

# Polyimides Containing 4,4'-Bipyridinium Units

C. Gaina, V. Gaina, A. Airinei, E. Avram

Institute of Macromolecular Chemistry "P.Poni," Aleea Gr.Ghica Voda 41 A, Iasi, Romania

Received 18 May 2004; accepted 25 June 2004

DOI 10.1002/app.21145

Published online in Wiley InterScience (www.interscience.wiley.com).

**ABSTRACT:** New polyimides containing 4,4'-bipyridinium units were synthesized by the reaction of bis(dichloromaleimide)arylene derivatives with 4,4'-bipyridine in *meta*-cresol. IR and  $^1\text{H-NMR}$  spectroscopy and elemental analysis as well confirmed their structures. The polymers were characterized by viscometric measurements, softening

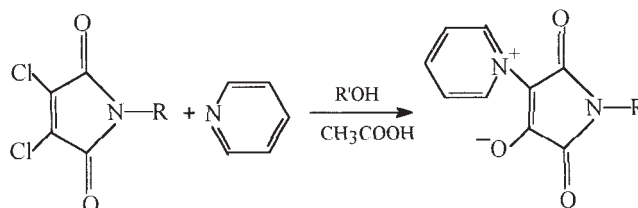
points, and thermogravimetric data. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 94: 2091–2100, 2004

**Key words:** viologene polymers; nucleophilic substitution; tetrachlorobismaleimide; polyimide

## INTRODUCTION

In the last three decades, the nucleophilic substitution reaction of bisdichloromaleimides has been effectively exploited in the synthesis of several classes of polymers. By displacement of chlorine in bis(dichloromaleimide) with bisphenols, diamine, bistiols poly(maleimide-ethers),<sup>1–3</sup> poly(maleimid-amines),<sup>4,5</sup> poly(maleimide-ethers),<sup>6</sup> etc. were prepared. The above-mentioned polymers possess good solubility in aprotic dipolar solvents, low flame retardance,<sup>4</sup> and good electric properties,<sup>2</sup> and are available for further curing reactions due to the presence of olefinic bonds in their structures.<sup>5</sup> The polymers containing 4,4'-bipyridyl units are an interesting class of materials that exhibit a wide range of properties due to the presence of viologen moiety. They exhibit electrical conductivity,<sup>7,8</sup> photochromism,<sup>8–10</sup> electrochromism,<sup>11</sup> thermochromism,<sup>12</sup> and photomechanical behavior.<sup>10</sup> Karten and coworkers<sup>13</sup> claimed that dichloromaleimides react with tertiary hetero-aromatic amines, such as pyridine, in alcohol or acetic acid to give betaine (Scheme 1). Recently, Koch and coworkers<sup>14</sup> obtained pyridinium-oxy zwitter ionic quinines by the reaction of *p*-chloroanil with pyridines. We studied a series of polymers synthesized by nucleophilic substitution of bis(dichloromaleimide) aromatic derivatives with bisphenols,<sup>15,16</sup> diamine,<sup>17,18</sup> and sodium sulfide.<sup>19,20</sup>

In this article, we describe the synthesis and characterization of polyimides containing viologen moiety by the reaction of bis(dichloromaleimides) with 4,4'-bipyridine in *meta*-cresol.



Scheme 1

## EXPERIMENTAL

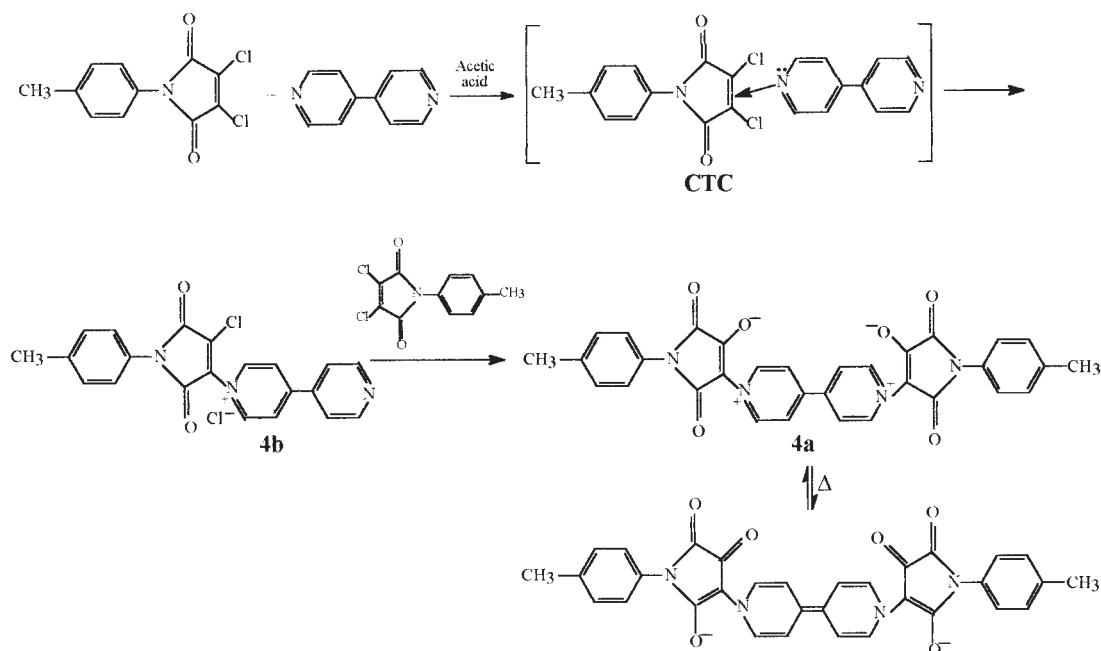
### General equipment

The IR absorption spectra were recorded on a Carl Zeiss Jena SPECORD M80 spectrophotometer (Tokyo, Japan) with KBr pellets. The  $^1\text{H-NMR}$  spectra were recorded on a Jeol C60-HL spectrometer using DMSO- $d_6$  as solvent and tetramethylsilane as an internal standard. The softening points were measured with a Gallenkamp hot-block melting point apparatus. Thermogravimetric (TG) measurements were made at a heating rate of 12°C/min in air using a MOM derivatograph. The UV-vis spectra were obtained on a Carl Zeiss Jena SPECORD M42 spectrophotometer in DMSO solutions using 10-mm quartz cells field poly(tetrafluoroethylene) stoppers.

UV irradiation was performed with a 350-W high-pressure mercury arc lamp at room temperature, and a suitable glass filter (365-nm) was used to obtain the irradiation light. The initial absorbance of the samples under study in the absorption band maximum was kept between 0.9 and 1.0.

The inherent viscosities of polymer solutions (0.5% w/v) in  $\text{H}_2\text{SO}_4$  were determined at 30°C by using an Ubbelohde suspended level viscometer. The polymer solubility was determined for 4 common solvents at a concentration of 1% (w/v) at 100°C for 12 h. To deter-

Correspondence to: C. Gaina (gcost@icmpp.tuiasi.ro).



Scheme 2

mine the equilibrium water absorption, the samples were previously conditioned at 120°C in an oven for 12 h. They were subsequently placed in a desiccator where 89% relative humidity (r.h.) was maintained by means of an over saturated aqueous solution of KCl at 20°C, and were periodically weighed.

### Reagents and materials

Maleic anhydride (mp 54–56°C, Aldrich) was resublimed before use. The thionyl chloride and *m*-cresol were freshly distilled before use. *p*-Toluidine was recrystallized from ethanol before use. The *p*-phenylen-

diamine, 2–4 toluenediamine, 4,4'-diaminodiphenylmethane, 4,4'-diaminodibenzil, and 4,4'-diaminodiphenylether were purified by recrystallization before use. The 4,4'-bipyridine was purchased from Fluka Company and used as received.

### Monomer synthesis

#### *N-p*-tolyl-3,4-dichloromaleimide

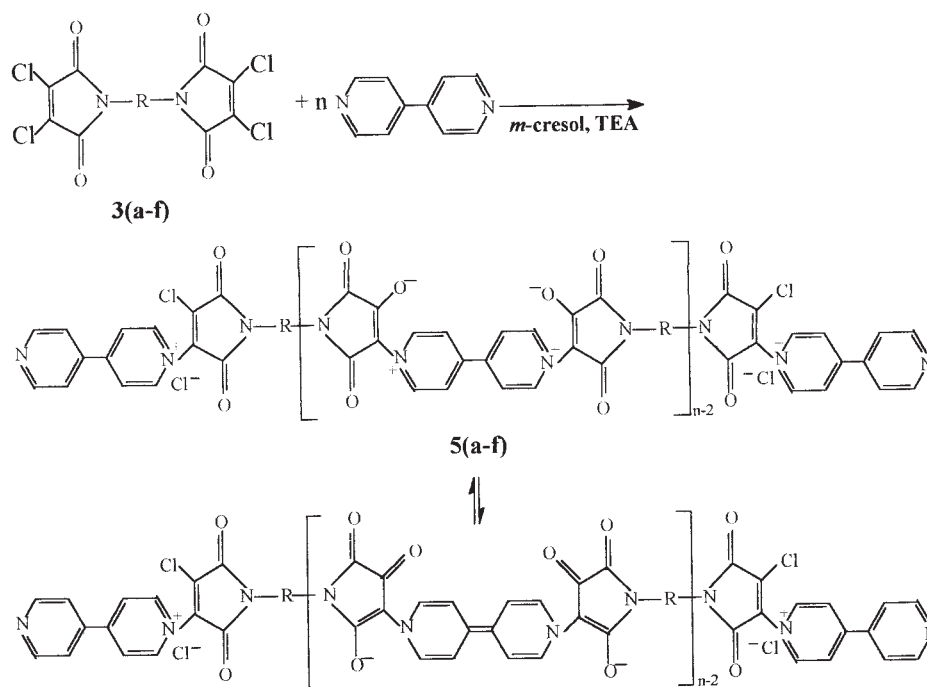
*N-p*-tolyl-3,4-dichloromaleimide was prepared from *N-p*-tolyl maleimide and pyridine in excess of thionyl chloride, according to a method proposed by Relles.<sup>21</sup>

TABLE I  
Properties of Monomers 2(a–e) and 3(a–e)

Polymer	Yield (%)	Recrystallization solvent	General appearance	Melting point (°C)		Reference
				Found	Literature	
2a	90	isopropanol	solid-pale yellow	141–143	136–141	[25]
2b	90	ethanol	light-yellow solid	340–343	347 <sup>a</sup>	[26]
2c	87	ethanol	white solid	173–174	172–174	[27]
2d	91	benzene	pale yellow powder	159–160	157–160	[26]
2e	88	toluene	pale yellow powder	253–254	254	[28]
2f	90	toluene	yellow powder	188–189	187–188	[26]
3a	83	chloroform-methanol	ochre solid	192–194	193–194	[29]
3b	68	chloroform-methanol mixture	pale yellow powder	239–243	242 <sup>b</sup>	[6]
3c	81	chloroform-cyclohexane mixture	yellow	223–225	223–224	[1]
3d	75	chloroform-methanol	ochre solid	223–225	225–226	[1]
3e	79	dichloromethane	ochre solid	>350		
3f	78	chloroform	ochre solid	265–267	260.5–261.5	[1]

<sup>a</sup> Polymerization.

<sup>b</sup> Decomposition.



Scheme 3

To a solution of 18.75 g (0.1 mol) of *N-p*-tolyl maleimide in 120 mL of thionyl chloride cooled at 0°C in an ice bath, 17 mL (0.21 mol) of pyridine were dropped in over 15 min. The reaction mixture was stirred and maintained for 2 h at 0°C. The ice bath was removed and the system was maintained 2 h at room temperature, then it was heated under reflux for 2 h. The excess of thionyl chloride was removed by vacuum distillation, and the residue was poured in 200 mL chloroform. The chloroform solution was extracted with 100 mL dilute HCl (to remove the excess of pyridine as pyridine hydrochloride), washed with 150 mL water, dried overnight with anhydrous magnesium sulfate, filtered, and evaporated of solvent to

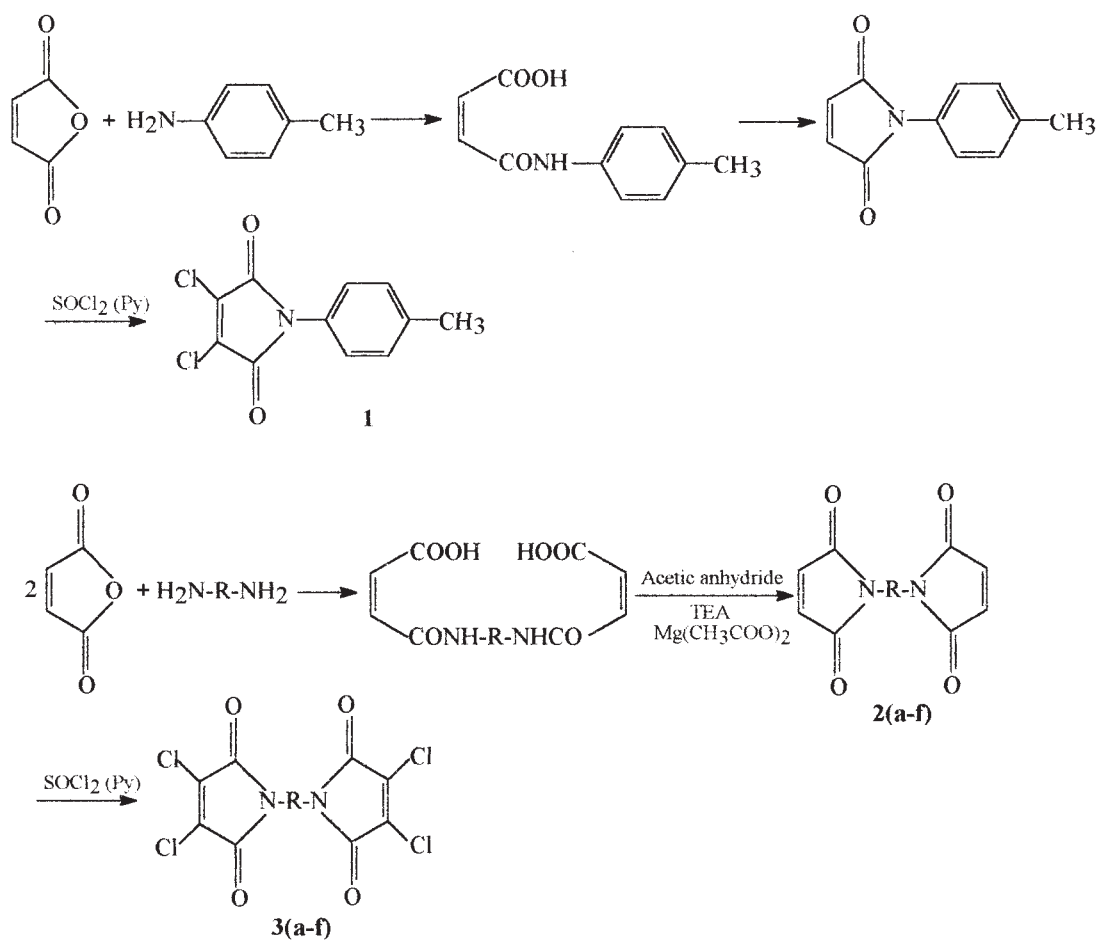
give 26 g of a solid residue. The crude product was recrystallized from ethanol resulting in 2.3 g (83.2% yield), mp = 194–196°C [lit.,<sup>22</sup> 191–192°C].


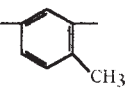
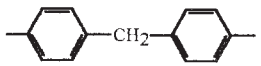
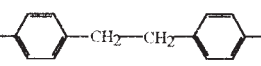
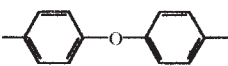
#### Tetrachlorobismaleimide synthesis

The bis(dichloromaleimide)s **3(a–f)** were prepared by the reaction of bismaleimides **2(a–f)** in the presence of thionyl chloride and pyridine, according to a method proposed by Relles<sup>21</sup> (Scheme 4). Bismaleimide **2a** was prepared by the reaction of maleic anhydride (2 mol) with hexamethylene diamine (1 mol) in boiling acetic acid, according to a method proposed by Gill et al.<sup>23</sup> The bismaleimides **2(b–f)** were prepared from

TABLE II  
Elemental Analysis of Polymers 5(a–f)

Polymer	Empirical formula (Formula weight)	Elemental analysis (%); calcd/(found)			
		C	H	N	Cl
5a	C <sub>24</sub> H <sub>20</sub> N <sub>4</sub> O <sub>6</sub> (460.444)	62.60 (61.56)	4.37 (4.33)	12.16 (12.33)	(2.67)
5b	C <sub>24</sub> H <sub>12</sub> N <sub>4</sub> O <sub>6</sub> (452.360)	63.72 (62.83)	2.67 (3.08)	12.38 (12.26)	(3.24)
5c	C <sub>25</sub> H <sub>14</sub> N <sub>4</sub> O <sub>6</sub> (466.387)	64.38 (67.40)	3.02 (3.61)	12.01 (12.56)	(2.37)
5d	C <sub>31</sub> H <sub>18</sub> N <sub>4</sub> O <sub>6</sub> (542.485)	68.64 (67.84)	3.34 (3.33)	10.32 (10.27)	(1.80)
5e	C <sub>32</sub> H <sub>20</sub> N <sub>4</sub> O <sub>6</sub> (550.512)	69.06 (68.14)	3.52 (3.60)	10.06 (10.26)	(2.04)
5f	C <sub>30</sub> H <sub>16</sub> N <sub>4</sub> O <sub>7</sub> (544.458)	66.18 (67.36)	2.96 (3.04)	10.20 (10.57)	(1.62)



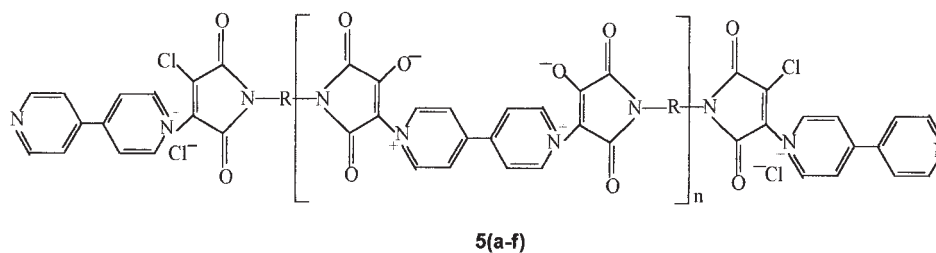
<b>R</b>	<b>2</b>	<b>3</b>
$-(\text{CH}_2)_6-$	a	a
	b	b
	c	c
	d	d
	e	e
	f	f

Scheme 4

aromatic diamines in dry acetone and cyclodehydrated *in situ* in the presence of acetic anhydride and triethylamine using anhydrous magnesium acetate as a catalyst, according to a method described in the

literature.<sup>24</sup> The properties of the obtained monomers are listed in Table I.

A typical procedure for the preparation of tetrachlorobis(maleimide) follows. To a solution of bis(maleimide)



Scheme 5

**2(a-f)** (0.05 mol) in 150 mL thionyl chloride cooled at 0°C in an ice bath, 17 mL (0.21 mol) of pyridine were dropped in over 30 min. The reaction mixture was stirred and maintained at 0°C for 2 h, at 20–25°C for 2 h, and at reflux for 1 h. The excess of thionyl chloride was removed in vacuum, and the solid residue was triturated with methanol, then filtered and recrystallized from adequate solvent.

#### Synthesis of model compound 4

To a solution of 2.56 g (10 mmol) of *N-p*-tolyl-3,4-dichloromaleimide and 1.4 mL (10 mmol) of triethylamine (TEA) in 50 mL glacial acetic acid, 0.781 g (5 mmol) of 4,4'-bipyridine was added, and the mixture was stirred at reflux for 6 h. The reaction mixture was cooled at room temperature, and the purple solid that resulted was filtered, then washed with 50 mL 3% Na<sub>2</sub>CO<sub>3</sub> solution and water and finally with acetone. The product was dried at 80°C for 12 h in a vacuum oven, resulting in 2.0 g (71% yield) product **4a**, mp = 460°C. The red solution obtained after filtration was poured into 200 mL water. The solid formed was filtered and washed with 30 mL 3% Na<sub>2</sub>CO<sub>3</sub> solution, then with water, and dried at 80°C for 12 h in a vacuum oven, resulting on 0.5 g of product **4b**, mp > 350°C.

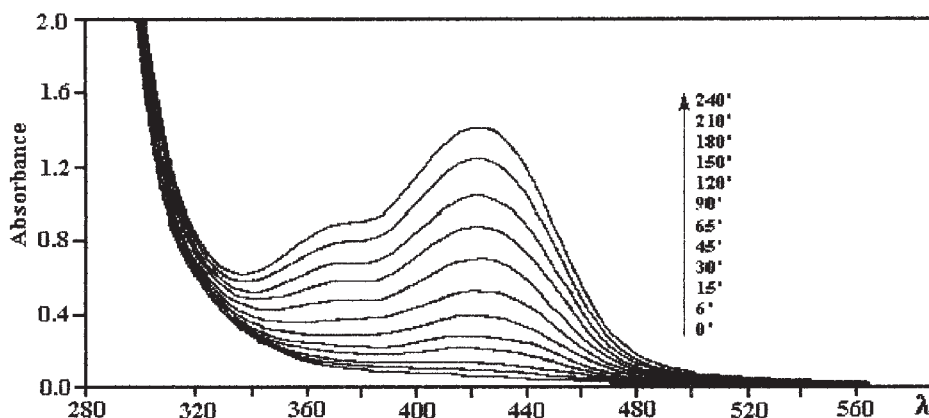
*Identification of compound 4a.* The IR spectrum of **4a** (KBr, cm<sup>-1</sup>): 3050 ( $\nu$ , = CH aromatic), 1770, 1700 ( $\nu$ , C = O symmetric and asymmetric), 1650 ( $\nu$ , quaternized -N<), 1610, 1500 ( $\nu$ , C = C aromatic), 1410, 1040 ( $\nu$ , C-N-C of imide ring and pyridine ring).

The <sup>1</sup>H-NMR spectrum (DMSO-d<sub>6</sub>, TMS),  $\delta$  (ppm): 9.73 (d, 4H aromatic proton *ortho* N<sup>+</sup>), 8.54 (d, 4H, J = 6.7 Hz, aromatic proton *meta* N<sup>+</sup>), 7.275 (d, 8H, J = 2.44 Hz, aromatic proton *p*-tolyl), 2.35 (s, 6H, CH<sub>3</sub>).

The UV-vis spectrum showed an absorption maximum at 500 nm in DMSO solution. The elemental analysis found (%): C, 69.05; H, 4.57; N, 10.13 corresponding to a molecular formula C<sub>32</sub>H<sub>24</sub>N<sub>4</sub>O<sub>6</sub> (560.544) and calculated (%), C, 68.57; H, 4.31; N, 9.98.

*Identification of compound 4b.* The IR spectrum of **4b** (KBr, cm<sup>-1</sup>) showed bands at: 3060 ( $\nu$ , = CH aromatic ring), 1740 ( $\nu$ , C = O asymmetric), 1645 ( $\nu$ , quaternized -N<), 1600, 1500 ( $\nu$ , C = C aromatic ring), 1415, 1040 ( $\nu$ , C-N-C of imide ring and pyridine ring), 890 ( $\nu$  -C-Cl maleimide ring).

The <sup>1</sup>H-NMR shift values (DMSO-d<sub>6</sub>, TMS),  $\delta$  (ppm): 9.73 (d, 2H, J = 6.7 Hz, aromatic protons *ortho* N<sup>+</sup>), 8.39 (d, 2H, J = 5.65 Hz, aromatic proton *meta* N pyridine), 8.54 (d, 2H, J = 6.7 Hz, aromatic proton *meta* N<sup>+</sup>), 8.03 (d, 2H, J = 5.65 Hz aromatic proton *ortho*



**Figure 1** The change in UV spectral characteristics during reaction of *N-p*-tolyl-3,4-dichloromaleimide with 4,4'-bipyridine in DMSO at  $2.5 \cdot 10^{-4}$  mol/L at room temperature.

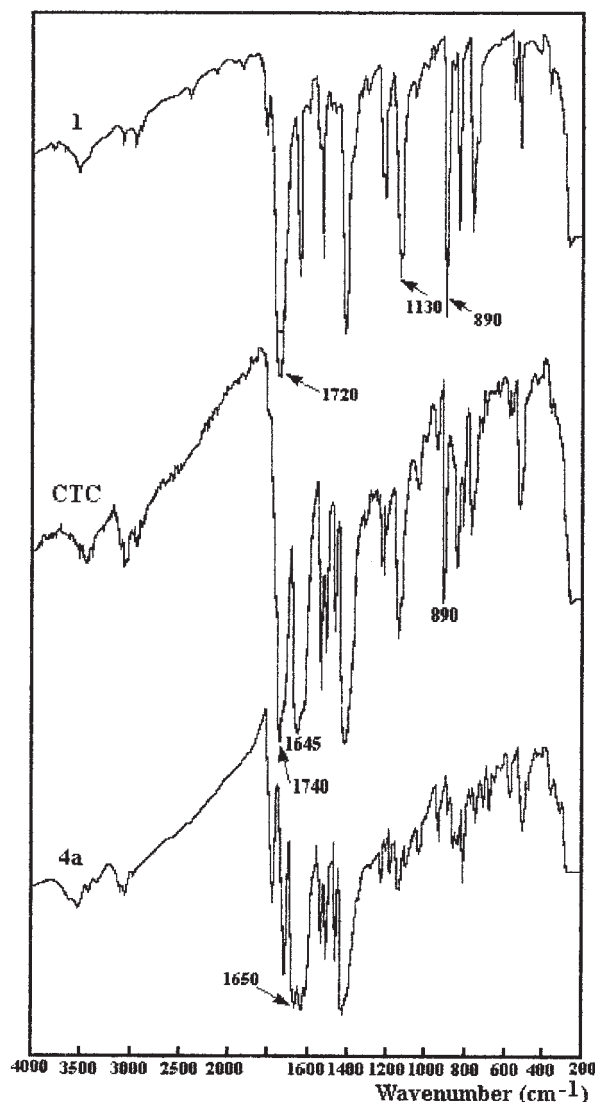


Figure 2 IR spectra of *N-p*-tolyl-3,4-dichloromaleimide (**1**) and model compound **4a**.

$\text{N}^+$ ), 7.275 (d, 4H,  $J = 2.44$  Hz, aromatic proton of *p*-tolyl), 2.35 (s, 3H,  $\text{CH}_3$ ).

The UV-vis spectrum showed absorption maxims at 370 and 430 nm.

Elemental analysis found (%), C, 61.38; H, 3.78; N, 9.78; Cl, 17.48 corresponding to a molecular formula  $\text{C}_{21}\text{H}_{15}\text{N}_3\text{O}_2\text{Cl}_2$  (412.257) and calculated analysis (%), C, 61.18; H, 3.66; N, 10.18; Cl, 17.19.

### Polymer synthesis

The reaction was run in *m*-cresol using equimolecular amounts of tetrachlorobismaleimide **3(a-g)** and 4,4'-bipyridine at 110–120°C for 10 h. The relative amounts of monomers and *m*-cresol were adjusted to maintain a solid content of 15% wt in the reaction mixture. A typical procedure for preparation of polymer was carried out as follows. A 100 mL three-necked flask, equipped with a mechanical stirrer, condenser, and thermometer was charged with a mixture of 2.092 g (5 mmol) of bis(dichloromaleimide) **3d**, 0.781 g (5 mmol) of 4,4'-bipyridine, and 1.4 mL of TEA in 20 mL *m*-cresol. The solution was stirred at room temperature for 15 min and then at 110–120°C for 10 h. The reaction mixture was cooled at room temperature and poured into 150 mL methanol. The resulting solid was extracted with hot methanol using a Soxhlet extractor for 6 h. The product was dried at 80°C for 10 h in a vacuum oven. The structures of polymers are presented in Scheme 3, and the properties are listed in Table II.

### RESULTS AND DISCUSSION

The *N-p*-tolyl maleimide (**1**) and the bismaleimide **2(b-f)** were prepared by the reaction of maleic anhydride with corresponding amine or diamine in two stage reaction according to the methods developed by Searle<sup>24</sup> (Scheme 4). The bismaleimide **2a** was pre-

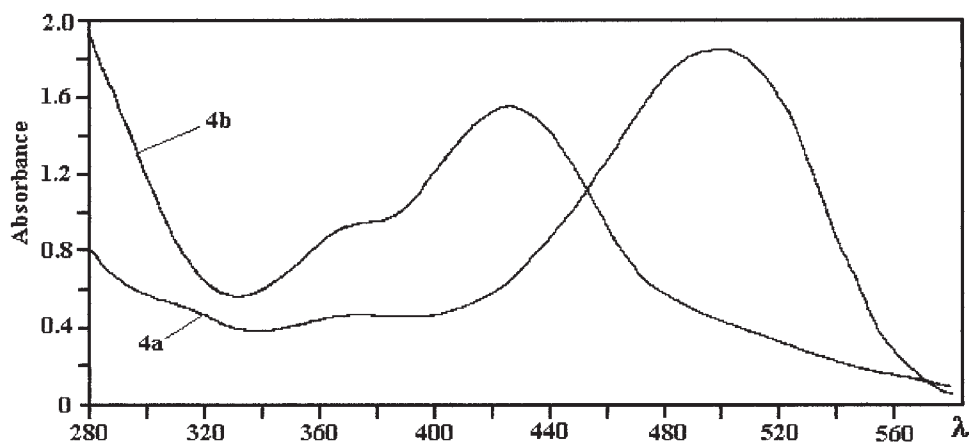


Figure 3 UV-vis absorption spectra of model compounds **4a** and **4b** in DMSO solution.



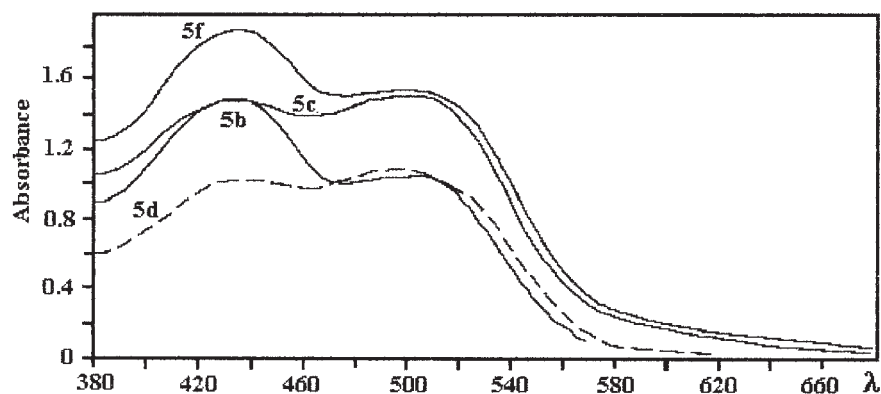


Figure 4 UV-vis absorption spectra of polymers 5(b-d) and 5f in DMSO solution.

pared directly from boiling acetic acid according to a method proposed by Gill et al.<sup>23</sup> The method of Relles<sup>21</sup> was used to prepare *N-p*-tolyl-3,4-dichloromaleimide and bis(dichloromaleimide)s 3(a-f) (Scheme 4).

The properties of the monomers 2(a-f) and 3(a-f) are presented in Table I. As can be seen, the melting points of the monomers showed good agreement between literature and experimental values. To facilitate the assignment of spectral data for polymers, a model compound 4a was prepared by reaction of *N-p*-tolyl-3,4-dichloromaleimide and 4,4'-bipyridine. Thus, by mixing of *N-p*-tolyl-3,4-dichloromaleimide with 4,4'-bipyridine in equimolar mixture in DMSO solution, a charge transfer complex obtained and the resulting bipyridine salts have maxim absorption bands at 370 and 420 nm (Fig. 1). Figure 1 shows a gradual increase of the absorption bands at 370 and 420 nm during the reaction. An analogue charge transfer complex has been reported.<sup>30</sup> Reaction of *N-p*-tolyl-3,4-dichloromaleimide with 4,4'-bipyridine in 2 : 1M ratio in glacial acetic acid in the presence of TEA at reflux resulted in a mixture of two compounds 4a and 4b (Scheme 2) in proportion of 71 and 29%, respectively. After spectral and elemental analysis identification, the product 4a corresponding to disubstituted bipyridine product and 4b corresponding to the monosubstituted bipyridine salt were found. The bipyridine salt is an intermediate product in the synthesis of bifunctional product 4a, according to a reaction mechanism proposed by Karten et al.<sup>13</sup>

The IR spectra of *N-p*-tolyl-3,4-dichloromaleimide and model compounds 4a and 4b are presented in Figure 2. The IR spectrum of bipyridine salt 4b in comparison with that of the compound resulting from the reaction of *N-p*-tolyl-3,4-dichloromaleimide with 4,4'-bipyridine in DMSO showed a decrease of the absorption band intensity of C-Cl at 890 cm<sup>-1</sup> and the appearance of absorption band for the quaternized pyridinium salt at 1640 cm<sup>-1</sup>. This confirmed that a chlorine atom is substituted with a viologen. Presence

of bipyridine in the structure of compound 4b is confirmed also by an increase of absorption band intensity at 1400–1385 cm<sup>-1</sup> attributed to C-N-C vibrations. The infrared spectra of model compound 4a showed the complete disappearance of the =C-Cl absorption peak from 810 cm<sup>-1</sup>.<sup>6</sup> Three consistent bands appeared at 1770, 1700, and 1650 cm<sup>-1</sup>. The bands at

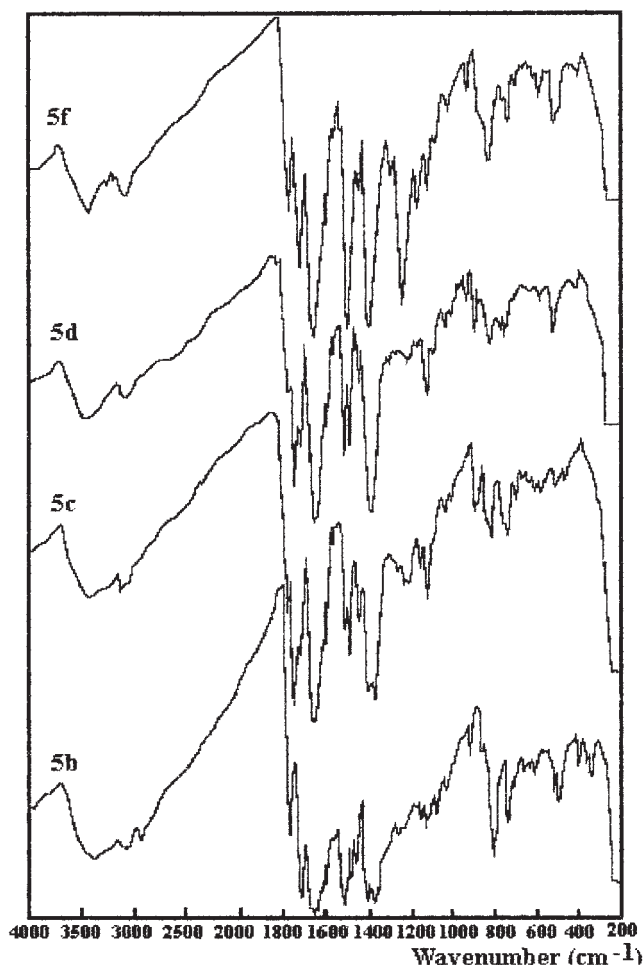


Figure 5 IR spectra of polymers 5(b-d) and 5f.

TABLE III  
The Properties of Polymers 5(a–f)

Polymer	Yield (%)	$\eta_{inh}^a$ dL/g	$M_w^b$	Solubility <sup>c</sup>			
				H <sub>2</sub> SO <sub>4</sub>	m-Cresol	DMF	DMSO
5a	67	0.18	~ 5300	S	S	PS	PS
5b	63	0.11	~ 4300	S	S	PS	PS
5c	69	0.13	~ 5900	S	S	PS	PS
5d	70	0.20	~ 7900	S	S	PS	PS
5e	68	0.18	~ 6900	S	S	PS	PS
5f	71	0.23	~ 8700	S	S	PS	PS

<sup>a</sup> Inherent viscosity measured in conc. H<sub>2</sub>SO<sub>4</sub> at the concentration of 0.5 g/dL at 30°C.

<sup>b</sup> Quantitative molecular weight values calculated from the chlorine end group content.

<sup>c</sup> Determined at a concentration 1% (w/v); S-soluble, PS-partially soluble.

1770 and 1700 cm<sup>-1</sup> were sharp, of medium to strong intensity, and the band at 1650 cm<sup>-1</sup> was broad and stronger. Previously it has been observed that the products obtained by nucleophilic substitution of dichloromaleimide with aromatic tertiary amines<sup>13</sup> presented the same absorption bands in the infrared spectrum.

The UV-vis spectra of model compounds **4a** and **4b** in DMSO solution (Fig. 3) showed two absorption maxims at 370 and 430 nm for the compound **4b** and an absorption maximum at 500 nm for the disubstituted compound **4a**.

The polymers were prepared by the reaction of bis-(dichloromaleimide)s **3(a–f)** with 4,4'-bipyridine in *m*-cresol resulting in 63–71% yield.

The structures of polymers **5(a–f)** are presented in Scheme 3. The elemental analysis (H, N%) of the polymers is in good agreement with the calculated values (Table II). The content of chlorine in all the polymers and the difference between calculated and found values for %C shows the presence of the monosubstituted bipyridinium units as end groups. The new structures of polymers were presented in Scheme 5.

These structures of the polyimides are supported by the UV spectra (Fig. 4) that presented two absorption band maxims at 430 and 510 nm.

The IR spectra of polymers **5(b–d)** and **5f** (Fig. 5) show good agreement with the IR spectrum of model

compound **4a**. The examination of IR spectra of all polymers **5(a–f)** reveals that all spectra contain prominent characteristic bands: the betaine structures<sup>13</sup> at 1770, 1700, and 1650 cm<sup>-1</sup>, the vibration of C–N–C imide ring at 1385–1400 cm<sup>-1</sup>, and distinct aromatic bands in the regions 3080–3000, 1510–1500, and 1200–800 cm<sup>-1</sup>. In addition, the IR spectrum of polymer **5f** showed an absorption band at 1270 cm<sup>-1</sup> attributed to the vibration of C–O–C from diphenylether structure. The properties of the polymers **5(a–f)** are presented in Table III. The inherent viscosities of the polymers **5(a–f)** measured in conc. H<sub>2</sub>SO<sub>4</sub> ranged between 0.11 and 0.23 dL/g. On the basis of proposed structures of the polymers (Scheme 5) and the chlorine analysis data, we calculated the corresponding molecular weight. All obtained polymers **5(a–f)** are soluble in sulfuric acid (Table III) at room temperature and *m*-cresol after heating at 100°C for 12 h and partially soluble in dipolar aprotic solvents.

The thermal behavior of the polymers **5(a–f)** was evaluated by DSC and TGA measurements (Table IV). The polymers did not soften below 350°C, and our attempts to identify a glass transition by DSC failed, proving that all the polymers are rigid enough, having  $T_g$  higher than the decomposition temperature.

The TGA traces of polymers show similar decomposition patterns, and the polymer samples exhibited weight loss below 4% at 340°C, due probably to the

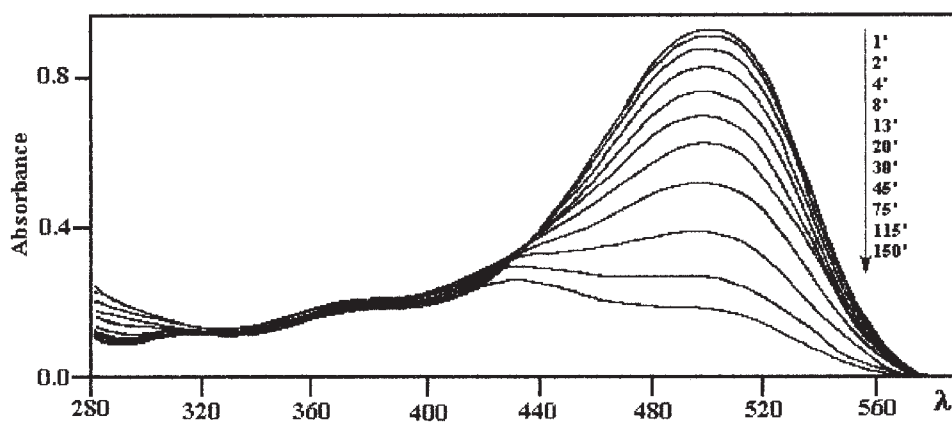
TABLE IV  
The Thermal Properties of the Polymers 5(a–f)

Polymer	IDT <sup>a</sup> (°C)	Temperature (°C) for % weight loss				Y <sub>c</sub> <sup>b</sup> (%)	Softening range (°C)
		5	10	20	30		
5a	298	320	342	389	423	35	>350
5b	330	365	382	418	460	41	>350
5c	325	342	367	400	430	38	>350
5d	328	348	370	415	450	40	>350
5e	315	335	355	395	425	39	>350
5f	335	362	375	425	470	37	>350

<sup>a</sup> Initial decomposition temperature.

<sup>b</sup> Char yield at 600°C.





**Figure 6** The change in UV-vis spectral characteristics during UV irradiation of model compound **4a** at differential interval of times.

elimination of residual solvent and chlorine content. The polyimides with aromatic structure and containing bipyridinium units **5(b–f)** begin to decompose at 315–335°C. Polyimide **5a** having aliphatic structure begins to decompose at 298°C.

Considering the temperature corresponding to 10% weight loss ( $T_{10}$ ) as a criterion of thermal stability, the following order may be given for the thermal stability of polymers:



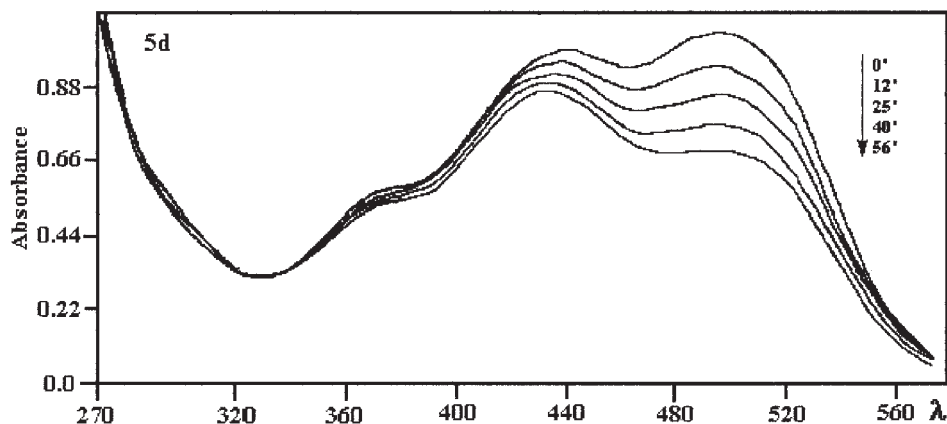
The  $T_{10}$  value of the polyimide **5a** containing alkyl linkages was lower compared with those of the polymer containing aromatic structures.

The photochemical behavior of the model compounds **4a** and **4b** and polymers **5(a–f)** was studied in DMSO solution by means of UV-vis absorption spectroscopy. The electronic absorption spectra of the compounds containing bipyridine units are characterized by absorption bands at 420 and 500 and a shoulder peak at 365 nm (Figs. 3 and 4). The absorption bands

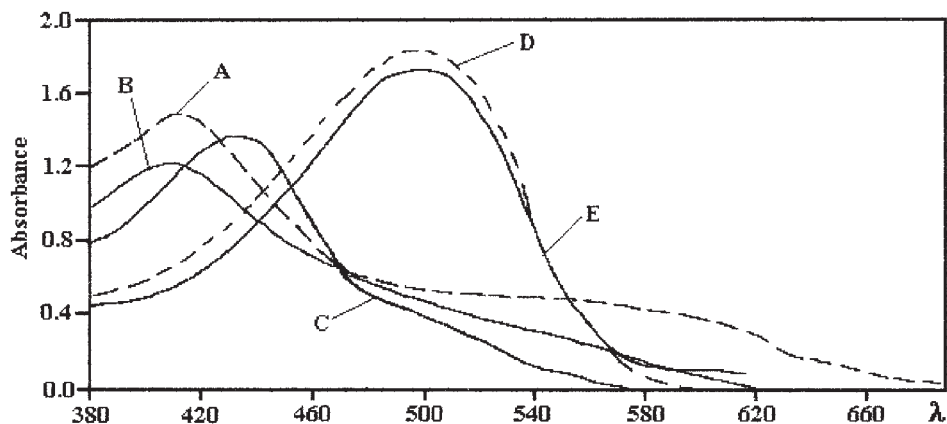
at 365 and 420 nm were assigned to the bipyridine salt obtained by mixing of *N-p*-tolyl-3,4-dichloromaleimide with 4,4'-bipyridine in DMSO solution at room temperature (Fig. 1).

The photochromic behavior of model compound **4a** and polymer **5d** by irradiation with a high-pressure mercury lamp was studied. Upon UV irradiation the intensity band at 500 nm decreased, and the compound **4a** solution turned to red along with keeping constant the peaks at 365 and 420 nm (Fig. 6). By UV irradiation of polymer **5d** in DMSO solution, both absorption bands at 420 and 500 nm decreased (Fig. 7).

The influence of pH on the visible absorption spectrum of model compound **4a** is presented in Figure 8. The position of absorption band of compound **4a** is not apparently influenced in acid solution (Fig. 8, curve D). In alkaline medium, on the other hand, the solution acquires a bluish to bluish-green color but this color disappears, probably, due to the decomposition of the imidic ring (Fig. 8).



**Figure 7** The change in the electronic absorption spectra during UV irradiation of polymer **5d**.



**Figure 8** Absorption spectra of protonated forms (E, D) and neoprotonated (A, B) of the model compound **4a** and model compound **4b**.

The X-ray diffraction study indicates that the polymers are amorphous.

### CONCLUSION

In this paper we reported the synthesis of novel polymers derived from tetrachlorobismaleimide and 4,4'-bipyridine by the polycondensation reaction. Due to their rigid structure, the polymers are soluble only in sulfuric acid at room temperature and partially soluble in dipolar aprotic solvents.

### References

- Relles, H. M.; Shluenz, R. W. *J Polym Sci Chem Ed* 1973, 11, 561.
- Edge, S.; Charlton, A.; Varma, K. S.; Underhill, A. E.; Hansen, T. K.; Becher, J.; Kathirgamanathan, P.; Khossari, E. J. *Polym Sci, Part A: Polym Chem* 1992, 32, 2773.
- Sava, M.; Chiriac, C.; Gaina, C.; Stoleriu, A.; Gaina, V. *J Macromol Sci -Pure Appl Chem* 1997, A34, 725.
- Kondo, H.; Sato, M.; Yokoyama, M. *Eur Polym Mater* 1980, 16, 537.
- Varma, J. K.; Fohlev, G. M.; Parker, J. A. *Polym Prepr* 1981, 22, 22.
- Srinivasan, P. R.; Mohadevan, V.; Srinivasan, M. *Eur Polym Mater* 1988, 24, 235.
- Ng, P. K.; Wong, C. T.; Han, S.; Chan, W. K. *Polym Prepr* 1994, 40, 1212.
- Simon, M.S.; Moore, P. T. *J Polym Sci Polym Chem Ed* 1975, 13, 1.
- Kamagawa, H.; Amemiya, S. *J Polym Sci: Polym Chem Ed* 1985, 23, 2413.
- Hashimoto, T.; Kohjaya, S.; Yamashita, S.; Irie, M. *J Polym Sci: Part A: Polym Chem* 1991, 29, 651.
- Sato, H.; Tamamura, T. *J Appl Polym Sci* 1979, 24, 1075.
- Moore, J. S.; Stupp, S. I. *Macromolecular* 1986, 19, 1815.
- Karten, M. J.; Shapiro, S. L.; Isaacs, E. S.; Freedman, L. *J Org Chem* 1965, 30, 2657.
- Koch, A. S.; Harbison, W. G.; Hubbord, J. M.; Kort, M.; Rol, B. A. *J Org Chem* 1996, 61, 5959.
- Gaina, C.; Gaina, V.; Stoleriu, A.; Chiriac, C.; Cozan, V.; Sava, M. *J Macromol Sci-Pure Appl Chem* 1996, A33, 1755.
- Gaina, C.; Gaina, V.; Sava, M. *J Macromol Sci-Pure Appl Chem* 1997, A34, 2525.
- Gaina, C.; Gaina, V.; Stoleriu, A.; Sava, M.; Chiriac, C. *Designed Monomers and Polymers* 1998, 1, 315.
- Gaina, C.; Gaina, V.; Sava, M. *High Perform Polym* 2001, 13, 269.
- Gaina, C.; Gaina, V.; Sava, M.; Chiriac, C. *High Perform Polym* 1999, 11, 185.
- Gaina, C.; Gaina, V.; Ivanov, D. *Macromol Rapid Commun* 2001, 22, 25.
- Relles, H. M. *J Org Chem* 1972, 37, 3630.
- Relles, H. M.; Schluentz, R. W. *J Org Chem* 1972, 37, 1743.
- Bryon Gill, G.; James, G. D.; Oates, K. V.; Pattenden, G. *J Chem Soc Perkin Trans 1* 1993, 2567.
- Searle, N. E. U.S. Patent 244,536, 1948; *ChemAbstr* 1948, 42, 7340.
- Cotter, R. J.; Sauers, C. K.; Whelan, J. M. *J Org Chem* 1961, 26, 10.
- Crivello, J. V. *J Polym Sci Polym Chem Ed* 1973, 11, 1185.
- Nanjan, M. J.; Sivaraj, K. *J Polym Sci: Part A Polym Chem* 1989, 27, 375.
- Tasaro, G. C.; Pendharker, S. M. *Polym Adv Technol* 1994, 5, 521.
- Boeus, N.; Schryver, F. C.; Smets, G. *J Polym Sci: Polym Chem Ed* 1975, 13, 201.
- Farcasiu, M.; Instratoiu, M. *Rev Roum Chim* 1970, 15, 253.