The far infra-red spectrum of poly(vinyl chloride)

M. Goldstein and D. Stephenson
Department of Chemistry, Sheffield City Polytechnic, Pond Street, Sheffield S1 1WB, UK

and W. F. Maddams
Group Research and Development Department, The British Petroleum Company Limited, Sunbury-on-Thames, Middlesex TW16 7LN, UK
(*Received* 27 *July* 1982; *revised* 17 *September* 1982)

The far infra-red spectrum of a poly(vinyl chloride) sample prepared by the urea clathrate (U–C) route has been measured at various temperatures in the range 60 to 320 K. The results, taken in conjunction with those for two less highly ordered polymers, indicate that a revision of the assignments of earlier workers, based on normal coordinate calculations and on the measured spectra of secondary alkyl chlorides such as 2-chlorobutane, is required. The band at 65 cm^{-1} is attributed to a lattice mode and is not indicative of weak hydrogen bonds of the type C–H···Cl–C–. However, it is suggested that the band at 185 cm^{-1}, which is particularly clear and sharp with the U–C polymer, probably originates from an interaction of this type, occurring specifically at tight chain folds.

Keywords Spectrum; far infra-red; poly(vinyl chloride); lattice; vibrational; folding

INTRODUCTION

The vibrational spectrum of poly(vinyl chloride) (PVC) in the mid infra-red region has been the subject of a number of detailed studies, particularly in the case of the carbon–chlorine stretching modes, which are specific for the various configurational and conformational isomers, and whose presence is now well established[1-3]. However, the far infra-red spectrum of PVC has attracted comparatively little attention. Three low frequency modes were observed by Krimm and coworkers[4,5], at 67, 89 and 180 cm^{-1}. These may be compared with the results of two sets of calculated values, based on normal coordinates analyses. The first, by Tasumi and Shimanouchi[6], related to a single syndiotactic chain. It predicted bands at 54 and 117 cm^{-1}, both involving vibrations that are predominantly torsional modes, and a third band at 127 cm^{-1} that corresponds to the C–Cl wagging modes. Somewhat later, Moore and Krimm[5] used a more realistic model and allowed for the presence of two syndiotactic chains in the orthorhombic unit cell; they also included an intermolecular force field to allow for weak interactions of the type C–H···Cl–C that had been used to account for the band at 64 cm^{-1} in the spectra of model secondary chlorides[7]. They then predicted bands at 29, 64 and 90 cm^{-1}. The first of these is a C–Cl···H bending mode, the second a hybrid torsion/bending mode of C–Cl···H and the third a torsional mode.

It is noteworthy that neither calculation accounts for the band at 180 cm^{-1}, which is comparable in intensity with those at 67 and 89 cm^{-1}. Furthermore, two X-ray diffraction studies provide evidence against general weak interactions of the type C–H···Cl. Wilkes *et al.*[8], from an examination of single crystals of a low molecular weight polymer of moderately high syndiotacticity, concluded that the C–H···Cl distance is 4.71 Å whereas the van der Waals' contact distance is only 4.1 Å. Recently, Conte *et al.*[9], have suggested that this type of weak interaction only occurs at chain folds and that this supramolecular structure is only present in highly syndiotactic polymers, implying that the 64 cm^{-1} band ought to occur only in the spectrum of the urea clathrate polymer (see Experimental). In view of these unresolved problems, a further study is warranted. The aim of the present work has been to obtain spectra from a wider range of samples and to make measurements over a range of temperatures, as a potential means for identifying lattice modes, in an attempt to obtain a fuller understanding of the infra-red-active low frequency modes.

EXPERIMENTAL

Samples

Three types of polymer, all more syndiotactic and more ordered than the commercial type of material, were examined.

(i) M–E: a commercial polymer made by the Montecatini–Edison Company, using a polymerization temperature of −30°C. It has a syndiotacticity of 63% (from ^{13}C n.m.r. measurements) and a viscometrically determined relative molecular mass of 60 000.

(ii) TBMC: four experimental polymers prepared by ionic polymerization at 0°C in tetrahydrofuran using tertiary butylmagnesium chloride as initiator[10]. Typically these materials have syndiotacticities, determined by ^{13}C n.m.r. spectroscopy, of about 70% and number average relative molecular masses in the range 3000–4000.

(iii) U–C: an experimental polymer made in a urea–canal complex[11], having a syndiotacticity of at least 90%[12].

These samples were examined in the form of discs, typically 0.1 mm in thickness. These were prepared by cold sintering the powders.

0032–3861/83/070823–04$03.00

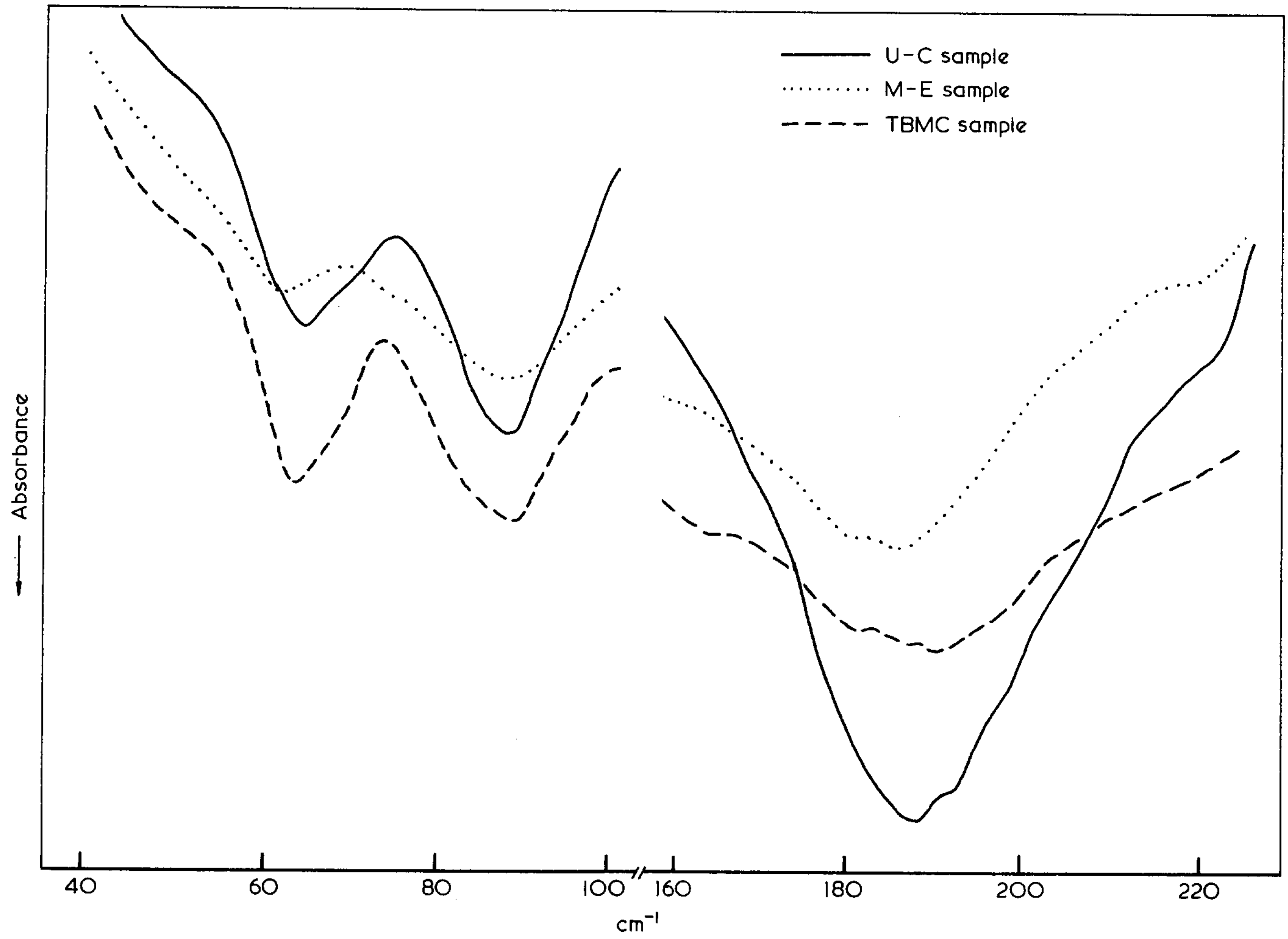

Figure 1 Far infra-red spectra of poly(vinyl chloride) samples prepared by three different methods (see Experimental)

Spectrometers

Far infra-red spectra were measured with a Beckman-RIIC FS-720 Fourier transform spectrometer. A sampling interval of 8 μm was used and the primary intensity data were recorded on paper tape for off-line processing on an IBM 1130 computer. 512 points were recorded on each interferogram, giving a resolution of about 2.5 cm^{-1}. Measurements below ambient temperature were made with a Cryogenic Technology model 20 cryodyne closed cycle helium cryostat. X-ray diffraction measurements were made with an Advanced Metals Research 3-202 diffractometer coupled to a Phillips 1130/00/60 generator; CuKα radiation was used.

RESULTS

In general, our results broadly confirm the experimental data of Krimm *et al.*[3,4]. However, we have studied a wider range of characterized PVC samples and have investigated more thoroughly the temperature dependence of the spectra. These additional results, together with the knowledge of more recent literature, have enabled a fuller and more critical assessment of the data to be made.

Measurements at ambient temperature

Figure 1 shows the far infra-red spectra, over the two ranges 40 to 100 cm^{-1}, and 160 to 220 cm^{-1}, for the urea clathrate polymer (U–C), the Montedison material (M–E) and one of the polymers prepared with tertiary butylmagnesium chloride as a catalyst (TBMC); the spectra of the three remaining materials of this latter type did not differ markedly. There are differences for each of the three observed bands but they are not particularly pronounced at 90 cm^{-1}, where the M–E material gives the broader, weaker profile. The 65 cm^{-1} band, well defined in the case of U–C and TBMC polymers, is broad and displaced to a lower frequency with the M–E polymer. Annealing of the discs at a temperature of 140°C for periods up to 30 hours produced some sharpening of the two bands with the U–C polymer but the spectra of the other two materials were not affected significantly by this annealing treatment. The pattern of differences between samples changes in the case of the band at about 185 cm^{-1}, as it is markedly sharper and more intense in the case of the U–C polymer. However, with all three, it does not change significantly upon annealing.

Measurements at low temperatures

Spectra were measured at various temperatures, covering the range 60 to 320 K. Only in the case of the U–C polymer was a detectable shift of band position with temperature observed and this was confined to the peak at about 65 cm^{-1}. Band position as a function of temperature is shown in *Figure 2*, where an error of ± 0.5 cm^{-1} in the former has been assumed. However, the scatter of results suggests a somewhat lower precision. Nevertheless, the results indicate that the band position is

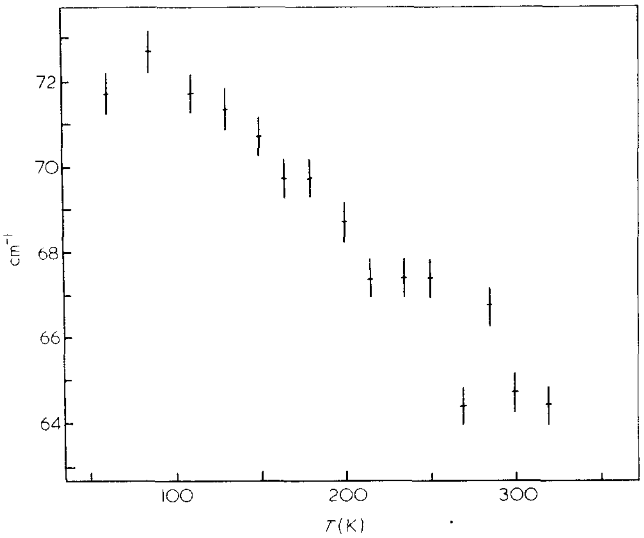

Figure 2 Position of the ~65 cm^{-1} band of poly(vinyl chloride), prepared by the urea clathrate route, as a function of temperature (*T*)

a linear function of temperature, moving from approximately 64 cm^{-1} at 320K to 73 cm^{-1} at 60K, a substantial change.

X-ray diffraction crystallinity indices

The X-ray diffractograms were interpreted using the method of Michel and Guyot[10]. Lines were drawn between the extremes of the baseline, constructed by joining the points on the diffraction profile at 2θ values of 14° and 32°, and the profile minimum at 21°. This triangular area A_3 is taken as a measure of the incoherent scattering from amorphous regions. The sum of the two areas, A_1 and A_2, above the triangular area is regarded as characterizing the coherent diffraction from crystalline regions. The crystallinity index is then obtained as the ratio $A_1+A_2/A_1+A_2+A_3$. This empirical approach, which has the merit of simplicity, gives somewhat larger values than those obtained by the use of the bimodal amorphous background of Rayner and Small[13]. Nevertheless, it is very useful for comparative purposes. The U–C polymer gave the value 83, which increased marginally after annealing at 140°C, as anticipated from the results of Baker *et al.*[12]. The TBMC material has a crystallinity index of 57 and the figure for the M–E material is 30. Here, also, small increases were observed after annealing.

DISCUSSION

The results for the 90 cm^{-1} band, which are in line with the earlier but less detailed measurements of Moore and Krimm[5], do not warrant detailed comment. The assignment to a torsional mode appears wholly logical. The broadening and weakening of the band that occurs with the M–E polymer, and is accentuated still further in the case of a commercial polymer also examined, is not unreasonable. As the degree of order and syndiotacticity decrease, bent isotactic and syndiotactic conformers will be present at higher concentrations. The torsional mode for these will almost certainly occur at slightly different frequencies, leading to band broadening. If their intensities are somewhat lower this will lead to a weakening of the composite band.

Warrier and Krimm[4] assigned the 65 cm^{-1} band to a localized vibrational mode involving an intermolecular interaction of the type C–H···Cl, from two lines of reasoning. The first is the appearance of a band in spectra of model liquid secondary chlorides[7] at ~67 cm^{-1} that was assigned to an interaction of this type. Secondly, having noted that the 65 cm^{-1} PVC band is only found with highly ordered polymers of the U–C type, and is therefore to be associated with the crystalline phase, they argue against its assignment as a lattice mode, although they observe an increase of 3 cm^{-1} in its frequency between ambient temperature and 77 K. Their evidence against this assignment is that it is forbidden in the infrared spectrum by symmetry and that the frequency shift on deuteration is inconsistent with this type of motion.

It is pertinent to examine these arguments in some detail. The studies on the model compounds, 2-chloropropane, 2-chlorobutane, 3-chlorobutane and meso-2,4-dichloropentane showed, both at room temperature and at 77 K, a band at 67 cm^{-1}. However, it did not persist in the vapour phase or in solution. These facts were interpreted as excluding rotational or translational–rotational motions, pseudolattice oscillations and intramolecular motions in general. Furthermore, changes in the frequencies of the three C–Cl stretching modes of 2-chlorobutane as a function of concentration in solution in a hydrocarbon solvent were regarded as indicative of hydrogen bonding.

However, the broad bands appearing in the far infrared spectra of polar liquids have now been the object of rather detailed studies[14–16]. It is now generally considered that they are caused largely by hindered rotation (libration) of the dipole in a cage of surrounding molecules, either of the same species or solvent molecules. It is therefore unnecessary to invoke hydrogen bonding to explain the appearance of this type of band in the spectra of liquids. Furthermore, in a subsequent X-ray diffraction study of single crystals of a low molecular weight PVC of moderately high syndiotacticity, Krimm and coworkers[8] concluded that a direct C–H···Cl hydrogen bond type of interaction in the solid state is excluded because the C–Cl distance is 4.71 Å, whereas the van der Waals' contact distance is 4.1 Å.

The experimental evidence against the assignment to a lattice mode consists of studies on three deuteriated polymers by Warrier and Krimm[4]. At 77 K the band position is 67.1 cm^{-1} for PVC, 65.8 cm^{-1} for $(CH_2CDCl)_n$, 67.1 cm^{-1} for $(CD_2CHCl)_n$ and 64.3 cm^{-1} for $(CD_2CDCl)_n$. Hence, the observed ratios for the hydrogen to deuterium frequencies are 1.020, 1.000 and 1.044, whereas the predicted values for a translational mode are 1.008, 1.016 and 1.024. Warner and Krimm concluded that the differences between the pairs of values are significant. However, they gave no estimate of the likely errors in the band positions. It is possible to obtain agreement between the measured and calculated values if the former are adjusted to 66.1, 66.6 and 64.3 cm^{-1}. The necessary adjustments are not markedly greater than the uncertainties in the determination of the peak position encountered in the present work; hence, the results on the deuteriated polymers cannot be regarded as significant evidence against the lattice mode assignment.

The positive evidence for this assignment comes from the systematic shift as a function of temperature. The slope of the frequency–temperature plot is approximately twice that obtained from the two temperature measurement of Warner and Krimm[4]. However, by the reasoning used in connection with their deuteration results, a somewhat greater difference between ambient temperature and 77 K is possible, although not so large as given by the present measurements. In view of the number of data points involved, these latter are to be preferred. There is then little doubt that the $65\,cm^{-1}$ band must be assigned to a lattice mode, with the clear implication that this type of vibration cannot be wholly forbidden.

The failure of the normal coordinate calculations to predict a band at $185\,cm^{-1}$ suggests that it may have its origin in weak intermolecular interactions, of a specific nature. Furthermore, the increasing intensity and sharpness of this band in the series M–E, TBMC and U–C, indicates that this interaction must be specific to the crystalline phase. It is instructive to consider the problem in terms of the chain folded model for PVC, proposed on theoretical grounds by Conte *et al.*[9]. Their calculations imply that tight (010) and (400) folds, and hence adjacent re-entry, may occur, the folds being stabilized by weak hydrogen bond interaction of the type –C–H·····Cl–C.

Unlike polyethylene, polyoxymethylene, long chain polyesters and several other polymers, there is no experimental evidence for chain folding in PVC. If it does occur it will only be found in highly ordered materials and this is a parameter which is both difficult to define and to measure with this particular polymer. The reflections observed in the X-ray diffractogram are of the type (*hk*0), indicating that the order is substantially lateral[17]. Only in the case of the U–C polymer[12] do (*hkl*) type reflections occur. Hence, the fact that the results of the present X-ray measurements indicate that the crystallinity indices for the U–C, TBMC and M–E polymers are in the approximate ratio 3:2:1 does not indicate comparable levels of three dimensional order. It is, undoubtedly, markedly greater in the case of the U–C polymer than for the other two materials, and there will, therefore, be a correspondingly greater disposition towards chain folding, if this does occur. It is therefore very significant that the $185\,cm^{-1}$ band is strongest and sharpest in the case of the U–C polymer. As the degree of three dimensional order decreases, and slightly disordered structures become more abundant, the interaction frequency may be spread over a limited range, thus accounting for the broadening of the band in the TBMC and M–E polymers. There is, therefore, some evidence for assigning the $185\,cm^{-1}$ band to –C–H···Cl–C interactions in tight chain folds in highly ordered regions, although the present work does not provide conclusive proof.

ACKNOWLEDGEMENT

We thank the SERC for a Research Grant. We are grateful to Dr A. Michel (CNRS France) and Dr J. Hay (University of Birmingham, UK) for gifts of samples.

REFERENCES

1 Krimm, S. *J. Polym. Sci.* (*C*) 1964, **7**, 3, and references therein
2 Pohl, H. U. and Hummel, D. O. *Makromol. Chem.* 1968, **113**, 190, 203
3 Robinson, M. E. R., Bower, D. I. and Maddams, W. F. *Polymer* 1978, **19**, 773
4 Warrier, A. V. R. and Krimm, S. *Macromolecules* 1970, **3**, 709
5 Moore, W. H. and Krimm, S. *Makromol. Chem. Suppl.* 1975, **1**, 491
6 Tasumi, M. and Shimanouchi, T. *Polym. J.* 1971, **2**, 62
7 Warrier, A. V. R. and Krimm, S. *J. Chem. Phys.* 1970, **52**, 4316
8 Wilkes, C. E., Folt, V. L. and Krimm, S. *Macromolecules* 1973, **6**, 235
9 Conte, G., D'Ilario, L., Pavel, N. V. and Giglio, E. *J. Polym. Sci. Polym. Phys. Edn.* 1979, **17**, 753
10 Michel, A. and Guyot, A. *J. Polym. Sci.* (*C*) 1971, **33**, 75
11 White, D. M. *J. Am. Chem. Soc.* 1960, **82**, 5678
12 Baker, C., Maddams, W. F. and Preedy, J. E. *J. Polym. Sci. Polym. Phys. Edn.* 1977, **15**, 1041
13 Rayner, L. S. and Small, P. A. (to Imperial Chemical Industries Ltd.). Br. Pat. 847,676 (October 30, 1951)
14 Davies, M., Pardoe, G. W. F., Chamberlain, J. E. and Gebbie, H. A. *Trans. Faraday Soc.* 1970, **66**, 273
15 Pardoe, G. W. F. *Trans. Faraday Soc.* 1970, **60**, 2699
16 Pardoe, G. W. F. *Spectrochim. Acta* 1971, **27A**, 203
17 Natta, G. and Corradini, P. *J. Polym. Sci.* 1956, **20**, 251