Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

New Poly(Bismaleimide-Ether)s Containing Functional Pendant Carboxylic Groups

C. Hulubei[a]; C. Cojocariu[a]; S. Pecincu[a]; F. Popescu[a]
[a] Institute of Macromolecular Chemistry, Iasi, Romania

To cite this Article Hulubei, C. , Cojocariu, C. , Pecincu, S. and Popescu, F.(1997) 'New Poly(Bismaleimide-Ether)s Containing Functional Pendant Carboxylic Groups', Journal of Macromolecular Science, Part A, 34: 6, 1085 — 1095
To link to this Article: DOI: 10.1080/10601329708015012
URL: http://dx.doi.org/10.1080/10601329708015012

J.M.S.—PURE APPL. CHEM., A34(6), pp. 1085-1095 (1997)

NEW POLY(BISMALEIMIDE-ETHER)S CONTAINING FUNCTIONAL PENDANT CARBOXYLIC GROUPS

C. HULUBEI, C. COJOCARIU, S. PECINCU, F. POPESCU
Institute of Macromolecular Chemistry
Aleea Gr. Ghica Voda 41A, Iasi-6600
Romania

ABSTRACT

New poly(bismaleimide-ether)s with functional pendant groups were synthesized by Michael addition polymerization of two monomers with functionality f > 2 (DL tartaric acid and methylene-5,5'disalicylic acid) to various bismaleimides with flexible groups (N,N'-4,4'-diphenylmethanebismaleimide, N,N'-4,4'-diphenyletherbismaleimide and N,N'-4,4'-dibenzylbismaleimide). The polymerization occurred in solution, through the addition of the OH groups to the C=C double bond of the maleimide rings. The polymers were obtained in good yields and they were characterized by elemental analysis, IR and ^{1}H NMR spectra, thermogravimetric analysis and viscozimetry.

INTRODUCTION

The materials based on maleimide polymers such as bismaleimide-ethers can be used in electrical industry as resistant sheets, molding resins with high thermal resistance and pressing materials containing miscellaneous fillers, enamels, lakes, insulated films, all having very good mechanical resistance [1-4]. Very often, the classical polymers cannot be used under unusual working conditions because they do not possess suitable properties. One of the existing methods to improve such properties consists in the preparation of polymers with different compositions by varying the nature and relative amount of the two monomer units in the new polymers. The functional pendant groups may also serve to modify the polymer properties directly and, as a tether for further attachment of various functional units at these sites of the polymer molecule. These functional pendant groups, specifically polar functional groups, may impart several important properties to polymeric systems such as: dyeability, wettability, adhesion, permeability, high strength (in case H-bonding functional groups) etc. [5]. The present paper deals with the synthesis of poly(bismaleimide-ether)s with carboxylic pendant groups.

EXPERIMENTAL

Measurements:

The IR spectra were recorded on a Specord M90 Carl Zeiss Jena Spectrophotometer by using the KBr pellet technique. ^{1}H NMR spectra were run on a Jeol 60 MHz NMR spectrometer at 50^0 C in DMSO-d_6 using TMS as the internal standard. The inherent viscosity of polymer solutions (0.5% w/v) in DMF was determined at 25±0.1^0 C by using an Ubbelohde Suspended Level Viscozimeter. Melting and softening points were determined with a Gallenkamp hot-block melting point apparatus. Thermogravimetric analysis (TGA) was carried out in air with an F. Paulik Derivatograph at a heating rate of 10^0 C/min.

Reagents and Materials:

Maleic anhydrid (Aldrich) was resublimated before use. 4,4'-diphenylmethane diamine (Aldrich), 4,4'-diamine dibenzyl (Aldrich), 4,4'- diphenylether diamine (Merck), acetic anhydride (Aldrich) were used as received. Acetone was distilled before use. N-methyl pyrrolidone (NMP) was distilled over P_2O_5 before use.

(DL) Tartaric acid anhydrous (Fluka) has been used as aliphatic diol and methylene-5,5'-disalicylic acid (Fluka) has been used as bisphenol.

Monomers Synthesis

N,N'-4,4'-diphenylmethanebismaleimide (I) and **N,N'-4,4'diphenyletherbismaleimide (II)** were synthesized following the literature [6] via reaction of maleic anhydride with the corresponding diamines.

(I): m.p. 153-156^{0}C. Yield: 85.7%

$C_{21}H_{14}N_2O_4$ (358.34)	Calc.(%)	C 70.39	H 3.9	N 7.82
	Found (%)	C 69.98	H 3.98	N 7.73

IR spectrum (KBr disc): 3100 (C=C), 2950 (-CH_2-), 1770, 1720 (imide ring, symmetrical and asymmetrical C=O stretching), 1600, 1505 (aromatic ring- stretching vibration), 1380 (C-N stretching), 1160 (C-N-C bending links), 830 (para disubstituted aromatic ring)

^{1}H NMR (DMSO-d_6): δ = 7.26-7.83 (aromatic ring), 7.14 (vinyl group), 4.12 (-CH_2-)

(II): m.p. 180-181^{0}C. Yield: 82.5%

$C_{20}H_{12}N_2O_5$ (360.32)	Calc.(%)	C 66.67	H 3.33	N 7.78
	Found (%)	C 66.21	H 3.40	N 7.52

IR spectrum (KBr disc): 3140 (C=C), 1735 (imide ring- symmetrical and asymmetrical C=O stretching), 1510 (aromatic ring), 1420 (C-N stretching), 1260 (C-O-C)

^{1}H NMR (DMSO-d_6) : δ = 7.3-7.96 (aromatic ring), 7.16 (vinyl group)

N,N'-4,4'-dibenzylbismaleimide (III) was carried out in two steps according to [7].

(III): m.p. 232-234 °C. Yield: 79.3%

$C_{22}H_{16}N_2O_4$ (372.36)	Calc. (%)	C 70.96	H 4.30	N 7.52
	Found (%)	C 70.23	H 4.65	N 7.12

IR spectrum (KBr disc): 3100 (C=C), 2930 ($-CH_2-CH_2-$), 1770 (imide ring, symmetrical and asymmetrical C=O stretching), 1605, 1510 (aromatic ring-stretching vibration), 1380 (C-N-C)

^{1}H NMR (DMSO-d_6): δ = 7.29-7.70 (aromatic ring), 7.10 (vinyl group), 2.66-2.95 ($-CH_2-CH_2-$)

Model Compounds Synthesis:

1-Phenylsuccinimide-3-(1',2'-dicarboxyethyl)-ether (IV), 1-Phenylsuccinimide-3-(o-carboxyphenyl)-ether (V)

A 250 ml four-necked flask fitted with a condenser, a thermometer, a dry nitrogen inlet, a mechanical stirrer was charged with a mixture of 8.65 g (0.05 mole) N-phenylmaleinimide and 25 ml DMF. 0.167 g (0.001 mole)2-mercaptobenzothiazole was utilized as catalist. A solution of 6.7 g (0.05 mole) malic acid [or 6.9 g salicylic acid] in 15 ml DMF was gradually introduced at 60°C. The reaction mixture was heated at 90 -110° C for 86-90 hours. The obtained product was precipitated into methanol, washed and dried at 50° C for 4 hours in a vacuum oven.

(IV) m.p.158-161 °C. Yield: 64.5%

$C_{14}H_{13}NO_7$ (307.24)	Calc.(%)	C 54.72	H 4.26	N 4.56
	Found(%)	C 53.92	H 5.05	N 4.03

(V) m.p.190-192 °C. Yield: 60.2%

$C_{17}H_{13}NO_5$ (311.34)	Calc.(%)	C 66.57	H 4.20	N 4.49
	Found(%)	C 65.94	H 4.66	N 4.37

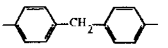
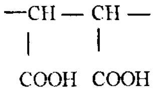
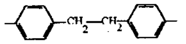
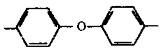
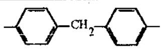
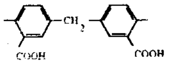
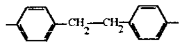
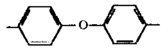
Polymer Synthesis:

The same synthesis system used to obtain the model compounds was charged with a solution of bismaleimide in a dry solvent. The glycol was introduced gradually, in a mole ratio glycol: bismaleimide = 2/1 (concentration of monomers in NMP was 40 %). N-triethylamine (TEA) or 2-mercaptobenzothiazole (0.001 mole) was utilized as catalysts. The entire system was continuously purged with dry nitrogen. The mixture was heated at 90-110° C for 12 hours. The obtained product was precipitated into methanol, washed and dried at 50° C for 5 hours in a vacuum oven. The properties of the obtained polymers are listed in Table 1.

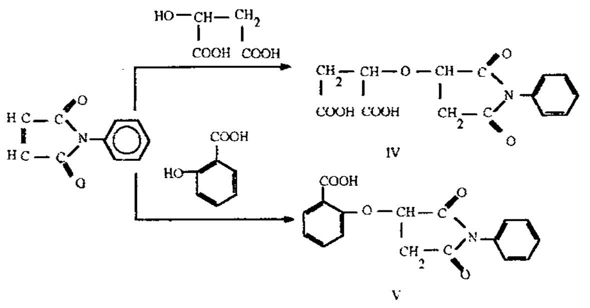
RESULTS AND DISCUSSION

Because of the flanking carbonyl groups , maleimide compounds possess double bonds with a low electron density. These double bonds are highly reactive. As a result, these compounds are susceptible to facile reduction, Diels-Alder reactions, as well as attack by a great number of nucleophilic agents.

TABLE 1 The properties of the obtained polymers

Polymers	R	R'	Yield, %	Softening point, ^{0}C	η^{a}_{inh}(dL/g)
VI		 $\underset{COOH}{-CH}-\underset{COOH}{CH}-$	81	>350	0.31
VII			74	>350	0.28
VIII			68	>350	0.30
IX			78	>350	0.35
X			80	>350	0.32
XI			75	>350	0.27

[a]Measured at the concentration of 0.5 g/dL in DMF at 25 ^{0} C.



Scheme 1

In order to facilitate the assigments of IR and ^{1}H NMR spectra, two model compounds (**IV** and **V**) where synthesized (Scheme 1).

The infrared spectra of these compounds (Fig.1) present a strong imide carbonyl band at 1720 and 1725 cm^{-1}, while the aromatic ring absorption band appears at 1510 and 1590-1605 cm^{-1}. The aliphatic ether absorption band appears at 1030 cm^{-1} and the aromatic ether absorption band a appears at 1200 and 1310 cm^{-1} . The band at 690 cm^{-1} is typical of monosubstituted phenyl ring absorption[12-13]. ^{1}H NMR spectra of the same model compounds in DMSO-d_6 (Fig.2) confirm the expected structures . COOH protons has been detected in offset at 11.8 ppm and 12.45 ppm, respectively. A multiple absorption at 7.25 ppm has been assigned to the aromatic protons. The peaks at 3.25 ppm and 2.92 ppm are due to the two aliphatic methylene protons in the succinimide ring. The peaks at 4.7 ppm and 5.25 ppm, respectively, represent the absorption of the methine protons adjacent to oxygen.

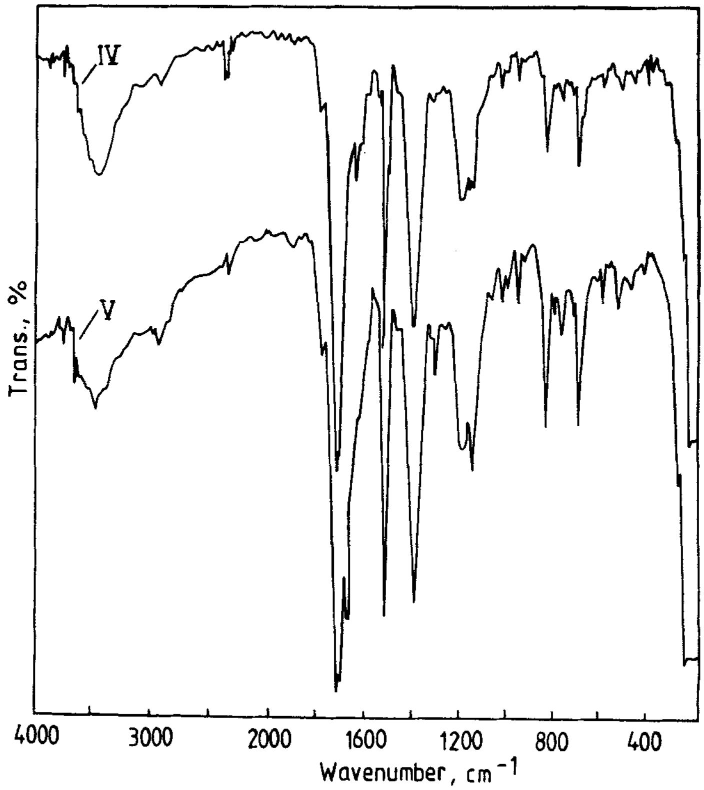


Fig. 1 IR spectra of model compounds IV and V on KBr disc

Six poly(bismaleimide-ether)s were prepared by Michael addition of tartaric acid and methylene-5,5'-disalicylic acid to various bismaleimide (8-12) (Scheme 2).

Elemental and thermogravimetric analysis data of the obtained polymers are presented in Table 2. IR and ^{1}H NMR spectra confirmed also the expected structures (Fig. 3 and Fig. 4). The IR spectra show the disappearance of characteristic absorption band at 3100 cm^{-1} (C=C), and the appearance of the aliphatic ether band at 1040-1050 cm^{-1} and the aromatic ether band at 1175-1300 cm^{-1} , respectively [12]. All the other representative bands are present in the polymer spectra: C-N-C at 1390 cm^{-1}, imide ring at 1165 cm^{-1} , imide carbonyl at 1720 cm^{-1} and aromatics at 830-760 cm^{-1}. The products derived from tartaric acid show distinctly bands for carboxylic pendant groups at 1200 cm^{-1}, while those derived from methylene-5,5' disalicylic acid show the similar bands at 1660 cm^{-1}.

The inherent viscosity measured at 25 ^{0}C in DMF (0.5 w/v) ranged between 0.27 and 0.35 dL/g. The thermal behavior of the obtained polymers was monitored by TGA. From thermogravimetric analysis data one can see that the polymers with aromatic structures

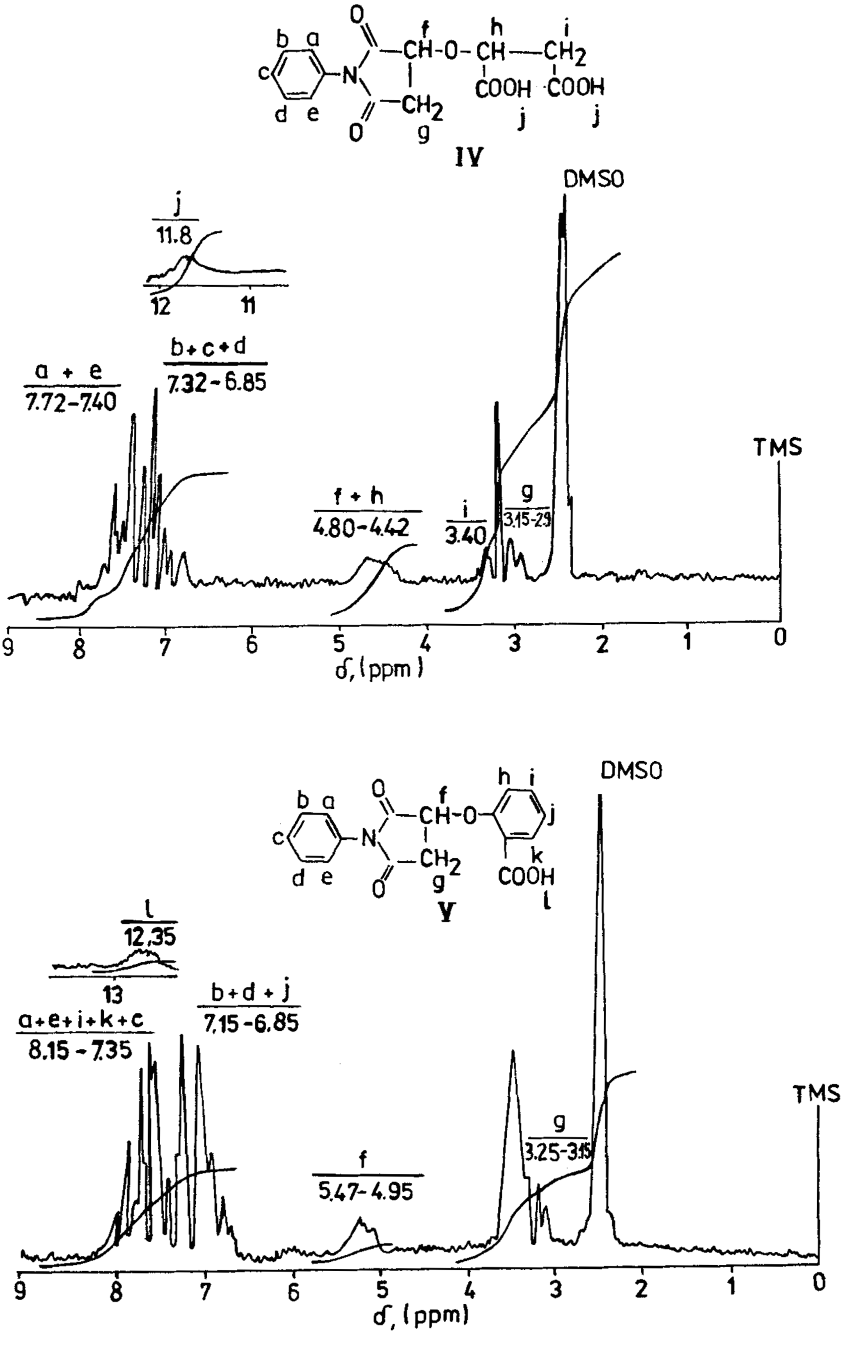
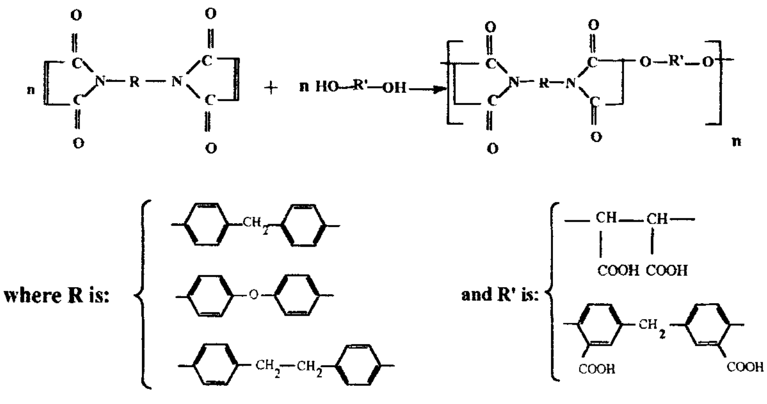


Fig. 2 ^{1}H NMR spectra of model compounds IV and V in DMSO-d_6



Scheme 2

TABLE 2 Elemental and thermogravimetric analysis of polymers

Polymers	Molecular formula (formula weight)		C, %	H, %	N,%	T_{decom}	ATG weight loss, % 400^0 C
VI	$(C_{25}H_{20}N_2O_{10})_n$	Calcd	59.05	3.93	5.51	355	20
	$(508)_n$	Found	61.3	4.14	6.07		
VII	$(C_{26}H_{22}N_2O_{10})_n$	Calcd	54.54	3.84	4.89	370	21
	$(522)_n$	Found	55.17	4.12	5.43		
VIII	$(C_{24}H_{18}N_2O_{11})_n$	Calcd	56.47	3.92	5.49	340	21
	$(510)_n$	Found	56.98	4.58	5.68		
IX	$(C_{36}H_{26}N_2O_{10})_n$	Calcd	66.87	4.04	4.33	370	19
	$(646)_n$	Found	67.03	4.91	5.08		
X	$(C_{37}H_{28}N_2O_{10})_n$	Calcd	69.09	4.24	4.24	370	16
	$(660)_n$	Found	68.53	5.15	4.58		
XI	$(C_{35}H_{24}N_2O_{11})_n$	Calcd	64.81	3.7	4.32	350	17
	$(648)_n$	Found	64.74	4.44	4.86		

were decomposed at higher temperature than those observed for the polymers based on aliphatic diols.

The qualitative solubility of poly(bismaleimide-ether)s were evaluated in various solvents (0.5%w/v) and are listed in Table 3.

CONCLUSIONS

The new poly(bismaleimide-ether)s with pendant carboxylic groups were synthesized by polyaddition reaction between bismaleimides and monomers with f >2.The products were

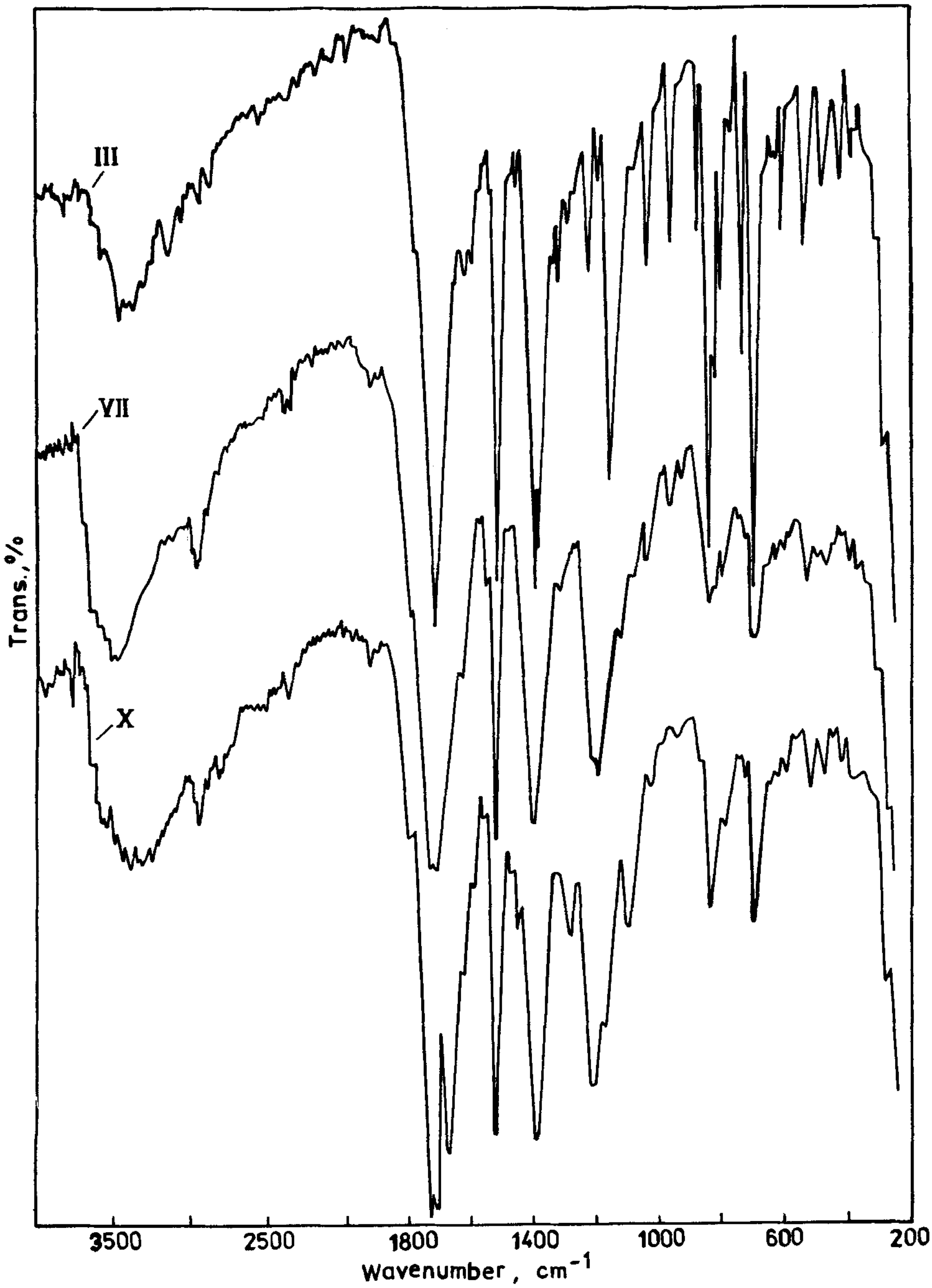


Fig. 3 IR spectra of bismaleimide III and polymers VII and X on KBr disc

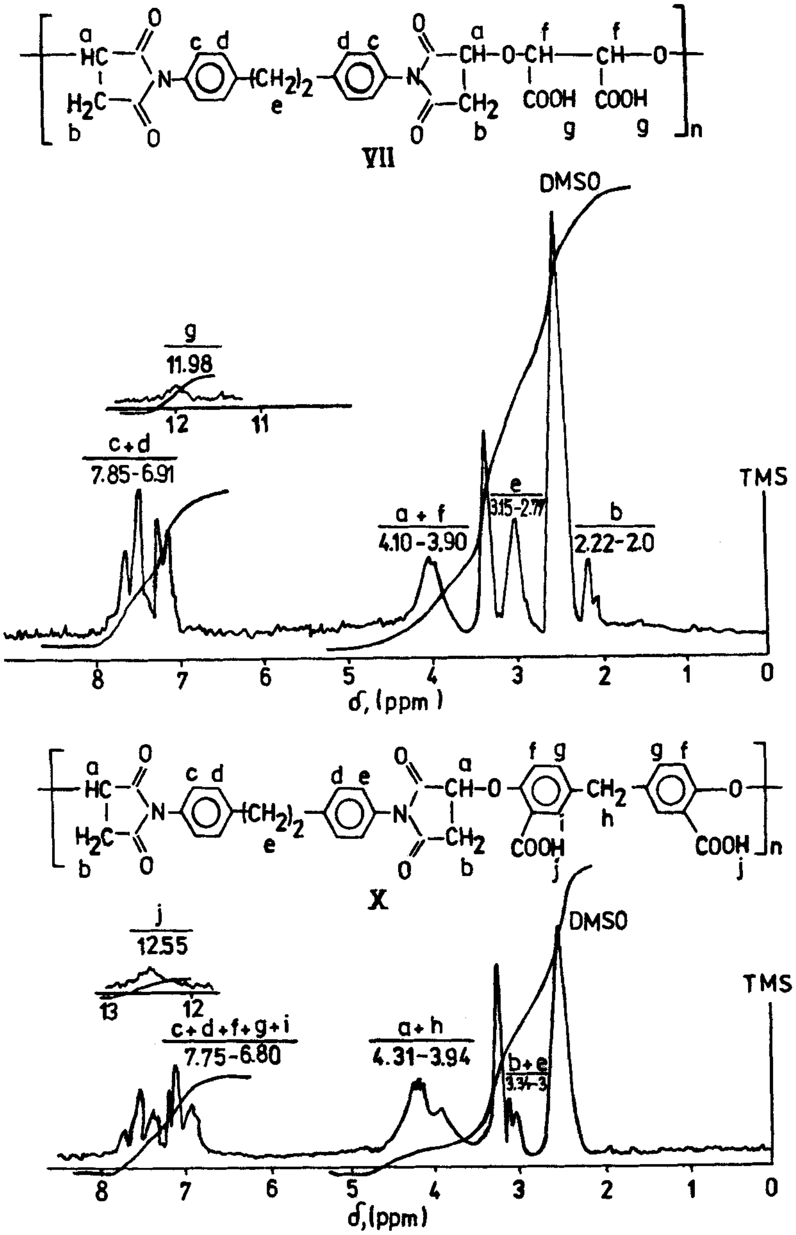


Fig. 4 ^{1}H NMR spectra of polymers VII and X in DMSO-d_6

TABLE 3 The solubility of poly(bismaleimide-ether)s

Polymer	**Solvents**							
	DMSO	DMF	NMP	THF	DCE	Chloroform	Acetone	Methanol
VI	++	++	++	++	–	–	–	–
VII	++	++	++	++	–	–	–	–
VIII	++	++	++	++	–	–	–	–
IX	+–	++	++	++	–	–	–	–
X	+–	++	++	++	–	–	–	–
XI	+–	++	++	++	–	–	–	–

++ high soluble; +– partially soluble; – insoluble

characterized by elemental analysis, inherent viscosity, IR and ^{1}H NMR spectra. Thermal stability was evidenced by TGA. The polymers present an acceptable high thermal stability and exhibit softening points higher than 350^0 C.

The new compounds are soluble in electro-donating organic solvent such as DMF, NMP, DMA, DMSO and chemical reaction at the pendant functional groups are possible in these media. These polymers may be used for composite materials with inorganic fillers, metal and other organic polymers. A more detailed study of this behavior is still underwork and will be reported.The investigation will be continued in order to prepare new functionalizated structures of poly(bismaleimide-ether)s and to extend their uses as well.

REFERENCES

1. J.A. Mikroyannidis, Eur. Polym. J. 25 (6), 557 (1989)
2. R. Vasiljev, P. Benko, Elektroizolacna Kablova Tech. 38 (3), 162 (1985), CA 106, 6081f, 1987
3. Ishii, Keiichiro; Suzuki, Kenichi; Shoji, Takechika, J.P. 61,233,017 (Oct.17, 1986), CA 106, 197523j, 1987
4. Liao, Yih Tyan; Lin, Chen Ron; Lin,Wen Liang J.Appl.Polym.Sci. 40 (11-12), 2239 (1990)
5. S.Ramakrishnan, Indian Journal of Technology 31, 293-301, 1993, CA 120, 218577m, 1994

6. Gh. Mandric; G. Gherasim; GH. Petrache, C. Chiriac, Rom Ro 70,247 (Mart.8, 1979), CA 96, 85417w, 1982
7. V.Taranu, S.Pecincu, in press
8. A. Renner; I.Forgo; W.Hofmann, Helv.Chim.Acta 61, 1443 (1978)
9. A. Mueller; T. Haug; A. Renner, Ger. Offen. 2,459,961 (July 3, 1975), CA 83, 194042x, 1975
10. G. Gherasim; I.Zugravescu, Revista de Chimie 32 (11), 1047 (1981), CA 96, 142574W, 1982
11. G.Luders; E.Merker; H.Rambach, Die Angew. Makromol. Chem. 182, 135 (1990)
12. V. Taranu, S.Pecincu, Macromolecular Reports A31 (Suppls.1&2), 45-52 (1994)
13. J.V.Crivello, J.P.S. Polym.Chem. 14, 159-182 (1976)