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Note

THE THERMAL BEHAVIOUR OF POLY-*N*-ARYLMALEIMIDES

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The polymerization and properties of *N*-*n*-alkyl- and *N*-arylmaleimides have been studied by many authors [1–9]. Recently, Barrales-Rienda et al. [10] have investigated the polymerization of *N*-fluorophenylmaleimide and discussed the structure–properties relationship of different polymers containing fluoro derivatives of *N*-phenylmaleimide. They found that there is not much change in the thermal stability of polymers by substitution of hydrogen by fluorine in the phenyl ring. However, it was reported that the position of fluorine substitution has a considerable effect on thermal stability.

In this paper, results on the thermal stability of poly-*N*-arylmaleimides with respect to different halogen atoms are reported.

EXPERIMENTAL

Materials

Commercial benzene was used after purification by the method reported in the literature [11]. Maleic anhydride was recrystallized from chloroform to yield white needles, m.p. 49°C. The amines were purified by distillation using zinc dust. Benzoyl peroxide was purified by crystallization from dry ether, m.p. 104 ± 1°C.

Preparation of N-arylmaleimides

The three maleimide compounds used in this work were synthesized, using a modification of the method of Searle [12], from maleic anhydride and the corresponding aromatic amines. The intermediate maleamic acids were cyclodehydrated using $(CH_3CO)_2O$ and fused CH_3COONa at 95°C. *N*-*p*-Fluorophenyl, *N*-*p*-chlorophenyl and *N*-*p*-bromophenyl maleimides were obtained in 60–70% yields; m.p. 154, 113 and 108°C, respectively.

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Polymerization of N-arylmaleimides

Polymerization of *N*-arylmaleimides was carried out in benzene solution at 80°C in nitrogen atmosphere. In a typical reaction 8 g of monomer were polymerized in 100 ml benzene using 0.25 g of benzoyl peroxide at 80°C in a three-necked flask with a mercury-sealed mechanical stirrer and cold water condenser. The polymer was isolated by filtration, and purified by several washes with hot dioxane; the polymer was finally dried at 60°C/10 mm for 20 h.

Analysis

Nitrogen estimation in the polymer samples was carried out on a Coleman nitrogen analyzer. IR spectra of the monomers and polymers were recorded on a UR-10 spectrophotometer (Carl-Zeiss) equipped with KBr, LiF and NaCl optics as KBr discs. Thermogravimetric (TG) and differential thermal analyses (DTA) were performed on a derivatograph (MOM, Budapest, Hungary) at a heating rate of 10°C min^{-1} in air.

RESULTS AND DISCUSSION

The polymerization of *N*-arylmaleimides was slow during the initial stage, with an induction period of about 30 min. After 30 min, the polymers in the form of solids started to separate out, and the polymerization was continued for a total period of 6 h. Yields of the polymers are high. The polymers are sparingly soluble in dimethylformamide, dimethylsulfoxide and tetrahydrofuran. Table 1 shows the percent yield and microanalysis of these polymers.

The cyclic compounds with carbonyl groups show two typical absorption peaks in their IR spectra between 1700 and 1800 cm^{-1} [13–15]. These two bands are clearly shown in the IR absorption maxima of *N*-arylmaleimides. The important IR absorption maxima of *N*-arylmaleimides and poly-*N*-arylmaleimides and their assignments are given in Table 2. In reference to the frequency assignments, it is revealed that the IR spectra of poly-*N*-arylmaleimides differ from the IR spectra of

TABLE 1

Percent yield and elemental analysis of poly-*N*-arylmaleimides

No.	Substance	Yield (%)	Nitrogen (%)		Halogen (%)	
			Reqd.	Found	Reqd.	Found
1b	Poly-*N*-*p*-fluorophenylmaleimide	97	7.33	7.59	9.95	9.98
2b	Poly-*N*-*p*-chlorophenylmaleimide	76	6.74	6.55	17.10	17.04
3b	Poly-*N*-*p*-bromophenylmaleimide	85	5.59	5.75	31.75	31.86

TABLE 2

IR spectral data of *N*-arylmaleimides and poly-*N*-arylmaleimides (ν cm^{-1})

No.	Substance	C=O stretch	C=C stretch	C–N–C stretch	=C–H stretch	C=C stretch aromatic	C=0 in plane and out-of-plane deformation vibration	C–H deformation vibration	C–X stretch
1a	*N*-*p*-Fluorophenylmaleimide	1710 sb 1770 w	1580 s	1310 w, 1390 s 1145 s	3100 s 3060 w	1460 m 1510 s	630 w 580 s	815 s 835 s	1020 s 1035 s 1070 s 1085 s 1230 s
1b	Poly-*N*-*p*-fluorophenylmaleimide	1705 sb 1775 w		1390 sb 1155 sb 1185 sb	3060 w	1460 w 1508 sb	650 s 580 s	830 sb	1015 s 1045 w 1095 m 1230 sb 1290 s
2a	*N*-*p*-chlorophenylmaleimide	1720 sb 1770 w	1585 s	1315 s 1385 sb 1150 s 1175 w	3085 s 3080 w	1455 m 1500 s 1550 w	680 s 580 s	640 s	650 s 710 s 750 s 765 s 780 m
2b	Poly-*N*-*p*-chlorophenylmaleimide	1710 sb 1770 w		1310 w 1385 sb 1185 sb	3080 w	1455 w 1495 sb	630 s 580 w	830 sb	650 sb 710 s 745 sb
3a	*N*-*p*-bromophenylmaleimide	1720 sb 1765 w	1580 s	1300 s 1375 b 1135 sb 1170 w	3090 s 3080 s	1450 s 1465 w 1510 sb 1540 w	670 s 580 s	820 sb	640 w
3b	Poly-*N*-*p*-bromophenylmaleimide	1700 sb 1765 w		1335 w 1375 sb 1170 sb	3080 w	1450 w 1490 sb 1530 w 1550 w	660 s 580 w	810 sb 850 w	540 w

s=Strong; b=broad; w=weak; m=medium.

TABLE 3

Evaluation of kinetic parameters for the thermal decomposition of poly-*N*-arylmaleimides by Reich's method [16]

No.	Substance	Decomposition exotherm	Peak start (°C)	Peak temp. (°C)	Peak end temp. (°C)	Order of decomposition	Energy of activation (kcal mole^{-1})
1b	Poly-*N*-*p*-fluorophenylmaleimide	First	355	400	455	0.66	69.33
		Second	485	530	615	0.67	50.93
		Third	660	750	790		
2b	Poly-*N*-*p*-chlorophenylmaleimide	First	320	350	385	0.95	86.54
		Second	470	510	550	0.92	93.50
		Third	560	610	700	1.24	64.19
3b	Poly-*N*-*p*-bromophenylmaleimide	First	325	400	430	0.89	84.48
		Second	430	545	600	0.93	42.63
		Third	695	780	820		

TABLE 4

Results of thermogravimetric analysis (TGA) of poly-*N*-arylmaleimides

No.	Substance	Initial decomposition temp. (°C)	% wt. loss at different temperatures in air (°C)					Order of decomposition [17]
			400	500	600	700	800	
1b	Poly-*N*-*p*-fluorophenylmaleimide	355	9.61	52.30	71.15	88.45	95.15	1.58
2b	Poly-*N*-*p*-chlorophenylmaleimide	320	29.23	51.54	81.55	89.45	89.45	1.09
3b	Poly-*N*-*p*-bromophenylmaleimide	325	9.37	58.13	73.13	88.45	96.07	1.91

N-arylmaleimides only with respect to the broadening of the major bands and the absence of ethylenic bands (1580–1585 cm^{-1}). From spectral and elemental analysis of these polymers, it is suggested that *N*-arylmaleimides undergo vinyl type free radical addition polymerization under the reaction conditions used in this work.

Table 3 gives the peak temperatures of poly-*N*-arylmaleimides 1b, 2b and 3b observed from the DTA thermograms. On comparing the values of peak starting temperatures, it is revealed that all these polymers are thermally stable up to about 320°C. Three decomposition exotherms are observed in all the polymers which indicate that the behaviour of thermal degradation is similar in all cases.

Table 4 presents the initial decomposition temperatures and percent weight loss at different temperatures observed from TG thermograms. A comparison of the results given in Table 4 makes it clear that all the poly-*N*-arylmaleimides studied here are thermally stable up to 320°C. Poly-*N*-*p*-fluorophenylmaleimide is comparatively more thermally stable than the other poly-*N*-arylmaleimides. The thermal stability trend is poly-*N*-*p*-fluorophenylmaleimide > poly-*N*-*p*-chlorophenylmaleimide = poly-*N*-*p*-bromophenylmaleimide. Generally, the fluorine atom increases the thermal stability of the polymers.

From the results of the kinetic parameters, it can be concluded that all these polymer samples follow approximately the same mechanism of degradation. The order of decomposition may be considered to be near to one as the calculated values of order of decomposition for each sample are around one within the possible range of uncertainty. From the literature survey [6], it is revealed that the energy of activation ranges from 24 to 40 kcal mole^{-1}; however, in most of the samples studied here it varies from 42 to 93 kcal mole^{-1}.

From the above results of DTA, TG and IR spectra, the structure of the polymers is more regular and stable, which is justified by the presence of the –CH–CH– group in the backbone.

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