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### New Poly(4-Chloro)Maleimides. I. Synthesis and Characterization of Poly[Ether-Ester-(4-Chloro)Maleimides]

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# NEW POLY(4-CHLORO)MALEIMIDES. I. SYNTHESIS AND CHARACTERIZATION OF POLY[ETHER-ESTER-(4-CHLORO)MALEIMIDES]

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## ABSTRACT

New poly[*N*-(ester)-3-(ether)-4-(chloro)]maleimides were synthesized by the reaction of *N*-(4-chlorocarbonylphenyl)-3,4-dichloromaleimide (**3**) with various bisphenols such as hydroquinone (**8a**), 2,2-bis(4-hydroxyphenyl)propane (**8b**), 4,4'-(hexafluoroisopropylidene)diphenol (**8c**), and 2,5-bis(4-hydroxybenzylidene)cyclopentanone (**8d**). The structures of the resulted polymers were confirmed by IR and elemental analyses. A series of model compounds (**4–7**) was synthesized to facilitate confirmation of the structure of the polymers. The polymer containing hydroquinone units (**9a**) exhibited LC behavior in the melt, as observed by PLM measurements.

## INTRODUCTION

Despite the well-known reactions of dichloromaleimides with alcohols, phenols, thiols, and azides [1–4], they are not often used in the synthesis of new, important polymers. In recent years poly(chloromaleimide-ethers) [5, 6], poly(maleimide-amines) [7, 8], and poly(maleimide-amine-ethers) [9] have been prepared by the reaction of bis(dichloromaleimides) (BDCMI) with bisphenols, diamines or tetramines, and *p*-aminophenol, respectively.

The above-mentioned polymers possess good solubilities in aprotic dipolar solvents and are available for further curing reactions due to the presence of an olefinic bond in their structures [8].

Recently Hoyt et al. [10] reported new bis(maleimide-esters) which exhibited TLC behavior.

The present work describes the synthesis and characterization of new poly(4-chloromaleimides) which contain both ester and ether groups on the backbone. The polymers were obtained by the reaction of *N*-(4-chlorocarbonylphenyl)-3,4-dichloromaleimide (**3**) with various bisphenols. Both the 3-chlorine atom and acid chloride groups in maleimide are involved in reactions leading to the ether and ester links, respectively.

Besides the polymers, a series of model compound (**4–7**) was also prepared.

## EXPERIMENTAL

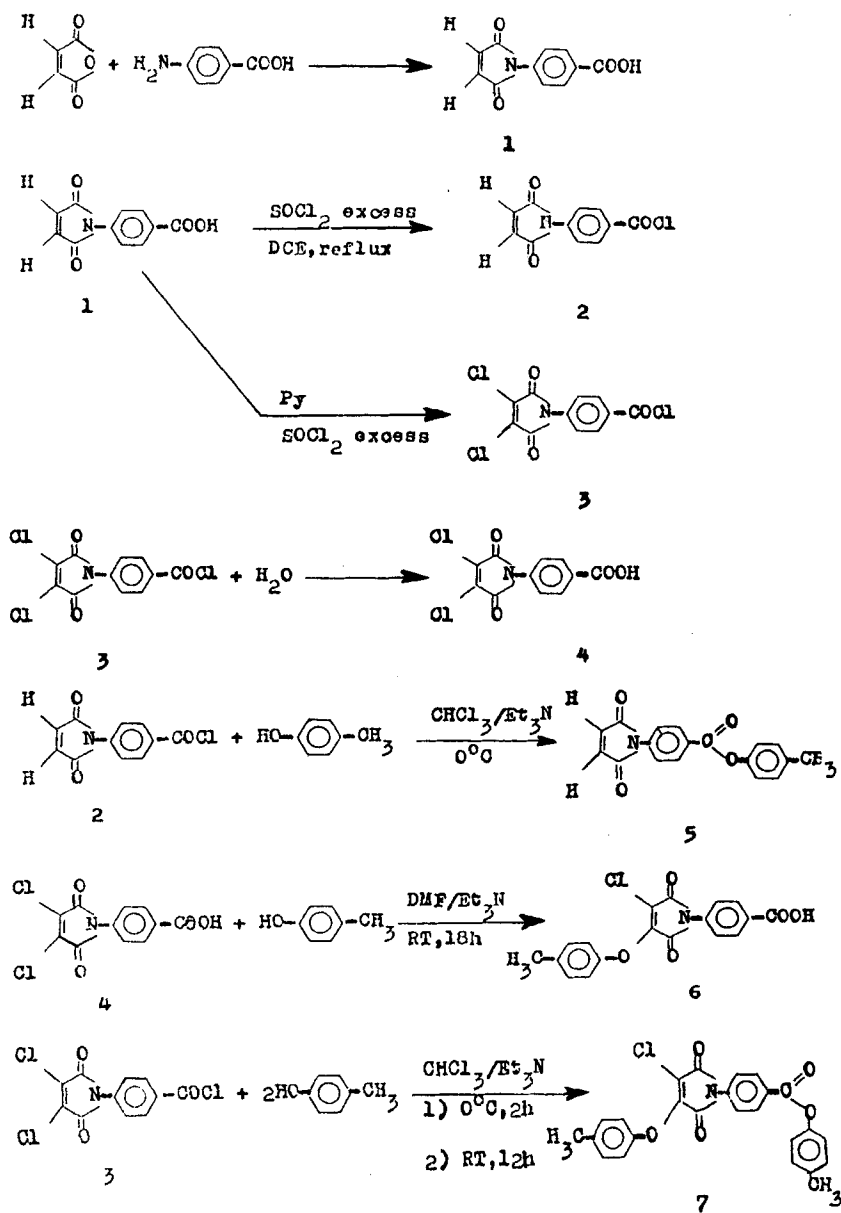
### Measurements

The IR spectra were recorded on a Specord M80 Carl Zeiss, Jena Spectrophotometer using the KBr pellet technique. Proton NMR spectra were run on a Jeol 60 MHz NMR spectrometer at 50°C in DMSO-*d*<sub>6</sub> using TMS as the internal reference. The inherent viscosities of polymers solutions (0.5% w/v) in DMSO were determined at 30°C by using an Ubbelohde Suspended Level Viscometer. Polymer solubilities were determined for 13 common solvents at a concentration of 1% (w/v) at room temperature. The solvents studied were (in order of increasing Hansen solubility parameter): toluene, chloroform, methyl ethyl ketone (MEK), acetone, cyclohexanone, dioxane, pyridine, nitrobenzene, *N*-methyl-pyrrolidin-2-one (NMP), *N,N*-dimethylformamide (DMF), dimethylsulfoxide (DMSO), methanol, water. The melting and softening points were observed with an IOR MC1 type polarizing microscope equipped with a heating stage. 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. Thermooptical analysis (TOA) was carried out in air at a heating rate of 7°C/min as described [11]. Thermogravimetric curves were obtained in air with an F. Paulik Derivatograph at a heating rate of 12°C/min.

### Reagents and Materials

2,5-Bis(4-hydroxybenzylidene)cyclopentanone (**8d**) was obtained as described [12] (mp 317–320°C; Ref. 12, 332°C). Maleic anhydride (mp 54–56°C, Aldrich) was sublimed before use. Thionyl chloride was freshly distilled before use. *N*-Methyl-pyrrolidin-2-one (NMP), 1,2-dichloroethane (DCE), and dichloromethane (DCM) were distilled over anhydrous calcium chloride before use. DMSO, pyridine (Py), triethylamine (TEA), 4-aminobenzoic acid, *p*-cresol, hydroquinone (**8a**), 2,2-bis(4-hydroxyphenyl)propane (**8b**), and 4,4'-(hexafluoroisopropylidene)diphenol (**8c**) (Fluka) were used as received.

The synthetic route of the monomer (**3**) and model compounds (**4–7**) are shown in Scheme 1.



SCHEME 1.

***N*-(4-Carboxyphenyl)maleimide, 1**

The product was obtained as described [13] (mp 248–255°C, methanol; Ref. 13, 239–241°C).

***N*-(4-Chlorocarbonylphenyl)maleimide, 2**

The product was prepared as described [14] (mp 165–168°C, DCE; Ref. 14, 170°C).

***N*-(4-Chlorocarbonylphenyl)-3,4-dichloromaleimide, 3**

A 250-mL four-necked flask fitted with a reflux condenser, nitrogen inlet, thermometer, and mechanical stirrer was charged with a solution of 15.0 g (69.07 mmol) of **1** in 140 mL thionyl chloride. After cooling at 0°C on an ice bath, 17 mL of dry pyridine were dropped in over 15 minutes and stirring was maintained for 1 hour at 0°C. After the addition of pyridine, the initial slurry was converted to a clear yellow solution. The ice bath was removed, then the system was heated under reflux for 2 hours. The excess of thionyl chloride was removed by distillation. Dichloromethane (50 mL) was added, and a white-yellow crystalline solid separated out. The product was filtered, dried, and recrystallized once from toluene. The yield after purification was 13.67 g (65%), mp 225–228°C.

Analysis. Calculated for  $C_{11}H_4Cl_3NO_3$  (304.508): C, 43.38; H, 1.32; Cl, 34.93; N, 4.60%. Found: C, 43.89; H, 1.50, Cl, 34.38; N, 5.02%. IR (KBr,  $cm^{-1}$ ): 3505 (OH), 1800 (sh), 1740 (imide I), 1780 (C=O, of COCl), 1600, 1510 (C=C, aromatic), 1410 (imide II), 1200 (C—O, of COCl), 1125 (imide III), 890 (C—Cl, of imide ring), 845 (1,4-phenylene ring), 735 (imide IV).  $^1H$ -NMR (DMSO- $d_6$ , TMS):  $\delta$  7.49 (d, 2H, ortho to imide), 8.04 (d, 2H, ortho to COCl).

***N*-(4-Carboxyphenyl)-3,4-dichloromaleimide, 4**

To a solution of 3.0 g (9.852 mmol) of compound **3** in acetone (10 mL) was added 10 mL water. After refluxing under stirring for 3 hours, the resulting solid was filtered, washed with methanol, dried, and recrystallized once from acetic acid. The yield after purification was 2.70 g (90%), mp 315–319°C.

Analysis. Calculated for  $C_{11}H_5Cl_2NO_4$  (286.063): C, 46.18; H, 1.76; Cl, 24.79; N, 4.90%. Found: C, 45.65; H, 1.70; Cl, 24.23; N, 4.50%. IR (KBr,  $cm^{-1}$ ): 3300–2500 (COOH), 1805, 1710 (imide I), 1745 (C=O, of COOH), 1640 (C=C, olefinic), 1620, 1525, 1440 (C=C, aromatic), 1415 (imide II), 1200 (C—O, of COOH), 1135 (imide III), 900 (C—Cl, of imide ring), 865 (1,4-phenylene ring), 735 (imide IV).  $^1H$ -NMR (DMSO- $d_6$ , TMS):  $\delta$  7.56 (d, 2H, ortho to imide), 8.125 (d, 2H, ortho to COOH).

***N*-[4-(Methylphenoxycarbonyl)]maleimide, 5**

The same synthesis system as previously described was used and charged with 0.611 g (5.6503 mmol) *p*-cresol, 30 mL chloroform, and 1.2 mL triethylamine. The mixture was purged with nitrogen, cooled at 0°C with an ice bath, 1.218 g (5.1693

mmol) of **2** was added, and the reaction mixture was stirred at 0°C for 2 hours, then at room temperature for 12 hours. The product was extracted by separation funnel with 100 mL of 0.1 N HCl, washed with water, and left overnight over anhydrous sodium sulfate until dried and then crystallized from ethanol to give 1.38 g yield, 87%, mp 168–172°C.

Analysis. Calculated for  $C_{18}H_{13}NO_4$  (307.291): C, 70.35; H, 4.26; N, 4.56%. Found: C, 70.73; H, 4.31; N, 4.74%. IR (KBr,  $cm^{-1}$ ): 3130, 3110 (=C–H, olefinic and aromatic), 1748 (C=O, of ester), 1725 (imide I), 1640 (C=C, olefinic), 1620, 1525 (C=C, aromatic), 1405, 1390 (imide II), 1225, 1215 (C–O, of ester), 1160 (imide III), 870, 845, 810 (1,4-phenylene ring), 705 (imide IV).  $^1H$ -NMR ( $CDCl_3$ , TMS):  $\delta$  2.45 (s, 3H,  $-CH_3$ ), 6.925 (s, 2H, olefinic), 7.20–7.425 (m, 4H, ortho to  $-O-CO-$ , ortho to  $-CH_3$ ), 7.65 (d, 2H, ortho to imide ring), 8.375 (d, 2H, ortho to  $-CO-O-$ ).

### ***N*-(4-Carboxylphenyl)-3-(4-methylphenoxy)-4-chloromaleimide, 6**

To a solution of 0.638 g (5.90 mmol) *p*-cresol and 0.8812 g (3.08 mmol) of **4** in DMF (15 mL) was added 0.6 mL triethylamine. Stirring was maintained for 3 hours at room temperature. The reaction mixture was poured into 100 mL water and the resulting solid was filtered, washed with methanol, and dried for 12 hours in vacuum at 60°C. The yield after recrystallization from ethanol was 0.85 g (70%), mp 233–237°C.

Analysis. Calculated for  $C_{18}H_{12}ClNO_5$  (357.736): C, 60.43; H, 3.38; Cl, 9.91; N, 3.91%. Found: C, 58.97; H, 3.82; Cl, 10.01; N, 4.24%. IR (KBr,  $cm^{-1}$ ): 3500–2500 (COOH), 1800, 1700 (imide I), 1740 (C=O, of COOH), 1660 (conjugation), 1615 (C=C, olefinic), 1590, 1510, 1410 (C=C, aromatic), 1397 (imide II), 1225, 1200 (C–O, of ether + COOH), 1175 (imide III), 895 (C–Cl, of imide ring), 860, 825, 805 (1,4-phenylene ring), 695 (imide IV).  $^1H$ -NMR ( $DMSO-d_6$ , TMS):  $\delta$  2.40 (s, 3H,  $CH_3$ ), 7.25 (m, 4H, ortho to ether, ortho to  $-CH_3$ ), 7.575 (d, 2H, ortho to imide ring), 8.1 (d, 2H, ortho to COOH).

### ***N*-[4-(Methylphenoxy)carbonylphenyl]-3-[4-(methyl)phenoxy]-4-chloromaleimide, 7**

The same synthesis system used for the preparation of monomer **3** was charged with 0.8591 g (7.944 mmol) *p*-cresol and 60 mL chloroform. The flask was cooled at 0°C, then 1.6 mL triethylamine and 1.107 g (3.6353 mmol) **3** were added and the system was maintained for 2 hours at 0°C, then for 12 hours at room temperature. The purification procedure was the same as discussed for monomer **3**. After recrystallization from ethanol the product gave 1.30 g yield, 80%, mp 183–186°C.

Analysis. Calculated for  $C_{25}H_{18}ClNO_5$  (447.854): C, 67.04; H, 4.05; Cl, 7.92; N, 3.13%. Found: C, 67.18; H, 4.63; Cl, 8.06; N, 3.13%. IR (KBr,  $cm^{-1}$ ): 1800 (imide I), 1738 (C=O, of ester + imide I), 1665 (conjugation), 1618 (C=C, olefinic), 1520 (C=C, aromatic), 1420 (C=C, aromatic + imide II), 1275 (aromatic ether), 1178 (imide III), 880 (C–Cl), 1025, 865, 835, 803 (1,4-phenylene ring), 700 (imide IV).  $^1H$ -NMR ( $CDCl_3$ , TMS):  $\delta$  2.45 (s, 6H,  $CH_3$ ), 7.20 (m, 8H, ortho to  $-CH_3$ , ortho to ether, ortho to  $-O-CO-$ ), 7.675 (d, 2H, ortho to imide ring), 8.39 (d, 2H, ortho to  $-CO-O-$ ).

### Polymer 9a-d Synthesis

A 100-mL three-necked flask, equipped with a mechanical stirrer, thermometer, and dry nitrogen inlet, was charged with a mixture of 0.459 g (2.0 mmol) of **8b**, 12 mL *N*-methyl-pyrrolidin-2-one, and 0.6 mL triethylamine. The flask was cooled at 0°C with an ice bath. 0.6093 g (2.0 mmol) of **3** was added and the system was maintained for 2 hours at 0°C, then for 10 hours at room temperature under vigorous stirring. The reaction mixture was poured into 100 mL 0.1 N HCl. The solid which formed was filtered and washed first with water and then with methanol. The polymer was dried for 10 hours under vacuum at 60°C.

All other polymers were obtained in the same manner and their properties are presented in Table 1.

## RESULTS AND DISCUSSION

To facilitate the analysis of spectral data of polymers, a series of model compounds **4-7**, besides monomer **3**, were prepared using the intermediates **1** and **2** as shown in Scheme 1, and good elemental analysis data confirmed the proposed structures.

No literature was found regarding the synthesis of monomer **3**. It was obtained using a 1:3 molar ratio of **1**:pyridine with an excess of thionyl chloride. The <sup>1</sup>H-NMR spectra of compounds **3** and **7** (Fig. 1) showed the disappearance of olefinic protons at 7.2 ppm, while the IR spectra showed the appearance of characteristic absorption bands at 1780 cm<sup>-1</sup> (COCl) and 890 cm<sup>-1</sup> (C-Cl, of imide ring). Four types of imide absorption bands (imides I-IV) were detected in the spectra of monomer **3**, model compounds **4-7**, and polymers **9a-d** and their significance is the same as reported in the literature [14].

Monomer **3** possesses two kinds of reactive functional groups, 3,4-dichloromaleimide and acid chloride. It is reasonable to expect a difference in their reactivities. The synthesis of model compound **5** was a good illustration of the reaction of acid chloride groups with a phenol at 0°C, while the synthesis of model compound **6** indicated there was interaction of the chlorine atom from the 3-position of the maleimide ring with a phenol at room temperature. Finally, the

TABLE 1. The Properties of Polymers **9a-d**

Polymer	Yield, %	Softening range, °C	Inherent viscosity, <sup>a</sup> dL/g
<b>9a</b>	80	150-170	0.09
<b>9b</b>	82	170-190	0.15
<b>9c</b>	85	218-240	0.11
<b>9d</b>	80	200-250	0.14

<sup>a</sup>Measured in DMSO at a concentration of 0.5 g/dL at 30°C.

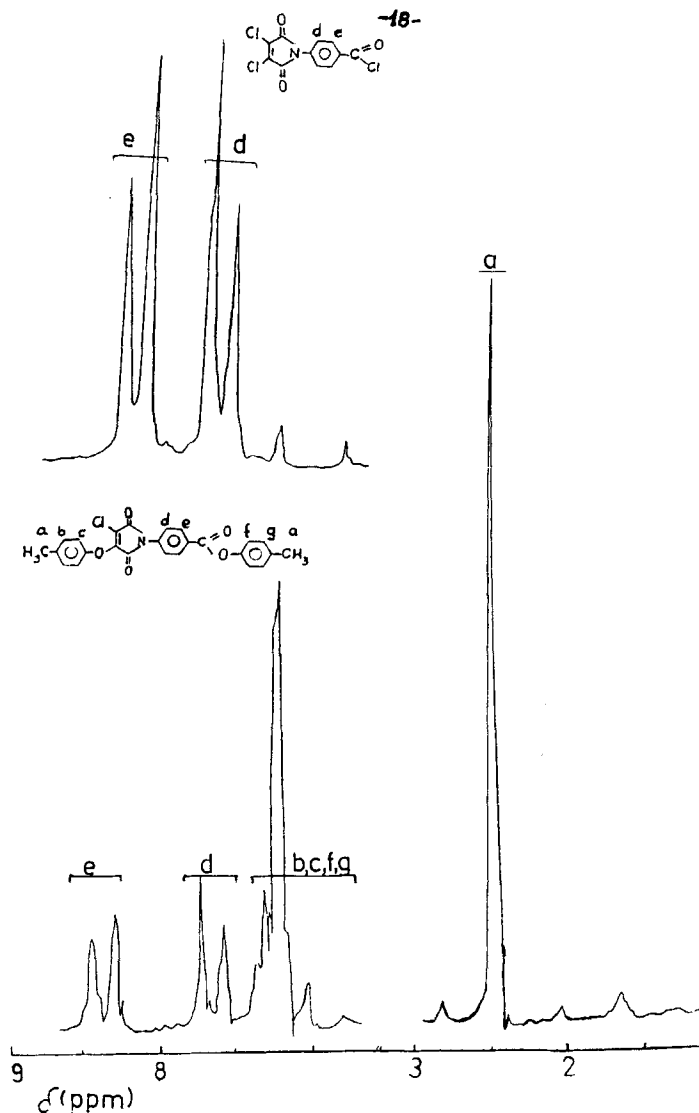
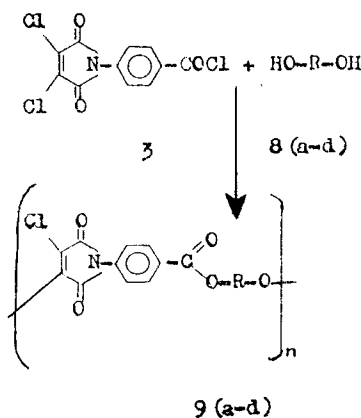



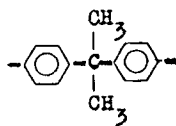
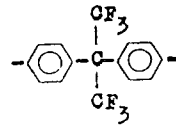
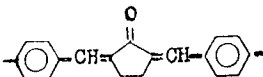
FIG. 1. The  $^1\text{H-NMR}$  spectra of monomer 3 and model compound 7.

synthesis of model compound 7 showed good interaction of both types of functional groups.

The synthesis of polymers is presented in Scheme 2. The elemental analysis values (Table 2) and spectral data confirmed the proposed structures. The IR spectra of polymers (Fig. 2) showed the complete disappearance of the  $\text{COCl}$  absorption peak at  $1780\text{ cm}^{-1}$  [15] and the appearance of some characteristic absorption bands at  $1740\text{ cm}^{-1}$  (ester),  $1275\text{ cm}^{-1}$  (aromatic ether), and  $1665\text{ cm}^{-1}$  (conjugation) which confirmed the presence of 4-chloromaleimide moieties in the polymer backbones [4].





R	8	9
	8a	9a
	8b	9b
	8c	9c
	8d	9d

SCHEME 2.

The polymers were softened in the 150–250°C range, and their inherent viscosities ranged between 0.08 and 0.14 dL/g. The polymers **9a** and **9b**, which have inherent viscosities of 0.09 and 0.08 dL/g respectively, are softened between 150 and 190°C, and they seem to be oligomers. Their thermal behaviors were monitored by DSC (Table 3, Fig. 3) and TOA (Fig. 4). Polymer **9a** showed an endothermic peak with a maximum at about 154°C in the first heating cycle. The second heating cycle showed a  $T_g$  at 127°C and a broad exotherm with a maximum at about 240°C due to the polymerization process. The TOA curve (Fig. 4a) confirmed the DSC observations showing a distinct transition temperature at 136°C. When polymer **9a** was analyzed by PLM, it was seen that it melted in the 150–170°C range and showed a strong birefringence in the melt. The TLC behavior for **9a** is not unexpected because the LC behavior of ester bismaleimides containing hydroquinone units has been reported [10].

The DSC curve of polymer **9b** (Fig. 3c) showed a melting endothermic peak at 185°C in the first heating cycle. In the TOA curve (Fig. 4d) this transition tempera-

TABLE 2. Elemental Analysis of Polymers 9a-d

Polymer	Empirical formula (formula weight)	C, %		H, %		Cl, %		N, %	
		Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found
9a	(C <sub>34</sub> H <sub>16</sub> Cl <sub>2</sub> N <sub>2</sub> O <sub>10</sub> ) (683.39)	57.75	60.06	2.36	3.61	10.37	6.97	4.10	4.75
9b	(C <sub>52</sub> H <sub>36</sub> Cl <sub>2</sub> N <sub>2</sub> O <sub>10</sub> ) (919.73)	67.90	67.38	3.94	4.19	7.71	5.60	3.04	4.68
9c	(C <sub>52</sub> H <sub>24</sub> F <sub>12</sub> Cl <sub>2</sub> N <sub>2</sub> O <sub>10</sub> ) (1135.61)	54.99	56.18	2.13	2.73	6.24	3.45	2.47	4.89
9d	(C <sub>60</sub> H <sub>36</sub> Cl <sub>2</sub> N <sub>2</sub> O <sub>12</sub> ) (1047.81)	68.77	67.24	3.46	4.42	6.77	4.52	2.67	4.78

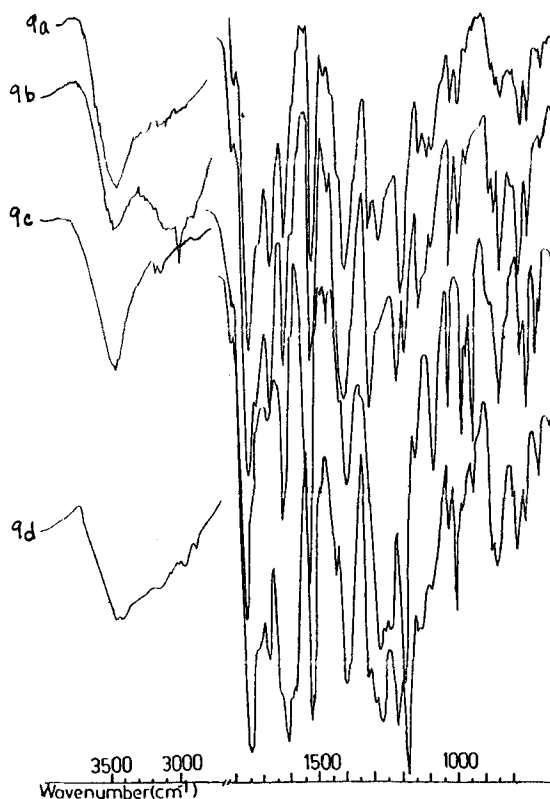


FIG. 2. The IR spectra of polymers **9a-d**.

TABLE 3. The Thermal Properties of Polymers **9a-d**

Polymer	TGA temperatures (°C) for various % decompositions						$T_g$ , °C	
	5	10	20	30	40	50	TOA <sup>a</sup>	DSC <sup>b</sup>
<b>9a</b>	225	278	350	430	475	513	136	127
<b>9b</b>	295	340	392	438	478	528	178	185 <sup>c</sup>
<b>9c</b>	318	370	453	490	512	558	177	—
<b>9d</b>	288	350	437	488	530	567	180	177

<sup>a</sup>TOA measurements in air.

<sup>b</sup>DSC measurements, second heating cycle in nitrogen.

<sup>c</sup>Melting temperature, first heating cycle.

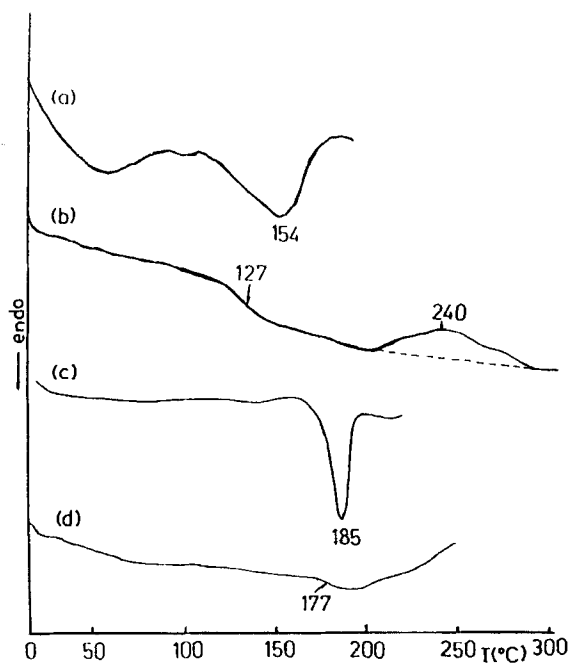


FIG. 3. The DSC curves (10°C/min) of polymers: (a) **9a** first heating scan, (b) **9a** second heating scan, (c) **9b** first heating scan, (d) **9d** second heating scan.

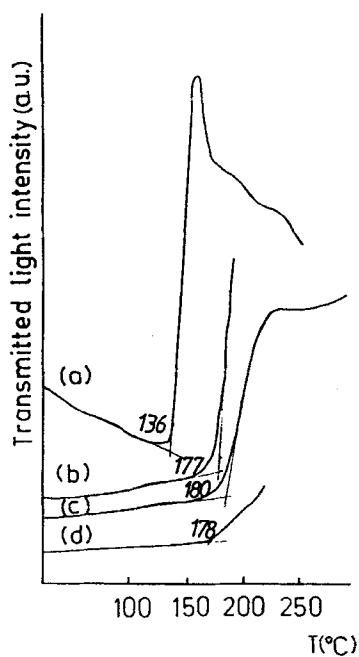


FIG. 4. The TOA curves (7°C/min) of polymers: (a) **9a**, (b) **9c**, (c) **9d**, (d) **9b**.

ture appeared at 178°C. The TOA curve of polymer **9c** (Fig. 4b) showed a transition temperature at 177°C. The PLM observations for polymers **9b** and **9c** showed that they softened in the 170–190°C and 218–240°C ranges, respectively, without the appearance of birefringence.

The DSC curve for polymer **9d** (Fig. 3d) showed a weak  $T_g$  at 177°C, but the TOA curve in Fig. 4c gave evidence of a strong transition at about 180°C. PLM observations showed that polymer **9d** softened between 200 and 250°C, and a small birefringence was observed.

The thermooxidative stability of the polymers was studied in air by TGA with a heating rate of 12°C/min (Table 3, Fig. 5). As can be seen, the polymers showed similar decomposition patterns, and the temperature at which 50% weight loss occurred ranged between 225 and 318°C. Polymer **9c** possessed the better thermooxidative stability, while **9a** had a poor one, as confirmed by its small viscosity value.

Solubilities room temperatures of poly(4-chloro)maleimides **9a–d** are given in Table 4. As can be seen, polymers **9a–c** had good solubility in common solvents, greater than that of polymer **9d**.

It is well known [7] the poly(chloromaleimide-amines) are generally insoluble due to their large hydrogen bond content. It seems to be reasonable to assume that the higher solubility observed in our case could be due to the absence of —NH— groups on the polymer backbone, i.e., a decreased level of hydrogen bonds.

Moreover, literature data [10] show that the solubilities of chloro-substituted maleimide-esters are greater than those of methyl-substituted or unsubstituted ones. This could be an additional explanation for the increased solubility observed in our case.

The limited range of solubility in the case of polymer **9d** could be due to the presence of the rigid dibenzylidenecyclopentanone moieties on the backbone, as reported for arylidene polyesters [17].

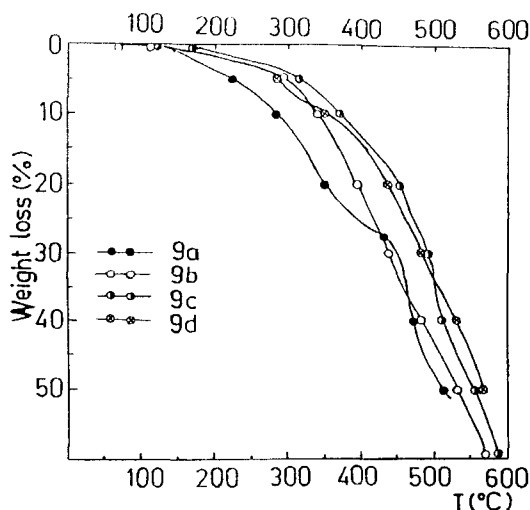


FIG. 5. The TGA curves of polymers **9a–d**.

TABLE 4. The Solubility of Polymers **9a-d**<sup>a</sup>

Test solvent	Solubility <sup>b</sup> parameter, $\delta$	Polymer			
		<b>9a</b>	<b>9b</b>	<b>9c</b>	<b>9d</b>
Toluene	8.90	I	I	I	I
Chloroform	9.21	I	I	SW	I
MEK	9.27	S	PS	S	PS
Acetone	9.75	S	PS	S	PS
Cyclohexanone	9.89	S	S	S	PS
Dioxane	10.01	S	S	S	PS
Pyridine	10.60	S	S	S	PS
Nitrobenzene	10.67	PS	S	S	PS
NMP	11.17	S	S	S	S
DMF	12.15	S	S	S	S
DMSO	13.04	S	S	S	S
Methanol	14.49	I	I	I	I
Water	23.43	I	I	I	I

<sup>a</sup>I = insoluble, SW = swollen, PS = partially soluble, S = soluble.

<sup>b</sup>Solvent solubility parameter in  $(\text{cal}/\text{cm}^3)^{1/2}$  [16].

From the solubility tests, solubility parameter values seem to be reasonable estimates for polymers, as follows for polymers **9a-c** in the 9.27–13.04 range and for polymer **9d** in the 11.17–13.04  $(\text{cal}/\text{cm}^3)^{1/2}$  range.

## CONCLUSIONS

The synthesis of a new 3,4-dichloromaleimide acid chloride monomer (**3**) opened an interesting way in the synthesis of new poly[4-chloromaleimides] containing both ester and ether links in the backbone.

The polymers had good solubilities in common solvents, higher than those reported for poly(chloromaleimide-amines) [7]. Acceptable thermal stability was provided by TGA measurements in air.

Polymer **9a**, which contained the hydroquinone moiety, exhibited TLC behavior.

## REFERENCES

- [1] R. Oda, Y. Hayashi, and T. Takai, *Tetrahedron*, **24**, 4051–4056 (1968).
- [2] M. Augustin and M. Kohler, *J. Prakt. Chem.*, **316**(1), 113–119 (1974).
- [3] D. M. Lynch and A. J. Crovetti, *J. Heterocycl. Chem.*, **9**(5), 1027–1032 (1972).
- [4] H. M. Relles and R. W. Schlunz, *J. Org. Chem.*, **37**(23), 3637–3645 (1972).

- [5] H. M. Relles and R. W. Schlunz, *J. Polym. Sci., Polym. Chem. Ed.*, **11**, 561–571 (1973).
- [6] S. Edge, A. Charlton, and K. S. Varma, *J. Polym. Sci., Part A: Polym. Chem.*, **30**, 2773–2780 (1992).
- [7] H. Kondo, M. Sato, and M. Yokoyama, *Eur. Polym. J.*, **16**, 537–541 (1980).
- [8] I. K. Varma, G. M. Fohlen, and J. A. Parker, *Polym. Prepr.*, **22**(1), 22–23 (1981).
- [9] P. R. Srinivasan, V. Mahadevan, and M. Srinivasan, *Eur. Polym. J.*, **24**(3), 255–258 (1988).
- [10] A. E. Hoyt and B. C. Benicewicz, *J. Polym. Sci., Part A: Polym. Chem.*, **28**, 3417–3427 (1990).
- [11] C. Vasile and A. Stoleriu, *Mater. Plast.*, **27**, 117 (1990).
- [12] M. A. Abd-Alla, M. M. Kandeel, K. I. Aly, and A. S. Hamman, *J. Macrom. Sci. — Chem.*, **A27**(5), 523–538 (1990).
- [13] J. O. Park and S. H. Jang, *J. Polym. Sci., Part A: Polym. Chem.*, **30**, 723–729 (1992).
- [14] I. A. Mikroyannidis, *J. Polym. Sci., Polym. Chem. Ed.*, **28**(3), 669–677 (1990).
- [15] A. E. Hoyt and B. C. Benicewicz, *J. Polym. Sci., Part A: Polym. Chem.*, **28**, 3403–3415 (1990).
- [16] C. M. Hansen, *Ind. Eng. Chem., Prod. Res. Dev.*, **8**, 2 (1969).
- [17] M. A. Abd-Alla and K. I. Aly, *J. Macrom. Sci. — Chem.*, **A28**(3–4), 251–267 (1991).

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