Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

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To cite this Article Cataldo, Franco , Ursini, Ornella , Ragni, Pietro , Lilla, Valentina and Angelini, Giancarlo(2009) 'Radiation-Induced Polymerization of Vinylidene Chloride in Bulk and Included in Thiourea Crystals', Journal of Macromolecular Science, Part A, 46: 1, 16 — 24

To link to this Article: DOI: 10.1080/10601320802511711

URL: http://dx.doi.org/10.1080/10601320802511711

Journal of Macromolecular Science®, Part A: Pure and Applied Chemistry (2009) **46**, 16–24

ISSN: 1060-1325 print / 1520-5738 online
DOI: 10.1080/10601320802511711

Radiation-Induced Polymerization of Vinylidene Chloride in Bulk and Included in Thiourea Crystals

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Received May 2008, Accepted June 2008

Vinylidene chloride (VDC) or 1,1-dichloroethylene was polymerized with γ radiation in bulk or as inclusion complex in thiourea crystals (inclusion polymerization). The resulting poly(vinylidenechloride) (PVDC) samples obtained from the two different polymerization techniques were characterized by FT-IR and electronic absorption spectroscopies, by ozonolysis and by thermal analysis (TGA, DTG and DTA). It was found that two selective secondary reactions occur in the two PVDC samples, respectively obtained from bulk polymerization or from inclusion polymerization. In the former case, the main reaction is only a crosslinking reaction, while in the latter case, with the PVDC included into the thiourea channels, the crosslinking reaction is fully inhibited and instead a dehydrohalogenation reaction takes place producing the polyene structures. The presence of polyene structures in the PVDC synthesized by the inclusion polymerization was demonstrated by electronic absorption spectroscopy and by ozonolysis experiments. The presence of polyene segments in the PVDC causes a reduction in the thermal stability of the polymer, lowers its melting point and reduces its crystallinity.

Keywords: Poly(vinylidenechloride), PVDC, radiation-induced polymerization, bulk polymerization, inclusion polymerization, inclusion complex, channel complex, thiourea, supramolecular chemistry, chemical structure, polyene chains, ozonolysis, FT-IR spectroscopy, UV-VIS spectroscopy, thermal analysis.

1 Introduction

Vinylidene chloride (VDC) or 1,1-dichloroethylene can be easily polymerized by free radical and ionic reactions (1). The resulting polymer, poly(vinylidenechloride) (PVDC) is known for a long time and finds applications in packaging, molding, extrusion and lacquer resins (1). Several copolymers of VDC are commercially important (1). VDC can also be polymerized with high energy radiation (2–4). In bulk conditions, the radiation-induced polymerization of VDC shows a polymerization rate proportional to the dose rate to the power of 0.48 (2), in line with the behavior of a number of different monomers (5). Higher molecular weight was measured on PVDC obtained at higher radiation doses (2). VDC has also been radiation-polymerized in emulsion and the polymerization rate was found to be dependent on 0.3 power of emulsifier concentration, whereas the molecular weight of the resulting PVDC increased with the degree of monomer conversion and with the emulsifier concentration (3). VDC has also been radiation-polymerized in solution in the presence of different solvents like bromoform, chloroform and benzene (4). The polymerization rate was increased in the presence of bromoform and chloroform rather than in benzene. It is well known that halogenated solvents may act as sensitizers for the free radical polymerization of certain monomers.

The inclusion polymerization of various monomers, the stereospecificity and the mechanism of this supramolecular synthesis has been discussed in detail in some reviews (7–9). For instance, the polymerization process involves the irradiation of a monomer occluded inside the channels of certain crystals like urea, thiourea and deoxycholic acid. The shape of the channels inside the crystals may act as a template conferring to the resulting polymer a stereospecific order. A typical example of such synthesis is the inclusion polymerization of 1,3-dimethylbutadiene monomer inside the channels of thiourea crystals (10). The resulting poly(dimethylbutadiene) is always obtained with a very high 1,4-trans content, while the bulk or emulsion polymerization with a free radical initiator yields a polymer

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with much less ordered chemical structure and relatively low trans content (10).

Although it has been reported that VDC forms complexes with thiourea (6), the radiation-induced inclusion polymerization or channel polymerization of VDC has never been studied in detail. The present paper is an account of the study of the inclusion polymerization of VDC in comparison with the bulk polimerization of VDC. Furthermore, some chemical and physical properties of the PVDCs obtained by the two polymerization routes (channel and bulk) are reported.

2 Experimental

2.1 Materials and Equipment

Vinylidene chloride was purchased from Fluka (Switzerland) and used as received. Thiourea was a high purity grade from Riedel de Haen (Germany). Chloroform was a spectrophotometric grade from Fluka and o-dichlorobenzene was from Aldrich (USA). Irradiations were made in a Gamma cell from Atomic Energy of Canada at a dose rate of 2.0 kGy/h.

The FT-IR spectra were recorded on samples embedded in KBr pellets in transmittance mode. Electronic absorption spectra were recorded on PVDC suspensions in $CHCl_3$ or solutions in o-dichlorobenzene. Spectrophotometric measurements were made on a Shimadzu UV160A spectrophotometer. Thermogravimetric analysis with simultaneous differential thermal analysis was recorded under a nitrogen flow at a heating rate of 10°C/min.

2.2 Bulk Polymerization of Vinylidene Chloride

Three vials were filled with vinylidene chloride (~10 g each) in a high vacuum line. The monomer was accurately degassed and the vials were sealed. The three vials were then irradiated in the gamma cell at room temperature at 150, 300 and 450 kGy. The doses used were sufficient to cause the complete polymerization of the monomer. After irradiation, the vials were carefully opened and in all cases a release of gaseous hydrochloric acid was observed. The PVDC was recovered by breaking the glass surrounding the polymer mass. In all cases, the PVDC was recovered as a cylindrical block which was powdered quite easily in a ceramic mortar. The yield was quantitative with respect to the initial monomer. In all the three cases, the PVDC was obtained as a cream-white powder.

2.3 Inclusion Polymerization of Vinylidene Chloride in Thiourea

2.3.1. *Run 1*

The sample was prepared by filling a glass flask with 17.15 g of thiourea moistened with 2.83 g of dry methanol and filled with 17.24 g of vinylidene chloride. The flask was stored three days at +15°C before irradiation. The irradiation was accomplished at 300 kGy in a tightly closed flask with a screw cap. After irradiation, the sample appeared as a unique block violet in color and somewhat friable. No visible detection of release of HCl was observed by opening the flask. The purification of the product was made by grinding the product in a mortar, transferring the powder in a flask and refluxing the mixture with 200 ml of distilled water and 25 ml of conc. HCl for 1 h. The thiourea dissolution (and hydrolysis) is complete. The purified PVDC was recovered by filtration with an aspirator. The polymer collected in the filter was washed with acetone and left to dry in air. The yield was 15.3 g. Even after purification, the PVDC appeared as a violet powder.

2.3.2. *Run 2*

This sample was prepared as the first sample described in run 1, but the proportions were: 17.88 g of thiourea, 5.79 g of methanol and 9.41 g of vinylidene chloride. After irradiation at 300 kGy in a tightly closed flask with screw cap, the work-up was exactly the same as described in run 1. The PVDC appeared darker than that prepared in run 1 but always violet in color. The yield was 8.6 g.

2.4 PVDC Ozonolysis in $CHCl_3$ Suspension

PVDC (300 mg) obtained by inclusion polymerization was suspended in 50 ml of chloroform. A violet suspension was obtained. The electronic absorption spectrum of the suspension was measured and then the suspension was transferred in a 500 ml round bottomed flask which was evacuated. Ozone/oxygen mixture (ozone $\approx$4% by weight) was admitted into the flask and was vigorously shaken. The originally violet color faded rapidly into a pink color. A sample of the reaction mixture was taken to record the UV and IR spectra and then a further ozone treatment was accomplished again by evacuating the flask and admitting ozone. The suspension turned from pink to light yellow. Again the UV and IR spectra of the sample were recorded.

2.5 PVDC Ozonolysis in Homogeneous Solution

PVDC (300 mg) obtained by inclusion polymerization was dissolved in o-dichlorobenzene (50 g). A dark brown homogeneous solution was obtained by heating at 150°C for 30 min. The solution was transferred in a 500 ml round bottomed flask which was evacuated and then filled with a ozone/oxygen mixture (ozone $\approx$4% by weight). After shaking, the solution changed its color from dark brown to light brown. The electronic absorption spectrum of the solution was recorded before and after the ozone treatment.

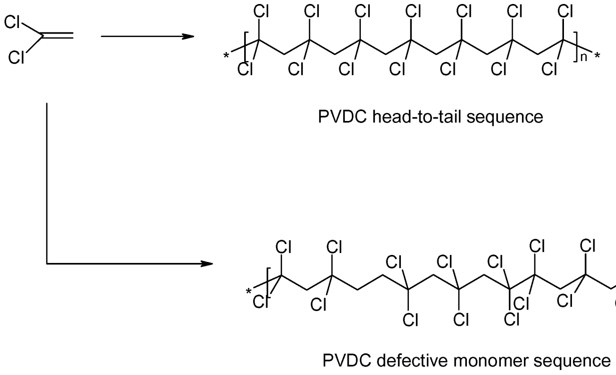
3 Results and Discussion

In the exploratory work of Brown and White (6), VDC was polymerized inside thiourea crystals by the action of an electron beam. A total dose ranging from 10 to 50 kGy was used in that work. Under those conditions, the PVDC yields reported were rather low (6). In fact, the VDC conversion to PVDC was comprised between 20–30%; only in one case 40% conversion was measured on weight of PVDC polymer on VDC monomer (6).

As shown in the experimental section, in the present work, the PVDC yields are quantitative both for the polymer produced in bulk, as well as that produced by inclusion polymerization. The merit of this result may be attributed to the fact that γ radiation is more penetrating than electron beam and the samples have been irradiated in a more uniform way. Furthermore, higher radiation doses have been used in the present work in comparison to the earlier work.

3.1 Chemical Structure of PVDC Prepared in Bulk and by Inclusion Polymerization

As shown in Scheme 1, PVDC has a regular structure and a high crystallinity (1). As a consequence of the head-to-tail connection of the monomeric units, the chlorine atoms are arranged in geminal position along the polymer backbone and are lying on the same plane. Defective structures in PVDC can arise from the anomalous head-to-head and tail-to-tail connection of the units as shown in Scheme 1. Such anomalies are rare. Figure 1 shows the FT-IR spectra of the PVDC prepared by radiation-induced polymerization in bulk and included in thiourea. The two spectra do not show any significant differences which may suggest important structural differences between the two PVDC samples. Thus, the inclusion polymerization of VDC in a constrained medium does not imply the introduction of additional chain defects due to wrong addition in the monomer unit sequence along the polymer backbone. The infrared spectrum of PVDC is well known (11, 12) and the stretching due to geminal CCl_2 moiety gives rise to a series of absorption bands at 750, 654, 598, 529 and 450 cm^{-1} (11), as shown in Figure 1. Other features of the PVDC spectrum are the CH_2 stretching bands at 2992 and 2932 cm^{-1} and the CH_2 bending mode at 1404 cm^{-1} (12). The two intense bands at 1071 and 1041 cm^{-1} are due to C–C skeletal vibrations (12).



Sch. 1. Regular PVDC is made by a sequence of monomeric units connected head-to-tail. PVDC with defective monomer sequence may have head-to-head and tail-to-tail connections in the monomeric unit sequence. Such defective structure appears negligible in the PVDC prepared by radiation polymerization both in bulk and as clathrate.

Figure 1 shows also the infrared spectrum of thiourea characterized by the C=S stretching bands at 1404 and 727 cm^{-1} while the NH_2-(C=S) infrared bands are located at 3370, 3140 and about 1600 cm^{-1} (13). The bands at 3268 and 1080 are due to the N–H stretching. The complex of thiourea including PVDC is similar to that of pure thiourea, although some band shift can be noticed due to the interaction between the host and the guest and the distortions introduced by the polymer guest formed in the thiourea matrix (Fig. 1). The spectra in Figure1 show also that thiourea can be washed away completely leaving a PVDC completely pure.

The cream-white color of the PVDC, prepared by radiation-induced polymerization prepared in bulk in comparison to the violet color of the PVDC which was prepared by inclusion polymerization does not find any explanation on the basis of the FT-IR spectroscopy.

3.2 Electronic Absorption Spectroscopy and Ozonolysis of PVDC Prepared by Inclusion Polymerization

Figure 2 shows the electronic absorption spectrum of PVDC obtained by inclusion polymerization and characterized by a violet color. Such material once suspended in chloroform shows an absorption spectrum with a maximum at 520 nm followed by a shoulder reaching 600 nm. It is worth remembering that long polyenes like poliacetylene chains show absorption maxima just at these wavelengths (14). More precisely, growing polyacetylene chains on Rh(I) catalyst display a maximum at 600 nm and also shows a series of bands at shorter wavelengths, namely at 500, 545 and at 590 nm (14). The polyenic origin of such absorption can be easily demonstrated by reacting the PVDC suspension in $CHCl_3$ with ozone (see Experimental section). The treatment with ozone rapidly discolors the suspension which initially turns into pink and by further ozone treatment it becomes clear yellow. Figure 2 shows the changes in the PVDC electronic absorption spectrum after the treatment with ozone. The absorption maximum at 520 nm with the shoulder at 600 nm completely disappeared as a result of the removal of the polyene moieties. It is well documented that ozone attacks and also oxidizes the conjugated double bonds of the polyene chains (15–17). Therefore, the ozone treatment demonstrated the presence of polyenes in the PVDC prepared by inclusion polymerization.

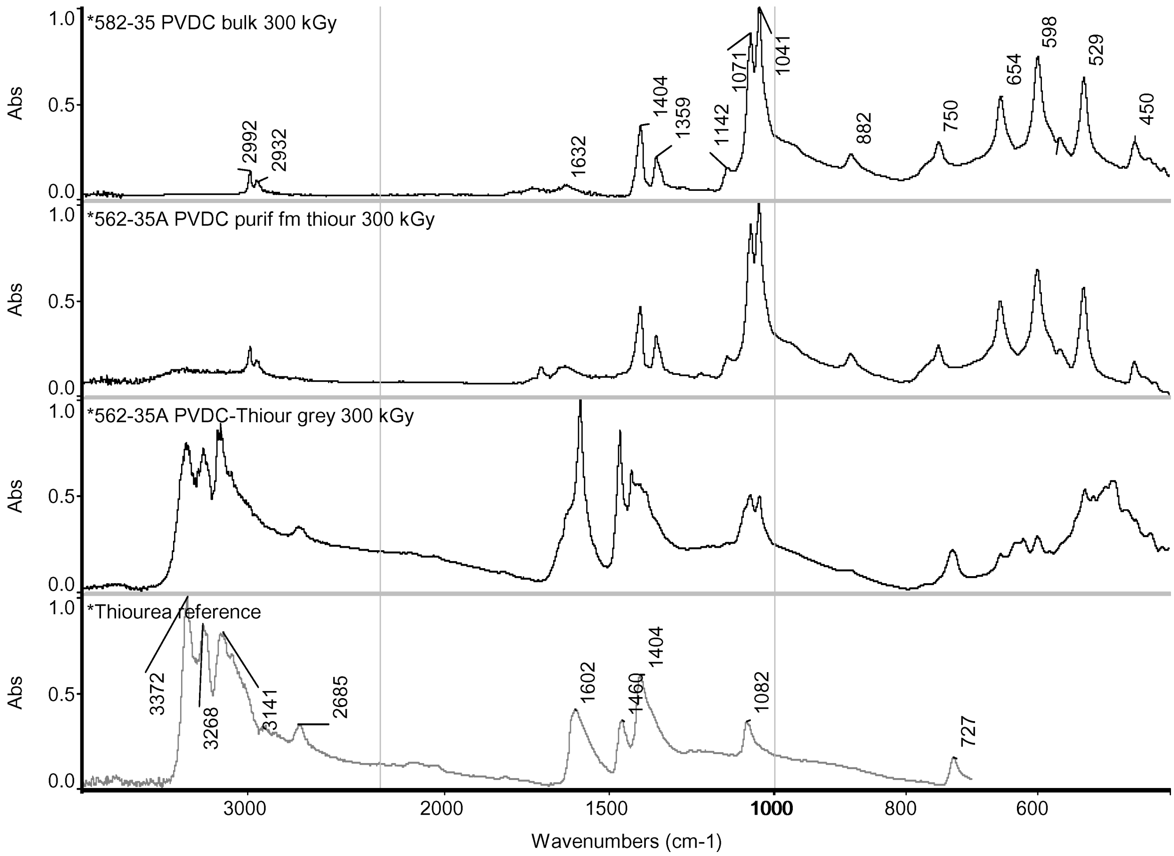


Fig. 1. FT-IR spectra of PVDC prepared by bulk polymerization at 300 kGy (first spectrum from top). The PVDC prepared by inclusion polymerization in thiourea crystals displays the same band pattern as the PVDC prepared in bulk (second spectrum from top). The third spectrum from top shows the complex between PVDC and thiourea before the purification and thiourea removal. The spectrum at the bottom of the figure is due to pure thiourea.

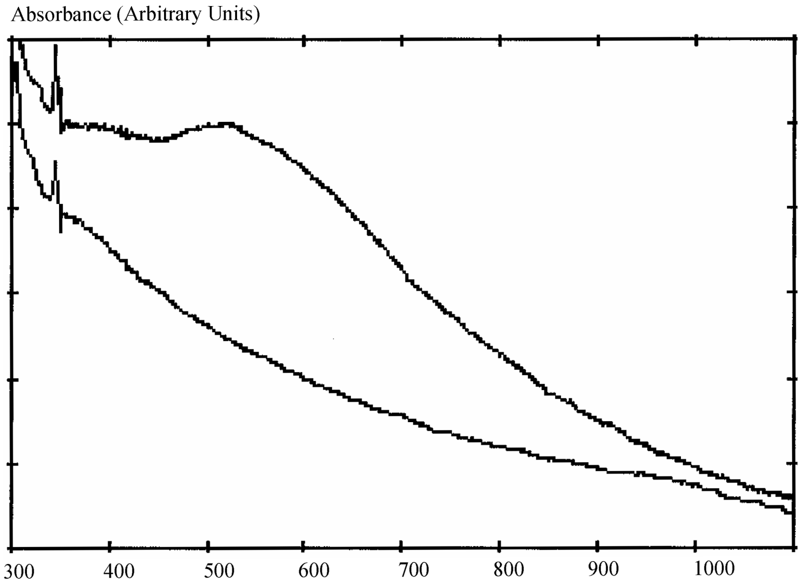


Fig. 2. Electronic absorption spectra of PVDC obtained by inclusion polymerization dispersed in $CHCl_3$. The violet color of this PVDC sample is responsible for the absorption maximum at 520 nm followed by a shoulder at 600 nm (upper absorption curve). The ozone treatment removes the absorption bands in the visible and the PVDC becomes yellow (lower absorption curve).

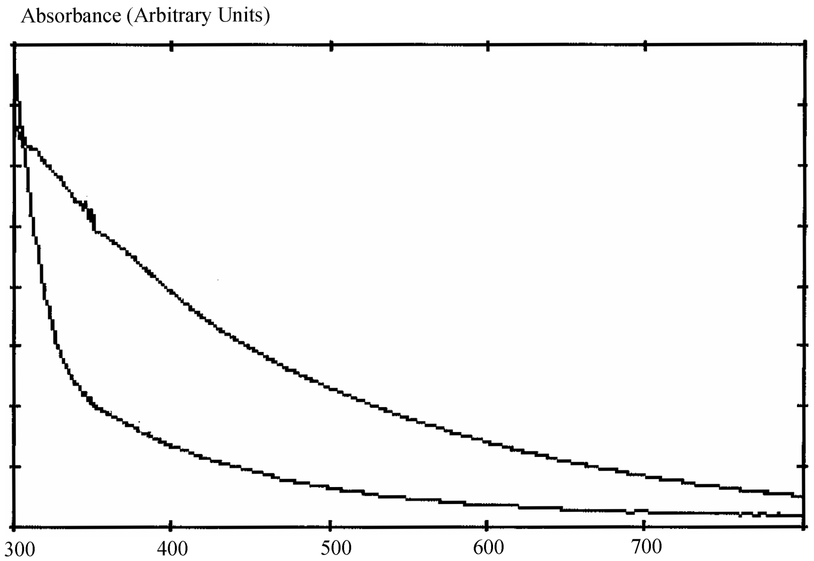
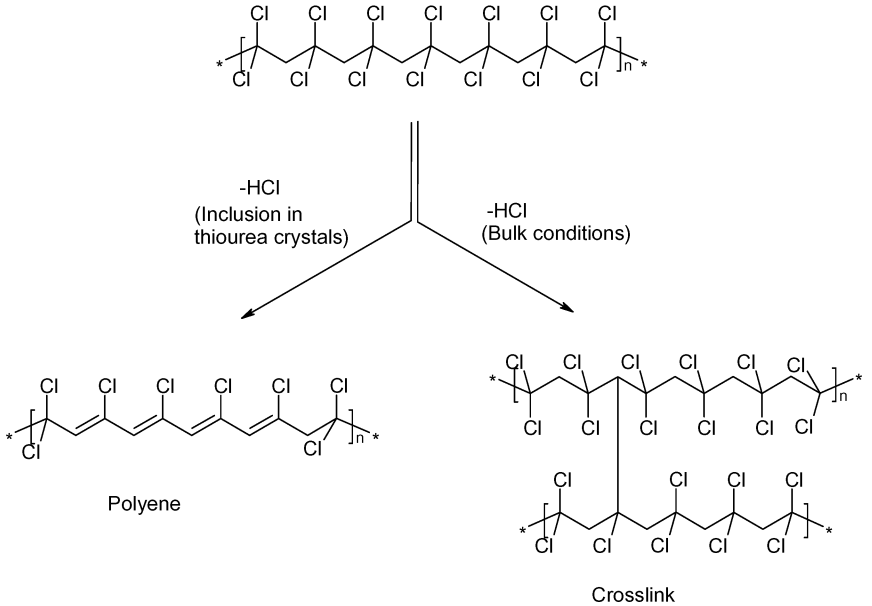


Fig. 3. Electronic absorption spectra of PVDC obtained by inclusion polymerization dissolved in o-diclorobenzene (upper absorption curve). The ozone treatment of such solution causes its discoloration in the visible as shown by the lower absorption curve.

A similar result can be achieved in a homogeneous solution obtained by dissolving PVDC in o-dichlorobenzene and treating the solution with a stream of ozone: the original absorption curve which has appreciable absorption intensity in the range comprised between 300 and 800 nm after the ozone treatment becomes much more transparent as reported in Figure 3.

The isolation of the PVDC after ozonation in $CHCl_3$, both at the pink and yellow color has permitted us to record the FT-IR spectra which are shown in Figure 4. From the spectra, it is evident that the ozonolysis has oxidized the polyene segments into ketonic groups. In more detail, the ozonolysis has caused the development of the absorption bands at 1720–1733 cm^{-1} which can be assigned to aldehyde and carboxylic acid moieties (13). Carboxylic acid groups are also suggested by the absorption band at about 3400 cm^{-1} in conjunction with the ketonic band at about 1720 cm^{-1}. Figure 4 shows an increase of the intensity of these bands at a higher degree of ozonation. The formation of aldheyde and carboxylic acid groups suggest that



Sch. 2. PVDC synthesized by inclusion polymerization produces chloropolyenes as secondary products while crosslinking reaction is favored in the case of bulk polymerization of vinylidene chloride.

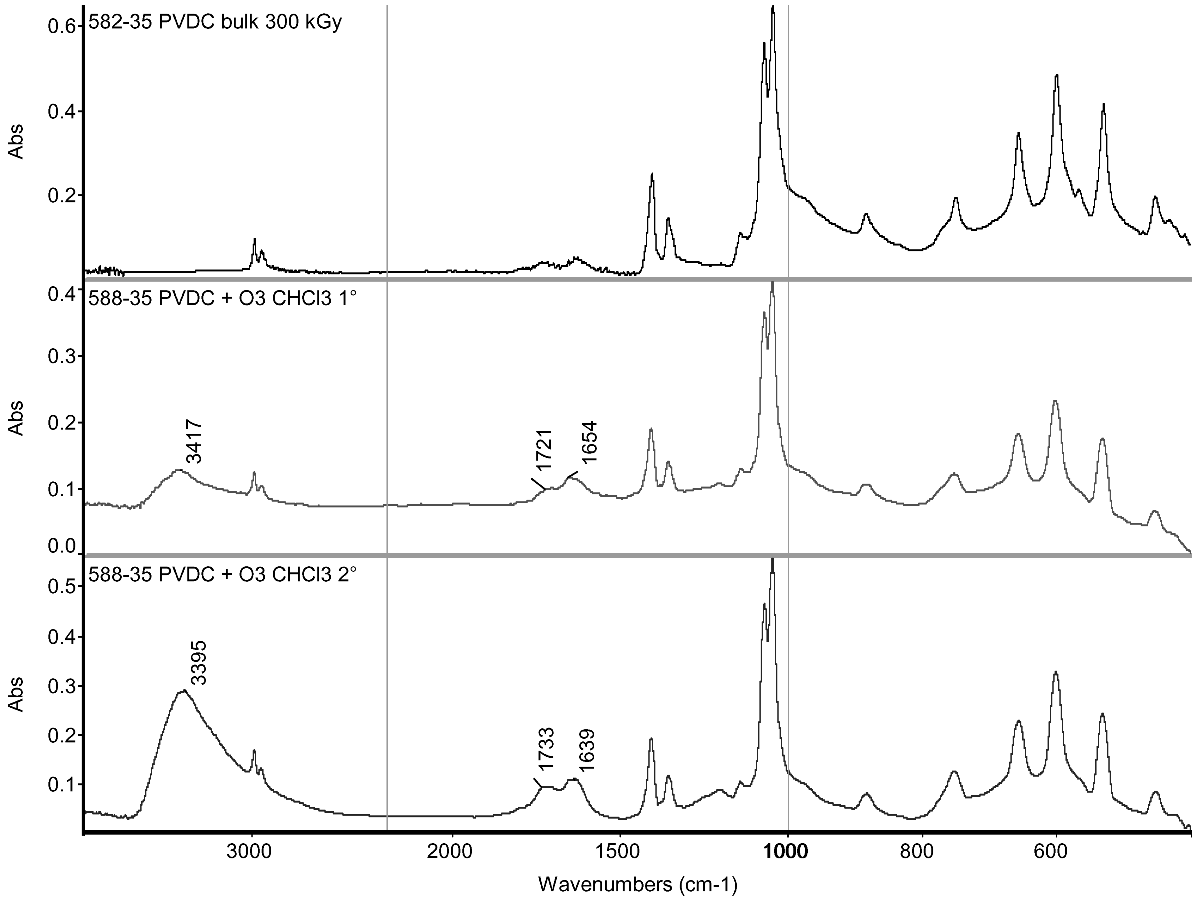


Fig. 4. FT-IR spectra of reference PVDC (top of the figure) and the ozonized PVDC samples (middle and bottom of the figure). The spectrum in the middle is PVDC from inclusion polymerization whose colour turned from violet to pink after ozone treatment. The spectrum at the bottom of the figure is PVDC from inclusion polymerization fully ozonated whose colour turned pink to white-yellow after ozone treatment.

the ozonolysis has led to chain scission of the PVDC backbone just in the correspondence of the polyene moieties. To justify the violet color of the PVDC prepared by inclusion polymerization we have advocated the presence of polyene segments and have demonstrated their presence by electronic absorption spectrophotometry and by ozonolysis experiments and FT-IR spectroscopy. However, the formation of polyene segments by the action of radiation on halogenated polymers is not a novelty. It is well known for quite a while (18, 19) that the irradiation of poly(vinylchloride) (PVC) produces the formation of polyene segments which are manifested by development of different colors in the PVC and which can be detected by electronic absorption spectroscopy with the development of absorption bands which can reach 500–600 nm (18). The polyene segments are formed by the radiation-induced dehydrochlorination of the chlorinated polymers. For instance, PVC releases HCl with a radiation chemical yield of 2.74 molecules/100 eV while hydrogen is released only with a radiation chemical yield of 0.15 molecules/100 eV (19). Thus, it is not a surprise that polyene segments are also formed in the radiolysis of PVDC and this phenomenon has been documented in the literature (20–23). The loss of HCl is accompanied both by chain scission and crosslinking reactions. Scheme 2 reports schematically, the formation of polyene chains and crosslinks in PVDC. Both are due to radiation-induced dehydrochlorination reactions. At first glance, it is quite surprising that the PVDC obtained by inclusion polymerization a 300 kGy is violet in color and rich in polyene segments, while this is not the case of PVDC polymerized in bulk at the same radiation dose (300 kGy) or even at a higher 450 kGy dose. In fact, the PVDC synthesized in bulk was just cream-white with minimal, if any, polyene content. The first explanation is that the PVDC polymerized in bulk was irradiated in the complete absence of oxygen, while this was not the case of PVDC synthesized by the inclusion polymerization approach. However, the amount of oxygen was minimal in the latter case because the flask was completely filled with the thiourea-VDC mixture and was tightly closed with a screw cap. It is known that the presence of oxygen favours the dehydrochlorination reaction and the formation of polyenes in halogenated polymers (24).

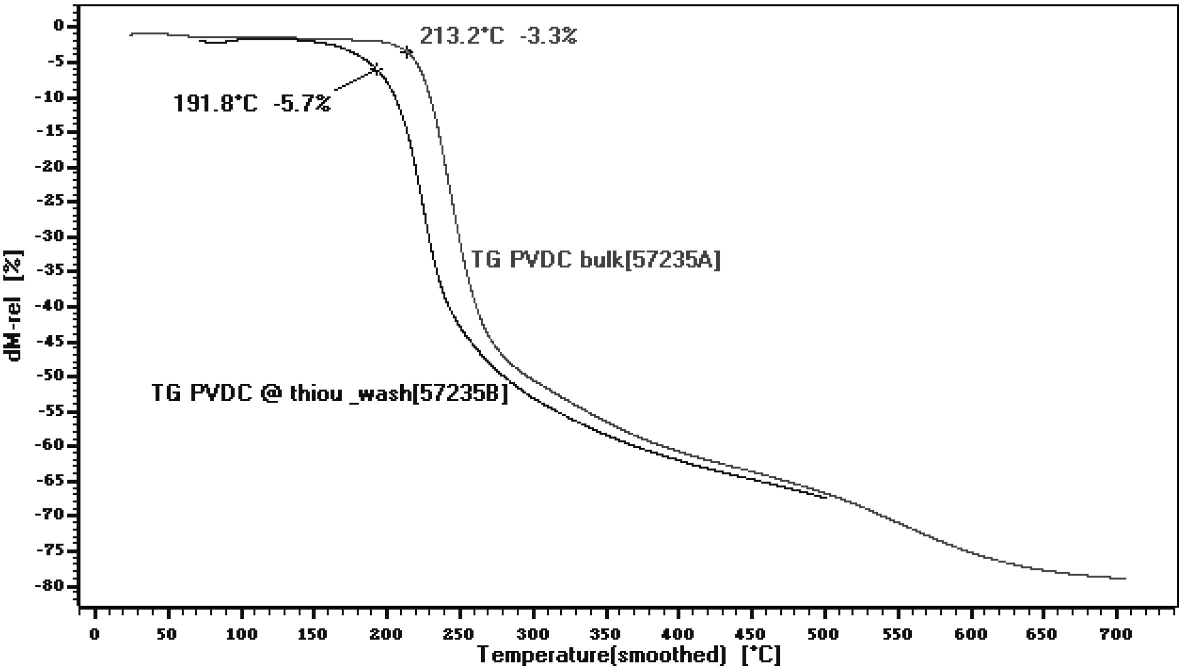


Fig. 5. Thermogravimetric analysis (under N_2 flow) of PVDC synthesized with bulk polymerization or as inclusion complex in thiourea channels. The TGA shows that the PVDC derived from inclusion polymerization is less stable than that polymerized in bulk.

However, in the present case, the vast differences between the products of bulk and inclusion polymerization cannot be attributed to oxygen. Another simple explanation may involve the fact that PVDC prepared in bulk is a solid block of plastic at room temperature with limited chain motion so that the dehydrochlorination is partially inhibited and instead, crosslinking reactions are more favoured. In contrast, the PVDC formed inside the channels of thiourea cannot crosslink at all, since each chain is isolated into the channels of the thiourea crystals and therefore, the main possible reaction is almost exclusively dehydrochlorination. Furthermore, the thiourea itself and the presence of methanol (used as an aid for complex formation) may contribute to the dehydrochlorination reaction.

As shown in Scheme 2, we propose that the inclusion polymerization of VDC promotes selectively the dehydrochlorination of the PVDC formed inside the thiourea channels. On the other hand the VDC polymerization in bulk leads to a polymer block where only crosslinking reactions can happen preferentially.

3.3 Thermal Analysis of the PVDC Prepared by Radiation-Induced Polymerization in Bulk and as Inclusion in Thiourea Crystals

The thermal behavior of the PVDC samples polymerized in bulk, and included inside thiourea crystals, was studied with thermogravimetry (TGA), differential termogravimetric analysis (DTG) and differential thermal analysis (DTA) in a nitrogen flow at a heating rate of 10°C/min.

The TGA curves are reported in Figure 5 and proved that the PVDC obtained in bulk is more thermally stable than the PVDC prepared with the inclusion technique. In fact, the former starts it decomposition at 213°C, while the latter shows an incipient decomposition already at 192°C. The different thermal stability of the two PVDC samples can be better visualized from the DTG curves (Fig. 6) which permit us to visualize the maximum decomposition rate of each sample. The PVDC sample polymerized in bulk shows a maximum decomposition rate at 243°C, while the sample prepared by inclusion polymerization reaches its maximum decomposition rate at 223°C i.e., 20°C lower temperature. The reason for such significantly different thermal stability is not fully understood, but should be interpreted again in terms of the presence of polyene structures in the case of the inclusion polymerization product. The polyene structures present in the PVDC from inclusion polymerization are chloro-polyene structures as shown in more detail in Scheme 2. Such structures are susceptible to further decomposition with liberation of other HCl and formation of acetylenic moieties (25–27). It appears plausible that the lower stability of PVDC prepared by inclusion polymerization resides just in the chloro-polyene structures.

In the early work on the inclusion polymerization of VDC, the resulting PVDC was obtained in relatively low yields and the melting point of the polymer was reported with a very large melting interval i.e., 120°–200°C or 150°–190°C (6). The melting point of the commercially available PVDC is 202°C (1). Figure 7 shows that the PVDC synthesized by bulk polymerization has a melting point just at

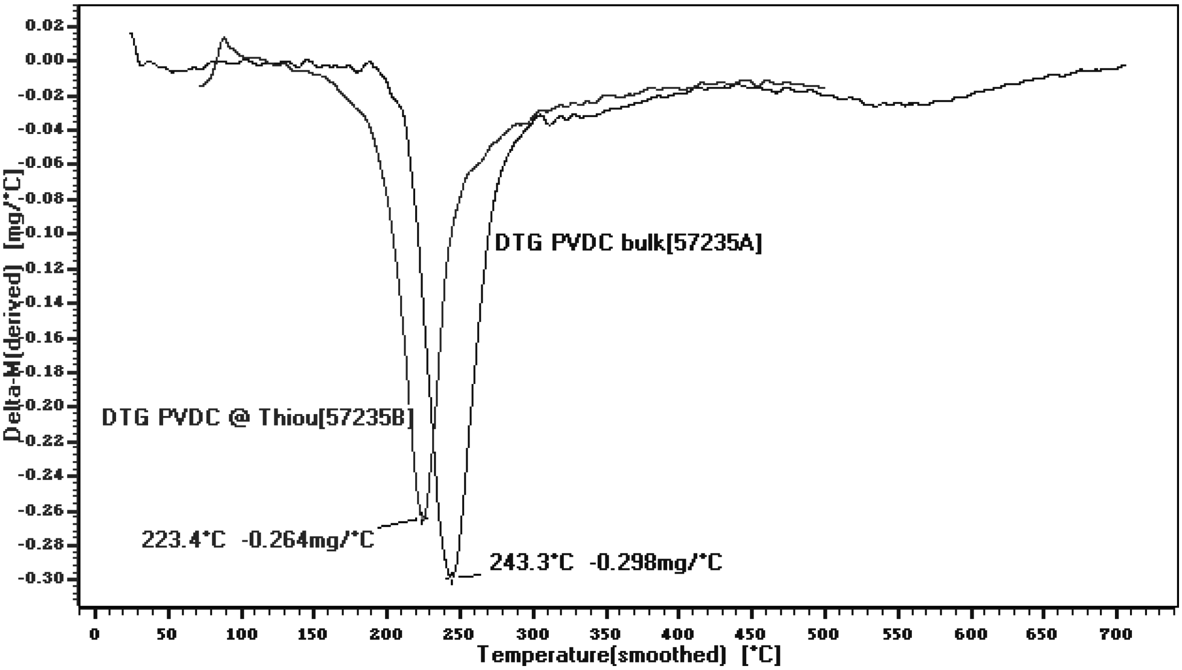


Fig. 6. The first derivatives of the two TGA curves reported in Figure 5 show that the maximum decomposition rate of PVDC obtained with the inclusion polymerization technique occurs at 223°C, a 20°C lower temperature than the regular PVDC prepared with polymerization in bulk.

203°C in agreement with literature data (1) and with "regular" PVDC. Instead, the PVDC sample prepared by inclusion polymerization shows an endothermal melting point at 184°C inside the melting interval reported by Brown and White (1). The DTA technique does not permit a quantitative measurement of the melting enthalpy, but a qualitative estimation can be inferred from Figure 7. It is evident from Figure 7 that PVDC from inclusion polymerization

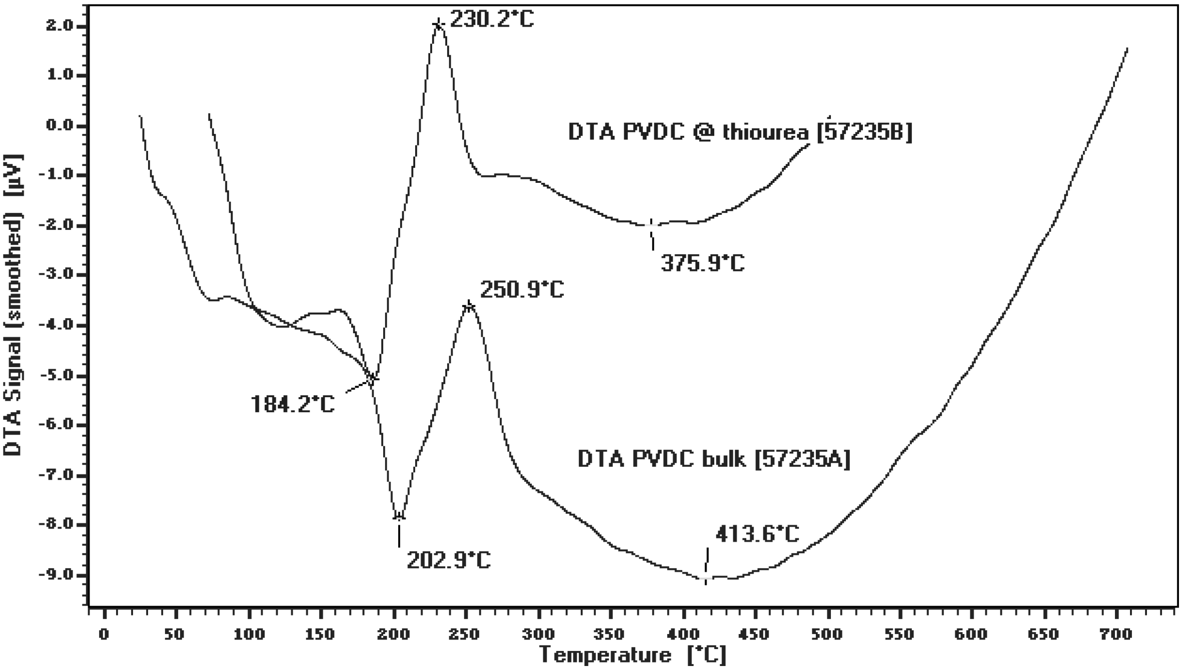


Fig. 7. The differential thermal analysis of PVDC shows that the bulk polymerized sample has a regular melting point of 203°C, while the sample prepared by inclusion polymerization has low melting point located at 184°C.

has a lower melting enthalpy than that of regular PVDC obtained from bulk polymerization. Consequently, lower crystallinity can be attributed to the PVDC obtained by inclusion polymerization. The lower level of crystallinity can be due to the presence of the chloro-polyene segments along the PVDC chains.

4 Conclusions

VDC can be easily polymerized with radiation-induced polymerization in quantitative yields into PVDC, both in bulk, or as an inclusion complex inside the channels of thiourea crystals. At 300 kGy dose, the PVDC samples prepared according to the two polymerization techniques do not show any significant differences in their FT-IR spectra. However, the PVDC obtained by inclusion polymerization is violet in color and shows an electronic absorption spectrum which suggests the presence of polyene moieties along the polymer chain. Such polyene structures are almost absent in the case of PVDC prepared with bulk polymerization. The ozonolysis of the PVDC obtained by inclusion polymerization selectively destroys the polyene structures.

It is suggested that two selective secondary reactions occur in the two PVDC samples, respectively obtained in bulk and as an inclusion complex. In the former case, the main reaction is only a crosslinking reaction, while in the latter case, being the PVDC included into the thiourea channels, the crosslinking reaction is fully inhibited and instead a dehydrohalogenation reaction takes place producing the polyene structures. The thermal behavior of the two PVDC samples has been studied by TGA, DTG and DTA. The PVDC obtained by inclusion polymerization shows lower thermal stability, lower melting point and a reduced degree of crystallinity in comparison to the PVDC prepared in bulk which instead has all the thermal parameters in line with the literature data.

Acknowledgements

This research work has been partially supported by the Italian Space Agency contract n. I/015/07/0 (Studi di Esplorazione del Sistema Solare).

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