#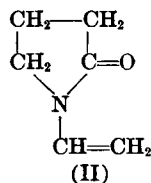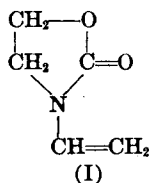 Nitrogen-Containing Monomers.   II.   Reactivity Ratios of N-Vinyloxazolidone and N-Vinylpyrrolidone with Vinyl Monomers*

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1. INTRODUCTION

The synthesis of N-vinyloxazolidone (I) and a brief description of its use as a monomer in vinyl polymerization was reported recently by Drechsel[1-3] and by Arend and Trieschmann.[4]   We have examined this new monomer, and this paper describes the results of reactivity ratio determinations with styrene, methyl methacrylate, decyl methacrylate, vinyl acetate, and vinyl chloride.   In addition, because of its structural similarity, the reactivity ratios of N-vinylpyrrolidone (II) with styrene, methyl methacrylate, and vinyl acetate were determined.   The Alfrey-Price Q and e values were calculated for both of the nitrogen-containing monomers in order to complete the comparison.

$$
\begin{array}{cc}
\begin{array}{c}
CH_2\!\!-\!\!O \\
| \qquad | \\
CH_2 \quad C\!\!=\!\!O \\
\diagdown \diagup \\
N \\
| \\
CH\!\!=\!\!CH_2
\end{array}
&
\begin{array}{c}
CH_2\!\!-\!\!CH_2 \\
| \qquad | \\
CH_2 \quad C\!\!=\!\!O \\
\diagdown \diagup \\
N \\
| \\
CH\!\!=\!\!CH_2
\end{array}
\\
\text{(I)} & \text{(II)}
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$$

2. EXPERIMENTAL

(a) Monomers

The N-vinyloxazolidone was prepared according to the general procedure used by Drechsel[3] with only minor modifications.   The crude monomer was distilled at 70° (0.3 mm.) giving pure product in 68% yield (calc.: for $C_5H_7O_2N$: N, 12.38%; found: N, 12.50%).

The N-vinylpyrrolidone was commercial material from Antara Chemical and was redistilled before use.   The styrene, methyl methacrylate, vinyl acetate, and decyl methacrylate were commercial grade materials and were carefully distilled before they were used.   The vinyl chloride was condensed from a pressure cylinder in Dry Ice and handled as a liquid.

(b) Polymerizations

General Procedures

The experimental methods were essentially those of Mayo and Lewis.[5] Polymerizations were carried out with 0.01 wt.-% azobisisobutyronitrile as the initiator in two-oz. screw-cap bottles fitted with Teflon gaskets and under a nitrogen atmosphere except in the case in which one monomer was vinyl chloride. In this case, the vinyl chloride was allowed to boil a few minutes in order to expel air before the bottle was capped. The polymers were precipitated by pouring the solutions into a nonsolvent and were purified by repeated reprecipitations from a solvent system into a nonsolvent system. The purified polymers were dried under high vacuum to constant weight, and the compositions of the copolymers were determined by elemental analysis.

The per cent nitrogen was determined by a modified Kjeldahl procedure involving digestion for 8 hr. instead of the usual 1–2 hr. The accuracy of the nitrogen analysis was checked by analyzing N-vinyloxazolidone and N-vinylpyrrolidone homopolymers. The results of these analyses were as follows.

1. ANAL. Poly-N-vinyloxazolidone (8 hr. digestion): Calc.: N, 12.38. Found: N, 12.37.

2. ANAL. Poly-N-vinylpyrrolidone (8 hr. digestion). Calc.: N, 12.61. Found: N, 11.6.

3. ANAL. Poly N-vinylpyrrolidone (2 hr. digestion). Calc.: N, 12.61. Found: N, 10.6.

These data indicate that, while little difficulty is involved in obtaining accurate nitrogen analyses for the N-vinyloxazolidone copolymers, it appears impossible to obtain accurate nitrogen analyses for the N-vinylpyrrolidone copolymers. Consequently, all the nitrogen analyses for the N-vinylpyrrolidone copolymers were corrected by the factor 12.61/11.6.

The reactivity ratios were determined from the differential form of the general copolymerization equation, both the method of intercepts[6] and the Fineman and Ross plots[7] being used.

TABLE I

Reactivity Ratio Data for Styrene (St) and N-Vinyloxazolidone.
Solution Polymerization in Benzene at 50°

Charge			Product		
St, g.	NVO, g.	Mole fraction NVO	Conversion, %[a]	N, %	Mole fraction NVO
12.00	13.00	0.50	4.85	0.44	0.033
9.51	15.49	0.60	3.24	0.67	0.050
7.60	12.40	0.60	3.37	0.60	0.045
7.07	17.93	0.70	1.80	0.90	0.067
5.67	14.33	0.70	7.34	0.90	0.067
3.74	16.26	0.80	4.80	1.46	0.109

[a] Based on the weight of copolymer obtained.

(c) Reactivity Ratio Determinations

N-*Vinyloxazolidone* (*NVO*)

With Styrene. Copolymerizations of NVO (M_2) with styrene (M_1) were run in benzene solution; the copolymers were precipitated with methanol and purified from benzene–methanol. Results are described in Table I. The r_1 and r_2 values obtained were $r_1 = 30$, $r_2 = 0.05$

With Methyl Methacrylate and Decyl Methacrylate. The copolymerizations of NVO (M_2) with methyl and decyl methacrylate were run in bulk and precipitated with methanol. Purification was by reprecipitation from benzene–methanol. The reactivity ratios as determined from the data in Tables II and III were: (*a*) with methyl methacrylate, $r_1 = 9.6$, $r_2 = 0.035$; (*b*) with decyl methacrylate, $r_1 = 12.8$, $r_2 = 0.015$.

TABLE II

Reactivity Ratio Data for Methyl Methacrylate (MMA) and *N*-Vinyloxazolidone.
Bulk Polymerization at 50°

Charge			Product		
MMA, g.	NVO, g.	Mole fraction NVO	Conversion, %[a]	N, %	Mole fraction NVO
2.24	22.76	0.90	1.80	5.21	0.392
4.53	20.47	0.80	1.44	3.43	0.254
6.87	18.13	0.70	1.44	2.32	0.170
9.29	15.71	0.60	1.52	1.73	0.126
12.98	12.02	0.45	2.08	1.01	0.073 .
16.83	8.17	0.30	2.16	0.57	0.042

[a] Based on the weight of copolymer obtained.

TABLE III

Reactivity Ratio Data for Decyl Methacrylate (DMA) and *N*-Vinyloxazolidone.
Bulk Polymerization at 50°

Charge			Product		
DMA, g.	NVO, g.	Mole fraction NVO	Conversion, %[a]	N, %	Mole fraction NVO
4.54	20.46	0.90	2.16	1.59	0.228
8.33	16.67	0.80	2.64	0.98	0.147
11.54	13.46	0.70	3.72	0.76	0.114
14.28	11.21	0.611	3.80	0.66	0.101
16.67	8.33	0.50	5.84	0.47	0.073

[a] Based on the weight of copolymer obtained.

With Vinyl Acetate. The bulk copolymerization of NVO (M_2) with vinyl acetate is described in Table IV. The polymers were precipitated in naphtha and purified from methylene chloride–naphtha. Reactivity ratio values of $r_1 = 0.52$, $r_2 = 1.90$ were obtained.

TABLE IV

Reactivity Ratio Data for Vinyl Acetate (VA) and *N*-Vinyloxazolidone.
Bulk Polymerization at 50°

Charge			Product		
VA, g.	NVO, g.	Mole fraction NVO	Conversion, %[a]	N, %	Mole fraction NVO
4.00	21.00	0.80	2.30	11.3	0.888
8.41	16.59	0.60	3.24	9.83	0.747
10.80	14.20	0.50	2.44	9.02	0.670
13.32	11.68	0.40	7.40	7.58	0.546

[a] Based on the weight of copolymer obtained.

With Vinyl Chloride. Copolymerizations of NVO (M_2) with vinyl chloride were run in bulk, and the polymers were precipitated with methanol. Purification was from dimethylformamide–methanol. Experimental data are described in Table V. Values of $r_1 = 0.84$, $r_2 = 0.35$ were calculated for this pair.

TABLE V

Reactivity Ratio Data for Vinyl Chloride (VCl) and *N*-Vinyloxazolidone.
Bulk Polymerization at 50°

Charge			Product		
VCl, g.	NVO, g.	Mole fraction NVO	Conversion, %[a]	Cl, %	Mole fraction NVO
11.1	39.2	0.339	9.14	18.3	0.462
17.8	32.2	0.500	9.22	24.5	0.578
26.3	23.7	0.667	6.46	32.1	0.701
33.5	15.6	0.795	8.12	38.6	0.792

[a] Based on the weight of copolymer obtained.

TABLE VI

Reactivity Ratio Data for Styrene (St) and *N*-Vinylpyrrolidone
Solution Polymerization in Benzene at 50°

Charge			Product		
St, g.	NVP, g.	Mole fraction NVP	Conversion, %[a]	N, %[b]	Mole fraction NVP
4.74	20.26	0.80	2.35	2.46	0.185
7.16	17.84	0.70	3.52	1.66	0.125
9.62	15.38	0.60	4.08	1.20	0.090
12.10	12.90	0.50	5.86	0.78	0.058
17.16	7.84	0.30	8.22	0.34	0.025

[a] Based on the weight of copolymer obtained.
[b] Corrected for low N determinations on poly-NVP.

N-Vinylpyrrolidone (NVP)

With Styrene. Benzene solution copolymerizations of NVP (M_2) with styrene (M_1) are described in Table VI. Polymers were precipitated from methanol and reprecipitated from benzene with methanol. From the data, values of $r_1 = 15.7, r_2 = 0.045$ were determined.

With Methyl Methacrylate. Copolymerizations of NVP (M_2) with methyl methacrylate were run in bulk and precipitated from carbon tetrachloride-petroleum ether. Purification was by reprecipitation from benzene with the same precipitating solvent. Values of $r_1 = 4.7, r_2 = 0.005$ were calculated from the data given in Table VII.

TABLE VII
Reactivity Ratio Data for Methyl Methacrylate (MMA) and N-Vinylpyrrolidone.
Bulk Polymerization at 50°

Charge			Product		
MMA, g.	NVP, g.	Mole fraction NVP	Conversion, %[a]	N, %[b]	Mole fraction NVP
4.59	20.41	0.80	4.46	3.65	0.269
6.97	18.03	0.70	2.88	3.40	0.249
11.85	13.15	0.50	3.84	2.07	0.150
14.36	10.64	0.40	4.44	1.60	0.116
16.94	8.06	0.30	4.60	1.19	0.086

[a] Based on the weight of copolymer obtained.
[b] Corrected for low N determination on poly-NVP.

With Vinyl Acetate. The copolymers of NVP (M_2) and vinyl acetate described in Table VIII were prepared by bulk polymerization and precipitated with naphtha. Reprecipitation was from acetone-naphtha. From the data, values of $r_1 = 0.205, r_2 = 3.30$ were calculated.

TABLE VIII
Reactivity Ratio Data for Vinyl Acetate (VA) and N-Vinylpyrrolidone.
Bulk Polymerization at 50°

Charge			Product		
VA, g.	NVP, g.	Mole fraction NVP	Conversion, %[a]	N, %[b]	Mole fraction NVP
8.52	16.48	0.60	3.8	11.0	0.841
13.43	11.57	0.40	3.8	9.66	0.717
16.09	8.91	0.30	3.1	8.48	0.614
18.91	6.09	0.20	2.0	7.24	0.510

[a] Based on weight of copolymer obtained.
[b] Corrected for low N determination on poly-NVP.

3. DISCUSSION

The results of the reactivity ratio determinations of N-vinyloxazolidone and N-vinylpyrrolidone are summarized in Table IX. The copolymers of

NVO with styrene, methyl methacrylate, and decyl methacrylate have smaller amounts of NVO than that originally charged as can be seen from the high r_1 and low r_2 values.

TABLE IX
Reactivity Ratios and Q and e Values of N-Vinyloxazolidone and N-Vinylpyrrolidone

Monomer M_1	Monomer M_2	r_1	r_2	Q_1	e_1	Q_2	e_2
Styrene	NVO	30.0 ± 0.5	0.05 ± 0.05	1.0	−0.8	0.043	−0.48
Methyl methacrylate	NVO	9.6 ± 0.2	0.035 ± 0.015	0.74	+0.4	0.052	−0.64
Decyl methacrylate	NVO	12.8 ± 0.5	0.015 ± 0.05	—	—	—	—
Vinyl acetate	NVO	0.52 ± 0.08	1.90 ± 0.10	0.028 0.01	−0.3 −0.5	0.062 0.020	−0.44 −0.61
Vinyl chloride[a]	NVO	0.84 ± 0.02	0.35 ± 0.02	0.074 0.024	+0.4 +0.2	0.054 0.023	−0.84 −0.90
Styrene	NVP	15.7 ± 0.5	0.045 ± 0.05	1.0	−0.8	0.087	−1.22
Methyl methacrylate	NVP	4.7 ± 0.5	0.005 ± 0.05	0.74	+0.4	0.074	−1.33
Vinyl acetate	NVP	0.205 ± 0.015	3.30 ± 0.15	0.028 0.01	−0.3 −0.5	0.170 0.067	−0.95 −1.12
Vinyl chloride[a]	NVP	0.53[a]	0.38[a]	0.074 0.024	+0.4 +0.2	0.085 0.034	−0.82 −1.07

[a] Different sets of values of Q and e for vinyl acetate and vinyl chloride were used because of the uncertainty of the actual values in the literature (see Alfrey et al., ref. 6).

Reactivity ratios of NVO with vinyl chloride show that copolymers can be prepared containing appreciable amounts of NVO and that the copolymer can contain higher or lower percentages of NVO than present in the charge. This system exhibits an azeotropic copolymerization composition at approximately 80 mole % vinyl chloride.

The copolymers of NVO with vinyl acetate are perhaps the most interesting of the series. In this case, r_1 is high and the copolymer is richer than the monomer charge in NVO.

Reactivity ratios of NVP with styrene and methyl methacrylate are similar to those for NVO with the same two monomers, although in the latter cases the r_1 is about twice the value as that for NVP. In any case, the NVP copolymerizes reluctantly with these monomers.

Similarity between NVP and NVO is also apparent in copolymers with vinyl acetate with r_2 (NVP) being greater than one. Reactivity ratios of $r_1 = 0.44$ and $r_2 = 0.36$ for the same system were reported by Hayashi and Smets.[8] The r_2 value differs from our determination; however, their value[8] was determined from a Kjeldahl nitrogen analysis. Applying our correction factor to these data, which we feel is necessary with NVP polymers (see Section 2 and also Breitenbach and Edelhauser[9]), an r_2 value very close to 3.3 is obtained. For completeness, we have also included in Table IX the reactivity ratios of NVP with vinyl chloride determined by
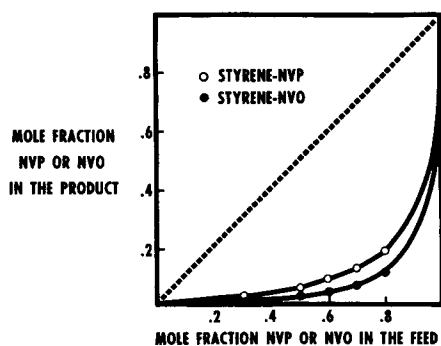
Fig. 1. Composition curves for copolymers: (O) styrene–NVP; (●) styrene–NVO.
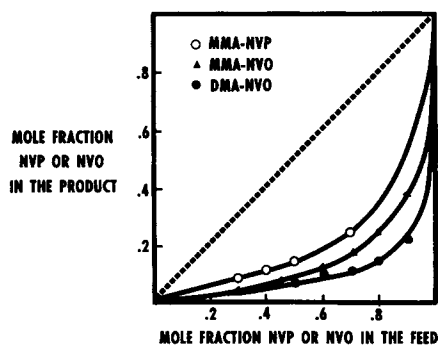

Fig. 2. Composition curves for copolymers: (O) MMA–NVP; (▲) MMA–NVO; (●) DMA–NVO.
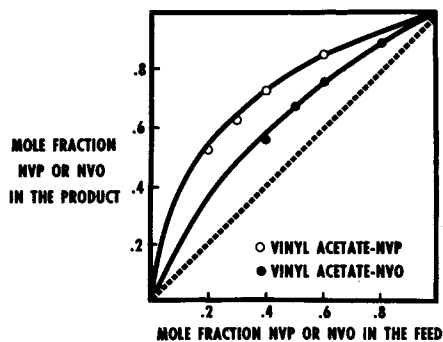

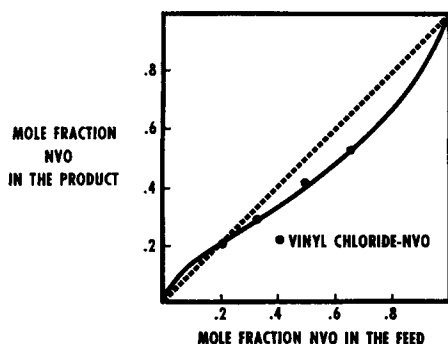Fig. 3. Composition curves for copolymers: (O) vinyl acetate–NVP; (●) vinyl acetate–NVO.

Fig. 4. Composition curve for vinyl
chloride–NVO copolymer.

Breitenbach and Edelhauser.[9] Composition curves for the various NVO
and NVP copolymers are shown in Figures 1–4.

The Alfrey-Price equations[6] were used to calculate the Q and e values
listed in Table IX.   For NVO, average values of $Q = 0.043$, $e = -0.63$
were found.   Different sets of values of Q and e for vinyl acetate and vinyl
chloride were used because of the uncertainty of the actual values in the
literature.[6]   Average values for NVP of $Q = 0.093$ and $e = -1.17$ were
calculated from our data.

From the results reported here, it can be seen that N-vinyloxazolidone is
similar but less reactive than N-vinylpyrrolidone as a monomer in copoly-
merization reactions.   Properties of the resultant copolymers, however,
differ considerably.

Note Added in Proof: Since our manuscript was submitted, a paper by R.
Hart and D. Timmerman (*Makromol. Chem.*, **31,** 223–229, 1959) on the "Copolymeriza-
tion of N-Vinyl-2-Oxazolidinone" has come to our attention. They have determined the
reactivity ratios of N-vinyl oxazolidone with methyl methacrylate, vinylidine chloride,
and vinyl acetate, and calculated the Q and e values as shown below:

Reference monomer (M_2)	r_2	r_2	Q_1	e_1	Q_2	e_2
Vinyl acetate	0.60	1.50	0.047	−0.3	0.086	−0.63
Vinylidine chloride	1.35	0.08	0.20	0.6	0.060	−0.89
Methyl methacrylate	6.00	0.03	0.74	0.4	0.073	−0.91

Although the values are not identical, our values agree quite well with those of Hart
and Timmerman.

We are indebted to Mr. Harry Ferber and Mr. William Coulman of our Analytical
Department for the polymer analysis.

References

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Synopsis

The reactivity ratios in the copolymerization of *N*-vinyloxazolidone with styrene, methyl methacrylate, decyl methacrylate, vinyl acetate, and vinyl chloride have been determined and the Alfrey-Price *Q* and *e* values calculated. Reactivity ratios in the copolymerization of *N*-vinylpyrrolidone with styrene, methyl methacrylate, and vinyl acetate have also been determined and the *Q* and *e* values determined. *N*-Vinyloxazolidone was found to be similar but less reactive than *N*-vinylpyrrolidone as a comonomer; however, the properties of the resultant copolymers differed appreciably.

Résumé

On a déterminé les rapports de réactivité dans la copolymérisation de la *N*-vinyloxazolidone avec le styrène, le méthacrylate de méthyle, le méthacrylate de décyle, l'acétate de vinyle et le chlorure de vinyle et partant, on a calculé les valeurs des *Q* et *e* d'Alfrey-Price. Les rapports des réactivités ont également été déterminés dans la copolymérisation de la *N*-vinylpyrrolidone avec le styrène, le méthacrylate de méthyle et l'acétate de vinyle et on a calculé les valeurs *Q* et *e*. Il a été trouvé que la *N*-vinyloxazolidone était similaire à la *N*-vinylpyrrolidone comme comonomère mais était moins réactionnelle. Toutefois, les propriétés des copolymères obtenus différaient appréciablement entre elles.

Zusammenfassung

Die Reaktivitätsverhältnisse wurden für die Copolymerisation von *N*-Vinyloxazolidon mit Styrol, Methylmethacrylat, Decylmethacrylat, Vinylacetat und Vinylchlorid bestimmt und die *Q*- und *e*-Werte nach Alfrey-Price berechnet. Ebenso wurden die Reaktivitätsverhältnisse für die Copolymerisation von *N*-Vinylpyrrolidon mit Styrol, Methylmethacrylat und Vinylacetat sowie die entsprechenden *Q*- und *e*-Werte bestimmt. Es wurde gefunden, dass *N*-Vinyloxazolidon sich als Comonomeres ähnlich wie *N*-Vinylpyrrolidon verhält, aber weniger reaktionsfähig ist; die Eigenschaften der erhaltenen Copolymeren unterschieden sich jedoch beträchtlich.