Application of infra-red digital subtraction techniques to the microstructure of polychloroprenes:
3. Effect of structural irregularities on the crystalline infra-red bands of chloroprene copolymers

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Infra-red digital subtraction techniques have been applied to chloroprene copolymers containing relatively low concentrations of methyl methacrylate, acrylonitrile or styrene. The 'crystalline' bands of these chloroprene copolymers were obtained by subtraction of the amorphous spectrum obtained at 85°C from that of the semi crystalline spectrum recorded at room temperature. The presence of these comonomer units does not cause frequency shifts of the infra-red crystalline bands of polychloroprene. From these and previous results it is postulated that only the inverted *trans*-1,4- and 2,3-dichloro-2-butenylene units are capable of being included into the crystalline lattice and of causing the observed frequency shifts.

INTRODUCTION

In the preceeding two papers of this series[1,2] we have been primarily concerned with the application of digital subtraction methods to the infra-red spectra of polychloroprenes in the amorphous state. It was demonstrated how this technique may be employed to accentuate the infra-red bands due to structural irregularities occurring in the polymer chain of predominantly *trans*-1,4-polychloroprenes, and how these results can lead to information regarding the mechanism of oxidative degradation. In this communication we describe how digital subtraction techniques may be used to gain information concerning the effects of specific structural irregularities on the 'crystalline' infra-red bands of chloroprene polymers.

The separation of the crystalline bands (or more accurately the bands characteristic of long lengths of the polymer chain in the preferred conformation) from the amorphous contribution to the infra-red spectrum has previously been reported[3]. For the sake of clarity this procedure is illustrated in *Figure 1* using a polychloroprene synthesized at −150°C[4]. This polymer consists of essentially pure *trans*-1,4- units with only approximately 2% as head-to-head placements. Spectrum A is that of the semicrystalline polymer recorded at room temperature. The spectrum of the same polymer in the amorphous state recorded at 85°C is denoted B. By subtracting spectrum B from spectrum A, employing the amorphous band at 602 $\mathrm{cm^{-1}}$ to determine the correct subtraction parameter[3], a difference spectrum (A − B) is obtained that is representative of the crystalline phase of the polychloroprene. Note particularly the relatively narrow and well resolved infra-red bands in the difference spectrum indicating a highly ordered preferred conformation of the translational repeat units in the polymer.

Previous studies on chloroprene polymers polymerized at temperatures in the range −20° to 40°C revealed that specific crystalline bands (obtained by the subtraction technique described above) were sensitive, in terms of frequency, to the number of structural irregularities present in the polymer[5]. When the results of these studies were reported the polychloroprene synthesized at −150°C was not available. Consequently, it is instructive to compare the observed frequencies of the 'crystalline' infra-red bands of this polymer to those of the polymers synthesized at −20°, 0° and 40°C, as in *Table 1*. The most sensitive bands are those at 959, 1009, 1250 and 1318 $\mathrm{cm^{-1}}$ (−150°C polymer). These are all highly coupled normal modes[6] involving the C—C stretch and various $\mathrm{CH_2}$ bending vibrations. It is well known that as the polymerization temperature is increased, the concentration of head-to-head *trans*-1,4-; *cis*-1,4-; 1,2- and 3,4- units also increases[4,7]. Furthermore, it was determined that analogous frequency shifts were also observed in the spectra of a chloroprene copolymer containing approximately 5 mol % of 2,3-dichloro-2-butenylene units. It was concluded from these studies that specific structural irregularities are incorporated into the crystalline lattice causing a perturbation of the vibrational force field which results in specific frequency shifts. In this communication we will consider in more detail the types of irregularities that can be incorporated into the crystal lattice by examining the crystalline bands of chloroprene polymers containing methyl methacrylate (MMA), acrylonitrile (AN) or styrene (Sty) comonomers.

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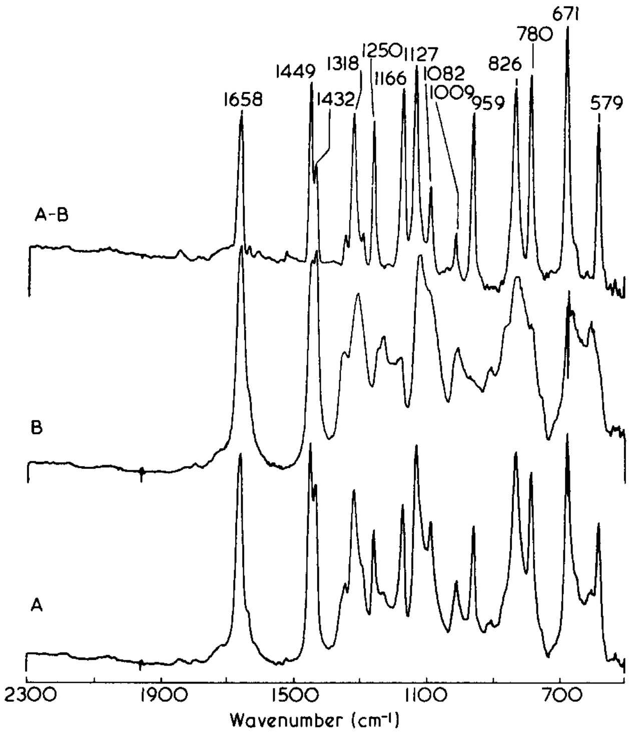


Figure 1 Fourier transform i.r. spectra of polychloroprene polymerized at –150°C in the range 500–2300 cm^{-1}. A, room temperature spectrum; B, spectrum recorded at 85°C; B–A, difference spectrum

EXPERIMENTAL

Chloroprene copolymers were synthesized at –20°C employing a MeOH/water emulsion system described below:

Water (purged with N_2)	392 g
Methanol (purged with N_2)	320 g
Lomar	2 g
Dextrose	2 g
Oleic Acid	16 g
Ammonia (28% soln in H_2O)	24 g
MEK perioxide	1.6 g
Chloroprene (redistilled)	Variable
Comonomer (MMA, AN or Sty)	Variable

Catalyst: 5% solution of sodium hydrosulphite

All the polymers used in this study were isolated before the extent of conversion had exceeded 10%. This procedure is essential to ensure random inclusion of the comonomer into the polymer chain. All three of the comonomers (MA, AN or Sty) are markedly less reactive than chloroprene[8] and it is necessary to use monomer feed ratios containing much larger concentration of the comonomer than required for the desired copolymer composition. Consequently feed ratios of chloroprene: comonomer of 70:30, 80:20, 90:10 and 95:5 were employed. The copolymers were isolated and reprecipitated twice from a carbon disulphide (CS_2) solution into a large volume of methanol. The comonomer content of the copolymers was determined by elemental analysis, infra-red and n.m.r. spectroscopy. The absorptivities of well-isolated, characteristic bands of polychloroprene [υ_s(= C) at 1660 cm^{-1}] and homopolymers of the comonomers [υ_s(C ≡ N) at 2240 cm^{-1} for PAN, and the ring stretching mode at 1601 cm^{-1} for PS] were determined from films of known weight. The copolymer composition was then estimated from the experimental spectra of the copolymers. Although significant errors can be introduced using this technique, it must be emphasized that highly accurate determinations are not needed for this particular study. However, the infra-red analyses of the chloroprene–AN copolymers were checked by elemental nitrogen analysis and were found to be in good agreement. In addition, the chloroprene–MMA copolymers are particularly amenable to analysis by proton n.m.r. spectroscopy. The OCH_3 group associated with the MMA unit has an isolated line at approximately 3.6 ppm[9] while the CH= group of the chloroprene unit absorbs at 5.5 ppm[10]. These results are summarized in *Table 2.*

For the infra-red studies, films were cast from carbon disulphide solutions onto potassium bromide windows. The samples were dried overnight under vacuum at room temperature to remove carbon disulphide. Each sample was then 'sandwiched' using a second potassium bromide plate and stored under vacuum in the absence of light.

The infra-red spectra were obtained on a Digilab Model FTS-15/B Fourier transform spectrometer. Each spectrum was recorded at a resolution of 2 cm^{-1} with a total of 100 scans. The spectra were stored in the system's memory for further data manipulations. The frequency scale is calibrated internally with a reference helium–neon laser to an accuracy of 0.2 cm^{-1}. The precision in the reported frequencies is 1 cm^{-1}. Infra-red spectra were recorded at room tempera-

Table 1 Crystaline vibration frequencies (cm^{-1}) of *trans*-1,4-polychloroprene as function of polymerization temperature

Temperature (°)			
–150	–20	0	40
1658	1660	1660	1660
1449	1449	1448	1447
1318	1318	1316	1313
1250	1250	1252	1254
1166	1167	1167	1167
1127	1127	1127	1127
1082	1083	1083	1083
1009	1007	1005	1004
959	958	954	953
826	826	826	826
780	780	779	778
671	671	671	671
579	177	176.5	576

Table 2 Analyses of the chloroprene copolymers

	Mol % of comonomer		
Copolymer	Infra-red analysis	Elemental analysis	P.n.m.r. analysis
Chloroprene–acrylonitrile			
CA1	1.4	1.0	
CA2	2.2	1.9	
CA3	3.5	3.2	
Chloroprene–styrene			
CS1	0.7		
CS2	2.3		
CS3	3.3		
Chloroprene–methylmethacrylate			
CM1			1.5
CM2			3.0
CM3			3.9

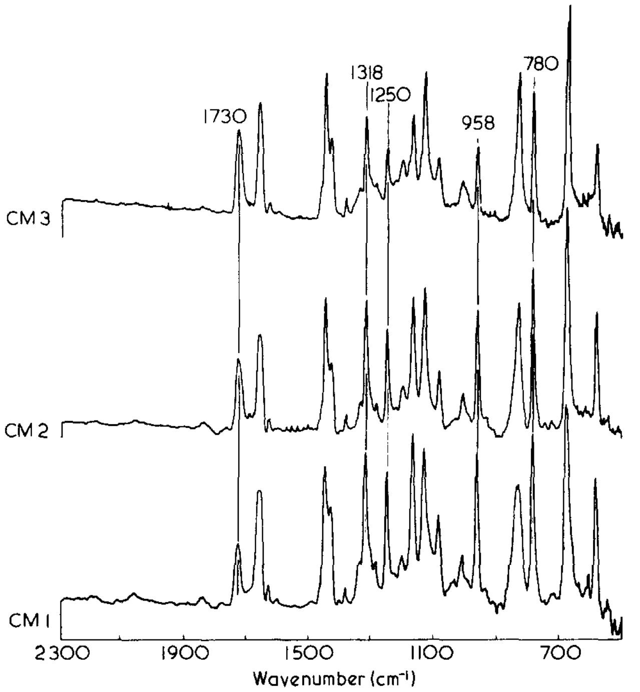


Figure 2 Fourier transform i.r. difference spectra of chloroprene–MMA copolymers in the range 500–2300 cm^{-1} obtained by subtracting the spectrum obtained at 85°C from that of the room temperature spectrum. CM1, 1.5 mol % MMA; CM2, 3.0 mol % MMA; CM3, 3.9 mol % MMA

ture and elevated temperatures (85°C) using a SPECAC automatic temperature controller which is accurate to ±2°C.

The p.n.m.r. spectra were obtained from solutions of the polymers in $CDCl_3$ using a Varian XL 100 spectrometer.

RESULTS

Figure 2 shows the infra-red difference spectra of the three chloroprene/MMA copolymers, designated CM1, CM2, and CM3 obtained by subtracting the amorphous spectrum recorded at 85°C from that of the semicrystalline copolymer recorded at room temperature. To reiterate, these copolymers were synthesized at –20°C and contain approximately 1.5, 3.0 and 3.9 mol % of MMA, respectively. We have implicitly assumed that the concentration and distribution of chloroprene structural units other than the head-to-tail *trans*-1,4-configuration (i.e. inverted *trans*-1,4-; *cis*-1,4-; 1,2- and 3,4-units) is the same as that for a homopolychloroprene synthesized under identical conditions and at the same temperature. This is a reasonable assumption since the concentration of these structural irregularities is primarily a function of temperature for the same free radical emulsion system. An examination of the difference spectra shows conclusively that the presence of MMA does not result in any additional frequency shifts of the polychloroprene crystalline bands. Note particularly the bands at 1318, 1250 and 958 cm^{-1} which appear at identical frequencies in the spectrum of the crystalline bands of homopolychloroprene synthesized at –20°C[5].

There are two aspects of these difference spectra which should be discussed. The first is that the absolute intensities of the crystalline bands, decrease with increasing MMA concentration. This is because there is a decrease in the degree of crystallinity with increasing MMA content which necessitates the subtraction of a larger fraction of amorphous material. Note, however, that all the spectra shown in *Figure 2* are scale expanded so that the band of strongest absorbance is plotted to full scale. The second point concerns the appearance in the difference spectrum of MMA bands characteristic of the polychloroprene crystalline phase. This does not mean that MMA units are incorporated into the crystal but is a consequence of the subtraction method. The difference spectrum is obtained by subtracting the spectrum of the completely amorphous polymer from that of the semicrystalline material. In order to eliminate precisely the amorphous bands in the latter spectrum it is necessary to subtract only a fraction of the former spectrum. Consequently, only a corresponding fraction of the MMA bands are subtracted, leaving some MMA bands in the difference spectrum.

Similar results are observed in the difference spectra of chloroprene copolymers containing Sty (see *Figure 3* – CS1, CS2 and CS3 which contain approximately 0.7, 2.3 and 3.3 mol % of Sty respectively) and those containing AN (*Figure 4* – CA1, CA2 and CA3 which contain approximately 1.2, 2.1 and 3.4 mol % of AN, respectively). The frequencies of the polychloroprene crystalline bands are again identical to those of the homopolychloroprene prepared at the same temperature.

DISCUSSION

It was surmised that a study of the crystalline bands of chloroprene polymers in which additional specific structural irregularities were incorporated might be informative. For example, it seems highly unlikely that a radically different comonomer unit (both in terms of chemistry and size) such as MMA, could be accommodated into the crystalline domain. Thus, if the comonomer is excluded from the crystalline lattice there should be no difference in the position of the crystalline infra-red bands of the copolymer when compared to that of a homopolymer prepared under the same

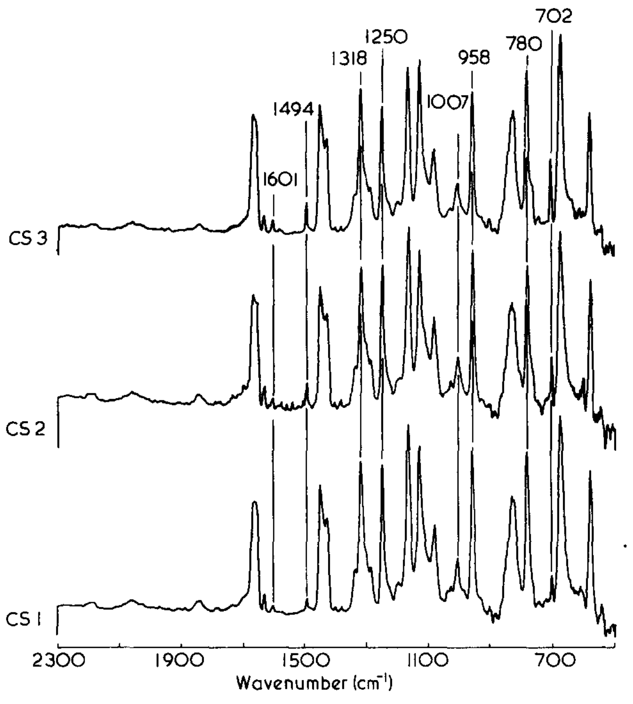


Figure 3 Fourier transform i.r. difference spectra of chloroprene–St copolymers in the range 500–2300 cm^{-1} obtained by subtracting the spectrum obtained at 85°C from that of the room temperature spectrum. CS1, 0.7 mol % Sty; CS2, 2.3 mol % Sty; CS3, 3.3 mol % Sty

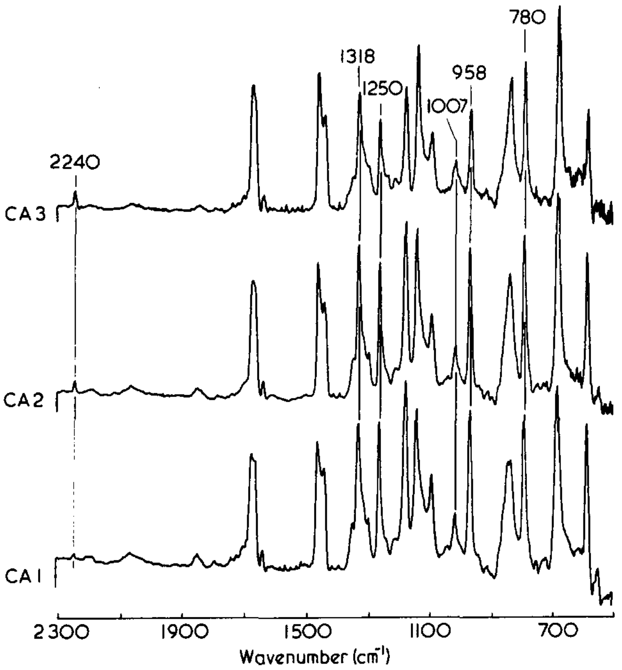
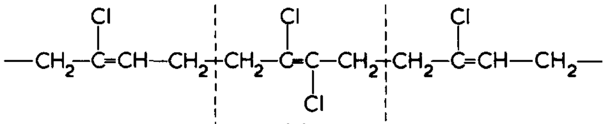


Figure 4 Fourier transform i.r. difference spectra of chloroprene–AN copolymers in the range 500–2300 cm^{-1} obtained by subtracting the spectrum obtained at 85°C from that of the room temperature spectrum. CA1, 1.2 mol % AN; CA2, 2.1 mol % AN; CA3, 3.4 mol % AN

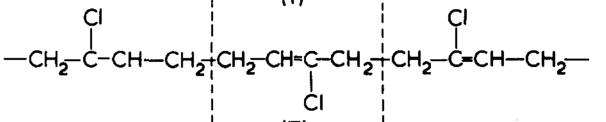
polymerization conditions, assuming random inclusion of the comonomer into the polymer chain. Naturally, the presence of comonomer units will affect the size of the crystalline domains and hence the ultimate degree of crystallinity that can be attained. The above results demonstrate that this hypothesis is correct and the presence of MMA, Sty or AN structural units in the chain of a polychloroprene synthesized at –20°C does not cause significant frequency shifts of the crystalline bands at 1318, 1250 and 958 cm^{-1}. It must be emphasized that a similar concentration of 2,3-dichloro-2-butenylene units introduced into the polychloroprene chain at –20°C does result in significant frequency shifts of these crystalline bands[5]. For example, the 1318 cm^{-1} band shifts to 1314 cm^{-1}, the 1250 cm^{-1} band to 1254 cm^{-1} and the 958 cm^{-1} band to 953 cm^{-1}. Furthermore, as mentioned previously, corresponding frequency shifts are observed in the homopolychloroprene polymerized at 40°C[5].

We believe that these results are convincing evidence for the premise that these frequency shifts of the crystalline bands in the polychloroprenes are caused by the inclusion of inverted *trans*-1,4- (or 2,3-dichloro-2-butenylene) units into the crystalline lattice. An examination of the molecular models of these two structural irregularities supports this conclusion. The presence of an inverted *trans*-1,4- unit in an otherwise head-to-tail *trans*-1,4-polymer causes a relatively minor perturbation of chain conformation and stacking of adjacent chains, permitting a slow incorporation into the lattice (see *Figure 4* of ref 11). Furthermore, the size of the inverted *trans*-1,4- 'defect' is identical to that of the head-to-tail unit, so that chain alignment is not disrupted. It is also significant that the copolymer of chloroprene and 2,3-dichlorobutadiene polymerized at –20°C which effectively introduces 2,3-dichloro-2-butenylene structural irregularities into the polymer chain, shows the same frequency shifts as the homopolymer synthesized at 40°C and indicates that this structural unit is incorporated into the crystalline lattice. The presence of a 2,3-dichloro-2-butenylene unit (I) in an otherwise *trans*-1,4- polychloroprene chain is somewhat analogous to the incorporation of an inverted *trans*-1,4- unit (II):



$$-CH_2-\overset{Cl}{C}=CH-CH_2-CH_2-\overset{Cl}{C}=\underset{Cl}{C}-CH_2-CH_2-\overset{Cl}{C}=CH-CH_2-$$

(I)



$$-CH_2-\overset{Cl}{C}=CH-CH_2-CH_2-CH=\underset{Cl}{C}-CH_2-CH_2-\overset{Cl}{C}=CH-CH_2-$$

(II)

In a previous publication[5] it was concluded, based on the available quantitative infra-red measurements[4], that the *cis*-1,4- structural unit was probably incorporated into the crystalline lattice. However, recent ^{13}C n.m.r. results[12] indicate that the concentration of *cis*-1,4- units in the chloroprene polymers has been considerably overestimated (e.g. 5.2% by ^{13}C n.m.r. compared to 13% by infra-red spectroscopy for the 40°C polymer). We now consider that the *cis*-1,4- structural unit is likely to be excluded from the crystalline lattice because it causes a major perturbation of the chain conformation. Similarly, the 1,2- and 3,4- structural units, together with MMA, Sty and AN units will be excluded from the lattice on the grounds of shape and size.

A theoretical consideration of the effect of these various defects on the vibrational spectrum of polychloroprene also leads to the conclusion that the crystalline defects are primarily due to the inclusion of the inverted *trans*-1,4- or 2,3-dichloro-2- butenylene units. In general, the effect of defects on the vibrational spectrum of a polymer chain can result in the appearance of localized or resonance modes[13,14]. Localized modes are those that lie outside the lattice bands of the ideal polymer chain and thus cannot exchange energy with them. The presence of radically different chemical units, such as MMA, Sty, or AN would give rise to such modes. The spectra presented above demonstrate that the vibrational modes of chloroprene are essentially unperturbed by a low concentration of such defects (frequency shifts and band broadening due to a difference in the sequence length and distribution of *trans*-1,4- units might be expected at higher defect concentrations[15], but at such concentrations the crystallinity of the polymer would also be completely disrupted). Defect units that are configurationally different (e.g. *cis*-1,4-, 1,2- or 3,4- units) could also give rise to such localized modes. In this case there is a more complex situation since there is the possibility of weak coupling between such chemically similar units. However, localized modes are observed for such defects, as demonstrated in the first paper of this series.

In contrast, resonance modes are located inside the lattice bands of the ideal polymer and are coupled to them. Clearly the inclusion of inverted *trans*-1,4- units would give rise to such modes. If we were to set up and compare the valence force constant matrix of a polymer chain which included such units with that of the ideal perfect chain, then the only difference would be in the order of the off-diagonal terms (the interaction force constants), since no new chemically distinct structure is being incorporated into the chain. Such changes in the force constant matrix can at their simplest be considered as a perturbation that would lead to the observed frequency shifts in the crystalline bands of *trans*-1,4-polychloroprene polymerized at various temperatures.

In summary, the presence of MMA, Sty and AN units in the polychloroprene chain does not cause frequency shifts of the crystalline bands. Furthermore, it is reasonable to infer that the *cis*-1,4-, 1,2- and 3,4- structural irregularities are also excluded from the crystalline lattice on the grounds of shape and size. Only the inverted *trans*-1,4- and the 2,3-dichloro-2-butenylene units may be accomdated into the crystalline lattice. This causes a perturbation of the vibrational force field resulting in the observed frequency shifts of specific crystalline bands.

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