of the residue indicated the presence of 23.7% XI, 7.1% XIII and 31.7% of VI.

The remaining residue afforded 0.41 g. (37.9%) of N,N-diphenylcarbamyl chloride when treated with alcohol. Alumina chromatography of the residue gave 0.02 g. (3.96%) of diphenyl disulfide, 0.08 g. (7.4%) of N,N-diphenylcarbamyl chloride, 0.16 g. (11.6%) of XII and 0.11 g. (7.78%) of VIII.

Reaction of XIII with I.—To 1.08 g. (4.65 mmoles) of N,N-diphenylcarbamyl chloride and 0.628 g. (4.65 mmoles) of XIII in 75 ml. of acetonitrile was added 4.65 mmoles of I in 25 ml. of acetonitrile. After 10 hours at 45–50°, 0.18 g. (47.9%) of sodium thiocyanate was obtained. Analysis of the residue (2.00 g.) indicated the presence of 33.4% XI, 11.5% of XIII and 15.7% of VI.

Chromatography of the remaining liquid gave 0.1 g. (19.8%) of diphenyl disulfide, 0.09 g. (8.3%) of N,N-diphenylcarbamyl chloride, 0.24 g. (17.5%) of XII and 0.19 g. (7.15%) of VIII.

Cyanide Cleavage of Methyl 5-(4-Nitrophenyl)-3,4-dithiapentanoate (IV).—Cleavage of 1.0 g. (3.66 mmoles) of IV in the usual manner with the exception that a nitrogen atmosphere was used afforded a green oil when the acetonitrile was removed. Addition of ether gave 0.12 g. (40.5%) of sodium thiocyanate. The vapor fractogram of the remaining oil (1.64 g.) indicated no volatile compo-

nents were present (30/60 mesh Celite columns containing 2% and 4% Carbowax were used over a temperature range of 90 – 140°). Authentic 4 - (5 - nitrophenyl) - 3 - thiabutanoate was not eluted under these conditions.

The oil was chromatographed on alumina and afforded three solid fractions which were recrystallized and identified as: 0.30 g. (35.3%) of N,N-diphenylcarbamyl chloride; 0.30 g. (48.7%) of p-nitrobenzyl disulfide, m.p. 122–124°; 0.26 g. (23.6%) of VIII. A fourth fraction, 0.005 g., m.p. 58–67°, was not identified. Although no pure sulfide could be obtained, the infrared spectrum of one of the liquid fractions was virtually identical to a spectrum of the authentic sulfide.

Reaction of IX with I.—A solution of 3.66 mmoles of I in 25 ml. of acetonitrile was added to 0.85 g. (3.66 mmoles) of N,N-diphenylcarbamyl chloride and 0.71 g. (3.66 mmoles) of IX[18] in 75 ml. of acetonitrile. Isolation of the products in the manner described gave 0.10 g. (33.8%) of sodium thiocyanate and a green oil, shown to contain no volatile products. Chromatography of the oil gave 0.30 g. (35.3%) of carbamyl chloride, 0.20 g. (32.5%) of p-nitrobenzyl disulfide and 0.05 g. (4.5%) of VIII. A liquid fraction exhibited a infrared spectrum essentially identical to authentic methyl 4-(4-nitrophenyl)-3-thiabutanoate, but no pure sulfide could be isolated.

(18) E. E. Reid, J. Am. Chem. Soc., **39**, 124 (1917).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF PENNSYLVANIA, PHILADELPHIA 4, PENNA.]

N,N-Divinylaniline and Its Polymerization

BY EUGENE Y. C. CHANG[1] AND CHARLES C. PRICE

N,N-Divinylaniline has been prepared by the pyrolysis of N,N-bis-(2-trimethylammonioethyl)-aniline dihydroxide. Radical polymerization and copolymerization of this monomer in dilute solutions gave soluble polymers with low residual double bond content. A cyclization polymerization mechanism is proposed. The copolymerization parameters for N,N-divinylaniline, divinyl sulfone and divinyl ether have been determined. The Q- and e-values for divinylaniline were found to be 0.15 and −1.6, respectively; those for divinyl sulfone were 0.14 and 1.4; and those for divinyl ether were 0.04 and −1.3. The higher Q-values of these divinyl monomers compared with those of the corresponding monovinyl monomers indicated enhanced reactivity due to direct interaction of neighboring double bonds. The stronger ultraviolet absorption of N,N-divinylaniline compared to that of N-phenylpyrrole also suggested the existence of resonance interaction between the two vinyl groups and the aromatic ring chromophore in N,N-divinylaniline. N,N-Divinylaniline showed a chain transfer constant of $C = 0.034$ in methyl methacrylate polymerization and $C = 0.013$ in styrene polymerization.

The similarity of the valence shell structures of nitrogen and oxygen suggests that N-vinyl compounds should have polymerization characteristics close to those of O-vinyl compounds and that a monomer such as N,N-divinylaniline should undergo a cyclization polymerization in the presence of a second monovinyl monomer similar to that of divinyl ether reported by Butler.[2]

The object of this work was therefore to prepare N,N-divinylaniline and to study its polymerization by radical catalysis. The copolymerization parameters of divinyl sulfone and divinyl ether were also determined for comparison.

Results and Discussion

Monomer Synthesis.—A process analogous to that for the preparation of N-methyl-N-vinyl-aniline[3] was adopted. N,N-Bis-(2-hydroxyethyl)-aniline was converted to N,N-bis-(2-bromoethyl)-aniline by treatment with phosphorus tribromide. The dibromide was treated with excess anhydrous trimethylamine in ethanol at room temperature to

give N,N-bis-(2-trimethylammonioethyl)-aniline dibromide. This quaternary ammonium bromide was then converted to the corresponding dihydroxide by silver oxide. N,N-Divinylaniline was obtained by pyrolysis of the diquaternary ammonium hydroxide at 150° under a nitrogen atmosphere. The compound absorbed two moles of hydrogen upon catalytic hydrogenation and the hydrogenated product was identical with N,N-diethylaniline.

Figure 1 illustrates the ultraviolet spectrum of N,N-divinylaniline together with those of several other reference compounds. The larger area covered by the bands of N,N-divinylaniline compared to N-phenylpyrrole indicates that there could be additional interaction arising in the divinylaniline molecule due to the freedom of rotation of the two vinyl groups to assume extra conjugating forms. The two "vinyl" groups in N-phenylpyrrole have restricted positions in a ring. Two possible conformations for the direct interaction between the two vinyl groups in divinylaniline are postulated as shown by formulas I and II.

In form I one vinyl group lies toward the back of the aniline plane and the other vinyl group lies toward the front. In form II the two vinyl groups lie toward the same side of the aniline plane. Simi-

(1) American Viscose Corp. Fellow, 1959–1960.

(2) G. B. Butler, Abstract of April, 1958, A.C.S. Meeting, San Francisco, Calif., p. 6-R. G. B. Butler, Abstract of Sept., 1958, A.C.S. Meeting, Chicago, Ill., p. 32-T.

(3) J. von Braun and G. Kirschbaum, Ber., **52**, 2261 (1919).

I   II

lar overlap of two orbitals can occur between the α-carbon atom of a vinyl group and the 1-carbon of the phenyl group, when the latter ring is perpendicular to the plane defined by the nitrogen and the vinyl carbons attached to it. The interatomic distance between the α-carbon atoms is estimated to be ca. 2.2 Å.

A similar type of interaction between the vinyl groups in divinyl and dipropenyl ether has been advanced by Price and Snyder.[4] The interatomic distance between the two α-carbon atoms in this case was also estimated to be ca. 2.2 Å.

Copolymerization Parameters.—As another experimental procedure for evaluating the ability of a nitrogen, oxygen or sulfone-sulfur atom to relay conjugation from a substituent on one side of the atom to that on the other, the copolymerization parameters of divinylaniline, divinyl ether and divinyl sulfone were measured. The evaluation of the reactivity ratios of these monomers was made by using a modified two-component composition equation similar to that which was used for the treatment of m-divinylbenzene[5] as shown in eq. 1.

This modified equation

$$r_2 = \frac{2M_1}{M_2}\left[\frac{m_2}{m_1}\left(1 + \frac{2M_1}{M_2}r_1\right)^{-1}\right] \quad (1)$$

where M_1 is the molar concentration of the divinyl monomer, is necessary in order to correct for the statistical factor of two for the divinyl monomers.

The results of the copolymerizations of N,N-divinylaniline with five other monomers, styrene, p-methylstyrene, methyl methacrylate, acrylonitrile and vinyl acetate, are summarized in Tables I to V. Those of divinyl sulfone with methyl methacrylate and styrene are given in Tables VI and VII; those of divinyl ether with methyl methacrylate and styrene are given in Tables VIII and IX. In most cases the compositions of divinylaniline copolymers were evaluated by nitrogen analysis, those of divinyl sulfone copolymers by sulfur analysis and those of divinyl ether by carbon analysis. In several cases when there were large discrepancies between the results of elementary analyses a value which would fit best in the composition curve was chosen. From the data in these tables the reactivity ratios r_1 and r_2 were estimated by the intersection method and Q- and e-values were calculated. The intersection method did not give adequate solutions of r_1 values for divinyl ether copolymerizations, a situation similarly encountered in the study of ethyl vinyl ether.[6] The method of simultaneous equations[6] was used in this case to obtain the Q- and e-

(4) W. H. Snyder, Doctoral Dissertation, University of Pennsylvania, June, 1961.

(5) R. H. Wiley and E. E. Sales, J. Polymer Sci., 42, 491 (1960).

(6) C. C. Price and T. C. Schwan, ibid., 16, 577 (1955).

Fig. 1.—Ultraviolet spectra of: N,N-divinylaniline,[a] ———; N-phenylpyrrole,[b] — — —; N,N-diethylaniline,[a] — — —; N,N-dimethylaniline.[c] — — — —.

[a] Present work. [b] J. Davoll, J. Chem. Soc., 3802 (1953). [c] H. Walba and G. E. K. Branch, J. Am. Chem. Soc., 73, 3342 (1951).

values. The copolymerization parameters for N,N-divinylaniline, divinyl sulfone and divinyl ether are listed in Tables X, XI and XII, respectively.

The high −e-values for N,N-divinylaniline and divinyl ether and the high +e-value for divinyl sulfone are as expected. The Q-values for divinyl sulfone and divinyl ether are markedly higher than

TABLE I

COPOLYMERIZATION OF N,N-DIVINYLANILINE (M_1) AND STYRENE $(M_2)^a$

$M_1{}^b$	$2M_1{}^c$	Time, hr.	Conversion, %	C, %	H, %	N, %	$m_1{}^d$
0.07	0.13	7	18	91.68	7.77	0.29	0.02
.18	.32	5	13	91.69	7.93	.63	.04
.28	.44	5	14	91.94	7.26	.74	.06
.41	.58	5	12	90.92	7.72	1.31	.10
.58	.73	4	7	89.76	7.80	2.09	.17
.71	.83	5	8	88.32	7.69	3.28	.28
.83	.91	5	8	87.88	7.69	4.29	.39
.95	.97	7	9	85.75	7.55	6.70	.63
.94	.97	8	11	84.87	7.88	7.15	.67

[a] Polymerized at 60° with 0.2–0.5% azoisobutyronitrile as catalyst. [b] Mole fraction of M_1 in the monomer mixture. [c] Mole fraction calculated as $2M_1/2M_1 + M_2$. [d] Mole fraction of M_1 in copolymer by nitrogen analysis.

TABLE II

COPOLYMERIZATION OF N,N-DIVINYLANILINE (M_1) AND p-METHYLSTYRENE $(M_2)^a$

$M_1{}^b$	$2M_1{}^c$	Time, hr.	Conversion, %	C, %	H, %	N, %	$m_1{}^d$
0.18	0.31	8	15	91.10	8.74	0.50	0.04
.24	.39	8	13	91.01	8.64	0.60	.05
.38	.55	8	15	90.32	8.57	1.05	.09
.46	.63	8	14	90.26	8.63	1.43	.12
.59	.74	11.5	15	89.37	8.33	2.13	.19
.73	.84	11.5	12	88.60	8.28	3.38	.30
.82	.90	12.5	10	87.44	8.22	4.05	.38
.94	.97	13.5	5	85.34	7.97	6.44	.63

[a] Polymerized at 66% monomer concentration in benzene at 60° with 0.4% azoisobutyronitrile as catalyst. [b] Mole fraction of M_1 in the monomer mixture. [c] Mole fraction calculated as $2M_1/2M_1 + M_2$. [d] Mole fraction of M_1 in copolymer by nitrogen analysis.

TABLE III
COPOLYMERIZATION OF N,N-DIVINYLANILINE (M_1) AND METHYL METHACRYLATE $(M_2)^a$

$M_1{}^b$	$2M_1{}^c$	Time, hr.	Conversion, %	C, %	H, %	N, %	$m_1{}^d$
0.31	0.41	3.5	9	67.97	7.84	3.24	0.23
.32	.48	7	20	67.69	7.88	3.21	.25
.45	.62	4	4	67.70	7.68	3.70	.30
.60	.75	7	10	70.05	7.97	4.31	.37
.78	.88	13	10	69.78	7.97	4.86	.43
.77	.87	2	12.5	73.23	4.38	5.77	.50
.83	.91	24	4	70.60	8.40	4.96	.42
.95	.98	34	12	75.23	8.02	6.76	.63

^{a} Polymerized at 30–100% monomer concentration in benzene at 60° with 0.02–0.5% azoisobutyronitrile as catalyst. ^{b} Mole fraction of M_1 in monomer mixture. ^{c} Mole fraction calculated as $2M_1/2M_1 + M_2$. ^{d} Mole fraction of M_1 in copolymer by nitrogen analysis.

TABLE IV
COPOLYMERIZATION OF N,N-DIVINYLANILINE (M_1) AND ACRYLONITRILE $(M_2)^a$

$M_1{}^b$	$2M_1{}^c$	Time, hr.	Conversion, %	C, %	H, %	N, %	$m_1{}^d$
0.06	0.11	4	4	74.02	6.73	18.10	0.20^d
.09	.16	4	11	74.38	6.96	16.94	.22^d
.02	.33	1.5	10	74.60	8.60	16.62	.34^e
.28	.44	4	10	73.26	6.70	16.09	.37^e
.39	.56	3.3	15	77.64	6.73	15.96	.42^d
.72	.84	0.5	11	75.93	7.63	14.46	.48^e

^{a} Polymerized at 30–100% monomer concentration in dimethylformamide at 60° with 0.2–0.5% azoisobutyronitrile. ^{b} Mole fraction of M_1 in monomer mixture. ^{c} Mole fraction calculated as $2M_1/2M_1 + M_2$. ^{d} Mole fraction of M_1 in copolymer by carbon analysis. ^{e} Mole fraction of M_1 in copolymer by nitrogen analysis.

TABLE V
COPOLYMERIZATION OF N,N-DIVINYLANILINE (M_1) AND VINYL ACETATE $(M_2)^a$

$M_1{}^b$	$2M_1{}^c$	Time, hr.	Conversion, %	C, %	H, %	N, %	$m_1{}^d$
0.14	0.24	72	0.5	73.64	7.60	6.99	0.55
.37	.54	72	1	77.73	7.73	8.36	.75
.49	.66	72	1.5	79.36	7.74	8.64	.82
.79	.88	72	2	80.73	7.85	10.46	.94
.91	.95	72	2	81.36	8.02	9.66	.97

^{a} Polymerized in bulk at 60° with 0.05–0.5% of azoisobutyronitrile as catalyst. ^{b} Mole fraction of M_1 in monomer mixture. ^{c} Mole fraction calculated as $2M_1/2M_1 + M_2$. ^{d} Mole fraction of M_1 in copolymer from the average of nitrogen and carbon analysis.

TABLE VI
COPOLYMERIZATION OF DIVINYL SULFONE (M_1) AND METHYL METHACRYLATE $(M_2)^a$

$M_1{}^b$	$2M_1{}^c$	Time, min.	Conversion, %	C, %	H, %	S, %	$m_1{}^d$
0.2	0.33	50	4.8	60.55	8.01	1.09	0.05
.4	.57	50	4.4	59.35	7.80	4.10	.13
.6	.75	75	7.0	54.72	7.51	7.32	.24
.8	.89	75	7.5	52.94	6.85	12.06	.40

^{a} Polymerized at 30% monomer concentration in benzene at 60° with 1% azoisobutyronitrile as catalyst. ^{b} Mole fraction of M_1 in the monomer mixture. ^{c} Mole fraction calculated as $2M_1/2M_1 + M_2$. ^{d} Mole fraction of M_1 in copolymer by sulfur analysis.

TABLE VII
COPOLYMERIZATION OF DIVINYL SULFONE (M_1) AND STYRENE $(M_2)^a$

$M_1{}^b$	$2M_1{}^c$	Time, hr.	Conversion, %	C, %	H, %	S, %	m_1
0.2	0.33	2.5	12	78.68	7.06	6.49	0.216^d
.4	.57	5.5	14	73.32	6.87	9.13	.32^e, 0.31^d
.6	.75	3.5	13	70.15	6.60	10.69	.40^e, .37^d
.8	.89	3.5	10	66.38	6.83	12.55	.47^e, .43^d

^{a} Polymerized at 30% monomer concentration in benzene at 60° with 1% azoisobutyronitrile as catalyst. ^{b} Mole fraction of M_1 in the monomer mixture. ^{c} Mole fraction calculated as $2M_1/2M_1 + M_2$. ^{d} Mole fraction of M_1 in copolymer by sulfur analysis. ^{e} Mole fraction of M_1 in copolymer by carbon analysis.

TABLE VIII
COPOLYMERIZATION OF DIVINYL ETHER (M_1) AND METHYL METHACRYLATE $(M_2)^a$

$M_1{}^b$	$2M_1{}^c$	Time, hr.	Conversion, %	C, %	H, %	O,^{d} %	$m_1{}^e$
0.2	0.33	1	6	60.35	8.10	31.55	0.06
.2	.33	2	12	60.26	8.05	31.69	.05
.4	.57	2	13	60.58	8.16	31.26	.10
.6	.75	2	12	60.88	8.11	31.01	.14
.8	.89	2	10	61.12	8.17	30.71	.18

^{a} Polymerized with 0.5% azoisobutyronitrile as catalyst at 60°. ^{b} Mole fraction of M_1 in the monomer mixture. ^{c} Mole fraction calculated as $2M_1/2M_1 + M_2$. ^{d} Obtained by difference from C,H analysis. ^{e} Calculated by %C in copolymer.

TABLE IX
COPOLYMERIZATION OF DIVINYL ETHER (M_1) AND STYRENE $(M_2)^a$

$M_1{}^b$	$2M_1{}^c$	Time, hr.	Conversion, %	C, %	H, %	O,^{d} %	$m_1{}^e$
0.2	0.33	6.5	6.2	92.24	7.55	0.21	0.002
.4	.57	6.5	6.1	92.15	7.90	..	.01
.6	.75	3.5	2.4	91.03	7.66	1.31	.08
.8	.89	6.5	2.0	90.20	7.69	2.11	.125

^{a} Polymerized with 1% azoisobutyronitrile as catalyst at 60°. ^{b} Mole fraction of M_1 in the monomer mixture. ^{c} Mole fraction calculated as $2M_1/2M_1 + M_2$. ^{d} Obtained by difference from C, H analysis. ^{e} Calculated by %C in copolymer.

TABLE X
COPOLYMERIZATION PARAMETERS FOR N,N-DIVINYLANILINE

M_2	r_2	r_1	r_1r_2	Q_2	e_2	Q_1	e_1
Styrene	13.0	0.045	0.585	1.0	-0.8	0.14	-1.5
p-Methylstyrene	11.8	.05	.59	1.0	-.9	.15	-1.6
Methyl methacrylate	2.0	.01	.02	0.74	.4	.16	-1.5
Vinyl acetate	0.1	2.0	.2	.01	-.3	.15	-1.6
Acrylonitrile	0.42	0.003	.0013	.68	.9	.16	-1.7
				.44	1.2	.06	-1.4
					Average	0.15	-1.6

TABLE XI
COPOLYMERIZATION PARAMETERS FOR DIVINYL SULFONE (M_1)

M_2	r_2	r_1	r_1r_2	Q_2	e_2	Q_1	e_1
Methyl methacrylate	8.5	0.045	0.38	0.74	0.4	0.13	1.4
Styrene	1.3	0.01	0.013	1.0	-0.8	0.15	1.3
					Average	0.14	1.4

TABLE XII

Copolymerization Parameters for Divinyl Ether (M_1)

M_2	r_2	$r_1{}^a$	$r_1 r_2$	Q_2	e_2	$Q_1{}^a$	$e_1{}^a$
Methyl methacrylate	10.0	0.006	0.06	0.74	0.4	0.04	−1.3
Styrene	40.0	0.02	0.8	1.0	−0.8	0.04	−1.3

^{a} Values obtained by method of simultaneous equations.

their analogous monovinyl monomers. Divinyl sulfone has a Q-value about twice that of methyl vinyl sulfone[7a] or phenyl vinyl sulfone[7b] (0.09 and 0.07) and divinyl ether has a value more than twice that of ethyl vinyl ether (0.015).[5] Divinylaniline, although no data of directly related analogous monovinyl monomers are available, has a Q-value about twice that of N-methyl-N-vinyl-p-toluenesulfonamide (0.09).[8] The increased reactivity of these divinyl monomers indicates extra stabilization of the intermediate radicals due to the presence of the second double bond. The added stabilization can be interpreted as involving a radical intermediate state anchimerically stabilized by a neighboring vinyl group as in the canonical form shown below, where X denotes either a nitrogen, oxygen or sulfone sulfur atom.

Structure of N,N-Divinylaniline Copolymers.—

When divinylaniline was polymerized with other monomers, such as styrene, methyl methacrylate, acrylonitrile, etc., in the absence of added solvent, an insoluble copolymer was always obtained. These insoluble copolymers must therefore contain a three-dimensional cross-linked network structure formed by random addition of each of the two vinyl groups with the growing radical chain. When divinylaniline was polymerized with the other monomers in the presence of a solvent such that the total concentration of the monomer mixture was not higher than 30%, a soluble copolymer could be obtained. Analysis for residual double bond in the soluble copolymers by infrared absorption in the

TABLE XIII

Copolymers of N,N-Divinylaniline (M_1) Polymerized in Solution

$M_2{}^a$	% $m_1{}^b$ by wt.	Mole of residual double bond ^{c}	ηinh^d
MMA	39	0.08	0.15
MMA	10	.25	.17
MMA	50	.0	.153^e
MMA	45	.07	.21
DEF	30	.15	..
p-MS	20	.21	..
STY	20	.0	..
STY	17	.09	0.36

^{a} MMA = methyl methacrylate, DEF = diethyl fumarate, p-MS = p-methylstyrene, STY = styrene. ^{b} % M_1 found in the copolymer. ^{c} Per mole of divinylaniline units in the copolymer. ^{d} Inherent viscosity = ln η_{rel}/c. ^{e} Mol. wt. = 10,000–22,000 by cryoscopic method.

(7) (a) C. C. Price and J. Zomlefer, J. Am. Chem. Soc., 72, 14 (1950), (b) C. C. Price and H. Morita, ibid., 75, 4747 (1953).

(8) J. Furukawa, T. Tsuruta, N. Yamamoto and H. Fukutani, J. Polymer Sci., 37, 215 (1959).

6.0 to 6.2 μ region showed negative results and catalytic hydrogenation indicated only a small amount in certain cases. The results of some of the analyzed samples are given in Table XIII.

The absence of residual double bond plus the high solubility of these copolymers prepared in dilute solutions strongly supported the view of a cyclization propagation step[1] with the formation of a favorable six-membered ring. The radical resulting from addition to one double bond of the divinyl monomer first adds to the double bond of the monovinyl monomer. In dilute solution, this radical evidently then cyclizes by attacking the second vinyl group of the divinyl monomer before it can react with a vinyl group in another monomer. The polymer chain would then contain structural units of the structure

A case showing a strong tendency to alternation of two monomers in copolymerization was demonstrated in the copolymerization of N,N-divinylaniline with diethyl fumarate, the results of which are given in Table XIV. Diethyl fumarate monomer, having widely different polarity from that of divinylaniline, and being reluctant to homopolymerize, polymerized with divinylaniline in widely different monomer concentration ratios to give copolymers of nearly constant two-to-one molar ratio composition. The solubility properties of these copolymers also supported the cyclization polymerization mechanism. The polymer chain should contain the repeating units below

TABLE XIV

Copolymerization of N,N-Divinylaniline (M_1) and Diethyl Fumarate (M_2)^a

M_1/M_2	Time, days	Conversion, %	C, %	H, %	N, %	$m_1/m_2{}^b$ by mole
1/0.2	5	5	64.71	7.31	3.25	1/1.7
1/0.6	23	23	64.61	7.21	3.57	1/1.5
1/1.4	5	8	63.85	7.29	2.99	1/2.0
1/3.2	6	15	63.79	7.18	2.95	1/2.0
1/4.0	5	4	63.39	7.21	2.62	1/2.1

^{a} Polymerized with 0.07–0.5% AIBN as catalyst at 60° with no added solvent. ^{b} Monomer ratio found in copolymer by N analysis.

Chain Transfer Properties.—

The presence of N,N-divinylaniline in the polymerization of methyl methacrylate or styrene caused a sharp decrease in molecular weights. This chain transfer property of N,N-divinylaniline is illustrated in Fig. 2 and

Fig. 2.—Chain transfer of N,N-divinylaniline in methyl methacrylate polymerization.

Fig. 3 by plotting $(1/P - 1/P_0)$ versus S/M according to eq. 2.

$$\frac{1}{P} = \frac{1}{P_0} + C \frac{S}{M} \qquad (2)$$

where P is the number average degree of polymerization, P_0 the degree of polymerization without divinylaniline, C the chain transfer constant, S the molar concentration of divinylaniline and M the molar concentration of the monomer to be polymerized. The concentrations of divinylaniline were held at very low levels such that the chain transfer (to monomer) of divinylaniline to its own monomer could be neglected. The slope of Fig. 2 gives $C = 0.034$ for methyl methacrylate polymerization and that of Fig. 3 gives $C = 0.013$ for styrene polymerization.

A possible mechanism for this chain transfer reaction could be postulated to involve at first the copolymerization of a divinylaniline molecule with a growing polymer radical in the cyclic manner. A hydrogen radical may then be abstracted from this cyclic radical chain end by another monomer molecule to start a new radical leaving a terminated polymer chain as shown in eq. 3.

$$(3)$$

This mechanism is in accord with that which was postulated for the chain transfer reaction of vinyl acrylate reported by Delmonte and Hays,[9] in which the proposed transfer step was that shown in eq. 4.

$$(4)$$

The decreased activity of divinylaniline as a chain transfer agent in styrene polymerization compared to methyl methacrylate polymerization is probably best explained by polar effects.

Homopolymerization.—N,N-Divinylaniline was polymerized to form low molecular weight homo-

(9) D. W. Delmonte and J. T. Hays, Abstract of Sept., 1959, A.C.S. Meeting, Atlantic City N. J., p. 1-T.

Fig. 3.—Chain transfer of N,N-divinylaniline in styrene polymerization.

polymers of about 30% conversion either with or without the presence of benzene solvent at 60° using azoisobutyronitrile catalyst. The polymers produced by bulk polymerization usually contained some gel particles whereas those produced by solution polymerization were always soluble. Infrared analysis and catalytic hydrogenation indicated the presence of about 50% of residual double bond per mole of divinylaniline units in the soluble portion of the bulk polymers and only negligible amount of double bond was detected in the solution polymers. The results of the experiments are illustrated in Table XV.

TABLE XV

PROPERTIES OF POLY-N,N-DIVINYLANILINE

Method[a]	Mole of residual double bond[b]	Conversion, %	η_{inh}[c]	M.p.,[d] °C.
Bulk	0.61	30	0.09[e]	160–170
Bulk	.53	30	.08	155–165
Soln.	.03	16	.05[f]	150–160
Soln.	.04	28	.06	152–161
Soln.	.06	28	.07	159–168

[a] Solution = 20–50% monomer in benzene. [b] Per mole of monomer unit, determined by hydrogenation. [c] Inherent viscosity. [d] Capillary tube method. [e] Cryoscopic method, mol. wt. 5000–7000. [f] Cryoscopic method, mol. wt. 4300.

From the results of bulk polymerization it is reasonable to assume that the soluble portion of the bulk polymers was formed by a cyclization polymerization scheme containing segments of the following structure, which accounts for the presence of

one residual double bond for every two monomer units. The substantial absence of double bonds in the solution polymers led to the postulation of a bicyclic structure[10]

(10) See also D. S. Trifan and J. J. Hoglen, J. Am. Chem. Soc., 83, 2021 (1961).

In this structure the bridge carbon atom may lie on either side of the rings to give two isomeric forms. The growing chain from the two ends of the bicyclic unit may also assume two isomeric configurations, *cis* and *trans*. A random distribution of the three different combinations of configuration in the chain would give a polymer amorphous in nature having a relatively low softening point as was found in the experiments.

Another alternative for the polymer chain to be linear and without residual double bond would be the formation of a four-membered ring by direct cyclization of the two double bonds in one monomer molecule to give the structural unit

However, this possibility was ruled out by infrared study of the CH_2 stretching frequencies of the polymers in the 2900 cm.$^{-1}$ region. The average of the asymmetric and symmetric CH_2 frequencies of the polymers tested lay in the range of 2892 and 2916 cm.$^{-1}$, corresponding to a strainless straight chain or strainless rings. A four-membered ring would correspond to an average value in the range of 2936 and 2969 cm.$^{-1}$.[11] Further support for the cyclized structural units in the polymer comes from the ultraviolet spectra data summarized in Table XVI. Both the lowered extinction coefficient for the 260 mμ band and the appearance of the 300 mμ band as a shoulder rather than a distinct maximum, indicate the similarity of the polymer chromophore to N-phenylpiperidine rather than to diethyl- or dibutylaniline.

TABLE XVI

ULTRAVIOLET ABSORPTION SPECTRA OF DIVINYLANILINE POLYMERS AND RELATED ANILINES

Compound	$\lambda_{max.}$ mμ	log ϵ	$\lambda'_{max.}$ mμ	log ϵ
Bulk polymer	260	3.97	298(sh)	3.36
Soln. polymer	260	3.93	298(sh)	3.23
N-Phenylpiperidine	254	3.94	292(sh)	3.0
N,N-Diethylaniline	260	4.18	302	3.34
N,N-Dibutylaniline	261	4.20	306	3.36

Experimental

Preparation of N,N-Divinylaniline. 1. N,N-Bis-(2-bromoethyl)-aniline.—N,N-Bis-(2-hydroxyethyl)-aniline (111 g., 0.61 mole) was melted and dropped slowly into 500 g. of phosphorus tribromide (1.84 moles) with stirring and gentle warming. The mixture was further heated for 3 hours on a steam-bath. An orange colored precipitate appeared during the reaction, probably a hydrobromide salt. Benzene, crushed ice and dilute caustic soda solution

(11) R. Zbinden and H. K. Hall, Jr., *J. Am. Chem. Soc.*, **82**, 1215 (1960).

were then added and the organic layer was separated, dried and passed through a column of activated alumina. After evaporation, the product was recrystallized from light petroleum ether; yield 135 g. (72%), m.p. 53–55° (lit.[12] 53–55°).

2. N,N-Bis-(2-trimethylaminoethyl)-aniline Dibromide. —A mixture of 130 g. (0.422 mole) of the above with 88 g. (1.49 moles) of anhydrous trimethylamine and 175 ml. of absolute ethanol was placed in a screw - capped flask and warmed to dissolve. The reactants were allowed to stand at room temperature for 3 or 4 days with occasional shaking. The precipitate formed was washed with ether and absolute ethanol to yield 145 g. (94%) of the dibromide. It was recrystallized from ethanol; m.p. 245–246° dec. *Anal.* Calcd. for $C_{16}H_{31}N_3Br_2$: C, 45.25; H, 7.35; N, 9.88. Found: C, 45.22; H, 7.17; N, 9.92.

3. N,N-Divinylaniline.—A solution of 33 g. (0.078 mole) of the quaternary ammonium salt in methanol was shaken with freshly-prepared moist silver oxide. After removing the silver bromide precipitate, the methanol solution was evaporated to a very viscous sirup. The viscous liquid was then dropped into a distilling flask kept at 150°. The decomposition products were carried over to a cooled receiver with a stream of nitrogen while the whole system was kept under a reduced pressure of 25 mm. The organic layer obtained was dried and distilled through a 30-cm. packed column and then through a Todd column to yield 8.0 g. (70%) of a colorless liquid, b.p. 81–81.7° (10 mm.), $n^{20}D$ 1.5734, d^{20}_4 0.955. The liquid became very viscous at −70° without crystallization. *Anal.* Calcd. for $C_{10}H_{11}N$: C, 82.71; H, 7.64; N, 9.65. Found: C, 82.68; H, 7.65; N, 9.84.

Purification of Monomers.—The liquid monomers were distilled through a 30-cm. packed column. The fractions were taken at the indicated boiling point: styrene, 38° (13 mm.); p-methylstyrene (Dow), 66° (18 mm.); methyl methacrylate, 100.5°; acrylonitrile, 76°; vinyl acetate, 72.5°; divinyl sulfone (Union Carbide), 102° (10 mm.); and divinyl ether (trade name Vinethene, Merck), 28°; diethyl fumarate (Eastman white label), undistilled. All samples were stored in the cold and in the absence of light.

Polymerization and Copolymerization Procedures.— Polymerizations were carried out in sealed tubes. Monomers, catalyst and solvent were weighed separately into an ampoule, the ampoule was then chilled in a Dry Ice–acetone-bath, evacuated and sealed under vacuum. From 0.1 to 1% by mole of azobisisobutyronitrile based on monomer was used as catalyst and benzene (dimethylformamide in the case of acrylonitrile monomer) was used as solvent in an amount equal or less than that of the monomer mixture. Catalysts such as benzoyl peroxide and hydroperoxides could not be used because they caused rapid discoloration of N,N-divinylaniline. Polymerization was carried out in a 60° bath.

The polymers were isolated by pouring the reactants into petroleum ether (boiling range 30–60°), filtering through fritted glass funnel, drying and reprecipitating by dissolving in a small amount of benzene or dimethylformamide and precipitating again in petroleum ether. The polymer was then collected by filtration and dried overnight under high vacuum.

The yields of homopolymers were generally lower than 30% even after a long period of time. The yields of copolymers were much higher except with very unreactive monomers such as vinyl acetate.

Polymerization of N,N-divinylaniline by boron trifluoride etherate gave very high yields (98%) of polymer at a very high reaction rate. A few drops of boron trifluoride etherate were dropped into a tube containing 1 g. of divinylaniline at −20°. After shaking for 10 min. and then gradually warming to room temperature for 1 hour, a light brown polymer insoluble in organic solvents was obtained. The polymer softened at 175–180°.

Analytical Methods.—*Elementary analyses* were done by Galbraith Laboratories, Knoxville, Tenn., and Microanalysis Inc., Wilmington, Del.

Viscosity determinations were run at 30° in benzene solution using an Ubbelohde dilution-type viscometer.

Infrared spectra were determined with a Perkin–Elmer recording infrared spectrophotometer model 21.

Ultraviolet spectra were obtained with a Process and Instruments model R 53.

(12) W. C. J. Ross. *J. Chem. Soc.*, 183 (1949).

Cryoscopic molecular weight determinations of the polymers was made by using a Beckmann thermometer and a Hershberg melting point apparatus. p-Nitrotoluene, m.p. 51.7°, K_f 0.78, was used as solvent.

Catalytic hydrogenation of N,N-divinylaniline was performed in a volumetric microhydrogenation apparatus. Raney nickel, 10% palladium-on-charcoal and platinum dioxide were all successfully used as catalyst. Either absolute ethanol or diglyme were used as solvent.

The product isolated from catalytic hydrogenation of N,N-divinylaniline formed a picrate salt as yellow needles, m.p. 140°. The melting point was identical to that of diethylaniline picrate prepared in the same way (lit.[18] 142°). Mixing the two picrates did not cause a lowering of the melting point.

Attempted preparation of the picrate of N,N-divinylaniline by the same method gave only a brown resinous material melting over a range of 114° to 125°.

Determination of residual double bonds in polymers and copolymers by catalytic hydrogenation was made according to the same general procedures as in the hydrogenation of the monomer. Diglyme was used as solvent in most cases on account of the solubility of the polymers. The polymers were introduced to the solvent–catalyst mixture after the system had been allowed to come to equilibrium either by dropping the preweighed sample from the sample container inside the vessel or by injecting into the system a measured quantity of the diglyme solution of the polymer. The latter method was necessary for many fluffy or powdery samples which could not be weighed properly in the sample

(13) R. I. Shriner and R. C. Fuson, "Systematic Identification of Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., 3rd. edition, 1948, p. 242.

container. Diglyme was prepurified to remove peroxide and kept under a nitrogen atmosphere. In each case the reaction was allowed to run at least 18 hours to ensure completion of the reaction.

The infrared spectrum of N,N-divinylaniline showed the pertinent peaks as shown in Table XVII.

TABLE XVII

INFRARED ABSORPTION BANDS FOR N,N-DIVINYLANILINE

Wave length, μ	Intensity	Wave length, μ	Intensity
3.30	Weak	8.32	V. strong
6.03sh	Medium	8.96	Weak
6.10sh	Strong	9.35	Weak
6.20sh	V. strong	9.45	Weak
6.28	V. strong	9.80	Weak
6.69	Strong	10.22sh	Medium
7.08	Medium	10.37	V. strong
7.30	Medium	10.62	Weak
7.42	Strong	12.30	V. strong
7.62	Strong	13.10	Strong
7.80	Strong	14.35	V. strong
8.06	V. strong	14.80	Medium

The disappearance or diminishing of the strong shoulders in the 6.0 to 6.2 μ region of the spectra of polymers and copolymers leaving only a sharp band at 6.25 μ similar to that of diethylaniline was used as a criterion for the reduced double bond content in addition to the catalytic hydrogenation analyses.

COMMUNICATIONS TO THE EDITOR

A COMPARISON OF THE ACYL-ENZYME INTERMEDIATES, CINNAMOYL-TRYPSIN AND CINNAMOYL-α-CHYMOTRYPSIN[1]

Sir:

The reaction of N-trans-cinnamoylimidazole with α-chymotrypsin proceeds by a mechanism involving a preliminary adsorptive step followed by two catalytic steps, acylation of the enzyme producing cinnamoyl-α-chymotrypsin then deacylation of this intermediate to give cinnamate and regenerate the enzyme.[2,3] It has now been demonstrated that the trypsin-catalyzed hydrolysis of N-trans-cinnamoylimidazole proceeds in the same fashion, and it is possible to compare the spectrophotometric and kinetic behavior of the two acyl-enzyme intermediates, cinnamoyl-trypsin and cinnamoyl-α-chymotrypsin.

The rates of acylation of trypsin and α-chymotrypsin by N-trans-cinnamoylimidazole and the rates of deacylation of cinnamoyl-trypsin and of cinnamoyl-α-chymotrypsin have been determined spectrophotometrically (Table I). The data in Table I indicate that at concentrations of enzyme which are equal to or greater than that of the substrate and at pH's around 4 or 5, the rate of acylation is much greater than that of deacylation for α-chymotrypsin, and reasonably greater for trypsin

(1) This research was supported by grants from the National Institutes of Health.

(2) M. L. Bender and B. Zerner, J. Am. Chem. Soc., 83, 2391 (1961).

(3) M. L. Bender, G. R. Schonbaum, G. A. Hamilton and B. Zerner, ibid., 83, 1255 (1961).

sin. This result indicates that it should be possible to prepare and observe reasonably stable acyl-enzymes at those pH's. Cinnamoyl-α-chymotrypsin can be prepared at pH 4 in a quantitative fashion by the stoichiometric reaction of N-trans-cinnamoylimidazole and α-chymotrypsin, and can be kept for hours at pH 4 with only slight decomposition. The difference spectrum of cinnamoyl-α-chymotrypsin vs. α-chymotrypsin is shown in Fig. 1.[4] The trypsin-catalyzed hydrolysis of N-trans-cinnamoylimidazole at pH 5.2 has been carried out at an [enzyme]/[substrate] ratio 23.7. Under these conditions the acylation and deacylation reactions can be considered to be two consecutive first-order reactions[2] in which the first step is 39 times as fast as the second. The maximum concentration of the intermediate, cinnamoyl-trypsin, formed transiently then can be calculated to be 90.0% of the initial substrate concentration. It then was possible to obtain a difference spectrum of cinnamoyl-trypsin vs. trypsin at the time of maximum concentration of the intermediate, correcting for the 2.3% of reactant and the 7.7% of product present. The difference spectrum of the intermediate also was computed from observations on a solution containing

(4) (a) In both difference spectra the absorbance due to the enzyme has been subtracted directly by an equivalent concentration of the appropriate enzyme in the reference cell of the spectrophotometer. (b) The cinnamoyl-α-chymotrypsin difference spectrum omits consideration of the small bumps observable in the enlarged view of the maximum shown in M. L. Bender, G. R. Schonbaum and G. A. Hamilton, J. Polymer Sci., 49, 75 (1961).