

Synthesis and Characterization of *N*-Substituted Poly(ethylenepyrrole): Functionalization of Ethylene–Carbon Monoxide Alternating Copolymers

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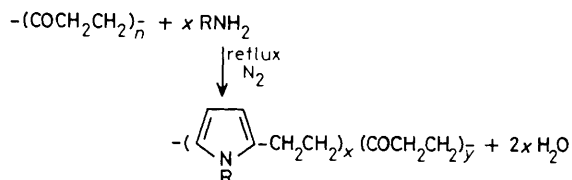
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The reactions of ethylene–carbon monoxide alternating copolymers with a variety of primary amines result in a new type of functionalized polymer derivative, *N*-substituted poly(ethylenepyrrole), containing a high density of pyrrolic units with versatile nitrogen-bound substituents in the molecular backbone.

In comparison with the huge array of heterocyclic polymers, simple chemical methods for forming polymer derivatives with pyrrole as the main component units in the polymer chain are relatively rare.¹ These types of polymers are expected to possess good thermal stability and good processability and

therefore, might be suitable as materials for speciality polymers.² We have taken advantage of the unique regular 1,4-dione moiety in the alternating copolymers of ethylene–carbon monoxide³ *via* facile chemical functionalization to synthesize a new class of polymer derivative, *N*-substituted



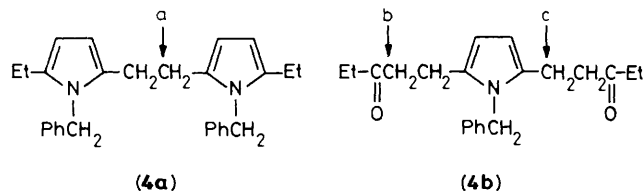
- (1) R = Prⁱ
 (2) R = Buⁿ
 (3) R = Ph
 (4) R = PhCH₂
 n = 2x + y

Scheme 1

poly(ethylenepyrrole) (PEP), which contain a high density of pyrrolic units with versatile *N*-substituents in the molecular backbone.⁴

The ethylene-carbon monoxide copolymers readily condensed with primary amines to give PEP as formulated in Scheme 1, to give the polymers (1)–(4). This derivatization process appears to be quite general. In a typical reaction, a suspension of ethylene-carbon monoxide copolymer (700 mg) in freshly distilled benzylamine (10 ml) was heated under reflux under nitrogen for 10 h. A brown homogeneous solution was gradually produced. Excess of amine was eliminated by evaporation. A dark yellow solid was recovered from CH₂Cl₂/EtOH in 60% yield.[†] With isopropylamine of low boiling point as the reactant, the reaction was manipulated in an autoclave which was immersed in a 100 °C oil bath and charged with 800 psi of N₂ during the reaction.

The major constituent units of PEP were identified as *N*-substituted 2,5-dimethylenepyrrole (Scheme 1), mainly based on spectroscopic data.[‡] The Paal-Knorr condensation of acetylacetone with amines to yield *N*-substituted 2,5-dimethylpyrroles is well known.⁵ A model reaction of tetradecane-3,6,9,12-tetraone⁶ with benzylamine was found to give two pyrrole-containing products which were identified as (4a) and (4b) in a relative yield of 9:1. Features of the n.m.r. spectra of (4a) and (4b) are worth comments.§ The



benzylic protons of (4a) and (4b) showed distinctly separated resonances which matched with the corresponding data for the *N*-benzyl-PEP. In the ¹³C n.m.r. spectra, the methylene carbon (C^a) in (4a) appeared at δ 26.48, whereas (4b) showed two methylene peaks at δ 41.17 (C^b) and 20.49 (C^c). These three signals are in good agreement with data for the methylene carbons in the PEP backbone. For the PEPs, the peaks at δ ca. 41 and ca. 20 always had almost identical intensity, and the δ 26 peaks were usually more than twice as intense as the other two. This evidence again supports the assigned structure.

The absence of unreacted 1,4-dione in the PEP indicated that the stability of the aromatic pyrrolic structures was an essential driving force for these reactions. The percentage of carbonyl conversion, 2x/(2x + y),[¶] had a scattered distribution, with no specific correlation with either amines or reaction conditions but a statistical outcome. Its average was 0.86, consistent with a mechanism in which the pyrrolic units were formed mainly through random cyclization of any 1,4-dione moiety in the ethylene-carbon monoxide copolymers with the amines.⁷ The average value of (x + y) for the PEPs was determined as 21, and the average molecular weight was estimated as 3000–4000.||

The relative reactivity of this derivatization reaction seems to be dominated by the steric effect of the amines and has little to do with the amine basicity. Amines containing a primary α-carbon, such as (2) and (4), showed better reactivity and the reaction could normally be completed within a few hours under typical conditions. Other amines having a non-primary α-carbon, e.g. (1) and (3), took more than 10 h for complete reaction. *t*-Butylamine had not reacted with ethylene-carbon monoxide copolymers at all after 24 h. This is consistent with the results of a reactivity study of the model reactions between acetylacetone and amines.

PEPs have reasonably good thermal stability. For example, thermogravimetric analysis of the benzyl derivatives did not show a weight loss until 400 °C. Unlike their parent ethylene-carbon monoxide copolymers, PEPs showed rather good solubility in many organic solvents. The substituent on the pyrrolic nitrogen is of direct relevance in tailoring their material properties.

[†] The yield was based on 650 mg weight yield and 88% CO conversion rate (*vide infra*).

[‡] Selected spectroscopic data: (1), n.m.r. (300 MHz, CDCl₃) ¹H: δ 5.74–5.95 (2.0H), 4.47 (0.9H), 2.95–2.99 (5.2H), 1.49–1.51 (6.3H); ¹³C: δ 209.11, 132.25, 130.90, 104.65, 103.97, 46.94, 42.01, 27.85, 22.43, 21.72. (2), i.r. (KBr, ν/cm⁻¹), 3097, 2954, 2927, 2867, 1710, 1636, 1590, 1501, 1462, 1422, 1367, 1297, 1258, 1085, 1023, 800, 744; ¹H n.m.r. 5.80–5.96 (2.0H), 3.76 (2.1H), 2.85–2.90 (5.6H), 1.61 (2.6H), 1.36 (3.6H), 0.94 (4.2H); ¹³C n.m.r. δ 208.92, 131.78, 130.64, 103.98, 103.73, 43.35, 41.57, 33.59, 26.25, 20.39, 20.24, 13.82. (3), ¹H n.m.r. 6.62–7.28 (7.8H), 5.67–5.78 (2.0H), 2.34–2.42 (6.3H), 1.02–1.11 (0.4H); ¹³C n.m.r. 138.33, 133.02, 131.99, 128.91, 128.34, 104.53, 26.86. (4), ¹H n.m.r. 7.15 δ (3.7H), 6.65 (2.1H), 5.80 (2.0H), 5.02, 4.84, 4.71 (1.9H in total), 2.60 (5.1H), 1.15 (0.37H); ¹³C n.m.r. 138.29, 132.44, 132.16, 131.51, 131.22, 128.59, 126.98, 125.35, 104.60, 46.23, 41.53, 26.35, 20.33, 12.79; anal.: calc. (based on 0.88 CO conversion): C, 83.6; H, 7.1; N, 7.1%. Found: C, 82.3; H, 6.9; N, 7.3%.

§ Compound (4a), ¹H: δ 7.20 (m, 6H), 6.76 (d, 4H), 5.88 (s, 2H), 4.87 (s, 4H), 2.68 (s, 4H), 2.42 (q, 4H), 1.16 (t, 6H); ¹³C: δ 138.58, 134.61, 132.16, 128.62, 126.93, 125.47, 104.45, 103.59, 46.24, 26.48, 19.85, 12.80. (4b), ¹H: δ 7.24 (m, 3H), 6.81 (d, 2H), 5.83 (s, 2H), 5.04 (d, 2H), 2.66, 2.63 (A₂B₂, 8H), 2.34 (q, 4H), 0.99 (t, 6H); ¹³C: δ 211.16, 210.40, 131.71, 130.74, 129.02, 128.26, 127.20, 125.54, 104.28, 46.43, 41.17, 35.90, 20.49, 7.73.

[¶] x and y respectively represent the average number of the pyrrolic units and of the unreacted carbonyls. The value of 2x/(2x + y) was estimated from the ¹H n.m.r. integration of the pyrrolic protons corresponding to 2x, and the integration of the methylene protons on the backbone corresponding to 4(x + y), so that 2x/(2x + y) = 0.88 for *N*-benzyl-PEP (4), 0.87 for (1), 0.83 for (2), and 0.86 for (3).

|| The integration of the terminal methyl peak at δ 1.15 in ¹H n.m.r. spectrum was defined as 6H. For *N*-benzyl-PEP, x + y = 21, \bar{M}_n = 3400, for *N*-phenyl-PEP, x + y = 24, \bar{M}_n = 3700.

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