On the vibrational spectra of poly-1,1,2,2-tetrachlorobutane—a model for head-to-head poly(vinylidene chloride)

M. M. Coleman, D. F. Varnell, B. A. Brozoski and P. C. Painter
Polymer Science Section, Materials Science and Engineering Department, The Pennsylvania State University, University Park, PA, 16802, *USA*
(*Received* 20 *October* 1980)

Infra-red and Raman spectra of poly (1,1,2,2-tetrachlorobutane), a model polymer for head-to-head poly(vinylidene chloride), are presented. Mutual exclusion of the infra-red and Raman spectra is observed and the polymer appears to be highly ordered. The preferred conformation of the polymer chain is inferred to be most probably in the form of a planar zigzag.

INTRODUCTION

During the past few years we have published several papers concerned with the interpretation of the vibrational spectra of two major classes of chlorinated polymers; poly(vinylidene chloride) (PVDC)[1–3] and the chlorodiene polymers *trans*-1,4-polychloroprene (TPC)[4–8] and *trans*-1,4-poly(2,3-dichlorobutadiene) (TPDCB)[8]. The studies of these two classes of polymers were carried out separately with little if any overlap. In the case of PVDC we were particularly interested in the application of vibrational spectroscopy and normal coordinate analysis to the determination of the preferred conformation of the crystalline polymer. Conversely, for TPC and TPDCB, the major aim of our work was to accurately assign the vibrational spectra of these polymers and to ascertain the effect of structural irregularities occurring in the polymer chain of these materials. The results presented in this paper represent a logical extension of the above studies and is in fact an intriguing fusion of this work. By mild chlorination of TPDCB one may prepare the polymer poly-1,1,2,2-tetrachlorobutane (PTCB) which is, in effect, a model polymer for head-to-head PVDC[9]. As we show below we have been able to obtain a highly ordered sample of PTCB and from infra-red and Raman studies are able to infer that the preferred conformation of the polymer is most probably in the form of a planar zig-zag.

EXPERIMENTAL

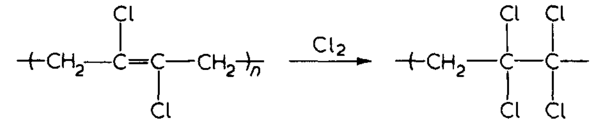
The TPDCB used in this study has previously been described[8]. Solution chlorination of TPDCB in *ortho*dichlorobenzene was performed by essentially following the procedure of Murayama and Amagi[9]. However, we increased the solution chlorination temperature from 50° to 60°C as it was found that our TPDCB sample precipitated from solution at the lower temperature. Following chlorination, the reaction mixture was cooled, neutralized with NaOH in MeOH, and the polymer isolated and washed thoroughly. After drying under vacuum, the polymer was stored in a refrigerator in the absence of light.

Samples of PTCB were prepared for mid-infra-red analysis by casting onto a potassium bromide disc from a suspension in acetone. The acetone was subsequently removed by vacuum dessication. Far-infra-red spectra were obtained from samples of PTCB suspended in caesium iodide. Raman spectra were acquired from a sample sealed in a capillary tube.

Infra-red spectra were obtained from a Digilab FTS-15/B Fourier transform infra-red (*FT*i.r.) spectrometer. Four hundred scans at a resolution of 2 cm^{-1} were signal averaged and stored on a magnetic disc system. The original spectra obtained in the mid-infra-red region exhibited a significant sloping baseline due to scattering effects associated with the method of sample preparation (i.e., an incoherent film prepared from a suspension of PTCB in acetone). Accordingly, a baseline correction to the spectrum was performed. Raman spectra were obtained on a Jobin-Yvon Ramanor HG-2S spectrometer. The 5145Å exciting line of a Spectra Physics argon-ion laser was employed and the laser power at the sample was approximately 300 mW. A scan speed of 30 cm^{-1}/min was used and the slit widths were 250, 150, 150, and 150μ respectively. The Raman spectrometer is interfaced to the Nova 3 computer associated with the *FT*i.r. spectrometer and four scans were signal averaged.

RESULTS AND DISCUSSION

The chlorination of TPDCB to produce PTCB (head-to-head PVDC) has previously been reported by Murayama and Amagi[9].



$$\left[\!-CH_2-C(Cl)=C(Cl)-CH_2-\right]_n \xrightarrow{Cl_2} \left[\!-CH_2-CCl_2-CCl_2-CH_2-\right]_n$$

TPDCB PTCB

These authors also included infra-red spectra in the range 600–2800 cm^{-1} of PVDC, PTCB and TPDCB. However, the spectra are of rather poor quality and indicate that the polymers are not highly ordered. (Note for example the

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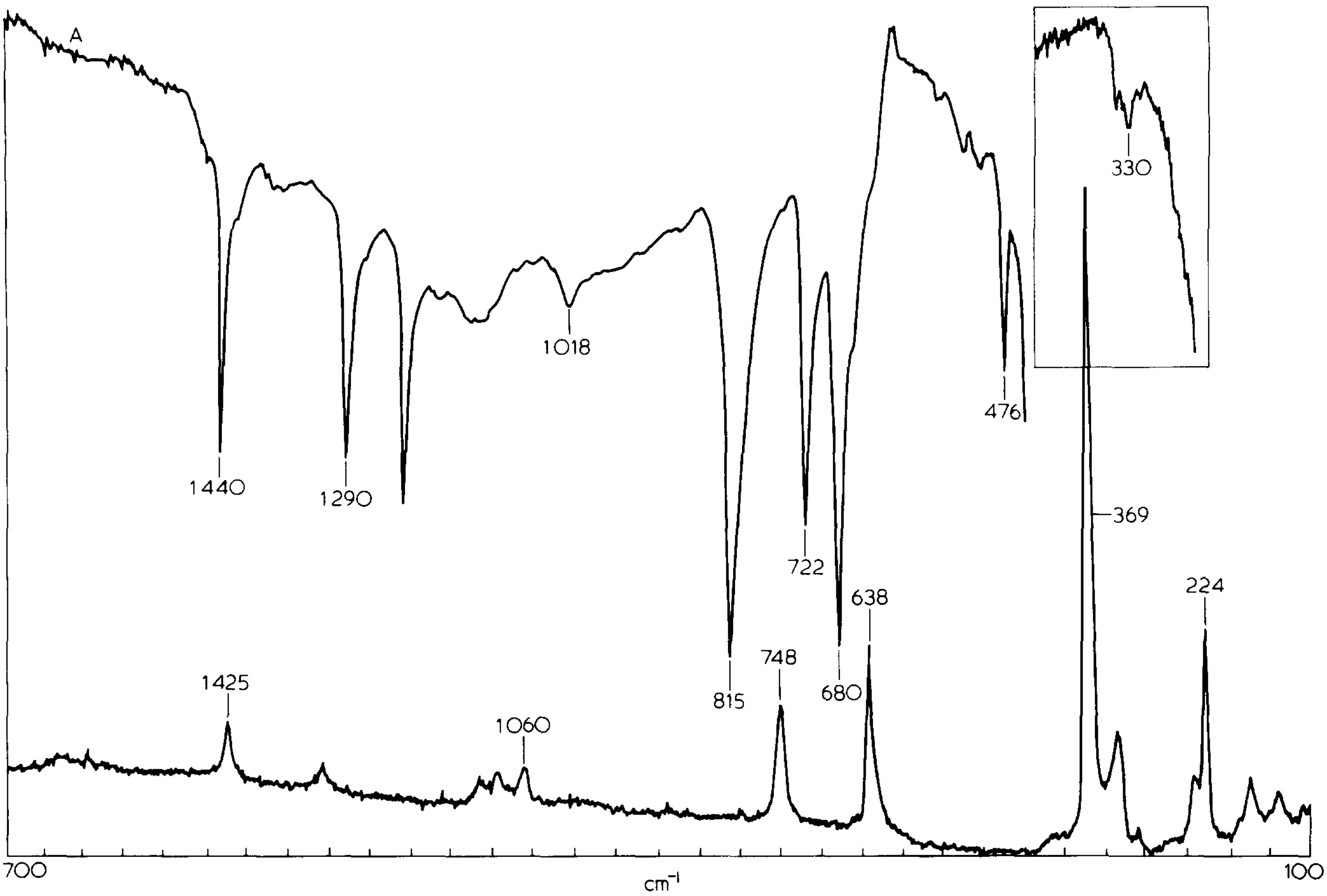

Figure 1 A, transmission infra-red spectrum of PTCB in the range 450–1700 cm^{-1}. Insert: Far infra-red region 250–450 cm^{-1}. B, Raman spectrum of PTCB in the range 100–1700 cm^{-1}

presence of the infra-red band at approximately 1640 cm^{-1} in the spectra of TPDCB which is associated with the C=C stretching vibration and is infra-red inactive in the preferred conformation[8]. Further in the spectrum of PVDC the bands are relatively broad, especially in the 900–1100 cm^{-1} range which suggests that the polymer contains a significant amount of non-preferred (amorphous) conformations[1].)

Figure 1 shows the infra-red and Raman spectra of PTCB in the range 100–1700 cm^{-1}. It is evident from the spectra of PTCB that we have produced a highly ordered polymer as evidenced by the sharp infra-red bands and Raman lines. More importantly it is immediately apparent that the infra-red and Raman spectra exhibit almost perfect mutual exclusion. This is illustrated in *Table 1* which lists the observed vibrational frequencies and tentative assignments, based on the normal coordinate calculations previously performed on PVDC[3] and TPDCB[8]. The infra-red and Raman spectra of the single crystal preparations of PVDC and TPDCB have previously been published[1,8].

Initially, it should be stated that the spectra obtained from the chlorinated sample of TPDCB is entirely consistent with the formation of PTCB. The Raman spectra of PTCB shows complete absence of any line in the 1600–1700 cm^{-1} region which would be indicative of unreacted olefinic bonds present in the original TPDCB. (The Raman line at 1643 cm^{-1} in TPDCB is the most intense line present in the spectrum[8].) Furthermore, there is no evidence that chlorination of the methylene groups on TPDCB occurs under the experimental conditions employed. If significant substitution of the methylene

Table 1 Vibrational spectroscopic data of poly-1,1,2,2-tetrachlorobutane

Raman (cm^{-1})	Infra-red (cm^{-1})	Tentative assignment
2950(w)	2955(m) 2920(m) 2870(sh) 2850(mw)	ν(CH$_2$)
1425(mw)	1440(s)	s(CH$_2$)
1310(vw)	1290(ms)	ω(CH$_2$)
	1218(s) 1130(w–br)	t(CH$_2$)
1110(vw)		t(CH$_2$)
1090(w) 1060(w)	1018(w)	ν(C–C)
885(vw)?	815(vw)	r(CH$_2$)
748(m) 638(ms)	722(s) 680(vs)	ν(CCl$_2$)
	476(m)	r(CCl$_2$)
369(vvs)		ω(CCl$_2$)
	345(w)	
331(m)	330(w)	s(CCl$_2$)?
305(vw)		
238(mw–sh)		r(CCl$_2$)?
224(ms)		δ(C–C–C)?
170(mw)		ω(CCl$_2$)?
138(w)		t(CCl$_2$)?

Key: s = strong, m = medium, w = weak, v = very, sh = shoulder, br = broad, ν = stretch, s = scissor, ω = wagging, t = twisting, r = rock, and δ = deformation groups had occurred we would not expect to obtain a highly ordered polymer and we would anticipate additional absorbances in the C–Cl region of the spectrum. Attempts to determine a crystalline melting point (T_m) from differential scanning calorimetry (d.s.c.) were unsuccessful. Presumably, PTCB degrades at temperatures below its T_m and, in fact, examination of the sample after the d.s.c. scan suggests extensive degradation (the sample was black and resembled carbonaceous material). Preliminary X-ray diffractometer studies on a powdered PTCB sample do suggest a semi-crystalline material. Diffraction peaks equivalent to *d*-spacings of 2.01 and 2.86Å were definitely observed.

As mentioned previously, the infra-red and Raman spectra of PTCB exhibit almost perfect mutual exclusion which infers a highly ordered polymer and in turn suggests that the structure of the preferred conformation contains a centre of symmetry. Given the chemical structure of PTCB, the simplest translational repeating unit is $(CH_2-CCl_2-CCl_2-CCl_2)_n$. Two conformations which satisfy the requirements of a centre of symmetry are the planar zig-zag and *cis*–planar conformations. The line group of an isolated chain in either conformation is isomorphous to the point group C_{2h}. Accordingly, 17 Raman active lines (9 A_g and 8 B_g) and 15 infra-red active bands (7 A_u and 8 B_u) are predicted which are mutually exclusive. These predictions are in good agreement with the observed frequencies shown in *Table 1*. Although we are unable to distinguish between the planar zigzag and *cis*–planar conformational models we tend to favour the former. In the latter the chlorine and hydrogen atoms are eclipsed and would be in closer proximity to one another. Conversely in the planar zigzag case the chlorine and hydrogen atom are farthest removed from one another. However, it must be emphasized that we cannot definitely rule out the *cis*–planar conformation on the basis of our vibrational studies.

From a consideration of the normal coordinate calculations of PVDC[3] and TPDCB[8] we have been able to confidently assign most of the major bands occurring in the spectra of PTCB. In common with the spectra of many polymers, the C–H stretching region is complicated in the infra-red spectrum due to Fermi resonance effects. Four bands are observed at 2955, 2920, 2870, and 2850 cm^{-1} whereas only two fundamentals are predicted. In the Raman spectra only one definitive band is observed at 2950 cm^{-1}. The two CH_2 scissor vibrations are assigned to the vibrations occurring at 1440 (out-of-phase, infra-red active) and 1425 cm^{-1} (in-phase, Raman active). These vibrations occur at similar frequencies to those observed for TPDCB (1441 and 1432 cm^{-1}) but are significantly different to those observed for PVDC (1403 and 1385 cm^{-1}). Unlike PVDC where each methylene unit is flanked by two CCl_2 units, in PTCB and TPDCB each methylene unit is flanked by another methylene unit and either a CCl_2 or $=CCl$ unit. The CH_2 wagging and twisting vibrations may be assigned to the bands occurring at 1310, 1290, 1218 and 1110 cm^{-1} which are in fair agreement to those calculated for TPDCB.

The vibrations occurring in the 800–1100 cm^{-1} region deserve further comment. In the infra-red spectrum of crystalline PVDC[1] the dominant bands are those occurring at 1070 and 1041 cm^{-1}. These bands have been assigned to predominantly a skeletal and CH_2 rocking mode respectively[3]. It is immediately apparent that only a very weak band occurs in this region of the spectrum in PTCB. Fortunately, this is readily explained from the normal coordinate results of PVDC and TPDCB. The intense CH_2 rocking mode at 1070 cm^{-1} in PVDC is associated with an isolated CH_2 unit. In TPDCB, where there are two methylene units in sequence, a similar rocking mode is calculated at 824 cm^{-1} and assigned to the intense infra-red band at 812 cm^{-1}. Accordingly, an assignment of the intense infra-red band at 815 cm^{-1} in PTCB to a CH_2 rocking vibration is entirely consistent. The relatively weak infra-red band at 1018 cm^{-1} is thus assigned to a skeletal mode similar to that observed at 1041 cm^{-1} in PVDC. Raman lines at 1090 and 1060 cm^{-1} are most probably also associated predominantly with C–C skeletal vibrations in PTCB (similar frequencies are observed in PVDC).

The four C–Cl stretching frequencies are readily assigned to the two Raman lines (in-phase) at 748 and 638 cm^{-1} and the two infra-red bands (out-of-phase) at 722 and 680 cm^{-1}. The medium intense infra-red band at 476 cm^{-1} and the very strong Raman line at 369 cm^{-1} may be assigned to CCl_2 rocking and wagging modes respectively. Similar modes are observed at 454 and 356 cm^{-1} in the spectra of PVDC. The remaining bands occurring below 350 cm^{-1} cannot be assigned with confidence. We have tentatively assigned several vibrations to CCl_2 deformations by analogy to the observed and calculated frequencies and intensities of PVDC.

Finally, there is no evidence for the presence of significant amounts of head-to-head placements in the homopolymer of PVDC. Characteristic frequencies for head-to-head placements as determined from the spectra of PTCB, especially the intense 815 cm^{-1} infra-red band and 369 cm^{-1} Raman line, are not observed in the spectra of PVDC.

ACKNOWLEDGEMENTS

The authors wish to acknowledge the financial support of the National Science Foundation, Grant DMR 7910841, Polymers Program.

REFERENCES

1 Coleman, M. M., Wu, M. S., Harrison, I. R. and Painter, P. C. *J. Macromol. Sci. Phys.* 1978, **B15**(3), 463

2 Wu, M. S., Painter, P. C. and Coleman, M. M. *J. Polym. Sci. Polym. Phys. Edn.* 1980, **18**, 95

3 Wu, M. S., Painter, P. C. and Coleman, M. M. *J. Polym. Sci. Polym. Phys. Edn.* 1980, **18**, 111

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

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

6 Coleman, M. M., Painter, P. C. and Koenig, J. L. *J. Raman Spect.* 1976, **5**, 417

7 Coleman, M. M., Petcavich, R. J. and Painter, P. C. *Polymer* 1978, **19**, 1243, 1249, 1253

8 Petcavich, R. J. and Coleman, M. M. *J. Macromol. Sci. Phys.* 1980, **B18**(1), 47

9 Murayama, N. and Amagi, Y. *J. Polym. Sci. Polym. Lett. Edn.* 1966, **4**, 119