



BEADED 4-VINYLPYRIDINE–STYRENE–DIVINYLBENZENE COPOLYMER: SYNTHESIS AND CATALYTIC ACTIVITY IN THE FORMATION OF ORGANIC CARBONATES FROM EPOXIDES AND CO₂

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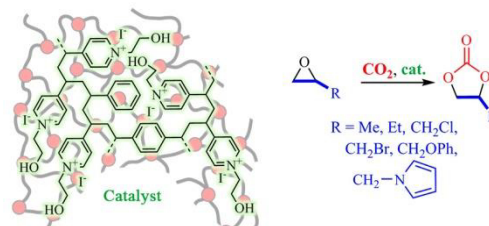
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Abstract

A beaded 4-vinylpyridine–styrene–divinylbenzene copolymer was obtained and modified by the quaternization of the pyridine units with 2-chloroethanol and the anion exchange with iodine. The resulting ionic polymer can be recycled for seven consecutive runs without loss of conversion in the addition of CO₂ to epoxides.

Key words: epoxides, CO₂ fixation, 4-vinylpyridine–styrene–divinylbenzene copolymer, suspension polymerization.



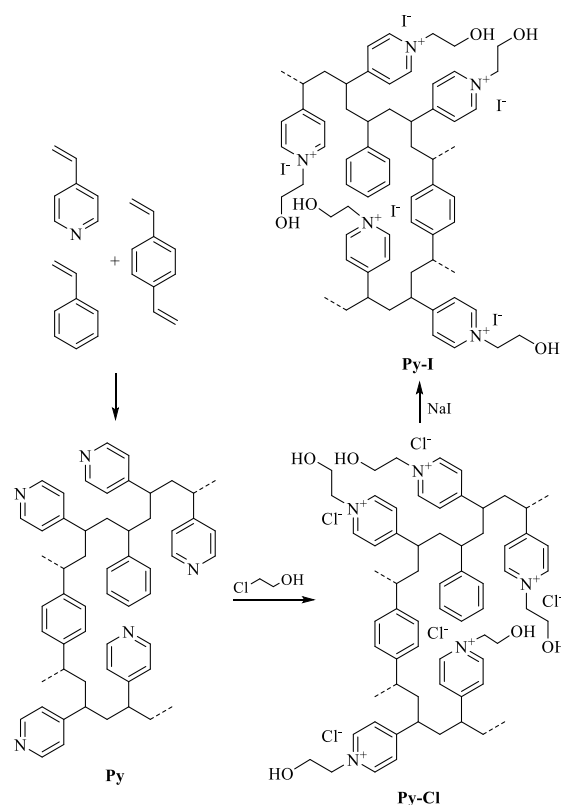
Introduction

Organic carbonates are widely used as fuel additives, polar solvents, in particular, in lithium-ion batteries, monomers for the production of polycarbonates and non-isocyanate polyurethanes [1]. One of the convenient approaches to the synthesis of organic carbonates is the addition of CO₂ to epoxides [2–4]. Nowadays, a variety of transition metal complexes, ionic liquids, as well as non-metallic catalysts such as organic ammonium, imidazolium, and phosphonium salts, including those covalently or weakly bound to solid carriers, are used as catalysts for this process [5–7]. The advantages of heterogeneous catalysts are the ease of separation from reaction products and the possibility of recycling. In this respect, beaded heterogeneous catalysts can be very convenient in use owing to the possibility of easy filtration. One of the approaches to the production of beads is the suspension polymerization, during which monomers (and an organic solvent) featuring low water solubility are dispersed with a stabilizer and agitation in the form of liquid drops to afford solid spherical particles after polymerization completion. The addition of a cross-linking agent to the system leads to the formation of interline bonds in the polymer, which enable the dissolution of the resulting polymer in any media. In the case of vinyl-containing polymers, the most commonly used cross-linking agent is divinylbenzene. One of the attractive candidates for the introduction of a nitrogen-containing polymeric moiety, which is necessary to obtain the catalysts for the addition of CO₂ to epoxides, is 4-vinylpyridine. Furthermore, it is known that the presence of hydroxy groups in the catalyst can provide an additional activating effect on this process [4, 8].

In this communication, we present the preparation of a beaded 4-vinylpyridine–styrene–divinylbenzene copolymer and its modification by the quaternization of the pyridine units with 2-chloroethanol, as well as the application of this new cross-linked anion-exchange resin in the addition of CO₂ to epoxides.

Results and discussion

The beaded copolymer (with the particle sizes of 0.4–0.8 mm) was obtained by the radical suspension copolymerization of 4-vinylpyridine, divinylbenzene, and styrene (70%, 6%, and 24%, respectively) in the presence of benzoyl peroxide at 80 °C for 8 h (Scheme 1). It should be noted that in the absence of



Scheme 1. Synthesis and modification of the pyridine-containing polymer.

styrene, the resulting granules are mechanically unstable and decompose during isolation and polymer-analogous transformations. Treatment of the product obtained with 2-chloroethanol in toluene resulted in a quaternized derivative (Scheme 1). The structure of the latter was confirmed using IR spectroscopy (Fig. 1). Thus, the characteristic absorption band of out-of-plane C–H vibrations of the 4-vinylpyridine and styrene units at 702 cm^{-1} appeared to be greatly weakened in the IR spectrum of the product, while the band at 819 cm^{-1} (Py) shifted to the higher frequencies (843 cm^{-1} , Py-Cl). A new intense band was observed at 1070 cm^{-1} , which can be attributed to the C–O stretching vibrations of the 2-ethanol moiety. The configuration of the bands that correspond to the bending vibrations of the pyridine units and aliphatic CH bonds at $1170\text{--}1620\text{ cm}^{-1}$ (Py) significantly changed, with the most characteristic difference being the shift of the intense band at 1596 cm^{-1} (Py) to 1620 cm^{-1} (Py-Cl). The IR spectrum of the product also showed a broad band of OH stretches at $3200\text{--}3400\text{ cm}^{-1}$.

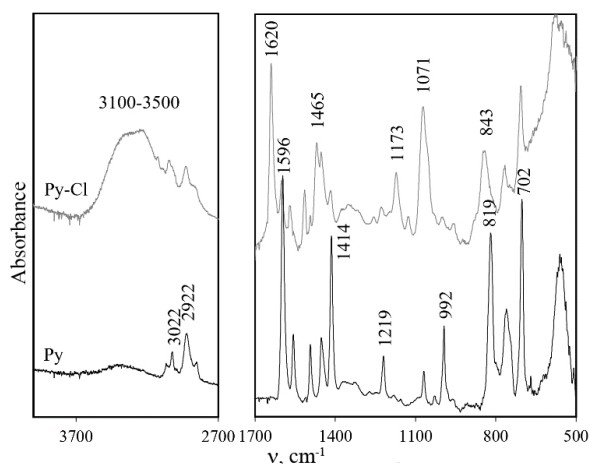
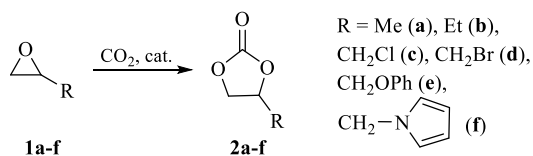


Figure 1. ATR IR spectra of the initial copolymer and the product of its interaction with 2-chloroethanol.

The quaternized product was treated with an aqueous solution of sodium iodide to substitute the chloride anion for iodide, which is a well-known technique for increasing the catalyst efficiency [9].

The resulting polymers (Py-Cl and Py-I) were tested for the catalytic activity in the reaction of CO_2 (10 atm) with propylene oxide (**1a**, Scheme 2) used as a substrate at $120\text{ }^\circ\text{C}$ for 4 h.



Scheme 2. Synthesis of organic carbonates.

The results obtained show that Py-I is much more effective than Py-Cl (Table 1, entries 1 and 2), which can be associated with the nature of the leaving groups (halide ions) in the catalytic cycle [4]. An increase in the CO_2 pressure in the case of Py-I positively affected the substrate conversion (entry 3). The following temperature rise to $130\text{ }^\circ\text{C}$ provided the quantitative conversion to target carbonate **2a** (entry 4). It

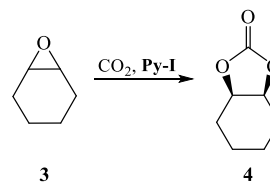
should be noted that the catalyst can be recycled, affording the complete conversion in seven consecutive runs, although a slight decrease in its efficiency was observed in the 8th run. The reaction with epoxide **1b** bearing a more electron-donating ethyl group compared to substrate **1a** (Scheme 2) required a longer time to achieve the complete conversion (entries 5, 6). The catalytic system also proved to be active in the case of monosubstituted epoxides **1c-f** (entries 7–10).

Table 1. Results of the catalytic experiments with the polymers obtained

Entry	Cat.	Oxirane	P, atm	T, $^\circ\text{C}$	t, h	Conversion (yield), %
1	Py-Cl	1a	10	120	4	10
2	Py-I	1a	10	120	4	80
3	Py-I	1a	56	120	4	87
4	Py-I	1a	56	130	4	100 (92) ^a
5	Py-I	1b	56	130	4	83
6	Py-I	1b	56	130	5	100 (91)
7	Py-I	1c	56	130	5	100 (91)
8	Py-I	1d	56	130	5	100 (92)
9	Py-I	1e	56	130	5	100 (90)
10	Py-I	1f	56	130	5	100 (87)

^a conversion after the 7th run: 100%, 8th run: 92%, 9th run: 87%.

In addition, catalyst Py-I effectively catalyzed the reaction of a challenging substrate, namely, cyclohexene oxide **3** with CO_2 (56 atm, $130\text{ }^\circ\text{C}$), affording 100% conversion in 20 h (Scheme 3).



Scheme 3. Addition of CO_2 to cyclohexene oxide.

Experimental section

General remarks

The ^1H (400.13 MHz) and ^{13}C (100.61 MHz) NMR spectra of the products of the catalytic experiments were recorded on a Bruker Avance 400 spectrometer in CDCl_3 . 4-Vinylpyridine, styrene, 80% divinylbenzene, benzoyl peroxide, 2-methyloxirane (**1a**), 2-ethyloxirane (**1b**), 2-chloromethyloxirane (**1c**), 2-bromomethyloxirane (**1d**), 2-(phenoxymethyl)oxirane (**1e**), and cyclohexene oxide (**3**) were purchased from commercial sources (Sigma-Aldrich or Acros). 1-(Oxiran-2-ylmethyl)-1-pyrrole (**1f**) was obtained according to the published procedure [10]. 4-Vinylpyridine was purified prior to the experiments by mixing with diethyl ether (1/2 volume ratio), centrifuging to remove oligomeric impurities, filtering through silica gel, and evaporating under reduced pressure to remove the solvent.

Syntheses

Copolymerization of 4-vinylpyridine, divinylbenzene, and styrene (synthesis of Py). A three-neck round-bottom flask equipped with a condenser, a thermometer, and an anchor stirrer was charged with 15 mL of an aqueous phase (NaNO_2 (0.015 g,

0.22 mmol), NaCl (4.95 g, 84.60 mmol), PVA (0.50 g; $M_w = 85000\text{--}124000$, 87–89% hydrolyzed), and KOH (0.20 g, 3.57 mmol) in 150 mL of deionized water). Then the organic phase containing 4-vinylpyridine (2.02 mL, 19.06 mmol), divinylbenzene (0.29 mL, 1.63 mmol), styrene (0.74 mL, 6.53 mmol), isobutanol (1.025 mL), octane (1.025 mL), and benzoyl peroxide (0.77 g, 2.38 mmol) was dispersed in the solution. The copolymerization was carried out under constant stirring at 400 rpm and 80 °C for 8 h. The resulting beads were filtered off, rinsed with acetone, ethanol, and deionized water. Then they were kept in a drying chamber at 60 °C for 3 h. Yield: 2.70 g (93%). Anal. Found: C, 81.14; H, 7.07; N, 8.78%.

Quaternization of copolymer Py with 2-chloropropanol (synthesis of Py-Cl). A three-neck round-bottom flask equipped with a condenser, a thermometer, and an anchor stirrer was charged with Py (0.50 g), 2-chloropropanol (0.317 mL), and toluene (3 mL). The reaction was carried out under constant stirring at 120 °C for 4 h. The resulting beads were filtered off, rinsed with acetone and deionized water. Then they were kept in a drying chamber at 80 °C for 2 h. Yield: 0.59 g. Anal. Found: C, 60.67; H, 6.80; N, 5.75; Cl, 11.49%.

Substitution of the chloride ion in the modified polymer for iodide (synthesis of Py-I). Py-Cl (0.45 g) was placed in a column with a frit and treated with 5% aqueous solution of NaI (30 mL). The target product was rinsed with water (10 mL) and acetone (5 mL) and then kept in a drying chamber at 80 °C for 2 h. Yield: 0.46 g. Anal. Found: C, 48.44; H, 5.47; N, 4.69; I, 29.00%.

Synthesis of carbonates 2a–f and 4 from epoxides. A 10 mL autoclave was charged with the mentioned polymer (30 mg) and the corresponding epoxide (6 mmol). Then CO₂ was introduced into the autoclave at 25 °C and the mixture was heated to the required temperature in a thermostat. After the reaction completion, the autoclave was cooled to 5 °C and CO₂ was released. The liquid products were separated from the beads using a Pasteur pipette. In the case of solid product 2e, CH₂Cl₂ (3 mL) was added, the beads were separated by filtration, and the carbonate solution was evaporated. The spectral characteristics of the resulting carbonates were in agreement with the previously published data [10–12]. The recycling was carried out by removing the resulting carbonate from the autoclave and adding the epoxide and CO₂ to the remaining beads.

Conclusions

Hence, the new beaded 4-vinylpyridine–styrene–divinylbenzene cross-linked copolymer was synthesized and modified by the quaternization of its pyridine units with 2-chloroethanol and subsequent substitution of the counterions for

the iodide anions. The resulting iodine-containing anion exchange resin exhibited high efficiency in the addition of CO₂ to epoxides. The ionic polymer can be reused for seven consecutive runs without loss of conversion. In addition, it is more convenient for the separation from the reaction products than the related powdered catalysts [13].

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