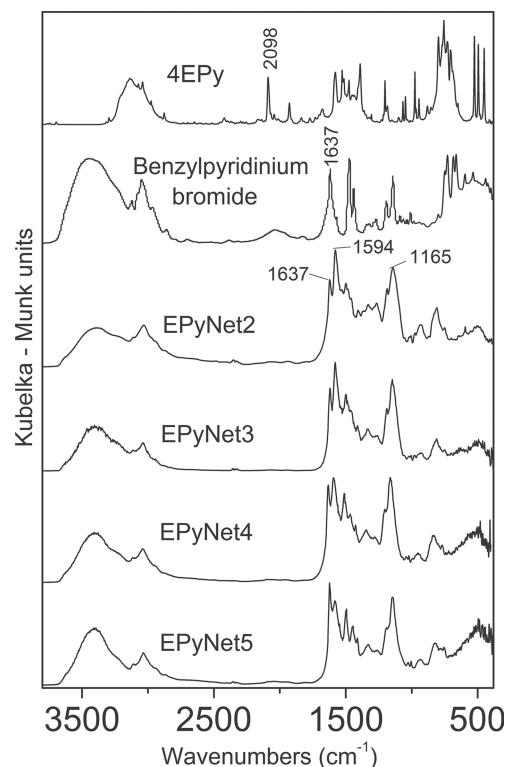


Figure 3. FTIR spectra of polymers from Table 2 and 4-ethynylpyridine and *N*-benzylpyridinium bromide. For codes of polymers see Table 2.

of the B type were either absent or present in a small amount (undetectable by ^{13}C CP/MAS NMR spectroscopy) in the polymers; ii) the N:N $^+$ mole ratio varied from 1.32 (EPyNet2) to 0 (EPyNet5); iii) the content of pyridiniumyl groups in the polymers, c_{N^+} , was in an interval from 2.36 mmol g^{-1} (EPyNet2) to 3.11 mmol g^{-1} (EPyNet5). The content of pyridyl groups in the polymers, c_{N} , varied from 0 mmol g^{-1} (EPyNet5) to 3.12 mmol g^{-1} (EPyNet2). Values of N:N $^+$, c_{N^+} , and c_{N} are summarized for individual polymers in Table 2; iv) the order in which the extent of polymers crosslinking was increasing can be estimated as follows: EPyNet2 < EPyNet3 < EPyNet4 < EPyNet5.

Figure 3 shows FTIR spectra of polymers from Table 2 together with spectra of 4Epy and *N*-benzylpyridinium bromide (see Experimental Section). The FTIR spectra of all the polymers contained a strong band at 1165 cm^{-1} that was assigned to the bending vibration of pyridinium ring. On the other hand, the signal due to the $\text{C}\equiv\text{C}$ bond stretching, well evident in the spectrum of 4Epy monomer at 2098 cm^{-1} , was not observed in the spectra of the polymers. The bands at about 1594 and 1637 cm^{-1} reflect C=C and C=N stretching of: i) main-chain double bonds, and ii) phenylene, pyridyl, and pyridiniumyl groups. The band at 1637 cm^{-1} was tentatively ascribed to the stretching of pyridiniumyl groups, since its position corresponded to that of the pyridiniumyl stretching

Table 3. Polymerization of 4EPy with various quaternizing agents: 1,4-bis(bromomethyl)benzene (QA1), 2,6-bis(bromomethyl)naphthalene (QA2), 4,4'-bis(bromomethyl)-1,1'-biphenyl (QA3), 2,2'-bis(bromomethyl)-1,1'-biphenyl (QA4), and (*R*)-2,2'-bis(bromomethyl)-1,1'-binaphthyl (QA5). N:Br mole ratio in the feed = 2:1, initial EPy concentration = 1.6 mol L⁻¹, solvent DMF, reaction time 72 h, reaction temperature 70 °C. Y is the yield of polymer, N:Br(polymer) is the N:Br mole ratio in the polymer, N:N⁺(polymer) is the mole ratio of non-quaternized and quaternized pyridine pendants in the polymer, c_N is the content of non-quaternized pyridine pendants in the polymer, c_{N+} is the content of quaternized pyridine pendants in the polymer, a_{CO₂,750 Torr} is the volume of CO₂ (in cm³ at STP) adsorbed on 1 g of a polymer sample at 20 °C (CO₂ pressure = 750 Torr).

Polymer code	QA	Y [%]	Units ^{a)}	N:Br (polymer)	N:N ⁺ (polymer)	c _{N+} [mmol g ⁻¹]	c _N [mmol g ⁻¹]	a _{CO₂,750 Torr} [cm ³ (STP) g ⁻¹]
EPyNet4	QA1	82	A, D	1.61:1	0.61:1	2.92	1.80	16.4
EPyNet6	QA2	81	A, D	1.60:1	0.60:1	2.68	1.61	12.2
EPyNet7	QA3	81	A, D	1.93:1	0.93:1	2.55	2.37	14.4
EPyNet8	QA4	72	A, D	1.97:1	0.97:1	2.50	2.43	4.7
EPyNet9	QA5	76	A, D	1.98:1	0.98:1	2.26	2.21	7.2

^{a)}Type of monomeric unit (Scheme 2) prevailing in the polymer.

band in the spectrum of *N*-benzylpyridinium bromide (see Figure 3). The band at 1594 cm⁻¹ might be contributed by the stretching of the pyridyl groups, since its wavenumber corresponds to that of pyridyl stretching in the spectra of 4EPy (see Figure 3) and 4-vinylpyridine.^[44] It is evident from Figure 3 that the ratio of intensities of bands at 1637 cm⁻¹ and 1594 cm⁻¹, I_{1637}/I_{1594} , in the spectra of the polymers increased in the polymer series from EPyNet2 to EPyNet5 (i.e., in parallel with decreasing N/N⁺ mole ratio in the polymers).

Table 3 summarizes the results of polymerizations of 4EPy with various QAs (mole ratio in the polymerization feed, N:Br = 2:1). Formulae of the applied QAs are given in Scheme 1, and the codes of the polymers prepared are listed in Table 3. High polymer yields ranging from 72 to 82% were achieved. The polymerizations were successful even if QAs with partly sterically hindered CH₂Br groups (i.e., QA4 and chiral QA5) were applied. The N:Br mole ratio in the polymers was in a narrow interval from 1.60:1 to 1.98:1. FTIR spectra of polymers from Table 3 are given in Figure S2 (Supporting Information). FTIR spectra confirmed absence of the ethynyl groups in the polymers. On the other hand, the variety in type of the QA used for the polymer synthesis was only marginally reflected in FTIR spectra: all the FTIR spectra were similar to that of EPyNet4 shown in Figure 3 and discussed above. The ¹³C CP/MAS NMR spectra of polymers shown in Figure 4 confirmed: i) the absence of ethynyl groups, and ii) presence of non-quaternized 4-pyridyl pendants [the signal at 150 ppm due to the resonance of N-C(ring) carbons] in all the polymers. Signals due to the resonance of ArCH₂Br carbons were not unambiguously confirmed in the spectra of any of the polymers, that is, linear units of the B type were either absent or present in a small amount (undetectable by ¹³C CP/MAS NMR spectroscopy) in the polymers from Table 3. On the other hand, signals due to the

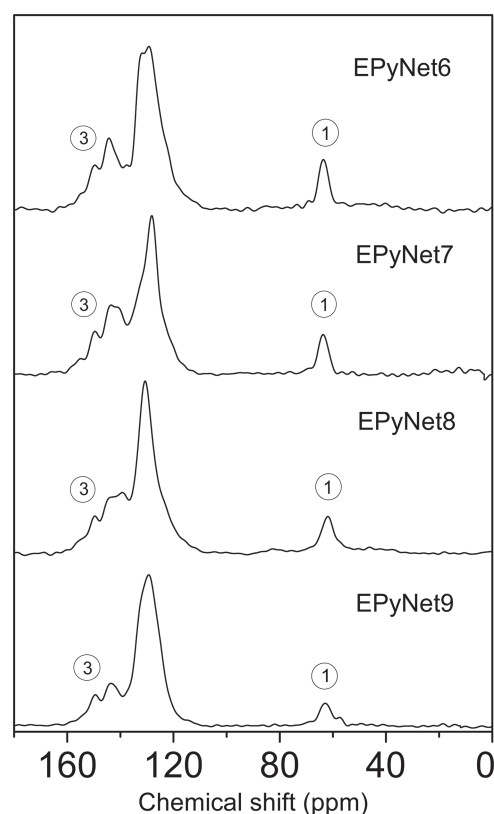


Figure 4. ¹³C CP/MAS NMR spectra of polymers from Table 3. For codes of polymers see Table 3.

resonance of N⁺-CH₂-Ar carbons at 62 ppm were present in the spectra of all the polymers. It can be thus concluded that polymers from Table 3 comprised predominantly A and D monomeric units.

The results summarized in Table 2 and 3 demonstrate the high efficiency and versatility of polymerization of 4EPy with bifunctional QAs. The reported highly

crosslinked pyridine-group-containing networks are easy to synthesize in the moderate to high yields. The composition and crosslinking extent of the networks can be partly controlled by the N:Br mole ratio in the polymerization feed and by the character of QAs. Two points are worth discussing in this connection: i) there are many contributions in the literature dealing with polymerization of equimolar mixtures of 2EPy with monofunctional QAs into linear soluble polymers (see Introduction). Polymers [reported as poly(*N*-alkyl-2-ethynylpyridinium halogenide)s] were mostly assumed to contain exclusively pyridiniumyl pendants connected to the polyene chains. Moreover, the quaternization of 2EPy was assumed as necessary for the 2EPy to be built into the polymer chain (as quaternized monomeric units). The results of our work showed that if the polymerization feed with the ratio of N:Br ≥ 2 was applied, the polymers contained (besides quaternized pyridiniumyl groups) also non-quaternized pyridyl pendants. Evidently, a certain amount of EPy units was incorporated into polymers without preceding quaternization under a shortage of QA in the reaction mixture. It may be probable that non-quaternized pyridyl-containing units could be, under proper conditions, incorporated into the linear polymers derived from EPys and monofunctional QA. ii) The high conversion of both CH_2Br groups of QA molecules incorporated into the polymer networks was achieved in the studied polymerizations. This ensured the high crosslinking extent of the products. The reaction of the first CH_2Br group of a QA molecule transformed this molecule into the part of *N*-[(4-(bromomethyl)benzyl)pyridinium-4-yl] pendant connected to the main chain. Considering the transformation of the remaining CH_2Br group of this pendant, one can assume two reaction modes: i) the CH_2Br group could react with an 4EPy molecule under the 4EPy quaternization followed by incorporation of the quaternized 4EPy as a new monomeric unit into the polymer chain (mechanism of Blumstein et al.). The latter stage of the reaction should be efficient since the reaction byproduct containing quaternized 4EPy in the pendant (units C in Scheme 2) was not detected in the polymers; ii) the CH_2Br group could be converted in a one-step reaction with the non-quaternized 4-pyridyl pendant of a properly oriented main chain segment.

3.2. Absorption and Photoluminescence Properties of Prepared Polymers

All the prepared polymers were brown-black brittle solids insoluble in tested solvents (DMF, THF, DMSO, CHCl_3 , ethanol, methanol, and water). Vis absorption spectra (Figure S3, Supporting Information) revealed the continuous absorption in the visible range either with no distinct maximum (EPyNet1, EPyNet8, and EPyNet9) or with

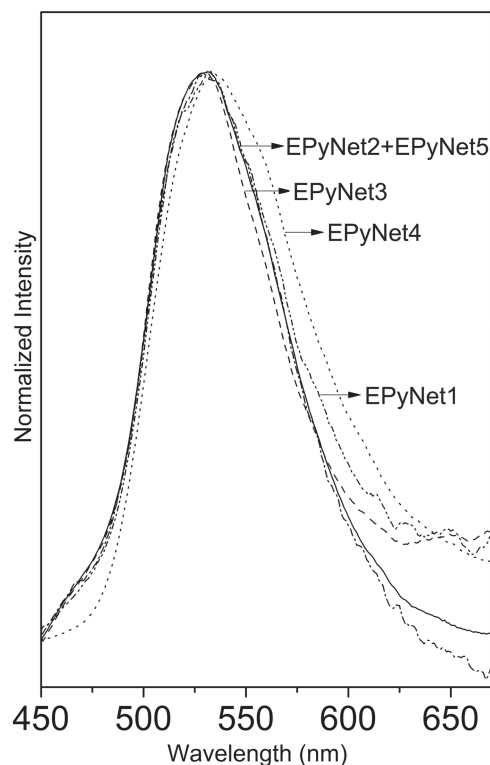


Figure 5. Photoluminescence spectra of polymers from Table 1 and Table 2. Excitation wavelength: 420 nm. For codes of polymers see Table 1 and Table 2.

a wide absorption maximum at 700–720 nm (other polymers). All the polymers exhibited PL when excited by light of wavelength 420 nm. The observed PL was most probably due to the conjugated main chains of polymers. The PL spectra of polymers containing QA1-derived linkers are shown in Figure 5: all the spectra contained similar broad PL emission bands with maximums ($\lambda_{\text{PL,max}}$) in the narrow wavelength interval from 530 to 535 nm without any systematic dependence on: i) the positional isomerism of the EPy monomer (2EPy or 4EPy) and ii) the N:Br mole ratio in the polymers. The PL spectra of polymers prepared from 4EPy and various QAs are shown in Figure 6. Polymers EPyNet4 and EPyNet8 exhibited similar broad PL bands with $\lambda_{\text{PL,max}} = 535$ nm. The PL emissions bands of EPyNet6, EPyNet7 and EPyNet9 were narrower and slightly blue shifted ($\lambda_{\text{PL,max}} = 529$). This blue-shift may reflect a lower extent of conjugation of EPyNet6, EPyNet7 and EPyNet9 compared with EPyNet4 and EPyNet8. The intensive absorption in the vis range (ascribed to the main chain conjugation) and PL with $\lambda_{\text{PL,max}}$ from 500 to 600 nm were reported for various linear poly(*N*-alkyl-2-ethynylpyridinium halogenide)s in the literature.^[35,38] Our results showed that these two properties were preserved also in the case of the crosslinked form of the EPy-based polyacetylenes reported herein.

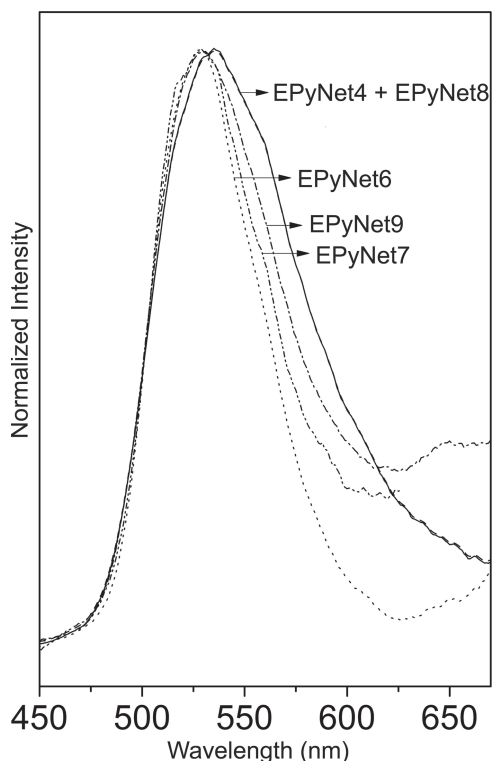


Figure 6. Photoluminescence spectra of polymers prepared from 4EPy and various QAs. Excitation wavelength: 420 nm. For codes of polymers see Table 2 and Table 3.

3.3. CO₂ Adsorption on Prepared Polymers

The prepared polymers were mostly highly crosslinked and possessed the high content of aromatic segments. These parameters indicated that the prepared polymers might exhibit micro/mesoporosity and activity in the gas adsorption. However, the standard characterization by nitrogen adsorption revealed that all the polymers adsorbed only negligible amounts of nitrogen at 77 K. On the other hand, all the polymers were found to be active in CO₂ capture at 293 K. Carbon dioxide adsorption/desorption isotherms on EPyNet1 and EPyNet4 are given in Figure 7. Both isotherms showed hysteresis down to low equilibrium pressures. The hysteresis reflected a difference in the mechanism of CO₂ adsorption and desorption and it simultaneously implied that CO₂ was captured into the pores of EPyNet1 and EPyNet4. This explanation is based on the supposition that some porosity is formed in EPyNet1 and EPyNet4 under the conditions of CO₂ capture despite the fact that no pores were recognized in these materials by N₂ adsorption. The polymer networks reported in this study (Scheme 1) contain CH₂ bridges between the aromatic cores of the QA-derived linkers and main chain units (see Scheme 1). These CH₂ groups may introduce certain conformation flexibility into the networks. We speculate that the networks possessed rather compact nonporous conformation at 77 K due

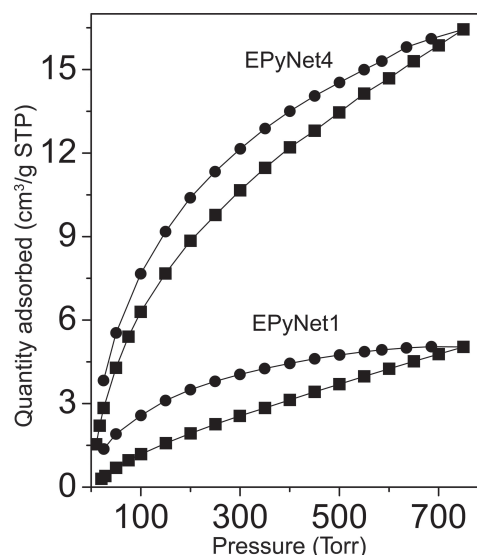


Figure 7. CO₂ adsorption/desorption isotherms (20 °C) on polymers EPyNet1 and EPyNet4 (adsorption – squares; desorption – circles). For codes of polymers see Table 1.

to the interactions between segments. The conformation compactness can be, however, disturbed with increasing temperature as the result of unrestricted rotation along–CH₂– bonds. This may lead to the formation of some pores accessible for CO₂ at 293 K. Moreover, the penetration of CO₂ into the polymer can induce formation of other non-permanent pores via the swelling mechanism as already discussed by Weber et al.^[45] in connection with gases being captured in the soft micro/mesoporous polymers. An indirect support for our hypothesis can also be found in the literature dealing with the CO₂ capture on various micro/mesoporous polymers. In some cases, the high CO₂ captures were reported for the materials with rather low specific surface area resulting from N₂ adsorption measurements at 77 K (e.g., microporous polyimide reported by Ritter et al.^[46]) exhibited CO₂ uptake of 1.58 mmol g^{−1} (273 K, 1 bar) although its specific surface area determined by N₂ adsorption at 77 K was only 57 m² g^{−1}.

Figure 7 shows that EPyNet1 exhibited a lower efficiency in CO₂ capture compared with EPyNet4. This may reflect the presence of B-type units in EPyNet1 (Scheme 2, Table 1) since these units do not contribute to the polymer crosslinking and simultaneously enhance the mass of the polymer. The comparison of CO₂ adsorption isotherms on polymers from Table 2 is given in Figure 8. The desorption branches on all the polymers had the character shown in Figure 7 (they were not incorporated into Figure 8 for a better clarity). The CO₂ uptakes, $a_{\text{CO}_2, 750 \text{ Torr}}$, are summarized in Table 2 where also the definition of this characteristic is given. The CO₂ uptake increased in the polymer series EPyNet2 < EPyNet5 < EPyNet3 < EPyNet4, that is, it passed through a maximum in dependence on the structural and

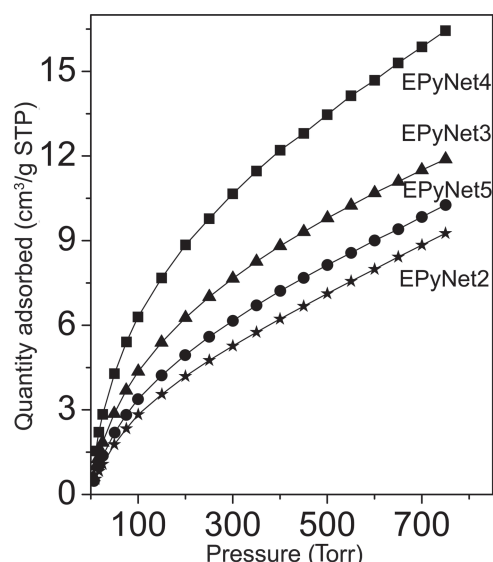


Figure 8. CO₂ adsorption isotherms (20 °C) on polymers from Table 2. For codes of polymers see Table 2.

compositional parameter of polymers from Table 2 (extent of crosslinking, c_{N+} , and c_N parameters). It is known from the literature that CO₂ uptake by micro/mesoporous materials is enhanced by functionalization of these materials with amine nitrogen-containing groups as a result of N to CO₂ attracting interactions.^[47–50] The presence of the D-type units with slightly basic pyridyl groups in our polymers may be assumed as favorable for the CO₂ capture. Nevertheless, the highest CO₂ uptake was not achieved for EPyNet2 (i.e., for the sample with the highest D unit content). This was most probably due to the reduced extent of crosslinking of EPyNet2. Evidently, there was an optimal composition and crosslinking extent of polymers derived from 4EPy and QA1 for an efficient CO₂ capture. The structure and composition of EPyNet4 probably approached the most this optimum.

The values of $a_{\text{CO}_2, 750 \text{ Torr}}$ for the polymers prepared from 4EPy and various QAs are summarized in Table 3. The CO₂ adsorption isotherms on these polymers are given as Figure S4 in the Supporting Information. QAs with sterically unhindered CH₂Br groups (QA1, QA2, and QA3) provided polymers with values of $a_{\text{CO}_2, 750 \text{ Torr}}$ ranging from 12.2 to 16.4 cm³(STP) g^{−1}. QAs with partly sterically hindered CH₂Br groups (QA4 and QA5) provided polymers with reduced $a_{\text{CO}_2, 750 \text{ Torr}}$ values (4.7 and 7.2 cm³(STP) g^{−1} respectively). The reduction of $a_{\text{CO}_2, 750 \text{ Torr}}$ values might be contributed by suppression of the pore formation in these polymers due to the partly restricted rotation along the CH₂– bonds. As is evident from Table 2 and 3, the highest $a_{\text{CO}_2, 750 \text{ Torr}}$ value achieved for our polymers was equal to 16.4 cm³(STP) g^{−1}. This corresponds to the medium CO₂ uptakes (at 293 K) reported for various micro-/mesoporous polymers in the literature.^[51,52]

4. Conclusion

The polymerization of 4EPy and 2EPy with quaternizing agents of the bis(bromomethyl)arene type is shown as an efficient tool for the preparation of highly crosslinked networks with pyridine-derived segments. The polymerization proceeded as a spontaneous catalyst-free reaction (i.e., the networks did not contain catalyst residue). The prepared partly conjugated networks consisted of polyacetylene main chains substituted by pyridiniumyl and pyridyl groups. The crosslinking was achieved via interconnection of pyridiniumyl pendants by –CH₂(arylene)H₂C– linkers. The ¹³C CP/MAS NMR and FTIR spectroscopy techniques were found to be efficient for the study of composition and structure of the networks. The variation of the ratio of the amount of 4EPy to that of the quaternizing agent in the polymerization feed allowed us to synthesize networks differing in: i) the content of pyridiniumyl and pyridyl groups, and ii) the extent of crosslinking. The easily accessible diversity in the networks composition and structure is beneficial for potential applications of these materials. The presence of non-quaternized pyridyl groups in the polymers may be interesting for eventual postpolymerization modifications involving reactions via the lone electron pair on the nitrogen atom (e.g., post-polymerization quaternization, complexation of metal ions, etc.).

The reported networks were photoluminescent when excited at 420 nm and captured carbon dioxide at 293 K. Moderate values of CO₂ uptakes up to 16.4 cm³(STP) g^{−1} were achieved (293 K, equilibrium CO₂ pressure 750 Torr). CO₂ is assumed to be captured into the pores created in the networks at room temperature owing to the conformation changes enabled by the presence of CH₂ groups in the linkers connecting the segments of the main chains.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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