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Ionic Polymerization of 1,2-Butylene Oxide: NMR Study of the Reaction Products

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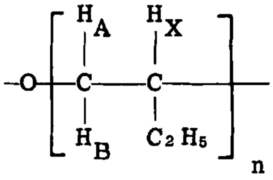
ABSTRACT

An NMR study on the reaction products of the ionic polymerization of 1,2-butylene oxide has been carried out. Polymers prepared via a cationic mechanism by using a trityl salt as the initiator are built up of repeat monomer units, and the propagation reaction follows Bernoullian statistics. Polymers prepared via an anionic mechanism with the use of sodium metal as initiator, on the other hand, are not made up of repeat monomer units, and the propagation reaction follows a first-order Markov statistics. In the cationic polymers the mean chemical shifts of the triads and tetrads move upfield on replacing m dyads by r dyads; however, the pentads move downfield on changing m by r. In the anionic polymers the mean chemical shifts for the triads and tetrads of the ethyl group along with the pentads of the methine protons move upfield whereas tetrads associated with the remaining methylenes move downfield on replacing m dyads by r dyads as well as on replacing o-$C_6H_4Cl_2$ by CCl_4 or DMSO-d_6 as the solvent for recording the spectrum. The anionic polymer M-b, which is rich in double bonds and hydroxyl groups, has relatively lower values for the geminal couplings J_{AB} and the vicinal couplings J_{AX} and J_{BX} as compared to those obtained with

polymer M-a, which has practically no double bonds and very few (if any) hydroxyl groups. The appearance of the methylene protons in polymer M-b as well as the coupling constants J_{AB}, J_{AX}, and J_{BX} vary on changing the solvent from o-$C_6H_4Cl_2$ to CCl_4 or DMSO-d_6.

INTRODUCTION

Studies on the ionic polymerization of 1,2-butylene oxide have been reported earlier from this laboratory [1-4]. In these it was pointed out that the molecular weight distributions of the reaction products obtained under cationic polymerization conditions [3, 4] were bimodal, consisting essentially of low molecular weight cyclic products on the one hand and linear high molecular weight polymers on the other. Double bonds and hydroxyl groups were absent from these products, and their overall structure, as analyzed by NMR, appeared to originate from monomer repeat units such as that shown in structure I.



$$-\mathrm{O}\left[\begin{array}{cc} H_A & H_X \\ | & | \\ -\mathrm{C}- & -\mathrm{C}- \\ | & | \\ H_B & C_2H_5 \end{array}\right]_n-$$

The molecular weight distribution of reaction products obtained under anionic polymerization conditions [4] were likewise bimodal; however unlike the previous study (cationic), these contained double bonds and hydroxyl groups. Furthermore these did not correspond to structure I.

It was suggested [4] that the reactants in the anionic polymerization, viz., the 1,2-butylene oxide monomer and the sodium-mirror initiator, react together to form a new product which then polymerizes to yield the resulting polymer. Similar arguments have been put forth, notably [5] in the case of the anionic polymerization of propylene oxide with a sodium mirror initiator, where the resulting products were rich in double bonds and hydroxyl groups. Others [6-10] are of the opinion that the formation of double bonds results exclusively from chain transfer reactions during the course of polymerization.

The NMR analyses reported in these earlier publications [1-4] on 1,2-butylene oxide were restricted to an evaluation of the different types of protons. More recently, it was noted that though the chemical shifts for protons of the main chains of cationically prepared poly(1,2-butylene oxide) already reported [3, 4] agreed with those suggested by Price and Fukutani [11] for the case of poly(tert-butylene oxide) [which has the same main chain as of poly(1,2-butylene oxide)], they are different to those suggested by Tani and Oguni [12], who studied poly(tert-butylethylene oxide). Assignments similar to those reported by Tani and Oguin [12] have also been proposed for poly(propylene oxide) [13-16] and for poly[(s)-isopropylethylene oxide] [17] by other groups. It was thus thought that a detailed study of the stereochemistry of poly(1,2-butylene oxide) in terms of triads, tetrads, and pentads would be of interest. Furthermore, the structures of the polymers obtained by the anionic mechanism which apparently does not correspond to the repeat units of 1,2-butylene oxide, were found to be very sensitive to stereochemical changes and yielded interesting data correlating the triads, tetrads and pentad sequences. The principal results of this study form the subject matter of the present communication.

EXPERIMENTAL

Preparation of reactants, experimental procedure and characterization of reaction products are described in details, in the earlier publications [1-4]. Only the reaction conditions and some of the characteristics of the polymers used in the present studies are listed in Table 1.

RESULTS AND DISCUSSION

Cationic Polymerization Products:

Effect of Solvent and Temperature on the Quality of the Spectra

It has been pointed out in the literature [18] that although the spin-lattice relaxation of polymer nuclei is not proportional to the macroscopic solution viscosity, the rate of local chain motion upon which the line width depends, does depend on the solvent viscosity. It is therefore recommended to use solvents of moderate viscosity. It has been further suggested [18] that in order to reduce dipolar broadening one must use elevated temperatures. In the present study, three solvents, viz., o-dichlorobenzene (o-$C_6H_4Cl_2$), carbon tetrachloride (CCl_4), and dimethyl sulfoxide (DMSO-d_6) were used in combination with TMS as the internal standard.

In Fig. 1 are shown the NMR spectra of the ethyl region of the T-2

TABLE 1. Polymerization Reaction Conditions

Sample no.	Ionic mode of polymerization	Initial monomer concentration $[M]_0$ (mole/liter)	Initiator	Initiator concentration $\times 10^3$ (mole/liter)	Reaction temperature (°C)	Reaction time (hr)	Yield (base-mole/liter)	Polymer molecular weights $\overline{M_w}$ (GPC)
T-2[a]	Cationic	2.42	Triphenylmethyl hexafluoro arsenate	2.44	0	0.7	0.32	288
B-16	Cationic	11.62	Triphenylmethyl hexafluoro phosphate	1.16	-10	144	4.84	6.7×10^4
M-a	Anionic	11.62	Sodium mirror	Excess	20	24	-	Tetramers
M-b	Anionic	11.62	Sodium mirror	Excess	20	24	-	Tetramers

[a] In dichloroethane.

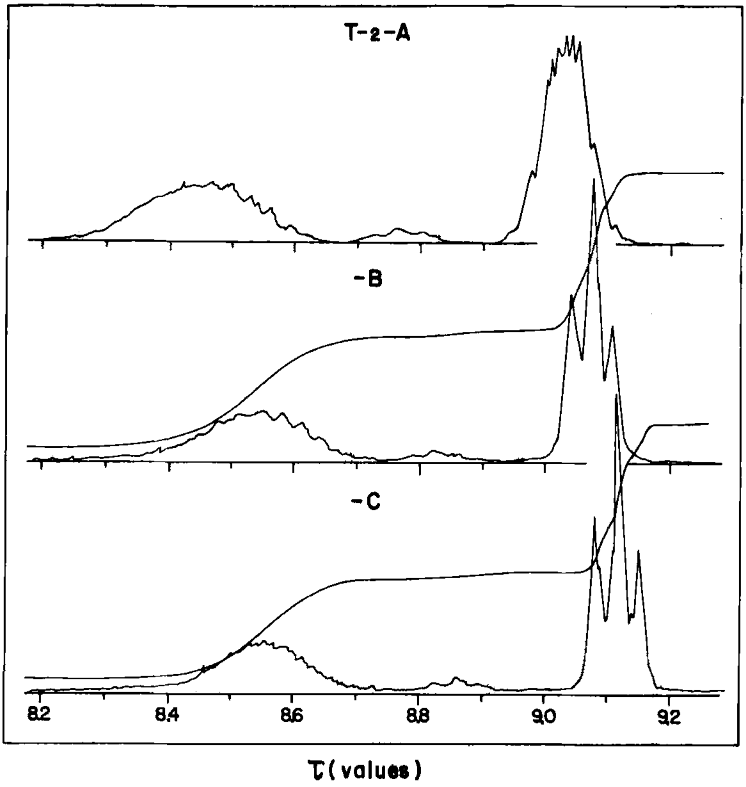


FIG. 1. 220 MHz NMR spectra of the side-chain ethyl protons of poly(1,2-butylene oxide) T-2 in 15% w/v solution of o-$C_6H_4Cl_2$ at 100°C (T-2-A), of CCl_4 at 75°C (T-2-B), and of DMSO-d_6 at 120°C (T-2-C) in the range of 8.2 to 9.2 τ.

products dissolved in each of these solvents. The methyl protons (between 8.9 and 9.2 τ) yield a multiplet when the spectrum was recorded in o-$C_6H_4Cl_2$ at 100°C (T-2-A) as solvent but show well resolved triplets when the solvent was CCl_4 (at 75°C) (T-2-B) or DMSO-d_6 (at 120°C) (T-2-C). Furthermore, the triplets do not appear at the same τ values when going from one solvent to other. In o-$C_6H_4Cl_2$ (T-2-A) these have peaks at 8.99, 9.02, and 9.05 τ, in CCl_4(T-2-B) at 9.05, 9.08, and 9.11 τ, and in DMSO-d_6 (T-2-C) at 9.08, 9.12, and 9.15 τ. Methylene protons (located between 8.2 and 8.7 τ) also appear at different chemical shifts, depending on the solvent. Such shifts in the values of τ (for a given set of protons) are not unusual and are frequently observed in the NMR spectra. These are attributed to the different shielding anisotropy of the solvents used. The results based on Fig. 1 clearly show how useful it can be to record the NMR spectra of a polymer in different solvents. Information which is not revealed with one solvent may be available with the other. In the present case it is difficult to compute the intensity of each peak of the triplet when $o\text{-}C_6H_4Cl_2$ is the solvent, but in CCl_4 and DMSO-d_6 the peaks are very well defined and their intensity can be easily computed.

Furthermore it is possible that a part of the spectra may be better resolved with one solvent while an other part is better resolved in another solvent. In Fig. 2 are shown the main chain methine and methylene protons of products T-2, as recorded in the same three solvents. The spectra obtained are quite different. The methine and methylene protons appear at τ values of 6.1-6.9 in $o\text{-}C_6H_4Cl_2$, 6.2-6.9 in CCl_4, and 6.2-6.7 in DMSO-d_6. This would indicate that these protons resolve in the spectra as merged together but not always to the same extent in the three solvents used. In $o\text{-}C_6H_4Cl_2$ the separation of methine and methylene protons appears to be best achieved.

In order to gather additional information regarding the structure of the polymer, NMR spectra of the T-2 products were recorded in $o\text{-}C_6H_4Cl_2$ CCl_4 and DMSO-d_6 but at 25° C. It was remarked, however, that the spectra obtained at 25° C resembled very much those obtained at the elevated temperatures. For this reason the spectra at 25° C are not shown here. Based on the above results it was decided to use $o\text{-}C_6H_4Cl_2$ at 100° C for recording the spectrum of another sample of poly(1,2-butylene oxide), viz., B-16, and analyze it in terms of triad, tetrad, and pentad sequences.

Analyses of the Spectra

In Fig. 3 is shown the NMR spectrum of the side-chain ethyl protons of high molecular weight poly(1,2-butylene oxide)B-16. The results of the analyses of the spectrum are presented in Table 2. The triplet located between 8.9 and 9.1 τ is due to the methyl protons and the three peaks at 8.99, 9.02, and 9.05 have intensity of 0.34, 0.48, and 0.18 respectively. These may be attributed to mm, mr, and rr triads in ascending order of magnetic field as has been done in the case of poly-p-isopropyl-α-methylstyrene [19], poly-α-methylstyrene [20], poly(methyl methacrylate) [21], polypropylene [22], and polyacetaldehyde [23]. Making use of the triad intensity in combination with equations relating configurational statistics and propagation mechanism [18] one arrives at the conclusion that the cationic polymerization of 1,2-butylene oxide (B-16) obeys Bernoullian propagation with $P_m = 0.58$. Based on this value of $P_m = 0.58$, the intensity of the six tetrads, viz., mmm, mmr, rmr, mrr, mrm, and rrr were calculated, and their τ values are shown in Table 2.

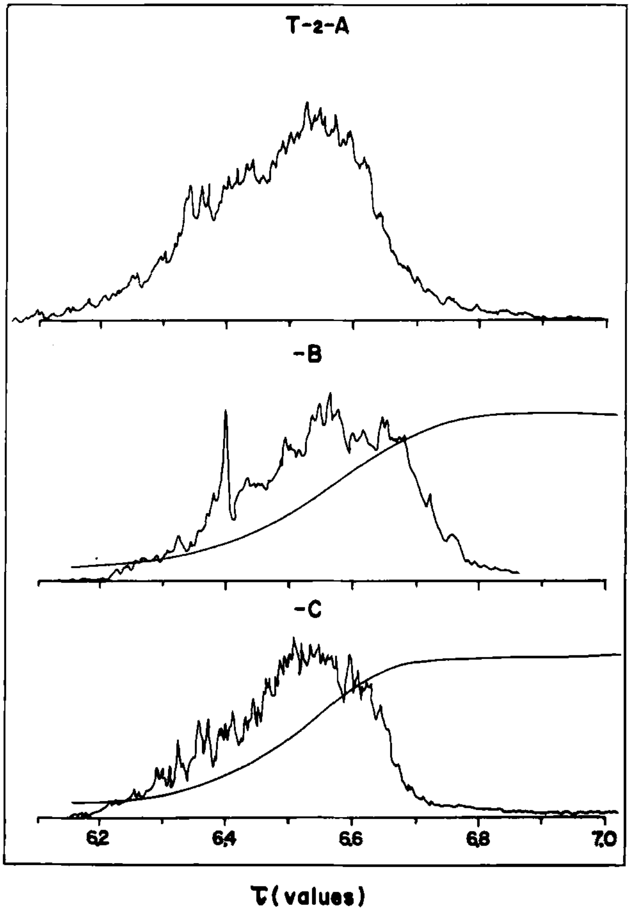


FIG. 2. 220 MHz NMR spectra of the main-chain protons of poly(1,2-butylene oxide) T-2 in 15% w/v solution of o-$C_6H_4Cl_2$ at 100°C (T-2-A), of CCl_4 at 75°C (T-2-B), and of DMSO-d_6 at 120°C (T-2-C) in the range of 6.0 to 7.0 τ.

In Fig. 3. the methylene protons are located between 8.2 and 8.6 τ with important peaks at regular intervals of 6.6 Hz, indicating that the quartets, which these protons are built up of have a J_{AB} = 6.6 Hz. By making use of this value in combination with the calculated intensity of the six tetrads, quartets bearing peak ratios of 1:3:3:1 were arranged to simulate the spectrum of the methylene protons between

TABLE 2. Assignment of Chemical Shifts, on the basis of the Triad Population for Various Tetrads for Poly(1,2-butylene Oxide) sample B-16, NMR Spectrum Observed in o-$C_6H_4Cl_2$ at 100°C

	Nature of protons		Important peaks			Configuration placement		
	Location	Type	τ values	Intensity based on area	Intensity based on tetrad placement	Sequence	Intensity based on P_m = 0.58	Center τ values
Triads[a]	Side chain	Methyl $-CH_2-\underline{CH_3}$		0.34		mm		8.99
				0.48		mr		9.02
				0.18		rr		9.05
Tetrads	Side chain	Methylene $-\underline{CH_2}-CH_3$	8.25	0.02	-			
			8.28	0.03	0.03			
			8.31	0.07	0.07			
			8.34	0.13	0.12	mmm	0.20	8.32
			8.37	0.20	0.19			
			8.40	0.23	0.23	mmr + rmr	0.28 0.10	8.38
			8.43	0.15	0.19	mrr	0.20	8.41
			8.46	0.10	0.11	mrm	0.14	8.44
			8.49	0.03	0.05	rrr	0.07	8.48
			8.52	0.02	0.01		J_{AB} = - 6.6 Hz	

Main chain	Methylene $-O-\underline{CH_2}-CH-O-$	6.43	0.02	0.03			
	(85%)	6.45	0.06	0.07			
		6.475	0.10	0.12	mmm	0.20	6.46
		6.50	0.16	0.19			
		6.53	0.24	0.23	mmr + rmr	0.28 0.10	6.52
		6.566	0.23	0.19	mrr	0.20	6.55
		6.60	0.14	0.11	mrm	0.14	6.58
		6.63	0.06	0.05	rrr	0.07	6.62
		6.66	0.01	0.01		J_{AB} = - 6.6 Hz	
Main chain	Methylene $-O-\underline{CH_2}-CH-O$	6.230	0.07	0.08			
		6.255	0.16	0.12	mmm	0.20	6.25
	(15%)	6.278	0.21	0.19	[mmr + rmr]	0.28 0.10	6.29
		6.300	0.19	0.22			
		6.320	0.16	0.15	mrr	0.20	6.31
		6.344	0.15	0.10	[mrm +	0.14	6.36
		6.364	0.06	0.08	rrr]	0.07	
						J_{AB} = - 5 Hz	

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[a] Bernoullian propagation with $P_m = 0.58$.

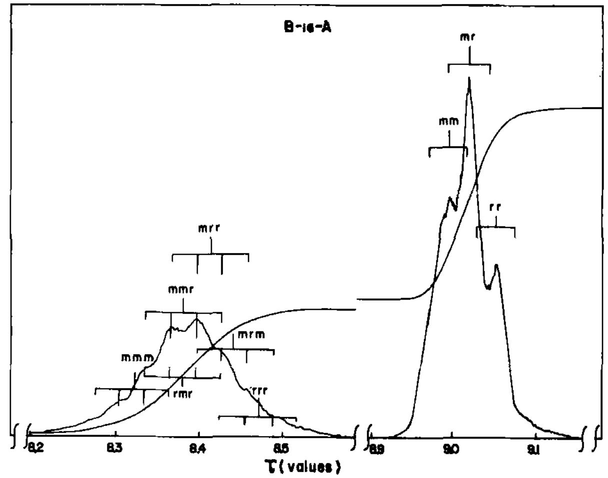


FIG. 3. 220 MHz NMR spectrum of the side-chain ethyl protons of poly(1,2-butylene oxide) B-16 in 15% w/v solution of o-$C_6H_4Cl_2$ at 100° C (B-16-A) showing the placement of three triads (8.9 to 9.2 τ) and six tetrads (8.2 to 8.6 τ) (cf. Table 2 for other data).

8.2 and 8.6 τ. It was noted that if the tetrads mmm, mmr + rmr, mrr, mrm, and rrr are placed at τ values of 8.32, 8.38, 8.41, 8.44, and 8.48, respectively, the resulting spectrum resembles that obtained experimentally. This is shown in Table 2, where the intensity based on the areas under the various peaks between τ = 8.2 and 8.6 and these based on tetrad placement agree quite well.

In Fig. 4 is shown the NMR spectrum of the main-chain methine and methylene protons of the poly(1,2-butylene oxide) B-16. The spectrum between τ = 6.45 and 6.7 resembles that of the side chain methylene protons (τ = 8.2 to 8.6). The important peaks between 6.45 and 6.7 τ also appear at regular intervals of 6.6 Hz. Keeping in mind the spectrum of the side-chain methylene protons (τ = 8.2 and 8.6), the left-hand side of the spectrum of the main chain methylene protons was traced in dotted lines. The area for these protons was calculated and compared with the total area between 6.2 and 6.7 τ. It was observed that the area for the methylene protons (44 cm^2) is less than a 2/3 of the total area (80 cm^2), suggesting that a part of the methylene protons must lie somewhere else in the spectrum. An analyses of the proton spectrum between 6.2 and 6.35 τ reveals that these have peaks appearing at 5 Hz interval and represent 8.0 sq cm of surface area. It is possible that this residue also belongs to the main-chain methylene protons. The sum of the areas between 6.2 and 6.35 τ and between 6.4 and 6.7 (main-chain methylenes) now

TABLE 3. Assignment of Chemical Shifts, on the Basis of the Triad Population, for Various Tetrads and Pentads for Poly(1,2-butylene Oxide) sample T-2, NMR Spectrum Observed in o-$C_6H_4Cl_2$ at 100° C

	Nature of protons		Important peaks			Configuration placement		
	Location	Type	τ values	Intensity based on area	Intensity based on tetrad placement	Sequence	Relative intensity $P_m = 0.58$	Center τ values
Triads[a]	Side chain	Methyl $-CH_2-\underline{CH_3}$		0.33		mm		9.00
				0.49		mr		9.04
				0.18		rr		9.08
Tetrads	Side chain	Methylene $-\underline{CH_2}-CH_3$	8.30	0.03	0.03			
			8.33	0.06	0.07			
			8.36	0.10	0.11	mmm	0.20	8.35
			8.39	0.14	0.14			
			8.43	0.18	0.17	mmr	0.28	8.41
			8.46	0.16	0.16	rmr	0.10	8.45
			8.50	0.14	0.14	mrr	0.20	8.48
			8.53	0.10	0.09	mrm	0.14	8.52
			8.56	0.06	0.04			
			8.59	0.03	0.03	rrr	0.07	8.58
							$J_{AB} = -6.6$ Hz	

(continued)

TABLE 3 (continued)

	Nature of protons		Important peaks			Configuration placement		
	Location	Type	τ values	Intensity based on area	Intensity based on tetrad placement	Sequence	Relative intensity P_m = 0.58	Center τ values
Tetrads	Main chain	Methylene $-O-\underline{CH_2}-\underset{\vert}{CH}-O-$	6.440	0.02	0.02			
			6.455	0.03	0.03			
			6.470	0.05	0.07			
			6.486	0.09	0.10			
			6.498	0.07	0.06	mmm	0.20	6.486
			6.507	0.05	0.07			
			6.525	0.10	0.10			
			6.534	0.05	0.05	mmr	0.28	6.507
			6.543	0.06	0.05			
			6.550	0.06	0.04			
						rmr	0.10	6.558
			6.568	0.10	0.10			
			6.584	0.06	0.05			
			6.589	0.05	0.05			
			6.593	0.03	0.03	mrr	0.20	6.589

		6.611	0.05	0.07			
					mrm	0.14	6.605
		6.618	0.04	0.05			
		6.636	0.04	0.04	rrr	0.07	6.664
		6.659	0.03	0.03			
						J_{AB} = - 6.6 Hz	
		6.698	0.01	0.01			
Pentads Main chain	Methine –O–CH₂–$\underline{\text{CH}}$–O	6.230	0.01	0.01			
		6.245	0.02	0.02	rrrr	0.03	6.245
		6.261	0.03	0.03			
		6.277	0.03	0.05	mrrr	0.08	6.273
		6.293	0.04	0.05			
		6.308	0.04	0.05	mrrm	0.06	6.298
		6.324	0.04	0.07	rmrr	0.08	6.320
		6.340	0.10	0.09	rmrm	0.12	6.339
		6.356	0.10	0.09	rmmr	0.06	6.357
		6.372	0.09	0.08	mmrr	0.12	6.368
		6.388	0.08	0.08			
		6.404	0.11	0.11	mmrm	0.16	6.400
		6.420	0.15	0.13	mmmr	0.16	6.420
		6.439	0.07	0.09	mmmm	0.11	6.439
		6.455	0.04	0.04			
		6.471	0.01	0.01	Line width 3.5 Hz		

[a] Bernoullian propagation with $P_m = 0.58$.

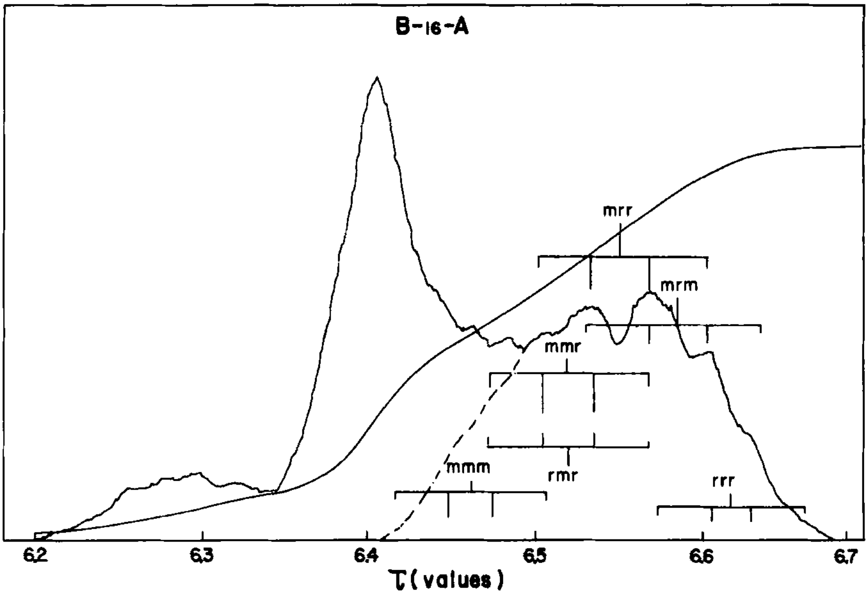


FIG. 4. 220 MHz NMR spectrum of the main chain protons of poly(1,2-butylene oxide) B-16 in 15% w/v solution of o–$C_6H_4Cl_2$ at 100° C (B-16-A) showing the placement of six tetrads (6.4 to.6.7 τ) (cf. Table 2 for other data).

represents 2/3 of the total main-chain protons ($O-CH_2-\underset{|}{C}H-O$). The τ values for the various tetrads (J_{AB} = -6.6 Hz) viz., mmm, mmr + rmr, mrr, mrm, and rrr (τ = 6.4 to 6.7) are 6.46, 6.52, 6.55, 6.58, and 6.62, respectively. The τ values for tetrads (for the residual methylene protons between 6.2 and 6.35 τ) mmm, mmr + rmr, mrr, and mrm + rrr are 6.25, 6.29, 6.31, and 6.36, respectively, with a J_{AB} of -5 Hz. The methine protons of the main chain appear centered at 6.41 τ. The pentad analyses of these protons was thus not possible in the case of poly(1,2-butylene oxide) B-16. However, in another sample of poly(1,2-butylene oxide), T-2, which has very low molecular weight, the analyses of both tetrads and pentads was possible and the results are discussed below.

In Fig. 5 is shown the NMR spectrum of the ethyl region of poly(1,2-butylene oxide) T-2 observed in o–$C_6H_4Cl_2$ at 100° C. The peaks located between 8.9 and 9.2 τ are due to the methyl protons and those at 9.0, 9.04, and 9.08 τ are attributed to mm, mr, and rr

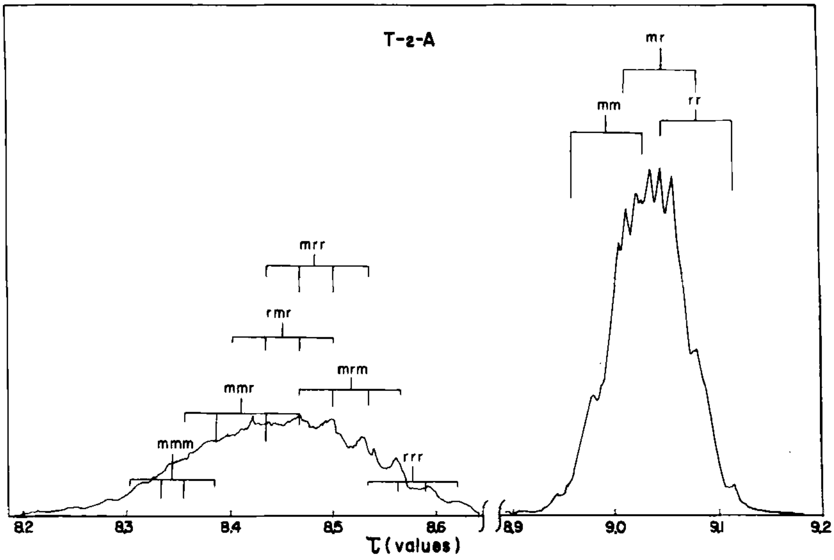


FIG. 5. 220 MHz NMR spectrum of the side-chain ethyl protons of poly(1,2-butylene oxide) T-2 in 15% w/v solution of o–$C_6H_4Cl_2$ at 100° C showing the placement of triads and tetrads (cf. Table 3 for other data).

triads, respectively, having relative intensity of 0.33, 0.49, and 0.18 (see Table 3). Once again, by making use of the triad intensity in combination with equations relating configurational statistics and propagation mechanism [18], it can be concluded that the cationic polymerization of 1,2-butylene oxide (T-2) obeys Bernoullian propagation with $P_m = 0.58$. Based on this value the intensity for the six tetrads, viz., mmm, mmr, rmr, mrr, mrm, and rrr are 0.20, 0.28, 0.10, 0.20, 0.14, and 0.07, respectively. Using these values, quartets representing all of the six tetrads were placed (stick plot on Fig. 5) between τ values of 8.3 and 8.6 in order to simulate the spectrum of the methylene protons. It was noted that the best fit was obtained when the tetrads mmm, mmr, rmr, mrr, mrm, and rrr were placed at 8.35, 8.41, 8.45, 8.48, 8.52, and 8.58 τ, respectively. The J_{AB} value for these quartets was found to be -6.6 Hz.

In Fig. 6 is presented the NMR spectrum of the main-chain methylene and methine protons of poly(1,2-butylene oxide) oligomeric products T-2 observed in o–$C_6H_4Cl_2$. The important peaks in this spectrum and their relative intensity are given in Table 3. Based on

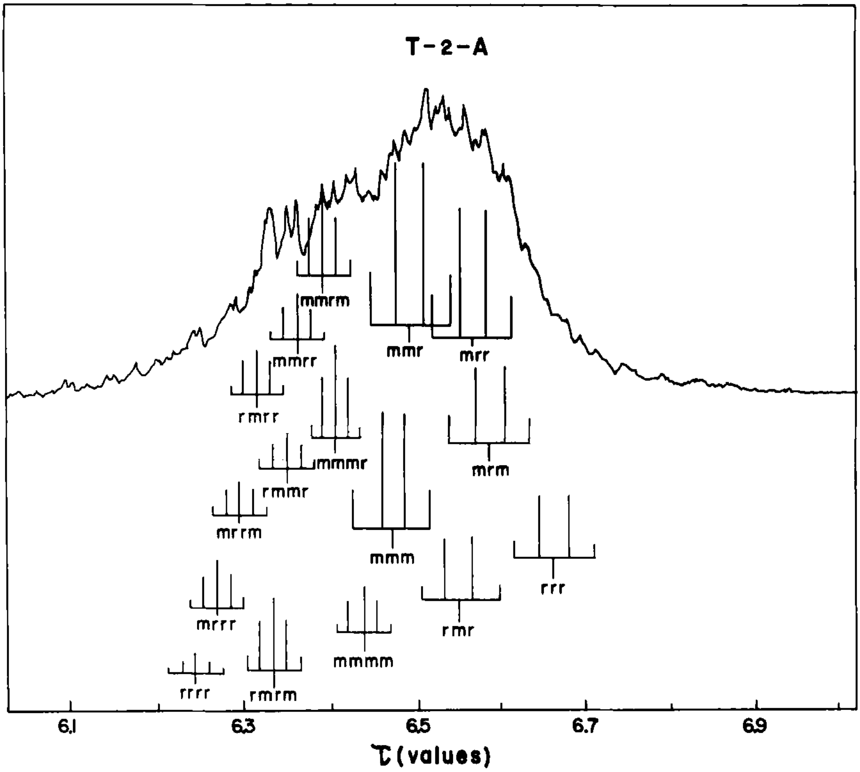


FIG. 6. 220 MHz NMR spectrum of the main-chain protons of poly(1,2-butylene oxide) T-2 in 15% w/v solution of o-$C_6H_4Cl_2$ at 100°C showing the placement of ten pentads (6.2 to 6.5 τ) and six tetrads (6.4 to 6.7 τ) (cf. Table 3 for other data).

the value of $P_m = 0.58$, the intensity of various tetrads and pentads were calculated. By making use of these intensity values, pentads and tetrads were traced and placed between τ values of 6.2 and 6.7 in order to simulate the spectrum of T-2 (Fig. 6). It was observed that the best fit between the experimental and the theoretical spectra was obtained when the six tetrads, viz., mmm, mmr, rmr, mrr, mrm, and rrr, were centered at 6.486, 6.507, 6.558, 6.589, 6.605, and 6.664 τ, respectively, whereas the ten pentads, viz., rrrr, mrrr, mrrm, rmrr, rmrm, rmmr, mmrr, mmrm, mmmr, and mmmm were placed at 6.245, 6.273, 6.298, 6.320, 6.339, 6.357, 6.368, 6.400, 6.420, and 6.439 τ, respectively (Table 3). The values of geminal coupling J_{AB}

for the meso- and racemic-centered tetrads were found to be -6.6 Hz. The values of the vicinal couplings J_{AX} and J_{BX} as determined from their line positions were 4.0 and 3.5 for the meso-centered tetrads and 1.6 and 5.2 for the racemic-centered tetrads, respectively. Furthermore although the mean tetrad chemical shift moves upfield on replacing m dyads by r dyads, the mean pentad chemical shifts show a reverse trend.

Anionic Polymerization Products

In an earlier publication [4] it was shown with the help of NMR spectra that the products of the anionic polymerization of 1,2-butylene oxide are not the conventional polymers with repeat monomer units. The IR spectra of one fraction M-b of the anionic products showed the presence of double bonds and hydroxyl groups whereas the other (M-a) did not. This second fraction did show, however, a strong peak at 1735 cm^{-1} corresponding to a certain C–O arrangement. In the previous study [4] an attempt was made to elucidate the reactions leading to the formation of products M-b and M-a. Although it was possible to speculate on the reaction leading to M-b, the formation of produce M-a could not be accounted for. In the present study some additional data have been obtained on the NMR of these polymers which may help to clarify the problem.

Analyses of Polymer M-b

In Fig. 7 are shown the NMR spectra of products M-a and M-b. On the basis of the NMR spectra of M-b it had been concluded earlier [4] that the main structure of this polymer must be derived from structures II or III.

$CH_3{-}CH_2{-}CH{=}CH{-}CH_2{-}\overline{O}$

II

$CH_3{-}CH_2{-}CH_2{-}CH{=}CH{-}\overline{O}$

III

This conclusion was reached solely on the basis that a well defined spectrum such as that of M-b must originate from repeat units of a single entity rather than from mixture of polymers which could also account for the observed proton intensity of the various groups responsible for the NMR spectrum (Fig. 7). In order to obtain

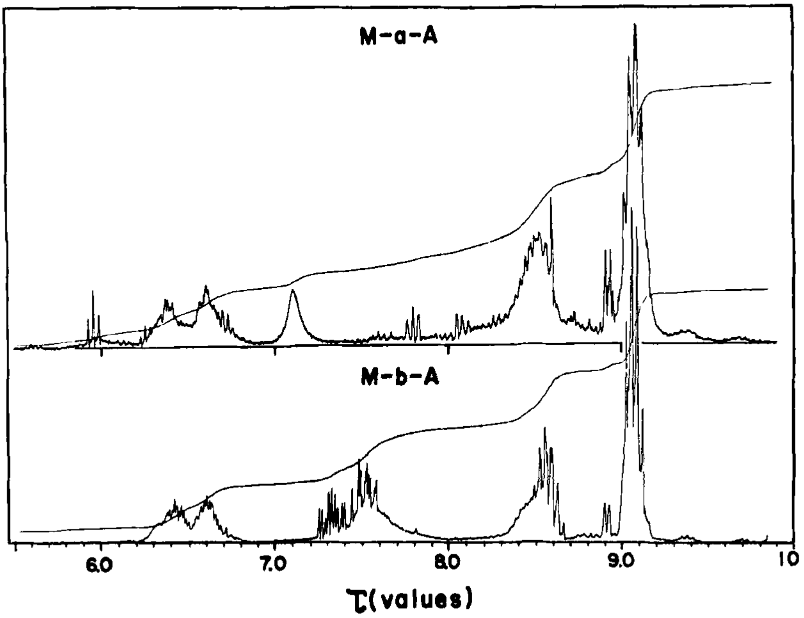
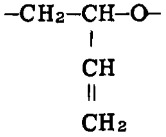


FIG. 7. 220 MHz NMR spectra of anionic products M-a and M-b in 15% w/v solution of o-$C_6H_4Cl_2$ at 100° C.

monomers of the type II or III, more than one molecule of 1,2-butylene oxide is required in the reaction with the sodium metal initiator. The reaction mechanism leading to the formation of II or III is hard to imagine.

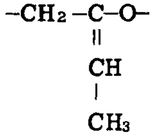
If, on the other hand, one considers the possibility that the products yielding the spectrum M-b are made up of mixture of polymers, then there are various structures which can yield double bonds and hydroxyl groups. In a first approach, one shall consider that one molecule of monomer reacts with the sodium initiator and that two protons are eliminated to form a double bond. Structures IV to VI represent the products of such reactions having both main-chain and side-chain protons.

In a second approach one must then consider the possibility that the reaction of 1,2-butylene oxide with sodium metal will eliminate only one proton to yield a double bond. In this reaction, all of the protons form a monofunctional chain as suggested by Simons and Verbanc [5] in their work on the polymerization of propylene oxide with sodium metal. Structures VII, VIII, and IX present such a case.



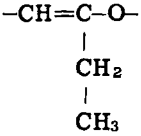
$$-CH_2-\underset{\begin{array}{c}|\\ CH\\ \|\\ CH_2\end{array}}{CH}-O-$$

IV



$$-CH_2-\underset{\begin{array}{c}\|\\ CH\\ |\\ CH_3\end{array}}{C}-O-$$

V



$$-CH=\underset{\begin{array}{c}|\\ CH_2\\ |\\ CH_3\end{array}}{C}-O-$$

VI

$CH_2=CH-CH_2-CH_2-\overline{O}$

VII

$CH_3-CH=CH-CH_2-\overline{O}$

VIII

$CH_3-CH_2-CH=CH-\overline{O}$

IX

In the earlier study [4] only the possibility of the presence of structures IV to VI was discussed, and it was pointed out that a mixture X of about 30% of structure IV, 4% of structure V and 66% of structure VI could yield the necessary proportions of the different proton groups observed. Similarly a mixture Y containing 23% of structure VII, 4% structure VIII, and 73% of structure IX could also satisfy the spectrum of M-b observed in o–$C_6H_4Cl_2$ at 100° C. In order to justify the concept that mixtures of different polymer structures are responsible for the NMR spectrum of M-b, it must be shown that the two methylene protons of structure IV, which are in different environment and which contribute in mixture X a major proportion towards the $-CH_2$ protons appearing between 7.0 and 8.0 τ, are equivalent. This should also be true for structure VII present in mixture Y whose three methylene protons are in different environment. These must also be equivalent in order that their τ values fall between 7.0 and 8.0.

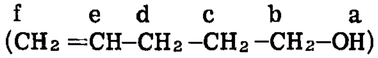
To verify this point the NMR spectra of three unsaturated alcohols, 3-buten-1-ol:

$(\overset{f}{CH_2}=\overset{e}{CH}-\overset{d}{CH_2}-\overset{b}{CH_2}-\overset{a}{OH})$

2-buten-1-ol:

$(\overset{i}{CH_3}-\overset{h}{CH}=\overset{g}{CH}-\overset{b}{CH_2}-\overset{a}{OH})$

and 4-penten-1-ol:



$$\overset{f}{(CH_2}{=}\overset{e}{CH}{-}\overset{d}{CH_2}{-}\overset{c}{CH_2}{-}\overset{b}{CH_2}{-}\overset{a}{OH)}$$

were observed in o–$C_6H_4Cl_2$ (100° C), CCl_4 (75° C), and DMSO-d_6 (110° C). The chemical shifts of the various protons in the three solvents are listed in Table 4. Furthermore the NMR spectra of 3-buten-1-ol, whose structure resembles that of structure VII, in three solvents is shown in Fig. 8. From Table 4 and Fig. 8 it can be seen that the three methylene protons b, d, and f in 3-buten-1-ol fall between (6.35-6.41), (7.69-7.78), and (4.91-5.01), respectively, when the spectrum was observed in o–$C_6H_4Cl_2$. These results tend to refute the concept that a mixture of different polymer structures is responsible for the final spectrum of M-b.

The possibility that polymer M-b is made up of structures II or III must next be considered. In both of these structures the ethyl protons $CH_3{-}CH_2\underline{-}$ should show identical chemical shifts. The methine protons $-CH{=}CH{-}\overline{O}$ of structure III should have slightly lower τ values as compared to those in structure II ($-C\underline{H}{=}C\underline{H}{-}\overline{CH_2}-$) because in the former structure these are attached to an electronegative oxygen atom which would move them downfield. However, this difference in the chemical shifts of the methine protons of structure II and III may not be sufficiently pronounced to establish which of the structures is the dominant one. The methylene protons ($={CH}{-}C\underline{H}_2{-}\overline{O}$) of structure II and those $-(CH_2{-}C\underline{H}_2{-}CH{=})$ of structure III, however, should yield conclusive evidence since each should show different chemical shifts. In structure II these are flanked by oxygen molecules and resemble those present in the cationic product B-16 discussed earlier. In the NMR spectrum of B-16 observed in o–$C_6H_4Cl_2$, these protons appeared between 6.43 and 6.66 τ. However, in the spectrum of M-b the same methylene protons appeared between 7.2 and 7.8 τ, which tends to refute structure II and supports structure III, whose methylene protons should appear at τ values higher than 6.66. Although the chemical shifts of the CH_2 protons lend support to their being part of structure III, their multiple peak spectrum would favor structure II as will be discussed later on. Thus both structures II and III have been retained for the present study.

From the results in Table 4, two interesting observations can be made: (1) changing the solvent and the temperature does not affect the chemical shifts of most protons except those attached to oxygen atoms; (2) protons attached to oxygen move to lower field on D_2O exchange as well as when the solvent is changed successively from o–$C_6H_4Cl_2$ to CCl_4 to DMSO-d_6.

The study of the downfield movement of protons attached to oxygen revealed a few other interesting observations. For example, in the

TABLE 4. τ Values for the Various Protons of 2-Buten-1-ol, 3-Buten-1-ol and 4-Penten-1-ol Dissolved in Different Solvents

Solvent-alcohol combinations	τ values for the various types of protons								
	a	b	c	d	e	f	g	h	i
o–$C_6H_4Cl_2$, 2-Bu-1-ol	7.83 7.47[a]	5.82-5.99	-	-	-	-	4.32	4.55	8.35-8.41
CCl_4, 2-Bu-1-ol	7.38	5.89-6.05	-	-	-	-	4.27	-4.55	8.30-8.36
DMSO-d_6, 2-Bu-1-ol	6.10	5.91-6.05	-	-	-	-	4.27	-4.64	8.36-8.42
o–$C_6H_4Cl_2$, 3-Bu-1-ol	7.69 7.44[a]	6.35-6.41	-	7.69-7.78	4.13-4.32	4.91-5.01	-	-	-
CCl_4, 3-Bu-1-ol	7.43	6.38-6.44	-	7.69-7.78	4.11-4.30	4.89-4.99	-	-	-
DMSO-d_6, 3-Bu-1-ol	5.94	6.49-6.55	-	7.76-7.85	4.07-4.25	4.92-5.04	-	-	-
o–$C_6H_4Cl_2$, 4-Pen-1-ol	7.85 7.45[a]	6.38-6.44	8.32-8.44	7.85-7.95	4.12-4.30	4.97-5.09	-	-	-
CCl_4, 4-Pen-1-ol	7.38	6.41-6.47	8.31-8.44	7.83-7.92	4.09-4.32	4.95-5.08	-	-	-
DMSO-d_6, 4-Pen-1-ol	6.18	6.52-6.58	8.40-8.52	7.88-7.97	4.10-4.29	4.95-5.08	-	-	-

[a] D_2O exchange.

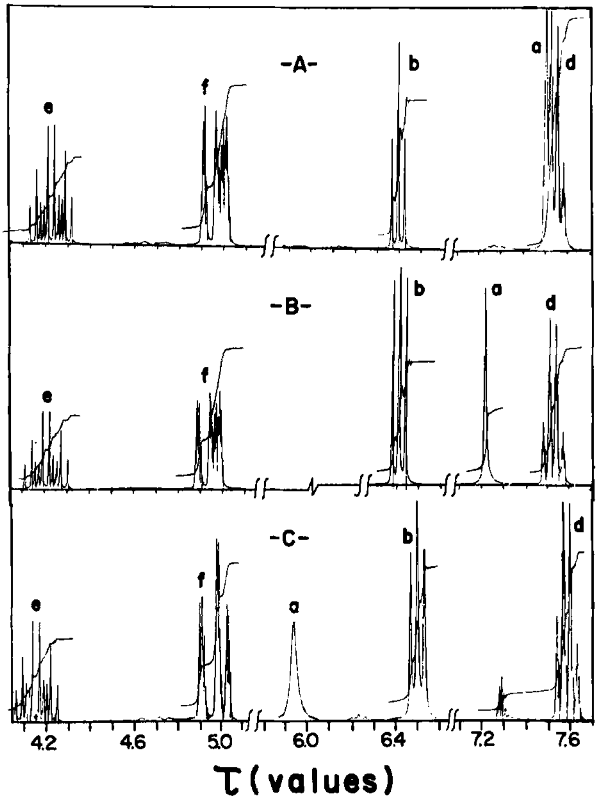


FIG. 8. 220 MHz NMR spectra of 3-buten-1-ol observed (A) in 15% w/v solution of o–$C_6H_4Cl_2$ at 100°C, (B) in CCl_4 at 75°C, and (C) in DMSO-d_6 at 110°C (cf. Table 4 for other data).

NMR spectrum of the $-CH_2OH$ part of 2-buten-1-ol observed in 15% solution of DMSO-d_6 at 110°C a doublet was seen at 5.96 and 5.98 τ with a slight hump at 5.99 τ, and a singlet was observed at 6.1 τ. When the NMR spectrum was recorded out of a 10% solution in DMSO-d_6 at 100°C, there was a downfield movement (to $\tau = 5.88$) of a part of the protons appearing at 5.98 τ. In this spectrum, the earlier singlet observed at 6.1 τ now appeared as a doublet at 6.09 and 6.11 τ as is shown in Fig. 9.

In yet another experiment, the NMR spectrum of the $-CH_2OH$ part of 4-penten-1-ol observed in 15% solution of DMSO-d_6 at 110°C yielded a singlet at 6.18 τ and a 1:2:1 triplet at 6.52, 6.55 and 6.58 τ

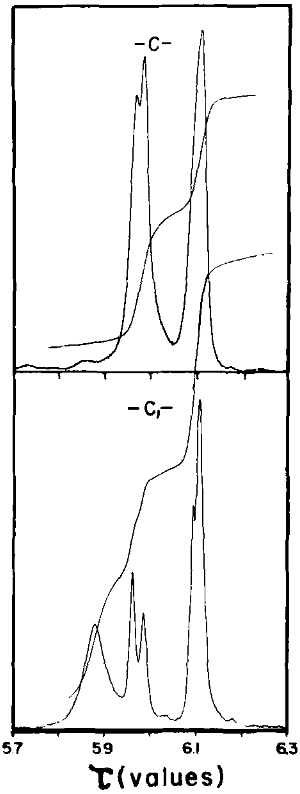


FIG. 9. 220 MHz NMR spectra of $-CH_2OH$ part of 2-buten-1-ol observed: (C) in 15% w/v solution of DMSO-d_6 at 110°C and (C_1) in 10% w/v solution of DMSO-d_6 at 100°C.

respectively. When the same spectrum was recorded in 10% solution of DMSO-d_6 at 100°C, the singlet at 6.18 moved downfield and appeared as a triplet at 5.93, 5.95, and 5.97 τ whereas the 1:2:1 triplet at 6.52, 6.55, and 6.58 τ became a quartet and appeared at 6.52, 6.545, 6.57, and 6.60 τ as shown in Fig. 10. These changes (multiple peaks in one case and singlet in the other) in the spectra of the $-CH_2OH$ protons may be attributed to the process of rapid proton-transfers between different alcohol molecules leading to collapse of spin-spin fine structure. Similar observations have been made in the case of ethyl alcohol [24].

These results clearly indicate the importance of making a proper choice of solvent for NMR studies on alcohols including polyalcohols

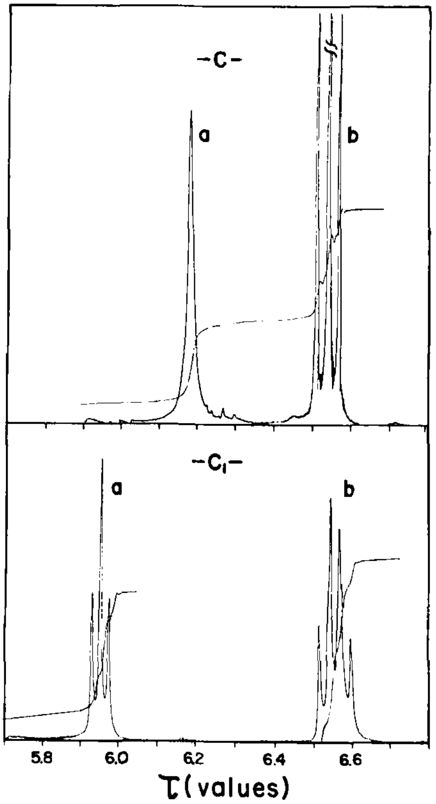


FIG. 10. 220 MHz NMR spectra of $-CH_2OH$ part of 4-penten-1-ol observed (C) in 15% w/v solution of DMSO-d_6 at 110°C and (C_1) in 10% w/v solution of DMSO-d_6 at 100°C.

as in the present case. Keeping this in mind the NMR spectrum of product M-b was observed in different solvents.

Effect of Solvent Type on the Quality of the Spectrum of Polymer M-b

In Fig. 11 are shown the NMR spectra of the ethyl region of the anionic products M-b observed in three solvents, viz., o-$C_6H_4Cl_2$, CCl_4, and DMSO-d_6. In o-$C_6H_4Cl_2$ the methyl protons show four peaks at 9.02, 9.05, 9.08, and 9.12 τ (Table 5), whereas in CCl_4

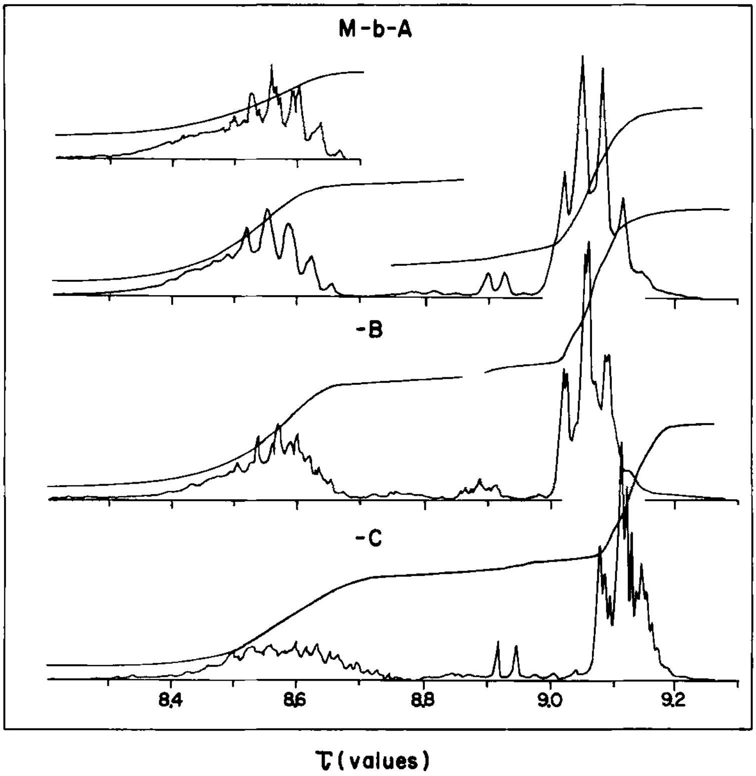


FIG. 11. 220 MHz NMR spectra of the ethyl region of polymer M-b observed (M-b-A), in 15% w/v solution of o–$C_6H_4Cl_2$ at 100° C, (M-b-B) in CCl_4 at 75° C, and (M-b-C) in DMSO-d_6 at 110° C.

(Table 6) these protons show only three peaks in the form of doublets, at (9.023, 9.030), (9.059, 9.064), and (9.091, 9.098) τ. In DMSO-d_6 (Table 7) these protons appear as three peaks in the form of triplets, at (9.084, 9.092, 9.100), (9.118, 9.127, 9.134), and (9.150, 9.159, 9.168) τ. These methyl protons appear at the same τ values in o–$C_6H_4Cl_2$ and in CCl_4, but move upfield on changing to DMSO-d_6 as the solvent. The same is true for the methylene protons of the ethyl groups which likewise move upfield on changing the solvent and follow the same trends as those of the methyl groups.

In Fig. 12 are shown the NMR spectra of the methylene protons (other than those in the ethyl protons) of polymer M-b observed in o–$C_6H_4Cl_2$, CCl_4, and DMSO-d_6 as solvents. In o–$C_6H_4Cl_2$, these

TABLE 5. Assignment of Chemical Shifts on the Basis of the Analyses of the Triad Population for Various Tetrads and Pentads for the Oligomeric Product M-b Originating from the Anionic Polymerization of 1,2-Butylene Oxide, NMR Spectrum Observed in o–$C_6H_4Cl_2$ at 100°C

		Important peaks				Configuration placement		
						Relative intensity		
	Nature of protons	τ values	Intensity based on area	Intensity based on tetrad placement	Sequence	1st order Markov $P_{m/r} = 0.61$ $P_{r/m} = 0.72$	From diads and triads	Center τ values
Triads[a]	Methyl $\underline{CH_3}$–CH_2–		0.21		mm			9.02
			0.37		mr			9.05
			0.29		rm			9.08
			0.13		rr			9.12
Tetrads	Methylene CH_3–$\underline{CH_2}$–	8.35	0.02	0.01				
		8.39	0.04	0.03	mmm	0.08	0.09	8.40
		8.42	0.07	0.06				
		8.45	0.09	0.11	mmr	0.26	0.30	8.46
		8.48	0.12	0.12				
		8.51	0.15	0.16	rmr	0.20	0.24	8.53
		8.545	0.22	0.23	mrm	0.24	0.20	8.56
		8.58	0.19	0.19	mrr	0.18	0.18	8.56

	8.62	0.07	0.07				
	8.65	0.01	0.01	rrr	0.04	0.03	8.65
					J_{AB} = -6.6 Hz		
Methylene $CH_3-CH_2-\underline{CH_2}$	7.250						
	7.264			Two AB type quartets			
	7.286			J_{AB} = -8.0 Hz			
	7.300	0.21		J_{AX} = 3.5 Hz	like		
	7.305			J_{BX} = 3.0 Hz	signs		
	7.323						
	7.341						
	7.355						
	7.382			Quartet and a singlet			
	7.395			J_{AB} = -11 Hz			
	7.439	0.28		J_{AX} = 11 Hz	unlike		
	7.477			J_{BX} = 10 Hz	signs		
	7.490						
	7.477						
	7.486						
	7.516			Two AB type quartets			
	7.525	0.35		J_{AB} = -8.5 Hz			

(continued)

TABLE 5 (continued)

		Important peaks				Configuration placement		
						Relative intensity		
	Nature of protons	τ values	Intensity based on area	Intensity based on tetrad place-ment	Sequence	1st order Markov $P_{m/r} = 0.61$ $P_{r/m} = 0.72$	From diads and triads	Center τ values
		7.539						
		7.545			$J_{AX} = 2.15$ Hz	unlike signs		
		7.577			$J_{BX} = 2.65$ Hz			
		7.584						
		7.6 to 7.9	0.16		No pattern			
Pentads	Methine $-CH{=}\underline{CH}-O$	6.341	0.06	0.07	mmmm	0.03		6.341
		6.366	0.07	0.11	mmrm	0.19		6.359
		6.386	0.10	0.12	mmmr	0.10		6.373
		6.410	0.11	0.14	mmrr	0.07		6.386
		6.431	0.17	0.15	mrmr	0.29		6.419
		6.457	0.13	0.13	rmmr	0.06		6.431
		6.475	0.13	0.10	mrrm	0.06		6.457
		6.486	0.07	0.08	rmrr	0.08		6.475

		6.500	0.06	0.06	mrrr	0.11	6.486
		6.525	0.08	0.03	rrrr	0.01	6.500
Pentads	Methine $-\underline{\mathrm{CH}}=\mathrm{CH}-\mathrm{O}$	6.525	0.06	0.07	mmmm	0.03	6.525
		6.543	0.11	0.11	mmrm	0.19	6.543
		6.568	0.13	0.12	mmmr	0.10	6.568
		6.586	0.14	0.14	mmrr	0.07	6.586
		6.610	0.12	0.15	mrmr	0.29	6.595
		6.631	0.10	0.13	rmmr	0.06	6.610
		6.648	0.15	0.10	mrrm	0.06	6.623
		6.661	0.09	0.08	rmrr	0.08	6.648
		6.677	0.05	0.06	mrrr	0.11	6.661
		6.700	0.04	0.03	rrrr	0.01	6.677

[a] $P_{m/r} = 0.61$; $P_{r/m} = 0.72$; $P_{m/r} + P_{r/m} = 1.33$. The propagation does not conform to Bernoullian statistics but to first-order Markov statistics as shown in the tetrad analyses.

TABLE 6. Assignment of Chemical Shifts on the Basis of the Analyses of Triad Population, for Various Tetrads and Pentads for the Oligomeric Product M-b Originating from the Anionic Polymerization of 1,2-Butylene Oxide, NMR Spectrum Observed in CCl_4 at 75° C

		Important peaks			Configuration placement		
	Nature of protons	τ values	Intensity based on area	Intensity based on tetrad placement	Sequence	Relative intensity	Center τ values
Triads[a]	Methyl $\underline{CH_3}$–CH_2			0.21	mm		9.023, 9.030
				0.56	mr		9.059, 9.064
				0.23	rr		9.091, 9.098
Tetrads	Methylene CH_3–CH_2–CH_2	8.37	0.01	0.01			
		8.40	0.03	0.03			
		8.43	0.05	0.07	mmm	0.09	8.415
		8.46	0.09	0.10			
		8.50	0.12	0.12	mmr	0.26	8.48
		8.53	0.14	0.13			
		8.56	0.23	0.21	rmr	0.15	8.545
		8.595	0.20	0.20	[mrm	0.15	
		8.625	0.10	0.08	mrr]	0.25	8.577
		8.65	0.03	0.01	rrr	0.10	8.637
					J_{AB} = -6.6 Hz		

	Methylene $CH_3-CH_2-\underline{CH_2}$	7.209					
		7.223			Two AB type quartets		
		7.264			$J_{AB} = - 12.5$ Hz		
		7.280	0.29		$J_{AX} = 3.6$ Hz, $J_{BX} = 3.2$ Hz, like signs		
		7.391					
		7.409					
		7.448					
		7.461					
		7.332	0.48		No pattern		
		7.468					
		7.475			Two AB type quartets		
		7.491			$J_{AB} = -5$ Hz		
		7.498	0.23		$J_{AX} = 2.7$ Hz, $J_{BX} = 1.8$ Hz, like signs		
		7.518					
		7.532					
		7.541					
		7.555					
Pentads	Methine $-CH{=}\underline{CH}-O$	6.380	0.01	0.02	mmmm	0.04	6.380
		6.395	0.03	0.03			
		6.406	0.05	0.05	mmmr	0.10	6.406

(continued)

TABLE 6 (continued)

Nature of protons	Important peaks			Configuration placement		
	τ values	Intensity based on area	Intensity based on tetrad placement	Sequence	Relative intensity	Center τ values
	6.418	0.05	0.07			
	6.432	0.11	0.08			
	6.445	0.07	0.07	mmrm	0.13	6.445
	6.452	0.07	0.05	mmrr	0.11	6.452
	6.459	0.07	0.07			
	6.473	0.12	0.11	⌈mrmr	0.18	6.473
	6.484	0.07	0.09	⌊rmmr	0.08	
	6.495	0.06	0.05	mrrm	0.07	6.484
	6.502	0.07	0.07			
	6.514	0.09	0.09	⌈rmrr	0.13	6.514
	6.527	0.07	0.06	⌊mrrr	0.11	
	6.539	0.05	0.03			
	6.550	0.03	0.02	rrrr	0.05	6.550
Methine $-\underline{CH}=CH-O$	6.561	0.02	0.01			

6.573	0.03	0.03	mmmm	0.04	6.580
6.580	0.04	0.04	mmmr	0.10	
6.591	0.05	0.05			
6.600	0.05	0.06			
6.611	0.07	0.07	mmrm	0.13	6.611
6.618	0.08	0.07			
6.629	0.08	0.08			
6.641	0.12	0.12	mrmr	0.18	6.641
6.655	0.08	0.11			
6.668	0.12	0.10	rmrr	0.13	6.668
6.684	0.07	0.10	rmmr	0.08	6.684
6.695	0.09	0.09	mmrr	0.11	
			mrrm	0.07	6.695
6.707	0.04	0.06	mrrr	0.11	6.707
6.718	0.02	0.03	rrrr	0.05	6.718

[a] $P_{m/r} = 0.57$; $P_{r/m} = 0.55$; $P_{m/r} + P_{r/m} = 1.12$. The propagation does not conform to Bernoullian statistics but to first-order Markov statistics.

TABLE 7. Assignment of Chemical Shifts on the Basis of the Analysis of Triad Population for Various Tetrads and Pentads for the Oligomeric Products M-b Originating from the Anionic Polymerization of 1,2-Butylene Oxide, NMR Spectra Observed in DMSO-d_6 at 110°C

		Important peaks			Configuration placement		
	Nature of protons	τ values	Intensity based on area	Intensity based on tetrad place-ment	Sequence	Relative intensity	Center τ values
Triads[a]	Methyl $\underline{CH_3}$–CH_2–		0.25		mm		9.084, 9.092, 9.100
			0.56		mr		9.118, 9.127, 9.134
			0.19		rr		9.150, 9.159, 9.168
Tetrads	Methylene CH_3–$\underline{CH_2}$	8.445	0.05	0.05	mmm	0.12	8.43
		8.473	0.09	0.08			
		8.510	0.13	0.12	mmr	0.26	8.49
		8.536	0.11	0.12	rmr	0.15	8.52
		8.562	0.12	0.12			
		8.590	0.15	0.16	mrr	0.23	8.605
		8.623	0.17	0.16	rrr	0.08	8.640
		8.659	0.12	0.12			

		8.690	0.06	0.07	mrm	0.16	8.675
		8.720	0.02	0.02	J_{AB} = -6.6 Hz		
	Methylene CH_3–CH_2–$\underline{CH_2}$–	6.8-7.2	0.71		No pattern		
		7.330					
		7.348					
		7.386			Two AB type quartets		
		7.405	0.29		J_{AB} = -12.5 Hz		
		7.527			J_{AX} = 4.0 Hz } like signs		
		7.545					
		7.582			J_{BX} = 4.0 Hz } like signs		
		7.600					
		7.468					
		7.477					
		7.486			DMSO-d_6 (nondeuterated residue)		
		7.495					
		7.502					
Pentads	Methine –CH=$\underline{CH}$–O	6.480	0.04	0.04	mmmm	0.05	6.486
		6.486	0.05	0.07	mmmr	0.12	
		6.493	0.05	0.05			
		6.500	0.05	0.05			

(continued)

TABLE 7 (continued)

Nature of protons	Important peaks			Configuration placement		
	τ values	Intensity based on area	Intensity based on tetrad placement	Sequence	Relative intensity	Center τ values
	6.507	0.06	0.06	mmrm	0.15	6.507
	6.514	0.04	0.04			
	6.518	0.04	0.03			
	6.527	0.08	0.07			
	6.541	0.09	0.11	mmrr	0.11	6.541
				mrmr	0.17	
	6.548	0.09	0.09			
	6.561	0.07	0.10	rmmr	0.07	6.561
	6.570	0.10	0.10	mrrr	0.09	6.570
				rmrr	0.13	
	6.584	0.07	0.09			
	6.593	0.08	0.06	mrrm	0.07	6.593
				rrrr	0.03	
	6.600	0.03	0.03			

Methine $-\underline{\mathrm{CH}}{=}\mathrm{CH}{-}\mathrm{O}$	6.600	0.04	0.04			
	6.609	0.07	0.07	mmmm	0.05	6.609
				mmmr	0.12	
	6.623	0.05	0.05			
	6.630	0.05	0.04			
	6.639	0.04	0.05	mmrr	0.11	6.639
	6.648	0.07	0.07			
	6.657	0.07	0.07			
	6.668	0.09	0.09	mmrm	0.15	6.657
	6.680	0.15	0.13	mrmr	0.17	6.680
	6.698	0.12	0.12			
	6.709	0.08	0.08	rmmr	0.07	6.698
	6.720	0.04	0.06	rmrr	0.13	
	6.727	0.04	0.06	mrrr	0.09	6.720
	6.739	0.03	0.03	mrrm	0.07	6.727
	6.750	0.01	0.01	rrrr	0.03	6.739

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[a] $P_{m/r} = 0.53$; $P_{r/m} = 0.59$; $P_{m/r} + P_{r/m} = 1.12$. The propagation does not conform to Bernoullian statistics but to first-order Markov statistics.

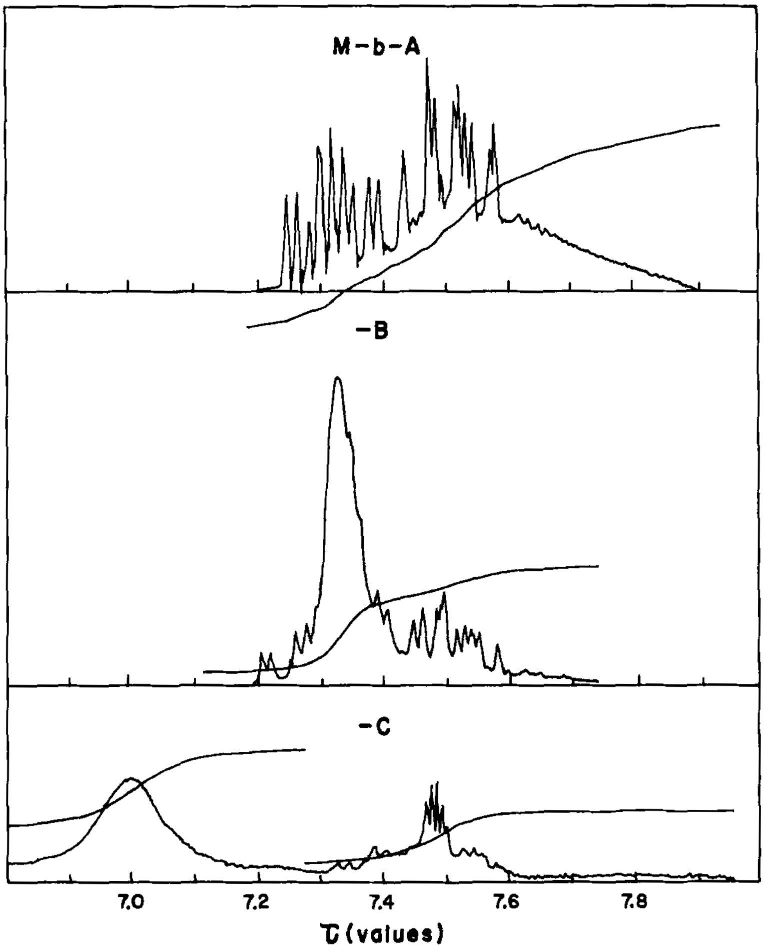

FIG. 12. 220 MHz NMR spectra of the methylene protons of polymer M-b observed (M-b-A) in 15% w/v solution of o–$C_6H_4Cl_2$ at 100° C, (M-b-B) in CCl_4 at 75° C, and (M-b-C) in DMSO-d_6 at 110° C.

protons appear between 7.2 and 7.9 τ, yielding 18 peaks (Table 5) which are located between 7.2 and 7.6 τ and represent 84% of this type of methylene protons, however, the region between 7.6 and 7.9 (remainder 16%) shows no trends. In CCl_4 these protons appear between 7.2 and 7.7 τ, with approximately 48% of the protons located at τ = 7.33 and the rest distributed evenly all over. In DMSO-d_6 these methylene protons appear between 6.8 and 7.6 τ with a major portion (71%) located between 6.8 and 7.2 τ and the rest between 7.2 and 7.6 τ. It may be noted that on changing the solvent from o–$C_6H_4Cl_2$ to CCl_4 and finally to DMSO-d_6 a portion of the methylene protons moves downfield. If a parallel is drawn between these results and those obtained with 3-buten-1-ol in different solvents, it may be concluded that these are not methylene portons but other protons attached to oxygen as are the hydroxyl protons. There are however some points which cast doubt on this conclusion. Firstly, the intensity of these protons is much too high since it would require nearly 3(–OH) groups per 2 monomer units to justify the high intensity (71%) of these protons appearing between 6.8 and 7.2 τ in DMSO-d_6 as the solvent. These protons then must form a part of the growing chain but the mechanism leading to the formation of such a monomer unit by the reaction of 1,2-butylene oxide with sodium metal is still more difficult to imagine. Such hydroxyl protons could not be located at the chain ends as these generally appear at τ values of about 5.4. It is quite possible that these protons form a part of the methylene protons which in DMSO-d_6 as solvent are brought very close to the oxygen atoms of the polymer, i.e., close enough for a loose hydrogen bonding to take place. In o–$C_6H_4Cl_2$ or in CCl_4 this effect is not so pronounced. It would appear that the strength of O- - -H bonding would follow the trend: o–$C_6H_4Cl_2$ < CCl_4 < DMSO-d_6.

In Fig. 13 are shown the NMR spectra of the methine protons observed in o–$C_6H_4Cl_2$ in CCl_4 and in DMSO-d_6. These protons appear between 6.2 and 6.7 τ in o–$C_6H_4Cl_2$, 6.36 to 6.8 in CCl_4, and 6.45 to 6.8 in DMSO-d_6. These protons move upfield on changing the solvent from o–$C_6H_4Cl_2$ to CCl_4 and finally to DMSO-d_6.

Analyses of the Spectra

Structures II and III were retained earlier in the text as these are thought to give NMR spectra similar to that observed for polymer M-b. With the object of obtaining further information and to simplify the spectra few additional experiments, e.g., spin decoupling and deuterium exchange, were carried out prior to analyzing these in terms of triad, tetrad, and pentad sequences. In Fig. 14 are shown a part of the NMR spectrum of polymer M-b observed in o–$C_6H_4Cl_2$ (M-b-A) along with that obtained after deuterium exchange (M-b-A_D).

In the region 7.2-7.6 τ instead of the 18 peaks in the NMR spectrum of the undeuterated polymer 19 peaks are present after the deuterium exchange. This helps us locating the 8th peak of the AB quartet in the region 7.25-7.355 τ. As for the methine protons, like the methylene protons, their chemical shifts move upfield after deuterium exchange which is not uncommon. Furthermore, the peak at 6.58 τ in the

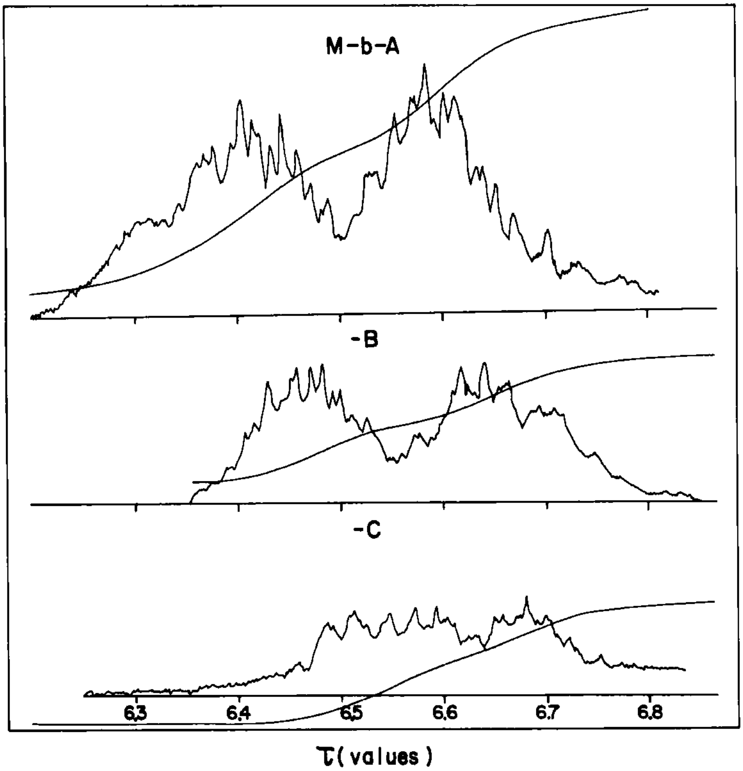

FIG. 13. 220 MHz NMR spectra of the methine protons of polymer M-b observed (M-b-A) in 15% w/v solution of o–$C_6H_4Cl_2$ at 100°C, (M-b-B) in CCl_4 at 75°C, and (M-b-C) in DMSO-d_6 at 110°C.

undeuterated polymer is displaced after the deuterium exchange, indicating that the methine protons, in a certain configuration sequence which appears at 6.58 τ, are affected by long-range coupling to protons attached to oxygen atoms.

In Fig. 15 are shown partial NMR spectra of polymer M-b observed in o–$C_6H_4Cl_2$ (M-b-A). The methine and the methylene protons between 6.0 and 8.0 τ have been decoupled from the methyls appearing between 9.0 and 9.2 τ by using spin decoupling technique. M-b-A-1 to M-b-A-4 (Fig. 15) show the decoupled protons irradiation being carried out at 9.12 τ, 9.08, 9.05, and 9.02 τ, respectively. When irradiation is carried out at 9.12, 9.08, and 9.05 τ there are no drastic changes in the resulting spectra of methine and methylene

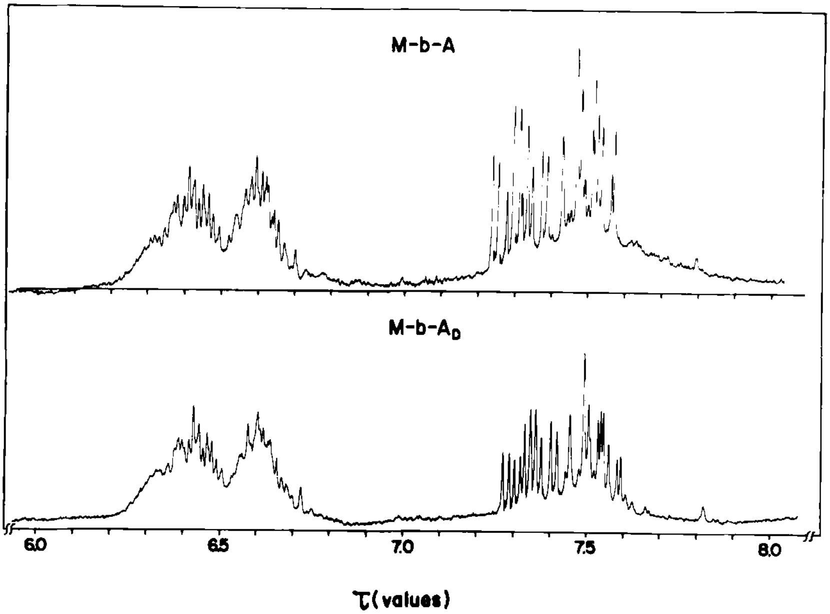

FIG. 14. 220 MHz NMR spectra of polymer M-b observed in 15% w/v solution of o–$C_6H_4Cl_2$ at 100° C: (M-b-A) before and (M-b-A$_D$) after deuteration in the range of 6.0 and 8.0 τ.

protons; however, irradiation at 9.02 τ has a very significant influence on the spectrum of the methine and methylene protons as witnessed by the degeneration of the spectrum instead of its improvement. It does indicate, nevertheless, that the methyl protons in a certain configuration appearing at 9.02 τ have a long range effect on the methine and the methylene protons. This is an additional point in favor of structures II or III (where methyl, methylene, and methine protons form part of the same chain) being retained as the structural model of polymer M-b. Based on the quality of the spectra shown in Figs. 11, 12, and 13 the placement of sequences is best shown with the spectra observed in o–$C_6H_4Cl_2$ as solvent. Thus the various parts of this spectrum have been expanded and greater emphasis has been placed on the discussion of the individual groups. The placement of sequences in the NMR spectra observed in CCl_4 and DMSO-d_6 has also been carried out and the results are listed in Tables 6, 7, and 8, however, these are not shown graphically.

In Fig. 16 is shown the NMR spectrum of the ethyl protons of polymer M-b. The four peaks at 9.02, 9.05, 9.08, and 9.12 τ have

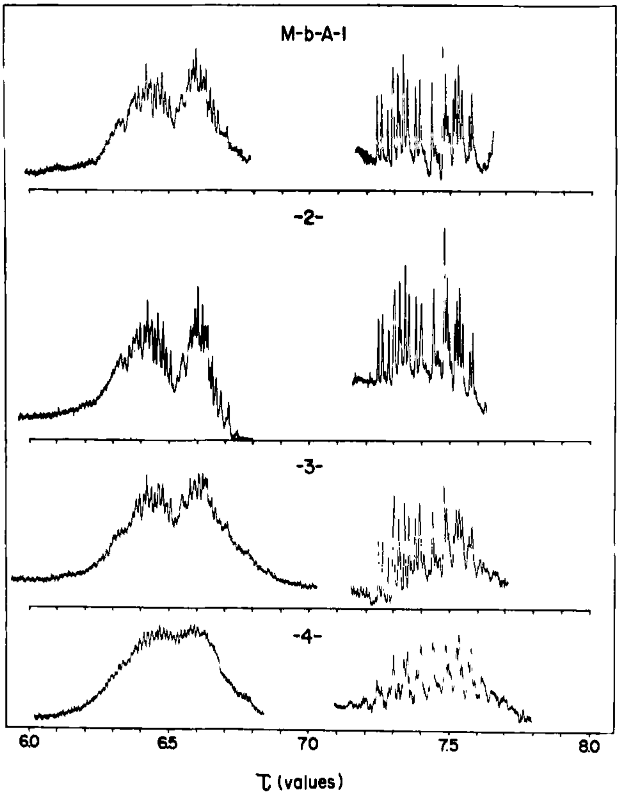

FIG. 15. 220 MHz NMR spectra of polymer M-b observed in 15% w/v solution of o-$C_6H_4Cl_2$ at 100° C in the range of 6.0 and 8.0 τ. Each spectrum was recorded after spin decoupling from a definite part of methyl protons by irradiation (M-b-A-1) at 9.12 τ, (M-b-A-2) at 9.08 τ, (M-b-A-3) at 9.05 τ, and (M-b-A-4) at 9.02 τ.

intensity of 0.21, 0.37, 0.29, and 0.13 (Table 5), which have been assigned to mm, mr, rm, and rr triads, respectively [19-23]. Making use of the triad intensity in combination with equations relating configurational statistics to the propagation mechanism [18] one arrives at the conclusion that the anionic polymerization of 1,2-butylene oxide leading to M-b does not obey Bernoullian propagation but rather conforms to a first-order Markov statistics with $P_{m/r} = 0.61$ and $P_{r/m} = 0.72$. Based on these values, the intensity of the six tetrads, viz., mmm, mmr, rmr, mrr, mrm, and rrr were calculated: 0.08, 0.26, 0.20, 0.24, 0.18, and 0.04, respectively.

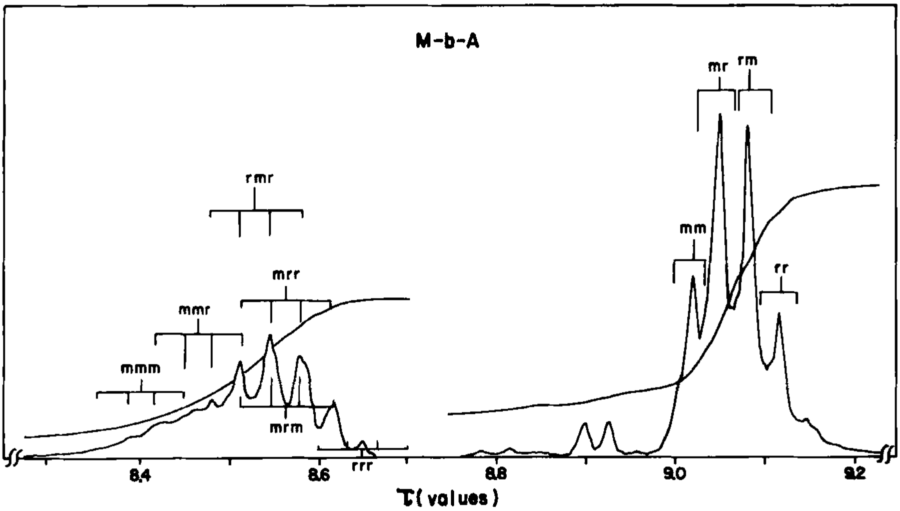

FIG. 16. 220 MHz NMR spectrum of the ethyl protons of polymer M-b observed in 15% w/v solution of o–$C_6H_4Cl_2$ at 100° C, showing the placement of four triads (9.0 to 9.2 τ) and six tetrads (8.25 to 8.7 τ) (cf. Table 5 for other data).

In Fig. 16 the methylene protons of the ethyl group appear between 8.25 and 8.7 τ, with important peaks at regular intervals of 6.6 Hz, indicating that the quartets, of which these methylene protons are built up, have a $J_{AB} = 6.6$ Hz. Making use of this value of J_{AB} in combination with the calculated intensity of the six tetrads quartets bearing peak ratios of 1:3:3:1 (stick spectra) were arranged to simulate the spectrum of the methylene protons. If the tetrads mmm, mmr, rmr, mrm + mrr, and rrr are placed at τ values of 8.40, 8.46, 8.53, 8.56, and 8.65, the resulting spectrum resembles that obtained experimentally. This is shown in Table 5, where the intensity based on areas under the various peaks between 8.35 and 8.7 τ and the intensity based on tetrad placement agree quite well.

In Fig. 17 is shown the NMR spectrum of the methylene protons which could be flanked by oxygen atoms and –CH-protons (structure II)

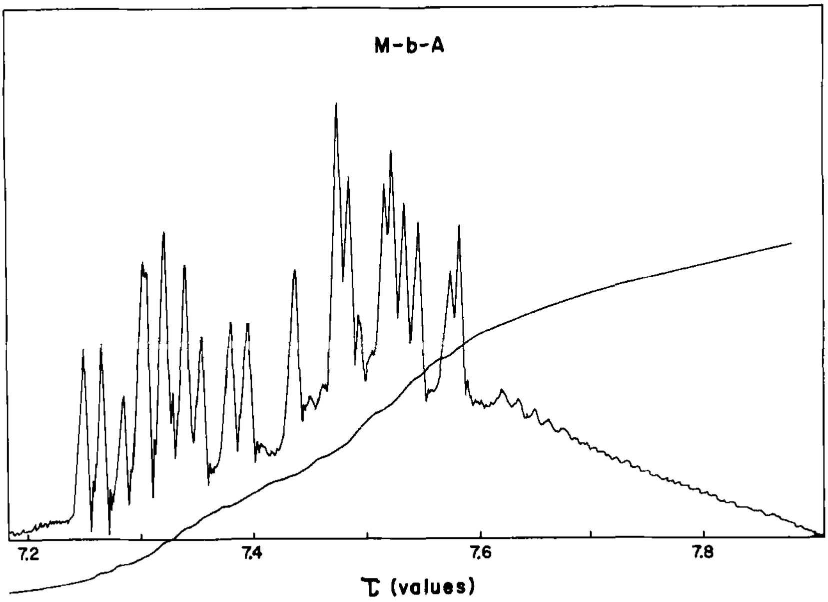

FIG. 17. 220 MHz NMR spectrum of the methylene protons of polymer M-b observed in 15% w/v solution of o–$C_6H_4Cl_2$ at 100° C in the range of 7.2 to 7.9 τ (cf. Table 5 for other data).

or $-CH_2$ and $=CH$ protons (structure III). These protons appear in the form of 18 peaks between 7.2 and 7.6 τ and between 7.6 and 7.9 τ where these show no trends. As discussed earlier, deuterium exchange on these protons gave rise to 19 peaks instead of the usual 18. The analysis of these peaks is summarized in Table 5. Between 7.25 and 7.355 there are eight peaks which resemble the peaks of two AB quartets with J_{AB} = -8.0 Hz, J_{AX} = 3.5 Hz, and J_{BX} = 3.0 Hz. These peaks have an intensity of 0.21. Between 7.382 and 7.490 τ the spectrum resembles that of a part of an AB quartet and a singlet with J_{AB} = -11 Hz, J_{AX} = 11 Hz, J_{BX} = -10 Hz and having an intensity of 0.28. Between 7.477 and 7.584 τ there are once again eight peaks which represent two quartets with J_{AB} = -.8.5 Hz, J_{AX} = 2.15 Hz, J_{BX} = 2.65 Hz having intensity of 0.35. Between 7.6 and 7.9, where the protons show no trends, the intensity is 0.16. The proton denoted by X in the calculation of the coupling constant is the nearest neighbor methine proton whether it be from structure II or III. Furthermore, the intensity of the methylene protons between 7.25 and 7.355 τ, 7.382 and 7.490 τ, 7.477 and 7.584 τ and 7.6 and 7.9 τ match the intensity of the methyls at 9.02, 9.08, 9.05, and 9.12 τ which have been assigned to mm, rm, mr, and rr triads. It would appear that for each of the four triad configurations there are corresponding proportions of methylene protons which in themselves exist in the meso and racemic forms. These resemble the intriguing combinations of geometrical and configurational isomerism in diene polymers [25] which can yield mixtures of cis-isotactic as well as trans-isotactic structures and so on. Although the multipeak spectrum of methylene protons gives rise to the speculation about the presence of geometrical and configurational isomerism, it also casts doubt on the possibility that structure III is the monomeric species responsible for polymer M-b. Structure II on the other hand could yield cis isotactic and trans isotactic type mixtures.

In Fig. 18 is shown the NMR spectrum of the –CH=CH– protons, observed in o–$C_6H_4Cl_2$ as solvent. Each of the two methine protons appear separately in the form of multiple peaks, the ones nearer to the electronegative groups, e.g., oxygen being downfield (6.34 to 6.52 τ) whereas the others are placed upfield (6.52 to 6.7 τ). The surface area of all of these peaks were calculated and are presented in Table 5. Based on the triad data of polymer M-b (Fig. 11A) and by making use of the equations established for the first-order Markovian model [18], the intensity of the ten pentads, viz., mmmm, mmrm, mmmr, mmrr, mrmr, rmmr, mrrm, rmrr, mrrr, and rrrr, were calculated and these are presented in Table 5. With the help of these pentad intensities, stick spectra of all of the ten pentads were traced and placed between 6.34 and 6.52 τ in order to simulate the spectrum of the methine protons appearing in that region. It was noted that on placing the ten pentads mentioned earlier at 6.341, 6.359, 6.373, 6.386, 6.419, 6.431, 6.457, 6.475, 6.486, and 6.500 τ, respectively, the intensity based on area and that based on the pentad placement agree well. Similar calculations were made for the methine protons appearing between 6.52 and 6.70 τ and it was noted that for the same order of pentad sequences the best fit is found on placing these at 6.525, 6.543, 6.568, 6.586, 6.595, 6.610, 6.623, 6.648, 6.661, and 6.677 τ, respectively. It appears that in polymer M-b on replacing the meso dyad by a racemic one, the mean chemical shifts move upfield when o–$C_6H_4Cl_2$ is used as solvent for observing the spectrum.

The graphical analyses similar to those presented in Figs. 16, 17, and 18 of the NMR spectra of polymer M-b observed in CCl_4 and DMSO-d_6 (cf. Figs. 11, 12, and 13) have not been included here; only the numerical data have been retained and are presented in Tables 6 and 7. The intensity of mm, mr, and rr triads (0.21, 0.66, and 0.13) in o–$C_6H_4Cl_2$ (Table 5), now have values of 0.21, 0.56, and 0.23, in CCl_4 and 0.25, 0.56, and 0.19 in DMSO-d_6. The differences are attributed to the resolving power of the solvent since the intensity

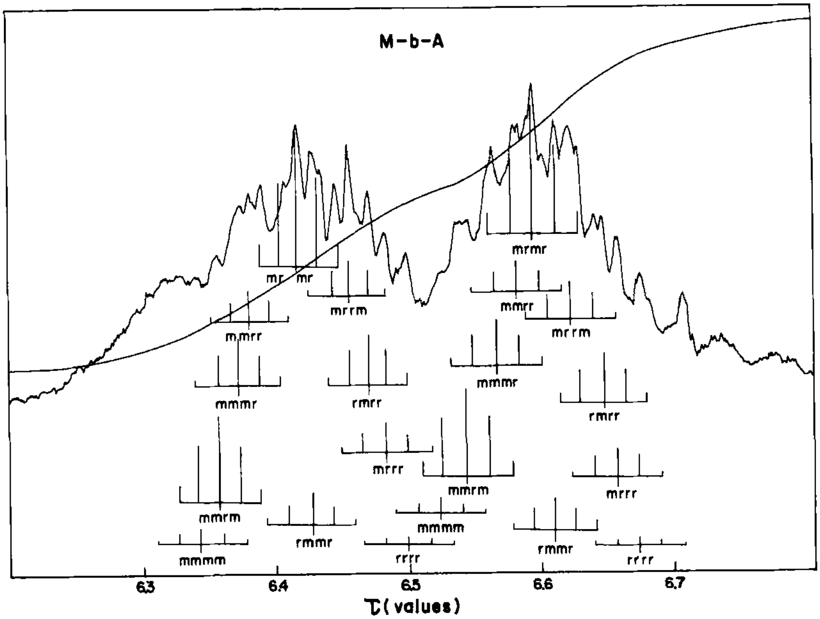

FIG. 18. 220 MHz NMR spectrum of the methine protons of polymer M-b observed in 15% w/v solution of o–$C_6H_4Cl_2$ at 100° C in the range of 6.2 and 6.8 τ showing the placement of the various pentads (cf. Table 5 for other data).

values of mm, mr, and rr triads for a given polymer sample are unique. An analysis involving NMR spectra of polymer M-b observed in CCl_4 and DMSO-d_6, in terms of tetrads and pentads, has been made on the methylene (CH_3–$\underline{CH_2}$–) and methine (–$\underline{CH}$=$\underline{CH}$–) protons, making use of the respective triad population data obtained in each of these solvents. The results are quite similar to those obtained with the spectrum of polymer M-b recorded in o–$C_6H_4Cl_2$ as solvent, viz., the mean chemical shift moves upfield on replacing the m dyads by r dyads. The methylene protons which appeared between 7.2 and 7.9 τ in o–$C_6H_4Cl_2$, 7.2 and 7.6 τ in CCl_4, and 6.8 and 7.5 τ in DMSO-d_6 do, however, show other interesting results. In CCl_4 these methylene protons appear as two AB type quartets between 7.2 and 7.46 τ with an intensity of 0.29 and J_{AB} = -12.5 Hz, J_{AX} = 3.6 Hz, and J_{BX} = 3.2 Hz. But another part of these methylenes, between 7.468 and 7.555 τ, has an intensity of 0.23 and shows two AB type quartets with J_{AB} = 5.0 Hz, J_{AX} = 2.7 Hz, and J_{BX} = 1.8 Hz. The rest of the methylenes appearing at 7.332 τ show no particular pattern.

Attempts to correlate these intensity values with those of the triad population (cf. Table 6) lead to the conclusion that within experimental error the two AB quartets between 7.21 and 7.46 τ correspond to the intensity of the mm triads, the two AB quartets between 7.468 and 7.555 correspond to rr triads, while those at 7.332 τ showing no particular patterns correspond to mr triads.

In DMSO-d_6, the same methylene protons appear between 6.8 and 7.2 τ with an intensity of 0.71 and show no patterns, while the remainder of these protons with intensity of 0.29 show two AB quartets having $J_{AB} = -12.5$ Hz, $J_{AX} = 4.0$ Hz, and $J_{BX} = 4.0$ Hz. These methylene protons with intensity of 0.29 correspond to mm triads (cf. Table 7) whereas those which show no trends represent the corresponding sum of mr and rr triads.

The results of the spectra analyses of the methylene protons of polymer M-b in three different solvents reveal a few curious observations. For example, the methylene protons with intensity of 0.29 (cf. Tables 6 and 7) which appear as two AB type quartets in CCl_4 and DMSO-d_6 and which have been related to mm triad configuration, have a $J_{AB} = -12.5$ Hz. When the spectrum of methylene protons related to mm triad configuration was analyzed in o–$C_6H_4Cl_2$ the J_{AB} value was found to be -8.0 Hz. Similarly the two AB quartets with intensity of 0.23 (Table 6, CCl_4 as solvent) and related to the rr triad configuration have a $J_{AB} = -5.0$ Hz, whereas there are no AB type quartets with this J_{AB} in either of the spectra observed in o–$C_6H_4Cl_2$ or DMSO-d_6. In the work of Hirano et al. [15] on poly(trans-propylene oxide-1-d), Tsuji et al. [17] on poly[(s)-isopropylethylene oxide] as well as Heatley and Bovey [26] on poly(vinyl chloride) when the spectra were recorded in different solvents the geminal coupling constants J_{AB} and the vicinal coupling constants J_{AC} and J_{BC} did not change by much. Furthermore, in these studies [15, 17, 26] the chemical shifts of the various protons also remain practically unchanged on changing the solvent.

The results obtained in this study may be attributed to geometrical and configurational isomerism similar to that observed in dienes [25] and epoxides [27] because of the presence of double bonds and oxygen atoms in polymer M-b.

As mentioned earlier, the intensity of the mm, mr, and rr triads calculated from the spectra recorded in o–$C_6H_4Cl_2$, CCl_4 and DMSO-d_6 is not the same. As the intensity of the tetrads and pentads listed in Tables 5, 6, and 7 were calculated from the intensity of the triad data obtained in the same solvent in which the spectrum was recorded, a comparison of their mean chemical shifts in different solvents may be questionable; however, to overcome this objection the data of triad intensity obtained from the spectrum recorded in o–$C_6H_4Cl_2$ (which appears to have the best resolution of all three solvents) was used to

TABLE 8. Comparison of Chemical Shifts for Various Tetrads and Pentads for the Oligomeric Product M-b Originating from the Anionic Polymerization of 1,2-Butylene Oxide, NMR Spectra Observed in o–$C_6H_4Cl_2$ at 100° C, CCl_4 at 75° C, and DMSO-d_6 at 110° C

			τ values		
	Nature of protons	Sequence	o–$C_6H_4Cl_2$	CCl_4	DMSO-d_6
Tetrads	Methylene $CH_3–\underline{CH_2}$	mmm	8.40	8.415	8.43
		mmr	8.46	8.48	8.49
		rmr	8.53	8.545	8.52
		mrm	8.56	8.58	8.575
		mrr	8.56	8.58	8.675
		rrr	8.65	8.64	8.575
Pentads	Methine $–CH{=}\underline{CH}–O–$	mmmm	6.343	6.380	6.486
		mmmr	6.373	6.406	6.486
		mmrm	6.359	6.445	6.507
		mmrr	6.381	6.452	6.541
		mrmr	6.419	6.473	6.541
		rmmr	6.427	6.473	6.561
		mrrm	6.455	6.484	6.593
		rmrr	6.471	6.514	6.570
		rrrm	6.482	6.514	6.570
		rrrr	6.500	6.550	6.593

Methine $-\underline{CH}=CH-O-$	mmmm	6.526	6.591	6.609
	mmmr	6.570	6.591	6.609
	mmrm	6.545	6.618	6.648
	mmrr	6.589	6.618	6.623
	mrmr	6.595	6.641	6.680
	rmmr	6.610	6.641	6.680
	mrrm	6.623	6.668	6.739
	rmrr	6.650	6.684	6.709
	rrrm	6.660	6.684	6.720
	rrrr	6.675	6.707	6.750

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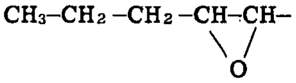
[a] All assignments based on the triad population data obtained with o–$C_6H_4Cl_2$ as solvent.

simulate the spectrum of methylene protons of the ethyl group as well as that of the methine –CH=CH– protons. These analyses are shown in Table 8, from which it can be seen that on replacing the meso dyads by racemic ones the mean chemical shifts of the tetrads and pentads move upfield on changing the solvent from o–$C_6H_4Cl_2$ to CCl_4 and finally to DMSO-d_6.

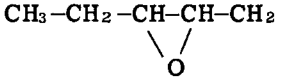
Analysis of Polymer M-a:

In an earlier publication [4] it was shown with the help of IR spectra that polymer M-a has certain C–O arrangement which are not necessarily ester linkages. Furthermore, the absence of double bonds and hydroxyl groups was also established for this polymer. In Fig. 7 is shown the NMR spectrum of this polymer in o–$C_6H_4Cl_2$ as solvent. By making use of the NMR and IR information it is proposed that a major part of polymer M-a is built up of structure X or XI or maybe both.



$CH_3{-}CH_2{-}CH_2{-}\underset{\diagdown\,O\,\diagup}{CH{-}CH}{-}$

X



$CH_3{-}CH_2{-}\underset{\diagdown\,O\,\diagup}{CH{-}CH}{-}CH_2$

XI

In Table 9 are summarized the results of a complete analyses of the NMR of polymer M-a as calculated from an expanded part of spectrum M-a-A in Fig. 7. As in polymer M-b, the propagation mechanism does not follow Bernoullian statistics but rather first-order Markov statistics. Furthermore, the chemical shifts of the methylenes of the ethyl CH_3-CH_2- and of the methine protons of the oxycyclic ring –O–CH–CH– exhibit the same tendency to move upfield on changing the m dyads by r dyads. The analyses of the remainder of the methylene protons between 7.1 and 8.33 show that the values of the geminal J_{AB} as well as vicinal couplings J_{AX} and J_{BX} as calculated from the AB type quartets are higher than the corresponding values obtained with polymer M-b.

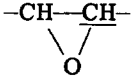
TABLE 9. Assignment of Chemical Shifts on the Basis of Analyses of the Triad Population for Various Tetrads and Pentads for the Oligomeric Product M-a Originating from the Anionic Polymerization of 1,2-Butylene Oxide, NMR Spectrum Observed in o-$C_6H_4Cl_2$ at 100°C

		Important peaks			Configuration placement		
	Nature of protons	τ values	Intensity based on area	Intensity based on tetrad placement	Sequence	Relative intensity	Center τ values
Triads[a]	Methyl $\underline{CH_3}-CH_2-$		0.18		mm		9.02
			0.31		mr		9.06
			0.29		rm		9.09
			0.22		rr		9.12
Tetrads	Methylene $CH_3-\underline{CH_2}-$	8.36	0.03	0.02	mmm	0.06	8.375
		8.39	0.07	0.05			
		8.42	0.08	0.09	mmr	0.22	8.43
		8.44	0.09	0.10			
		8.47	0.16	0.13	rmr	0.19	8.485
		8.50	0.17	0.17			
		8.53	0.15	0.15	mrr	0.26	8.515
		8.56	0.13	0.13	mrm +	0.17	8.58
		8.60	0.09	0.10	rrr	0.10	
		8.63	0.03	0.03	J_{AB} = -6.6 Hz		

(continued)

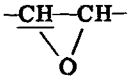
TABLE 9 (continued)

		Important peaks			Configuration placement		
	Nature of protons	τ values	Intensity based on area	Intensity based on tetrad placement	Sequence	Relative intensity	Center τ values
Tetrads	Methylene $-CH_2-\underline{CH_2}-$	7.100	0.28		No pattern		
		7.410					
		7.441					
		7.473					
		7.510	0.14		Two AB type quartets		
		7.564			$J_{AB} = -14$ Hz		
		7.600					
		7.632			$J_{AX} = 8$ Hz	like signs	
		7.664			$J_{BX} = 8$ Hz		
		7.755					
		7.764			Quartet and a singlet		
		7.791	0.14		$J_{AB} = -7$ Hz		
		7.818			$J_{AX} = 7$ Hz	unlike signs	
		7.827			$J_{BX} = 7$ Hz		

		7.927					
		7.955	0.08		Quartet $J_{AB} = -8$ Hz		
		7.982					
		8.018					
		8.041					
		8.050			Quartet and a singlet		
		8.082	0.14		$J_{AB} = -8$ Hz		
		8.114			$J_{AX} = 8$ Hz ⎤ unlike signs		
		8.123			$J_{BX} = 8$ Hz ⎦		
		8.100					
		8.132					
		8.164			Two AB type quartets		
		8.195	0.22		$J_{AB} = -14$ Hz		
		8.223			$J_{AB} = 7$ Hz ⎤ like signs		
		8.259			$J_{BX} = 7$ Hz ⎦		
		8.291					
		8.327					
Pentads	Methine 	6.30	0.02	0.02	Line width 3.5 Hz		
		6.31	0.08	0.06	mmmm	0.02	6.31
		6.325	0.10	0.11	mmmr mmrm	0.08 0.12	6.325

(continued)

TABLE 9 (continued)

Nature of protons	Important peaks			Configuration placement		
	τ values	Intensity based on area	Intensity based on tetrad placement	Sequence	Relative intensity	Center τ values
	6.34	0.13	0.15	mmrr	0.10	6.34
	6.36 6.368	0.18	0.17	mrmr	0.21	6.368
	6.38	0.12	0.13	rmmr mrrm	0.07 0.08	6.38
	6.395	0.10	0.10			
	6.41	0.14	0.12	rmrr	0.16	6.41
	6.425	0.08	0.10	mrrr	0.12	6.425
	6.44	0.05	0.05	rrrr	0.05	
				Line width 3.5 Hz		
	6.52	0.03	0.03	mmmm	0.02	6.52
	6.535	0.06	0.07	mmmr	0.08	6.535
	6.555	0.11	0.10	mmrm	0.12	6.555
	6.573	0.11	0.10	mmrr	0.10	6.573

6.587	0.09	0.12	rmmr	0.07	6.587
6.605	0.18	0.16			
6.62	0.17	0.16	mrmr	0.21	6.605
6.635	0.10	0.12	mrrm	0.08	6.62
			rmrr	0.16	
6.65	0.08	0.08	mrrr	0.12	6.65
6.665	0.06	0.04	rrrr	0.05	

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[a] $P_{m/r} = 0.63$; $P_{r/m} = 0.56$; $P_{m/r} + P_{r/m} = 1.19$. The propagation does not conform to Bernoullian statistics but to first-order Markov statistics as shown in the tetrad analyses.

CONCLUSIONS

The principal conclusions to be drawn from this work are outlined briefly as follows.

The cationic polymerization of 1,2-butylene oxide yields products which are repeat units of the monomer and the propagation mechanism follows Bernoullian statistics. The mean chemical shifts of the triads and tetrads move upfield on replacing m dyads by r dyads. However, the pentads move downfield on replacing m dyads by r dyads. Recording the spectra of the cationic products in different solvents did not affect the chemical shifts of various protons.

The anionic polymerization of 1,2-butylene oxide, on the other hand, yields products which are other than repeat units of monomer, and the propagation mechanism follows first-order Markov statistics. The mean chemical shifts of the triads and tetrads associated with the ethyl group along with the pentads of the methine protons move upfield whereas the tetrads associated with the remaining methylenes move downfield on replacing m dyads by r dyads and on replacing o–$C_6H_4Cl_2$ by CCl_4 or DMSO-d_6 as the solvent for recording the spectrum.

Further work on the ionic polymerization of 1,2-butylene oxide is in progress, and the results of these studies will be reported in due course.

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