

The Copolymerisation of Maleimide

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(Eingegangen am 27. Januar 1964)

SUMMARY:

The Q and e values for maleimide amount to 0.41 and 1.33 respectively.

The chemical reactivity and the IR-spectrum of polymaleimide are discussed.

ZUSAMMENFASSUNG:

Die Q- und e-Werte für Maleimid betragen 0,41 bzw. 1,33.

Es werden die chemische Reaktionsfähigkeit und das IR-Spektrum von Polymaleimid besprochen.

Introduction

It has been generally known that the radical homopolymerisation of 1,2-disubstituted ethylenes proceeds only with great difficulty, even if some of these compounds display a strongly marked reactivity in copolymerisations. A classical example is provided by maleic anhydride, which is being used on industrial scale for the syntheses of numerous copolymers. However, until recently it was not believed to be able to form homopolymers. In the recent literature, the homopolymerisation of maleic anhydride is mentioned^{1,2}). Maleimide and its derivatives being far more reactive³⁻⁶), the copolymerisation of maleimide as well as some characteristics of the homopolymer will be dealt within this article.

Experimental

1. Monomers and solvents

Maleimide is prepared by making maleic anhydride react with urea, dehydrating the resulting maleuric acid, and converting the obtained N-carbamyl maleimide⁷). Instead of performing the decomposition to maleimide in dimethyl formamide at approximately 100°C. and recrystallizing the impure product from ethyl acetate⁷), we preferred to prepare maleimide by dry pyrolysis of the carbamyl maleimide under vacuum at approximately 180°C. The raw maleimide is further purified by sublimation at 150°C. under a vacuum of 0.5 mm. Hg. Yield of the conversion of N-carbamyl maleimide: 50.3%.

$C_4H_3O_2N$ (97.07)	Calcd. N 14.42
	Found N 14.14–14.31

M.p. 94°C., (Lit.: 92°C.).

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Vinylidene chloride is prepared by dehydrochlorination of 1,1,2-trichloroethane⁸); B.p. 31°C.

Methyl methacrylate and *styrene* are commercial products. The inhibitor is removed from both products by washing with alkali, and the products are distilled under nitrogen before use.

Cyclohexanone and *chlorobenzene* are dried and distilled under nitrogen, while eliminating the head- and the tail-fraction.

2. Polymerisation

The copolymerisations with maleimide are performed in cyclohexanone with azo-bis-isobutyronitrile as the initiator. The total amount of monomer is from 2 to 2.75 mole/l. and the amount of initiator is from 6 to $8 \cdot 10^{-3}$ mole/l. The polymerisation tubes are sealed off and heated in an oil thermostat at 75°C., till a yield of approximately 10% of polymer is obtained. The polymer solution is then poured out in ether (vinylidene chloride, methyl methacrylate) or methanol (styrene) and the polymer is purified by dissolving two times in tetrahydrofuran and precipitating in ether or ethanol.

Maleimide is polymerised at 90°C. in chlorobenzene (5% solution) with 6% dibenzoyl peroxide as the initiator. The precipitate is filtered after three hrs., dissolved in acetone-methanol (1:1) and precipitated in hexane. Yield: 95%, $[\eta]_{\text{DMF}}^{25} = 0.12$ dl./g.

$\text{C}_4\text{H}_3\text{O}_2\text{N}_2$ (97.07) Calcd. C 49.49 N 14.42

Found C 50.77 N 13.63 Cl 0.20

Potentiometric titration in pyridine/water (9:1) with aqueous solution of sodium hydroxide: $9.54 \cdot 10^{-3}$ equiv./g. (theoretically $10.30 \cdot 10^{-3}$).

Chlorine analysis indicates the presence of chlorophenylene units in the polymer chain; UV-spectroscopy reveals phenyl or benzoyl end groups originating from the initiating radicals.

Polymaleimide, prepared by polymerisation in bulk at 135°C. for 18 hrs., is partly insoluble. The N-percentage (soluble polymer) is from 14.49 to 14.78.

3. Infrared spectra

The IR-spectra of the products, dissolved in dimethyl sulfoxide, are registered by means of an Infracord (Perkin-Elmer). The solutions are saturated previously with sodium chloride in order to reduce the attack of the cells by dimethyl sulfoxide. The registration is restricted to the field between 2 and 9 μ .

The infrared examination is carried out on products in solution in order to eliminate the occasional influence of differences in the crystal structure of the reference product on the absorption spectra⁹).

Results and Discussion

1. Copolymerisation

The results of the copolymerisations are given in Tables 1, 2, and 3. The mentioned N- and Cl-analyses constitute the averages of at least two values.

Table 1. Copolymerisation of styrene (M_1)/maleimide (M_2); polymerisation time: 8–15 min.

M_2	Conversion %	N %	m_2
0.05	3	4.08	0.297
0.1	10	5.54	0.399
0.2	12	5.66	0.405
0.3	10.7	6.18	0.445
0.4	11.2	6.66	0.479
0.5	10	7.28	0.522
0.6	9.8	7.38	0.528
0.7	8.3	7.68	0.548
0.8	12.2	8.09	0.570
0.9	2.5	8.72	0.618

Table 2. Copolymerisation of vinylidene chloride (M_1)/maleimide (M_2); polymerisation time: 60–120 min.

M_2	Conversion %	Cl %	m_2
0.1	10.2	66.28	0.094
0.2	5.8	56.64	0.226
0.3	10.2	47.81	0.347
0.4	8.3	43.47	0.406
0.5	11.2	40.20	0.451
0.6	12	34.77	0.525
0.7	8	28.88	0.605
0.8	12.2	21.14	0.711
0.9	12.2	10.88	0.851

Table 3. Copolymerisation of methyl methacrylate (M_1)/maleimide (M_2); polymerisation time: 18–30 min.

M_2	Conversion %	N %	m_2
0.1	12.2	0.63	0.045
0.2	12.8	1.24	0.088
0.3	4.8	1.84	0.131
0.4	5	2.62	0.186
0.5	14.5	3.46	0.244
0.6	10	4.50	0.318
0.7	10	5.83	0.411
0.8	3.8	7.22	0.507
0.9	11	10.33	0.721

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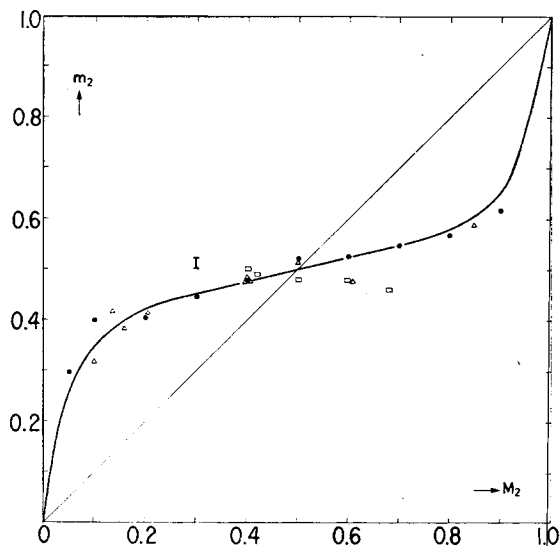


Fig. 1. Copolymerisation diagram:

I: Styrene (M_1)/maleimide (M_2) (\bullet). The experimental values of styrene-N-butyl maleimide⁹⁾ (\square) and styrene-N-methyl citraconimide¹⁶⁾ (\triangle) are supplied for comparison

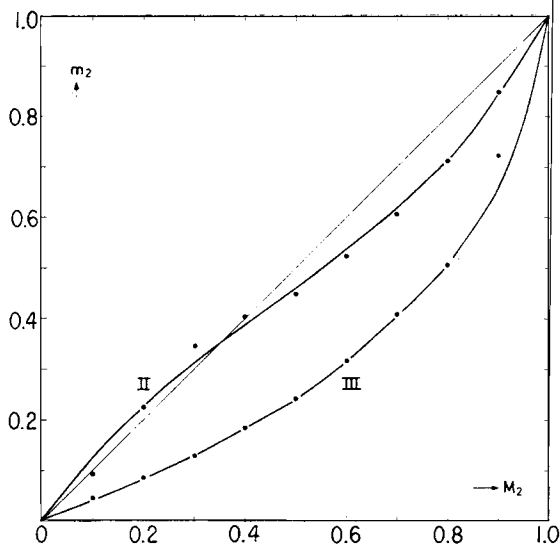


Fig. 2. Copolymerisation diagram:

II: Vinylidene chloride (M_1)/maleimide (M_2)

III: Methyl methacrylate (M_1)/maleimide (M_2)

The experimental points are given in Fig. 1 and Fig. 2. The values M_2 are the initial molar fractions of maleimide in the mixtures of monomers, whereas the values m_2 are the molar fractions of maleimide in the copolymers. The polymerisation curves are determined by inserting successive values of r_1 and r_2 in the fundamental equation of copolymerisation¹⁰⁾ (Eq. (1)), until the best fit of the resulting curve with the experimental points is obtained (Figs. 1 and 2).

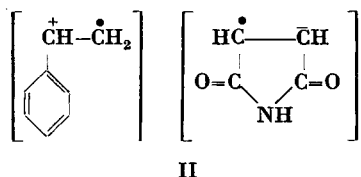
$$\frac{m_1}{m_2} = \frac{M_1}{M_2} \cdot \frac{r_1 M_1 + M_2}{r_2 M_2 + M_1} \quad (1)$$

The reactivity of maleimide (Q_2) and the polarity of its double bond (e_2) are calculated using the equation of ALFREY-PRICE¹¹⁾ with the values of r_1 and r_2 . The calculated values of Q and e are given in Table 4.

Table 4. Copolymerisation of maleimide (M_2) with (M_1)

M_1	r_1	r_2	Q_1	e_1	Q_2	e_2
styrene	0.1	0.1	1	-0.8 ¹²⁾	(1.8)	1.34
vinylidene chloride	0.71	0.48	0.20	0.29 ¹³⁾	0.39	1.33
methyl methacrylate	2.50	0.17	0.74	0.4 ¹²⁾	0.43	1.32
				average:	0.41	1.33

In the calculation of the average value of Q_2 , the high value from the copolymerisation with styrene is not taken into account. This abnormal value can be explained by the formation of molecular complexes in the transition state between styrene and maleimide in much the same manner as the electron-donor-acceptor complexes between *e.g.* conjugated carbonyl, nitrilo or nitro compounds (quinones, tetracyanoethylene, tri-nitrobenzene) and aromatic groups¹⁴⁾. These structures (II) formed by the transfer of an electron of the styrene double bond to the maleimide radical



give rise to the pronounced alternation in this copolymerisation in the same way as was assumed for maleic anhydride¹⁵⁾.

The same alternation can be noticed in the copolymerisation of styrene with N-butyl maleimide³⁾, and with N-methyl citraconimide¹⁶⁾. The values of these monomers plotted in Fig. 1 approximate to the values on the copolymerisation curve of maleimide. The Q and e values of N-methyl citraconimide recalculated from literature data¹⁶⁾, are given in Table 5. They are situated in the same range as the values obtained for maleimide. A higher Q value is also found for the copolymerisation with styrene. It is impossible, however, to compare the Q and e values of N-butyl maleimide with our results because of insufficient literature data concerning the copolymerisations with this monomer³⁾.

Table 5. Copolymerisation of N-methyl citraconimide (M_2) with (M_1)

M_1	r_1	r_2	Q_2	e_2
styrene	0.135	0.24	0.95	1.05
methyl methacrylate	3.24	0.15	0.32	1.25

2. Characteristics of polymaleimide

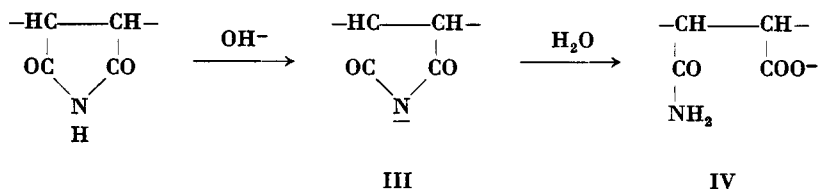
Solubility

Polymaleimide is soluble in dimethyl formamide, formamide, dimethyl sulphoxide, pyridine and in mixtures of acetone, butanone, dioxane and tetrahydrofuran with water (up to 40–50 % of water) and in mixtures of acetone and ethyl acetate with methanol. It is insoluble in water, lower alcohols, benzene, chlorobenzene, cyclohexanone, butyl acetate, tetrahydrofuran, dioxane, ether, hexane, carbon tetrachloride, and chloroform.

Reactivity

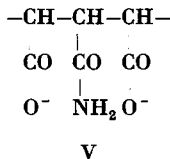
Polymaleimide is chemically not very reactive and in this respect analogous to polyacrylamide. After shaking for three weeks in water at room temperature it has scarcely changed. Even after refluxing for fifty hours in water the N-contents of the treated polymer remains almost unaltered. At 110°C. in a pressure tube the imide functions start hydrolysing gradually while the polymer dissolves. In a mixture of dioxane and water wherein the polymer is soluble, a slow hydrolysis occurs at 50°C. Polymaleimide does not react with alcohols; the polymerisation of the monomer may even be performed in methanol or ethanol.

Polymaleimide dissolves in an alkaline aqueous medium, probably because of the formation of an imide salt (III) which in water hydrolyses to maleamic acid (IV).



The polymaleimide can be recovered unaltered from ammoniacal water on condition that the polymer is precipitated immediately after dissolution. Under analogous conditions partly hydrolysed polymer is obtained from diluted sodium hydroxide solution. The polymaleimide is precipitated from a solution in pyridine by ammonia gas. A quantitative saponification to poly(maleic acid) is very difficult, owing to the precipitation of the partly saponified polymer from the reaction medium. This phenomenon is also observed during the titration of poly(maleic acid) with alkali¹⁾.

The most important reason why the amide functions are only saponifiable with great difficulty is probably due to the electrostatic repulsion of the attacking hydroxyl ions by the carboxylate ions on the polymer chain, which are shielding the amide groups¹⁷⁾:



Infrared spectrum

A close analogy exists between the spectra of succinimide and polymaleimide dissolved in DMSO (Fig. 3 and Table 6).

The absorption bands on 3.16μ and 3.31μ indicate associated NH-groups, although RANDALL¹⁸⁾ did not observe hydrogen bonding in succinimide. The band on 2.90μ , possibly due to a less firmly associated NH-group, is more intense in DMSO solution than the same absorption band in the spectrum recorded in potassium bromide, whereas the 5.90μ band of the record in KBr is shifted towards 5.83μ in DMSO. These changes in the spectra, as well as the fact that polymaleimide only dissolves in strong polar solvents can be explained by the rupture of hydrogen bonds.

The band on 6.00μ is rather difficult to explain. As a matter of fact, this absorption band which otherwise could be ascribed to traces of water,

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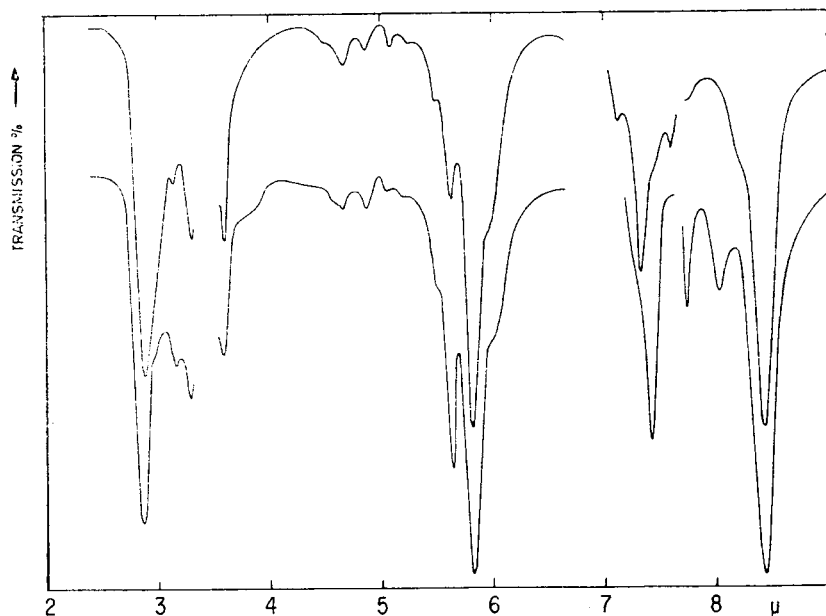
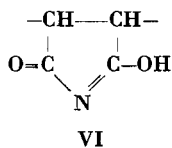


Fig. 3. Infrared spectrum of succinimide (lower spectrum) and polymaleimide (upper spectrum) dissolved in DMSO (the spectral ranges where DMSO interferes are omitted from the graph)

Table 6. Comparison of the infrared bands in the spectra of succinimide and polymaleimide dissolved in DMSO

Polymer (μ)	Succinimide (μ)	Interpretations
2.90; 3.16; 3.31 ± 3.60	2.90; 3.20; 3.32 ± 3.60	NH-valency (see text) possible overtone
5.50	5.52	?
5.65; 5.83	5.65; 5.83	$\nu_{C=O}$
6.00	6.00	see text
7.35; 8.45	7.43; 8.45	ν_{C-N}
	7.74; 8.05	$-CH_2$ -groups?

does not disappear on carefully drying the products. This absorption could be assigned to a $C=N-$ bond, suggesting a partial enolization of the imide function (VI).



In this case the OH-vibration near $3\ \mu$ would not be observable because of overlapping with the NH-band.

We are indebted to Dr. R. JANSSEN, head of the Laboratory for Organic Analysis, and to Ing. H. RUYSSCHAERT, for the interpretation of the infrared spectra.

We further wish to thank Prof. Dr. A. VAN DORMAEL, director of Chemical Research, and Dr. A. CONIX, head of the Polymer Department, for their kind interest in this work.

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