Effect of plasticizer concentration and annealing on the structure of PVC

H. R. Brown*, G. M. Musindi and Z. H. Stachurski**
Department of Materials Engineering, Monash University, Clayton, Victoria, 3168, *Australia*
(*Received* 13 *October* 1981)

Samples of poly(vinylchloride) with various amounts of di-2-ethylhexyl phthalate plasticizer have been prepared by casting from solution. The enthalpy of fusion of these samples has been measured using differential scanning calorimetry. The results presented show the dependence of the enthalpy of fusion on plasticizer concentration, annealing time and annealing temperature to which the samples were subjected. The results indicated that the addition of plasticizer has surprisingly little effect on the crystallinity of commercial PVC. Small angle X-ray scattering measurements have also been carried out on samples of PVC plasticized with two different plasticizers. There was considerable similarity found between the two samples. Therefore SAXS results cannot be taken on the whole as a measure of crystallinity in this material.

Keywords Poly(vinyl chloride); plasticizer; structure; differential scanning calorimetry; small angle X-ray scattering; annealing; spinoidal decomposition; morphology

INTRODUCTION

Plasticized PVC derives its useful mechanical properties partly from the fact that it is a gel rather than a true solution. It was suggested many years ago that the crosslink points within the gel are crystallites[1,2] and the existence of a small degree of crystallinity has been demonstrated by a number of techniques in concentrated PVC gels[3,4]. In dilute gels the existence of crystallites has been inferred from the mechanical behaviour of the gels, also from small angle X-ray scattering (SAXS)[2,5], and from wide angle X-ray scattering (WAXS) on dried gels[6,7].

There is no direct evidence on the morphology of the crystallites which contribute to the mechanical properties of PVC gels, though it has been assumed that they must be of a fringed micelle type[2,5,6]. Recently it has been shown that a portion of the crystallites is unlikely to contribute to the gel mechanical properties[6]. Work on the morphology of the plasticized PVC would therefore be of value in an endeavour to explain the mechanical properties of the material.

The majority of work on PVC morphology has been done on unplasticized material. By the use of WAXS it has been shown that the unit cell is approximately the same for all PVCs independent of their tacticity, and is of an extended syndiotactic structure[8-10]. The crystallinity is found to increase fairly rapidly with syndiotacticity (which increases with decreasing polymerization temperature) and figures of around 5–10% are normally quoted for commercial material which is polymerized at ~50°C[11-13]. This type of material is normally found to have syndiotacticity of 0.55 to 0.60[6,14-16]. If the polymerization is assumed to be random, minimum sequence lengths ($\omega_{\min}$) of 5–7 monomer units have been estimated from the crystallinity and syndiotacticity[15,9,11]. X-ray broadening estimates of crystal size are not compatible with this figure[6,13], requiring values of $\omega_{\min} \simeq 12$. Three suggestions have been made to explain this discrepancy: (a) that the polymerization is not random[6], (b) that a number of isotactic units are incorporated in the crystals[14], and (c) that a portion of the apparently crystalline material is, in fact, in a mesomorphic condition with only two dimensional order and presumably incorporates isotactic sequences[14]. In addition Hay *et al.*[17] used a different equation from the usual one in relating syndiotacticity to sequence length distributed and thereby removed the problem.

SAXS has been used to examine both rigid and plasticized PVC[13,18-22]. Results from unplasticized material have been shown to be consistent with a two phase structure, i.e. crystallites in an amorphous matrix with a wide size range of randomly organized crystallites. On annealing the crystallites become sufficiently organized to give a broad Bragg peak corresponding to a period of around 10–15 nm[13,19,20]. When the material was quenched from high temperature it was found to be amorphous by WAXS technique and with no structure by SAXS measurements[13,20].

The addition of a plasticizer has been shown by WAXS to have no noticeable effect on the crystal structure of PVC. However it causes small increases in crystallinity for concentrations of up to 20 pph of DOP in PVC. For concentrations above this value the crystallinity drops, but only down to 50% of its original value at 60 pph of DOP[3]. Infra-red absorption studies also showed that the plasticizer did not penetrate the crystalline regions of PVC and that concentrations up to 50% DOP did not greatly affect the crystallinity of the material[4].

The annealing and melting of PVC crystallites have been studied by a number of workers using thermal analysis techniques[15,17,23-25]. It has been found that commercial material as-received tends to show a broad melting range from 100°–220°C[23], the latter figure being controlled by the limits of thermal stability of the material. Quenching from a high temperature into iced water or liquid nitrogen results in reduced or zero crystallinity, and

---

* Present address: Dept. of Macromolecular Science, Case Western Reserve University, Cleveland, Ohio 44106, USA

** Present address: Ministry of Transport and Communication, P.O. Box 11873, Nairobi, Kenya

0032-3861/82/101508-07$03.00

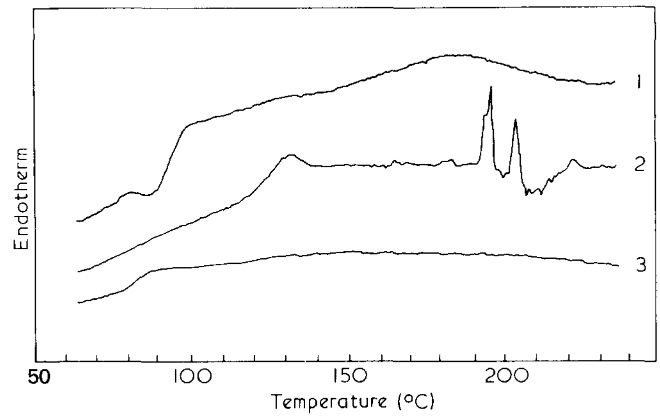

Figure 1 Thermograms of PVC scanned at 10°C min^{-1} using sensitivity of 1 mcal s^{-1}. (1) Compacted PVC powder; (2) UPVC cast film heated for 1 h at 110°C and cooled freely in air at room temperature; (3) sample (2) further heated at 220°C for 20 s and quenched in ice-water

annealing at temperatures above T_g produces a distinct endotherm at temperatures not very far above the annealing temperature[15,24,25]. The size of this endotherm is dependent on annealing time and temperature but in general is greatest for annealing temperatures in the range 120°–130°C. The difference in detailed results between the various workers can probably be explained by the different crystallization rates of the particular materials used, and also different sample sizes.

It is hard to relate the measured enthalpies to crystallinities, as estimates of the enthalpy of fusion of PVC crystals vary between 650 and 2700 cal/mole[26–29]. It is not clear whether the material which melts over the relatively small temperature range after annealing is the vast majority of the crystallites in the material[25], or just secondary crystallites and mesomorphous material[15].

SAXS work on plasticized PVC shows a peak whose position has been studied as a function of plasticizer concentration, plasticizer type and processing conditions[18,21,22]. Long periods vary between 10 nm for low plasticizer concentrations to ~30 nm for gels containing only 10% polymer[5]. It has been suggested that a model of crystallites existing in an amorphous plasticized matrix will explain these results. However it is hard to imagine the cause for the regularity of the crystalline position necessary to give an interference peak when the crystallites are perhaps only 1% volume fraction of the total. The intensity of scattering is also slightly larger in the dilute gels than might be expected with this rather simple model[5].

It is clear from the above discussion that a study of the effect of plasticizer level on the annealing and melting properties of plasticized PVC is therefore of value in relating the work done on rigid materials to the structure of the plasticized materials in which the crystallinity probably has a much greater effect on the mechanical properties.

EXPERIMENTAL

The polymer used in this study was a commercial PVC Geon 103 EP/M supplied by Goodrich Chemical Company (Australia). This is a suspension polymerized material manufactured in the temperature range 50°–60°C with $M_w = 60\,000$. A commercial di-2-ethylhexyl phthalate (DOP) was used as plasticizer (except in one of the SAXS samples where a permanent plasticizer Diolpate 195 was used). The samples were stabilized by an octyl thiotin compound used at 2 parts per hundred of PVC (pph) concentration. All samples were cast from tetrahydrofuran (THF) solutions by drying the solutions at 45°C for between 5 and 13 days. They were then heated to 110°C for one hour in an attempt to remove any remaining traces of the solvent. This treatment has been effective in thin samples used for infra-red work[4], but may not have been equally effective for the thicker samples used here (see Results). After drying, in order to remove the crystallinity caused by the drying process, the samples were heated for a short time in a silicone oil bath to 220°C, then quenched in iced water. The heating time was calculated to be sufficient to raise the temperature in the centre of the specimen to 200°C, and was typically around 30 s.

After quenching the samples were annealed in a hot air oven and finally quenched in liquid nitrogen or iced water. The liquid nitrogen quenched materials were sealed in d.s.c. sample pans before annealing and quenching, as contact with the liquid nitrogen seemed to turn the samples into a brown colour. They were tested immediately after quenching. The water quenched materials however were sealed in d.s.c. pans after quenching and often stored for a few days at −20°C before testing.

SAXS was measured and examined using a standard Kratky camera and proportional counter with Cu Kα radiation. Flat plate WAXS patterns were taken from a few samples using either Cu Kα or Mo Kα radiation depending on the sample thickness.

Thermal measurements were made on a Perkin-Elmer DSC-2 equipped with Scanning Auto Zero attachment. Sample sizes of around 10 mg, and testing rates of 20°C min^{-1} were normally used. Problems were experienced with corrosion in the sample cell due to the evolution of HCl gas.

RESULTS

Figure 1 shows d.s.c. thermograms of the original PVC powder together with an unplasticized sample before and after heating in the silicone oil and quenching. The original powder shows a clear T_g and a broad melting transition. The 'dried' sample shows no T_g within the measured temperature range (due to the plasticization effects of residual THF), a melting transition a little above the final drying temperature, and sharp peaks due to foaming of the material by boiling THF at the high temperatures. In the 'quenched' material there is essentially no residual THF and little obvious crystallinity. The thermogram for this sample is not entirely straight for temperatures above T_g so there could be a very small degree of residual crystallinity within the material.

A figure of WAXS patterns is not shown here but the following observations are made. The absence of the double ring around $2\theta = 18°–20°$ (Cu Kα), and its reappearance on annealing demonstrates that for the plasticized material most of the crystallinity is removed in the heating/quenching process. It can be mentioned here that this was not the case for highly plasticized materials which did show some crystallinity by WAXS after quenching, although their d.s.c. thermograms were

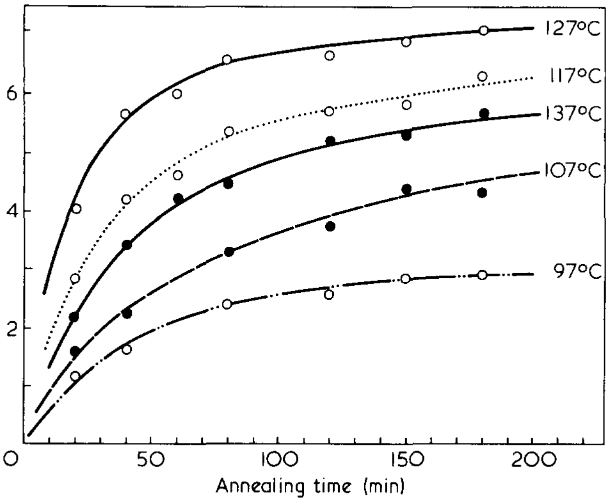

Figure 2 Dependence of enthalpy of fusion in unplasticized PVC on annealing time and temperature. The samples were annealed and then quenched in ice-water

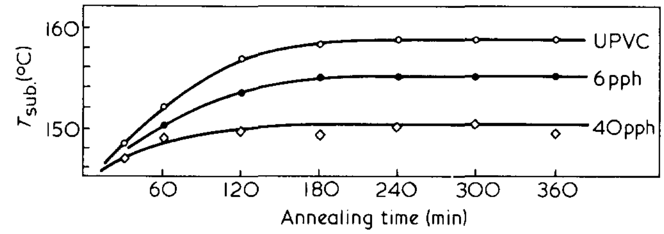

Figure 3 Dependence of melting peak temperature of PVC on annealing time and plasticizer concentration. T_a = 127°C

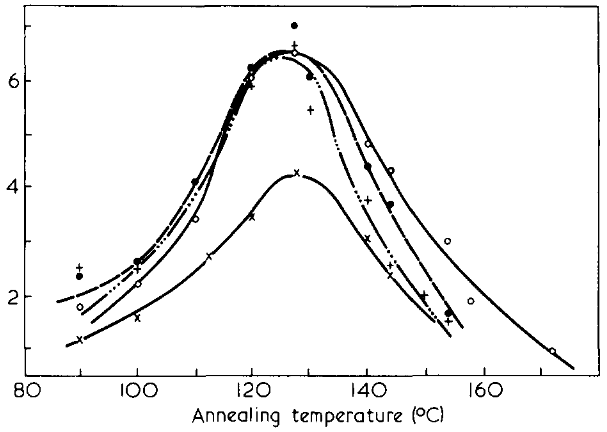

Figure 4 Dependence of enthalpy of PVC on annealing temperature and plasticizer concentration for annealed and ice-water quenched samples. (○) UPVC, (●) 6 pph DOP, (+) 20 pph DOP, and (X) 40 pph DOP. Annealing time = 2 h

equally smooth. Presumably these crystallites melted at temperatures below the start of the d.s.c. runs.

On annealing the specimens, all thermograms developed endothermic peaks at temperatures above the annealing temperatures. These were very similar to the peaks reported by Illers[24], Ohata *et al.*[25] and Grey and Gilbert[15]. The enthalpy of melting, ΔH, and the temperature of the peak, T_{sub}, were measured as a function of annealing time, annealing temperature and plasticizer content. The results for samples quenched in iced water after annealing were a little different from those for the liquid nitrogen quenched samples and so are given separately.

Figure 2 shows the enthalpy of fusion as a function of annealing time for unplasticized water quenched material at a series of annealing temperatures. The enthalpies were all calculated per gram of PVC. Very similar results were obtained for plasticized materials of 6, 20 and 40 pph DOP, the only difference being that the absolute values of enthalpy changed a little with DOP content.

Figure 3 shows the effect of annealing time at one temperature on the melting peak, T_{sub}, for three types of samples. One can see from *Figures 2* and *3* that both enthalpy and T_{sub} reach constant values at approximately the same annealing time and that T_{sub} varies a little with plasticizer content. The effect of a wide range of annealing temperatures was studied for the same materials at a constant annealing time of 2 h, and the results are shown in *Figure 4*.

To study the effect of plasticizer content on melting enthalpy the range of materials was widened, the annealing time was kept constant at 2 h, but only three annealing temperatures were used. These results are shown in *Figure 5*. Similar measurements were made on the nitrogen quenched samples. *Figure 6* shows the variation of fusion enthalpy with annealing time at one annealing temperature (137°C) for three plasticizer levels. Similar results were found at other annealing temperatures. As before these results show a saturation at long times.

A constant annealing time of three hours was chosen for a further study of the effect of annealing temperature on melting enthalpy for the three materials. The results are

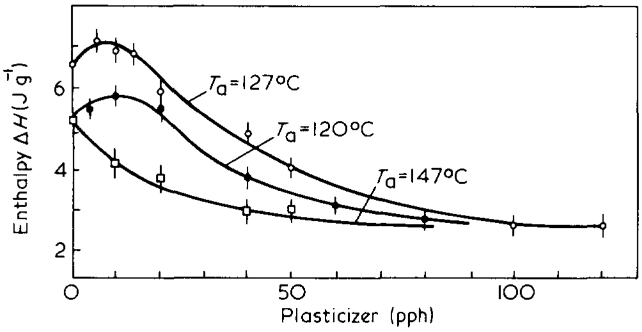

Figure 5 The effect of plasticizer concentration on enthalpy of PVC annealed and quenched in ice-water. Annealing time = 2 h

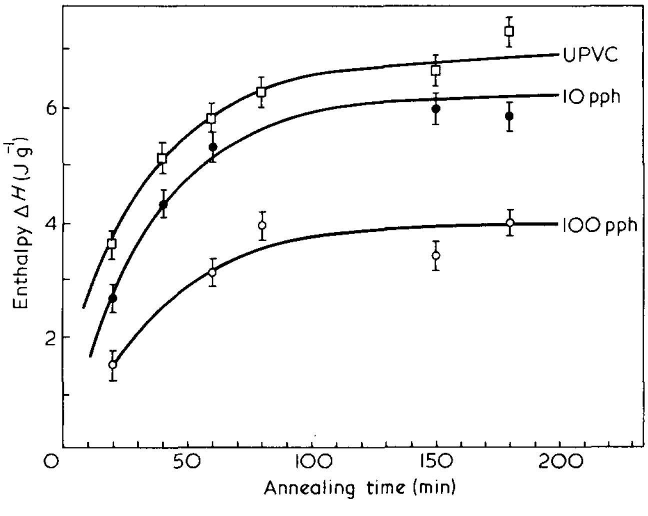

Figure 6 Dependence of enthalpy of PVC on annealing time and plasticizer concentration. The samples were quenched in liquid nitrogen. T_a = 137°C

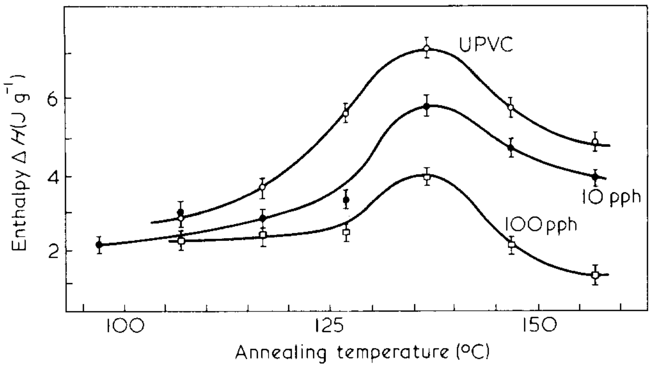

Figure 7 Dependence of enthalpy of PVC on annealing temperature and plasticizer concentration for annealed and liquid nitrogen quenched samples. Annealing time = 3 h

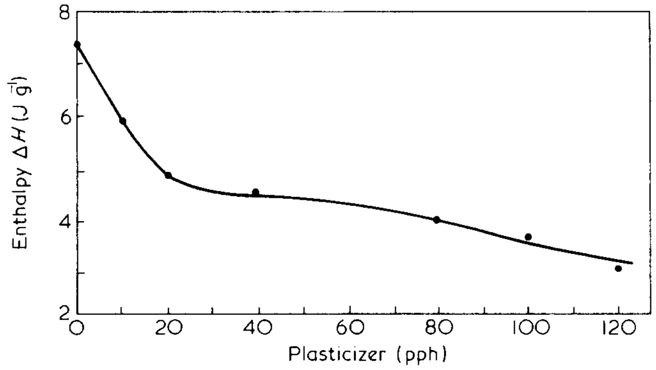

Figure 8 The effect of plasticizer concentration on enthalpy of PVC annealed and quenched in liquid nitrogen. Annealing time = 3 h; T_a = 137°C

shown in *Figure 7*. A temperature of 137°C, the temperature of the maximum in *Figure 7*, was chosen for studying the effect of plasticizer level on melting enthalpy, the results being shown in *Figure 8*. The temperature of the melting peak, T_{sub}, decreased a little with increasing plasticizer content for the nitrogen quenched materials. The variation of T_{sub} with annealing temperature for a number of materials is shown in *Figure 9*.

SAXS patterns were measured on two materials, one containing 60 pph DOP and the other 60 pph Diolpate 195. The specimens were dried at 70°C for 24 h but never heated in the silicone oil bath nor quenched. They were measured before and after annealing at 130°C for 3 h. The results of the slit smeared scattering are given in *Figures 10* and *11*. The relatively low accuracy of these curves did not justify desmearing, particularly as the main interest was in relative changes on annealing. The invariants $Q = \Sigma I(s)s$, where s is the scattering vector, were also measured for these patterns in arbitrary units and are shown in *Table 1*.

DISCUSSION

The removal of crystallinity in some types of rigid PVC on quenching from temperatures above 200°C has also been observed before[24,25,30], and much higher temperatures have also been used[13]. Some authors have found that in their materials the quenching reduces rather than removes the crystallinity[4,15].

On heating quenched materials some workers have observed 'cold crystallization' exothermic peaks at temperatures a little above T_g[15,24]. These were not

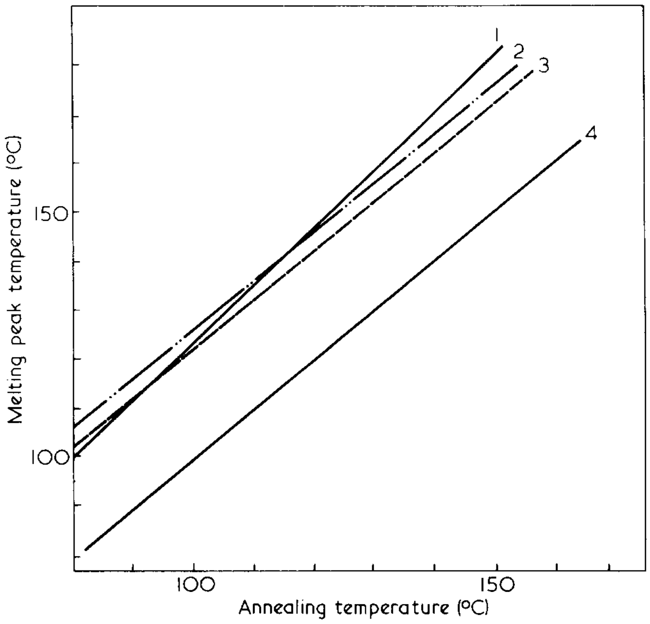

Figure 9 Dependence of melting peak temperature of PVC samples on annealing temperature (annealing for 2 h). (1) UPVC (WQ samples); (2) 20 pph DOP (WQ samples); (3) all compositions of NQ samples, and (4) $T_a = T_{sub}$

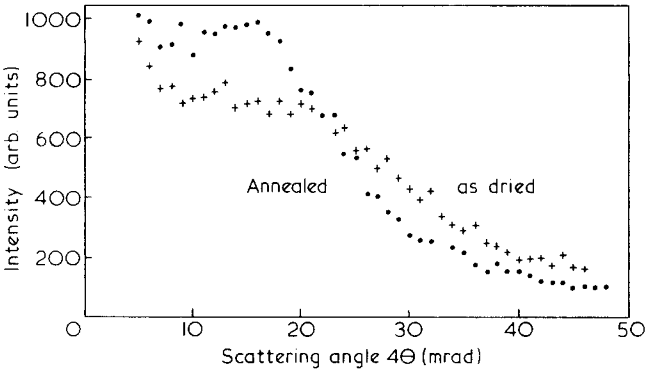

Figure 10 Small angle X-ray scattering of a sample of PVC with 60 pph of Diolpate before and after annealing

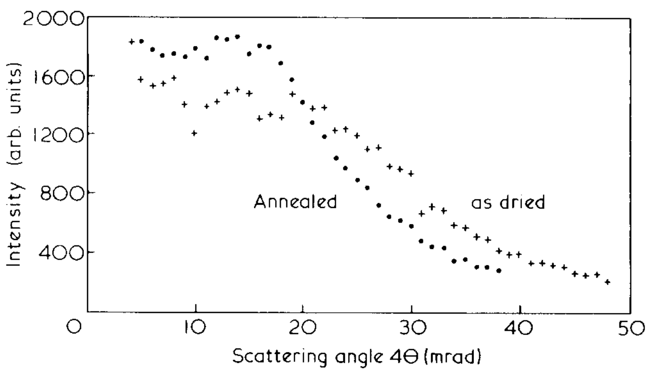

Figure 11 Small angle X-ray scattering of a sample of PVC with 60 pph of DOP before and after annealing

Table 1 SAXS invariants

	60 pph DOP	60 pph Diolpate
Before annealing	420 000	215 000
After annealing	401 000	201 000

observed in this work although the authors have seen them in other grades of PVC. It seems likely that melting points and crystallization rates are material dependent as they are functions of syndiotacticity and molecular weight, so this disparity between results is not surprising.

The size of the melting endotherms measured here at temperatures a little above the annealing temperatures was similar to, or slightly larger than, those measured by other workers[14,15,24,25]. For example the maximum endotherm measured was 6.6 J g^{-1}, which can be compared with 2.5 J g^{-1} measured by Ohata *et al.*[25], and 3.8 J g^{-1} from Grey and Gilbert[15]. The results from 100°C annealing agree very well with Juijn *et al.*[23].

The existence of a temperature at which the melting enthalpy is a maximum has been observed before[15], and is in agreement with Witenhafer's results for the effect of annealing on crystallinity as measured by i.r. spectroscopy. The reason for this maximum is not clear, particularly when one notes that its position is independent of plasticizer concentration. If T_m is the temperature at which the last crystallites melt, then an increase of crystallinity on decreasing the annealing temperature from T_m is to be expected from Flory's theory of the crystallization of copolymers[31]. T_m, however, is expected to depend on the plasticizer content, as it is normally given by the expression[26]:

$$1/T_m - 1/T_m^\circ = RV_u(v_1 - \chi V_1^2)/\Delta H_u V_1 \qquad (1)$$

where T_m° is the value of T_m with no plasticizer, ΔH_u is the enthalpy of melting per repeat unit, V_1 and V_u the molar volumes of the plasticizer and one repeat unit of the polymer, v_1 is the volume fraction of the plasticizer and χ is the Flory–Huggins interaction parameter of the system. This equation has been found to fit the melting of dilute solutions of PVC in several plasticizers[26,32] and is one way of measuring ΔH_u. For PVC–DOP system χ is believed to be close to zero[26,32], so the decrease in melting point should vary approximately as the volume fraction of the plasticizer. Taking $v_1 = 0.5$ (71 pph DOP) the estimated decrease in T_m is in the range 30°–33°C. However there is some evidence that χ is a function of v_1 for this system[33], but it was found to decrease at $v_1 > 0.5$, thereby increasing the expected melting point depression. One would therefore expect that in the higher annealing temperature region, where the enthalpy is decreasing with increasing temperature, the curves would shift to lower temperatures with increasing plasticizer concentrations. This was not observed.

It has been suggested by Witenhafer[30] that the decrease of crystallinity at lower annealing temperatures is a kinetic effect, and for the system he studied there was a decreasing crystallization rate as the temperature was lowered. Both Ohata *et al.*[25] and Grey and Gilbert[15] considered that the maximum in enthalpy at annealing temperatures of 120°–140°C was a reflection of the normal observation that crystallite or spherulitic growth rates go through a maximum at temperatures between T_g and T_m. Ohata had evidence from an Avrami analysis that the growth rate did go through a maximum for his system but there is no evidence that this was the case for Grey and Gilbert's work or for the results reported here. However it is no explanation why the 'equilibrium' crystallinity should go through a maximum with decreasing annealing temperature. In addition, if rate effects are important, then one would expect that the addition of plasticizer, which increases the segmental mobility, will increase the rate of crystallization in the low temperature region where mobility effects are expected to be important. This is, as we know, the main cause of solvent induced crystallization[34].

A possible explanation for the decrease in apparent crystallinity at lower temperatures observed here is that at low temperatures the longer syndiotactic units, instead of forming relatively good crystallites with other longer units, form very poor crystallites with the shorter units. These very poor crystallites are so little ordered (may be mainly in two dimensions) that they have a low enthalpy of fusion. The fact that the melting point varies only with the annealing temperature is consistent with this point of view.

The effect of plasticizer level on melting enthalpy (shown in *Figures 5* and *8*) is also a surprising result. The main observation is that significant plasticizer levels decrease the enthalpy, although at certain annealing temperatures a small increase may be seen at low plasticizer levels. The observation of a small increase and then a decrease is entirely in agreement with the infra-red crystallinity measurements of Lebedev *et al.*[3]. It can be seen that the increase is just a feature of small shape changes in the curves of *Figure 5*. It is not very significant and will not be considered here. The decrease in crystallinity in the high temperature region could follow directly from the Flory theories of copolymer crystallization and melting point depression by diluent as discussed above. Perhaps the poorly ordered and possibly nematic crystallinity formed in the low temperature region is particularly affected by a diluent because its enthalpy per repeat unit is low. In this context it is worth noting that DOP is an unusually good solvent of PVC with strong dipole–dipole interactions (which can be seen by i.r. spectroscopy[4]) and a positive enthalpy of mixing[33].

We can now consider the reasons for the differences in the results obtained for the water quenched and nitrogen quenched materials. These could come either from the increased cooling rate of the nitrogen quenched materials, which could suppress crystallization on cooling, or from the fact that the nitrogen quenched materials were sealed from the atmosphere. This sealing could have two effects. It could decrease the plasticizer losses on annealing (though subsidiary experiments showed that the losses were small anyway), and it could decrease oxidation on annealing, which could affect the crystallinity.

An Avrami analysis was attempted on the results and the exponent was found to be approximately 1, in agreement with Ohata *et al.*[25]. It is not clear whether this analysis has much meaning in this system as there is no evidence that the degree of crystallization approaches 1. Also, over the relatively short time range studied ($1\frac{1}{2}$ decades) the Avrami analysis is not distinguishable from the crystallization vs. log time analysis which fits results over a larger time range in highly plasticized materials[5]. For the majority of published results the time for half crystallization is about 20–60 min[15,23,25] in agreement with this work. Witenhafer's material apparently crystallized much more rapidly with the equivalent time for half crystallization at 120°C being approximately 1 min. This might however be a feature of the i.r. technique which measures the concentration of straight syndiotactic sequences rather than crystallinity directly[35].

The most noticeable feature of the SAXS results is the considerable similarity between the results obtained with the two different plasticizers both before and after annealing. The chemical structure of the plasticizers is quite different as Diolpate 195 is a polypropylene adipate end capped with glycol, and of molecular weight around 2000. This suggests that the structure which gives the SAXS is independent of plasticizer type. It means that a two phase model of crystallites in a plasticized matrix could be applicable[5,18,20,22]. If this is the case then the effect of annealing is to remove some of the small crystallites, decreasing the tail of the scattering curve, and making the intercrystal distance larger and more regular. The small decrease of the invariants shows that the total crystallinity decreased if anything during annealing. It should be emphasized that these materials were not heated to 200°C and quenched before annealing. A number of the specimens, including the X-ray specimens, were to some extent oriented on first drying. Guerrero *et al.*[7] had observed the same effect. On annealing the dimensions within the plane of the specimen contracted by about 10% with essentially no change in mass. One might expect this to cause an equivalent decrease in the Bragg spacing from SAXS emphasizing that the increase observed in this work is a real effect.

There is a factor of 2 difference in the invariant between the two plasticizers (see *Table 1*). This is a little hard to explain as in a two phase model the invariant is given by $\varphi_1(1-\varphi_1)(\Delta\xi_e)^2$ where φ_1 is the volume fraction of one phase and $\Delta\xi_e$ is the difference in electron density between the two phases. Assuming additivity of volumes the ratio of the two invariants is approximately 1.46 when reasonable values (1.475 and 1.38) for the crystalline and amorphous densities of PVC are used. The specimen thicknesses and absorptions were not significantly different. This therefore provides evidence against the two phase model.

As mentioned in the introduction, this simple two phase model has a number of problems. It is hard to see the reason for the regularity in structure that would be required to give an interparticle interference maximum at only a few per cent volume fraction. In addition, if the crystallites are 6–12 repeat units in length in the chain direction and if most crystallizable material is incorporated into the crystallites, it is hard to see how they can be as far as 200–300 Å apart assuming that the polymerization is random and the intercrystalline material is Gaussian random coil. Also, reasonable estimates of the modulus of unplasticized PVC above T_g have been obtained from rubber elasticity assuming only 43 monomer units between crosslinks[11], a value that agreed well with estimates from syndiotacticity. Even allowing a 50% reduction in crystallinity by plasticizer, 80 monomer units too few to form a random chain between crystallites that are 200–300 Å apart. Other estimates of the molecular weight between crosslinks of plasticized PVC also suggest values of 80–100 monomer units between crosslinks[36]. There is n.m.r. evidence that plasticized PVC should be considered as a three phase material consisting of rigid crystallites, a semi-rigid phase, and a flexible phase[37]. Perhaps the material undergoes a phase separation or spinodal decomposition within the amorphous material on cooling or drying, and it is these density fluctuations that are the main contributors to the SAXS patterns. With larger volume fractions and smaller density differences it is much easier to see how interference peaks can appear in SAXS. They are in fact normally predicted for spinodal decompositions[38]. It seems, therefore, that the properties of plasticized PVC come partly from fluctuations in plasticizer content within the amorphous regions.

CONCLUSION

There are two main conclusions to be drawn from this work. The first is on the effect of plasticizer on the crystallization properties of PVC and the second is on the structure of the amorphous regions in plasticized PVC.

It was shown that the addition of plasticizer had surprisingly little effect on the crystallinity of 'commercial' PVC and in particular on the annealing and melting properties of these crystallites. Doubt was thrown on the customary kinetic explanation for the existence of an annealing temperature which maximizes the melting enthalpy. It was suggested that the correct explanation may be in terms of the variation of crystal 'quality' with annealing temperature and in particular in the formation of mesomorphic material at lower temperatures. The morphology of the crystallites is not known at this stage.

The second conclusion is that the SAXS results cannot be taken on the whole as more evidence for or measure of crystallinity in this material. Whereas the crystallites give rise to X-ray scattering, there is another feature in the structure of the material which results in electron density fluctuations, also causing scattering of X-rays and giving rise to the Bragg peak. We suggest, perhaps rather than conclude, that this structural feature occurs in the amorphous region of the plasticized PVC as a result of phase separation, maybe as spinodal decomposition.

As a final remark we would like to point to the great sensitivity of PVC to plasticization. Even the residual traces of THF in the dried samples shifted the T_g to lower temperatures by a substantial amount. This prompts us to make the comment that great care and control must be exercised in preparing PVC samples for any research work.

REFERENCES

1 Alfrey, Jr. T., Wiederhorn, N., Stein, R. and Tobolsky, A. *Ind. Eng. Chem.* 1949, **41**, 701
2 As above *J. Coll. Sci.* 1949, **4**, 211
3 Lebedev, V. P., Derlyukova, L. Ye., Razinskaya, I. N., Okladnov, N. A. and Shtarkman, B. P. *Polym. Sci. USSR* 1965, **7**, 366
4 Tabb, D. L. and Koenig, J. L. *Macromolecules* 1975, **8**, 929
5 Dorrestijn, A., Keijzers, A. E. M. and te Nijenhuis, K. *Polymer* 1981, **22**, 305
6 Lemstra, P. J., Keller, A. and Cudby, M. *J. Polym. Sci., Polym. Phys. Edn.* 1978, **16**, 1507
7 Guerrero, S. J., Keller, A., Soni, P. L. and Geil, P. H. *J. Polym. Sci., Polym. Phys. Edn.* 1980, **18**, 1533
8 Natta, G. and Corradini, P. *J. Polym. Sci.* 1956, **20**, 251
9 Lebedev, V. P., Tsvankin, D. Ya and Glazkovskii, Yu. V. *Polym. Sci., USSR* 1972, **14**, 1123
10 Gouinlock, E. V. *J. Polym. Sci., Polym. Phys. Edn.* 1975, **13**, 961
11 Manson, J. A., Iobst, S. A. and Acosta, R. *J. Macromol. Sci., Phys.* 1974, **B9**, 301
12 D'Amato, R. J. and Strella, S. *Appl. Polym. Symp.* 1969, **8**, 275
13 Wenig, W. *J. Polym. Sci., Polym. Phys. Edn.* 1978, **16**, 1635
14 Juijn, J. A., Gisolf, J. H. and de Jong, W. A. *Kolloid.-Z.u.Z. Polymere* 1973, **251**, 456
15 Grey, A. and Gilbert, M. *Polymer* 1976, **17**, 44
16 Pezzin, G. *Plast. Polym.* 1969, **37**, 295
17 Hay, J. N., Biddlestone, F. and Walker, N. *Polymer* 1980, **21**, 985
18 Bonart, R. *Kolloid-Z.u.Z., Polymere* 1966, **1**, 213
19 Neilson, G. F. and Jabarin, S. A. *J. Appl. Phys.* 1975, **46**, 1175
20 Blundell, D. J. *Polymer* 1979, **20**, 934

21 Singleton, C. J., Stephenson, T., Isner, J., Geil, P. H. and Collins, E. A. *J. Macromol. Sci. Phys.* 1977, **B14**, 29
22 Shtarkman, B. P., Lebedev, V. P., Yatsynina, T. L., Kosmynin, B. P., Gerasimov, V. I., Genin, Ya. V. and Tsvankin, D. Ya. *Polym. Sci., USSR* 1972, **14**, 1826
23 Juijn, J. A., Gisolf, J. H. and de Jong, W. A. *Kolloid-Z.u.Z. Polymere* 1969, **235**, 1157
24 Illers, K. H. *J. Macromol. Sci. Phys.* 1977, **B14**, 471
25 Ohata, S., Kajiyama, T. and Takayanagi, M. *Polym. Eng. Sci.* 1976, **16**, 465
26 Anagnostopoulos, C. E., Coran, A. Y. and Gamrath, H. R. *J. Appl. Polym. Sci.* 1960, **4**, 181
27 Lyngaae-Jørgensen, J. *Polym. Eng. Sci.* 1974, **14**, 342
28 Gouinlock, E. V. *J. Polym. Sci., Polym. Phys. Edn.* 1975, **13**, 1533
29 Kockolt, D. *Kolloid. Z.u.Z. Polymere* 1964, **198**, 17
30 Witenhafer, D. E. *J. Macromol. Sci. Phys.* 1970, **B4**, 915
31 Flory, P. J. *Trans. Faraday Soc.* 1955, **51**, 848
32 Nakajima, A., Hamada, H. and Hayashi, S. *Macromol. Chem* 1966, **95**, 40
33 Su, C. S., Patterson, D. and Scheiber, H. P. *J. Appl. Polym. Sci.* 1976, **20**, 1025
34 Desai, A. B. and Wilkes, G. L. *J. Polym. Sci., Polym. Symp.* 1974, **46**, 291
35 Baker, C., Maddams, W. F. and Preedy, J. E. *J. Polym. Sci., Polym. Phys. Edn.* 1977, **15**, 1041
36 Guzeyev, V. V., Malinskii, Yu. M. and Shkalenko, Zh. I. *Polym. Sci. USSR* 1975, **17**, 2124
37 Hassan, A. M. *Crit. Rev. Macromol. Sci.* 1972, **1**, 399
38 Langer, J. S., Bar-on, M. and Miller, H. D. *Phys. Rev. A.* 1975, **11**, 1417