Polymer Bulletin 41, 153–160 (1998)

Polymer Bulletin

New imide-copolymers with coronand structure

Nils Kottner, Elisabeth Klemm[*]

Institut für Organische Chemie und Makromolekulare Chemie,
Friedrich-Schiller-Universität Jena, Humboldtstrasse 10, D-07743 Jena, Germany

Received: 23 April 1998/Revised version: 8 June 1998/Accepted: 10 June 1998

SUMMARY

The Diels-Alder reaction of bis-(2-pyrone) **2** with various aliphatic and aromatic bismaleimides **1** in dilute solution was carried out to produce linear soluble copolymers with a coronand structure. NMR spectra and model reactions confirm the structure **4** (3). The polymers show weight losses at about 440°C determined by thermogravimetric analysis (Tab. 1).

INTRODUCTION

Synthesis of linear polyimides with coronand structures via Diels-Alder reaction was reported first in 1993 /1/. The polyaddition of aliphatic bismaleimides **1a-c** and bispyrone **2** leads to linear polyimides **3a-c** /2/. The polymers are soluble in common solvents and form thermally stable films on glass or metal surfaces (1).
Structure **3** is proved by the synthesis of a tetra(maleimide) as intermediate compound in the linear polyaddition of bismaleimides **1a** and **1f** with bis(2-pyrone) **2**. The reaction of this tetra(maleimide) with (α-pyrone in dilute toluene solution leads to the coronandcyclization, equivalent to (2) /1/. The yields of the polyimides **3** reach 64%, the missing 36 mass-% include the macrocyclic oligomers **3** (m = 1...8), polyimides with cyclic end-groups $\mathbf{3}^*$, and the dimer $\mathbf{3}^*$ with m'= 0 (1). We obtained these results by means of the matrix-assisted laser desorption/ionization technique (MALDI) /3/.

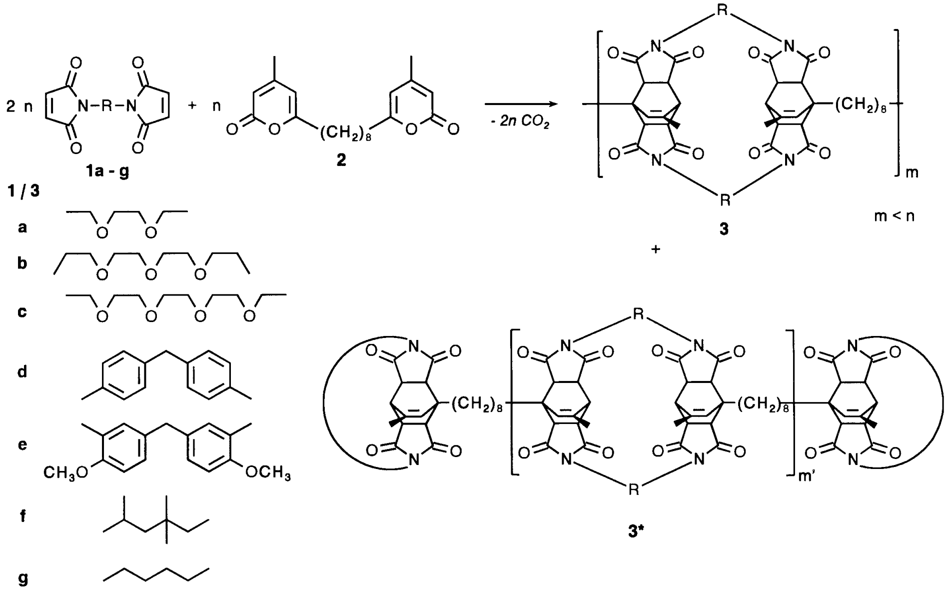
Aromatic bismaleimides (**1d**, **1e**) form insoluble networks /2/. The polymers have no coronand structure. Copolymers of aliphatic and aromatic bismaleimides with bispyrones are unknown. The aim of this publication is to give results of the copolymerization process and to propose the copolymer structure.

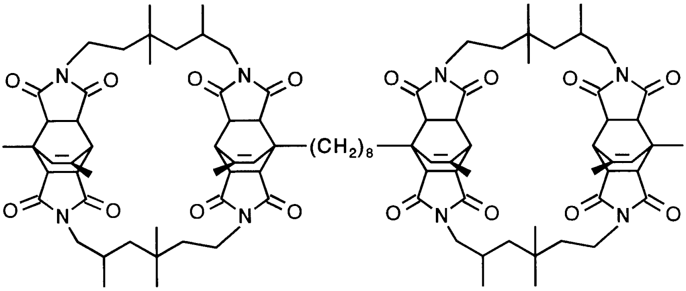
RESULTS AND DISCUSSION

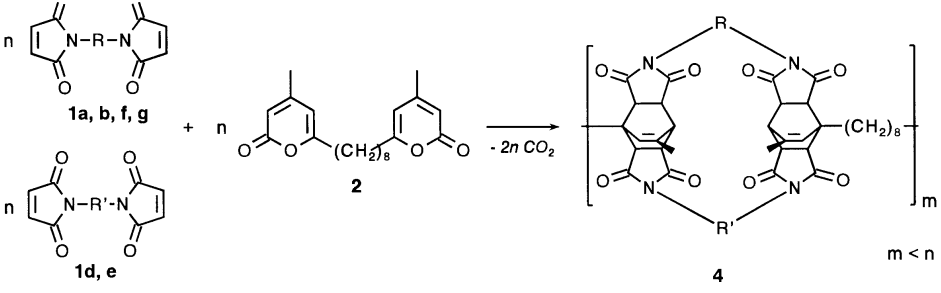
As starting materials we used the aliphatic bismaleimides **1a**, **1b**, **1f**, **1g**, the aromatic bismaleimides **1d**, **1e**, and the bispyrone **2**, in molecular proportions of 1 : 1 : 1. The total maleimide concentration was 0,07 mol/l (3). The polyadditions were done in 1,2,5-trichlorobenzene at 210°C for 24 hours. Complete conversion of bismaleimides and bispyrone was achieved. The polymers **4** were precipitated in n-hexane. They are soluble in various solvents such as chloroform, N,N-dimethylformamide, and dimethyl sulfoxide. Table I summarizes the results of the polyaddition.

---

[*] Corresponding author


2 n
1a - g
+ n
(CH2)8
2
- 2n CO2
R
N
O
(CH2)8
m
3
m < n
+
1 / 3
a
b
c
d
e
CH3O
OCH3
f
g
m'
3*


O
N
(CH2)8


n
N-R-N
1a, b, f, g
n
N-R'-N
1d, e
+ n
(CH2)8
2
- 2n CO2
R
R'
(CH2)8
m
m < n
4

Tab. 1: Structure, thermal stability and number-average molecular weights of polyimides **4**.

polymer	maleimide R 50 mol-%	maleimide R' 50 mol-%	TGA* 10 % [°C]	M_n (VPO) [g/mol]	yield [%]
4a	**1d**	**1a**	435	11900	70
4b	**1d**	**1b**	415	4900	68
4c	**1d**	**1f**	440	2180	40
4d	**1d**	**1g**	390	7400	20
4e	**1e**	**1a**	405	6500	62
4f	**1e**	**1b**	425	7900	70

* TGA were recorded with a heating rate of 10 K min^{-1} in air

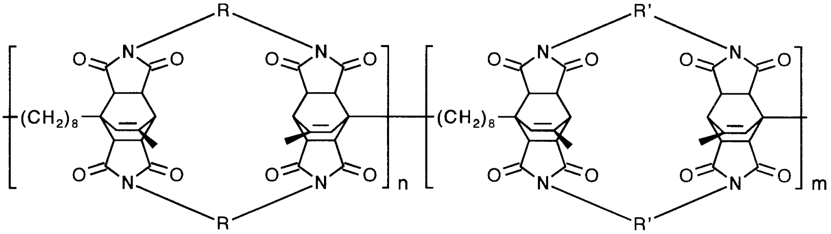
The difference to 100% yield is an insoluble crosslinking polymer /2/. We assume that the uncommonly low yields of soluble copolymeric products **4c** and **4d** result from the lower flexibility of alkane and isoalkane spacer (**1g**, **1f**) in comparison with the o-alkyl spacer groups **1a** - **1c**. From this point of view coronand structures become more and more unlikely and the consequence is an intermolecular reaction and the formation of insoluble polymer networks (polymer **4c**, **4d**). ^{1}H-NMR spectroscopy was used to determine the ratio of maleimides (R and R') in the copolymers **4**. Fig. 1 shows the polymer **4b**.

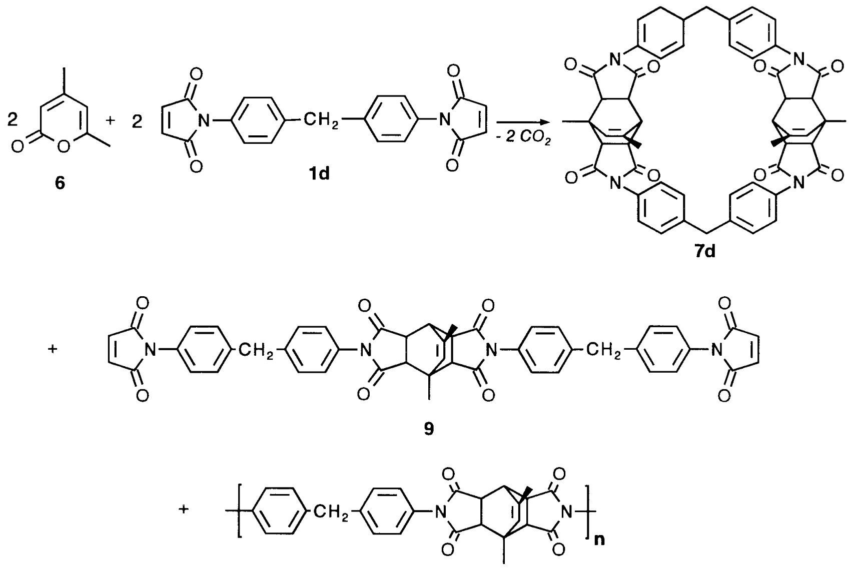
The integral ratio of the signals of the methylene protons of diphenylmethane in **1d** (3,9 ppm) to the protons (5,2-5,5ppm) in the copolymer permits conclusions as to the copolymer structure. The integral ratio of 1:1 shows the equivalence of **1g** and **1d** in the copolymer. On the basis of these integrals we calculated the values of aromatic bismaleimides in the complete Diels-Alder copolymers **4**. In all cases we determined a nearly 1:1 ratio of bismaleimide: Diels-Alder adduct (Tab. 2). A typical GPC curve of copolymers is illustrated in Fig. 2.

Tab. 2: Mol Ratios of aromatic maleimide vs. Diels-Alder adduct in the polymers **4a-f**.

polymer	ratio aromatic maleimide : Diels-Alder adduct
4a	1 : 1,1
4b	1 : 1,0
4c	1 : 1,3
4d	1 : 1,1
4e	1 : 1,0
4f	1 : 1,2

It is impossible to specify the exact structure of the polymer **4**. Block copolymers with structure **5** can be excluded (4). Model experiments to synthezise the cycle 7 (5) led to 75 % linear polymer **8** (Mn = 19900 g/mol) and to 25% low molecular weight products /4/. In this lower fraction we determined three substances by MS and GPC : 2 % maleimide **1d**, 15 % substance 9, and 5 % cycle **7d**. This shows that flexibility and volume of the maleimide spacer play an important role in the mechanism of this reaction.

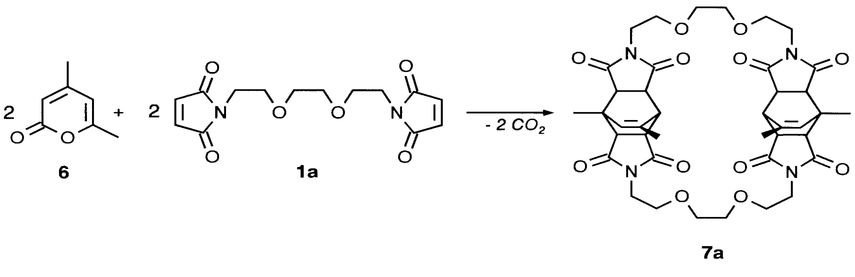




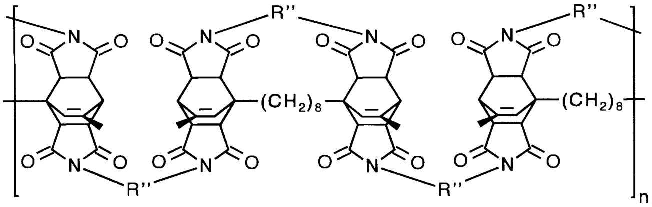
8

In comparison, to produce a cycle by adding triethyleneglycolbismaleimide **1a**, which is a more flexible maleimide, to dimethylpyrone **6**, we isolated the expected cycle **7a** as the main product, and only up to 5 % linear polymer (5). Intermolecular reactions to form polymer networks are preferred when with aromatic maleimides are used.

We exclude branched coronand structures. Polymers with such structures should show maleimide or pyrone groups in NMR spectra. They are missing. From these considerations, we assume that the polymers have the ideal structure **4** (3). The contribution of homocyclic or heterocyclic groups in the polymer structure is very low. On the basis of our earlier results the coronand structure **10** is unlikely /2/.



(5)



R'' = R or R'

10

EXPERIMENTAL

Synthesis of monomers Cf. our previous publications /1, 2/.

Copolymer Synthesis

General procedure for polymerization reactions

In 200 ml sealed bottles, 0,454 mmol aliphatic bismaleimide (**1a**, **1b**, **1f**, **1g**), 0,454 mmol aromatic bismaleimide (**1d**, **1e**), 0.454 mmol bis-α-pyrone **2**, and 10 mg di-tert-butyl-p-cresol in 1,2,4-trichlorobenzene or chlorobenzene were heated at 210°C for 24 hours at the concentration of 0,07 mol/l (with regard to maleimide). After cooling the polymers were precipitated in hexane and washed with hexane. The products were precipitated twice from methylenechloride / methanol and dried at 10^{-2} Torr and 50°C about 24 hours.

Poly-{[1^9,5^9-dimethyl-1^{1,3,5,7},5^{1,3,5,7}-octaoxo-1,5-hexadecahydro-8,11-dioxa-2,4-(1,4)-dibenzena-1,5(2,6)-bis-(4,8-etheno-pyrrolo[3,4-f]isoindola)-cyclotridecaphane-1^4,5^4-diyl]-octane-1,8-diyl} 4a

Yield: 70%. TGA: 435°C. Tg: 321°C. M_n = 11900 g/mol. ^{13}C-NMR ($CDCl_3$): 176,7 (C-9); 175,5 (C-8); 141,1 (C-10); 139,2 (C-2); 129,7 (C-12); 129,4 (C-13); 127,9 (C-1); 126,4 (C-11); 69,8 (C-17); 67,0 (C-16); 45,1 (C-5); 44,2 (C-6); 43,9 (C-7); 41,1 (C-14); 38,5 (C-4); 38,3 (C-15); 21,5 (C-3); 21,4-42,0.

ANAL. Calcd. for$C_{53}H_{56}N_4O_{10}$ $(909,05)_n$: H 6,21% N 6,16%. Found: H 6,78% N 5,81%

Poly-{[1^9,5^9-dimethyl-1^{1,3,5,7},5^{1,3,5,7}-octaoxo-1,5-hexadecahydro-9,12,15-trioxa-2,4-(1,4)-dibenzena-1,5(2,6)-bis-(4,8-etheno-pyrrolo[3,4-f]isoindola)-cyclooctadecaphane-1^4,5^4-diyl]-octane-1,8-diyl} 4b

Yield: 68 %. TGA: 415°C. M_n = 4900 g/mol. ^{13}C-NMR ($CDCl_3$): 176,6 (C-9); 175,5 (C-8); 141,1 (C-10); 139,7 (C-2); 129,6 (C-12); 129,3 (C-13); 127,9 (C-1); 126,3 (C-11); 70,2 (C-19); 69,8 (C-18); 68,4 (C-17); 44,2 (C-5); 43,8 (C-6); 43,4 (C-7); 41,1 (C-14); 38,5 (C-4); 36,1 (C-15); 27,8 (C-16); 21,3 (C-3); 22,0-32,0.

ANAL. Calcd. for $C_{57}H_{64}N_4O_{11}$ $(981,16)_n$: H 6,57% N 5,71%. Found: H 6,27% N 4,99%

Poly-{[1^9,5^9,7,9,9-pentamethyl-1^{1,3,5,7},5^{1,3,5,7}-octaoxo-1,5-hexadecahydro-2,4-(1,4)-dibenzena-1,5(2,6)-bis-(4,8-etheno-pyrrolo[3,4-f]isoindola)-cycloundecaphane-1^4,5^4-diyl]-octane-1,8-diyl} 4c

Yield: 40 %. TGA: 440°C. M_n: 2180 g/mol. ^{13}C-NMR (CDCl3): 176,3 (C-9); 175,1 (C-8); 141,2 (C-10); 139,8 (C-2); 129,7 (C-12); 129,4 (C-13); 128,0 (C-1); 126,4 (C-11); 44,3 (C-5); 44,0 (C-6); 43,8 (C-7); 41,1 (C-14); 38,5 (C-4); 21,5 (C-3); 21,4-48,9. ANAL. Calcd. for $C_{56}H_{62}N_4O_8$ $(919,13)_n$: C 73, 18% H 6,80% N 6,10%. Found: C 72,74% H 6,70% N 6,47%.

Poly-{[1^9,5^9-dimethyl-1^{1,3,5,7},5^{1,3,5,7}-octaoxo-1,5-hexadecahydro-2,4-(1,4)-dibenzena-

1,5(2,6)-bis-(4,8-etheno-pyrrolo[3,4-f]isoindola)-cyclotridecaphane-1^4,5^4-diyl]-octane-1,8-diyl} 4d

Yield: 20%. TGA: 390°C. M_n = 7400 g/mol. ^{13}C-NMR ($CDCl_3$): 176,7 (C-9); 175,5 (C-8); 141,1 (C-10); 139,7 (C-2); 129,6 (C-12); 129,3 (C-13); 127,9 (C-1); 126,3 (C-11); 44,2 (C-5); 43,8 (C-6); 43,4 (C-7); 41,1 (C-14); 38,5 (C-4); 37,8 (C-15); 27,3 (C-16); 26,1 (C17); 21,5 (C-3); 22,0-32,0. ANAL. Calcd. for $C_{53}H_{56}N_4O_8$ $(877,05)_n$: C 72,58% H 6,44% N 6,39%. Found: C 71,97% H 7,23% N 6,45%

Poly-{[2^6,4^4-dimethoxy-1^9,5^9-dimethyl-$1^{1,3,5,7}$,$5^{1,3,5,7}$-octaoxo-1,5-hexadecahydro-8,11-dioxa-2,4-(1,3)-dibenzena-1,5(2,6)-bis-(4,8-etheno-pyrrolo[3,4-f]isoindola)-cyclotridecaphane-1^4,5^4-diyl]-octane-1,8-diyl} 4e

Yield: 62 %. TGA: 405°C. Tg = 283°C. M_n = 6500 g/mol. ^{13}C-NMR ($CDCl_3$): 176,7 (C-9); 175,5 (C-8); 153,1 (C-11); 139,1 (C-2); 133,1 (C-14); 131,2 (C-13); 129,5 (C-12); 120,5 (C-10); 112,2 (C-15); 69,9 (C-20); 67,0 (C-19); 56,0 (C-17); 44,6 (C-5); 44,2 (C-6); 43,8 (C-7); 39,4 (C-16); 38,5 (C-4); 37,8 (C-18); 20,7 (C-3); 22,0-32,0. ANAL. Calcd. for $C_{55}H_{60}N_4O_{12}$ $(969, 10)_n$: H 6,24% N 5,78%. Found: H 6,47% N 5,86%

Poly-{[2^6,4^4-dimethoxy-1^9,5^9-dimethyl-$1^{1,3,5,7}$,$5^{1,3,5,7}$-octaoxo-1,5-hexadecahydro-9,12,15-trioxa-2,4-(1,3)-dibenzena-1,5(2,6)-bis-(4,8-etheno-pyrrolo[3,4-f]isoindola)-cyclotridecaphane-1^4,5^4-diyl]-octane-1,8-diyl} 4f

Yield: 70%. TGA: 425°C. Tg = 254°C. M_n = 7900 g/mol. ^{13}C-NMR (CDCl3): 176,7 (C-9); 175,5 (C-8); 153,1 (C-11); 139,2 (C-2); 134,1 (C-14); 133,0 (C-13); 128,0 (C-12); 120,5 (C-10); 112,2 (C-15); 70,5 (C-22); 70,2 (C-21); 68,5 (C-20); 55,9 (C-17); 44,6 (C-5);44,2 (C-6); 43,9 (C-7); 38,5 (C-16); 38,3 (C-4); 36,1 (C-18); 27,8 (C-19) 20,6 (C-3); 22,0-32,0. ANAL. Calcd. for $C_{59}H_{68}N_4O_{13}$ $(1040,48)_n$: H 6,58% N 5,38. Found: H 6,48% N 5,31%.

Model Synthesis: $1^{4,9}$,$10^{4,9}$-Tetramethyl-dodecahydro-4,7,13,16-tetraoxa-1,10(2,6)-bis-(4,8-etheno-pyrrolo[3,4-f]isoindola)-cyclotetradecaphane-$1^{1,3,5,7}$,$10^{1,3,5,7}$-octaone 7a

In 120 ml toluene 1,5 g (4,87 mmol) bismaleimide **1a**, 0,604 g (4,87 mmol) 4,6-dimethyl-pyran-2-one **6** and 20 mg di-tert-butyl-p-cresol are refluxed for 50 hours. The product is purified with column-chromatography (ethylacetate : toluene- 13 : 1, silica gel 60, 70-230 mesh ASTM).

Yield: 35%. Fp: 234°C. TGA: 370°C. MS (CI-CH_4): m/z 777,3 ($M+H^+$). ^{13}C-NMR ($CDCl_3$): 176,3 (C-9); 175,6 (C-8); 139,2 (C-2); 127,0 (C-1); 69,6 (C-12); 67,6 (C-11); 48,7 (C-5); 43,8 (C-6); 40,9 (C-7); 38,5 (C-4); 37,9 (C-10); 21,8 (C-3); 19,6 (C-13).

ANAL. Calcd. for $C_{40}H_{48}N_4O_{12}$: (776,33): C 61,85% H 6,23% N 7,21%. Found: C 61,13% H 6,36% N 7,16%.

$2^{4,9}$,$6^{4,9}$-Tetramethyl-2,6-dodecahydro-1,3,5,7(1,4)-tetrabenzena-2,6(2,6)-bis-(4,8-etheno-pyrrolo[3,4-f]isoindola)-cyclooctaphane-$2^{1,3,5,7}$,$6^{1,3,5,7}$-octaone 7d

In 120 ml chlorobenzene 1,79 g (5,00 mmol) diphenylmethanebismaleimide **1d**, 0,621 g (5,00 mmol) 4,6-dimethyl-pyran-2-one **6**, and 20 mg di-tert-butyl-p-cresol are refluxed for 50 hours. The product is purified with column-chromatography (ethylacetate : toluene- 1:1, silica gel 60, 70-230 mesh ASTM and isolated by preparative thin layer chromatography, (ethylacetate).

Yield: 5%. MS (CI: H_2O) : m/z 878 ($M+H^+$) $C_{54}H_{44}N_4O_8$ (876,97). ^{13}C-NMR ($CDCl_3$): 176,3 (C-9); 175,6 (C-8); 169,4 (MI); 141,1 (C-10); 140,2 (MI); 139,2 (C-2); 129,6 (C-12); 129,3 (C-13); 127,0 (C-1); 126,3 (C-11); 48,7 (C-5); 43,8 (C-6); 41,1 (C-14); 40,9 (C-7); 38,5 (C-4); 21,8 (C-3); 19,6 (C-15).

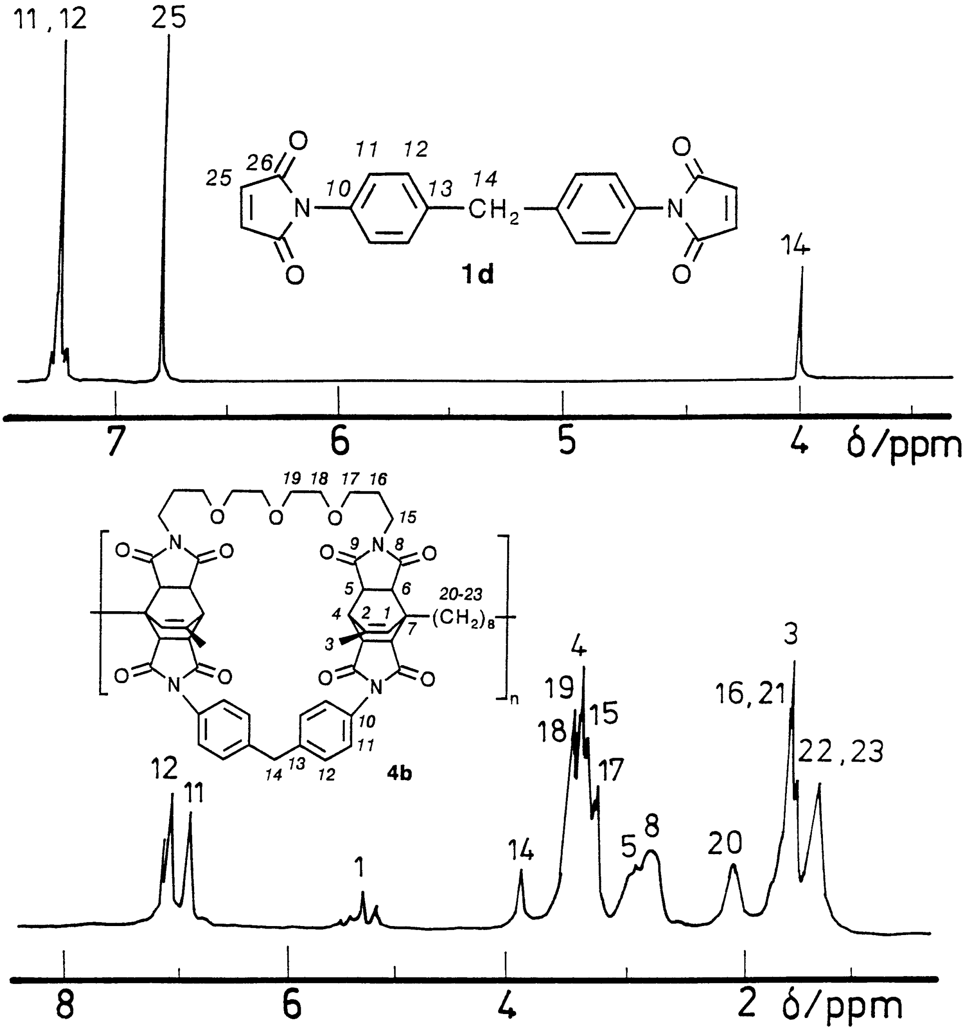


Fig. 1. ^{1}H-NMR (CDCl$_3$) spectra of maleimide **1d** and copolymer **4b**

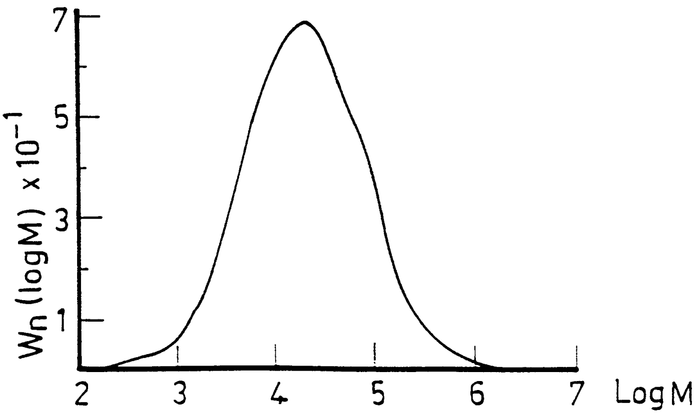


Fig. 2. GPC curve of copolymer **4f**

REFERENCES

/1/ E. Klemm, G. Alhakimi, H. Schütz, *Makromol. Chem.* **194**, 353 (1993)
G. Alhakimi, H. Görls, E. Klemm, *Macromol. Chem. Phys.* **195**, 1569 (1994)
G. Alhakimi, E. Klemm, *J Polym. Sci.: Part A: Polymer Chemistry* **33**, 767 (1995)
G. Alhakimi, E. Klemm, H. Görls, *J Polym. Sci.: Part A: Polymer Chemistry* **33**, 1133 (1995)

/2/ N. Kottner, E. Klemm, *Angew. Makromol. Chem.* **254**, 39 (1998)

/3/ N. Kottner, R. Bublitz, E. Klemm, *Macromol. Chem. Phys.* **197**, 2665 (1996)

/4/ J.K. Stille, *Fortschr. Hochpolym.-Forsch.* **3**, 48 (1961)
E.A. Kraiman, *US-Patent 2890206* (1959)