

THERMAL BEHAVIOUR OF POLY-*N-p*-METHYLPHENYLMALEIMIDE

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(Received 5 February 1981)

ABSTRACT

N-p-Methylphenylmaleimide was polymerized at 80°C in benzene solution using benzoyl peroxide as initiator. The yield of polymer obtained was about 80% and its \bar{M}_n was 10 000. The thermal behaviour of poly-*N-p*-methylphenylmaleimide (PMPMI) was studied using TG and DTA techniques and a mechanism of degradation is suggested.

INTRODUCTION

The polymerization and properties of *N-n*-alkyl- and *N*-acrylmaleimides have been studied by many authors [1–9]. Recently Barrales-Rienda et al. [10] investigated that 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 the fluorine substitution has a considerable effect on the thermal stability.

In this paper, results on the thermal behaviour of poly-*N-p*-methylphenylmaleimide (PMPMI), its structural changes during heating, and the mechanism of degradation are suggested.

EXPERIMENTAL

Materials

Commercial benzene was treated several times with concentrated sulphuric acid in order to remove thiophene, then washed with distilled water, dried over anhydrous CaCl₂, and distilled under an atmosphere of nitrogen. The fraction boiling at 78–79°C was collected and stored over sodium wire in an atmosphere of nitrogen. Maleic anhydride was recrystallized from chlo-

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roform to yield white needles (m.p. 49°C); *p*-toluidine was distilled using zinc dust to yield lustrous plates (m.p. 45°C); the benzoyl peroxide was purified by crystallization from dry ether (m.p. 104 ± 1°C). All the reagents were dried and stored in tight-capped bottles in an atmosphere of nitrogen.

Synthesis of N-p-methylphenylmaleimide

N-p-Methylphenylmaleimide was prepared according to the standard procedure [11] involving a two-stage process:

(i) formation of *N-p*-methylphenylmaleamic acid from maleic anhydride and *p*-toluidine using carbon tetrachloride as solvent at room temperature;

(ii) cyclodehydration of *N-p*-methylphenylmaleamic acid using acetic anhydride and fused sodium acetate to yield *N-p*-methylphenylmaleimide at 95°C.

Polymerization of N-p-methylphenylmaleimide

The polymerization of *N-p*-methylphenylmaleimide was carried out in benzene solution at 80°C in an atmosphere of nitrogen. In a typical reaction 8 g of monomer were polymerized in 100 ml of 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. The purification was carried out by dissolving the polymer in chloroform and re-precipitated by methanol. The procedure was repeated twice and the polymer was dried at 60°C/10 mm for 20 h.

Characterization

Estimation of nitrogen in the polymer sample was carried out using a Coleman nitrogen analyzer. IR and NMR spectra of the monomer and polymer were recorded on a UR-10 spectrophotometer (Carl Zeiss) in KBr, and a 60 MHz Varian XL-60 spectrophotometer in CDCl₃ solution, respectively. The intrinsic viscosities of the polymer sample were determined in chloroform, dimethylformamide and cyclohexanone at 30°C using an Ubbelohde viscometer. The \bar{M}_n was determined in chloroform at 37°C on a Hewlett-Packard (U.S.A.) vapour pressure osmometer model 302B. Thermogravimetric (TG) and differential thermal analysis (DTA) were performed in air on a MOM derivatograph (Budapest, Hungary) at a heating rate of 10°C min⁻¹.

RESULTS AND DISCUSSION

The monomer and its polymer were characterized by their melting points and microanalysis data (Table 1). The cyclic compounds having carbonyl groups show two typical absorption peaks in their IR spectra between 1700 and 1800 cm⁻¹ [12–14]. These two bands are clearly shown in the IR spectrum (Fig. 1) of *N-p*-methylphenylmaleimide. Apart from bands at 1775 and 1715 cm⁻¹ (C=O stretching), the spectrum has the following characteristic

TABLE 1

Characteristics of *N-p*-methylphenylmaleamic acid, *N-p*-methylphenylmaleimide and poly-*N-p*-methylphenylmaleimide

Compound	Colour	Nitrogen (%)		M.p. (°C)		Yield (%)
		Reqd.	Found	Obsd.	Lit.	
<i>N-p</i> -Methylphenylmaleamic acid	Yellow	6.83	6.81	206	206 [11]	95
<i>N-p</i> -Methylphenylmaleimide	Yellow	7.48	7.50	145	149 [11]	55
Poly- <i>N-p</i> -methylphenylmaleimide	White	7.48	7.22			82

absorptions; 3096 and 1583 cm^{-1} (C=C stretching), 1320 and 1130 cm^{-1} (C—N—C stretching), 1550–1450 cm^{-1} (aromatics), and 800–700 cm^{-1} (C—H bending for aromatics). The NMR spectrum of the monomer has absorptions at 6.97, 6.52 and 2.30 δ which can be assigned to aromatic, vinyl and methyl protons, respectively.

Polymerization of *N-p*-methylphenylmaleimide was slow during the initial stage, with an induction period of about 30 min. After 30 min, the polymer started to separate out in the form of a white solid, and the polymerization was continued for a total period of 6 h. The yield of the polymer was 82%.

The IR spectrum of the polymer (Fig. 2) shows the disappearance of the double bond, indicating polymerization to have taken place at the ethylenic double bond. All the other characteristic bands of the monomer were observed in the polymer spectrum. The NMR spectrum of the polymer also shows three peaks at 7.06, 6.55 and 2.20 δ due to aromatic, methine and methyl protons, respectively. From these spectra, it seems that the structure of the polymer is more regular and may be due to the presence of —CH—CH— linkages without affecting other functional groups of the monomer. The polymer is appreciably soluble in chloroform, dimethylformamide, dimethylsulphoxide, tetrahydrofuran, dioxane and cyclohexanone.

The intrinsic viscosities $[\eta]$ of PMPMI at 30°C in chloroform, dimethylformamide and cyclohexanone were found to be 0.162, 0.137 and 0.074 dl

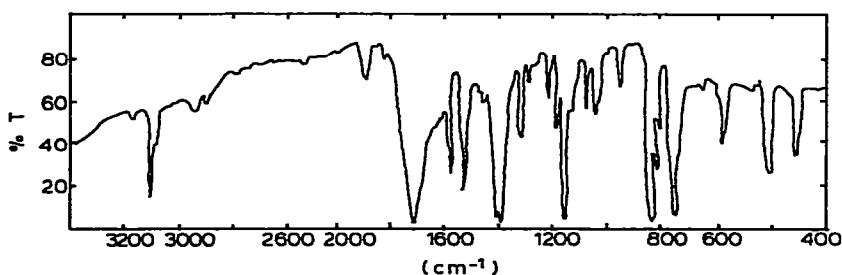


Fig. 1. IR spectrum of *N-p*-methylphenylmaleimide in KBr.

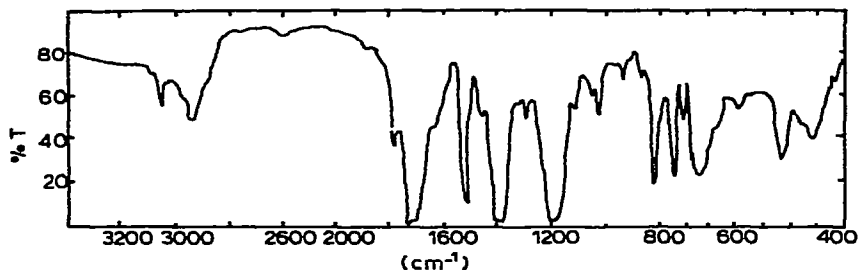


Fig. 2. IR spectrum of poly-*N-p*-methylphenylmaleimide in KBr.

g^{-1} , respectively. The data show the trend of intrinsic viscosities of the polymer in different solvents to be: chloroform > dimethylformamide > cyclohexanone. This may be due to the fact that the coil swells differently in different solvents and therefore has different sizes [15].

The number average molecular weight of the PMPMI (10 000) was determined by VPO. The comparatively low molecular weight product obtained during this reaction of addition polymerization by free radical initiator is due to the structure of the monomer itself. It is known [6] that the double bond of maleimide is characterized by an appreciable steric hindrance, taken as responsible for its low polymerization tendency in contrast to vinyl monomers which yield high molecular weight polymers.

TG and DTA curves for PMPMI are presented in Fig. 3. The TG curve clearly shows that the polymer is thermally stable up to 340°C, above which it slowly starts to lose weight and up to 430°C the weight loss is about 37%. This is corroborated by DTA data which show an exothermic peak at 340°C, indicating the onset of degradation reaction in the polymer. Beyond 430°C the weight loss was much slower, probably due to simultaneous chain rupture and crosslinking.

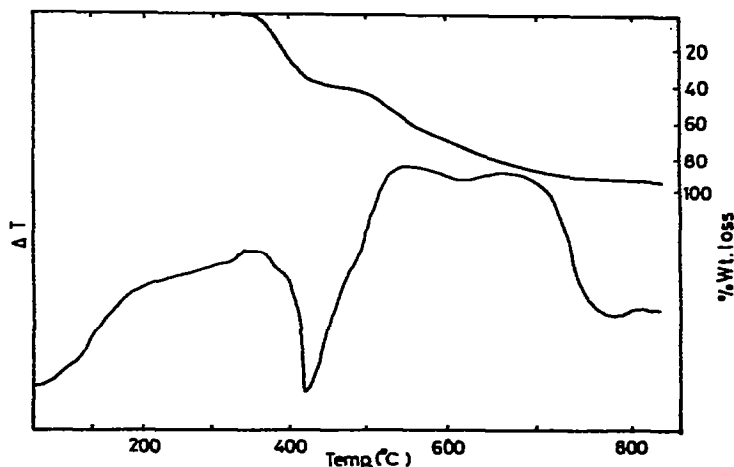


Fig. 3. DTA and TGA thermograms of poly-*N-p*-methylphenylmaleimide in air at 10°C min^{-1} .

TABLE 2
DTA data for poly-*N-p*-methylphenylmaleimide

Decomp. exotherm	Peak start temp. (°C)	Peak temp. (°C)	Peak end temp. (°C)	Order of decomp.	Energy of activation (kcal mole ⁻¹)
First	335	345	355		
Second	510	520	620	1.21	53.07
Third	620	665	775	1.45	49.45

From the above observations in DTA and TG data, it may be suggested that in the temperature range 345–430°C, the polymer chains undergo rupturing and crosslinking simultaneously, resulting in a more stable residue of the polymer than the initial polymer sample. At around 520°C, further degradation occurs and additional crosslinking is imparted, resulting in a more stable residue. Beyond 665°C, the residue instantaneously undergoes degradation into the volatile products.

The Reich method [16] was used for the evaluation of kinetic parameters of the thermal degradation of PMPMI. From the results (Table 2) it can be seen that the order of decomposition is close to 1, which is similar to the values reported in the literature [6]. However, the activation energies were in the range 49–54 kcal mole⁻¹, in contrast to the values of 42–93 kcal mole⁻¹ observed by Barrales-Rienda and Gonzalez Ramos [6].

Degradation behaviour

The polymer is stable up to 340°C, but on prolonged heating at 340–350°C degradation starts. The data on degradation at 340–350°C with respect to time are given in Table 3. The gaseous products of degradation were collected over the temperature range 340–350°C in air and tested with lime water, which showed the presence of carbon dioxide. The condensates on the wall of the reaction tube were collected and separated into different constituents by column chromatography on silica gel using ethyl acetate,

TABLE 3
Thermal degradation data for poly-*N-p*-methylphenylmaleimide at 340–350°C

Heating time (min)	Initial wt. of sample (g)	Wt. of residue (g)	Wt. loss (g)	% Wt. loss	Colour of residue
60	1.4246	1.2277	0.1969	13.8	Light brown
120	1.7731	1.4801	0.2930	16.5	Brown
180	1.9213	1.4062	0.5151	26.8	Dark brown

TABLE 4

Analysis of volatilized products from poly-*N-p*-methylphenylmaleimide at 340–350°C

No.	Volatilized substance	M.p. (°C)		Nitrogen (%)	
		Obsd.	Lit.	Reqd.	Found
1	<i>N-p</i> -Methylphenylsuccinimide	148	150	7.41	7.40
2	Dimer and trimer of <i>N-p</i> -methylphenylmaleimide			7.48	7.20
3	<i>N,N'</i> -Di- <i>p</i> -tolylurea	256	260	11.67	11.52

benzene and acetone (3 : 6 : 1) as eluant. After purification, the chemical structures of the isolated substances were determined on the basis of elemental analysis, IR spectra, the presence of a double bond, and melting points. The results are summarized in Table 4.

Original PMPMI is soluble in chloroform and dimethylformamide (DMF). However, the degraded polymer is insoluble in chloroform and sparingly soluble in DMF. Therefore, the degraded polymer was separated into two fractions by heating at 100°C with an excess of DMF. The dissolved fraction was separated by precipitation with excess methanol. The results are shown in Table 5.

The wt. % of the fraction insoluble in DMF increases with increase in heating time. This trend suggests that at a constant temperature range, the number of crosslinks of the polymer chains depends upon the time of heating of the original polymer sample. As the time of heating increases, the number of crosslinks increases. The 99% weight insoluble fraction at about 3 h indicates the maximum number of crosslinks.

The IR spectra of DMF-insoluble fractions of the degraded PMPMI are shown in Fig. 4. From examination of the IR spectra, it appears that all samples retain their PMPMI pattern. However, the appearance of unsaturation was indicated by the presence of a band at 1595 cm⁻¹ which may be due to C=C. The intensities of all important absorption bands decrease as the time of heating is increased.

TABLE 5

Fractionation data for degraded poly-*N-p*-methylphenylmaleimide at 340–350°C

Heating time (min)	Wt. residue (g)	Soluble in DMF (g)	Colour of soluble fraction	Insoluble in DMF (g)	Colour of insoluble fraction	Insoluble fraction (wt. %)
60	1.2277	0.2705	Dark green	0.9572	Light green	78.0
120	1.4801	0.1305	Brown	1.3496	Brown	91.1
180	1.4062	0.0070	Brown	1.3992	Reddish brown	99.5

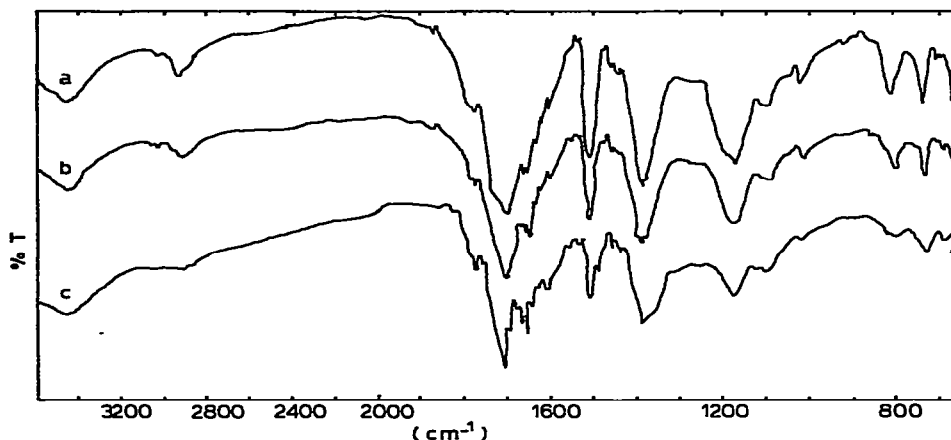


Fig. 4. IR spectra of DMT — insoluble fractions of poly-*N-p*-methylphenylmaleimide in KBr. Polymer sample heated for (a) 60 min at 340–350°C; (b) 120 min at 340–350°C; and (c) 180 min at 340–350°C.

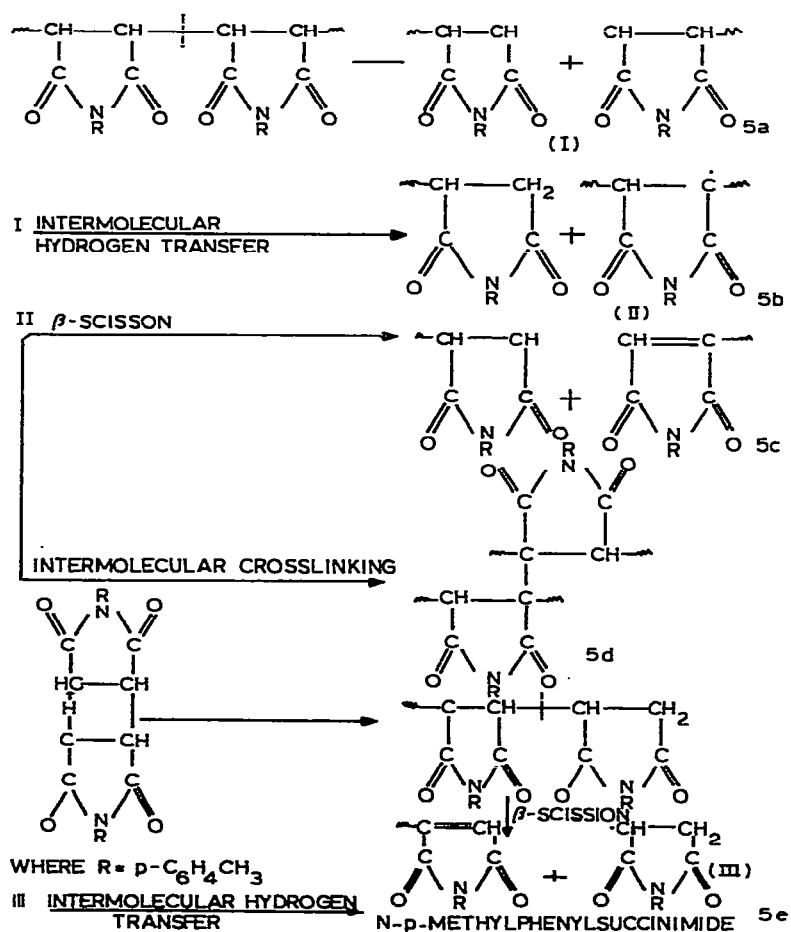


Fig. 5. Mechanism of degradation of PMPMI.

Degradation mechanism

The initial degradation of PMPMI may be due primarily to random scissions in the main chains, as shown in Fig. 5(a). The carbon atoms in the main chains of PMPMI are tertiary and C—C bonds in the main chains are in the β -position to the carbonyl groups. Furthermore, the degradation products consist mainly of *N-p*-methylphenyl succinimide, the dimer and trimer of *N-p*-methylphenylmaleimide, and *N,N*-di-*p*-tolylurea; no monomer is isolated. From the above results it is assumed that the thermal scission of the C—C bonds in the main chains at the β -position is accompanied by inter- and intramolecular hydrogen transfers, as shown in Fig. 5 (b and c). The intramolecular hydrogen transfers are due to a back-biting reaction, in which the hydrogen atoms attached to the 4-, 5- and 6-position carbons are abstracted by the end radicals. Abstraction of the hydrogen atom attached to the 4-position carbon leads to the formation of *N-p*-methylphenylsuccinimide (Fig. 5e). Similarly, abstraction of the hydrogen atoms attached to the 5- and 6-position carbons leads to the formation of the dimer and trimer of *N-p*-methylphenylmaleimide. The scission of both the C—C bonds and C—H bonds in the main chain is accompanied by scission of the imide rings, which results in the formation of *N,N'*-di-*p*-tolylurea and crosslinkage.

From these studies, it can be concluded that the thermal stability of PMPMI is almost the same as the fluorophenylmaleimides reported in the literature [10]. However, the thermal degradation process is complex. The mechanism of degradation is proposed as the scission in the main chains, inter- and intramolecular crosslinking, based on the observation of the degraded products.

ACKNOWLEDGEMENTS

The authors express their gratitude to the 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 discussions.

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