Application of infra-red digital subtraction techniques to the microstructure of polychloroprenes: 2. Mechanism of oxidative degradation at 60°C

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Experimental results obtained from the application of infra-red digital subtraction techniques to oxidized polychloroprenes are presented. These results demonstrate the involvement of 1,2- and 3,4-structural irregularities in the initial stages of oxidative degradation at 60°C. A free radical mechanism consistent with these observations is proposed.

INTRODUCTION

In the first paper of this series[1] we demonstrated the potential of digital subtraction techniques to accentuate and measure the infra-red bands associated with structural irregularities present in predominantly *trans*-1,4-polychlororenes. We will show in this communication how this technique may be employed to gain significant information concerning the oxidation of polychloroprene. Specifically, we will present infra-red spectral evidence for the involvement of 1,2- and 3,4-structural units in the initial stages of oxidation at relatively low temperatures (~60°C). In addition, we will advance a simple free radical mechanism that is consistent with the experimental results.

The oxidative degradation of polychloroprene has previously been studied by several investigators[2–7]. The majority of these studies have been carried out at elevated temperatures (90°–500°C) on samples where the degree of oxidative degradation is extensive. However, most commercial polychloroprenes find wide application as elastomeric materials and are generally employed in the –30° to 120°C range. Slight oxidation, which may result in chain scission and crosslinking reactions, can have a marked effect on the physical properties of the material. Consequently, we believe the initial stages of oxidation at moderate temperatures to be particularly relevant to the end use applications of polychloroprene.

Bailey[4] studied the oxidative degradation of polychloroprene using a variety of techniques, including infra-red spectroscopy, in the temperature range of 90°–120°C. On the basis of his results, Bailey proposed a free radical mechanism for the oxidation of polychloroprene. This mechanism involved peroxy radical attack on the α-methylene hydrogen contained in the main-chain *trans*-1,4-unit. Subsequent oxidation yields cyclic peroxides which decompose to give acid chlorides and aldehydes. Infra-red bands observed at 1802 and 1734 cm^{-1} in the spectrum of the oxidized polymer were assigned to the υ_s (C=O) stretching frequencies of acid chlorides and aldehydes, respectively, consistent with the final two products. However, this mechanism seems unlikely because it invokes adjacent cyclic peroxides which are sterically unfavourable and because it does not take into account the fact that polychloroprenes contain a significant concentration of structural irregularities that are highly reactive and susceptible to oxidation. More recent studies have been carried out by Gardner and McNeill[5–7] but their papers are mainly concerned with a comparison of the degradation of polychloroprene with that of poly(vinyl chloride). The experiments involved much higher temperatures where elimination of HCl and the formation of conjugated sequences is significant.

EXPERIMENTAL

The polymers used in the experiments have been previously described in the first paper of this series[1]. Films used in the infra-red studies were cast from 10% carbon disulphide solution onto potassium bromide plates. The samples were dried under vacuum at room temperature for several hours to remove residual carbon disulphide. Infra-red spectra were taken at 60°C (±2°C) using a SPEAC automatic temperature controller. Oxidation was carried out within the sample chamber of the spectrometer.

The infra-red spectra were obtained on a Digilab Model FTS 15B Fourier transform spectrometer. Each spectrum was recorded at a resolution of 2 cm^{-1} utilizing 100 scans. The spectra were stored in the systems memory for further data manipulations. The frequency scale is accurate to 0.2 cm^{-1} and the precision of the reported frequencies is 1 cm^{-1}.

RESULTS AND DISCUSSION

We have previously described an infra-red digital subtraction technique where the spectrum of an amorphous polychloroprene (heated to 70°C) synthesized at 20°C was subtracted from that of polychloroprene synthesized at 40°C[1]. The resulting difference spectrum was shown to reflect the variation in concentration of structural irregularities (*cis*-1,4-; 1,2- and 3,4- units) between the two polymers. A similar method was used to accentuate the changes that occur in the initial stages of oxidation of the 40°C polymer. *Figure 1* shows the amorphous infra-red spectra (recorded at 60°C)

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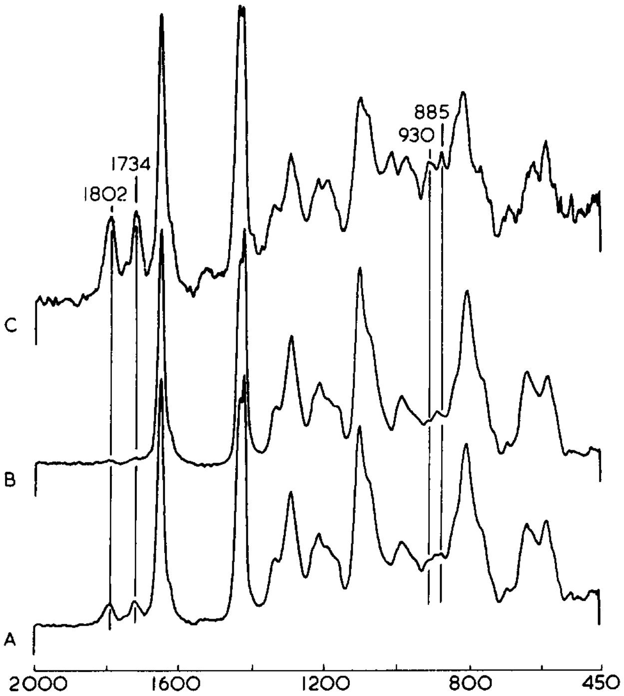


Figure 1 Fourier transform i.r. spectra at 60°C in the range 450–2000 cm^{-1}. A, Polychloroprene polymerized at 40°C and oxidized for 3 h at 60°C; B, unoxidized polychloroprene polymerized at −20°C; C, difference spectrum

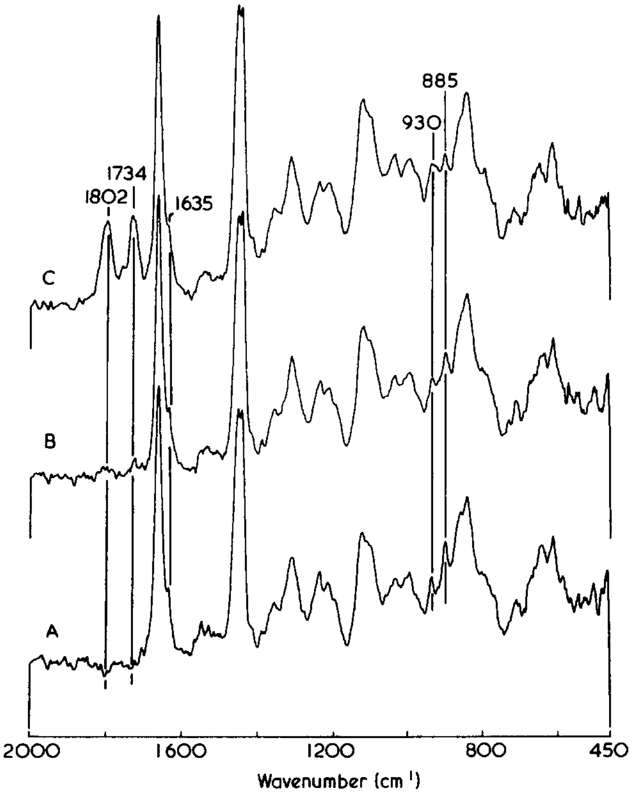


Figure 2 Fourier transform i.r. difference spectra at 60°C in the range 450–2000 cm^{-1} obtained by subtracting the spectrum of polychloroprene polymerized at −20°C from the spectra of polychloroprene polymerized at 40°C and oxidized at 60°C for 5 min (A), 1.5 h (B) and 3 h (C)

of a slightly oxidized 40°C polymer (A), an unoxidized −20°C polymer (B) and the difference spectrum (C) obtained by subtracting B from A. The criterion for subtracting the spectral contribution of the regular *trans*-1,4 units is the same as that described in the preceding paper. Note particularly the accentuation of the bands at 1802 and 1734 cm^{-1} assigned to acid chlorides and aldehydes. We will be particularly interested in the bands associated with the 1,2- and 3,4 structural units which are observed at 930, 885 and 1635 cm^{-1} (ref 1).

Figure 2 shows the difference spectra obtained by subtracting the amorphous spectrum of the unoxidized −20°C polychloroprene from that of the 40°C polychloroprene after (A) 5 min; (B) 1.5 h and (C) 3 h at 60°C. In effect, we are employing the −20°C polymer as an identical standard with which to remove the major *trans*-1,4 contribution. This in turn, accentuates the changes that occur upon oxidation. The spectrum designated A is that of the essentially unoxidized polymer, while B reflects that of the polymer where oxidation can only just be detected (note the infrared bands at 1802 and 1734 cm^{-1}). Spectrum C is that of a clearly oxidized polychloroprene. However, it should be emphasized that oxidation is still not extensive. The intense bands associated with acid chlorides and aldehydes, 1802 and 1734 cm^{-1}, respectively, are still relatively weak (see *Figure 1*) and only appear relatively strong in the difference spectrum after the main contribution of the *trans*-1,4- units has been eliminated. It is evident from a comparison of the three spectra in *Figure 2* that the bands at 1635, 930 and 885 cm^{-1} have decreased in intensity as a function of oxidation. *Figure 3* shows an expansion of the 760–1160 cm^{-1} region of the spectra. The decrease in intensity of the 930

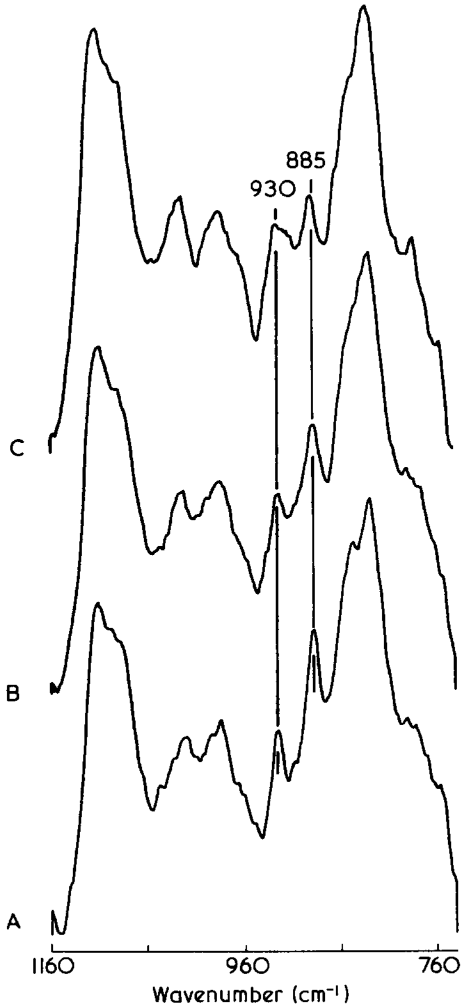


Figure 3 Expanded Fourier transform i.r. difference spectra in the range 760–1160 cm^{-1} shown in *Figure 2*

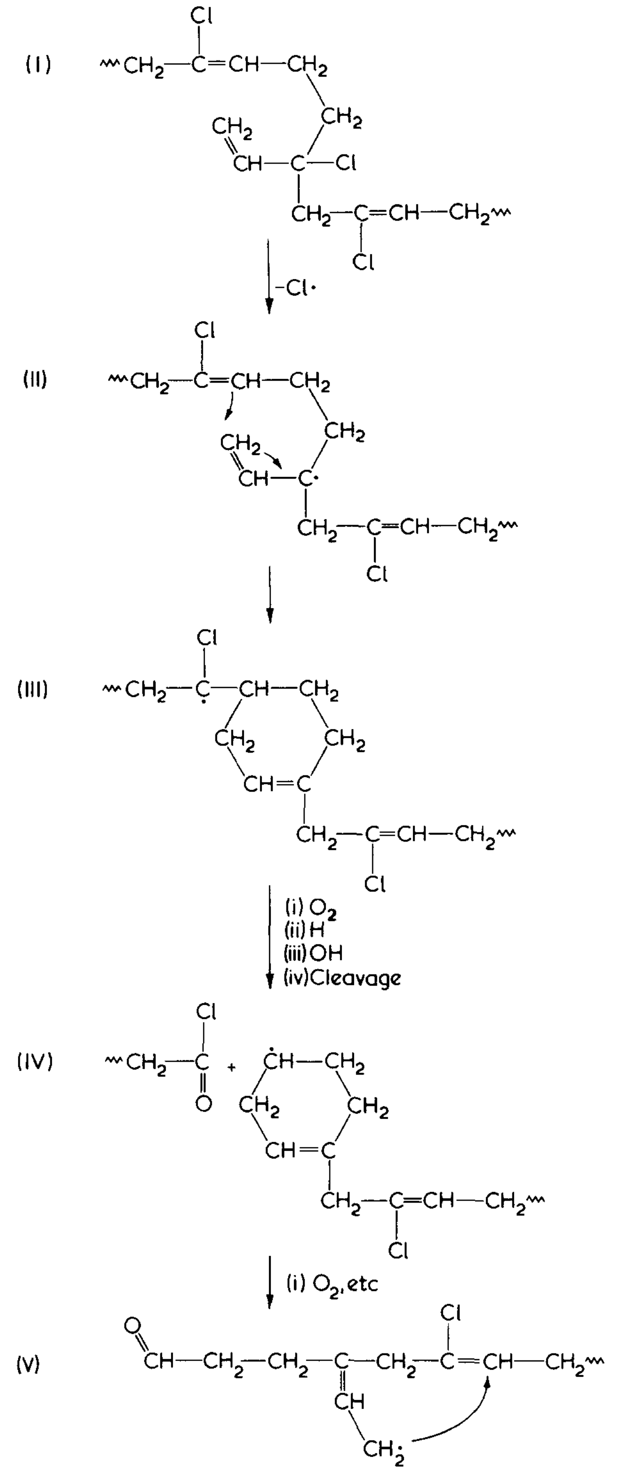


Figure 4 Proposed mechanism for the oxidation of polychloroprene at 60°C

and 885 cm^{-1} bands is pronounced upon oxidation. These two bands are associated with 1,2- and 3,4- structural units respectively[1]. It is well known that tertiary allylic chlorines and hydrogens are very reactive, and the above results show conclusively that the 1,2- and 3,4- structural units are attacked preferentially in the initial stages of oxidation. Note particularly spectrum B which shows a significant decrease in the intensities of the 930 and 885 cm^{-1} bands compared to the unoxidized spectrum, A, even though at this stage in the oxidation the 1802 and 1734 cm^{-1} bands are not definitive.

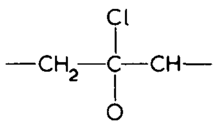
A simple mechanism, consistent with the involvement of the 1,2- and 3,4- units in the oxidation of polychloroprene at 60°C is shown in *Figure 4*. Essentially, the mechanism includes the following:

(1) Abstraction of a tertiary allylic chlorine or hydrogen (from 1,2- or 3,4- units) yielding a tertiary carbon radical (II) which is stabilized by resonance:

$$\dot{C}\text{–CH=CH}_2 \leftrightarrow \text{C=CH – }\dot{C}\text{H}_2$$

(2) Intramolecular cyclization by rearrangement yielding a cyclohexene and a chlorine substituted tertiary carbon radical (III).

(3) Oxidation of (III), followed by abstraction of H^0 to yield a hydroperoxide which decomposes to give the structure:

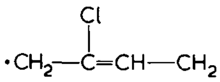


$$\text{—CH}_2\text{—}\overset{\text{Cl}}{\underset{\text{O}}{\text{C}}}\text{—CH—}$$

Cleavage of the chain results in the formation of an acid chloride (one of the observed products) and a secondary carbon radical (IV).

(4) Further oxidation of (IV), similar to that outlined in (2) above, results in the formation of an aldehyde (the second major product) and an allylic carbon radical (V).

(5) The radical (V) is identical to that of radical (II), and the above process can now be repeated by attack of radical (V) on the other side of the chain or, alternatively, it could terminate by abstracting another allylic chlorine or hydrogen from another chain [i.e. repeat the process from step (1)]. In either case, the mechanism predicts the formation of acid chlorides and aldehydes which are reported to increase proportionately as a function of oxidation[4]. Furthermore, if both sides of the chain are attacked by radicals (II) and (V) we are left with the allylic main chain radical:



$$\cdot\text{CH}_2\text{—}\overset{\text{Cl}}{\text{C}}\text{=CH—CH}_2$$

A back-biting mechanism involving a six-membered cyclization process can be invoked, similar to that described above, which also predicts the formation of acid chlorides and aldehydes.

Summarizing, we believe that the infra-red results presented in this communication conclusively demonstrate the involvement of 1,2- and 3,4- structural irregularities in the initial stages of the thermal oxidation of polychloroprenes at 60°C. In addition, a simple free radical mechanism is presented which is consistent with our experimental results. This mechanism suggests that polychloroprenes could possibly be stabilized against oxidative degradation by the elimination of the 1,2- and 3,4- structures. The concentration of these structural units does decrease on reducing the temperature of the free radical polymerization into the range 40° to −40°C, (see *Table 1* of ref 1) but only by a factor of 2 or 3. Furthermore, reducing the temperature also increases the *trans*-1,4- content which increases the crystallinity so that the material is no longer elastomeric. Presumably, 2,3-dichlorobutadiene could be used as a comonomer to overcome this latter difficulty. However, chemical modification after synthesis of the polymer would be the most efficient way of completely eliminating the 1,2- and 3,4- structures. As mentioned previously, both these structures are chemically reactive and saturation of the vinyl double bonds (e.g. bromination, hydrohalogenation, etc.) or nucleophilic substitution of the allylic chlorine is feasible. This is currently under investigation in our laboratory.

ACKNOWLEDGEMENTS

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