Polymer Vol. 39 No. 23, pp. 5827–5838, 1998
0032-3861/98/$ – see front matter

PII: S0032-3861(98)00076-7

Synthesis and material properties of soluble poly(1,1′-ferrocenylene-*alt*-*p*-oligophenylenes)

Ralf Knapp, Ulf Velten and Matthias Rehahn*
Polymer-Institut, Universität Karlsruhe, Kaiserstrasse 12, D-76128 Karlsruhe, Germany
(Accepted 22 January 1998)

A series of poly(1,1′-ferrocenylene-*alt*-*p*-oligophenylenes) has been prepared via Pd-catalysed polycondensation, i.e. poly(1,1′-ferrocenylene-*alt*-*p*-terphenyl-4,4″-ylene), poly(1,1′-ferrocenylene-*alt*-*p*-quinquephenyl-4,4⁗-ylene), and poly(1,1′-ferrocenylene-*alt*-*p*-septiphenyl-4,4″″″-ylene), which bear two solubilising *n*-hexyl or *n*-dodecyl side chains at every repeating unit. The homogeneous constitution of all soluble polymers has been proved using high-resolution ^{1}H and ^{13}C n.m.r. spectroscopy, and the degrees of polymerization have been shown to vary from $P_n = 15$ to 55. The material properties of the poly(1,1′-ferrocenylene-*alt*-*p*-oligophenylenes) have been analysed in bulk and solution using t.g.a., d.s.c., WAXS, g.p.c., viscosimetry and light scattering. Some of the results are contrasted with those of measurements on poly(*p*-phenylene) and poly[2,9-(*o*-phenanthroline)-*alt*-*p*-oligophenylene] reference polymers showing that the main chains of the poly(1,1′-ferrocenylene-*alt*-*p*-oligophenylenes) are by no means rodlike, like those of the poly(*p*-phenylenes) but assume randomly coiled conformations. However, the coils are less densely packed and significantly more flexible than those of the poly[2,9-(*o*-phenanthroline)-*alt*-*p*-oligophenylenes]. © 1998 Published by Elsevier Science Ltd. All rights reserved.

(Keywords: coordination polymers; ferrocene-containing polymers; Pd-catalysed polycondensation)

INTRODUCTION

Ferrocene-containing polymers are of considerable interest because of their excellent thermal, redox and spectroscopic properties[1–5]. Moreover, polymetallocenylenes with metal–metal distances of less than approx. 7 Å, or with metallocenylene moieties linked 1,1′-heteroannularly via π-conjugated bridges, are additionally of interest because of their promising electronic, optical and magnetic properties arising from interactions of the transition metal complexes along the polymer chains [6–16]. Hence, much effort was spent during recent decades to make available derivatives of these latter polymers in particular. Finally, in the early 1990s, three research groups succeeded in developing efficient syntheses of such materials. Manners *et al.* took advantage of the ring-opening polymerization of [*n*]ferrocenophanes and prepared an impressive variety of polymetallocenylenes in which the metallocenylenes are spaced by only a few ångstrøms[2,3]. Simultaneously, Rosenblum *et al.* published an elegant synthetic access to alkyl-substituted polymetallocenylenes in which stacked metallocenylenes are held together by short, π-conjugated naphthylene bridges[9–14]. Finally, we applied the Pd-catalysed aryl–aryl coupling reaction for the synthesis of the *n*-hexyl substituted poly(1,1′-ferrocenylene-*p*-terphenyl-4,4″-ylenes) **1a** of homogeneous structure and high molecular weights (*Scheme 1*)[17]. In these latter polymers **1a**, rigid, rod-like *p*-terphenylene residues alternate with flexible ferrocenylene moieties, a structural feature which should give rise to interesting properties in bulk and solution. In order to examine systematically this novel class of metal-containing polymers, we have now prepared further poly(1,1′-ferrocenylene-*alt*-*p*-oligophenylene) derivatives such as **1b**, **2a,b**, and **3a,b** with longer *p*-oligophenylene bridges and/or longer flexible side chains (*Scheme 1*). In this paper, we describe the synthesis of these novel polymers as well as some of their properties in bulk and solution. Moreover, the properties of polymers **1a** are contrasted with those of poly(*p*-phenylene) (PPP) derivatives **8** and **9**, and those of the poly[2,9-(*o*-phenanthroline)-*alt*-*p*-oligophenylenes] **11** (*Scheme 2*)[18]. The latter polymers have a constitution which is very similar to that of **1a** but have conformationally rigid *o*-phenanthroline residues in the backbone instead of the nearly freely rotating ferrocenylene moieties.

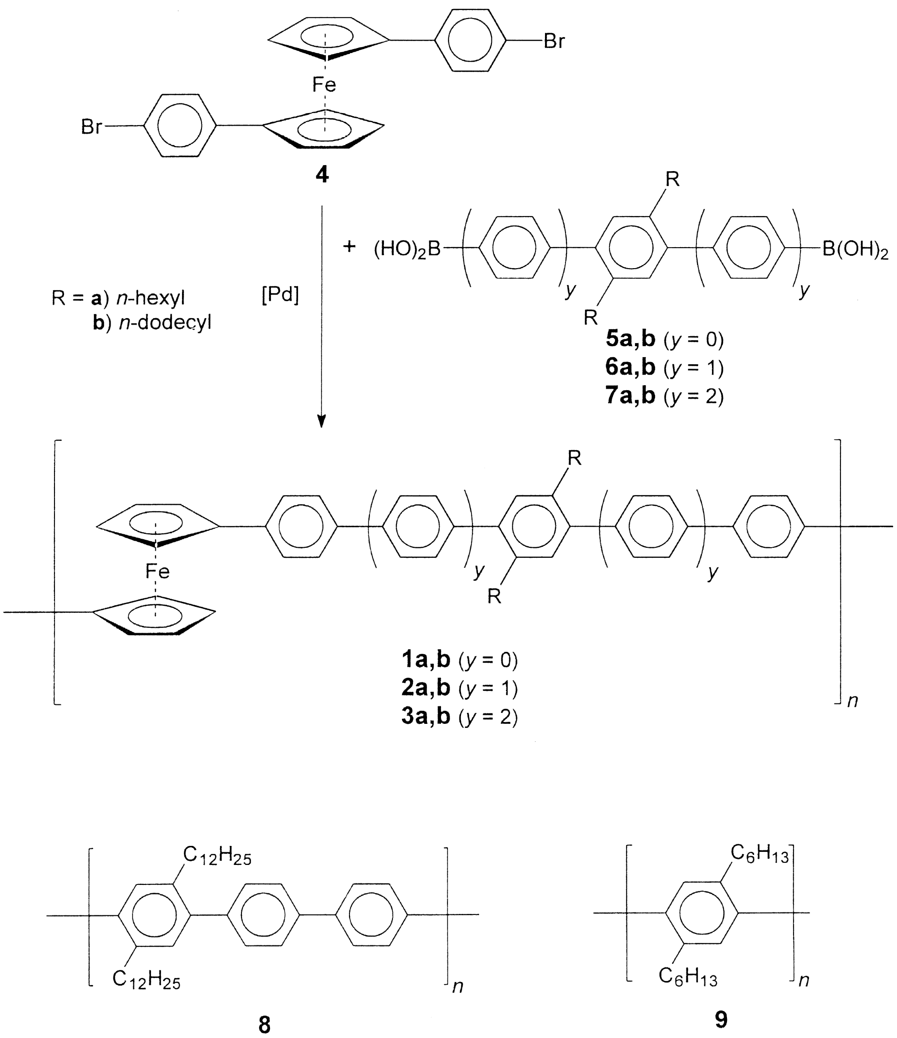
RESULTS AND DISCUSSION

Syntheses

1,1′-Bis(*p*-bromophenyl)ferrocene **4**[19], 2,5-dialkylbenzene-1,4-diboronic acids **5a,b**[20], and the *p*-oligophenylenediboronic acid derivatives **6a,b** and **7a,b**[20,21] were prepared according to synthetic procedures published recently. Subsequently, equimolar amounts of monomer **4** and the respective diboronic acid derivative were reacted in the heterogeneous system of toluene and 1 M aqueous Na_2CO_3, using 0.1–1 mol.% of $[Pd(PPh_3)_4]$ as the precursor complex of the catalytically active Pd species (*Scheme 1*). For the preparation of samples with lower molecular weights, small amounts of bromobenzene were additionally added to the reaction mixtures which act as monofunctional species and thus generate end groups. While polymers **1a,b** and **2b** were found to remain soluble over the whole reaction time, polymers **2a** and **3a,b** precipitated during the polycondensation reaction. After the conversions were completed, bromobenzene was added to the reaction mixtures to convert the remaining boronic acid functionalities into phenyl end groups. The former would prevent light-scattering investigations due to their pronounced aggregation tendency[22]. After precipitation of the products in methanol, all polymers except **2a** and **3a,b** were found to be readily soluble in a variety of organic solvents such as toluene, chloroform and tetrahydrofurane. Polymer **3b** redissolved completely only in 1,1,2,2-tetrachloroethane while polymers **2a** and **3a** were hardly soluble even in hot tetrachloroethane.

---

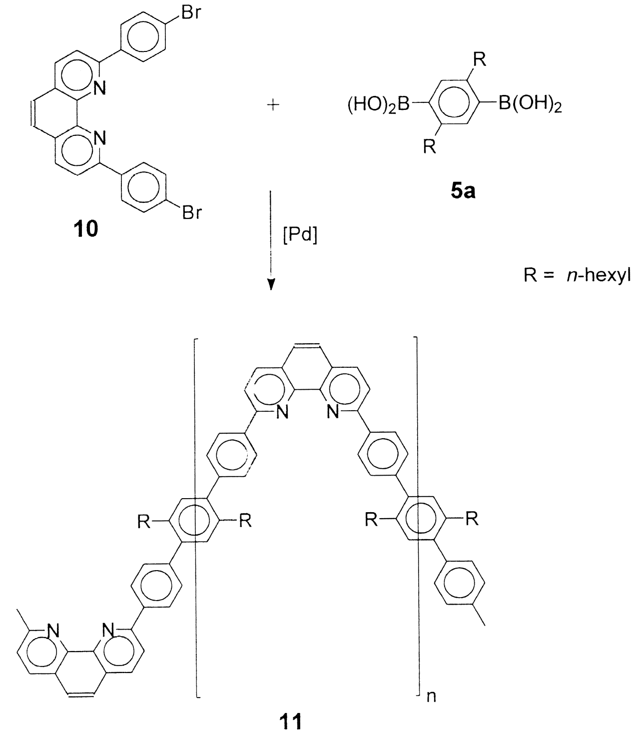
*To whom correspondence should be addressed. E-mail: rehahn@polyibm2.chemie.uni-karlsruhe.de



Scheme 1

The constitutional homogeneity of the soluble products or product fractions was analysed using ^{1}H and ^{13}C n.m.r. spectroscopy. For all those polymers which remained soluble over the whole time of polycondensation, only absorptions were found in the n.m.r. spectra which clearly correspond to the hydrogen and carbon atoms of the inner-chain repeating units of the expected polymers. No evidence was found of structural defects or end groups showing that structurally homogeneous and high-molecular-weight polymers **1a,b** and **2b** were made available. As an example, *Figure 1* displays the ^{1}H n.m.r. spectra of polymers **1a** (A) and **2b** (B) while *Figure 2* shows the ^{13}C n.m.r. spectrum of polymer **2b** together with the full signal assignment. On the other hand, small additional absorptions were detected in the spectra of all those polymers which precipitated during the polymer synthesis, i.e. of polymers **2a**, **3a** and **3b**. By means of tabulated increments and reference spectra, it was possible to show that these small absorptions originate from either bromine or phenyl chain termini rather than from structural defects within the chains. Thus, in these latter cases the formation of structurally regular but only low-molecular-weight polymers was evident from the n.m.r. spectra.

In full agreement with n.m.r. spectroscopy, vapour pressure and membrane osmometry showed the soluble fractions of the highest molecular weight samples of the presented polymers to have average degrees of polycondensation of $P_n = 62$ (**1a**), 43 (**1b**), 10 (**2a**), 25 (**2b**), 5 (**3a**)



Scheme 2

and 12 (**3b**). These results demonstrate that the values of P_n of the readily soluble polymers are in the same order of magnitude as those found for many other polyaromatics prepared via Pd-catalysed polycondensation[23–30]. On the other hand, the chain growth stops immediately—or is at least dramatically slowed down—when the growing species precipitate in the oligomeric state. Consequently, *p*-quinquephenylene bridges are the longest rigid units that can be used in poly(1,1′-ferrocenylene-*alt-p*-oligophenylenes) with only two *n*-dodecyl side chains per repeating unit when readily soluble and really high-molecular-weight materials are aimed at.

In addition to the polymers **1**–**3** with long *p*-oligophenylene bridges, we were also interested in the preparation of poly(1,1′-ferrocenylene-*p*-phenylenes) **12a** or **12b** where the ferrocenylene moieties are connected by only one phenylene ring. Hence, we carried out Pd-catalysed polycondensation reactions using various combinations of monomers such as those shown in *Scheme 3*[19]. Unfortunately, we did not succeed in finding reaction conditions under which the Pd-catalysed ferrocenyl-phenyl bond formation process proceeds selectively and quantitatively enough to give soluble, high-molecular-weight polymers **12**: under all conditions tested, side reactions of the electron-rich ferrocene monomers and of the catalytically active species led to the formation of lower oligomers **12a,b** and insoluble, presumably crosslinked products. As an example, *Figure 3* depicts the ^{1}H n.m.r. spectrum of the soluble fraction of a polymer **12a** ($P_n = 9$) prepared from 1,1′-diiodoferrocene **16** and 2,5-dihexylbenzene-1,4-diboronic acid **5a** (route B, *Scheme 3*). In addition to the intense absorptions of the inner-chain repeat units, signals of chain end-groups are clearly detectable. Since further optimization of the coupling conditions was not possible, we stopped our efforts directed towards the synthesis of polymers **12**.

To conclude, while *p*-septiphenylene bridges like those of polymers **3** are beyond the upper limit of the length of the rigid blocks for solubility reasons, a single *p*-linked phenylene moiety is beyond the lower limit because of chemical restrictions—at least when the presented synthetic strategy is applied. Finally, reference polymers **8**[20], **9**[30] and **11**[18] were prepared in analogy to the procedure described for polymers **1**–**3**, and subsequently analysed using n.m.r. spectroscopy and osmometry. Their constitution was found to be homogeneous in all cases (see, for example, the ^{1}H n.m.r. spectrum of **11** shown in *Figure 4*), and the degrees of polycondensation vary from $P_n = 20$ to 60.

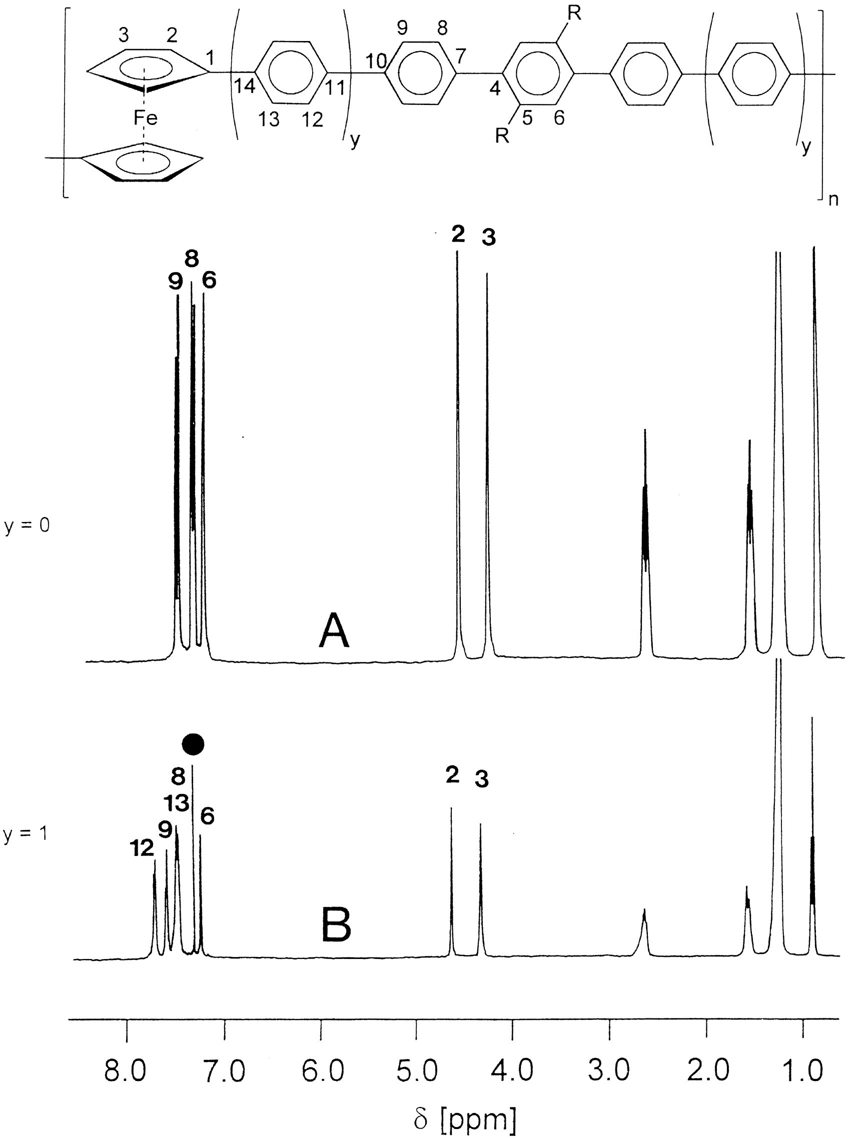


Figure 1 ^{1}H NMR spectra of polymers **1a** (A) and **2b** (B), recorded in $CDCl_3$ (●) at room temperature

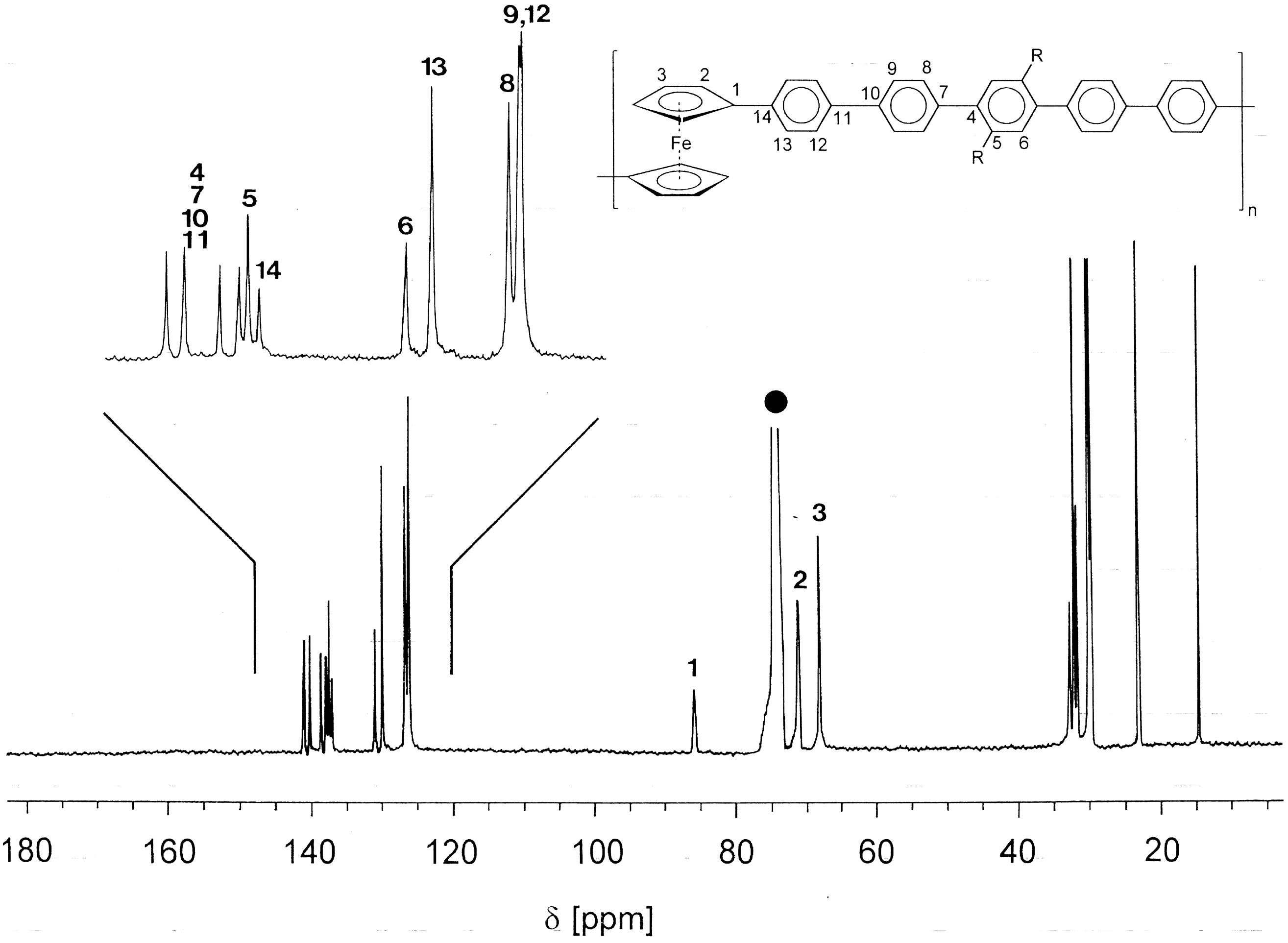
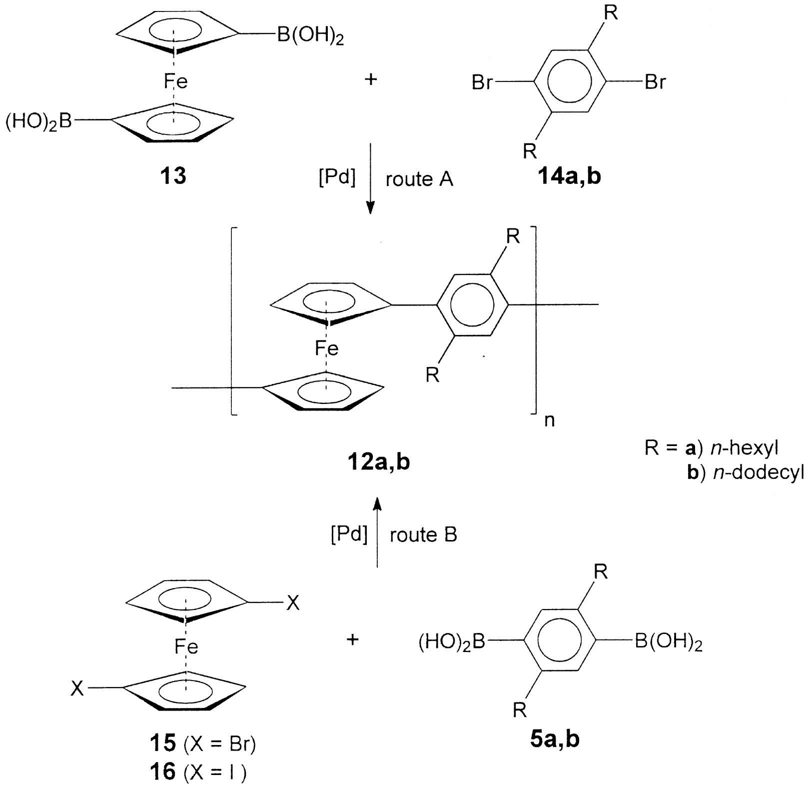


Figure 2 ^{13}C n.m.r. spectrum of polymer **2b**, recorded in $CDCl_3$ (●) at room temperature



Scheme 3

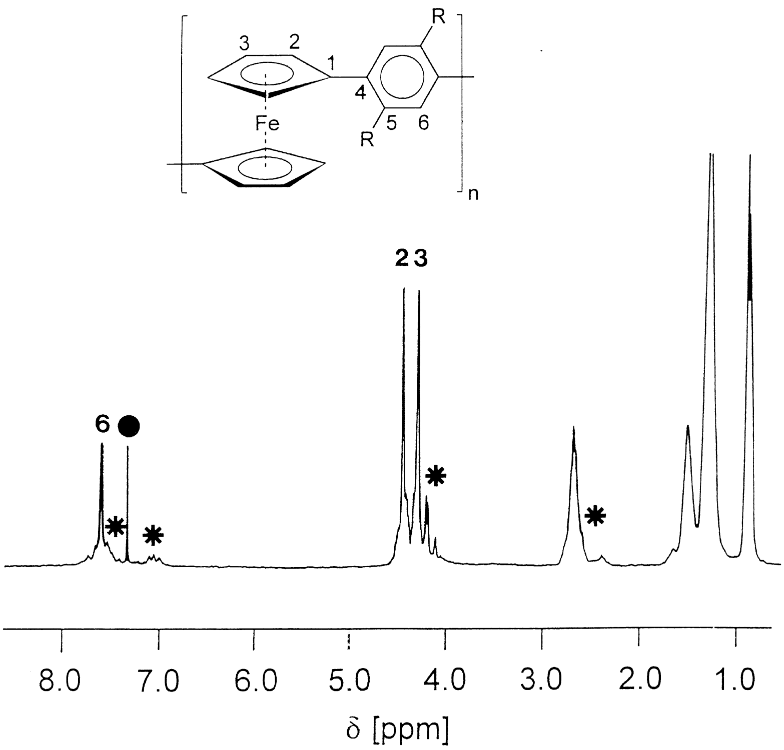


Figure 3 ^{1}H n.m.r. spectrum of polymer **12a**, recorded in $CDCl_3$ at room temperature; absorptions corresponding to the solvent (●) and end-groups or defect structures (*) are assigned. See text for details

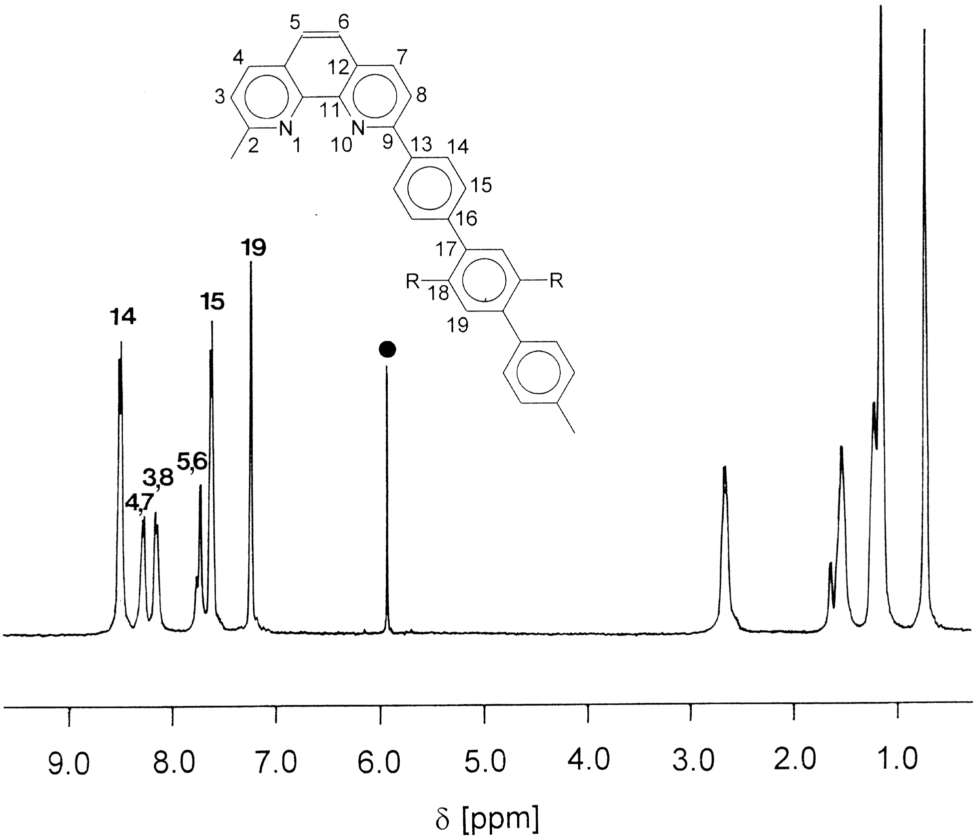


Figure 4 ^{1}H n.m.r. spectrum of polymer **11**, recorded in $C_2D_2Cl_4$ (●) at room temperature

Solution properties

An interesting first aspect concerning the conformational behaviour of polymers **1**–**3**, **11** and **12** was the question whether or not formation of cyclic oligomers occurs during the Pd-catalysed synthesis: on the one hand, the ferrocenylene moieties should allow growing chains to assume a nearly arbitrary conformation because rotation around the Cp···Fe···Cp axes (Cp = cyclopentadienyl) has a very low activation energy of only a few kJ mol^{-1}. Thus, a certain amount of cyclic oligomers was expected to be formed here. The *o*-phenanthroline moieties, on the other hand, impose 60° tilt angles into the otherwise rod-like polymer backbones of **11** and thus should also enable the growing chains to assume a conformation allowing ring closure (*Figure 5*). Therefore, cyclic oligomers were expected here as well in addition to the linear polymer chains.

To check whether or not cyclo-oligomerization occurs, gel permeation chromatography (g.p.c.) investigations were carried out using representative product mixtures of the readily soluble polymers **1a,b**, **2b** and **11**. *Figure 6* shows the g.p.c. traces of (A) a high- and (B) a low-molecular-weight polymer **1a**. Rather unexpectedly, no peaks were detected at high elution times which would point towards the formation of cyclic oligomers. A completely different behaviour was found, on the other hand, upon analysing the *o*-phenanthroline-based polymers **11**: in this case, the formation of cyclic oligomers was immediately evident from the g.p.c. traces. *Figure 7A* shows the g.p.c. trace of a representative product mixture of polymer **11** as received by pouring the whole reaction solution into methanol. A distinct peak appears at high elution times, in addition to the broad peak which corresponds to the linear high polymers **11**. Extraction with acetone allows quantitative separation of the oligomeric fraction (*Figure 7B*), thus making available the pure polymer **11** (*Figure 7C*). Finally, the extracted oligomeric material could be identified using FD mass spectrometry to be nearly exclusively the cyclic trimer **11a**[18].

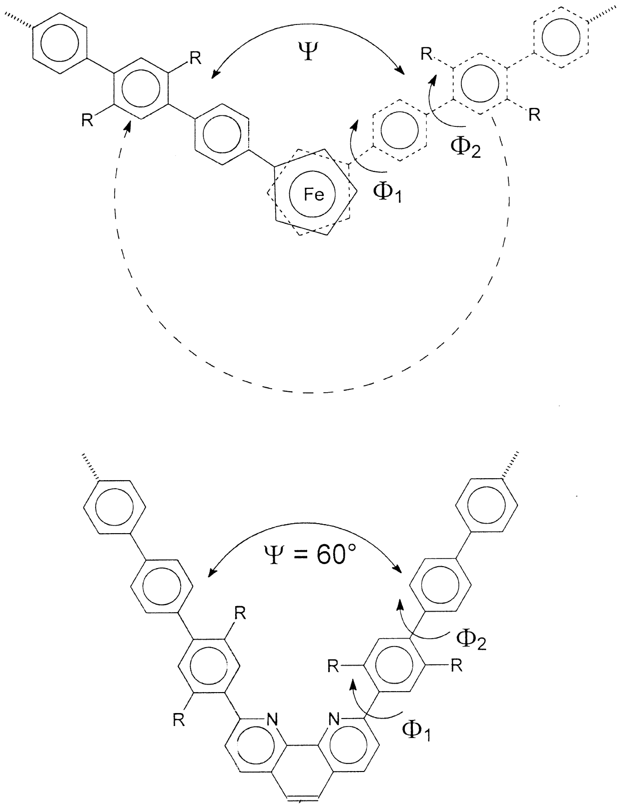


Figure 5 Top-view of the tilted substructures, i.e. 1,1′-ferrocenylene and *o*-phenanthroline, respectively, of polymers **1a** and **11**

The obvious difference in the polymerization behaviour of the ferrocenylene- and the *o*-phenanthroline-based polymeric systems was rather surprising at first glance. It might be caused by different chain conformations assumed by these two systems under the conditions of the Pd-catalysed polycondensation reaction. To prove this assumption, we analysed the solution properties of polymers **1a** and **11** using viscosimetry and light scattering: two series of polymers **1a** and **11** were prepared, with four and three different degrees of polymerization, respectively. Polymers **1a** were analysed as received and thus unfractionated but the *o*-phenanthroline-based polymers **11** were extracted with acetone prior to subsequent experiments to remove the cyclic oligomers. The values of P_n and M_n, determined using osmometry, are listed in *Tables 1* and *2*: while M_n ranges from 6400 to 31 900 for **1a**, the values of M_n of polymers **11** lies between 11 000 and 22 500. The intrinsic viscosities, $[\eta]$, determined using these polymers are given in *Tables 1 and 2*, and the Huggins plots are shown in *Figure 8* (**1a**) and *Figure 9* (**11**).

Throughout, the intrinsic viscosities of polymers **1a** were found to be significantly larger than those of polymers **11** of

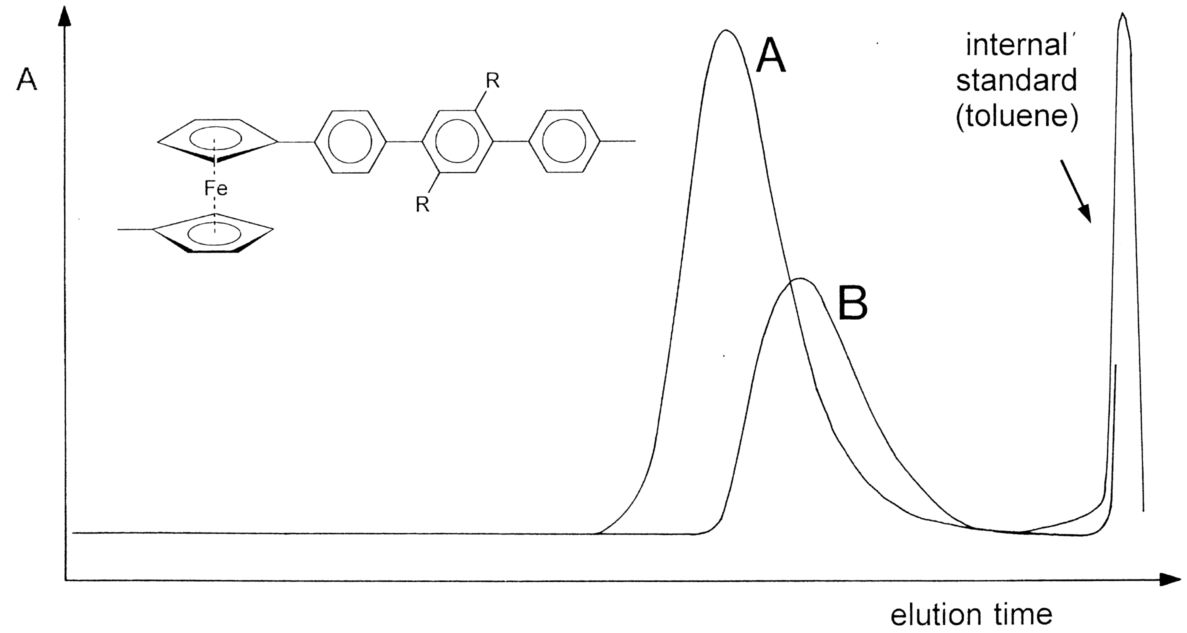


Figure 6 G.p.c. elution curves of (A) a high-molecular weight and (B) a low-molecular-weight polymer **1a**; the eluent was chloroform

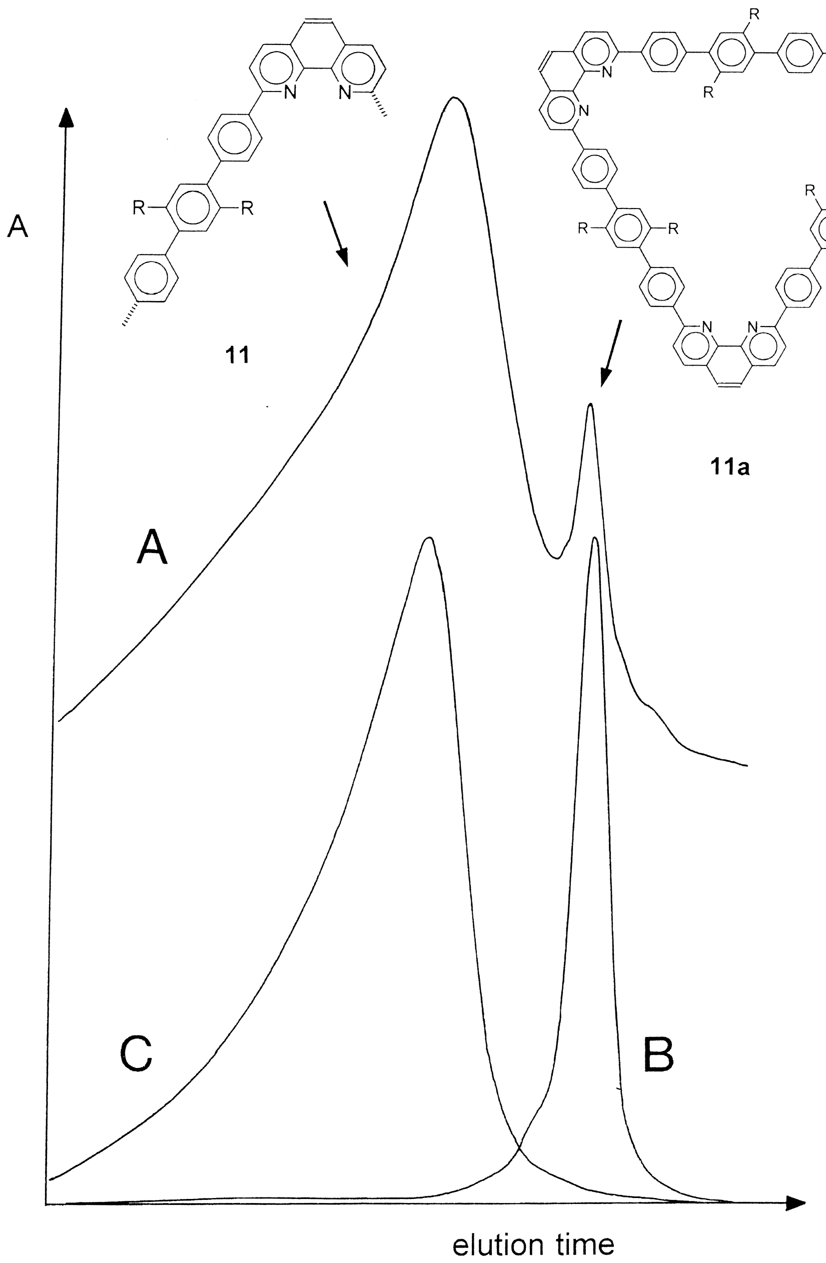


Figure 7 G.p.c. elution curves of (A) a representative product mixture of polymer **11**, of (B) the cyclic trimer **11a**, and of (C) the high-molecular-weight fraction of **11**; the eluent was chloroform

Table 1 Characterization of poly(1,1′-ferrocenylene-*alt*-*p*-terphenylenes) **1a**

Polymer	$M^a_{\mathrm{n,OS}}$	$P_{\mathrm{n,OS}}{}^a$	$M^b_{\mathrm{w,LS}}$	M_w/M_n	$[\eta]$ (mL $g^{-1})^c$
1a/1	6400	11			17.8
1a/2	14 500	25			30.1
1a/3	17 400	30	35 500	2.0	33.5
1a/4	31 900	55	5100	1.6	40.8

[a] Toluene, 30°C
[b] 1,1,2,2-Tetrachloroethane, 30°C
[c] 1,1,2,2-Tetrachloroethane, 30°C

comparable molecular weights: while, for example, polymer **1a/3** ($M_n = 17\,400$) has a value of $[\eta] = 33.2$ mL g^{-1} in tetrachloroethane at 30°C, polymer **11/2** ($M_n = 18\,400$) has an intrinsic viscosity of only $[\eta] = 20.4$ mL g^{-1} under the same conditions. This result confirms the above assumption that the *o*-phenanthroline-based polymers **11** form more

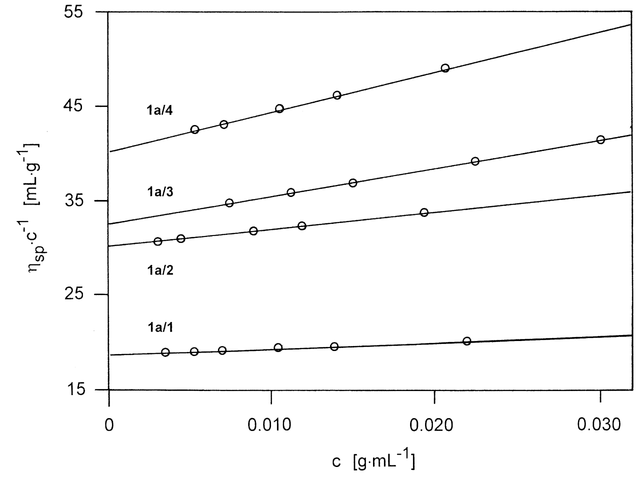


Figure 8 Huggins plots of polymers **1a/1**, **1a/2**, **1a/3** and **1a/4**, measured in tetrachloroethane at 30°C. For details see text and *Table 1*

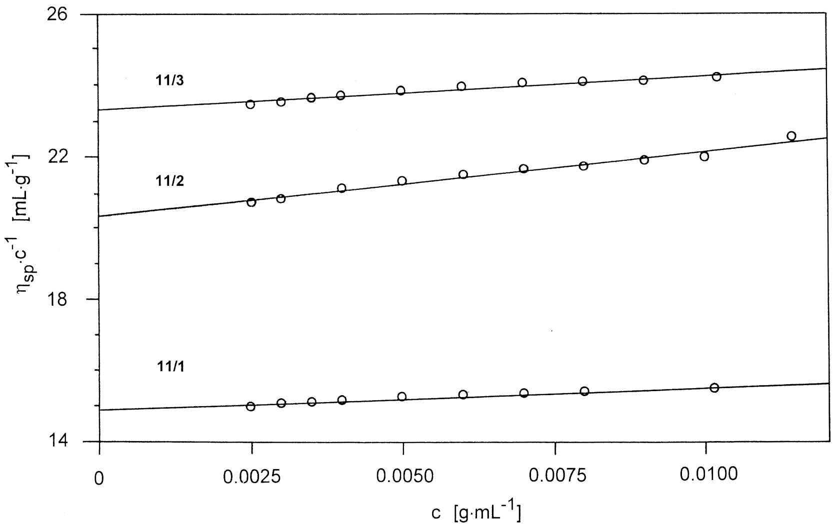


Figure 9 Huggins plots of polymers **11/1**, **11/2** and **11/3**, measured in tetrachloroethane at 30°C. For details see text and *Table 2*

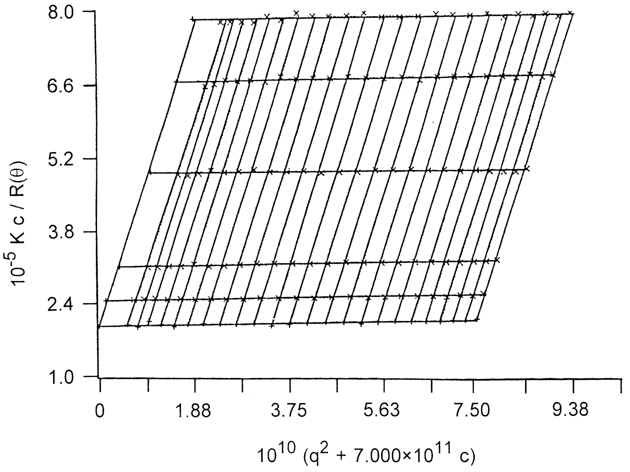


Figure 10 Zimm plot of the light-scattering intensities of polymer **1a/3**, recorded in tetrachloroethane at 30°C

Table 2 Characterization of poly[2,9-(*o*-phenanthroline)-*alt*-*p*-oligophenylenes] **11**

Polymer	$M^{a}_{n,OS}$	$P^{a}_{n,OS}$	$M^{b}_{w,LS}$	M_w/M_n	[η] (mL g^{-1})^{c}
11/1	11 400	20	18 500	1.6	14.9
11/2	18 400	32	31 200	1.7	20.4
11/3	22 500	39	44 400	2.0	23.3

[a] Toluene, 30°C
[b] 1,1,2,2-Tetrachloroethane, 30°C
[c] 1,1,2,2-Tetrachloroethane, 30°C

compact coils in solution than the poly(1,1′-ferrocenylene-*alt*-*p*-terphenylenes) **1a**, causing their higher tendency to cyclo-oligomerize. Nevertheless, it is also evident from the viscosimetric studies that the ferrocenylene-based polymers assume a coiled chain conformation as well. To make this point clear, we compared the intrinsic viscosity of polymer **1a/3** ($P_n = 30$, $M_n = 17\,400$) with that of the really rodlike PPP derivative **8** ($P_n = 32$; $M_n = 17\,800$): while the intrinsic viscosity of **1a/3** is only $[\eta] = 33.2$ mL g^{-1}, the PPP **8** has a value of $[\eta] = 168$ mL g^{-1} under the same conditions.

To corroborate the results of the osmometric and viscosimetric investigations, polymers **1a** and **11** were also investigated by light scattering (see *Tables 1 and 2*). The weight-average molecular weights, M_w, thus determined were in good agreement with the values of M_n obtained using osmometry: polydispersities of $M_w/M_n = 1.6$ to 2.0 were found for all polymers investigated by light scattering. Moreover, the Zimm plots show the ferrocenylene-based polymers **1a** to have larger radii of gyration than the *o*-phenanthroline-based polymers **11** in all cases. As an example, *Figure 10* displays the Zimm plot of polymer **1a/3** ($P_n = 30$, $M_n = 17\,400$), and *Figure 11* that of polymer **11/2** ($P_n = 32$, $M_n = 18\,400$). From these data, radii of gyration of $r_G = 13$ and 11 nm were deduced for polymers **1a/3** and **11/2**, respectively.

To conclude, viscosimetry as well as the light scattering data both allow the explanation of the higher tendency to cyclo-oligomerize in the course of the synthesis of polymers **11**: as the *o*-phenanthroline moieties introduce bend angles into the main chains that are fixed to precisely 60°, they fold back the attached chain segments much more efficiently than the ferrocenylene moieties which can rotate nearly freely. The other way round, the experiments allow the conclusion that the average bent angle that each ferrocenylene moiety imposes into its polymer chain must be significantly larger than 60°, but clearly less than 180°.

Bulk properties

The bulk properties of the poly(1,1′-ferrocenylene-*p*-oligophenylenes) were investigated using high-molecular-weight samples of polymers **1a,b** and **2b**, and compared with those of poly(2,5-dihexyl-*p*-phenylene) **9** and poly[2,9-(*o*-phenanthroline)-*alt*-*p*-oligophenylene] **11**. Prior to the analysis of the thermal phase behaviour, however, we had to determine the thermal stability of the materials under investigation: it is well-established that the introduction of *n*-alkyl side chains into aromatic polymers reduces their thermal stability drastically. For example, unsubstituted poly(*p*-phenylene) is stable up to temperatures of above 500°C, but decomposition starts at about 250–300°C when aliphatic side chains are attached to these polymers. Hence, to ensure that the following measurements are not affected by thermal cleavage of the aliphatic side groups, thermogravimetric analyses were performed. Representative t.g.a. plots are shown in *Figure 12* for polymers **1a** (A), **1b** (B) and **9** (C).

The t.g.a. curves clearly show the considerably higher thermal stability of the poly(1,1′-ferrocenylene-*alt*-*p*-oligophenylenes) in comparison with the PPP reference polymer that does not contain ferrocenylene moieties: while weight loss starts in the latter systems at approx. 300°C already, the ferrocenylene-based polymers are stable up to 400°C. Obviously, the ferrocenylenes inhibit the thermal cleavage of the *n*-alkyl side chains and thus increase the thermal stability of these materials by about 100°C. Therefore, the analysis of the thermal phase behaviour of the ferrocenylene-containing polymers **1**–**3** is possible up to temperatures of 400°C. In this, we started with the *p*-terphenylene-bridged polymers **1a**,**b** and **11**. All these polymers were found to be semicrystalline according to d.s.c. and WAXS investigations if obtained by precipitation from solution. When heated up for the first time, the weak reflexes in the WAXS pattern disappear, and intensive endothermic peaks appear in the d.s.c. curves at 110°C (**1a**, *Figure 13A*) and 65°C (**1b**, *Figure 13B*) respectively. Simultaneously, the originally brittle materials change into isotropic melts. When the molten materials were cooled down again, recrystallization could not be achieved any more, neither by cooling down extremely slowly nor by annealing at various temperatures. Throughout, brown, transparent and completely amorphous glasses were obtained (WAXS, polarization microscopy). Consequently, the second heating run gave only the glass transitions at 80°C (**1a**, *Figure 13C*) and 30°C (**1b**, *Figure 13D*). Obviously, the high melt viscosity prevents recrystallization of the once molten materials.

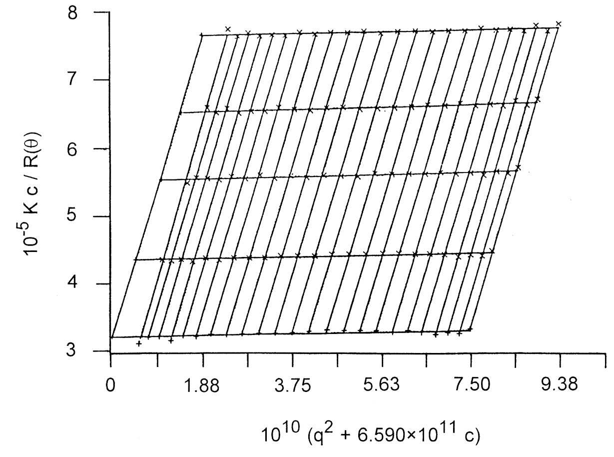


Figure 11 Zimm plot of the light-scattering intensities of polymer **11/2**, recorded in tetrachloroethane at 30°C

The poly[2,9-(*o*-phenanthroline)-*alt*-*p*-oligophenylenes] **11** are also found to be semicrystalline at room temperature when obtained by precipitation from solution. However, their thermal phase behaviour is quite different from that of polymers **1a**. When heated up for the first time in a d.s.c. experiment (*Figure 14A*), a glass transition is observed at approx. 190°C which is followed by an intensive exothermic peak at 220°C which could be assigned to a recrystallization process by WAXS studies and polarization microscopy: above 200°C, the originally powdery material softens, but shortly after this it resolidifies, giving a birefringent solid. Obviously, the crystallinity is rather low in the precipitated material and increases as soon as the chain segments reach a sufficient mobility for their reorganization and thus shortly above the glass transition temperature. No further phase transition could be observed when the heating was continued up to temperatures where decomposition starts. (The weak endotherm at approx. 270°C might be due to the loss of coordinated water.) Thus, the thermal stability of polymer **11** is insufficient to reach the isotropic melt. In the second and all subsequent heating runs, the glass transition at 190°C is the only phase transition that could be observed

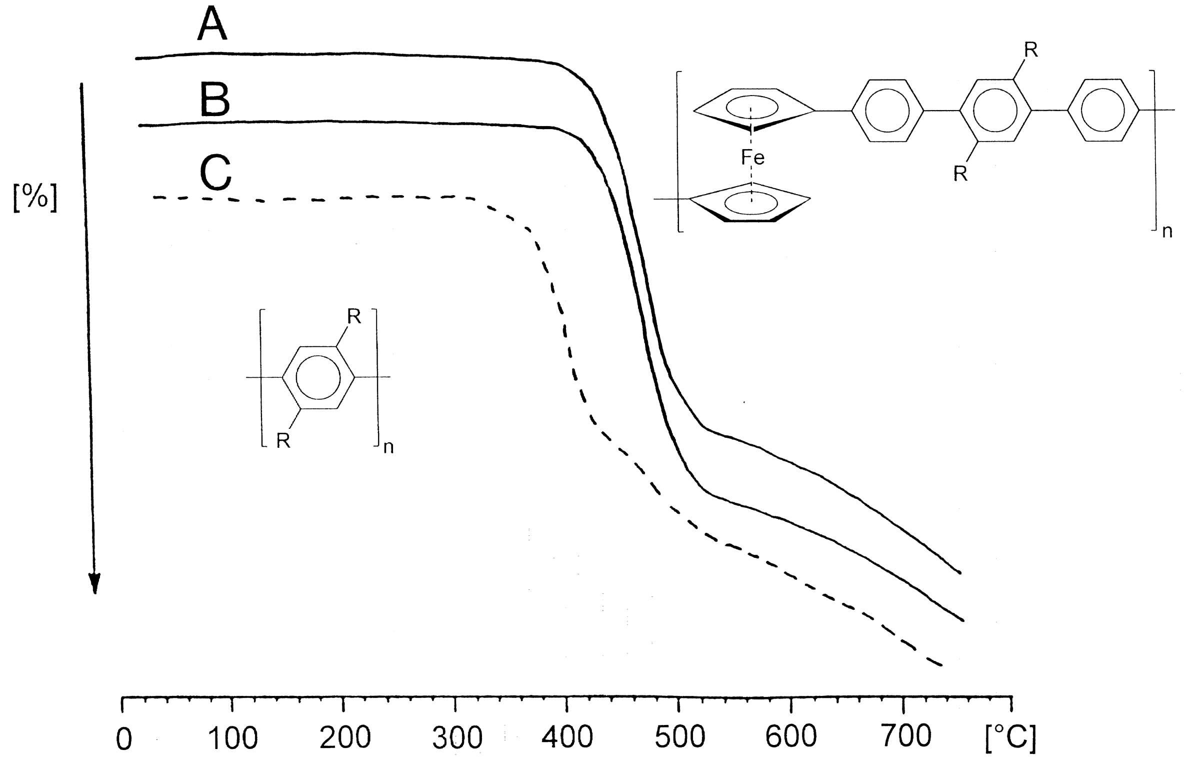


Figure 12 T.g.a. plots of polymers **1a** (A), **1b** (B) and **9** (C), measured under an atmosphere of nitrogen and at a heating rate of 5 K min^{-1}

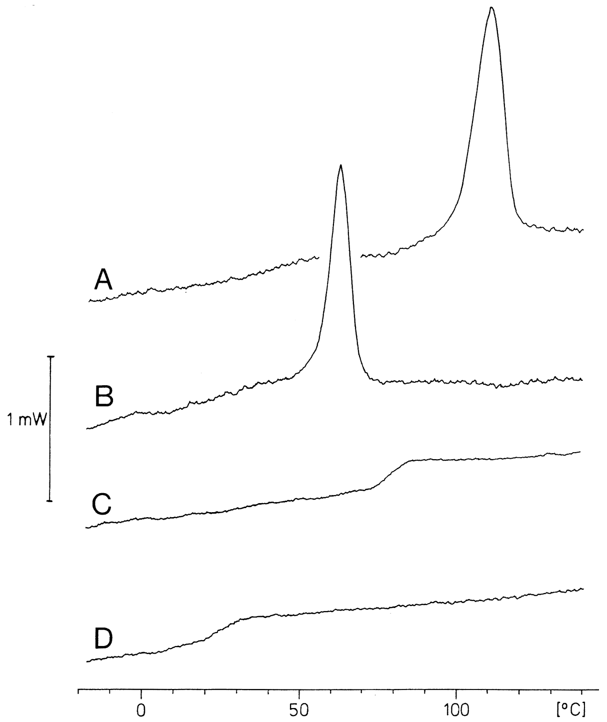


Figure 13 D.s.c. plots of polymers **1a** (first heating run: A; second heating run: C) and **1b** (first heating run: B; second heating run: D), measured under an atmosphere of nitrogen and at a heating rate of 5 K min^{-1}

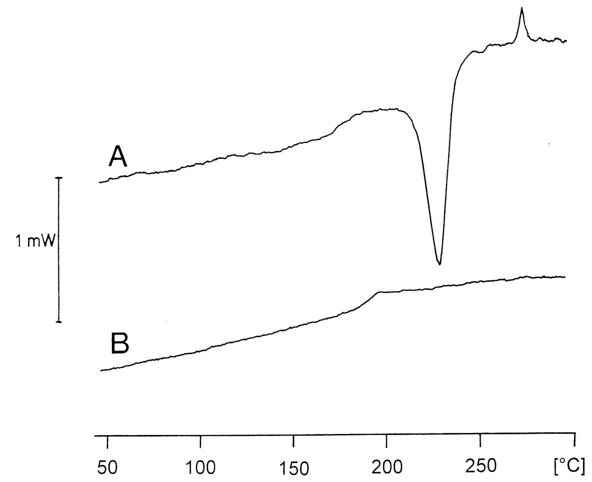


Figure 14 D.s.c. plots of polymer **11** (first heating run: A; second heating run: B), measured under an atmosphere of nitrogen and at a heating rate of 5 K min^{-1}

(*Figure 14B*), showing that the material remains semicrystalline also after thermally induced recrystallization. To conclude, the experiments showed that the thermal behaviour of the ferrocenylene-containing polymers **1** and of their *o*-phenanthroline counterpart **11** is quite different. As in solution, the differences can be interpreted as the consequence of the considerably higher conformational freedom of the ferrocenylene-based polymers.

A thermal behaviour which was again quite different was found for the *n*-dodecyl substituted poly(1,1′-ferrocenylene-*alt*-*p*-quinquephenylenes) **2b**. When these polymers were heated up for the first time, an endotherm T1 was observed at approx. 70°C. We interpret this transition as a side-chain melting process. When the material is heated further, two more endotherms are found at 160°C (T2) and at 185°C (T3). In-between T2 and T3, moreover, a pronounced exothermic signal E is found (*Figure 15A*).

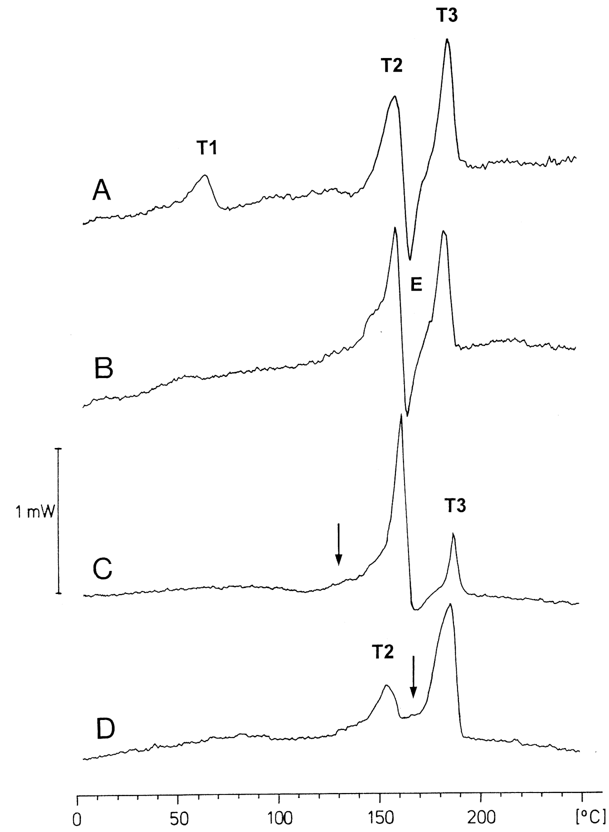


Figure 15 D.s.c. plots of polymer **2b** (first heating run: A; second heting run: B; after annealing at 130°C: C; after annealing at 165°C: D) measured under an atmosphere of nitrogen and at a heating rate of 5 K min^{-1}; see text for details

With the aid of WAXS and polarization microscopy, endotherm T3 could be identified as the transition into the isotropic melt. To make sure that the exotherm E between T2 and T3 corresponds to a phase transition from a low-temperature crystalline modification into a high-temperature modification, various annealing experiments were performed. *Figure 15C* and *D* display d.s.c. curves obtained after annealing at 130°C and 165°C, respectively. When the material is annealed at 130°C and, thus, below T2, three transitions are observed in the following heating run, the intensive endotherm T2, the exotherm E, and the endotherm T3. When, on the other hand, the material is annealed at 165°C and, thus, at a temperature between T2 and T3, the enthalpy of T2 decreases significantly in the following heating run. Moreover, a much more pronounced enotherm T3 is found, and exotherm E has disappeared. Based on these observations and additional WAXS experiments, we assign endotherm T2 to the melting of the low-temperature crystalline modification, and exotherm E corresponds to the recrystallization of the material in a high-temperature crystalline modification. The occurrence of a liquid-crystalline mesophase, on the other hand, can be excluded on the basis of these experiments. Clarification of what the difference is between the low- and the high-temperature modification is presently under way.

CONCLUSIONS

The present work shows the preparation of readily soluble, constitutionally homogeneous and high-molecular-weight poly(1,1′-ferrocenylene-*alt*-*p*-oligophenylenes) through the Pd-catalysed polycondensation reaction. While polymers containing short *p*-oligophenylene bridges are readily soluble, neither flexible side chains nor the flexible ferrocenylene links guarantee sufficient solubility of the polymers containing more than five phenylenes in the rigid *p*-oligophenylene moieties. The properties in bulk and solution were analysed and compared with those of poly[2,9-(*o*-phenanthroline)-*alt*-*p*-oligophenylene] reference polymers. The intrinsic viscosities and the radii of gyration have been found to be smaller for the *o*-phenanthroline-based polymers **11** compared with their more flexible ferrocenylene analogs **1a**. This allows an explanation of the experimental finding that in the course of the polymer syntheses only the *o*-phenanthroline-based systems form cyclic oligomers. Obviously, the ferrocenylene moieties introduce tilt angles greater than 60° into the otherwise highly rigid polymer chains. Moreover, they provide the chains with a considerable dynamic flexibility as is evident from, for example, the low glass-transition temperatures of polymers **1a,b**. Thus, the presented investigations demonstrate the enormous influence of both, the degree of flexibility and the tilt angles of the bending units on the solution properties and on the thermal phase behaviour of these novel macromolecular systems containing rodlike moieties and bent structures in an alternating fashion.

EXPERIMENTAL

All chemicals and solvents were purchased from Fluka, Aldrich, and Strem Chemical Co. in p.a. quality, and used without further purification. 1,1′-Bis(*p*-bromophenyl)ferrocene **4**[19], 2,5-dialkylbenzene-1,4-diboronic acids **5a,b**[20], *p*-oligophenylenediboronic acids **6a,b** and **7a,b**[20,21], 2,9-bis(*p*-bromophenyl)-*o*-phenanthroline **10**[18] and $[Pd(PPh_3)_4]$[31] were prepared according to the literature; $PdCl_2$ was a gift of the Degussa Chemical Co. Polymers **8**[20], **9**[30] and **11**[18] were prepared according to the procedures described recently.

^{1}H and ^{13}C n.m.r. spectra were recorded on a Bruker AC 400 spectrometer at 400 MHz (^{1}H) and 100 MHz (^{13}C), respectively. Chloroform-d_1 and tetrachloroethane-d_2 (Deutero GmbH) were used as the solvents, TMS as the internal standard. Measurements were carried out at 30°C unless otherwise stated. Signal assignment is done according to the numbering of the protons and carbons given in *Figures 1–4*. Membrane osmometry was done using a Knauer 0100 Membrane osmometer at 50°C in toluene. Knauer Y1245-membranes (regenerated cellulose) were used. Vapour pressure osmometry was performed using a Knauer vapour pressure osmometer (35°C, chloroform). Gel permeation chromatography was done on a 5 mm Styragel column in chloroform at a flow rate of 1 mL min^{-1} with u.v. detection (254 nm). Viscosity measurements were carried out using Ubbelohde viscosimeters (SCHOTT company, diam. = 0.5 mm, type 0C) with the LAUDA process viscosimetry system PVS 2.03. Light-scattering intensities were determined using a SOFICA-P6D-42000 apparatus equipped with a laser operating at 633 nm. All measurements were done at 30°C using tetrachloroethane as the solvent. The refractive index increments (dn/dc) were measured with a Brice-Phoenix differential refractometer at two different wavelengths and extrapolated to 633 nm. Thermal gravimetric analysis measurements were performed using a Mettler TG 50 and a Netzsch STA 409 apparatus under an atmosphere of nitrogen. The heating rate was 5 K min^{-1}. D.s.c. investigations were carried out using a Mettler d.s.c. 30 (heating rate: 5 K min^{-1}). WAXS measurements were performed on a Siemens D-5000 diffractometer using CuK_α radiation ($\lambda = 1.542$ Å). Elemental analyses were carried out on a CHN-RAPID apparatus of Elementar Analysensysteme GmbH.

Polymer syntheses; general procedure:

1,1′-bis(p-bromophenyl)ferrocene **4** (0.496 g; 1.0 mmol), diboronic acid derivative **5a,b**, **6a,b**, or **7a,b** (1.0 mmol) and $Pd[P(C_6H_5)_3]_4$ (1×10^{-6} mol) are refluxed and vigorously stirred in the heterogeneous system of toluene (5 mL)/ aqueous Na_2CO_3 (1 M, 7 mL) for 5 days. Bromobenzene (1 mL) is added and refluxing and stirring is continued for one further day.

Work-up for readily soluble polymers. After the mixture is cooled down to room temperature, the layers are separated, and the organic one is washed with water (2x50 mL), dried ($MgSO_4$) and filtered. The polymer is precipitated from this solution with methanol, recovered by filtration through a Büchner funnel and dried *in vacuo* over P_4O_{10}. Further purification is possible by redissolving the polymers in chloroform (10 mL) followed by precipitation in methanol (200 mL).

Work-up for scarcely soluble polymers. In the case of polymers which precipitate during the polycondensation reaction, the whole reaction mixture is diluted with water (200 mL) and toluene (200 mL), the aqueous layer is separated off, and the organic layer is washed with water (2 × 200 mL). The organic layer is concentrated down to about 50 mL, and methanol (200 mL) is added. The precipitate is filtered off, washed with methanol (100 mL) and dried *in vacuo* over P_4O_{10}.

Analytical data of soluble polymers:

Polymer **1a**: ^{1}H n.m.r. ($CDCl_3$): $\delta = 0.80$ (t; 6H CH_3), 1.20 (m; 12H, CH_2), 1.50 (m; 4H, Ar–CH_2–C$\underline{H}_2$–R), 2.61 (t; 4H, Ar–CH_2–R), 4.26 (m; 4H, H3), 4.56 (m; 4H, H2), 7.17 (s; 2H, H6), 7.27 (m; 4H, H8), 7.44 (m; 4H, H9); ^{13}C n.m.r. ($CDCl_3$): $\delta = 14.04$ (q; CH_3), 22.54, 29.35, 31.47, 31.59, 32.83 (5t; CH_2), 68.04 (d; C3), 70.94 (d; C2), 85.86 (s; C1), 125.66, 129.28 (2d; C8,9), 130.85 (d; C6), 136.91 (s; C10), 137.54 (s; C5), 139.74, 140.55 (2s; C4,7).

Elemental analysis:	Calcd:	C 82.74	H 7.64
$(C_{40}H_{44}Fe)_n$	Found:	C 82.54	H 7.59

Polymer **1b**: ^{1}H n.m.r. ($CDCl_3$): $\delta = 0.85$ (t; CH_3), 1.23 (m; 36H, C$\underline{H}_2$), 1.51 (m; 4H, Ar–CH_2–C$\underline{H}_2$–R), 2.61 (t; 4H, Ar–C$\underline{H}_2$–R), 4.20 (m; 4H, H3), 4.58 (m; 4H, H2), 7.17 (s; 2H, H6), 7.27 (m; 4H, H8), 7.45 (m; 4H, H9); ^{13}C n.m.r. ($CDCl_3$): $\delta = 14.14$ (q; CH_3), 22.69, 29.36, 29.43, 29.59, 29.66, 29.66, 29.69, 31.56, 31.92, 32.81 (10t; CH_2), 67.88 (d; C3), 71.11 (d; C2), 85.73 (s; C1), 125.63, 129.27 (2d; C8,9), 130.83 (d; C6), 136.91 (s; C10), 137.54 (s; C5), 139.64, 140.49 (2s; C4,7).

Elemental analysis:	Calcd:	C 83.39	H 9.15
$(C_{52}H_{68}Fe)_n$	Found:	C 83.57	H 9.26

Polymer **2b**: ^{1}H n.m.r. ($CDCl_3$): $\delta = 0.85$ (t; CH_3), 1.23 (m; 36H, CH_2), 1.53 (m; 4H, Ar–CH_2–C$\underline{H}_2$–R), 2.58 (t;

4H, Ar–CH_2–R), 4.29 (m; 4H, H3), 4.58 (m; 4H, H2), 7.18 (s; 2H, H6), 7.41, 7.42, 7.53, 7.65 (4d; 8H, H8,9,12,13); ^{13}C n.m.r. ($CDCl_3$): $\delta = 14.14$ (q; CH_3), 22.69, 29.37, 29.68, 31.52, 31.93, 32.60 (16t; CH_2), 67.76 (d; C3), 70.79 (d; C2), 85.66 (s; C1), 126.30, 126.78, 129.79, 130.95 (4d; C6,8,9,12,13), 137.23, 137.56, 138.11, 139.06, 140.31, 140.77 (6s; C4,5,7,10,11,14).

Elemental analysis:	Calcd:	C 85.30	H 8.51
$(C_{64}H_{76}Fe)_n$	Found:	C 85.18	H 8.63

ACKNOWLEDGEMENTS

The authors are grateful to Professor M. Ballauff, Karlsruhe, for his support of this work. Financial support by the *Deutsche Forschungsgemeinschaft* is gratefully acknowledged.

REFERENCES

1. Ciardelli, F., Tsuchida, E. and Wöhrle, D., *Macromolecule–Metal Complexes*. Springer, Berlin, 1996.
2. Manners, I., *Angew. Chem.*, 1996, **108**, 1713.
3. Manners, I., *Adv. Organomet. Chem.*, 1995, **37**, 131.
4. Neuse, E. W., *J. Macromol. Sci.-Chem.*, 1981, **A16**(1), 3.
5. Neuse, E. W. and Rosenberg, H., *J. Macromol. Sci. Rev. Macromol. Chem.*, 1970, **C4**(1), 1.
6. Mueller-Westerhoff, U. T., *Angew. Chem. Int. Ed. Engl.*, 1986, **25**, 702.
7. Morrison, W. H. and Hendrickson, D. N., *Inorg. Chem.*, 1975, **14**, 2331.
8. Kramer, J. A. and Hendrickson, D. N., *Inorg. Chem.*, 1980, **19**, 3330.
9. Rosenblum, M., Nugent, H. M., Jang, K. S., Labes, M. M., Cahalane, W., Klemarczyk, P. and Reiff, W. M., *Macromolecules*, 1995, **28**, 6330.
10. Rosenblum, M., *Adv. Mater.*, 1994, **6**, 159.
11. Nugent, H.M., Rosenblum, M. and Klemarczyk, P., *J. Am. Chem. Soc.*, 1993, **115**, 3848.
12. Foxman, B. M. and Rosenblum, M., *Organometallics*, 1993, **12**, 4805.
13. Foxman, B. M., Gronbeck, D. A. and Rosenblum, M., *J. Organomet. Chem.*, 1991, **413**, 287.
14. Arnold, R., Matchett, S. A. and Rosenblum, M., *Organometallics*, 1988, **7**, 2261.
15. Bayer, R., Pöhlmann, T. and Nuyken, O., *Macromol. Chem., Rapid Commun.*, 1993, **14**, 359.
16. Hmyene, M., Yassar, A., Escorne, M., Percheron-Guegan, A. and Garnier, F., *Adv. Mater.*, 1994, **6**, 564.
17. Knapp, R. and Rehahn, M., *Makromol. Chem., Rapid Commun.*, 1993, **14**, 451.
18. Velten, U. and Rehahn, M., *Macromol. Chem. Phys.*, 1998, **199**, 127.
19. Knapp, R. and Rehahn, M., *J. Organomet. Chem.*, 1993, **452**, 235.
20. Rehahn, M., Schlüter, A. D. and Wegner, G., *Makromol. Chem.*, 1991, **1990**, 191.
21. Galda, P. and Rehahn, M., *Synthesis*, 1996, p. 614.
22. Schmitz, L. and Ballauff, M., *Polymer*, 1995, **36**, 879.
23. Vanhee, S., Rulkens, R., Lehmann, U., Rosenauer, C., Schulze, M., Köhler, W. and Wegner, G., *Macromolecules*, 1996, **29**, 5136.
24. Schlüter, A. D. and Wegner, G., *Acta Polymer.*, 1993, **44**, 59.
25. Rau, I. U. and Rehahn, M., *Acta Polymerica*, 1994, **45**, 3.
26. Rau, I. U. and Rehahn, M., *Makromol. Chem.*, 1993, **194**, 2225.
27. Schmitz, L., Rehahn, M. and Ballauff, M., *Polymer*, 1993, **34**, 646.
28. Helmer-Metzmann, F., Rehahn, M., Schmitz, L., Ballauff, M. and Wegner, G., *Makromol. Chem.*, 1992, **193**, 1847.
29. Rehahn, M., Schlüter, A. D. and Wegner, G., *Makromol. Chem., Rapid Commun.*, 1990, **11**, 535.
30. Rehahn, M., Schlüter, A. D., Feast, W. J. and Wegner, G., *Polymer*, 1989, **30**, 106031.
31. Coulson, D. R., *Inorg. Synth.*, 1972, **13**, 121.