Application of infra-red digital subtraction techniques to the microstructure of polychloroprenes: 1. Accentuation and assignment of bands due to structural irregularities

M. M. Coleman, R. J. Petcavich and P. C. Painter
Polymer Science Section, The Pennsylvania State University, University Park, Pa 16802, USA
(Received 25 March 1978)

Infra-red digital subtraction techniques have been employed to accentuate and assign the bands associated with the structural irregularities present in predominantly *trans*-1,4- polychloroprenes. The spectral contribution of the *trans*-1,4- configuration was removed from the spectra of polychloroprenes synthesized at different temperatures revealing contributions due to *cis*-1,4-, 1,2- and 3,4- structural irregularities. In addition bands associated with end-groups were also observed. The results demonstrate the potential of infra-red digital subtraction techniques to determine, both qualitatively and quantitatively, relatively small concentrations of structural irregularities in polychloroprenes.

INTRODUCTION

Infra-red spectroscopy has traditionally been one of the most widely employed tools for the characterization of polymeric materials. However, there has been one major drawback. In many cases the detection of analytical infra-red bands due to relatively small concentrations of other structural units or irregularities in the polymer chain is of particular importance. Such defects have a marked effect on the chemical and physical properties of the polymer. Unfortunately, infra-red bands attributed to these structural irregularities, which can arise from sequential or structural isomerization of the monomer, incorporation of a comonomer, oxidative or thermal degradation etc., are often masked by the strong absorbance of the unmodified structural units of the polymer. Previously, attempts have been made to eliminate this background by introducing a wedge of unmodified material in the reference beam of a dual beam spectrometer. This balancing technique is time-consuming but it has been employed successfully over limited spectral ranges. During the past few years, with the proliferation of dedicated mini-computers, it has become relatively easy to perform mathematical manipulations upon infra-red spectral information. Although data processing is not strictly limited to Fourier transform infra-red spectrometers, the fact that the spectral information is necessarily stored digitally in a dedicated minicomputer permits routine subtraction or addition of absorbance spectra.

Difference absorbance spectra obtained from polymeric systems are more readily interpreted when there is little or no significant vibrational coupling between the chemical repeat units that make up the polymer chain. In this case it is possible to subtract the contribution of the main structural unit which in turn accentuates the presence of the remaining structural irregularities.

Consequently, we postulated that detection and identification of the changes in the microstructure of polychloroprenes prepared as a function of polymerization temperature would be particularly amenable to digital subtraction techniques. Normal coordinate calculations indicate that the structural units in *trans*-1,4-polychloroprene are not significantly coupled[1]. Structural irregularities occurring in predominantly *trans*-1,4-polychloroprenes include *cis*-1,4-; 1,2-, isomerized-1,2-, 3,4- and inverted *trans*-1,4- units[2–4]. All these structural irregularities increase in concentration as the polymerization temperature is increased[2,4] which in turn leads to a decrease in the maximum degree of crystallinity that the polymer may attain[5]. Quantitative measurements of the concentration of the various types of structural units present in polychloroprene chains synthesized at temperatures in the range −150° to 90°C have recently been obtained by Coleman and Brame using ^{13}C n.m.r. spectroscopy[3,4]. *Table 1* summarizes these results and presents data concerning the amount of *trans*-1,4- (TH), inverted *trans*-1,4- (TH), inverted *trans*-1,4- (HT), *cis*-1,4-, 1,20, isomerized 1,2- and 3,4- structural units. These results conflict somewhat with previous infra-red studies[6] especially on the amount of *cis*-1,4- present as a function of temperature. ^{13}C n.m.r. is an excellent technique for studying the microstructure of polychloroprenes, but it is time consuming and not readily amenable to routine analysis.

Infra-red spectroscopy has previously been employed to estimate the concentration of structural irregularities in polychloroprenes[7]. However the results were subject to considerable error due to the presence of the strongly absorbing background of the predominant *trans*-1,4- units and the uncertainty of drawing baselines. Ferguson[8] attempted to improve the accuracy of the analysis of *cis*-1,4- units by a curve fitting technique employing the C=C stretching frequency. In this communication we report the results of the

0032–3861/78/111243–06$02.00

application of digital subtraction methods to the characterization of polychloroprenes containing different amounts of structural irregularities.

EXPERIMENTAL

Preparation of polymers

Chloroprene was either polymerized at temperatures below 0°C or in the MeOH/H_2O emulsion system described previously[9], or at 0°C and above, essentially with the recipe of McFarland and Pariser[10]. The chain transfer agent, CCl_3Br, was employed in varying amounts in all cases to yield number-average molecular weights in the 100 000 range, as determined by gel permeation chromatography. The polymers were isolated in MeOH, containing a phenolic antioxidant and reprecipitated twice from CS_2 solution into a large volume of MeOH before use.

Essentially all *trans*-1,4-polychloroprene was synthesized by irradiation of the crystalline monomer at −150°C[6]. Only 0.1 g of this polymer was available.

Model compounds

The preparation and purification of the model compounds used in this study, *cis* and *trans*-chloro-4-octene; 3-chloro-1-butene; 2-chloro-1-butene and 1-chloro-3-methyl-2-butene, have been described in a previous publication[3].

Instruments

The infra-red spectra were obtained on a Digilab Model FTS-15/B Fourier transform spectrophotometer. 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}.

For the infra-red studies, films were cast from carbon disulphide solutions onto potassium bromide plates. The samples were dried overnight under vacuum at room temperature to remove carbon disulphide. The samples were then sandwiched between potassium bromide plates and stored under vacuum in the absence of light until infra-red spectra were obtained.

Infra-red spectra were taken at temperatures in the range of 70°–85°C using a SPECAC automatic temperature controller which is accurate to ±2°C. Solution studies were carried out at room temperature in 10% w/v of the polymer in carbon disulphide using a sealed cell having a pathlength of 0.1 mm. Because of the very limited quantity of the all *trans*-1,4-polychloroprene (polymerized at −150°C) available, an accurate 10% w/v solution was not prepared.

RESULTS AND DISCUSSION

Polychloroprenes are semicrystalline materials and infra-red spectra acquired at room temperature are composed of contributions from the crystalline (or more accurately, the preferred conformation of the polymer chain) and the amorphous phases. We have previously shown[11] that there are subtle changes in the frequencies of specific 'crystalline' bands as a function of polymerization temperature. This has been interpreted as being due to the inclusion of defects in the crystalline lattice (see paper 3 of this series for a further discussion of this topic). In any event, one consequence of this behaviour is that meaningful data concerning structural defects cannot be obtained from the subtraction of the room temperature spectra of polychloroprenes prepared at different temperatures. This is due to variations in the degree of crystallinity and changes in the band shapes and frequencies. However, we surmized that digital subtraction techniques might be successful if carried out above the crystalline melting points of the polymers. The infra-red bands will broaden, in this case, due to the distribution of conformational arrangements in the amorphous state. This implies that the spectral contribution from the *trans*-1,4-structural units in the molten polychloroprene will have a similar distribution of conformational states regardless of the temperature of polymerization and the presence of a varying concentration of structural irregularities. Thus by digitally subtracting the amorphous spectrum (acquired at 70°C) of a more structurally regular polychloroprene from that of a polymer containing a higher concentration of structural irregularities, it should be possible to accentuate the infra-red bands due to these structural irregularities. *Figure 1* demonstrates this procedure. Spectra A and B are those obtained at 70°C from the polychloroprene samples polymerized at −20° and 40°C respectively. The scale expanded difference spectrum (B − A) was obtained using the bands attributable to *trans*-1,4- units at 1660, 1305, 1118 and 825 cm^{-1} to determine the correct subtraction parameter. In terms of experimental technique, it should be emphasized that to obtain high signal-to noise difference spectra it is essential that the films employed should be of comparable thickness (<0.5 μm) and be within the absorbance range where the Beer–Lambert law is obeyed.

The infra-red bands observed in the difference spectrum are attritubutable to the *cis*-1,4-, 1,2- and 3,4- structural units and represent a difference of approximately 4, 1 and 1% respectively based on the ^{13}C n.m.r. results (see *Table 1*). Of particular interest is the fact that it was possible to resolve the C=C stretching vibration of the *cis*-1,4- unit at 1652 cm^{-1} from that of the very strongly absorbing 1660 cm^{-1} C=C stretch of the predominant *trans*-1,4- unit. This region of the spectrum is shown on an expanded frequency scale in *Figure 2*. The major bands occurring in the difference spectrum are given in *Table 2*. We have also included the infra-red spectral data reported by Ferguson[7] for the predominantly *cis*-1,4-polychloroprene synthesized by Aufdermarsh and Pariser[12]. Dr Aufdermarsh kindly supplied a copy of the original infra-red spectrum of this polymer from which we determined the infra-red frequencies. The major bands due to the *cis*-1,4- unit, (i.e. 1652, 1440, 1430, 1340, 1285, 1225, 1200, 1105, 1030, 850, 800, 690 and 654 cm^{-1}), observed in the difference spectrum are consistent with the infra-red spectrum of the *cis*-1,4-polychloroprene. The infra-red spectrum of the isolated *cis*-1,4- unit in polychloroprene will be similar to that of the *cis*-1,4- homopolychloroprene due to the large repeat unit and the absence of significant vibrational coupling along the chain. Although it was inferred from chemical and spectroscopic means that the polymer synthesized by Aufdermarsh and Pariser[12] was indeed predominantly *cis*-1,4-polychloroprene, the above results from the difference spectrum prove this conclusively. Infra-red analysis of the model compounds *cis* and *trans*-4-chloro-4-octenes in the liquid state was not very helpful. Apart from the significant difference in the frequencies of the C=C stretching vibration (1662 cm^{-1} for *trans*; 1653 cm^{-1} for *cis*) the only characteristic bands that could be related to the *cis*-1,4-polychloroprene were those observed at 1232, 1105, 680

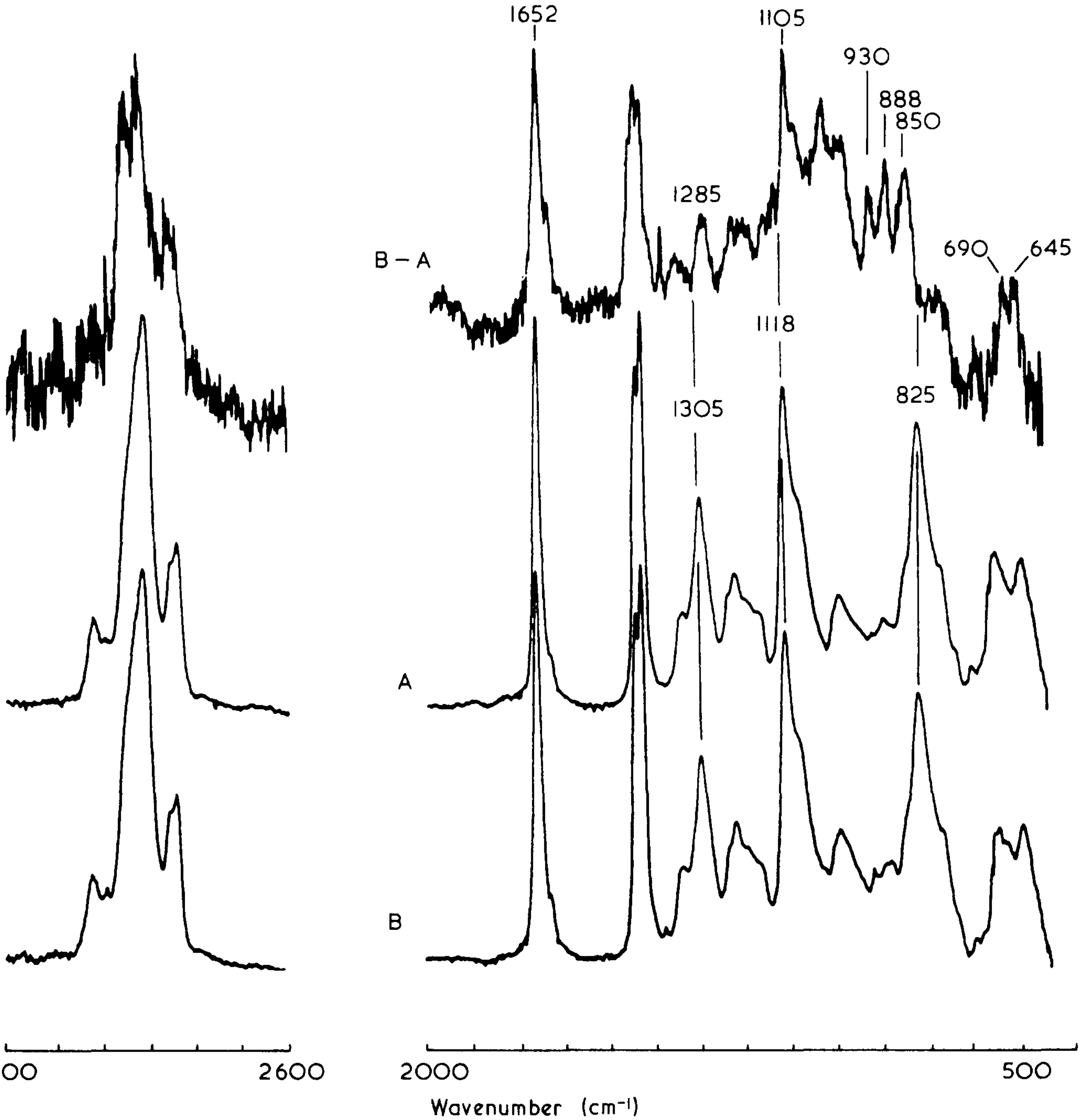

Figure 1 Fourier transform i.r. spectra at 70°C in the range 500–3200 cm^{-1}: A, polychloroprene polymerized at −20°C; B, polychloroprene polymerized at −40°C; B–A, difference spectrum

and 645 cm^{-1}. In model compounds of this type coupling of the vibrations of the methyl end groups with those of the chloroprene repeat unit can significantly affect the spectrum.

The 1,2- unit is readily identified spectrum by the well isolated bands at 985 cm^{-1}. The compound 3-chloro-1-butene which is a model for the 1,2- structural unit in polychloroprene[3] has characteristic bands at 989 (ms), 930 (vvs) 1024 (vs) and 1644 (m). The latter two frequencies contribute to the bands at 1030 and 1638 cm^{-1} observed in the difference spectrum.

The 3,4- unit is identified by a band at 888 cm^{-1} in the difference spectrum which is consistent with one of two dominant bands (878 cm^{-1}) observed in the infra-red spectrum of model compound 2-chloro-1-butene. The other intense band in the model compound occurs at 1633 cm^{-1} and contributes to the band at 1638 cm^{-1} observed in the difference spectrum.

There are no isolated bands that can be unambiguously assigned to the isomerized 1,2- unit. The compound 1-chloro-3-methyl-2-butene, which is a model for the isomerized-1,2 unit[3] has extremely intense bands at 840 and 670 cm^{-1}. No isolated bands are observed at these frequencies in the difference spectrum, but examination of *Table 1* reveals that the concentration of isomerized 1,2-units is within experimental error for both the 40°C and −20°C polymers. Therefore, if the band exists it would be eliminated by the subtraction technique.

The above results suggest that digital subtraction of the infra-red spectrum of an amorphous all *trans*-1,4-polychloroprene from that of an amorphous sample of a polychloroprene containing structural irregularities is a viable and

Table 1 ^{13}C n.m.r. analysis of polychloroprenes prepared at different temperatures[1]

Polymerization temperature (°C)	*trans*-1,4-)%)			Isomerized (%)			
	Total	HT	TH	1,2-	1,2-	3,4-	*cis*-1,4-
40	90.8	9.2	81.6	1.7	0.8	1.4	5.2
0	95.9	5.5	90.4	1.2	1.0	1.1	1.8
–40	97.4	4.2	93.2	0.8	0.6	0.5	0.7
–150	~100.0	2.0	98.0	n.d.*	n.d.*	n.d.*	n.d.*

* Estimated to be ⩽ 0.2%.

[1] From the data of Coleman and Brame – ref 4

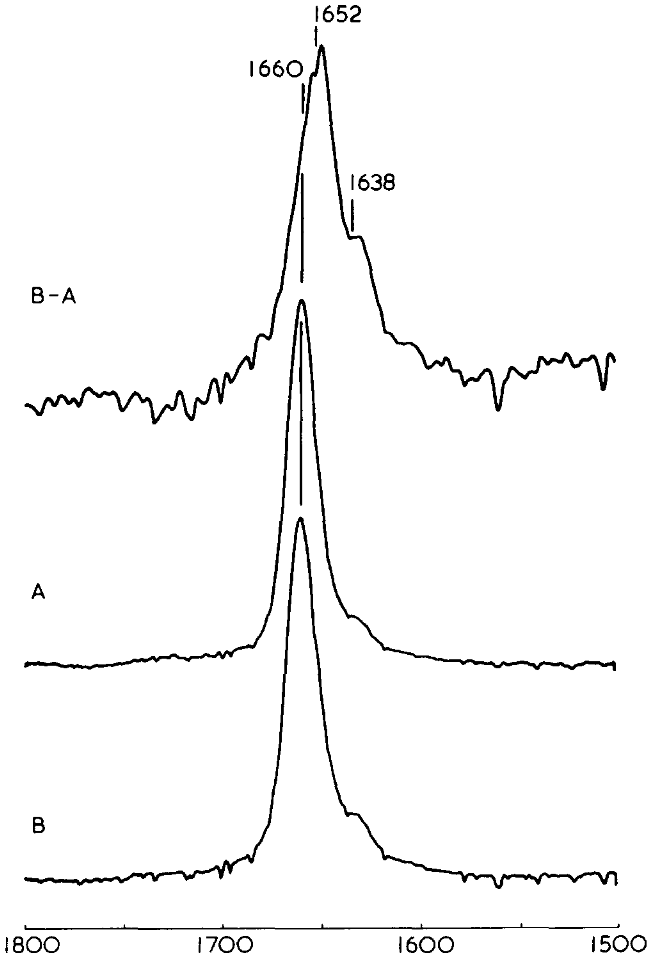

Figure 2 Expanded Fourier transform i.r. spectra at 70°C in the range 1500–1800 cm^{-1}: A, polychloroprene polymerized at –20°C; B, polychloroprene polymerized at 40°C; B–A, difference spectrum

efficient method for qualitative analysis, and also suggests that quantitative analysis is feasible. However, it must be emphasized that we have been unable to perform this procedure in a desirable routine manner. Although we have obtained difference spectra similar to that shown in *Figure 1* many times on different samples we have also failed on several occasions to produce difference spectra that do not exhibit considerable band distortions. One important factor is that the absolute absorbance values of both samples must correspond closely for optimum results. But this is not the only criterion for successful subtraction. In fact, we have . been unable to obtain acceptable difference spectra employing the essentially all *trans*-1,4-polychloroprene (i.e. polymerized at –150°C) in the molten state at temperatures up to 85°C. It was this failure that led us to attempt the subtractions in solution. Carbon disulphide (CH$_2$) was chosen as the solvent for the polymer because it has relatively few infra-red bands and there is a 'window' in the 1400–600 cm^{-1} spectral range.

Figure 3 shows the infra-red spectrum of CS$_2$ solutions of the polychloroprene samples synthesized at –150° and 40°C (A and B respectively). The difference spectrum (B – A) was obtained by subtracting A from B using the band at 1118 cm^{-1} to determine the correct subtraction parameter. Although this appears somewhat subjective, it is relatively

Table 2 Frequencies and assignment of major bands in the Infrared difference spectrum of polychloroprene taken at 70°C

cis-1,4-polychloroprene[1] (cm^{-1})	Difference spectrum (cm^{-1})	Assignment
1652 (vs)	1652 (vs)	υ_s(C=C) *cis*-1,4-
	1638 (m–sh)	υ_s(C=C) 1,2-; 3,4-
1440 (s)	1440 (s)	δ(CH$_2$)
1430 (s)	1430 (s)	
1345	1340 (w–br)	*cis*-1,4-
1284 (m)	1285 (m)	*cis*-1,4-
1225 (ms)	1225 (m–br)	*cis*-1,4-
1196 (ms)	1200 (m–br)	*cis*-1,4-
1105 (s)	1105 (vs)	*cis*-1,4-
	1090 (m–sh)	?
1030 (ms)	1030 (s)	*cis*-1,4-; 1,2-
	985 (m–br)	1,2-; *trans CH* wag
	930 (m)	1,2-; CH$_2$ wag
	888 (m)	3,4-; CH$_2$ wag
850 (s)	850 (m)	*cis*-1,4-
800 (s)	800 (w–br)	*cis*-1,4-
690 (m)	690 (m)	*cis*-1,4; *cis CH* wag
645 (m)	645 (m)	*cis*-1,4-

[1] Taken from the data of Ferguson

[2] Infra-red spectrum of polychloroprene synthesized at –20°C subtracted from spectrum of polychloroprene synthesized at 40°C

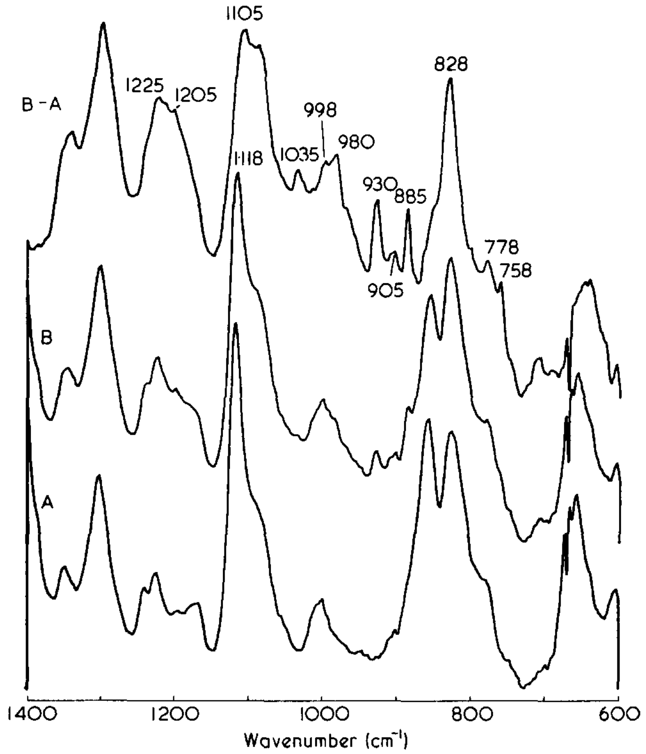

Figure 3 Fourier transform i.r. spectra of polychloroprene in CS$_2$ solution in the range 600–1400 cm^{-1}: A, polychloroprene polymerized at –150°C; B, polychloroprene polymeized at +40°C; B–A, difference spectrum

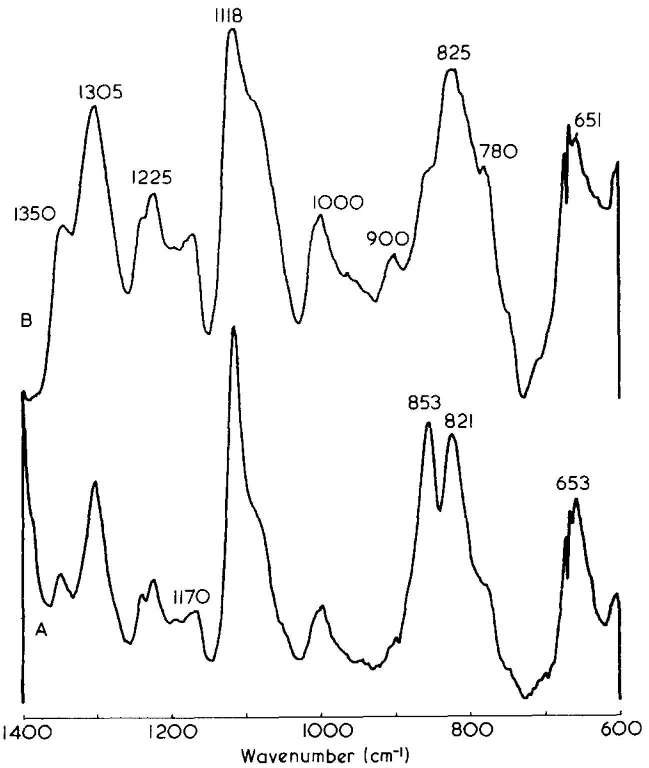

Figure 4 Fourier transform i.r. spectra of polychloroprene polymerized at −150°C in the range 600–1400 cm^{-1}: A, CS_2 solution at room temperature; B, molten state at 85°C

easy to observe oversubtraction as distortion to the band shapes of the total spectrum occurs. It can be seen that the bands due to the 1,2- and 3,4- structural units at 930 and 885 cm^{-1} respectively are very well resolved and are in fact superior to those observed in the molten state experiments. Other bands are also resolved more clearly in this difference spectrum and we will comment on these later. Before proceeding with a detailed discussion, it is interesting to comment on the differences observed between the molten (85°C) and CS_2 solution spectra of the −150°C polymer. *Figure 4* compares these infra-red spectra in the 600–1400 cm^{-1} region. It can be seen that the CS_2 solution spectrum contains infra-red bands that are significantly sharper than the bands in the molten state. Note particularly the bands at 1305, 1118, 821 and 653 cm^{-1}. It should be remembered that the spectrum taken in the molten state is a higher temperature (–85°C) compared to room temperature solution spectrum. However, apart from a few exceptions where local order is postulated in solution, one would anticipate that the infra-red spectrum of a polymer solution would contain broad bands typical of an unordered material. In addition, frequency shifts attributed to polymer/solvent interaction may also be observed. The bands observed in the 750–900 cm^{-1} region of the spectrum can reasonably be assigned to predominantly CH_2 rocking modes[1]. In the crystalline state two bands are observed at 826 and 789 cm^{-1} [11,13] while in the molten state we can identify four bands at 900 (w), 853 (m–sh), 825 (s) and 780 (m) cm^{-1}. The 900 and 853 cm^{-1} bands are likely to be CH_2 rocking modes associated with non-preferred conformations (i.e. rotations about the CH_2–CH_2 sequence) of the all *trans*-1,4-polychloroprene. CH_2 does have a weak infra-red band at 852 cm^{-1} which contributes to the absorbance observed at 853 cm^{-1}. Nevertheless the CS_2 solution spectrum indicates that a narrower distribution of conformational states exists in CS_2 solution compared to that of molten polymer. The main point, however, is that this effect does not appear to prevent the successful subtraction of the all *trans*-1,4- polymer from the other polychloroprene samples.

Figure 5 shows the difference spectra obtained by subtraction of the spectrum of all *trans*-1,4-polychloroprene in CS_2 from that of the polychloroprenes synthesized at −20°, 0° and 40°C (A, B, and C respectively). It must be emphasized that these three spectra have been scale-expanded to accentuate the infra-red bands and are not plotted on the same absolute absorbance scale. Thus the total absorbance of spectrum C is considerably less than that of B which in turn is less than A. As mentioned previous, the bands at 930 and 885 cm^{-1} attributable to the 1,2- and 3,4- placements are well isolated, resolved, and useful for quantitative measurements.

By plotting the difference spectra on identical absorbance scales the relative peak heights (or areas) of the 930 and 883 cm^{-1} bands can be measured for the three polychloroprene samples polymerized at −20°, 0° and 40°C. Each of these samples was prepared accurately as a 10% w/v solution and the spectra recorded from the same infra-red cell. Although the precise concentration of the all *trans* −150°C polymer was not known, this polymer solution can be used as a standard to remove the contribution of the *trans*-1,4- units from each of the three polymer solutions and hence the relative concentrations of various structural irregularities. The ratio of the absorbances of the 930 cm^{-1} band in the difference spectra was measured as 1:1.5:2.2 for the −20°, 0° and 40°C polymers respectively. This is in good agreement with the ^{13}C n.m.r. results which gives a corresponding ratio of 1:1.3: .9 for the 1,2- units (see *Table 1*). Similarly, for the 885 cm^{-1} band a ratio of 1:1.6:3.2 was determined by infra-red which is compared to

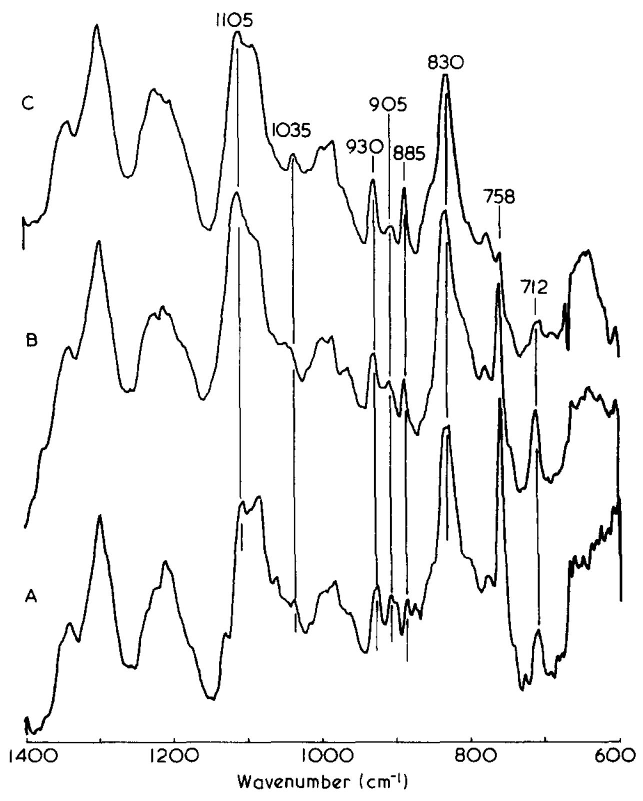

Figure 5 Fourier transform i.r. CS_2 solution difference spectra obtained by subtracting the spectrum of the polychloroprene polymerized at −150°C from the spectra of polychloroprenes polymerized at −20°C (a), 0°C (b) and 40°C (c)

a corresponding ratio for the 3,4- units of 1:2.2:2.8 by ^{13}C n.m.r.

These results form the basis for a fast, reasonably accurate method for the quantitative analysis of the 1,2- and 3,4- structural units in polychloroprenes. Having obtained a solution spectrum of the all *trans*- −150°C polymer this can be permenently stored on tape or disc system and used as a standard to remove the *trans*-1,4- contribution from an unknown polychloroprene sample. The absorbance of the 930 and 885 cm^{-1} bands can be calibrated by ^{13}C n.m.r. using a well characterized polychloroprene synthesized at say 40°C. Once this is achieved it is only necessary to obtain the spectrum a 10% solution of the unknown polychloroprene, remove the *trans*-1,4- contribution and measure the absorbance of the 930 and 885 cm^{-1} bands. Unfortunately, there does not appear to be such a convenient band with which to measure *cis*-1,4- content. Bands at 1225, 1105, and 830 cm^{-1} can be assigned to the *cis*-1,4- unit but they are complicated by being broad and poorly defined.

The sharp band at 758 cm^{-1} is assigned to CCl_3 end groups. The CCl_3 group has an intense characteristic band at this frequency (e.g. in $CHCl_3$ at 758 cm^{-1}). The CCl_3 end groups are formed by chain transfer to CCl_3Br during polymerization.

$$R\cdot + CCl_3Br \rightarrow RBr + CCl_3\cdot$$

$$CCl_3\cdot + CH_2{=}CCl{-}CH{=}CH_2 \rightarrow CCl_3{-}CH_2{-}CCl{=}CH{-}CH_2\cdot$$

where R· is an initiator or polymer radical.

This, again, demonstrates the potential of digital subtraction techniques for the identification and measurement of relatively small concentrations of structural features such as end-groups. It must be emphasized that the apparent large relative increase of the 758 cm^{-1} band as a function of decreasing polymerization temperature, as shown in *Figure 5*, does not necessarily mean that the absolute concentration of end-groups has increased (which in turn implies a corresponding decrease in molecular weight). These spectra are not plotted on the same absorbance scale. In fact, if measurements are made on identical absorbance scales the ratio of the absorbances of the 758 cm^{-1} band is approximately 1:1.7:1.5 for the 40°, 0° and −20°C polychloroprenes respectively. Without appropriate extinction coefficients it is not possible to estimate molecular weights from this data.

The infra-red band observed in the difference spectra at 712 cm^{-1} cannot be unambiguously assigned. The ratio of absolute absorbances is 1:2:1 for the 40°, 0° and −20°C polymers respectively. This trend is similar to that measured by ^{13}C n.m.r. for the isomerized 1,2- unit (see *Table 1*). However, the 712 cm^{-1} band should then correspond to the 670 cm^{-1} band observed in the model compound 1-chloro-3 methyl-2-butene. The 32 cm^{-1} difference is too large for an unambiguous assignment of the 712 cm^{-1} band to isomerized 1,2-units. Another possibility is tha the band is a C−Cl end-groups formed by chain termination of the growing polymer to the allylic chlorine contained in the 1,2- unit of an already formed polymer chain. In effect, a branching reaction, that is well known to occur in the free radical polymerization of chloroprene. The weak band at 905 cm^{-1} is present in all three difference spectra and is probably a −CH out of plane vibration and may be associated with the alkene formed in a branching reaction. However, this can only be assumed to be reasonable speculation at this stage.

ACKNOWLEDGEMENTS

The authors would like to thank Drs R. R. Garrett and C. A. Aufdermarsh Jr. of the Elastomer Chemicals Department, E. I. DuPont de Nemours and Company for their contributions to this study. Dr Garrett kindly prepared and supplied the all *trans*-1,4- polychloroprene; a copy of the original infra-red spectrum of the polymer was provided by Dr Aufdermarsh. This research was carried out with financial support of the National Science Foundation, Grant DMR 76-84444, Polymers Program.

REFERENCES

1 Tabb, D. L. and Koenig, J. L. *J. Polym. Sci. (Polym. Phys. Edn)* 1975, **13**, 1159

2 Maynard, J. T. and Mochel, W. E. *J. Polym. Sci.* 1954, **13**, 251; 1955, **18**, 227

3 Coleman, M. M., Tabb, D. L., and Brame Jr, E. G. *Rubber Chem. Technol.* 1977, **50**, 49

4 Coleman, M. M. and Brame, Jr, E. G. *Rubber Chem. Technol.* submitted for publication

5 Maynard, J. T. and Mochel, W. E. *J. Polym. Sci.* 1954, **13**, 235

6 Garrett, R. R., Hargreaves II, C. A. and Robinson, D. N. *J. Macromol. Sci. (A)* 1970, **4**, 1679

7 Ferguson, R. C. *J. Polym. Sci. (A-2)* 1964, 4735

8 Ferguson, R. C. *Anal. Chem.* 1964, **36**, 2204

9 Coleman, M. M. and Fuller, R. E. *J. Macromol. Sci. (B)* 1975, **11**, 419

10 McFarland, J. W. and Pariser, R. *J. Appl. Polym. Sci.* 1963, **7**, 675

11 Tabb, D. L., Koenig, J. L. and Coleman, M. M. *J. Polym. Sci. (Polym. Phys. Edn)* 1975, **13**, 1145

12 Aufdermarsh Jr, C. A. and Pariser, R. *J. Polym. Sci. (A-1)* 1964, 4727

13 Coleman, M. M., Painter, P. C., Tabb, D. L. and Koenig, J. L. *J. Polym. Sci. (Polym. Lett. Edn)* 1974, **12**, 577