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(2) The mechanism of the regulating effect of the diethylamine during isoprene and butadiene polymerization by alkali metals have been explained.

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STUDIES IN CYCLIC POLYMERIZATION AND COPOLYMERIZATION—XIII. CYCLIC POLYMERIZATION OF N-SUBSTITUTED DIALLYLAMINES*

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BUTLER has shown that the polymerization of quarternary diallyl ammonium salts in aqueous solution in the presence of *tert*.-butyl hydroperoxide or an **azo-initiator**, leads to the formation of linear-cyclic polymers on the following scheme [1,2].



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Our attempts to polymerize the free base of diallylamine or tertiary diallylalkylamines (diallylmethylamine and diallylbenzylamine) by means of radical initiators were unsuccessful. This fact is an obvious example of the influence of the polarity of the molecule on the reactive capacity of monomers [3]. The capacity of diallyl derivatives of quarternary ammonium salts for radical polymerization is probably connected with the polarizability of the allyl groups which is due to displacement of the electron density (π -electrons) of the double bond under the influence of the electron acceptor ammonium nitrate. On the basis of this it is to be expected that if polar groups, which give the nitrogen its electron repulsing property, are introduced to the diallylamine, the substituted diallylamines will show a tendency to radical polymerization. It must be said that we have already noted the influence of polar substituents on the polarization of substituted 1,6heptadienes [4, 5].

Our aim in the present work was to study the ability of N-substituted diallylamines to undergo cyclic polymerization as a function of the nature of its substituent. As was to be expected, when polar substituents containing negative groups were introduced to the diallylamine nitrogen, the N-substituted diallylamines show a tendency to polymerize in the presence of free radical initiators. The conditions for polymerization are given in the Table, and the properties of the resulting polymers of the series of N-substituted diallylamines synthesized by us: N,N-diallyl acetamide, N,N-diallyl chloroacetamide, N,N-diallyl propionamide, N,N-diallyl benzamide, N,N-diallyl benzene sulphamide, N,N-diallyl-p-toluene sulphamide, methyl diallyl carbomate and diallyl cyanamide.

It is interesting to note that only the substituted diallylamines in which the electron acceptor groups (CO, CN, SO₂) of the substituent are directly bonded with the nitrogen, can be polymerized. If these groups are removed from the nitrogen on one or two carbon atoms, the N-substituted diallylamines will not polymerize. For instance, the ethyl diallylaminoacetic acid and N-(β -cyanethyl) diethylamine which we synthesized, produced no polymers under analogous conditions of polymerization. The increase in the electron repulsing activity of the substituent promotes polymerization; for instance, for N,N-diallylamides the influence of the substituent can be given in the following series:

$$ClCH_{3}CO > CH_{3}CO > CH_{3}CH_{2}CO.$$

It can be seen from the Table that the degree of monomer conversion in the presence of dinitril azo-isobutyric acid (DAA) is considerably higher than in the presence of benzoyl peroxide (BP). Increased initiator concentration also raises the polymerization rate. If the polymerization temperature is raised above 80° this causes a reduction in the polymer yield. The maximum degree of N-substituted diallylamine transformation under the polymerization conditions studied was about 35%. For N,N-diallyl acetamide and diallyl cyanamide, Fig. 1 shows the influence of polymerization time (up to 16 hours) on the polymer yield at 80° in the presence of two moles per cent DAA (of monomers).

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All the polymers of N-substituted diallylamines obtained are smooth powdery substances soluble in organic solvents (benzene, chloroform and so on). For the five synthesized polymers the molecular weights determined by the ebullioscopic method, were between 7200 and 24,000 (see Table).



FIG. 1. Dependence of depth of transformation on polymerization time in the presence of 2 mol.% DAA at 80°: 1-diallyl cyanamide; 2-N,N-diallyl acetamide.

In purified specimens of the products of N-substituted diallylamine polymerization, there is practically no residual unsaturation, which is confirmed by spectral analysis in the double bond region, of the N,N-diallyl-*p*-toluene sulphamide polymer for instance (Fig. 2f). As the absorption bands of the carbonyl group (C=O) for N,N-disubstituted amides[6] and the double carbon—carbon bond (C=C) lie in the near range (1630–1660 cm⁻¹), the degree of unsaturation of the polymers can be assessed by the non-planar strain vibrations, and also by the valency vibrations of the C—H bonds of the vinyl groups (=CH₂) of the monomers. For instance, in the IR absorption spectra of the N,N-diallyl acetamide and diallyl cyanamide monomers intensive bands are seen, which are typical of nonplanar strain and valence vibrations of the C—H bond of the vinyl group with a frequency of 920, 985 and 3075 cm⁻¹ (Fig. 2a and d), while these frequencies, which are typical of an unsaturated state, are absent in the polymers obtained (Fig. 2b, e, f).

The solubility and fusibility of the resulting polymers, and also the absence of residual unsaturation in them, indicate that polymerization has occurred through the two double bonds of the N-substituted diallylamines with formation of linear polymers with cycles in the chain. The cyclic units in the polymer chain were also found by studying the IR spectra. In the spectra (Fig. 2b, e, f) of the N,N-diallyl acetamide, diallyl carbamic acid ether and N,N-diallyl-p-toluene sulphamide polymers, have strong absorption bands around 2870, 2880, 2930 and 2950 cm⁻¹. As follows from published data [7], these are the results of valency vibrations of the C—H bonds of the piperidine ring CH₂ groups. Besides this, comparing the IR spectra of the poly-N,N-diallyl acetamide with that of the N-acetyl piperidine,

CH ₂ =CHCH ₂ CH ₂ =CHCH ₂ where R:	Concentration of initiator, mol. %		Poly- meriza- tion	Poly- meriza- tion	Polymer yield,	Melting point of	Molecular weight of
	BP	DAA	°C	time, hr	%	°C	polymer
CH ₃ CO-	_	2	80	32	25.5		
		3	80	32	32.3	85-95	22,650
	-	2	100	32	21.0		
$CH_{3}CH_{2}CO -$	-	2	80	39	22.5	66-78	-
$ClCH_2CO-$	_	2	80	11	21.2		-
_	-	2	80	32	30.2	70-107	_
<co< td=""><td>2</td><td></td><td>80</td><td>46</td><td>11.4</td><td></td><td></td></co<>	2		80	46	11.4		
	_	2	80	46	13.3		
	_	3	80	46	18.9	98-116	24,000
	-	2	100	46	12.8		, í
CH ₃ OCO	2	l —	80	60	11.9	76-98	13,680
	—	2	80	20	18.0		
	_	3	80	20	$24 \cdot 2$		
	-	2	100	60	14.3	Ì	
	2	1 _	80	30	12.0		
	_	2	80	39	21.5	103 - 125	13,750
		3	80	35	31.6	1	
	-	2	100	35	26.7	ł	
CH ₃ SO ₂ -	2	_	80	35	14.8		
	Ì	2	80	39	$32 \cdot 1$	105 - 120	7260
	_	3	80	35	36.0		
		2	100	35	29.5	Í	
N ≡ C	1	_	70	6	6.1		
	_	1	70	6	11.0		
	2	-	70	30	12.5		
	_	2	70	30	26.3		
	-	1	80	42	$24 \cdot 4$	400-450	-
	l <u> </u>	2	80	32	23.6	-	
		3	80	32	31.2		
	2		130	30	7.1		
		2	130	30	18.0		

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which is a structural model of its units, a similarity was found between the absorption bands of the valence and strain vibrations of the C—H bonds of the ring (Fig. 2b, c).

Thus the polymerization of N-substituted diallylamines containing polar groups at the nitrogen atoms follows a cyclic mechanism with formation of piperidine cycles in the main chain of the polymer, similar to the polymerization of the quarternary diallyl ammonium salts. S. G. MATSOYAN et al.



FIG. 2. IR absorption spectra: a-N,N-diallyl acetamide; b-polymer of N,N-diallyl acetamide; c-N-acetyl acetyl piperidine; d-diallyl cyanamide; e-methyl diallyl carbamate; f-polymer of N,N-diallyl-p-toluene sulphamide.

Of the products of the cyclic polymerization of N-substituted diallylamines obtained, particular interest attaches to the polydiallyl thianamide, which is distinguished by poor solubility and high fusibility. It is insoluble in the ordinary organic solvents (benzene, chloroform etc.) and also in the monomer proper and it precipitates in the process of drop polymerization, in the form of a light yellow hard powder. The diallyl thianamide polymer on the other hand, is soluble in *m*-cresol and in hot piperidine. Its characteristic viscosity in *m*-cresol at 20° is 0.06.

Polydiallyl thianamide is softened and fused in a sealed capillary at around $400-450^{\circ}$. To study the temperature stability we took the curve for the variation in the weight of the polymer specimen when heated in air (Fig. 3). The specimen was weighed in an open crucible after holding at given temperature for 20 minutes; the polymer became dark at $300-350^{\circ}$. It follows from Fig. 3 that the intensive oxidizing degradation of polydiallyl cyanamide does not begin until around 350° .



FIG. 3. Variation in weight of polydiallyl cyanamide on heating.

As is to be expected, when the polydiallyl cyanamide was heated with 30% sulphuric acid the nitrile group was hydrolized with subsequent decarboxilation; in this way the product of the cyclic polymerization of diallylamine was obtained.



Unlike the starting polymer, the resulting polydiallylamine had a melting point around $120-150^{\circ}$, is soluble in low alcohols and swells in water. There is a 3340 cm^{-1} absorption band in the IR spectrum of the polymer, corresponding to valence vibrations of the N—H bond. Methyl iodide has the effect of forming the tertiary ammonium salt of polydiallylamine in the form of a soluble powder which becomes soft at high temperature.

EXPERIMENTAL

Diallyl cyanamide was obtained by the reaction of calcium cyanamide with allyl bromide [8].

N,N-diallyl benzene sulphamide and N,N-diallyl-p-toluene sulphamide were obtained by the interaction of the corresponding sulphochlorides with diallylamine [9, 10].

N,N-diallyl chloroacetamide was synthesized by the reaction of the chloroanhydride of monochloroacetic acid with diallylamines [11]. The constants of the resulting compounds were the same as published figures.

N,N-diallyl acetamide. A mixture of 3 g diallylamine and 5 g acetic anhydride was heated with a flowback cooler at 100-115° for 4 hours. After vacuum distillation of the reaction mixture 3.9 g (90% of theoretical) N,N-diallyl acetamide was obtained with b.p. $92-93^{\circ}/11$ mm, n_D^{20} 1.4691, d_4^{20} 0.9310.

Found, %: N 10.02; MR_D 41.63. C₈H₁₃NO. Calculated, %: N 10.07; MR_D 42.03.

N,N-diallyl propionamide. Into a round-bottom triple-necked flask with an agitator, reverse cooler and dropping funnel, was placed 3.1 g diallylamine and a solution of 1.35 g caustic soda in 3.1 ml water, and after this 2.95 g propionyl chloride was added drop by drop. Then the reaction mixture was heated in a water bath at 50-60° for 3 hours with vigorous stirring. The reaction mixture was treated with an aqueous solution of potash, extracted with ether and dried with magnesium sulphate. 2.1 g was obtained (42.6% of theoretical). N,N-diallyl propionamide with b.p. $96-97^{\circ}/10 \text{ mm}$, n_D^{20} 1.4664, d_4^{20} 0.9238.

Found, %: N 9.40; MR_D 45.96. C₉H₁₅NO. Calculated, %: N 9.13; MR_D 45.74.

N,N-diallyl benzamide. The experiment was similar to the previous one. From 3 g diallylamine, 1.35 g caustic soda in 3.1 ml water and 4.8 g benzyl chloride, was obtained 4.3 g (68.6% of theoretical) N,N-diallyl benzamide with b.p. $108-109^{\circ}/2 \text{ mm}, n_D^{20} 1.5398, d_4^{20} 1.0364.$

Found, %: N 7.46; MR_D 60.90. C₁₂H₁₅NO. Calculated, %: N 6.96; MR_D 61.65.

Methyl diallyl carbamate. The experiment was similar to that described above. 3.2 g methyl ester of chlorocarbonic acid was added drop by drop to a mixture of 3.09 g diallyl-amine and a solution of 1.4 g caustic soda in 3.5 ml water. After the usual treatment 3.62 g was obtained (yield 73.4% theoretical) of methyl diallyl carbamate with b.p. $72-73^{\circ}/12$ mm, n_D^{20} 1.4548, d_4^{20} 0.9583.

Found, %: N 9.08; MR_D 44.07. C₈H₁₃NO₂. Calculated, %: N 9.03; MR_D 43.67.

Ethyl diallyl amino acetate. A mixture of 6 g diallylamine in 60 ml absolute ether and 3.78 g ethyl chloroacetate was boiled in a water bath for 5 hours. The reaction solution was filtered off from the diallylamine hydrochloride and after removing the ether from the filtrate the residue was distilled in a vacuum. 2.3 g was obtained (40% of theoretical) of ethyl diallyl amino acetate with b.p. 87-88°/13 mm, n_D^{20} 1.4472, d_4^{20} 0.9308.

Found, %: N 8.10; MR_D 52.60. C₁₀H₁₇NO₂. Calculated, %: N 7.65; MR_D 53.04.

N- $(\beta$ -cyanethyl)-diallylamine. A mixture of 5 g diallylamine and 4 g acrylonitrile was heated in a sealed ampoule at 100–110° for 4 hours. The reaction mixture was vacuum distilled and 5.2 g (66.4% of theoretical) of N- $(\beta$ -cyanethyl)-diallylamine was obtained with b.p. 102°/12 mm, n_D^2 1.4637, d_A^{20} 0.9004.

Found, %: N 18.90; MR_D 45.99. C₉H₁₉N₂. Calculated, %: N 18.66; MR_D 46.31.

Polymerization of N-substituted diallylamines. Weighed portions (0.5-2 g) of the monomers and BP or DAA (1-3 mol. % of monomer) were put into ampoules. After removing the air with nitrogen and evacuating, the ampoules were sealed and heated in a thermostat at a definite temperature. In all cases, with the exception of the diallyl cyanamide, the resulting

polymer was liberated from the unreacted monomer and cleaned by reprecipitation from a chloroform or benzene solution with petroleum ether. The polymers, which contained sulphamide groups at the nitrogen atom, are soluble in chloroform but insoluble in benzene.

Polydiallyl cyanamide was precipitated in the process of polymerization as a white powder which was washed in benzene or again precipitated from the solution in *m*-cresol with alcohol.

The polymers obtained were passed through a glass filter and dried to constant weight at 56° . The softening and melting temperatures were determined by heating powder specimens in a sealed capillary. The molecular weights were determined by the ebullioscopic method in benzene or chloroform. The results of the polymerization are shown in the Table.

Hydrolysis of polydiallyl cyanamide. Into a two-neck flask with a mixture and reverse cooler, was placed 0.56 g polymer and 4 ml 30% sulphuric acid. Stirring vigorously the mixture was heated at $100-120^{\circ}$ until the polymer was completely dissolved (about 3 hours). The product of the hydrolysis was precipitated by introducing a 20% solution of caustic soda to the reaction mixture. The precipitate was filtered off, dissolved in alcohol and precipitated with acetone. 0.4 g (90% of theoretical) polydiallylamine was obtained in the form of a light yellow powder which is easily soluble in low alcohols and acids, and has a melting point around $120-150^{\circ}$.

Found, %: N 15.30.
$$(C_6H_{11}N)_n$$
. Calculated, %: N 14.43.

When the anhydrous methanol solution of the polymer was boiled with methyl iodide an iodine methylate of the polydiallylamine was formed as a brown powder soluble in water, which softened and turned black at 260° , but did not melt.

The spectra were taken on a IKS-14 instrument. The range 700–1800 cm⁻¹ was taken with a prism of NaCl in paste and vaseline oil (for the polymers), and the valence vibration range of the C-H bonds, in a solution in CCl₄ using LiF prisms.

CONCLUSIONS

(1) A number of N-substituted diallylamines have been synthesized and their capacity for cyclic polymerization in dependence on the nature of the substituent has been studied.

(2) It has been found that if polar substituents whose electron acceptor groups (CO, SO₂, CN) are immediately bound with the nitrogen atom, are introduced to the diallylamine, the N-substituted diallylamines show a tendency to radical polymerization.

(3) The properties of the polymers have been studied and it has been found that under conditions of radical polymerization chain growth is the result of alternating inter- and intramolecular reaction with formation of piperidine rings in the main polymer chain.

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THE THERMAL AND THERMAL-OXIDATIVE DEGRADATION OF POLYFORMALDEHYDE—I. THE ORDER OF REACTION IN THERMAL DEGRADATION*†

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IMPROVEMENT of the heat stability of formaldehyde polymers is of particular importance because their cieling temperature [1], and consequently the processing temperature, is below the melting point. Therefore in order to prevent degradation during processing purely kinetic retardation is necessary.

The study of the heat stability of polyformaldehydes of low molecular weight polyoxymethylenes—was begun by Staudinger in the 1920's. It has been found [3] that in the temperature interval of $100-300^{\circ}$ in the absence of oxygen depolymerization of the macromolecules from the ends of the chains occurs, passing at higher temperatures to breakdown of the C—O—C bonds. The simple outline of the process proposed by these authors does not indicate the mechanism of the reaction as a whole and does not explain the low activation energy, which is lower than the heat effect of polymerization [4]. The patent literature [5] and the paper by MacDonald [6], dealing with the heat stability of high-molecular polyformaldehydes, do not give additional information on the mechanism of degradation.

In a series of papers, beginning with this communication, some kinetic relationships of the thermal and thermal-oxidative degradation of α -polyoxymethylene and high-molecular polyformaldehyde in the temperature interval of 120–346° will be examined. The purpose of the work is the elucidation of the mechanism of the process and examination of the possibility of raising the heat stability of the polymers.

- * Vysokomol. soyed. 5: No. 6, 861-867, 1963.
- [†] Part of the experimental work was carried out by O. M. Koz'minykh.