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Copolymerization Behavior of N-Vinylcarbazole and Other N-Vinyl Monomers

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SUMMARY:

N-vinylcarbazole has been copolymerized with methyl methacrylate, methyl acrylate, styrene and vinylidene chloride. From the reactivity ratios found and from literature data, the Q and e values were calculated according to the ALFREY-PRICE scheme:

$$Q = 0.30 \qquad e = -1.2$$

Values of the resonance factor q and the electrical factor ε were calculated using the equations of SCHWAN and PRICE:

$$q = -2.3 \text{ kcal/mole}$$

$$\varepsilon = -0.39 \cdot 10^{-10} \text{ e.s.u.}$$

Q and e values for several N-vinyl monomers were plotted on a Q-e map.

ZUSAMMENFASSUNG:

N-Vinylcarbazol wurde mit Methylmethacrylat, Methylacrylat, Styrol und Vinyliden-chlorid copolymerisiert. Aus den bestimmten Copolymerisationsparametern und aus Literaturangaben wurden die Werte für Q und e nach der Beziehung von ALFREY-PRICE berechnet:

$$Q = 0,30 \qquad e = -1,2$$

Werte für den Resonanzfaktor q und den elektrischen Faktor ε wurden nach den SCHWAN-PRICE-Gleichungen berechnet:
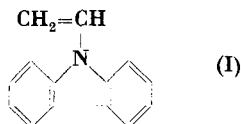
$$q = -2,3 \text{ Kcal/Mol}$$

$$\varepsilon = -0,39 \cdot 10^{-10} \text{ e.s.E.}$$

Die Q- und e-Werte für verschiedene N-Vinylmonomere wurden verglichen.

1. Introduction

Few data concerning the copolymerization of N-vinylcarbazole (I) with other monomers are available in the literature[1-3].

$$CH_2=CH$$

In this study N-vinylcarbazole has been copolymerized with methyl methacrylate, methyl acrylate, styrene and vinylidene chloride. Its reactivity Q and polarity e were determined and compared to those of other N-vinyl monomers.

The resonance and electrical factors q and ε were also calculated and compared to previously reported values.

2. Experimental

(by D. Timmerman)

a) *Materials*

N-Vinylcarbazole, a commercial product, was recrystallized from methanol. Polymerization tests indicated that is was free from inhibiting sulfur containing impurities[4].

The other *monomers* and the polymerization *solvent* (benzene free of thiophene) were carefully purified and freshly distilled under nitrogen before use.

b) *Procedure*

All the copolymerization experiments were carried out in benzene solution, at 75°C., in glass tubes sealed under nitrogen atmosphere, in the presence of 7.3 mole/l. azo-bis-isobutyronitrile. The total concentration of the monomers was comprised between 1.1 and 1.9 mole/l. The polymerizations were stopped at low conversions.

The copolymers were purified by repeated dissolution in methylene chloride or butanone and precipitation in methanol.

The composition of the copolymers was evaluated by Kjeldahl nitrogen determinations; the composition of the copolymers with vinylidene chloride was calculated from Schöniger chlorine determinations[*].

[*] We are indebt to Dr. L. Moelants, Head of our Analytical Department, for the polymer analysis.

[1] T. Alfrey, Jr. and S. L. Kapur, J. Polymer Sci. 4 (1949) 215.

[2] T. Alfrey, Jr. and B. Mazel, unpubl. results; cf. T. Alfrey, Jr., J. J. Bohrer, and H. Mark, "Copolymerization", Interscience, New York, 1952, p. 39.

[3] S. N. Ushakov and A. F. Nikolaev, Izvestia Akad. Nauk SSSR, Otdel. Khim. Nauk, (1956) 83; C.A. 50 (1956) 13867.

[4] H. Davidge, J. appl. Chem. 9 (1959) 241.

c) *Results*

The results of the copolymerizations are described in Tables I, II, III, and IV and in Fig. 1 and 2. M_2 and m_2 are the mole fractions of vinylcarbazole respectively in the monomer feed and in the copolymer.

Table I. Copolymerization of methyl methacrylate and N-vinylcarbazole (M_2)

M_2	Conversion (%)	N-content (%)	m_2
0.100	6.8	0.62	0.046
0.200	4.5	1.28	0.100
0.400	9.5	2.41	0.205
0.500	9.5	2.96	0.263
0.600	5.7	3.31	0.303
0.800	2.8	4.29	0.429
0.900	12.2	5.09	0.549

Table II. Copolymerization of methyl acrylate and N-vinylcarbazole (M_2)

M_2	Conversion (%)	N-content (%)	m_2
0.200	8.2	2.92	0.231
0.400	15.0	4.19	0.379
0.500	5.6	4.50	0.421
0.600	3.1	4.58	0.433
0.800	7.5	4.83	0.470
0.900	4.7	5.53	0.588

Table III. Copolymerization of styrene and N-vinylcarbazole (M_2)

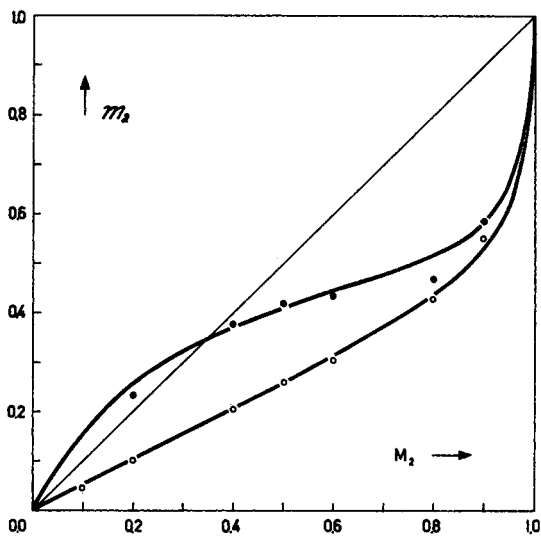| M_2	Conversion (%)	N-content (%)	m_2
0.103	5.4	0.34	0.026
0.200	3.2	0.57	0.044
0.400	3.0	1.18	0.095
0.500	2.7	1.33	0.108
0.600	3.8	2.00	0.170
0.800	2.8	3.21	0.300
0.849	3.6	4.01	0.400
0.900	4.5	4.83	0.519

Fig. 1. Composition curves for the copolymerization of N-vinylcarbazole (M_2) with methyl methacrylate (○) and with methyl acrylate (●)
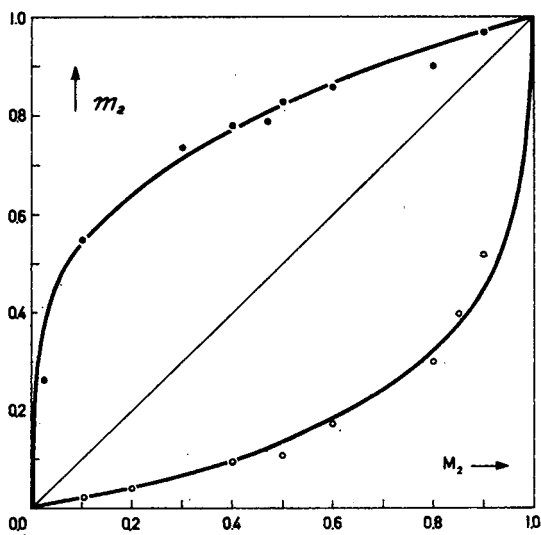

Fig. 2. Composition curves for the copolymerization of N-vinylcarbazole (M_2) with styrene (○) and with vinylidene chloride (●)

Table IV. Copolymerization of vinylidene chloride
with N-vinylcarbazole (M_2)

M_2	Conversion (%)	Cl-content (%)	m_2
0.025	3.5	42.49	0.266
0.100	8.2	21.32	0.550
0.300	1.2	11.29	0.734
0.400	9.2	9.06	0.781
0.466	5.8	8.68	0.789
0.500	7.5	—	0.827 *)
0.601	15.7	5.65	0.857
0.800	5.5	3.86	0.900
0.900	2.5	1.10	0.971

*) calculated from N-content (6.56% N).

3. Discussion

The reactivity ratios, r_1 and r_2 were calculated by the method of inter-cepts proposed by MAYO and LEWIS[5], using the integrated copolymeri-zation Eq. (1) and by fitting the best curve through the experimental points (Fig. 1 and 2)

$$r_2 = \frac{M_1}{M_2} \left[\frac{m_2}{m_1} \left(1 + \frac{M_1}{M_2} r_1 \right) - 1 \right] \tag{1}$$

The values found are indicated in Table V, together with pertinent literature data.

The reactivity Q_2 of N-vinylcarbazole and the polarity e_2 of its double bond were calculated from the parameters r_1 and r_2, using Eqs. (2) and (3) derived from the ALFREY-PRICE equations[6].

$$e_2 = e_1 \pm (- \ln r_1 r_2)^{1/2} \tag{2}$$

$$Q_2 = \ln \frac{Q_1}{r_1} - e_1 (e_1 - e_2) \tag{3}$$

The values obtained for each copolymerization system are shown in Table V. The values of Q_1 and e_1 for reference monomers are indicated in Table VI[7].

[5] F. R. MAYO and F. M. LEWIS, J. Amer. chem. Soc. 66 (1944) 1595.

[6] T. ALFREY, Jr. and C. C. PRICE, J. Polymer Sci. 2 (1947) 101.

[7] C. C. PRICE, J. Polymer Sci. 3 (1948) 772.

Table V. Reactivity ratios for the copolymerization of N-vinylcarbazole (M_2) with various monomers (M_1)

M_1	r_1	r_2	Q_2	e_2	Ref.
methyl methacrylate	2.0	0.040	0.20	—1.20	*)
methyl methacrylate	2.0	0.20	0.25	—0.56	[1]
methyl acrylate..........	0.50	0.050	0.26	—1.32	*)
styrene	5.7	0.035	0.48	—2.07	*)
styrene	5.5	0.012	0.68	—2.45	[1]
vinylidene chloride	0.020	3.7	3.8	—1.01	*)
vinyl acetate	0.126	2.68	0.30	—1.34	[3]
2,5-dichlorostyrene	8.0	0.016	0.12	—1.03	[2]

*) This study.

Table VI. Q and e values of reference monomers [7]

M_1	Q_1	e_1
styrene	1.0	—0.8
methyl methacrylate	0.74	0.4
methyl acrylate...........	0.42	0.6
vinyl acetate	0.028	—0.3
vinyl chloride	0.024	0.2
vinylidene chloride	0.20	0.6
acrylonitrile	0.44	1.2
2,5-dichlorostyrene	1.67	0.4

The data of Table V agree quite satisfactorily with the exception of the more negative polarity found with styrene and the very large value of Q obtained with vinylidene chloride. It is most probable that the approximations of the ALFREY-PRICE scheme are not valid in these two cases owing to polarity factors for the copolymerization with styrene (both monomers are strongly negatively charged) and to steric factors for the copolymerization with vinylidene chloride (both monomers bear voluminous substituents). It should, however, be pointed out that in this last case, the determination of Q_2 is subjected to a rather large error since r_1 is very small and accordingly lacks precision.

Neglecting these abnormal values, the following mean values can be attributed to N-vinylcarbazole:

$$Q = 0.30 \qquad e = -1.2$$

SCHWAN and PRICE[8] have recently derived new equations which take account of the temperature factor and express the electrical factor ε in terms of e.s.u. and the resonance factor q in kcal/mole:

[8] T. C. SCHWAN and C. C. PRICE, J. Polymer Sci. **40** (1959) 457.

$$\varepsilon_2 = \varepsilon_1 \pm 0.372 \cdot 10^{-10} (-RT \ln r_1 r_2)^{1/2} \qquad (4)$$

$$q_2 = RT \ln r_1 + q_1 + 7.225 \cdot 10^{20} \varepsilon_1 (\varepsilon_1 - \varepsilon_2) \qquad (5)$$

Using these equations and the reference values given by SCHWAN and PRICE the q_2 and ε_2 values of N-vinylcarbazole were calculated from the reactivity ratios r_1 and r_2 reported in Table V. The results are shown in Table VII.

Table VII. q_2 and ε_2 values calculated from the copolymerization of N-vinylcarbazole (M_2) with various monomers (M_1)

Monomer M_1	Temp. (°C.)	q_2 [a]	ε_2 [b]	Ref.
methyl methacrylate	75	—2.0	—0.42	[*]
methyl methacrylate	70	—2.1	—0.22	[1]
methyl acrylate	75	—2.2	—0.42	[*]
styrene	75	—2.5	—0.63	[*]
styrene	70	—2.8	—0.75	[1]
vinylidene chloride	75	—4.4	—0.39	[*]
vinyl acetate	65	—2.5	—0.43	[3]
2,5-dichlorostyrene	70	—1.7	—0.48	[2]

[a] expressed in terms of kcal/mole. [b] expressed in terms of 10^{-10} e.s.u.
[*] this study.

From these data N-vinylcarbazole can be characterized by following values:

$$q_2 = -2.3 \text{ kcal/mole}; \qquad \varepsilon_2 = -0.39 \cdot 10^{-10} \text{ e.s.u.}$$

SCHWAN and PRICE have indicated different values: $q_2 = -1.2$ kcal/ mole; $\varepsilon_2 = +0.33 \cdot 10^{-10}$ e.s.u. The calculation of e and ε from Eqs. (2) and (4) necessitates a choice between two solutions. For chemical reasons it seems that a negative value for N-vinylcarbazole should be preferred.

The copolymerization behavior of N-vinylcarbazole can indeed be compared with data published lately on the copolymerization of other N-vinyl monomers. To get comparable results we recalculated literature data using a homogeneous set of Q_1 and e_1 values for the reference monomers (Table VI). In some cases, where r_1 or r_2 values were equal to zero, e_2 values were determined, as suggested by PRICE[9], from the results of two different copolymerization systems, using Eqs. (6) or (7).

$$e_2 = [\ln (Q'_1 r_1 / Q_1 r'_1) + e^2_1 - e'^2_1] / (e_1 - e'_1) \qquad (6)$$

$$e_2 = \ln (Q_1 r_2 / Q'_1 r'_2) / (e_1 - e'_1) \qquad (7)$$

[9] C. C. PRICE and R. D. GILBERT, J. Polymer Sci. 8 (1952) 577.

In Table VIII the reactivity ratios and the Q and e values of following N-vinyl monomers are reported:

N-vinylpyrrolidone (II), N-vinyloxazolidinone (III), N-vinyl-N'-ethylurea (IV), ethyl N-vinylcarbamate (V), N-vinylmercaptobenzothiazole (VI), N-vinylsuccinimide (VII) and N-vinyl-N-methyl-p-toluenesulfonamide (VIII). Data concerning vinyl isocyanate (IX) and isopropenyl isocyanate (X) are also mentioned although these N-vinyl monomers are not strictly comparable to the preceding compounds.
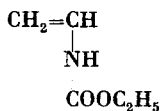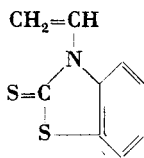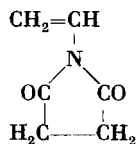
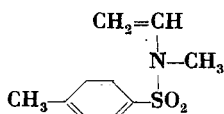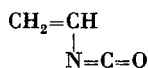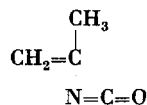$$CH_2=CH$$
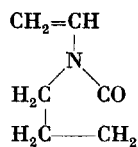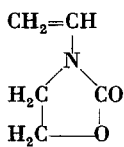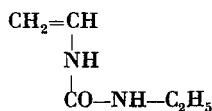
(II)   (III)   (IV)

(V)   (VI)   (VII)

(VIII)   (IX)   (X)

All these monomers are characterized by a negative polarity of their double bond. For compounds I to VIII, where the vinyl double bond is not conjugated with another unsaturated bond, this negative polarity can be explained by considering the mesomeric forms which can be attributed to N-vinyl derivatives [*]. The only possible charge on one of the carbon atoms of the double bond is a negative charge:

$$CH_2=CH-N\diagup \longleftrightarrow \overset{\ominus}{CH_2}-CH=\overset{\oplus}{N}\diagup$$
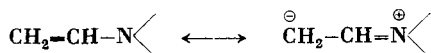
The importance of this effect will of course depend on the nature of the other substituents of the nitrogen atom. This appears clearly if one

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[*] See also ref. [14] and [15].

considers e.g. N-vinylpyrrolidone (II) ($e = -1.4$) and N-vinylsuccin-imide (VII) ($e = -0.26$) wherein the nitrogen atoms are substituted by respectively one and two electron acceptor groups ($-CO-$). The polarity of the vinyl bond of N-vinylsuccinimide is less negative than that of N-vinylpyrrolidone.

Table VIII. *Copolymerization parameters of N-vinyl monomers*

Monomer M_1	M_2	r_1	r_2	Q_2	e_2	Ref.
Styrene	II	15.7	0.045	0.10	−1.39	[11]
Methyl methacrylate	II	4.7	0.005	0.072	−1.54	[11]
Vinyl acetate	II	0.38	0.44	0.11	−1.64	[10]
Vinyl acetate	II	0.205	3.30	0.16	−0.92	[11]
Vinyl chloride	II	0.53	0.38	0.035	−1.07	[12]
Styrene [a]	III	30	0.05	—	—	[11]
Methyl methacrylate	III	6.0	0.03	0.073	−0.91	[13]
Methyl methacrylate	III	9.6	0.035	0.051	−0.64	[11]
Vinyl acetate	III	0.60	1.50	0.19	−0.62	[13]
Vinyl acetate	III	0.52	1.90	0.056	−0.41	[11]
Vinyl chloride	III	0.84	0.35	0.022	−0.90	[11]
Vinylidene chloride	III	1.35	0.08	0.060	−0.89	[13]
Styrene	IV	20	0.020	0.11	−1.76	[14]
Methyl methacrylate	IV	1.8	0.015	0.19	−1.50	[14]
Vinyl acetate	IV	0.45	0.63	0.087	−1.42	[14]
Vinyl acetate	V	0.33	0.33	0.13	−1.79	[15]
N-Vinylpyrrolidone [b]	V	2.0	0.42	0.090	−1.82	[15]
Methyl methacrylate	VI	0.1	1.0	1.7	−0.92	[16]
Styrene	VII	7.0	0.09	0.083	−0.12	[17]
Vinyl acetate [a]	VII	0.18	6.05	—	—	[17]
Methyl acrylate	VII	1.2	0.4	0.21	−0.26	[17]
Acrylonitrile	VII	0.54	0.16	0.12	−0.36	[17]
n-Butyl vinyl ether [c, d] . . .	VII	0	15	0.19	−0.13	[17]

[10] K. HAYASHI and G. SMETS, J. Polymer Sci. **27** (1958) 275.

[11] J. F. BORK and L. E. COLEMAN, J. Polymer Sci. **43** (1960) 413.

[12] J. W. BREITENBACH and H. EDELHAUSER, Ricerca sci., Suppl. **25** (1955) 242.

[13] R. HART and D. TIMMERMAN, Makromolekulare Chem. **31** (1959) 223.

[14] R. HART and D. TIMMERMAN, Bull. Soc. chim. belges **67** (1958) 123.

[15] L. GHOSEZ and G. SMETS, J. Polymer Sci. **35** (1959) 215.

[16] R. J. KERN, J. Polymer Sci. **43** (1960) 549.

[17] J. FURUKAWA, T. TSURUTA, N. YAMAMOTO, and H. FUKUTANI, J. Polymer Sci. **37** (1959) 215.

Table VIII (continued)

Monomer M_1	M_2	r_1	r_2	Q_2	e_2	Ref.
Styrene	VIII	12.3	0 [c]	0.092	−0.96	[17]
Methyl methacrylate	VIII	4.68	0 [c]	0.098	−0.77	[17]
acrylonitrile	VIII	0.42	0 [c]	0.086	−0.88	[17]
Styrene	IX	8.13	0.08	0.072	−0.13	[18]
Styrene	IX	6.9	0.1	0.089	−0.19	[19]
Methyl methacrylate	IX	5.57	0.16	0.12	+0.06	[18]
Methyl methacrylate [e]	IX	3.4	0.12	0.15	−0.55	[19]
Methyl acrylate	IX	1.38	0.14	0.14	−0.68	[18]
Vinylidene chloride	IX	1.46	0.33	0.082	−0.25	[18]
Acrylonitrile	IX	0.19	0.16	0.24	−0.67	[18]
Styrene	X	7.0	0.14	0.16	−0.94	[20]
Styrene	X	8.12	0.07	0.22	−1.55	[21]
Methyl acrylate	X	0.8	0.08	0.19	−1.09	[20]
Methyl acrylate	X	0.69	0.11	0.23	−1.00	[21]
Methyl methacrylate	X	3.10	0.14	0.17	−0.51	[21]
Vinylidene chloride	X	0.85	0.31	0.12	−0.55	[21]
Acrylonitrile	X	0.24	0.10	0.18	−0.73	[21]

[a] Q_2 and e_2 were not calculated when the product $r_1 r_2$ was greater than unity. [b] The Q_1 and e_1 values used are means of the values given in this table for vinylpyrrolidone ($Q_1 = 0.10$, $e_1 = −1.4$). [c] The Q_2 and e_2 values are calculated from pairs of copolymerization systems, according to the method of PRICE[7]. [d] $Q_1 = 0.015$, $e_1 = −1.6$.
[e] These data were kindly communicated by Dr. G. WELZEL; they differ slightly from previously published values[19].

For N-vinyl compounds such as vinyl and isopropenyl isocyanates, the carbon-carbon double bonds of which are conjugated with a carbon-nitrogen double bond, a somewhat different interpretation of the experimental results has been given[20].

In Fig. 3 the Q and e values of N-vinyl monomers are plotted on a Q-e map in relation to the position of some reference monomers. Concerning the high Q value of N-vinyl mercaptobenzothiazole it should be noted that this value has been calculated from only one single copolymerization system.

[18] Y. IWAKURA, M. SATO, T. TAMIKADO, and T. MIZOGUCHI, Kobunshi Kagaku, Chem. High Polymers Japan 13 (1956) 390; C.A. 51 (1957) 18694.
[19] G. WELZEL and G. GREBER, Makromolekulare Chem. 31 (1959) 230.
[20] R. HART and A. VAN DORMAEL, Bull. Soc. chim. belges 65 (1956) 571.
[21] Y. IWAKURA, M. SATO, T. TAMIKADO, and S. MIMASHI, Kobunshi Kagaku, Chem. High Polymers Japan 13 (1956) 390; C.A. 51 (1957) 4045.
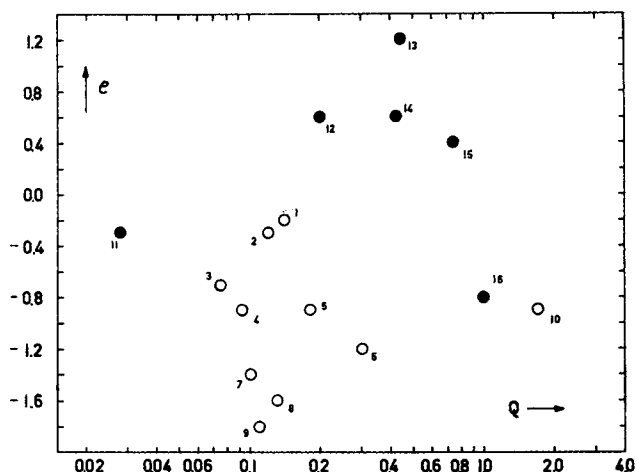
Fig. 3. Q-e map for N-vinyl monomers (○) and some reference monomers (●):
(1) N-vinylsuccinimide, (2) vinyl isocyanate, (3) N vinyloxazolidinone, (4) N-vinyl-N-methyl-p-toluenesulfonamide, (5) isopropenyl isocyanate, (6) N-vinylcarbazole, (7) N-vinylpyrrolidone, (8) N-vinyl-N'-ethylurea, (9) ethyl N-vinylcarbamate, (10) N-vinyl mercaptobenzothiazole, (11) vinyl acetate, (12) vinylidene chloride, (13) acrylonitrile, (14) methyl acrylate, (15) methyl methacrylate, (16) styrene

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