

Copolymerization of Acrylonitrile with N-substituted Maleimides

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SUMMARY:

Acrylonitrile was copolymerized with three N-arylmaleimides as well as with N-octadecylmaleimide in dimethylformamide (DMF) using azobisisobutyronitrile (AIBN) as initiator. The monomer reactivity ratios were calculated by the Fineman-Ross and the Kelen-Tüdös methods from which the Q- and e-parameters of these monomers were evaluated. The prepared copolymers were characterized by viscosity measurements and thermal analysis. The intrinsic viscosity decreases by increasing the maleimide content in the copolymer. Thermogravimetry TG and differential thermal analysis (DTA) data showed a remarkable improvement in the thermal behaviour of the investigated copolymers. A mechanism for the participation of the maleimide units in the nitrile oligomerization was also proposed. The investigation of the dyeing properties of the copolymers with the exception of those containing octadecylmaleimide, showed good affinity towards basic dyes as well as an appreciable improvement in their colour fastness towards UV light.

ZUSAMMENFASSUNG:

Acrylnitril wurde sowohl mit drei N-Arylmaleimiden als auch mit N-Octadecylmaleimid in Dimethylformamid (DMF) mit Azobisisobutyronitril als Initiator copolymerisiert. Die Copolymerisationsparameter wurden nach Fineman-Ross und nach Kelen-Tüdös bestimmt und hieraus die Q- und e-Werte der Monomeren berechnet. Die hergestellten Copolymeren wurden durch Viskositätsmessungen und Thermoanalysen charakterisiert. Die Grenzviskosität der Polymeren sinkt mit steigendem Gehalt an Maleimideinheiten. Die durch Thermogravimetrie (TG) und Differential-Thermoanalyse (DTA) erhaltenen Werte zeigen eine bemerkenswerte Verbesserung des thermischen Verhaltens der untersuchten Copolymeren. Ein Mechanismus für die Beteiligung der Maleimideinheiten an der Oligomerisierung der Nitrilgruppen wurde vorgeschlagen. Die Untersuchung der Färbereigenschaften aller Copolymeren mit Ausnahme derer, die Octadecylmaleimid enthalten, ergab sowohl eine gute Affinität bezüglich basischer Farbstoffe als auch eine recht gute Verbesserung der Farbbeständigkeit gegen UV-Strahlung.

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1. Introduction

The technological importance of polyacrylonitrile (PAN) is known to suffer from several disadvantages: Weak moldability, colour instability, and weak dyeability. Besides other efforts to abolish these difficulties, N-substituted maleimides have been used as comonomers for the production of acrylonitrile copolymers with improved properties. Thus, introducing N-arylmaleimides into the PAN backbone is reported to improve the moldability, while keeping the excellent mechanical properties of the polymer¹. N-phenylmaleimide improves the extrudability and leads to a polymer of greater strength². Incorporation of 10–50 mol-% of N-arylmaleimides (mainly halogen containing derivatives) increases the softening point of PAN to 115–250 °C while the moldable properties^{3,4} are retained. The discoloration of PAN at 120–200 °C caused by nucleophilically initiated nitrile group condensation, was effectively inhibited by the introduction of some maleimides or their N-substituted derivatives into the polymer chain^{5,6}. The stiffness of the polymaleimide chains together with their helicoidal conformation suggests an enhanced thermal stability of the polymers as well as of their copolymers⁷. One should therefore expect an improvement of the thermal properties of the arylmaleimide copolymers with acrylonitrile.

Copolymerization of acrylonitrile with different comonomers has also been used as an effective way for improving the polymer's dyeability with various kinds of dyes^{8,9}. Our preliminary studies have indicated that poly-(N-arylmaleimides) absorb basic dyes to a greater extent.

The above mentioned factors were the basis, upon which the present study was conducted. This work describes the determination of the reactivity ratios of acrylonitrile with four maleimide derivatives. Data of the thermal behaviour and dyeing properties of these copolymers are also presented.

2. Experimental

2.1 Materials

Acrylonitrile (BDH) was purified by distillation before polymerization. Four N-substituted maleimides were prepared by the original method of Searle¹⁰. The final products were purified by repeated crystallization from aqueous ethanol: N-2-chlorophenylmaleimide (2CMI), mp 77 °C, N-4-chlorophenylmaleimide (4CMI), mp 110 °C, N-2-bromophenylmaleimide (2BMI), mp 84–85 °C, and N-octadecylmaleimide (ODMI), mp 65 °C. The purity of the monomers was checked by thin layer

Copolymerization of AN

chromatography (TLC). Azobisisobutyronitrile (AIBN) was purified by repeated crystallization from methanol, DMF (Prolabo) was used as received. Three basic dyes "Methylene Blue" (C. I. Basic Blue 9,52015), "Maxilon Orange" (4RL) and "Maxilon Yellow-Brown" (2GL, Ciba-Geigy) were used for the present investigation without further purification.

2.2 Copolymerization Procedure

Polymerization ampoules of pyrex glass were charged with the monomers, the solvent, and the initiator ($2 \cdot 10^{-2}$ mol/l). The ampoules were covered with serum caps, cooled, and purged with a slow stream of purified nitrogen. The polymerization was then carried out in a water thermostat at 70 °C. The reaction was terminated by opening the ampoules and pouring the contents into a large amount of ethanol. The precipitated materials were collected and washed repeatedly with hot ethanol. The copolymers were dried to constant weight at 60 °C. The copolymer compositions were calculated on the basis of their halogen and/or nitrogen contents.

2.3 Thermal Analysis

Thermal analysis was performed in air using a Derivatograph thermoanalyser, (made in Hungary), which gives the TG and DTA thermograms simultaneously at a heating rate of 10 °C/min.

2.4 Dyeing Method

The fine homogeneous powdered polymer samples were immersed at room temperature in the dye bath using a dye/liquor ratio of 1:100. The pH was adjusted at 3–4 using acetic acid/sodium acetate buffer mixture. The temperature was then gradually increased to 95 °C in 30 min and was kept at this temperature for another 50 min. The dye bath was cooled to 60 °C and the sample was centrifuged, rinsed, and dried¹¹. The amount of dye absorbed on the sample was measured by the conventional colorimetric method to measure the concentration of dye remaining in the dye bath.

3. Results and Discussion

The composition of the initial monomer feed mixtures and that of the copolymers for the four investigated systems are compiled in Tab. 1–4. The data in the tables were analysed by the Fineman-Ross method¹² and the

Tab. 1. Copolymerization data for the system acrylonitrile (M_1) and 2CMI (M_2) in DMF at 70°C.

No.	$X = \frac{[M_1]}{[M_2]}$	Conversion (%)	Amount of Cl (wt.-%)	$Y = \frac{[m_1]}{[m_2]}$	$[\eta]$ (ml/g)
1	19.00	5.00	2.7	20.92	0.288
2	9.00	7.80	5.5	8.26	0.255
3	4.00	7.0	9.0	3.52	
4	2.33	9.50	11.2	2.06	
5	1.5	9.00	12.7	1.35	0.137
6	1.00	7.50	13.7	0.97	
7	0.66	10.8	14.6	0.66	
8	0.43	7.50	15.5	0.40	
9	0.25	9.40	16.2	0.22	
10	0.11	9.30	16.6	0.11	

Tab. 2. Copolymerization data for the system acrylonitrile (M_1) and 4CMI (M_2) in DMF at 70°C.

No.	$X = \frac{[M_1]}{[M_2]}$	Conversion (%)	Amount of Cl (wt.-%)	$Y = \frac{[m_1]}{[m_2]}$	$[\eta]$ (ml/g)
1	19.00	11.00	2.95	18.80	
2	9.00	11.50	5.20	8.97	0.182
3	4.00	9.50	8.00	4.45	
4	2.33	7.00	10.00	2.78	
5	1.50	8.00	12.50	1.44	0.125
6	1.00	5.50	13.50	1.04	
7	0.66	6.00	14.4	0.73	
8	0.43	7.00	15.25	0.47	0.042
9	0.25	8.50	15.85	0.31	
10	0.11	6.00	16.40	0.17	

Kelen-Tüdös equation¹³. Least square method was used throughout the calculations for the determination of the slopes and intercepts. Correlation coefficients were found to be higher in the Fineman-Ross treatment. Averaged values were used to construct theoretical composition curves. The fit with the experimental points was rather good as illustrated in Fig. 1. The Kelen-Tüdös plots for the four systems are shown in Fig. 2. The intercept of the line at $\xi = 1$ is equal to r_1 and that at $\xi = 0$ is equal to r_2/α^{14} , where

Copolymerization of AN

$$\eta = \frac{G}{F + \alpha}, \quad \xi = \frac{F}{F + \alpha}$$

and α is an arbitrary constant ($\alpha = \sqrt{F_{\max} \cdot F_{\min}}$)

$$G = \frac{X(Y-1)}{Y}, \quad F = \frac{X^2}{Y}$$

where

$$X = \frac{[M_1]}{[M_2]}, \quad Y = \frac{d[M_1]}{d[M_2]}$$

Tab. 5 summarizes the r_1 and r_2 data.

Tab. 3. Copolymerization data for the system acrylonitrile (M_1) and 2BMI (M_2) in DMF at 70°C.

No.	$X = \frac{[M_1]}{[M_2]}$	Conver- sion (%)	Amount of Br (wt.-%)	$Y = \frac{[m_1]}{[m_2]}$	$[\eta]$ (ml/g)
1	19.00	5.00	3.50	38.52	0.195
2	9.00	5.50	7.25	16.06	
3	4.00	9.50	11.30	8.61	
4	2.33	9.00	15.50	4.98	0.058
5	1.50	11.00	18.85	3.25	
6	1.00	10.50	21.00	2.43	
7	0.66	8.50	23.60	1.64	0.015
8	0.43	9.90	25.75	1.09	
9	0.25	10.80	29.00	0.45	
10	0.11	7.00	30.13	0.25	

The reactivity ratios show the expected trend. The 2BMI and ODMI have the lowest reactivity, a direct consequence of the bulky groups. It was also observed that the position of the chlorine atom in the phenyl ring has a slight effect upon the reactivity of the monomer. From the obtained values of r_1 and r_2 the Q- and e-parameters of the four monomers were estimated. Two values are usually obtained for each e-parameter where the higher positive values were chosen based on structural considerations due to the fact that the two carbonyl groups in the imide ring draw the electrons away from the

Tab. 4. Copolymerization data for the system acrylonitrile (M_1) and ODMI (M_2) in DMF at 70°C.

No.	$X = \frac{[M_1]}{[M_2]}$	Conver- sion (%)	Amount of N_2 (wt.-%)	$Y = \frac{[m_1]}{[m_2]}$	$[\eta]$ (ml/g)
1	19.00	12.00	23.60	45.82	0.352
2	9.00	13.20	20.80	19.69	0.360
3	4.00	8.00	17.50	9.96	
4	2.33	9.30	14.50	5.79	
5	1.50	3.00	12.00	3.65	
6	1.00	5.00	10.00	2.40	
7	0.66	3.50	8.50	1.65	
8	0.43	1.50	7.20	1.09	
9	0.25	2.00	6.10	0.67	
10	0.11	2.50	4.80	0.24	

Tab. 5. Reactivity ratios and Q-e-parameters for the copolymerization of acrylonitrile (M_1) and N-substituted maleimides (M_2).

M_2	Kelen-Tüdös method		Fineman-Ross method		Parameters	
	r_1	r_2	r_1	r_2	Q_2	e_2
2CMI	0.96	1.04	0.90	1.05	0.65	1.39
4CMI	0.97	0.73	0.97	0.73	0.99	1.81
2BMI	2.10	0.40	2.03	0.33	0.49	1.80
ODMI	2.36	0.40	2.36	0.38	0.31	1.55

Literature values¹⁴: $Q_1 = 0.48$, $e_1 = 1.23$

double bond rendering it relatively positively charged. The obtained values are somewhat different from those previously obtained for the 2CMI and 4CMI¹⁵, though being still in the range reported for the substituted maleimides^{7,16}. In general, one should be particularly cautious when comparing the Q- and e-values of the same monomer in different systems¹⁷.

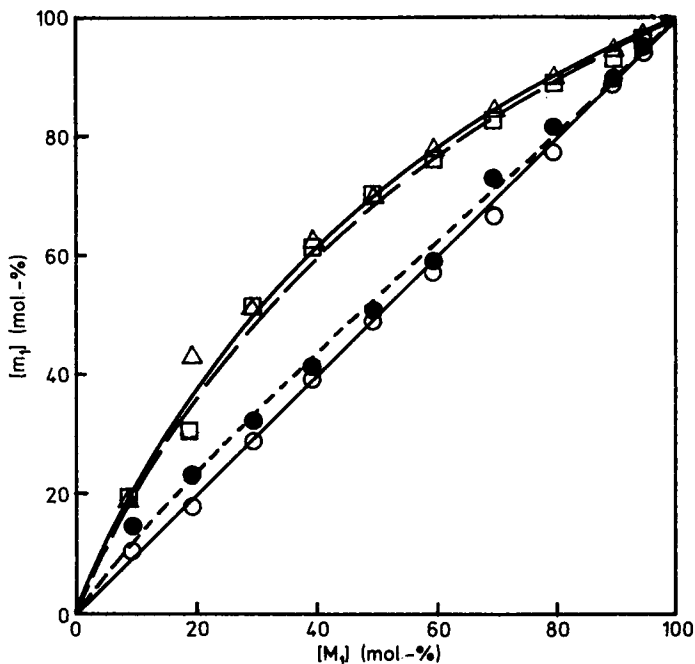


Fig. 1. Copolymer composition diagram of AN (M_1) and different N-substituted maleimides; solvent DMF, initiator AIBN ($2 \cdot 10^{-2} \text{ mol l}^{-1}$), temperature 70°C , total monomer concentration = 2 mol l^{-1} ; \circ 2CMI, \bullet 4CMI, \square 2BMI, \triangle ODMI.

The lines are constructed theoretically using values of r_1 and r_2 in Tab. 5; points are experimental values.

3.1 Thermal Behaviour of the Copolymers

The TG and DTA curves of polyacrylonitrile (PAN), poly(N-2-chlorophenylmaleimide) (P2CMI) together with some representative copolymers are given in Fig. 3 and 4, respectively. The thermal analysis of PAN shows the usual thermogram with an initial decomposition temperature at 250°C and an exotherm with a maximum at 280°C , which results from the oligomerization of the nitrile groups and formation of some aromatic structure¹⁸. On the other hand, the thermogram of P2CMI shows a different behaviour. Its TG curve contains two steps with initial decomposition temperatures at 360 and 480°C , where the corresponding DTA curve has only two small exo-

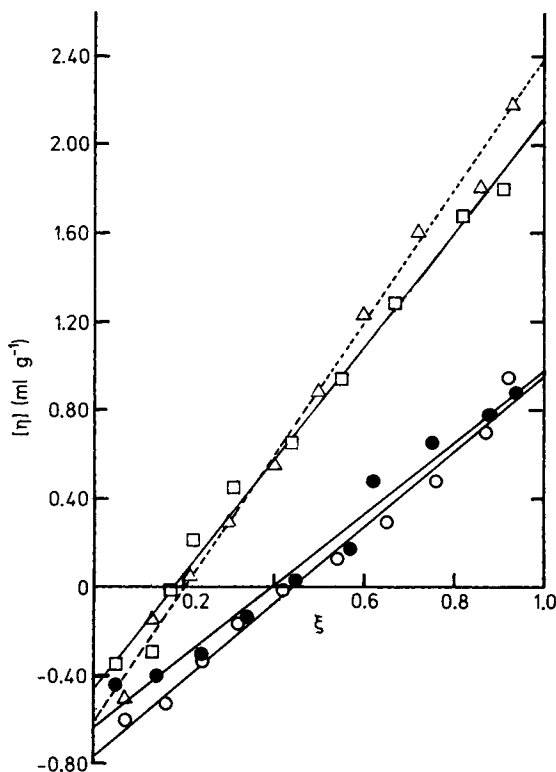


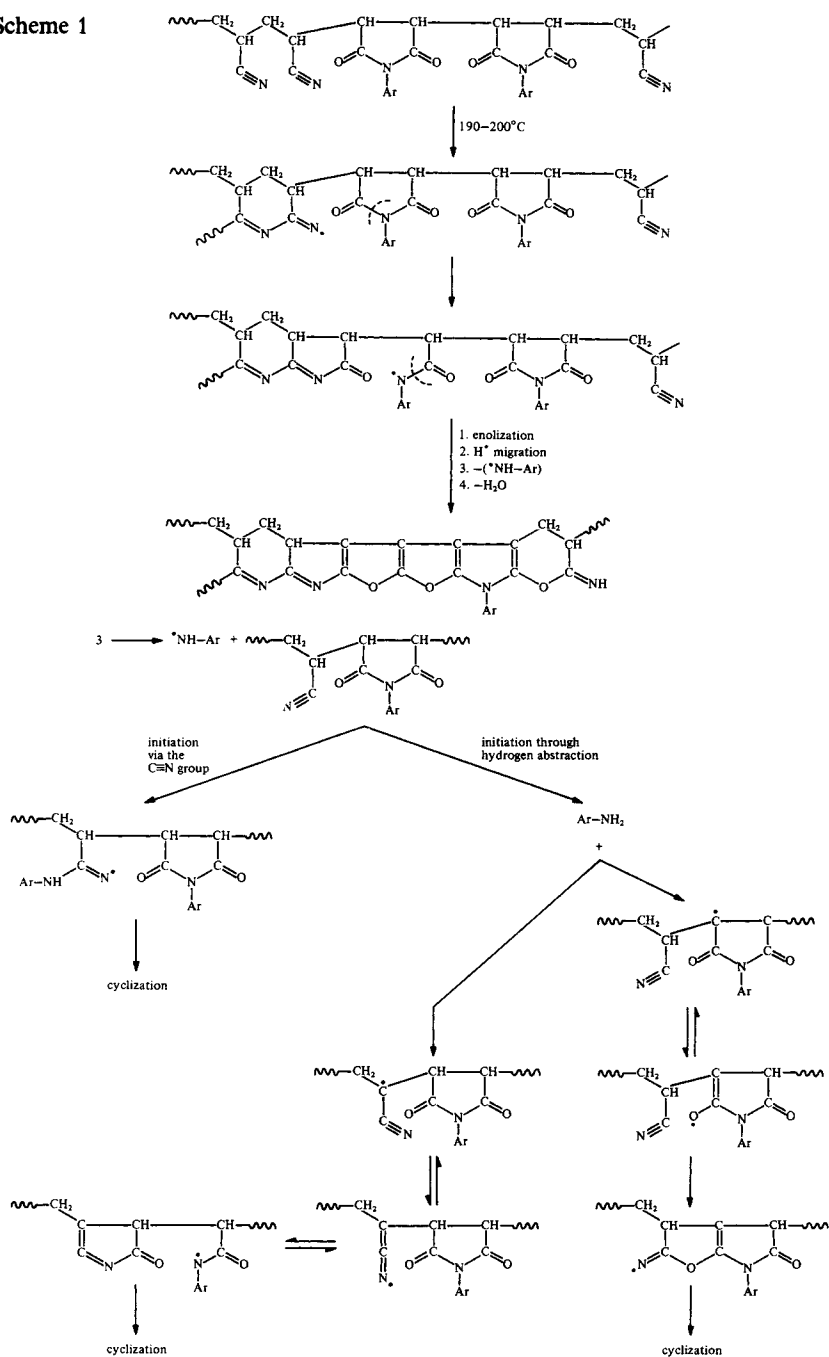
Fig. 2. Kelen-Tüdös plot for AN/N-substituted maleimides; ○ 2CMI, ● 4CMI, □ 2BMI, △ ODMI.

therms with maxima at 380 and 430°C followed by a greater one at 530°C. In spite of the fact that the copolymers have degradation curves similar to those of PAN, the exotherm maximum at 280°C is reduced significantly due to the presence of 2–5 mol-% bromo- or chlorophenylmaleimides as comonomers and is further reduced by increasing their molecular amounts in the copolymer (compare curve 2 with 4 in Fig. 4). This is probably due to the participation of the maleimide units in the nitrile oligomerization process, which leads to elimination of both water and anilino radicals (ArNH^\bullet). The eliminated radical probably abstracts a hydrogen atom from a neighbouring molecule or attacks a nitrile group, thus initiating the cyclization reaction of the attacked chain.

A mechanism which is based on the experimental results can be suggested as follows:

Copolymerization of AN

Scheme 1



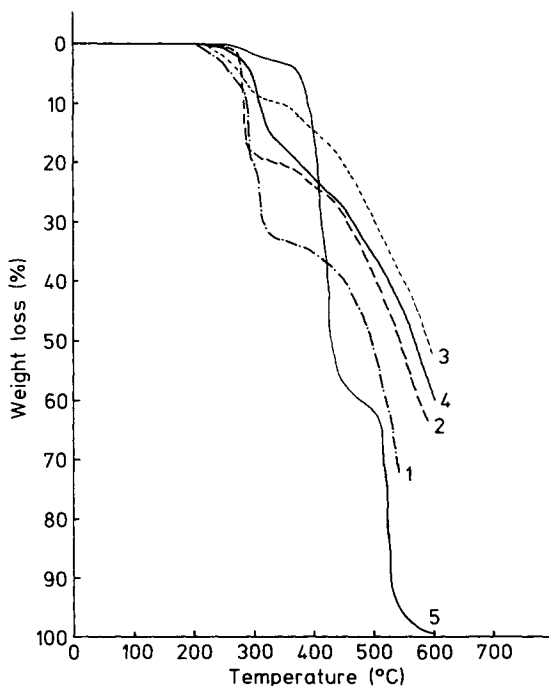


Fig. 3. TG curves for AN/N-substituted maleimide polymers and copolymers, heating rate $10^{\circ}\text{C}/\text{min}$ in air; 1) PAN, 2) AN/5 mol-% 2CMI, 3) AN/2.8 mol-% 2BMI, 4) AN/10 mol-% 2CMI, 5) P2CMI.

From the obtained values of r_1 and r_2 together with the similarity of the polarity of the double bonds in the AN and N-substituted maleimide one can assume¹⁹ with high certainty that the probability of AA diads and AAA triads in the copolymers will be high, thus justifying the composition of the copolymer shown in scheme 1.

A positive evidence in favour of this mechanism is gained by detecting a primary aromatic amine among the products of the thermal degradation of the copolymers (AN/10 mol-% 2CMI). This experiment was conducted by heating the copolymer in a sealed tube at 200°C for 60 minutes and then extracting the residue with alcohol. The positive diazotization test confirmed the presence of a primary aromatic amine. The acrylonitrile moiety adjacent to the maleimide group can participate in the reaction through the readily formed $-\text{C}=\text{N}^{\bullet}$ radical, which attacks the imide linkage and breaks the

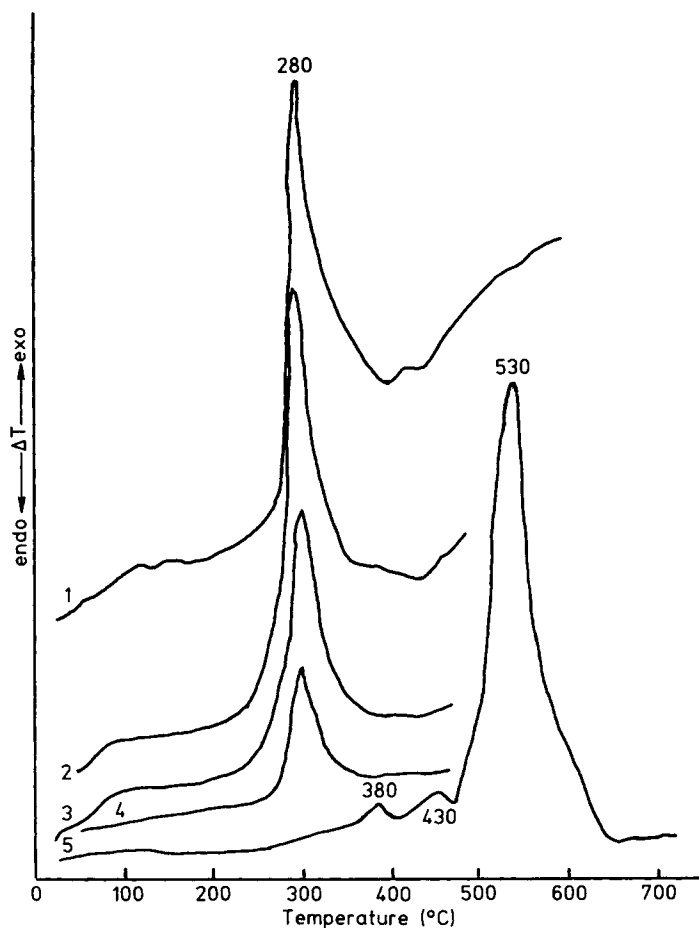


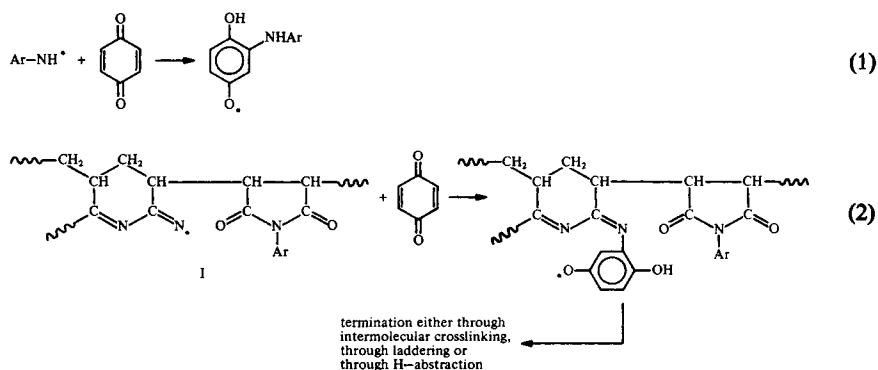
Fig. 4. DTA curves for AN/N-substituted maleimide polymers and copolymers, heating rate 10°C/min in air; 1) PAN, 2) AN/5 mol-% 2CMI, 3) AN/2.8 mol-% 2BMI, 4) AN/10 mol-% 2CMI, 5) P2CMI.

C—N bond. The rupture of the latter bond will be followed by the elimination of the Ar-NH^\bullet radical as previously postulated. The participation of both the nitrile and imide groups at the initial stage of the heating process was evidenced by the rapid disappearance of their corresponding bands in the IR spectrum of the copolymer after heating. The presence of the maleimide groups causes a decrease in the intensity of the exotherm.

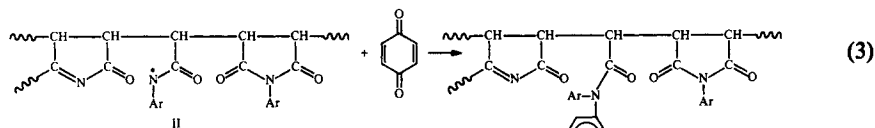
A direct experimental proof for the mentioned radical mechanism was obtained by trapping the anilino radical formed as a result of the thermal degradation of the copolymer by a known radical trap. For this, p-benzoquinone was mixed in different concentrations with the copolymer. The mixture was then heated in a sealed tube as previously described, and the extracted residue with alcohol was subjected to both diazotisation test and a sensitive colour reaction characteristic for the quinone and its substituted derivatives known as Craven test²⁰. According to this test, the material being investigated is treated with a mixture of equal volumes of concentrated solutions of ammonia and ethyl alcohol followed by the addition of few drops of ethylcyanoacetate. A green or blue colour is developed whenever the quinone derivative still retains an unsubstituted position in the quinonoid ring. The intensity of the developed colour increases with the number of the unsubstituted positions. Moreover, the test is so sensitive that it can differentiate easily between the parent p-benzoquinone and its quinonoid derivatives as various colours are developed in each case. The absence of free aromatic amine in the extract and formation of a stable green colour in the Craven test for the extracted products as well as the extensively washed solid residue of the copolymer provide a strong evidence supporting the radical nature of the oligomerization mechanism of PAN.

A mechanism for trapping the degradative intermediates by p-benzoquinone is proposed as follows:

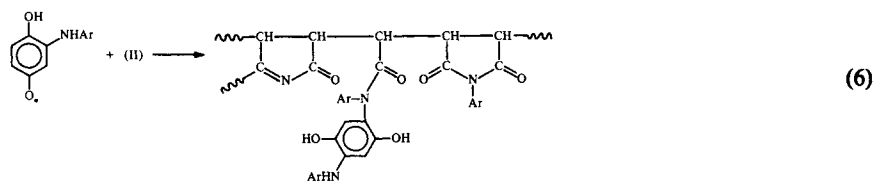
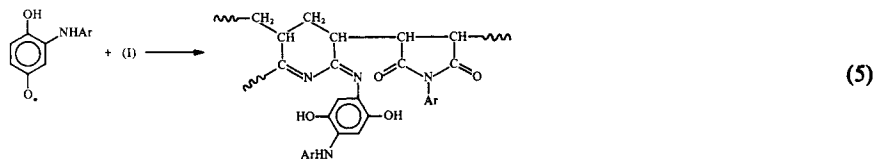
Scheme 2



Copolymerization of AN



termination either through
intermolecular crosslinking,
through laddering or
through H-abstraction



Eq. 4 is not probable to occur as no anilino derivatives were detected in the extracted products. On the other hand, the reaction of p-benzoquinone with the imino radical as represented in equation 2 is responsible for the positive Craven test of the solid residue. This is because the anilino derivatives of quinone are known to give negative results with the mentioned test²¹.

The TG curves (Fig. 3) indicate also that the thermal stability of the copolymers has been substantially improved as reflected in the amount of weight loss. On the other hand, Tab. 6 gives more information on the thermal degradation behaviour of these copolymers. It can be noticed that the bromo derivative provides the lowest weight loss value even when its content is very low (≈ 2 mol-%) in the copolymer.

The thermal degradation of PAN and its copolymers in air as well as under nitrogen atmosphere has been investigated by Coleman et al.²²⁻²⁴ using FTIR. Intramolecular cyclization, intermolecular crosslinking, and water elimination have been proposed. Oxidative reactions were a major

Tab. 6. Weight loss data of acrylonitrile copolymers after heating at 200  C for various periods of time.

Copolymer compositon (mol-%)	Heating time (min)	Colour	Weight loss (%)
PAN	40	yellow	6.0
	80	brown	8.5
	130	black	8.7
AN/5% 2CMI	40	pale yellow	2.3
	80	pink	5.1
	130	dark brown	6.5
AN/10% 2CMI	40	pale yellow	1.6
	80	yellow	2.2
	130	brown	2.5
AN/2.5% 2BMI	40	pale yellow	1.8
	80	dark brown	2.1
	130	dark brown	2.2
AN/5% 2BMI	40	brown	1.9
	80	dark brown	2.3
	130	dark brown	2.4
AN/5% 4CMI	40	brown	2.5
	80	black	4.0
	130	black	17.0
AN/10% 4CMI	40	brown	1.6
	80	dark brown	4.2
	130	black	16.5

factor with subsequent heating. Grassie and McGuchan^{25,26} have investigated the effect of copolymerization on the oligomerization of the nitrile groups of PAN on heating. It has been argued that since the comonomer is an integrated part of the polymer chain, it may influence the cyclization reaction of the nitrile groups either by initiation, participation or inhibition. Acrylic acid and acrylamide act as initiators for the cyclization reaction. A free radical mechanism followed by homolytic scission of the amide C—N bond has been proposed. Methyl- and benzylacrylates together with methylmethacrylate participate in the cyclization process and cause a decrease in the intensity of the exotherm without a strong initiating effect. Styrene, α -methylstyrene, vinyl pyridine and vinylacetate on the other hand, act as

blocking agents for the nitrile oligomerization. The exotherm is accordingly strongly suppressed and the total amount of heat evolved is reduced.

From the aforementioned mechanism, one can assign the maleimide derivatives in the second category of the Grassie classification²⁶.

3.2 Dyeing and Fastness Properties of the Copolymers

The various homopolymers and their copolymers were dyed with three basic dyes, methylene blue, maxilon orange, and maxilon yellow-brown. A comparison between the amount of absorbed dyes by the different samples for the three dyes is given in Tab. 7. These values were calculated from the determinations carried out for the concentrations of the dyes in the dye bath before and after dyeing, as it was not possible to extract the dye completely from the dyed samples. The data clearly indicate the higher affinity of the

Tab. 7. Dye absorption data of the acrylonitrile/N-substituted maleimides copolymers and homopolymers.

Copolymer composition (mol-%)	Amounts of dye absorbed (wt.-%)		
	Methylene blue	Maxilon orange	Maxilon yellow
PAN	27.00	63.85	34.65
AN/5% 2CMI	58.00	77.20	49.20
AN/10% 2CMI	66.50	97.20	61.20
AN/5% 2BMI	80.00	92.70	55.00
AN/10% 2BMI	82.70	94.00	57.50
AN/5% ODMI	73.00	55.00	71.00
AN/10% ODMI	79.00	52.00	72.00
AN/5% NPMI*	67.50	96.40	77.00
AN/10% NPMI	93.50	97.80	81.00
AN/5% 4HPMI**	56.50	80.20	77.50
AN/10% 4HPMI	32.00	55.30	25.00
P2CMI	97.00	94.30	96.70
PNPMI	48.00	96.40	72.00

* NPMI = N-phenyl maleimide.

** 4HPMI = N-4-hydroxyphenyl maleimide.

maleimide homopolymers and their copolymers towards the absorption of basic dyes compared with that of PAN. This affinity bears very small relation to the nature of the N-substituted group in the maleimide moiety except for the ODCMI where the amount of the dye absorbed was found to decrease with increasing content in the copolymer. This is most likely to be due to the hydrophobic nature of the long methylene chain. When the phenyl ring of the maleimide contains an —OH group as in the case of N-4-hydroxyphenylmaleimide, the same behaviour was observed. In this case the formation of hydrogen bonding could hinder the diffusion of the dye.

The colour fastness of dyes towards light is known to depend much on the substrate fibers. For example, basic dyes have usually low colour fastness when used for silk and wool. However, they can show much better colour fastness when used for dyeable polyacrylonitrile²⁷. As the colour fastness towards UV light is considered to be an accelerated light fastness test, it is of interest to investigate if the presence of the maleimide derivatives as comonomers with AN affects the light fastness property of the latter and in what way. Tab. 8 illustrates the grades of the UV fastness of different dyed samples when exposed to a low pressure mercury lamp up to 100 min. These

Tab. 8. UV fastness of the dyed samples exposed to a low pressure mercury lamp.

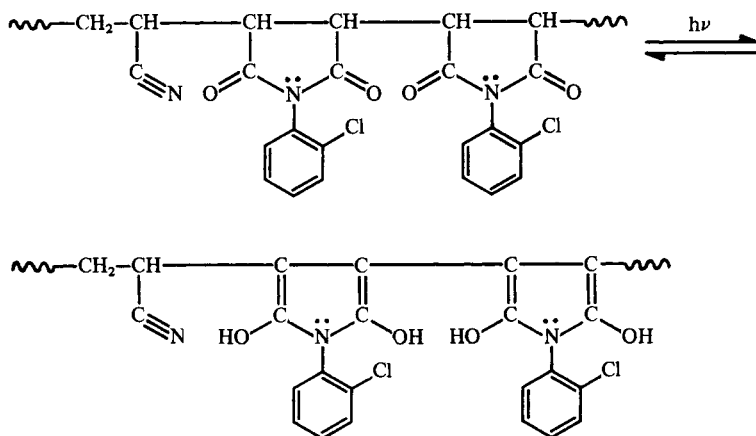
Copolymer composition (mol-%)	Methylene blue	Maxilon orange	Maxilon yellow
PAN	VP	M	G
AN/5% 2CMI	P	VG	VG
AN/10% 2CMI	P	VG	VG
AN/5% 2BMI	M	VG	G
AN/10% 2BMI	M	M	M
AN/5% ODMI	VP	G	G
AN/10% ODMI	VP	G	G

VG: very good, G: good, M: moderate, P: poor, VP: very poor

Exposure temperature reached to about 85°C. Exposure time: 100 min.

grades were obtained by matching the exposed samples with the originals. The surrounding temperature was ca. 85°C while the distance from the source was kept constant at 10 cm. The results show an appreciable improve-

ment of the colour fastness as a result of copolymerization with 2CMI, while it is lowered when ODMI was used as a comonomer. The improved fastness might be attributed to the highly conjugated system created on the N-aryl-maleimide as a result of keto/enol tautomerism which may act as an UV absorber:



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