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MINISTRY OF TECHNOLOGY

EXPLOSIVES RESEARCH AND DEVELOPMENT ESTABLISHMENT

REPORT No. 6/R/66

Synthesis and Characterisation of Hydroxy - Terminated Polybutadienes

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Synthesis and Characterisation of Hydroxy-Terminated Polybutadienes

by

D.H. Richards, D.A. Salter and R.L. Williams

Approved for Circulation:

L.J. BELLAMY
DIRECTOR

4th January 1967

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CONTENTS

Reference: WAC/173/06

1. SUMMARY

An adaptation of the Szwarc 'living' polymer method has been used to synthesise hydroxy-terminated polybutadienes up to 11,000 molecular weight which ~~have been~~ were characterised by infra-red and nuclear magnetic resonance spectroscopy. The latter technique indicates that the materials are predominantly 1,2- linked, and analysis by chemical and physical methods shows that the production of hydroxy-terminal groups is virtually quantitative.

It is possible to react these polymers with ~~TDI~~ 2,4-TOLUENE DI-ISOCYANATE to yield thermoplastics, which can be crosslinked with castor oil to give good quality rubbers.

2. INTRODUCTION

Composite propellants using crosslinked polybutadienes as binder-fuels have some distinct advantages in physical and combustion properties over both double-base and polyurethane rubber systems. They have been extensively investigated in the U.S.A., but in this country work has been concentrated mainly on a polyisobutene-based plastic propellant. Although this material and the linear polybutadienes have useful properties, there are limitations to the charge sizes which can be prepared without permanent deformation of the charge under its own weight. This can be overcome after incorporation of the oxidiser by suitably crosslinking the polymer to furnish a rubbery product. The American work on polybutadiene in this connection has been recently reviewed (1).

Two approaches have been made; the first consists of copolymerising butadiene with monomers containing functional groups such as acrylic acid and methacrylic acid, with acrylonitrile sometimes being added to form a terpolymer. Diepoxides and aziridines are used as curing agents. The second method is either to introduce terminal groups by direct attack on an anionic polybutadiene with the appropriate reagent, or to use for the polymerisation, catalysts and chain transfer agents which contain the required group. The chain transfer technique has met with some success and a number of U.S. companies manufacture carboxyl terminated polybutadienes (CTPBs) by this method. The products, however, are expensive and the batch reproducibility is not good. Attempts to synthesise CTPB by anionic methods have, until recently, produced indifferent results, probably due to side reactions at the carboxylation stage producing ketone groupings (2). Moreover, the rubbery propellants prepared from CTPB have shown some temperature instability which has been attributed to the ester bonds formed in the crosslinking process. This defect could be avoided by using hydroxy-terminated polybutadiene (HTPB) and reacting it with a di-isocyanate to produce urethane links. Only one company (3) produces HTPB commercially, but batch reproducibility is open to suspicion and the functionality of the polymer is greater than two so that reaction with a di-isocyanate produces a rubber directly.

/Recently .....

Recently HTPB has been prepared by the Szwarc anionic 'living' polymer method (4). Using this technique the functionality cannot exceed two and a material with a very sharp (Poisson) molecular weight distribution is produced. This report describes the adaptation of this method to produce 150 g. batches of hydroxy-terminated polymer for propellant evaluation. The results of an examination of various polybutadienes by infra-red and nuclear magnetic resonance (NMR) spectroscopy are also discussed, and quantitative methods for determining the molecular weight and structure of the polymer are considered briefly.

3. EXPERIMENTAL

3.1 Materials

3.1.1 Lithium

Lithium metal of B.D.H. reagent grade was washed with ether to remove oil, dried and cut into small pieces under argon, and weighed before transferring into the reaction vessel.

3.1.2 Naphthalene

Naphthalene of B.D.H. micro-analytical reagent grade was used without further purification.

3.1.3 Ethylene Oxide

Ethylene oxide, supplied by B.D.H., was purified as described in Section 3.3.3.

3.1.4 Butadiene

Butadiene cylinders from British Hydrocarbon Chemicals were connected directly to the purification train described in Section 3.3.2.

3.1.5 Tetrahydrofuran

Tetrahydrofuran, B.D.H. reagent grade, was refluxed with potassium hydroxide, distilled, the distillate refluxed with sodium-potassium alloy, and distilled once more. This material was immediately transferred to the vacuum line and further purified as given in Section 3.3.1.

3.1.6 Other Reagents

All other reagents, benzene, ether, etc., were of laboratory reagent grade and were not further purified.

/3.2 .....

3.2 Apparatus

The experimental method differs from that given in the literature (4) in that the operations were carried out entirely in vacuo rather than under argon. The apparatus for the preparation of reagents and for the polymerisation is shown in Figures 1 (a) to (d) and Figure 2.

Figure 1 (a) shows the pumping arrangement for the main apparatus. It enables the mercury diffusion pump to be by-passed via two routes, each equipped with a liquid nitrogen trap, so that volatiles may be continuously extracted from substances attached to the line.

Figures 1 (b) to (d) illustrate those parts of the apparatus concerned with the purification of tetrahydrofuran, butadiene, and ethylene oxide respectively, and the polymerisation vessel is shown in Figure 2. These will be described in detail in the following sections of the report. The interconnections not specifically mentioned in the following text, however, were used for easy flushing and degassing of apparatus in between runs, and to enable more than one operation to be carried out simultaneously on the line.

3.3 Methods

3.3.1 Purification of Tetrahydrofuran (THF)

THF was introduced via the sidearm into the 2-litre flask a (Figure 1 (b)) which contained naphthalene, sodium and potassium, and a magnetic stirrer. The sidearm was sealed after cooling the solvent with an isopropanol-solid carbon dioxide bath, and the system thoroughly degassed. The liquid was allowed to return to room temperature and stirred until eventually a dark green colour characteristic of the sodium-naphthalene complex was formed. THF was then distilled at -78°C into bulb b which contained the same ingredients as a. On this occasion the green colour formed immediately and the solution was used as a stock solution, aliquots being distilled into the measuring cylinder as required. All stopcocks in this part of the apparatus were metal to prevent solvent attack.

3.3.2 Purification of Butadiene

Two cylinders containing argon and butadiene respectively were joined to the apparatus as shown in Figure 1 (c). The argon was used merely to flush the apparatus after a run or to introduce an inert atmosphere to any part of the system. Butadiene passed from the cylinder via a three-way tap through three scrubbing bottles c containing anhydrous ethylene glycol in which sodium had been dissolved. The rate of gas flow could be judged by turning the three-way tap to allow the butadiene to pass via a bubbler to waste. From the scrubbers the gas passed via the Drierite column d into the subsidiary manifold, and thence was condensed in the measuring cylinder e by use of an isopropanol-solid carbon dioxide bath. During this and subsequent distillations the system was

/connected .....

connected to the mercury manometer f (Figure 1 (b)) via stopcock g to ensure no pressure build up. A middle cut of the monomer, still at -78°C, was distilled from e via stopcock h into measuring cylinder c cooled in liquid nitrogen. This was warmed to -78°C and the required amount distilled into the reaction vessel attached at j (Figure 1 (c)) which was also at this temperature.

3.3.3 Purification of Ethylene Oxide

Ethylene oxide was introduced into a round bottom flask containing calcium hydride attached at k(Figure 1 (d)). The liquid was degassed after cooling and stirred magnetically for 6 to 7 hours with further periodic degassings. A receiver possessing a constriction and a breakseal was sealed on to the apparatus at l, and cooled in an isopropanol - solid carbon dioxide bath. The ethylene oxide was distilled into the flask after first passing through two towers packed with soda-lime (m). The rate of distillation was controlled by closing stopcock n and making the vapour pass through the fine capillary tube in parallel (shown by a dotted line). The distillation pressure was monitored with the manometer o. After collecting the required quantity of ethylene oxide, the ampoule was sealed at the constriction and stored in a freezer until required.

3.3.4 Polymerisation and Termination of Polybutadiene

The reaction vessel which was essentially a modified three-litre flask is shown in Figure 2. The sides were fluted and three glass paddles were sealed on as indicated in order to prevent laminar flow of the stirred solution. It is important that a fresh liquid surface is continually presented to the gaseous monomer during polymerisation in order to obtain a sharp molecular weight distribution. An ampoule containing ethylene oxide was sealed to the reaction vessel as shown and the required amounts of lithium metal and naphthalene (about 5 per cent excess of theoretical) introduced under argon. The flask was then quickly attached at j, Figure 1 (c), and evacuated. Known quantities of THF were distilled from c into the flask which was immersed in an isopropanol - solid carbon dioxide bath, and the whole magnetically stirred for 1 to 2 days at room temperature. Over this period the dark green colour of the naphthalene - lithium complex appeared and the lithium metal was slowly dissolved. At this point 10 per cent of the purified butadiene in the measuring cylinder was pumped away at -78°C and the calculated volume distilled over a period of about five hours into the reaction vessel which had also been cooled to this temperature. The rate of flow was controlled by stopcocks and the pressure monitored with manometer f. The colour of the THF solution changed to a light red characteristic of the butadienyl anion, which remained with unchanged intensity throughout the addition. After introduction of the required amount of butadiene, about 10 per cent of the monomer remained in c and was pumped away. The reaction mixture was stirred for a further hour before magnetically breaking the seal of the ethylene oxide ampoule with a glass encased iron hammer. The polymer solution on contacting the ethylene oxide gelled and became colourless where reaction had taken place. The

/solution .....

solution was warmed to room temperature and stirred for several days until the ethylene oxide had penetrated the initially formed gel and the whole system had become colourless and solid. This gelling on termination with ethylene oxide has been observed with 'living' polystyrene (5) and has been explained as being due to ion pair formation.

3.3.5 Extraction of Polymer

The reaction vessel was filled with argon and removed from the line. Addition of about 25 ml. of water (plus 0.5 ml. of 2,6-di-tert-butyl-4-methylphenol antioxidant) destroyed the gel and produced a non-viscous solution. This was poured into two litres of water, the separated organic phase washed with 1 litre of hot water and allowed to stand for an hour. The washing procedure was repeated a further five times, the final separated organic layer being dissolved in benzene and dried with anhydrous magnesium sulphate.

The solution was filtered and the benzene evaporated off. The viscous polymer remaining still contained most of the naphthalene used as catalyst and at first this was sublimed off using a rotary high vacuum evaporator. However, infra-red studies showed that even after two days at 90°C, significant amounts of naphthalene still remained. Accordingly a sublimator designed by Simkins and Smith (6) was used and, although naphthalene could still be detected by infra-red spectroscopy, this resulted in a more efficient method of extraction.

The details of three polymer preparations are listed in Table 1.

3.4 Polymer Analysis

3.4.1 End Group Analysis

The acetylation method developed by Blay (7) was used with minor modifications to determine the hydroxyl number of the polybutadienes.

3.4.2 Infra-red Spectra

Spectra were measured over the range 4,000 - 400 cm^{-1} with a Perkin Elmer 337 grating spectrometer. Samples were examined as films cast from carbon disulphide or chloroform solution on potassium bromide plates.

3.4.3 Nuclear Magnetic Resonance Spectra

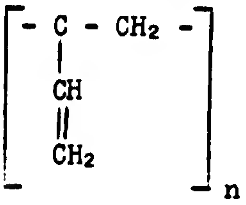
Proton magnetic resonance spectra were obtained at 60 Mc/s with a Perkin Elmer R10 spectrometer. Carbon disulphide solutions of the samples were used, tetramethyl silane being added as internal marker. Particular care was taken with the integration measurement to avoid saturation effects and usually the mean of at least ten integrals run both upfield and downfield was taken as the correct value. The determination of the degree of polymerisation, n, and fraction of 1,2-polymer, x, is considered in Section 4.

/4. .....

4. RESULTS AND DISCUSSION

The experimental details and results of three preparations are given in Table 1. The theoretical molecular weight is calculated from the relationship, mol. wt. = 2 × monomer (g.)/catalyst (moles), but in order to determine the weight of added monomer from its volume, the density of liquid butadiene at -78°C is required, and this has not been evaluated. An approximate value of 0.73 was therefore taken by extrapolation of published density data for the temperature range 60° to -20°C (8). The molecular weights calculated on the basis of two hydroxyl groups per chain (Table 2) agree quite closely with the theoretical figures. This implies that nearly every chain is terminated at both ends with hydroxyl groups and consequently that the polymerisation technique can produce the required hydroxyl-terminated polybutadiene. This is confirmed by the molecular weights as determined by NMR (see later) and also 2,4-tolyene di-isocyanate (TDI) reacts with the polymers to give thermoplastics which, after addition of castor oil, yield good quality rubbers (9).

Polymerisation of 1,3-butadiene can take place by either 1,2- or 1,4-addition, the former yielding a polymer with pendant vinyl groups (I), while the latter gives rise to either a poly-cis- (II) or poly-trans- (III) ethylene.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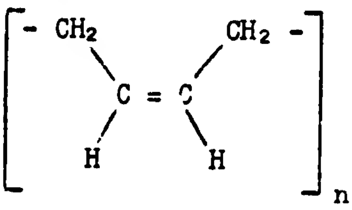
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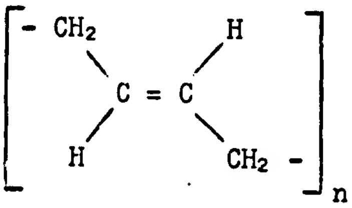
III

The situation with the poly-1,2-butadiene is further complicated by the possibility of stereoregularity along the polymer chain, giving rise to either syndiotactic, isotactic or atactic arrangements. The relative abundances of these three configurations depend on the polymerisation method and conditions. Generally for anionic polymerisation, the solvent and the polymerisation temperature are the two most important parameters. The higher the temperature the less 1,2- addition is obtained, whereas the addition of diethyl ether to the THF solvent increases 1,2- bond formation. The physical properties of the polymer, and of any rubbers produced from it, will depend largely on the composition of the polybutadiene so that a knowledge of the microstructure of the polymers produced is of great importance.

Several methods have been used to determine the microstructure, but that most extensively employed so far has been the infra-red spectrum. Both Natta (10) and Binder (11) have interpreted the spectra of various polybutadienes in terms of the structural units I, II and III. For example, the spectrum of trans-poly-1,4-butadiene, Figure 3, shows the following bands:

/3030 .....

3030 - 2980	m	CH stretch of trans -CH=CH-
2950	s)	Antisymmetrical CH_2 stretch
2910	s)	
2840	s	Symmetrical CH_2 stretch
1440	ms	CH_2 deformation
1350	w	CH in plane deformation of trans -CH=CH-
1235	m	
1052	m	
964	vs	CH out of plane deformation of trans -CH=CH-
910	mw	
770	mw	
440	mw	

The very intense band at 964 cm^{-1} is particularly characteristic of the trans-ethylenic unit. The spectrum of cis-poly-1,4-butadiene is shown in Figure 4, bands being assigned as follows:

3002	vs	CH stretch of cis -CH=CH-
2940	vs	Antisymmetrical CH_2 stretch
2850	s	Symmetrical CH_2 stretch
1650	m	C=C stretch
1440	ms	CH_2 deformation
1400	m	CH in plane deformation of cis -CH=CH
1300	m	CH deformation of cis -CH=CH
1240	mw	
992	m	
910	w	
738	vs br	cis -CH=CH out of plane deformation.

/Like .....

Like the trans-compound, the out of plane CH deformation is characteristic of the cis-linkage lying at 738 cm^{-1}. However, in the case of this compound the C=C stretching vibration of 1645 cm^{-1} is active and the =CH stretching vibration at 3002 cm^{-1} is very intense.

No sample of any of the forms of poly-1,2-butadiene was available for measurement, but it was evident by comparison of the spectrum of an anionic polymerised butadiene (Figure 5) with those published by Natta (10) and Binder (11), that this was a predominantly 1,2-polymer. The bands listed below are derived from this spectrum with appropriate amendment where necessary by reference to the published data.

3075	s	CH$_2$ stretch of CH$_2$=CH- group
2975	s	Antisymmetrical CH$_2$ stretch
2910	vs	
2840	s	Symmetrical CH$_2$ stretch
1830	m	Overtone of CH$_2$= out of plane deformation
1645	s	C=C stretch
1450	m	CH$_2$ deformation
1420	s	CH$_2$ in plane deformation of CH$_2$=CH-
1345	m	CH in plane deformation of CH$_2$=CH-
1290	m	
1225	w	
1070	w	
995	s	CH out of plane deformation of CH$_2$=CH-
910	vvs	CH$_2$ out of plane deformation of CH$_2$=CH- (?)
805	w	
685	s	CH out of plane deformation of CH$_2$=CH-
475	w	

/There .....

There are slight differences in the infra-red spectra of the syndiotactic and isotactic forms of poly-1,2-butadiene (10) but these occur only in the presence or absence of weak bands in the 1300 - 1200 cm^{-1} region and are not recorded above. The most characteristic features of the spectrum are the strong bands at 3075 cm^{-1}, 995 and 910 cm^{-1} due to the vinyl group.

It is evident that an analysis of any mixture of polybutadienes could be based on the intensities of the bands at 964 cm^{-1} for the trans-1,4- form, 995 and 910 cm^{-1} for the poly-1,2- form and 738 cm^{-1} for the cis-1,4- form, and attempts to do this have been made by Morero et al (12). However, in practice it is better to estimate the latter by difference since it has been shown subsequently (13) that the position of the band near 738 cm^{-1} depends on the percentage of the cis- form, shifting to lower frequencies as the cis- content falls. Moreover, the overall intensity in this region is complicated by an absorption at 685 cm^{-1} arising from the 1,2- form. Because of this difficulty, and especially the need for pure samples as calibrants, attention was turned to the NMR spectrum as an alternative means of analysis.

This has the advantage that the method is an absolute one and is also rapid, but has the drawback that its accuracy is not as high as an infra-red method. Moreover, Durbetaki and Miles (14) have already indicated the potentiality of NMR when they determined the olefine content of polybutadienes. They did not, however, extend the method further.

The NMR spectrum of an anionic polybutadiene is shown in Figure 6. The principal absorptions are as follows:

τ p.p.m. relative to $SiMe_4$	Assignment
8.84	CH_2 of $-(CHVi-CH_2-)_n$
8.08	CH of $-(CHVi-CH_2-)_n$ CH_2 of $-(CH_2-CH=CH-CH_2)_n$
6.54	CH_2 of terminal $-CH_2\boxed{CH_2}OH$ end group
5.36 5.24 5.07	CH_2 of $CH_2=CH-$ group
4.39 4.78	CH of $CH_2=CH-$ and $-CH=CH-$ groups
3.09 (variable in position)	OH of $-CH_2CH_2OH$ end group

/Since .....

Since the absorptions due to olefinic hydrogens, lying in the $\tau = 6$ region, are well separated from those due to saturated hydrogens, $\tau = 8.5$, it is possible to relate the fraction of form I to the areas of olefinic absorption, and saturated absorption, as follows:

If x is the fraction of 1,2-polymer then

1-x = fraction of combined cis- and trans-1,4-polymer

$$\frac{\text{Olefinic signal}}{\text{Saturated Hydrogen absorption}} = R = \frac{\text{No. of olefinic protons}}{\text{No. of saturated protons}}$$

$$= \frac{3x + 2(1-x)}{3x + 4(1-x)}$$

$$= \frac{2 + x}{4 - x}$$

$$\text{whence } x = \frac{4R - 2}{R + 1} \qquad \ldots\ldots \ 1$$

Table 3 gives the results for a number of samples of anionic polybutadiene and also some of commercial origin. The values are probably accurate to (x ± 7) per cent in the region of x = 0 per cent to (x ± 4) per cent in the region of x = 100 per cent. It can be seen that the two research samples of poly-1,4-butadiene are pure 1,4- forms within experimental error. Inspection of their infra-red spectra however shows that there is a weak band at 910 cm^{-1} in the cis- spectrum and a second at 972 cm^{-1} indicating small amounts of 1,2- and trans-1,4-polymer, a 1,2- content of perhaps a few per cent. In the trans-1,4- spectrum there is also a weak band at 910 cm^{-1} again showing a 1,2- content of a few per cent. The commercial samples are also predominantly 1,4-polymers. The anionic material on the other hand is principally 1,2-polymer and this view is confirmed from its infra-red spectrum. If this is compared with those spectra published by Natta (10), it is evident that the material is largely poly-1,2-butadiene, with some trans-poly-1,4-butadiene as the other component. It is not possible to say how much cis-1,4-polymer is present though it must be small. On the other hand, the poly-1,2- component of the spectrum is consistent with these being a major syndiotactic component and a smaller isotactic component.

The anionically polymerised butadienes were terminated with ethylene oxide to give $-CH_2CH_2OH$ end groups. These are shown by the presence of a weak 1:2:1 triplet at $\tau = 6.54$ resulting from the methylene of the CH_2OH end group, and by a singlet at $\tau = 3.09$ arising from the OH. The identity of these two assignments being established by their chemical shifts, multiplicity and intensity ratio of 2:1, it is possible to estimate a molecular weight for the samples from these intensities as follows:

/Let .....

Let n be the mean degree of polymerisation, x the fraction of 1,2-pplymer, 1-x the fraction of 1,4-pplymer. Then

$$\frac{\text{Area of } CH_2OH \text{ signal}}{\text{Area of signal from all other protons}} = \frac{4}{n[3x + 3x + 4\,(1-x) + 2\,(1-x)] + 4}$$

$$= \frac{4}{6n + 4} = R_1$$

$$\text{whence } n = \frac{1 - R_1}{1.5\,R_1} \qquad \ldots\ldots \underline{2}$$

Alternatively

$$\frac{\text{Area of } CH_2OH \text{ signal}}{\text{Area of Olefinic signal}} = \frac{4}{n[3x + 2\,(1-x)]} = \frac{6}{n\,(x + 2)} = R_2$$

$$\text{whence } n = \frac{4}{R_2\,(x + 2)} \qquad \ldots\ldots \underline{3}$$

Values of degrees of polymerisation determined from Equation 2 and 3 are compared in Table 2 with values determined by acetylation end group analysis and with values calculated from the quantities of starting material used in the synthesis. It can be seen that the agreement is very satisfactory. The method is limited to lower molecular weight ranges, it being estimated that values greater than 5,000 would be undetectable with the present form of NMR spectrometer. However, two methods could be employed to increase this range. Firstly, esterification of the hydroxyl with an acid containing many protons in the same environment e.g. triphenylpropionic, would increase the maximum by a factor of 15/2, i.e. to about 35,000. Secondly, use of computer averaging techniques now being introduced with NMP spectrometers can easily raise the signal/noise ratio by 5 to 10 times, giving an overall molecular weight maximum in the 150,000 and 350,000 range.

/5. .....

5. CONCLUSIONS

The anionic polymerisation technique can readily produce well characterised polybutadienes which are predominantly of the poly-1,2- form, with hydroxyl groups terminating each end of the polymer chain.

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/TABLE 1 .....

TABLE 1

Experimental Polymerisation Data

Sample	Li (g.)	Naphth (g.)	Butadiene (g.)	THF (ml.)	Ethylene/oxide (ml.)	Mol. Wt. (Calc.)
1	1.04	20.2	160	900	20	2,140
2	1.04	20.2	150	900	15	2,000
3	0.217	4.204	177	900	5	11,300

TABLE 2

Molecular Weights of Polybutadienes

Sample	NMR (Eqn. 2)	NMR (Eqn. 3)	OH Analysis	Mol. Wt. (Calc.)
1	2,280	2,200	2,400	2,140
2	1,710	1,740	1,930	2,000
3	-	-	11,600	11,300

TABLE 3

Analysis of 1,2- and 1,4- forms by NMR

Source	Sample	% 1,2-	% 1,4-
Anionic	1	68.2	31.8
	2	72.8	27.1
	3	85.5	14.5
Sinclair	R-15-M	18.5	81.5
Petrochemicals	R-45-M	18.0	82.0
Thiokol Chem.	HC 434	10.5	89.5
Phillips Petroleum Co.	trans-1,4-	0	100
Polymer Corpn. Ltd., Sarnia.	cis-1,4-	0	100

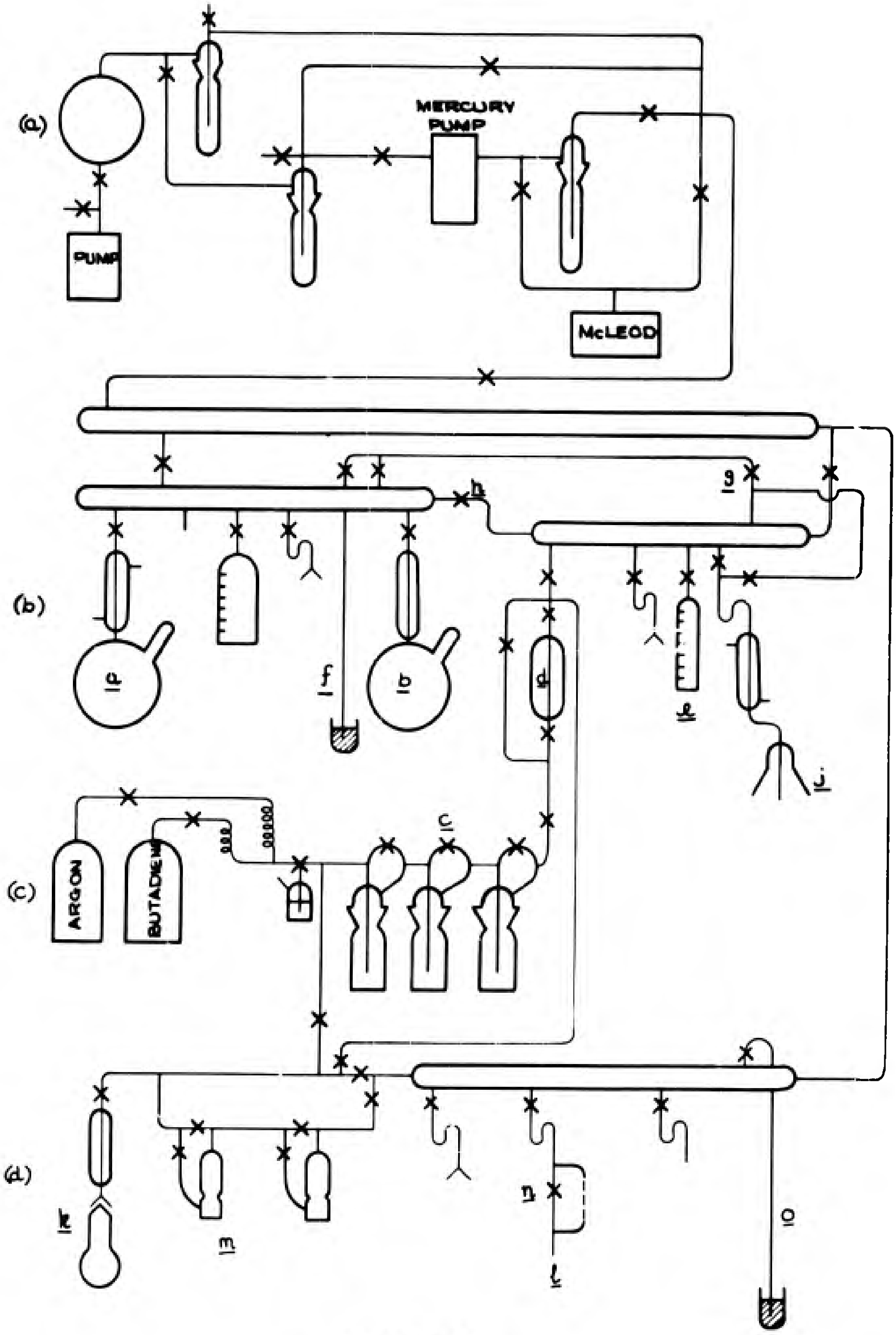
(a)
MERCURY PUMP
PUMP
McLEOD
(b)
h
g
a
f
b
d
e
j
(c)
ARGON
BUTADIENE
c
(d)
k
m
n
l
o

FIGURE 1.

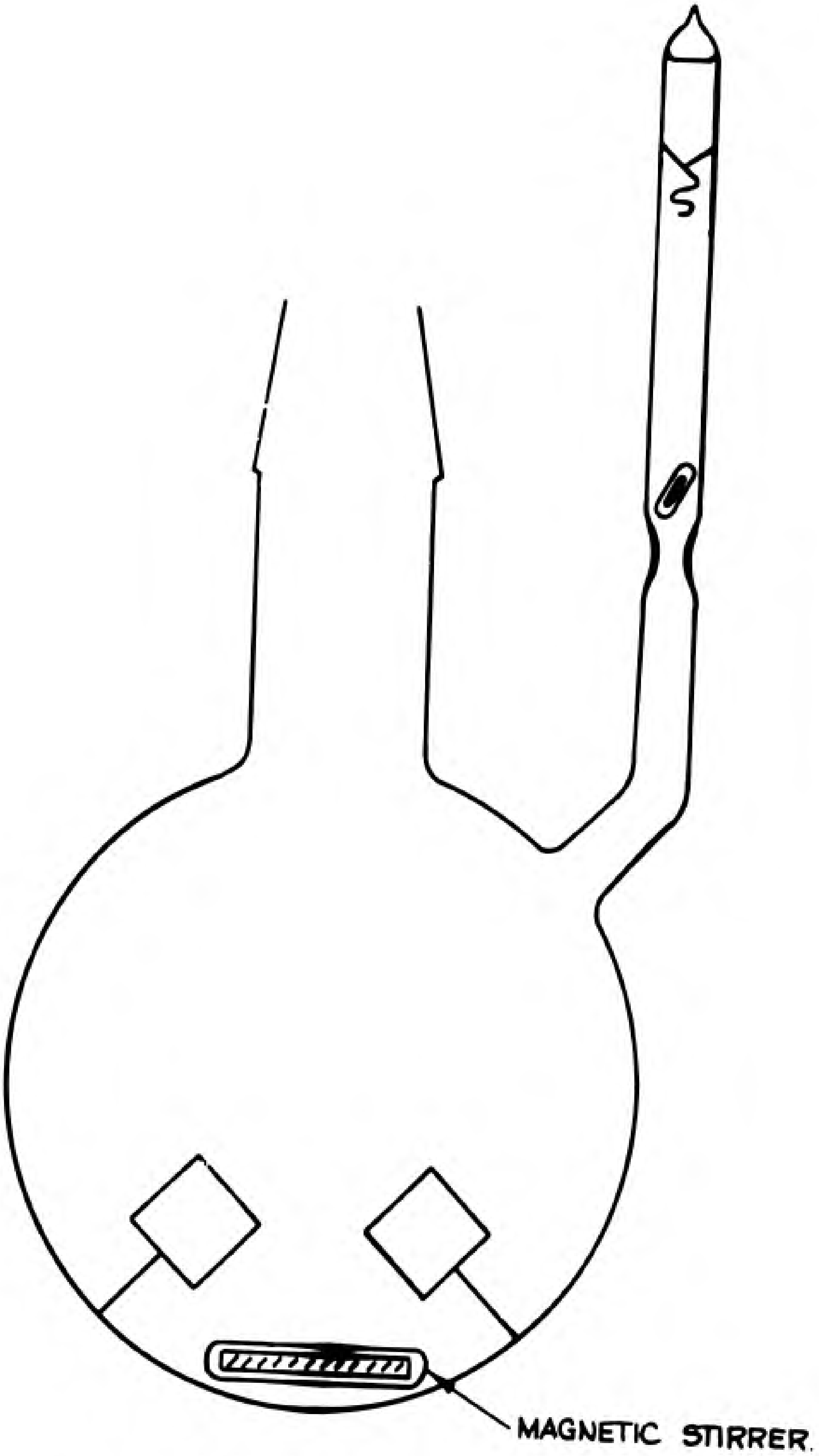

FIGURE 2.

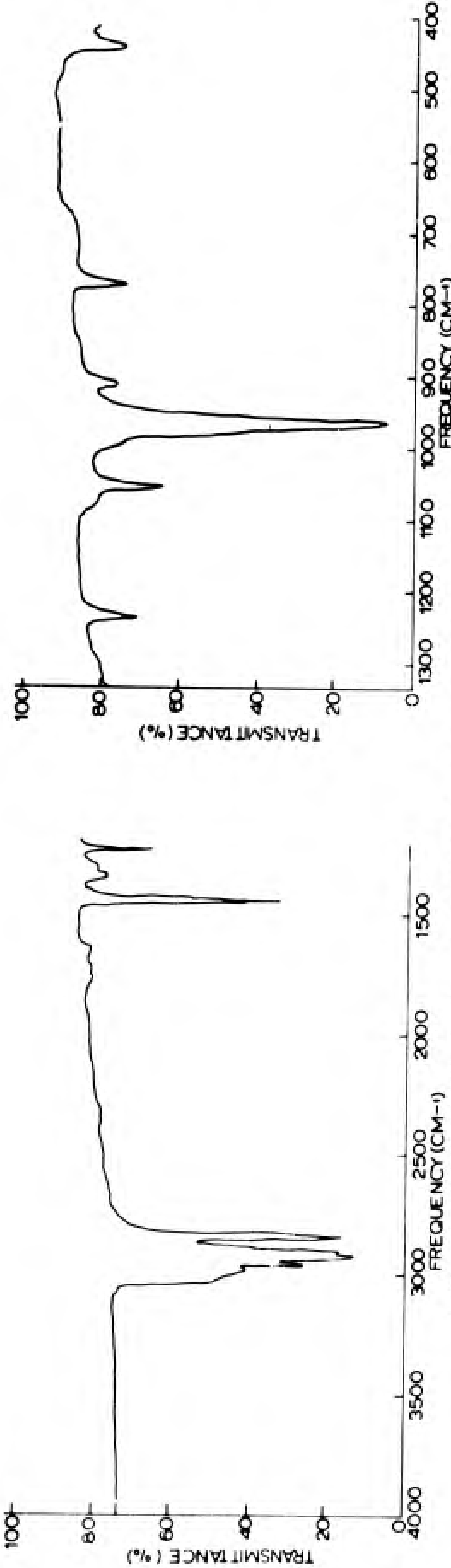

FIG. 3. THE INFRA-RED SPECTRUM OF TRANS-POLY - 1, 4 - BUTADIENE.

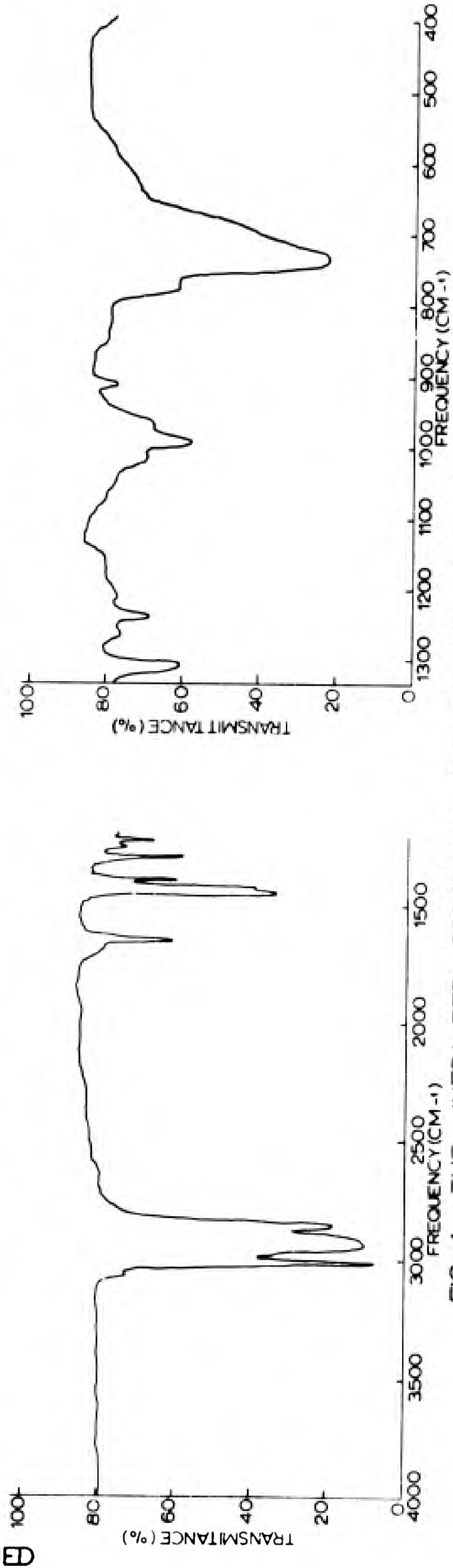

FIG. 4. THE INFRA-RED SPECTRUM OF CIS-POLY - 1, 4 - BUTADIENE.

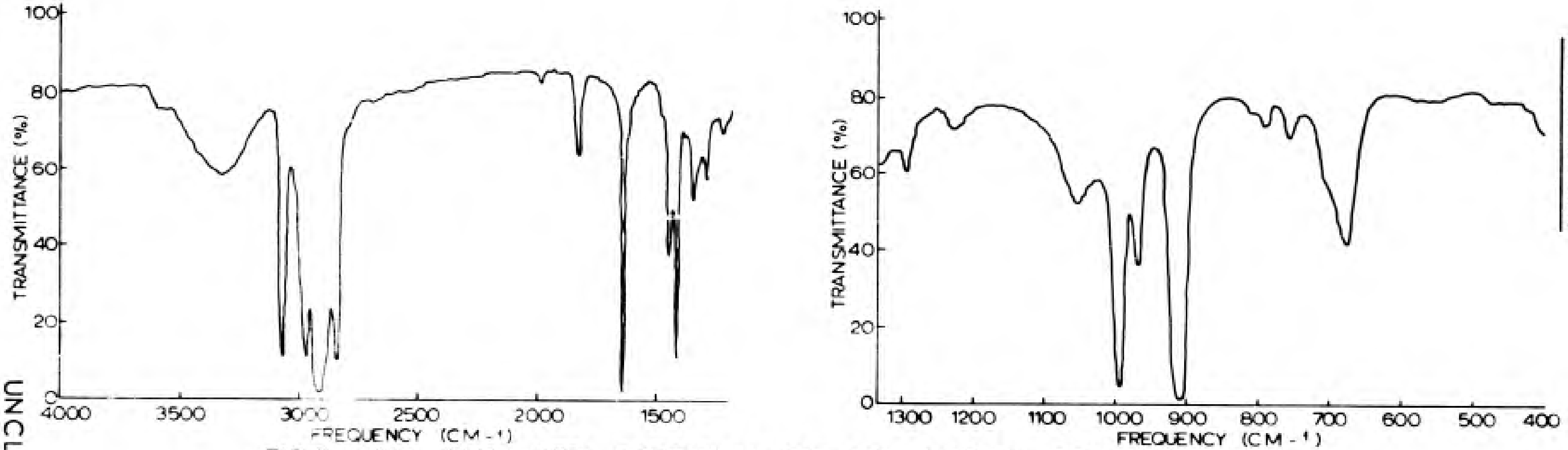

FIG 5. THE INFRA-RED SPECTRUM OF AN ANIONIC POLYBUTADIENE

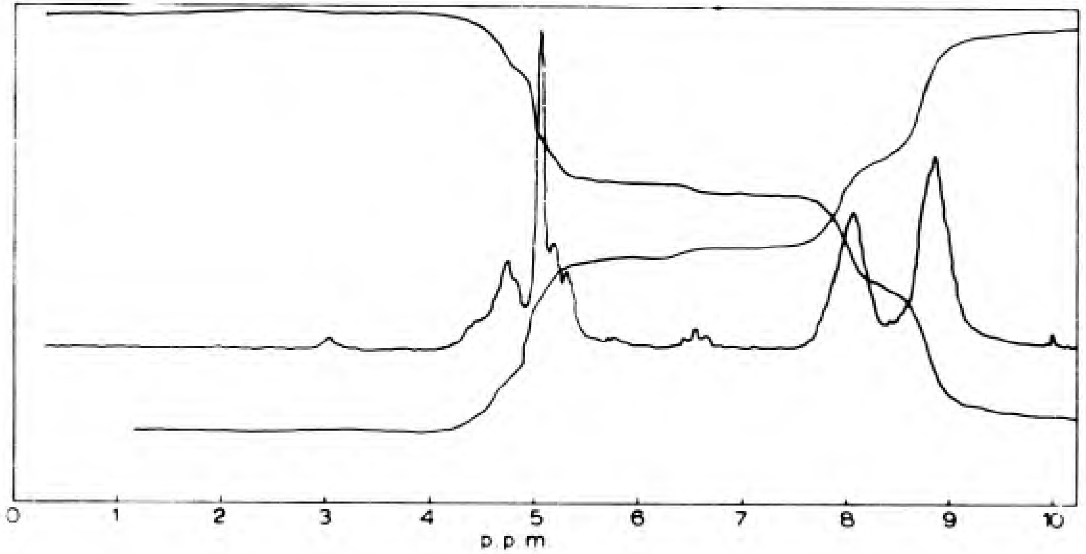

FIG.6. THE ^{1}H NMR SPECTRUM OF AN ANIONIC POLYBUTADIENE