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Polymer 44 (2003) 4487–4490

polymer

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Preparation of a new poly(p-phenylene) type polymer, poly(pyrazine-2,5-diyl), with a coplanar structure

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Received 10 March 2003; received in revised form 26 May 2003; accepted 26 May 2003

Abstract

Poly(pyrazine-2,5-diyl), PPyrz, was prepared by organometallic dehalogenative polycondensation of 2,5-dibromopyrazine. PPyrz was soluble in conc. H_2SO_4 and showed an η/c value of 0.45 dl g^{-1}. PPyrz exhibited the UV–vis peak at the longest wavelength ($\lambda_{max} = 439$ nm) among the poly(p-phenylene) type polymers. The polymer afforded a simple CP-MAS solid ^{13}C NMR pattern with peaks at δ 143.3 and 148.5. Microwave-assisted synthesis was effective.

Keywords: Poly(pyrazine-2,5-diyl); Poly(p-phenylene) type polymer; Coplanar structure

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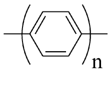
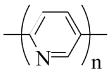
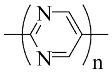
1. Introduction

Poly(p-phenylene), PPP, is one of the most fundamental π-conjugated polymers [1–4], and modification of PPP by replacing the CH group of PPP by nitrogen(s) has been carried out to produce, e.g. poly(pyridine-2,5-diyl), PPy [5], and poly(pyrimidine-2,5-diyl), PPyrim [6].

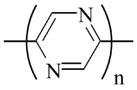

PPP


PPy


PPyrim

According to the CH-to-N replacement, the polymers attain interesting chemical properties such as metal complex forming reactivity and higher chemical and electrochemical reducibility.

Preparation and revealing chemical properties of poly(pyrazine-2,5-diyl), PPyrz, have also attracted attention [7,8], however, successful preparation of PPyrz has not been reported.


PPyrz

The CPK molecular model of PPyrz indicates that this polymer forms a planar main chain which is advantageous for formation of highly π-conjugated main chain. On the other hand, the previously prepared polymer such as PPy and PPyrim are considered to receive o-hydrogen repulsion to cause twisting of the bond in the main chain; if synthesis of head-to-tail type PPyrim is possible, the polymer is also considered to have a coplanar structure.

Herein we report synthesis of PPyrz via an organometallic polycondensation using a zerovalent nickel complex. Microwave-assisted organic synthesis including polymer synthesis [9] is currently attracting interest and applicability of this method for the present polymer synthesis has also been tested.

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doi:10.1016/S0032-3861(03)00442-7

2. Experimental

2.1. Synthesis of PPyrz

The monomer, **1**, 2,5-dibromopyrazine, was prepared according to the literature [10,11]. Dehalogenative polycondensation [1,5–8] of the monomer was carried out by using a mixture of bis(1,5-cyclooctadiene)nickel(0), Ni(cod)$_2$, and 2,2′-bipyridyl, bpy, with and without irradiation with microwave. For the polycondensation under irradiation with microwave, a CEM Discover apparatus was used.

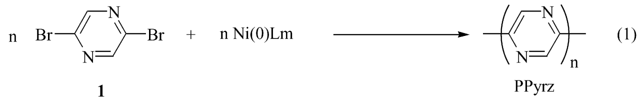
A dry DMF (35 ml) solution containing **1** (620 mg, 2.62 mmol), Ni(cod)$_2$ (1.44 g, 5.23 mmol), bpy (830 mg, 5.28 mmol), and 1,5-cyclooctadiene (570 mg, 5.23 mmol) was stirred at 60 °C for two days. The reaction mixture was poured into methanol. The precipitate was separated by filtration and worked-up including treatment with an aqueous ammonia solution of dimethylglyoxime and ensuing washing with diluted hydrochloric acid [12] to obtain 162 mg (yield = 79%) of PPyrz. Use of a larger polymerization system with 2.6 g of **1** gave PPyrz in a higher yield (93%). Use of toluene as the polymerization solvent, instead of DMF, and the polymerization under irradiation with microwave also gave PPyrz. PPyrz's prepared under the various conditions gave the same IR spectrum. The polycondensation under irradiation with microwave was carried out in a smaller (about 1/10) scale due to the limitation of the cavity (yield = 83%). In this case, 10 min of the polymerization time was enough. PPyrz seems to contain hydration water, similar to cases of N-containing heteroaromatics (e.g. bpy) and heteroaromatic polymers. CP-MAS solid ^{13}C NMR: δ : 143.3, 148.5. Anal. calcd for $(C_4H_2N_2)_n$: C, 61.54%; H, 2.58%; N, 35.88%. Calcd for $(C_4H_2N_2\ 0.25\ H_2O)_n$: C, 58.18%; H, 3.05%; N, 33.92%. Found: C, 58.86%; H, 3.53%; N, 32.85%; Br, 0%.

2.2. Measurements

UV–vis and photoluminescence (PL) spectra were recorded on Shimadzu UV-3100PC and Hitachi F-4010 Spectrometers, respectively. Solid ^{13}C NMR spectra were obtained with a JEOL EX 270 spectrometer. Viscosity was measured with an Ubbelohde viscometer.

3. Results and discussion

The dehalogenative polycondensation of 2,5-dibromopyrazine, **1**, with the zerovalent complex under usual conditions [1,5–8] gave PPyrz in high yield.



(1)

For purification of PPyrz, washing with an aqueous solution of dimethylglyoxime [12] was effective to remove nickel complex(es) included in the crude polymer; PPyrz showed almost negligible content of ash. It was difficult to remove well the nickel complex(es) included in the crude polymer by washing the crude polymer with an aqueous solution of EDTA, although this washing method was effective to remove nickel from usual π-conjugated polymers such as PPP and PPy [1,5–8]. This is considered to be due to a strong coordinating ability of PPyrz with nickel, and may be the reason why the tried preparation (or isolation) of PPyrz was unsuccessful.

As described above, PPyrz could be obtained without irradiation with microwave, however, irradiation with microwave contributed much to shorten the polymerization time in accord with the previous report [9]. PPyrz prepared without irradiation with microwave was assigned to PPyrz-1, and that prepared under irradiation with microwave to PPyrz-2; PPyrz-2 seemed to have a higher molecular weight as discussed later.

PPyrz was a brown polymer and soluble in conc. H_2SO_4. The brown color of the conc. H_2SO_4 solution was similar to that of solid PPyrz. This result suggests the interaction of PPyrz with H_2SO_4 is not so strong. Addition of the conc. H_2SO_4 solution of PPyrz into an excess amount of water gave a brown solid, and treatment of the brown solid with aqueous ammonia recovered original PPyrz as judged from IR data.

Fig. 1 shows CP-MAS solid ^{13}C NMR spectrum of PPyrz-1. The ^{13}C NMR spectrum shows a simple pattern with two absorption peaks in accord with the structure of PPyrz.

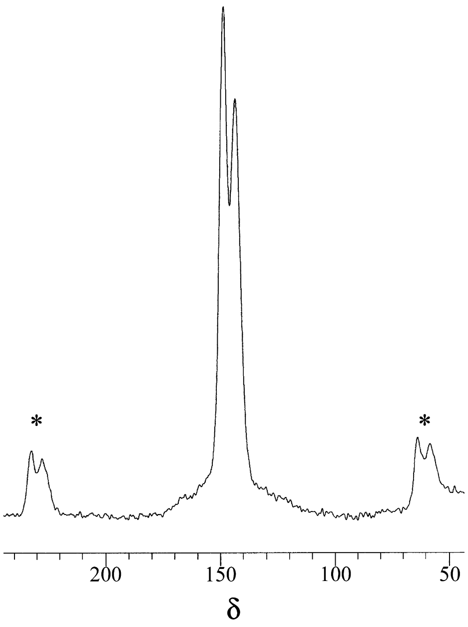
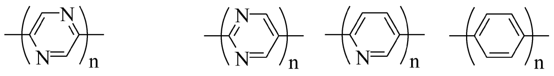


Fig. 1. CP-MAS solid ^{13}C NMR spectrum of PPyrz-1. The peaks with the * mark are due to spinning side band.

Fig. 2 compares UV–vis spectra of pyrazine and PPyrz in conc. H_2SO_4. According to the expansion of the π-conjugation system, the $\pi-\pi^*$ absorption peak of pyrazine at 284 nm is shifted to 439 nm for PPyrz-1, as shown by the chart (b) in Fig. 2. The absorption peak of PPyrz is located at the longest wavelength among the poly(*p*-phenylene) type polymers as expected from the coplanar structure of PPyrz.



PPyrz PPyrim PPy PPP

λ_{max} 439 nm > 360 - 380 nm
(e.g., 361 nm for PPyrim in conc. H_2SO_4 [6])

The chart (b) in Fig. 2 exhibits a shoulder peak at about 455 nm, and this shoulder peak becomes stronger for PPyrz-2 prepared under irradiation with microwave as seen in the chart (c) in Fig. 2. Since molecular assembly of π-conjugated polymer often causes a red shift of the UV–vis peak due to intermolecular electronic interaction [8], the shoulder peak may be assigned to a $\pi-\pi^*$ transition in assembled PPyrz molecules. This assembly, if it occurs, seems to take place more preferably with PPyrz-2 prepared under irradiation with microwave, since the peak at the (459 nm) becomes the major peak for PPyrz-2 as shown in Fig. 2. The conc. H_2SO_4 solutions of PPyrz-1 and PPyrz-2 gave η/c values of 0.25 and 0.45 dl g^{-1} (dl = 100 ml) at c = about 0.2 g dl^{-1} at 30 °C. These data indicate that PPyrz-2 has a higher molecular weight. Molecular interaction of π-conjugated polymers in solutions seems to be enhanced by the increase in the molecular weight [14].

Broadening of the chart (c) in Fig. 2, especially the rise of the absorption band in a range of about 500–570 nm, suggests formation of molecular aggregate(s) with a higher order of aggregation for PPyrz-2. For example, it is conceivable that the peak at 459 nm originates from a bimolecular adduct and the molecular aggregates with higher orders of aggregation give absorption bands in the range of 500–570 nm.

PL spectrum of PPyrz-1 shows a main peak at 477 nm, a sub-peak at 507 nm, and a small shoulder peak at about 550 nm. Appearance of a similar couple of main and sub-PL peaks has often been observed with π-conjugated molecules including π-conjugated polymers [5,15–19], and the PL peak at a longer wavelength has sometimes been assigned to emission from assembled π-conjugated molecules. The observed PL peaks at 477 and 507 nm for PPyrz-1 seem to correspond to the onset positions of the absorption bands at 439 and 455 nm, respectively, and are tentatively assigned to emissions from the single polymer molecule and the molecular assembly composed of two polymer molecules. The weak shoulder PL peak at 550 nm may be due to the aggregate with the higher order of aggregation. An interesting finding about PL is that both excitation spectra monitored at the PL peaks of 477 and 507 nm give essentially the same excitation spectrum with peaks at 436 and 457 nm; both the peaks correspond well to the 439 and 455 nm absorption peaks of PPyrz-1. This indicates that even the absorption at 457 nm (or at 455 nm in the UV–vis spectrum) can cause emission at 477 nm, and implies that the bimolecular assembly, if it is formed, can release photoactivated single polymer molecule, which emits 477 nm light, after absorption of 457 nm light. Irradiation with 457 nm light caused emission of the couple of the 477 nm main peak and 507 nm sub-peak and a weak peak at

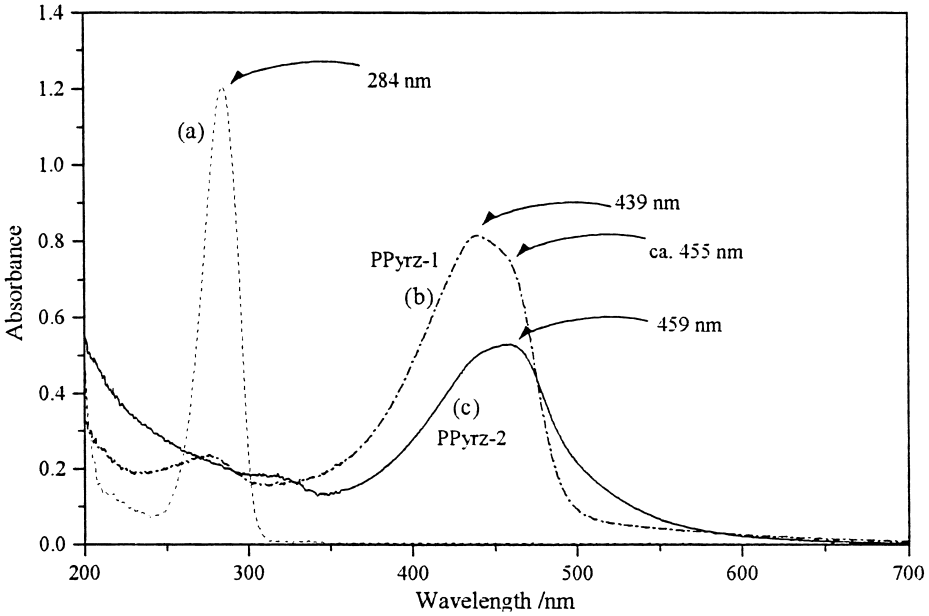


Fig. 2. UV–vis spectra of pyrazine and PPyrz prepared in DMF. (a) Pyrazine. (b) PPyrz-1 prepared without irradiation with microwave. (c) PPyrz-2 prepared under irradiation with microwave. All the spectra were measured in conc. H_2SO_4. Pyrazine gives the UV–vis peak at 261 nm in usual organic solvents [13].

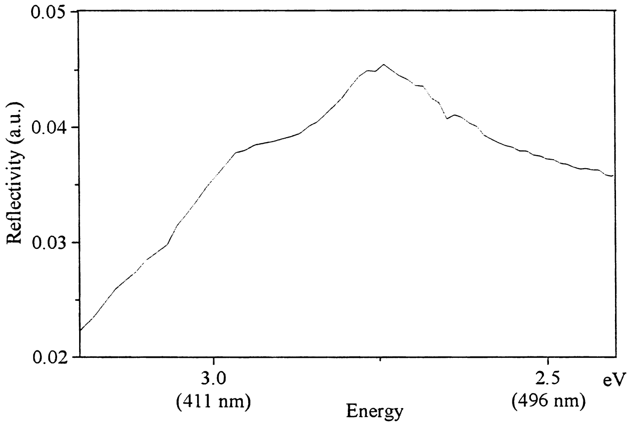


Fig. 3. Reflection spectrum of PPyrz-1. Compressed powder was used.

about 550 nm. Such a small Stokes shift from 457 to 477 nm is rare for PL of organic and inorganic molecules. PPyrz-2 gave essentially the same PL and excitation spectra and no obvious PL in longer wavelength was observed. These findings, particularly the latter finding, suggest that the molecular aggregates with the higher order of aggregation, which show the UV–vis absorption in the range of 500–570 nm as described above, did not contribute much to the PL.

PPyrz seems to be protonated, at least partly, in conc. H_2SO_4, although the degree of the protonation is not considered to be high as discussed above. Measurement of UV–vis absorption of non-protonated PPyrz was difficult since PPyrz was not soluble in non-acidic solvents. However, the reflection spectrum of a pressed pellet of PPyrz shown in Fig. 3 indicates that PPyrz has the UV–vis absorption peak at the position comparable to that observed in conc. H_2SO_4. The similarity in color between the powder of PPyrz and the conc. H_2SO_4 solution of PPyrz supports this view.

In summary, a new poly(*p*-phenylene) type polymer, PPyrz, which is considered to have a coplanar structure, has been prepared and characterized.

Acknowledgements

We are grateful to Professor T. Kanbara and Mr T. Kushida of our laboratory for helpful discussion. This research was partly supported by the 21st Century COE program.

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