

Copolymerization of *N*-Vinylurethane*

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The synthesis of *N*-vinylurethane has been described recently by Hart.¹ It was obtained by addition of ethyl alcohol to vinylisocyanate. The corresponding polymer, the polyvinylurethane, is an important starting material for the synthesis of the polyvinylamine.

The availability of a new *N*-vinyl derivative affords the possibility for examining the influence of this type of substitution $\text{CH}_2=\text{CH}-\text{N}-\text{C}=\text{O}$ with respect to the reactivity and the polarity of the double bond, and to compare the different monomers carrying the same structural feature.

EXPERIMENTAL RESULTS

All the copolymerization experiments were carried out in methanol solution in sealed tubes at 65°C. in the presence of 0.01 mole/l. azoisobutyronitrile as initiator. The monomers were freshly distilled under a nitrogen atmosphere. The copolymers with vinyl acetate and acrylic acid were precipitated by pouring the solution into diethyl ether. After redissolving in dioxane these copolymers were isolated by freeze drying and dried in vacuum at 40°C. Their composition was calculated from a Kjeldahl nitrogen determination; the acrylic acid content was also determined by conductometric titration.

The copolymers with vinylpyrrolidone were purified by repeated precipitation in dry diethyl ether; their composition was determined by infrared analysis using the urethane absorption band at 1525 cm^{-1} (solvent: chloroform; cell thickness: 0.1 mm.; Perkin-Elmer 21 double-beam spectrometer).

The copolymers with maleic anhydride precipitate during formation. They were purified by several washings with benzene. The urethane content was evaluated by Kjeldahl nitrogen determination. At high vinylurethane concentration, the copolymer is always an alternating 50/50 copolymer; at low vinylurethane concentration, the solution discolored and no copolymer was obtained.

With vinyl chloride the yields were always very low (maximum 5%) even after several hours.

* Presented at the International Symposium on Macromolecules, Prague, September 9-15, 1957.

In the Tables I–III, M_1 and m_1 indicate the molar fraction of *N*-vinylethylurethane in the initial mixture of monomers and in the copolymer, respectively. M'_1 is the corrected molar fraction of the solution which takes into account the amount of monomer which was polymerized.

TABLE I
Copolymerization of *N*-Vinylethylurethane–Vinyl Acetate

No.	M_1	M'_1	m_1	% N_2	Time, min.	Yield, %
11	0.802	0.813	0.687	9.1	470	15.7
12	0.071	0.058	0.112	2.11	470	28.1
13	0.203	0.180	0.292	4.32	720	29.3
14	0.502	0.500	0.515	7.15	720	36.6
15	0.340	0.323	0.401	6.15	470	38.5

TABLE II
Copolymerization of *N*-Vinylethylurethane–*N*-Vinylpyrrolidone

No.	M_1	M'_1	m_1	Time, min.	Yield, %
21	0.792	0.795	0.65	55	5.8
22	0.895	0.900	0.78	80	8.8
23	0.575	0.585	0.39	40	8.8
24	0.864	0.877	0.74	—	18.3
25	0.479	0.500	0.33	50	18.6
26	0.315	0.333	0.205	—	24.3

TABLE III
Copolymerization of *N*-Vinylethylurethane–Acrylic Acid

No.	M_1	M'_1	m_1	Urethane, %	Acrylic acid, %	Total	Yield, %
1	0.672	0.742	0.340	45	56	101	10.6
2	0.882	0.910	0.708	79.5	19.5	99	22.1

From these data of Tables I–III, r_1 and r_2 values have been calculated using the differential equation at low yields (<15%). In all other cases the integrated equation has been used.^{2,3}

INTERPRETATION

The copolymerization reactivity ratios of *N*-vinylethylurethane with vinyl acetate and vinylpyrrolidone have been calculated from these data. Using the Q and e values of 0.028 and -0.3 indicated by Price for vinyl acetate,⁴ and 0.105 and -2.03 indicated by Smets and Hayashi⁵ for vinylpyrrolidone, the corresponding values of the reactivity and the polarity of *N*-vinylethylurethane have been evaluated. The results are summarized in Table IV.

TABLE IV

Comonomer M_2	r_1	r_2	$r_1 r_2$	e_1	Q_1
Vinyl acetate	0.33	0.33	0.109	-1.79	0.132
<i>N</i> -Vinylpyrrolidone	0.42	2.	0.84	-2.03	0.105
			<i>Av.</i>	-1.91	0.118

The agreement between the Q and e values in Table IV may be considered as satisfactory. From Table IV it appears that the cross-propagation reactions, as measured by the reciprocal value of $r_1 r_2$, are more pronounced with vinyl acetate than with vinylpyrrolidone; this is also evident

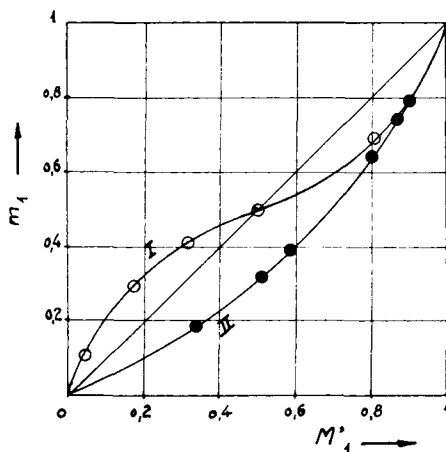


Fig. 1. Copolymerization of *N*-vinylethylurethane with vinyl acetate (O) and with *N*-vinylpyrrolidone (●). Curve I: $r_1 = r_2 = 0.33$. Curve II: $M_1 = 0.43$; $r_2 = 2$.

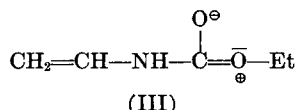
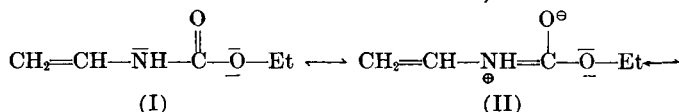
from Figure 1 which shows the usual copolymerization diagram. This behavior is evident on the basis of Table V.

TABLE V

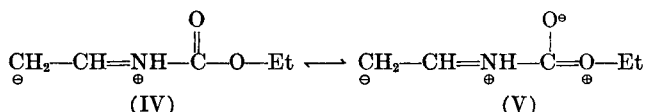
Monomer	e	Q	Ref.
<i>N</i> -Vinylethylurethane	-1.91	0.12	
<i>N</i> -Vinylethylurea	-1.6	0.14	6
<i>N</i> -Vinylpyrrolidone	-1.64	0.11	5
Vinyl acetate	-0.3	0.028	4
Vinyl ethyl ether			

Indeed, for monomers with low reactivity, the propagation reaction will be determined principally by the differences in polarity between the monomers. The high negative polarity value is somewhat surprising, although of the same range as that of *N*-vinylpyrrolidone and *N*-vinylethylurea.

Besides the usual electromeric formula,



an appreciable contribution by structures (IV) and (V) must be admitted. In these the basic properties of the nitrogen atom increase the negativity of the vinyl double bond.



The authors are indebted to Gevaert Photoproducten N.V. and to the Centre des Hauts Polymères for laboratory equipment, and to I.R.S.I.A. for the fellowship given to one of them (L. Gh.).

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Synopsis

N-Vinylurethane (M_1), prepared by the method of Hart, has been copolymerized with vinylacetate, vinylpyrrolidone, acrylic acid, and maleic anhydride. From the copolymerization reactivity ratios with vinyl acetate ($r_1 = 0.33$; $r_2 = 0.33$) and with vinylpyrrolidone ($r_1 = 0.42$; $r_2 = 2$), Q and e values were evaluated, in agreement with the Alfrey-Price equation, to 0.12 and -1.91 , respectively. These results are compared to those of other *N*-vinyl-substituted monomers.

Résumé

Le *N*-vinyluréthane (M_1), préparé par la méthode décrite par Hart, a été copolymérisé avec l'acétate de vinyle, la vinylpyrrolidone, l'acide acrylique et l'anhydride maléique. Aux dépens des rapports de réactivité à l'égard de l'acétate de vinyle ($r_1 = 0,33$, $r_2 = 0,33$) et de la vinylpyrrolidone ($r_1 = 0,42$, $r_2 = 2$) on a évalué en accord avec l'équation d'Alfrey-Price les valeurs de Q et e à 0,12 et $-1,91$ respectivement. Ces résultats sont comparés à ceux d'autres monomères vinyliques substitués à l'azote.

Zusammenfassung

N-Vinylurethan (M_1), das nach der von Hart beschriebenen Methode dargestellt wurde, wurde mit Vinylacetat, Vinylpyrrolidon, Acrylsäure und Maleinsäureanhydrid copolymerisiert. Aus den Reaktionsfähigkeits-verhältnissen mit Vinylacetat ($r_1 = 0,33$, $r_2 = 0,33$) und Vinylpyrrolidon ($r_1 = 0,42$, $r_2 = 2$) wurden nach der Beziehung von Alfrey-Price die Werte für Q und e zu 0,12 bzw. $-1,91$ ermittelt. Die Ergebnisse werden mit denen für andere, am Stickstoff substituierte Vinylmonomere verglichen.