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Reaction behaviour of *N*-methacryloyl pyrrole in radical polymerizations

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Summary

N-methacryloyl pyrrole NMP was synthesized via the pyrrylpotassium salt and radically polymerized. Thereby crosslinked and partially insoluble products were obtained. Synthesis of the model system N-acetyl pyrrole 1 and carefully directed reactions thereon made the explanation of the way of the radical polymerization possible.

Introduction

Pyrrole containing polymers are an interesting topic for several applications. Side reactions are expected to occur at the aromatic system by choosing the radical polymerization of suitable monomers as a simple polymerization method. Thus Conant et al.[1] pointed out the addition of triphenylmethylradicals at the α-positions of pyrrole in 60 % yield. On the other hand, Vernin et al.[2] observed a substitution of one α-hydrogen during the reaction of N-alkylpyrroles with benzoyloxy radicals. In our study we selected N-methacryloyl pyrrole NMP as monomeric compound. The installation of the carbonyl group at nitrogen was expected to decrease the π-electron density on the α-carbon to lower radical attack.

Experimental

Synthesis of N-acyl pyrroles

10.5 mmol freshly distilled pyrrole were mixed with 10 mmol potassium under argon in 10 ccm of dry toluene. The reaction mixture was stirred for 2 h at reflux temperature. After removal of the solvent, the pyrrylpotassium was dried in vacuo overnight. For the acylation reaction the pyrrylpotassium was suspended under argon in 10 ccm of dry ether. A solution of 10 mmol methacryloylchloride in 5 ccm of dry ether was added slowly at 0°C and the reaction mixture was stirred for an additional 1 h at room temperature. The solution was then filtered and the precipitate washed with ether. After solvent evaporation the residue was distilled under reduced pressure over a Vigreux-column (NMP: bp_{1mbar}: 27°C; n_D^{20}: 1.5185; yield: 90 %; 1: bp_{9mbar}: 60°C).

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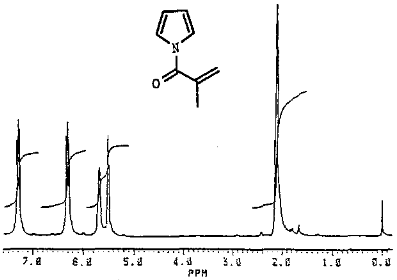


Fig. 1: *^{1}H-NMR spectrum of NMP*

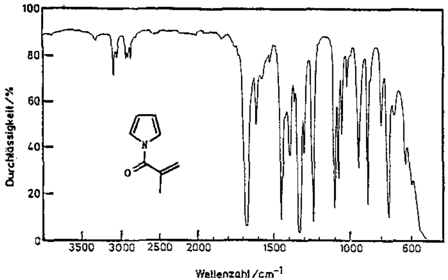


Fig. 2: *IR spectrum of NMP*

Polymerizations

The polymerization reactions were carried out under argon in screw-sealed, pressure-proof testtubes. Tab. 1 gives the reaction conditions and results.

Table 1: *Radical polymerization of NMP at 60°C with AiBN*

Exp.-Nr.	m_{NMP} (g)	m_{AIBN} (mg)	n_{AIBN} (mol%)	t (h)	Solv. (ml)	Col. PNMP	m_{PNMP} (mg)	Conv. (%)	Gel-form.	Solubility
1	1.019	2.6	0.21	23	/	white	26.4	2.6	?	?
2	10.66	20	0.15	29	/	white	929.6	8.7	+	-
3	2.171	25.2	0.96	17	/	white	164.7	7.6	±	±
4	1	10.9	0.9	27	THF (1)	white	34.5	3.5	-	+
5	1	10.9	0.9	264	THF (5)	orange	52.5	5.3	-	+
6	1	102	8.4	74	Tol. (20)	/	/	/	/	/

Measurements

The ^{1}H-NMR samples were prepared by dissolving 10 to 20 mg of substance in 0.5 ccm chloroforme-d_1 and measured at 37°C on a Bruker WP 80 SY instrument using tetramethylsilane (TMS) as an internal standard. IR spectra were recorded on a Perkin Elmer 398 IR spectrometer as thin films or in CCl_4 on NaCl disks or as KBr pressings. GC-MS were measured on a Finnigan Incos 50 GC Varian 3400-MS.

Results and discussion

The products resulting from radical polymerization of NMP were crosslinked and partially insoluble. Molecular weight decreases with increasing dilution of the reaction mixture until forming only low molecular weight products in exp.-no. 6 (see Tab. 1).

Spectroscopic data of the polymers point to side reactions in considerable amounts, but also to normal vinyliden polymerization. The IR spectrum shows two carbonyl bands at 1640 and 1680 cm^{-1}, the latter one resulting from the abolition of the

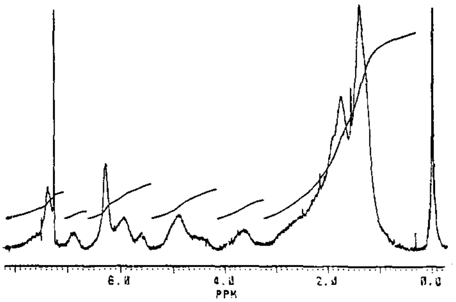


Fig. 3: ^{1}*H-NMR spectrum of PNMP*

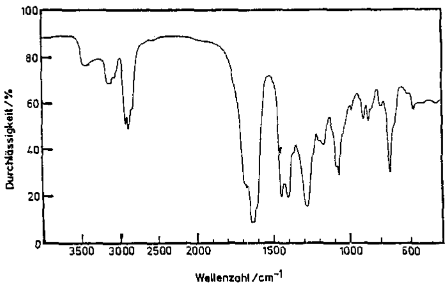
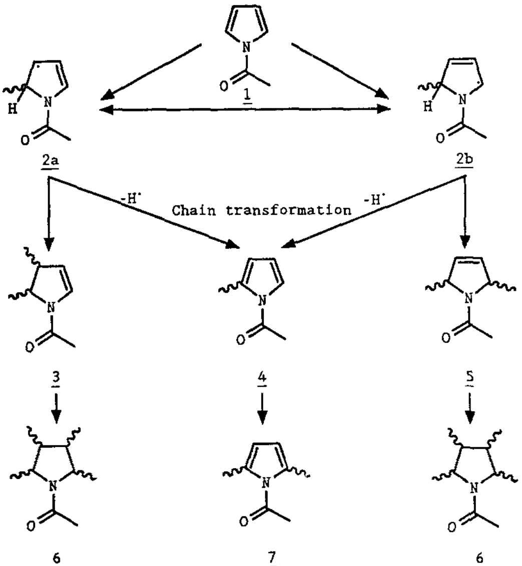


Fig. 4: IR spectrum of PNMP

conjugation with the vinyliden double bond (C=O in NMP: 1665 cm^{-1}). In the ^{1}H-NMR spectrum the peaks at 6.3 ppm (β-C) and 7.3 ppm (α-C) must be interpreted accordingly. Many other signals appear (see Figs. 3 and 4) which can not be explained by normal vinyliden polymerization. The reaction behaviour was investigated at the model system N-acetyl pyrrole 1 where only the vinyliden double bond is absent of. Scheme 1 shows possible reaction paths of this compound 1 with free radicals.

Scheme 1: Possible reaction paths of 1 with free radicals



If 1 is able to react with radicals by chain transfer, the molecular weights of poly(styrene)s synthesized under the same conditions should decrease with increasing amounts of 1 in the reaction mixture. However, molecular weights determined by GPC increase with increasing concentration of 1 (see Tab. 2). Therefore chain transfer reactions can be excluded. Radical 2 was expected to have a long lifetime due to mesomeric stabilization and thus should have a retarding influence on the styrene polymerization. The increase in molecular weight would then exclusively be conditioned by chain termination by coupling. An alternative explanation arises from the possibility of radical 2 to be incorporated in chain growth reaction. Studies of the rate of reaction in a dilatometer show no influence of 1 on the bulk polymerization of styrene (see Tab. 3).

That 1 is in fact built in the polymer chain is demonstrated by the synthesis of a styrene-1 copolymer with 12 mol% 1 de-

Table 2: *Change in molecular weight of poly(styrene)s from radical bulk polymerization with various concentrations of 1*

Exp.-no.	c_1 (g/l)	n_1 (mol%)	M_n (g/mol)	Conv. (%)
1	/	/	74300	8.7
2	0.46	0.05	78500	8.8
3	0.92	0.1	78800	8.7
4	1.84	0.19	80300	8.8
5	3.68	0.39	80500	8.7

reaction conditions: t = 4 h, T = 60°C,
c_{AiBN} = 1.0033 g/l = 0.07 mol%

Table 3: *Influence of 1 to the radical bulk polymerization of styrene at 60°C in a dilatometer*

Exp.-no.	c_1 (mol/l)	n_1 (mol%)	Slope (mm/min)	r (%)
1	/	/	3.56	99.989
2	0.0135	0.16	3.65	99.992
3	0.1304	1.5	3.42	99.988
4	0.3026	3.47	3.48	99.957
5	/	/	3.49	99.989

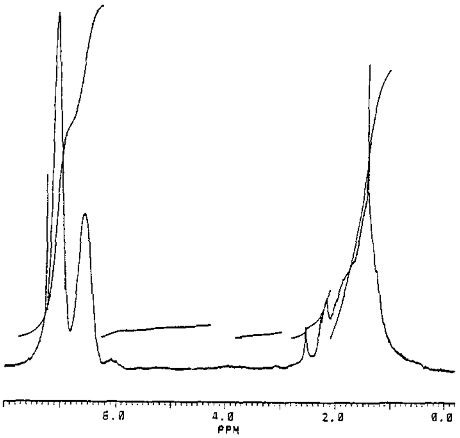
c_{AiBN} = 0.0289 mol/l = 0.33 mol%

termined by ^{1}H-NMR (see Tab. 4, Fig. 5). Therein the signals from the methyl group of 1 appear at 2.2 and 2.5 ppm.

Table 4: *Radical bulk copolymerization of 1 with styrene*

Styrene			1			Conditions			Copolymer		
m (mg)	n (mol%)	Conv. (%)	m (mg)	n (mol%)	Conv. (%)	t (h)	T (°C)	m_{AiBN} (mg)	m (mg)	Styr. (%)	1 (%)
376	45.6	2.9	469.8	54.4	0.3	5	60	3.2	12.3	88	12

Fig. 5: *^{1}H-NMR spectrum of a styrene-1-copolymer*



The reaction of 1 with AiBN gives a wide variety of low molecular weight and oligomeric products according to the corresponding gelpermeation chromatogramm. However, from pyrrole itself far less products are formed under similar conditions (see Fig. 6). In the reaction of 1 succeeded a separation of the regioisomer 8 from the stereoisomers 9 and 10 by flash chromatography on silica gel. The compounds were characterised by ^{1}H-NMR, IR and GC-MS (see

Figs. 8 - 10). Fig. 7 shows the main products and Tab. 5 shows the reaction conditions.

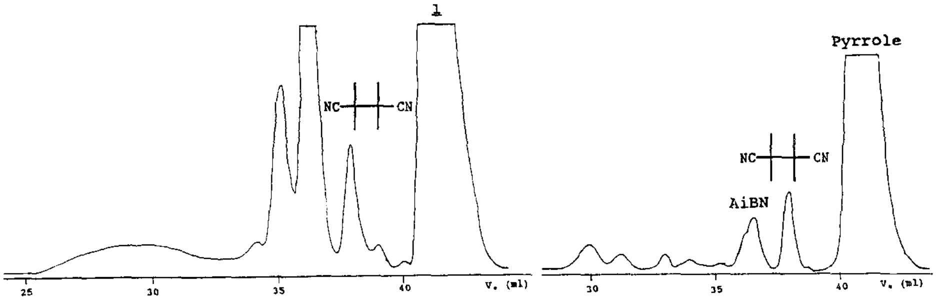
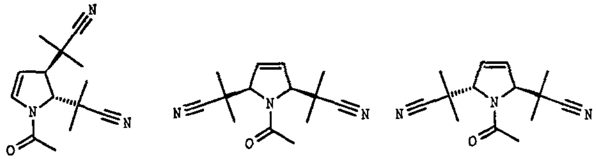


Fig. 6: *Gelpermeation chromatogramms of the reactions of 1.58 g 1 with 107 mg AiBN after 40 h at 60°C (left) and of 3 ccm of pyrrole with 155 mg AiBN after 76 h at 60°C (right)*

Fig. 7: *Main products of the reaction of 1 with AiBN*



trans-1-Acetyl-4, 5-bis-isobutyronitrilo-2-pyrroline

8

cis-1-Acetyl-2, 5-bis-isobutyronitrilo-3-pyrroline

9

trans-1-Acetyl-2, 5-bis-isobutyronitrilo-3-pyrroline

10

Table 5: *Reaction of 1 with AiBN after 9 days at 60°C*

	Educts		Products		
	1	AiBN	8	9	10
m (mg)	1580	107	8	6.5	8
M (g/mol)	109	164	245	245	245
Yield (%)	52	/	5	4.2	5

- the procentual values of the products are in relation to AiBN

The reaction to the products 8 - 10 is rather important considering that only 4.5 mol% AiBN relative to 1 were used. In addition to the gelpermeation chromatogramm the fact that solely 52 % 1 can be recovered points to an intensive oligomer formation. The cis-isomer of compound 8 is not formed because of the enormous steric hindrance of the molecule. This is already manifested in a splitting of the iso-butyronitrile groups in the ^{1}H-NMR spectrum of the trans-compound 8. For the same steric reason more often 1.4- than 1.2-addition takes place (ratio 1.8 : 1). The absence of the double bond in 8 causes to shift the ring protons comparing with 1 to higher field density and correspondingly the carbonyl band to smaller wavenumbers (1640 cm^{-1}) due to the electron pushing effect of the ring double bond. There is no conjugation possible between the carbonyl group and the aromatic system because of infringing the electron octet at nitrogen. Beyond that appear the C≡N- and C=C-stretching vibrations at 2205 cm^{-1} and at 1620 cm^{-1}.

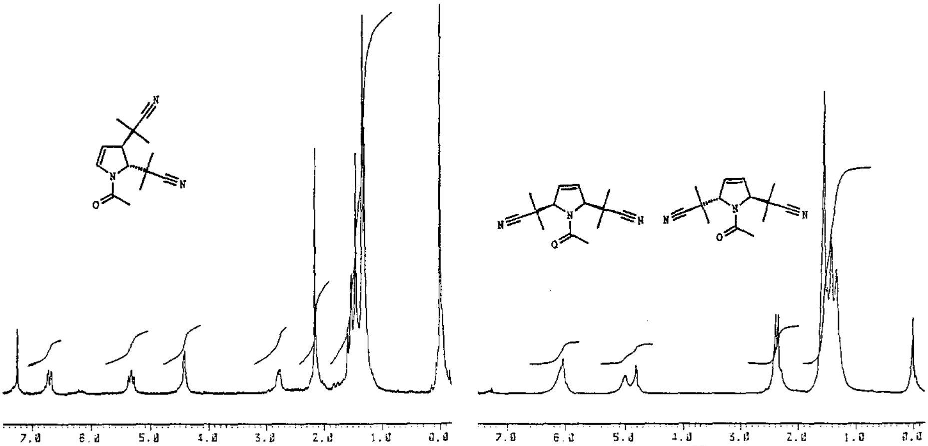
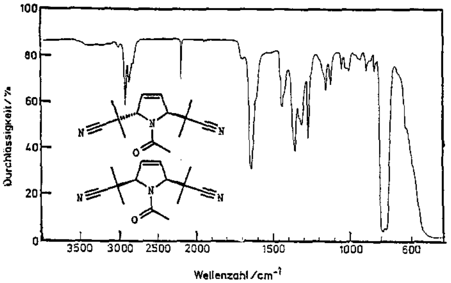


Fig. 8: *^{1}H-NMR spectra of compound 8 (left) and compounds 9 and 10 (right) in ratio 9 : 10*



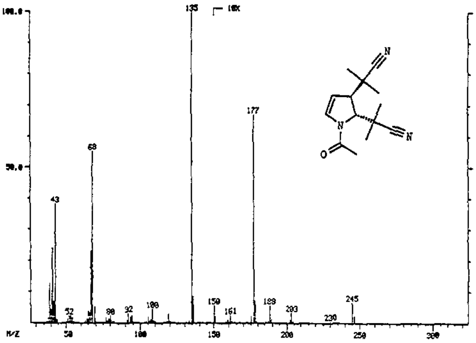
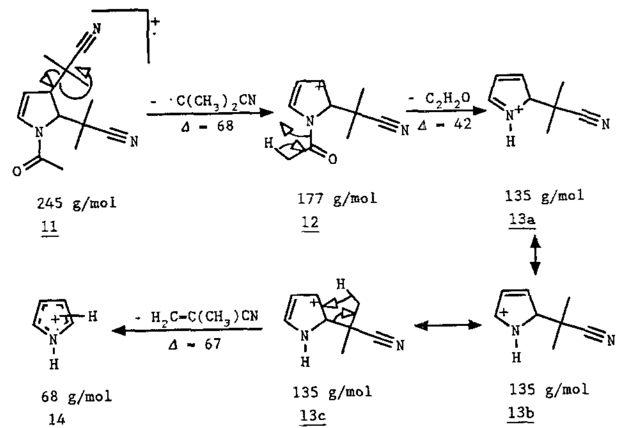


Fig. 9: *IR spectrum of stereoisomers 9 and 10 in relation 9 : 10*

Fig. 10: *GC-MS of compound 8*

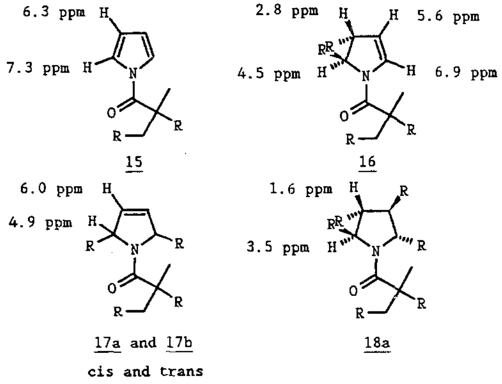
The GC-MS spectra of compounds 8 - 10 show characteristic molecule fragments by which the following scheme of fragmentation is proposed (see Scheme 2).
At first an iso-butyronitrile group splits off from the β-position (Δ = 68) followed by a decomposition of the amide bond of the resulting compound 12 giving a well stabilized intermediate 13 (base peak). Thereafter a second iso-butyronitrile group splits off and a protonated pyrrole ring remains.
The ^{1}H-NMR spectrum of the stereoisomers 9 and 10 shows also a splitting of the iso-butyronitrile methyl groups of the cis-compound 9, while the symmetric, sterically non hindered trans-product 10 gives a singlett (see Fig. 8). The IR and GC-MS spectra of the stereoisomers 9 and 10 are similar to those of the regioisomer 8. The corresponding explanations are counting for them, too. The results of the studies at the model system 1 confirm the suggested addition at the aromatic double bond during the formation of PNMP. Basing on these

Scheme 2: Possible scheme of fragmentation of compound 8



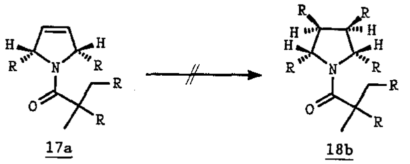
facts the following ^{1}H-NMR coordination for the structure of PNMP was taken. The structure 18 could not be proved directly but is resulting from a simple consideration. The aromatic α-protons of pyrrole are shifted about 0.7 ppm to lower field density by fixing the acyl group at nitrogen. However, the value for the β-protons does not change. Supposing the same effect for the pyrrolidine system a shift from 2.8 to 3.5 ppm results. This value was found in PNMP exactly. Another indication for this structure delivers the considerable decrease in molecular weight of poly(styrene)s synthesized by radical bulk polymerization with various concentrations of 1. It was proved that 1 acts as a comonomer, but this fact itself could not explain the jumpwise decrease in molecular weight. Considering pyrrolidine structures two additional chains will be fixed at the ring by which the molecular weight of those molecules doubles. Since the content on pyrrolidine structures in PNMP is about 18 % (see Fig. 12), the molecular weight of poly(styrene) rises vehemently.

Fig. 11: ^{1}H-NMR coordination for the structures in PNMP



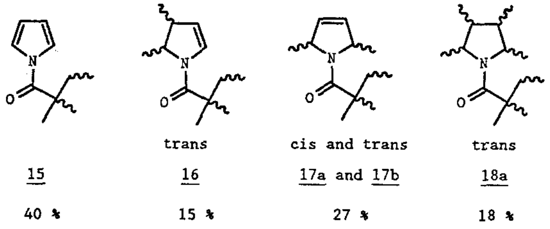
An important restriction of the way of reaction must be taken into account. A cis-N-acetyl-4,5-bis-isobutyronitrilo-2-pyrroline could not be indicated at the model system for steric reasons. Therefore a cis-3-pyrroline 9 does not further react because a second substituent has to be bound in cis position at the neighbouring C-atom. Additional proof for the way of reaction assumed is the good agreement of the wavenumbers of carbonyl bands of the isolated compounds 8 - 10 (1640 cm^{-1}) with the band observed in PNMP (1640 cm^{-1}). The diminution of the electron pulling effect of the pyrrole ring by addition

Scheme 3: *Steric hindrance of a cis-2.5-substituted pyrroline 9 against second addition because not all substituents R can occupy the thermodynamic favoured trans-position*



of radicals at the aromatic double bond implies the shift of the carbonyl band about 25 cm^{-1} to smaller wavenumbers, while the reaction at the vinyliden group increases the wavenumber of the carbonyl group about 15 cm^{-1} due to the abolition of the conjugation with the vinyliden bond. The approximate composition can be specified as following due to the coordination in Fig. 11 determined by ^{1}H-NMR.

Fig. 12: *Structures of a radically synthesized PNMP*



The polymerization exclusively happens to about 40 % at the vinyliden group, while 60 % of all pyrrole rings react under addition. The ratio found at the model system of 1.4- to 1.2-addition of 1.8 : 1 is also observed in PNMP, while the different reaction possibilities of the pyrroline derivatives 8 - 10 to the pyrrolidine derivative 18 were not considered in the calculation. The insolubility of PNMP was caused especially at higher molecular weights by the structures 16 - 18 which are generating a network assuming a total reaction at the vinyliden group. The acceptor influence of the carbonyl group must be held responsible for the activation of the pyrrole ring against radicalic attack. The decrease in aromaticity - recognizable at the large difference of the chemical shifts of the ring protons about 1 ppm - uses such a compound to behave rather as conjugated diene than as aromate.
Because of these facts pyrrole derivatives seem to be no useful monomers in radical polymerizations.

Acknowledgement

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