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Cyclopolymerization. IX. Effect of β-Substituents on the Cyclopolymerization of Diallylamines

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Cyclopolymerization. IX. Effect of β-Substituents on the Cyclopolymerization of Diallylamines

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ABSTRACT

ESR studies and analysis of the products from the cyclopolymerization of substituted diallylamines show that the cyclization may not involve a concerted process, and that the proportion of piperidine rings formed is increased by the use of bulky or conjugated β-substituents, or increased reaction temperatures, factors which favor thermodynamic control of the direction of ring closure. Increased piperidine ring content causes a small reduction in the basicity of the polymers.

INTRODUCTION

Diallylamine and its N-substituted derivatives have been shown to undergo radical-induced cyclization with the formation of pyrrolidine derivatives instead of the often-postulated isomeric piperidines [1]. The polymers formed in these reactions have also been shown to be essentially derivatives of poly(3,4-dimethylene pyrrolidine) [2].

These polymers, together with the related triallylamine polymers, form the basis of a series of commercially-important ion-exchange resins [3]. The effects of different N-substituents on polymer structure and resin basicity have been described in other papers in this series [4].

Radicals derived from 1,6-alkadienes can cyclize with the formation of both cyclopentane and cyclohexane derivatives, and the nature of the substituents and the 2- and 6-positions of the alkadiene can affect the statistical ratio of these rings in the cyclized products [5]. However, the effects of β-substituents on the cyclopolymerization of the analogous diallylamines were largely unknown, and there was a need to investigate these, both as a potential means for modifying polymer ion-exchange properties by the introduction of a proportion of piperidine rings, and for a better understanding of the mechanisms of the cyclopolymerization process.

In this paper we describe the effects of various β-allylic substituents and different reaction conditions on the products of the azobisisobutyronitrile-initiated cyclopolymerization of diallylamines, together with some preliminary ESR studies on the radicals formed by these monomers.

EXPERIMENTAL

Methods

PMR spectra were obtained using a Varian T-60 spectrometer; chemical shifts in $CDCl_3$ were calculated relative to internal TMS δ 0.00. Infrared spectra (IR) were measured in KBr disks or as thin films. Mass spectra (MS) were recorded with a Hitachi-Perkin Elmer RMU-6D spectrometer with heated inlet sampling at 200° C and 70 eV ionization potential. ESR spectra were obtained by using a Varian V-4501 spectrometer and Scanco variable temperature liquid flow cell at 25° C; $NH_2\cdot$ of $OH\cdot$ were generated in acid media by reaction between Ti^{3+} and NH_2OH or H_2O_2 respectively [6]. Microanalyses were performed by the Australian Microanalytical Service. Melting points are corrected; boiling points are uncorrected.

Reagents

Azobisisobutyronitrile (AIBN) was Fluka pure grade and was used as received. The monomers studied, together with the abbreviations

used in the discussion were: N-methyldiallylamine (MDAA); N-methylbis(2-methylallyl)amine (MDMA); N-methylbis(2-ethylallyl)amine (MDEtA); N-methylbis(2-isopropylallyl)amine (MDPrA); N-methylbis(2-tert-butylallyl)amine (MDBuA); N-methylbis(2-phenylallyl)amine (MDPhA); N-methylbis(2-carboethoxyallyl)amine (MDCA).

MDAA used a redistilled commercial sample. The other monomers were prepared by reaction of the respective allyl chlorides or bromides with 25% aqueous methylamine and an equivalent amount of 4 N NaOH at 60° C for 6 hr; MDBuA required 48 hr reaction at 60° C; MDCA required 2 hr at 5° C. The properties of the monomers are given below, together with references for the synthetic methods for the allyl halides.

N-Methylbis(2-methylallyl)amine

RCl (Aldrich). Bp 130° C/760 Torr; 92° C/150 Torr. PMR: C=CH_2 δ 4.92; N–CH_2, δ 2.85; N–CH_3, δ 2.23; C–CH_3, δ 1.78. Picrate, mp 75-80° C. Analysis. Found: C, 49.1%; H, 5.6%; N, 15.5%. Calculated for $C_{15}H_{20}N_4O_7$: C, 48.9%; H, 5.4%; N, 15.2%.

N-Methylbis(2-ethylallyl)amine

RBr, bp 62° C/70 Torr [7, 8]. BP 98° C/55 Torr. PMR: C=CH_2, δ 4.87; N–CH_2, δ 2.85; N–CH_3, δ 2.10; C–C_2H_5, δ 2.12, 1.06 Picrate, mp 45-47° C. Analysis. Found: C, 51.5%; H, 6.1%; N, 14.2%. Calculated for $C_{17}H_{24}N_4O_7$: C, 51.5%; H, 6.1%; N, 14.1%.

N-Methylbis(2-isopropylallyl)amine

RBr, bp 59° C/50 Torr [7, 8]. Bp 86-88° C/15 Torr. PMR: C=CH_2, δ 4.93-4.85; N–CH_2, δ 2.94; N–CH_3, δ 2.12; C–$CH(CH_3)_2$, δ 2.29, 1.08. Picrate, mp 73-74° C. Analysis. Found: C, 53.9%; H, 6.7%; N, 13.3%. Calculated for $C_{19}H_{21}N_4O_7$: C, 53.7%; H, 6.6%; N, 13.2%.

N-Methylbis(2-tert-butylallyl)amine

RBr, bp 67° C/35 Torr [9]. Bp 109-112° C/15 Torr. PMR: C=CH_2, δ 4.97, 5.12; N–CH_2, δ 3.02; N–CH_3, δ 2.12; C–CH_3, δ 1.08. Picrate, mp 147-148 C. Analysis. Found: C, 55.5%; H, 7.1%; N, 12.3%. Calculated for $C_{21}H_{32}N_4O_7$: C, 55.7%; H, 7.1%; N, 12.4%.

N-Methylbis(2-carboethoxyallyl)amine

RBr [10, 11]. Bp 96-100° C/0.1 Torr. IR: C=O, 1725 cm^{-1}; C=C, 1638 cm^{-1}. PMR: C=CH_2, δ 5.73, 6.18; CH_2–O, δ 4.10; N–CH_2, δ 3.22; N–CH_3, δ 2.23; CH_3–C, δ 1.47. Picrate, mp 100-101° C. Analysis. Found: C, 47.4%; H, 4.9%; N, 11.6%. Calculated for $C_{19}H_{24}N_4O_{11}$: C, 47.6%; H, 5.0%; N, 11.6%.

N-Methylbis(2-phenylallyl)amine

RBr [12]. Bp 122°C/0.1 Torr; mp 10° C. PMR: Ph, δ ca. 7.3; $C=CH_2$, δ 5.45, 5.20; $N-CH_2$, δ 3.37; $N-CH_3$, δ 2.18. Picrate, mp 102° C.

N,N- Dimethyl-2-tert-butylallylamine

RBr + $(CH_3)_2NH$. Bp 60° C/44 Torr. Picrate, mp 77-78° C. Analysis. Found: C, 47.2%; H, 5.7%; N, 15.6%. Calculated for $C_{14}H_{20}N_4O_7$: C, 47.2%; H, 5.7%; N, 15.7%.

Model Compounds for ^{13}C-NMR and Mass Spectroscopy

1,3,4-Trimethylpyrrolidine [13], 1,3,5-trimethylpiperidine [14], and 1,3,3,5,5-pentamethylpiperidine [15] have been described previously and were prepared by $LiAlH_4$ reduction of the respective N-methyl succinimides and glutarimides.

3,4-Diethyl-1,3,4-trimethylpyrrolidine

1,2-Diethyl-N-1,2-trimethylsuccinimide, bp 80° C/0.3 Torr, was prepared by distillation of the methylammonium salt of 1,2-diethyl-1,2-dimethylsuccinic acid [16] and reduced by refluxing with excess ethereal $LiAlH_4$ for 8 hr, yielding the pyrrolidine, bp 87-88° C/15 Torr. Picrate, mp 136-138° C. Analysis. Found: C, 51.3%; H, 6.7%; N, 14.3%. Calculated for $C_{17}H_{26}N_4O_7$: C, 51.2%; H, 6.6%; N, 14.1%. Although the succinic acid was a mixture of meso and racemic isomers, only one pyrrolidine isomer was obtained.

3,4-Diisopropyl-1,3,4-trimethylpyrrolidine

3,4-Diisopropyl-1,3,4-trimethylpyrrolidine, bp 114° C/15 Torr, was similarly prepared from 1,2-diisopropyl-1,2-dimethylsuccinic acid [16], N-methylimide, bp 85-98° C/0.4 Torr. Picrate, mp 101° C. Analysis. Found: C, 53.4%; H, 7.1%; N, 13.0%. Calculated for $C_{14}H_{30}N_4O_7$: C, 53.5%; H, 7.1%; N, 13.1%.

1,3,3,4,4-Pentamethylpyrrolidine

Bp 62° C/40 Torr. This was similarly prepared from 1,1,2,2-tetramethylsuccinic acid [16], N-methylimide, bp 140° C/15 Torr. Picrate, mp 250-260° C (decomp.). Analysis. Found: C, 48.4%; H, 6.1%; N, 15.2%. Calculated for $C_{15}H_{22}N_4O_7$: C, 48.6%; H, 6.0%; N, 15.1%.

The mass spectra of the various pyrrolidines were characterized by the appearance of a prominent radical ion m/e 57, $[CH_3N(CH_2)_2]^{+\cdot}$, whereas the spectra of the piperidines were characterized by the ion

m/e 58, $[(CH_3)_2NCH_2]^+$. The respective appearance of ions m/e 57 and 58 allows a convenient means for differentiation between N-methyl-β-substituted pyrrolidines and piperidines as discussed previously [2]. The ^{13}C-NMR spectra of the model compounds are described in another paper [17].

Reaction of N-Methylbis(2-methylallyl)amine Hydrochloride with AIBN at 60° C

MDMA (14.0 g, 100 mmole), HCl (3.6 g, 96 mmole), AIBN (8.2 g, 50 mmole) were heated together in ethanol (50 ml) under N_2 at 60° C for 55 hr. The products were separated into a nonbasic fraction [2] containing isobutyronitrile, ethyl isobutyrate, and tetramethylsuccinodinitrile, a basic fraction, which on distillation yielded recovered MDMA (36 mmole), a bicyclics fraction (1.4 g), bp 60-120° C/0.3 Torr, and a high boiling residue (4.2 g). Molecular distillation of this residue at 100-150° C/0.1 Torr gave a viscous fraction (0.5 g) containing a mixture of nitrile, amide, and ester components which, after hydrolysis and reesterification with ethanol, followed by preparative GLC fractionation, yielded ethyl 3-(1,3,4,4-tetramethyl-3-pyrrolidinyl)-2,2-dimethylpropionate (XIII), identified by its mass spectrum: $C_{15}H_{29}NO_2$, m/e 255 (intensity 24), 210 (29), 140 (24), 126 (17), 110 (15), 84 (65), 57 (100), 44 (17); IR: C=O 1736 cm^{-1}.

The bicyclic fraction was separated into its four components by preparative GLC. Their structures were assigned on the basis of their infrared and mass spectra. The ^{13}C-NMR assignments are discussed elsewhere [17].

Component i

1,3,5,7,7-Pentamethylbicyclo[3,3,1]nonan-6-one (XIIb, 5% of fraction). MS: $C_{13}H_{25}NO$, m/e 209 (intensity 61), 194 (25), 181 (5), 166 (7), 153 (100), 138 (12), 125 (8), 122 (8), 110 (14), 96 (9), 84 (11), 70 (8), 58 (60), 44 (16). IR: C=O, 1708 cm^{-1}.

Component ii

1,3,5,7,7-Pentamethylbicyclo[3,3,1]nonan-6-imine (XIb, 17% of fraction). MS: $C_{13}H_{26}N_2$, m/e 208 (intensity 82); 193 (81), 165 (27), 152 (100), 137 (88), 124 (41), 122 (47), 109 (66), 98 (17), 94 (14), 84 (19), 70 (11), 68 (12), 58 (57), 44 (16). IR: C=NH, 1627, 869 cm^{-1}. Dipicrate, mp 215-220° C (decomp.). Analysis. Found: C, 45.1%; H, 4.4%; N, 17.5%. Calculated for $C_{25}H_{32}N_8O_{14}$: C, 45.0%; H, 4.5%; N, 17.5%. Hydrolysis with hot dilute HCl yielded the ketone (i).

Component iii

cis-2,3a,6,6,7a-Pentamethylperhydroisoindol-5-one (IXb, 63% of fraction). MS: $C_{15}H_{25}NO$: m/e 209 (intensity 36), 194 (4), 152 (4), 140 (2), 122 (4), 112 (27), 110 (51), 108 (13), 96 (5), 94 (4), 84 (4), 70 (9), 67 (6), 57 (100), 44 (16). IR: C=O, 1718 cm^{-1}. Picrate, mp 148-149°C. Analysis. Found: C, 52.2%; H, 6.0%; N, 12.7%. Calculated for $C_{15}H_{26}N_4O_8$: C, 52.1%; H, 6.0%; N, 12.8%.

Component iv

trans-2,3a,6,6,7a-Pentamethylperhydroisoinol-5-one. (IXb, 14% of fraction). MS: $C_{15}H_{25}NO$: m/e 209 (intensity 46), 194 (4), 150 (10), 140 (12), 122 (6), 112 (36), 110 (70), 108 (15), 96 (6), 84 (7), 81 (8), 71 (7), 67 (7), 57 (100), 44 (36). The MS sample was obtained pure by analytical GLC; preparative GLC yielded samples contaminated with the isomeric ketone (iii).

Reaction of N-Methylbis(2-methylallyl)amine Hydrochloride with AIBN at 30°C

A solution of MDMA (14 g, 100 mmole), HCl (3.6 g, 96 mmole), and AIBN (2 g, 12 mmole) in ethanol (50 ml) was irradiated at 30°C with an 80-W high-pressure Hg lamp for 100 hr. The products included a bicyclics fraction (0.1 g), which was not investigated further, and polymer (2 g).

Reaction of N-Methylbis(2-methylallyl)amine Hydrochloride with AIBN at 135°C

A solution of MDMA (14 g, 100 mmole), HCl (5.3 g, 145 mmole), and AIBN (8.2 g, 50 mmole) in ethoxyethanol (50 ml) was added dropwise over 15 min to ethoxyethanol (20 ml) maintained at 135°C under an N_2 atmosphere. The basic products contained the bicyclic amines isolated from the 60°C reaction products (1.8 g; 20% i, 10% ii, 60% iii, 10% iv, and polymer (2.0 g).

Reaction of N-Methylbis(2-methylallyl)amine with AIBN at 60°C

A mixture of MDMA (14.0 g, 100 mmole) and AIBN (7.4 g, 45 mmole) was heated in benzene (40 ml) for 72 hr. GLC examination of the

products showed the absence of the bicyclic aminoketones i, iii, iv and presence of the imine ii and the putative imino precursors to iii and iv. Workup with aqueous reagents yielded basic products containing bicyclics (2.4 g; 9% i, 40% ii, 48% iii, 3% iv, and polymer (2.7 g).

A similar reaction at 30° C with UV irradiation of the MDMA-AIBN solution yielded less than 0.5 g of basic products.

Reaction of N-Methylbis(2-methylallyl)amine Hydrosulfate with $(NH_4)_2S_2O_8$ under Pressure

A solution of MDMA (5.9 g, 43 mmole), H_2SO_4 (2.6 g, 54 meq), $(NH_4)_2S_2O_8$ (0.46 g, 2 mmole) in water (to 20 g) was heated under N_2 at 80° C for 24 hr. The basic products yielded polymer (1.5 g, 25% conversion). A smaller volume of a similar solution was heated at 80° C under 8 Kbar hydrostatic pressure for 24 hr; the products contained polymer (0.2 g) equivalent to 7% of the monomer (1.3 g).

Reactions of N-Methyldiallylamine with AIBN

A series of reactions of MDAA·HCl with AIBN at 30, 60, and 135° C, MDAA with AIBN at 60° C; and MDAA · $\frac{1}{2}H_2SO_4$ with $(NH_4)_2S_2O_8$ at 80° C/8 Kbar, similar to those of MDMA described above, yielded polymers which were examined by using ^{13}C NMR spectroscopy. The other products of the reactions of MDAA with AIBN have been described previously [2].

Reaction of N-Methylbis(2-ethylallyl)amine Hydrochloride with AIBN

A solution of MDEtA (8.5 g, 51 mmole), HCl (1.85 g, 51 mmole), and AIBN (4.2 g, 25 mmole) in ethanol (40 ml) was heated at 60° C under an N_2 atmosphere for 80 hr. The basic products included recovered MDEtA (6.2 g, 37 mmole), a bicyclics fraction, bp 98-106/2 Torr (1.9 g), and polymer (0.7 g). The bicyclics fraction contained an imine (IR: C=NH, 3250, 1628, 870 cm^{-1}) and a small quantity of a ketone (IR: C=O, 1715 cm^{-1}). The imine was separated by preparative GLC and identified as 1,5-diethyl-3,7,7-trimethylbicyclo[3,3,1]-nonan-6-imine (XIc). MS: $C_{15}H_{28}N_2$ m/e 236 (intensity 7), 221 (11), 207 (26), 193 (4), 179 (30), 165 (24), 151 (66), 137 (19), 125 (11), 123 (14), 58 (100), 44 (55). ^{13}C-NMR [17]. Dipicrate, mp 220-230° C (decomp.). Analysis. Found: C, 47.1%; H, 4.9%; N, 16.3%. Calculated for $C_{27}H_{34}N_8O_{14}$: C, 46.7%; H, 4.9%; N, 16.1%. The imine

was resistant to mild acid hydrolysis, but treatment with 10 M HCl in a sealed tube at 120° C for 48 hr yielded 1,5-diethyl-3,7,7-trimethylbicyclo[3,3,1]nonan-6-one (XIIc), identical with the minor component of the bicyclics fraction. MS: $C_{15}H_{27}NO$, m/e 237 (intensity 51), 222 (22), 208 (11), 194 (4), 180 (4), 167 (100), 152 (31), 138 (13), 124 (7), 122 (5), 58 (15), 44 (22). ^{13}C-NMR [17]. Picrate, mp 136-140° C. Analysis. Found: C, 53.9%; H, 6.5%; N, 12.1%. Calculated for $C_{21}H_{30}N_4O_8$: C, 54.1%; H, 6.5%; N, 12.0%.

Reaction of N-Methylbis(2-isopropylallyl)amine Hydrochloride with AIBN

A solution of MDPrA (14.4 g, 74 mmole), HCl (2.7 g, 74 mmole), and AIBN (6.0 g, 37 mmole) in ethanol (40 ml) was heated under N_2 at 60° C for 80 hr. The basic products included recovered MDPrA (10 g, 51 mmole) a bicyclics fraction, bp 90-98°C/0.0005 Torr (1.5 g), and high-boiling residue (0.4 g). The bicyclics fraction contained essentially one component, 1,5-diisopropyl-3,7,7,-trimethylbicyclo[3,3,1]nonan-6-imine (XId). IR: C=NH, 3250, 1628, 870 cm^{-1}. MS: $C_{17}H_{32}N_2$, m/e 264 (intensity 21), 249 (18), 221 (100), 207 (13), 193 (16), 181 (5), 178 (5), 165 (46), 150 (6), 138 (6), 58 (30), 44 (12), ^{13}C-NMR [17]. Analysis. Found: C, 53.9%; H, 6.7%; N, 13.3%. Calculated for $C_{17}H_{32}N_2$: C, 53.7%; H, 6.6%; N, 13.2%. Heating the imine with 10 M HCl at 120° C for 48 hr resulted in 50% hydrolysis to 1,5-diisopropyl-3,7,7-trimethylbicyclo[3,3,1]nonan-6-one (XII d). IR: C=O, 1716 cm^{-1}. MS: $C_{17}H_{33}NO$, m/e 265 (intensity 46), 250 (23), 222 (32), 194 (6), 181 (73), 166 (70), 150 (5), 138 (6), 136 (6), 58 (40), 44 (100).

Reaction of MDPrA·H_2SO_4 with $(NH_4)_2S_2O_8$ at 80° C under 8 Kbar pressure yielded no polymer.

Reaction of N-Methylbis(2-tert-butylallyl)amine Hydrochloride with AIBN and with HO·

Treatment of MDBuA·HCl with ethanolic AIBN at 60° C as described above resulted in negligible yields of basic products and an almost quantitative recovery of MDBuA. Treatment of MDBuA·HCl with an equimolar amount of HO·, generated from Fenton's reagent at 5° C, yielded only a small quantity of basic, acyclic products, most of the MDBuA being recovered.

Reaction of N-Methylbis(2-phenylallyl)amine Hydrochloride with AIBN

A solution of MDPhA (9.8 g, 38 mmole), HCl (1.4 g, 38 mmole), and AIBN (3.1 g, 19 mmole) in ethanol (30 ml) was heated under N_2 at 60°C for 72 hr. The basic products included recovered monomer (2 g, 8 mmole) and polymer tenaciously retaining traces of monomer, which was detectable by thin-layer chromatography. There were no bicyclic amines analogous to those found in other diallylamine/AIBN reaction products.

Reaction of N-Methylbis(2-carboethoxyallyl)amine Hydrochloride with AIBN

A solution of MDCA (9.0 g, 35 mmole), HCl (1.3 g, 36 mmole), and AIBN (1.5 g, 9 mmole) in ethanol (30 ml) was irradiated at 30°C with an 80-W high pressure Hg lamp for 70 hr, yielding 9.7 g of basic polymer. There was no residual monomer or bicyclic amines in the product.

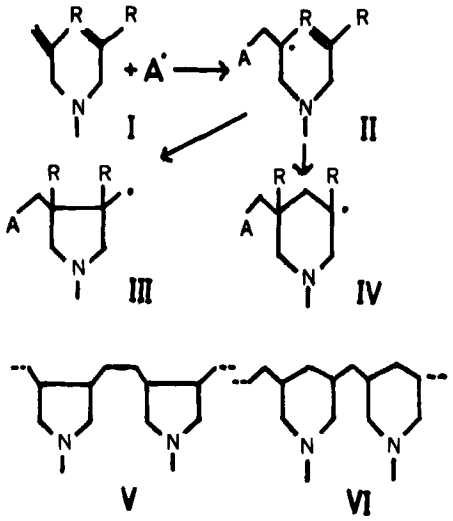
Basicity of Polymers

In previous papers in this series, methods were described for the potentiometric titration of crosslinked, water-insoluble diallylamine polymers. A modified and rapid procedure suitable for small quantities of polymer was used for the present study. Solutions containing approximately 1 meq of basic polymer in 2:1 dioxane-water (60 ml) were titrated with 0.2 N $HClO_4$, the apparent pH of the mixture being measured by using a Pye Unicam pH meter and Philips combined glass/reference electrode. The endpoints were the titers (V) corresponding to $\partial PH/\partial V$ maxima, and the sharpness of the endpoints were estimated from the pH differences between titers corresponding to 90% and 110% neutralization.

RESULTS

ESR Studies of Radical Structure

In previous papers [4, 6] we reported that diallylamine, various N-substituted diallylamines, e.g. Ia, and triallylamine reacted with



where

(a) R = –H
(b) R = $-CH_3$
(c) R = $-C_2H_5$
(d) R = –CH
(e) R = $-C(CH_3)_3$
(f) R = $-C_6H_5$
(g) R = $-CO_2 \cdot C_2H_5$

$HO^{\cdot}$, $NH_2^{\cdot}$, and other radicals in acidic media giving ESR spectral quartets assignable to pyrrolidinyl-methylene radicals, e.g. IIIa, as the sole observable species.

N-Methylbis(2-methylallyl)amine (MDMA, Ib) reacted with $NH_2^{\cdot}$ and $OH^{\cdot}$, giving ESR spectra consisting of a strong triplet, splitting 21.8 G assignable to the radical (IIIb), superimposed on a much weaker unidentified multiplet, possibly arising from radical (IVb). Computer simulation of the ESR spectra indicates that the concentration of radicals (IIb) and/or (IVb) is only about 0.1 that of radical (IIIb). N-Methylbis(2-ethylallyl)amine (MDEtA, Ic) reacted with $NH_2^{\cdot}$ giving a triplet, splitting 22.5 G, assigned to radical IIIc, superimposed on a strong multiplet, 137 G width, of which only the wings were resolved. These consisted of 1:2:3:2:1 quintets, splitting 5.4 G.

N-Methylbis(2-isopropylallyl)amine (MDPrA, Id) reaction with $NH_2^{\cdot}$ gave a 28-line multiplet of 115G width, containing quintets, splitting 5.4G, suggestive of radical (IId, A = NH_2) which contains two β-nitrogen atoms, as reaction of MDPrA with $OH^{\cdot}$ gave a weaker multiplet spectrum having apparent 1:1:1 triplet fine structure expected for radical (IId, A = OH). Radical IVd would have a spectrum with similar triplet

fine structure, but the observed spectrum lacked the additional multiplicity resulting from non-equivalence of the axial and equatorial ring hydrogens which was observed in the MDCA/NH_2' spectrum. There was no evidence of radical (IIId).

N-Methylbis(2-tert-butylallyl)amine (MDBuA, Ie) reactions with OH' and NH_2' yielded complex spectra which differed between themselves and also with those of the N,N-dimethyl-2-tert-butylallylamine with OH' or NH_2'. While the acyclic radical (IIe) is probably the predominant species, only acyclic products being obtained from the MDBuA/OH' reaction, the spectra could have been complicated by the steric effects of the tert-butyl groups preventing free bond rotation and resulting in several observable species.

Detailed ESR studies of the MDEtA, MDPrA, and MDBuA systems are still in progress.

Reaction of N-methylbis(2-phenylallyl)amine (MDPhA, If) with NH_2' gave a spectrum consisting of two broad superimposed triplets, splitting 17.8 G and 21.5 G, assignable to cis and trans isomers of radical (IIIf), together with a weaker multiplet component with 1:1:1 triplet structure, splitting 3.5 G, indicative of radical IVf.

Reaction of N-methylbis(2-carboethoxylallyl)amine (MDCA, Ig) with NH_2' gave a 1:2:1 triplet, splitting 31.5 G, of incompletely resolved sextets, splitting approximately 4.6 G. Radical IVg is probably the observed species as the MDCA-AIBN reaction products contain polymer which predominantly derived from piperidyl radicals (IVg). Steric effects of the two carboethoxy substituents (R) would hinder ring motions and cause markedly different splitting by the equatorial and axial ring hydrogen atoms; additional fine splitting would arise from the $-CO_2-CH_2-$ groups.

NMR Studies of Polymer Structure

The structures of the polymers were largely deduced from the ^{13}C-NMR spectra, the details of which are discussed elsewhere [18]. PMR of the MDAA, MDMA, and MDCA polymers showed that these were essentially saturated. IR of the polymers indicated the presence of nitrile, ester, and amide endgroups derived from the cyano-isopropyl initiating radical. ^{13}C-NMR spectra also showed the presence of methyl endgroups in the polymers. The ratios of pyrrolidine rings to piperidine rings in the various polymers, and the polymerization conditions are summarized in Table 1. Reaction of MDAA or MDMA free base with AIBN in benzene at 60°C appeared to yield polymers with ring-size ratios similar to those observed for polymers formed from the hydrochlorides at 60°C although there were some differences, still

TABLE 1. Ring-Size Ratios of Polymers

Polymer	Reaction temperature/ pressure (°C/bar)	Pyrrolidine: piperidine ratio
MDAA	30-135	> 10:1
MDMA	30	3:2
	60	1:1
	80/1	1:1
	80/8000	7:3
	130	2:3
MDEtA	60	2:3
MDPrA	60	acyclic
MDBuA	60	acyclic
MDPhA	60	1:1
MDCA	30	< 1:100

being investigated, between the ^{13}C-NMR spectra of the polymers formed from the free bases and those formed from the amine salts. The MDPrA and MDBuA polymers appeared to be acyclic, and the MDEtA polymer contained a small proportion of acyclic units in addition to pyrrolidine and piperidine units.

The degrees of polymerization (DP) were estimated from ^{13}C-NMR assay of terminal methyl groups, and by gel-permeation chromatography. The MDCA polymer had high DP, MDAA and MDMA polymers prepared at 30°C had DP of approximately 10, while the other polymers had DP of 5 or less.

Basicity of Polymers

The apparent pH at the endpoints in the potentiometric titration of the polymers with 0.2 N perchloric acid in 2:1 dioxane-water, and the slopes of the titration curves in the vicinity of the endpoints are listed in Table 2. The N-butyldiallylamine (BuDAA) and N,N-dimethylallylamine (DMAA) polymers were prepared earlier [2]. 1,3-Dimethylpiperidine is included for reference as a cyclomonomeric base.

TABLE 2. Basicity of Polymers

Base	Polymerization temperature (°C)	pH at endpoint	$\partial pH/\partial V$ at endpoint (ml^{-1})
1,3-Dimethyl-piperidine	–	5.30	5.7
$(DMAA)_n$	60	3.95	2.9
$(MDAA)_n$	60	4.15	4.1
$(BuDAA)_n$	60	4.40	5.2
$(MDMA)_n$	30	3.75	3.8
$(MDMA)_n$	135	3.60	3.4
$(MDCA)_n$	30	3.00	0.9

DISCUSSION

In this study of the cyclopolymerization of β-substituted diallylamines we have used techniques previously employed for the study of the N-substituted diallylamine systems, namely, ESR spectroscopy of diallylamine-derived radicals, structural analysis of low molecular weight basic products, plus detailed ^{13}C-NMR analysis of the polymers.

ESR and Radical Intermediates

The ESR spectra described in the Results indicate that increasing bulk of the alkyl substituents in the monomer series MDAA, MDMA, MDEtA, MDPrA, MDBuA favors formation of the piperidyl radical (IV), or alternatively stabilizes the acyclic radical (II) which appears to be the predominant observed species in the reactions of MDPrA and MDBuA. The observation of radicals IIc, IId, and IIe is the first substantive indication of the intermediacy of uncyclized radicals in the cyclopolymerization of diallylamines. The increase in ESR signal strength in the same series also reflects a reduction in radical reactivity because of steric shielding by the more bulky alkyl substituents. Examination of molecular models indicates that cyclization of radical II to the pyrrolidine derivative (III) would be hindered by the bulky alkyl substituents at both reactive centers; cyclization to

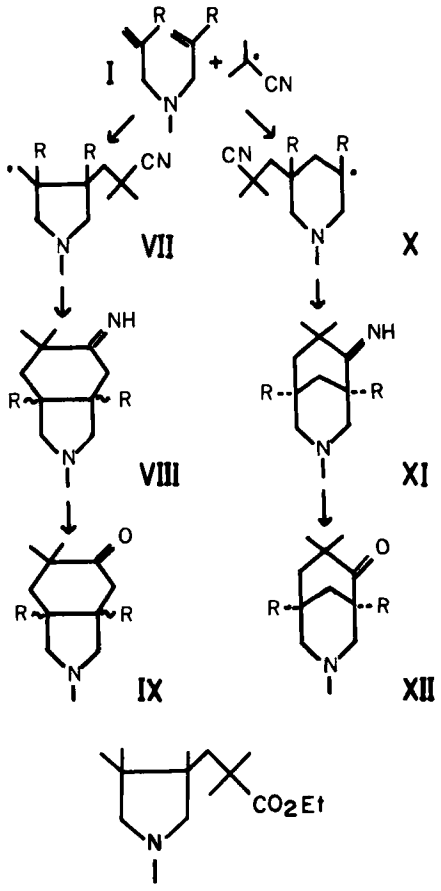
the piperidine (IV) involves attack on an unsubstituted terminal methylene and would be less subject to hindrance by the β-substituents.

The ESR observation of the putative acyclic radical (II) suggests that the cyclization is not a concerted reaction involving the two geminal N-allyl groups, but a sequential process in which attack of radical II on its geminal N-allyl group is favored on a statistical basis. This hypothesis is in agreement with recent proposals of Smith concerning the cyclization of oxa analogs of I and II [19]. It is interesting that in the MDMA and MDEtA reactions, where both the pyrrolidinyl methylene radical (III) and the acyclic radical (II) and/or piperidyl radical (IV) are observed together, the concentration of the radical (III) is greater than that expected from the proportion of pyrrolidine moieties in the total AIBN reaction products, suggesting that the secondary piperidyl radical (IV) is more reactive than its primary radical isomer (III), contrary to expectations. This observation is puzzling and will be a subject for further investigation. The difference is unlikely to result solely from the different initiating radicals, as AIBN and other initiators at the same reaction temperature yield products with similar ring-size ratios.

Effects of Substituents and Reaction Conditions on Product Ring-Size Ratios

The basic products from the various N-methylbis(2-alkylallyl)amine-AIBN reactions consist of bicyclic aminoketones and/or aminoimines, and polymers. Attempts were made to chemically degrade the polymers into products which could be used for quantitative PMR differentiation between piperidine and pyrrolidine moieties. The methods used included the classic Hoffmann and Von Braun procedures, but it was found that side reactions resulted in an impractical proliferation of spectroscopic species. However ^{13}C-NMR chemical shifts of the N-methyl-substituents permitted an unambiguous, semiquantitative differentiation between piperidine and pyrrolidine units of the polymer [17]. The present study was therefore confined to the N-methyldiallylamine derivatives.

The polymers from MDAA (Ia) contained only pyrrolidine units. Changes in reaction temperature, pressure, or media did not result in the appearance of piperidine units in the products. The use of higher reaction temperatures which should have favored the intermediacy of the thermodynamically more stable piperidine radical (Xa) instead resulted in increased yields of the bicyclic aminoketone (IXa) and reduction in yield of polymer, i.e., increased rate of intramolecular reaction of the pyrrolidine radical (VIIa).



where

(a) R = –H
(b) R = $-CH_3$
(c) R = $-C_2H_5$
(d) R = $-CH(CH_3)_2$
(e) R = $-C(CH_3)_3$

The polymers from MDMA (Ib) however showed an increase in piperidine content from 40% to 60% with increase in polymerization temperature, suggesting that the cyclization of radical IIb becomes more subject to thermodynamic control [19], at higher temperatures,

i.e., becomes more an equilibrium process in which six-membered ring formation is favored. This, coupled with the apparent greater reactivity of radical IVb observed from ESR spectra, would result in products containing a greater proportion of piperidine units. The MDMA polymers were saturated, and the isolation of the pyrrolidine derivative (XIII) shows that the termination reaction in ethanolic media occurs by hydrogen abstraction from the solvent, acetaldehyde being detected in the volatile reaction products. Terminal methyl groups were observed in the ^{13}C-NMR spectra of the MDAA polymers, in agreement with this termination mechanism. Increases in reaction pressure resulted in reduced polymer piperidine content, suggesting that the transition state for the formation of radical IV requires greater volume than that for radical III and becomes kinetically less favorable at higher reaction pressures.

The MDEtA (Ic) polymer contained a higher piperidine content than the MDMA polymers, and also contained a small proportion of acyclic units, shown by the presence of allylic unsaturation in its ^{13}C-NMR spectrum. The MDPrA oligomer (Id) was obtained in low yield, and appeared to be entirely acyclic.

The yields of polymers and their degree of polymerization were both reduced by bulky β-substituent groups, MDBuA (Ie), for example, yielding negligible amount of polymer, even when HO$^{\bullet}$ was used as initiator. These observations confirm the ESR results, which show that steric effects of the β-substituents retard the rates of both the intramolecular cyclization and intermolecular propagation reactions.

The MDPhA (If) polymer contained about 50% piperidine units, approximately the proportion expected from operation of steric effects. The MDCA (Ig) polymer, however, contained virtually 100% piperidine units, and the polymer was of high molecular weight and represented complete conversion of the monomer, indicating that steric effects were not responsible for the high piperidine content in this case. Earlier studies [5] with hydrocarbyl analogs of radical II had shown that β-substituents such as cyano, phenyl, or carboalkoxy stabilize the radicals and favor cyclization to the thermodynamically preferred six-membered ring radical rather than to the kinetically preferred five-membered ring isomer. The carboethoxy substituents of MDCA have a similar effect, but the weaker influence of the phenyl substituents of MDPhA was unexpected, and might be due to steric effects preventing coplanarity of the conjugated system.

The bicyclic aminoketones and aminoimines obtained from the bis(2-alkylallyl)amine-AIBN reactions also reflects the steric influences of the substituents. MDAA yielded only cis isomer of the pyrrolidine aminoketone (IXa), formed by back-biting cyclization of the radical VIIa and hydrolysis of the resultant imine (VIIIa) [2].

MDMA yielded both cis and trans isomers of the pyrrolidine aminoketones (IXb), together with a smaller amount of the piperidine aminoketone (XIIb) and its imino precursor (XIb), while MDEtA and MdPrA yielded only the piperidine bicyclic derivatives XIc, and XIIc and XId, respectively.

The bicyclic amine formation represents an alternative to propagation of the radicals VII or X, and is apparently favored by increase in reaction temperature or by reactions of AIBN with the less reactive unprotonated diallylamines. Steric effects which hinder radical propagation also result in increased bicyclic amine formation, for example, the bicyclic amine being the major product from the MDPrA-AIBN reaction.

The resistance of the bicyclic aminoimines (XI) to hydrolysis is surprising in view of the lability of the nonconjugated acyclic and alicyclic ketimines. This stability can be ascribed to steric shielding of the imine group by the adjacent geminal methyls and bridgehead alkyl substituents.

Basicity and Neighboring Amino Group Interaction

Polymers derived from diallylamines and triallylamine have been used as ion-exchange resins in water treatment. Polymerization of these monomers has been shown to proceed via radical intermediates such as IIIa [6]. The triallylamine polymers are now believed to consist predominantly of pyrrolidine chains crosslinked by further reaction of the pendent allyl groups [1, 2]. The diallylamine polymers are usually crosslinked by copolymerization, for example, with tetrafunctional monomers such as bis(diallylamino)alkanes [3].

One of the most important considerations in polymers of the above type is the basicity which is dependent on a number of factors. Of particular relevance is the degree of crosslinking which controls the swelling of the ionized polymer in water, and hence the separation, and degree of interaction between neighboring amino groups. The effects of such interaction have been previously demonstrated by the examples of bis(diallylamino)ethane and -propane, which have lower basicities than bis(diallylamino)butane and higher homologs [3] which allow greater separation between neighboring ionized amino groups. The ratio of piperidine and pyrrolidine rings would also affect the basicities of the polymers for, although monomeric substituted pyrrolidines and the analogous substituted piperidines have similar basicities, the basicity of a poly-3,4-dimethylenepyrrolidine (V) would be expected to differ from that of the analogous poly-3,5-piperidylmethylene (VI), as the dissimilar geometrics of the molecular

chains would result in differing degrees of restraint on the interactions between neighboring amino groups. The extent of this restraint is difficult to predict, as examination of Dreiding models of structures V and VI shows that they have similar maximum and minimum distances for amino group separation, despite the difference in the number of exocyclic methylene links.

Poly(MDMA) prepared at 30 and 130°C, containing respectively 40 and 60% piperidine units (Table 1), have similar potentiometric titration curves, but the slightly lower endpoint pH and $\partial pH/\partial v$ values found for the 130°C polymer (Table 2) indicate a reduction in basicity, apparently due to greater amino group interaction with increasing piperidine content. The polymers were completely soluble in the titration medium, so this increased interaction probably results from a reduction in average intramolecular ammonium group separation. The MDMA polymers were less basic than the MDAA and BuDAA polymers having virtually 100% pyrrolidine content, but this difference would be in part due to the methyl substituents in the former, as introduction of β-methyl substituents has been shown to cause a small reduction in the pKa values of monomeric pyrrolidines and piperidines through weak electronic effects [15].

Poly(MDCA), having virtually 100% piperidine content, in turn has a much lower basicity than the MDMA polymers, again indicative of greater amino group interaction with increasing piperidine content, although the differences in electronic and steric effects between the carboethoxy and methyl substituents would limit any rigorous comparison between the two polymers.

CONCLUSION

Our results show that the radical-induced cyclization of diallylamines does not necessarily involve a concerted reaction as acyclic radical intermediates were observed in reactions of sterically-hindered monomers. The direction of ring closure of the acyclic radical is susceptible both to steric and conjugative effects of β-substituents, and to a lesser extent, increases in reaction temperature, all of which favor an increase in the proportion of piperidines in the products, reflecting increased cyclization to the thermodynamically preferred piperidyl radical.

Increased piperidine content in the soluble diallylamine polymers results in increased interaction between neighboring ionized amino groups and a decrease in polymer basicity. Although an increase in piperidine content of poly(MDMA) could be obtained by use of higher polymerization temperatures, this increase was accompanied by reduction in the degree of polymerization and conversion.

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