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Synthesis of poly(phenylene acetylene) from poly(phenylene vinylene)

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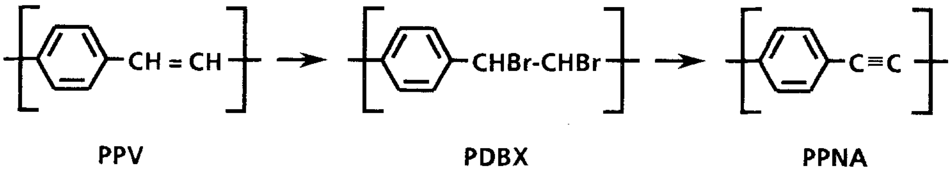
Summary

The objective of this work was to prepare films of poly(phenylene acetylene) from films of a precursor polymer, namely poly(α, α'-dibromoxylylene). This polymer was obtained by selective bromination of the vinylene groups of poly(phenylene vinylene) films in bromine/$CHCl_3$. Pyrolytic dehydrobromination of the brominated films under argon atmosphere gave dark yellow films which showed about 65 wt% of desired phenylene acetylene units.

Introduction

Poly(p-phenylene acetylene) (PPNA) this reported in the literature has been prepared most often by the Heck Reaction, involving palladium catalyzed reaction between a dihaloaryl and an acetylenic compound [1-4]. Electroreduction of 1,4-bis-(trichloromethyl)benzene [5] and self-condensation of copper p-iodophenylacetylenide [6] have also been described. Typically, PPNA was obtained as a low molecular weight, powdery material. Several soluble PPNA derivatives with reasonably high molecular weights were recently prepared from dialkoxylated monomer via Heck Reaction [7]. (Note that PPNA is used to avoid confusion with polyphenyl acetylene which is abbreviated as PPA.)

Recently, precursor routes to fully conjugated, intractible polymers such as polyacetylenes [8], polyphenylene [9] and poly(phenylene vinylene) [10-12] have been widely practiced. In this paper we describe our attempts on the preparation of previously inaccessible parent PPNA films via the transformation shown in the following scheme. The starting PPV films were prepared via the well-known sulphonium polyelectrolyte precursor-route [10-12]. In principal, bromination of PPV should give poly(α, α'-dibromoxylylene) (PDBX). This polymer may serve as the precursor polymer to PPNA by dehydrobromination. We also demonstrate herein the preparation of a copolymer composed of phenylene vinylene (PV) and phenylene acetylene (PA) units by partial bromination of PPV, followed by dehydrobromination.



Experimental

IR spectra were recorded on a Perkin-Elmer 1750 Fourier transform spectrometer. UV-VIS spectra were recorded on a Hewlett-Packard 8451A diode array spectrophotometer. Elemental analyses were performed at Galbraith Laboratories, Inc. Poly(p-phenylene vinylene) films with thickness of 5 to 15 um were prepared according to the reported procedure [10-12] by heating the corresponding precursor polymer, poly(xylylidene tetrahydrothiophenium chloride), at 300 °C for 18 hours under argon atmosphere. The resulting brown yellow PPV films gave the following elemental analysis data: %C 93.40, %H 5.95, %Cl < 0.06, %S 0.09, which is in good agreement with the theoretical values of %C 94.12 and %H 5.88. One molar bromine/chloroform solution was sufficent for complete bromination of PPV films of about 10 um thick and was thus used for most of bromination reactions unless specified otherwise. Typical bromination procedure is as follows: five pieces of PPV films (ca. 1.5 x 1.5 cm^2) with total weight of ca. 10 mg were placed in an 1 M $Br_2/CHCl_3$ solution (3.2 g/20 ml) contained in an enclosed vial. After reaction at room temperature for a desired time interval, the films were picked up with a tweezer and were washed twice in chloroform and then air dried. The brominated films are code named PDBX-n, where n is the number of hours used in bromination. The brominated films were then heated under a flow of argon at 200-250 °C for 2 hours and then at 300 °C for 14 hours to give brown films.

Results and Discussion

Bromination of PPV films in bromine/chloroform solutions was found to be very effective. Qualitatively, the reaction time is proportional to the film thickness and inversely proportional to the concentration of bromine. The progress of the reaction can be monitored by IR spectroscopy. This is presented in Figures la-ld (next page), where comparative IR spectra for PPV and brominated films at reaction time intervals of three, six and nine hours are given. These brominated films are denoted as PDBX-3, -6 and -9 respectively. The disappearing vinylene groups with time is reflected by the diminishing signals associated with *trans*-vinylene C-H, the stretching and out-of-plane deformation peaks at 3024 and 966 cm^{-1} respectively. This is accompanied by the formation of C-Br stretching bands between 600 and 617 cm^{-1}. Most vinylene groups are reacted after 6 hours as the peaks associated with vinylene C-H are no longer detectable. The 1214 and 759 cm^{-1} peaks of PDBX-3 and -6 are due to epoxy C-O stretching and ring vibration respectively. These peaks are no longer apparent in the spectrum of PDBX-9, indicating that the majority of the epoxy groups are gone. The ring opening of epoxy groups should result in an increase in alcohol groups. This is indeed reflected in a slight increase in intensity for the tertiary alcohol peak at 1140 cm^{-1} (see Figures lc and ld). Bromination of PPV films with a large excess of bromine at 0°C for 16 hours or with 1 M bromine/$CHCl_3$ in the presence of P_2O_5 for 16 hours gave a product, namely PDBX-O, with a similar IR spectrum as shown in Figure le. Distinctively different from the previous spectra is the 1709 cm^{-1} peak which indicates the presence of conjugated ketone groups. (see Table 1 for a detailed peak assignment.)

To account for the above results, plausible reaction paths, which were similar to those found for the bromination of triphenylethylene [13], were proposed. As shown in the following scheme, a vinylene unit reacts with a molecule of Br_2 to give a *vic*-dibromide unit 1. Elimination of HBr from 1 gives vinyl bromine 2. The liberated HBr may add back to form a *gem*-dibromide 3 according to Markovnikov's rule [14]. Unit 1 can also be hydrolyzed to 4 and then 5. Both of them can lead to the formation of 9 through the depicted paths. In addition, 5 may

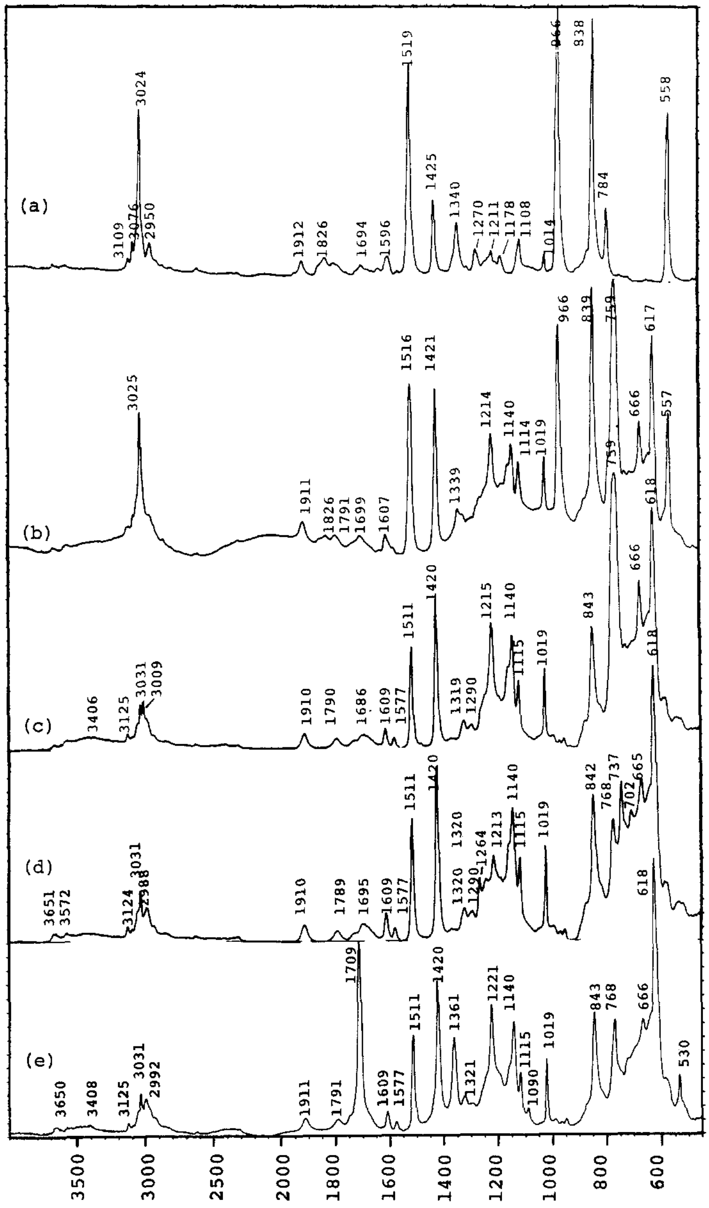
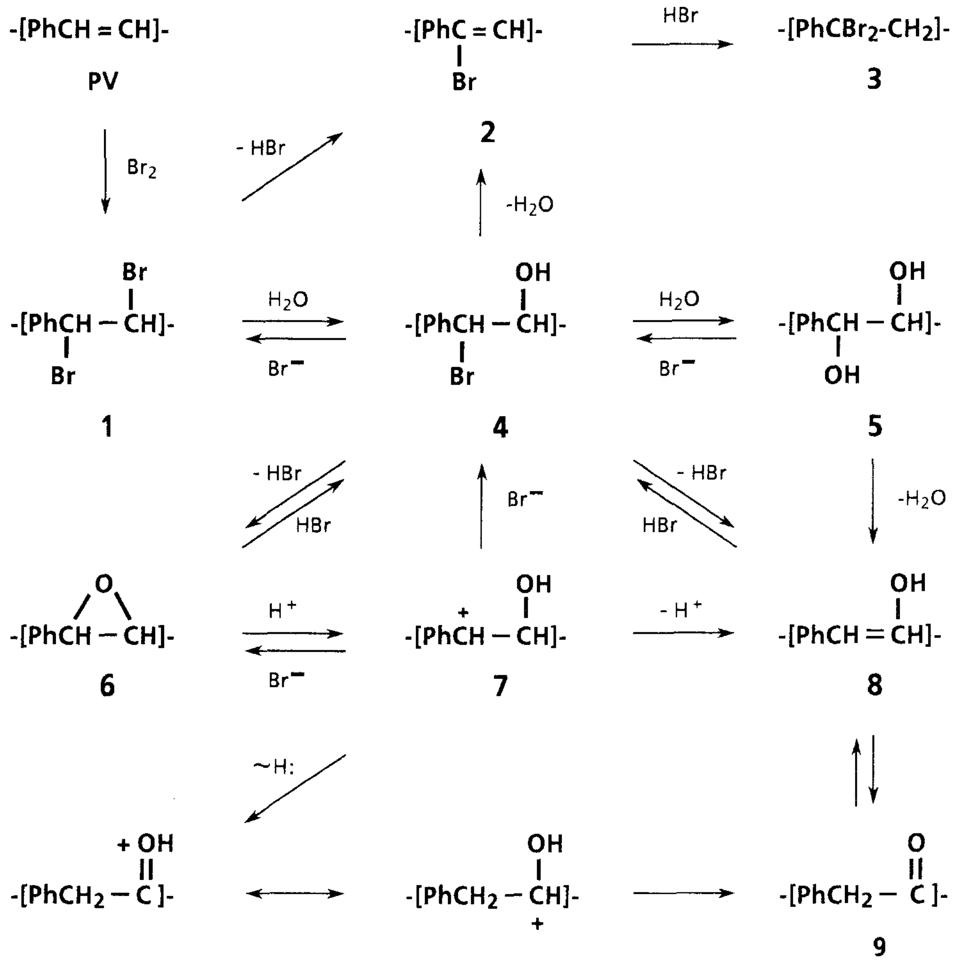


Figure 1. IR spectra for (a) PPV, (b) PDBX-3, (c) PDBX-6, (d) PDBX-9, (e) PDBX-O

Table 1. Peak Assignments for IR spectra (values given in cm^{-1})

PPV	PDBX-6	PDBX-O	PPNAs	Assignment
3109 w 3070 w	3125vw 3031 w	3125 w 3031 w	3027 m	Ar — H stretching
3024 s			3027 m	Trans = C — H stretching
2950 w	3009 w	2992 w		Alkane C — H stretching
			2211vw	Alkyne C≡C stretching
1912 w 1826 w 1791 w 1694 w	1910 w 1790 w 1686 w	1911 w 1791 w	1910 w 1790 w 1670 w	Overtone & combination bands due to Ar — H out-of-plane deformation
		1709 s		Ketone C = O stretching
1596 w	1609 w 1577 w	1609 w 1577 w	1600 m	'Quadrant' ring C = C stretching due to inperfac-tion^{10} or conjugation^{18a}
1519 s	1511 m	1511 s	1516 s	'Semi-circle' ring C = C stretching
1425 m	1420 s	1420 s	1407 m	Same as above^{10} or alcohol O — H in-plane def.
		1361 s		CH_2 def in $ArCH_2COAr^{20b}$
1340 m			1309 w	Not assigned
1270w 1178w 1108 w 1014 w	1115 w 1019 m	1115 w 1019 m	1244 w 1179 w 1106 w 1017 m	Ar — H in-plane deformation
		1221 s		Ar — CO str ^{20b} & Ar — H in-plane def
	1215 s			Epoxy C-O stretching
1211 w				= C — H in-plane deformation^{10}
	1140 s	1140 s		Alcohol C — O stretching
966 s				Trans = C — H out-of-plane deformation^{10}
			963 v **906 v**	May be ≡C — Ar stretching^{20c}
838 s	843 s	843 s	836 s	para-Ar — H out-of-plane deformation
784 m			872 v	Not assigned
		768 s	**784 v**	May be BrC = C — H out-of-plane def.^{20d}
	759 s			Epoxy ring vibration
	666 m 618 s	666 m 618 s		C — Br stretching or ring in-plane def.
			592 v	May be C = C — Br stretching
558s			548 m	Ring deformation^{10}

Note: (1) w: weak, m: medium, s: strong, vw: very weak, vs: very strong, v:variable.



give rise to **9** via **7** or **8**.

Elemental analysis data for PDBX-6 and -9 as well as the theoretical values for **1** and **2** are given in the following table. If the respective missing weight percent of 3.24 or 1.17 is attributed to oxygen, one may postulate, in conjunction with the IR results, that reaction is taking place in the sequence of PV → **1** → **4** or **5** → **6**. Also taking place is the reverse sequence of **6** → **4** or **5** → **1** or **2**. The fact that PDBX-9 shows a high %C of 39.15 may suggest the presence of **2**. Based on the results so far one may conclude that, under the present bromination condition, reaction time of at least 10 hours is needed to eliminate the oxygen containing

	%C	%H	%Br	%Total	%O
PDBX-6	35.75	2.30	58.71	96.76	3.24
PDBX-9	39.15	2.88	56.80	98.83	1.17
1	36.64	2.29	61.07	100	-
2	53.04	2.76	44.20	100	-

groups completely. (We speculate that chlorination of PPV would be less complicated because hydrolyses may not be as prone.) The occurrance of **9** in the presence of P_2O_5 was unexpected because the initial purpose of adding P_2O_5 to $Br_2/CHCl_3$ solution (the resulting mixture was allowed to stand overnight before use) was to prevent hydrolysis. The exact route that leads to the formation of **9** is not clear. But, it is possible that P_2O_5 could facilitate dehydration of **5** to give **8** and thus favor the formation of **9**.

Dehydrohalogenation of alkyl halides with hot alcoholic NaOH or KOH is very common. Polyvinylidene fluoride films have been dehydrofluorinated with NaOH or KOH in the presence of a phase transfer catalyst [15,16] or with the assistance of ultrasound [17]. However, hydrolysis and bond cleavage appeared to be the major reactions when the brominated films were treated under these conditions. This was indicated by the IR spectra of the resulting films showing vibrational peaks of carboxylic acid groups at 3400 and 1680 cm^{-1}. And, no acetylene stretching peaks were observed.

Thermal dehydrobromination was also investigated. Brominated films, PDBX-6, -9 and -18, were heated to give dark yellow films, PPNA-6, -9, -18 respectively. Their elemental analysis data and the theoretical values for ideal PPNA are given in the following table. Dehydrobromination was incomplete in all cases, as indicated by the high wt% of bromine. Most of the missing wt% of 13.53 in PPNA-6 may again be due to oxygen. Such an increase in oxygen content, as compared with 3.24 wt% for PDBX-6, is likely due to crosslinking involving epoxy groups and replacement of bromine by hydroxy groups. PPNA-9 showed a lower degree of dehydrobromination than PPNA-18. The data for PPNA-18 correspond well with the expected values of %C 79.32, %H 3.52 and %Br 17.16 for a polymer that consists of about 65% of PA unit, 10% of 1 or 3 and 25% of 2. The incomplete dehydrobromination could be a result of reversibility associated with most pyrolytic dehydrohalogenation [18].

	%C	%H	%Br	%Total
PPNA-6	71.05	3.49	11.93	86.47
PPNA-9	75.19	3.39	21.69	100.27
PPNA-18	79.20	3.67	17.98	100.85
PPNA	96.00	4.00	-	100.00

The presence of acetylene groups in PPNA-6, -9, and -18 was indicated by their IR spectra. They were basically identical, as exemplified in Figure 2a for PPNA-9, except for a slight intensity variation for the peaks at 963,906, 784 and 591 cm^{-1}. Our observation was that the intensities of these peaks were inversely proportional to the degree of dehydrobrominaiton. For instance, the IR spectrum of PPNA-18 showed relatively weak intensities at these positions. And, the IR spectrum of a sample which was heated at 250°C for 6 hours showed very strong bands at these frequencies. The weak peak at 2211 cm^{-1} is attributable to the stretching of acetylene groups. Its weak intensity suggests that most of the acetylene groups are reasonablly symmetrical [1,2]. Therefore, the polymer chains of PPNA-9 and -18 may consist of blocks of PNA that are interrupted by bromine containing units **1**, **2** or **3**. (For detailed peak assignment for PPNA, see Table 1.) A partially brominated, light yellow PPV film was also converted to give a copolymer film composed of PV and PA units. This IR spectrum of the copolymer film is given in Figure 2b showing distinctive peaks associated with each polymer unit.

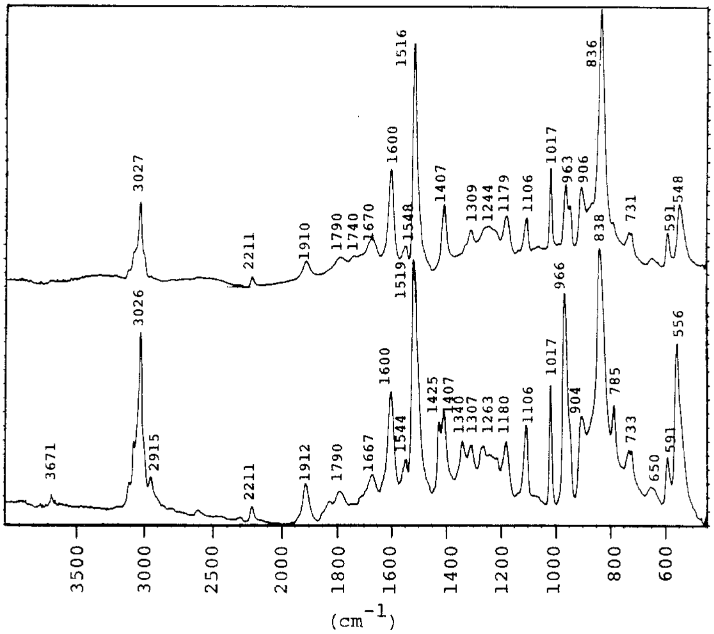


Figure 2. IR specta for PPNA-9 (top) and a PPV-co-PPNA film (bottom)

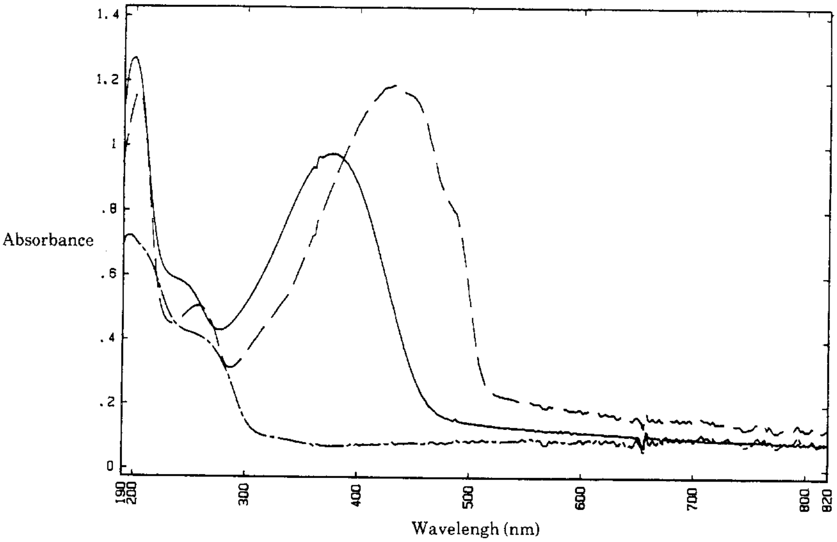


Figure 3. UV-VIS spectra for PPV (— — —), PDBX (—-—-—) and PPNA (——)

A thin PPV film was deposited on a quartz plate and was brominted in an 1M bromine/$CHCl_3$ solution for 30 minutes and the resulting film was then heat treated as described. The UV-VIS spectra of the thin films are given in Figure 3. The PPV absorption band disappears after bromination. And, after heating, a new band appears. The respective λ_{max}'s for PPV and the dehydrobrominated films are 432 and 376 nm which correspond to band gaps of 2.87 and 3.30 eV. These values are very close to the calculated values of 2.5 eV for PPV and 3.4 eV for PPNA [19]. One would expect a relatively high degree of dehydrobromination for thin PDBX films because the eliminated HBr can quickly diffuse out of the film and thus reduce the tendency of the reversed reaction.

In conclusion, complete and selective bromination of the vinylene groups in PPV films can be achieved by using bromine/chloroform solutions. The brominated films can be used as the precursors for the preparation of PPNA films by dehydrobromination. However, more research is needed in order to develop dehydrobromination methods for a complete trasformation.

References

1. Sanechika, K.; Yamamoto, T.; Yamamoto, A. *Bull. Chem. Soc. Jpn.*, 1984, **57**, 752.
2. Trumbo, D. L.; Marvel, C. S. *J. Polym. Sci., Polym. Chem. Ed.* 1986, **24**, 2311.
3. Wright, M. E. *Macromolecules* 1989, **22**, 3256. (Heck)
4. Heitz, W. Abstract in The 4th International Conference on Unconventional Photoactive Solids, San Jose, Oct. 15-18, 1989, p17.
5. Lakshmikantham, M. V.; Vartikar, J.; Jen, K.-Y.; Cava, M. P.; Huang, W. S.; MacDiarmid, A. G. *Polym. Prepr.* 1983, 24(2),75.
6. Tateishi, M.; Nishihara, H.; Aramaki, K. *Chem. Lett.* 1987, 1727.
7. Schulz, R. C.; Reiner, G. *Makromol. Chem.* 1990, **191**, 857.
8. Edwards, J. H.; Feast, W. J. *Polymer* 1981, 21, 595.
9. Ballard, D. G.; Courtis, A.; Shirley, I. M.; Taylor, S. C. *J. Chem. Soc. Chem. Commun.* 1983, 954.
10. Wessling, R. A.; Zimmerman, R. G. US Patent 3,706,677.
11. Machado, J. M. Ph.D. Dissertation, University of Massachusetts, 1988, chapter 3.
12. Bradley, C. D. C. *J. Phys. D: Appl. Phys.* 1987, **20**, 1389.
13. Kakis, F. J.; Brase, D.; Oshima, A. *J. Org. Chem.* 1971, **36**, 4117.
14. March, J. "Advanced Organic Chemistry"; Wiley and Sons: New York, 1985, p680.
15. Dias, A. J.; McCarthy, T. J. *Macromolecules*, 1984, **17**, 2529.
16. Percec, V.; Hahn, B. *J. Polym. Sci., Polym. Chem. Ed.* 1987, **25**, 783.
17. Urban, M. W.; Salazar-Rojas, E. M. *Macromolecules*, 1988, **21**, 372.
18. March, J. Advanced Organic Chemistry; Wiley and Sons: New York, 1985, p916.
19. Bredas, J. L.; Chance, R. R.; Baughman, R. H.; Silbey, R. *J. Chem. Phys.* 1982, **76**, 3673.
20. (a) Socrate, G. Infrared Characteristic Group Frequencies, 1980, Wiley and Son, Chichester, p 84; (b) p 62, Table 10.3; (c) p 38; (d) p35, Table 3.2.

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