J. Braz. Chem. Soc., Vol. 7, No. 6, 491-496, 1996.
Printed in Brazil.

Article

Raman and Infrared Spectra of Polychlorotrifluoroethylene

Yoshio Kawano* and Sérgio Carvalho de Araujo

Instituto de Química, Universidade de São Paulo, C.P. 26.077,
05599-970 São Paulo - SP, Brazil

Received: June 17, 1996

Espectros vibracionais Raman e infravermelho de polímeros homólogos do policlorotrifluoroetileno (PCTFE) foram obtidos. Tentativa de atribuição das bandas vibracionais observadas foi efetuada pela comparação com as atribuições vibracionais do politetrafluoroetileno e seus oligômeros, do monômero clorotrifluoroetileno e das medidas de polarização Raman efetuadas para os homólogos do PCTFE de baixa massa molar, em estado líquido (Kel-F-10, óleo Fluorolube e graxa Fluorolube). Os espectros Raman destes homólogos são semelhantes e mostraram bandas polarizadas em 389, 448, 495, 666 e 1124 cm^{-1}. Estas bandas foram atribuídas aos modos vibracionais totalmente simétricos. Os espectros infravermelho destes homólogos, também apresentaram semelhanças. Os espectros Raman e infravermelho de PCTFE, em fase sólida, apresentaram pequenos deslocamentos em algumas bandas em comparação com os valores de PCTFE em fase líquida. Estes deslocamentos foram atribuídos às diferentes conformações da cadeia polimérica em fase líquida e sólida. As duas amostras de PCTFE sólidas apresentaram espectros vibracionais semelhantes, apesar de apresentarem pequenas diferenças no grau de cristalinidade.

Raman and infrared vibrational spectra of homologous of polychlorotrifluoroethylene (PCTFE) polymers have been obtained. Tentative assignments of vibrational Raman and infrared bands have been made by comparison with the assignments of vibrational bands of polytetrafluoroethylene and its oligomers, the monomer chlorotrifluoroethylene and the polarized Raman bands. The polarized Raman bands for the homologous of PCTFE of low molecular weight in liquid state or grease (Kel-F-10 oil, Fluorolube oil and grease) are similar and shown polarized bands at 389, 448, 495, 666 and 1124 cm^{-1}. These bands were assigned to totally symmetric vibrational modes. The infrared spectra of these homologous are also similar. The Raman and infrared spectra of solid PCTFE shown small shift in some bands in comparison to the bands of liquid PCTFE. This shift were assigned to conformational differences between the PCTFE chain in liquid and solid state. The two samples of solid PCTFE have shown similar vibrational spectra, although the small differences in the degree of crystallinity.

Keywords: *polychlorotrifluoroethylene, Raman, infrared*

Introduction

Polychlorotrifluoroethylene (PCTFE) with a constitutional repeating unit (-CFCl-CF_2-), was first reported as solid homopolymer in 1937. It is synthesized by the polymerization reaction of the monomer chlorotrifluoroethylene (CFCl=CF_2). This polymer is of interest because of its chemical inertness, low solubility, high softening point, and satisfactory electrical and mechanical properties.

High molecular weight PCTFE is a fluorine-containing homopolymer of commercial importance, partially crystalline resin that has special uses due to vapor-barrier properties, superior thermal stability and resistance to strong oxidizing agents. The crystal structure of PCTFE has been determined by X-ray diffraction[2]. The pseudohexagonal lattice parameters are a = 0.644 nm and c = 4.15 nm. The polymer chain configuration is a helical one, with an average of 16.8 monomer units in one turn of the helix. The skeletal angles on the CF_2 and CFCl units differ by 5-7°. The polymer chain accommodates these alternating angles by twisting around the axis of the helix.

Low molecular weight PCTFE are oils, waxes or greases used for lubricants' purposes due to its performance under severe environments without chemical degradation or decomposition, and is commercially known as Kel-F or Fluorolube oil, wax or grease.

In PCTFE, replacement of one of the fluorine atoms of polytetrafluoroethylene (PTFE) with a chlorine atom lowers the molecular symmetry and show different physical and chemical properties compared to those of the PTFE.

In this work the Raman (apparently has not been reported previously) and infrared (IR) vibrational spectra of oil, viscous oil, grease and solid PCTFE are recorded and tentative assignments of vibrational bands are presented.

Experimental

Commercial samples of PCTFE of different molecular weight, in pellet or rod (Chemplast Inc.), Kel-F-10 oil (3M), Fluorolube oil (Aldrich) and Fluorolube grease (Fisher Scientific Co.) were used in this investigation.

The Raman spectra were obtained using a Renishaw Raman Microscope spectrometer, system 3000, with CCD detection, equipped with a Spectra Physics, model 127-35 He-Ne laser, operating at 632,8 nm in a backward scattering geometry. The polarized Raman spectra of liquid samples were obtained using adequate coupling of polarizer and half-wave plates incorporated before the entrance horizontal slit of the monochromator. The samples for Raman spectroscopy were prepared as pellet or rod for solid samples and in capillary or in aluminum pan for liquid samples.

The infrared spectra were obtained by using a Nicolet Màgna 550 FT-IR spectrometer and a Bomem DA3 FT-IR spectrometer and a photoacoustic accessory of MTEC, model 200. The IR spectra, in the range of 4000-450 cm^{-1}, were recorded as hot pressed films for solid sample in Bomem spectrometer, KBr beam splitter, DTGS/KBr detector, and 128 scans, with 4 cm^{-1} resolution or as pellets for photoacoustic infrared spectrum, 128 scans with 4 cm^{-1} resolution, mirror velocity of 0.05 cm/s, and carbon black was used as reference. The spectra of liquid film in KBr plates were obtained using the Nicolet spectrometer equipped with CsI beam splitter, DTGS/CsI detector, and 128 scans with 2 cm^{-1} resolution.

Results

The Raman spectra of PCTFE of different molecular weight are shown in Fig. 1, in the range of 100 - 1500 cm^{-1}. Low molecular weight PCTFE spectra show several weak or very weak peaks that are absent in high molecular weight samples spectra (900, 1044, 1102 and 1234 cm^{-1}). The solid samples show a band at 180 cm^{-1} that is not observed in the liquid spectra. This band certainly may be a crystalline mode. In the solid Raman spectra the bands at 339, 447 and 1293 cm^{-1} appear shifted to high wavenumber region compared to the liquid samples spectra (329, 439 and 1283 cm^{-1}). The solid samples show also a band splitting at 622 and 639 cm^{-1} compared to a singlet band at 633 cm^{-1} for liquid samples.

The polarized Raman spectra of homologous liquid samples are very similar to each other, and show polarized bands at 389, 448, 496, 666 and 1124 cm^{-1}. Typical polarized Raman spectra of Fluorolube oil are shown in Fig. 2. The polarized Raman spectra obtained with the polarizer parallel (Fig. 2, spectrum A) and the polarizer perpendicular plus the half-wave plate (spectrum B) show a low fluorescence in the high wavenumber region compared to the spectrum of the same sample without polarizer (Fig. 1, spectrum D).

The transmission IR spectra of low molecular weigh PCTFE are shown in Fig. 3, in the region of 400-1500 cm^{-1}. The main differences among these spectra are related to the changes in the relative intensities of several absorption bands. The band at 439 cm^{-1} appears as a shoulder in the

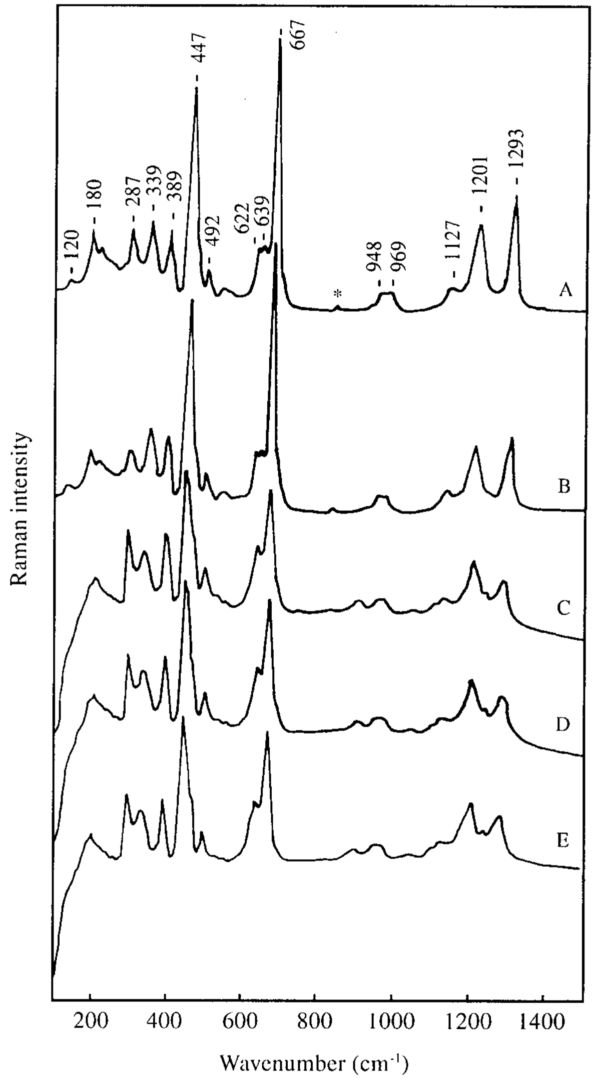

Figure 1. Raman spectra of PCTFE. (A) PCTFE pellet, (B) PCTFE rod, (C) Fluorolube grease, (D) Fluorolube oil and (E) Kel-F-10 oil. * Plasma line.

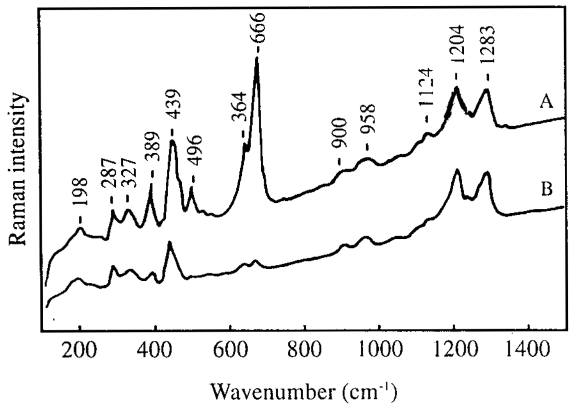

Figure 2. Polarized Raman spectra of Fluorolube oil. (A) Parallel polarization and (B) perpendicular polarization.

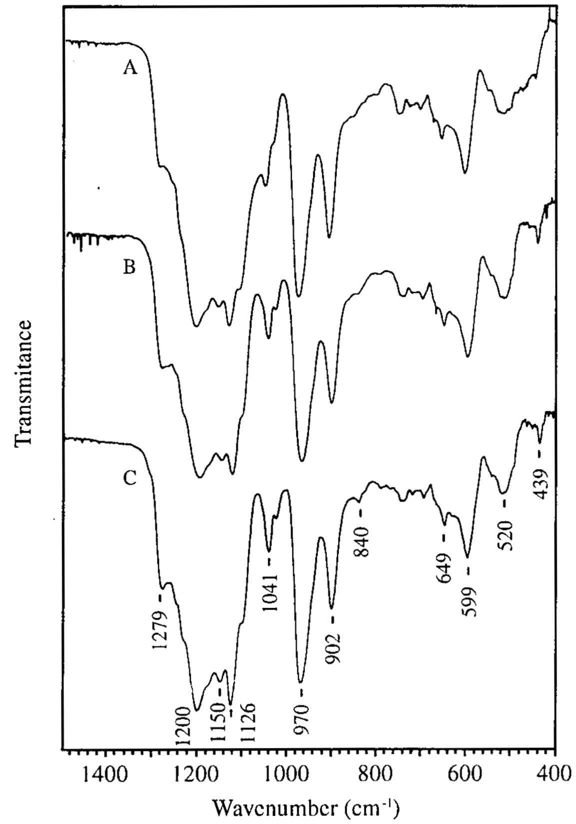

Figure 3. Infrared spectra of low molecular weight PCTFE. (A) Fluorolube grease, (B) Fluorolube oil and (C) Kel-F-10 oil.

Fluorolube grease spectrum and occur as a weak band in the spectra of Kel-F-10 and Fluorolube oil. The band at 840 cm^{-1} is weak in Kel-F-10 and appears as a shoulder in the Fluorolube oil and in grease spectra. The remarkable change is observed around 1000 - 1100 cm^{-1} in the spectrum of grease due to the intensity increase of the band at 1126 and the shoulder at 1100 cm^{-1}.

The transmission IR spectrum of hot pressed PCTFE solid film is shown in Fig. 4. This spectrum agree very well with that reported by Liang and Krimm[3] for PCTFE, in the region of 400 - 2000 cm^{-1}. A new band at 493 cm^{-1} appears in this spectrum, and the band at 584 cm^{-1} appears shifted to low wavenumber region compared to the liquid spectra (598 cm^{-1}). The band at 666 cm^{-1} appears with a higher intensity. Several bands that are very weak in the liquid spectra are absent in the solid film spectrum. The band that appears at 902 cm^{-1} in the liquid spectra disappears in the solid film spectrum. The bands at 1025 and 1041 cm^{-1} in the liquid spectra disappear also in the solid film spectrum. The band at 1128 cm^{-1} appears with increased intensity and the same is true for the band at 1290 cm^{-1}, which has shifted to high wavenumber region in solid film spectrum.

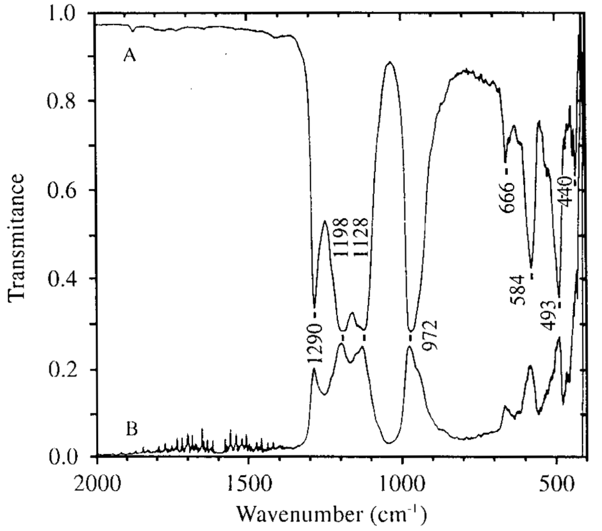

Figure 4. Infrared spectra of PCTFE pellet. (A) Transmission infrared spectrum of hot pressed film and (B) photoacoustic infrared spectrum of pellet.

Comparing the transmission IR spectrum of solid film with the photoacoustic IR spectrum (Fig. 4, spectrum B) of pellet PCTFE of the same resin, we observed a good agreement between the wavenumbers of both spectra.

The comparison between Raman and IR spectra of each homologous of PCTFE show bands that appear exclusively in Raman spectrum (Table 1; 448, 633 and 958 cm^{-1}) or in IR spectrum (Table 2; 599, 649, 740, 970 and 1150 cm^{-1}).

Discussion

A model may be postulated for the purpose of determining the symmetry species with a cyclic group that is a factor group of the one-dimensional space group of the infinite helix. From the factor group analysis one obtains the symmetry species, irreducible representations, total number of normal modes under the irreducible representation, and the selection rules for fundamentals in the Raman and IR spectra. This model for PCTFE assumes an infinitely long helical chain containing 16.8 monomer units (-CFCl-CF$_2$-) per one turn of the helix. According to this model a very high number of active fundamentals modes will be obtained for symmetry species actives in both Raman and IR spectra[4] and it should be not possible to identify all the predicted Raman and IR active fundamentals. However, there are also some difficulties to assign completely the vibrational spectra of PCTFE, because since its tacticity, the different conformations of the samples, their molecular weight, their degree of crystallinity for solid samples, and the number of molecular chains per unit cell are not known.

A satisfactory assignment can be made, however, as a result of the comparison among the spectra of PTFE[3,5-7], its oligomers[8,9], chlorotrifluoroethylene[10] and PCTFE of different molecular weight. By comparison of the results, it is possible to identify reasonably the CF_2 group vibrations. The remaining bands in the spectra are undoubtedly due to vibrations associated with the CFCl group, and those can be assigned without difficulty on the basis of the wavenumber region. The resulting interpretation of the spectra are given in Table 1 and 2.

Since the motions of the atoms in the chain gives rise to a highly coupled systems of oscillators, the designation of the characters of the vibrations is only meant to be suggestive of the approximate physical nature of the vibrations.

The polarized Raman bands at 389, 448, 495, 666 and 1124 cm^{-1} can be unambiguously assigned to symmetric vibrational modes. The band at 389 cm^{-1} is assigned to CCC

Table 1. Raman bands of homologous of PCTFE (cm^{-1})

KELF-10 (oil)	FLUOROLUBE (oil)	FLUOROLUBE (grease)	PCTFE (rod)	PCTFE (pellet)	Assignment
1283 m	1283 m	1283 m	1293 m	1293 m	ν (CF)
1235 w	1235 w	1234 w	1232 vw	1232 vw	ν_{as} (CF_2)
1204 m	1204 m	1203 m	1201 m	1201 m	ν_{as} (CF_2)
1124 w	1124 w	1125 w	1127 w	1127	ν_s (CF_2)
1098 sh	1099 sh	1102 sh			
1044 w	1043 w	1044 vw			
			969 w	969 w	ν (CCl)
957 w,br	958 w,br	958 w,br	948 w	948 w	ν (CCl)
900 w	900 w	900 w			ν (CCl)
666 s,p	666 s,p	666 s,p	667 s	667 s	ν (CC)
633 w	634 w	633 w	639 w	639 w	ν (CC)
			622 w	622 w	ν (CC)
		556 vw	542w,br	542 w,br	ω (CF_2)
	532 vw	532 vw			
495 w,p	496 w,p	494 w,p	492 w	492 w	δ (CF_2)
462 sh	462 sh	462 sh	465 sh	465 sh	ω (CFCl)
	448 sh	447 sh,p	448 s	447 s	
439 s	439 s	439 s			δ (CFCl)
389 m,p	389 m,p	389 m,p	389 m	389 m	
329 m	327 m	329 m	339 m	339 m	ρ (CF_2)
288 m	287 m	288 m	287 m	287 m	δ (CFCl)
			267 vw	267 vw	ω (CF_2)
			205 w	205 w	δ (CFCl)
196 w	198 w	198 w			δ (CFCl)
			180 m	180 m	lattice mode ?
			116 vw	120 vw	

Intensity: br= broad, m= medium, p= polarized, s= strong, sh= shouldes, v= very, w= weak.

Vibrations modes: ν = stretching, ν_{as} = asymmetric stretching, ν_s = symmetric stretching, δ = deformation, ω = wagging, ρ = rocking and t = twisting.

Table 2. Infrared bands of homologous of PCTFE (cm^{-1})

Kel-F-10 (oil-film)	FLUOROLUBE (oil-film)	FLUORLUBE (grease-film)	PCTFE (solid film)	PCTFE* (pellet)	Assignment
1279 w	1278 w	1279 w	1290 s	1285 s	ν (CF)
1211 sh	1211sh				
1200 vs	1199 vs	1199 vs	1198 s	1202 s	ν_{as} (CF_2)
1150 s	1149 s	1149 s	1150 sh		ν_s (CF_2)
1126 vs	1126 vs	1126 vs	1128 s	1130 s	ν_s (CF_2)
1100 sh	1100 sh	1100 sh			
1041 w	1041 w	1043 w			
1025 vw	1025 vw	1025 vw			
970 s	970 s	969 s	972 s	973 s	ν (CCl)
902 m	902 m	902 m			ν (CCl)
840 w					
741 w	739 w	744 w			
721 vw	720 vw	720 vw			
697 vw	697 w	696 w			ν (CC)
	668 vw	668 vw	666 w	660 w	ν (CC)
649 w	649 w	649 w			ν (CC)
599 m	598 m	598 m			ω (CF_2)
			584 m	582 m	ω (CF_2)
520 w	521 w	515 w			δ (CF_2)
			493 s	490 m	δ (CF_2)
439 w	436 w	439 vw	440 w		δ (CFCl)

*Photoacoustic IR spectra; Intensity: m= medium, s= strong, sh= shoulder, v=very, w=weak.
Vibrations modes: ν = stretching, ν_s = symmetric stretching, ν_{as} = asymmetric stretching, δ = deformation and ω = waggin.

skeletal deformation, in comparison with band that appears in PTFE oligomers[8] at 382 cm^{-1}. The band at 448 cm^{-1} is assigned to CF_2 deformation. The band at 495 cm^{-1} is assigned to CF_2 scissoring, that appears at 517 cm^{-1} in chlorotrifluoroethylene spectrum[10]. The strong band at 666 cm^{-1} is assigned to CC skeletal stretching, which is lower than that observed for PTFE, at 735 cm^{-1}. The weak band at 1124 cm^{-1} is assigned to CF_2 symmetric stretching, which is lower than that at 1382 cm^{-1} assigned for PTFE[5] and at 1155 cm^{-1} for C_3F_8 oligomer[8]. The relative intensity of this band is surprisingly weak in the Raman spectrum and very strong in IR spectrum, considering it as a symmetric stretching vibration.

The vibrational bands of PCTFE near 1000-1300 cm^{-1}, are assinged fo CF stretching mode and CF_2 asymmetric stretching modes. The bands of PCTFE occur at lower wavenumber in comparison to the bands of PTFE[5]. The CF stretching band appears at 1293 cm^{-1} in solid PCTFE and at 1283 cm^{-1} in low molecular weight samples. The CF_2 asymmetric stretching modes appear at 1232 and 1201 and the CF_2 symmetric stretching appear at ~1127 and 1150 cm^{-1} for both, the low and high molecular weight PCTFE. The unassigned weak or shoulder bands in Raman and IR spectra of low molecular weight samples can be attributed to terminal group vibrations, which could be the CF_3 group. It is also possible to be the vibrational modes of different chain conformations.

The bands in the 1000-800 cm^{-1} range should be associated to CCl stretching vibrations. In the Raman spectrum, a not well-resolved weak and broad peak appears in this region. In the IR spectrum it is clear the presence of two bands (902 and 970 cm^{-1}) in liquid samples and only a band (972 cm^{-1}) in solid PCTFE sample. It is possible to assign the band at 972 cm^{-1} to a C-Cl stretching mode of a conformation that is predominant in the solid and liquid states, and the band at 902 cm^{-1} to the other conformation, that is practically absent in solid and has a medium intensity in liquid state PCTFE.

The bands around the 600-800 cm^{-1} could be assigned to CC skeletal stretching vibrations. The Raman spectra of liquid samples show two peaks at 666 and 633 cm^{-1}, and the solid samples show three peaks at 666, 639 and 622 cm^{-1}. The IR spectrum of the solid sample shows a weak band at 666 cm^{-1} and that of the liquid samples shows a weak band at 649 cm^{-1}. The ratio of relative intensities of peaks at 666 and 639 cm^{-1} in solid state Raman spectra is ~4.7 (I_{666}/I_{639}) and in liquid state Raman spectra is ~2.2 (I_{666}/I_{633}). From these results we concluded that only one type of conformation is predominant in the solid state, and there for at least two conformations are present in the liquid state. The difference in conformation may be more reazonable than a difference in chain configuration. These results are also clear in the IR spectrum, where one observes a weak band at 666 cm^{-1} the absence of band at 649 cm^{-1} in the solid state spectrum, and the absence of the band at 666 cm^{-1} in liquid state spectra. The noncoincidence between Raman (633 cm^{-1}) and IR (649 cm^{-1}) bands assigned to same vibrational modes, may be due to both modes belonging to different symmetry species with different activities. The Raman spectra of solid PCTFE show in this region a band splitting (639 and 622 cm^{-1}) that may be associate to crystalline effect.

The degree of crystallinty determined by differential scanning calorimetry showed ~30% for PCTFE pellet and ~37% for PCTFE rod, considering the heat of fusion of 43 J/g for PCTFE with 100% of crystallinity[11]. The difference in the degree of crystallinity (~7%) between PCTFE pellet and rod showed no change in Raman and IR spectral profile for both PCTFE samples.

The bands below 600 cm^{-1} may be assigned to deformation vibrations. With exclusion of polarized Raman lines, which were already assigned, the remaining bands were assigned considering that the vibrational modes of CF_2 groups should have higher wavenumbers than CFCl groups[10], and by comparison with assignments done for PTFE[5,6] and its oligomers[7] and to chlorotrifluoroethylene[10]. The assignments are shown in Tables 1 and 2.

Conclusion

The Raman and IR spectra of five homologous of PCTFE (three of them in liquid state and two in solid state) were important to interpret the vibrational bands of PCTFE. For liquids samples, the polarized Raman spectra were important to assign the symmetric vibrational modes. The results have shown the presence of at least two different chain conformations, with the predominance of one of them in the solid state and the presence of both conformations in the liquid state.

Acknowledgments

S.C.A. thanks CNPq for a fellowship and Y.K. thanks CNPq for a research fellowship and FAPESP, PADCT/ FINEP for financial support.

References

1. Mark, H.F.; Bikales, N.M.; Overberger, C.G.; Menges, G.; Kroschwitz, J.I. *Encyclopedia of Polymer Science and Engineering;* John Wiley: New York, 1989.
2. Mencik, Z. *J. Polymer Sci., Polymer Phys. Ed.* **1973**, *11*,1585.
3. Liang, C.Y.; Krimm, S. *J. Chem. Phys.* **1956**, *25*, 563.
4. Painter, P.C.; Coleman, M.M; Koenig, J.L. *The Theory of Vibrational Spectroscopy and its Application to Polymeric Materials*; John Wiley: New York, 1982.
5. Cutler, D.J; Hendra, P.J; Rahalkar, R.R.; Cudby, M.E.A. *Polymer* **1981**, *22*, 726.
6. Peacock, C.J.; Hendra, P.J.; Willis, H.A.; Cudby, M.E.A. *J. Chem. Soc. (A)* **1970**, 2943.
7. Koenig, J.L.; Boerio, F.J. *J. Chem. Phys.* **1969**, *50*(7), 2823.
8. Pace, E.L.; Plaush, A.C.; Samuelson, H.V. *Spectrochim. Acta* **1966**, *22*, 993.
9. Risgin, O.; Taylor, R.C. *Spectrochim. Acta* **1959**, *12*, 1036.
10. Mann, D.E.; Acquista, N.; Plyler, E.K. *J. Chem. Phys.* **1953**, *21*(11), 1949.
11. Khanna, Y.P.; Kuhn, W.P.; Macur, J.E.; Messa, A.F.; Murthy, N.S.; Reimschuessel, A.C.; Schneider, R.L.; Sibila, J.P.; Signorelli, A.J.; Taylor, T.J. *J. Polymer Sci., Polymer Phys.* **1995**, *33*, 1023.

FAPESP helped in meeting the publication costs of this article