Irradiation of Poly(vinyl Chlorides). Part II. Effect of Dynamic Mechanical Properties*

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Synopsis

The dynamic Young moduli of purified PVC and PVC derivatives were measured at room temperature during the course of irradiation by ultraviolet light at 2537 A. wavelength. The PVC derivatives with copper salicylate, ferrocene, or copper phthalocyanine were prepared by Friedel-Crafts reaction as described in the previous paper. The loss tangent decreased monotonically with irradiation time, while the dynamic modulus appeared to pass through a maximum. More pronounced variations in both E and tan δ were observed for the PVC derivatives than for the purified PVC, owing to enhanced crosslinking and scission in the presence of the substituents. The gel permeation chromatograms of irradiated PVC samples have been observed to skew to the left, where low molecular weight material occurs. The decrease in E after long exposure was discussed in terms of molecular polydispersity of the soluble fractions of PVC.

INTRODUCTION

In Part I of this study[1] the crosslinking and the scission of polyvinyl chloride and its derivatives by ultraviolet irradiation were investigated. The derivatives had the structure of
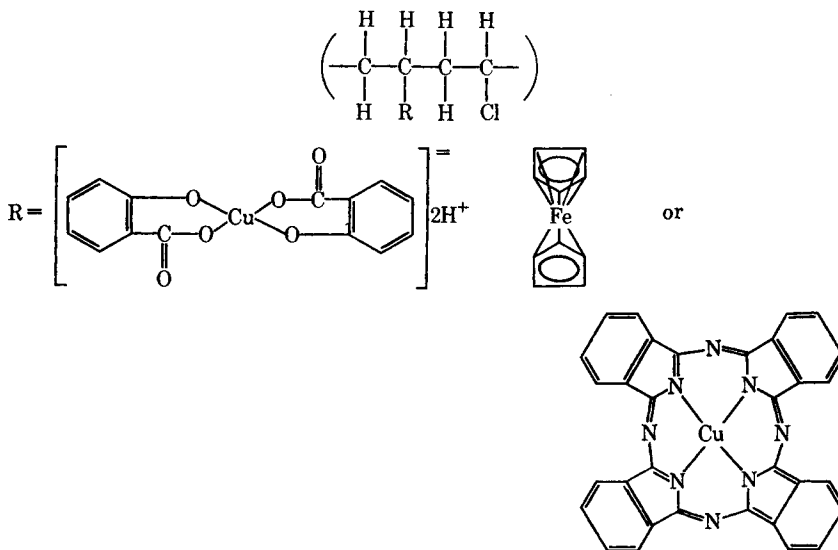
Substitution of R occurred on the rings. This report describes a concurrent study of the dynamic mechanical properties of the irradiated polymers and the dependence of these properties on the molecular weight distribution of the materials.

Experimental

PVC films, less than 1 mil in thickness, were cast from 10% solutions in redistilled tetrahydrofuran on a glass plate, air-dried, and then vacuum-dried at 40°C. overnight. Small pieces of the films were clamped on glass slides and irradiated at 40°C. for various intervals in a Rayonet chamber reactor at a distance of 2 in. from the lamps. The wavelength was 2537 A.

Since Geon 101 EP (B.F. Goodrich Co.) contained additives and surfactants, it was purified by three times precipitating a 2% tetrahydrofuran solution into eight times its volume of methanol. PVC derivatives were prepared as described previously. The intrinsic viscosity of Geon was 1.08 dl./g. in tetrahydrofuran at $25 \pm 0.05°C$.; its $\bar{M}_w$ was calculated to be 83,200 from the equation $[\eta] = 1.91 \times 10^{-4}\bar{M}_w{}^{0.75}$ given by Kolinsky et al.[2] The ratio $\bar{M}_w/\bar{M}_n$ was estimated by gel permeation chromatography to be 2.84.

The dynamic Young moduli E and loss tangents tan δ of irradiated PVC and its derivatives were measured by a Vibron Dynamic Viscoelastometer at room temperature and 110 cps.

Results and Discussion

The dynamic Young modulus E of purified PVC is 2.4×10^{11} dynes/cm.[2] at room temperature. It increases with irradiation time, reaching a maximum of 2.8×10^{10} at about 10 hr. and then decreases to an approximately constant value of 2.0×10^{10} after 20 hr.; see Figure 1. The moduli–dose (time) curves for the other PVC samples are similar to that of the purified PVC; therefore, only the latter will be discussed in detail.

Charlesby has shown in the irradiation of polyethylene,[3-5] which is highly crystalline, that the crosslinking process increases the Young
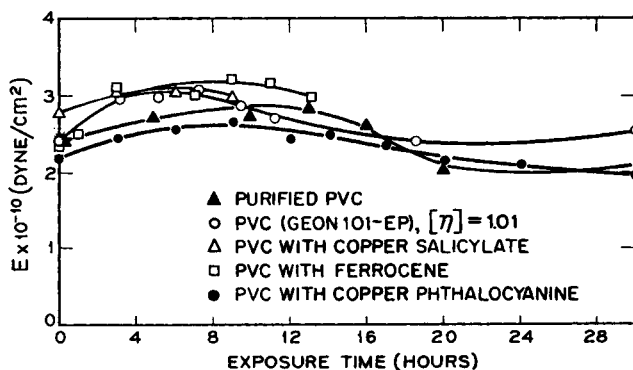

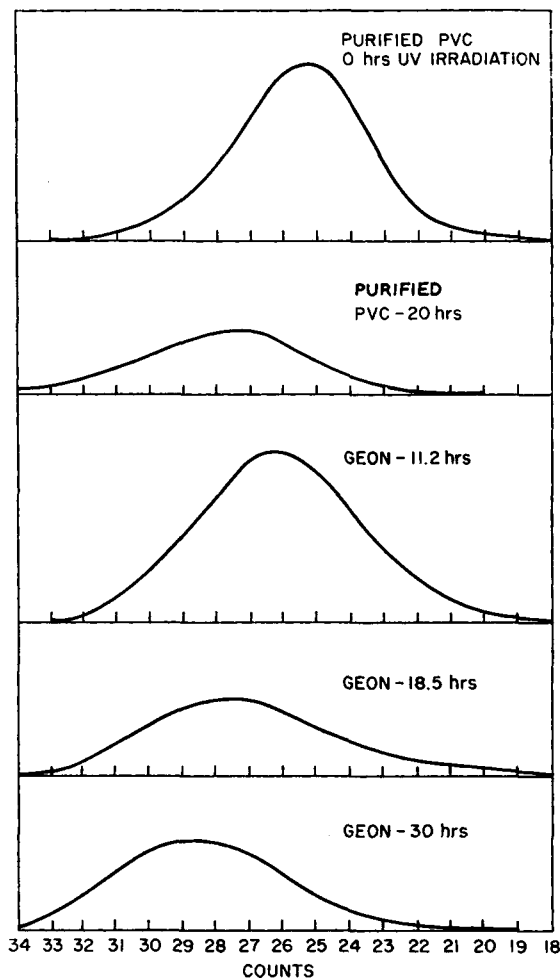Fig. 1. Modulus change of PVC and its derivatives during irradiation.

Fig. 2. Gel permeation chromatograms of purified PVC and Geon 101 EP before and after irradiation.

modulus while the destruction of crystallinity causes it to drop.   In the case of PVC, however, the molecular order is very poor,[6,7] and it is unlikely that the same explanation can be used to account for the decrease in the modulus of PVC.   Instead, we shall attempt to discuss the observed modulus change in terms of the formation of crosslinks compensated by the production of low molecular weight fragments from scission reactions. It is known that molecular polydispersity tends to lower the modulus of a polymer.   Although the study of the effect of polydispersity was carried out mostly for rubbery polymers,[8] a qualitative picture may also be expected for glassy polymers.   We have, therefore, examined the molecular weight distributions of the irradiated samples at different dosages by gel permeation chromatography.   Typical chromatograms are shown in

TABLE I

Molecular Weight Distribution for Soluble Fractions of Ultraviolet-Irradiated PVC

Irradiation time, hr.	$\bar{M}_n$ ($\times 10^{-4}$)	$\bar{M}_w$ ($\times 10^{-5}$)	$\bar{M}_w/\bar{M}_n$
0 (purified PVC)	4.16	1.41	3.40
13.0 (incipient gel.)	2.32	1.70	7.35
20.0 (postgel.)	1.38	0.49	3.53
0 (Geon)	2.93	0.83	2.84
11.2 (pregel.)	4.87	2.29	4.70
13.3 (pregel.)	2.10	2.71	12.90
18.5 (pregel.)	2.63	4.94	18.70
29.9 (postgel.)	1.57	2.00	12.80

Figure 2. Since irradiation produces branched molecules, an accurate calculation of $\bar{M}_n$ or $\bar{M}_w$ of the irradiated polymer from the chromatograms is not expected by this method. For the purpose of comparison we have calculated $\bar{M}_n$ and $\bar{M}_w$ as if all molecules were linear. These values are listed in Table I to give a qualitative indication of the relative polydispersity in PVC samples. The actual $\bar{M}_n/\bar{M}_w$ ratios for the irradiated samples would have been larger as a result of branching.

A detailed mathematical treatment by Charlesby[9] has shown that $\bar{M}_w$ tends to increase to infinity at gel point, while $\bar{M}_n$ reaches a finite value if degradation is neglected. It may be seen from Table I that the ratio $\bar{M}_w/\bar{M}_n$ of purified PVC is about 3.4 (some low molecular weight fractions have been removed from Geon in the precipitating process). When incipient gelation has been reached at 13 hr. of ultraviolet irradiation, the ratio $\bar{M}_w/\bar{M}_n$ increases to 7.35. In the postgelation period (20 hr. of ultraviolet irradiation) both $\bar{M}_w$ and $\bar{M}_n$ of the soluble fractions decrease, since the large molecules have mostly been incorporated into the gel fractions. Although these values are not exact, it is evident that substantial
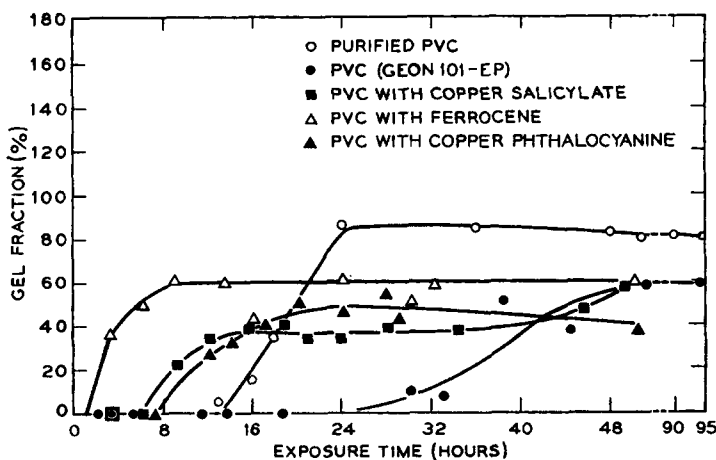

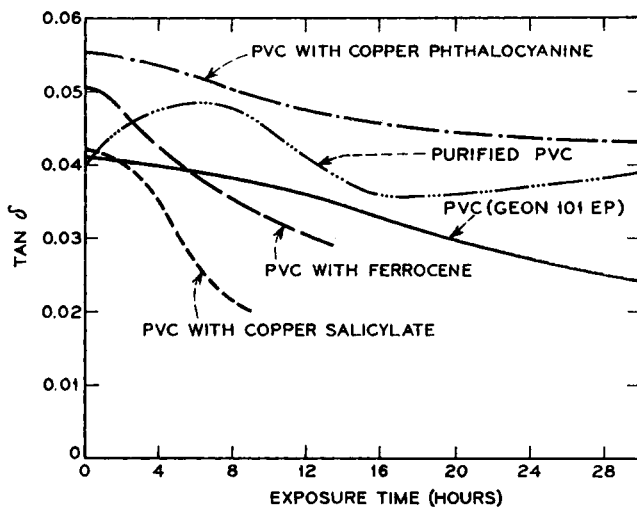Fig. 3. Gelation behavior of PVC and its derivatives during irradiation.

Fig. 4. Loss tangent curves of PVC and its derivatives during irradiation.

quantities of low molecular weight fractions are present in the irradiated samples after incipient gelation has been reached. The gelation behavior of the PVC samples is shown in Figure 3 for comparison.

The molecular weights of irradiated Geon are also shown in Table I. The experimental results are complicated by the fact that surfactants and other additives are present in Geon which may participate in chain-transfer reactions[1] and affect the distribution in molecular weights. Qualitatively, $\bar{M}_w$ increases in the pregelation period, while $\bar{M}_n$ appears to increase first and decrease later, as degradation becomes important. In the postgelation stage the $\bar{M}_w$ of the soluble fraction is still higher than the original value, but the $\bar{M}_n$ is less. The ratio $\bar{M}_w/\bar{M}_n$ increases from 2.8 to as high as 18.7. Geon shows a much larger polydispersity than purified PVC in both pre-gelation and postgelation periods.

We now proceed to discuss the modulus change of purified PVC in terms of crosslinking and scission processes. Prior to gelation the observed increase in modulus may be attributed to the formation of crosslinks in the polymer. The modulus of a polymer in the glassy state, however, shows only a weak dependence on the degree of crosslinking.[10,11] It is, therefore, understandable that only a small increase in the magnitude of E has resulted. At the same time, the presence of low molecular weight fragments produced by chain-scission reactions tends to lower the modulus of the material. A maximum in the modulus–time curve is produced by these two opposing contributions at about 12 hr., which is near the point of incipient gelation at which the number of crosslinks per primary molecule approaches 2. Further irradiation results in a decrease of E, although the gel content continues to increase. It is likely that after incipient gelation the contribution of small molecules derived from scission processes to the

change in E becomes predominant over that of crosslinks. The modulus of the sample remains unchanged with dosage after gel content becomes constant. This indicates a balance between the crosslinking and scission reactions. The effect of substituents on the dynamic mechanical behavior of PVC during irradiation by ultraviolet light may be attributed mostly to the variations in gelation patterns (Fig. 3) that govern the occurrence of maxima in the moduli–dose (time) curves.

Figure 4 shows the loss tangents of PVC and its derivatives with copper phthalocyanine, copper salicylate, and ferrocene during irradiation by ultraviolet light. The mobility of polymer segments has been related to the loss tangent.[11] The reductions in tan δ for the PVC samples can then be ascribed to the decreased mobilities of polymer segments resulting from crosslinking reactions.

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