

DIFFERENTIAL THERMAL ANALYSIS OF POLY(VINYLDENE CHLORIDE) CRYSTALS

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(Received September 3, 1981)

The melting behavior of poly(vinylidene chloride) (PVDC) was studied using differential thermal analysis (DTA). Crystals were grown isothermally from 0.1% and 0.02% dilute solutions of the polymer in 1,2-dibromoethane and monobromobenzene. Both 'solid' and 'oil' samples were used for the DTA experiments. 'Solid' samples are defined as dried down crystals and 'oil' samples are crystals which have been suspension exchanged in silicone oil without letting them dry out. Thermal curves of 'solid' samples are similar to those obtained previously with as-polymerized crystals, that is they show two endotherms. The lower temperature peak corresponds to the melting of lamellae as formed. The upper peak at around 200°C, may be due to the melting of crystals which have reorganized during heating. Thermal curves of 'oil' samples show two extra small peaks in addition to those of the 'solid' samples. From the results of annealing and degradation experiments, these two peaks may correspond to a small portion of the crystals which have been partially degraded to form double bonds and thus possess lower melting points. An alternative explanation is that there is an as yet unreported second crystal form of PVDC.

Most melting experiments on PVDC have been performed using DTA although X-ray diffraction and hot stage microscopy have also been employed [1]. Only one melting point at about 200° was obtained by X-ray diffraction and hot stage microscopy. However, a typical DTA curve of dried down PVDC crystals contains two endotherms. The upper peak at about 200° appears independent of crystallization conditions. The size and temperature of the lower peak depends on preparation conditions (crystallization temperature, solvent, etc.). The temperature of the lower peak increases with a decrease in the degree of undercooling, i. e. difference between crystallization temperature and dissolution temperature (ΔT_C). The lower peak is predicted to merge with the upper peak as ΔT_C approaches zero. The lower peak supposedly represents the melting of lamellae grown at the polymerization or crystallization temperature. However, the origin of these two peaks is still not fully understood.

The purpose of this paper is twofold: 1) to investigate the melting process of PVDC single crystals as it is influenced by crystallization temperature, annealing, quenching and heating rates, 2) to try to explain the origin of the multiple endotherms. In this work, 1,2-dibromomethane and bromobenzene were found not to

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degrade the crystals appreciably at crystallization temperatures as high as 95°. The crystals were not discolored after crystallization. Crystallization could not be carried out isothermally below 80° at 0.1% concentration since at this bath temperature crystals appeared before the sample reached equilibrium.

A novel technique has recently been developed by Harrison [2, 3] to obtain a much narrower melting range for DTA curves than had previously been reported. Using polyethylene, a broad peak was resolved to yield three single sharp peaks. This was achieved by exchanging a suspension of polyethylene crystals in xylene to silicone oil and never permitting the crystals to dry down. Each of these peaks was reported to relate to different reorganizational phenomena. This technique was employed in the present study in order to obtain more detailed information on the melting process of PVDC crystals.

Experimental

PVDC single crystals were crystallized from dilute solution at crystallization temperatures of 85, 90, and 95°. The melting points were investigated using DTA and various annealing, quenching and heating rate conditions. The morphologies were examined using transmission electron microscopy.

1. Material preparation

All chemicals are reagent grade. PVDC homopolymer was kindly provided by Dr. R. A. Wessling of the Dow Chemical Company (Midland, Michigan). 100 ml of solvent were heated to about 130° in a 3-neck flask under nitrogen. 0.1 g of polymer was then added and dissolved in the solvent. Crystallization tubes were preheated to the desired crystallization temperature (T_c) in an oil bath. The 0.1% dilute solution was then transferred to the crystallization tubes immediately after the polymer was completely dissolved. This was normally determined as the point at which polymer particles were no longer visible. Previous hot filtration experiments confirmed the reliability of this method, for this system. In most cases, crystals appeared within one hour. The crystals were left in the tubes for about two hours for complete crystallization. The crystals were then washed with fresh solvent at the crystallization temperature before the tubes were allowed to cool to room temperature. Crystals of 0.02% concentration were prepared using a similar technique. All crystals prepared in this manner show no discoloration after crystallization.

2. Microscopy

Transmission electron microscopy was performed using a Philip's EM 300 electron microscope. Samples to be examined in the electron microscope were obtained directly from the crystallization tube after crystallization and washing. A drop of crystal suspension was placed on a carbon-coated copper grid and the solvent was allowed to evaporate. In order to facilitate lamellar thickness measurements, a dilute water suspension of 2540 Å latex particles was placed on the grid surface and

allow to dry. The sample grid was lightly shadowed with chromium in an evaporator and then examined directly under the microscope.

3. *Differential thermal analysis*

Transition temperatures were measured using a DuPont 990 DTA instrument. Crystals obtained from the crystallization tubes were divided into two parts. One part was washed by centrifugation five times with xylene, exchanged to silicone oil and any residual xylene removed under high vacuum. This is the 'oil' sample. The other part was washed five times with acetone and dried under vacuum. This is the 'solid' sample. Both of these samples were placed under a high vacuum of 10^{-5} torr in order to remove residual solvent. The samples were then packed in 2 mm diameter DTA capillary tubes to the desired depth (~ 4 mm for oil sample and ~ 2 mm for solid sample). The temperature scale was calibrated from the melting points of a number of high purity organics. The transition temperatures of the PVDC samples were taken as the peak maxima.

4. *Chemical dehydrochlorination*

Dehydrochlorination of PVDC crystallized at 90° from bromobenzene was carried out at room temperature and at 45° with pyridine [4]. Crystals obtained from the crystallization tubes were centrifuged, the supernatant was discarded and the crystals were stirred in a nonsolvent of isopropyl alcohol to which pyridine was later added. The crystal suspension was placed in a water bath at the appropriate temperature for different periods of time.

5. *Annealing and quenching*

Annealing and quenching experiments were performed using the duPont 990 DTA Samples to be annealed were placed in capillary tubes and isothermally heated to the desired temperature. They were kept at this temperature for appropriate periods of time and then cooled to room temperature. Quenched samples were isothermally heated to the desired temperature and then immediately cooled to room temperature at approximately $90^\circ/\text{min}$. For electron microscopic studies, thermally treated samples were washed 10 times with xylene to remove silicone oil and then examined under the microscope.

Results

The thermal curves obtained in this work consist of two, three or four peaks depending on the method of preparation and subsequent conditioning. Both position and area of these peaks change as a function of the various experimental conditions. Unless specifically mentioned the observations reported are for 'oil' samples of crystals grown from bromobenzene run at $20^\circ/\text{min}$.

Figure 1 shows DTA curves of 'solid' and 'oil' samples. Four peaks were initially obtained from the 'oil' samples as opposed to two for the 'solid' samples. 'Solid' samples apparently melt at higher temperatures than 'oil' samples. This is probably

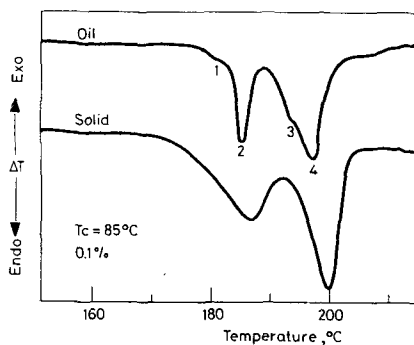


Fig. 1. DTA curves of PVDC crystals grown from bromobenzene at the indicated temperature and concentration

due to poor thermal conductivity of the 'solid' samples [3]. For convenience, the four peaks of the 'oil' sample curve are assigned as first, second, third and fourth in order of increasing temperature as indicated in Fig. 1. The 2nd and the 4th peak of the 'oil' sample apparently corresponds to the lower and upper peak of the 'solid' sample, respectively. One important point concerning the sample packing should be noted. Contamination of the inside wall of the capillary tube by the sample should be avoided as it causes an undesirable drift of the base line. With "solid" samples this can readily be achieved by tamping the tube with a small rod of appropriate diameter. "Oil" samples can be directly introduced into the bottom of the sample tube using a hypodermic syringe.

In these studies we will occasionally be concerned with "peak ratios". This is defined as the ratio of the area of third and fourth peaks to that of the first and second. Baseline construction is always a problem. We have normally joined the point at which the trace first deviates from the initial straight horizontal baseline, to the point at which it is judged to return to a flat baseline. Peak areas are separated by drawing a vertical line from the minimum between peaks two and three to the constructed baseline. Of course, this is subjective. However, we are careful to consider only trends and are concerned only with ratios of peak areas and not absolute values.

A. Effects of crystallization temperature

Table 1 lists the positions of all melting peaks for 'oil' samples of PVDC crystallized at different temperatures. Note that for some preparations, the first peak is too small to be identified or does not exist at all. The reason for this will be discussed later. As shown in Table 1 and Fig. 2, the temperature of the first and second peaks increase with increasing crystallization temperature i. e. $(T_4 - T_2)$ decreases as T_c increases. The positions of peaks T_3 and T_4 vary only slightly as a function of crystallization conditions. The peak area ratio remains approximately the same with different crystallization conditions. In Fig. 3, the positions of the second

Table 1
Effect of crystallization temperature on melting of PVDC single crystals

T_c	Peak position, °C	1st	2nd	3rd	4th
1,2-dibromoethane	85	—	185.0	195.5	197.0
	90	181.0	187.0	194.5	198.0
	95	184.0	189.5	195.0	198.5
Monobromobenzene	85	180.0	185.5	194.0	197.0
	90	182.0	187.3	194.3	197.5
	95	184.5	189.5	195.5	198.0

— peak too small to be identified.

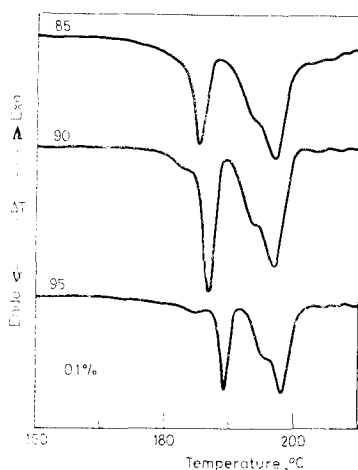


Fig. 2. Effect of crystallization temperature on the melting behavior of PVDC. The number on the left indicate the crystallization temperature in °C

peak for 'oil' samples are compared with those obtained by Wessling et al. with as-polymerized crystals formed from bromobenzene [1]. The second peak of the 'oil' samples apparently corresponds to the lower peak of the solid as-polymerized PVDC crystals reported previously.

B. Effects of crystallization concentration

Figure 4 shows the effects of changing the concentration of PVDC, in the crystallization stage, on the melting behavior of the resulting crystals. The positions of all peaks are unchanged for different concentrations and the area of the first and

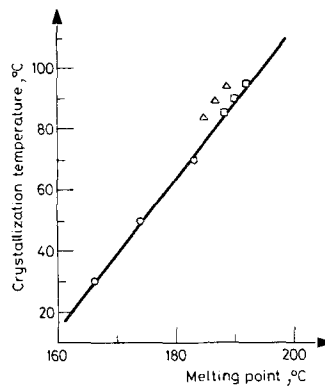


Fig. 3. A comparison of melting temperature versus crystallization temperature for this study and that of Wessling et. al. [1]. Crystals grown from bromobenzene. ○ — data of Wessling [1], solid samples, lower peak. □ — this study, "solid" samples, lower peak. △ — this study, "oil" samples, second peak

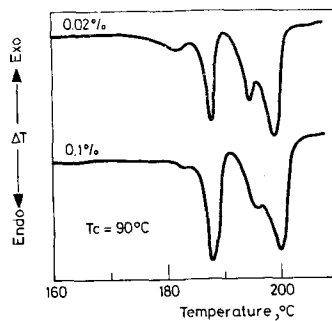


Fig. 4. The effect of crystallization concentration on the melting of PVDC crystals. Crystals were grown from bromobenzene at 90°. The concentration of polymer in the crystallization liquid is given on the figure

third peak apparently increases with decreasing concentration. These effects of concentration on the first peak area seem quite peculiar and no satisfactory explanation could be found. However, some DTA curves of the 0.1% samples also show the same first peak area as those of 0.02% samples. As previously mentioned, the appearance of the first peak is not consistent among different sample preparations. It was thought that the appearance of the first peak may be due to incomplete dissolution during sample preparation. In order to enhance dissolution, PVDC/solvent slurries, were introduced into the boiling solvent instead of the normal dry powder. When this was done the DTA curves of both concentrations showed no first peak, and the third peak became smaller. It is therefore assumed that there is no effect of PVDC concentration at the crystallization stage, on the melting behavior of the resulting crystals. At this point in the study it was presumed that the first peak arose as a result of incomplete dissolution. It will become clear later that this is not the case.

C. Effects of annealing and quenching

The effects of annealing on the melting process are shown in Figs 5 and 6. It should be noted that because of overlap of peaks many of the observations made regarding peak position and size can only be qualitative. For an annealing time of

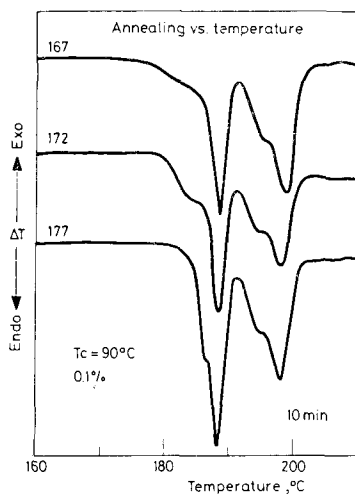


Fig. 5. The effect of annealing temperature on the melting of PVDC crystals. Crystals were initially grown from bromobenzene at 90°C , 0.1%. They were then annealed for 10 mins. at the indicated temperatures, $^{\circ}\text{C}$

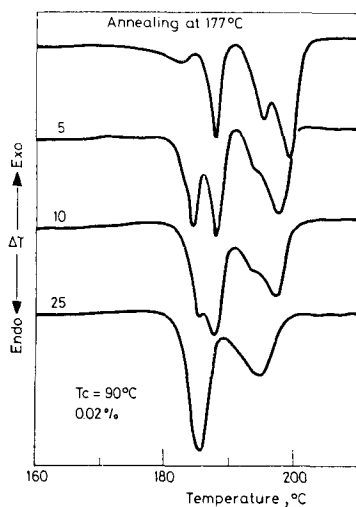


Fig. 6. Effect of annealing time on melting of PVDC crystals. Crystals were initially grown from bromobenzene at 90°C , 0.02%. They were then annealed at 177° for the indicated times in minutes

10 minutes, curves show no obvious changes up to 167°. As annealing temperature increases above 167°, the size and temperature of the first peak increases and shows a tendency to merge with the second peak. The temperature of the second peak is apparently unchanged. The third and fourth peaks, however, move to slightly lower temperatures. In addition, Table 2 shows that the peak area ratio decreases as annealing temperature increases.

Table 2

(a) Effect of annealing temperature on the peak area ratio with annealing time of 10 minutes. (Peak area ratios as defined in the text.)

(b) Effect of annealing time on the peak area ratio with annealing temperature of 177°C

a.		b.			
Temperature, °C	Ratio	0.02%		0.1%	
		time, mins	ratio	time, mins	ratio
167	1.32	5	1.0	10	0.82
172	1.28	10	0.72	20	0.68
177	0.82	25	0.57	30	0.50

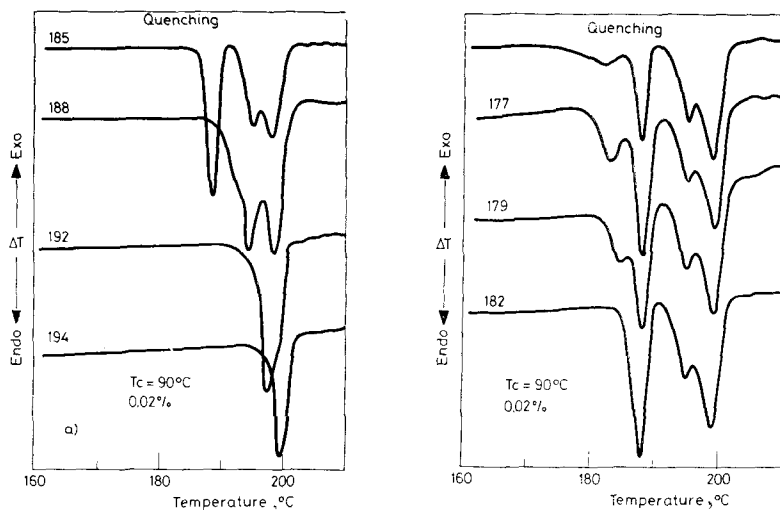
As shown in Fig. 6, increasing annealing time at a constant temperature of 177° shows an effect similar to that of increasing annealing temperature. As annealing time increases, the first peak increases both in size and temperature and finally merges with the second peak. At the same time, the third and fourth peak move to lower temperatures and then merge with each other. The peak area ratio also decreases as indicated in Table 2.

Figures 7 and 7a show the effects of quenching on melting behavior. Quenching does not show any effect up to 172°. At a quenching temperature of 177°, the size and position of the first peak starts to increase and merge with the second peak (~ 182°) while the upper two peaks show no change. A quench temperature of 188° causes this merged second peak to move upward and merge with the third peak while the fourth peak still remains unchanged. Finally, as quenching temperature is further increased, the new third peak merges with the fourth peak and it moves to higher temperatures.

It seems that there is a threshold condition in annealing and quenching below which no effect is shown. It has been noted that some curves show no first peak. However, when annealing or quenching is applied to such samples the first peak appears and behaves in exactly the same way as if it were initially present.

D. Effects of heating rate.

The effects of heating rate on melting are shown in Fig. 8. There is no apparent effect on the positions of the first and second peaks up to 20°/min. Their positions decrease very slightly at 50°/min. This may be due to broadening and overlap of these peaks. The temperatures and peak ratios decrease as heating rate increases.



Figs 7 and 7a. Effect of quenching temperature on the melting of PVDC crystals. Crystals were grown from bromobenzene at 90°C , 0.02%. They were then heated to the indicated temperature ($^{\circ}\text{C}$) at $20^{\circ}\text{C}/\text{min}$. and quenched to room temperature

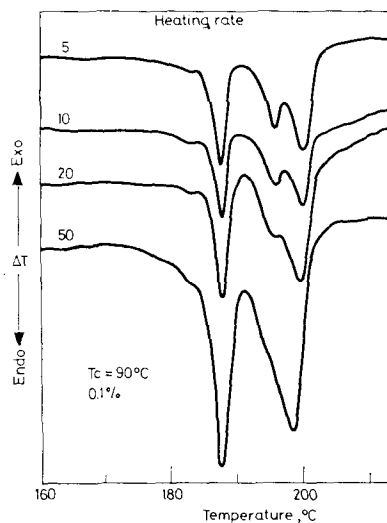


Fig. 8. Effect of heating rate on the melting of PVDC crystals. Crystals were grown from bromobenzene at 90°C , 0.1%. The heating rates are indicated in $^{\circ}\text{C}/\text{min}$

The apparent temperature decrease is almost certainly due to broadening and overlap of these peaks. Table 3 shows the values for the peak area ratios as heating rate increases. These results generally agree with those obtained by Wessling with solid samples [1].

Table 3

Effect of heating rate on peak area ratio as defined in the text

Heating rate °/min	Ratio	Concentration	
		0.02%	0.1%
5		4.0	3.6
10		3.3	3.1
20		3.0	2.2
50		2.8	1.5

Table 4

Effect of chemical dehydrochlorination on the peak area ratio. (Crystals were grown from bromobenzene at 90°.)

Time, h	Peak area ratio
5	3.3
10	3.2
20	2.4
40	2.3
60	2.0
80	1.8

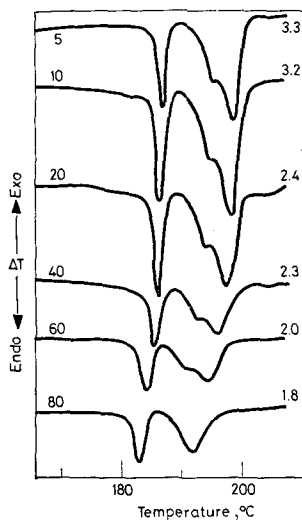


Fig. 9. Effect of time of chemical dehydrochlorination on melting of PVDC crystals. Reaction time in hours is shown on the left. The numbers on the right indicate the peak area ratio

E. Chemically dehydrochlorinated PVDC crystals

DTA curves of crystals dehydrochlorinated at room temperature are the same as those without dehydrochlorination. Curves of PVDC dehydrochlorinated at 45° are shown in Fig. 9. The first peak is not shown in these preparations, but it appears when the sample is annealed. No changes occur in the thermal curves for dehydrochlorination times up to 10 hours. As the time of dehydrochlorination is increased beyond 10 hours, all peak positions are lowered and the third and fourth peaks seem to merge with each other. As shown in Table 4, the peak area ratio decreases as time of dehydrochlorination decreases. These changes are quite similar to those observed for annealed samples.

F. Microscopy

Figure 10 shows electron micrographs of PVDC crystals grown at 90°. The morphology of these crystals is generally lath-shaped with branches extended out at a fixed crystallographic angle. Similar micrographs were obtained from crystals grown at different temperatures. The thickness of the crystals, obtained from the shadow length, is approximately 75 ± 10 Å. Within the error of the experiment no differences in thickness could be measured for crystals with T_c at 85, 90 or 95°. This is presumably due to the poor accuracy of the shadowing technique. The value of 75 Å is however in good agreement with those obtained by Okuda [5] using a small angle X-ray technique on solution grown PVDC crystal mats. However, these values are somewhat lower than those obtained by Wessling et al. with crystals formed from cyclopentanone [6].

Micrographs of annealed samples are shown in Fig. 11. The edges of the crystals are no longer as well defined as in the unannealed samples. This may be due to the fact that the edges of neighboring branches fuse together or interpenetrate in some way.

Micrographs of chemically dehydrochlorinated samples are shown in Fig. 12. The morphology of these crystals does not differ noticeably from crystals prior to dehydrochlorination.

Discussion

The thermal curves obtained in this work are similar to those obtained by Wessling [1] in three respects.

1. As shown in Table 1 and Fig. 2, both the first and second peaks increase in temperature with increasing crystallization temperature. The second peak falls on a straight line extrapolated from Wessling's data. Thus the second peak observed in oil samples corresponds to the lower peak of the curves of as-polymerized solid samples.

2. The positions of the upper peaks (3 and 4) do not vary appreciably as a function of crystallization temperature.

3. The peak area ratio decreases with an increase in heating rate.

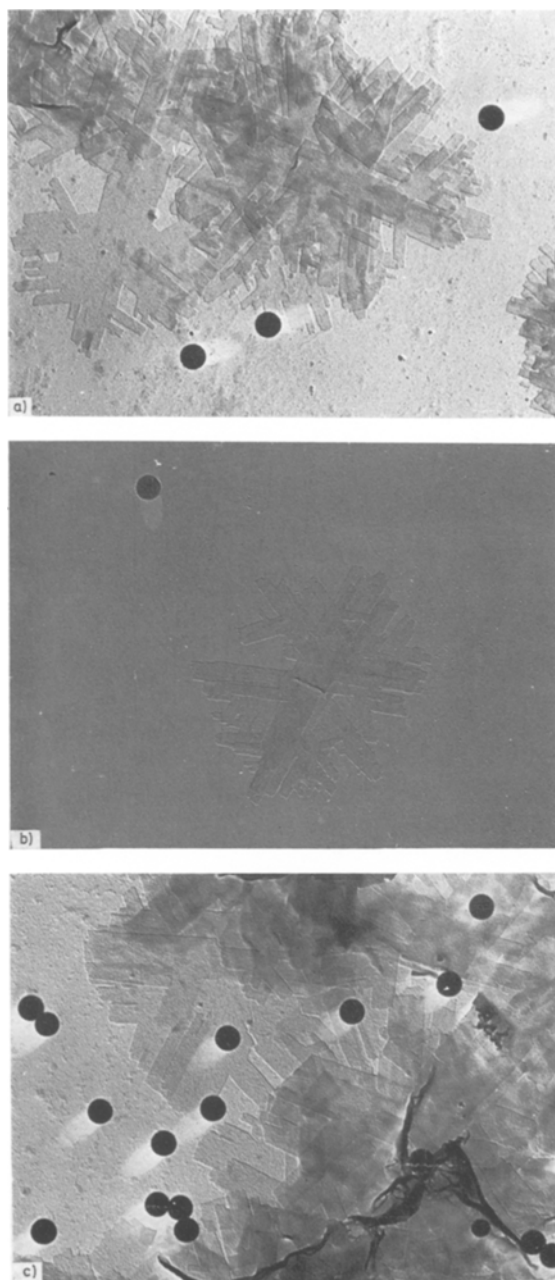


Fig. 10. Micrographs of PVDC crystallized at 90° , chromium shadowed. Latex particles are 2540 \AA . (a) 0.1% in bromobenzene, (b) 0.02% in bromobenzene, (c) 0.1% in 1,2-dibromoethane

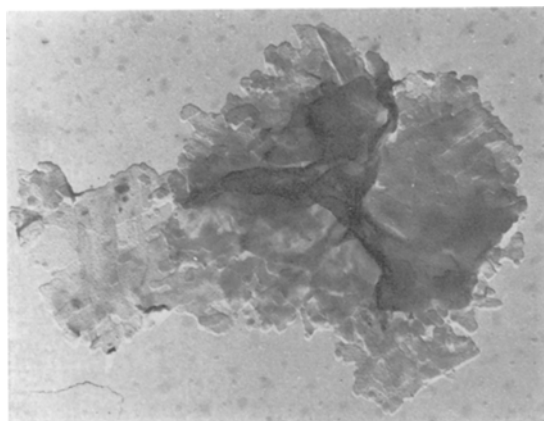


Fig. 11. Micrograph of PVDC crystallized from 0.02% bromobenzene at 90°C, chromium shadowed, magnification approximately 10,000 \times . Annealed at 177° for 5 minutes

Wessling [1] suggested that the lower peak of the as-polymerized crystals, represented melting of lamellae grown by crystallization from solution during polymerization. The upper peak represented the melting of PVDC polymerized in the solid phase. He also predicted that a DTA curve would show only one endotherm for solution crystallized PVDC. However, from the results of this study, curves of solution grown PVDC crystals consist of three or four peaks.

Multiple peaked endotherms have been explained in terms of partial melting followed by partial recrystallization [2, 7–9] and in many cases the heating rate dependence of these peaks is interpreted as evidence of reorganization [8, 10]. The faster the heating rate, the less the material undergoes reorganization. As shown in Table 3, the peak area ratio decreases as heating rate increases.

On this basis one can separate out two groups of peaks. The first and second peaks remain unchanged in position with increasing heating rate. The third and fourth peaks show a decrease in position and intensity relative to the first two peaks on increasing the heating rate. It appears that peaks 3 and 4 are due to the melting of crystals which have already undergone some reorganization.

Turning to the first two peaks, what are their origins? An initial suggestion must surely be that they represent the melting of lamella grown at the crystallization temperature. However, there are two peaks, does this imply two lamella thicknesses?

One explanation for the first small peak could be that it is due to a low molecular weight contaminant. That is, low molecular weight polymer may be left in solution after higher molecular weight material crystallizes. On cooling the low molecular weight material crystallizes out at lower temperatures. This possibility can be ignored as there are no differences in the DTA curves of crystals washed with solvent after crystallization and those which were not washed. Incomplete crystallization may also be ruled out, the DTA curves are the same for samples crystallized for 2 hours or for 24 hours.

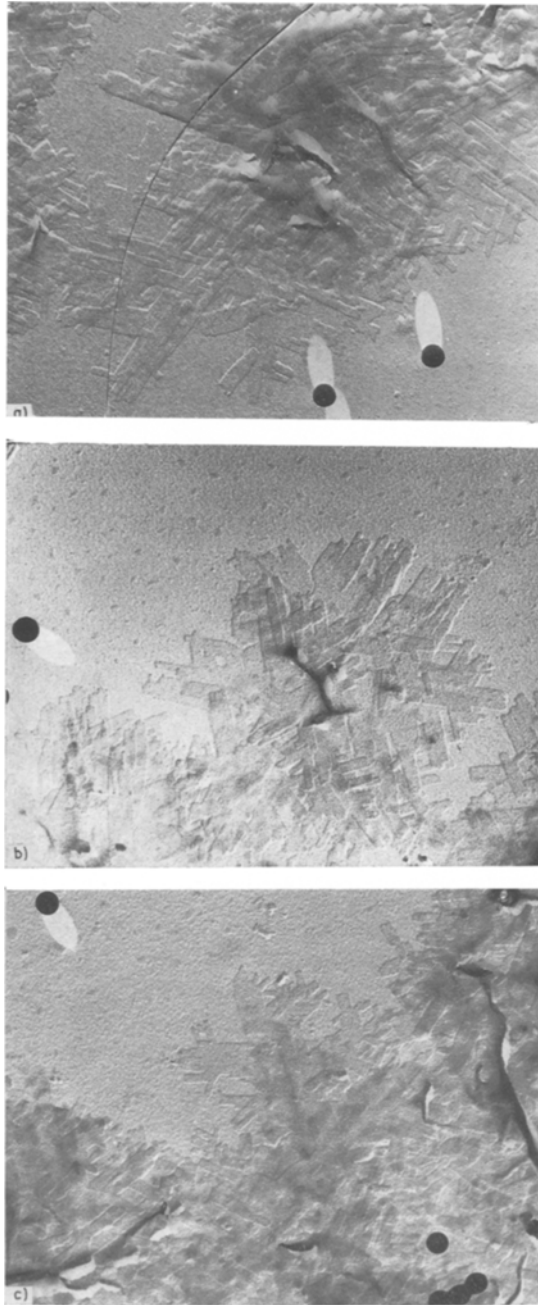


Fig. 12. Micrographs of PVDC crystals after dehydrochlorination. Latex particles are 2540 Å.
(a) Dehydrochlorinated for 10 hrs. (b) Dehydrochlorinated for 20 hrs. (c) Dehydrochlorinated for 80 hrs

From the results shown in Fig. 4, it was thought that the size of the first peak was a function of the concentration of polymer in the crystallization solution. If the sample is prepared in such a way that complete dissolution is obtained, this concentration dependence no longer exists. The first peak appeared to be related to incomplete dissolution. However, when the sample is annealed the first peak again appears and behaves in the same way as those shown in figs 5, 6, 7, and 7a.

It is thought that annealing of polyethylene single crystals in a narrow temperature range below the melting point causes reorganization of part of the crystal [11]. In the early stages of annealing, lamellar thickening occurs only at the edges of the crystals [12–14]. If this is the case in PVDC, one would expect a small peak to occur at a higher temperature than the second peak. The small amount of material on the edges of an annealed crystal will have a higher lamellar thickness and therefore a higher melting point. This assumes that the second peak which is normally the larger of the two represents the melting of the original as crystallized lamella which has not undergone reorganization or degradation. However, degradation can also occur during annealing. The lamellar surface and presumably the edges of PVDC crystals were found to be more susceptible to chemical degradation than the rest of the crystal [4]. An increase in fold period may therefore lead to the incorporation of defects (dehydrochlorinated units) into the crystals. This in turn would lead to a decrease in melting point. One could then argue that if the effect due to degradation exceeded that due to a fold period increase a peak should be observed on the low temperature side of the "main peak". This, in fact, is observed.

With regard to the second peak one observation at least is in line with accepted crystallization theory. Namely, the peak temperature increases as crystallization temperature increases. However, the annealing behavior is somewhat unusual. In the case of PE, annealing at increasing temperatures or at one temperature for increasing times shows an increase in melting point. With PVDC annealing under similar relative conditions shows either no change or a decrease of the second peak as time increases; Figs 5 and 6.

Degradation of PVDC begins at about 130° and annealing of PVDC is believed to take place in the range 130°–160° [15]. Degradation results in a lowering of the melting point since it introduces double bonds which may increase surface energy or act as defects within the crystal [4]. With annealing temperatures between 130°–167°, the effect of annealing leading to lamellar thickening may not be observable, alternatively it may be offset by degradation. Hence no change of melting temperature is observed. As annealing time or temperature increases, the effect of degradation may prevail over that of lamella thickening and cause a lowering of the melting point.

Assuming that cross-linking, which results from degradation, is not serious at this time [16–18], reorganization of polymer chains is possible and the upper peaks still exist. However, peaks 3 and 4 become smaller as annealing time increases. This implies that partial crosslinking may occur which prevents parts of the crystals from undergoing reorganization. Alternatively, one can argue that a copol-

mer system is produced by the degradation. The defective chains do not crystallize as rapidly as homopolymers and the upper peaks decrease in size.

The third peak seems to be related to the first peak in such a way that changes of the first peak are accompanied by a change of the third peak. The third peak may therefore represent the melting of crystals of the first peak which have undergone reorganization. Annealing can be carried out for short time periods at higher temperatures. Under these conditions the effects of degradation are minimized and one observes an increase in melting point; Figs 7 and 7a.

The hypothesis that degradation occurs during annealing and causes a lowering of the melting point can be supported by the results of chemical dehydrochlorination. The melting peaks of the annealed samples move to lower temperatures in the same way as those of chemically dehydrochlorinated samples and the peak area ratio also decreases with increase of dehydrochlorination time.

With particular reference to Fig. 6 an alternative explanation suggests itself for the annealing behavior. If two different forms of PVDC existed then the first and second peaks could represent their melting points. Further, peaks 3 and 4 might represent the melting of these forms after reorganization. This idea is entirely consistent with the thermal behavior seen in Fig. 6. Here we envision that annealing causes an additional reorganization from one form to another. In the unannealed sample we see that the second and fourth peaks are the main peaks. After annealing the main peaks are at positions initially occupied by the first and third peaks. Unfortunately, there is no evidence in the literature for two different forms. However, since there are several proposed structures for PVDC one might argue that the existence of two different forms is not unlikely.

We are sure that the informed reader will be able to propose a number of additional experiments which could potentially distinguish between the alternative explanations given here. We have, in fact, spent a considerable amount of time and effort on FTIR and X-ray methods. Unhappily the data obtained from these methods are themselves ambiguous. This stems in part from the relative positions and intensities of bands associated with unsaturation to those of other bands in the system. Further, X-ray diffraction from polymers is generally quite poorly resolved and is particularly difficult with PVDC which has an extremely high electron density for a polymer, and judging by previous work, a very low symmetry. Redissolving the polymers also presents problems since this is a quite thermally sensitive material. At this time, we are therefore forced to let the thermal data stand by itself.

Conclusions

1. PVDC single crystals can be prepared from a dilute solution of monobromobenzene or 1,2-dibromoethane with T_c up to 95° without serious degradation.
2. Oil suspensions of PVDC crystals have narrower endotherms than those of dry solid crystals and the peak maxima of oil samples are at slightly lower temperatures than those of solid samples. Four endotherms are seen on most oil samples.

3. The change of peak area ratio as a function of heating rate supports the suggestion of reorganization occurring during melting.
4. The first two peaks are sensitive to crystallization temperature.
5. The first peak is greatly enhanced by annealing and quenching. It is suggested that the first peak may correspond to a small portion of the crystal which is located at the edges of the crystal.
6. An alternative explanation for annealing behavior can be proposed if two different forms of PVDC can be shown to exist.

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The authors wish to thank the NSF Materials Division for support of this work under grants DMR 72-03292 A01 and A02.

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ZUSAMMENFASSUNG — Das Schmelzverhalten von Poly(vinylidenchlorid (PVDC) wurde unter Einsatz der Differentialthermoanalyse (DTA) untersucht. Die Kristalle wurden unter isothermen Bedingungen aus 0.1% und 0.02% verdünnten Lösungen des Polymeren in 1,2-Dibromäthan und Monobrombenzol gezüchtet. Sowohl »feste« als auch »ölige« Proben wurden für die DTA-Versuche eingesetzt. Als »feste« Proben wurden getrocknete Kristalle definiert und »ölige« als solche, bei welchen die Suspension im Siliconöl verblieb, ohne sie austrocknen zu lassen. Die thermische Kurven der »festen« Proben sind den bereits früher mit polymerisierten Kristallen erhaltenen ähnlich, d. h. sie zeigen zwei Endotherme. Der Peak bei der niedrigeren Temperatur entspricht den Schmelzen der gebildeten Lamellen. Der obere Peak bei etwa 200° kann dem Schmelzen von während der Aufheizung reorganisierten Kristallen zugeschrieben werden. Die thermische Kurven der »öiligen« Proben zeigen zwei zusätzliche kleine Peaks außer denen an »festen« Proben. Aus den Ergebnissen der Temper- und Zersetzungsversuche dürften

diese beiden Peaks einen kleinen Anteil der teilweise unter Bildung von Doppelbindungen zersetzten Kristalle entsprechen, welche auf diese Weise niedrigere Schmelzpunkte haben. Eine alternative Erklärung ist, daß es eine bisher nicht beschriebene zweite Kristallform von PVDC gibt.

Резюме — С помощью дифференциального термического анализа (ДТА) изучен характер плавления поливинилиденхлорида. Кристаллы полимера были выращены изотермически из разбавленных растворов полимера (концентрация 0.1% и 0.02%) в 1.2-дибромэтаноле и монобромбензоле. Для ДТА измерений были использованы «твердые» и «масляные» образцы полимера. «Твердые» образцы представляли собой высушенные кристаллы, а масляные — кристаллы, выделенные суспензионным обменом из силиконового масла, без последующего их высушивания. ДТА-кривые «твердых» образцов подобны ранее полученным для полимерных кристаллов и показали наличие двух эндотерм. Более низкий температурный пик соответствует плавлению образующихся слоев. Пик около 200° С может быть обусловлен плавлением кристаллов, переориентированных в процессе нагрева. На кривых «масляных» образцов, кроме этих двух пиков, проявлялись два чрезвычайно малых пика. Из экспериментальных результатов по отжигу и распаду этих образцов, очевидным является то, что эти два пика могут соответствовать небольшой части кристаллов, частично подвергшихся распаду с образованием двойных связей. Вследствии этого они имеют более низкие точки плавления. Другим объяснением этого факта может быть наличие второй кристаллической формы этого полимера, которая все еще не установлена.