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Polypentamethylnadimides obtained by Diels–Alder reaction

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Abstract

The reactions between benzylbromide or α,α′-dibromo-*meta*-xylene (DBMX) and sodium 1,2,3,4,5-pentamethylcycopenta-1,3-dienide ($CpMe_5^{\ominus}$, $Na^{\oplus}$) give only the expected pentamathylcyclopentadiene derivatives with a good yields. These products lead to endo isomer adducts via a Diels–Alder reaction with maleimide.

New low molecular weight polypentamethylnadimides were obtained in this way from the Diels–Alder polymerization of bispentamethylcyclopentadiene monomers and commercial or synthetic bismaleimides. The polyadducts were characterised by size exclusion chromatography (SEC), matrix assisted laser desorption ionization-time of flight (MALDI-TOF), nuclear magnetic resonance (NMR) and thermogravimetric analyses (TGA).

The low molecular weight was attributed to methyl steric hindrance. For the lowest molecular weight products, two different endcapped oligomers were observed. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: α,α'-bis (1,2,3,4,5-pentamethylcyclopenta-2,4-dienyl)-*meta*-xylene; Bismaleimides; Diels–Alder polymerization

1. Introduction

The aromatic polyimides are a class of high performance polymers *exhibiting* a good thermal stability, chemical resistance and a good mechanical properties [1]. For their obtaining, the process which consists in the chain extension by Diels–Alder's reaction between bisdienes and bismaleimides represents an interesting alternative to the polycondensation of amines with tetraacides derivatives [2]. The use of bismaleimides as bisdienophiles is very useful because the double bond of maleimides is very reactive towards electron rich dienes, to give a normal demand Diels–Alder cycloaddition. Thus BMIs were used to obtain linear polyimides by reaction with several kind of dienes [3–8]. However the dienes are often difficult to prepare [8] and functionnalized diene have been used.

Furane terminated oligomers react with BMIs at 70°C leading to an oxygen containing cycloadduct [9–14] which can react with acetic anhydride to give an aromatic imide [15,16].

The reaction of a bis-arylcyclopentadienone with a BMI gives a ketonic adduct [17,18]. The carbon monoxyde evolution proceeds spontaneously but the final aromatization is then difficult to perform.

The pyrones behave as diene and react with bismaleimides giving a bis-cycloadduct [19–22]. By heating, carbon dioxyde extrusion takes place with formation of bis diene. This reaction was used to prepare a polyimide with a bicyclooctene structure [8].When heated, benzocyclobutene reacts as a bis-methylene cycloadiene and polyaddition with maleimide has been showed [23].

Meador et al., recently reported that a 2,5-diaroyl p.xylene give a transcent photoenol able to react with a BMI giving a poly-1,2,3,4,5,6,7,8-octahydroanthracene cycloadduct [3].

In previous works [24,25] having for objective the preparation of biscyclopentadienes monomers for a Diels–Alder polymerization with some BMIs, we showed that the condensation of a benzylbromide with sodium cyclopentadienide yields several oligomers. The expected monobenzylcyclopentadiene is in fact a transcient product reacting according to two pathways. The first is a proton transfer with the cyclopentadienyl carbanion, giving a mixture of new isomeric benzylcyclopentadienylcarbanions. The second is a Diels–Alder reaction between the different

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cyclopentadienes present in the reaction medium [24]. When α,α′-dibromo-*meta*-xylene (DBMX) was used instead of benzylbromide, a mixture of linear and macrocyclic oligomeric products was obtained [25]. Such behaviour can be explained by considering that the four protons of a benzyl cyclopentadiene are more acidic than those of cyclopentadiene. As a consequence pure bis cyclopentadienes were not prepared and it was impossible to get the expected polynadimide by condensation with the BMIs.

In this work we present a selective condensation of benzylbromide and DBMX with sodium 1,2,3,4,5-penta methylcycopenta-1,3-dienide ($\mathrm{CpMe}_5^{\ominus}$, $\mathrm{Na}^{\oplus}$). Pure benzylpentamethylcyclo-pentadiene and α,α′-bis(pentamethylcyclopentadienyl)-*meta*-xylene (bisCpMe$_5$) were obtained. The Diels–Alder reaction of the diene and bisdiene with maleimide were investigated and the obtained polypentamethylnadimides were characterized.

2. Experimental

($\mathrm{CpMe}_5^{\ominus}$, $\mathrm{Na}^{\oplus}$) solution in tetrahydrofuran (0.5 M), benzylbromide and DBMX were purchased from Aldrich and used as received.

Anhydrous THF was obtained by the procedure as described by Vogel [26].

2.1. Techniques

2.1.1. Nuclear magnetic resonance

Proton and carbon-13 nuclear magnetic resonance (NMR) spectra were recorded on a Brucker AC 250 instrument operating at 250 and 62.9 MHz, respectively, using $CDCl_3$ as solvent in most cases. Chemical shifts are given as δ and ppm relative to tetramethylsilane (TMS) used as internal standard.

2.1.2. Size Exclusion chromatography (SEC)

A WATERS 510 GPC apparatus, fitted with a refractive index and UV detectors was used. It was equipped with a PSS gel mixed B column (60 cm). The operating solvent was THF (1 ml/min).

The volume of injected sample solution (1 mg/ml) was 20 μl. Narrow molecular weight polystyrene standards were used for the calibration curve.

2.1.3. HPLC-MS analyses (purity determination of bismaleimides (BMIs))

Analyses were conducted with a Hewlett Packard 1100 instrument equipped with MS and UV ($\lambda = 260 \pm 10$ nm) detectors.

Mobile phases A (water + trifluoroacetic acid pH = 2.45) and B (acetonitrile) were used with an elution gradient A/B from 30/70 to 0/100 in 30 min. Flow-rate: 0.5 ml/min.

The columns were Chrompack Inertsil ODS-5 μm–(150 × 3) mm and a precolumn.

The MS conditions used for the identification of the peaks detected by UV were: Ionization: atmospheric pressure chemical ionization (positive mode), Gas: dry nitrogen (350°C, 4 l/min), nebulizer pressure: 60 psig, capillary voltage: 2000 V.

Vaporizer temperature: 400°C, Corona current: 8 μA.

2.1.4. Differential scanning calorimetry (DSC) (melting point determination of the BMIs)

Melting points of the BMIs were determined with a DuPont 2000 V4.0B with linear temperature programming (10°C/min^{-1}) from 40 to 350°C in an argon atmosphere.

2.1.5. Liquid secondary ion mass spectroscopy (LSIMS)

LSIMS experiments were carried out on a ZAB2-SEQ mass spectrometer (Micromass) working in an MCA (Multi Channel Accumulation) scanning mode. The detected mass range was between 100 and 1200 amu in a scan time of 15 s. Mass spectrometer resolution was set at 2000.

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

2.1.6. Electron impact mass spectrometry analysis

All the electron ionization spectra obtained were obtained on a ZAB2-SEQ mass spectrometer (Micromass) set in standard acquisition mode. The ion source was operated at an accelerating voltage of 8 kV, an ionizing electron energy of 70 eV and an ion source temperature of 200°C.

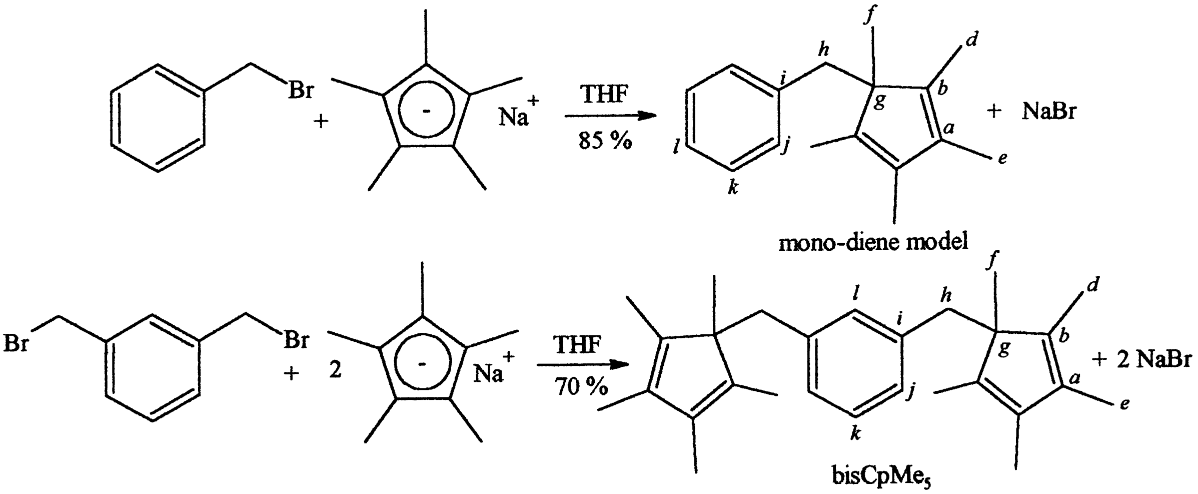
2.1.7. Matrix assisted laser desorption ionization–Time of flight (MALDI-TOF)

MALDI-TOF analyses were conducted with a Voyager-DE STR (Applied Biosystems). The instrument was equipped with a nitrogen laser ($\lambda = 337$ nm, pulse duration = 4 ns). Laser desorbed positive ions were analyzed after being accelerated by 25 kV and acquisition was in both linear and reflector mode. External calibration was carried out using a peptide mixture provided by Applied Biosystems.

2.1.7.1. Preparation of the samples for MALDI-TOF determination. One volume of a polymer solution in THF or $CHCl_3$ (10 mg/ml) was added to 10 volumes of a solution of 10 mg of 2,5-dihydroxybenzoic acid in 1 ml of THF. The runs were performed with 1 μl pipetted onto 1 of 100 roughed 2.5 mm diameter sample positions on a stainless steel plate.

2.1.8. Thermogravimetric Analyses (TGA)

Dynamic thermogravimetric analyses (TGA) of isolated polymer powders were obtained with a Hi-Res TGA 2950 Thermogravimetric analyzer (TA Instruments) at a heating



Scheme 1. Synthesis of the mono-diene model and bisCpMe$_5$.

rate of 5°C/min^{-1} from 30 to 350°C under nitrogen for the polymers and from 30 to 600°C for the adduct models.

2.2. Synthesis of monomers and models

2.2.1. Synthesis of 1-benzyl-1,2,3,4,5-pentamethylcyclopenta-2,4-diene (mono-diene model) (Scheme 1)

30 ml of CpMe$_5$Na solution (15 mmol of CpMe$_5^{\ominus}$ anion) were added through a septum with a syringe to 2.309 g (13.5 mmol) of benzylbromide in 10 ml of anhydrous THF stirred under nitrogen at 0°C. The immediate formation of an NaBr precipitate was observed. After complete addition of CpMe$_5$Na, the temperature was maintained at 0°C for 1 h and then at room temperature for 3 h. Fifty ml of diethylether were then added and the mixture was washed with 30 ml of a saturated solution of NH$_4$Cl. The organic layer was washed with distilled water until neutral pH and dried over sodium sulfate. After solvent removal, a crude yellow oil still contained 1,2,3,4,5-pentamethylcyclopenta-2,4-diene (hydrolyzed excess of CpMe$_5^{\ominus}$ anion). Finally, 2.587 g of yellowish oil of pure benzylpentamethylcyclopentadiene was obtained by filtration of the crude product in silica gel column with hexane as eluent. Yield = 85%.

Calculated for $C_{17}H_{22}$: C,90.20, H,9.80

Found: C,90.07, H,9.93

Mass spectroscopy (EI): *m/Z*, calculated: 226.36, found: 226.2

^{1}*H NMR*:(solvent: CDCl$_3$); δ1.05 (s, 3H, H_f), 1.63 (s, 6H, H_e^*), 1.82 (s, 6H, H_d^*), 2.74 (s, 2H, H_h), 6.86–6.91 (m, 2H, H_j), 7.09–7.13 (m, 3H, H_k and H_l), $^{3}J_{jk} = 7.34$ Hz

^{13}*C NMR*: (solvent: CDCl$_3$); δ 10.3$_7$ (2C, C_e^*), 10.7$_8$ (2C, C_d^*), 21.7$_0$ (C_f), 41.6$_0$ (C_h), 56.7$_6$ (C_g), 125.52 (C_f), 126.7$_9$ (2C, C_k), 128.5$_3$ (2C, C_j), 134.5$_3$ (2C, C_a), 138.6$_0$ (C_i), 139.1$_8$ (2C, C_b).

*: assignments can be reversed

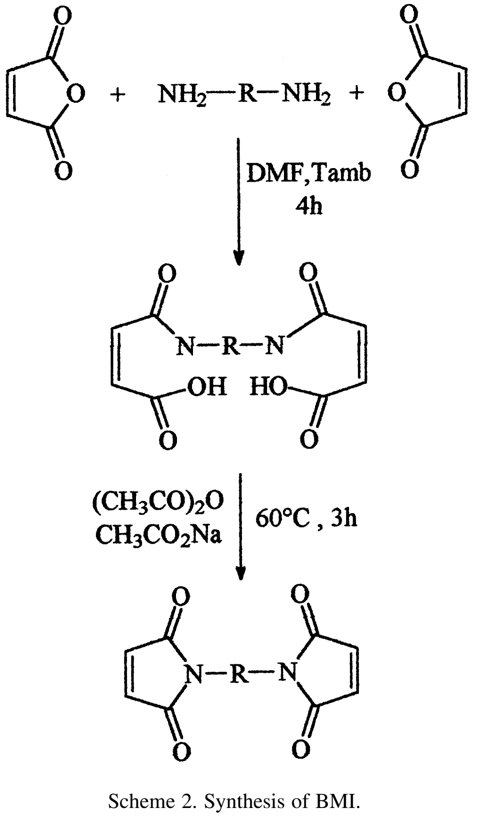
2.2.2. Synthesis of bisCpMe$_5$ (Scheme 1)

The preparation of bisCpMe$_5$ from 50 ml of CpMe$_5$Na solution (24.7 mmol) and 2.97 g (11.2 mmol) of DBMX in 15 ml of THF was carried out as described above. Recrystallization from methanol gave 2.734 g (70%) of the bisdiene (Fig. 2).

Melting Point: 64.5°C (DSC)

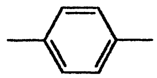
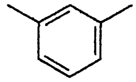
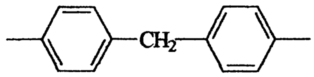
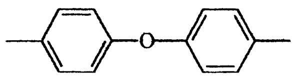
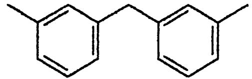
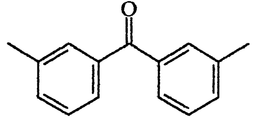
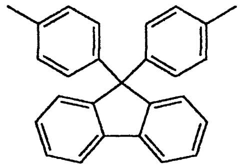
Calculated for $C_{28}H_{38}$: C,89.78, H,10.22

Found: C,89.65, H,10.34



Scheme 2. Synthesis of BMI.

Table 1
Results of BMI synthesis: yields and purity

BMI	–R–	Yield (%) (crude)	Yield (%)[a] (pure prod.)	Mp litt. (°C)	Mp mes.[b] (°C)	Purity[c] (%)
I[d]		–	–	> 345	–	96.8
II[e]		–	–	198	205.5	99.2
III[f]		–	–	156–8	156	98
IV		70	45	173–6	178.5	93
V		67	40	–	196.8	97
VI		53	30	–	209	94.3
VII		88	72	335	339.7	96.7

[a] Yield calculated after two recystallizations in methanol or in a mixture of methanol/ chloroform.

[b] Melting point determined by DSC.

[c] Purity determined by HPLC.

[d] Purchased from Fluka and used as received.

[e] Available in the laboratory, purified by silica gel column chromatography.

[f] Purchased from Sigma-Aldrich, purified by two recystallizations in methanol.

Mass spectroscopy (EI): *m*/*z*, calculated: 374.60, found: 374.3

^1H *NMR:* (solvent: $CDCl_3$); δ 0.98 (s, 6H, H_f), 1.62 (s, 12H, H_e^*), 1.71 (s, 12H, H_d^*), 2.58 (s, 4H, H_h), 6.49 (s, 1H, H_l), 6.57–6.62 (m, 2H, H_j), 6.78–6.85 (m, 1H, H_k), $^3J_{jk} = 7.34$ Hz, $^4J_{jl} = 1.76$ Hz

^{13}C *NMR*: (solvent: $CDCl_3$); $\delta 10.3_7$ (4C, C_d^*), 10.8_9 (4C, C_e^*), 21.8_8 (2C,C_f), 41.6_0 (2C,C_k), 56.6_6 (2C,C_g), 126.0_2 (3C,$C_j + C_k$), 129.4_0 (C_l), 134.0_6 (4C, C_a), 137.6_2 (2C, C_i), 139.7_8 (4C, C_b).

*: assignments can be reversed

2.2.3. Synthesis of N-(4-benzoyl)-phenylmaleimide (MI)

This monomaleimide was synthesized by the method described in our recent publication [24].

2.2.4. Synthesis of bismaleimides

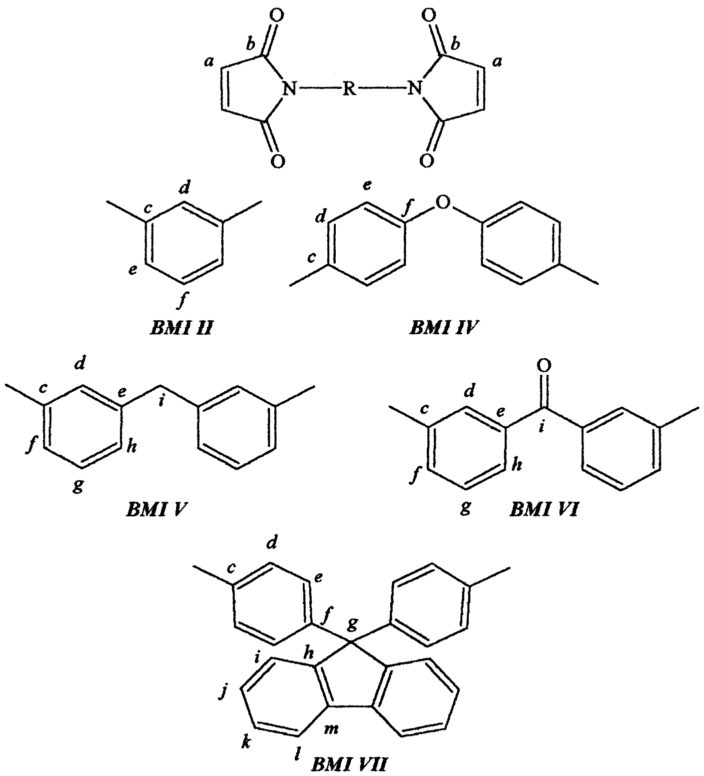
2.2.4.1. Starting materials. Diamines purchased from Sigma-Aldrich and Lancaster were high purity commercial products, used as received. Maleic anhydride (Sigma-Aldrich), was recrystallized from acetic acid. *N*,*N*-dimethylformamide (DMF) was dried by refluxing with CaH_2 and distilled.

2.2.4.2. General procedure (Scheme 2). According to the method reported in the literature [27,28], several bismaleimides were prepared with some modifications.

0.04 mol of the diamine dissolved in 40 ml of DMF was added were dropped into a suspension of 8.63 g (0.08 mol) of maleic anhydride in 70 ml of DMF at room temperature under nitrogen and was stirred mechanically. The mixture was left for 4 h at room temperature. Additional solvents (85 ml DMF + 120 ml dry acetone) were added to the solution (to avoid the precipitation of amide acid).

For cyclization, 2 g of fused sodium acetate and 25 ml of acetic anhydride were added and the mixture was heated for 3 h at 60°C. After cooling, the mixture was poured into ice water and the bismaleimide was filtered off, washed

Table 2
Chemical shifts and attributions of ^{13}C NMR spectra of BMI



Chemical shifts[a]

BMI	a	b	c	d	e	f	g	h	i	j	k	l	m
II	134.95	169.87	132.38	124.96	126.19	129.49	–	–	–	–	–	–	–
IV	134.91	170.13	127.39	128.87	119.28	155.97	–	–	–	–	–	–	–
V	134.86	170.06	132.06	[b]	141.84	[b]	[b]	[b]	40.90	–	–	–	–
VI	135.00	169.86	132.31	[c]	137.53	[c]	[c]	[c]	194.16	–	–	–	–
VII	134.92	170.02	130.52	126.91	128.38	145.04	64.82	150.33	126.33	128.38	128.38	120.90	139.86

[a] Solvent: DMSO.

[b] 124.80–129.22 ppm.

[c] 127.64–130.91 ppm.

with a saturated solution of $NaHCO_3$ and with water until neutrality.

A purified sample was obtained by successive recrystallizations from methanol or a mixture of $CHCl_3$/MeOH. Yields, melting points and purity are reported in Table 1. The results of carbon NMR of the BMI synthesized are shown in Table 2.

2.2.5. Synthesis of mono-adduct model (MAM) (Scheme 3)

A solution of 1.047 g (3.7 mmol) of MI in 15 ml of THF was added to a solution of 0.818 g (3.6 mmol) of the monodiene in 5 ml of THF. The mixture was left at room temperature for 24 h under nitrogen and was concentrated by removing the majority of solvent. Purification involved silica gel column chromatography with hexane/ethyl acetate (75/25) as eluent and then by recrystallization from methanol, yielding 1.035 g (75%) of pure product.

Melting Point: 164°C (DSC)

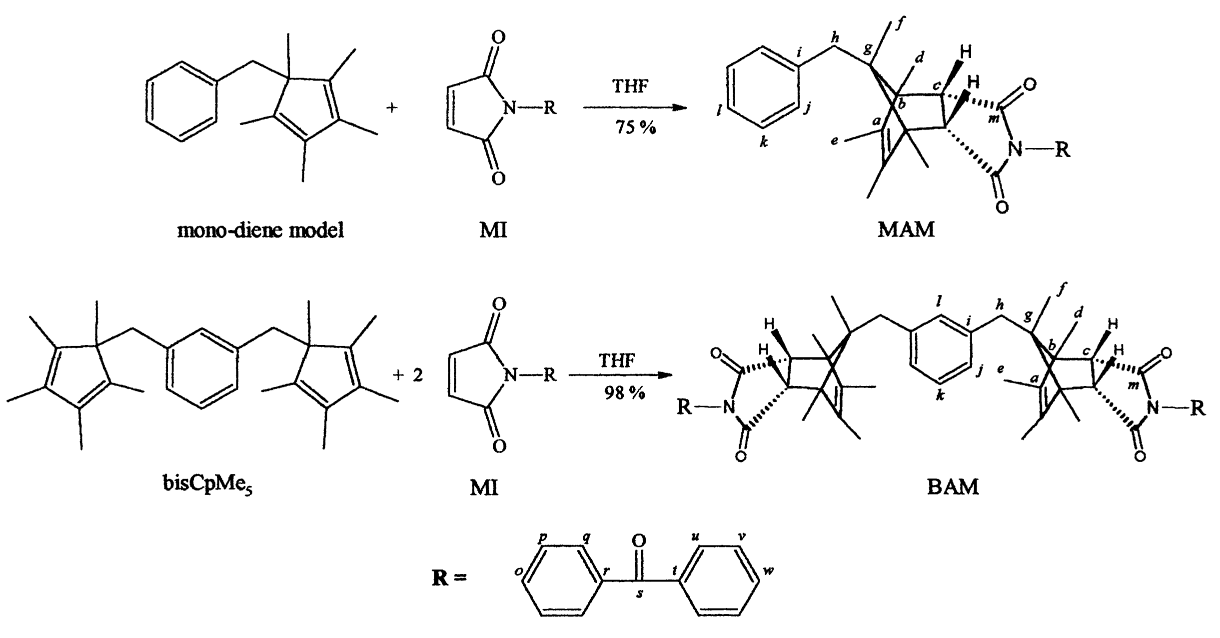
Calculated for $C_{34}H_{33}NO_3$:C,81.08, H,6.60, N,2.78, O,9.53

Found: C,81.09, H,6.59, N,2.64, O,9.75

Mass spectroscopy (EI): *m/Z*, calculated: 503.63, found: 503.2

^{1}*H NMR:* (solvent: $CDCl_3$); δ 0.98 (s,3H,H_f), 1.16 (s,6H,H_d), 1.69 (s,6H,H_e), 2.56 (s,2H,H_h), 3.07 (s,2H,H_c), 7.06–7.10(m, 2H, H_j), 7.21–7.27(m,$CDCl_3$ + 4H, $H_q + H_k + H_l$), 7.44–7.49(m, 2H, H_v), 7.56–7.64 (m,1H,H_w), 7.79–7.82 (m, 2H, H_u), and 7.84–7.88 (m, 2H, H_p). $^3J_{jk} = 7.63$, $^3J_{u,v} = 8.22$, $^3J_{vw} = 7.34$, $^4J_{uw} = 1.47$ Hz.

^{13}*C NMR*: (solvent: $CDCl_3$); δ 11.6_1 and 12.0_7 (4C,C_d^* and C_e^*),15.5_5 (C_f), 38.6_8 (C_h), 51.3_3 (2C, C_c), 60.9_5 (2C,C_b), 67.7_9(C_g), 132.4_6 (C_w), 135.4_7 (3C,$C_a + C_i$), 136.8_8 and



Scheme 3. Synthesis of MAM and BAM.

137.0_6 (2C, C_r^* and C_t^*), $138.7_8(C_o)$, 125.9_7–130.6_4 (13C, the rest of C_{arom}), $176.3_1(2C,C_m)$, 195.4_2 (C_s)

*: assignments can be reversed

2.2.6. Synthesis of the bis-adduct model (BAM) (Scheme 3)

The procedure used to prepare the BAM was similar to that used for the synthesis of the MAM. Reagent quantities were 0.5 g (1.3 mmol) of bisCpMe$_5$ in 5 ml of THF and 0.814 g (2.9 mmol) of MI in 10 ml of THF.

After purification of the compound by silica gel column chromatography 1.17 g (98%) were obtained.

Melting Point: 244°C (DSC)

Calculated for $C_{62}H_{60}N_2O_6$: C,80.14, H,6.51, N,3.01, O,10.33

Found: C,79.93, H,6.56, N,3.19, O,10.32

Mass spectroscopy(LSIMS): *m/Z*, calculated: 929.1, found:,929.6 [$M^{+\cdot}$], 651.3 [$(M - MI)^{+\cdot}$], 412.2 [(MI + CpMe$_5$)], 278.1[$(MI + H)^+$]. MI: *N*-(4-benzoyl)-phenyl-maleimide

^{1}*H NMR:* (solvent: CDCl$_3$); δ 0.98 (s,6H,H_f), 1.19 (s,12H,H_d), 1.70 (s,12H,H_e), 2.53 (s,4H,H_h), 3.07 (s,4H,H_c), 6.83(s,1H,H_l), 6.88–6.91(d,2H,H_j), 7.12(t,1H,H_k), 7.23–7.28(d,4H, H_q), 7.48(t,4H,H_v), 7.59(t,2H,H_w), 7.78–7.82(d,4H,H_u), 7.84–7.88(d,4H,H_p).

^{13}*C NMR:* Table 5.

2.3. Diels–Alder polymerization (Scheme 4)

Equimolar quantities of bisCpMe$_5$ and BMI dissolved in DMF containing hydroquinone as a free radical scavenger were added to a three-necked 100 ml round-bottom flask with a nitrogen inlet, a condenser and a mechanical stirrer. The solution was stirred at room temperature under nitrogen for 2 h, then heated gradually to 140°C and maintained for 24 h. The polymer solution was then cooled to room temperature.[1] The polymer was precipitated by the dropwise addition of the reaction mixture into rapidly stirred methanol, collected by filtration, and dried under vacuum.

3. Results and discussion

3.1. Synthesis of the mono-diene model and the bisdiene monomer

The benzylpentamethylcyclopentadiene model and the bisdiene monomer (bisCpMe$_5$) were prepared by reacting benzylbromide and DBMX with CpMe$_5^{\ominus}$ anion in THF as solvent (Scheme 1).

Proton and ^{13}C NMR spectra of bisCpMe$_5$ are shown in Fig. 1a and b.

In both cases, starting from either benzylbromide or DBMX, the reaction yielded only the expected product with no side reactions.

There are two possible reasons for this selectivity compared to the reaction of the unsubstituted cyclopentadienide anion with the same brominated products [24,25]. First, since the pentamethylcyclopentadienyl anion is symmetrical, only one position is available for nucleophilic attack on the benzylic carbon carrying the bromine.

On the other hand, the benzylic methylene group (–CH$_2$–) obtained by the nucleophilic substitution (Scheme 1) is

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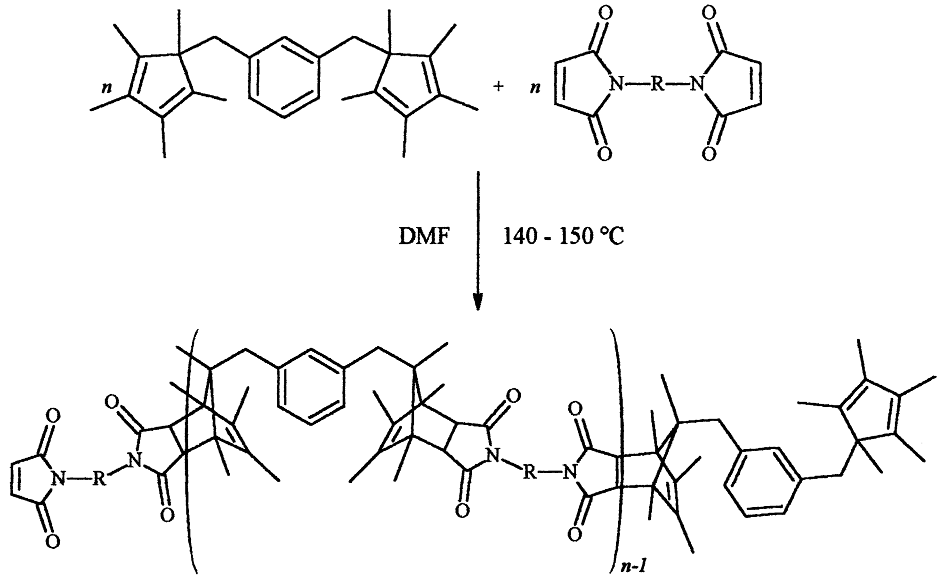
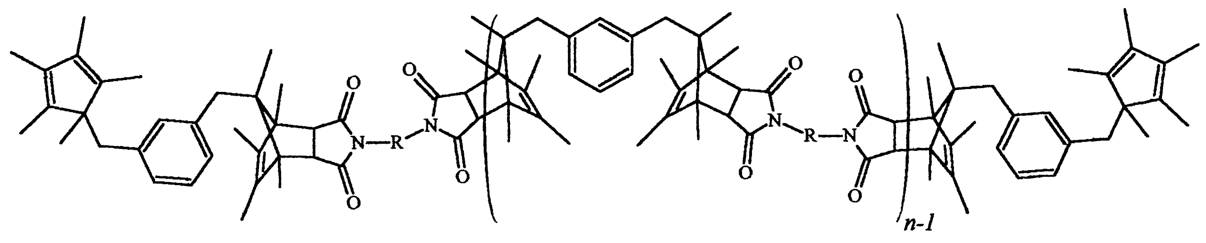
[1] In the case where precipitate appeared during the cooling, the solution was diluted by the addition of chloroform.



a - distribution type : MI••••••Cp



b - distribution type : Cp••••••Cp

Scheme 4. Diels–Alder polymerization of bis$CpMe_5$ with BMI.

probably protected by methyl steric hindrance of the pentamethylcyclopentadienyl substituant and can thus not yield give a carbanion; the reaction stops after formation of the expected product.

As seen in the spectra, only one benzyl methylene group is present in the structure ($\lambda = 2.58$ ppm for the proton and 41.6 ppm for the carbon). The spectra also show one methyl group on sp^3 carbon ($\lambda = 0.98$ ppm for the proton and 21.8 ppm for the carbon) and two different symmetrical methyl groups on the cyclopentadiene ring. These data confirm the presence of only one structure.

3.2. Synthesis of the bismaleimides (BMI)

The general synthesis of the BMI (Scheme 2) was carried out according to published procedures [27,28] with minor modifications, without isolation of the amic acid that was dehydrated by adding a mixture of acetic anhydride and sodium acetate to the reaction mixture.

The BMI used are listed in Table 1.

The results of the carbon NMR analyses of the BMI synthesized are shown in Table 2.

Purity was determined by HPLC and the indicated yield was calculated by taking purity into account.

The DSC traces agree with the classical behavior of the BMI. A sharp endotherm corresponding to melting is followed by a broad exotherm attributable to BMI polymerization.

3.3. Synthesis of the MAM and the BAM by Diels–Alder reaction

The Diels–Alder model reactions (Scheme 3) were run at room temperature in THF with an excess of maleimide (2.7% for the MAM and 11.5% for the BAM) No side reactions were observed and the yields for the MAM and the BAM were 75 and 98%.

The endo–exo isomerization of the Diels–Alder adducts is well documented [29] and occurs via a reverse Diels–Alder thermal reaction. Proton NMR spectra of the MAM and the BAM (Fig. 2a and b), however, showed only one signal for the 'c' proton, from the maleic double bond after the Diels–Alder cycloaddition.

The benzyl and methyl groups on 'g' carbon are

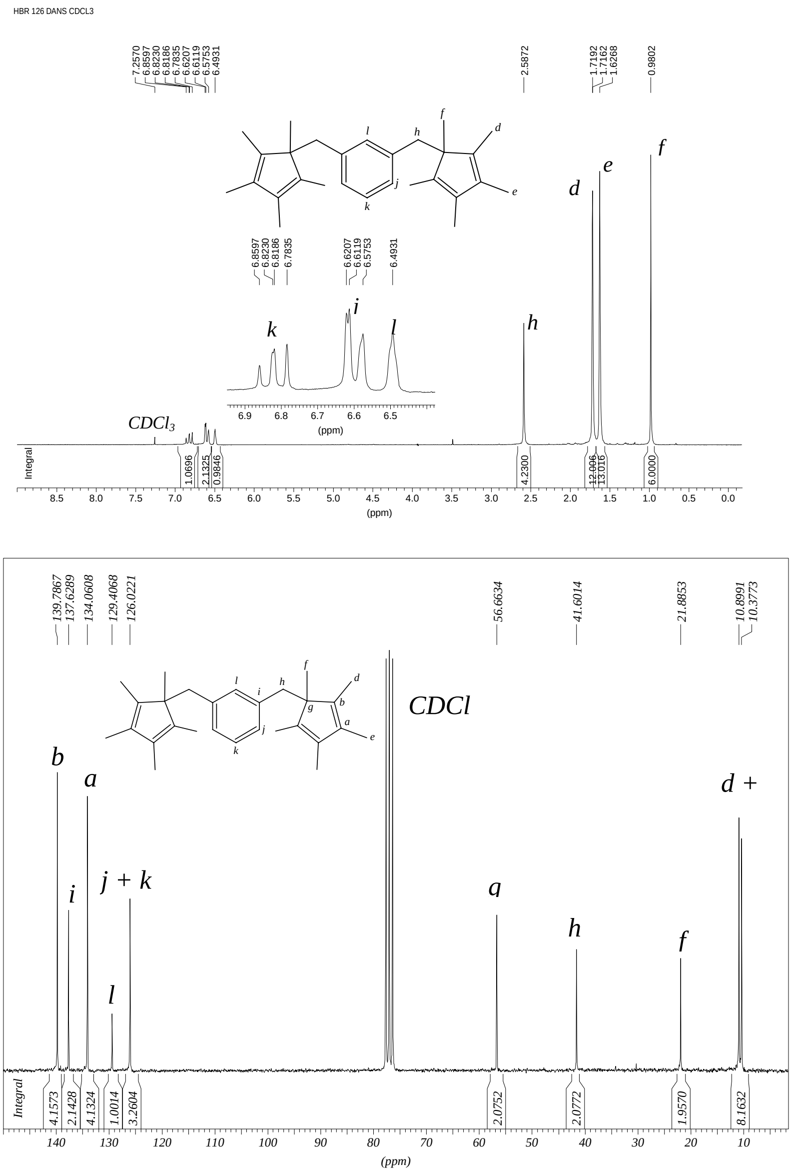


Fig. 1. (a) ^{1}H NMR spectrum of bisCpMe$_5$ (b) ^{13}C NMR spectrum (quantitative conditions) of bisCpMe$_5$.

responsible for considerable steric hindrance and the endo isomer, usually obtained in the Diels–Alder reaction, is probably more stable in this case than nadimide, that exhibits two signals for the corresponding ‘c’ protons [30].

No starting material, maleimide or cyclopentadiene, was observed by NMR spectroscopy.

Electron impact mass spectroscopy of the MAM and LSIMS of the BAM with thioglycerol as a matrix confirmed the formation of the expected adduct $m/z = 503.2$ (MAM) and $m/z = 929.6$ amu (BAM).

The spectra also show the presence of the starting material maleimide (MI) and diene. Bearing in mind that these products were not observed in NMR, this means that a reverse Diels–Alder (RDA) took place during mass spectra determination.

3.4. Reaction of the BMIs with the bisdiene: synthesis and characterization

Polyimides were synthesized by the Diels–Alder reaction of bisCpMe$_5$ and BMI (Scheme 4) in DMF at 140–150°C because of the low solubility of the BMIs. The initial concentration of the equimolar reactants was between 40 and 85 mmol per liter.

SEC (Table 3) shows that the Diels–Alder adducts exhibited a moderate mean molecular weight, between 3000 and 12,000 Da. Even when the purest BMIs were used (I, II, III), molecular weight was relatively low, suggesting small competitive self-BMI cross-linking, leading to an unbalanced polyaddition responsible for the low

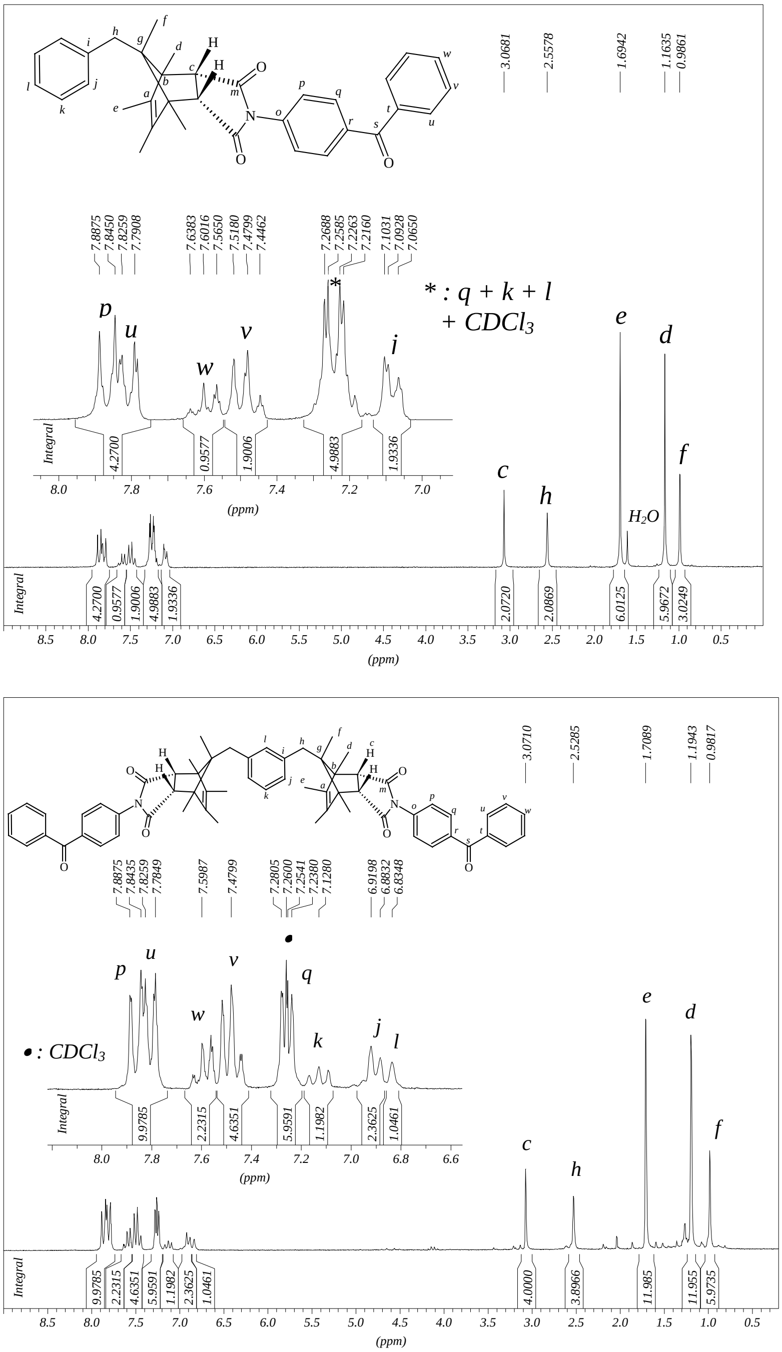


Fig. 2. (a) ^{1}H NMR spectrum of MAM. (b) ^{1}H NMR spectrum of BAM.

molecular weight. Since BMI systems are insoluble, SEC takes into account only linear polymers.

MALDI-TOF determinations were carried out with 2,5-dihydroxybenzoic acid as matrix. Table 4 summarizes the molecular weight obtained in linear mode for each polymer. The data show that polymers 2, 3 and 5 had the highest molecular weight and confirm that insoluble materials 2 and 5 are probably linear polymers.

It is noteworthy that in the case of low molecular material, MALDI-TOF furnishes a very precise determination of the terminal groups, e.g. polymers 2, 3, 5, 6 and 7 are end-capped with one MI and one CpMe$_5$ (Scheme 4a). In the case of polymers 1 and 4, however, there was a new distribution, with two CpMe$_5$ as end-capping groups (Scheme 4b).

Fig. 3 shows the MALDI-TOF spectrum of polymer 3 (with only one distribution) and Fig. 4 the spectrum of polymer 4 (with two distributions).

Formation of the bispentamethylcylopentadiene telechelic oligomers in the case of the BMI 1 and 4 can be explained

Table 3
Polymer synthesis: experimental parameters, yields and SEC results

Polymer code	BMI	BMI Purity (%)	C_0[a] (mmol/l)	Reaction temp. (°C)	Reaction time (h)	Yield (%)	Mn	Mp	Ip
1	I	98	65	140	4.5	76	3,730	14,320	3.8
2	II	99.2	45	R.T. 140	14 60	80	Insol.	–	–
3	III	98	82	140	24	95	11,800	37,390	3.2
4	IV	93	45	140	74	87	3,050	8,500	2.8
5	V	97	42	140	14	85	Insol.	–	–
6	VI	94.3	42	140	14	58	3,180	9,860	3.1
7	VII	96.7	65	150	17	67	7,260	30,000	4.1

[a] Initial concentration of equimolar mixture of $BiCpMe_5$ and BMI in DMF.

by considering that there is more self-cross linking of BMI. The formation of a BMI network is impossible to detect by MALDI-TOF analysis and probably by NMR, so we cannot observe a significant difference between the molecular weight determined by SEC and MALDI-TOF.

Figs. 5 and 6 show the proton spectrum of polymer 3 with $M_n = 11,800$ obtained with 4,4′-bismaleimidodiphenylmethane and a low molecular weight oligomer 4 obtained with 4,4′-bismaleimidodiphenylether.

The interpretation of proton NMR spectra and attributions of proton chemical shifts is relatively difficult. For both polymers, however, we observed only one type of ‘c’ protons ($\delta = 3.01$ and 3.02 ppm), probably due to the endo configuration, in agreement with the BAM product ($\delta = 3.07$ ppm). This selectivity, even at 140°C, is due to steric hindrance.

In addition, polymer 3 revealed only one type of ‘f’, ‘d’, ‘e’ methyl protons and one type of benzylic ‘h’ proton. The spectrum of polymer 4 shows different signals for the similar protons, but this difference is due to the influence of the $CpMe_5$ end group As confirmation of the low molecular weight, the ‘z’ proton of the maleimide end group appears at $\delta = 7.05$ ppm only in the low molecular weight oligomer.

Carbon NMR was performed only with polymers 3, 6 and 7 whose solubility was sufficient for the determination (Table 5).

The main feature of the spectra is the presence of only one ‘c’ carbon ($\delta = 51.25$ ppm for polymer 3, $\delta = 51.98$ ppm for the polymer 6 and $\delta = 51.23$ ppm for polymer 7) as observed with the spectrum of the BAM ($\delta = 51.29$ ppm). These data agree with the presence of only one isomeric nadimide.

Thermogravimetric analyses were performed with a heating gradient of 5°C/min^{-1} under nitrogen or air with a 10% loss in weight (Table 6). It can be seen that the extent of degradation in air or an inert atmosphere is very close for the first step of the degradation. The loss of weigh in air is lower than in an inert atmosphere (Fig. 7). This can be explained by the fact that degradation in an inert atmosphere is governed only by the kinetics of the reverse Diels–Alder reaction and oxidation in air could hinder the simple reverse Diels–Alder reaction.

4. Conclusion

The condensation of sodium pentamethylcyclopentadienide with DBMX is simpler than the preparation of monosubstituted cyclopentadiene. The reaction yields only one product. $BisCpMe_5$ reacts with commercial or synthetic BMIs. Probably as a result of steric hindrance by the pentamethyl group, the Diels–Alder reaction does not take place as in the case of unsubstituted cyclopentadiene,

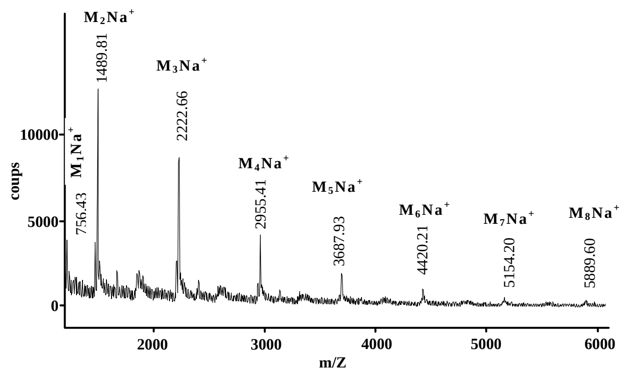


Fig. 3. Linear mode MALDI-TOF spectrum of polymer 3.

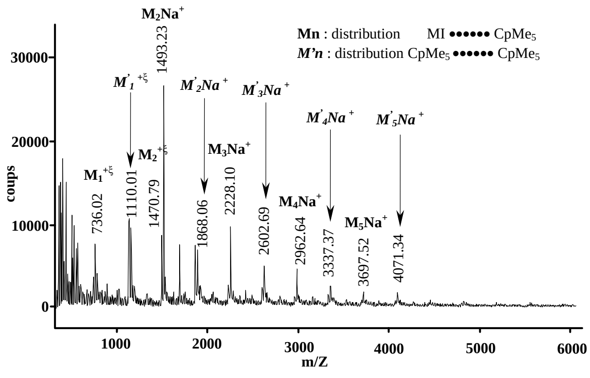


Fig. 4. Linear mode MALDI-TOF spectrum of polymer 4.

Table 4
MALDI-TOF results of polymers (distribution type: MI···CpMe$_5$ is observed in common polymers, Distribution type: CpMe$_5$···CpMe$_5$ is present only in polymer 1 and polymer 4)

	Polymer 1							
	Distribution type: MI···CpMe$_5$				Distribution type: CpMe$_5$···CpMe$_5$			
	Calc. M$^{+\cdot}$	Found M$^{+\cdot}$	Calc. MNa$^+$	Found MNa$^+$	Calc. M$^+$	Found M$^+$	Calc. MNa$^+$	Found MNa$^+$
$n = 1$	642.35	642.57	665.34	665.10				
$n = 2$	1284.69	1287.03	1307.68	1310.12				
$n = 3$	1927.04	1930.93	1950.03	1952.78				
$n = 4$	2569.39	–	2592.38					
$n = 5$	3211.74	–	3234.73					
$n = 6$	3854.08	–	3877.07					

	Polymer 2				Polymer 3			
	Distribution type: MI···CpMe$_5$				Distribution type: MI···CpMe$_5$			
	Calc. M$^{+\cdot}$	Found M$^{+\cdot}$	Calc. MNa$^+$	Found MNa$^+$	Calc. M$^{+\cdot}$	Found M$^{+\cdot}$	Calc. MNa$^+$	Found MNa$^+$
$n = 1$	642.35	–	665.34	–	732.39	–	755.38	756.43
$n = 2$	1284.69	1285.75	1307.68	1308.58	1464.79	–	1487.78	1489.81
$n = 3$	1927.04	1928.13	1950.03	1950.26	2197.18	–	2220.17	2222.66
$n = 4$	2569.39	2569.77	2592.38	2592.08	2929.57	–	2952.56	2955.41
$n = 5$	3211.74	3211.39	3234.73	3233.62	3661.96	–	3684.95	3687.93
$n = 6$	3854.08	3852.77	3877.07	3874.93	4394.36	–	4417.35	4420.21
$n = 7$	4496.43	4493.43	4519.42	4516.26	5126.75	–	5149.74	5154.20
$n = 8$	5138.78	5136.30	5161.77	5158.10	5859.14	–	5882.13	5889.60
$n = 9$	5781.13	–	5804.12	5799.60				
$n = 10$	6423.47	–	6446.46	6440.70				
$n = 11$	7065.82	–	7088.81	7080.10				
$n = 12$	7708.17	–	7731.16	7725.90				
$n = 13$	8350.51		8373.50	8359.10				

	Polymer 4							
	Distribution type: MI···CpMe$_5$				Distribution type: CpMe$_5$···CpMe$_5$			
	Calc. M$^{+\cdot}$	Found M$^{+\cdot}$	Calc. MNa$^+$	Found MNa$^+$	Calc. M$^{+\cdot}$	Found M$^{+\cdot}$	Calc. MNa$^+$	Found MNa$^+$
$n = 1$	734.37	736.02	757.36	758.71	1108.66	1110.01	1131.65	1133.05
$n = 2$	1468.73	1470.79	1491.72	1493.23	1843.03	1844.95	1866.02	1868.06
$n = 3$	2203.10	–	2226.09	2228.10	2577.40	–	2600.39	2602.69
$n = 4$	2937.47	–	2960.46	2962.64	3311.77	–	3334.76	3337.37
$n = 5$	3671.84	–	3694.83	3697.52	4046.13	–	4069.12	4071.34

	Polymer 5				Polymer 6			
	Distribution type: MI···CpMe$_5$				Distribution type: MI···CpMe$_5$			
	Calc. M$^{+\cdot}$	Found M$^{+\cdot}$	Calc. MNa$^+$	Found MNa$^+$	Calc. M$^{+\cdot}$	Found M$^{+\cdot}$	Calc. MNa$^+$	Found MNa$^+$
$n = 1$	732.39	733.56	755.38	756.57	746.37	–	769.36	–
$n = 2$	1464.79	1467.63	1487.78	1489.59	1492.73	1494.39	1515.72	1517.67
$n = 3$	2197.18	2200.61	2220.17	2222.34	2239.10	–	2262.09	2264.73
$n = 4$	2929.57	2933.38	2952.56	2954.98	2985.47	–	3008.46	3011.51
$n = 5$	3661.96	–	3684.95	3686.95	3731.84	–	3754.83	3759.78
$n = 6$	4394.36	–	4417.35	4419.82	4478.20	–	4501.19	4505.65
$n = 7$	5126.75	–	5149.74	5152.20				
$n = 8$	5859.14	–	5882.13	5883.60				
$n = 9$	6591.53	–	6614.52	6616.00				
$n = 10$	7323.93	–	7346.92	7350.40				
$n = 11$	8056.32	–	8079.31	8068.80				

	Polymer 7			
	Distribution type: MI···CpMe$_5$			
	Calc. M$^{+\cdot}$	Found M$^{+\cdot}$	Calc. MNa$^+$	Found MNa$^+$
$n = 1$	882.44	–	905.43	–
$n = 2$	1764.87	–	1787.86	1789.82
$n = 3$	2647.31	–	2670.30	2671.70
$n = 4$	3529.75	–	3552.74	3552.98
$n = 5$	4412.19	–	4435.18	4434.39
$n = 6$	5294.62	–	5317.61	5315.50
$n = 7$	6177.06	–	6200.05	6197.30

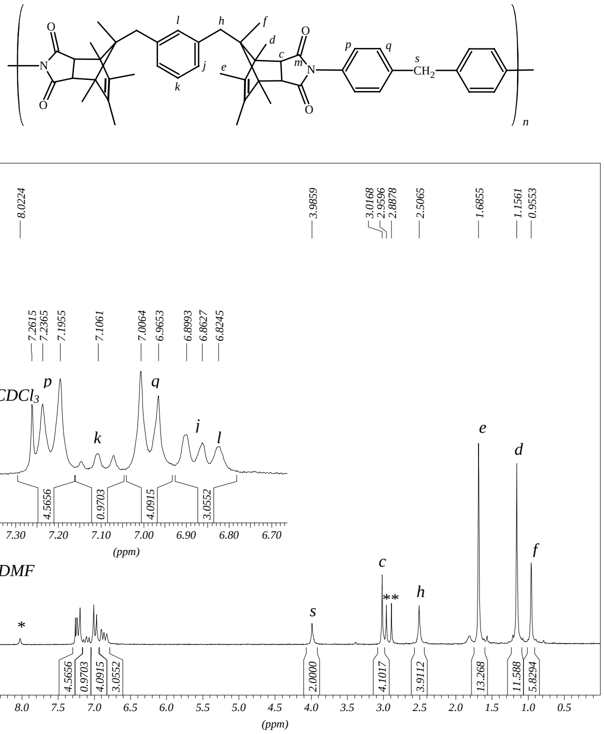


Fig. 5. ^{1}H NMR spectrum of polymer 3.

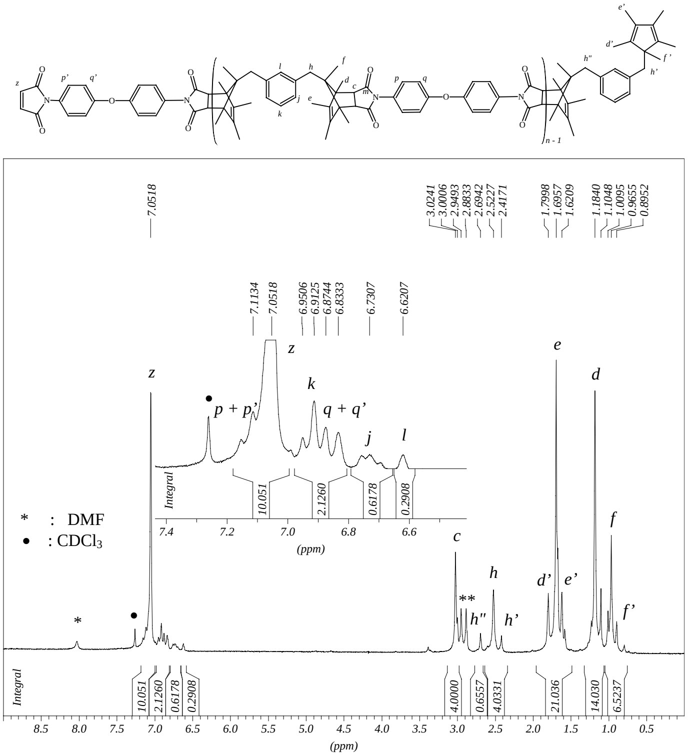
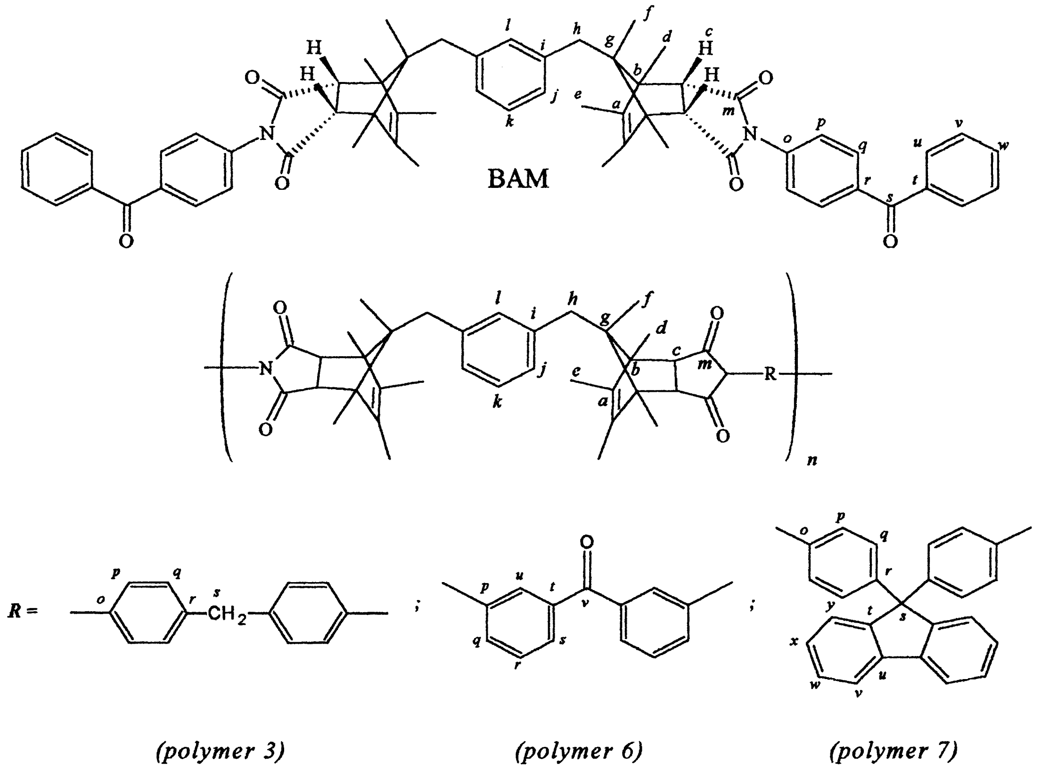


Fig. 6. ^{1}H NMR spectrum of polymer 4.

Table 5
Chemical shifts and attributions of ^{13}C NMR spectra of the BAM and the polymers 3, 6 and 7



Chemical shifts[a]

Product	a	b	c	d	e	f	g	h	i	j	k	l
BAM	135.47	60.96	51.29	11.60[b]	12.16[b]	15.52	67.70	38.65	135.37	128.53	127.30	132.70
Polymer 3	135.47	60.84	51.25	12.07[b]	11.45[b]	15.44	67.62	38.74	138.54	128.42	127.19	132.77
Polymer 6	136.16	61.55	51.98	12.08[b]	12.69[b]	16.10	68.32	39.33	132.91	129.49	129.49	133.36
Polymer 7	135.44	60.85	51.23	11.44[b]	12.05[b]	15.44	67.64	38.73	138.50	127.64	127.17	132.72

Product	m	o	p	q	r	s	t	u	v	w	x	y
BAM	176.28	138.37	126.06 to	130.64	136.90[b]	195.46	137.02[b]	126.06	130.64	132.48	–	–
Polymer 3	176.47	130.22	126.43	129.44	140.40	40.92	–	–	–	–	–	–
Polymer 6	176.70	–	138.39[b]	129.30	To	130.91	139.08[b]	128.77	193.99	–	–	–
Polymer 7	176.44	130.57	126.21	128.65	145.44	64.82	150.19	139.97	119.97	128.65	128.65	127.55

[a] Solvent: $CDCl_3$.

[b] Assignments can be reversed.

Table 6
Thermogravimetric results of polymers (dynamic TGA determined on powdered samples at a heating rate of 5°C/min^{-1} under nitrogen atmosphere)

Polymer	Temperature of 10% weight loss under air atmosphere (°C)	Temperature of 10% weight loss under nitrogen atmosphere (°C)
1	270	270
2	290	300
3	297	320
4	330	315
5	342	318
6	350	315
7	290	300

where several products were obtained. The formation of only one isomeric substituted polynadimide (endo) was observed and polyaddition did not yield high molecular weight polypentamethylnadimide. The low molecular weights are probably the consequence of a small degree of cross-linking of BMIs, leading to an unbalanced polyaddition. This hypothesis is being explored. For the smallest oligomers the formation of two types was observed. One was end-capped with one maleimide and one pentamethylcyclopentadiene as expected, and the second was end-capped with two pentamethylcyclopentadienes. The 10% weight loss of these polyadducts occurred

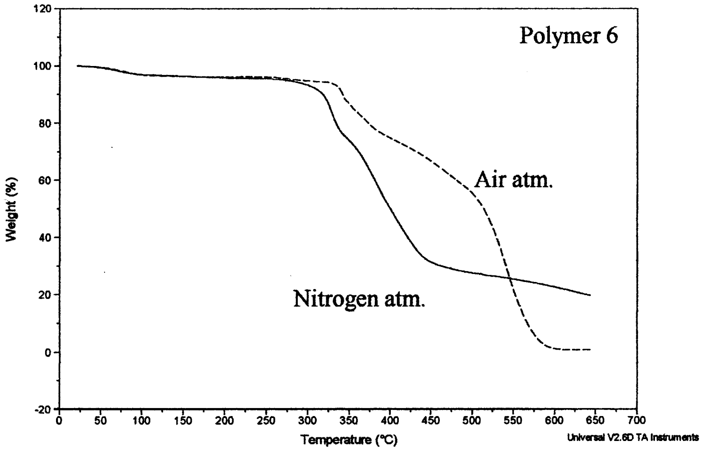


Fig. 7. TGA diagram of polymer 6 in air and nitrogen.

between 270 and 340°C. The reverse Diels–Alder and the thermo-oxidative behaviors of these polymer are under investigation.

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