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Unsaturated Carbonic Acid Derivatives III

Copolymerization Behavior of S-, O- and N-Vinyl Derivatives of Carbonic Acid

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SUMMARY:

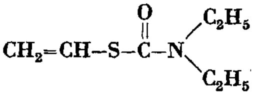
S-Vinyl-N-diethyl monothiolcarbamate, O-Vinyl-N-diethyl carbamate, and N-Vinyl-N-methyl-S-ethyl monothiolcarbamate were copolymerized with styrene and vinyl acetate. The Alfrey-Price Q- and e-values were calculated and compared with those of other S-, O-, and N-vinyl monomers. The S-vinyl thiolcarbamate was found to be more reactive as a comonomer than the N- or O-vinyl compounds.

ZUSAMMENFASSUNG:

S-Vinyl-N-diäthyl-monothiocarbamat, O-Vinyl-N-diäthylcarbamat und N-Vinyl-N-methyl-S-äthyl-monothiocarbamat wurden mit Styrol und Vinylacetat copolymerisiert. Die Q- und e-Werte wurden nach der Beziehung von Alfrey und Price berechnet und mit den Werten bekannter S-, O- und N-Vinylverbindungen verglichen. S-Vinylthiocarbamat ist reaktionsfähiger als die entsprechenden O- und N-Vinylverbindungen.

I. *Introduction*

The synthesis and the polymerization of S-, N- and O-vinyl derivatives of carbonic acid have been described recently¹⁾. In connection with investigations on nitrogen and sulfur containing polymers²⁾, we have been interested in the copolymerization behavior of these monomers, especially in the polarity and reactivity of the S-vinyl group. This paper describes the copolymerization of S-vinyl-N-diethyl monothiolcarbamate (I), N-vinyl-N-methyl-S-ethyl monothiolcarbamate (II) and O-vinyl-N-diethyl carbamate (III).



$$CH_2{=}CH{-}S{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}N\begin{matrix}\diagup C_2H_5\\ \diagdown C_2H_5\end{matrix}$$

(I)

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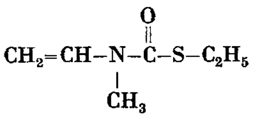
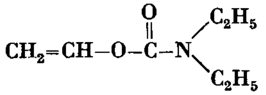


$CH_2{=}CH{-}N(CH_3){-}C({=}O){-}S{-}C_2H_5$ (II)



$CH_2{=}CH{-}O{-}C({=}O){-}N(C_2H_5)_2$ (III)

Styrene and vinylacetate were used as comonomers. The Q- and e-values were determined and the results were compared with those of other S-, O- and N-vinyl monomers.

II. *Experimental*

a) *Purification of Reagents*

Styrene and vinylacetate were twice shaken with a 3% sodium hydroxide solution and washed with water until neutral. Both monomers were dried over molecular sieves and distilled under nitrogen. Middle fractions were used for the polymerization experiments (styrene, b.p.$_{12}$ 43 °C.; vinylacetate, b.p.$_{763}$ 73 °C.). Benzene, methanol and petroleumether were distilled before use.

b) *Preparation of the monomers*

The monomers were prepared by dehydrohalogenation of S-, O- and N-β-chloroethyl carbamates.

S- and O-β-Chloroethyl-N-diethyl Carbamates$^{1)}$

To a stirred solution of 2 moles of diethylamine in 200 ml of ether at 0 °C., a solution of 1 mole of S-β-chloroethyl chlorothiolformate$^{3)}$ or O-β-chloroethyl chloroformate in 100 ml. of ether was added over a period of 30–60 min. The white precipitate of the amine salt was formed immediately. After completion of the addition, the slurry was stirred at 30 °C. for 1 hr. The amine salt was filtered; the ether was washed with dilute sulfuric acid and water, and dried over magnesium sulfate. The ether was removed and the residue vacuum distilled, S-β-chloroethyl-N-diethyl monothiolcarbamate$^{1)}$: yield 93%; b.p.$_{0.3}$ 64 °C.; n_D^{23} 1.5036. O-β-chloroethyl-N-diethyl carbamate$^{1)}$: yield 82%; b.p.$_{0.8}$ 61 °C.; n_D^{21} 1.4464.

S-Ethyl-N-β-chloroethyl-N-methyl Thiolcarbamate$^{1)}$

The substance was prepared by reaction of N-methylaziridin with S-β-chloroethyl chlorothiolformate in ether, yield 80%; b.p.$_{0.3}$ 72 °C.; n_D^{21} 1.5210.

S-, O- and N-Vinyl Carbonic Acid Derivatives$^{1)}$

The β-chloroethyl compounds were dissolved in absolute t-butanol and added dropwise to a freshly prepared equimolar solution of potassium t-butoxide in absolute t-butanol. The temperature was kept at 50–70 °C. during the reactions. After the addition was completed, the slurries were stirred for at least 1–2 hrs., usually until the reaction mixtures were neutral or only weak basic. The reaction mixtures were cooled, neutralized with glacial acetic acid and ether was added to complete the precipitation of the salt. The slurries were filtered, the solvent evaporated and the residues vacuum distilled.

S-Vinyl-N-diethyl monothiolcarbamate[1] (I): yield 83%; b.p.$_{1.2}$ 58–59°C.; n_D^{25} 1.3043.

O-Vinyl-N-diethyl-carbamate[1] (III): yield 45%; b.p.$_{4.8}$ 49°C.; n_D^{25} 1.4345.

N-Vinyl-N-methyl-S-ethyl monothiolcarbamate[1] (II): yield 62%; b.p.$_{0.7}$ 47°C.; n_D^{25} 1.5299.

c) *Copolymerization Experiments*

The polymerizations (in bulk) were carried out in sealed glass tubes, which had been flushed with nitrogen. 2,2'-Azobisisobutyronitrile (0.25–0.3% b.wt.) was used as a catalyst. The polymerization temperature was 66°C. The polymerizations were stopped at low conversions.

The copolymers were precipitated from methanol or pentane and purified by repeated dissolution in benzene and precipitation in methanol or pentane. The copolymers with styrene were dried for six days at 70°C and 0.1 mm. Hg, the copolymers with vinylacetate were freeze dried from dilute benzene solutions.

The composition of the copolymers was evaluated by KJELDAHL nitrogen determinations. The % N given in Tables 1–6 are an average of two analyses. The analyses were performed at A. BERNHARDT, Microanalytical Laboratories, Mülheim/Ruhr, Germany.

d) *Results*

The experimental data are given in Tables 1–6. The reactivity ratios r_1 and r_2 were determined by use of the integrated copolymerization equation of MAYO and LEWIS[4].

Table 1. Copolymerization of S-Vinyl-N-diethyl monothiolcarbamate (M_1) with Styrene (M_2)

Exp. No.	M_1/M_2 *)	Conversion (%)	% N	m_2/m_1 **)
a	2.305	8.65	3.79	2.06
b	0.982	6.3	2.02	5.13
c	0.450	7.9	1.29	8.75
d	0.264	11.3	0.71	18.8
e	0.168	12.5	0.52	24.4

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*) M_1, M_2 = initial concentration of the two monomers (mole).

**) m_1, m_2 = concentration of monomers in the copolymer (mole).

Table 2. Copolymerization of S-Vinyl-N-diethyl monothiolcarbamate (M_1) with Vinylacetate (M_2)

Exp. No.	M_1/M_2 *)	Conversion (%)	% N	m_2/m_1 **)
a	0.926	6.5	7.25	0.395
b	0.702	6.6	6.61	0.612
c	0.347	8.1	6.14	0.801
d	0.194	8.07	5.40	1.113
e	0.115	9.08	4.16	2.062
f	0.093	4.7	3.84	2.388

Table 3. Copolymerization of O-Vinyl-N-diethyl carbamate (M_1) with Styrene (M_2)

Exp. No.	M_1/M_2 *)	Conversion (%)	% N	m_2/m_1 **)
a	3.0760	3.55	1.17	10.13
b	2.0942	4.55	0.70	17.85
c	1.0706	3.82	0.38	37.20
d	0.5473	3.91	0.26	50.37
e	0.4135	5.82	0.18	73.39

Table 4. Copolymerization of O-Vinyl-N-diethyl carbamate (M_1) with Vinylacetate (M_2)

Exp. No.	M_1/M_2 *)	Conversion (%)	% N	m_2/m_1 **)
a	0.554	7.8	3.15	3.504
b	0.358	5.6	2.28	5.477
c	0.306	5.0	2.02	6.394
d	0.139	5.5	1.11	12.997
e	0.068	6.7	0.61	25.02

Table 5. Copolymerization of N-Vinyl-N-methyl-S-ethyl monothiolcarbamate (M_1) with Styrene (M_2)

Exp. No.	M_1/M_2 *)	Conversion (%)	% N	m_2/m_1 **)
a	4.465	6.12	2.45	4.10
b	2.002	7.95	1.46	7.82
c	0.549	2.96	0.50	25.50
d	0.305	4.25	0.45	28.51
e	0.193	3.08	0.25	52.36

Table 6. Copolymerization of N-Vinyl-N-methyl-S-ethyl monothiolcarbamate (M_1) with Vinylacetate (M_2)

Exp. No.	M_1/M_2 *)	Conversion (%)	% N	m_2/m_1 **)
a	0.217	8.0	5.6	1.219
b	0.485	9.1	5.15	1.473
c	0.401	7.7	4.71	1.770
d	0.173	6.0	2.63	4.508
e	0.102	7.3	1.98	6.550

III. *Discussion*

The results of the parameter (r_1, r_2) determination of the monomers I, II and III are summarized in Table 7. The copolymer composition plots are given in figures 1 and 2.

Table 7. Copolymerization Parameters of S-, N- and O-Vinyl Carbamates (M_1)

Monomers	r_1	r_2	e_1	Q_1
S-Vinyl-N-diethyl monothiolcarbamate (I)			−1.49[a]	0.33[a]
Styrene (M_2)	0.14 ± 0.03	4.4 ± 0.6	−1.49	0.40
Vinylacetate (M_2)	1.5 ± 0.3	0.16 ± 0.08	−1.49	0.25
N-Vinyl-N-methyl-S-ethyl monothiolcarbamate (II)			−1.86	0.18
Styrene (M_2)	0.025 ± 0.01	13.0 ± 3	−1.86	0.18
Vinylacetate (M_2)	1.3 ± 0.2	0.6 ± 0.1	−0.88[b]	0.044
O-Vinyl-N-diethyl carbamate (III)			−1.10[a]	0.021[a]
Styrene (M_2)	0.03 ± 0.01	32.0 ± 5	−1.01	0.029
Vinylacetate (M_2)	0.25 ± 0.08	1.8 ± 0.4	−1.19	0.012

[a] Average of the following two values.

[b] The negative polarity of monomer II as derived from these copolymerization data is unusually small compared with known data of analogue N-vinylmonomers[5–8].

The copolymerization parameters r_1, r_2 show that the reactivities of the three monomers in copolymerization reactions with a free radical, derived from styrene or vinyl acetate, is of the following order:

S-Vinyl > N-Vinyl > O-Vinyl

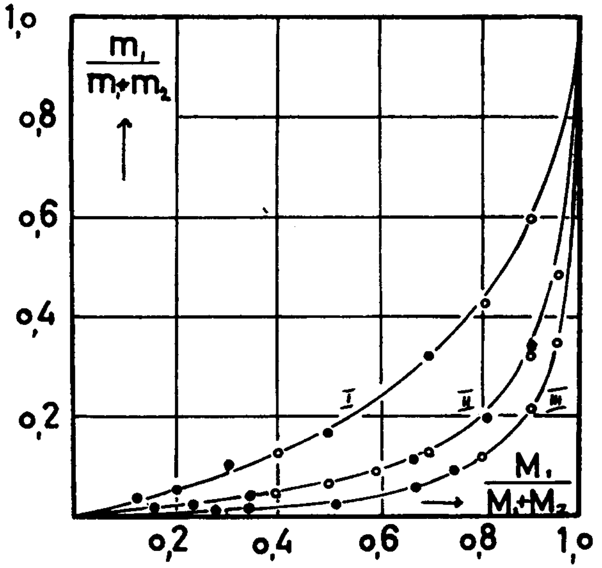


Fig. 1. Copolymer composition plots (● found, ○ calculated)

Curve I: S-Vinyl-N-diethyl monothiolcarbamate and styrene
Curve II: N-Vinyl-N-methyl-S-ethyl monothiolcarbamate and styrene
Curve III: O-Vinyl-N-diethyl carbamate and styrene

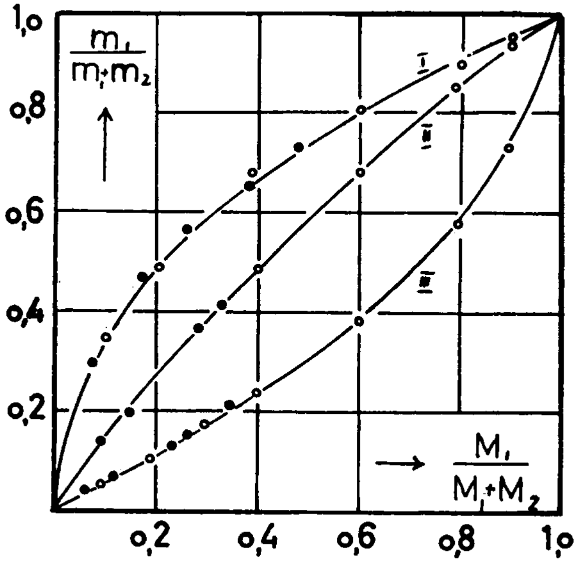
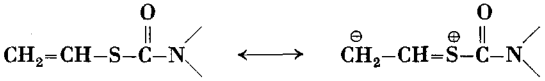


Fig. 2. Copolymer composition plots (● found, ○ calculated)

Curve I: S-Vinyl-N-diethyl monothiolcarbamate and vinylacetate
Curve II: N-Vinyl-N-methyl-S-ethyl monothiolcarbamate and vinylacetate
Curve III: O-Vinyl-N-diethyl carbamate and vinylacetate

All monomers are less reactive than styrene, but only O-vinyl-N-diethyl carbamate (III) shows a smaller copolymerization tendency than vinylacetate.

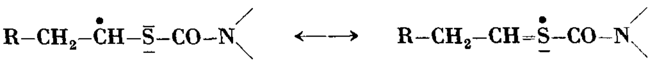
The reactivities (Q_1) of the monomers and the polarities (e_1) of their double bonds were calculated from the parameters r_1 and r_2 using the Alfrey-Price equation[9]. The Q- and e-values of 0.028 and −0.3 as indicated by Price[10] for vinylacetate were used. The values obtained for each copolymer system are given in Table 7 too. All three monomers are characterized by a negative polarity as can be visualized, considering the following electron distributions:



$$\mathrm{CH_2{=}CH{-}S{-}\overset{\overset{O}{\|}}{C}{-}N\langle} \longleftrightarrow \mathrm{\overset{\ominus}{C}H_2{-}CH{=}\overset{\oplus}{S}{-}\overset{\overset{O}{\|}}{C}{-}N\langle}$$

The basic properties of the hetero atoms increase the negativity of the vinyl double bond. Due to the electron-donating character of the amino, the sulfide and the ether group, one would expect to find the most negative polarity for the N-vinyl compound*). This is in agreement with the findings.

The fact that the S-vinyl compound (I) is more reactive than the other monomers (II, III) in copolymerizations, finds its explanation in its relatively high Q-value, indicating a considerable resonance stabilization of the adduct radical



$$\mathrm{R{-}CH_2{-}\overset{\bullet}{C}H{-}\underline{\overline{S}}{-}CO{-}N\langle} \longleftrightarrow \mathrm{R{-}CH_2{-}CH{=}\underline{\overset{\bullet}{S}}{-}CO{-}N\langle}$$

This resonance stabilization of the radical involves expansion of the sulfur octet, which is in agreement with other chemical evidence and already suggested by Price, Zomlefer, and Scott to explain the relatively high Q-values of methyl vinyl sulfide[11] and divinylsulfide[12].

Table 8 summarizes the known Q- and e-values of S-vinyl sulfides and S-vinyl thiolesters.

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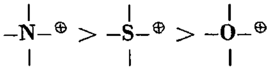
*) The tendency of amines, sulfides and ethers to form "Onium" salts is of the following order



$$\mathrm{-\overset{|}{\underset{|}{N}}-^{\oplus} > -\overset{|}{\underset{|}{S}}-^{\oplus} > -\overset{|}{\underset{|}{O}}-^{\oplus}}$$

Table 8. Copolymerization Parameters of S-Vinyl Sulfides and S-Vinyl Thiolesters

Monomer	Q	e	Lit.
S-Vinyl-N-diethyl monothiolcarbamate ..	0.32	−1.49	[a]
S-Vinyl thiolacetate	0.31	−1.46	[b]
Methyl vinyl sulfide	0.32	−1.45	[11]
Phenyl vinyl sulfide	0.34	−1.40	[14]
Divinyl sulfide	0.58	−1.11	[12]
Pentachlorophenyl vinyl sulfide	0.22	−0.58	[14]
Ethyl vinyl sulfide	0.37	−0.12	[14]

[a] This paper.

[b] Calculated from datas given by C. G. OVERBERGER, H. BILETCH, and R. G. NICKERSON[13].

The second substituent on the sulfur does not seem to have a remarkable influence on the reactivity of the double bond. This was also confirmed by the Q- and e-values of S-vinyl thiolacetate, which were calculated from copolymerization data given by OVERBERGER, BILETCH and NICKERSON[13]. The two S-vinyl esters, monomer I and vinyl thiolacetate, and the S-vinyl sulfides (methyl vinyl sulfide and phenyl vinyl sulfide) have nearly identical copolymerization parameters.

Positive e-values and low Q-values of S-vinyl compounds are only known for methyl vinyl sulfone ($Q = 0.11$; $e = +1.2$)[11] and n-butyl vinyl sulfonate ($Q = 0.02$; $e = +0.8$)[15].

Both the sulfone and the sulfonate group are electron withdrawing, and the sulfur in these oxygenated groups cannot expand its valence shell as suggested for the sulfides and thiolesters.

Contrasted to these results for S-vinyl sulfides and thiolesters, the e-values of analogue O-vinyl compounds differ noticeably, *e.g.* from −1.64 for n-butyl vinylether to +0.42 for vinyl butyrate (Table 9).

Table 9. Copolymerization Parameters of O-Vinyl Ethers and O-Vinyl Esters

Monomer	Q	e	Lit.
n-Butyl vinyl ether	0.014	−1.64	[14]
Diethyleneglycol monovinyl ether	0.046	−1.39	[14]
Ethyl vinyl ether	0.032	−1.17	[16]
O-Vinyl N-diethyl carbamate (III)	0.019	−1.10	this paper
Vinyl formate	0.20	−0.83	[17]
Vinyl acetate	0.028	−0.30	[6]
Vinyl laurate	0.012	0.06	[14]
Vinyl butyrate	0.038	0.42	[14]

This may be explained by the fact that for monomers with Q-values close to zero, slight differences in the polarity of the double bond play an important roll in the copolymerization behavior of these monomers.

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