

Rigid-rod polyelectrolytes: carboxylated poly(*para*-phenylene)s via a novel precursor route

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The synthesis of a soluble poly(*para*-phenylene) (PPP) derivative with two *p*-carboxyphenoxyethylene substituents in the 2,5-positions of every alternate phenylene moiety is described, transforming a bromomethylene-substituted precursor PPP in a two-step reaction sequence. Both of these steps, namely a Williamson reaction and an ester cleavage using anhydrous potassium hydroxide, occur selectively and almost quantitatively (>98%, n.m.r.). Structurally homogeneous, rigid-rod polyelectrolytes with 80–130 phenylene rings attached to each other may be obtained by this method.

(Keywords: poly(*para*-phenylene)s; rigid-rod polyelectrolytes; precursor routes)

Introduction

Rigid-rod polymer electrolytes are of growing importance for both fundamental and applied science (for reviews, see refs 1–4). In contrast to flexible-chain polyelectrolytes, their persistence length is independent of the ionic strength. Furthermore, the formation of lyotropic mesophases is expected, which are determined by the electrostatic interactions.

Although much effort has been made to develop appropriate synthetic strategies for preparing well defined, rigid-rod polyelectrolytes, very few such compounds are available today^{5–9}. Recently, Wallow and Novak^{10–13} reported the elegant synthesis of a carboxylated poly(*para*-phenylene) (PPP) derivative. A water-soluble polymer was obtained by Pd-catalysed polycondensation. Nevertheless, comprehensive structural proof and the determination of the degrees of polycondensation (\overline{DP} s) achieved raised difficulties in their work.

In a previous paper¹⁴, we reported on the synthesis of a soluble, structurally homogeneous PPP derivative having two reactive bromomethylene functionalities in the 2,5-positions of every alternate phenylene moiety. When solutions of that precursor polymer were treated with sodium phenolate derivatives, the bromomethylene groups reacted selectively and nearly quantitatively in a Williamson reaction¹⁵ leading to the corresponding phenoxyethyl-substituted PPP. This conversion was applied for preparing a PPP derivative with lateral cyano functionalities. Beyond that, a variety of other PPP derivatives should become available by analogous conversions, depending on the substitution pattern of the phenolate derivative used for the etherification.

The aim of the present paper is to extend the new route for preparing a soluble, structurally well defined PPP polyelectrolyte. Based on precursor PPP 1 the synthesis of a carboxylated, high molecular weight PPP derivative 3 is reported via its ester intermediate 2 (Scheme 1).

Experimental

General. All reagents were purchased from Fluka or Aldrich Chemical Co. and were used without further

purification. Toluene, dimethyl formamide (DMF) and 1,2-dimethoxy ethane (DME) were dried using standard procedures. Precursor PPP 1 was synthesized as described previously¹⁴. All reactions were carried out under a nitrogen atmosphere. Other methods and techniques were as described elsewhere¹⁴. The signal assignment of the absorptions in the ¹H and ¹³C n.m.r. spectra is made according to the numerals given in Figure 2.

Poly(2,5-dihexyl-1,4-phenylene-co-2,5-di(4-ethylbenzoatoxymethylene)-1,4-phenylene) (2). Polymer 1 (400 mg, 1 equiv.), *p*-hydroxyethyl benzoate (0.6564 g, 3.95 mmol, 2.5 equiv.), sodium tert-butanolate (0.2657 g, 2.765 mmol, 1.7 equiv.), potassium iodide (50 mg), toluene (100 ml) and DMF (100 ml) were stirred and refluxed for 1 day. About 50 ml of the solvent was distilled off from the obtained solution. Polymer 2 was precipitated by pouring the concentrated solution into methanol (200 ml). A colourless polymer 2 was recovered by filtration and dried *in vacuo*. Yield: 508 mg (95%).

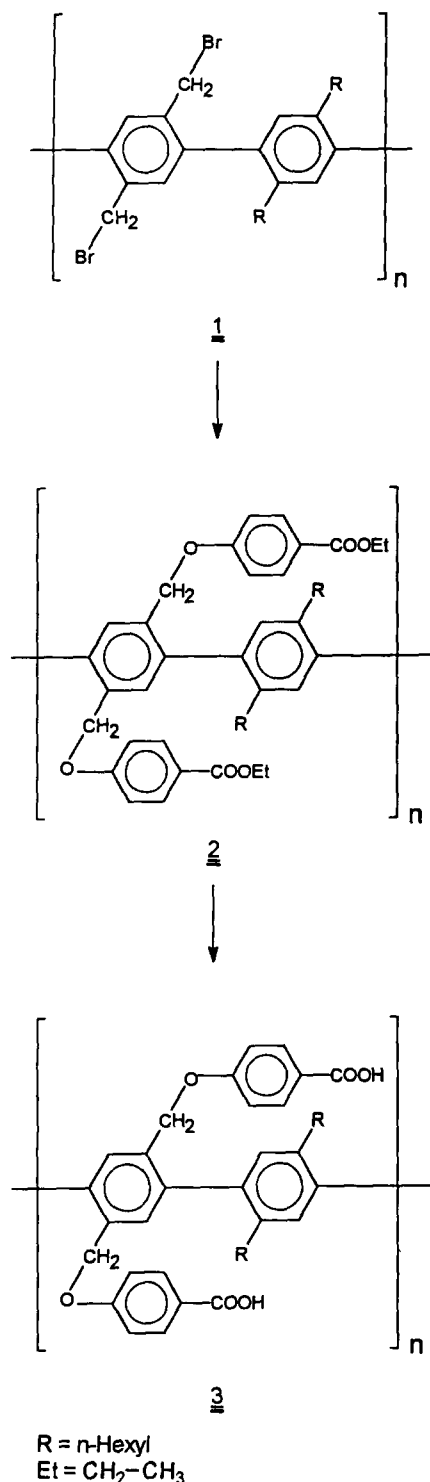
¹H n.m.r. (C₂D₂Cl₄, 363 K) δ 0.80 (t; 6H, (CH₂)₅-CH₃), 1.13, 1.32 (2m; 22H, CH₂-(CH₂)₄-CH₃, O-CH₂-CH₃), 2.36 (m; 4H, Ar-CH₂-R), 4.28 (m; 4H, O-CH₂-CH₃), 4.82, 4.95 (2m; 4H, Ar-O-CH₂-Ar'), 6.78 (d; 4H, aromatic-H⁸), 7.18 (s; 2H, aromatic-H⁶), 7.49 (broad s; 2H, aromatic-H³), 7.86 (d; 4H, aromatic-H⁹).

¹³C n.m.r. (C₂D₂Cl₄, 363 K) δ 14.06, 14.54 (2q; (CH₂)₅-CH₃, O-CH₂-CH₃), 22.62, 29.24, 29.42, 31.07, 31.70, 32.99, 33.16 (7t; (CH₂)₅-CH₃), 60.75 (t; O-CH₂-CH₃), 68.57 (t; aryl-CH₂-O), 114.65, 114.91 (2d; aromatic-C⁸), 123.85 (s; aromatic-C¹⁰), 130.78, 131.65 (2d; aromatic-C³, C⁶, C⁹), 134.20 (s; aromatic-C²), 138.21, 138.70 (2s; aromatic-C¹, C⁵), 140.32 (s; aromatic-C⁴), 162.59, 162.75 (2s; aromatic-C⁷), 166.26 (s; COOEt).

Analysis calculated for (C₄₄H₅₂O₆)_n: C, 78.07; H, 7.75%. Found: C, 76.70; H, 7.85; Br, 0.19%.

Poly(2,5-dihexyl-1,4-phenylene-co-2,5-di(para-carboxyphenoxyethylene)-1,4-phenylene) (3). Polymer 2 (327 mg, 1 equiv.) was dissolved in toluene (85 ml). Potassium tert-butanolate (1.0846 g, 9.665 mmol, 10 equiv.) and water (35 μ l, 1.9330 mmol, 2 equiv.) were added. The

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Scheme 1

mixture was stirred at room temperature for 1 day. DME (85 ml) was added and the reaction mixture was stirred for a further 2 days at room temperature. Water (100 ml) was added and stirring was continued for a further 4 h. The emulsion-like reaction mixture obtained was then acidified with hydrochloric acid (2 M). Colourless polymer 3 precipitated. It was isolated by filtration and dried *in vacuo* (0.1 mbar, P_4O_{10}). However, it was not possible to remove water quantitatively. Polymer 3 contained water even if it was dried for several days, as could be seen from the ^1H n.m.r. spectra; the apparent yields were > 100% (328.7 mg), but owing to the presence

of water an exact determination of the yield was not possible. On the other hand, no further polymer was found when the acidified solution was evaporated to dryness. Thus, the material was obtained quantitatively by acidifying.

^1H n.m.r. (DMSO- d_6 , 363 K) δ 0.78 (t; 6H, $(\text{CH}_2)_5\text{-CH}_3$), 1.10 (m; 24H, $\text{CH}_2\text{-CH}_2\text{-(CH}_2)_3\text{-CH}_3$), 1.28 (m; 4H, $\beta\text{-CH}_2$), 2.34 (m; 4H, $\alpha\text{-CH}_2$), 4.91, 5.00 (2m; 4H, aryl- $\text{CH}_2\text{-O}$), 6.88 (d; 4H, aromatic- H^8), 7.20 (s; 2H, aromatic- H^6), 7.52 (m; 2H, aromatic- H^3), 7.83 (d; 4H, aromatic- H^9).

^{13}C n.m.r. (DMSO- d_6 , 363 K) δ 13.01 (q; CH_3), 21.28, 27.79, 28.05, 29.63, 30.33, 31.75 (6t; $(\text{CH}_2)_5\text{-CH}_3$), 67.37 (t; aryl- $\text{CH}_2\text{-O}$), 113.99 (d; aromatic- C^8), 123.25 (s; aromatic- C^{10}), 129.73, 130.60 (2d; aromatic- $\text{C}^3, \text{C}^6, \text{C}^9$), 133.38 (s; aromatic- C^2), 136.93, 137.54 (2s; aromatic- C^1, C^5), 139.18 (s; aromatic- C^4), 161.34 (s; aromatic- C^7), 166.17 (s; COOH).

Analysis calculated for $(\text{C}_{40}\text{H}_{44}\text{O}_6)_n$: C, 77.39; H, 7.15%. Found: C, 68.60; H, 6.59%.

Results and discussion

As was evident from our earlier investigations¹⁴, the bromomethylene-substituted PPP 1 should be a suitable precursor for the synthesis of a broad variety of PPP derivatives. On the one hand, the flexible hexyl side chains bond at every alternate phenylene moiety and guarantee a good solubility of PPP 1 in solvents appropriate for a number of well-established conversions. On the other hand, advantageous reactivity of the bromomethylene functionalities, even under mild reaction conditions with, for example, sodium phenolate derivatives, means that polymer 1 is an ideal candidate for preparing carboxylated PPP derivatives according to the route shown in *Scheme 1*. Nevertheless, optimized reaction conditions must be found that ensure both complete conversion of the bromomethylene functionalities and stability of the ester groups during etherification. Reacting precursor PPP 1 in a homogeneous mixture of toluene, DMF, sodium tert-butanolate and an excess of *p*-hydroxyethyl benzoate was an appropriate procedure. A colourless, fibrous material was obtained in nearly quantitative yields. It dissolved readily and completely in conventional organic solvents such as chloroform, *o*-dichlorobenzene or toluene. Thus the quality of the conversion and the structural homogeneity of PPP 2 could be examined by high field n.m.r. spectroscopy.

From the ^1H n.m.r. spectrum of the obtained polymer (*Figure 1B*) it is evident that almost 100% of the bromomethylene functionalities had reacted selectively, leading to the desired ether groups. The etherification process resulted in the complete disappearance of the signals of α -methylene protons of PPP 1 at 4.35 and 4.48 ppm (see *Figure 1A*) and an equivalent appearance of signals at 4.82 and 4.95 ppm corresponding to α -methylenes of PPP 2. The additional doublets at 7.86 and 6.78 ppm and the multiplet at 4.28 ppm (*Figure 1B*) were assigned unambiguously to the attached *p*-(carboxyethyl)phenol ether. This assignment was verified by ^{13}C n.m.r. spectroscopy (*Figure 2*). The carbon spectrum of PPP 2 (*Figure 2B*) exhibits the correct number of absorptions required for the supposed structure. With the aid of model compounds¹⁴, tabulated increments¹⁶ and distortionless enhancement by polarization transfer

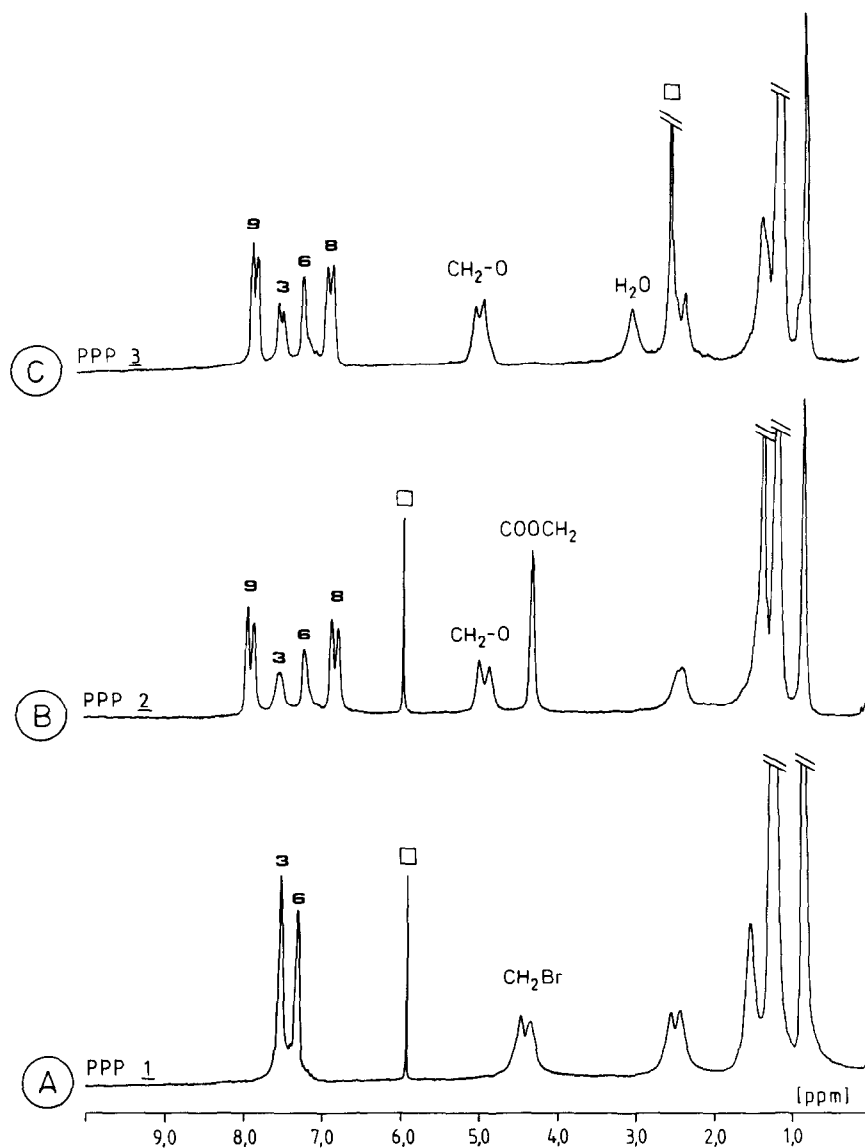


Figure 1 ^1H n.m.r. spectra of PPP derivatives **1** (A) and **2** (B) recorded in 1,1,2,2-tetrachloroethane (\square) at 90°C , and ^1H n.m.r. spectrum of PPP **3** (C) recorded in dimethyl sulfoxide (DMSO) (\square) at 90°C

experiments, a full signal assignment could be made (see *Figure 2* and Experimental). The lack of further absorptions permits the exclusion of the formation of structural irregularities within the accuracy of the n.m.r. method. Additional proof of the nearly 100% conversion of the bromomethylene functionalities of precursor **1** was achieved using elemental analysis. Almost no bromine was found in polymer **2** ($<0.2\%$), indicating a conversion of more than 99% of the bromomethylenes. The observed difference between the calculated and found carbon contents of PPP **2** (see Experimental) is presumably due to incomplete combustion and thus carbonization of the material, as found earlier for other PPP derivatives as well^{10-14,17}.

In order to exclude chain degradation during conversion of the PPPs, a comparison was required of the *DP*s of the precursor used and the PPP **2** obtained. As PPP **2** dissolves readily in many organic solvents, its *DP* could be determined directly by membrane osmometry (m.o.) in *o*-dichlorobenzene. In a representative experiment, a *DP* of 25 ($\bar{M}_n \approx 17\,000$) was found for a PPP **2** made from a precursor having exactly the same

DP of 25 (m.o.). Thus, according to these investigations, the *DP*s are unchanged within the limits of error of the m.o. method.

Finally, the ester groups of PPP **2** had to be cleaved to achieve the desired rod-like polyelectrolyte **3**. Rather unexpectedly, no hydrolysis was achieved by stirring and refluxing PPP **2** in the two-phase system of water (NaOH)/toluene. Unchanged material was recovered from that procedure. On the other hand, a nearly 100% ester cleavage was achieved when a homogeneous solution of polymer **2** in toluene was treated with 10 equivalents of potassium tert-butanolate and only two equivalents of water¹⁸. The small amount of water immediately hydrolyses a portion of the butanolate, leading to a small amount of anhydrous potassium hydroxide. Under these conditions the potassium salt of PPP **3** has been formed within 3 days at room temperature. After hydrolysis of the excess butanolate, the polyacid **3** is obtained as a colourless, brittle solid by acidifying the emulsion-like reaction mixture. Polymer **3** dissolves readily in organic solvents such as dimethyl sulfoxide, DMF and dimethyl acetamide. For that

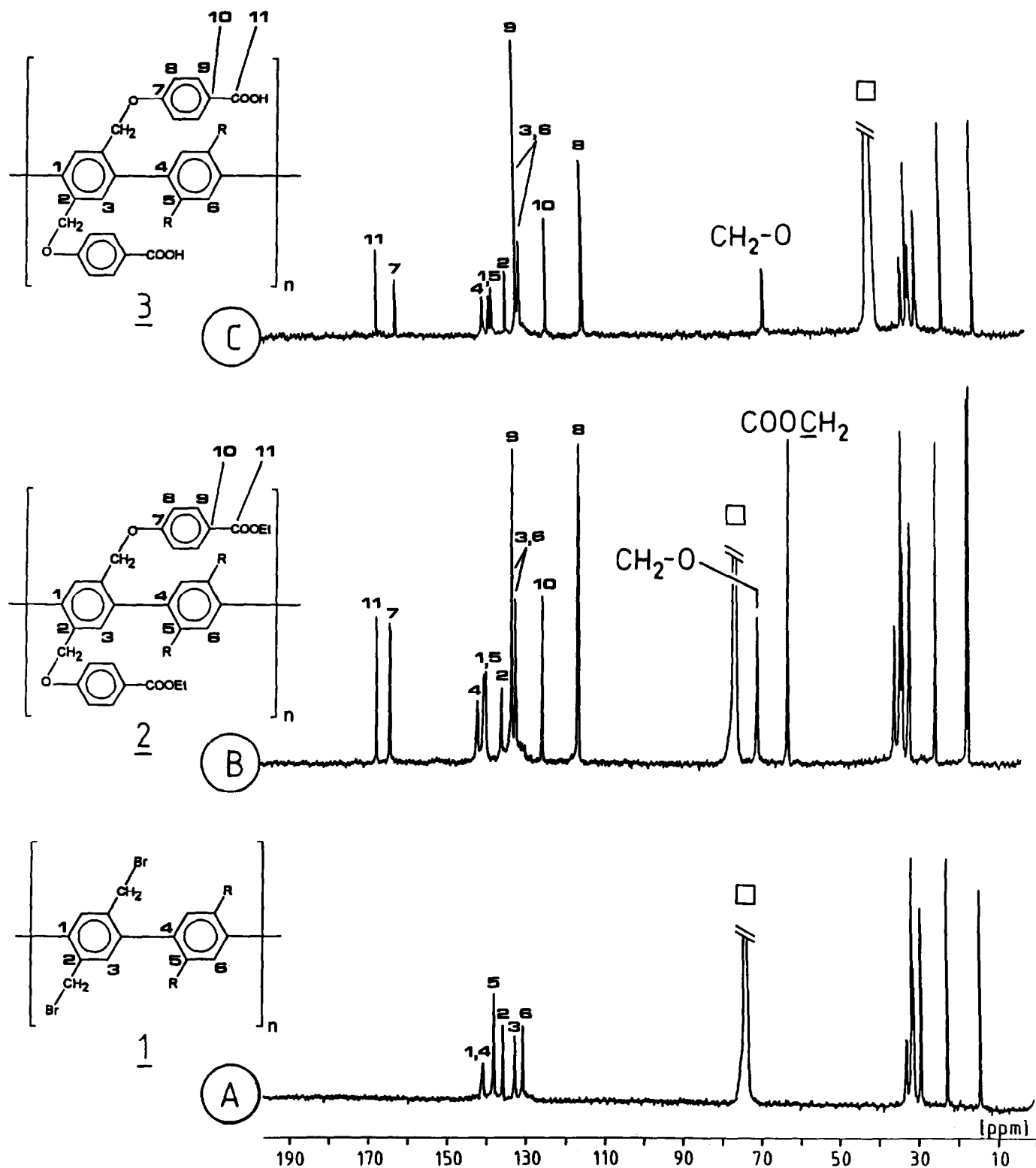


Figure 2 ^{13}C n.m.r. spectra of PPP derivatives 1 (A) and 2 (B) recorded in 1,1,2,2-tetrachloroethane (\square) at 90°C , and ^{13}C n.m.r. spectrum of PPP 3 (C) recorded in DMSO (\square) at 90°C

reason, the completeness and selectivity of the hydrolysis process and thus the homogeneity of the molecular constitution of PPP 3 could be established by n.m.r. spectroscopy.

The ^1H n.m.r. spectrum (Figure 1C) shows four absorptions of aromatic protons in the correct intensity ratios, namely two doublets at 7.83 and 6.88 ppm corresponding to the hydrogens H^9 and H^8 of the lateral phenolic substituents, and two broad and slightly

structured absorptions at 7.52 and 7.20 ppm corresponding to the protons H^3 and H^6 of the polymer main chain. Besides the signals of the other aliphatic protons absorbing from 0.77 to 2.34 ppm, an absorption is detected at 4.95 ppm. This split absorption arises from the aryloxymethylene protons. A further important fact is the complete disappearance of the signal at 4.28 ppm arising from the ester methylenes in PPP 2. The presence of a large amount of water, which was not completely

removed from that polymer, is manifested by the strong absorption at 3.20 ppm. This water also prevented exact evaluation of the yields of polymer **3**, which were, however, in the region of 100%. The nearly quantitative ester cleavage and the lack of further absorptions pointing towards structural irregularities is also supported by the ^{13}C n.m.r. spectrum shown in *Figure 2C*. It is evident from the given signal assignment that all features of these n.m.r. spectra are consistent with the proposed structure for polymer **3** and constitute unambiguous proof of its structure. The narrow splitting of some of the absorptions in the ^1H as well as in the ^{13}C n.m.r. spectra is due to the presence of atropisomers within the polymer chains, which is discussed elsewhere in more detail¹⁴. A direct determination of the \overline{DP} of PPP **3** by m.o. was not possible because of the large amount of water present in the material. However, the conversion of polymer **2** leading to PPP **3** occurred almost quantitatively under mild reaction conditions, and no evidence for cleavage of carbon-carbon bonds was found in the n.m.r. spectra. Thus the same \overline{DP} can be assumed for PPP **3** as found for the PPP **2** used for its preparation. Consequently, depending on the \overline{DP} of the precursor PPP used, carboxylated PPPs having an average of 50–130 phenylene rings per chain were obtained during the investigations presented here.

Conclusions

In conclusion, the conversion of the bromomethylene-substituted PPP derivative **1** with sodium phenolate derivatives in a Williamson reaction is established as an effective route to carboxylated PPP derivatives of regular structure and high \overline{DP} . This synthesis provides access to an interesting new class of rigid-rod polyelectrolytes, the

physical properties of which will form the subject of subsequent publications.

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