

It must be noted that nothing is mentioned about the proportions of the components of the liquids *absorbed* by crosslinked or insoluble polymers which may be very different from that in the ambient mixture. Some reservations must also be made concerning the use of relative weight increases in view of the different densities of the pure materials involved; it is necessary, for a common basis, to express all

results as relative volume increase.

CONCLUSIONS

A method for the calculation of most efficient mixtures of three, two or single component solvents for resins has been developed. This method, because of its rapidity using modern computers, is capable of screening many

combinations. The best of these may then be tested experimentally.

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Letters

The microstructure of polychloroprene determined by ^{13}C -nuclear magnetic resonance

The properties of polydienes are dependent upon the configurations of the diene units within the chains, the distribution of these units along the chain and upon the relative orientations of the units, i.e. whether they are in head-head, head-tail or tail-tail arrangements. ^{13}C nuclear magnetic resonance (^{13}C n.m.r.) spectroscopy can be used not only to distinguish between polybutadienes and polyisoprenes with regular microstructures¹ but also to determine the relative amounts and the distributions of diene units with different configurations within polymers of irregular microstructure²⁻¹². It has been shown also that for polyisoprenes, ^{13}C n.m.r. can be used to identify and measure the relative amounts of head-head, head-tail and tail-tail linkages involving 1,4- units^{11,12}.

For polychloroprenes, proton magnetic resonance spectroscopy can be used to detect head-head and tail-tail linkages between 1,4- units¹³ and also, if high field strengths are employed, to determine the relative amounts of *cis*-1,4- and *trans*-1,4- enchainment¹⁴. As yet, there have been no publications describing the use of ^{13}C n.m.r. to determine the microstructure of polychloroprenes, although the technique has been used to give some limited information regarding the microstructure of some chloroprene-methyl methacrylate copolymers¹⁵.

The Figure shows the methylene carbon resonances obtained at 20 MHz

(Varian CFT20 spectrometer) for a sample of polychloroprene prepared by bulk thermal polymerization under nitrogen at 25°C. The spectrum is the result of 30K pulses on a 10% w/v solution of the polymer in CDCl_3 with an acquisition time of 0.5 sec and a pulse width of 12 μsec (corresponding to a nuclear tip angle of $\sim 51^\circ$). There was no additional delay between pulses. 4096 data points were used in the accumulation of the spectrum over a spectral width of 4000 Hz, and the usual 'white noise' proton decoupling procedure was employed. The relative areas of the peaks in the spectrum were not affected by small changes in

pulse width and acquisition time and therefore the areas can be expected to give reliable quantitative results.

The pattern of methylene resonances is very like that observed for free radically prepared polyisoprenes^{11,12} showing the presence of both *cis*- and *trans*-1,4- units and a mixture of head-head, head-tail and tail-tail linkages. (The absence of any characteristic olefinic methylene carbon resonances in the full spectrum indicates that this polymer contains no 1,2- or 3,4- units). By analogy with polyisoprene spectra, the following assignments may be made for the methylene resonances:

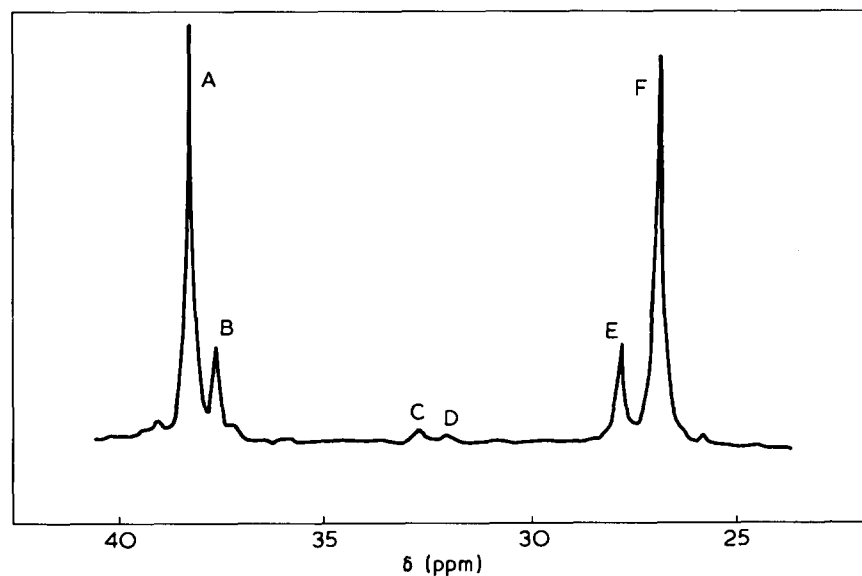
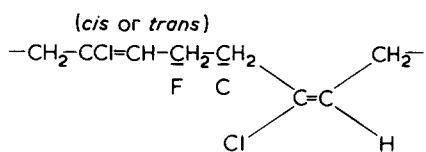
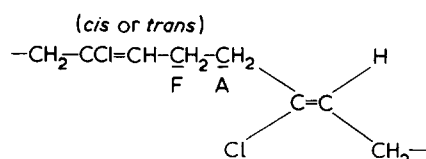
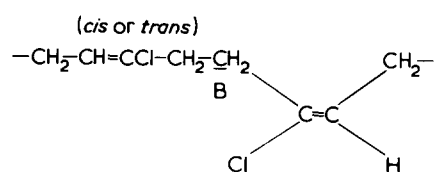
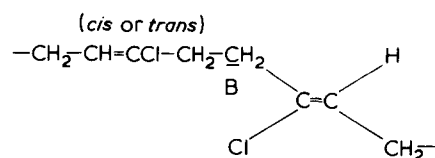


Figure 1 Methylene carbon resonances in polychloroprene (Peak assignments are given in the text)

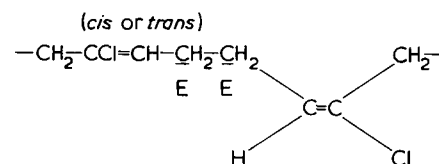
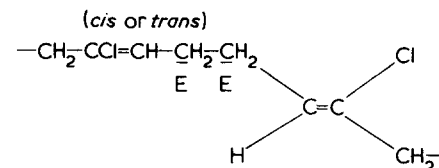
1,4-1,4 (head-tail) linkages



4,1-1,4 (head-head) linkages



1,4-4,1 (tail-tail) linkages



Methylene carbon	Chemical shift (ppm relative to TMS)
A	38.4
B	37.7
C	32.7
D	32.0
E	27.7
F	26.9

Measurements of the areas of the methylene carbon peaks suggest the following microstructure for the polychloroprene:

Type of unit	Fraction of total (%)
trans-1,4-	94
cis-1,4-	6
cis-1,4- in 4,1-1,4 linkages	1
trans-1,4- in 4,1-1,4 linkages	9
cis- and trans-1,4- in 1,4-4,1 linkages	10

Thus, ¹³C n.m.r. enables some features of the microstructure of polychloroprenes to be determined readily and for the free radical sample described here gives results comparable with those for similar polychloroprenes that have been obtained by proton magnetic resonance^{13,14}. As expected the polychloroprene contains equal amounts of 1,4-4,1 and 4,1-1,4 linkages.

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Analysis of multicomponent electric birefringence transients: data for proteoglycan solutions

In recent years a number of electro-optical methods have been developed and harnessed for the characterization of biopolymers in aqueous solution. Electrically-induced birefringence studies are the most common^{1,2}. In these, one applies a d.c. pulsed electric field and investigates the induced molecular orientation and relaxation by recording the transient changes in the birefringence of the bulk solution. Regular transient responses, of which Figure 1a is a typical example, are usually reported. The birefringence is established as the solute molecules become aligned until a steady-state situation is attained. Termination of the field is then accompanied by a field-

free decay of the birefringence as the molecules revert to a random array. Analysis of this decay rate leads to molecular relaxation times (τ) and hence to information on the molecular geometry^{1,3}.

Non-regular transients have been encountered, especially when studying conducting media. Such irregularities have often been rejected as anomalous. Occasionally, proposals have been made for their origins in terms of complex molecular behaviour⁴⁻⁷ or of the influence of more than a single relaxation process⁸⁻¹² in the system under study.

Recently, we have been engaged in electric birefringence studies on aqueous

solutions of the complex biopolymer proteoglycan, which is a constituent of cartilage connective tissue. The proteoglycan molecule consists of an extended protein backbone to which flexible chondroitin sulphate and keratan sulphate polysaccharide chains are attached radially in a 'bottle-brush' structure¹³. Electric birefringence measurements were made using a conventional apparatus¹ working in the linear detection mode¹⁴. Pulsed rectangular electric fields of up to 6 kV/cm amplitude and of 6 msec duration were applied to solutions of pig laryngeal proteoglycan¹⁵ in deionized water (at a pH of about 5.5) and 0.71 mg/ml concentration. Figure 1 records a