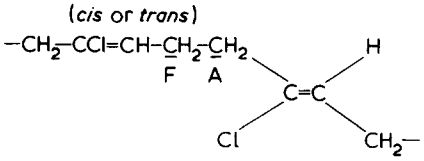
*1,4–1,4 (head–tail) linkages*

(*cis* or *trans*)



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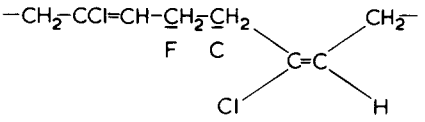
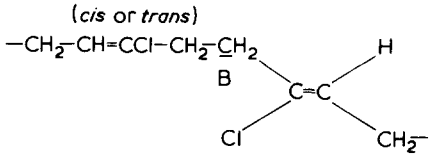
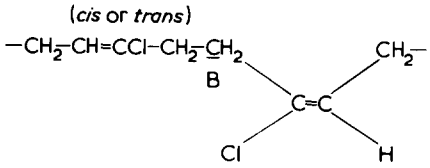


*4,1–1,4 (head–head) linkages*

(*cis* or *trans*)

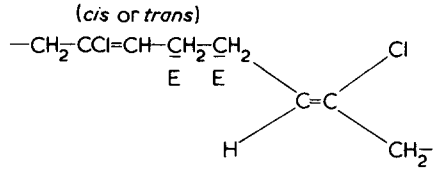


(*cis* or *trans*)

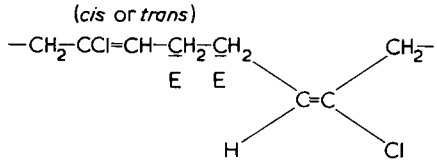


*1,4–4,1 (tail–tail) linkages*

(*cis* or *trans*)



(*cis* or *trans*)



| 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, $^{13}C$ 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 ($\tau$) 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 behaviour[4–7] or of the influence of more than a single relaxation process[8–12] 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' structure[13]. Electric birefringence measurements were made using a conventional apparatus[1] working in the linear detection mode[14]. Pulsed rectangular electric fields of up to 6 kV/cm amplitude and of 6 msec duration were applied to solutions of pig laryngeal proteoglycan[15] in deionized water (at a pH of about 5.5) and 0.71 mg/ml concentration. *Figure 1* records a

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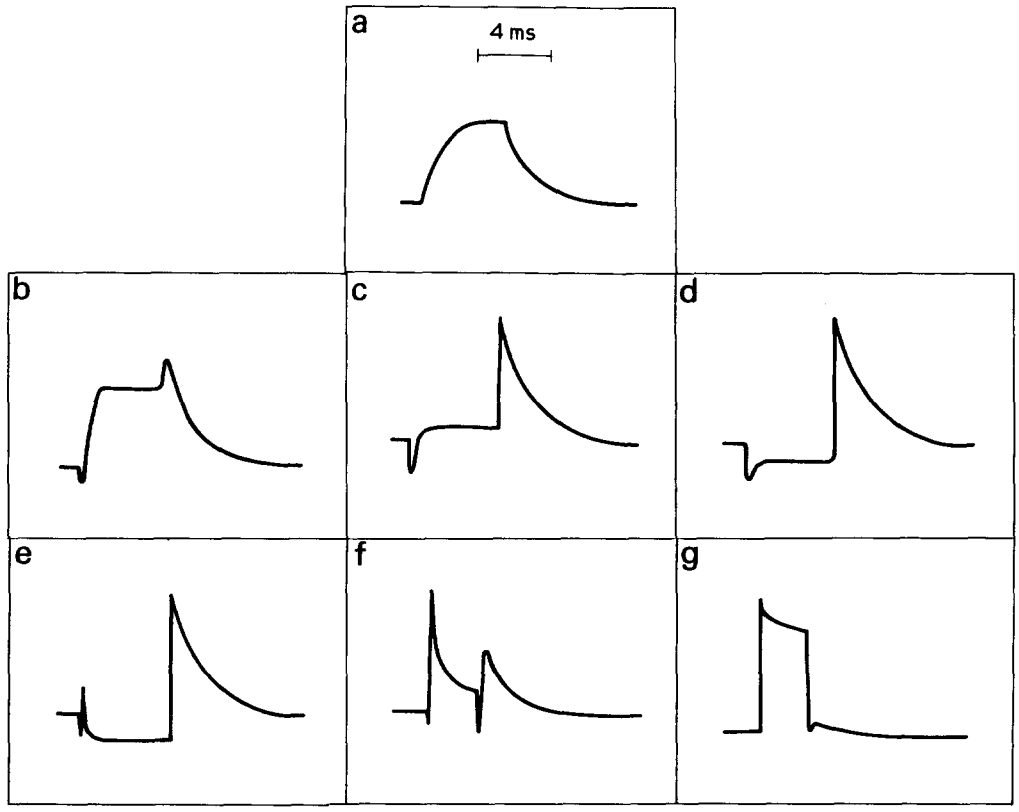


*Figure 1* Transient electric birefringence traces for a proteoglycan solution with increasing electric field amplitudes. Frames (a) to (g) are for pulsed d.c. fields of 200, 680, 1300, 1600, 2200, 2400 and 5300 V/cm, respectively. Time runs from left to right, with the same time scale in each case. Frames (b) to (f) have the same ordinate magnitude, whilst (a) and (g) are 0.5 and 10 times this, respectively

sequence of transient birefringence responses as the field amplitude was increased. We note the following:

(a) the transients became increasingly complex with field amplitude;

(b) the ultimate decay of all transients was characterized by the same relaxation time;

(c) the decay was characterized by more than a single process in frames (b) to (g), indicating the presence of more than a single discrete relaxation event. This multicomponent feature also is evidenced in the establishment of the transient;

(d) at any given field strength, the transients were reproducible.

An interpretation of these traces is as follows. For low amplitude fields, regular transients such as that of *Figure 1a* were recorded. The birefringence, corresponding to the plateau region, varied as the square of the applied field thus obeying the Kerr law[1]. With increasing field strength ($E$) the birefringence became increasingly independent of $E$ as complete orientation of the responsible molecular entity was attained. Fields in excess of 700 V/cm did not induce any further birefringence *from this* component, which we refer to as component I. From the transient decay, it corresponds to a molecular species with a relaxation time of the order of 3 msec.

In the intermediate field strength range [frames (b) to (d)] a second relaxation component II is increasingly manifest. It gives rise to a birefringence of opposite sign to that of component I, involves a faster relaxation time (in the range 400 to 800 $\mu$sec) and requires the relatively larger electric field amplitude to cause significant birefringence. A smaller (or more flexible) molecular species generally does have a shorter $\tau$ and needs a higher $E$ to cause orientation owing to its smaller electrical anisotropy. In this case, its contribution is increasingly significant once component I has begun to approach a field amplitude sufficient to cause its complete orientation. Hence, a full description of the behaviour in *Figure 1d* is as follows. The initial fast negative response of component II is reduced as the slowly increasing positive contribution from component I is encountered. At statistical equilibrium a plateau is established between these two contributions. Upon termination of the pulse, the faster negative contribution II decays rapidly leaving the slower positive component I to decay with its slow characteristic relaxation time.

At even higher field amplitudes, a third, even faster component (III) becomes evident [frames (e) to (g)] giving rise to a positive birefringence. At the field amplitudes sufficient to cause a significant birefringence from component III, species I has been fully oriented and can contribute no more to the observed birefringence whilst species II has gone beyond its $E^2$ dependent region. From frame (g) of *Figure 1*, it is seen that at very large fields process III dominates the birefringence. The existence of the three contributions can be appreciated if one considers the decay processes seen in frames (e) to (g) of *Figure 1*. Upon termination of the field, the fast positive component III rapidly decays, followed by the remnant of the slower negative component II. Finally the slowest component I is the sole remaining contributor which brings the birefringence to its prefield value.

The widely different relaxation rates for each of these three processes enabled us to isolate their contributions to the observed birefringence transients. The procedure was as follows. In frames (b) to (d) one could extrapolate the final relaxation process back to the condition of field termination, thereby defining the magnitude

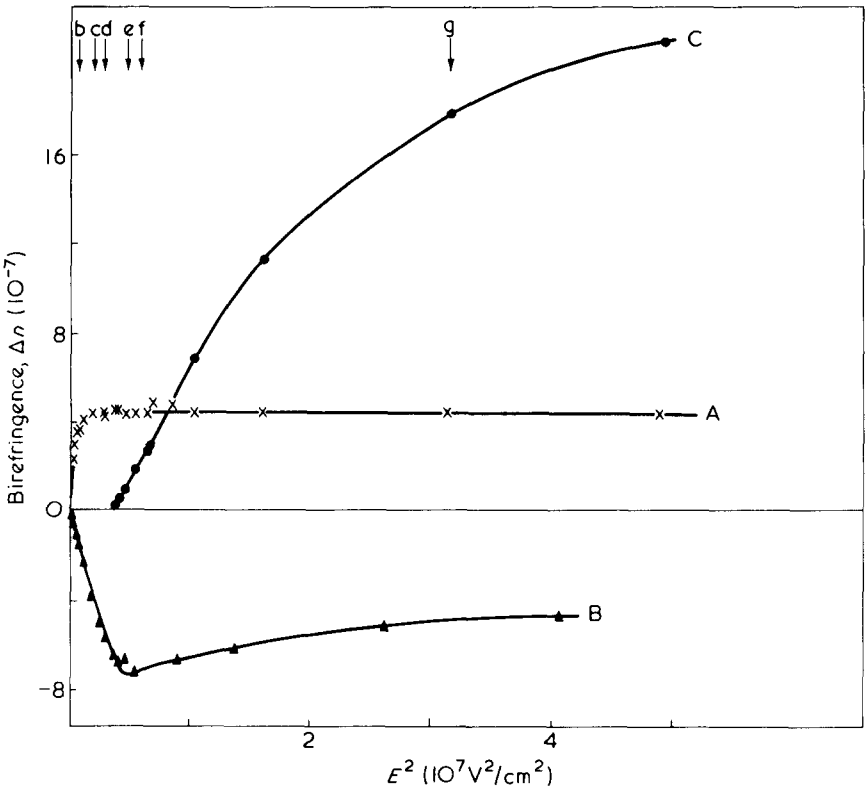


*Figure 2* Variation of the birefringence amplitudes of each component I, II and III with the square of the applied field strength. A, I; B, II; C, III. The conditions for the transients of *Figure 1* are designated by arrows labelled (b) to (g). Figure 1a is too close to the ordinate to display

of the positive birefringence from component I at this field strength. The magnitude of the birefringence due to component II was the difference between this value and the plateau observed before the termination of the field pulse. Such analysis showed that, by the conditions of *Figure 1c*, the birefringence due to species I had reached its maximum value (*Figure 2*). At the higher field amplitudes, component III was predominant and could be estimated. As a first approximation, it was assumed that the initial peak in *Figure 1g* represented the amplitude of this component alone. Hence, the contribution from species II could be estimated from the plateau of the transient after allowing for the species I contribution. Such an analysis enabled the field dependence of the birefringence from each component to be compiled as in *Figure 2*.

Realistic assignments can be made for each of these three contributions in terms of the proteoglycan molecules. Independent studies in this research group on solutions of chondroitin sulphate indicate that these molecules, which constitute the side chains of proteoglycan, have a relaxation time of the order of 1 μsec and give rise to a birefringence field dependence which is strikingly similar in both form and sign to that of component III in *Figure 2*. Secondly, the dimensions of single proteoglycan molecules[13] are consistent with a prolate ellipsoid which, through Perrin's equations[16] correspond to a rotary relaxation time of some 600 μsec. This is similar to the value recorded here for component II. The value of $\tau = 3$ msec observed herein for component I can be interpreted as arising from the rotation of an ellipsoid of twice the length but of equal cross-section to that of independent proteoglycan molecules. This is the model for an end-to-end dimer. Recent studies indicate the presence of aggregates consisting of only a few proteoglycan molecules in solution under various conditions of pH and ionic strength[17,18]. For the conditions of the present experiments, we have used additives which inhibit and disrupt end-to-end bonding in proteoglycans. Such additives have been accompanied by drastic diminutions of component I in the observed electric birefringence responses. Full details of these additional experiments will be reported elsewhere.

It would thus appear that the complex birefringence transients indicate the presence of three independent molecular relaxation processes corresponding to the tumbling motions of an end-to-end dimer (component I), of the single molecule (component II) and to the orientation of flexible chondroitin sulphate side chains (component III). At sufficiently high field strengths, the positive birefringence of the chondroitin sulphate predominates. This is consistent with the fact that this polysaccharide accounts for some 90% of the weight of proteoglycan molecules[13].

In conclusion it appears that, in certain circumstances, unusual electric birefringence transients have their origin in multicomponent relaxation processes associated with the structure of complex macromolecules. Such transients should not be ignored as they may afford a means of characterizing molecules, their aggregates and side chains in the presence of each other.

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## Effect of high pressure in free radical terpolymerizations

Unlike the study of two-component vinyl polymers, the much larger field of three-component polymers has received relatively little attention. Likewise the pressure effect has not been examined in these systems, the quantitative work on high pressure multicomponent polymerizations being centred on free radical copolymerizations[1], so that the present contribution has to be regarded as an exploratory investigation.

Terpolymerization reactions were carried out at 50.0°C in stainless steel tubes or PTFE capsules (at high pressure). The distilled monomers, the initiator (lauroyl peroxide), the solvent (acetone) were introduced in the tube and weighed. After isolation and drying, the polymer was analysed by microanalysis. The yield was limited to 5–10% in all experiments to ensure that the mean composition of the terpolymers was close to the instantaneous composition.

We have examined the pressure effect (3000 bar) first on the contour maps for terpolymer composition, and secondly on azeotropy in terpolymerization systems.

### *Pressure effect on the contour maps for terpolymer composition*

Applying the relationship connecting the feed composition with the instantaneous composition of a multicomponent polymer[2,3]:

$$d[M_1]/d[M_2]/\ldots/d[M_n] = [M_1]\sum_{i=1}^{n}\frac{[M_i]}{r_{1i}}\Big/[M_2]\sum_{i=1}^{n}\frac{[M_i]}{r_{2i}}\Big/\ldots\Big/[M_n]\sum_{i=1}^{n}[M_i]\frac{r_{n1}}{r_{ni}}$$

where $r_{ni}$ is the reactivity ratio of monomer $n$ *versus* monomer $i$; we have calculated the terpolymer composition which requires the knowledge of six binary reactivity ratios. The relation between the molar composition of the terpolymers and the corresponding composition of monomer feed is represented in the form of triangular plots[4].

Using the method developed by O'Driscoll[5], we have computed the contour lines for each monomer; these have been drawn with increments of 0.1 in units of mole fraction. As an example, using the reactivity ratios shown in *Table 1* for the system: acrylonitrile ($M_1$)–diethyl fumarate ($M_2$)–styrene ($M_3$) and replacing them in the above equation, we obtained the contour lines at 1 and 3000 bar, respectively, for the three monomers (*Figure 1*). It should be noticed that variations of position in the composition lines may be considerable (especially for styrene) which gives evidence for the influence of pressure on terpolymer composition. This is due to the pressure effect on reactivity ratios (see *Table 1*) related to the differences in activation volumes for homo- and cross-propagation[8].

### *Pressure effect on azeotropy in terpolymerization systems*

*Ternary azeotrope.* A true azeotrope in terpolymerization would occur, when the mole fraction of all three monomers in the polymer initially produced were the same as those in the feed. For example, we have found that two systems present a true ternary azeotrope

*Table 1* Pressure effect on the reactivity ratios in the system acrylonitrile (1)–diethyl fumarate (2)–styrene (3)

| | 1 bar | 3000 bar | Reference |
|---|---|---|---|
| $r_{12}$ | 5.5 | 9.2 | 6 |
| $r_{21}$ | 0.15 | 0.10 | 6 |
| $r_{13}$ | 0.02 | 0.05 | 6 |
| $r_{31}$ | 0.65 | 0.53 | 6 |
| $r_{23}$ | 0.06 | 0.15 | 7 |
| $r_{32}$ | 0.15 | 0.25 | 7 |

(*Table 2*). According to the results given in this Table, the coordinates are practically not affected by pressure. This result is rather surprising, since, with the exception of α-methylstyrene, combinations of all other comonomers lead to reactivity ratios which are pressure dependent. This point must be

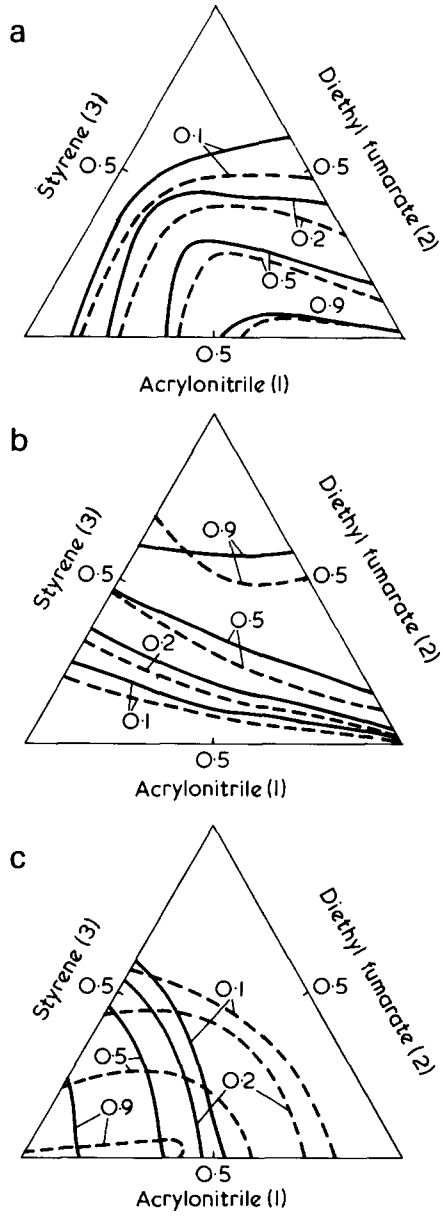


*Figure 1* Effect of pressure on the contour maps for the three monomers of system A. ——, 1 bar; – – – –, 3000 bar

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