

Infrared Study of Combined Effect of γ -Radiation and Elevated Temperature on Poly(vinyl Chloride)

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Synopsis

Infrared absorption spectroscopy has been used to investigate the combined effect of γ -radiation and heat on poly(vinyl chloride) (PVC). The recorded spectra showed that exposure of PVC samples to gamma doses from 0.5 to 15 Mrad results in remarkable changes in the absorbances of their absorption bands. Also, the exposure to doses from 3 to 15 Mrad results in an appearance of a C=O band at 1720 cm^{-1} and O—H band at 3450 cm^{-1} . The nature of the formation of these bands was discussed in terms of peroxide-mediated oxidative degradation mechanism. Moreover, it was found that heat treatment of PVC samples over the temperature range $25\text{--}180^\circ\text{C}$ causes no noticeable changes in their spectra apart from slight changes in the absorbances of the bands. On other hand, it was found that heat treatment of the irradiated samples causes considerable increase in the intensity of the C=O band. In addition to the well-defined and sharp band appearing at 1720 cm^{-1} , the spectra of the samples irradiated with 10 and 15 Mrad exhibited two bands at 1070 and 1120 cm^{-1} . The obtained data led also to the conclusion that the C—Cl bands cannot be used as a measure of crystallinity of PVC.

INTRODUCTION

Effect of radiation or elevated temperature on PVC has been investigated in these past years¹⁻⁵ while the combined effect of both has received much less attention.⁶ Dehydrochlorination, discoloration and formation of free radicals are characteristics of both radiolytic and thermal decomposition. Polyene chains with long sequences are formed as a result of dehydrochlorination and produce intense color in PVC irradiated *in vacuo*.⁷ γ -Irradiation of PVC results in bond cleavage giving free radicals which, in the presence of oxygen, react rapidly with the oxygen to give peroxy radicals which lead ultimately to the formation of carbonyl and hydroxyl groups.^{8,9} Rates of oxygen consumption and formation of oxidative products have been determined in γ -initiated oxidation of PVC at 25°C .¹⁰ The radiation thermal aging behavior of PVC and PE were also investigated.⁶

The aim of this paper is to investigate the joint effect of γ -radiation and elevated temperature on PVC by using IR spectroscopy.

EXPERIMENTAL

The polymer used in this study is a commercial high molecular weight polyvinylchloride (PVC) obtained from Fluk Ltd.

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The sample was ground and the powder was then sieved to a particle size of diameter ranging from 0.075 to 0.63 mm.

The powder was irradiated by a ^{60}Co sources Noratom control A.S. gamma 3500 unit 40 r/s. The unirradiated and irradiated powdered samples were heated in an atmosphere of air at a series of increasing temperature up to 180°C for 3 h.

The infrared spectra (IR) were recorded on the PYE UNICAM full automatic double beam spectrophotometer Model SP3 - 300. The spectra of the powder were obtained as KBr discs. The obtained intensities of the infrared absorption bands are the averages of four replicate runs. The accuracy of the measured values was found to be 2%.

RESULTS AND DISCUSSION

Commercial samples of high molecular weight PVC were exposed to various doses of gamma radiation viz. 0.5, 1, 2, 3, 4, 5, 6, 10, and 15 Mrad. Then, the IR spectra of unirradiated and irradiated samples were recorded and are shown in Figure 1.

It appears from Figure 1 that the spectrum of PVC in the C—Cl region ($600\text{--}700\text{ cm}^{-1}$) is very simple. It consists of two clearly defined bands at 605 and 685 cm^{-1} , together with ill defined band at about 635 cm^{-1} .

As can be seen from Figure 1 that exposure of PVC samples to gamma doses from 0.5 to 15 Mrad results in remarkable changes in the intensities of its absorption bands. The exposure to gamma radiation from 1 to 15 Mrad results in an appearance of a broad band of medium intensity at about 3450 cm^{-1} . This band is due to the O—H stretching vibration of hydroxyl groups. Also, the exposure of the samples to gamma doses from 3 to 15 Mrad results in an appearance of a band at about 1720 cm^{-1} , the intensity of which

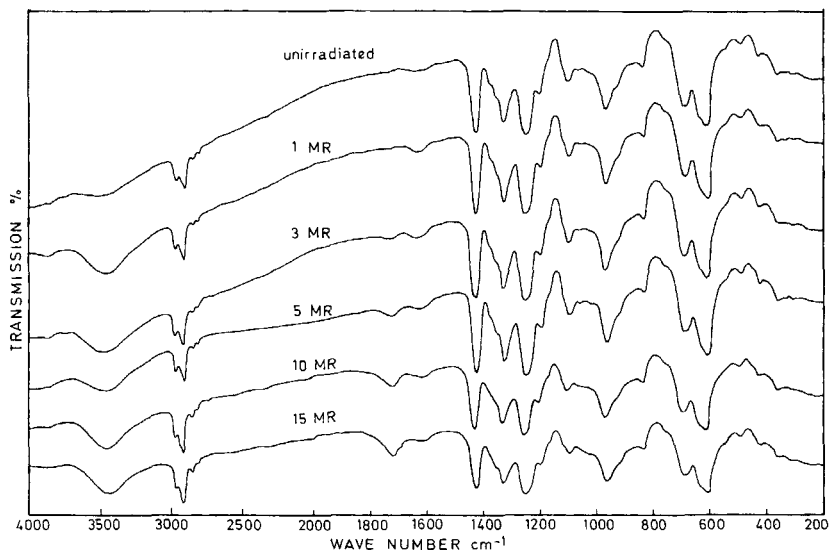


Fig. 1. IR spectra of γ -irradiated PVC.

increases with increasing doses. This band is due to the formation of carbonyl groups.

The absorbances of all absorption bands were determined by using the base line method. Base lines were drawn from 460 to 780 cm^{-1} , from 790 to 1140 cm^{-1} , and from 1150 to 1480 cm^{-1} across the bands 605 and 685 cm^{-1} , 830 , 965 and 1095 cm^{-1} and 1195 , 1250 , 1325 , and 1420 cm^{-1} , respectively. The absorbances are plotted against gamma doses in Figure 2.

Figure 2 indicates that the relationships between the absorbances and gamma doses for all the bands have similar behavior. The characteristic features of this relation are (a) slight decrease followed by, (b) an increase followed by, (c) a decrease followed by, (d) an increase followed by, (e) sharp decrease followed by, (f) final levelling off.

The rapid decrease in the absorbances can be attributed to the oxidative degradation of the polymer.

In case of much less ordered polymers, including the commercial materials, various workers have used the absorbance ratios A_{602}/A_{690} and A_{640}/A_{690} as measures of the proportion of syndiotactic units in a planar conformation and have then frequently inferred that this will also be a

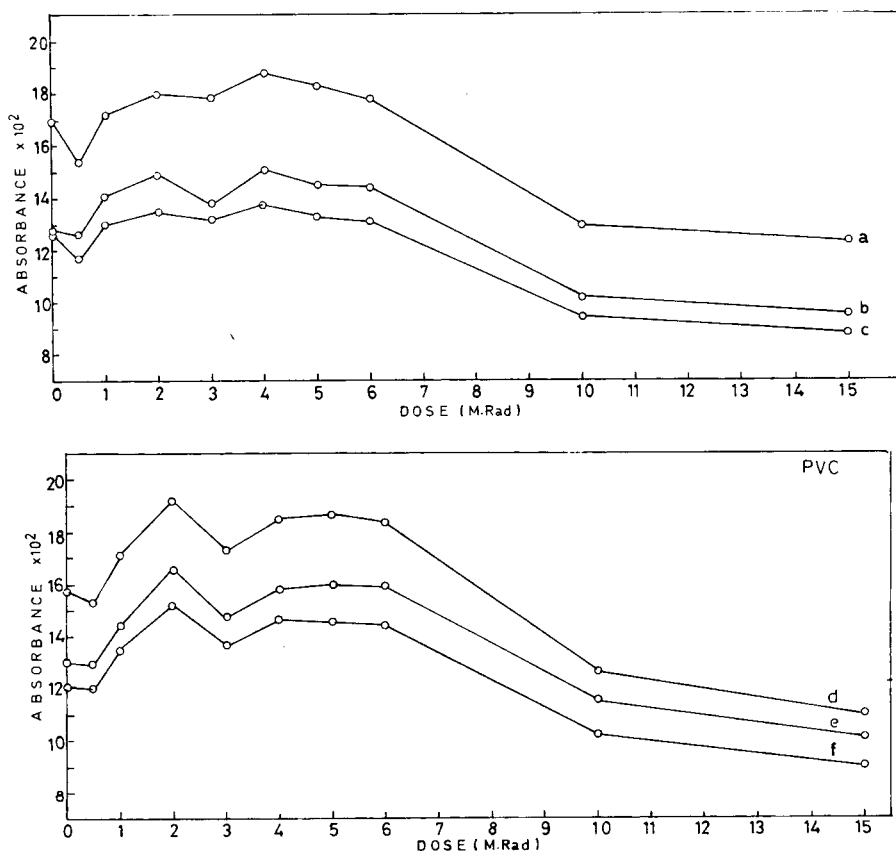


Fig. 2. Variation of the absorbances of γ -irradiated PVC bands with doses: (a) $\nu = 605\text{ cm}^{-1}$; (b) $\nu = 965\text{ cm}^{-1}$; (c) $\nu = 685\text{ cm}^{-1}$; (d) $\nu = 1250\text{ cm}^{-1}$; (e) $\nu = 1420\text{ cm}^{-1}$; (f) $\nu = 1325\text{ cm}^{-1}$.

measure of the crystallinity. Bockman¹¹ Crugnola et al.,¹² Crugnola and Danusso,¹³ and Baker et al.¹⁴ pointed out that, although the absorbance ratios A_{602}/A_{690} and A_{640}/A_{690} can prove useful as a semiempirical measure of the content of planar syndiotactic units in PVC samples, this information will not be of value in predicting their crystallinities. The two ratios are a measure of the structural units which may, in favorable circumstances, form parts of crystalline regions. Biasis et al.¹⁵ found that the optical density ratio 638/695 can characterize fringed micelles type crystallites if the sample has not been milled with KBr. This index cannot characterize the crystallinity of all mass and suspension PVC. They also mentioned that the index 604/695 allows one to follow the concentration of ribbon type crystals.

In the present study the ratio of the absorbances of the band at 605 cm^{-1} to that of 685 cm^{-1} (A_{605}/A_{685}) was calculated for the unirradiated and irradiated samples. These values are given below:

Dose	0	0.5	1	2	3	4	5	6	10	15
A_{605}/A_{685}	1.34	1.32	1.32	1.33	1.35	1.36	1.38	1.36	1.37	1.4

It is evident that the variation in the A_{605}/A_{685} for different doses are in the range of the experimental error and can be neglected. This means that gamma doses causes no significant changes in this ratio.

The unirradiated and irradiated samples were then heated in atmosphere of air at a series of increasing temperatures up to 180°C . The IR spectra of the unirradiated heated samples are shown in Figure 3.

It appears from Figure 3 that heat treatment of unirradiated PVC samples over the temperature range $25\text{--}180^\circ\text{C}$ causes no noticeable changes in their spectra in the region from 200 to 1800 cm^{-1} apart from slight changes in the absorbances of the bands. It appears also that heating the samples above 60°C increases the intensity of the OH band appearing at 3450 cm^{-1} .

Figure 4 indicates that heat treatment of the sample irradiated with 1 Mrad above 118°C results in an appearance of a C=O band at about 1720 cm^{-1} . This band is appearing in the spectra of the samples irradiated with 3, 4, 5, and 6 Mrad. Heat treatment of these samples at a series of increasing temperatures causes slight increase in its intensity. The spectra of the samples heated at 170 and 180°C show two shoulders on both sides of this band at about 1680 and 1760 cm^{-1} .

It is apparent from Figure 4 that heat treatment of the samples irradiated with 10 and 15 Mrad induces considerable changes in their spectral features. The weak C=O band appearing at 1720 cm^{-1} becomes a well-defined sharp band of medium intensity in the spectra of the heated samples. In addition to this band, the spectra of these heated samples show two new sharp bands at 1070 and 1120 cm^{-1} . The intensities of the 1720 , 1120 , and 1070 cm^{-1} are temperature-dependent. Elevation of temperature to 170°C causes remarkable decreases in the intensities of all absorption bands. In general, the spectra of these samples show considerably better resolution in the C—H stretching region.

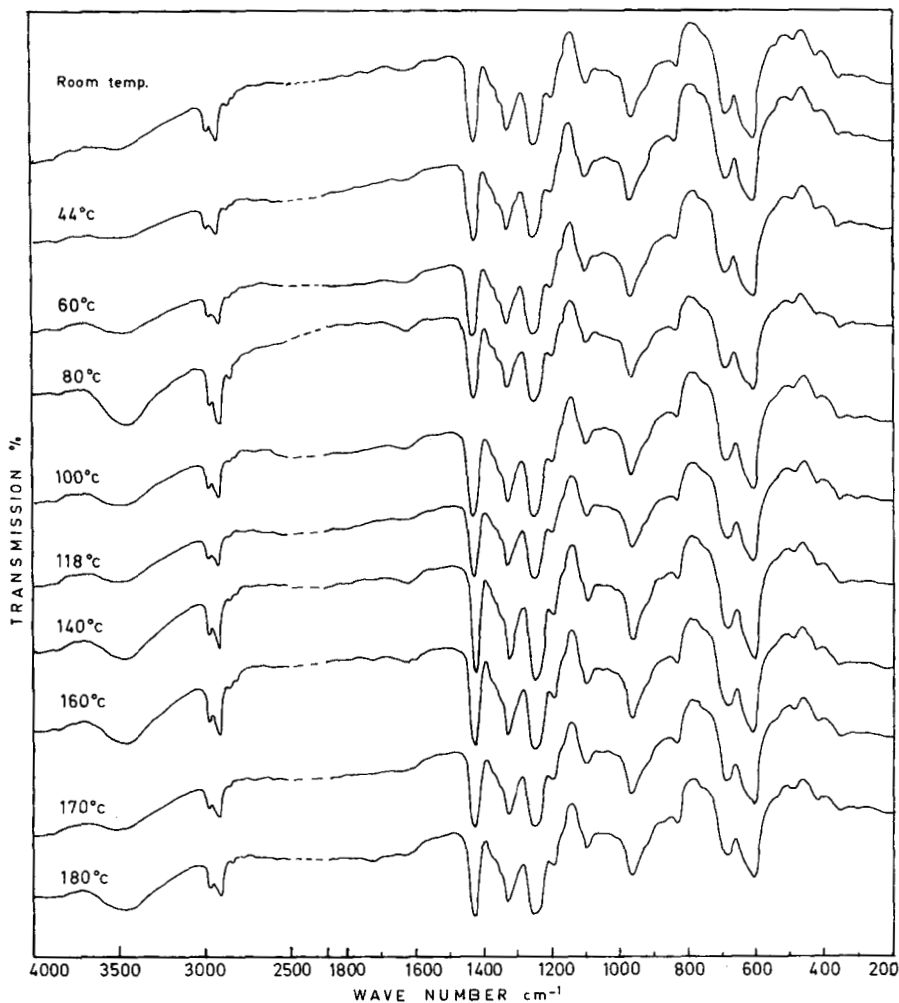


Fig. 3. IR spectra of thermally treated PVC.

The absorbances of C=O band at 1720 cm^{-1} of the samples irradiated with 10 and 15 Mrad were determined. A base line was drawn across this band from 1540 to 1840 cm^{-1} . The degree of oxidation was measured by the carbonyl index. This is simply the ratio of the carbonyl peak at 1720 cm^{-1} to CH₂ peak at 1428 cm^{-1} . The measured values are given in Table I.

The table reveals that heat treatment of the samples irradiated with 10 and 15 Mrad above room temperature increases the degree of oxidation, but this increase is not regular. The highest degree of oxidation is obtained at 170°C for 15 Mrad and at 60°C for 10 Mrad while the lowest value is obtained at 80°C and 118°C for the samples irradiated with 10 and 15 Mrad, respectively.

The time of heating was also taken into consideration. The sample irradiated with 3 Mrad was heated at 60°C and 118°C for different periods up to 5 h.

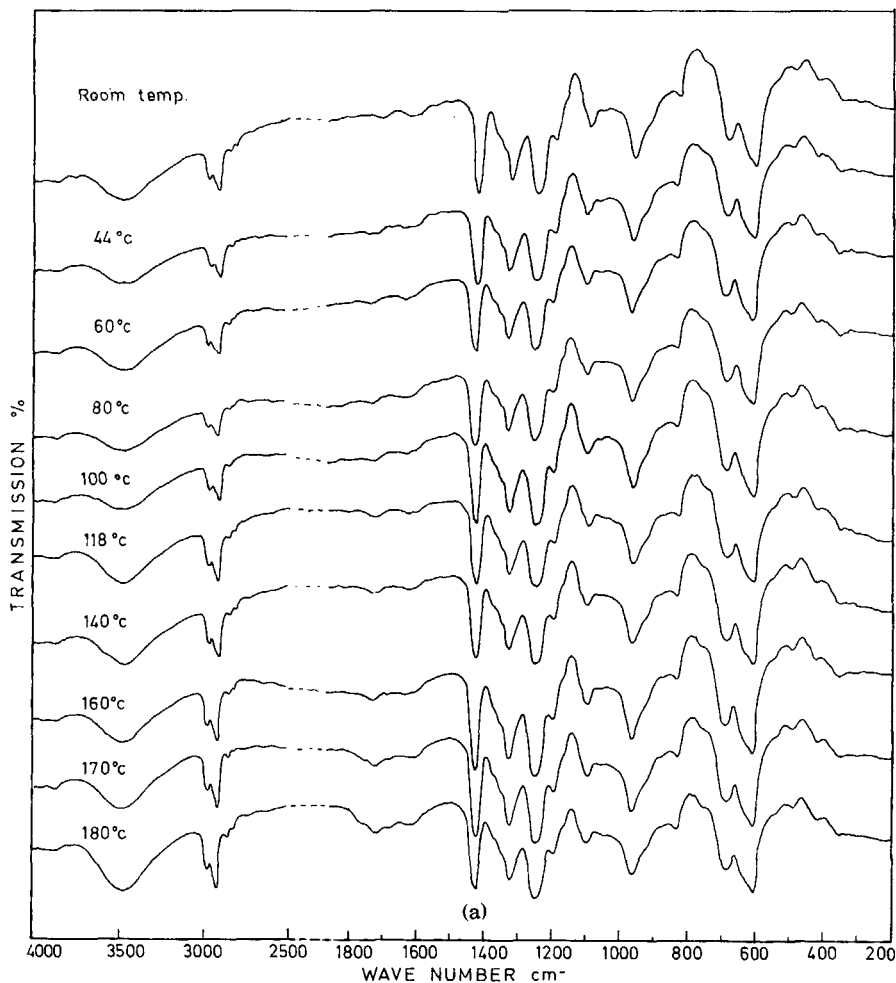


Fig. 4. IR spectra of thermally treated γ -irradiated PVC: (a) 30 Mrad, (b) 10 mRad, (c) 15 mRad.

It was found that the time of heating from 0.5 to 5 h has no remarkable effect on the intensity of the C=O band at 1720 cm^{-1} .

Clough and Gillen⁶ reported tensile elongation data for PVC and PE samples aged in environments of (1) room temperature radiation (4.5 krad/h, 25°C), (2) elevated temperature radiation (4.5 krad/h, 80°C), and (3) elevated temperature in the absence of radiation (80°C). They found that the combined effect of radiation and elevated temperature results in dramatically enhanced degradation compared with elevated temperature alone or radiation at room temperature. The joint effect of gamma radiation and elevated temperature was also found to occur when the two environments were applied in a sequential fashion, but only when the experiments were performed in the order: radiation at room temperature followed by elevated temperature. The IR spectra obtained on polyethylene samples from their combined radiation elevated temperature environment experiments showed a correlation between deterioration in mechanical properties and the formation and growth of strong peaks in the carbonyl region ($\lambda_{\text{max}} \sim 1710\text{ cm}^{-1}$).

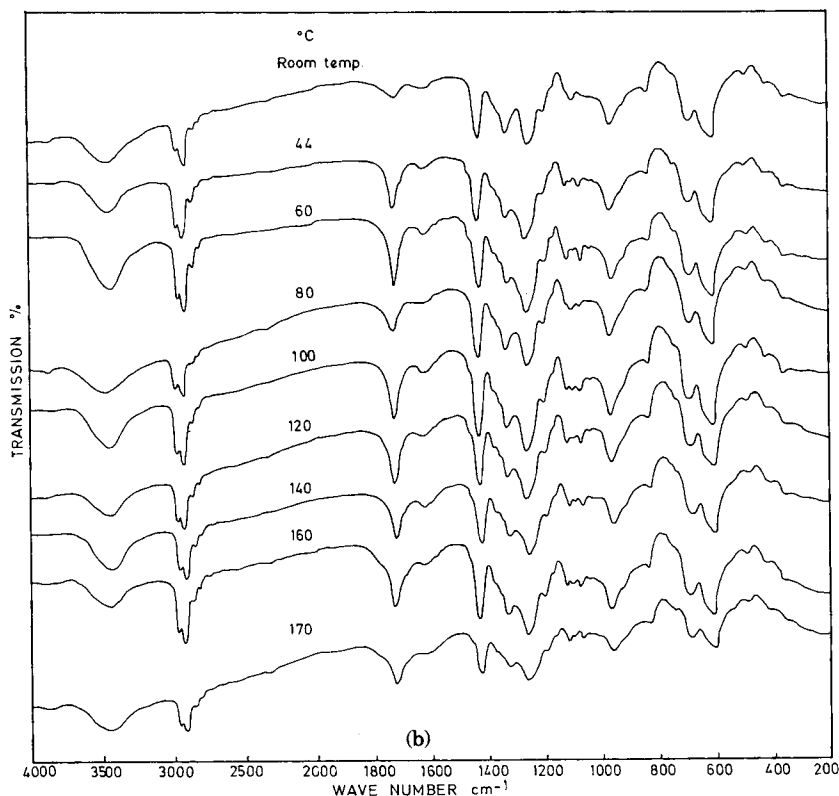


Fig. 4. (Continued from the previous page.)

They interpreted the aging behavior of PVC and PE in terms of a peroxide-mediated oxidative degradation mechanism. Gamma-irradiation of the polymers results in bond cleavage giving free radicals, which, in the presence of oxygen, react by a chain mechanism to form oxidation products that include hydroperoxides (Dole,¹⁶ Rabek,¹⁷ and Reich and Stivala¹⁸). The hydroperoxides are thermally labile; breakdown yields more free radicals which can initiate new chain reactions with oxygen to give further oxidation including formation of more hydroperoxides. The radical steps set in motion during the course of the reactions include pathways which lead to polymer chain scission and crosslinking.

They further confirmed the importance of oxygen by carrying out the experiments in simultaneous environment of radiation and elevated temperature, but under an inert atmosphere of nitrogen, here, the degradation was found to be completely blocked. For the sequential experiments, an oxidative degradation mechanism, involving substantial amounts of thermally induced peroxide breakdown, would require the participation of oxygen in both the radiation step and the thermal step.

On the basis of the above-mentioned considerations, one can come to the conclusion that the combined effect of radiation and elevated temperature results in formation and growth of strong peak in the carbonyl region at 1720 cm⁻¹. The formation of these carbonyl groups can be interpreted on the basis of the peroxide mediated oxidative degradation mechanism proposed by Clough and Gillen.⁶

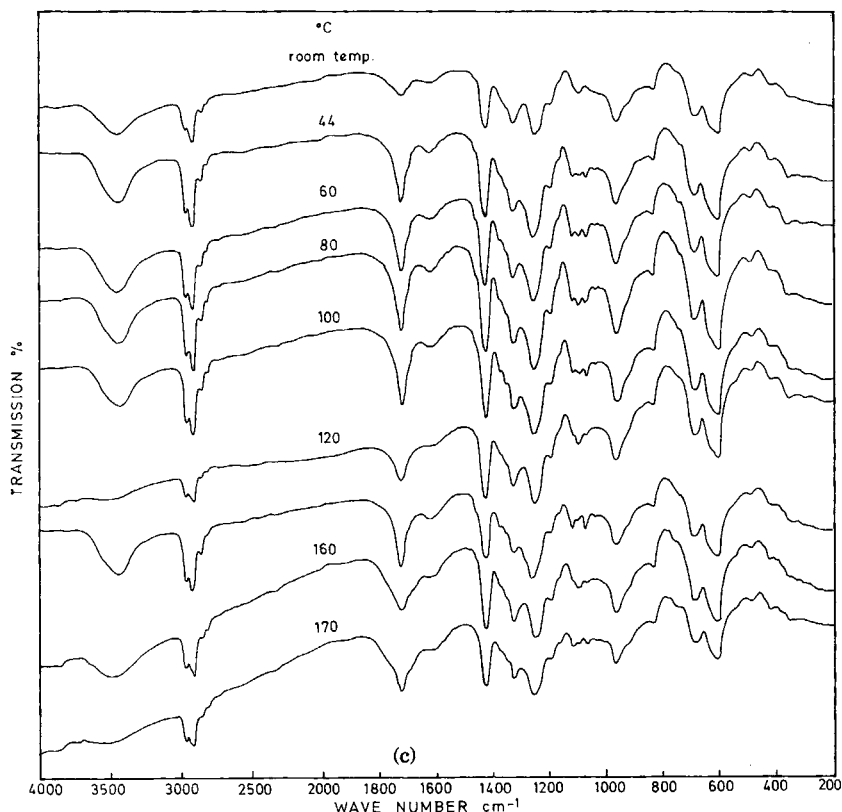


Fig. 4. (Continued from previous page.).

The ratio A_{605}/A_{685} was determined for the samples under investigation. It was found that the difference between the measured values is small and can be neglected. This means that heat treatment of unirradiated and irradiated PVC has no effect on the ratio A_{605}/A_{685} .

Biais et al.¹⁵ found that by heating the PVC film above 140°C both 615/695 and 638/695 cm^{-1} ratios decrease. Baker et al.¹⁴ found that when PVC

TABLE I
Variation of Degree of Oxidation of γ -Irradiated PVC with Temperature

Temp. (°C)	Dose (Mrad)			
	10 Mrad		15 Mrad	
	Absorbances of the C=O band at 1720 cm^{-1}	Carbonyl index	Absorbances of the C=O band at 1720 cm^{-1}	Carbonyl index
25	0.385	0.26	0.245	0.38
44	0.122	0.94	0.081	0.84
60	0.117	1.19	0.117	0.76
80	0.140	0.48	0.053	0.73
100	0.146	0.86	0.102	0.91
120	0.066	0.91	0.094	0.49
140	0.119	0.87	0.081	0.84
160	0.087	0.91	0.089	0.94
170	0.102	1.08	0.071	1.31

was annealed at a series of increasing temperatures up to 180°C the crystallinity increases steadily with annealing temperature. Furthermore, as the temperature is raised some amorphous material is converted to a nematic phase, and this may crystallize during the subsequent cooling. IR spectrum did not change, in agreement with the prediction of Moore and Krimm¹⁹ that there is no observable band splitting from interchain interaction in crystalline regions, thus indicating that these C-Cl bands cannot be used as a measure of crystallinity.

The above mentioned considerations lead to the conclusion that the C-Cl bands (605, 635, 687 cm^{-1}) cannot be used as a measure of crystallinity of PVC.

References

1. A. A. Miller, *J. Phys. Chem.*, **63**, 1755 (1959).
2. S. Ohnishi, S. Sugimoto, and I. Nitta, *J. Polym. Sci.*, **A1**, 625 (1963).
3. D. Braun, *Pure Appl. Chem.*, **26**, 173 (1971).
4. Z. Mayer, *J. Macromol. Sci. C*, **10**, 263 (1974).
5. G. Avrey, B. C. Head, and R. C. Poller, *J. Polym. Sci., Macromol. Rev.*, **8**, 1 (1974).
6. R. Clough and K. Gillen, *Radiat. Phys. Chem.*, **18**, 3-4 (1981).
7. G. J. Atchison, *J. Appl. Polym. Sci.*, **7**, 1471 (1963).
8. R. Salovey and R. G. Gebauer, *J. Polym. Sci., A-1*, **10**, 1533 (1972).
9. G. Zeppenfel and A. Bartl, *J. Polym. Sci. C*, **11**, 4369 (1969).
10. C. Decker, *J. Appl. Polym. Sci.*, **20**, 3336 (1976).
11. O. C. Bockman, *J. Polym. Sci., A*, **3**, 3399 (1965).
12. A. Crugnola, M. Pegoraro, and F. Danusso, *J. Appl. Polym. Sci.*, **6**, 1705 (1968).
13. A. Crugnola and F. Danusso, *J. Polym. Sci. B*, **6**, 535 (1968).
14. C. Baker, W. F. Maddams, and J. E. Preedy, *J. Polym. Sci., Polym. Phys. Ed.*, **15**, 1041-1054 (1977).
15. R. Biais, M. Geny Chuong, and M. Carrega, *Br. J. Polym.*, 179 (1980).
16. M. Dole, *Adv. Radiat. Chem.*, **4**, 303 (1974).
17. J. Rabek, *Oxidative Degradation of Polymers*, I. Bamford and C. Tipper, Eds., *Comprehensive Chemical Kinetics*, **14**, *Degradation of Polymers*, Elsevier, Amsterdam, 1975, chap. 4, p. 425.
18. L. Reich and S. Stivala, *Elements of Polymer Degradation*, McGraw-Hill, New York, 1971.
19. W. H. Moore and S. Krimm, *Makromol Chem. Suppl.*, **1**, 491 (1975).

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