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Cyclopolymerization of Diallylamides and Diallylsulphonamides

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SUMMARY

High resolution carbon-13 nuclear magnetic resonance spectroscopy is used to study the structure of N-amide and N-sulphonamide derivatives of polydiallylamines and shows that these have the poly(3,4-pyrrolidinediylethylene) structure common to most polydiallylamines, not the previously reported poly(3,5-piperidinediylmethylene) structure.

INTRODUCTION

In recent years the structures of a number of cyclopolymers from 1,6 diene monomers have had to be revised (SOLOMON 1975) in line with new evidence provided by techniques such as ^{13}C nuclear magnetic resonance (NMR) spectroscopy. In particular, the diallylamino monomers first polymerized by BUTLER and INGLEY (1951) and assigned polypiperidine structures, have recently been shown to have poly-(3,4-pyrrolidinediylethylene) structures (JOHNS et al. 1976, HAWTHORNE et al. 1979, LANCASTER et al. 1976) except where certain highly polar or bulky groups are present (HAWTHORNE and SOLOMON 1976, HAWTHORNE et al. 1976). These monomers have generally been polymerized as quaternary ions in an aqueous acidic medium, but it does not necessarily follow that polymerization of the neutral compounds in bulk, especially where strong electron withdrawing groups are present on the nitrogen atom, will give similar polymer structures.

Three different groups of diallylamide monomers have been polymerized previously. These are: diallyl cyanamide (I) (UNO et al. 1968) diallylamides (II) (MATSOYAN et al. 1963) and diallylsulphonamides (III) (CRAWSHAW and JONES 1972) with R'=H or CH_3, R=CH_3 or C_6H_5. In each case the polymers were assigned the polypiperidine structure on very limited evidence. BRACE (1971) carried out cyclizations of a number of these monomers in the presence of an efficient chain transfer agent to give monomeric pyrrolidines, and hence suggested that pyrrolidine structures were present in the polymers. Subsequent polymerization and copolymerization studies with these monomers have still favoured the six membered ring (CRAWSHAW and JONES 1972, DANIELYAN et al. 1979, SAYADYAN et al. 1977).

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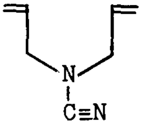
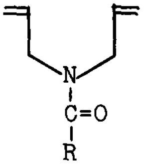


I



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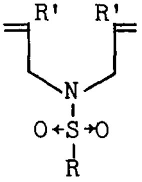


III

We have repeated polymerizations with these monomers and used the ^{13}C NMR technique to restudy the structures of the polymers formed. Only monomers with R'=H are reported in this paper as the monomers containing R'=CH_3 gave distinctly different and more complicated polymer structures which will be the subject of a subsequent publication.

RESULTS

The monomers II and III, (R=CH_3 and C_6H_5, R'=H) were prepared and purified by methods described previously (see experimental): they were polymerized in bulk in sealed tubes using either azobisisobutyronitrile (AIBN) or benzoyl peroxide as initiators under the conditions shown in TABLE I.

TABLE I.
Polymerization of diallylamine monomer, $RN(CH_2{-}CH{=}CH_2)_2$

R=	Concentration of Initiator,[a] moles/l		Time (hr)	Temp.	% Conversion to polymer( )		Polymer Solubility
	A	B					
CH_3CO	0.30		12	70°	35%	(IV)	$CHCl_3$ sol.
		0.20	16	70°	14%	(IV)	
CH_3SO_2		0.30	5	70°	68%	(V)	$CHCl_3$ insol.
		0.20	100	20°	70%	(V)	DMSO sol.
CN	0.30		10	70°	22%	(VI)	60% sol. in $CHCl_3$
		0.20	10	70°	15%	(VI)	40% sol only in hot DMSO
C_6H_5CO	0.28		16	70°	25%	(VII)	$CHCl_3$ sol.
$C_6H_5SO_2$	0.20		30	70°	30%	(VIII)	$CHCl_3$ sol.

[a] A = Azobisisobutyronitrile: B = Benzoyl peroxide.

The ease of polymerization varied considerably with individual monomers and initiators, with the diallysulphonamides giving the best yields under quite mild conditions. The polymers were generally soluble in chloroform and could be purified readily by precipitation from this solvent using diethyl ether. The diallylcyanamide polymerizations yielded two fractions, the major one soluble in chloroform and the other only soluble in dimethylsulphoxide above 100°. The infrared spectra of these two fractions were similar, but ^{13}C NMR indicated that the cyano groups in the insoluble product had undergone a number of side reactions. Highly purified polymer V was only slightly soluble in chloroform but was very soluble in DMSO; the ^{13}C spectra were obtained in both solvents.

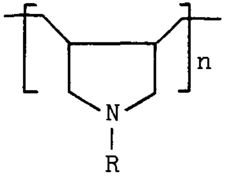
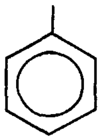
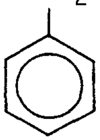
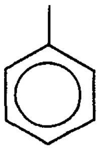
The results of the ^{13}C NMR analyses are shown in TABLE II and the spectrum of polymer IV is shown in Fig. I. The infrared spectrum of polymer VI was essentially identical to that previously reported (UNO et al. 1968).

DISCUSSION

The ^{13}C NMR spectra of the polymers in TABLE II are similar to those obtained from previous diallylamine polymers (JOHNS et al. 1976, HAWTHORNE et al. 1979, cf N-phenyl derivative in TABLE II) which were shown to be a mixture of cis- and trans-polypyrrolidines. The differences observed in the chemical shifts of the respective carbons in the different polymers are consistent with the substituent shift parameters of the different N-substituents. In the case of the amide derivatives (IV and VII) the spectra are complicated by a doubling of the peaks arising from the pyrrolidine ring-methylene and methine carbons. These double peaks reflect the partial double bond character of the amine C-N bond which leads to both cis- and trans-forms of the amide group (PHILLIPS 1955). Similar spectra have been obtained from the model, N-acetylpyrrolidine, which has peaks in the ambient temperature ^{13}C spectrum in DMSO at 46.6 and 44.9 ppm (trans- and cis-C2), 25.6 and 24.1 (trans- and cis-C3), 21.9 (methyl) and 167.7 (carbonyl). This phenomenon is temperature dependent and the spectrum at 140°, in which the cis- and trans-amide forms equilibrate at a rate greater than the resonance frequency of the spectrometer, is comprised of single resonance peaks for the C2 and C3 carbons respectively at 45.9 and 24.9 ppm. The 130° spectrum of the polymer (IV) in DMSO is also simplified by coalescence of the C2 and C3 resonances in both the cis- and trans-substituted structures to averaged singlet signals and resembles the previous polypyrrolidine spectra (JOHNS et al. 1976, HAWTHORNE et al. 1979) and those of the other polymers in TABLE II.

As additional proof of structure, the two polymers IV and V were synthesized by an alternative route using polypyrrolidine itself, formed by polymerization of diallylamine hydrochloride in aqueous solution using redox initiators (HODGKIN et al. 1981). This polymer was converted to IV and V by treatment with acetyl chloride and sulphonyl chloride respectively. The ^{13}C chemical shifts of all the carbon atoms in the polymers synthesized by the two methods were identical but as seen in Fig. 1 the proportion of trans-form in polymer IV synthesized from the monomer (≈33%) is higher than for the polymer formed by acetylation of polypyrrolidine (≈16%). LANCASTER et al. (1976) mentioned the occurrence of relatively high levels of trans-pyrrolidine structure in poly(diallylguanidine) but most other workers have

TABLE II.
^{13}C Chemical Shifts[a] of Substituted Polypyrrolidines from diallylamines.

 Carbon	R=	IV $-C{=}O$ $\vert$ CH_3	Polymer Structure V $-SO_2$ $\vert$ CH_3	VI $-C{\equiv}N$	VII $-C{=}O$ 	VIII $-SO_2$ 	(b) 
backbone methylene	cis	26.3	25.7	25.6	25.3	25.7	26.8
" "	trans	30.7	30.5	30.4	29.0	31.1	33.0
ring methene	cis	40.6,42.4	41.8	41.9	40.6,42.4	41.8	41.6
" "	trans	43.7,45.4	44.9	44.6	43.4,45.4	44.7	44.5
ring methylene	cis	49.5,51.3	51.4	54.1	50.2,51.8	51.7	52.0
" "	trans	53.1,54.8	53.0	55.7	53.1,55.0	53.0	53.6
amide carbonyl	cis	169.7	-	-	170.0	-	-
" "	trans	169.3	-	-	169.6	-	-
nitrile				117.6			
				117.4			
methyl		22.3	35.6,34.9	-	-	-	
aromatic		-	-	-	127.1,128.4	127.3,129.2	111.5,115.5
		-	-	-	130.1,136.7	133.0,137.2	129.2,142.9
methyl chain ends	cis	13.2	13.0	12.9	12.9	13.1	
" " "	trans	16.1	15.9	15.9	16.7	16.0	

[a] ppm from TMS. Solvent $CDCl_3$ [b] from JOHNS et al. 1976

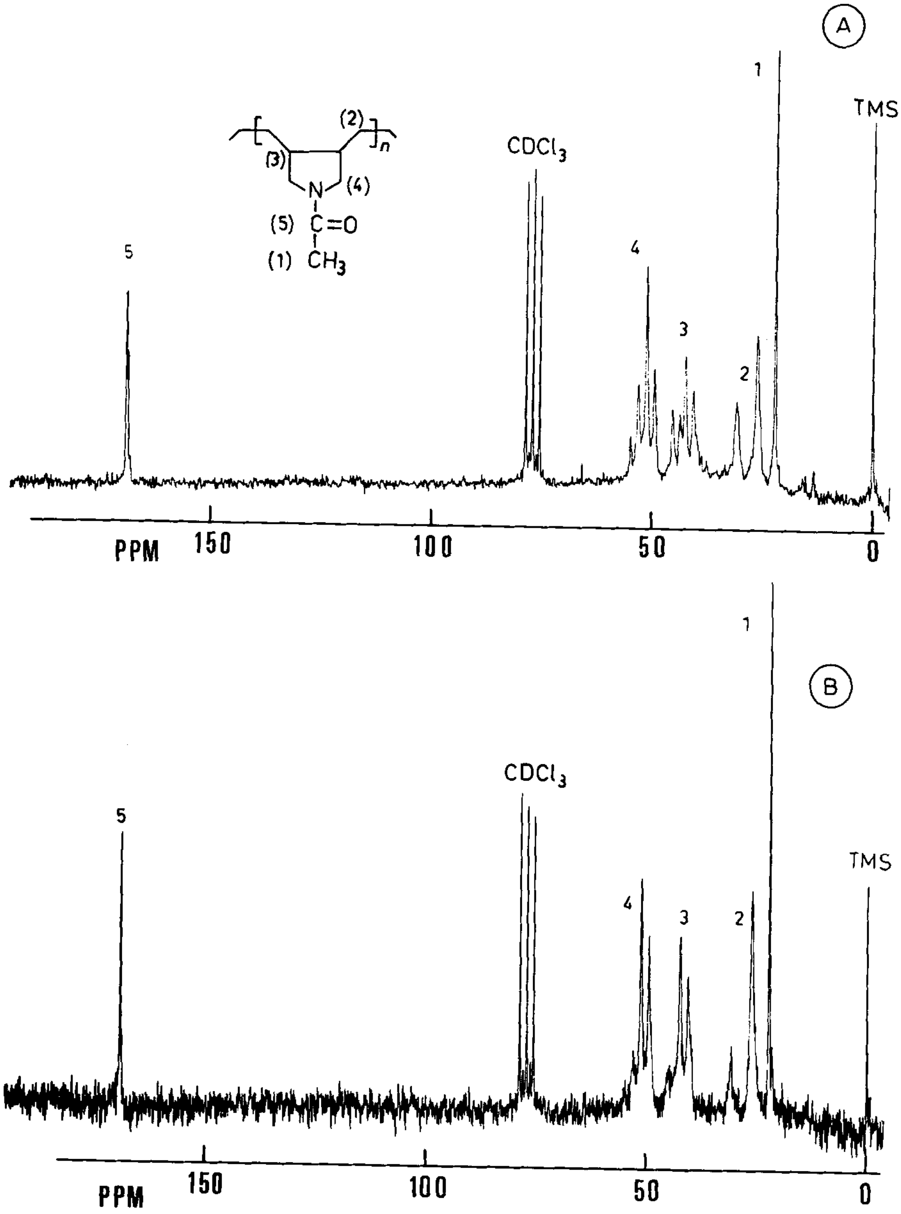


Fig. 1 ^{13}C-NMR spectra of polymer IV (A) synthesized directly from monomer ($CDCl_3$) (B) synthesized from poly (3,4-pyrrolidinediylethylene) and acetyl chloride ($CDCl_3$).

found an approximately 5:1 ratio of cis- to trans-ring structures.

All of the signals in the ^{13}C NMR spectra of the polymers have been assigned to the polypyrrolidine structures and as no other signals are observed which correspond to polypiperidines it is suggested that the level of such structures in the polymers is less than 5%.

The report of UNO et al. (1968) on polydiallylcyanamide stressed the presence of terminal allyl groups and suggested various chain transfer mechanisms which would explain this. CRAWSHAW and JONES (1972), however, found no double bonds in the polydiallylsulphonamide derivatives and we likewise were unable to observe any trace of residual double bonds by NMR or infrared in any of our purified polymers. In contrast we obtained the characteristic cis- and trans-terminal methyl signals at approximately 13 and 16 ppm resulting from hydrogen abstraction by the propagating radical (HAWTHORNE et al. 1979). The intensity of these end group peaks and comparison with previous polypyrrolidines whose molecular weights were determined by vapour phase osmometry (HODGKIN and DEMERAC 1980) indicated that most of the polymers were between 20 and 50 units in length.

EXPERIMENTAL

Materials: The amide monomers were prepared by the methods of BRACE (1971) and the sulphonamides by the methods of CRAWSHAW and JONES (1972). Diallylcyanamide was a commercial product from Borden Inc. Monomer-Polymer Laboratories. The monomers were purified by distillation under vacuum and polymerized in bulk under nitrogen, in sealed tubes, as for the above reference. Poly(3,4-pyrrolidine) was synthesized as described previously (HODGKIN et al. 1981) or by the polymerization of diallylamine hydrochloride in sealed tubes using 3% of 2,2'-azobis(isobutyramidine)dihydrochloride as initiator. Acetylation of this polymer was carried out by treatment with acetyl chloride and pyridine and methylsulphonylation using methanesulphonyl chloride and pyridine.

The amide and sulphonamide polymers were purified by repeated precipitation from chloroform solution using diethyl ether; except for the methylsulphonamide polymers which were reprecipitated from dimethylsulphoxide solution.

^{13}C NMR:

^{13}C NMR spectra were measured at ambient temperature (≈30°C) at 20 MHz on approximately 15% w/v solutions of the polymers in $CDCl_3$ over spectral widths of 4000 Hz with 4000 data points. Chemical shifts are reported in ppm from internal tetramethylsilane.

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