



## NEW POLYMERS WITH ALKYLIDENESUCCINIMIDE STRUCTURES BASED ON BISMALIMIDES AND BISCITRACONIMIDES

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New polymers containing alkylidenesuccinimide structures prepared from phosphorous ylides of bismaleimides or biscitraconimides and aromatic dialdehydes by the Wittig reaction, are reported for the first time in the literature. Phosphorous ylides of bismaleimides or biscitraconimides were synthesized *in situ* by the reaction of bismaleimide or biscitraconimide or AB monomers containing both maleimide and aldehyde or citraconimide and aldehyde groups with triphenylphosphine in *meta*-cresol or acetic acid. The structures of monomers and polymers were confirmed by FTIR, <sup>1</sup>H-NMR and UV-visible spectroscopy and elemental analysis. The thermal behaviour of polymers was studied by thermogravimetric analysis and differential calorimetric measurements.

### INTRODUCTION

Bismaleimides can be used as versatile monomers in polymer synthesis by polymerization, Michael polyaddition or cycloaddition reactions.<sup>1-3</sup> Their resins are attractive for composites because the maleimide moieties have unsaturated end-groups that undergo thermal addition polymerization without by-product elimination that can lead to the formation of voids within the composite. The most desirable properties include high tensile strength and modulus, excellent chemical and corrosion resistance, good thermal stability and performance at elevated temperatures. Crosslinked and/or linear polymers can be obtained from bismaleimides by thermal curing, conjugate addition, polymerization with diamines, bisphenols or bistiols, curing reactions with diallyl phenols monomers or cycloaddition reactions.<sup>4-5</sup> The preparation and the reactions of stable phosphorous ylides derived from maleimides or citraconimides<sup>6-12</sup> have received some attention, although they are not often used in the synthesis of new important polymers.

We have already reported on the synthesis of polymers by the polyaddition reaction between bismaleimides or biscitraconimides and diamines

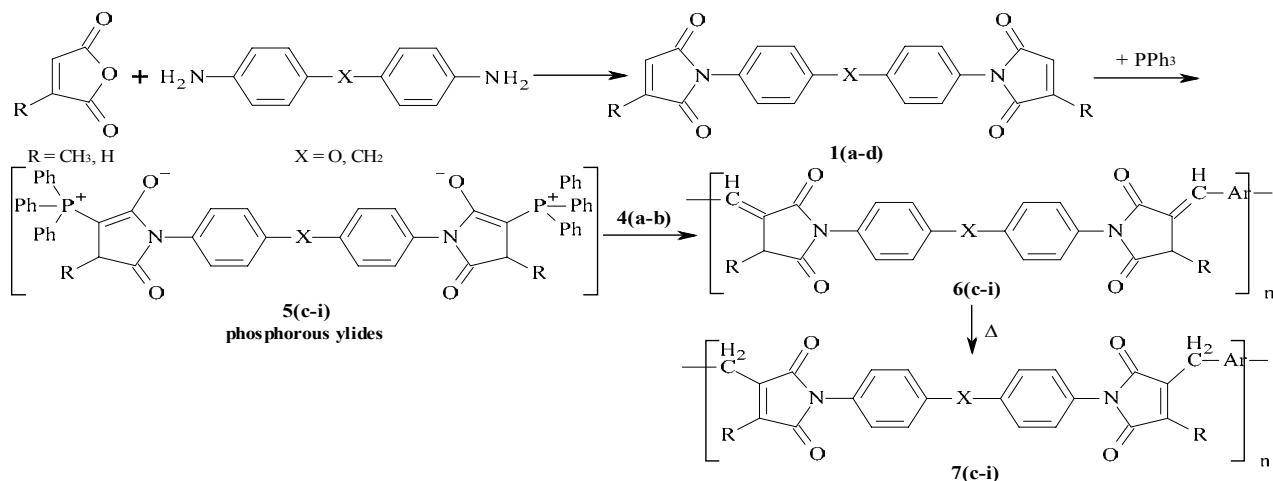
or bistiols<sup>13-17</sup> or by cycloaddition reaction.<sup>17-21</sup> Recently, we reported on the synthesis of polyimides containing 3,3'-bipyrrrolidine-2,2',5,5'-tetrone units by ring-coupling reaction of  $\alpha,\alpha'$ -bis(chlorosuccinimide)s.<sup>22</sup> The present work describes a new reaction for the synthesis of polymers based on bismaleimides or biscitraconimides and dialdehydes in the presence of triphenylphosphine (the Wittig reactions) and their properties are investigated.

### RESULTS AND DISCUSSION

The bismaleimides and biscitraconimides **1(a-d)** were prepared according to the method described in the literature and their synthesis is illustrated in Scheme 1.<sup>20</sup>

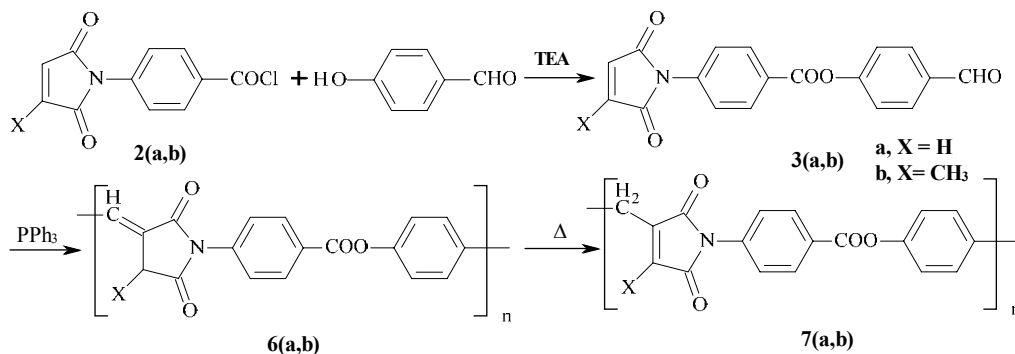
The monomers AB containing both maleimide and aldehyde groups **3(a,b)** were obtained by the condensation reaction of 4-maleimido-or 4-citraconimidobenzoic acid chloride **2(a,b)** with 4-hydroxybenzaldehyde (Scheme 2). Dialdehyde **4b** was prepared according to a method described in the literature (Scheme 3).<sup>24</sup> The structure of these monomers was confirmed by FTIR and <sup>1</sup>H-NMR spectroscopy and elemental analysis.

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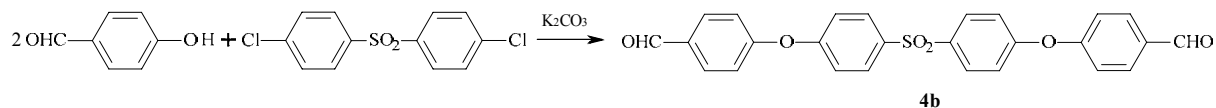


R	X	1	Ar	5-6
H	CH <sub>2</sub>	a		c
CH <sub>3</sub>	CH <sub>2</sub>	b	idem	d
H	O	c	idem	e
CH <sub>3</sub>	O	d	idem	f
H	CH <sub>2</sub>	a		g
CH <sub>3</sub>	CH <sub>2</sub>	b	idem	h
H	O	c	idem	i

Scheme 1



Scheme 2



Scheme 3

The polymers having alkylidensuccinimide structures were prepared by two ways: (i) by the Wittig reaction of bismaleimides or citraconimides **1(a-d)** with dialdehyde **4(a,b)** in the presence of triphenylphosphine (Scheme 1); (ii) by the Wittig reaction of monomers AB **3(a,b)** with

triphenylphosphine (Scheme 2). The structure of polymers **6(a-i)** was confirmed by the FTIR and <sup>1</sup>H-NMR spectroscopy and elemental analysis (Table 1 and 2). Elemental analysis data are in good agreement with the calculated values (Table 3).

The FTIR spectrum of the ylidic derivative **5c** (Figure 1) shows the disappearance of the absorption bands at  $3101\text{ cm}^{-1}$  attributed to  $\nu_{\text{CH}}$  of maleimide, at  $1150\text{ cm}^{-1}$  corresponding to  $\nu_{\text{C-N-C}}$  and at  $830\text{ cm}^{-1}$ , and the appearance of a new absorption band at  $1107\text{ cm}^{-1}$ , and increase of the absorption band intensity at  $1178\text{ cm}^{-1}$ . By reaction

of the ylide derivative **5c** with dialdehyde, the polymer **6c** is obtained. The spectrum of this polymer shows a decrease of the absorption bands intensity corresponding to  $\nu_{\text{C=O}}$  of ylide and their shifting from  $1641\text{ cm}^{-1}$  to  $1655\text{ cm}^{-1}$ , and the absorption bands attributed to  $\nu_{\text{C-N-C}}$  were shifted to  $1380\text{ cm}^{-1}$  and  $1171\text{ cm}^{-1}$ .

Table 1

The FTIR data of polymers **6(a-i)** (wavenumbers,  $\text{cm}^{-1}$ )

Sample	Imide structure	Olefinic bond	Aromatic ring	Other structures
<b>6a</b>	1775, 1710, 1393, 1193, 693	1609	1608, 1513, 817	1269 (C-O-C of ester)
<b>6b</b>	1780, 1716, 1386, 1166, 688	1650*	1592, 1507	2973, 2932, 1446 (C-CH <sub>3</sub> ), 1266 (C-O-C of ester)
<b>6c</b>	1770, 1710, 1380, 1170, 692	1655	1602, 1512, 820	
<b>6d</b>	1771, 1711, 1387, 1169, 688	1653	1598, 1503, 819	2930 (C-CH <sub>3</sub> )
<b>6e</b>	1771, 1711, 1384, 1168	1654	1604, 1501, 831	1241 (Ph-O-Ph)
<b>6f</b>	1773, 1707, 1394, 1166, 692	1650*	1604, 1501, 829	2921 (C-CH <sub>3</sub> ), 1241 (Ph-O-Ph)
<b>6g</b>	1770, 1711, 1381, 1160	1653	1588, 1488	1323, 1160 (SO <sub>2</sub> ), 1242 (Ph-O-Ph)
<b>6h</b>	1778, 1711, 1384, 1169	1652	1586, 1513	1323, 1158 (SO <sub>2</sub> ), 1243 (Ph-O-Ph), 2930 (C-CH <sub>3</sub> )
<b>6i</b>	1770, 1711, 1388, 1165, 691	1655	1586, 1501, 832	1321, 1158 (SO <sub>2</sub> ), 1241 (Ph-O-Ph)

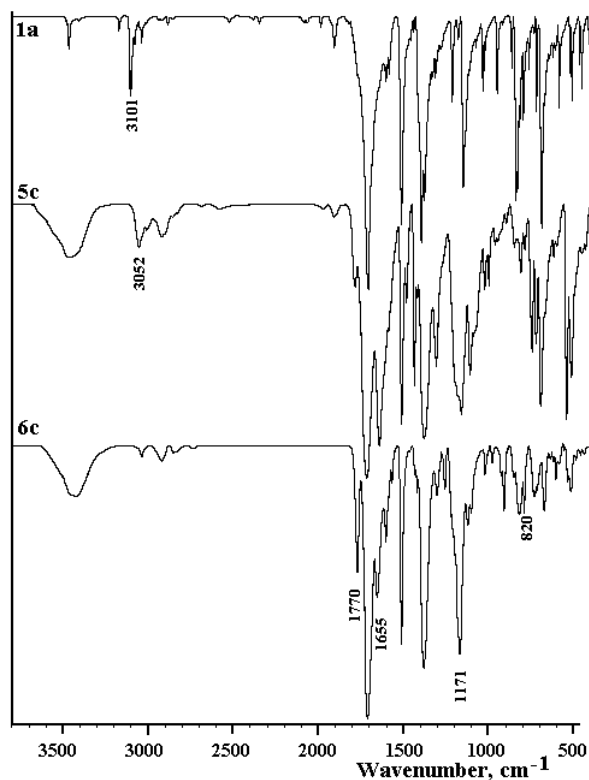
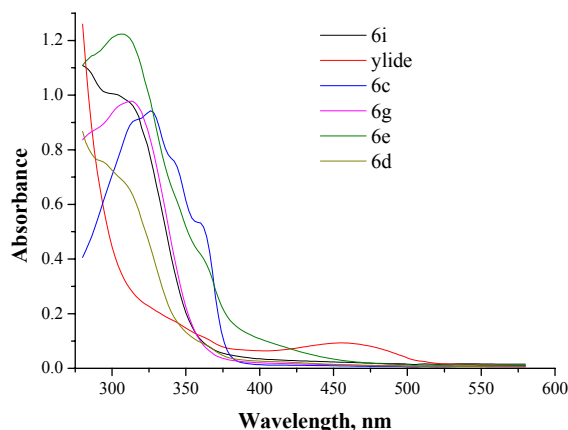
\*overlaps on the absorption band at  $1710\text{ cm}^{-1}$ Fig. 1 – The FTIR spectra of the compounds **1a**, **5a** and **6a**.Fig. 2 – The UV-vis spectra of polymers **6(c-i)**.

Table 2

The <sup>1</sup>H-NMR data of polymers **6(a-i)**

Sample	The <sup>1</sup> H-NMR chemical shifts (δ, ppm) and assignments
<b>6a</b>	8.25 (d, 2H, aromatic protons), 7.82 (d, 2H, aromatic protons), 7.58 (d, 2H, -CH=), 7.48 (d, 2H, aromatic protons), 7.52 (d, 2H, aromatic protons), 3.56 (s, 2H, CH <sub>2</sub> of succinimide ring)
<b>6b</b>	8.27 (d, 2H, aromatic protons), 7.84 (d, 2H, aromatic protons), 7.67 (d, 2H, -CH=), 7.55 (d, 2H, aromatic protons), 7.46 (d, 2H, aromatic protons), 3.78 (m, 2H, CH of succinimide ring)
<b>6c</b>	7.81 (s, 4H, aromatic protons), 7.64 (d, 2H, -CH=), 7.43 (d, 4H, aromatic protons), 7.32 (d, 4H, aromatic protons), 4.17 (s, 2H, -CH <sub>2</sub> -), 3.93 (s, 2H, CH <sub>2</sub> of succinimide ring)
<b>6d</b>	7.83 (s, 4H, aromatic protons), 7.67 (d, 2H, -CH=), 7.52 (d, 4H, aromatic protons), 7.29 (d, 4H, aromatic protons), 4.00 (s, 2H, -CH <sub>2</sub> -), 3.86 (m, 2H, CH of succinimide ring), 2.06 (d, 6H, CH <sub>3</sub> of succinimide ring)
<b>6e</b>	7.88 (dd, 4H, aromatic protons), 7.78 (d, 2H, -CH=), 7.64 (d, 4H, aromatic protons), 7.35 (d, 4H, aromatic protons), 3.57 (m, 4H, CH <sub>2</sub> of succinimide ring)
<b>6f</b>	7.87 (dd, 4H, aromatic protons), 7.69 (d, 2H, -CH=), 7.58 (d, 4H, aromatic protons), 7.36 (d, 4H, aromatic protons), 3.78 (m, 4H, CH of succinimide ring), 2.12 (d, 6H, CH <sub>3</sub> of succinimide ring)
<b>6g</b>	7.98 (m, 4H, aromatic protons), 7.78 (d, 2H, -CH=), 7.60 (m, 2H, aromatic protons), 7.42 (dd, 4H, aromatic protons), 7.30 (dd, 4H, aromatic protons), 7.22 (m, 10H, aromatic protons), 4.00 (s, 2H, CH <sub>2</sub> ), 3.85 (d, 2H, CH of succinimide ring)
<b>6h</b>	7.96 (m, 4H, aromatic protons), 7.70 (d, 2H, -CH=), 7.20-7.35 (m, 20H, aromatic protons), 4.03 (s, 2H, CH <sub>2</sub> ), 3.18 (m, 2H, CH of succinimide ring), 2.19 (d, 6H, CH <sub>3</sub> of succinimide ring)
<b>6i</b>	7.98 (m, 4H, aromatic protons), 7.79 (m, 4H, aromatic protons), 7.61 (d, 2H, -CH=), 7.42 (m, 4H, aromatic protons), 7.19-7.33 (m, 12H, aromatic protons), 3.85 (s, 2H, succinimide ring)

Table 3

The properties of polymers **6(a-i)**

Sample	$\eta_{inh}$ (dL/g)	Elemental analysis						$T_g^a$ (°C)	IDT <sup>b</sup> (°C)	$T_{5\%}^c$ (°C)	$T_{10\%}^c$ (°C)	$T_{20\%}^c$ (°C)	$Y_c^{700}^d$ (%)
		C %		H %		N %							
		Calcd	Found	Calcd	Found	Calcd	Found						
<b>6a</b>	0.230	70.82	71.03	3.63	3.72	4.59	4.37	193	407	445	460	515	18
<b>6b</b>	0.187	71.45	71.27	4.10	3.97	4.38	4.27	187	398	430	450	490	16
<b>6c</b>	0.305	75.64	76.03	4.38	4.54	6.08	5.73	185	412	450	475	545	55
<b>6d</b>	0.133	76.22	76.83	4.95	5.07	5.73	5.37	175	385	408	435	497	33
<b>6e</b>	0.140	72.72	73.08	3.92	4.27	6.05	5.67	221	380	397	430	493	37
<b>6f</b>	0.213	73.46	74.00	4.52	4.87	5.71	5.17	209	370	395	428	487	32
<b>6g</b>	0.221	71.92	72.43	4.11	4.59	3.57	3.03	188	405	413	446	486	40
<b>6h</b>	0.170	72.58	72.98	4.23	4.71	3.45	2.97	193	425	435	460	495	38
<b>6i</b>	0.120	70.22	70.87	3.84	4.37	3.56	3.07	135	360	565	370	413	17

<sup>a</sup> The glass transition temperatures by DSC measurements for polymers **7(a-i)**; <sup>b</sup> Initial decomposition temperature; <sup>c</sup> Temperature for 5, 10 and 20 % weight loss; <sup>d</sup> Char yield at 700°C.

The <sup>1</sup>H-NMR spectrum of the polymer shows the disappearance of the signals due to the maleimide protons at 7.20 ppm and the appearance of the chemical shifts ascribed to the succinimide protons at 3.92 ppm and 7.65 ppm attributed to the benzylidene proton, respectively.

The UV-vis spectra of polymers performed in DMSO are presented in Figure 2. From this figure is observed the disappearance of absorption band maximum at 456 nm corresponding to the ylide and the appearance of new absorption bands in the range 300 and 335 nm attributed to the benzylidene group.

Viscosities of polymers ranged between 0.120 and 0.305 dL/g. All polymers were soluble in dipolar aprotic solvents. Thermal behaviour of

polymers **6(a-i)** was investigated using the DSC and TGA measurements and the thermal data obtained by processing TGA and DSC curves are presented in Table 3. The thermogravimetric curves of the copolymers presented a single stage of decomposition in the range 360-425°C and the temperature for 10% weight loss varied between 370 and 475°C. The residue left after heating at 700°C in air of the polymers **6(a-i)** ranged between 16 and 55%. The polymers **6(a-b)** have the lowest value of the residue due to the ester bonds. By heating of polymers **6(a-i)** over 200°C, polymers **7(a-i)** are obtained (Scheme 1 and 2).<sup>25-26</sup> The DSC curve for polymer **6d** at the first and second heating is illustrated in Figure 3.

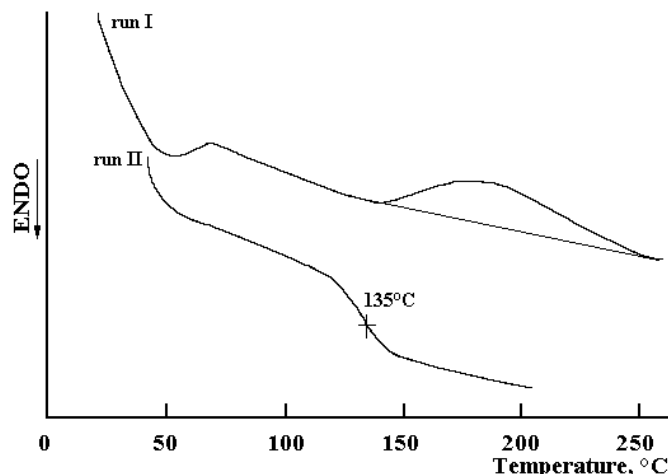


Fig. 3 – The DSC scan of polymer **6d** at the first and second heating run.

As can be seen, the DSC curve at the first heating cycle presents a broad exothermic peak in the range 135–245°C attributed to the rearrangement of alkylidenesuccinimides to alkylmaleimides. The glass transition temperature of polymers **7(a-i)**, determined by DSC measurements of polymers **6(a-i)** during the second heating cycle, varied in the range 135–221°C.

## EXPERIMENTAL

**Measurements.** The FTIR spectra were recorded on a Bruker Vertex 70 spectrophotometer. The <sup>1</sup>H-NMR spectra were recorded on a Bruker NMR spectrometer, Avance DRX 400 MHz, using DMSO-*d*<sub>6</sub> as solvents and tetramethylsilane as an internal standard. Melting and softening points were determined with a Gallenkamp hot-block point apparatus. Thermogravimetric analysis (TGA) was carried out in air with a F. Paulik Derivatograph at a heating rate of 10°C/min. Differential scanning calorimetry (DSC) measurements were done using a Mettler TA Instrument DSC 12E with a heating rate of 10°C/min, in nitrogen. The inherent viscosities of the polymer solutions (measured at a concentration of 0.5 g/dl) in NMP were determined at 25°C using an Ubbelohde suspended level viscometer.

**Reagents and Materials.** Maleic anhydride (Aldrich), citraconic anhydride (Aldrich), 4-aminobenzoic acid (Aldrich), 4,4'-methylenedianiline (Aldrich), 4,4'-oxydianiline (Aldrich), 4-hydroxybenzaldehyde (Aldrich), 4,4'-terephthalaldehyde (**4a**) (Aldrich), acetone, acetic anhydride and triphenylphosphine were used as received. Thionyl chloride and *m*-cresol were freshly distilled before use. Monomers **1(a-d)** were prepared following the literature<sup>17,23</sup> via the reaction of maleic or citraconic anhydride with the corresponding diamines, in dry acetone, followed by cyclodehydration *in situ* in the presence of acetic anhydride and triethylamine using anhydrous magnesium acetate as catalyst. 4-Maleimido- and 4-citraconimidobenzoic acid chloride **2(a,b)** were prepared according to our previous paper.<sup>20</sup>

**Synthesis of monomers 3(a-b).** The monomers **3(a-b)** were prepared by the condensation reaction of 4-maleimidobenzoic acid chloride or 4-citraconimidobenzoic acid chloride with

4-hydroxybenzaldehyde. The detailed procedures are presented below. To a solution of 4-hydroxybenzaldehyde (1.22 g, 0.01 mol) in dry acetone (80 ml) at 0–5°C, triethylamine (1.4 ml) and 4-maleimidobenzoic acid chloride (2.36 g, 0.01 mol) were added. The reaction mixture was stirred for 3 hours at room temperature and the resulting white solid was filtered, washed with acetone and dried for 10 hours at 60°C in vacuum.

***N*-(4-formyl phenoxy-carbonylphenyl)maleimide 3a** was recrystallized from dioxane, yield 92%, mp=224–227°C. FTIR (KBr, cm<sup>-1</sup>): 3100 (ν<sub>CH</sub>), 1723, 1390, 1160, and 695 (imide I-IV), 1750, 1608, 1520, 1270, 840. <sup>1</sup>H-NMR (DMSO-*d*<sub>6</sub>), δ (ppm): 7.20 (s, 2H, -CH=CH-), 7.62 (d, 2H, aromatic protons), 7.71 (d, 2H, aromatic protons), 8.15 (d, 2H, aromatic protons), 8.37 (d, 2H, aromatic protons), and 10.30 (s, 1H, CHO).

***N*-(4-formyl phenoxy-carbonylphenyl)citraconimide 3b** was obtained in 87% yield. Elemental analysis calcd. for C<sub>19</sub>H<sub>13</sub>NO<sub>5</sub> (335.31): C, 68.08; H, 3.91; N, 4.18. Found: C, 68.31; H, 3.82; N, 4.31 %. FTIR (KBr, cm<sup>-1</sup>): 3100 (ν<sub>CH</sub>), 1723, 1390, 1160, and 698 (imide I-IV), 1700, 1650, 1515, 1270, 840. <sup>1</sup>H-NMR (DMSO-*d*<sub>6</sub>), δ (ppm): 2.12 (s, 3H, CH<sub>3</sub>), 6.57 (s, 1H, CH), 7.52 (d, 2H, *J*=8.4 Hz, aromatic protons), 7.82 (d, 2H, *J*=8.8 Hz, aromatic protons), 8.02 (d, 2H, *J*=8.8 Hz, aromatic protons), 8.10 (d, 2H, *J*=8.4 Hz, aromatic protons), and 10.30 (s, 1H, CHO).

**4,4'-[sulphonylbis-(4,1-phenyleneoxy)]dibenzaldehyde 4b** was prepared by the reaction of 4,4'-dichlorodiphenylsulfone with *p*-hydroxybenzaldehyde in the presence of anhydrous potassium carbonate according to the method described in the literature.<sup>24</sup>

Elemental analysis calcd. for C<sub>28</sub>H<sub>18</sub>SO<sub>6</sub> (458.48): C, 68.11; H, 3.96; S, 6.99. Found: C, 68.27; H, 4.01; S, 6.73 %. FTIR (KBr, cm<sup>-1</sup>): 1700 (CHO), 1330, 1165 (SO<sub>2</sub> vibrations), 1250 (ether), 1025, 840 (aromatic ring). <sup>1</sup>H-NMR (DMSO-*d*<sub>6</sub>), δ (ppm): 6.89–7.28 (m, 8H, *ortho* to -O-), 7.84–8.04 (m, 4H, *ortho* to SO<sub>2</sub>, and 4H, *ortho* to CH=O), 10.13 (s, 2H, -CHO).

**Polymer synthesis.** A 100 mL three-necked flask, equipped with mechanical stirrer, dry nitrogen inlet and reflux condenser, was charged with monomer **1b** (0.77 g, 2 mmol), *m*-cresol (20 mL) and triphenylphosphine (1.1 g, 4.2 mmol) and stirred at 80°C/1 hour, then the compound **4b** (0.917 g, 2 mmol) was added. The reaction mixture was heated at 100–110°C/10 hours. The polymer was poured into 70 mL methanol, filtered, washed with methanol and then extracted

with ethylic ether for 6 hours using a Soxhlet extractor. The product was dried at 60°C for 6 hours in a vacuum oven. The same synthesis was used to prepare all polymers.

## CONCLUSIONS

New polymers having alkylidenesuccinimide groups are reported for the first time in the literature, which were prepared by the Wittig reaction of phosphorous ylides with dialdehyde. The polymers have the thermal stability in the range 370 and 475°C and are soluble in dipolar aprotic solvents.

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