Synthesis of new polymers containing carbanions in the backbone chain

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The literature data on polymers with carbanions in the backbone chain are lacking. However, the synthesis and study of such polymers are of considerable interest since polymers bearing anionic charges in side chains occur widely in living nature and exhibit a variety of biological activities.¹

The first representatives of such polymers were synthesized by the reaction of 1,4-phenylenediisocyanate with glycol cyanoacetates $1a,b^2$ in the presence of triethylamine. Similar reactions with the use of monofunctional reagents were described earlier. Apparently, the first step of the process includes the deprotonation of cyanoacetate 1 and the reaction of the resulting carbanion 2 with diisocyanate to give N-anion 3. The prototropic $C \rightarrow N$ migration in anion 3 yields polyamide 4 containing carbanions in the backbone chain (Scheme 1).

The composition and structure of polymers **4a,b** were confirmed by elemental analysis data and IR and ¹H NMR spectra. Treatment of salt **4b** with a hydrochloric acid solution gave free CH acid **5**.

The above examples of the synthesis of polymers 4 elucidate the general principle of construction of polymers with carbanions in the backbone chain. To obtain the latter, diisocyanates should be introduced into the

reaction with bismethylene compounds capable of being deprotonated *in situ* by an organic base to give salts of the corresponding CH acids.

¹H NMR spectra were recorded on a Bruker AMX-400 spectrometer (400.13 MHz) in DMSO-d₆. IR spectra were recorded on a Magna-IR750 FT-IR spectrometer (Nicolet) in KBr pellets.

Polymer 4a. Triethylamine (1.73 mL, 12.5 mmol) was added to a mixture of 1,4-phenylenediisocyanate (1.0 g, 6.25 mmol) and ethylene glycol cyanoacetate (**1a**) (1.22 g, 6.25 mmol) in 20 mL of dry DMF (reaction is slightly exothermic). The reaction mixture was stirred for 4 h in an atmosphere of dry nitrogen, left at ~20 °C for 3 days, and then transferred into CH₂Cl₂ (50 mL). The precipitate was filtered off, washed with CH₂Cl₂, and kept *in vacuo* (50–60 °C, 1 Torr) to give a light powder (3.12 g, 89.6%) with limited solubility in DMF, DMSO, and formamide; $\eta_{\rm sp}$ 0.34 (1% solution in DMF). Found (%): C, 60.14; H, 7.41; N, 15.07. Calculated (%): C, 60.32; H, 7.36; N, 15.08. ¹H NMR, δ : 1.17 (t, 18 H, C $\underline{\rm H}_3$ CH₂N, ${}^3J_{\rm H,H}$ = 7.2 Hz); 3.09 (q, 12 H, CH₃C $\underline{\rm H}_2$ N, ${}^3J_{\rm H,H}$ = 7.2 Hz); 4.10, 7.29 (both s,

Scheme 1

$$m \text{ NCCH}_2\text{C}(O)\text{O}(\text{CH}_2)_n \text{O}(O)\text{CCH}_2\text{CN} + 2m \text{ Et}_3\text{N} \implies m \text{ NCCHC}(O)\text{O}(\text{CH}_2)_n \text{O}(O)\text{CCHCN}$$

$$2m \text{ Et}_3\text{NH}$$

$$2a,b$$

$$m \text{ 2} + m \text{ 1,4-OCN-C}_6\text{H}_4\text{-NCO} \xrightarrow{2m \text{ Et}_3\text{N}} \left\{ \text{C}(O)-\bar{\text{N}}-\text{C}_6\text{H}_4-\bar{\text{NC}}(O)\text{HCC}(O)\text{O}(\text{CH}_2)_n \text{O}(O)\text{CHC}} \right\}_m$$

$$3a,b$$

$$3a,b$$

$$- \left\{ \text{C}(O)-\text{NH-C}_6\text{H}_4-\text{NHC}(O)\bar{\text{CC}}(O)\text{O}(\text{CH}_2)_n \text{O}(O)\text{CC}} \right\}_m$$

$$2m \text{ Et}_3^+\text{NH}$$

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$$4a,b$$

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4 H each, OCH₂, H arom.); 8.91, 10.49 (both s, 2 H each, C(O)NH, N⁺H). IR, ν /cm⁻¹: 1597 (C(O)N); 1627 (C(O)O); 2185 (CN); 2674 (N⁺H).

Polymer 4b. Under the above conditions, a light yellow powder (3.88 g, 88.2%) was obtained from cyanoacetate **1b** (1.57 g, 6.25 mmol), Et₃N (1.73 mL, 12.5 mmol), and 1,4-phenylene-diisocyanate (1.0 g, 6.25 mmol); η_{sp} 0.4 (1% solution in DMF). Found (%): C, 62.04; H, 8.14; N, 14.04. Calculated (%): C, 62.54; H, 8.14; N, 13.68. ¹H NMR, δ: 1.16 (t, 18 H, CH₃CH₂N, ³ $J_{\rm H,H}$ = 7.2 Hz); 1.36 (s, 4 H, OCH₂CH₂CH₂); 3.10 (q, 12 H, CH₃CH₂N, ³ $J_{\rm H,H}$ = 7.2 Hz); 3.35 (s, 4 H, OCH₂CH₂); 3.95 (t, 4 H, OCH₂, ³ $J_{\rm H,H}$ = 6.2 Hz); 7.32 (s, 4 H, H arom.); 8.91, 10.48 (both s, 2 H each, C(O)NH, N⁺H). IR, ν/cm⁻¹: 1598 (C(O)N); 1633 (C(O)O); 2179 (CN); 2687 (N⁺H); 3196 (NH).

Polymer 5. A solution of 35% HCl (0.5 mL) in 5 mL of water was added to a solution of salt **4b** (2 g) in 20 mL of MeCN—water (1:1). The reaction mixture was stirred for 2 h. The precipitate was filtered off, washed with acetone, and kept *in vacuo* (50–60 °C, 1 Torr) for 2 h to a constant weight. The yield of the resulting colorless powder was 1.31 g (98%); η_{sp} 0.20 (1% solution in DMF). Found (%): C, 58.41; H, 5.20; N, 13.53. Calculated (%): C, 58.25; H, 4.85; N, 13.59. ¹H NMR, δ : 1.33, 1.57,

4.10 (all m, 4 H each, OCH₂CH₂CH₂, OCH₂CH₂, OCH₂); 4.90 (br.s, 2 H, CH, $\Delta v = 120$ Hz); 7.45 (s, 4 H, H arom.); 10.66 (s, 2 H, NH). IR, v/cm^{-1} : 1642 (C(O)N); 1750 (C(O)O); 2210 (CN); 3193 (NH).

The thermomechanical properties and molecular weights of all polymers will be reported elsewhere.

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