

## NEW N-(DIMETHYLAMINOPHENYL)MALEIMIDES AS COMPONENTS OF THE INITIATION SYSTEM TERTIARY AMINE-BENZOYL PEROXIDE

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Received March 18th, 1976

A number of crystalline N-(dimethylaminophenyl)maleimides copolymerizable with other ethylenically unsaturated monomers have been prepared, their melting points and solubilities have been determined, and the IR and NMR spectra have been measured. The rate constants of the reaction between benzoyl peroxide and the imides were determined in a benzene solution at 25°C and evaluated with respect to the structure of the imides. The initiation activity of the system benzoyl peroxide-imide was verified in the block polymerization of styrene.

The initiation systems benzoyl peroxide-N,N-dialkylaromatic amine are employed especially in dental surgery in cold-curing the methacrylate resins<sup>1,2</sup>. Their disadvantage consists in the possibility of diffusion of unreacted low-molecular weight tertiary amines and reaction products from the resulting polymers into the surrounding medium. The undesirable diffusion of toxic amines can be reduced by substituting the methyl substituents on the nitrogen atom with bulky alkyl substituents<sup>3</sup>, or completely eliminated by using polymers or copolymers containing tertiary amino groups<sup>4</sup> instead of low-molecular weight amines. However, in the two latter cases the reactivity of the tertiary amino groups with peroxide is weakened.

On curing methacrylate resins with newly prepared 2-(N-aryl-N-methylamino)ethyl methacrylates, which in the form of a copolymer with methyl methacrylate are incorporated in the cured resin we attained approximately the same curing rates as with commonly used N,N-dimethyl-p-toluidine<sup>5</sup>. 2-(N-Aryl-N-methylamino)ethyl methacrylates are liquid compounds and with 2,2'-azobis(isobutyronitrile) can be polymerized to soluble homopolymers.

We prepared a number of N-(dimethylaminophenyl)maleamic acids (*I*) (Table I), and from them crystalline N-(dimethylaminophenyl)maleimides (*II*) (Table II), which undergo homopolymerization with difficulty, but readily copolymerize with other common monomers. The maleimides were as follows: N-(2-dimethylaminophenyl)maleimide (*IIa*), N-(3-dimethylaminophenyl)maleimide (*IIb*), N-(4-dimethylaminophenyl)maleimide (*IIc*), N-(2-dimethylamino-5-methylphenyl)maleimide (*IId*), N-(3-dimethylamino-6-methylphenyl)maleimide (*IIe*), N-(4-dimethylamino-2,6-dimethylphenyl)maleimide (*IIf*), of which only *IIc* has been described in the literature<sup>6</sup>.

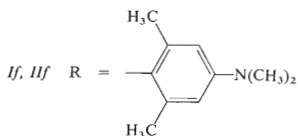
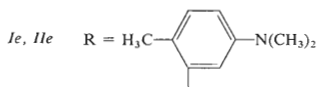
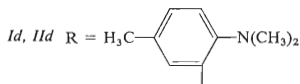
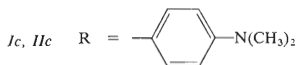
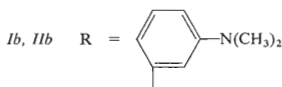
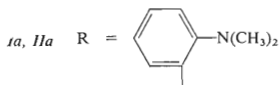
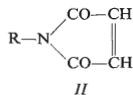
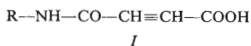


TABLE I

Characteristics of N-Substituted Maleamic Acids of the General Formula R-NH-CO-CH=CH-COOH (*I*)

<i>I</i>	Molecular formula (mol. weight)	Yield <sup>a</sup> %	M.p., °C	Calc./Found			Colour
				% C	% H	% N	
<i>a</i>	C <sub>12</sub> H <sub>14</sub> N <sub>2</sub> O <sub>3</sub> (234.3)	39	150-1	61.51	6.03	11.97	green-yellow
				60.94	6.09	11.62	
<i>b</i>	C <sub>12</sub> H <sub>14</sub> N <sub>2</sub> O <sub>3</sub> (234.3)	94	172-4	61.51	6.03	11.97	orange-yellow
				61.53	6.05	11.79	
<i>c<sup>b</sup></i>	C <sub>12</sub> H <sub>14</sub> N <sub>2</sub> O <sub>3</sub> (234.3)	80	200-3	—			deep red
<i>d</i>	C <sub>13</sub> H <sub>16</sub> N <sub>2</sub> O <sub>3</sub> (248.3)	60	102-4	62.87	6.50	11.29	green-yellow
				62.61	6.62	11.19	
<i>e</i>	C <sub>12</sub> H <sub>16</sub> N <sub>2</sub> O <sub>3</sub> (248.3)	86	134-5	62.87	6.50	11.29	orange
				62.75	6.48	11.08	
<i>f</i>	C <sub>14</sub> H <sub>18</sub> N <sub>2</sub> O <sub>3</sub> (262.3)	91	152-4	64.10	6.92	10.68	orange-red
				63.68	6.75	9.90	

<sup>a</sup> With respect to aniline; <sup>b</sup> Described in ref.<sup>6</sup>.

The assumed structure of N-(dimethylaminophenyl)maleimides is confirmed by their IR spectra (Fig. 1). The absorption values in the range from 670 to 840  $\text{cm}^{-1}$  correspond to the characteristic out-of-plane vibrations of the C—H bonds of the benzene ring, to which one may also assign three absorption maxima near 1455, 1515 and 1615  $\text{cm}^{-1}$ . In the range from 900 to 1100  $\text{cm}^{-1}$  the spectrum of homopolymers *Ile* and *Ilf* (with a saturated imide ring) contains one pronounced absorption band near 1040  $\text{cm}^{-1}$ , while monomers possess further three bands in the same region at 950, 980 and 1070  $\text{cm}^{-1}$ . The valency vibration of the C=C bond in the imide ring of the monomer can be responsible for the absorption maximum near 1580  $\text{cm}^{-1}$ , which is missing in the spectrum of homopolymers *Ile* and *Ilf* (in the spectrum of *Ila* it is probably overlapped by an adjacent band). The maleimide ring is clearly distinguished from the maleisoimide ring by the absorption of the CO group near 1720  $\text{cm}^{-1}$ ; the carbonyl group of the latter ring absorbs at a wave number higher than 1800  $\text{cm}^{-1}$ . The absorption maxima in the range from 2800

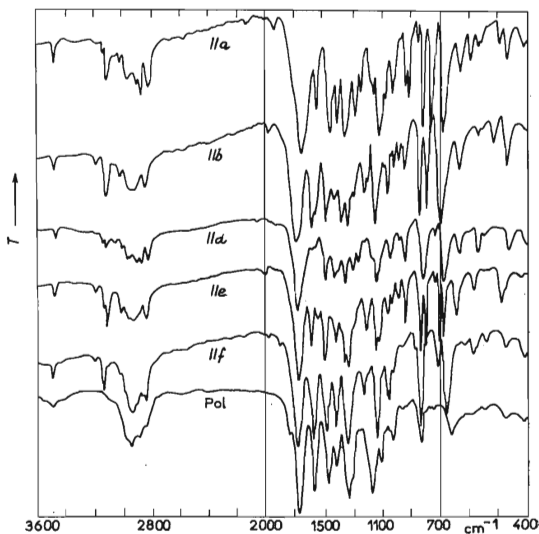


FIG. 1  
IR Spectra of N-(Dimethylaminophenyl)maleimides *Ila,b,d,e,f* and of Homopolymer *Ilf* (Pol)

to  $3000\text{ cm}^{-1}$  correspond to the characteristic valency vibrations, while the band in the range from  $1360$  to  $1380\text{ cm}^{-1}$  corresponds to the deformational vibrations of the  $\text{CH}_3$  groups. A pronounced maximum near  $3100\text{ cm}^{-1}$  is exhibited by all monomers, but not by the homopolymer. It can probably be assigned to the vibrations of the  $=\text{C}-\text{H}$  bonds in the imide ring of monomers *IIf*–*IIf*.

The chemical shifts of protons in the NMR spectra of imides *IIf*–*IIf* are summarized in Table III. The higher screening of the b protons in *IIf* and *IId* indicates that the electron density on the nitrogen atom of their tertiary amino group is lower than on the nitrogen atom of imides *IIf*, *IIf*, *IIf*. The intensities of signals at the recorded  $\tau$  values are proportional to the number of the respective protons *a*, *b*, *c*, *d*.

#### Reaction of N-(Dimethylaminophenyl)maleimides with Benzoyl Peroxide

The rate constants (*k*) of a bimolecular reaction of peroxide with the dimethylamino group of monomers *IIf*–*IIf* were calculated using the determined time losses of  $\text{Bz}_2\text{O}_2$  in mixtures with N-(dimethylaminophenyl)maleimides (starting concentra-

TABLE II

Characteristics of N-Substituted Maleimides of the General Formula  $\text{R}-\text{N} \begin{array}{l} \diagup \text{CO}-\text{CH} \\ \diagdown \text{CO}-\text{CH} \end{array} \quad (\text{II})$

<i>I</i>	Molecular formula (mol. weight)	Yield <sup>a</sup> %	M.p., °C	Calc./Found			Colour (absorption part of spectrum)
				% C	% H	% N	
<i>a</i>	$\text{C}_{12}\text{H}_{12}\text{N}_2\text{O}_2$ (216.2)	27	104–6	66.64	5.60	12.96	light-yellow
				66.56	5.72	12.69	(violet)
<i>b</i>	$\text{C}_{12}\text{H}_{12}\text{N}_2\text{O}_2$ (216.2)	61	98–9	66.64	5.60	12.96	yellow
				66.63	5.68	12.98	(blue)
<i>c</i> <sup>b</sup>	$\text{C}_{12}\text{H}_{12}\text{N}_2\text{O}_2$ (216.2)	80	153–4	—			red-brown (green-blue)
<i>d</i>	$\text{C}_{13}\text{H}_{14}\text{N}_2\text{O}_2$ (230.3)	50	59–61	67.79	6.13	12.18	yellow
				67.31	6.10	11.98	(blue)
<i>e</i>	$\text{C}_{13}\text{H}_{14}\text{N}_2\text{O}_2$ (230.3)	76	85–6	67.79	6.13	12.18	orange
				67.44	6.12	12.09	(green-blue)
<i>f</i>	$\text{C}_{14}\text{H}_{16}\text{N}_2\text{O}_2$ (244.3)	54	136–8	68.83	6.60	11.47	yellow-orange
				68.71	6.74	11.37	(green-blue)

<sup>a</sup> With respect to maleamic acid; <sup>b</sup> Described in ref.<sup>6</sup>.

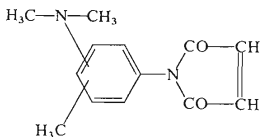
tions of both compounds  $36.6 \text{ mmol dm}^{-3}$  and 2,2-diphenyl-1-picrylhydrazyl ( $9.3 \text{ mmol dm}^{-3}$ ) at  $25^\circ\text{C}$ .

Imide <i>II</i> :	<i>a</i>	<i>b</i>	<i>c</i>	<i>d</i>	<i>e</i>	<i>f</i>
$k \cdot 10^4, \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$	0.35	3.93	11.5	1.29	11.5	9.01

The accuracy of determinations by the described procedure lies within  $\pm 5\%$ .

Similarly to 2-(*N*-aryl-*N*-methylamino)ethyl methacrylates<sup>7</sup>, for *N*-(dimethylaminophenyl)maleimides one can also see a relation between their rate constant with  $\text{Bz}_2\text{O}_2$  and electron density on the nitrogen atom of their tertiary amino group. The chemical shifts ( $\tau$ ) of the protons *b* in Table III indicate that the tert-amino group of imides *IIa*, *IIc* is the weakest electron donor with respect to benzoyl peroxide. Both these imides possess the dimethylamino group on the benzene ring in the position *ortho* with respect to the imido group, and the rate constant of their reactions with benzoyl peroxide is lower by an order of magnitude than that of the other imides. The correlation just mentioned cannot probably be assumed in the group of imides *IIb, c, e, f*; the differences between the rate constants of their reactions with benzoyl peroxide can rather be a consequence of different pre-exponential factors

TABLE III  
Characteristics of the H-NMR Spectra of *N*-(Dimethylaminophenyl)maleimides



Imide	Chemical shift ( $\tau$ ) of protons on ppm <sup>a</sup>			
	(a)	(b)	(c)	(d)
<i>IIa</i>	—	7.40	3.18	2.53—3.0; 3.20—3.25
<i>IIb</i>	—	7.10	3.25	2.65—2.83; 3.27—3.49
<i>IIc</i>	—	7.05	3.24	2.84; 2.92; 3.22; 3.30
<i>IIc</i>	7.70	7.44	3.20	2.74—3.08; 3.22—3.61
<i>IIe</i>	7.99	7.10	3.21	2.74—2.91; 3.24—3.61
<i>IIf</i>	7.93	7.07	3.17	3.50

<sup>a</sup> Belongs to protons (a): in methyl groups of phenyl ring, (b): in methyl groups of nitrogen, (c): of maleimide ring, (d): of phenyl ring

than of insignificant changes in the activation energies corresponding to the differences between the  $\tau$  values of the b protons.

Although the rate constants of reactions of  $Bz_2O_2$  with imides *IIf*, *Ic*, *e*, and *f* in the benzene solution were lower by an order of magnitude than those with N,N-dimethyl-*p*-toluidine<sup>8</sup> ( $0.0126 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ ), the initiation system  $Bz_2O_2$ -*Ic* was more effective in the isothermal polymerization of styrene (25°C) than the system  $Bz_2O_2$ -N,N-dimethyl-*p*-toluidine. By using the former, we obtained in 5 h 8.5% and in 48 h 35.2% of the crosslinked copolymer of styrene with *Ic*, while the latter yielded respectively 8% and 9.9% of the soluble low-molecular weight polystyrene ( $[\eta] = 20 \text{ cm}^3/\text{g}$  (benzene, 25°C)). It should also be noted that with the system  $Bz_2O_2$ -*Ic* the amount of the polymer was still increasing after staying for 48 h, while the initiation system  $Bz_2O_2$ -N,N-dimethyl-*p*-toluidine was virtually exhausted after 7 h of the reaction. The observed differences between the two initiation systems are in accordance with the assumed chain course of the reaction of  $Bz_2O_2$  with tertiary amines<sup>8</sup>, which even in styrene is not completely suppressed. The incorporation of the tertiary amino group into crosslinked polymer chains probably reduces the reaction rate of the benzoyloxy radical with the tertiary amino group



and of the termination reactions of the C-amine radicals with the polystyrene radicals. (The crosslinking of polymers with the tertiary amino groups by means of benzoyl peroxide has been explained earlier<sup>9,10</sup>.)

The colour of the imides is related to changes in the rate constants. Table II shows that absorptions in the visible part of the spectrum are shifted from the long-wave range (blue-green) to the short-wave range (violet) in the order *Ic*, *Ie*, *IIf*, *IIf*, *IId*, *IId*, *IId*, in which the rate constants of reactions of imides with benzoyl peroxide also decrease. The dependence indicates that the light absorption in the ultraviolet and visible parts of the spectrum can become a sensitive indicator of the electron-donor ability of the tertiary amino group of N-(dimethylaminophenyl)maleimides, and thus also of the effectivity of the initiation systems imide-benzoyl peroxide. An investigation of this dependence and of the relationship between the structure of imides and the characteristics of their homopolymerization or copolymerization is still in progress.

## EXPERIMENTAL

## Starting and Model Compounds

Dimethylaminoanilines were prepared from the respective nitroso- or nitro-N,N-dimethylanilines by reducing them with stannous chloride<sup>11</sup>. They were chromatographically pure and their boiling points or melting points corresponded to the literature data: 2-dimethylaminoaniline<sup>12</sup>, b.p. 102.5°C/1300 Pa, from 2-nitro-N,N-dimethylaniline<sup>13</sup>; 3-dimethylaminoaniline<sup>14</sup>, b.p. 81°C/13 Pa, from 3-nitro-N,N-dimethylaniline<sup>15</sup>; 4-dimethylaminoaniline<sup>11</sup>, b.p. 133°C/1800 Pa, m.p. 41°C, from 4-nitroso-N,N-dimethylaniline<sup>11</sup>; 2-dimethylamino-5-methylaniline<sup>16</sup>, b.p. 113°C/1800 Pa, from 2-nitro-4,N,N-trimethylaniline<sup>17</sup>; 3-dimethylamino-6-methylaniline<sup>18</sup>, m.p. 50°C, from 3-nitro-4,N,N-trimethylaniline<sup>18</sup>; 4-dimethylamino-2,6-dimethylaniline, b.p. 94°C/13 Pa, from 4-nitroso-3,5,N,N-tetramethylaniline<sup>19</sup>. Maleic anhydride, acetic anhydride and potassium iodide were reagent grade. Benzoyl peroxide was 99% (iodometrically). The solvents used ("pure") were redistilled on a Bruun column with 32 theoretical plates.

N-(Dimethylaminophenyl)maleamic acids (*Ia*–*If*) were prepared from the above anilines and maleic anhydride similarly to N-phenyl maleamic acid<sup>20</sup>. They were purified by crystallization from ethanol, ethyl acetate or benzene (Table I). They are readily soluble in 5% solution of sodium hydrocarbonate, ethanol, acetone, chloroform, acetic acid, dimethylformamide, in hot water and in hot ethyl acetate. Their solutions in dilute (5%) hydrochloric acid and acetic acid are colourless. In a solution of acetic anhydride the acids *Ia*–*If* were dehydrocyclized to yield the corresponding N-(dimethylaminophenyl)maleimides<sup>20</sup> (*Ila*–*IIf*, Table II). They were purified by dissolving in 5% aqueous solution of hydrochloric acid, precipitation with 5% solution of NaHCO<sub>3</sub> and crystallization of the dried precipitate from cyclohexane. They dissolve readily in aromatic and halogenated hydrocarbons, ethers, esters, ketones and in dilute mineral acids.

## Analytical Techniques

Dimethylaminoanilines were analyzed by using a gas chromatograph Chrom 3, Laboratorní přístroje, Prague, packed with 10% SE on Chromosorb W. The IR spectra of N-(dimethylaminophenyl)maleimides were recorded with a Perkin-Elmer 621 spectrometer by employing the KBr technique; the NMR spectra were measured with a PS-100 (JEOL) spectrometer at 100 Mc/s with HMDS as the internal standard ( $\tau = 9.95$ ). 10% (*W/v*) solutions of imides in CDCl<sub>3</sub> were prepared for measurements of the NMR spectra.

## Experimental Techniques

The reaction rate of benzoyl peroxide with N-(dimethylaminophenyl)maleimides was investigated iodometrically<sup>18</sup> in a benzene solution at 25°C and at an equimolar concentration of both components corresponding to 36.6 mmol dm<sup>-3</sup>. 2,2-Diphenyl-1-picrylhydrazyl was used in an amount of 9.3 mmol dm<sup>-3</sup>. From samples of the reaction mixture, N-(dimethylaminophenyl)maleimides were extracted with 0.2M solution of hydrochloric acid prior to the determination of the peroxide content. The block polymerization of styrene initiated with the systems N,N-dimethyl-*p*-toluidine–benzoyl peroxide and N-(4-dimethylaminophenyl)maleimide–benzoyl peroxide was carried out in sealed glass ampoules free from oxygen at 25°C. The equimolar concentration of both initiation components corresponded to 36.6 mmol dm<sup>-3</sup>. Polystyrene was precipitated from the polymerization mixture with a sevenfold volume of ethanol and dried at room temperature to constant weight. Heating of the solution of N-(dimethylaminophenyl)maleimide (0.5 g)

and 2,2'-azobis(isobutyronitrile) (0.003 g) in benzene (0.6 g) at 70°C for 24 h followed by diluting the solution with a sevenfold volume of ethanol yielded colourless homopolymers of *Ile* and *Ilf*.

*The authors are indebted to Dr H. Pivcová and Dr P. Schmidt for measurements of the IR and NMR spectra and for assistance in their interpretation.*

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Translated by L. Kopecká.