Thermochimica Acta, 53 (1982) 163–173
Elsevier Scientific Publishing Company, Amsterdam—Printed in The Netherlands

SYNTHESIS AND THERMAL STUDY OF POLY-*N-p*-SUBSTITUTED PHENYLMALEIMIDES

RAJENDRA D. PATEL *, M.R. PATEL ** and I.S. BHARDWAJ

Research Centre, Indian Petrochemicals Corporation Ltd., Vadodara-391 346 (India)

(Received 10 August 1981)

ABSTRACT

Poly-*N-p*-bromomethylphenylmaleimide was synthesized from poly-*N-p*-methylphenylmaleimide at 80°C in benzene solution using *N*-bromosuccinimide as a brominating agent with a trace amount of benzoyl peroxide. The alcoholysis, aminolysis and Wurtz reaction of poly-*N-p*-bromomethylphenylmaleimide were carried out using various alcohols, amines and sodium metal, respectively. The polymers obtained were characterized on the basis of elemental analysis, IR spectra and molecular weight measurements. The thermal behaviour of these polymers was studied by DTA and TG methods and the probable mechanism of degradation and crosslinking reactions are proposed.

INTRODUCTION

The maleimide functional group is particularly versatile in the synthesis and reactions of polymers. Examples involving bis-maleimides include Diels–Alder polymerization with bis-dienes or pseudobis-dienes [1], photo-polymerization via $2\pi + 2\pi$ cyclo-addition [2], free radical [3] and thermal [4] polymerization, thermal addition polymerization to 1,1-diphenylethylene [5] and substituted bis-quinoxalines [6], Diels–Alder crosslinking of polymers containing pendant furan groups [7], and peroxide- [8] and radiation-promoted [9] crosslinking of unsaturated polymers. Several papers have been published concerning photo-cycloaddition polymerization of bis-maleimides with benzene [10] and alkylbenzene [11] and the corresponding photo-crosslinking with polystyrene [12–19].

Literature survey reveals that bromination of *N-p*-methylphenylmaleimide and its polymer using *N*-bromosuccinimide has not yet been studied. In order to observe the effect of the various substituents, if any, on the thermal stability of poly-*N*-phenylmaleimide, various poly-*N-p*-substituted phenylmaleimides were synthesized from poly-*N-p*-bromomethylphenylmaleimide. The results for the synthesis and thermal stability of the substituted maleimides shown in Fig. 1, are reported here.

---

* To whom correspondence should be addressed.

** Department of Chemistry, S.P. University, Vallabh Vidyanagar-388 120, Gujarat, India.

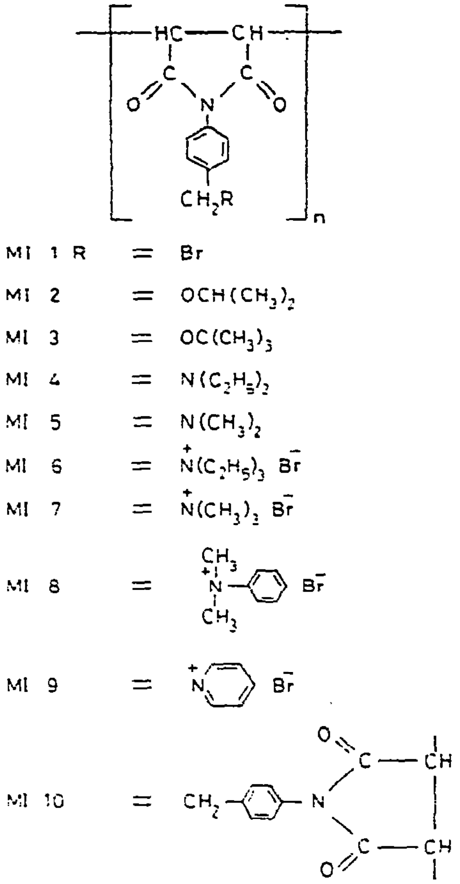


Fig. 1. Structures of poly-*N*-*p*-substituted phenylmaleimides.

EXPERIMENTAL

Materials

Benzene, maleic anhydride, *p*-toluidine and benzoyl peroxide were purified as described previously [20]. Reagent grade *N*-bromosuccinimide, isopropanol, *t*-butanol, diethylamine, triethylamine, dimethylamine, trimethylamine, aniline, pyridine and sodium metal were obtained from S.M. Chemicals (Baroda, India) and were used as received. The purity of the reactants was in the range 90–99%.

Synthesis of N-p-*methylphenylmaleimide*

N-*p*-Methylphenylmaleimide was prepared according to the procedure given in the literature [21].

Polymerization of N-p-methylphenylmaleimide

The polymerization of *N*-*p*-methylphenylmaleimide was carried out according to the process described previously [20].

Polymer reactions

Bromination

Poly-*N*-*p*-methylphenylmaleimide (0.2139 mole), *N*-bromosuccinimide (49.0 g) and benzoyl peroxide (1.0 g) were mixed in benzene (400 ml) and refluxed to boiling temperature for 12 h with continuous stirring. The reaction mixture was cooled, and the polymer was filtered and washed several times with boiling benzene to remove the succinimide formed during the reaction. After completion of the reaction, the red coloured product (MI1) was dried at 60°C/10 mm for 10 h; yield 97%.

Alcoholysis

Poly-*N*-*p*-bromomethylphenylmaleimide (0.0301 mole) was added to a solution of sodium isopropoxide in isopropanol (40 ml). The reaction mixture was refluxed at 80°C for 40 h with continuous stirring. The polymer (MI2) was filtered from the reaction mixture, washed with hot distilled water and dried in vacuum at room temperature; yield 98%.

The *t*-butanol derivative of the above brominated polymer (MI3) was prepared by a technique similar to that used in the isopropanolysis, except that isopropanol was replaced by *t*-butanol.

Aminolysis

Poly-*N*-*p*-bromomethylphenylmaleimide (0.0037 mole) was treated with the following amines as described for the alcoholysis:

(a) diethylamine (20 ml) (MI4)
(b) triethylamine (20 ml) (MI5)
(c) dimethylamine (20 ml) (MI6)
(d) trimethylamine (20 ml) (MI7)
(e) dimethylaniline (5 ml) in benzene (30 ml) (MI8)
(f) pyridine (5 ml) in benzene (30 ml) (MI9)

All the products were obtained in 89–98% yield.

Wurtz reaction

Poly-*N*-*p*-bromomethylphenylmaleimide (0.0303 mole) was treated with sodium metal (10.0 g) in toluene (200 ml) in a manner similar to the isopropanolysis for 65 h. The product, poly-*N*,*N*′-4,4′-(α,β-diphenylethane)bis-maleimide (MI10), was obtained in 99% yield.

Characterization

Nitrogen and halogen estimations in the polymer samples were carried out on a Coleman nitrogen analyzer and by Carius method, respectively.

IR spectra of the polymers were recorded on a UR-10 spectrophotometer (Carl Zeiss) in KBr.

The $\overline{Mn}$ was determined in chloroform at 37°C on a Hewlett-Packard (U.S.A.) model 302B vapour pressure osmometer.

Thermogravimetric (TGA) 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 bromination and other reactions studied are associated with the colour changes. Table 1 shows the preparation conditions, % yield, colour characteristics, elemental analysis and molecular weights of poly-*N*-*p*-substituted phenylmaleimides. The bromination of poly-*N*-*p*-methylphenylmaleimide occurs at benzylic carbon when *N*-bromosuccinimide is used as brominating agent. The polymers are insoluble in most of the organic solvents and sparingly soluble in dimethylformamide and dimethylsulphoxide. The mechanism for the bromination of poly-*N*-*p*-methylphenylmaleimide using NBS and benzoyl peroxide is similar to the allylic type mechanism.

The IR spectra of poly-*N*-*p*-bromomethylphenylmaleimide and poly-*N*-*p*-*t*-butoxymethylphenylmaleimide are shown in Figs. 2 and 3. The characteristic peaks of poly *N*-*p*-methylphenylmaleimide have been discussed previously [20]: however, additional peaks due to C–Br (500–600 cm^{-1}), CH_2–N (1430–1556 cm^{-1}), $CH_2-\overset{+}{N}$ (1400–1440 cm^{-1}), $CH(CH_3)_2$ (1140–1170, 1370–1390 cm^{-1}), $OC(CH_3)_3$ (720–770, 820–920, 100–1040, 1155–1200 cm^{-1}), Ph–$N(CH_3)_2$ (2800 cm^{-1}) and CH_2 – Ph (1430–1445 cm^{-1}) were observed in the spectra.

The number average molecular weight of the poly-*N*-*p*-methylphenylmaleimide is about 10000. The same polymer was used for the bromination, alcoholysis, aminolysis and Wurtz synthesis. Since the substituted phenylmaleimides are insoluble in most of the solvents, their molecular weights have been calculated by adding the weight of the substituents in the starting polymer, assuming that no cleavage of backbone takes place during the course of reaction.

The DTA and TG thermograms of poly-*N*-*p*-bromomethylphenylmaleimide (I) and poly-*N*,*N'*-(α,β-diphenylethane)bis-maleimide (II) are shown in Fig. 4. TGA thermogram I indicates that the weight loss starts at 170°C and increases rapidly up

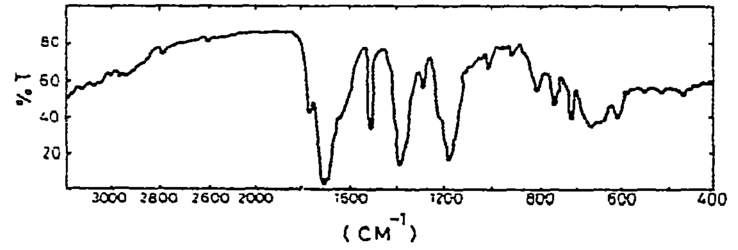


Fig. 2. IR spectrum of poly-*N*-*p*-bromomethylphenylmaleimide in KBr.

TABLE 1

Preparation conditions and elemental analysis of poly-*N*-*p*-substituted phenylmaleimides (MI1–MI10)

Compound No.	Solvent	Time of reaction	Yield %	Colour	Nitrogen %		Halogen %		$\overline{M}n$
					Calcd	Found	Calcd	Found	
	Benzene	6	82	White	7.48	7.22			10000
MI1	Benzene	12	97	Red	5.26	5.54	30.07	29.52	14100
MI2	Isopropanol	40	98	Yellow	5.71	5.58			13000
MI3	*t*-Butanol	22	99	Yellow	5.40	5.36			13700
MI4	Diethylamine	5	98	Brown	10.58	10.88			13700
MI5	Dimethylamine	16	99	Light green	12.17	11.60			12200
MI6	Triethylamine	5	90	Grey	7.63	7.94	21.80	21.20	19400
MI7	Trimethylamine	11	91	Dark grey	8.61	8.28	24.61	24.35	17200
MI8	Benzene	7	89	Dark green	7.24	7.14	20.67	20.26	20500
MI9	Benzene	7	89	Brown	8.12	8.10	23.19	23.14	18300
MI10	Toluene	65	99	Dark brown	7.53	7.56			19700

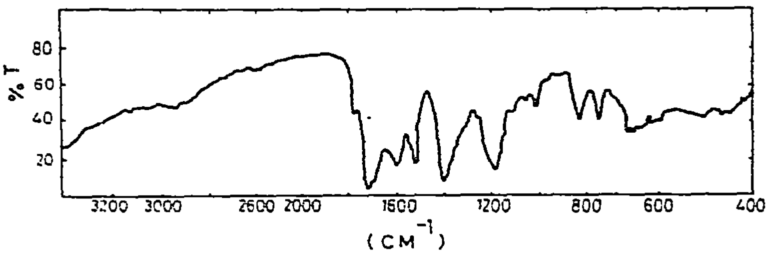
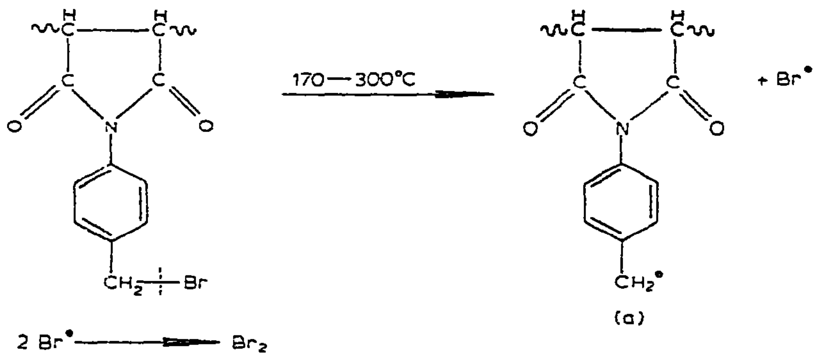


Fig. 3. IR spectrum of poly-*N*-*p*-*t*-butoxymethylphenylmaleimide in KBr.

to 300°C. The percentage weight loss up to 300°C is nearly 28%. This is mainly due to dehalogenation of the polymer (calculated Br 30%). The elimination of bromine suggests that the initial thermal cleavage occurs at CH_2–Br. This is expected in accordance with the difference in C–C (83 kcal mole^{-1}) and C–Br (51 kcal mole^{-1}) bond dissociation energies.



The polymer radical (a) thus formed can combine with another radical and give a product like (b) or it can abstract a proton from a neighbouring polymer to yield (c)

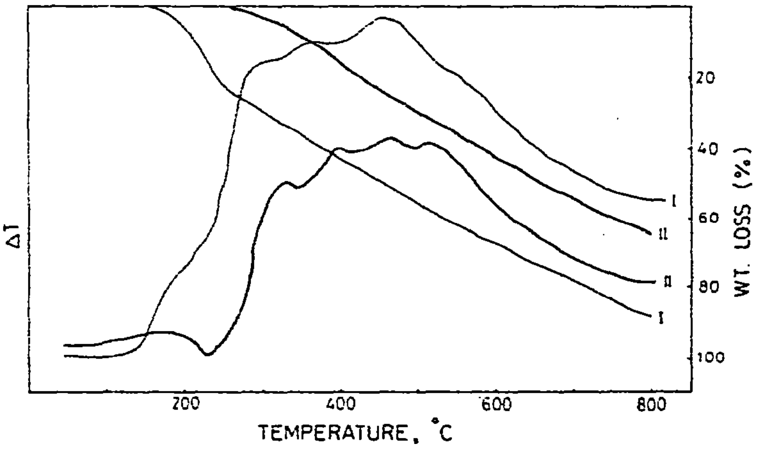
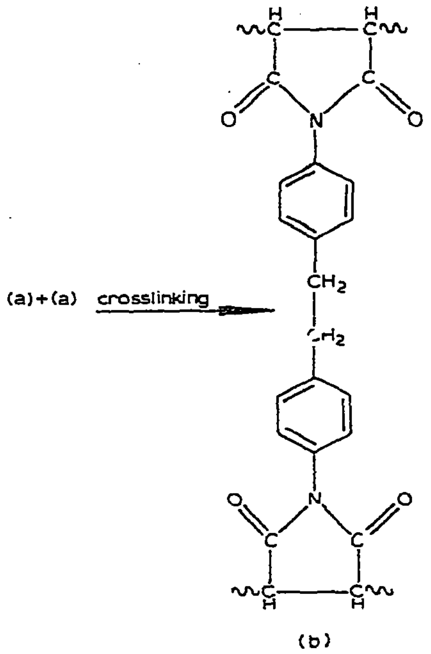
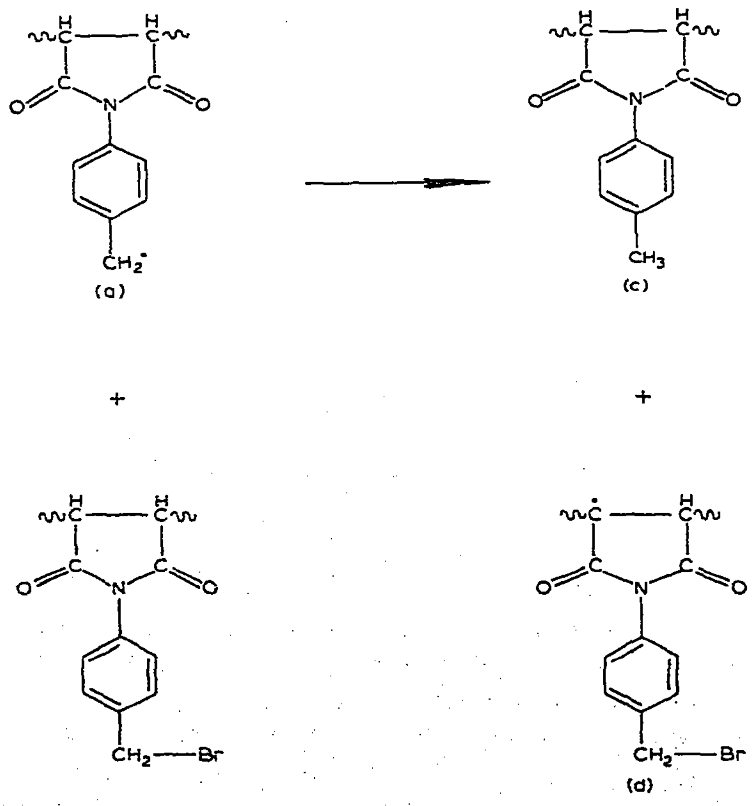
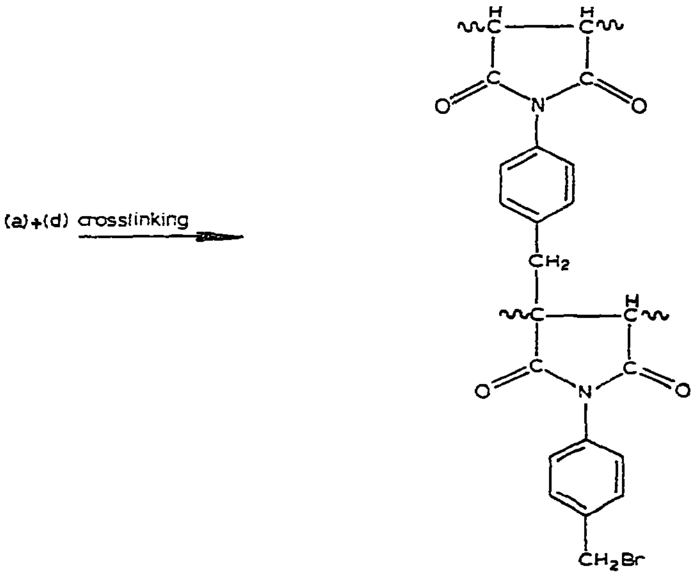


Fig. 4. DTA and TG curves of poly-*N*-*p*-bromomethylphenylmaleimide (I) and poly-*N*,*N*'-4,4'-(α,β-diphenylethane)bis-maleimide (II) in air at 10°C min^{-1}.

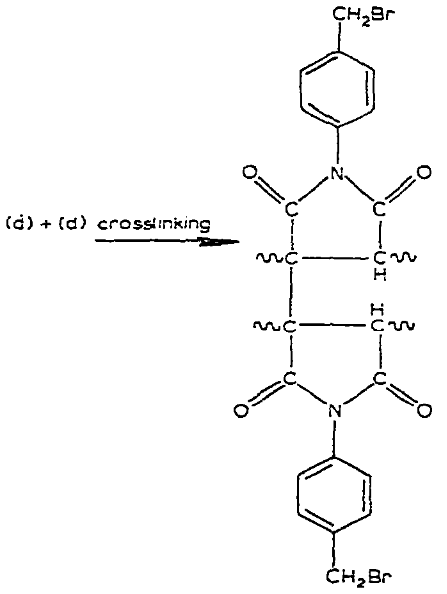
and another polymer radical (d) which can combine either with (a) or (d) to yield (e) and (f), respectively. This is shown schematically as







(e)



(f)

The TG thermogram II has no appreciable weight loss up to 300°C. Beyond this temperature the thermogravimetric analyses of both I and II are very similar; this may be due to transformation of I into II by dehalogenation as explained earlier.

The DTA thermogram of I shows a small endotherm at 255°C, which is due to C–Br bond rupture. Apart from this there are three exotherm peaks at 325, 400 and 460°C. The DTA thermogram of II differs from I with respect to the starting decomposition temperature. The remainder of thermogram II is similar to that of I and has similar exotherm peaks at 305, 370 and 470°C. DTA and TG thermograms of poly-*N*-*p*-isoproproxymethylphenylmaleimide (III) and poly-*N*-*p*-*t*-butoxymethylphenylmaleimide (IV) are shown in Fig. 5. The DTA thermogram of III shows endotherms at 135 and 140°C due to cleavage of the C–O bond. The DTA

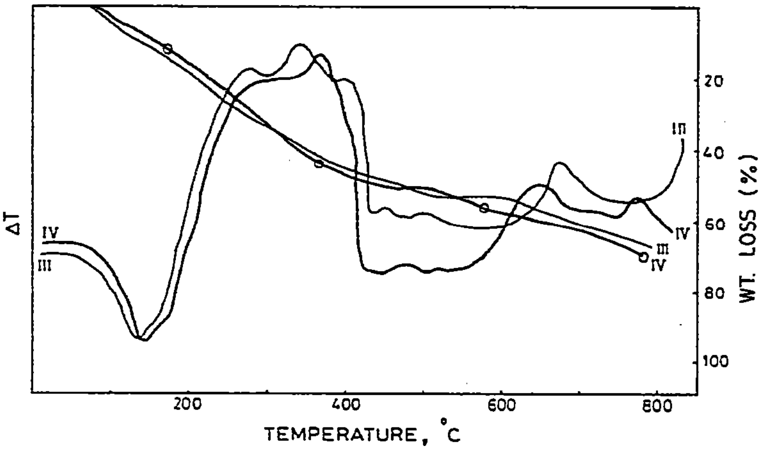


Fig. 5. DTA and TG curves of poly-*N*-*p*-isopropoxymethylphenylmaleimide (III) and poly-*N*-*p*-*t*-butoxymethylphenylmaleimide (IV) in air at 10°C min^{-1}.

thermogram of III shows two broad exotherms at 340 and 670°C with shoulders at 275 and 400°C, and three exotherms at 450, 500 and 780°C. Two broad exotherms at 300 and 645°C with a shoulder at 360°C and three small exotherms at 480, 520 and 770°C in the DTA thermogram IV are due to degradation of the polymer.

The TG curve of III reveals that there is a rapid change in weight loss up to 150°C. From 150–230°C the change in weight loss is slow. From 230–440°C the change in weight loss is again rapid, thereafter 440° to 670°C it is very slow. Above 670°C, there is an instantaneous change in weight loss. The TG curve of IV shows a similar change in weight loss as in the TG curve of III.

The TG and DTA results of poly-*N*-*p*-substituted phenylmaleimides are given in Tables 2 and 3. Table 2 gives the correlation between decomposition exotherm peak temperatures in the polymer. From Tables 2 and 3, it is observed that almost all

TABLE 2

DTA data for poly-*N*-*p*-substituted phenylmaleimide

Compound No.	Decomposition endotherm peak temp. (°C)	Decomposition exotherm peak temperature (°C)			Order of decomposition [22]	Energy of activation (kcal mole^{-1})
		First	Second	Third		
	430	345	520	665	1.21	53.07
MI1	225	325	400	460	0.38	26.29
MI2	135	340	670		0.84	20.03
MI3	140	300	645		0.61	21.79
MI4	115	400	500	560	0.73	24.06
MI5	125	380	510	560	0.38	29.32
MI6	125	400	500	560	0.54	26.68
MI7	135	380	510	560	0.80	17.67
MI8	95	440	520	560		
MI9	135	440	520	560	0.45	35.00
MI10	–	305	370	470	1.04	29.20

TABLE 3

Results of TGA for poly-*N*-*p*-substituted phenylmaleimides

Compound No.	Initial decomposition temp. (°C)	%Wt. loss at different temperatures (°C) in air							
		100	200	300	400	500	600	700	800
	355				27.04	42.93	71.48	87.80	92.60
MI1	170		6.35	29.80	42.50	56.75	70.46	78.54	88.75
MI2	70	4.16	16.16	33.34	48.51	53.01	54.34	62.50	68.34
MI3	70	4.54	18.19	34.10	46.14	50.91	57.93	63.63	72.73
MI4	60	8.81	15.43	26.43	38.10	49.28	61.90	73.10	80.50
MI5	70	7.61	19.56	28.26	41.30	53.27	64.13	75.01	85.65
MI6	60	9.21	13.43	34.21	52.60	63.16	79.07	86.84	94.73
MI7	60	12.50	27.75	38.00	50.00	61.27	74.50	85.00	83.74
MI8	80	5.00	7.14	12.50	19.64	37.51	55.37	72.14	86.80
MI9	80	4.81	12.03	22.96	43.89	57.58	68.52	76.88	85.17
MI10	255	–	–	2.10	16.00	29.50	42.50	53.10	63.00

these polymers follow approximately the same mechanism of degradation. The order of reaction may be considered to be nearly equal to one and the energy of activation ranges from 17 to 72 kcal mole^{-1} [22].

CONCLUSIONS

(i) From the results of TG and DTA it seems that poly-*N*-*p*-substituted phenylmaleimides are thermally less stable than poly-*N*-arylmaleimides.

(ii) The route for the synthesis of poly-*N*,*N'*-4,4'-(α,β-diphenylethane)bismaleimide is novel.

ACKNOWLEDGEMENTS

The authors express their gratitude to IPCL Research Centre for providing analytical facilities, Prof. Dr. R.D. Patel for continuous encouragement during this work, and Dr. Y.N. Sharma for useful discussion for writing the manuscript.

REFERENCES

1 J.K. Stille, J. Macromol. Sci. Chem., 3 (1969) 1043.
2 F.C. De Schryver, Pure Appl. Chem., 34 (1973) 213.
3 Societé Rhodiaceta, Neth. Appl. 6, 514, 767 (1966).
4 D.O. Hummel, K.-U. Heinen, H. Stenzenberger and H. Siesler, J. Appl. Polym. Sci., 18 (1974) 2015.
5 W.N. Emmerling and M.L. Hallenleben, Eur. Polym. J., 13 (1977) 179.
6 A.A. Berlin, T.V. Zelenetskaya and R.M. Asseva, Zh. Vses. Khim. Ova., 15 (1966) 591.
7 J.M. Craven, U.S. Pat. 3, 435, 003 (1969).
8 P. Kovacic and R.W. Hein, J. Am. Chem. Soc., 81 (1959) 1187, 1190.
9 S.M. Miller, R. Roberts and R.L. Vale, J. Polym. Sci., 58 (1962) 737.
10 Y. Musa and M.P. Stevens, J. Polym. Sci., Part A-1, 10 (1972) 319.
11 W. Kardush and M.P. Stevens, J. Polym. Sci., Part A-1, 10 (1972) 1093.
12 M.P. Stevens, in S.S. Labana (Ed.), UV Light Induced Reactions of Polymers, American Chemical Society Symposium Series No. 25, American Chemical Society, Washington, DC, 1976, p. 64.
13 M.P. Stevens, J. Polym. Sci., Polym. Chem. Ed., 17 (1979) 3675.
14 D.C. Phillips, D.H. Davies and J.A. Jackson, Makromol. Chem., 177 (1976) 3049.
15 K. Nakamura and S. Kikuchi, Bull. Chem. Soc. Jpn., 40 (1967) 2684.
16 L.M. Minsk and H.L. Cohen, U.S. Pat. 3, 308, 075 (1967).
17 J.F. Klebe and T.J. Windish, S. Afr. Pat. 7,003,454 (1970).
18 K. Ichimura, S. Watanabe and H. Ochi, J. Polym. Sci., Polym. Lett. Ed., 14 (1976) 207.
19 G. Smets, in E.B. Mano (Ed.), Proc. Int. Symp. Macromol, Rio de Janeiro (1974), Elsevier, Amsterdam, 1975.
20 R.D. Patel, M.R. Patel and I.S. Bhardwaj, Thermochim. Acta, 48 (1981) 11.
21 N.E. Searle, U.S. Pat. 2,444,536 (1948).
22 L. Reich, Macromol. Chem., 123 (1969) 42.