

This article was downloaded by:

On: 24 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597274>

Synthesis and Characterization of Poly(Maleimide-Ethers) from the Reaction of Bis(dichloromaleimides) with 4,4'-(Hexafluoroisopropylidene)diphenol

M. Sava^a; C. Chiriac^a; C. Gaina^a; A. Stoleriu^a; V. Gaina^a

^a "Petru Poni" Institute of Macromolecular Chemistry, ROMANIA

To cite this Article Sava, M. , Chiriac, C. , Gaina, C. , Stoleriu, A. and Gaina, V.(1997) 'Synthesis and Characterization of Poly(Maleimide-Ethers) from the Reaction of Bis(dichloromaleimides) with 4,4'-(Hexafluoroisopropylidene)diphenol', *Journal of Macromolecular Science, Part A*, 34: 4, 725 – 733

To link to this Article: DOI: 10.1080/10601329708014998

URL: <http://dx.doi.org/10.1080/10601329708014998>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

SYNTHESIS AND CHARACTERIZATION OF POLY(MALEIMIDE-ETHERS) FROM THE REACTION OF BISDICHLOROMALEIMIDES WITH 4,4'-(HEXAFLUOROISOPROPYLIDENE)DIPHENOL

M. SAVA, C. CHIRIAC, C. GAINA,
A. STOLERIU AND V. GAINA

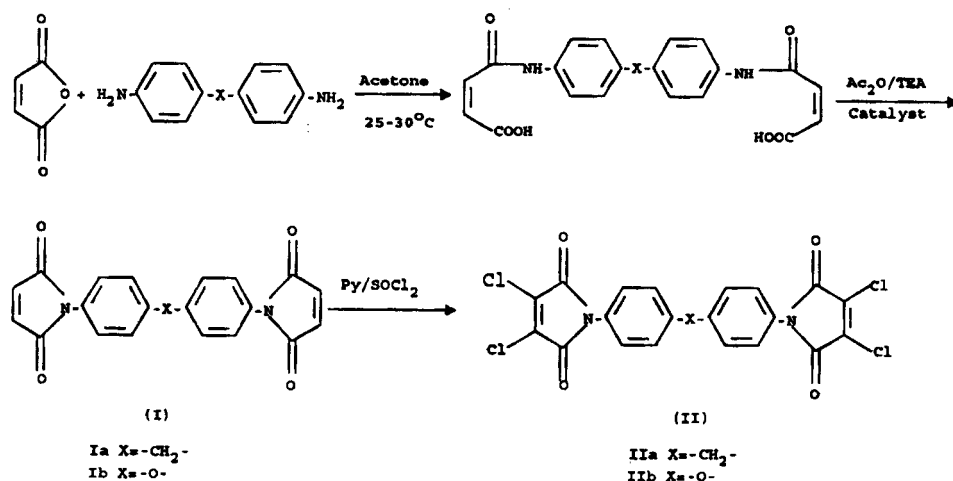
"Petru Poni" Institute of Macromolecular Chemistry
Aleea Gr.Ghica Voda No.41A
RO-6600 ROMANIA

ABSTRACT

New poly(maleimide-ethers) containing chlorine and fluorine were synthesized and characterized. They were prepared by reacting bisdichloromaleimides with 4,4'-(hexafluoroisopropylidene)diphenol. Polymers were characterized by inherent viscosity measurements and infrared (IR) spectroscopy. Thermal characterization of monomers and polymers were accomplished by differential scanning calorimetry (DSC), thermogravimetric analysis (TGA) and differential thermogravimetry (DTG). GPC was employed for characterization of polymer IIIb. In addition, the thermal stability of the polymers was evaluated by isothermal gravimetric analysis (IGA). The properties of these polymers are discussed and compared with polymers derived from bisphenol A.

INTRODUCTION

Polymers containing aromatic and/or heterocyclic structures, such as polyquinoxalines, polybenzothiazoles and polyimides are known to have excellent thermal stability because of their minimal number of oxidizable hydrogen atoms and the high extent of conjugation. Polyimides are one of the most attractive classes of polymers because of their usual chemical, thermal and oxidative stability and



Scheme 1

especially the possibility of processing to molding adhesive, films etc [1-4]. Addition type polyimides can be easily processed and can be homopolymerized without the evolution of volatiles. However, the major disadvantage is their brittleness due to the extensive crosslinking attained during polymerization [5-8]. Ether bridges (-O-) inserted into the macromolecular chain of these polymers make the chain more flexible. This paper deals with synthesis and characterization of these new poly(maleimide-ethers).

EXPERIMENTAL

Bismaleimide (I)

The aromatic bismaleimides (I) used in the reaction were prepared from aromatic diamines (1 mol) with maleic anhydride (2 mol) in dry acetone at reflux temperature under a nitrogen atmosphere according to a method described in the literature [9] (Scheme 1). Intermediate bismaleamic acid was cyclodehydrated *in situ* with acetic anhydride, triethylamine using magnesium acetate as a catalyst. The final product was recrystallized from toluene and dried under vacuum, Mp Ia: 155-158°C; Mp Ib: 178-183°C. IR (Kbr)cm⁻¹ for Ia: 3100(H-C=), 1785, 1710(imide I), 1610(maleimide C=C), 1512(aromatic rings), 1390(imide II), 1145(imide III), 710(imide IV). IR (Kbr)cm⁻¹ for Ib: 3125(H-C=), 1790, 1725(imide I), 1625 (maleimide C=C), 1515(aromatic rings), 1410(imide II), 1155(imide III), 715(imide IV). In addition, monomers Ib showed a strong absorption band at 1250 cm⁻¹ assigned to the aromatic ether.

Table 1. Thermal properties and elemental analysis^a of the monomers.

Mono-mer	Mp ^b (°C)	Texo ^c (°C)	GT ^d (s)	Tg ^e (°C)	Elemental analysis			
					C%	H%	N%	Cl%
Ia	160	240	35	475	69.92 (70.38)	3.64 (3.93)	8.14 (7.86)	-
IIa	210	268	-	375	51.48 (50.83)	1.96 (2.03)	6.01 (5.64)	29.14 (28.30)
Ib	182	260	60	485	67.02 (66.66)	3.51 (3.35)	7.98 (7.77)	-
IIb	267	300	-	378	48.47 (48.22)	1.87 (1.61)	5.35 (5.62)	28.21 (28.47)

^aRequired values are given in parantheses.

^bMelting point by DSC.

^cExothermal peak temperature by DSC.

^dGel time at 225°C.

^eTemperature at 10% decomposition by TG.

Bisdichloromaleimides(II)

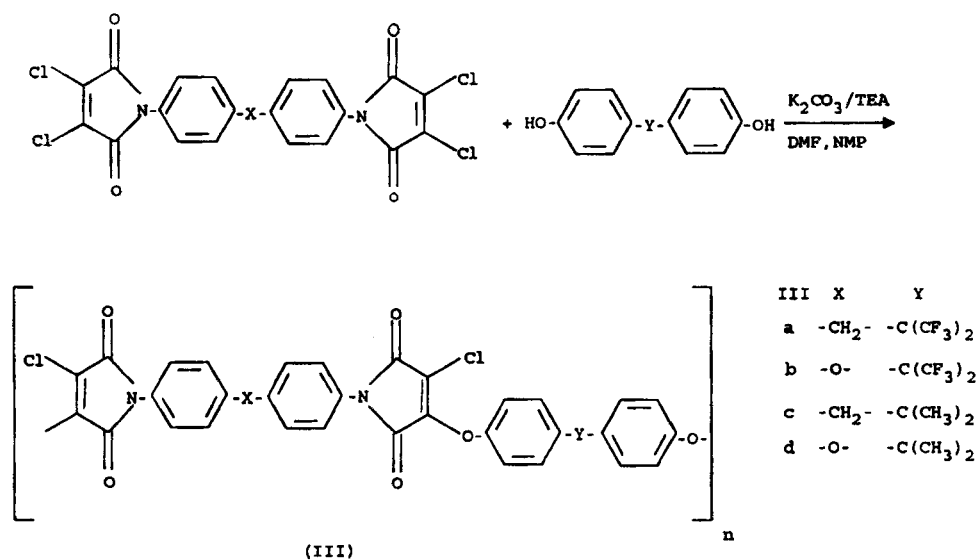
Bismaleimides are converted to (II) by treatment with pyridine and thionyl chloride according to Scheme 1. The mixture was stirred at 0°C for 8 hours and then refluxed for 2 hours. The excess thionyl chloride was removed *in vacuo*; the solid residue was washed several times with methanol and then recrystallized from chloroform [10], Mp IIa:202-210°C; Mp IIb:265-269°C. IR (KBr)cm⁻¹ for IIa: 1810 (maleimide ring), 1745(C=O), 1640(C=C). IR (KBr)cm⁻¹ for IIb: 1810 (maleimide ring), 1750(C=O), 1645(C=C), 1275(Ar-O-Ar). The properties and elemental analysis data of the obtained monomers are listed in Table 1.

4,4'-(Hexafluoroisopropylidene)diphenol was supplied by Fluka and used without further purification, Mp 160-163°C.

4,4'-Isopropylidene diphenol(bisphenol A) was obtained commercially (Fluka) and purified by recrystallization from toluene.

Synthesis of the polymers

The general procedure for the preparation of poly(maleimide-ethers) was as follows [11]. In a 100-mL three-necked flask equipped with mechanical stirrer and



Scheme 2

thermometer, a solution of bisdichloromaleimide (0.003 mol) in DMF (25 mL) was placed and 4,4'-(hexafluoroisopropylidene)diphenol (0.003 mol) in DMF (10 mL) was added at 0-10°C over a period of 10 minutes. Then anhydrous K₂CO₃ (0.013 mol) and 1.5×10⁻⁵ mol of triethylamine were added and the suspension was stirred at 10-15°C for 6-10 hours. The excess K₂CO₃ was filtered by pouring the suspension through a bed of glass-wool. The viscous solution was added slowly to 75 mL of methanol and 10 mL of 1N HCl which were being stirred vigorously in a blender. The precipitated polymer was filtered, washed with methanol, and dried *in vacuo* at 90°C. This polymer was redissolved in CHCl₃, filtered through celite to remove dust particles and reprecipitated by adding to aqueous acidic methanol (Scheme 2).

Measurements

The IR spectra were recorded on a Specord M90 Carl Zeiss Jena Spectrophotometer using the KBr pellet technique. The inherent viscosities of polymer solutions (0.5% w/v) in CHCl₃, were determined at 20°C using an Ubbelohde Suspended Level Viscometer. Differential scanning calorimetry (DSC) measurements were done by using a Mettler TA, instrument DSC 12E with a heating rate of 10°C/min. in nitrogen. Gel permeation chromatograms were obtained by using a PL-EMD Evaporative Light Scattering Detector instrument and DMF as eluent, at a flow rate of 1 mL min⁻¹. Gel time was measured in the following

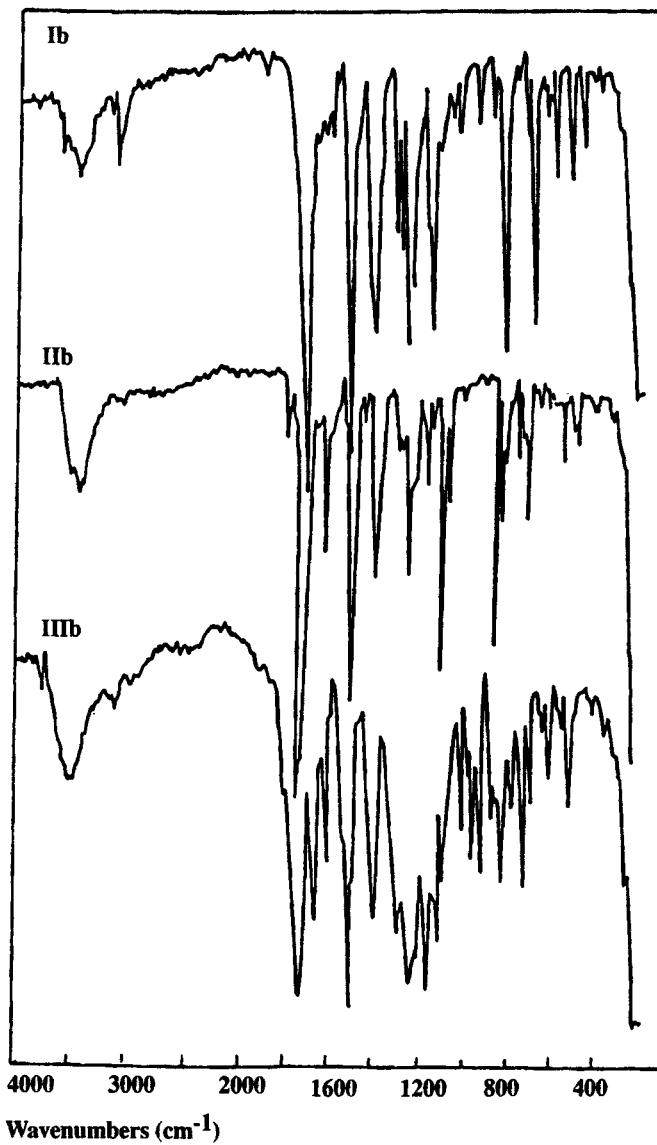


Figure 1. IR spectra of monomers Ib, IIb and of polymer IIIb.

Table 2. Characterization of the Polymers III (a-d)

Poly- mer	a (dL/g)	T _g ^b (°C)	PDT ^c (°C)	Elemental analysis ^d				
				C%	H%	N%	Cl%	F%
IIIa	0.34	189	315	56.38	2.88	3.89	9.72	14.71
				(56.93)	(2.38)	(3.68)	(9.33)	(15.00)
IIIb	0.40	193	340	55.60	2.40	3.43	9.61	15.13
				(55.21)	(2.11)	(3.67)	(9.31)	(14.97)
IIIc	0.46	172	305	65.94	3.90	4.05	10.53	-
				(66.36)	(3.71)	(4.29)	(10.88)	
IIId	0.35	175	325	64.39	3.73	4.18	10.48	-
				(64.34)	(3.39)	(4.28)	(10.85)	

^aMeasured at a concentration of 0.5 g/dL in chloroform at 20°C.

^bDetermined by DSC at a heating rate of 10°C/min in nitrogen.

^cPolymer decomposition temperature by DTG.

^dRequired values are given in parantheses..

manner. Bismaleimide monomers were heated at 225°C on a brass plate, and tack-free time was measured and defined as gel time.. Differential thermal analysis (DTA) and thermogravimetric analysis (TGA) were performed on a F. Paulik Derivatograph in air at a heating rate of 20°C/min.

RESULTS AND DISCUSSION

The structure of poly(maleimide-ethers) were identified by IR spectra and elemental analysis. Figure 1 presents typical IR spectra of monomers Ib, IIb and polymer IIIB. The IR spectra of polymer IIb showed the appearance of some characteristic absorption bands at 1660 cm⁻¹ (conjugation), 1215-1180 cm⁻¹ of the perfluoromethyl group and the decrease of the frequency (Cl-C=) band at 890 cm⁻¹ of bisdichloromaleimide (IIb). Elemental analysis data for C,H,N,Cl,F are in good agreement with the calculated values (Table 2). Inherent viscosities are in the range 0.035-0.46 g/dL in chloroform at a concentration of 0.5 g polymer/100 mL solution at

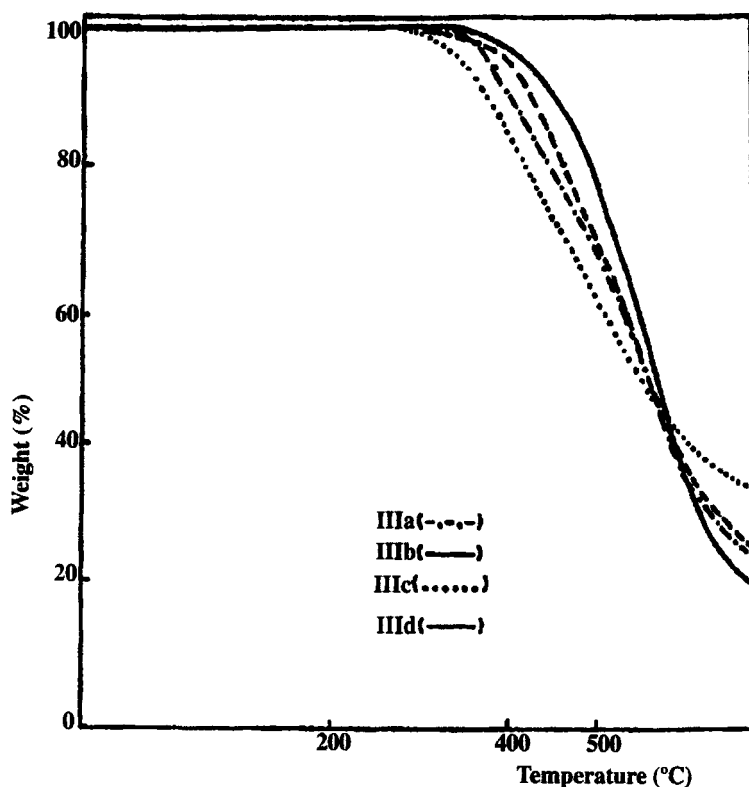


Figure 2. Thermogravimetric analysis of polymers III (a-d) in air (12°C/min).

20°C (Table 2). Comparison of inherent viscosity of polymers III(a-d) showed that the polymer derived from 4,4'-diaminodiphenylmethanebis(dichloromaleimide) and bisphenol A had a high value. The GPC curve indicated that M_n value of polymer IIIb was 13,000 and the M_w/M_n ratio as a measure of molecular weight distribution was 1.3. All polymers gave flexible films by casting 12% (w/w) polymer solutions on to glass plates. The polymers III(a-d) dissolved in a wide range of solvents such as chloroform, DMF, DMAc, NMP but are only partly soluble in DMSO and are insoluble in benzene. The polymers IIIa and IIIb are more soluble, probably caused by the incorporation of perfluoromethyl group into polymer chains. The thermal properties of the poly(maleimide-ethers) were investigated by differential scanning calorimetry (DSC), thermogravimetric analysis (TGA) and differential thermogravimetry (DTG).

The DSC measurements revealed the existence of one endotherm in the heating trace for all polymers. The polymers had glass transition temperatures between 172 and 193°C depending on the bisphenol component structures and no melting point up to 250°C. The large temperature range between T_g and the

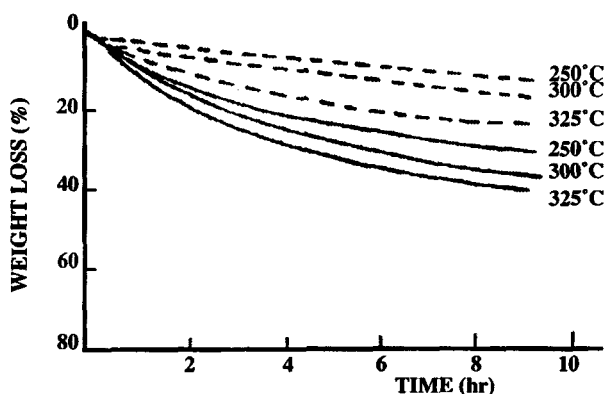


Figure 3. IGA traces of polymer IIIa (—) and polymer IIIb (---) in static air at 250, 300 and 325°C.

decomposition temperature makes the polymers attractive for processing in the air atmosphere, the starting temperatures of weight loss are from 270°C for polymer IIIc to 310°C for polymer IIIb. As can be seen in Figure 2, the polymers showed similar decomposition patterns, and the temperature at which 5% weight loss occurred ranges from 350 to 415°C. Polymer IIIb possessed better thermooxidative stability (caused mainly by the incorporation of perfluoromethyl group into the polymer chain). The present investigation was expanded to include evaluation of thermooxidative stability of polymers III(a,b) by IGA. Figure 3 presents IGA traces of those polymers at 250, 300 and 325°C in static air. After isothermal aging at these temperatures for 8 hours, a weight loss of 34.5, 36.0 and 40.0% for the polymer IIIa and 12.5, 18.0 and 22.5% for polymer IIIb was observed.

REFERENCES

1. W. A. Feld, B. Ramlingam and F. W. Harris, *J. Polym. Sci., Polym. Chem. Ed.*, **21**, 319-328 (1983).
2. S. S. Hirsch and S. L. Kaplan, *Coatings and Plastics Preprints*, **34**, 162 (1974).
3. C. E. Sroog, *Prog. Polym. Sci.*, **16**, 561-694 (1991).
4. J. O. Park and S. Hjang, *J. Polym. Sci., Part A: Polym. Chem.*, **30**, 723-729 (1992).
5. H. Stenzenberger, *Br. Polym. J.*, **20**, 383 (1988).
6. H. Takeda, H. Akiyamata and H. Kakinchi, *J. Appl. Polym. Sci.*, **35**, 1341-1350 (1988).
7. B. S. Rao, *J. Polym. Sci., Part A: Polym. Chem.*, **27**, 2509-2518 (1989).

8. J. Goldfarb, W. A. Feld, and J. Saikumer, *Polymer*, 34 (4), 813 (1993).
9. L. R. Dix, J. R. Ebdon, N. J. Flint, P. Hodge and R. O'Dell, *Eur. Polym. J.*, 31 (7), 647-652 (1995).
10. P. R. Srinivasan, V. Mahadevan and M. Srinivasan, *Eur. Polym. J.*, 24 (3) (1988).
11. H. M. Relles and R. W. Schluenz, *J. Org. Chem.*, 37, 363 (1972).