Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

Cyclopolymerization. III. Electron Spin Resonance Studies of Diallylamines with Redox Systems

A. L. J. Beckwith[a]; A. K. Ong[b]; D. H. Solomon[b]
[a] Organic Chemistry Department, The University of Adelaide, Adelaide, South Australia, Australia [b] Division of Applied Organic Chemistry, CSIRO, Melbourne, Victoria, Australia

To cite this Article Beckwith, A. L. J. , Ong, A. K. and Solomon, D. H.(1975) 'Cyclopolymerization. III. Electron Spin Resonance Studies of Diallylamines with Redox Systems', Journal of Macromolecular Science, Part A, 9: 1, 125 — 147
To link to this Article: DOI: 10.1080/00222337508068651
URL: http://dx.doi.org/10.1080/00222337508068651

J. MACROMOL. SCI.—CHEM., A9(1), pp. 125-147(1975)

Cyclopolymerization. III. Electron Spin Resonance Studies of Diallylamines with Redox Systems

A. L. J. BECKWITH

Organic Chemistry Department
The University of Adelaide
Adelaide, South Australia 5001, Australia

and

A. K. ONG and D. H. SOLOMON

Division of Applied Organic Chemistry
CSIRO
Melbourne, Victoria 3001, Australia

ABSTRACT

The reaction of a series of diallylamines and related compounds with free radicals in aqueous acid solution has been studied in a flow system using ESR spectroscopy. The initiation was by radicals generated from titanium trichloride-hydrogen peroxide (hydroxyl radicals) and titanium trichloride-hydroxylamine (amino radicals) systems, respectively. The observed ESR spectra were assigned to five-membered ring radicals as the major radical species present in the system. However, the dimethallyl-amine series gave both five- and six-membered ring radicals.

INTRODUCTION

Electron spin resonance (ESR) spectroscopy has a ready application in polymer science since it enables direct observation of radical species present in a polymerization mixture. The well-established flow technique developed by Dixon and Norman [1, 2] has made it possible to observe ESR spectra of short-lived free radicals in aqueous media. This technique has been widely applied in studying the radical polymerization of a variety of vinyl monomers in recent years [3-14].

The purpose of this investigation is to obtain information on the mechanism of cyclopolymerization by measuring the ESR spectra of propagating radicals produced from diallylamines and related compounds. In the flow system used for these experiments the conditions are similar but not identical to the polymerization process sometimes used [15]. Consequently the hyperfine splitting of the ESR spectra should provide information on the structure (particularly the ring size) of the propagating radicals.

ESR studies of monomers capable of forming cyclopolymers may give some insight into the mechanism of cyclopolymerization reactions and hence to the possible structure of the polymer formed [16].

RESULTS AND DISCUSSION

The radicals were generated in the cavity of an ESR spectrometer using the flow technique previously described [1, 2]. The amine radical HOA· and NH_2A·, A = (1), were generated from the appropriate amines as shown in Eqs. (1)-(IV).

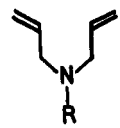
$$Ti^{3+} + H_2O_2 \rightarrow Ti^{4+} + HO^- + HO\cdot \quad (I)$$

$$HO\cdot + A \rightarrow HOA\cdot \quad (II)$$

$$Ti^{3+} + NH_2OH \rightarrow Ti^{4+} + HO^- + NH_2\cdot \quad (III)$$

$$NH_2\cdot + A \rightarrow NH_2A \quad (IV)$$

The spectrum of the radical resulting from addition of hydroxyl radicals to N,N-diallylamine (1, R = H) consists of a triplet (splitting from α-protons) of doublets (from β-protons) as shown in Fig. 1.



(I)

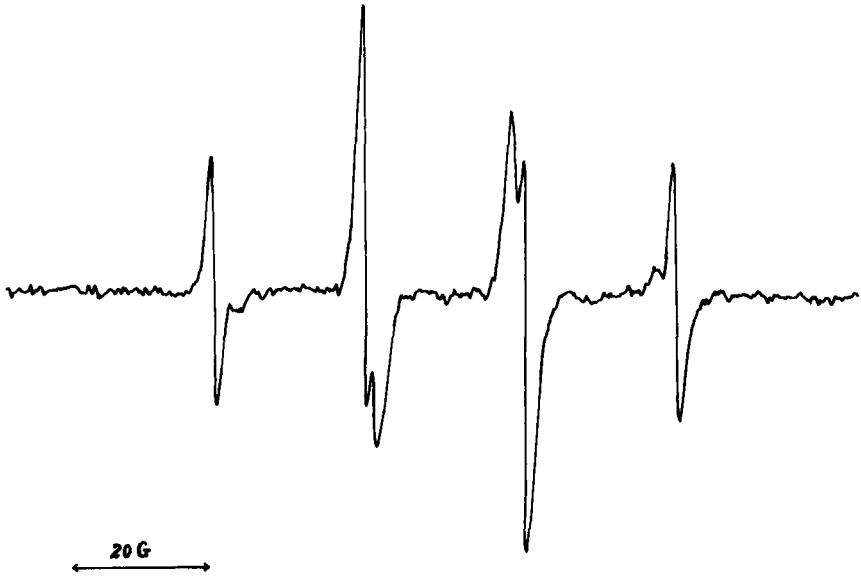
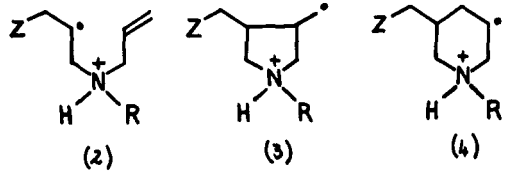


FIG. 1. ESR spectrum of radicals formed from N,N-diallylamine and ·OH radicals.

where R = H, CH_3, C_2H_5, n-C_3H_7, iso-C_3H_7, sec-C_4H_9, tert-C_4H_9, C_6H_5, $C_6H_5CH_2$, $CH_3OCH_2CH_2$, cyclohexyl, and $CH_2CH = CH_2$.

The spectrum can be assigned to the five-membered ring radical (3), but not the six-membered ring radical (4) or the uncyclized radical (2) [17].



When N,N-diallylamine (1, R = H) is treated with amino radicals, the ESR spectrum (Fig. 2) shows an evenly spaced quartet splitting pattern with an intensity distribution of 1:3:3:1. This is due to an overlapping of the triplet of doublets (cf. Fig. 1) because the couplings with α- and β-protons are practically equal. Again this hyperfine

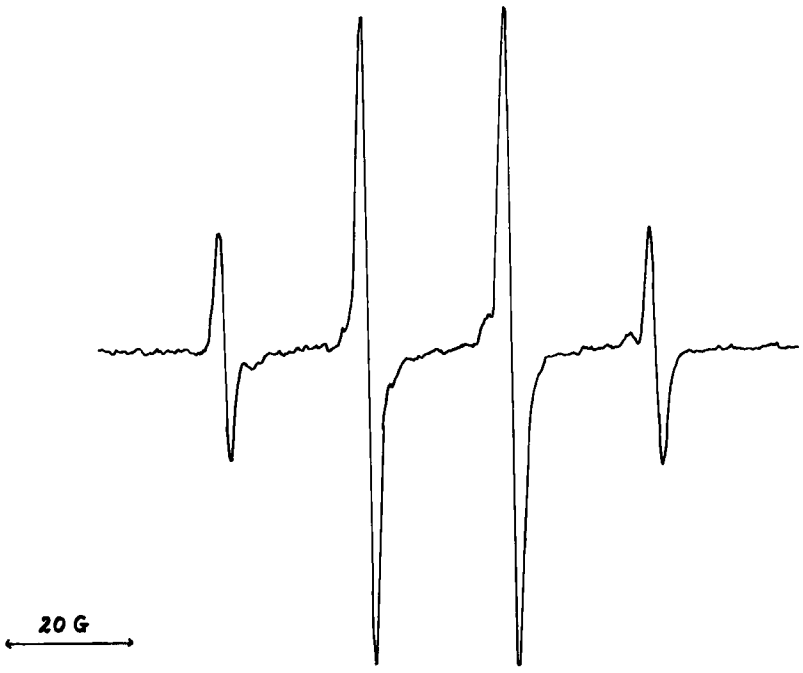


FIG. 2. ESR spectrum of radicals fromed from N,N-diallylamine and $\cdot NH_2$ radicals.

splitting pattern is consistent with the formation of the five-membered ring radical (3) but not the six-membered ring (4) or the uncyclized radicals (2).

Similarly, the other members of the diallylamine series (1) when treated with hydroxyl or amino radicals gave ESR spectra which indicated the formation of five-membered ring radicals (3). The splitting constants are set out in Table 1.

The data presented in Table 1 indicate that there is a slight increase in the splitting constant when the substituent R is bulky, e.g., phenyl or t-butyl. This change probably reflects an increase in the value of $a(\beta\text{-H})$ arising from the effects of nonbonded interactions between the N-substituent and the carbinyl group on the rotamer population of the latter.

Figure 3 shows the ESR signal recorded when hydroxyl ($\cdot OH$) radicals are generated in the presence of N,N-diallylbenzylamine (1, R = $C_6H_5CH_2$). The predominant species present is the five-membered cyclic radical (3). The weaker signal cannot be

TABLE 1. ESR Spectra of Radicals Derived from Diallylamines (1)

	HO·			NH_2·	
R	a(α-H)	a(β-H)	g	a(α-H)=a(β-H)	g
H	22.4 (t)[a]	23.8 (d)[a]	2.0026	22.6 (q)[a]	2.0026
CH_3		22.4 (q)	2.0025	21.1 (q)	2.0026
C_2H_5		22.4 (q)	2.0025	22.1 (q)	2.0025
C_3H_7		22.4 (q)	2.0026	22.1 (q)	2.0026
iso-C_3H_7		22.4 (q)	2.0026	21.8 (q)	2.0025
iso-C_4H_9		22.4 (q)	2.0026	22.1 (q)	2.0025
sec-C_4H_9		22.4 (q)	2.0025	22.0 (q)	2.0025
t-C_4H_9		22.6 (q)	2.0026	22.4 (q)	2.0025
C_6H_5		22.6 (q)	2.0026	22.4 (q)	2.0025
$C_6H_5CH_2$		22.3 (q)	2.0025	21.7 (q)	2.0025
Cyclohexyl		22.4 (q)	2.0026	22.0 (q)	2.0025
$CH_3OCH_2CH_2$—		22.5 (q)	2.0025	22.0 (q)	2.0025
CH_2=$CHCH_2$—		22.4 (q)	2.0026	22.2 (q)	2.0025

[a]Hyperfine splitting factor in gauss; (d), doublet; (t), triplet; (q) quartet. In each case the relative intensities of the absorptions were in the ratio of the coefficients of the appropriate binomial expansion.

unambiguously analyzed or assigned. It could arise either from the product (5) of ·OH addition to the aromatic ring, or from the benzylic radical (6) formed by hydrogen atom abstraction from the monomer (1, R = $C_6H_5CH_2$). We prefer the former suggestion since the general pattern of the weaker signal (comprising two widely separated multiplets) is similar to that exhibited by other aromatic ·OH adducts [18].

The quartet multiplicity of the signal recorded when triallylamine is treated with either ·NH_2 or ·OH radicals in consistent with the bicyclic structures (7, 8) as well as the monocyclic structure (3, R = allyl). The latter explanation is preferable because of the very close similarity of the hyperfine splitting constant to those of the monocyclic radicals formed from diallylamines. It may be relevant that the related alkyl radical (9) has been shown to cyclize as illustrated, with the first step proceeding very much more rapidly than the second [19].

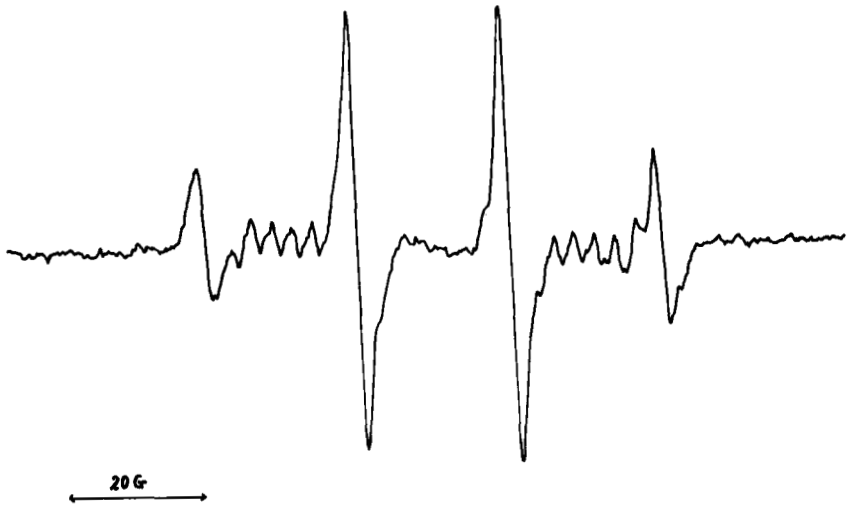
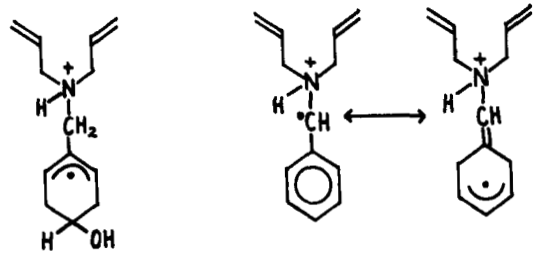


FIG. 3. ESR spectrum of radicals formed from N,N-diallylbenzylamine and ·OH radicals.

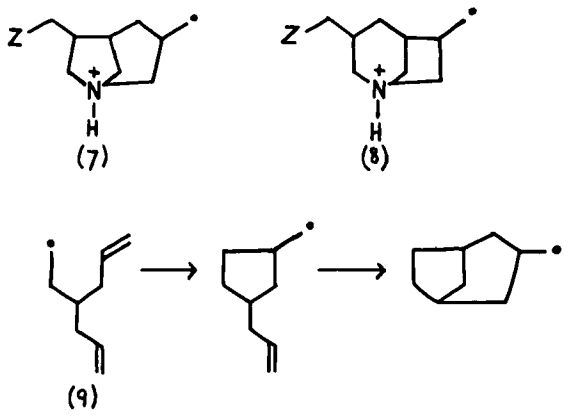


(5) (6)

In order to demonstrate that the radicals produced were independent of the initiating radical, N,N-diallylmethylamine (1, R = CH_3) was treated with Ti^{3+}/tert-butylhydroperoxide in the presence of EDTA. A spectrum was obtained similar to that from amino or hydroxyl radical attack on N,N-diallylmethylamine.

Cyclization of the initial radical (e.g., 2) to a five-membered ring radical (e.g., 3) would be expected to be inhibited by bulky substituents at the β-position of the allyl group.

The ESR signal recorded when dimethallylamine (10, R = H) is treated with ·OH radicals (Fig. 4) comprises two overlapping spectra.



The spectrum of triplet multiplicity is assigned to the five-membered cyclic radical (11). When the reaction is initiated with $\cdot NH_2$ radicals, the signal also comprises two overlapping spectra: a triplet assigned to the cyclic radical (11) and a spectrum of much higher multiplicity. Since the latter spectrum is identical to that observed when the reaction is initiated with ·OH radicals, we are able to exclude the

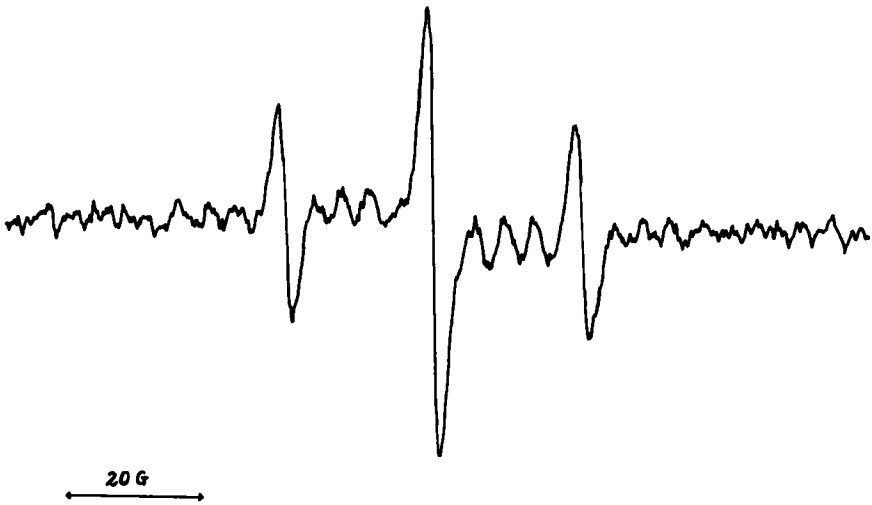
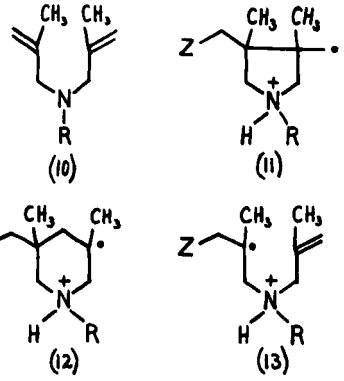


FIG. 4. ESR spectrum of radicals formed from dimethallylamine and ·OH radicals.

uncyclized radical (13) and we conclude, therefore, that it arises from the six-membered cyclic radical (12).



R = H, C_2H_5, n-C_3H_7, or methallyl

Both five-membered (11) and six-membered (12) cyclic radicals are similarly formed from the substituted dimethallylamine monomers (10, R = C_2H_5, n-C_3H_7, or methallyl). The splitting constants for the five-membered radicals are given in Table 2.

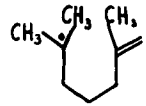
It is difficult to determine the relative stationary concentrations of five- and six-membered cyclic radicals formed from dimethallyl monomers (10). The signal attributed to the six-membered cyclic radical is superficially less intense than that attributed to the five-membered radical, but its multiplicity is much higher (theoretical

TABLE 2. ESR Spectra of Radicals Derived from Dimethallylamine Monomers (10)

	HO·		NH_2·	
R	a(α-H)	g	a(α-H)	g
H	22.2 (t)[a]	2.0026	22.3 (t)	2.0025
C_2H_5	22.0 (t)	2.0025	-	-
n-C_3H_7	22.2 (t)	2.0025	22.2 (t)	2.0026
Methallyl	22.1 (t)	2.0026	-	-

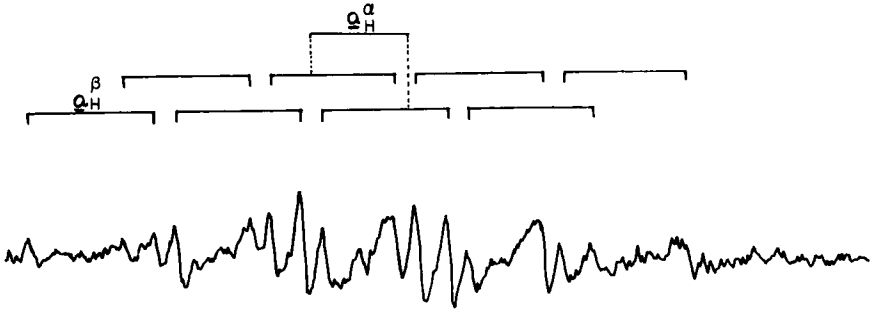
[a](t) = triplet.

multiplicity $\geqslant 60$), and preliminary calculations indicate that the actual integrated intensity is greater for radical (12) than it is for radical (11). We tentatively conclude that dimethallyl monomers (10) preferentially form six-membered cyclic radicals (12). A similar tendency has been noted in related carbon radicals (14) and has been attributed to the steric effect of the methyl substituents [20].



(14)

By contrast, bulky substituents in the γ-position of the allyl group might be expected to alter the whole pathway of radical formation and cyclization. The ESR spectrum of N,N-dicrotyl-n-propylamine (15) treated with hydroxyl radicals consists of a doublet of doublets of quartets (Fig. 5). This is consistent with the five-membered ring radical (17), with $a_H^{\alpha} = 16.5$ (d), $a_H^{\beta} = 21.6$ (d), and $a^{CH_3} = 25.2$ (q) G. The ESR signals are too weak for any six-membered ring (18) or the uncyclized radicals (16) to be detected. When the amino radical



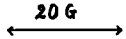


FIG. 5. ESR spectrum of radicals formed from N,N-dicrotyl-n-propylamine and ·OH radicals.

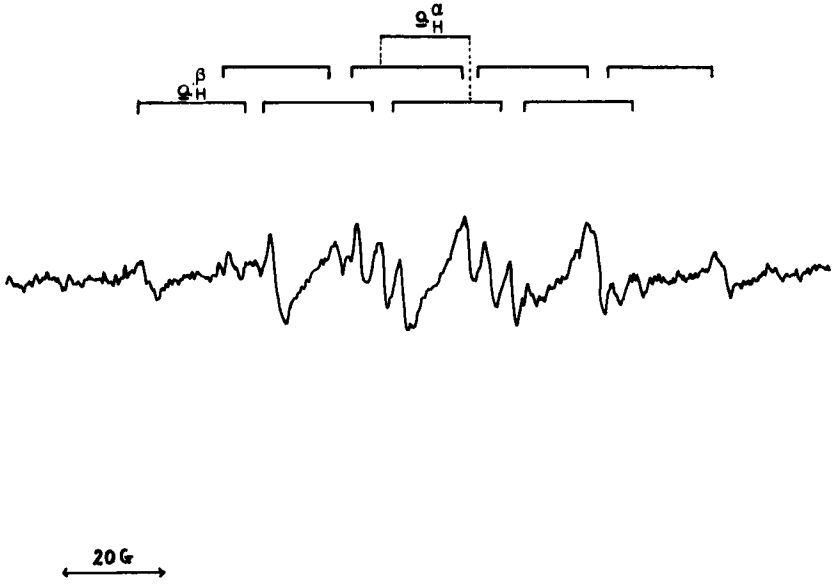


FIG. 6. ESR spectrum of radicals formed from N,N-dicrotyl-n-propylamine and $\cdot NH_2$ radicals.

is used as initiator, the ESR spectrum (Fig. 6) shows a doublet of doublets of quartets. This is again consistent with the five-membered ring radical (17), with a_H^{α} = 17.1 (d), a_H^{β} = 22.41 (d), and a^{CH_3} = 25.4 (q) G.

The radicals from allylamines were compared with those from a but-3-enylamine. The ESR spectrum of N,N-di(but-3-enyl)-propylamine (19) treated with hydroxyl radicals consists of a doublet of quintets with splitting constants a_H^{α} = 24.2 (d) and a_H^{β} = 22.2 (quintet, qn) G (Fig. 7). The spectrum is consistent with the formation of the uncyclized radical (20). When this monomer (19) was attacked by amino radicals, the ESR spectrum became a doublet of quintets of triplets (Fig. 8) which confirms the formation of the uncyclized radical (20), with a_H^{α} = 26.4 (d), a_H^{β} = 22.6 (qn), and a_N = 5.4 (t) G.

In view of the potential usefulness of bis(diallylamino)alkanes as cross-linking monomers, we examined their radical patterns, even though we anticipated similar results to those of the mono(diallylamino)-alkanes. When bis(diallylamino)alkanes (21) where x is 2 to 10 are

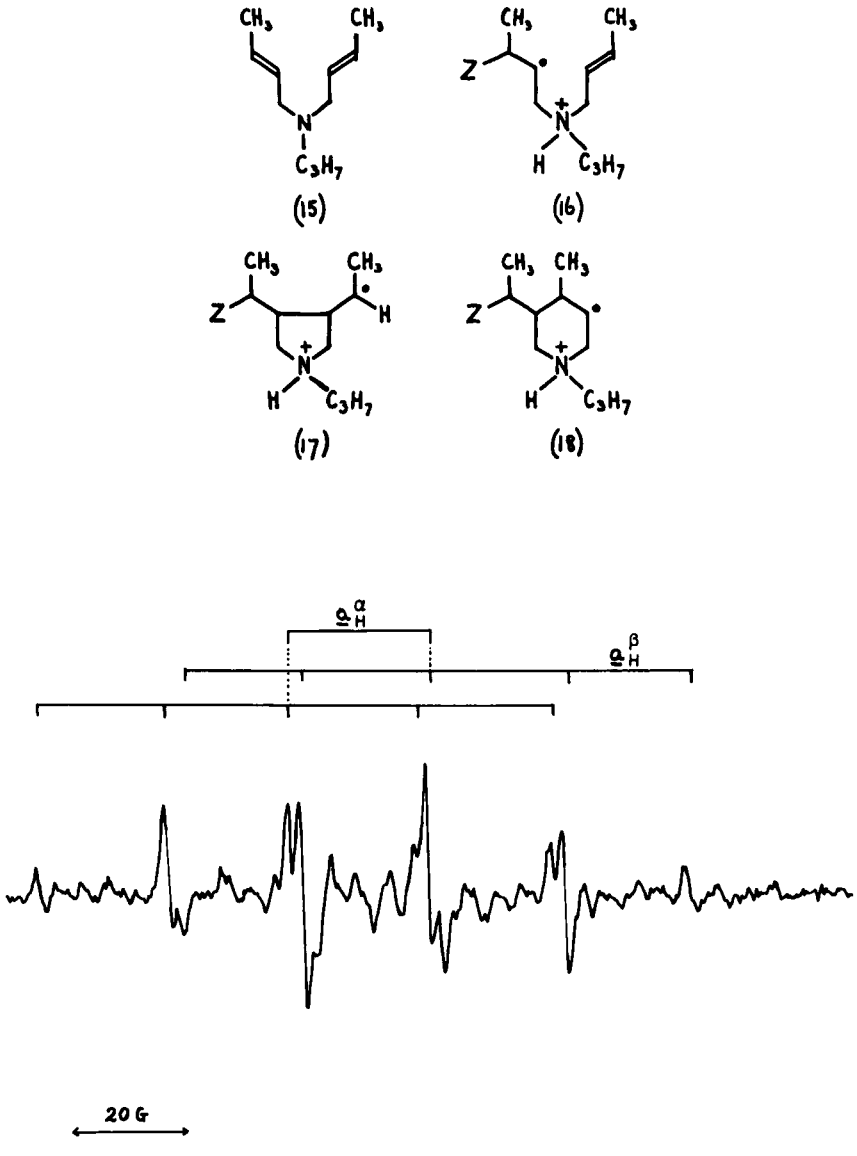


FIG. 7. ESR spectrum of radicals formed from N,N-di(but-3-enyl)-n-propylamine and ·OH radicals.

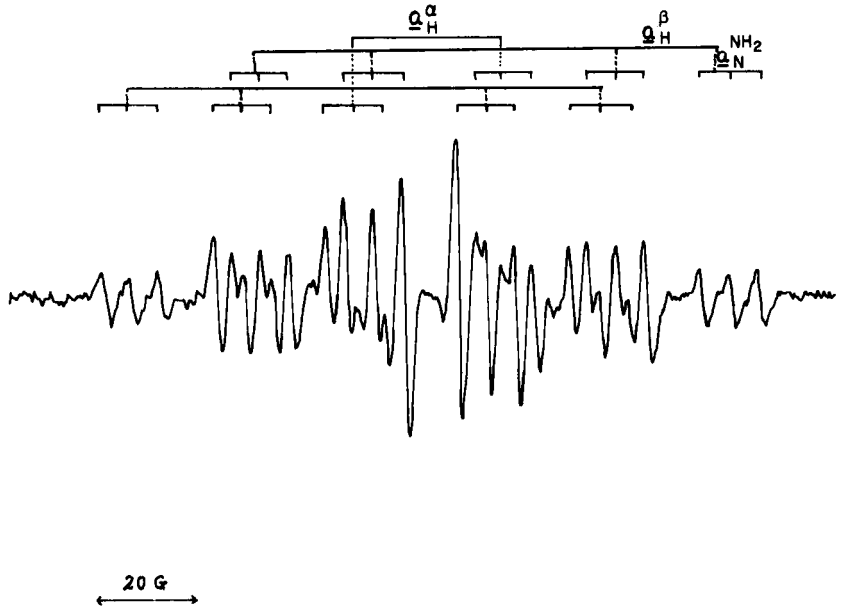
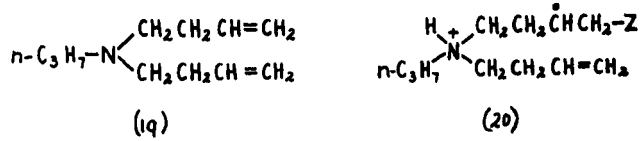
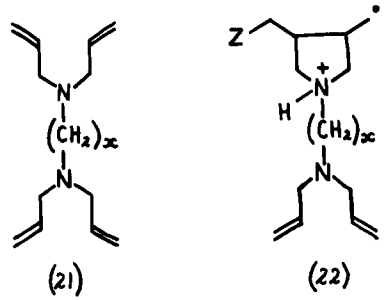


FIG. 8. ESR spectrum of radicals from N,N-di(but-3-enyl)-n-propylamine and $\cdot NH_2$ radicals.



reacted with hydroxyl or amino radicals, the ESR spectra produced show hyperfine quartet splitting similar to the spectra of the diallylamine series (1). This splitting pattern is consistent with the formation of five-membered ring radicals (22). The splitting values are tabulated in Table 3. Again no six-membered ring or uncyclized radicals or the radical resulting from the reaction of the allyl groups between the two nitrogen atoms were observed in the spectra.

The ESR spectra recorded when 1,2-bis(diallylamino)ethane (21, x = 2) is treated with amino radicals, shows splitting on the two outer peaks as shown in Fig. 9. This splitting is difficult to explain but possibly results from the unresolved peaks of the two isomeric five-membered ring radicals, i.e., cis- and trans-isomers (23) and (24),



(21) (22)

x = 2 to 10

TABLE 3. ESR Spectra of Radicals Derived from 1,X-bis(Diallylamino)alkanes (21)

	HO·		NH_2·		
X	a(α-H) = a(β-H)	g	a(α-H)	a(β-H)	g
2	22.5 (q)[a]	2.0025	cis 21.4	trans 22.3	2.0025
3	22.4 (q)	2.0025	22.1 (q)		2.0025
4	22.4 (q)	2.0025	22.1 (q)		2.0025
5	22.4 (q)	2.0025	22.0 (q)		2.0026
6	22.4 (q)	2.0025	22.1 (q)		2.0026
7	22.4 (q)	2.0025	22.1 (q)		2.0026
8	22.4 (q)	2.0025	21.9 (q)		2.0026
9	22.5 (q)	2.0025	22.1 (q)		2.0025
10	22.5 (q)	2.0025	21.9 (q)		2.0026

[a](q) = quartet.

respectively. The larger splitting constant, a(H) = 22.3 G is assigned to the trans-isomer (24) because inspection of models reveals that nonbonded interactions between the two substituents in the cis-isomer (23) increase the energies of those rotamers expected to show large values of β-H coupling. However, the absence of a similar observation for the diallyl series does not support this contention.

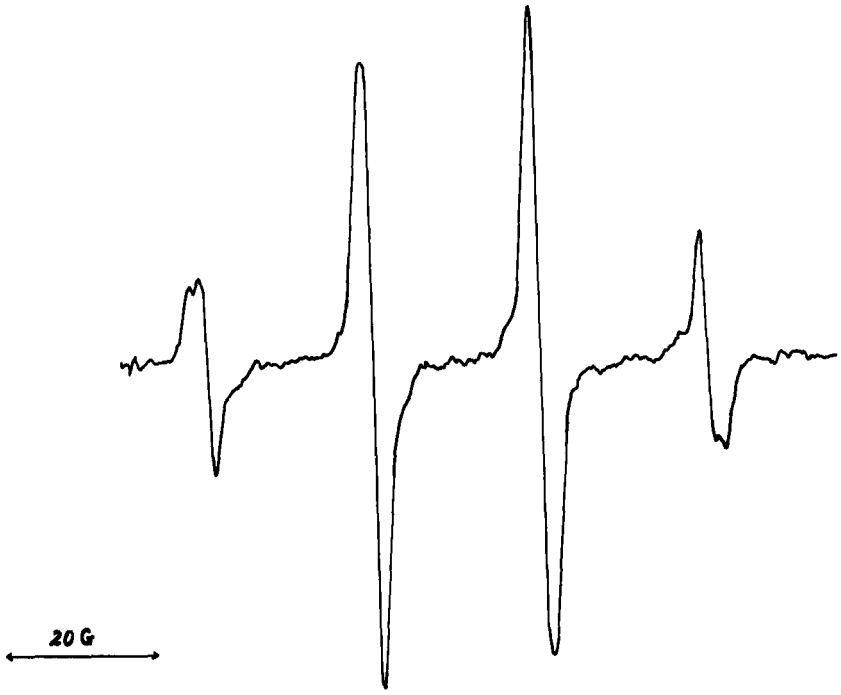
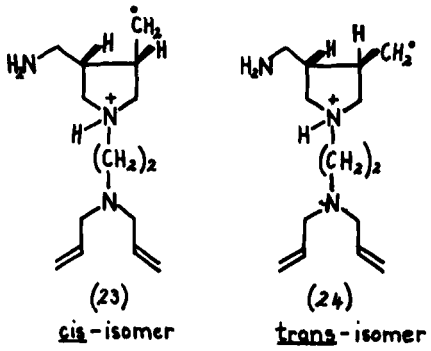


FIG. 9. ESR spectrum of radicals formed from 1,2-bis(diallylamino)-ethane and $\cdot NH_2$ radicals.



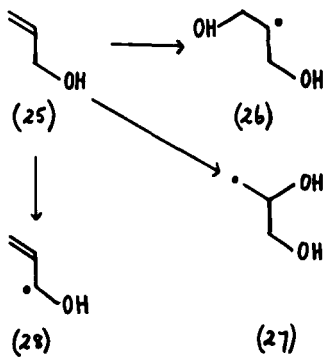
In conclusion, this part of the work has shown that the free radical attack on diallylamines and related systems gives predominately the five-membered ring radical (3); under the experimental conditions used, the uncyclized radical (2) is not observed. The recorded spectra show no indications of the formation of other radicals, except with the dimethallyl monomer (10) where a six-membered ring product is also present.

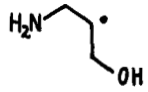
Cyclopolymerization of 1,6-dienes can occur via either a stepwise process or through a concerted mechanism. If the polymerization proceeds by a stepwise process, the radicals which would be expected to form are the uncyclized (2) and cyclized ring radicals. On the other hand, if the polymerization proceeds through a concerted mechanism, only cyclized radicals are expected. The stepwise mechanism is supported by the following observations.

ESR studies of monoallyl compounds have shown that hydroxyl radicals are capable of attacking β- and γ-carbon atoms of allyl monomers [21, 22]. For example, the observed ESR spectrum when allyl alcohol (25) is attacked by ·OH radicals indicates that reaction is predominately on the γ-carbon atom (26), 5 to 7% on the β-carbon atom (27), and a trace component assigned to the allylic radical (28) formed by hydrogen abstraction. Reaction of the same monomer (25) with amino radicals gives the radical (29) as the predominant species [23].

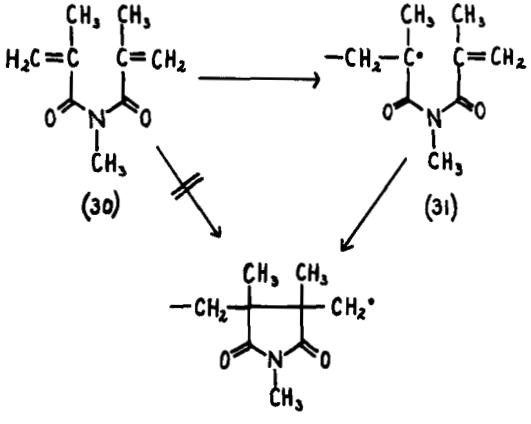
Recently, Kodaira and co-workers [24] showed that solid-state polymerization of N-methyldimethacrylamide (30) by γ-irradiation proceeds in a stepwise way (Scheme 1). The ESR spectrum obtained is consistent with the uncyclized radical (31).

Further evidence of the stepwise mechanism is provided by the polymerization of diallylamine hydrochloride (33) to yield cross-linked polymer under certain conditions [25]. This is consistent with some units undergoing cyclopolymerization and some propagating





(29)

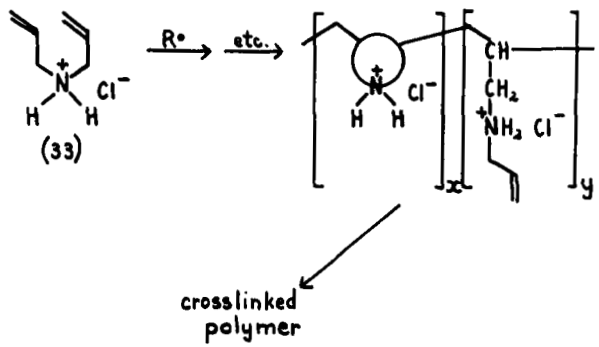


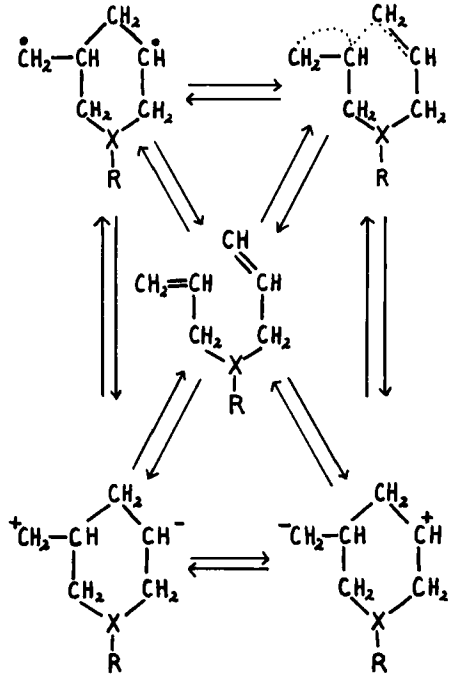
(30) (31) (32)

SCHEME 1.

before cyclization to form a polymer with pendent allyl groups which can then cross-link.

The concerted mechanism finds support in Butler's initial proposal that the cyclopolymerization involves a homoconjugative interspectral interaction [26] between the double bonds (Scheme 2). This view is also



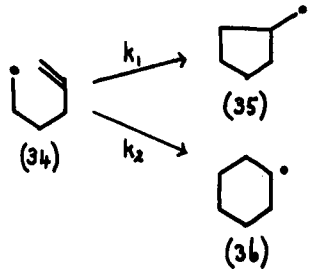


SCHEME 2.

supported in a recent study of a series of substituted silanes [27] by UV spectroscopy.

The formation of a five-membered ring is in accord with the cyclization of the hex-5-en-1-yl [28-34] radical (34) to the cyclopentyl carbinyl radical (35) rather than the supposedly more stable cyclohexyl radical (36). This is of interest because such a reaction proceeds by way of a less stable primary intermediate which is contrary to the classical theory that radical addition to double bonds occurs to yield the most stable radical product. This observation indicates that cyclization is under kinetic control; that is, the rate of formation of five-membered rings is very much faster than that of six-membered rings ($k_1 \gg k_2$).

Walling and Pearson [34] suggested that steric reasons may be the determining factor involved in the cyclization, but an alternative suggestion by Capon and Rees [35] is also attractive. The latter pointed out that in intramolecular additions much less time elapses between formation and interaction with the double bond of the initial radical.



This radical will therefore be much less selective, the transition state will resemble the initial state more closely, and bond formation will occur at the end of the double bond which the radical approaches more readily. Models show that the number of available conformations in which attack is at position 5 is greater than those for attack at position 6.

Struble and co-workers [36] suggested that the initial stages of the addition process involve interaction of the unpaired electron with the lowest unoccupied orbital of the π-system and along a line extending almost vertically from one of the terminal carbon atoms. This will give the preferred five-membered ring product.

The familiar triangular arrangement transition state is not acceptable in hex-5-en-1-yl (34) cyclization because it will lead to the six-membered ring radical (36).

ESR spectra showed that five- and six-membered ring radicals were formed from dimethallyl monomers (10). The formation of the six-membered ring radical (12) can be attributed to the steric effect of the methyl substituents on the transition states altering the relative rates of formation of five- and six-membered rings. However, the reaction is still under kinetic and not thermodynamic control.

The failure of N,N-di(but-3-enyl)propylamine (19) to cyclize is consistent with the results of Marvel and co-workers [37, 38] on α,ω-olefins, $CH_2{=}CH{-}(CH_2)_n{-}CH{=}CH_2$, where n = 2 to 18. They found that the degree of cyclization of the diolefins falls sharply as the ring size rises above six atoms.

EXPERIMENTAL

ESR Spectra

The ESR spectra were recorded with a Varian E9 EPR spectrometer equipped with 100 KHz modulation and an X-band Klystron. The splitting constants were measured to within ±0.1 G, and g-values to within ±0.0001. The instrument was calibrated by adding an aqueous solution of Fremy's salt (g = 2.0055, α = 13.09 G).

The procedure used for generation of hydroxyl and amino radicals was similar to those described in the preceding paper [17].

Materials

Some of the monomers were prepared and purified as described in the literature and had physical constants in agreement with those previously recorded, and NMR spectra in accord with the assigned structure: N,N-diallyl-iso-propylamine [39]; N,N-diallyl-sec-butylamine [40]; N,N-diallyl-iso-butylamine [41]; N,N-diallyl-tert-butylamine [39]; N,N-diallylbenzylamine [39]; N,N-diallylcyclohexylamine [39]; 1,2-bis(diallylamino)ethane [42]; 1,3-bis(diallylamino)propane [43]; 1,4-bis(diallylamino)butane [44]; 1,5-bis(diallylamino)pentane [44]; 1,6-bis(diallylamino)hexane [43]; 1,7-bis(diallylamino)heptane [43]; 1,8-bis(diallylamino)octane [43]; 1,9-bis(diallylamino)nonane [43]; and 1,10-bis(diallylamino)decane [43].

1,X-bis(diallylamino)alkanes (X = 2, 3, 6, 7, 8, 10) were prepared from 1,X-dibromoalkanes and diallylamine by heating the appropriate mixture under reflux for 24 hr. The purity of the product was assessed by GLC.

The following monomers were redistilled and the purity checked by GLC: N,N-diallylamine (Koch-Light Laboratories Ltd., England); N,N-di-methallyl amine and trimethallylamine (Aldrich Chemical Co., U.S.A.); N,N-diallylmethylamine, N,N-diallylethylamine, N,N-diallyl-n-propylamine, and triallylamine [provided by ICI (Australia)]; and N,N-di-methallylethylamine (provided by Dr. D. G. Hawthorne).

N, N-Dicrotylpropylamine

Crotyl bromide (27.0 g, 0.2 mole) and sodium hydroxide (40 g in 100 ml H_2O) were added dropwise at the same time from two dropping funnels to n-propylamine (5.91 g, 0.1 mole). After the addition was completed, the mixture was heated to reflux for 24 hr. After cooling, the crude amine layer was separated, dried over solid sodium hydroxide, and distilled; yield 12.67 g (75%), bp 78-80°C at 17 mm. (Found: C, 78.68, H, 12.52. $C_{11}H_{21}N$ requires C, 78.96; H, 12.66%) ν_{max} (liquid film): 3025 (sh), 2950 (s), 2860 (w), 2750 (s), 1664 (w), 1450 (m), 1380 (m), 1360 (w), 1340 (w), 1290 (w), 1260 (w), 1225 (w), 1152 (m), 1130 (m), 1100 (sh), 1080 (m), 1030 (m), 960 (s), 905 (w), 860 (w), 840 (w), 740 (w), and 680 (w) cm^{-1}. NMR ($CDCl_3$): 5.73-5.33 m, 4H (olefine protons); 3.20-2.83 m, 4H (methylene protons of crotyl group); 2.53-2.10 m, 2H ($N-CH_2$ protons of propyl group); 1.76-1.10 m, 8H (methyl protons of crotyl group and methylene protons of propyl group); and 0.83 t, 3H (methyl protons of propyl group). Mass spectrum:

M/e 167 (4%, M^+), 152 (2), 138 (39), 126 (3), 84 (34), 72 (10), 56 (15), 55 (100), 43 (22), 42 (28), 41 (36), 38 (29), 30 (96), and 29 (64).

N,N-Dimethallyl-n-propylamine

N,N-Dimethallylpropylamine was prepared by a similar procedure to that used for N,N-dicrotylpropylamine using β-methallyl chloride (45.20 g, 0.5 mole), sodium hydroxide (80 g in 200 ml H_2O) and N-propylamine (11.82 g, 0.2 mole). Distillation of the crude amine gave the required product; yield 20.20 g (61%), bp 34-35°C at 0.3 mm. (Found: C, 79.23; H, 12.68. $C_{11}H_{21}N$ requires C, 78.96; H, 12.66.) ν_{max} (liquid film); 3095 (w), 2990 (s), 2860 (sh), 2800 (s), 1795 (w), 1655 (m), 1455 (s), 1380 (m), 1340 (w), 1290 (w), 1285 (sh), 1240 (w), 1170 (w), 1135 (m), 1090 (sh), 1080 (m), 1042 (m), 1020 (m), 980 (w), 970 (w), 900 (s), 860 (w), 830 (w), and 750 (w) cm^{-1}. NMR ($CDCl_3$): 4.93 s, 4H (olefin protons); 2.86 s, 4H, (methylene protons of methallyl group); 2.30 t, 2H ($N-CH_2$ protons of propyl group); 1.76 s, 6H (methyl protons of methallyl group); and 1.70-0.66 m, 5H (CH_3CH_2- protons of propyl group). Mass spectrum: m/e 167 (7%, M^+), 152 (1), 138 (72), 126 (22), 84 (50), 82 (13), 72 (11), 67 (12), 56 (18), 55 (100), 43 (24), 42 (27), 41 (35), 39 (24), 30 (25), and 29 (38).

N,N-Di(but-3-enyl)-n-propylamine

N,N-Di(but-3-enyl)-n-propylamine was prepared by a similar procedure to that used for N,N-dicrotylpropylamine using 4-chloro-1-butene (27.0 g, 0.2 mole), sodium hydroxide (40 g in 100 ml water), and n-propylamine (5.91 g, 0.1 mole) to yield N,N-di(but-3-enyl)-n-propylamine, 9.75 g (56%), bp 30-32°C at 0.22 mm. The purity of product was checked by GLC. (Found: C, 79.19; H, 12.57. $C_{11}H_{21}N$ requires C, 78.96; H, 12.66%.) ν_{max} (liquid film): 3100 (w), 2950 (s), 2795 (s), 1830 (w), 1640 (m), 1465 (m), 1442 (sh.), 1400 (w), 1380 (w), 1360 (sh.), 1340 (w), 1330 (w), 1280 (m), 1220 (w), 1180 (m), 1080 (m), 998 (m), and 9.5 (s) cm^{-1}. NMR spectrum ($CDCl_3$): 6.23-5.50 m, 2H (methine olefinic protons); 5.30-4.83 m, 4H (methylene olefinic protons); 2.76-1.93 m, 10H ($N-CH_2CH_3$ protons of but-3-enyl group and $N-CH_2$ protons of propyl group); 1.46 sextet, 2H (methylene protons of propyl group); and 0.86 t, 3H (methyl protons of propyl group). Mass spectrum: M/e 167 (2%, M^+), 138 (11), 128 (11), 127 (30), 126 (100), 98 (12), 84 (30), 72 (24), 56 (18), 55 (83), 44 (11), 43 (22), 42 (36), 41 (28), 39 (16), 30 (22), and 29 (22).

N,N-Diallylaniline

N-N-Diallylaniline was prepared by a similar procedure to that used for N,N-dicrotylpropylamine using allyl bromide (48.4 g, 0.4

mole), sodium hydroxide (80 g in 200 ml water), and aniline (18.6 g, 0.2 mole). The reaction mixture was refluxed for 30 hr to yield N,N-diallylaniline, 30.0 g (88%), bp 120-122°C at 16 mm (lit. [45] bp 123°C at 18 mm). The IR and NMR spectra were in accord with the assigned structure.

ν_{max} (liquid film): 3080 (w), 2998 (sh), 2900 (w), 2850 (sh), 1642 (w), 1603 (s), 1580 (w), 1516 (s), 1460 (w), 1442 (w), 1422 (w), 1396 (m), 1364 (m), 1350 (sh), 1290 (w), 1238 (s), 1182 (m), 1162 (sh), 1130 (w), 1070 (w), 1042 (w), 1000 (m), 970 (sh), 930 (s), 870 (w), 758 (s), and 700 (s) cm^{-1}. NMR ($CDCl_3$): 7.40-6.40 m, 5H (aromatic protons); 6.23-5.53 t of t, 2H (methine olefinic protons); 5.36-4.90 m, 4H (methylene olefinic protons); and 3.86 d, 4H (methylene protons of allyl groups with allylic splitting).

β-Methoxyethyldiallylamine

β-Methoxyethyldiallylamine was prepared by a similar procedure to that used for N,N-dicrotylpropylamine using allylchloride (76.5 g, 1.0 mole), sodium hydroxide (40 g in 100 ml water), and 2-methoxyethylamine (37.5 g, 0.5 mole). The reaction mixture was heated at 70°C for 4 hr. After cooling, the organic layer was separated and dried over solid sodium hydroxide. The amine was distilled under reduced pressure; bp 61-62°C at 15 mm, yield 55 g (71%). The product was checked by GLC. (Found: C, 69.30; H, 10.98; N, 9.03. $C_9H_{17}NO$ requires C, 69.63; H, 11.03; N, 9.02%.) ν_{max} 3100 (w), 3000 (sh), 2900 (sh), 2880 (s), 2840 (s), 1840 (w), 1641 (m), 1450 (m), 1422 (m), 1358 (m), 1338 (sh), 1260 (w), 1200 (m), 1150 (sh), 1120 (s), 1060 (sh), 1000 (s), 970 (sh), 921 (s), 870 (w), 820 (w), 820 (w), and 670 (w) cm^{-1}. NMR ($CDCl_3$): 6.20-5.53 m, 2H (methine olefinic protons); 5.42-4.94 m, 4H (methylene olefinic protons); 3.66-3.04 m, 9H, (methoxyl protons at 3.34, methylene protons of allyl groups and $N-CH_2$ protons); and 2.65 t, 2H (methylene protons, CH_2-OCH_3). Mass spectrum: M/e 155 (5%, M^+), 140 (1), 124 (1), 111 (6), 110 (100, 41 (43), and 42 (8).

ACKNOWLEDGMENT

We wish to thank Dr. D. G. Hawthorne (CSIRO) for helpful discussions.

REFERENCES

[1] W. T. Dixon and R. O. C. Norman, Nature, 196, 891 (1962).
[2] W. T. Dixon and R. O. C. Norman, J. Chem. Soc., 1963, 3119.

[3] H. Fischer, Z. Naturforsch., 18a, 1142 (1963).
[4] H. Fischer, Ibid., 19a, 267 (1964).
[5] H. Fischer, Ibid., 19a, 866 (1964).
[6] H. Fischer, J. Polym. Sci., B2, 529 (1964).
[7] H. Fischer, Macromol. Chem., 98, 179 (1966).
[8] H. Fischer and G. Giacometti, J. Polym. Sci., C, 16, 2763 (1967).
[9] K. Takakura and B. Ranby, Ibid., B, 5, 83 (1967).
[10] H. Yoshida and B. Ranby, Ibid., C, 16, 1333 (1967).
[11] K. Takakura and B. Ranby, Ibid., C, 22, 939 (1969).
[12] Y. Doi and B. Ranby, Ibid., C, 31, 231 (1970).
[13] K. Takakura and B. Ranby, Ibid., A, 8, 77 (1970).
[14] K. Izumi and B. Ranby, Ibid., Polym. Chem. Ed., 11, 1903 (1973).
[15] C. D. McLean, A. K. Ong, and D. H. Solomon, J. Macromol. Sci.—Chem., In Press, and references cited therein.
[16] D. H. Solomon, J. Macromol. Sci.—Chem., A9, 97 (1975).
[17] A. L. J. Beckwith, A. K. Ong, and D. H. Solomon, J. Macromol. Sci.—Chem., A9, 115 (1975).
[18] W. T. Dixon and R. O. C. Norman, J. Chem. Soc., 1964, 4857.
[19] A. L. J. Beckwith and C. Moad, Unpublished Observations.
[20] A. L. J. Beckwith and I. A. Blair, Chem. Comm., In Press.
[21] B. Ranby, J. Macromol. Sci.—Chem., A6, 904 (1972).
[22] P. Smith and P. B. Wood, Can. J. Chem., 45, 649 (1967).
[23] C. Corvaja, H. Fischer, and G. Giacometti, Z. Phys. Chem., [N.F.] 45, 1 (1965).
[24] T. Kodaira, K. Marishita, H. Yamaoka, and H. Aida, J. Polym. Sci., Polym. Lett. Ed., 11, 347 (1973).
[25] G. B. Butler and Angelo, J. Amer. Chem. Soc., 79, 3128 (1957).
[26] G. B. Butler, J. Polym. Sci., 48, 279 (1960).
[27] G. B. Butler and B. Iachia, J. Macromol. Sci.—Chem., A3, 803 (1969).
[28] C. Walling, J. H. Cooley, A. A. Ponaras, and E. J. Racah, J. Amer. Chem. Soc., 88, 5361 (1966).
[29] J. K. Kochi and T. W. Beethea, J. Org. Chem., 33, 75 (1968).
[30] R. C. Lamb, P. W. Ayers, M. K. Toney, and J. F. Garst, J. Amer. Chem. Soc., 88, 4261 (1966).
[31] J. F. Garst, P. W. Ayers, and R. C. Lamb, Ibid., 88, 4260 (1966).
[32] R. F. Gapwood, C. J. Scott, and B. C. L. Needon, Chem. Comm., 1965, 14.
[33] R. C. Lambe, P. W. Ayers, and M. K. Toney, J. Amer. Chem. Soc., 85, 3483 (1963).
[34] C. Walling and M. S. Pearson, Ibid., 86, 2262 (1964).
[35] B. Capon and C. W. Ree, Ann. Rep., 61, 221 (1964).
[36] D. L. Struble, A. L. J. Beckwith, and G. E. Gream, Tetrahedron Lett., 1968, 3701.
[37] C. S. Marvel and W. E. Garrison Jr., J. Amer. Chem. Soc., 81, 4737 (1959).

[38] C. S. Marvel and J. K. Stille, Ibid., 80, 1740 (1958).
[39] S. Harada and K. Arai, Makromol. Chem., 107, 78 (1967).
[40] G. B. Butler and S. D. Squibb, J. Chem. Eng. Data, 10, 404 (1965).
[41] G. F. Hennion and R. H. Ode, J. Org. Chem., 31, 1975 (1966).
[42] G. B. Butler, and R. L. Bunch, J. Amer. Chem. Soc., 74, 3453 (1952).
[43] G. B. Butler and R. J. Angelo, Ibid., 78, 4797 (1956).
[44] G. B. Butler and R. J. Angelo, Ibid., 77, 1767 (1955).
[45] F. L. Carrahan and C. D. Hurd, Ibid., 52, 4586 (1930).