

CHARACTERISATION OF POLY(VINYLCHLORIDE)

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Abstract - $0.5 \cdot 10^{-3}$ Long branch and $5 \cdot 10^{-3}$ chloromethyl group per monomer unit (m.u.) possibly originating from head-to-head monomer placement are found in industrial PVC (fewer in low-temperature polymerized products). Tertiary chlorine atoms, if any, correspond to long branches ; internal double bonds ($0.05 \cdot 10^{-3}$ per m.u. and over) can start polydiene sequences.

^1H and ^{13}C NMR spectroscopy shows that syndiotactic placement is slightly favored over isotactic, depending only on polymerization temperature (PT). The number of aggregates in solution is very sensitive to PT, increasing with syndiotacticity, and heating up gives molecular solutions. Crystallizability increases with syndiotacticity, and two types of crystals exist ; crystallinity is higher in virgin powder, and fusion range covers 120° to 220°C . Annealing over 110°C develops a lower order detectable by DSC. A zone of higher density disappearing at 210°C is seen at the center of virgin PVC "one micron granules". The temperature of pseudofusion in plasticizers depends on heat treatment, and the kinetics of impregnation reveals morphological heterogeneities.

INTRODUCTION

This lecture is intended to survey the matter published since the last PVC symposium in Prague in 1970 ; some reference to work done in the author's laboratory will also be made.

Four subjects will be covered :

- Structure of the chain : long and short branching, double bonds, tacticity.
- Solution properties and aggregates.
- Order in solid PVC studied by X-rays, infra-red spectroscopy (IR), calorimetry.
- Morphology of the powder resin and of the latex studied mainly by electron microscopy (EM) and optical microscopy.

STRUCTURE OF THE PVC CHAIN

Long branches

De Vries (1) showed that tetrahydrofuran (THF) solution of PVC fractions in the molecular weight range 6400 - 650 000 g/mole obeyed the following Mark-Houwink relation :

$$[\eta]_{\text{THF}}^{25^\circ\text{C}} = 1.63 \cdot 10^{-2} M^{0.760}$$

Solutions were heated at 110°C for 2 hours before light-scattering measurements. Deviation from the above relation was minimal and compatible with one long branch per chain at most. Lyngaae-Jorgensen (2) confirmed this result by GPC ; taking $[\eta] M$ as proportional to the hydrodynamic volume of the polymer chain and assuming trifunctional branch points and using the theory of Stockmayer he found less than $0.6 \cdot 10^{-3}$ long branch per monomer unit (m.u.) (at 99 % statistical confidence level) ; this is equivalent to less than one long branch per chain for molecular weight under 100 000 g/mole.

In another argument the same author found that the kinetics of the polymerization reaction could not give rise to more than $0.12 \cdot 10^{-3}$ long branch per m.u. if $2.0 < M_w/M_n < 2.2$; this is less convincing since for some PVC samples values slightly lower than 2 have been found by the author (1.90 for laboratory emulsion PVC : PVC-E).

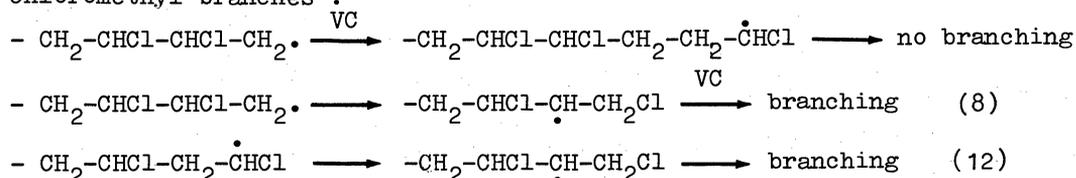
New results by Andersson (3) and Abdel-Alim (4) confirmed that abnormal behaviour of solutions originates from nothing other than molecular aggregates to get rid of which autoclaving was the right means. So it is confirmed that PVC is a fairly linear polymer as far as long branches are concerned.

An indirect method was used to measure the number of branches viz. hydrogenation of PVC into the corresponding hydrocarbon PVCH. Hydrogenation was carried out in the usual manner with $AlLiH_4$ (ALH) in tetrahydrofuran.

It was supposed that during the treatment no C - C bond was cut. Secondary C - C bonds were not cut since the number average degree of polymerization DP_n was approximately preserved (5,6). If tertiary C - C bonds were cut it would diminish DP_n and the weight average degree DP_w by a factor of approximately two in the case of only one long branch per chain, and this was not found to be the case. So there are very few long branches, if any, in PVC, PVCH has the same structure as the original PVC. In model compounds we did not find modifications of the carbon atom chain by the ALH treatment (6).

Short branches

Study of the methyl content of the PVCH was one of the ways of measuring the total branch content of PVC. Since the optical density at 1378 cm^{-1} is sensitive to the number of carbon bonds between the methyl group and the next tertiary carbon atom, prior knowledge of the length of the branch is necessary. In this way, Baker (7) could explain major discrepancies between results of different authors; corrected values were restricted to the range 1.8 to $16 \cdot 10^{-3}$ branch per m.u.. Lyngaae-Jorgensen found 4 to $7 \cdot 10^{-3}$ branch with no variation during polymerization, and no ethyl groups. We have found 4 to $6 \cdot 10^{-3}$ branch per m.u. in dozens of industrial products and for the conversion range of 0.08 to 0.86 with slightly higher values ($+ 10\%$) at 0.935 conversion. Rigo (8) found by radiolysis of PVCH that branching density did not vary with conversion; radiolysis gave methane and butane as Schröder (9) had already found; that was only compatible with an intramolecular process. Authors proposed the following mechanisms leading to chloromethyl branches:



Head-to-head monomer addition was said to exist by Shimitzu (10) and Maruyama (11) but was not detected by NMR spectroscopy (12). No explanation was given for the occurrence of the C_4 compounds. Abbas (12) using ^{13}C NMR spectroscopy found $6 \cdot 10^{-3}$ methyl per C_2 in PVCH, these methyls being directly attached to the main chain; that confirmed the radiolysis results. Methyls at the end of branches more than 6 carbons long were few: $2 \cdot 10^{-3}$ per C_2 or approximately one per molecule. Bovey (13), reducing PVC with the deuteride $AlLiD_4$, confirmed that the branches were mainly chloromethyls attached at a CH site which excluded tertiary chlorine atoms; this confirmed the work of Caraculacu (14) who could not detect those atoms by phenolysis. To decide between the two proposed branching mechanisms Bovey proposed to prepare PVC from deuterium-labelled monomers. (13)

To sum up the branching problem in PVC: $0.5 \cdot 10^{-3}$ long branch per m.u. seems to be a maximum acceptable value for PVC up to 0.90 conversion, i.e. less than 1 long branch at molecular weight of $100\,000 \text{ g/mole}$; 4 to $6 \cdot 10^{-3}$ chloromethyl branch per m.u. (less for low temperature polymerized PVC) is representative of short chain branching; tertiary chlorine atoms are not detected, their number is at most equal to that of long branches since they

cannot correspond to short ones.

Double bonds

Trans vinylene groups were long ago detected in PVCH and we (6) showed that LAH could not saturate double bonds in PVC or in polyethylene, which was confirmed by others (15); moreover we found (16) that a LAH solution immediately darkens a solution of poly(1,2-dichloro ethylene) in THF, which proved the dechlorinating effect of the reagent on $-(\text{CHCl}-\text{CHCl})-$ units. So the double bonds in PVCH are not necessarily limited to those preexisting in PVC. We found that this unsaturation level is remarkably constant, $6-8 \cdot 10^{-3}$ per C_2 , in PVCH prepared from industrial PVC and from many different low-temperature polymerized PVCs (LTP). Abbas and Bovey found $4 \cdot 10^{-3}$ double bonds per C_2 not too close to chain ends by ^{13}C NMR spectroscopy. These authors could not directly see chlorovinyl groups which we postulated to explain the difference in methyl content of PVCH before and after treatment with Raney nickel in the presence of potassium hydroxide (6). Direct measurements of double bonds in PVC have been attempted by resonance Raman spectroscopy (17), a highly sensitive technique. Spectra display fine bands at 1115 and 1500 cm^{-1} , Peitscher claimed to have detected one long sequence -(C-C)_n ($n = 10$ to 20) in $10\,000$ molecules ($M_n = 35\,000 \text{ g/mole}$).

Zil'berman (18,19) by a bromination method found $4.3 \cdot 10^{-3}$ double bond per m.u. which could correspond to 1.4 to $3.4 \cdot 10^{-3}$ internal double bond per m.u.. The values found were higher for PVC-E than for suspension and bulk PVC (PVC-S, PVC-M) with a minimum at 0.55 conversion. In any case practical stability was not correlated to these values. Although the different model molecules mimicking all the possible situations of double bonds have been studied by ^1H NMR, the complexity of the results rules out any opportunity of distinguishing the different cases if occurring simultaneously in real PVC (30). Two indirect methods have been proposed which do not distinguish between isolated and conjugated double bonds, but which are useful for evaluating the length of chain between double bonds: oxidation by potassium permanganate in N-dimethylacetamide (21) and ozonolysis (22). From variation of intrinsic viscosity Braun calculated 0.3 to $2.5 \cdot 10^{-3}$ $-(\text{C}=\text{C})$ or $-(\text{C}=\text{C})_n$ per m.u. with results higher for PVC-S than for PVC-M. Correlation between the values found and the sensitivity to dehydrochlorination were only found for laboratory products; this fact could be a consequence of the complexity of real industrial polymerization recipes. Results obtained by ozonolysis seem to be lower: $0.05 \cdot 10^{-3}$ (22) but constant over the $0.51 - 0.91$ conversion range. The last-mentioned authors insisted on controlled ozonolysis conditions as opposed to the finding of Abbas (23). Lindenschmidt (24) found the permanganate method reproducible but not necessarily exact and the molecular distribution of the oxidated material considerably spread.

Summing up: polydiene sequence length can be evaluated by UV and Raman spectroscopy; degradative methods, if carried out under precise conditions, can give reliable results; it is worthwhile studying the distribution of the oxidated products. No method of direct observation has up to now distinguished between the different types of double bonds in PVC.

Tacticity evaluation

Three methods are available: ^1H and ^{13}C NMR, IR. With the exception of PVC prepared in butyraldehyde solution (25), the tacticity depends on polymerization temperature. From the occurrence of diads, triads, etc... measured by NMR in PVC prepared at different temperatures one obtains the differential enthalpy and entropy change $\Delta(\Delta H)$ and $\Delta(\Delta S)$ between isotactic and syndiotactic placement.

$$\left. \begin{aligned} \Delta(\Delta H)_S^i &= 510 - 700 \text{ cal/mole} \\ \Delta(\Delta S)_S^i &= 1.1 - 1.7 \text{ e.u.} \end{aligned} \right\} \quad (25-27)$$

from triad study it has been shown that ss placement is favored over si and is more than ii (26).

From the abundance of syndiotactic, isotactic and heterotactic triads it is possible to check whether the statistics is Bernoullian (no effect by the penultimate unit). Mitani (28) found no deviation from Bernoullian statistics but Pham (27) and Adel-Alim (26) found it non-Bernoullian outside the 30° - 50° range of polymerization temperature. Inoue (29) has shown that the spin-lattice relaxation time T_1 of ^{13}C is the same irrespective of the tactic configuration and of the molecular weight, so the intensities of the observed ^{13}C resonances are directly related to the real concentration of carbon atoms in each configuration as for instance for the tetrads measured by Carman (30). Since the syndiotactic index measured for diadic placement is 0.54 - 0.56 for industrial PVC (0.50 is the purely atactic random case) the probability of only five syndiotactic successive placements (six m.u.) is $(0.55)^5 = 0.05$ (Bernoullian statistics). The ^1H NMR spectrum at high field is well understood from analysis of up to pentads the latest works being those of Hassan (β -proton spectrum) (25), Abdel-Alim (α -protons spectrum) (26) and the theoretical calculation of Ando (31) by the CNDO/2 method. The ^{13}C NMR spectrum at 25.2 MHz of tetrads was described by Carman (30) and of triads by Pham (27) with small differences in assignment of methylenic carbon signals. Evaluation of tacticity by IR is not independent of the state of the sample since measurements are often carried out on solids (film, powder) and not on solutions, so only an index of tacticity is measured by the ratio of characteristic band intensity such as D_{615}/D_{690} , the actual tacticity being obtained on solutions by the Germar method. Table 1 gives some examples of values of the D_{635}/D_{690} ratio for two types of samples: KBr disks pressed from the virgin polymer powder and cast films after evaporation of the solvent (cycloheptanone) at room temperature. PVC-E appears by IR more "syndiotactic" than PVC-M and PVC-S at the same polymerization temperature, which is a general result.

TABLE 1. D_{635}/D_{690} ratio for some PVC samples

	Polymerization Temperature °C	$(D_{635}/D_{690})_D$	$(D_{635}/D_{690})_{CF}$
PVC-S	56.5	1.20	1.75
PVC-M	45	1.25	1.75
PVC-M	-15	1.50	2.20
PVC-M	-40	1.62	2.40
PVC-M	-60	1.60	2.55
PVC-M	-90	2.28	3.30
PVC-E	42	1.55	2.15
PVC-E	-5	1.52	2.20

D : KBr disk.
CF : cast film

PVC behaviour has been correlated with tacticity : aggregation and crystallinity will be dealt with in later paragraphs. Dehydrochlorination to long polyene sequences is favored by high syndiotacticity (32).

SOLUTION PROPERTIES AND AGGREGATES

Since de Vries' paper (1) on PVC solutions, two points have been confirmed and thoroughly studied :

a) molecular weight distribution is of the most probable type with $M_w/M_n = 2$ with little deviation from that value (2,33). We found however on some PVC-E prepared under poorly controlled conditions values as high as 2.6, and in some low-temperature polymerized PVC (LTP) Solovey (34) and Andersson (3) found values higher than 2. This is not normally the case for all LTP since some authors were misled by the presence of aggregates (33), but we have found on a PVCH obtained from a bulk PVC prepared at -25°C with a special catalyst (peroxide and organo-metallic compound) a ratio M_w/M_n of 4.5 similar to that of some high-density polyethylenes.

b) solutions contain aggregates which can only be dissolved at high temperature. We exclude here aggregates containing suspending agents from PVC-S (35). Systematic studies (3,4,34,36) have shown that high molecular weight, syndiotacticity, higher concentration, separately or together, favor

aggregation ; precipitation from dilute solutions makes subsequent solubilization more difficult. Abdel-Alim (33) observed that two types of aggregates could exist in THF solution : strong ones, soluble at 200°C after 2 hours with a 4300 Å size, made of the high molecular weight part of LTP and weak ones, soluble at 100°C with a 2500 Å size composed of all types of molecular weight molecules. Lyngaae-Jorgensen (37) calculated a radius of gyration of 330 Å for those aggregates ; he postulated that they were made up of ten to twelve linear molecules with a small common dense core. The abundance of the last type was very sensitive to the polymerization temperature ; this enabled Abdel-Alim (4) to draw an Arrhenius plot between $1/T$ and the difference of the areas under the GPC traces before and after heating the solution. He found (33) that the molecular weight of LTP leveled off below -15°C which contradicted some previous data in the literature ; the need for filtering the solution before viscosity measurement could have led to the erroneous conclusion of a maximum at -15°C. For not too low polymerization temperature (over 0°C) solution viscosity of LTP is not very sensitive to aggregates in contrast to light-scattering. Osmometry is particularly insensitive to aggregates (38). Syndiotactic segments are more rigid in the glassy state (39) or in solution, and conversion level between 0.06 and 0.79 was found to be without influence (37). From the previous results it has been postulated that aggregates originate from molecular entanglements favored by long chains, and by kinks as a secondary factor (40). These two factors could explain the growing tendency of PVC to aggregate with diminishing polymerization temperature. If the crystallinity has been proposed as the main factor it is only because of the observed correlation between the tendency of PVC to aggregate and its syndiotacticity and crystallisability. But it must be remembered that aggregates appear non-crystalline (X-ray diffraction) until they have dried and annealed (35,41).

ORDER IN SOLID PVC

IR, X-rays, electron microscopy (EM), calorimetry have been used to study order in solid PVC.

X-rays

Three types of studies are performed on PVC by X-ray techniques :

- Wide angle X-ray diffraction (WAXD) ; Bragg angle 2θ Cu $K\alpha$ between 10° and 40°.
- Small angle X-ray diffraction (SAXD) ; 2θ between 0.2° and 2.0°.
- Small angle X-ray scattering (SAXS) ; 2θ between 0.06 and 1.0°.

WAXD was performed on PVC more than two decade ago (42) but refined values of the parameters of the orthorhombic cell for the syndiotactic planar PVC chain have been given more recently by Wilkes (43) with a calculated density of 1.53 g/cm³. Crystallinity evaluation varies somewhat from one author to another, samples of industrial PVC being attributed values ranging from 0 to 15 % (41,44,45). Sample preparation is of course important ; it must be stressed that when using the radiation of a Cu-target only the upper thin layer of the sample is analysed because of the small penetration of this radiation into PVC. For instance, pressed samples must be relaxed, otherwise preferential orientation due to sample superficial memory to stresses could affect the spectrum, but the relaxing treatment (annealing) might in turn alter the sample. This shows that even for ascertaining maximum crystallisability of a product, exact knowledge of the thermomechanical history of the sample is needed if reliable results are expected.

Some authors consider industrial PVC non-crystalline when quenched after heating at 200°C. This procedure affords samples of minimum crystallinity, but it is not certain that this minimum is nil. Owing to the fact that amorphous fractions of crystalline polymers gives in WAXD the same type of halo as quenched PVC, the intensity of the PVC halo has been subtracted from that of annealed samples in order to measure crystallinity (41,45). Such a measurement provides a total degree of order with more than one origin : the orthorhombic Natta crystals (period $c = 5.10 \text{ \AA}$) and those of another structure (period $c = 4.10 \text{ \AA}$) observed by Biaisi (46). When subjecting a PVC sample to elongation, Natta crystals give rise to equatorial reflexes ($h k 0$) and the others (4.10 \AA) to meridional reflexes ($0 0 1$). So Natta crystals could be of the folded type and the other ones of the fringe micelle type. Diffraction by the fringe micelle type has been mentioned in polyethylene and quite recently in isotactic polystyrene (47). In the case of PVC, the structure observed by Biaisi could characterize isotactic sequences $S_{H,H'}$ and not

syndiotactic sequences S_{HH} . This explanation seems to be more acceptable than a syncrystallization of two types of such different structure (5.10 Å and 4.10 Å). The 4.10 Å period corresponds to the pseudo planar isotactic extended chain postulated by Juijn (48).

Minimum sequence length of syndiotactic units for the existence of crystallites has been evaluated to be 5 to 7 from WAXD, using the Flory theory for copolymer crystallization (44,49). In order to explain the resistance to long-term creep of plasticized PVC it has been proposed that numerous small crystallites act as crosslinks of the gel network. This is substantiated by persistence of characteristic (110) spacing observed by WAXD in plasticized PVC by Geil and coworkers (50-52) and by similar results obtained by IR spectroscopy (53). Lebedev (54) measured 8 % crystallinity in industrial PVC and 4 % after plasticizing with 60 % of dioctylphthalate (DOP). In order to locate the crystallites, SAXD studies have been done, but no completely satisfactory correlation has been found between SAXD and EM on plasticized more or less processed samples. Generally SAXD does not detect long spacing in unplasticized PVC and no structure identified by EM has been related to crystallites.

SAXS studies are few in the literature and interpretation of the results are conflicting (55,56).

Infra-Red

IR spectrum is sensitive to configuration (tacticity) and conformation of chains and also to the interchain force field. Normal vibration analysis was carried out (57) down to very low frequencies. From the spectrum the accepted force field ruled out interchain hydrogen bonds :



A dipolar interaction was suggested. The same conclusion was reached (43) from the measured distance of 4.71 Å between the C atom of one chain and the Cl of its neighbour in the crystalline cell, and from the PVC behaviour in solvents (58). Although assignment of "crystalline-syndiotactic" bonds was done on highly syndiotactic samples uncertainties remained for the less tractable spectrum of industrial PVC. Moreover, it is well known that results are influenced by the way the sample is prepared. Witenhafer (59), using a compensation method directly observed those bands which are stronger in an annealed sample than in the corresponding quenched one. Taking the 2960 cm^{-1} band as the reference, this author measured crystalline bands and particularly that at 1250 cm^{-1} . He found that annealing over T_g enhanced the 1250/2960 band density ratio and that the process was a linear t^g increasing function of the logarithm of time, the maximum relative rate being observed at 110°C. The activation energy of 90 Kcal/mole (mole = one m.u.) is the same as that of the glass transition suggesting a similar process. Heating the sample above 110°C gradually melted out the developed structure, the 1250/2960 density ratio decreasing steadily and leveling off at over 220°C. The process was reversible. Kockott (60) had found a similar result by WAXD. Tabb (53) recently observed the same ordering process between T_g and 110°C with a Fourier Transform IR spectrometer, the compensation between the spectrum of the quenched and the annealed sample being made easier by the computer. He observed by the same method the "crystalline" part of the spectrum in a plasticized sample, confirming the X-ray result that the plasticizer does not destroy crystalline organization (50-54).

Calorimetry

No fundamentally new DSC results have appeared in the literature since the work of Illers (61) ; Gray (49,62) recently published the same type of work but focused on the endotherms obtained over T_g , he confirmed that annealing below T_g decreases free volume and increases density but does not change crystallinity (WAXD) ; this was also apparent from Illers who showed that xylene absorption was slowed down but reached the same final value. Annealing at 90°C, on the contrary, very much slowed absorption but also diminished the final value. In conclusion it can be recognized that heat treatment below T_g only changes the free volume of the amorphous glass.

Above T_g unplasticized PVC crystallizes rather quickly, with a maximum rate at 100 - 110°C as shown by IR (53,59), by adiabatic calorimetry (63) and DSC. Heating over 110°C reversibly melts out a part of that order (IR) but simultaneously develops new order, not detectable in WAXD, but which is manifested as an endotherm in DSC 20°C over the annealing temperature. That order might be two-dimensional. We (64) exemplified this temperature dependency by annealing the same sample for 15 minutes at successive temperatures 172°, 142°, 114°, 83°C ($= T_g$) in the DSC apparatus before cooling down to room temperature at 30°C/min. Heating then at the same rate (30°C/min.) gave rise to separate endotherms at 92°, 132°, 160°, 187°C, the same temperature we observed by separate successive annealings. It can be seen in Fig. 1B that the area under the 132°C endotherm is larger than the corresponding one in Fig. 1A; this means that only that part of the matter not already ordered by the two previous annealing periods at 172°C and 142°C was still available for the third one. It is amazing to compare the rate of development of that order measured by the area under the endotherm after a 5 minute annealing period and the maximum elongation at break of the same product as a function of the temperature (Fig. 2).

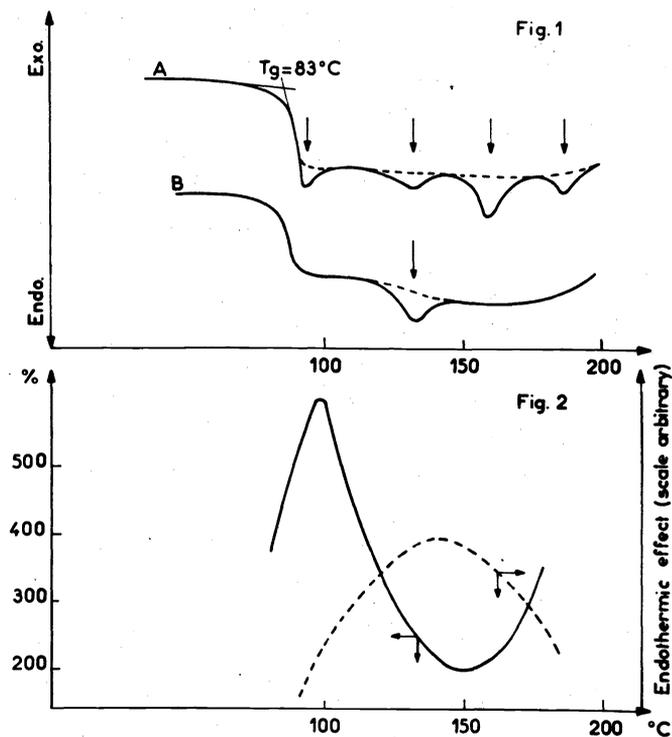


Fig. 1 Thermograms for PVC film : A, after annealing at 4 successive temperatures (172°, 142°, 114°, 83°C). B, after annealing at one temperature (114°). Curves (---) correspond to the unannealed sample.

Fig. 2 Elongation at break for a PVC sample (—) and DSC endothermic effect measured after a 5 minute annealing at the same temperature (---).

It is found that a maximum elongation corresponds to the range of rapid maximum crystallization : 90 - 110°C, then a minimum occurs corresponding to the range of maximum rearrangement rate ; above 160°C, this rate diminishes, the crystalline part goes on melting and the normal behaviour of a non rubbery melt prevails, allowing flow.

POWDER RESIN MORPHOLOGY

Macroscopic morphology of the different types of PVC-(S,E,M) was described by Tregan (65-67) and since that time by many others.

PVC-E is normally observed after drying, it looks like egg-shells (67) containing granules which are clusters of dry latex particles. When particle diameter before drying is to be measured a comparison of the different physical means of measurement is interesting. A long time ago Benoit (68) compared the electron microscopy with the light-scattering method (LS); it appeared that LS was quite sensitive to aggregation and gave higher results than EM. The advantage of LS is that it "sees" the real state of the matter, by EM it is the eye of the experimenter who decides on the reality of the aggregation. Higher order Tyndall spectra, successive maxima in LS (Mie theory) (69), ultra-centrifugation seems to give close results (70), ultra-centrifugation may be precise and rapid (71-73) but it is rarely used without calibration.

Transmission electron microscopy (TEM) is convenient for monodisperse latexes but an image analyzer is necessary to count the 10 000 to 20 000 particles necessary to obtain a good approximation of a broad distribution (74). Claver (75) showed that PVC latexes were particularly sensitive to electron irradiation during EM, so diameters too short by 20 to 25 % were not uncommon. In our laboratory Bonnemayre has confirmed those results and shown that a latex particle shrinks when losing HCl but that the outer diameter is more preserved when the beam current is lower and the time of irradiation longer for a constant total irradiation.

PVC-S is known for its pericellular membrane, Filisko (36) showed that its IR spectrum was not the simple combination of the spectra of PVC and of poly(vinylalcohol) which substantiated the hypothesis of a chemical association. Pluricellular PVC particles or monocellular ones are composed of cells which are originally spherical but much deflated in the end-product. The lost volume could correspond to more than the change in density from the monomer to the polymer, each cell containing liquid and gaseous monomer during polymerization. Although the external aspects of PVC-S and PVC-M are different, the internal structure of a PVC-S cell is not very different of that of a PVC-M grain. Ultra-thin sections of grains buried in epoxy resin or in PMMA observed by TEM shows the same structure of one-micron granules in both cases. This internal structure can also be seen by (66) scanning electron microscopy (SEM) on low-temperature fracture or on cuts after embedding the grains in poly(vinylacetate) latex, the latter does not penetrate the internal porosity of the grains. Morphogenesis of grains and their porosity can be observed by this method. TEM has revealed an elementary subparticle 200-300 Å in diameter in the swelled granule (PMMA) (76). Recently Bonnemayre (77) has shown that in the core of each "one-micron granule" of virgin PVC a zone of higher absorption for the electron beam does exist. This zone is approximately 0.2 micron in diameter. Since it is no longer visible if the grain has been heated in the 180-200°C range it is thought that this zone might represent a region of primary crystallinity. Organization of the matter is certainly favored by the high mobility of the PVC chain during the first 70 % of the polymerization time. PVC, when swelled with more than 20 % monomer, has a very low glass transition temperature (78) and the mobility of the chain has been recognized by NMR (79). Denser zones have also been observed by TEM (80) in PVC powder processed above 210°C; these were considered microfibrils 300 Å thick and were found not to be swelled by the methylmethacrylate. These microfibrils were the last distinct feature remaining after separation of microgranules by processing.

Testing methods using an optical microscope are of great interest for the practical knowledge of PVC, authors have observed the behaviour of PVC powder in plasticizer under a hot-stage microscope. Lalet (81) studied the pseudofusion of PVC-S in dioctylphthalate (DOP) when heating at 2°C/minute. He observed that the temperature of pseudofusion (PFT) was a little higher for high conversion products. By the same technique Glöckner (82) measured the time necessary to obtain pseudofusion of PVC-S and PVC-E samples: drying temperature, rate of precipitation from solution, milling, swelling by organic vapors followed by drying modified the PFT. These effects were easily rationalized by assuming that a higher PFT meant a more ordered structure.

PVC-E after heating, quenching and annealing was not as resistant to DOP action as the virgin product, this pointed to a higher order in that product which could not be restored. This is in line with remarks made by Juijn (82) during DSC experiments. Our observation by IR confirms also the particular ordering obtained during emulsion polymerization.

Since the space between granules is more or less densely filled with polymer, the state of compaction is an important factor of processability. Many authors have measured porosity by high pressure mercury porosimetry and surface area by BET technique. Others (84-86) used chromatography and characterized the powder by the time of retention of organic vapor on a column packed with the PVC powder. The kinetics of swelling by plasticizers or other liquids can better reveal morphological heterogeneities (87,88); this is the basis of a method developed many years ago by Tregan (89) who uses quinoline as swelling agent to differentiate between PVC powders by "microdiffusion". The kinetics of microdiffusion is measured by the determination of the rate of impregnation of the grain; this rate varies in a broad range of time according to the properties of the powder resin and increases exponentially with the temperature. Gausso-logarithmic representation of the phenomenon gives a Galton's straight line, the slope of which yields the specific parameter of the method viz. the homogeneity index. In the same way, diluent-powder interaction at room temperature as a function of time is the basis of "epidiascopy"; by this method Tregan can distinguish in PVC five main types of grain texture (90).

CONCLUSION

PVC has very few long branches ($0.5 \cdot 10^{-3}$ per m.u.) and few chloromethyl groups as short branches which can be formed when a head-to-head placement occurs.

PVC solution behaviour is only disturbed by aggregates which can be dissolved in most cases by autoclaving. These aggregates are favored by syndiotacticity and experimental conditions known to favor crystallization of polymers, but themselves are not crystalline. Tacticity depends on polymerization temperature but in any case sequences are short. Crystallinity (tridimensional order) exist even in industrial products polymerized around 60°C, in the latter case it is highest in the virgin product. Natta's orthorhombic crystals originate from syndiotactic sequences, but isotactic short sequences, always present, could form fringe micelle crystals. The syndiotactic crystallizable part melts between 120 and 220°C. Annealing in this temperature range develops lower level order, which influences PVC processing behaviour. A denser zone is recognizable at the core of the micro-granules in virgin powder resin and this inhomogeneity is lost by heating around 190°C. Processing desintegrates the PVC grain into separate granules which melt at over 200°C, losing their identity. Since PVC crystals are necessarily extremely small, WAXD gives no sharply defined spectra and TEM can only distinguish between relatively large zones of different mean density. This is informative but not sufficient to correlate precisely the structure and physico-mechanical properties of PVC, which may be considered as a sequenced crystallisable copolymer. The processability of PVC compounds depends on thermal history and grain morphology which is conveniently studied by optical microscopy in the presence of liquids.

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