

# ADDITION OF PHENOL AND BENZIMIDAZOLE TO THE DOUBLE BOND OF N-PHENYLMALEIMIDE

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## Summary

The characteristics of the polyaddition of bismaleimides and bifunctional nucleophilic compounds were studied by means of model compounds. The nucleophilic addition of *N*-phenylmaleimide and phenol was found to proceed with good yield in the presence of tetraethylammonium chloride and sodium phenolate catalysts. The reaction of *N*-phenylmaleimide and benzimidazole yielded 2-(*N*-phenylsuccinimide)-benzimidazole. The optimum conditions for the nucleophilic addition reaction were established. The results indicated that the range of monomers used to produce bismaleimide-based polymers can be extended to include compounds containing phenol and benzimidazole groups.

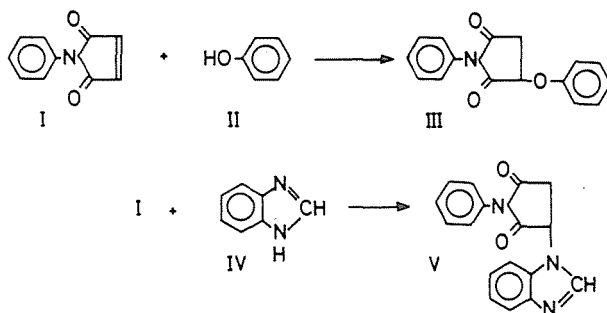
Intense investigations on the synthesis of polymers by the polyaddition of bisimides of unsaturated acids with various nucleophilic reactants [1-9] are of great interest, since the polymers obtained have very good properties in use, only slightly inferior to those of aromatic polyimides, while their processing can be carried out under relatively mild conditions, without volatiles being evolved.

In this series, polyaspartimides have been studied in greatest detail [1, 2, 9]. They are obtained in the reaction of *N,N'*-bismaleimides with aliphatic and aromatic diamines and their commercialization has been started [3, 9].

By reason of the great practical value of such polymers, it appeared of interest to extend the range of monomers utilized for this purpose, allowing to formulate more general characteristics of the process. In this context, modelling of the chemical processes taking place in polymer formation gain importance, in view of the presence of the two reactive groups of the bisimide and consequently the possibility of side reactions taking place.

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In this work we studied—as model reaction—the addition of phenol and benzimidazole to *N*-phenylmaleimide:



### Experimental

*N*-phenylmaleimide (I) was obtained with a yield of 65% from maleic anhydride and aniline in acetone, in the presence of sodium acetate and acetic anhydride. M. p. 89–90 °C (from cyclohexane), agreeing with the data in the literature [10].

Phenol (II) was purified by distillation. M.p. 43 °C.

Benzimidazole (IV) was obtained with a yield of 89% by heating *o*-phenylene diamine in formic acid. M.p. 170–172 °C (from water). Literature data 170–172 °C.

3-Phenoxy-*N*-phenylsuccinimide (III) is a finely crystalline white substance, soluble in acetone, chloroform, alcohols, amide solvents. M. p. 198–200 °C (from *n*-butanol).  $C_{16}H_{13}NO_3$ .

Calcd. %: C 71.16; H 4.86; N 5.24.

Found, %: C 71.69; H 4.90; N 5.37.

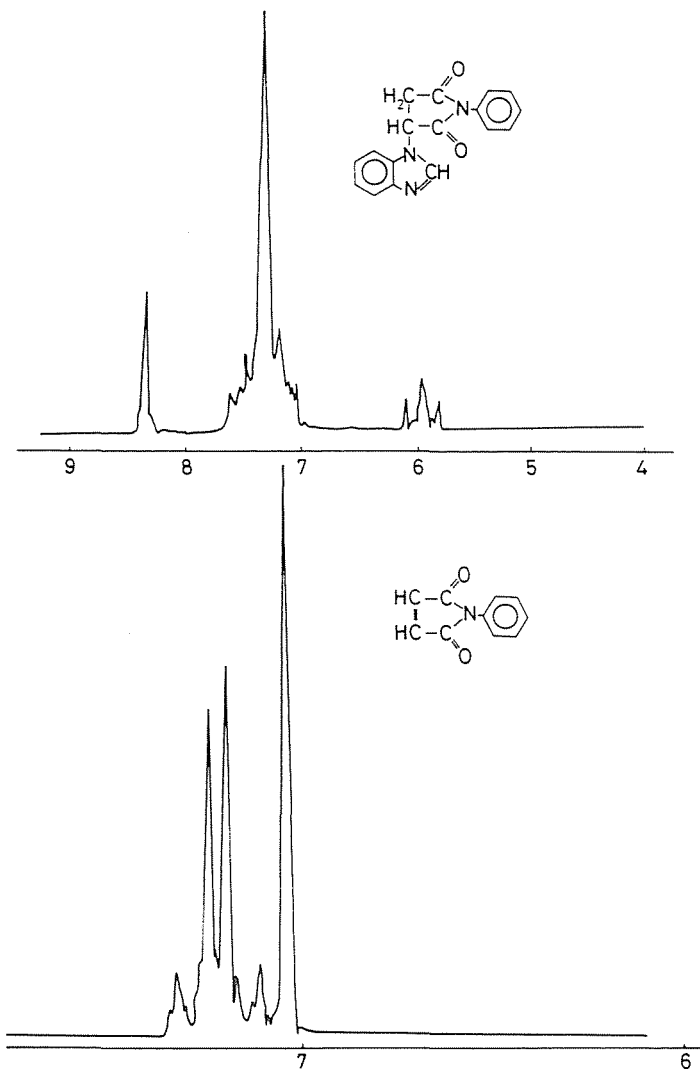
Molecular mass determined by mass spectroscopy: 267. Calculated: 267.192. IR spectrum ( $\nu$ ,  $cm^{-1}$ ): 1700 intense, 1770 weak (C=O), 1220 (=C—O—), 700, 760 ( $C_6O_5$ —). PMR spectrum ( $\sigma$ , ppm): 3.16 (m) 1H; 3.01 (m) 2H, 8.32 10H ( $C_6H_5$ ). UV spectrum ( $\lambda$ , nm): 204.5 (lg  $\epsilon$  4.36); 219.3 (lg  $\epsilon$  4.32); 268.6 (lg  $\epsilon$  3.32); 275 (lg  $\epsilon$  3.19).

2-*N*-Phenylsuccinimidebenzimidazole (V). White crystalline substance soluble in acetone, dioxan, *N,N'*-dimethylformamide. It was recrystallized from a mixture of acetic acid and water and did not melt before decomposition.

Calcd. %: C 73.63; H 4.72; N 10.10

Found, %: C 73.56; H 4.69; N 10.05.

IR spectrum ( $\nu$ ,  $cm^{-1}$ ): 1700 intense, 1770 weak (C=O); 1400 (—CH<sub>2</sub>—CO—); 1500, 1510, 1620 (aromatic and condensad systems); 700, 760 ( $C_6H_5$ , —O— $C_6H_4$ ).



*Instruments.* IR absorption spectra were recorded with an UR-20 spectrophotometer in the range of 400 to 3600  $\text{cm}^{-1}$ , using 0.1–4 mg samples prepared with optical grade KBr. PMR spectra were taken with a Tesla BS-497 spectrometer (100 MHz) in  $(\text{CD}_3)_2\text{CO}$  and  $\text{CDCl}_3$ . Electron spectra were recorded with a Specord UV-VIS spectrophotometer in ethanolic solution (concentration:  $10^{-4}$  mol/l). Mass spectra were taken with a MS-902 spectrometer at 180 °C and 11 Torr pressure.

## Discussion of the results

The presence of C=O groups (strong electron acceptors) in maleic acid derivatives including maleimides results in the desactivation of the C=C bond in electrophilic activation reactions, that is, the double bond is less reactive towards halogens, hydrogen halides and similar electrophilic compounds. For such bonds, nucleophilic addition reactions are characteristic. However, our attempts to carry out the reaction of N-phenylmaleimide with phenol in the melt and in solution, using polar organic solvents, were unsuccessful even at temperatures exceeding 170 °C. This is presumably explainable by the lesser nucleophilicity of phenol as compared to amines. Detailed studies demonstrated that 3-phenoxy-N-phenylsuccinimide formation takes place when N-phenylmaleimide is heated with excess phenol in the presence of catalytic amounts of tetraethylammonium chloride (TEAC). According to the data in Table 1, the yield of (III) increases from 2% to 44%, when the temperature is

Table 1

Synthesis conditions of 3-phenoxy-N-phenylsuccinimide in melt

Catalyst	Amount of catalyst, %*	Temperature °C	Time, min	Yield, %
—	—	170—180	300	—
Triethyl amine	5	150—170	300	—
TEAC	5	150	300	2
TEAC	5	180	300	44
C <sub>6</sub> H <sub>5</sub> ONa	5	70—80	25	58
C <sub>6</sub> H <sub>5</sub> ONa	5	50—55	25	57
C <sub>6</sub> H <sub>5</sub> ONa	5	50—55	35	60
C <sub>6</sub> H <sub>5</sub> ONa	3	70—80	180	36
C <sub>6</sub> H <sub>5</sub> ONa	3	70—80	25	25
C <sub>6</sub> H <sub>5</sub> ONa	1,5	50—55	15	20

\* Relative to the total equivalent mass of the initial reactants

raised from 150 °C to 180 °C. The phenol excess present ensures protonization of the anions being formed, preventing anionic polymerization of the N-phenylmaleimide.

In the IR spectrum of the addition product 3-phenoxy-N-phenylsuccinimide a slight shift ( $\nu = 10 \text{ cm}^{-1}$ ) of the valence absorption band of the carbonyl group towards the low-frequency range is observed; the characteristic signals of *cis*-vinyl protons are absent in the PMR spectrum ( $\sigma = 1.05 \text{ ppm}$ ). Also, the bathochromic shift of the benzene chromophoric group and the hyperchromic effect in the electron spectrum as compared to that of the initial N-phenylmaleimide correspond to the addition product of one mol of phenol to the C=C bond of N-phenylmaleimide, not interfering with the imide cycle.

Both reaction temperature and time could be substantially reduced by using sodium phenolate as catalyst. 60% yields could be attained at temperatures as low as 50–80 °C after 25–40 minutes. Further increase of reaction time does not practically affect yield.

The data in Table 1 indicate that reduced amounts of sodium phenolate result in lower yields. However, higher amounts of the catalyst might promote the alternative path, i.e. anionic polymerization of N-phenylmaleimide.

It is known from literature data that side reactions may occur in polyaspartimide synthesis, such as peramidation of the imide cycles of maleimide or aspartimide fragments [12], or else the formation of intermolecular C=N bonds [13], interfering with the polymer formation process. In modelling the polyaddition processes on the system phenol-N-phenylmaleimide, these phenomena are obviously unlikely to occur, since even when N-phenylmaleimide and 3-phenoxy-N-phenylmaleimide was heated with a 7-time excess of phenol, only 3-phenoxy-N-phenylmaleimide was separated from the melt.

The capability of benzimidazoles to act both as basic and acid substances makes these compounds highly interesting objects for polyaddition reactions. In the given case, the reactant being more nucleophilic than phenol, it combines the catalytic-property with inhibiting anionic polymerization. 2-N-phenylsuccinimidebenzimidazole (V) was obtained by heating equimolar amounts of N-phenylmaleimide and benzimidazole, dissolved in N,N'-dimethylformamide, for 60-80 minutes to 115–120 °C. The structure of the compound (V) formed was confirmed by the results of elemental analysis and IR spectroscopy.

Summing up: the investigations demonstrated that phenols and benzimidazoles can be utilized in polyaddition reactions, and the conditions for their nucleophilic addition to the double bonds of bisimides of unsaturated acids were established. These findings should be taken into account in the synthesis of polymers.

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