Double Bonds in Poly(vinyl Chloride)

Several attempts[1-4] have been made to determine quantitatively double bonds in poly(vinyl chloride) (PVC) and to correlate their amounts with thermal instability of polymers. Physical methods, essentially spectrographic (UV, IR, NMR), appear to be insufficiently accurate, so it seems necessary to use chemical methods.

Oxidative cuts by potassium permanganate[5] or ozone[6-8] did not lead to satisfactory results: if the carboxylic groups thus created are not analyzed, one must measure the variation of the intrinsic viscosity of polymer solution. Consequently, it is impossible to appreciate the double bonds situated in the neighborhood of chain ends, and it is difficult to interprete the purely statistical results that are obtained.

Gas-phase bromination[1,3,4,12] also led to poor results: the accessibility of the large molecules of bromine to reaction sites is not easy, nor homogeneous, when these sites are located in the center of PVC particles which can be more or less porous. In any case, the weight increase is so slight that it is difficult to measure it accurately, so the results[3,4,12] exhibit marked discrepancies, especially when the PVC samples include water-sensitive substances such as emulsifying agents.[4]

It seems that the best method is that described by Morikawa,[9] which is based on liquid-phase bromination. It was found to be both accurate and reproducible, provided the experimental procedure is cautious.

Reaction of bromine with double bonds is conducted in 1,2-dichloroethane solution, with mercuric acetate as a catalyst, in the dark. Bromine excess is titrated by iodine and thiosulfate, the final titration being controlled by fixed current potentiometry. Under these conditions, a determination of 2×10^{-3} double bonds per monomer unit is made with a dispersion of $\pm 0.1 \times 10^{-3}$.

One limitation in validity which should be noted is that this method cannot be used to analyze vinyl chloride/vinyl acetate copolymers nor chlorinated PVC.

In order to present the results in terms of macromolecular chains, the relation

$$\overline{DP}_n = 2.5 \, (IVA)^{1.2}$$

was used, where IVA is the Afnor viscosity index:

$$IVA = 50 \frac{t - t_0}{t_0}$$

where t is the flow time of PVC solution, t_0 is the flow time of pure solvent, the solvent is cyclo-

TABLE I
Bromine Double Bond Contents of Some Commercial PVC Samples

Lucovyl	Polymerization process	Polymer-ization degree $\overline{DP}_n$	Br double bond content		Thermal stability, min[a]
			Per 1000 monomer units	Per macro-molecule	
RB 8010	Bulk	450	2.2	1.0	70
GB 1150	Bulk	710	1.7	1.2	80
GB 1550	Bulk	1055	1.35	1.4	100
RS 8000	Suspension	495	3.05	1.5	75
RS 1100	Suspension	665	1.8	1.2	85
GS 1400	Suspension	915	2.15	1.95	100
PE 1151	Emulsion	760	1.5	1.15	70
PE 1801	Emulsion	1250	1.5	1.85	70

[a] Blackening time for test pieces, placed in aerated drying stove at 180°C; formulation as follows: Polymer, 100; lead dibasic stearate, 1.5; lead dibasic phosphate, 0.5; calcium stearate, 0.5; "Hartwachs" wax, 0.6.

TABLE II
Br Double Bond Content of Special PVC Samples

| PVC sample | Polymer- ization degree $\overline{DP}_n$ | Br double bond content | | Thermal stability, min[a] |
		Per monomer units	Per macro- molecule	
A (oxygen)	440	2.6	1.15	<75
Control	495	3.05	1.5	110
B (gas phase)	625	0.6–1.4	0.4–0.9	<75
Control	665	1.8	1.2	>120

[a] See Table I.

hexanone, and concentration of PVC is 0.5 g per 100 cm^3. Temperature is 25°C. The above relation was derived from the generally accepted formula

$$[\eta] = 163 \times 10^{-4} \, \overline{M}_w^{0.766} \tag{7}$$

taking (as is usual for PVC) $\overline{M}_w/\overline{M}_n = 2$.

RESULTS AND DISCUSSION

Commercial PVC Samples

Bromine double bond contents of commercial PVC samples selected so as to cover the range of current products are presented in Table I.

Three remarks can be made: (a) Significative differences exist between these samples; Br double bond content is not an invariant for PVC. (b) The number of Br double bonds in a macromolecular chain always exceeds 1, but never exceeds 2. There seems to be an increase in Br double bond content together with polymerization degree; but this in only a tendency which may be reversed under the influence of other factors. (c) The different polymerization processes do not lead to important differences in Br double bond contents; higher values might be observed in samples obtained by suspension process.

Thermal Instability and Br Double Bonds

From the above results, it can be observed that the variations of Br double bonds content do not coincide with known variations of thermal instability.

It is interesting to examine laboratory samples especially prepared to be highly unstable. As it is commonly admitted that thermal stability of PVC is strongly affected by the presence of oxygen in the reactor at the beginning of polymerization,[11-13] and by polymerization under such conditions, that pressure is below the normal vapor pressure of the monomer,[14,15] double bond content was analyzed for two laboratory samples, A and B. Sample A was obtained by suspension polymerization in the presence of approximately 0.3 wt % of oxygen (with regard to monomer). Sample B was obtained by a suspension process with continuous feeding of 90% of monomer, pressure being maintained below the normal vapor pressure of the monomer.

Results are presented in Table II, jointly with those for control samples normally polymerized and having similar a polymerization degree; thermal stability is also indicated.

It can be observed that the Br double bond content does not increase when polymerization is conducted under the above-mentioned conditions. Since thermal stability is, however, strongly affected, one can conclude that it cannot be related in a simple and unequivocal way to the Br double bond content of the product.

Origin of Double Bonds

Analyzing samples taken during the course of polymerization (Table III), it appears that the Br double bond content stays approximately constant all through the reaction, but is slightly higher in the early stage. This indicates that formation of Br double bonds is not due to a reaction that

TABLE III
Br Double Bond Content and Conversion Rate (Bulk Polymerization)

Polymer-ization tempera-ture, °C	Conversion %	Polymer-ization degree DP_n	Br double bond content	
			Per 1000 monomer units	Per macro-molecule
50	3.04	726	2.1	1.55
	65	1055	1.35	1.4
68	30	470	2.2	1.05
	50	470	2.2	1.05
	70	470	2.2	1.05

would start from a given stage of polymerization, but is a phenomenon inherent to the polymerization itself.

It is known that chain transfer by monomer is of great importance in vinyl chloride polymerization. This mechanism can account for a number of double bonds which can be evaluated to be 0.8–0.9 per macromolecule, according to polymerization conditions, for commercial products. The excess of Br double bonds above these figures should be compared with the continuous evolution of HCl all through the process of polymerization as studied by Enomoto[10] and Bauer.[11]

It seems reasonable to conclude that radical polymerization of vinyl chloride is associated with simultaneous dehydrochlorination, HCl evolution, and creation of supplementary double bonds in the PVC chains.

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J. BOISSEL

Centre de Recherches
Rhône-Poulenc
Aubervilliers, France