INTERACTION BETWEEN AMINES AND POLY(*N*-PHENYLMALEIMIDES)

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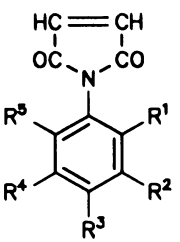
Dedicated to Professor Otto Wichterle on the occasion of his 80th birthday.

The interactions of substituted poly(*N*-phenylmaleimides) with low- and high-molecular-weight amines were studied. Colourless chloroform solutions of polymers, which carry electron-attracting substituents in benzene rings, turn intensively red on addition of amines in neutral or basic media depending on the nucleophilicity and accessibility of amino groups. Absorption spectra of the solutions in the visible range suggest that the formation of colour complexes consists in an interaction of free electron pairs of amines with adjacent carbonyl groups of the polyimides.

In an earlier paper we described interactions between carbonyl and amine groups which take place in copolymers of 2-dimethylaminoethyl methacrylate with *N*-phenylmaleimide[1]. Using potentiometric titration and UV-visible spectroscopy, we demonstrated that such interaction results in the formation of energetically favourable chromophores which give rise to an intensive red colour of the copolymers. This study concerns the interactions of homopolymers of *N*-phenylmaleimides *I* with low- and high-molecular-weight amines leading to the formation of chromophores absorbing in the range of wavelengths 494 – 510 nm.



I

I	R^1	R^2	R^3	R^4	R^5
a	H	Me_2N	H	H	H
b	H	Me_2N	H	H	Me
c	Cl	H	Cl	H	Cl
d	Br	H	Br	H	Br
e	Cl	Cl	Cl	Cl	Cl
f	Br	Br	Br	Br	Br

EXPERIMENTAL

Materials

N-(3-Dimethylaminophenyl)maleimide (*Ia*) (m.p. 98 °C), *N*-(2-methyl-5-dimethylaminophenyl)maleimide (*Ib*) (m.p. 85 °C), *N*-(2,4,6-trichlorophenyl)maleimide (*Ic*) (m.p. 134 °C), *N*-(2,4,6-tribromophenyl)maleimide (*Id*) (m.p. 142 °C), *N*-(pentachlorophenyl)maleimide (*Ie*) (m.p. 152 °C), *N*-(pentabromophenyl)maleimide (*If*) (m.p. 215 °C), were prepared by cyclodehydration of the corresponding maleamic acids[2].

Commercial amines were distilled at normal or reduced pressure in a stream of nitrogen prior to use. Tribenzylamine and 1,4-diazabicyclo[2.2.2]octane were used without special purification. Diisopropylethylamine was obtained by the reaction of diisopropylamine and ethyl iodide (mole ratio 2 : 1) in acetone and purified by distillation, b.p. 127 °C. The synthesis of 2-dimethylaminoethyl pivalate was described previously[3].

Poly(*N*-phenylmaleimides) and poly(*N*-butylmaleimide) were prepared by the radical polymerization of monomers *Ia* – *If* and *N*-butylmaleimide[4] in benzene or chloroform solutions using azobis(isobutyronitrile) as initiator[5,6]. The number-average molecular weights of poly(*Ia*) – poly(*If*) were 3 000, 3 300, 1 100, 1 650, 1 380, 2 270, respectively. Alternating copolymers of imides and styrene were obtained in a similar way. Poly(2-dimethylaminoethyl methacrylate) was prepared by radical polymerization[7].

Methods

Visible spectra were recorded in chloroform solutions immediately after mixing of the components using a Hewlett–Packard 8541 A spectrometer and a 1 cm cell. The concentration of monomeric units of poly(*N*-phenylmaleimides) was about 0.003 mol/l. The number-average molecular weights of poly(*Ia*) – poly(*If*) were determined in benzene with a Perkin–Elmer osmometer, model 115.

RESULTS AND DISCUSSION

Poly(*N*-phenylmaleimides) prepared by radical polymerization of *I* are white powdery substances, readily soluble in chloroform to colourless solutions. After addition of some amines the solutions of poly(*I*) turn immediately intensively red. The experiments carried out to elucidate this phenomenon gave the following results:

a) Colour changes take place only in solutions of those poly(*N*-phenylmaleimides) in which the phenyl rings carry chlorine or bromine substituents (Table I). If the rings are substituted with dimethylamino or methyl groups no colour appears. Similarly, poly(*N*-butylmaleimide) or unsubstituted poly(*N*-phenylmaleimide) does not cause any colouration.

b) In the series of amines, colouration with poly(*Ic*) is developed by low- and high-molecular-weight aliphatic amines, but not by aniline and its *N*-methyl derivatives or tribenzylamine.

c) Chloroform solutions of monomeric imides *Ia* – *If* and *N*-butylmaleimide remain colourless on addition of triethylamine.

d) Alternating copolymers prepared by the copolymerization of monomers *Ic* – *If* with styrene[8] do not form coloured solutions with triethylamine.

e) In all the coloured poly(*N*-phenylmaleimide)–amine complexes the absorption maxima vary within a narrow range between 494 and 510 nm (Table I).

f) Acidification of coloured solutions brings about their discolouration. The process is reversible: the solutions get coloured again if alkalized.

The results suggest that a necessary condition for the formation of a colour complex is the cumulation of *N*-phenylmaleimide units. This means that the formation of the chromophore involves an interaction of adjacent imide units in the polymers with a low- or high-molecular-weight amine similarly to the interaction of the carbonyl and amino groups in low-molecular-weight compounds[1]. The interaction is facilitated by the presence of halogen substituents which change the polarity of the C=O bond. Other things being the same, the increasing number of halogen substituents in the phenyl ring enhances the intensity of colouration (molar absorptivity) of the complex with triethylamine. The nature of halogen substituents in aromatic rings also influences the intensity of colouration; the molar absorptivities of bromo derivatives are higher than those of the corresponding chloro derivatives (Table I). The interaction disappears on acidifying the solution, as the free electron pair of the amino group is no more available. Since the measured absorption maxima of all complexes under investigation lie in a very narrow range (Table I), one may assume that their spatial arrangement will be sufficiently uniform and almost independent of the content and the kind of halogen substituents in the phenyl ring and on the type of amine participating in the complex formation. Since no colour complex is formed with alternating copolymer *N*-phenylmaleimide–styrene the carbonyl–amine–carbonyl interaction takes place obviously only between two adjacent *N*-phenylmaleimide units. Figure 1 shows a typical dependence of the molar absorptivity on the molar ratio of amine/imide units in the chloroform solution of

TABLE I
Absorption spectral data of poly(*N*-phenylmaleimide)–amine complexes

Polymer complex	ε, m^2mol^{-1}	λ_{max}, nm
Poly(*Ic*)–poly(2-dimethylaminoethyl methacrylate)	4.6	510
Poly(*Ic*)–2-dimethylaminoethyl pivalate	9.5	502
Poly(*Ic*)–diisopropylethylamine	12.4	500
Poly(*Ic*)–diisopropylamine	15.7	500
Poly(*Ic*)–1,4-diaza[2.2.2]bicyclooctane	18.0	499
Poly(*Ic*)–ethylamine	18.0	494
Poly(*Ic*)–diethylamine	19.5	504
Poly(*Ic*)–triethylamine	12.6	504
Poly(*Id*)–triethylamine	14.8	506
Poly(*Ie*)–triethylamine	32.5	500
Poly(*If*)–triethylamine	46.9	506

poly(*Ic*)–triethylamine. It can be seen in the plot that in a dilute solution the molar absorptivity is independent of the molar ratio only if it exceeds 30. If we assume that the interaction between the amine and imide units accompanied by complex formation is an equilibrium one, then the thirtyfold excess of amine is sufficient for practically complete bonding of the imide units in the complex. From the data presented in Fig. 1, we tried to estimate the constant of complexity (K), and the number of amine molecules (m) and of imide units (n) bound in the complex in equilibrium

$$m \text{ amine} + n \text{ imide} \overset{K}{\rightleftharpoons} \text{complex},$$

where

$$K = \frac{[\text{complex}]}{[\text{amine}]^m [\text{imide}]^n}.$$

By using the iterative least square method[9] we calculated $K \sim 3$, $m \sim 0.6$, and $n \sim 0.7$ for the complex poly(*Ic*)–triethylamine, i.e. the ratio amine/imide units is close to unity in the complex under consideration.

It is difficult to estimate the effect of the constitution of amine on the complex formation. Apparently, basicity is not the property which would define in a straightforward way the strength of interaction. Thus, e.g., a relatively strong base, tribenzylamine, in a mixture with poly(*Ic*) yields no colour complex at all, unlike weaker bases such as 1,4-diazabicyclo[2.2.2]octane. Neither is the effect of substituent size in the amine unequivocal: the sterically hindered diisopropylethylamine causes a colour change in the solution of poly(*Ic*) in contrast to aniline whose nitrogen is more accessible.

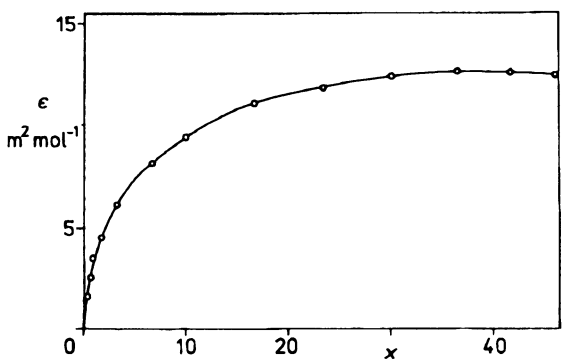


FIG. 1.
Dependence of the molar absorptivity at λ_{max} of the poly(*Ic*)–triethylamine complex in $CHCl_3$ on the molar ratio (x) triethylamine/imide units

Poly(2-dimethylaminoethyl methacrylate) yields a colour complex with poly(*Ic*) which is the least stable (the lowest ε, Table I). This fact can be attributed to the difficult access of most amino groups of polyamine to the carbonyl groups of adjacent units in the polyimide. A certain influence may also be exerted by the somewhat reduced basicity[10] of the polymethacrylate similarly to the low-molecular-weight 2-dimethylaminoethyl pivalate.

CONCLUSION

The colour complexes poly[*N*-(halogenophenyl)maleimide]–amine are formed by an interaction between the amino group and the carbonyl groups of the adjacent units of the polyimide. Apparently, nucleophilicity and accessibility of the amino group play an important role in the formation of this complex.

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