Ultraviolet Irradiation of Poly(vinyl Chlorides).
Part I. Effect of Substituents on
Radiation Parameters*

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Synopsis

The crosslinking and main-chain scission of PVC and its derivatives by ultraviolet radiation at 2537 A. were investigated. Examination of the relationship between gel fraction and radiation dose showed that the number of crosslinks formed in pure PVC per 100 e.v., G_c, was 0.29 and did not vary greatly from pure PVC to commercial PVC. However, the efficiency of scission was lowest ($G_s = 0.06$) for purified PVC, increased to 0.23–0.26 for commercial PVC, and increased further when chelates were substituted on PVC at Cl atoms. G_s for PVC with copper thalocyanine was 0.62, with copper salicylate was 1.38, and was 6.20 with ferrocene. G_c values also increased in the same order, from 0.40 to 3.10. The ratio of main-chain fractures to number of crosslinks formed (β/α) increased again in this order from 0.1 for purified PVC to 1.0 for PVC–ferrocene. For purified PVC, β/α increased after 36 hr. of ultraviolet irradiations. In the presence of copper salicylate and ferrocene, ion-radical reactions probably contribute towards the high β/α ratio. Ability of the aromatic substituents to enter chain-transfer reactions with polymeric radicals followed by coupling reactions may contribute partly towards crosslinking in PVC.

INTRODUCTION

Flory[1] and Charlesby[2] have developed theories which permit the evaluation of random crosslinking and main-chain scission in polymers subjected to irradiation. Although the literature on ultraviolet irradiation of poly-(vinyl chloride) (PVC) is extensive, little has been mentioned about the effect of additives on crosslinking and main-chain fracture efficiencies. The object of the present study was to determine these efficiencies in the presence of additives and substituents.

PVC was reacted with chelates such as copper salicylate, ferrocene and copper phthalocyanine, to obtain PVC derivatives with the structure I:

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* The Editors have been informed by Professor Kryszewski that reference to prior work of Mrs. Kwei-Ping Shen Kei and Mr. J. P. Luongo was unintentionally omitted from a communication by M. Kryszewski and M. Mucha that appeared in *J. Polymer Sci. B*, **5**, 1095 (1967) and reported studies similar to those described here. The work of Kwei and Luongo evidently has priority since it was presented at the ACS Meeting in Miami Beach in April 1967 and was further disseminated through *Polymer Preprints*, **8**, 588 (1967).

I
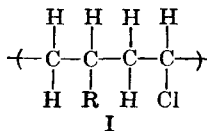
where R may be R_1–R_3.

R_1 R_2 R_3
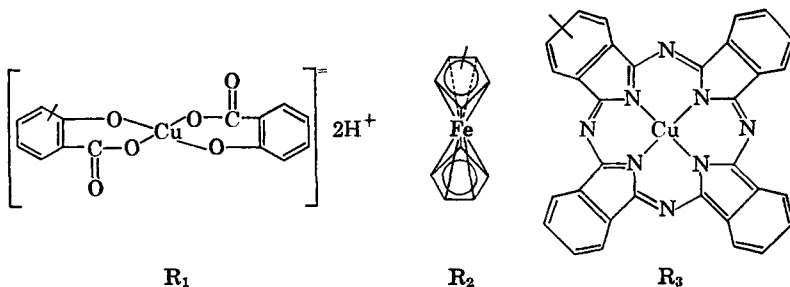
The substitution of R occurred on the rings, but the position of substitution was not determined. The PVC derivatives contained 1.3%, 0.2%, and 6.8% of the chelates of R_1, R_2, and R_3, respectively. These compounds absorb light both in the ultraviolet and the visible regions. Observation of gelation behavior as a function of radiation dose and of original weight-average molecular weight permitted us to calculate the efficiencies of crosslinking and scission.

EXPERIMENTAL

Preparation of PVC and Derivatives

Commercial PVC (Geon 101-EP, B. F. Goodrich) was reprecipitated from tetrahydrofuran solution into a large volume of methanol to remove additives such as surfactants, etc., which were present in the polymer. The purified PVC absorbed light weakly at 280 mμ. The intrinsic viscosity of the polymer in tetrahydrofuran was 1.08 dl./g. at $25 \pm 0.1°C$.

PVC derivatives with copper salicylate and with ferrocene were each prepared by the Friedel-Crafts method with using $AlCl_3$ or $ZnCl_2$ as catalyst. Reaction of PVC with benzene by Friedel-Crafts method has been reported by Teyssié and Smets[3] to vary widely from an extremely slow rate to violent gelation, depending largely on the solvents and the temperatures used. Mild conditions were selected in order to prepare PVC derivatives with low degrees of substitution at the Cl atoms. Copper salicylate was allowed to react with PVC in cyclohexanone for 24 hr. at room temperature; ferrocene was allowed to react with PVC in dichloroethane for 3 hr. at 0°C. The resulting polymers were purified by reprecipitating the tetrahydrofuran solutions three times in eight volumes of methanol and then drying in vacuum at 40°C. overnight. A colorless product was obtained.

The product derived from PVC and copper phthalocyanine was prepared as follows. A film was cast from a suspension of copper phthalo-

cyanine in PVC–tetrahydrofuran solution, then bombarded with excited helium gas for 1 hr. and dissolved to give a 2% solution in tetrahydrofuran. Excess copper phthalocyanine was removed by centrifugation of the solution at 9000 rpm for 1 hr. The polymer was precipitated in methanol, vacuum-dried, and redissolved to give a 1% solution in tetrahydrofuran, which was poured through a Sephadex G-25 column to separate once more trace amounts of unreacted copper phthalocyanine. The first few fractions of green solution were collected and allowed to stand overnight at room temperature. A green polymer separated out from the clear PVC solution. It was found by x-ray fluorescence analysis that the green polymer contained 6.8% of copper phthalocyanine/g. polymer, but that the clear solution contained no copper at all.

Characterization of PVC Derivatives

To determine the extent of reaction of copper salicylate or ferrocene with PVC, an x-ray fluorescence method was used. The fluorescence curves were calibrated by using mixtures of PVC and each chelate in tetrahydrofuran. The PVC derivatives were found to contain 1.3% copper salicylate, 0.2% ferrocene, or 6.8% copper phthalocyanine by weight. Their absorption spectra in the far-ultraviolet and visible region were carried out on a Cary Model 14 spectrophotometer, and showed absorption bands near 665 and 285 mμ. The metal–ligand absorption bands shifted from 700 to 665 mμ when the chelates were attached to PVC.

The absorption of the PVC ferrocene derivative at 665 mμ was very weak. The existence of this derivative was therefore confirmed by turbidity titration[4] at 700 mμ. PVC gave a maximum turbidity with 8.50 ml. of methanol in 10 ml. 0.2% tetrahydrofuran solution, and the ferrocene derivative showed maximum turbidity at 9.25 ml. of methanol. This indicated that a product other than PVC itself was obtained, and also that the product was not a mixture of PVC with ferrocene which would have shown two maxima in turbidity titrations.

Ultraviolet Irradiation of PVC Films

Thin films of PVC and its derivatives, less than 1 mil in thickness, were cast from 10% redistilled tetrahydrofuran solutions. They were air-dried and then vacuum-dried overnight at 40°C. Small pieces were clamped on micro slides and irradiated at a distance of 2 in. from the lamps in a Rayonet chamber reactor in air. The intensity of the light at 2537 A. wavelength and 2 in. apart from the lamps corresponded to an energy dissipation of 5.7 × 10^{16} e.v./sec./g. PVC. The temperature in the chamber was 40 ± 2°C.

Determination of Gel Content

Gel fractions of the irradiated films were determined by weighing films which had been extracted for 30 hr. with tetrahydrofuran and vacuum-

dried at 90°C. to constant weight. The volume of solvent used for extraction was greater than 1600 ml./g. polymer. Before extraction, the films were weighed and wrapped in weighed Dextalose papers (C. H. Dexter Co. Windsor Locks, Conn.) which had also been extracted for 24 hr. and vacuum-dried at 90°C. overnight. The wrapped films were then put in extraction thimbles for extraction. Elaborate precautions against oxidative degradations were considered unnecessary[5] during the low-temperature extraction of crosslinked PVC with tetrahydrofuran.

RESULTS

Weight-Average Molecular Weights

The $\bar{M}_w$ of PVC was calculated from its intrinsic viscosity, which was 1.08 dl./g. at 25 ± 0.01°C. in tetrahydrofuran, by using the equation of Kolinsky et al.[6]

$$[\eta] = 1.91 \times 10^{-4} \bar{M}_w 0.75 \tag{1}$$

$\bar{M}_w$ was calculated to be 83,200. The number-average molecular weight was determined by osmometry to be 29,300. Both $\bar{M}_w$ and $\bar{M}_n$ agree with the values obtained from gel permeation chromatography, which gave the ratio $\bar{M}_w/\bar{M}_n$ as 2.84. Both $\bar{M}_w$ and DP_n were needed in the calculation of crosslinking efficiency. The $\bar{M}_w$ values for PVC derivatives were also corrected to include the substituent groups. These values are listed in Table I.

TABLE I
Radiation Parameters of PVC Irradiated by Ultraviolet in Air at 40°C.

Additive	$\bar{M}_w \times 10^{-4}$	$(DP_n)_0$	β/α	G_c	G_s
Pure PVC	8.32	470	0.10	0.29	0.06
Surfactants					
(Geon 101-EP)	8.32	470	0.62	0.21	0.26
Copper					
phthalocyanine	8.58	470	0.78	0.41	0.62
Copper salicylate	8.43	470	0.96	0.72	1.38
Ferrocene	8.34	470	1.00	3.1	6.2
Darvic[a]	—	800	0.35	0.33	(0.23)[b]
Geon 101[c]	10.30	—	0.28	—	—

[a] Data of Charlesby and Pinner.[5]
[b] Calculated from G_c.
[c] Data of Miller.[7]

Treatment of Gel Content Data

Gel contents were studied as a function of irradiation dose by using Charlesby's theories,[2] which assumed that random molecular weight distribution occurred in the initial polymer, and that both random crosslinking and scission occurred, with each process proportional to the radiant energy dissipation within the polymer. One method of plotting the ex-
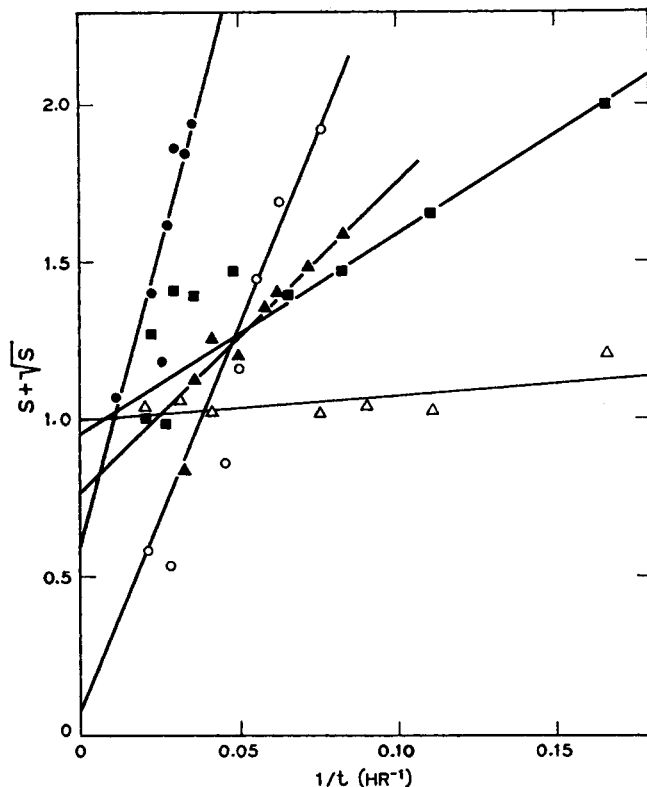
Fig. 1. $(S + \sqrt{S})$ vs. $1/t$ for PVC and PVC derivatives; (O) purified PVC; (●) Geon 101-EP; (■) PVC with copper salicylate; (△) PVC with ferrocene; (▲) PVC–copper phthalocyanine.

perimental data, which was proposed by Charlesby and Pinner,[5] was applied here. The soluble weight fraction, $S = 1 - g$, was related to dosage by

$$S + \sqrt{S} = (\beta/\alpha) + [1/\alpha(\overline{DP}_n)R] \qquad (2)$$

where g is weight fraction gel. The β/α ratio is the ratio between number of main-chain fractures and number of crosslinked units formed. Since the ultraviolet radiation dosage was proportional to the time of irradiation, R could be represented by t. This linear plot has the advantage of giving β/α directly from the intercept plus the fact that α could be obtained from slope and initial number-average degree of polymerization. The plots of $(S + \sqrt{S})$ versus $1/t$ are shown in Figure 1.

The G_c and G_s values for number of crosslinks, and number of main-chain fractures per 100 e.v. were calculated from eqs. (3) and (4), respectively.[7]

$$G_c = \frac{100 \, N}{2 \, \overline{M}_{w_0} R^* [1 - (\beta/2\alpha)]} \qquad (3)$$

$$G_s = (2\beta/\alpha)G_c \qquad (4)$$

Here R^* is the observed incipient gelation dose, N is the Avogadro number, and $\bar{M}_{w_0}$ is the weight-average molecular weight of original polymer. Both G_c and G_s values should be allowed for experimental errors of $\pm 20\%$ or more.

DISCUSSION

Poly(vinyl Chloride)

The G_c, G_s, and β/α values for purified PVC without additives are listed in Table I. Close agreement of $G_c = 0.29$ with other reported values is seen (i.e., 0.33 by Charlesby[5] and 0.28 by Miller[7]), even though $\bar{M}_w$ were slightly different and high energy radiation rather than ultraviolet radiation was used. The gelation behavior of purified PVC fits the straight line with $\beta/\alpha = 0.10$ up to about 36 hr. of irradiation. A slight decrease in the amount of gel is observed upon further irradiation. This indicates that more soluble materials have been produced on prolonged irradiation due to an increase in main-chain scission. Degradative formation of low molecular weight fragments in irradiated poly(1,1-dihydroperfluorobutyl acrylate) has also been reported by Shultz and Bovey.[8]

PVC Derivatives

The effect of the various additives, covalently attached to PVC (at Cl atom) through their aromatic groups, towards the efficiencies of crosslinking and main-chain scission in PVC can be examined in Table I. The G_c values for PVC derivatives with copper phthalocyanine (0.40), and copper salicylate (0.72) are slightly higher than that of purified PVC. Although $\pm 20\%$ experimental uncertainty should be allowed in these values, the aromatic groups appear to increase crosslinking efficiency in PVC. Substitution of ferrocene on PVC, however, gives an unusually high G_c value of 3.1. Its efficiency of main-chain scission is also high, with $G_s = 6.2$ scissions per 100 e.v. The G_s values for other PVC derivatives are all higher than purified PVC ranging from 0.26 in the presence of surfactants to 1.38 for the derivatives. Without additives, PVC manifests a low efficiency for scission for $G_s = 0.06$ only.

A comparison of the β and α values is listed in Table II. It is of interest that purified PVC is relatively resistant to crosslinking and scission under ultraviolet irradiation in air. The aromatic groups which substituted the chlorine atoms on PVC accelerated both crosslinking and scission. The great enhancement of these reactions in the PVC–ferrocene derivative is particularly unique. Its β/α ratio is 1.0. A plausible explanation is that a redox reaction occurs between ferrocene and traces of polymeric peroxides which may exist as intermediates. It is known that ferrocene can be oxidized by chemical reagents to ferricenium ion, $Fe(C_{10}H_{10})^+$;[9] so an ion-radical chain degradation may have occurred in the PVC–ferrocene derivative during ultraviolet irradiation. The dehydrochlorination reaction in

PVC also appears to be accelerated by the presence of ferricenium ion because the polymer turned dark brown at very early stages of UV irradiation. Discoloration in PVC has been interpreted as the formation of polyenic structures[10] by dehydrochlorination. An excess of polyenic structure may then lead to high crosslinking efficiency of PVC. Other PVC samples also showed discoloration but at later stages of irradiation than PVC–ferrocene derivative.

TABLE II
Comparison of β,α Values of PVC and Derivatives

Additive	$\alpha \times (\overline{DP}_n)_0$	$\alpha \times 10^4$	α/α_{ppvc}	$\beta \times 10^4$	β/β_{ppvc}
Pure PVC (ppvc)	0.027	0.58	1	0.06	1
Geon 101-EP	0.027	0.58	1	0.36	6
Copper phthalocyanine	0.102	2.17	4	1.69	29
Copper salicylate	0.158	3.36	6	3.23	56
Ferrocene	0.486	10.35	18	10.35	178
Darvic[a]	0.033	0.41	—	0.14	—
		(0.70)[b]	(1.22)[b]	(0.25)[b]	(4)[b]

[a] Data of Charlesby and Pinner.[5]
[b] If $(\overline{DP}_u)_0$ for Darvic were 470 instead of 800.

Berlin et al.[11] observed rapid reactions between some aromatic compounds and polymeric peroxy radicals of PVC; the resulting product radical, if active, can abstract an atom from PVC to reinitiate the chain radical. Our additives may fulfill the same role. The reinitiated chain radical may then undergo disproportionation leading to C—C rupture, or it may couple with another similar radical. Coupling may also occur between the radicals on the side-chain groups in PVC derivatives. The observed enhancement of crosslinking in PVC derivatives with copper phthalocyanine, copper salicylate, ferrocene, and surfactants, then may be attributed partly to the ability of their aromatic or aliphatic groups to enter chain-transfer reactions with polymeric radicals followed by coupling reactions.

Copper (II) phthalocyanine is known to remain intact when peroxides react with the porphyrin ring.[13] Copper (II) salicylate, however, may dissociate via oxidation to give ion-radical fragments.[14] Ion-radical chain reactions, then, may also play a part in main-chain scission of this PVC derivative under ultraviolet irradiation to give a high β/α ratio of 0.96.

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