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Polymer 41 (2000) 3183–3191

polymer

Reaction of cyclopentadienide carbanion with α,α′-dibromometaxylene: an unexpected example of polyanionic substitution

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Received 25 March 1999; received in revised form 23 June 1999; accepted 9 July 1999

Abstract

The reaction of α,α′-dibromometaxylene (DBMX) with sodium cyclopentadienide (CpNa) gives several oligomers, which were characterized by Size Exclusion Chromatography (SEC) and Liquid Secondary Ion Mass Spectroscopy (LSIMS). The obtained oligomers came from two competitive mechanisms after an anionic substitution of the DBMX by CpNa. The first was based on the proton transfer between the monosubstituted DBMX and CpNa giving a transcient monobrominate carbanion which is the propagating species of a polyanionic substitution. The second one is a classical Diels–Alder reaction between two oligomers containing substituted cyclopentadienes (CPDs) and also between an oligomer and the CPD formed in situ by hydrogen transfer.

Keywords: Biscyclopentadiene; α,α′-dibromometaxylene; Sodium cyclopentadienide

1. Introduction

The condensation of α,α′-dibromoxylene with sodium cyclopentadienide (CpNa) was previously used in order to get biscyclopentadiene (bis CPD) monomers [1,2] (Scheme 1 (Theoretical synthesis of biscyclopentadiene monomer)), but the authors pointed out the formation of some polymeric side products. In addition, in the case of methylCPD the presence of three isomers (Scheme 2 (Isomers of methylcyclopentadiene according to [3])) has been proved [3].

We have recently shown that the reaction of benzylbromide with CpNa did not allow the isolation of the expected benzylCPD. Two types of reactions took place in the reaction medium. One is based on the formation of benzylCPD carbanion, which reacts with the benzylbromide. The second one is a Diels–Alder addition between the dienes present in the medium [4]. According to these observations, α,α′-dibromometaxylene (DBMX) should react with the CpNa with the formation of polymeric products and the purpose of this paper is the characterization of the reaction products by Size Exclusion Chromatography (SEC) and Liquid Secondary ion mass spectroscopy (LSIMS).

2. Experimental

2.1. Condensation of DBMX with CpNa

CpNa solution in tetrahydrofuran (THF, 2.0 M), DBMX and anhydrous THF were purchased from Aldrich and used as received.

CpNa solution is added with a syringe and a septum to 2.64 g (10.0 mmol) of DBMX in 15 ml of anhydrous THF stirred at 0°C under nitrogen atmosphere. Amounts of CpNa added and reaction time are described in Table 1. The immediate formation of a white precipitate is observed. The mixture is stirred at 0°C and then filtered. The sodium bromide (NaBr) is washed with 3 × 10 ml of diethylether, and the washings are added to the filtrate which is washed in turn several times with 15 ml of distilled water until neutral pH. Following this, the organic layer is dried over sodium sulfate. Finally, the solvent is stripped off and a brown viscous oil is obtained. The latter must be stored at cold temperatures (less then 0°C), otherwise it would cross-link at ambient temperature.

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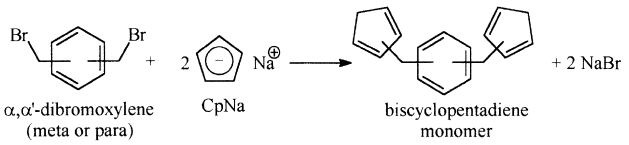
0032-3861/00/$ - see front matter
PII: S0032-3861(99)00464-4



Scheme 1.

NaBr is dried under vacuum and isolated in quantitative yield (95–98%). During reaction, samples are removed periodically for SEC analysis.

2.2. Proton NMR determination

Proton NMR spectra were recorded on a Brucker AC 250 instrument using Sample 4 after work up. The solvent was $CDCl_3$.

2.3. SEC

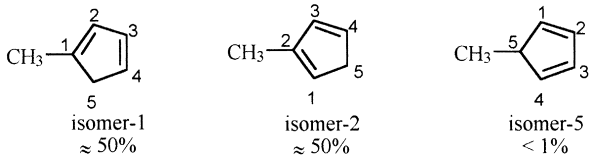
A WATERS GPC apparatus, fitted with refractive index and UV detectors is used (only the latter is used for this work). It is equipped with a series of three columns (μStyragel HR 0.5 + μStyragel HT 3 + μStyragel 10^3 Å) able to separate masses in the range of 10–10 000. The operating solvent is THF (1 ml/min).

Samples of 0.1 ml picked from the reaction mixture are diluted in 10 ml of THF, and 20 μl from this solution are injected through the Millipore filter.

2.4. LSIMS analyses

The LSIMS experiments were carried out on FISONS instruments ZAB2-SEQVG mass spectrometer working in a MCA (Multi Channel Accumulation) scanning mode. The detected mass range is between 350 and 2000 amu with a scan time of 15 s. The resolution of the mass spectrometer is set at 2000.

Sample preparation starts in by positioning a large drop of matrix (*m*-nitrobenzylalcohol) upon the probe tip. The sample (5 mg) is dissolved in 30 μl of THF and then deposited (3 μl) on the matrix. The probe is introduced into the ionisation chamber under high vacuum (10^{-8} mbar) and bombarded by a beam of Cs^+ ions accelerated at 35 kV.



Scheme 2.

3. Results and discussion

3.1. Condensation and SEC analysis

The condensation of CpNa with DBMX took place at 0°C in anhydrous THF under nitrogen atmosphere. Immediately after the first addition of CpNa (Sample 1, Table 1) a NaBr white precipitate appears. After the total addition (Samples 3 or 4, Table 1) the NaBr yield was ranging between 95 and 98%. After filtration, the organic phase was stored at 0°C.

The four Samples 1–4 obtained with different [CpNa] over [Br] ratios were analysed by SEC.

Fig. 1(a) shows the SEC trace obtained with 0.25 Cp^-/Br molar ratio. The peaks 1 and 2 were, respectively, attributed to CPD and DBMX and at least three products (peaks 3–5) are formed.

By increasing the Cp^-/Br molar ratio (Sample 2, Table 1), the peak 2 corresponding to DBMX decreases and another product (peak 6) appears (Fig. 1(b)).

With molar ratio equal to 1 (Fig. 1(c) and (d)), we observed a disappearance of the peak 2 and the formation of some higher molecular weight products. After work up including solvent evaporation, the SEC Trace (1e) was very similar to Trace (1c) and Trace (1d), but the peak 1 (CPD) was eliminated.

3.2. LSIMS

The reaction product corresponding to the 1e trace after work up has been analyzed by LSIMS with *m*-nitrobenzylalcohol as a matrix. The spectra are shown in Fig. 2. Traces 2(a–c) allow us to identify four oligomeric groups. For each group the difference between each peak is 168 amu. In these groups (indicated by roman numbers I, II, III, IV) the importance of the successive ions (indicated by Arabic numbers 1, 2, 3…) looks like a decreasing exponential.

A formula attribution for each peak has been done by taking into account the possible moieties (Table 2) which could participate in the oligomers formula. By different combinations of these "stones" we can build different oligomers having a molecular weight in agreement with the experimental data for the different series (Table 3).

Considering the group I, the most abundant ion I_1 (M/Z = 402) can be represented by the formula 3a (with $n = 1$) shown in Scheme 3 and the reaction mechanism for the formation of the sequence I would be a polyanionic substitution.

Formula 3a takes into account for the propagation an hydrogen transfer only on the terminal CPD. However, for the oligomers with a polymerization degree equal or superior to one, two other sites, the benzylic hydrogen or the hydrogen of disubstituted CPD, can give a carbanion by exchange with CpNa. And as a consequence, branched oligomers such as 3b, 3c and 3d can be produced.

In group II product II (M/Z = 468) can be explained by involving Diels–Alder reactions either by the dimerization

Table 1
Procedure used for the condensation of DBMX with CpNa (DBMX = 10 mmol; THF = 17 ml; $T = 0°C$)

Samples analyzed by SEC	Sample 1	–	Sample 2	Sample 3	Sample 4
CpNa added (mmol)[a]	5	5	5	5	–
Molar ratio (Cp^-/Br)	0.25	0.5	0.75	1	1
t (min)	40	40	40	40	90
SEC Trace (Fig. 2)	1a	–	1b	1c	1d

[a] Sodium cyclopentadiene solution in THF (2.0 M).

of a substituted CPD oligomer 4a (Scheme 4) or by the cycloaddition of CPD monomer on a mono or disubstituted CPD in the chain oligomers 5a, 5b (Scheme 5).

In Group III products III seem to be coming from a Diels–Alder addition of CPD on the group II_n products either on the oligomers 4a or on oligomers 5a and 5b.

Comparing group IV with group I, we observe a difference of 65 amu between IV_1 and I_2, IV_2 and I_3, etc. hence, the products IV_n could be the cyclic oligomers corresponding to the linear group I (Formula 3e, Scheme 3).

3.3. Attempts for NMR determinations

Proton NMR spectra were recorded at 250 MHz. As it can be seen on Fig. 3 the spectrum is rather complex due to the presence of a lot of oligomers with different isomeric structure.

However, the five groups of protons can be attributed to the different structure in agreement with the formulae 4b, 5a, 5b.

3.4. Reaction mechanism

Considering the mechanism responsible for the oligomers formations: the first step is the nucleophilic substitution of one DBMX bromine by the C_pN_a (Scheme 3, Eq. (1)).

The key point is probably that the reaction exchange between the monosubstituted product 3i and CpNa (Eq. (2)) is faster than the substitution of the second DBMX bromine by CpNa, because a substituted CPD is

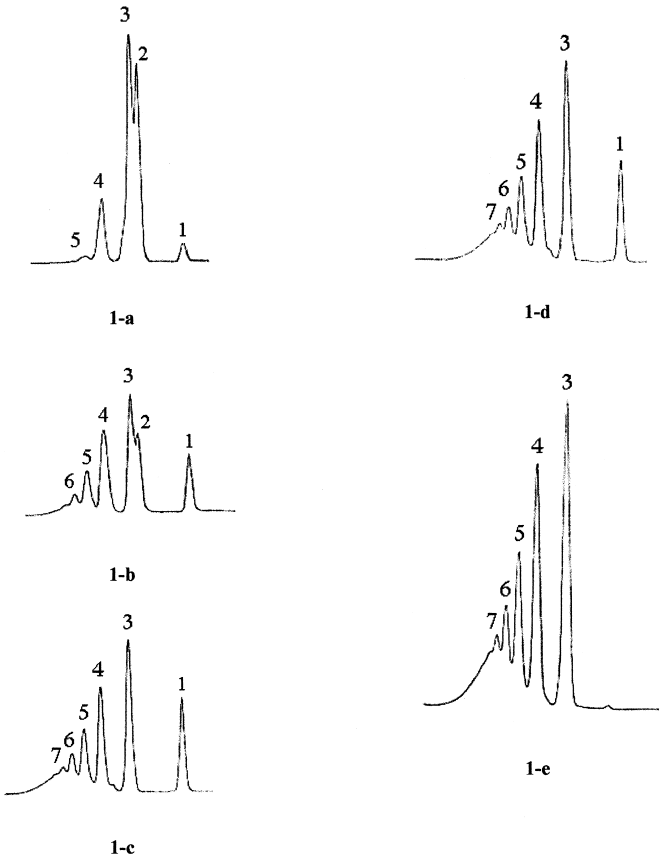
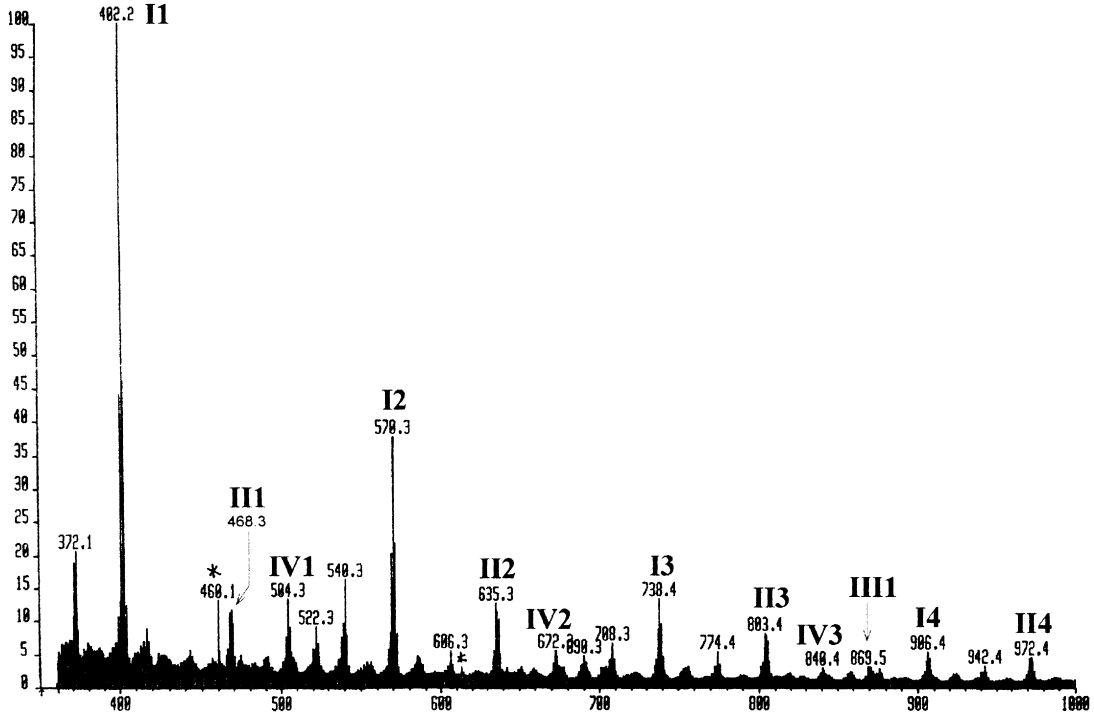


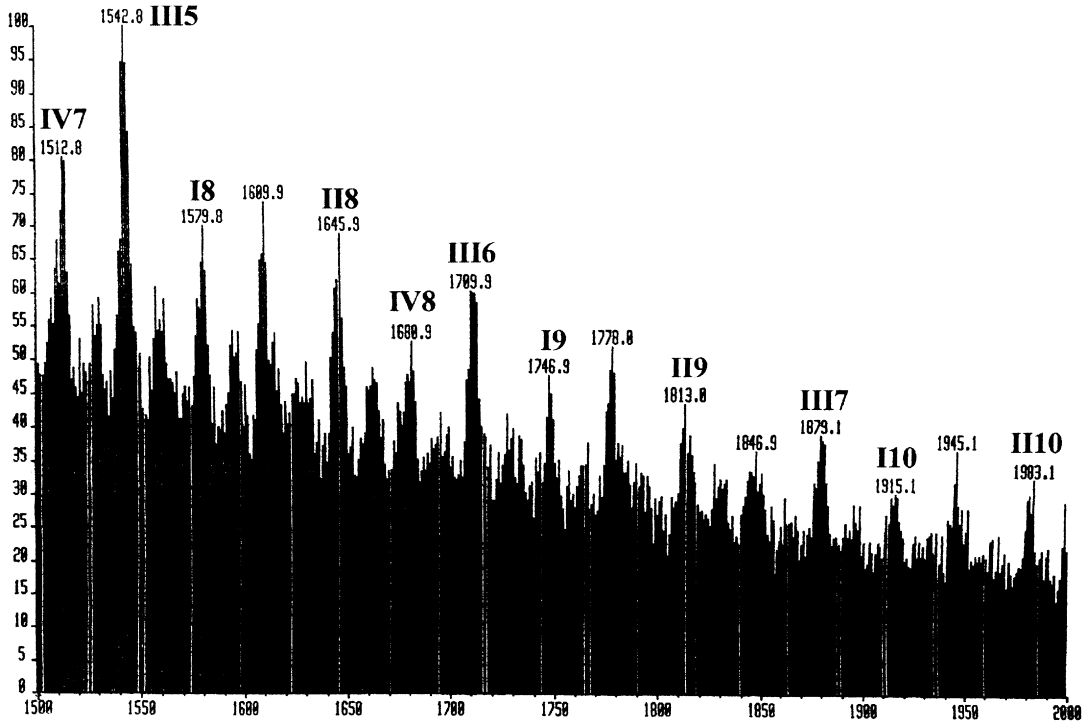
Fig. 1. (a)–(e) SEC traces recorded during condensation of DBMX with CpNa. (1) cyclopentadiene monomer (28.8 min); (2) : α, α′-dibromometaxylene (26.3 min); (3–7) : oligomers (25.6; 24.2; 23.0; 22.4; 21.6 min).



(a)

(b)

Fig. 2. LSIMS spectra of products coming from condensation of DBMX with CpNa. Trace 2(a): (350–1000 amu). Trace 2(b): (1000–1500 amu) standardized with regard to most intense peak (1037.2 amu). Trace 2(c): (1500–2000 amu) standardized with regard to most intense peak (1542.8 amu).



(c)

Fig. 2. (*continued*)

more acidic than the CPD itself. As a result the bromocarbanion, $3^{(-)}$, is the initiator of a polynucleophilic substitution.

But different pathways are possible for the polymerization:

(I) Reaction of $3^{(-)}$ with DBMX followed by exchange between the new substituted CPD with CpNa giving a new substituted cyclopentadienide etc.

(II) AB polysubstitution of the $3^{(-)}$ intermediate.

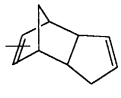
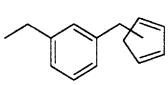
(III) Exchange with a disubstituted CPD in the chain and grafting by reaction with DBMX leading to 3b, 3c, 3d.

The termination of the polysubstitution reactions could take place either by substitution of a bromine by CpNa or by intramolecular substitution leading to the macrocyclic compounds 3e.

Another possibility for the linear or grafted oligomers termination is a hydrogen transfer from the solvent to a substituted cyclopentadienide.

However, the LSIMS results cannot be completely explained by the polysubstitution reaction, and different Diels–Alder additions must be taken into account. Not only Diels–Alder polyaddition between oligomers (which contain substituted CPD) (Scheme 4), but also Diels–Alder between an oligomer and the CPD formed in situ from CpNa must be considered.

Table 2
Symbols and mass moieties used in the interpretation of LSIMS spectra

Molecule/group	Notation	Mass
	CPD	66
	Cp	65
	CA	131
	Z–Cp	169

4. Conclusion

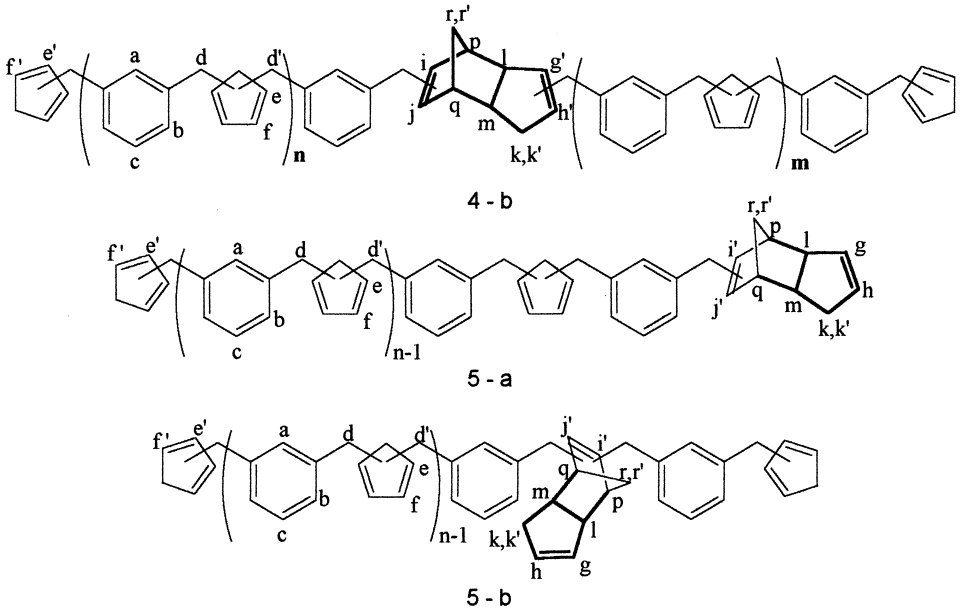
The reaction of sodium cyclopentadienide with DBMX leads to the formation of oligomeric materials.

According to SEC and LSIMS data, the reaction proceeds mainly through a polyanionic substitution probably due to hydrogen transfer between the transcient substituted CPD

Table 3
Characterization of observed ions in the spectra of products resulting from condensation of DBMX with CpNa

Distribution ion numbering	Observed mass (amu)[a]	Calculated mass	Proposed structure	Formulae
I_0	Not observed	234	Cp–Z–Cp	Scheme 3a–d ((a) Proposed structures of series I_n; (b-d) Examples of branched structures proposed for oligomers I_2 (M/Z = 570); (e) Proposed structures of series IV_n).
I_1	402	402	Cp–Z–Cp–Z–Cp	
I_2	570	570	(I_1–H) + Z–Cp	
I_3	738	738	(I_2–H) + Z–Cp	
I_4	906	906	(I_3–H) + Z–Cp	
I_5	1074	1074	(I_4–H) + Z–Cp	
I_6	1243	1242	(I_5–H) + Z–Cp	
I_7	1411	1410	(I_6–H) + Z–Cp	
I_8	1579	1579	(I_7–H) + Z–Cp	
I_9	1747	1747	(I_8–H) + Z–Cp	
I_{10}	1915	1915	(I_9–H) + Z–Cp	
II_1	468	468	$I_0 + I_0/I_1$ + CPD[b]	Scheme 4a and b (The first proposed mechanism that gives series II_n).
II_2	635	636	$I_1 + I_0/I_2$ + CPD	
II_3	803	804	$I_1 + I_1/I_3$ + CPD	
II_4	972	972	$I_1 + I_2/I_4$ + CPD	
II_5	1140	1140	$I_1 + I_3/I_2 + I_2/I_5$ + CPD	
II_6	1309	1308	$I_1 + I_4/I_2 + I_3/I_6$ + CPD	
II_7	1477	1476	$I_1 + I_5/I_2 + I_4/I_3 + I_3/I_7$ + CPD	
II_8	1646	1645	$I_1 + I_6/I_2 + I_5/I_3 + I_4/I_8$ + CPD	
II_9	1813	1813	$I_1 + I_7/I_2 + I_6/I_3 + I_5/I_4 + I_4/I_9$ + CPD	
II_{10}	1983	1981	$I_1 + I_8/I_2 + I_7/I_3 + I_6/I_4 + I_5/I_{10}$ + CPD	
III_1	869	870	II_3 + CPD	Scheme 5a and b (The second proposed mechanism that gives series II_n).
III_2	1037	1038	II_4 + CPD	
III_3	1206	1206	II_5 + CPD	
III_4	1374	1374	II_6 + CPD	
III_5	1543	1542	II_7 + CPD	
III_6	1710	1711	II_8 + CPD	
III_7	1879	1880	II_9 + CPD	
IV_1	504	505	I_2–Cp	Scheme 3e
IV_2	672	673	I_3–Cp	
IV_3	840	841	I_4–Cp	
IV_4	1008	1009	I_5–Cp	
IV_5	1176	1177	I_6–Cp	
IV_6	1345	1345	I_7–Cp	
IV_7	1513	1514	I_8–Cp	
IV_8	1681	1682	I_9–Cp	

[a] Most intense ion of the isotopic contributions.
[b] Cp–Z–Cp–Z–CA.



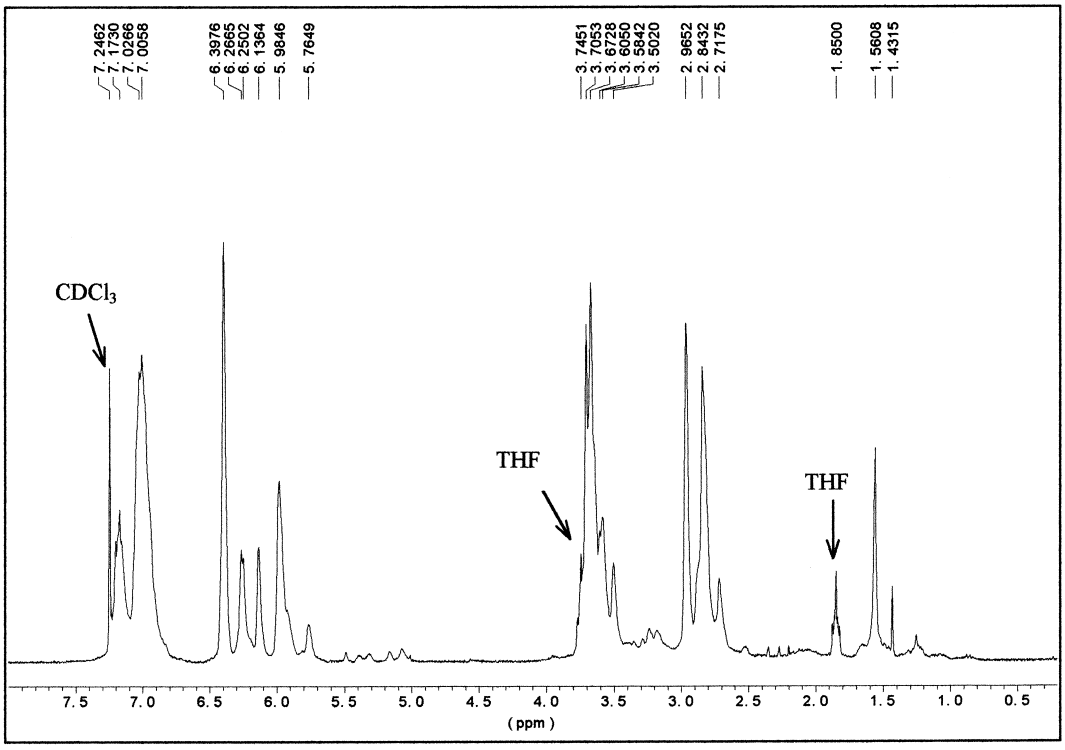
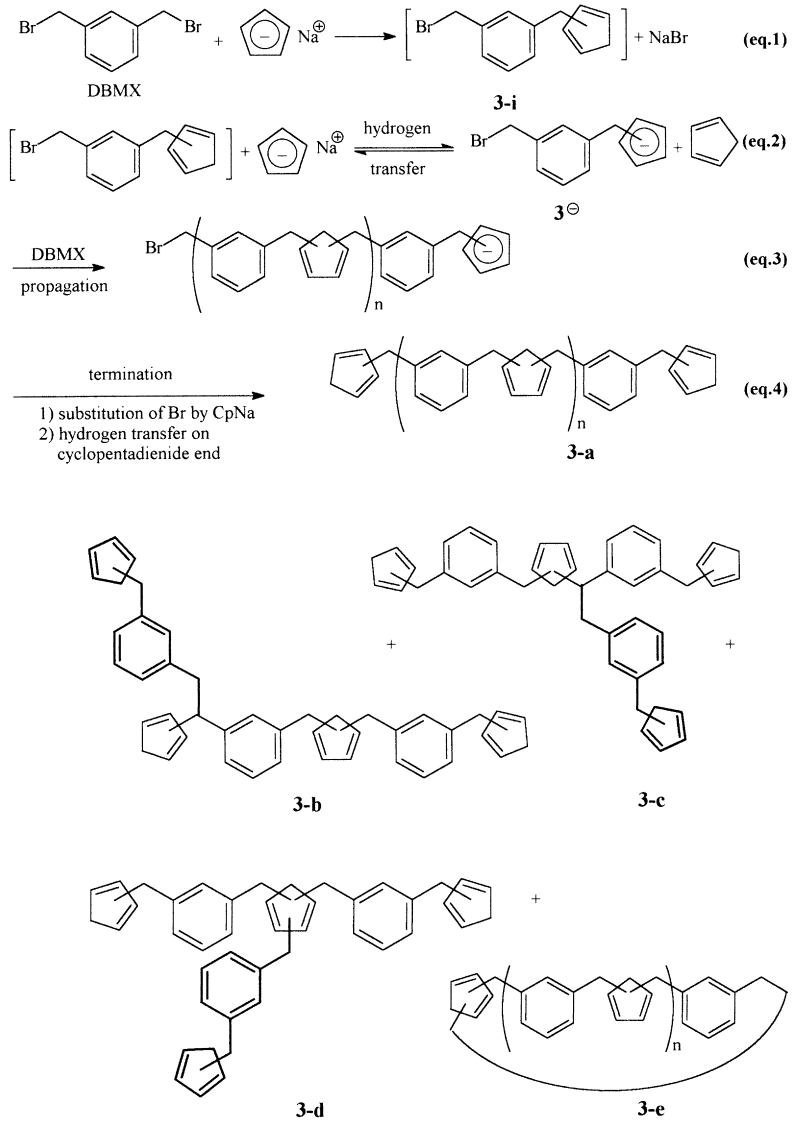
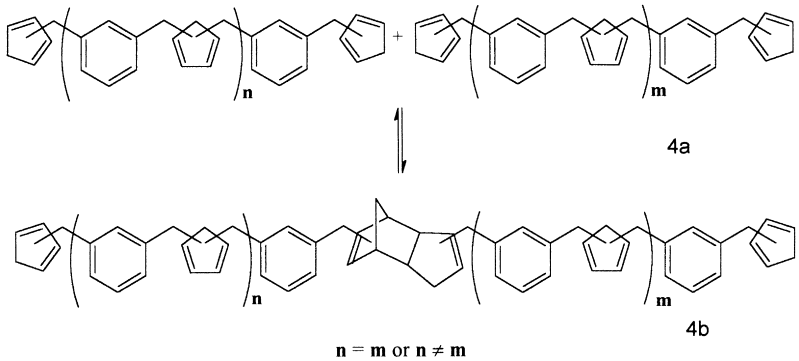


Fig. 3. NMR spectrum of Sample 4. 1.3–1.7 ppm: protons (r, r′); 2.6–3.3 ppm: cyclopentadienyl allylic protons (k, k′, l, m, p, q) + $-CH_2-$xylene protons (d′); 3.4–4.0 ppm: $-CH_2-$ xylene protons (d); 5.0–6.5 ppm: vinylic protons (e, f, e′, f′, g, h, g′, h′, i, j, i′, j′); 6.8–7.5 ppm: aromatic protons (a, b, c).



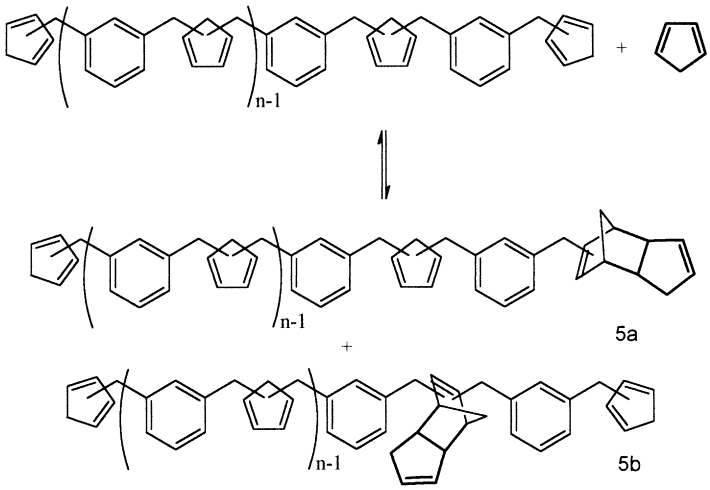
Scheme 3.



n = m or n ≠ m

n = m = 0 ⇒ **II**$_1$ (M/Z = 468), n = 0 and m = 1 ⇒ **II**$_2$ (M/Z = 636), n = m = 1 ⇒ **II**$_3$ (M/Z = 804)…

Scheme 4.



Scheme 5.

initially formed and sodium cyclopentadienide giving a new carbanion, which is the propagation species (Scheme 3). LSIMS data suggest the presence of linear and cyclic oligomers. Besides polysubstitution, Diels–Alder addition takes place between the different molecules containing a CPD ring present in the backbone and also with the free CPD formed in situ during the hydrogen transfer.

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