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

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To cite this Article Benedikt, George M.(1992) 'NMR Spectroscopy of Poly(Vinyl Chloride) Defects. ^{1}H-NMR Analysis of the 1,2-Dichloroethyl End Group to the Triad Level', Journal of Macromolecular Science, Part A, 29: 2, 85 — 98
To link to this Article: DOI: 10.1080/10101329208052154
URL: http://dx.doi.org/10.1080/10101329208052154

J.M.S.—PURE APPL. CHEM., A29(2), pp. 85–98 (1992)

NMR SPECTROSCOPY OF POLY(VINYL CHLORIDE) DEFECTS. ^{1}H-NMR ANALYSIS OF THE 1,2-DICHLOROETHYL END GROUP TO THE TRIAD LEVEL

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ABSTRACT

We synthesized and analyzed by ^{1}H NMR the mixture of meso (**m**) and racemic (**r**) 1,2,4,5-tetrachloropentane, as well as the mixture of **mm**, **mr**, and **rr** isomers of 1,2,4,6,7-pentachloroheptane and its precursor 1,2,6,7-tetrachloroheptane-4-ol as models for PVC 1,2-dichloroethyl end group. We were able to correct previous assignments as well as extend the ^{1}H-NMR analysis of this end group in PVC to the triad level.

INTRODUCTION

Establishing a relationship between poly(vinyl chloride) (PVC) thermal stability and its microstructure has been a long sought goal of several major studies performed in the last 20 years. An important role in this continuing activity was played by the members of an IUPAC international group, the results of which were published in 1985 [1]. NMR spectroscopy has played an increasing role as a preferred method for the study of the PVC defects or unusual end groups which appear in the PVC microstructure and which may affect its thermal stability.

With the increase in NMR field strength from 60 MHz for protons [2] to 200 MHz [3], to 270 MHz [3, 4], and subsequently to 350 MHz [5–9], more details regarding the unsaturated as well as saturated defect structures were obtained. (Unfortunately, some errors in assignments also occurred, and they will be discussed below.)

Regarding branching, the reductive PVC dehalogenation method leading to a polyethylene, pioneered by Cotman [10] in 1953, was used in the early seventies to obtain the degree of branching from the ratio of CH_3/CH_2 in the ^{1}H-NMR spectra [11]. The reduction method was later perfected by Starnes [12] and Hjertberg [13], and was subsequently followed by ^{13}C-NMR analysis. This constituted a sensitive method to detect the types of branches as well as to confirm the mechanism of PVC polymerization.

More recently, 2D NMR ^{1}H-^{13}C heteronuclear and ^{1}H-^{1}H homonuclear correlation spectroscopy has been used to confirm stereochemical sequence assignments in PVC [14–16].

Despite the above work, there is still a lot of ambiguity in the interpretation of the ^{1}H-NMR resonances due to the 1,2-dichloroethyl PVC end group, especially when the solvent used is CD_3COCD_3/CS_2 (5:3 by volume) [7]. In order to obtain a more consistent interpretation of this group, we synthesized and examined at 500 MHz the following models: 1,2,4,5-tetrachloropentane (**1**), 1,2,4,6,7-pentachloroheptane (**2**), and its precursor 1,2,6,7-tetrachloroheptane-4-ol (**3**). The symmetrical models **2** and **3**, containing three chiral centers, allow for the observation at 500 MHz of all four 1,2-dichloroethyl ends of the three diasteomers possible. In PVC this would translate into the observation of the end group to the triad level. In other words, we should be able to observe and assign all four chloromethyl end groups attached to **mm**, **rr**, **mr**, and **rm** monomer triads.

EXPERIMENTAL

Preparation of 1,2,4,5-Tetrachloropentane (1)

1,4-Pentadiene (5 g) from Aldrich Chemical Co. was dissolved in 25 mL carbon tetrachloride, cooled in an ice bath to below 5°C, and chlorine gas was passed from a lecture bottle under subdued light through the solution at a slow rate in order to control the reaction exotherm. The end of the reaction was monitored by the disappearance of the unsaturation in the proton NMR. The solution was first purged with nitrogen until the excess dissolved chlorine was eliminated, then washed with an aqueous 5% sodium bicarbonate solution, the solvent layer dried with anhydrous magnesium sulfate, and the solvent subsequently evaporated *in vacuo*. Fractionation by distillation at 0.2 mmHg and 80–85 °C afforded about 1.5 g 1,2,4,5-tetrachloropentane (93% pure by GC) containing the meso and racemic forms in about equal amounts.

Preparation of 1,2,6,7-Tetrachloroheptane-4-ol (3)

1,6-Heptadiene-4-ol (5 g) from Aldrich Chemical Co. was treated in a manner similar to the one described above with chlorine gas until no unsaturation remained by proton NMR. The product after a similar work-up was distilled at 0.2 mmHg and the 2.5-g fraction distilling at 130–135°C was sufficiently pure for NMR analysis. It contained a mixture of **mm**, **rr**, and **rm** isomers with a total of four different 1,2-dichloroethyl ends. A further separation was achieved by preparative LC sepa-

ration using a Whatman Partisil M9 column (50 cm × 9.4 mm ID) and eluting with isocratic methylene chloride. A fraction containing one of the symmetrical isomers (**mm**) was first separated, then a mixture of the same isomer and the nonsymmetrical one (**rm**), followed by a mixture of the **rm** isomer and the second symmetrical one **rr**. The NMR spectra of the three fractions allowed for the assignments of each individual isomer in the mixture.

Preparation of 1,2,4,6,7-Pentachloroheptane (2)

1,2,6,7-Tetrachloroheptane-4-ol (2.3 g) was refluxed with 15 mL thionyl chloride for 16 h. After removal of the excess reagent by rotary evaporation under vacuum, the residue was taken up in methylene chloride, washed with aqueous 5% sodium bicarbonate, the organic layer dried with anhydrous magnesium sulfate, and the solvent evaporated. ^{13}C- and ^{1}H-NMR analysis showed the presence of some starting alcohol in the mixture. The residue was redissolved in methylene chloride and extracted with concentrated sulfuric acid. The remaining organic layer was evaporated and fractionated at 0.6 mmHg to yield a fraction distilling at 108–115°C, containing the three **mm**, **rm**, and **rr** isomers of 1,2,4,6,7-pentachloroheptane (**2**). The mixture was analyzed by ^{1}H and ^{13}C NMR and showed four different 1,2-dichloroethyl ends as discussed in more detail below.

Low Molecular Weight PVC Extract

A commercial PVC resin was extracted with diethyl ether in a Soxhlet apparatus for 16 h, the solvent was partially removed by rotary evaporation, and subsequently methanol was added to precipitate the low molecular weight PVC extract. The solid product was filtered and dried in vacuum for 24 h at 50°C.

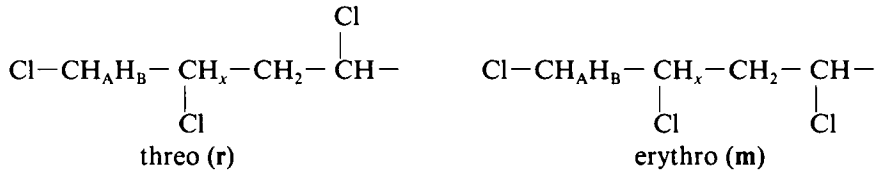
NMR Spectroscopy

The spectra were obtained on a Bruker AMX-500 NMR Spectrometer operating at 500.14 MHz for ^{1}H observation in several solvents, as shown below, and were referenced to TMS.

RESULTS AND DISCUSSION

Previously reported ^{1}H-NMR spectra of low molecular weight PVC resins at 270 MHz in acetone-D_6 [4] and 350 MHz in acetone-D_6/carbon disulfide (5:3 by volume) [7] show in the 3.8–4 ppm region a complicated overlapping pattern composed of two groups, one centered at 3.9 ppm and another at 3.85 ppm, which were ascribed to the AB part of the end ABX proton system in the threo and, incorrectly, to the same AB part in the erythro 1,2,4-trichlorobutyl end group [8, Fig. 9]. As shown below, the multiplet centered at 3.85 ppm represents only half of the erythro AB part of the ABX system. In $CDCl_3$ the same AB part was shown to appear as two doublets of doublets at 3.85 and 3.7 ppm assigned to the threo end (or first

racemic diad end) and a pair of doublets at 3.79 ppm assigned to one of the two AB protons of the erythro end (or first meso diad end) [8].



We decided to improve the analysis of the 1,2-dichloroethyl (or actually 1,2,4-trichlorobutyl) end group in various solvents by extending the system to the meso-meso (**mm**), racemic-racemic (**rr**), meso-racemic (**mr**), and racemic-meso (**rm**) triads at the end of the chain. In order to simplify the NMR spectra, we synthesized symmetrical models 1,2,4,5-tetrachloropentane (**1**), containing both **m** and **r** diastereomers and 1,2,4,6,7-pentachloroheptane (**2**), containing the three **mm**, **rr** and **mr** isomers, the former two exhibiting only one ABX pattern each (which one might call ABX**mm** and ABX**rr**), while the latter showing both ABX**mr** and ABX**rm** patterns at slightly different chemical shifts. The precursor for **2**, 1,2,6,7-tetrachloroheptane-4-ol (**3**) provided an additional example for the effect of the third chiral center, 6 atoms away from the AB proton system, on its NMR spectrum.

Since tetrahydrofuran is an excellent solvent for PVC in all ranges of molecular weight, we used its 99.95% deuterated form (THF-D_8) as our preferred NMR solvent. With its own residual proton resonances due to THF-D_7 at 3.58 and 1.72 ppm, this solvent allows for a clear observation of the most important PVC end groups. Moreover, the ^{1}H-NMR spectrum of a low molecular weight extract of a commercial radical initiated PVC resin in THF-D_8 appears very similar to the one previously published in the acetone/carbon disulfide mixture. The region of interest for our purpose, from 3.1 to 6.0 ppm, is shown in Fig. 1 for such a low molecular weight PVC in acetone-D_6/carbon disulfide (5:3 by volume), THF-D_8, and $CDCl_3$.

Before discussing in more detail the above spectra, we shall analyze the new models we synthesized.

I. 1,2,4,5-Tetrachloropentane (1)

The distillation fraction prepared as shown in the experimental part contained about equal amounts of the expected **m** and **r** isomers. We obtained easily the full assignment of the ^{1}H- and ^{13}C-NMR spectra of each of the diastereomers by analyzing their 2D ^{1}H-^{1}H homonuclear [17] (COSY) and ^{13}C-^{1}H heteronuclear correlation spectra [15, 18]. The double quantum filtered phase sensitive COSY spectrum in $CDCl_3$ is shown in Fig. 2 while the heteronuclear correlation spectrum is shown in Fig. 3. The 1D ^{1}H spectrum appears on the side of the 2D spectra.

The proton assignments start in Fig. 2 from the most obvious doublet of triplets at 2.65 ppm which is due to one of the two protons at carbon 3 in the meso form equally coupled to the two protons at carbons 2 and 4. This proton is probably the one situated in the closer proximity of the two chlorine atoms at carbons 2 and 4. The other proton at carbon 3 in the **m** isomer appears centered at 2.28 ppm and from the COSY spectrum appears clearly coupled to the proton centered at 4.28 ppm, which in turn is coupled to the narrower AB part of the ABX system (4 lines

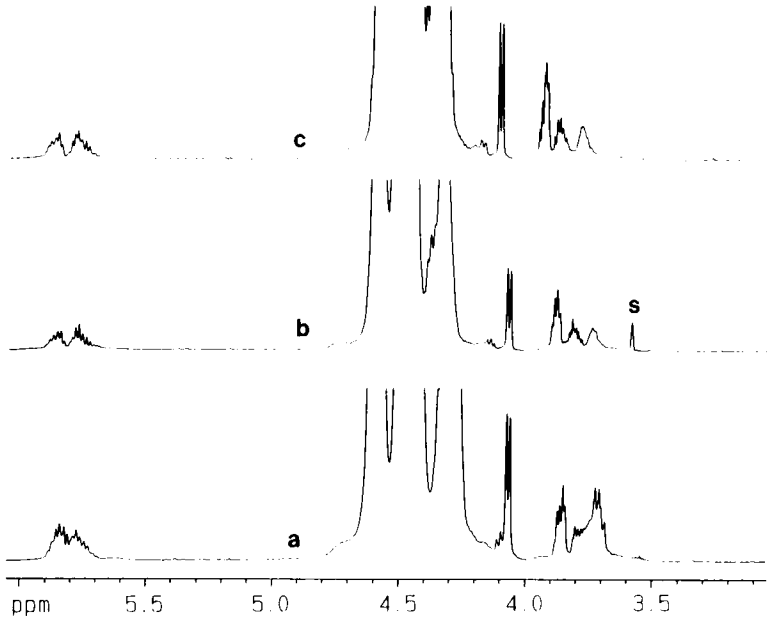


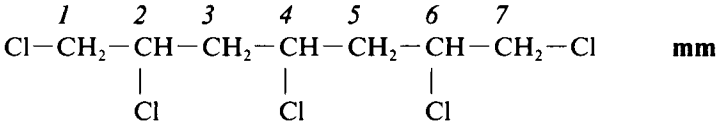
FIG. 1. Low field, 3.1 to 6.0 ppm region of the ^{1}H-NMR spectrum of a low molecular weight poly(vinyl chloride) in deuterated chloroform (a), tetrahydrofuran (b), and acetone/carbon disulfide (5:3 v/v) (c), "s" represents residual solvent.

for A and 4 for B noticeable between 3.85 and 3.74 ppm). Both protons at carbon 3 in the **r** isomer appear centered at 2.3 ppm, and they are coupled to the protons at carbons 2 and 4 centered at 4.37 ppm, which in turn are coupled to the broader AB part of the ABX pattern between 3.87 and 3.67 ppm.

Once the proton resonances have been established, one can obtain the carbon resonance assignments from the heteronuclear correlation spectrum in Fig. 3. The ^{13}C chemical shifts are shown in Table 1.

II. 1,2,4,6,7-Pentachloroheptane (2)

The mixture of the three isomers, **mm**, **rm** and **rr** prepared as described in the Experimental Section was expected to contain all four AB patterns for the $Cl-CH_2-$ groups at the end of the three triads. Due to their symmetry, the **mm** and **rr** isomers were expected to show identical AB patterns for protons at carbons 1 and 7 (ABX**mm** and ABX**rr**) while the **rm** isomer was expected to show two different, equal area, AB patterns for the ABX**mr** and ABX**rm** ends.



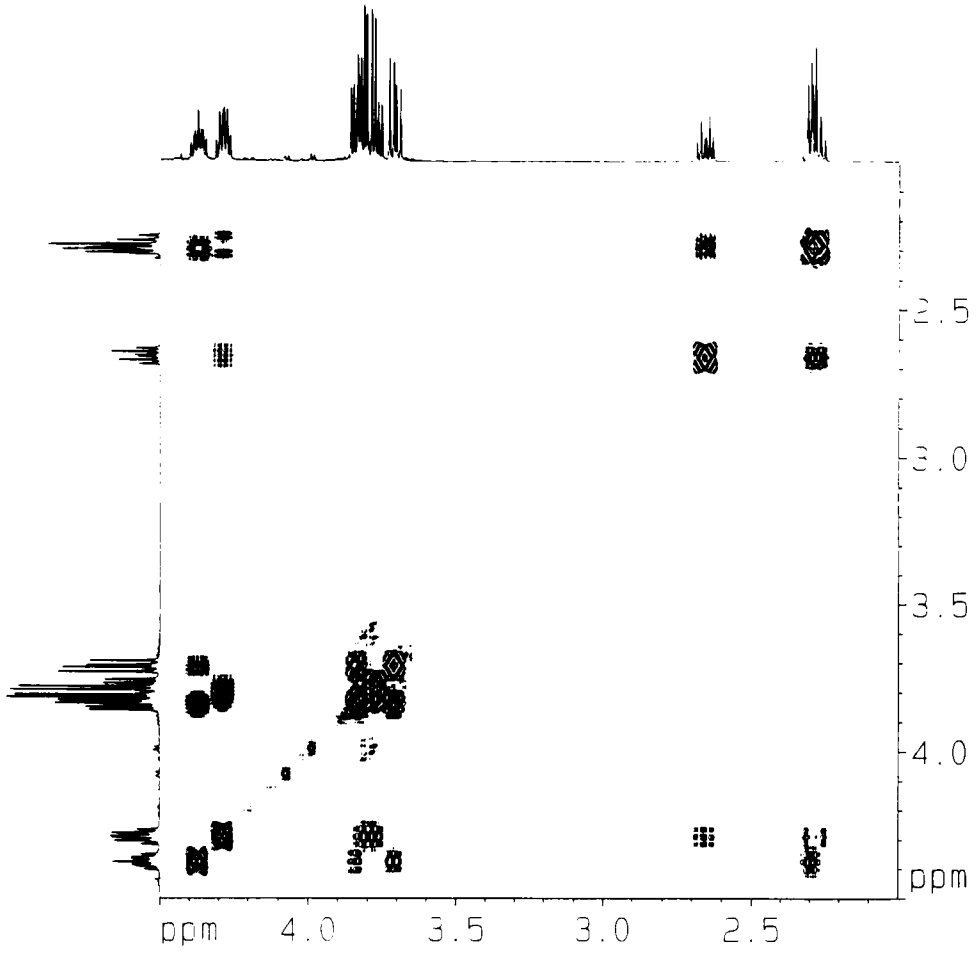
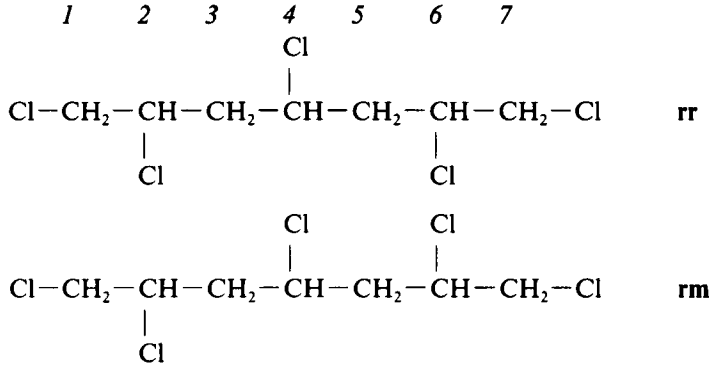


FIG. 2. Double quantum filtered phase sensitive 2D COSY spectrum of the mixture of meso and racemic 1,2,4,5-tetrachloropentane (1) in $CDCl_3$. (See Fig. 3 for assignments.)



The ^{1}H-NMR spectrum of the mixture of the three isomers appears on the axis of the 2D NMR double quantum filtered phase sensitive COSY spectrum of the mixture in $CDCl_3$ shown in Fig. 4. Three of the four expected AB patterns are

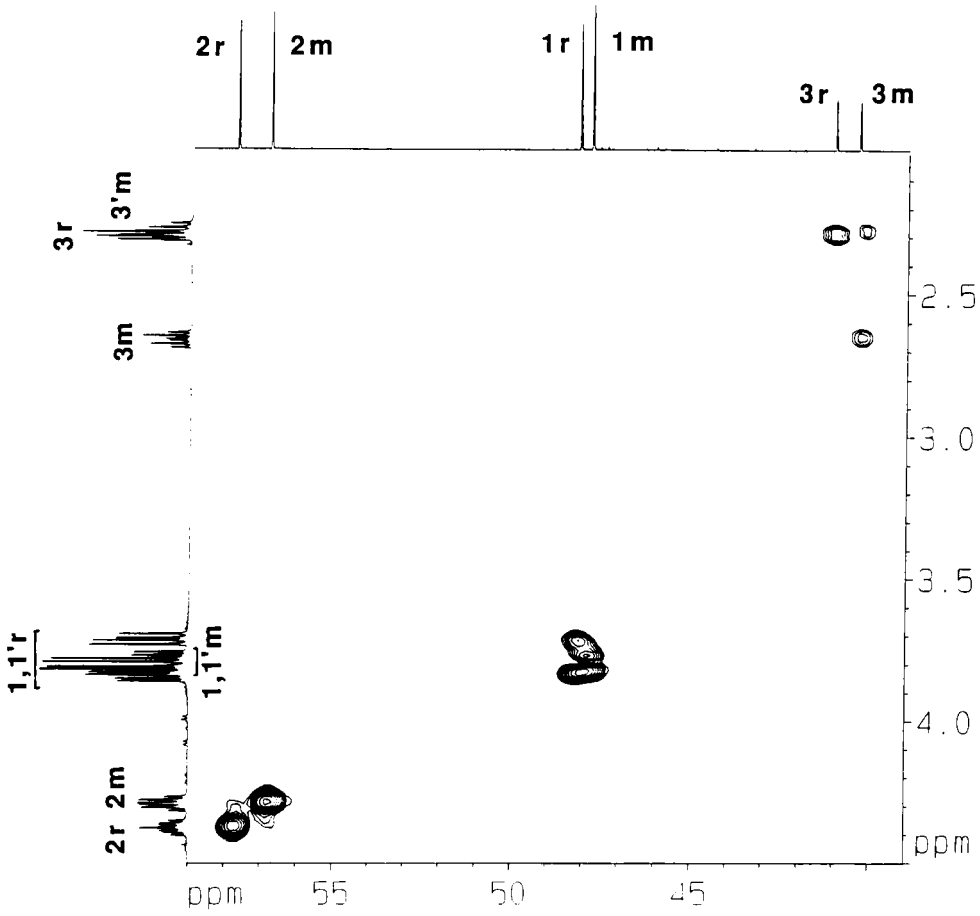


FIG. 3. 2D ^{1}H-^{13}C heteronuclear correlation spectrum of the mixture of the meso and racemic 1,2,4,5-tetrachloropentane (**1**) in $CDCl_3$.

TABLE 1. ^{13}C Chemical Shifts for 1,2,4,5-Tetrachloropentane in $CDCl_3$ (ppm)

Carbon	Isomer	Chemical shift
1	**m**	40.34
1	**r**	41.02
2	**m**	47.81
2	**r**	48.14
3	**m**	56.80
3	**r**	57.72

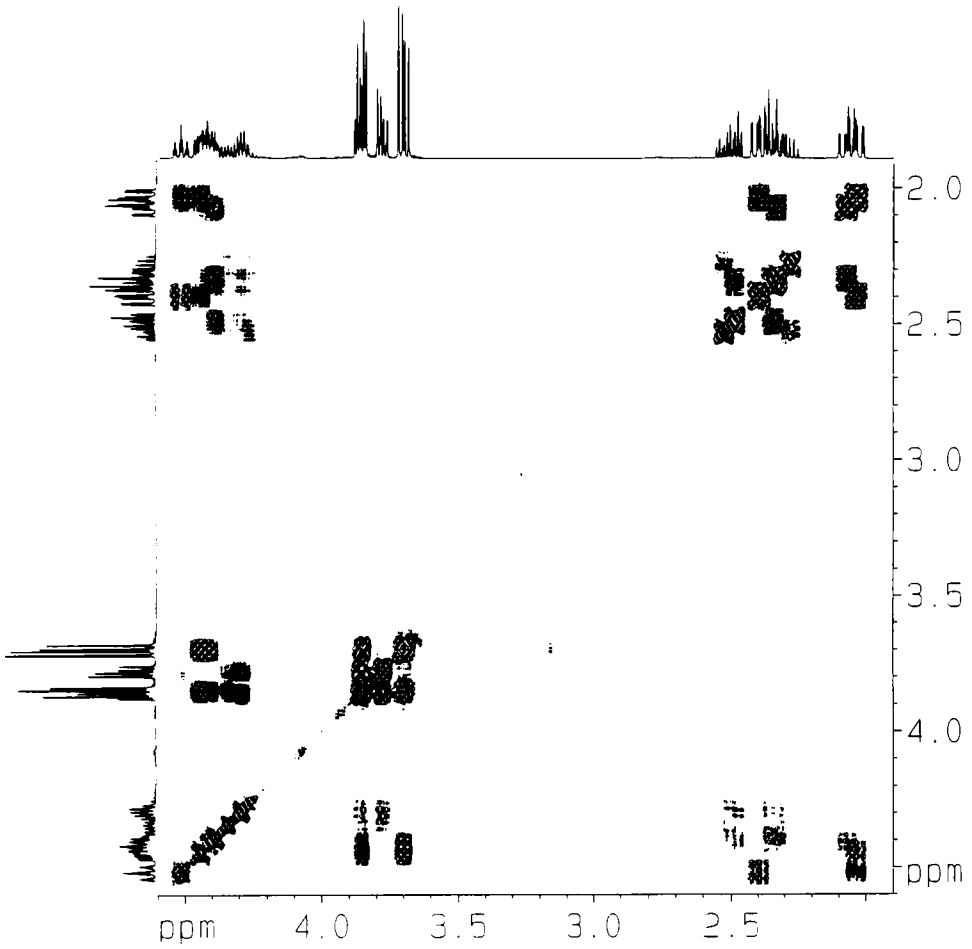


FIG. 4. Double quantum filtered phase sensitive 2D COSY spectrum of the mixture of **mm**, **rm**, and **rr** isomers of 1,2,4,6,7-pentachloroheptane (**2**) in $CDCl_3$. (See Fig. 5 and Table 2 for assignments.)

noticeable in the region from 3.6 to 3.9 ppm, with one being coincident (see also bottom trace in Fig. 6). A complete assignment for each of the three components of the mixture based on the correlation peaks, the perceived relative isomer ratios, and the several well resolved individual proton patterns may be made. For instance, one can start just as above in the case of Compound **1** with the obvious two doublets of triplets between 2.45 and 2.57 ppm, the lowest field one belonging to one of the two protons in Position *3* (and the identical one in Position *5*) of the **mm** isomer, the highest field one to one of the protons in Position *5* of the **rm** isomer. The assignments are further facilitated by the heteronuclear correlation spectrum of the mixture, the expansions of which are shown in Fig. 5. The assignments are given in Tables 2 and 3.

In the ^1H spectrum plotted on the axis of Fig. 5(2), three out of four ABX 1,2-dichloroethyl patterns are noticeable through the B part as doublets of doublets.

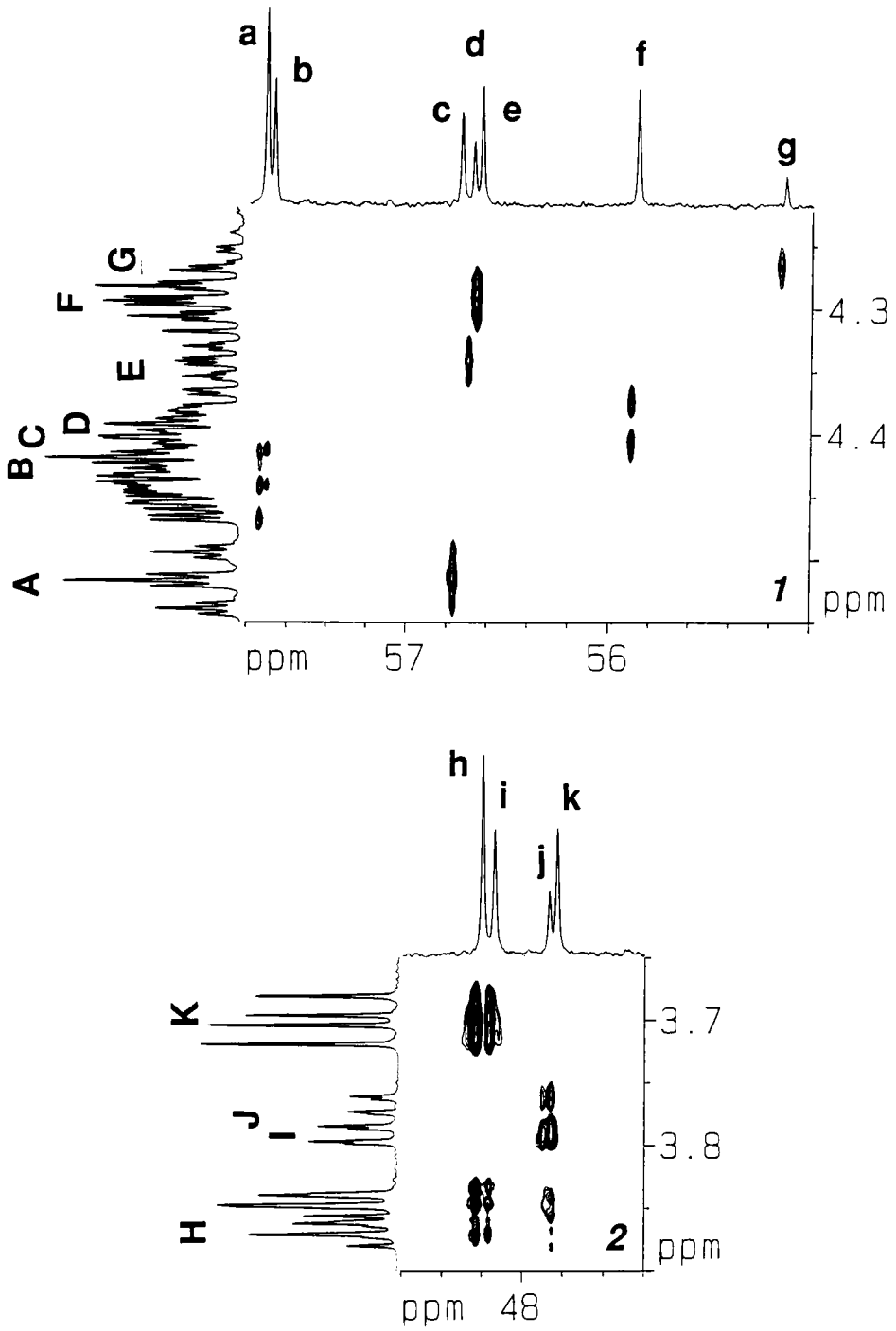


FIG. 5. Expansions of the 2D ^{1}H-^{13}C heteronuclear correlation spectrum of the mixture of **mm**, **rm**, and **rr** isomers of 1,2,4,6,7-pentachloroheptane (**2**) in $CDCl_3$. (See Tables 2 and 3 for assignments.)

(continued)

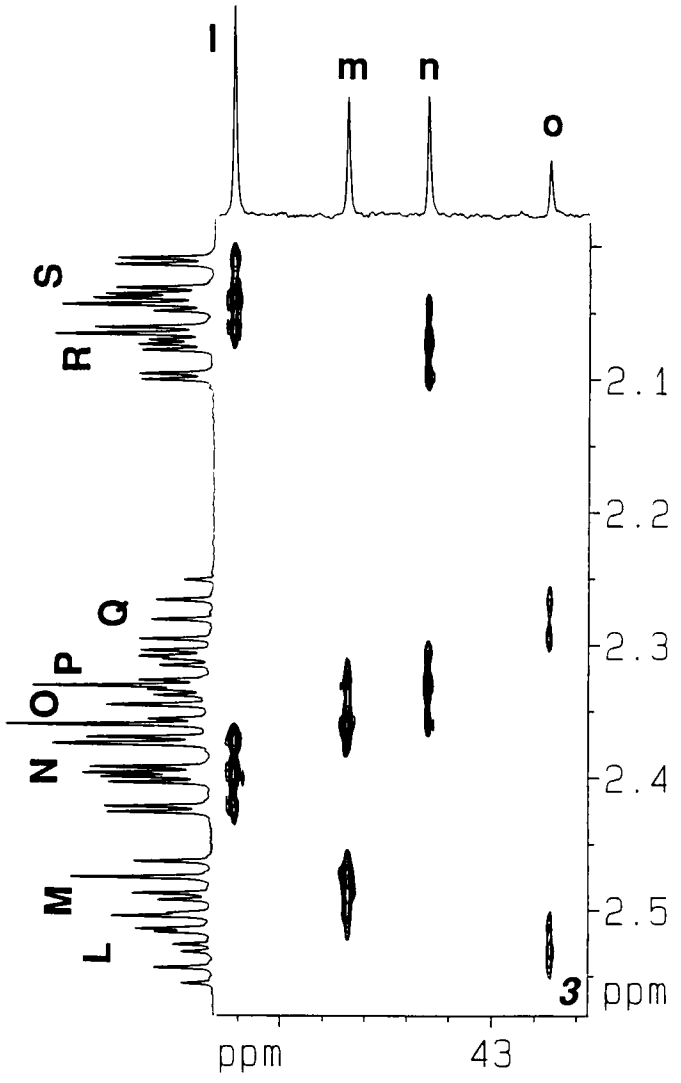


FIG. 5. Continued.

Despite the coincidence of the third and fourth pattern in the 1D NMR spectra, the 2D spectra are able to separate them.

Since our preferred solvent for PVC is THF-D_8, we decided to obtain the 1D proton NMR spectrum of the same mixture of isomers in a series of mixed THF-D_8/$CDCl_3$ covering the entire range of relative ratios (see Fig. 6). This allowed us to follow the solvent-induced change in the chemical shifts up to the point of 50/50 ratios where all four B parts of the ABX patterns became directly noticeable. In other words, the chloromethyl end group was resolved to the triad level in the proton NMR spectrum.

In pure THF-D_8 the spectrum in this region became a group of two multiplets containing at higher field the B part of the ABX**rr** and ABX**rm** ends, well resolved,

TABLE 2. ^{1}H Chemical Shifts for 1,2,4,6,7-Pentachloroheptane **(2) mm, rm,** and **rr** Isomers in $CDCl_3$ (ppm)

H (isomer)	Chemical shift	Assignment	Fig. 5 lables
1′,7′ all	3.85–3.9	A part of ABX in all isomers	H
1,7**mm**	3.76–3.85	B part of ABX (doublet of doublets)	I
7**rm**	3.755–3.8	B part of ABX (doublet of doublets)	J
1**rr**	3.69–3.73	B part of ABX (doublet of doublets)	K
1**rm**	3.69–3.73	B part of ABX (doublet of doublets)	K
3′,5′**mm**	2.5–2.55	Doublet of triplets	L
5′**rm**	2.45–2.52	Doublet of triplets	M
3′,5′**rr**	2.37–2.43	Doublet of doublets of doublets	N
5**rm**	2.32–2.39	Doublet of triplets	O
3′**rm**	2.31–2.37	Doublet of doublets of doublets	P
3,5**mm**	2.26–2.31	Doublet of triplets	Q
3**rm**	2.03–2.11	Doublet of doublets of doublets	R
3,5**rr**	2.0–2.08	Doublet of doublets of doublets	S
4**rr**	4.48–4.55	Triplet of triplets	A
2,6**rr**	4.41–4.49	Overlapping multiplet	B
2**rm**	4.4–4.45	Overlapping multiplet	C
4**rm**	4.36–4.43	Overlapping multiplet	D
2.6**mm**	4.32–4.37	Overlapping multiplet	E
6**rm**	4.27–4.32	Overlapping multiplet	F
4**mm**	4.25–4.29	Overlapping multiplet	G

TABLE 3. ^{13}C Chemical Shifts for 1,2,4,6,7-Pentachloroheptane **(2) mm, rm,** and **rr** Isomers in $CDCl_3$ (ppm)

Carbon	Isomer	Chemical shift	Fig. 5 labels
1,7	**rr**	48.20	h
1	**rm**	48.14	i
1,7	**mm**	47.87	j
7	**rm**	47.83	k
2,6	**rr**	57.71	a
2	**rm**	57.67	b
4	**rr**	56.74	c
2,6	**mm**	56.68	d
6	**rm**	56.64	e
4	**rm**	55.87	f
4	**mm**	55.13	g
3,5	**rr**	44.22	l
5	**rm**	43.68	m
3	**rm**	43.30	n
3,5	**mm**	42.73	o

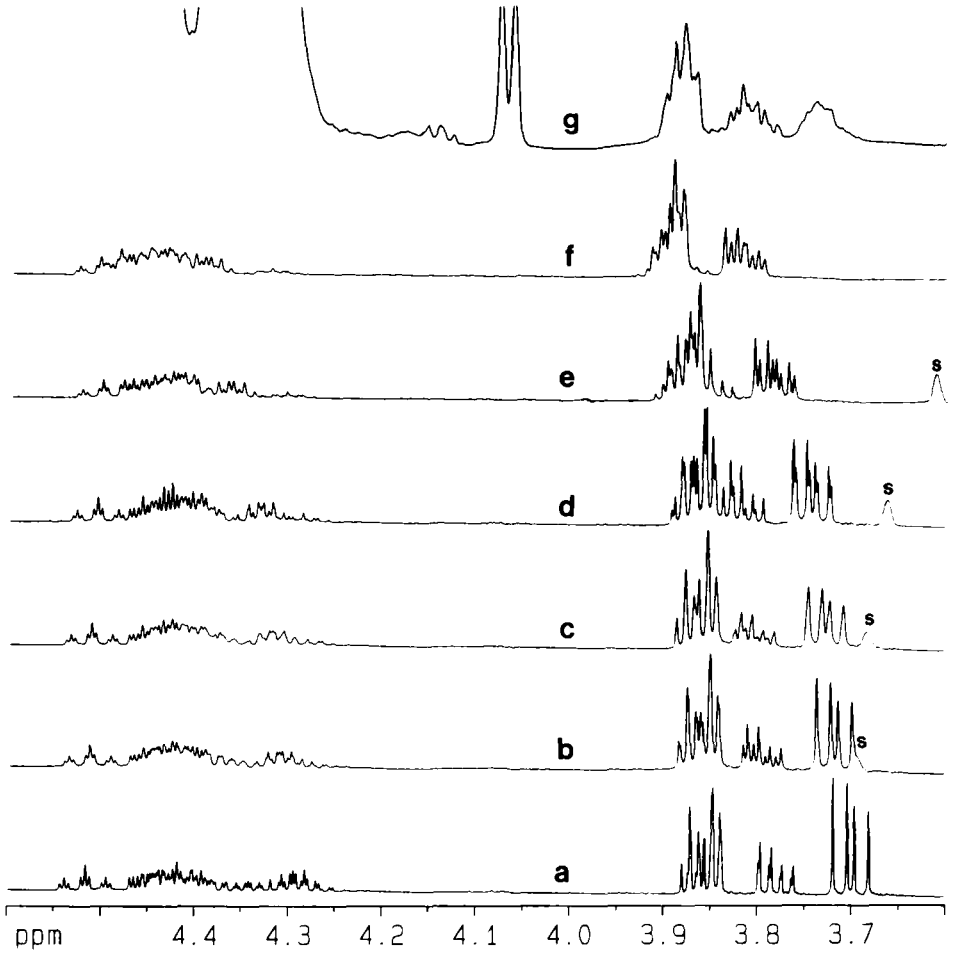


FIG. 6. Expansion of the ^{1}H-NMR spectrum of the mixture of **mm**, **rm**, and **rr** isomers of 1,2,4,6,7-pentachloroheptane (**2**) in mixtures of deuterated chloroform and tetrahydrofuran (v/v): 100/0 (a), 67/33 (b), 56/44 (c), 50/50 (d), 33/67 (e), 0/100 (f), and the low molecular weight PVC from Fig. 1 in THF-D_8 (g). "s" represents one of the residual protons in tetrahydrofuran-D_7.

while at lower field a multiplet representing all the A parts of the four ABX ends and the B parts of the remaining ABX**mr** and ABX**mm** ones.

The spectra are plotted in Fig. 6 together with the corresponding region of the low molecular weight PVC extract. It is clear now that the previous assignments for the two multiplets centered at 3.87 and 3.8 ppm, respectively, as the terminal chloromethyl groups in the threo and erythro polymer ends [8] is wrong. The lower field multiplet belongs, at the diad level, to the terminal chloromethyl protons in the threo and half of the erythro end, while the multiplet centered at 3.8 belongs to only half of the erythro end. In PVC the only additional overlap at 3.8 ppm would be due to the ABX pattern of the pendant chloromethyl branch.

III. 1,2,6,7-Tetrachloroheptane-4-ol (3)

The ^{1}H-NMR spectrum of a distillation fraction of **3** containing all three diastereomers in the mixture showed in $CDCl_3$ a pattern very similar to that of **2** above, except for the terminal ABX methylene protons. The B part of the pattern showed all four well resolved doublet of doublets at 3.79 ppm (ABX**mm**), 3.76 (ABX**mr**), 3.713 (ABX**rm**), and 3.711 (ABX**rr**). The assignments were facilitated by subsequent liquid chromatographic fractionations as shown in the Experimental Section. The three fractions obtained containing the **mm** isomer, the **mm** and **rm** in a mixture, and the **rm** and **rr** in a mixture, respectively, allowed for a complete assignment of the ^{1}H- and ^{13}C-NMR spectra. They are not given here because they are beyond the purpose of the present paper.

CONCLUSION

The 1D and 2D-NMR study of the models presented here allowed for a correction of the assignments for the 1,2-dichloroethyl end group in radical-initiated poly(vinyl chloride). The 500 MHz ^{1}H-NMR pattern for this end group was resolved to the triad level. Other end groups in PVC are expected to be assigned to the same level.

ACKNOWLEDGMENTS

Thanks are due to the BFGoodrich Company for the approval to publish this work and to Lee Traynor and Brian Goodall for their support.

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Received April 28, 1991
Revision received June 7, 1991