INTERNATIONAL UNION OF PURE AND APPLIED CHEMISTRY

MACROMOLECULAR DIVISION

COMMISSION ON POLYMER CHARACTERIZATION AND PROPERTIES

WORKING PARTY ON STRUCTURE AND PROPERTIES OF COMMERCIAL POLYMERS

DEFECTS IN THE MOLECULAR STRUCTURE OF POLYVINYLCHLORIDE AND THEIR RELATION TO THERMAL STABILITY

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Estimation of Defects in the Molecular
Structure of Polyvinylchloride**

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Abstract – Thirteen samples of polyvinylchloride especially prepared by different laboratories of the sub-group members were investigated. Quantitative data obtained from spectroscopic, chemical and physical methods of analysis of these samples are summarized in this report. The report also takes into account, for comparison, recent data published in the literature. The need for standardization of thermal stability testing, currently based on dechlorination tests in solution or the solid state, on coloration tests, or rheological measurements, is highlighted.

Correlation between structural defects and degradation rate remains far from clear. The degradation is accepted to be a chain process including initiation, propagation and termination steps; the mechanism of this process, whether radical or ionic, remains under discussion and there is some degree of reversibility. Structural defects are believed to be connected mainly with the initiation process. Further work is needed to reach a better agreement between the data from ^{1}H and ^{13}C NMR spectra.

When the IUPAC Sub-Group on Defects in the Molecular Structure of Polyvinylchloride (PVC) and their relation with thermal stability, was started in May 1977 one year after the Second International Symposium on PVC (Lyon 1976) this topic was far from clear. The situation at that time was described in some reviews[1,2]. From the model compounds studied, it was stated that the"regular" head-to-tail structures of the polymer were expected to be very stable at processing temperatures while structures including allylic chlorine or tertiary chlorine or oxygen containing structures were prone to dehydrochlorination; studies with polymer enriched with such structures through designed copolymerization have confirmed these statements. However, the presence of such structures in commercial PVC was not clearly stated (at least for tertiary chlorine) or indirectly deduced (for allylic chlorine through the presence of internal unsaturation). Chain end allylic chlorine had been identified but model compound studies revealed that such allylic chlorine was rather stable. It was generally believed that the molecular weight limitation came from a mechanism of transfer on the monomer, but the proof of the actual existence of the expected chain ends was not given. The more advanced data available dealt with the problem of branches: it was shown that the main branch structure was a chloromethyl branch; that statement was established from ^{13}C NMR analysis of the deuterated polyethylene which results from the reduction of PVC with tributyltindeuteride[3,4]. The mechanism of formation of these chloromethyl branches was believed to be from a sequence of head-to-head additions, radical isomerisation from a 1-2 migration of the terminal chlorine atom, and propagation reaction from the isomerised radical later on. The same reduction techniques have shown also the presence of 2-4 dichlorobutyl branches[5].

On the other hand the discussion at that time revealed that a universal definition of thermal stability was not yet accepted, because it may be based on either dehydrochlorination tests or colouration tests; in addition the presence of a variety of stabilizer recipes adds a number of extraneous parameters in these tests.

So the purpose of the Sub-Group was double; the first objective was concerned with the search for quantitative data about the various possible defects using both spectroscopic methods (NMR, IR, UV, Raman) or chemical methods, and eventually physical methods. The second objective was to establish the possible relationship between the number of these defects and the initial thermal degradation rate; to do that a re-examination of the various tests was necessary.

The work of the group was based on 13 PVC samples, specially produced either on the pilot plant or laboratory scale with very well defined conditions, simulating as closely as possible the conditions used for a commercial production.

The results obtained from 1977 to 1982 and the experimental methods used by the various members listed, belonging to laboratories either in industry or university, are published elsewhere in detail (seven different reports to be published in the Journal or Vinyl Technology[6].) The present report is only a summary of these reports, which also takes into account, for comparison, other recent data published independently by some of the members of the group as well as by other authors. To facilitate comparison between the results, the different laboratories are given arbitrary designations A.B.C... These designations vary from table to table.

BASIC DATA ABOUT THE SAMPLES

The 13 samples have been selected on the basis of the kind of process (bulk, suspension, emulsion), polymerization temperature, presence or absence of oxygen, nature of the initiator and presence of associated impurities, final conversions, pressure of the monomer, final thermal treatments. The main characteristics of these polymerization conditions are briefly reported in Table 1.

The molecular weight distribution of these polymers was studied by GPC,using Benoit's[7] universal calibration concept and using the following Mark-Houwink law for viscosity[8].

$$\{\eta\} = 1.5. \quad 10^{-4} \ M^{0.77} \ ml/g$$

The results are reported in Table II. It may be seen that the use of sub-saturation conditions (or high conversion or final overheating) causes a broadening of the molecular weight distribution. The weight average molecular weight was also obtained from light scattering in tetrahydrofuran.

From a combination of viscosity and GPC, the long chain branching may be obtained by the procedure of Drott and Mendelson[9] which assumes that the branch points are trifunctional. The data shows that only sample III, prepared under conditions of low pressure, has a significant degree of long chain branching: 0.75 branches per 1000 carbon atoms (see Table II).

STRUCTURAL ANALYSIS

Tacticity
Only spectroscopic methods have been used. By far and away the best analysis is ^{13}C NMR. Analysis at a temperature high enough in O.dichloro-benzene with a high resolution apparatus (not less than 50 MHz) is to be recommended, because of the excellent resolution and the fact that the results are not sensitive to the fortuitous presence of microgels in the solution. Typical data reported in Table III show an excellent reproduc-ibility (error less than $\pm2\%$). Within the error limits none of the polymers deviates from the Bernouillian propagation statistics. Such results have been confirmed by other workers[10,11].

From the infrared analysis, only semi-quantitative results (ranking of the various samples) can be obtained: the three ratios of absorbance A1428/ A1435; A610/A693 and A635/A693 increase with the amount of syndiotactic diads. But these ratios depend upon the method of preparation of the samples (conformational changes upon mechanical stress).

Short chain branching
After reduction with trialkyltin-hydride[12] (which is definitely a better method than those using lithium aluminium hydride initially proposed by Cotman[13]) the total number of branches can be obtained from compensated infrared spectra. However, a correction for the normal chain ends is necessary and some uncertainties remain because the reduction of unsaturated chain ends is not always complete; in addition the amount of unreduced chlorine can vary. Typical data, eliminating the results from non-compensated spectra, are reported in Table IV.

A few results have been obtained in the Group from ^{13}C NMR analysis of the reduced samples: the number of methyl groups has been found lower than expected from the IR data. This difference was attributed to the presence of butyl branches and also of a few ethyl branches. Use of γ radiolysis followed by gas chromatography, according to Bowner and O'Donnel[14] has shown the presence of some C_4 and C_2 branches. These findings are now supported by recent work of Starnes et al[15] as well as of Hjertberg and Sörvik[16] through ^{13}C NMR studies of reduced samples of various origin. It can now be stated that such methods are the preferred method for short chain branch analysis.

Saturated chain ends
Direct NMR analysis with high resolution apparatus (350 MHz) is now able to study the saturated chain-ends of the main chain and of the short branches[17].

The ^{1}H NMR spectra of low molecular weight extract of X, XII and XIII allows a clear identification of the signals from $- CHCl - CH_2Cl$ and $- CH_2 - CH_2Cl$ end groups (3.65 to 3.8) (3.8 to 3.9 ppm in deuterochloroform).

Table I – Main characteristics of polymerization conditions of thirteen IUPAC PVC samples

Samples	Polymerization process	Initiator	Polymerization temperature (°C)	Conversion (%)	Observations
I	Bulk	cumylhydroperoxide	- 30	15	continuous polymerization with stationary conversion
II	Bulk	ethylpercarbonate	56	56.5	pressure maintained at 8.4 kg/cm². No final overheating subsaturation pressure : 6.2 kg/cm²
III	Suspension	ammonium peroxisulfate	55		
IV	Bulk	ethylpercarbonate	56	82.5	pressure maintained at 8.4 kg/cm² final overheating (85-95°C)
V	Bulk	lauroylperoxide	70	62.6	no final overheating.pressure : 12 kg/cm²
VI	Suspension	azodiisobutyronitrile	54	81.4	presence of oxygen
VII	Suspension	lauroylperoxide	54	80	
VIII	Emulsion	potassiumpersulfate	55	87	
IX	Suspension	lauroylperoxide	54	70	without oxygen
X	Suspension	azodiisobutyronitrile	60	85	subsaturation
XI	Suspension	azodiisobutyronitrile	60	20	normal condition
XII	Bulk	cyclohexylperoxidicarbonate	56	83.5	final overheating.pressure : 8.3 kg/cm²
XIII	Bulk	cyclohexylperoxidicarbonate	56	54.7	pressure : 8.3 kg/cm². No overheating

Table II – Molecular weight measurements of IUPAC PVC samples from GPC, Light Scattering and Viscosity

Samples	$\overline{Mn}.10^{-3}$						Average $\overline{Mn}$	$\overline{Mw}.10^{-3}$						Average $\overline{Mw}$	Average $\overline{Mw}/\overline{Mn}$	$\overline{Mw}$ laboratory Light scattering (THF)		LCB/1000 GPC
	A	B	C	D	E	F		A	B	C	D	E	F			D	G	
I	38.2	47.1	53.9	57					175.3	258	144							
II	21.5	33.4	42.0	37.0	39.1	39.0	38.0	88.7	83.8	91.3	94.0	96.6	80	89.0	2.3	97	96	0.09
III	21.5	22.0	21.8	23.0	21.3	27.0	22.7	67.0	62.2	80.3	73.0	74.7	70	71.2	3.1	110	—	0.75
IV	27.7	25.9	27.7	30.0	26.0	30.0	27.8	84.8	81.3	91.7	90.0	82.9	75	84.2	3.0	80	96	0.38
V	27.5	26.9	29.6	26.0	32.3	34.0	29.3	64.0	60.2	67.6	62.0	69.3	60	63.8	2.2	70	70.3	0.47
VI	42.0	39.3	42.4	38.0	43.3	67.0	41	100.0	104.9	106.0	105.0	96.5	108	103.4	2.5	106	108.5	0.19
VII	50.4	48.5	47.2	40.0	47.2	54.0	47.8	103.3	104.8	108.0	103.0	103.3	91	102.2	2.1	102	111	0.23
VIII	45.9	45.0	46.4	40.0	48.8	58.0	45.2	125.5	97.7	115.0	103.0	109.7	117	111.3	2.5	107	105	0.31
IX	46.2	43.7	45.6	39.0	49.2	61.0	44.7	101.0	103.4	101.0	101.0	114.9	104	104.2	2.3	104	108	0.09
X		39.6	40.6		38.4	44.0	40.6		87.8	106.0		82.4	89	91.2	2.2		113.5	
XI		40.0	43.4		46.2	46.0	43.9		82.3	97.0		80.7	97	89.2	2.0		92.5	
XII		39.1	37.5			36.0	37.5		97.5	99.0			79	91.8	2.4		94.5	
XIII		41.6	45.5			43.0	43.3		85.8	101.0			96	94.2	2.2		96.5	

(*) LCB : long chain branching (number of branches per 1000 carbon atoms)

Table III - Tacticity values expressed as triad concentrations

| | 1H NMR | | | | | | 13C NMR | | | | | |
| | % Syndiotactic | | % Heterotactic | | % Isotactic | | % Syndiotactic | | % Heterotactic | | % Isotactic | |
Samples	A	B	A	B	A	B	C	D	C	D	C	D
I							32	35.9	50	46.6	18	17.5
II	32	33	50	49	18	18	29	30.3	46	48.2	25	21.5
III	31	31	50	49	19	20	30	30.6	46	47.1	24	22.3
IV	31	--	50	--	19	--	30.6	31.6	46.3	47.4	23.1	21.0
V	30	30	49	48	21	22	30.6	30.5	47.3	47.1	21.7	22.4
VI	33	29	49	49	18	22	31.7	32.0	48	46.2	20.3	21.8
VII	34	31	48	48	18	22	26.9	31.2	47.5	48.0	25.6	20.8
							25.5		52		19.8	
VIII	32	29	49	47	19	24	30.2	31.6	46.9	48.6	22.8	19.8
IX	31	31	48	47	21	22	30.9	31.6	47.4	48.3	21.7	20.2
X	33		47		20							
XI	35		48		17							
XII	34		47		19							
XII Extract	29		49.5		21.5							
XIII	32		51		17							
XIII Extract	28.5		51		20.5							

Table IV - Methyl branch contents from infrared analysis of samples after reduction (CH₃ per 1000 monomer units)

| | CH$_3$ | CH$_3$ | Cl[a] % | CH$_3$ | Cl[a] % | CH$_3$ | Cl[a] % |
Samples	A	B		C		D	
I	1.86	--	2.36	2.29	0.65	2.8	2.5
II	5.22	4.84	2.48	5.26	0.54	5.8	0.4
III	8.68	7.54	2.90	9.30	0.54	9.6	4.0
IV	6.28	6.20	2.86	6.96	0.36	6.1	1.4
V	6.40	5.70	2.80	5.90	0.40	5.8	1.4
VI	6.44	7.96	3.12	6.24	0.56	5.4	1.4
VII	5.40	5.52	2.46	5.46	0.43	5.0	2.1
VIII	4.28	7.50	3.10	5.10	0.18	5.2	2.8
IX	5.20	6.30	3.33	5.0	0.43	5.2	1.4
X	--	--	--	7.34	0.30	-	-
XI	--	--	--	6.40	0.24	-	-
XII	--	--	--	7.34	0.17	-	-
XIII	--	--	--	6.76	0.15	-	-

(a) the reduction process is never completed. The residual chlorine content (%) is given when available

Table V - 1H NMR analysis of saturated chain ends

Samples	Amount of extract (%)	$\overline{Mn}$	Resonance between 3.5 and 3.8 ppm ($-CH_2-CH_2Cl$)	3.8 and 4.0 ppm ($-CHCl - CH_2Cl$)
			as number of chloromethyl group per 1000 units (b)	
X	-	40 600	4.0	5.1
X$_e$ [a]	0.6	3 950	20.1	22.5
XII	-	37 500	4.2	4.4
XII$_e$ [a]	1.3	2 400	28.7	29.1
XIII	-	43 300	3.5	5.1
XIII$_e$ [a]	0.5	3 000	11.5	20.5

a) Samples obtained in solution by extraction by a tenfold volume of a mixture of hexane (75 %) – acetone (25 %) 20 hours at 20°C and then dried under vacuum at 30°C

b) Both values of the number of structures are to be corrected because of interference with the chloromethyl branches

The amount of the latter is lower in sample XIII with the lower conversion.
The quantitative estimate of these structures (Table V), however, is not
carried out with certainty because of the interference with the chloromethyl
branches which are more important in the whole polymer than in the low
molecular weight extract.   Other data were published recently by Van der
Heuvel[18].

Unsaturation

The following points are of concern: total number of double bonds (total
unsaturation), their localization inside of the polymer chain (internal
unsaturation) or at the chain ends and the sequence distribution of the
polyene.

Total unsaturation   Among the chemical methods, catalytic hydrogenation
was found to be incomplete, even at the rather high pressure (100 bar) used;
however complete hydrogenation of the low molecular weight fraction was
reported[22].   Two other chemical methods give reliable results with a
good reproducibility ($\pm$2%): bromine addition according to the method of
Morikawa[19] improved by Boissel[20], and ICI addition according to the
method of Wijs[21].   Results are reported in Table VI, together with some
results of spectroscopic methods.   Among them, the band at 1667 cm^{-1} in the
infrared spectrum can be used although the proper extinction coefficient has
not been determined directly.   The ^{1}H NMR spectrum using all the absorption
around 5.9 ppm from tetramethylsilane, gives reliable results if a high
resolution apparatus (at least 200 MHz) is used.

Chain end unsaturation   The structure - CH = CH - CH$_2$Cl initially proposed
by Petiaud and Pham[23] is now well confirmed.   It gives a well defined
doublet from the chloromethyl group at 4.05 - 4.10 ppm in solution in
deuterochloroform and appears at 4.2 ppm in dimethylsulfoxide-d6.   Its
formation is explained as a head-to-head addition mechanism through decomp-
osition of an isomerized radical, which gives a chlorine radical.   The
latter is able to reinitiate polymerization, thus explaining the presence
of CH$_2$Cl - CHCl - saturated end groups;   the whole mechanism is now accepted
as the true transfer mechanism which limits the molecular weight in PVC.
The amount of the structure - CH = CH - CH$_2$Cl is estimated between 0.5[17]
and 0.8[15] per molecule.

Internal unsaturation   The only method available is ozonolysis at low temp-
erature (- 20°C) according to Michel et al[24,25].   This method does not
give the number of internal double bonds, but the number of sequences of
internal double bonds because the result is based on the difference in the
number average molecular weight of the polymer before and after ozonolysis.
The accuracy of the method, tested in only one laboratory is acceptable, but
rather large deviations are observed between two laboratories, most probably
because the molecular weight determinations were carried out using two
different methods (viscometry and GPC).   The results are reported in
Table VII.

Obviously more data are necessary to give a clear conclusion as well as the
possibility of checking with a direct method.   Attempts to use catalytic
metathesis with a low molecular weight olefin were not successful.

Polyene distribution   UV visible spectroscopy is a well-established method
of describing the distribution of polyene sequences after thermal or photo
degradation.   Few data are available for virgin PVC.   Some work has been
carried out in the group and the results are reported in Table VII for short
sequences.   In addition a few attempts have been made to use Raman resonance
spectra (exciting wave length 514.5 cm^{-1}) which gives a semi-quantitative
estimate of a selected polyene sequence (n) by comparing the intensity of
ν(C = C)$_n$ with a convenient non-resonant band in the spectrum ($\gamma_{(CH_2)}$).

It may be concluded that the most striking feature of the unsaturation is
the chain end structure - CH = CH - CH$_2$Cl.   By comparing the more reliable
result of ozonolysis (molecular weight measurement by GPC) and the data of
NMR, it may be concluded that most of the internal double bonds are isolated
double bonds.   Polyene sequences are observed for high conversion polymers
and for polymers produced in subsaturation conditions or in the presence of
oxygen.

Tertiary chlorine atoms

A safe estimate of these is provided by ^{13}C NMR measurements after reduction
with ter-butyl tin deuteride; the data here comes mainly from Starnes'
team[15] and that of Sörvik[26].   The values obtained correspond to the sum
of the long chain and the short branches, other than chloromethyl branches.

Table VI – Total unsaturation per 1000 monomer units

Samples	Bromine addition A a	A b	B	C	D	ICI addition E*	F**	G*	IR E	^{1}H-NMR E	H
I						0.6			1.6		
II	1.7	1.6	1.5	1.4	1.7	1.6	2.1	1.6	1.7	1.7	1.8
III	3.7	4.0	3.1		3±0.6	2.2	2.8	2.2	2.5		2.7
IV	2.0	2.5	2.0	1.9	2.7	2.2	2.7	2.2	2.3	1.7	
V	1.9	2.4	2.1		2.4	2.4	2.9	2.3	2.2	1.0	2.2
VI	1.7		1.5		2.0	1.4	1.9	1.5			1.7
VII	1.2	1.4	1.5		1.5	1.6	1.9	1.4	2.0		1.8
VIII	1.6	1.6			1.5	1.6	1.7	1.5	2.1	1.3	1.5
IX	1.0		1.8		1.4	1.9	1.5	1.7	2.0		1.8
X					1.5	1.85	2.0	1.7			1.5
XI						2.0	2.2	1.3			2.2
XII						2.2	2.4	1.9	2.3	2.3	2.9
XIII						1.9	2.0	1.6	2.1	2.0	1.5

a : Cardiff Meeting ; b : Gothenburg Meeting   * X-Ray fluorescence ; ** ^{125}I labelled ICI

Table VII – Data on unsaturation in PVC samples

Samples	Internal unsaturation C=C/1000 monomer units from ozonolysis (a) A	B	C	Conjugated unsaturation (Mole.l^{-1}x10^5) by UV spectroscopy trienes	tetraene	Octene (D)	Conjugated unsaturation by résonance Raman spectroscopy $I(C=C)_{13}/I_\delta(CH_2)$ E	F	Chain end unsaturation/1000 monomer units ^{1}H NMR A	B
I					0.97	20	0.09			
II	0.07	0.3	0.06		0	0	0			
III	0.76	0.8	0.6	140	71	8	0.33	0.38		
IV	0.25	0.44	0.42	1070	41	7	1.53	1.50		
V	0.11				0	0	0			
VI	0.16			270	22	3	0.35	0.41		
VII	0.08			−	0	0	0			
VIII	0.13			−	0	0	0	−		
IX	0.004		0.32	−	0	0	0	−		
X	0.52		0.22						0.6	
Xe									10.5	9.4
XI	0.48		0.10						0.8	
XII	0.52		0.22						11.6	
XIIe										
XIII	0.24		0.12						0.75	
XIIIe									13.2	

a) $\overline{Mn}$ determination by viscosimetry (A, B) or GPC (C)

Table VIII – Labile chlorine atoms per 1000 monomer units

Sample	Phenolysis A	B	C a	C b	Thiophenolysis D	SOCl$_2$ ^{36} B
II	0.9	1.2	1.6	0.9	1.4	0.9
III	2.5	2.5	7.0	5.4	12.0	2.2
IV	1.4	1.6	2.0	1.8	2.5	1.3
V	1.0	1.2	1.9	1.7	3.7	0.6
VI	1.2	0.6	1.4	1.1	0	0.8
VII	1.0	0.6	1.4	1.1	8.1	0.5
VIII	0.9	1.0	1.2	0.7	3.8	0.8
IX	0.8	0.8	1.1	1.0	3.7	1.0
X	1.5	1.3	1.4	1.5	1.0	
XI			1.2	0.9		
XII	1.4	1.0	1.5	1.9	1.6	
XIII	1.0	1.1	1.1	1.6	1.5	

a) washed with water ; b) precipitated

Labile chlorine atoms

Some chemical methods are sensitive to a limited number of chlorine atoms including allylic and tertiary chlorine and possibly other atoms of unknown origin.   These methods are phenolysis, the exchange of chlorine with $SO^{36}Cl_2$, both methods developed by Caraculacu[27,28] and thiophenolysis according to Michel[29].   Results are reported in Table VIII.   The phenolysis method is to be recommended but care must be taken to avoid contamination by free phenol as well as the loss of low molecular weight polymers in the purification treatment.

Head-to-head structures

The method suggested by Shimizu and Ohtsu[30] has been tested in a few samples by one laboratory.   Based on separate investigation of other fractionated polymer, it was considered that the method measures the content of the saturated 1-2 dichloroalcane chain end.[31].

Oxygenated structures

The infrared spectra of all samples show some carbonyl groups (bands between 1715 and 1748 cm^{-1}) which can be assigned to impurities from the initiator, or additives such as phthalic esters used to dissolve the initiator.   The actual presence of oxygen in sample VI does not cause a specific increase of such bands.

Peroxide and hydroperoxide groups can also be detected in the polymer by reaction with potassium iodide in acetic acid, but again, they may correspond to residual initiator more than to specific structures.   The application of Zeppenfeld's[32] method which is claimed to be specific to hydroperoxide has given results between 0.03 (sample IV and VIII) and 0.24/1000 C (sample III).

THERMAL STABILITY

The simplest methods concern dehydrochlorination tests of pure polymer (without stabilizer), either in solution or in the solid state.   They are based on the measurement of the HCl evolved from a sample put in a thermostated cell, under a stream of gas carrying the HCl into a measurement apparatus, most often a conductimeter.   The results are concerned with the initial dehydrochlorination rate (HCl yield less than 0.3%).

The reproducibility of a solid state dehydrochlorination test in the same laboratory has been shown to be quite good.   But, as shown in Table IX there are rather large discrepancies between different laboratories for the same samples;   these discrepancies have to be attributed to small differences between the various tests; morphology of the sample, purity of the gas and the rate of flow of that gas, the cell design and material of construction (avoid any metal pieces), nature and sensitivity of the detector.   The major interest of these tests is that the various laboratories have given the same order of ranking of the samples.   There is obviously a need for standardization.

Some of the difficulties in the solid state test are certainly due to the effect of the morphology of the samples on the diffusion of HCl from the solid polymer under given conditions.   However the situation is worse, because the reproducibility within one laboratory is not as good.   In addition, different laboratories observed different shapes of the dehydrochlorination curve;   initial deceleration and then a constant rate or initial acceleration and then a constant rate.   In spite of these discrepancies, the same order of stability is generally found.   Recently, Bert and Michel[33] have shown that reproducible results can be obtained if the following two conditions are obeyed: temperature lower than 150°C, concentration of the polymer less than 0.1%.   But it must be noted that such conditions involve a drastic purification of the solvent and a very sensitive detector (actually a differential conductimeter[34]).

A large number of experiments have been carried out to assess the thermal stability of PVC in the presence of stabilizers.   They include dehydrochlorination tests, again based upon the measurement of the induction time before dehydrochlorination is observed (time necessary to reach pH = 3.9 or to observe the blue discolouration of congo red paper), or on the measurement of the dehydrochlorination rate after the induction period.   They also include colouring tests such as blackening time in a colour card, or the yellowing index using a colorimeter in static tests.   Finally, other tests have been carried out using either a plastograph, or a capillary rheometer.
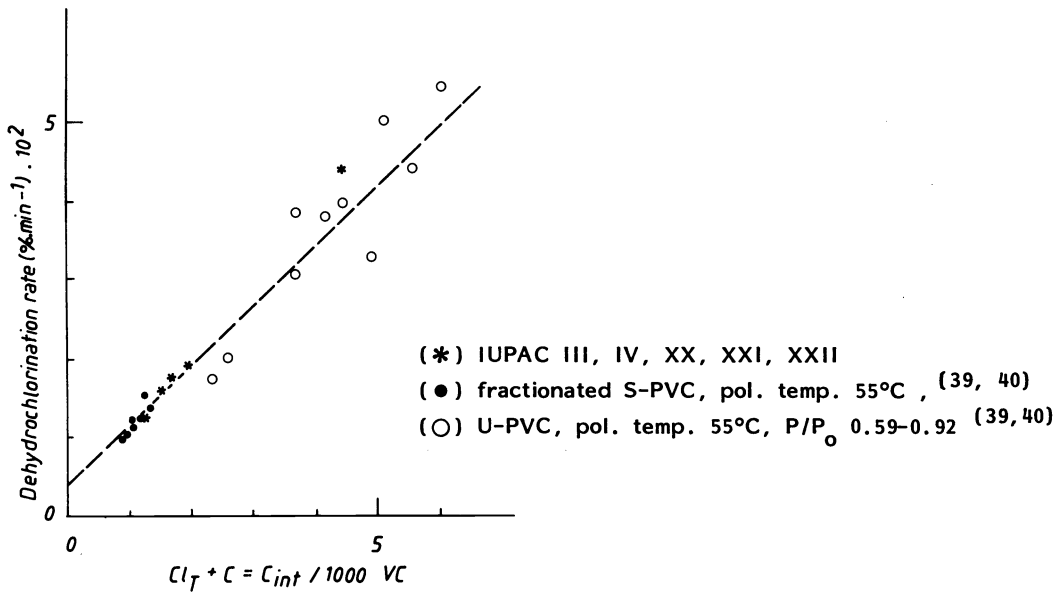
Fig. 1. Dehydrochlorination rate versus tertiary chlorine atoms + internal double bonds

Table IX – Degradation rate in solid state at 180°C, under inert atmosphere HCl $\%.min^{-1}.10^3$

Sample	A	B	C	Sample	A	B	C
I	2.72	3.0	7.3	VIII	5.4	4.9	9
II	6.55	6.5	15.0	IX	5.45	4.7	11.6
III	23.8	22.7	34	X	8.1	8.7	10.1
IV	10.85	8.2	14	XI	6.7	–	5.85
V	8.20	7.1	12.3	XII	7.9	6.42	7.0
VI	8.1	6.9	33	XIII	7.4	5.52	4.57
VII	5.35	4.3	20.6				

Table X – Heat stability of samples processed in the presence of tin thioglycolate (1 phr)

	Sample	V	IX	XII	XIII
	Oven ageing	Blackening time	(min)		
Laboratories	T°C				
A	180	120	150	90	150
A	200	50	60	40	60
B	190	55	110	50	110
	Brabender test	Stability time	(min)		
Laboratories	Load (g)	T°C			
A	30	180	9.5	6.5	< 6	8.5
B	60	180	26	9	9	19.5
–	––	200	12.5	6.5	5	8
–	––	220	7.5	4	3	5
C	64	180	15	10.5	9	11.8
–	––	200	9.5	6.8	6.2	7
D	65	180	12.1	8.5	6	7.7
–	––	200	7.5	6.6	4.3	5.6
Instron Rheometer 180°C		Stability time	(min)		
Laboratory A		23	25	16	35

The interpretation of these results and inter-laboratory comparison are even
more difficult because a number of new parameters have to be considered: the
nature and the amount of stabilizer, the initial processing of the mixture
to prepare the sheets, i.e. the thermal and shear history of the sample
before the tests, the influence of molecular weight upon the melt viscosity
of the polymer, the mechanism of gelation and fusion which will vary
according to the machine used for the test, the lubricant or plasticizing
properties of the stabilizers or other additives of the recipe, the actual
temperature reached during the test (which may be governed by shearing
stresses in dynamic tests), and finally the catalytic properties of the
metal chlorides which are by-products of the stabilizers.

A limited amount of standardization has been obtained using a series of
samples being processed initially by one laboratory and then distributed to
the others.   Then, even if there remain large inter-laboratory discrepan-
cies concerning, for instance, the results of dehydrochlorination or the
blackening time tests, some agreement was obtained concerning the relative
order of stability;   in this respect the same order can be observed between
pure static and capillary rheometer tests (Table X);   however, deviation
from that order is observed in the plastograph test due to shearing and
morphology effects.   But obviously, as in the case of simple dehydro-
chlorination tests, it is necessary to make an effort to standardize the
different kinds of test.

CONCLUSIONS

Although a few attempts have been carried out to correlate structural
defects and degradation rate[35,36], the situation is far from satisfactory
at the moment.   The degradation process is accepted to be a chain process
including initiation, propagation and termination steps.   The mechanism of
the process, whether radical or ionic, remains under discussion and there is
some degree of reversibility.   The structural defects are believed to be
connected mainly with the initiation process, but degradation tests such as
dehydrochlorination rate measurements, are sensitive to the whole process so
that not only do the initiation sites have an influence, but also the
termination sites, the sequence distribution of the configuration [37] and
the conformation as well as the distribution of the defects inside the chain.
Unfortunately, many defect structures from sample to sample are intercorre-
lated due to the nature of the polymerization mechanisms.

However, as suggested recently by Hjertberg[38] a rather good correlation
seems to be obtained between the dehydrochlorination rate in the solid state
and the total amount of internal unsaturation plus the number of tertiary
chlorine atoms, which corresponds to the sum of the number of branches
longer than chloromethyl branches.   As shown in Figure 1 the IUPAC samples
can be included in that correlation, which shows that a few other groups
should be involved in the initiation process.

Recent investigation by the IUPAC group leads to the following estimate of
numbers of defects for a polymer produced under regular conditions
(suspension 55°C), the polymerization being stopped just as the pressure
drop is observed;

Branches per 1000 monomer units: chloromethyl 3.8;   chloro-2-ethyl 0.2;
                                   dichloro-2-4-butyl 0.6;   long branches 0.1.

Unsaturated chain ends:-   - CH = CH - CH_2Cl : 1.1

Total - CH_2Cl groups: 7.1 (branches, saturated and unsaturated chain ends)

However, further work is needed to reach a better agreement between the data
from ^1H and ^{36}C NMR spectra.   Finally, it is believed that future progress
in the analysis of structural defects will come mainly from analysis.

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