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Cyclopolymerization. VII. The ^{13}C NMR Spectra of Cyclopolymers Obtained from N,N-Diallyamines*

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ABSTRACT

Pulsed Fourier transform ^{13}C natural abundance nuclear magnetic resonance spectroscopy has been used to determine the structures of the polymers formed by the radical-induced cyclopolymerization of N-substituted-N,N-diallylamines and

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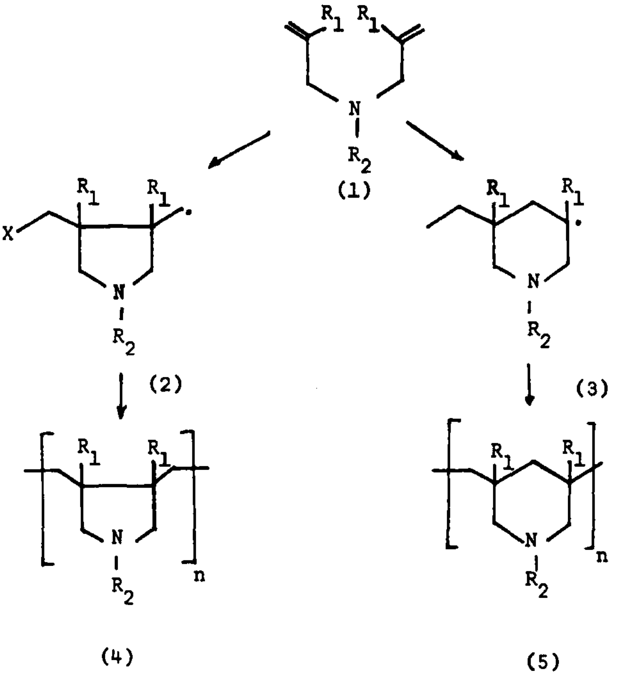
*This paper also constitutes Part III in the series, "Stereochemical Studies," by S. Middleton et al. For Part II, see Austral. J. Chem., 24, 865 (1971).

N-methyl-N,N-bis(2-alkylallyl)-amines. The polymers of N,N-diallylamines all contain cis- and trans-substituted pyrrolidine rings in the ratio 5:1. The polymers of N-methyl-N,N-bis(2-alkylallyl)amines give complex spectra due to the presence of both cis- and trans-pyrrolidine and -piperidine rings, but the difference in chemical shifts of the N-methyl signals from the different structural types allows the spectra to be analyzed.

INTRODUCTION

Electron spin resonance (ESR) studies have shown that the radicals formed from N-substituted-N,N-diallylamines (1, $R_1 = H$) in the presence of $TiCl_3/H_2O_2$ or $TiCl_3/H_2NOH$ initiators are five-membered cyclic species (2, $R_1 = H$); the alternative six-membered cyclic radicals (3, $R_1 = H$) are not observed [1, 2]. It seems likely, therefore, that the polymers formed from such monomers under similar conditions would be composed of pyrrolidine (4) rather than piperidine



(5) units. The polymers formed from N-substituted-N,N-bis(2-alkylallyl)amines (1, R_1 = alkyl), on the other hand, might well contain both five- and six-membered cyclic units, since radicals of types (2) and (3) are both detected in similar ESR studies of N-substituted-N,N-bis(2-methylallyl)amines (1, R_1 = Me) using the same radical-initiating systems [2].

A potential weakness in the above argument lies in the assumption that the radicals detected in the ESR cell are the same as those involved in polymer formation. It is possible that these latter radicals have very short life-times (thereby precluding their detection) and that the radicals detected are stable, nonpropagating species. It was therefore decided to investigate the structures of the polymers themselves by using nuclear magnetic resonance (NMR) spectroscopy.

Although proton NMR spectroscopy has been used extensively in the study of polymers [3, 4], the line broadening inherent in proton polymer spectra has severely limited the potential of the technique in this field. In contrast, the extended chemical shift range, the absence of significant dipolar line broadening and the simplicity of proton decoupled ^{13}C NMR spectra, in which each carbon resonates as a singlet, make these spectra extremely useful for the study of polymers [4, 5]. Moreover, the use of the pulsed Fourier transform technique [6], which greatly reduces accumulation time, permits the measurement of natural abundance ^{13}C spectra, while the off-resonance decoupling technique [7], in which the substitution at a particular carbon is reflected in the multiplicity of the respective signal, can be used to determine such substitution.

^{13}C natural abundance pulsed Fourier transform NMR spectroscopy has now been used to distinguish the different structural features of the polymers formed by radical-induced cyclopolymerization of a series of N,N-diallylamines (1, R_1 = H or alkyl), polymerization being initiated by hydroxyl and/or cyanoisopropyl radicals. It has been found that both the ring size and stereochemistry can be determined, and measurement of the relative intensities of the signals from similar carbons in the different structural moieties permits an estimate of the proportions of these units in the polymer structure.

RESULTS AND DISCUSSION

Cyclopolymerization of N-Methyl-N,N-diallylamine

The proton-decoupled ^{13}C NMR spectrum of the polymer formed by the cyanoisopropyl radical-induced cyclopolymerization of N-methyl-N,N-diallylamine at 30° C [8] is shown in Fig. 1. The polymer obtained

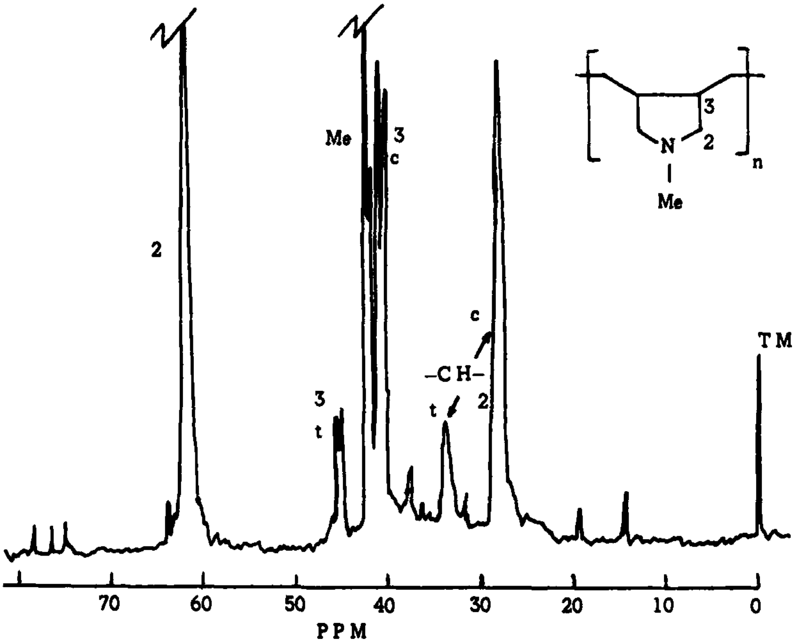
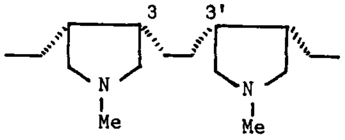


FIG. 1. Proton-decoupled ^{13}C NMR spectrum of a 20% solution in $CDCl_3$ of the polymer from N-methyl-N,N-diallylamine.

by using hydroxyl radicals as initiator gives an essentially identical spectrum. A comparison of this spectrum (Fig. 1) with those of a series of β,β-substituted pyrrolidines [9, 10] and piperidines [10] shows that the cyclic moieties in the polymer structure are of the pyrrolidine type (4, $R_1 = H$); no piperidine-type units (5, $R_1 = H$) are present. Further, the existence of both cis- and trans-substituted pyrrolidine residues in the polymer is revealed by the chemical shifts of the signals from the C3,4 methine carbons of the pyrrolidine rings and from the methylene carbons of the ethylene bridges between successive rings.

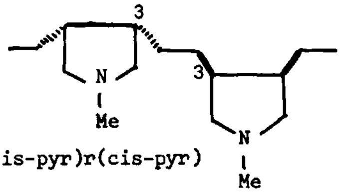
The following assignments can be made to the signals in the spectrum (Fig. 1). The downfield peak at 62.7 ppm, a triplet in an off-resonance decoupled spectrum, can be assigned to the C2,5 methylene carbons in both cis- and trans-pyrrolidine rings since the chemical shift is in close agreement with those of the C2,5 methylene carbons of cis- and trans-3,4-diethyl-1-methylpyrrolidine (62.4 and 62.6 ppm, respectively) [9], the broadened signal in the polymer spectrum preventing resolution into two peaks.

The two peaks at 41.9 and 41.5 ppm can be assigned to the C3,4 methine carbons of cis-substituted rings and the two peaks at 45.9 and 45.5 ppm to the corresponding carbons of trans-substituted rings, since the shifts are in good agreement with the appropriate signals in the spectra of cis- and trans-3,4-diethyl-1-methylpyrrolidine (42.9 and 47.0 ppm, respectively) when an upfield shift of approximately 1.5 ppm is allowed for the γ-substituent in the polymer structure. Comparison of the relative intensities of these pairs of signals indicates a cis:trans ratio of approximately 5:1, their appearance as doublets reflecting differences in the manner in which the cis and trans units are assembled in the polymer chain. Specifically, due to the asymmetric nature of the C3,4 carbons of each pyrrolidine unit, six different types of diad structures (6-11) are possible.



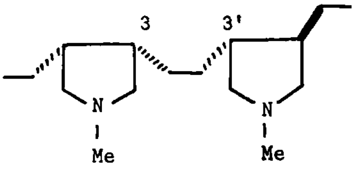
(cis-pyr)m(cis-pyr)

(6)



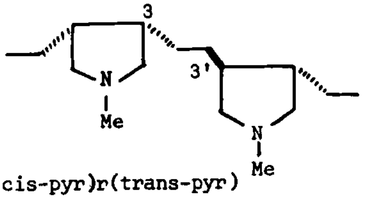
(cis-pyr)r(cis-pyr)

(7)



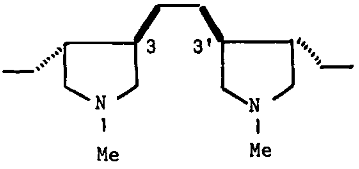
(cis-pyr)m(trans-pyr)

(8)



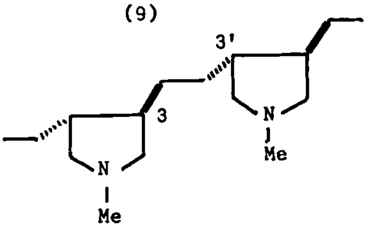
(cis-pyr)r(trans-pyr)

(9)



(trans-pyr)m(trans-pyr)

(10)



(trans-pyr)r(trans-pyr)

(11)

In considering the chemical shifts of the methine carbons in these different structures, it is convenient to focus attention on the "inner" methine carbons of each diad (labeled 3 and 3' in each case). We then propose that the chemical shift of any particular one of these carbons is determined primarily by the stereochemistry of the pyrrolidine unit in which it resides, and secondarily by the relative chiralities at C3 and C3' of the appropriate diad. On this basis, the methine carbons fall into two main groups, each of which has two subgroups:

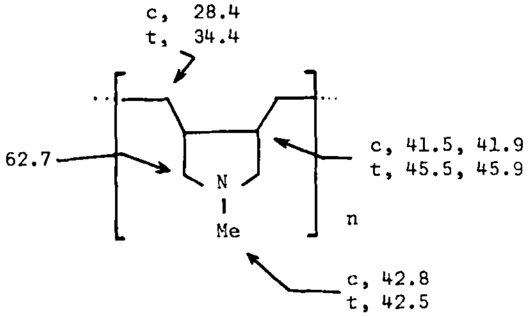
Group I: Methines of cis-pyrrolidine units
- (i) Those in which there is a meso (m) relationship between C3 and C3' of the appropriate diad
  See C3 of (6), C3' of (6), C3 of (8)
- (ii) Those in which there is a racemic (r) relationship between C3 and C3' of the appropriate diad
  See C3 of (7), C3' of (7), C3 of (9)

Group II: Methines of trans-pyrrolidine units
- (i) m relationship between C3 and C3'
  See C3' of (8), C3 of (10), C3' of (10)
- (ii) r relationship between C3 and C3'
  See C3' of (9), C3 of (11), C3' of (11)

Two doublets would thus be expected, in agreement with the observed result.

The pair of signals at 42.8 and 42.5 ppm can be assigned to the N-methyls of cis- and trans-pyrrolidine units, respectively, since the shifts are in excellent agreement with those of the N-methyl signals of cis- and trans-3,4-diethyl-1-methylpyrrolidine (42.9 and 42.7 ppm, respectively). The remaining broadened signals at 28.4 and 34.4 ppm can be assigned to the methylene carbons of bridging ethylene groups, the two peaks being attributable to methylene groups attached to cis- and trans-pyrrolidine units, respectively, since they are 6 ppm downfield from the methylene signals of the ethyl groups of cis- and trans-3,4-diethyl-1-methylpyrrolidine (22.4 and 28.3 ppm, respectively). The substitution of an ethyl group by a propyl group produces a 10 ppm downfield shift in the methylene carbon attached to the pyrrolidine ring as is shown by comparison of the shifts in cis- and trans-1,3,4-trimethyl-3,4-diethylpyrrolidine (27.7 and 28.2 ppm) and in cis- and trans-1,3,4-trimethyl-3,4-dipropylpyrrolidine (38.2 and 38.3 ppm) [10]. This downfield shift is caused by the addition of the β-methyl substituent and the reason for the subsequent 4 ppm upfield shift observed in the polymer spectrum is the presence of the additional two γ-substituents (carbons 2 and 4 of second the pyrrolidine ring).

All the above assignments are summarized in (12). The other low-intensity signals in the spectrum (Fig. 1) are thought to arise from initiating and terminating moieties and will be the subject of a subsequent communication.

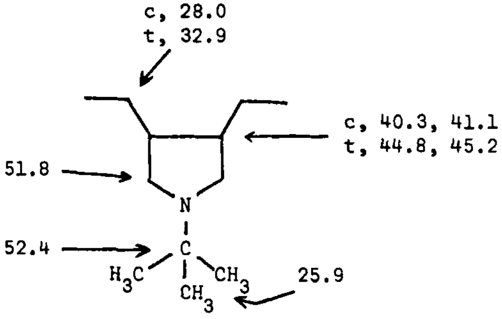


(12)

Cyclopolymerization of N-(tert-Butyl)-N,N-diallylamine

The proton-decoupled ^{13}C NMR spectrum of the $TiCl_3/H_2O_2$ radical-initiated cyclopolymer from N-(tert-butyl)-N,N-diallylamine may be interpreted in the same manner. Again the observed chemical shifts (13) are in good agreement with those to be expected on the basis of the data for the isomeric 1-(tert-butyl)-3,4-diethylpyrrolidines [9]. Thus the doublets at 40.3/41.1 and 44.8/45.2 ppm may be correlated with the C3 methine carbon signals from the cis and trans model compounds (42.4 and 46.1 ppm, respectively), the doublet character again reflecting the presence of different diad structures. The relative intensities of the two doublets indicate a cis:trans ratio of approximately 5:1, as with the polymer from the N-methyl amine above.

The same conclusion follows from consideration of the relative intensities of the signals from the bridging methylene carbons at 28.0 and 32.9 ppm which may be correlated with the signals for the methylene carbons of the ethyl groups of the cis and trans model compounds (21.9 and 27.0 ppm, respectively). The only other polymer signal which can be confidently assigned is that due to the tert-butyl methyl carbons at 25.9 ppm, in excellent agreement with the values found for the two model compounds (cis 25.9, trans 25.8 ppm). The remaining signals at 51.8 and 52.4 ppm may be tentatively assigned to the C2 methylene carbons and the quaternary carbons of the tert-butyl groups respectively of cis-pyrrolidine units, since the shifts correspond closely with those for the respective carbons in the cis model compound (51.6 and 52.5 ppm). Some overlapping is possible in the polymer spectrum, however, since the corresponding signals for the trans model compound have shifts of 52.5 and 52.1 ppm, respectively.



(13)

Cyclopolymerization of N-Benzyl (and substituted benzyl)-N,N-diallylamines

The benzylic methylene carbons of N-benzylpyrrolidines give signals at 60-61 ppm, whereas the corresponding carbons of N-benzylpiperidines have shifts of 63-64 ppm [9, 10]. It is therefore significant that there are no peaks in this latter region of the proton decoupled spectrum of the $TiCl_3/H_2O_2$ radical-induced cyclopolymer from N-benzyl-N,N-diallylamine. There is, however, a peak at 61.0 ppm, thereby establishing that the polymer contains only pyrrolidine-type units.

Assignment (14) of the other peaks in the polymer spectrum is again facilitated by reference to the spectra of model compounds, in this case the isomeric 1-benzyl-3,4-diethylpyrrolidines [9]. The relevant chemical shift data for these latter compounds are as follows: methylenes of ethyl groups (cis 22.4, trans 28.2); C3, 4 methines (cis 42.1, trans 46.2); C2,5 methylenes (60.2); benzylic methylenes (cis

61.2, trans 60.8); Cl' of phenyl group (139.4); C2' (128.2); C3' (128.9); C4' (126.9). As before, the polymer spectrum contains clear evidence of the presence of both cis- and trans-substituted pyrrolidine rings, the cis:trans ratio again being approximately 5:1 and the C3 methine carbon signals again appearing as doublets.

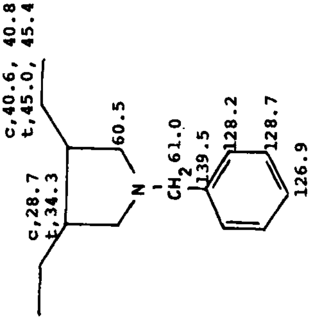
Assignments for the various peaks in the proton decoupled ^{13}C spectra of the $TiCl_3/H_2O_2$ radical-initiated cyclopolymers from a series of N-(substituted benzyl)-N,N-diallylamines [11] are shown (15-18). They are generally consistent with those for the unsubstituted N-benzyl polymer (14). In each case, the signals associated with the aromatic ring are sharp, indicative of the relatively high freedom of motion of these groups. Individual carbons in these rings may be assigned, as shown, from a knowledge of the different substituent parameters [5].

None of these N-(substituted-benzyl) polymers contains piperidine units, as evidenced again by the absence of benzylic methylene peaks in the region 63-64 ppm. Only for (15) and (16), however, do these methylenes have shifts in the range 60-61 ppm given above for simple N-benzylpyrrolidines. Steric crowding by the ortho phenolic hydroxyl group in (17) induces an upfield shift of 1.5 ppm in the benzylic methylene carbon signals and an even larger shift of 2.1 ppm as seen in Fig. 2 for (18), in which there is an additional methyl group ortho to the hydroxyl group.

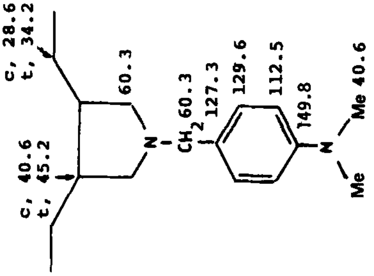
The number and relative intensities of the C3,4 methine and bridging methylene carbon resonances of the polymers (15-18) indicate that all the polymers are stereochemically very similar to that obtained from the unsubstituted N-benzyl amine. The same may also be said for the related pyrrolic polymer (19), whose "benzylic" methylene carbon resonates at relatively high field (51.9 ppm). The shifts of the backbone-carbon signals are, however, unexceptional.

Cyclopolymerization of N-Aryl-N,N-diallylamines

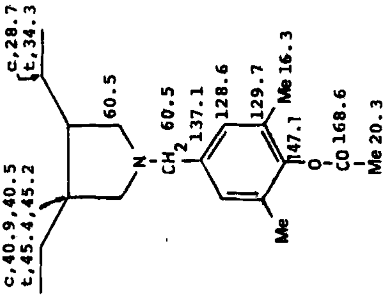
The proton-decoupled ^{13}C NMR spectrum of the $TiCl_3/H_2O_2$ radical-induced cyclopolymer from N,N-diallylaniline is shown in Fig. 3. A polypyrrolidine structure is again indicated by the correspondence between the observed chemical shifts (20) and those of the corresponding carbons of cis- and trans-3,4-diethyl-1-phenylpyrrolidine [9]. The relevant chemical shift data for these latter compounds are as follows: methylenes of ethyl groups (cis 20.6, trans 25.8); C3,4 methines (cis 43.2, trans 45.8); C2,5 methylenes (cis 51.6, trans 53.5); Cl' of phenyl group (cis 148.1, trans 148.0); C2' (cis 111.2, trans 111.5); C3' (cis 129.1, trans 129.2); C4' (cis 115.0, trans 115.3).



(14)



(15)



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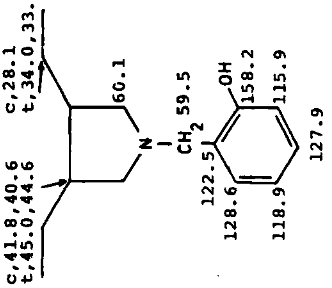

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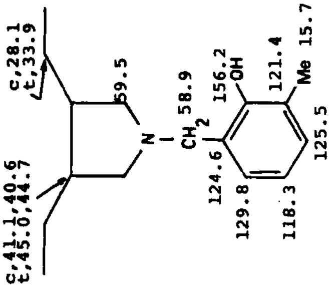
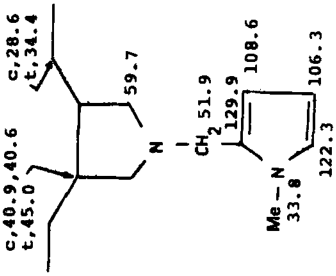


(18)



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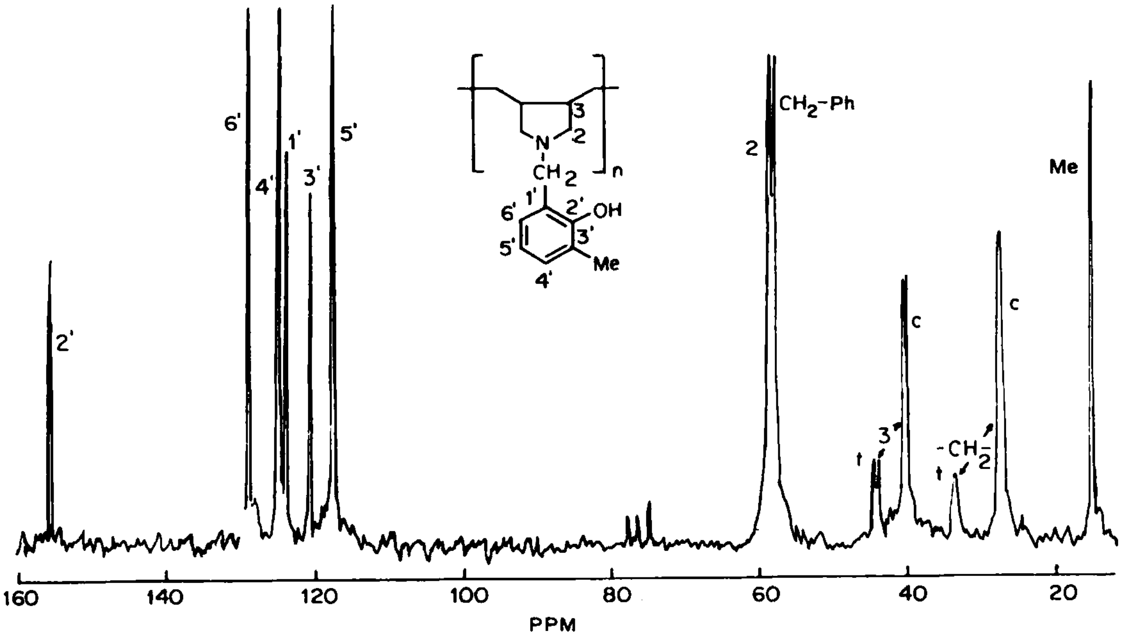


FIG. 2. Proton-decoupled ^{13}C NMR spectrum of a 20% solution in $CDCl_3$ of the polymer from N(2'-hydroxy-3'-methyl-benzyl)N,N-diallylamine.

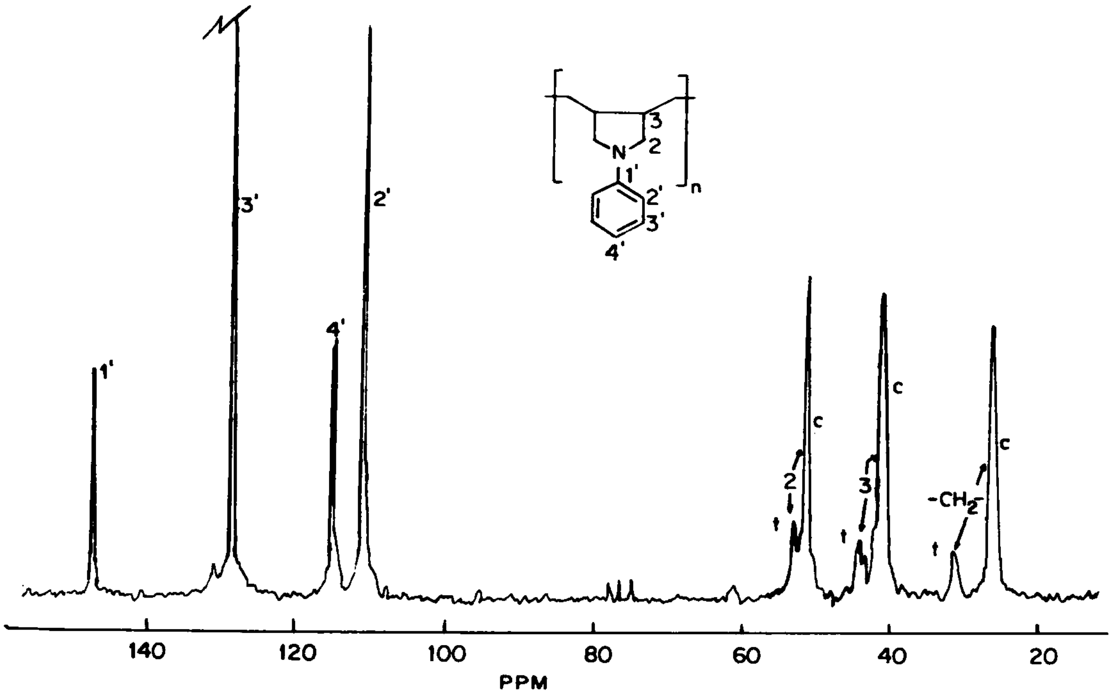
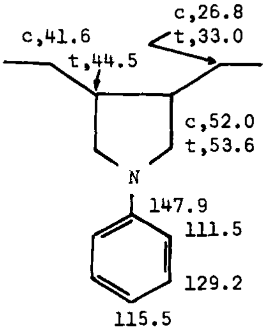


FIG. 3. Proton-decoupled ^{13}C NMR spectrum of a 20% solution in $CDCl_3$ of the polymer from N-phenyl-N,N-diallylamine.



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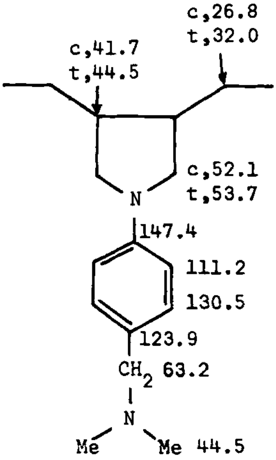

(21)

A 5: 1 preponderance of cis- over trans-pyrrolidine residues in the polymer is indicated by the relative intensities of the two C3,4 methine and the two bridging methylene carbon signals, as with the other diallylamine cyclopolymers discussed thus far, but also by the relative intensities of the two C2,5 methylene carbon signals. The fact that the shifts of these latter carbons are quite different in this case for cis- and trans-substituted pyrrolidine rings results from the close proximity of the anisotropic phenyl group. A similar effect is seen in the data for the para-substituted polymer (21).

Cyclopolymerization of N-Methyl-N,N-bis(2-alkylallyl)amines

The proton-decoupled ^{13}C NMR spectrum of the cyanoisopropyl radical-induced cyclopolymer from N-methyl-N,N-bis(2-methylallyl)amine is shown in Fig. 4. When compared with that of N-methyl-N,N-diallylamine (Fig. 1), the complexity of the new spectrum is immediately apparent. N-Methyl signals (quartets in the off-resonance decoupled spectrum), having chemical shifts (44.2 and 47.1 ppm) similar to those [10] of the model compounds 1,3,4-trimethyl-3,4-dipropylpyrrolidine (44.3 ppm) and 1,3,3,5,5-pentamethylpiperidine (47.1 ppm), indicate the presence of both pyrrolidine-type (4) and piperidine-type (5) structures in the polymer. The relative intensities of these signals in the spectrum (Fig. 4) from the polymer

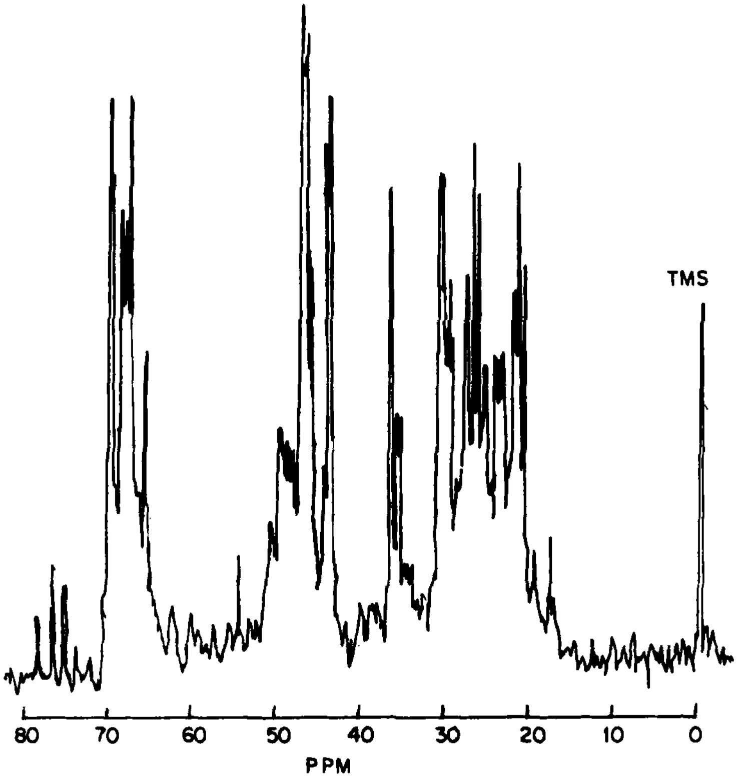

FIG. 4. Proton-decoupled ^{13}C NMR spectrum of a 20% solution in $CDCl_3$ of the polymer from N-methyl-N,N-bis(2-methylallyl)amine.

obtained at 60° C [8] show that the two different structural types are present in approximately equal proportions. The spectra of polymers prepared under different reaction conditions, however, show different pyrrolidine/piperidine ratios [8]. The complexity of these spectra can be explained and the different signals assigned when the possible combinations of the two structural types are considered. Since both cis- and trans-forms of both pyrrolidine and piperidine units are theoretically possible, there are 28 different types of diad structures which fall into four groups (Table 1). Although all 28 diad types need not necessarily afford distinctly different resonance signals, the variety of possibilities can account for the multiplicity of signals within the chemical shift ranges for the respective carbons.

TABLE 1. Types of Diad Structures

Group	Structural type	Inter-ring bridge	Possible different types
I	-pyr-pyr-	$-CH_2-CH_2-$	6
II	-pyr-pip-	$-CH_2-CH_2-$	8
III	-pip-pyr-	$-CH_2-$	8
IV	-pip-pip-	$-CH_2-$	6

The low field signals between 66.0 and 69.0 ppm can be assigned to C2 methylene carbons of pyrrolidine and/or piperidine residues in all diad types, since the equivalent signals in the model compounds cis- (66.7 ppm) and trans- (68.0 ppm)-1,3,4-trimethyl-3,4-dipropylpyrrolidine and 1,3,3,5,5-pentamethylpiperidine (69.1 ppm) all fall in this chemical shift range. The group of signals between 48.0 and 50.0 ppm can be assigned to C4 methylene carbons of piperidine rings (diad groups II, III, IV) and to bridging methylene groups (diad groups III, IV), both of which have similar environments to that of the C4 methylene carbon of 1,3,3,5,5-pentamethylpiperidine (50.4 ppm). The signal at 46.3 ppm can be assigned to pyrrolidine C3 carbons since the shift is in close agreement with that (46.7 ppm) of the C3 signal in both cis- and trans-1,3,4-trimethyl-3,4-diethyl- (and -3,4-dipropyl)-pyrrolidine.

The peaks between 36.0 and 37.0 ppm can be assigned to the methylene bridges (diad groups I, II) as these show the expected γ-substituent (1-2 ppm) upfield shift from the 38.2 and 38.3 ppm shifts of the propyl methylenes attached to the pyrrolidine ring in cis- and trans-1,3,4-trimethyl-3,4-dipropylpyrrolidine. The peaks between 30.0 and 31.0 ppm can be assigned to the quaternary C3 carbons of piperidine units (diad groups II, III, IV) since the shifts are approximately the same as that of C3 in 1,3,3,5,5-pentamethylpiperidine (31.5 ppm). Finally, the peaks at 20.0-22.0 and 26.0-28.0 ppm may be assigned to the C-methyl signals of pyrrolidine and piperidine units respectively. The first of these assignments is based on the shifts observed for the C-methyl signals of cis- and trans-1,3,4-trimethyl-3,4-dipropylpyrrolidine (20.7 and 21.8 ppm, respectively). The second assignment above is based on the shift observed for the C-methyl signal of 1,3,3,5,5-pentamethylpiperidine (29.8 ppm), an upfield shift of approximately 3-4 ppm being expected in the polymer spectrum since a similar upfield shift is observed for the C-methyl signals of cis- and trans-1,3,4-trimethyl 3,4-dipropylpyrrolidine (20.7 and 21.8 ppm) compared with the corresponding signal for 1,3,3,4,4-pentamethylpyrrolidine (24.0 ppm).

The spectrum of the polymer formed from N-methyl-N,N-bis(2-ethylallyl)amine shows the same complexity as that of the 2-methylallyl polymer. A similar comparison of the relative intensities of the N-methyl signals at 44.1 and 47.3 ppm permits estimation of the pyrrolidine/piperidine ratio within the polymer [8]. No equivalent spectra could be obtained from the involatile fractions of the products obtained on attempted polymerization of N-methyl-N,N-bis(2-isopropylallyl)amine and N-methyl-N,N-bis(2-tert-butylallyl)amine [8].

EXPERIMENTAL

The polymers used in this work were prepared and purified by methods which are described in accompanying papers [8, 11]. The natural abundance pulsed Fourier transform ^{13}C NMR spectra were obtained from approximately 20% solutions of polymers in $CDCl_3$ on either a Varian CFT20 or a Bruker WH90 spectrometer. All chemical shifts are reported relative to internal TMS (0.0 ppm).

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