Crystallinity in poly(vinyl chloride)

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Introduction

Free radical polymerized poly(vinyl chloride) has a low degree of crystallinity unless of low molecular weight and prepared in the presence of effective transfer agents[1], when more crystalline materials are produced. Stereoregularity also has a pronounced effect, and syndiotactic polymers prepared from the monomer–urea–clathrate are 60–70% crystalline[2]. Previous studies[3] have indicated that although the degree of crystallinity of commercial PVC is low, it is associated with a supermolecular structure which persists in the moulded article unless the crystallinity is removed by heating above 350K. This supermolecular structure stabilizes the primary crystallized particles and prevents ingress of stabilizers and plasticizers. Differential scanning calorimetry has produced some interesting information on the nature of the crystalline entities in PVC.

Experimental

A mass polymer, Breon, supplied by BP Chemicals Ltd, with number-average molecular weight of 3×10^4 and polydispersity of 2.7 as measured by g.p.c., was used throughout. 3% Dibutyl tin stabilizer, Ciba–Geigy's Irgastab 17M, was compounded with the powdered polymer in a Papenmeier high speed mixer.

The urea–clathrate polymer was kndly given by B. F. Goodrich Ltd as a research sample.

A Perkin–Elmer differential scanning calorimeter, DSC-2, was used with powdered, or moulded polymer samples of 5–20 mg. Glass transition temperatures and melting points were measured at different heating rates and extrapolated to zero rate, and zero wt. The procedure and calibration of the calorimeter is described elsewhere[4].

Results

Thermal analysis. The shape and temperature of the thermal transitions, observed by d.s.c., varied in a complex way with the thermal history of the PVC sample (*Figure* 1). Two distinct effects were observed in different temperature regions, at the glass transition temperature and above. Samples heated for the first time exhibited a marked glass transition with an endothermic process immediately following it, and two further endothermic processes between 380 and 480 K. On cooling at 10 K min^{-1} and reheating at the same rate, as initially, the endotherm at the glass transition disappeared, and the two other endotherms shifted to higher temperatures and lower intensities (see c and r of *Figure* 1). However, on rapid cooling through the glass transition at 180 K min^{-1} all the endothermic processes were replaced by exothermic ones, i.e. q of *Figure* 1. These thermal transitions were reproducible on slow cooling and quenching and subsequent heating under standard conditions. The highly-crystalline urea–clathrate polymer exhibited no detectible glass transition, nor endotherms. An exothermic process was observed above 500K, characteristic of its dehydrochlorination reaction, and the product removed from the calorimeter after such heat treatment was black. The mass polymer heated to 500K had yellowed, and some decomposition had occurred at this temperature, but not below.

The two distinct endothermic processes will be considered separately.

Glass transition temperature. The extrapolated glass transition temperature for quenched polymer, at zero rate of heating, was 348 ± 2K. The endotherm at the transition was characteristic of the physical aging of the amorphous polymer[5] and is associated with the continuation of the glass formation which set in on cooling below the transition. This consolidation of the glass was accompanied by a change in volume and heat content and is reversed on reheating above the transition[5]. Aging continues over a narrow temperature region below the glass transition, and the magnitude of the extent of aging is characterized by the heat of the endothermic process as measured by d.s.c.[5].

Aging was reversible and eliminated, as far as d.s.c measurements were concerned, by heating above the transition temperature and quenching. This procedure was adopted in measuring the extent of aging from the difference in heat content over the glass transition region between aged and quenched material (*Figure* 2). The rate of aging was markedly temperature dependent, reaching a maximum value at 339K and decreasing at lower temperatures. Aging was not observed at 295K in mass polymer over 6 months, within the detection limit of d.s.c. The extent of aging increased logarithmically with time at each temperature.

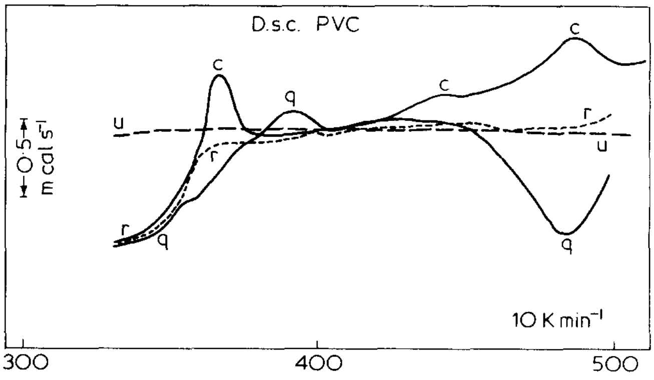

Figure 1 Differential scanning calorimeter analysis of PVC. c:— as received; q:— quenched from 500 K; r:— cooled at 10 K min^{-1} from 500 K; u:— urea–clathrate polymer

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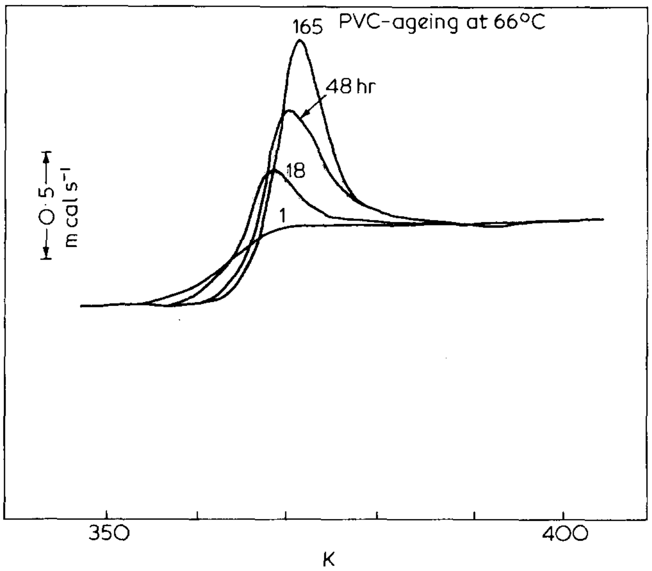

Figure 2 Aging of PVC — d.s.c. endotherms at the glass transition temperature

High temperature processes. The endothermic processes of the initial and the exothermic trace of the quenched polymer samples had similar magnitudes and appeared to be reversible, and thus not associated with the polymer's discoloration reaction. They were considered to be due to crystallization and melting of the PVC. Samples were melted initially at 350K, and quenched to various preset temperatures below 350K. Above the glass transition temperature, the calorimeter evolved heat progressively over 10–20 min from the first equilibration of the temperature (*Figure* 3). This was not associated with the equilibration of the calorimeter, since setting the temperature below the glass transition temperature, the calorimeter equilibrated within 20–30 s, and further quenching the specimen to the required temperature and reheating after various lapse periods at this temperature produced progressively larger melting curves at a higher temperature (see the inset melting curves in *Figure* 3). The slow progressive decrease in rate of evolved heat was considered to be due to a slow crystallization process, and an Avrami equation was used to analyse the conversion–time relationship, i.e.:

$$-\ln(1-X_c)=Zt^n \tag{1}$$

in which Z is a composite rate constant, n an integer constant characteristic of the crystallization mechanism, and X_c the degree of crystallinity[6]. An Avrami exponent, n, of approximately unity was observed for the progress of the crystallinity, consistent with the growth of predetermined rods, or lamellae.

On reheating once, crystallization was apparently complete. Two distinct melting endotherms were observed (*Figure* 4) defined by melting points T_m and T_l. The lower one, T_l, increased with increasing crystallization temperature, T_c, while the upper one, T_m, was invariant. Defining the melting point as the last trace of crystallinity, and correcting for thermal lag, the lower temperature T_l increased according to the Hoffman and Weeks relationship[7]:

$$T_l = T_m/(1-2B) + T_c/2B \tag{2}$$

in which B is unity if equilibrium conditions approximate during the crystallization (*Figure* 5). The higher observed value of T_m which was independent of T_c, was similar to the value of T_m of equation (2) obtained by extrapolation of T_l against T_c to the equilibrium conditions $T_l = T_c$.

These dependences can be interpreted in terms of extended and once-folded lamellae being produced, the stem lengths are limited by some irregularity which does not crystallize. The higher melting point is thus restricted by a structural constraint. The lower melting point T_l, corresponding to folded-lamellae is restricted by nucleation characteristics.

The melting point of an extended-chain lamella is restricted by the stem length degree of polymerization[8,9], since the melting point is lowered by terminal unit effects, i.e.:

$$T_m = T_m(1 - 2RT_m^0\ln(n)/n\Delta h - 2\sigma_e/n\Delta h) \tag{3}$$

in which R is the gas constant, T_m^0 the equilibrium melting point of an infinitely extended chain, and Δh the heat of fusion per monomer mole of the totally crystalline polymer. Neglecting σ_e, the lateral surface free energy, since it is normally of the order of Δh, and using a value of 11.3 kJ monomer mol^{-1} for the heat of fusion, and 546K for T_m^0[10], the stem length was determined to be about 16 monomer units. A range of about 12–16 monomer units straddled the melting region of the extended lamellae.

The observed heat of fusion of the mass polymer varied considerably with crystallization temperature, but was in the range 3–5% crystalline, i.e. 0.35–0.55 kJ monomer mol^{-1}.

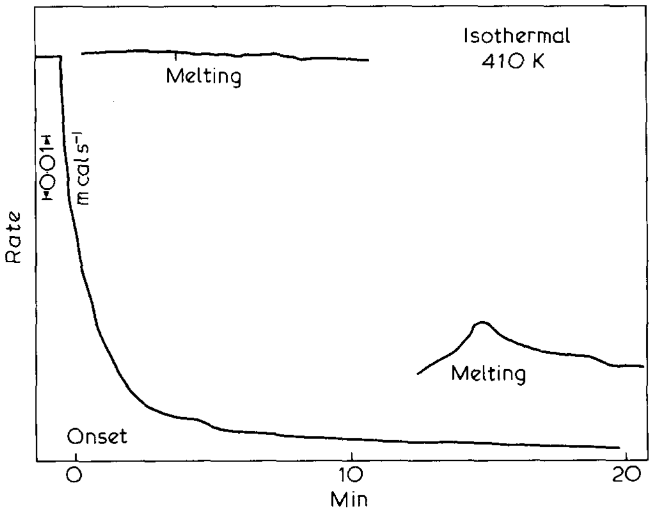

Figure 3 Isothermal crystallization of PVC

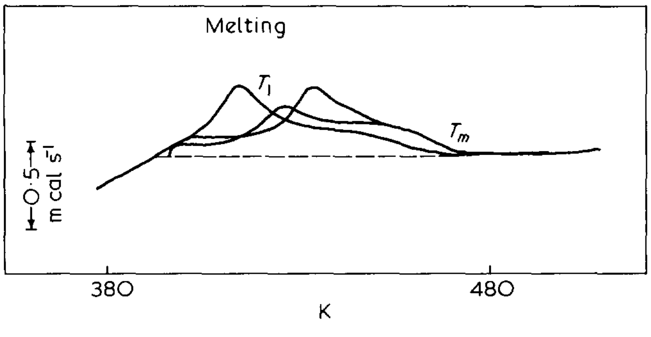

Figure 4 Melting endotherms of PVC

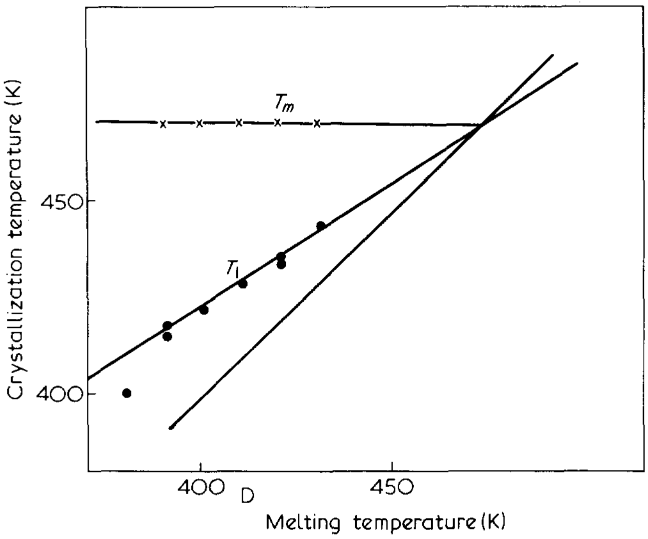

Figure 5 Variation of the melting points with crystallization temperature

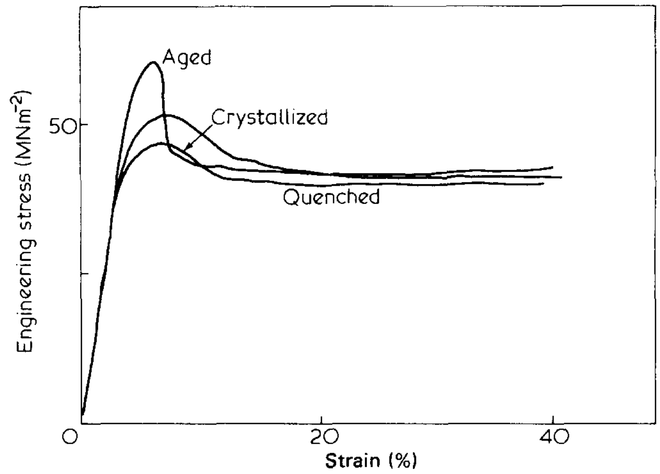

Figure 6 Tensile properties of thermally treated PVC

Free radical polymers prepared under similar temperature conditions are normally 60% syndiotactic[11] from which it was calculated that the weight fraction of material containing 16 syndiotactic monomer units would be 0.005 if the syndiotactic sequences were the result of random placement of the stereochemical units. In general for a sequence of n monomer units, the weight fraction of sequence is $n(n-1)/2 \cdot (1-s)^2 s^n$ in which s is the fractional degree of syndiotacticity. Summing the weight fraction over the sequence range 12–16 produced a maximum value to the crystallizability of the polymer of 5% — in remarkable agreement with the degree of crystallinity observed considering the assumptions involved. Calculations also indicate that higher stem lengths would be present but to less than 0.001 weight fraction and the d.s.c. would be unlikely to detect them. This would seem to account for the upper melting range observed.

Accordingly, PVC mass polymer crystallizes from a limited number of chain-folded and chain-extended lamellae, whose stem lengths are determined both by nucleation conditions and restricted by the degree of syndiotacticity of the polymer. In order to confirm these conclusions, a polymer prepared at 243K by free radical means (a gift from Dr G. Parkes, UWIST) was also studied. It was more crystalline in that the glass transition temperature was less well-defined, but it did not melt below its decomposition temperature. While this is clearly in line with the above studies, no quantitative conclusions can be drawn from them. It does, however, emphasize the severe limitations of the low decomposition temperature on a study of the bulk crystallization of PVC especially with highly crystalline samples.

Mechanical properties

Although thermal aging of PVC had considerable effect on the mechanical properties of the PVC sample, the relatively low degree of crystallinity exhibited by the sample, 3%, did not substantially alter the tensile yield properties or the impact strength, nor did it alter the progress of aging. As can be seen from *Figure* 6, the crystalline sample had an increased yield and drawing stress, by about 10%, but the general shape of the diffuse neck which developed on yielding did not alter. Specimens of 2 mm thickness were brittle in the Charpy impact test with notch tip radius below 1 mm, a brittle-to-ductile transition occurred between 1–2 mm notch tip radii with both quenched and crystalline material. In general, the low degree of crystallinity developed had little effect on the ultimate properties of the polymer. However, this was not the case with aged specimens which were brittle even with a 2 mm notch tip radius, and yielded at a substantially higher stress, up to 50% greater. These effects of aging are in keeping with what has been observed with other amorphous polymers[12] and will be dealt with in detail later.

References

1 Burnett, G. M., Ross, F. L. and Hay, J. N. *J. Polym. Sci.* (*A*-1) 1967, **5**, 1467
2 Wenig, W. *J. Polym. Sci.* (*Polym. Phys. Edn*) 1978, **16**, 1635
3 Walker, N. and Mills, N. Private communication
4 Gilmour, I. W. and Hay, J. N. *Polymer* 1977, **18**, 281
5 Struik, L. C. E. 'Physical Aging in Amorphous Polymers and Other Materials', Elsevier, Amsterdam, 1978
6 Hay, J. N. and Przekop, Z. J. *J. Polym. Sci.* (*Polym. Phys. Edn*) 1979, **17**, 951
7 Hoffman, J. D. and Weeks, J. J. *J. Res. Nat. Bur. Stand.* 1962, **A66**, 13
8 Hay, J. N. *J. Polym. Sci. Chem.* 1976, **14**, 2845
9 Hay, J. N. and Wiles, M. *Makromol. Chem.* 1976, **178**, 623
10 Brandrup, J. and Immergut, E. H. 'Polymer Handbook' Interscience, New York 1976
11 Pezzin, G. *Plastics and Polymers* 1969, **37**, 295
12 Adam, G. A., Hay, J. N., Parsons, I. W. and Haward, R. N. *Polymer* 1976, **17**, 51