On the Irradiation of Poly(vinyl chloride)

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Received November 20, 1968

ABSTRACT: Irradiated poly(vinyl chloride) was examined on postirradiation storage by electron spin resonance and ultraviolet-visible absorption spectroscopy. In the absence of reactive additives, a stable concentration of polyenyl free radicals and an increase in the concentration of conjugated double bonds are observed. A radiation-induced radical chain dehydrochlorination is inferred. The presence of reactive additives suppresses the formation of polyenyl radicals and optical absorption.

Free-radical decay and an increase in visible absorption follow the exposure of poly(vinyl chloride) to energetic irradiation.[1] Ultimately, an intensely colored product results. Attempts have been made to relate radical decay and color formation in irradiated poly(vinyl chloride).[2] The process is complicated by the identification of three radical species and conjugated double bond structures (polyenes) containing long sequences of unsaturation.[2,3] It was reported that visible absorption was inversely proportional to the concentration of the long-lived radical species implying that these were related.[2] Electron spin resonance and visible absorption measurements were made following the irradiation and storage of poly(vinyl chloride) under vacuum and in the presence of a scavenger in order to clarify the radiolytic mechanism.

Experimental Section

Poly(vinyl chloride) powder (Opalon-660, Monsanto Chemical Co.) was molded under vacuum at 127° and 5700 psi to produce colorless, transparent films, 4 mils thick. In addition, poly(vinyl chloride) was dissolved in boiling tetrahydrofuran (1 g/30 cc) containing 0.025% butylated hydroxytoluene preservative and the solvent evaporated to yield 2-mil films.

Molded and cast films of poly(vinyl chloride) were placed in Pyrex tubes and evacuated for 6 hr at 10^{-5} mm. Several tubes were opened to air following evacuation. All samples were irradiated at 15° in air or under vacuum in Pyrex tubes with a beam of 1-MeV electrons from a van de Graaff generator at a dose rate of about 4 Mrad/min to a total dose of 8 Mrad.[4] Several of the sealed tubes were opened to air following irradiation.

For electron spin resonance studies, samples were irradiated at one end of 4 mm (o.d.) tubes while the other end was shielded from the electron beam. After irradiation, tubes were inverted and irradiated samples examined in an undamaged portion of the tube.[5] Measurement of ultraviolet and visible absorption was accomplished in flattened Pyrex tubes. Samples were irradiated as previously described in a rounded portion of the tube (8 mm o.d.) and moved to an unirradiated flattened section for absorption studies.

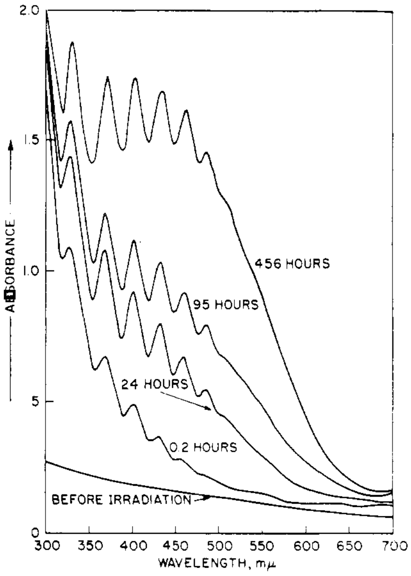

Figure 1. Absorption spectra of irradiated poly(vinyl chloride) following storage under vacuum.

Visible and ultraviolet absorption were recorded at 25° using a Cary 14 spectrophotometer from 700 to 300 mμ on samples set in place and untouched during repeated scans. Ultraviolet absorption spectra of poly(vinyl chloride) films prepared from tetrahydrofuran solution were also examined to 200 mμ.

Electron spin resonance spectra were obtained at 25° for samples in sealed and in open tubes using a Varian spectrometer with 20-db attenuation to avoid saturation effects. During intensity measurements film surfaces were aligned parallel to the magnetic field.

Results and Discussion

A series of absorption peaks between 300 and 700 mμ characterizes the optical density of vacuum molded poly(vinyl chloride) films irradiated and measured under vacuum (Figure 1). The absorption increases under vacuum at 25° and the optical density at 400 mμ is plotted as a function of postirradiation storage time (Figure 2). The most rapid increase occurs in the first few hours after irradiation.

First derivative electron spin resonance spectra of films molded, irradiated and studied under vacuum reveal a symmetric singlet about 25 G wide (Figure 3). Repeated measurements (on five samples) under vacuum, over a time interval similar to the optical absorption data, indicate no change in radical concentration, within experimental error. Average relative peak to

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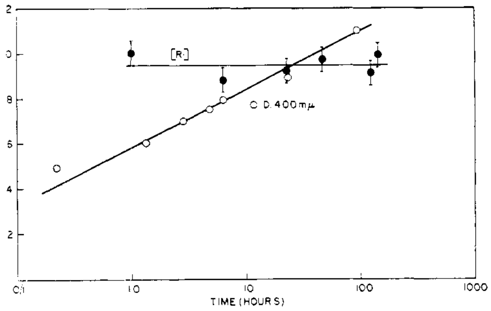

Figure 2. Optical density at 400 mμ and relative radical concentration in irradiated poly(vinyl chloride) following storage under vacuum.

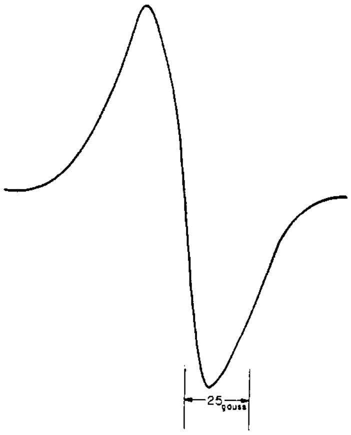

Figure 3. Electron spin resonance spectra of irradiated poly(vinyl chloride).

peak heights on a first derivative electron spin resonance spectrum at several times are appended to Figure 2.

Vacuum molded films of poly(vinyl chloride) exposed to air during or after irradiation produce a similar and increasing optical absorption spectrum which is reduced in intensity. Corresponding electron spin resonance spectra are similar, but decay to about 70 and 5% of the initial intensity after 1 day and 1 week, respectively.

Poly(vinyl chloride) films prepared from tetrahydrofuran solution and irradiated do not indicate any radiation induced optical absorption. Such samples evidence only small (~10% of previous intensities) electron spin resonance absorptions with a different pattern that decay on storage in air or under vacuum. Independent of irradiation, a large ultraviolet absorption is observed at 280 mμ and assigned to the hydroxytoluene additive.

Samples molded, irradiated and observed under vacuum are likely to reflect the intrinsic radiation process most closely. Optical absorption spectra are consistent with the presence of long sequences of conjugated double bond structures that increase in concentration subsequent to irradiation.[2] The examination of long-chain polyenes resulting from dehydrohalogenation of poly(vinyl chloride) in alkaline solution has been reported.[6] For irradiated poly(vinyl chloride) a comparison with model compounds[7,8] led to the conclusion that the double bond chain length approximated 16 conjugated double bonds.[2] Since regular ultraviolet maxima were observed (Figure 1) and the wavelength of the absorption maxima depends on sequence length, it was inferred that a specific polyene is selectively produced.[2] Surprisingly, at all times of post-irradiation storage the absorption maxima appear at the same wavelength but increase in intensity (Figure 1). This suggests that a particular sequence length is formed soon after irradiation and polyene sequences increase in length to this stable value. A more reasonable explanation is that at high enough values of the sequence length, the optical absorption spectra converge.[9] Vinylene unsaturation, dienes and trienes absorb at wavelengths below 300 mμ and are not observed in these studies.[7] A broad band underlying the absorption peaks may be due to the absorption of polyenes with a distribution of sequence lengths.[2] An additional complicating factor is the likelihood that the conjugated structures are polyenyl free radicals, rather than polyenes.

Any mechanism for the post-irradiation color formation under vacuum must preserve the concentration of free radicals (Figure 2). This is in agreement with certain electron spin resonance measurements[1] and contrasts with others.[2,3] In the electron spin resonance studies cited, irradiated poly(vinyl chloride) samples were either exposed to air or transferred in inert atmospheres. It is believed that the trapped radicals are exceedingly sensitive to traces of reactive additives and to chemical inhomogeneities in the polymer chain that may be introduced by molding in air or on subsequent transfer. Therefore, we examined electron spin resonance and optical absorption of samples molded under vacuum and contained in the same evacuated and sealed tubes used for irradiation. The delocalization of the electron associated with a long chain of conjugated unsaturation produces a singlet in electron spin resonance.[10] Alternatively, electron spin resonance spectra due to various polyenes may overlap and yield a broad single peak.[11] The polyenyl radical is very stable under vacuum. In the presence of oxygen, polyenyl free radicals are scavenged and the radical concentration decays.

Energetic irradiation of poly(vinyl chloride) results in carbon–chlorine bond scission to yield polymeric free radicals and chlorine atoms.[1a] Successive dehydrochlorination reactions adjacent to the free radical may generate long chain polyenyl free radicals at constant radical concentration. A free-radical chain dehydrochlorination was suggested to account for the formation of conjugated unsaturation. However, intermediate abstraction by chlorine atoms to yield the unstable polymer radical $-\dot{C}HCH(Cl)-$ was postu-

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lated.[1a,12] Polyenyl free radicals may undergo chain transfer to poly(vinyl chloride) to yield polyenes and polymeric radicals. As the conjugated sequence length of a polyenyl free radical increases, the radical is increasingly stabilized and transfer is less likely.

The effect of a reactive additive present during irradiation is indicated in films prepared from tetrahydrofuran solutions. The presence of a small concentration (0.75 wt %) of hydroxytoluene effectively suppresses conjugated unsaturation on irradiation. This protective effect is also indicated in electron spin resonance spectra in which the singlet associated with polyenyl free radicals is absent.

Conclusions

Electron irradiation of poly(vinyl chloride) induces a radical chain dehydrochlorination reaction, which, under vacuum, yields stable polyenyl free radicals with sequences of conjugated double bonds. Delocalization of the electron in polyenyl free radicals produces a singlet in electron spin resonance. At high enough values of the sequence length, the optical absorption spectra may converge. The presence of reactive additives or chemical inhomogeneities in the polymer chain suppresses the formation of polyenyl radicals and optical absorption.

Acknowledgments. We thank R. F. Westover and W. I. Vroom for vacuum molding of poly(vinyl chloride) films and Dr. F. A. Bovey for stimulating discussions.

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Structural Investigation of Chlorinated Polyethylenes by Pyrolysis–Gas Chromatography

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ABSTRACT: The distributions of chlorinated polyethylenes with various chlorine–carbon ratios were studied by use of direct pyrolysis–gas chromatography. The experimentally obtained results, in which the conception of random terpolymer between ethylene ($-CH_2CH_2-$), vinyl chloride ($-CH_2CHCl$), and 1,2-dichloroethylene ($-CHClCHCl-$) was adopted, were in fairly good agreement with those reported by ir.

Chlorinated polyethylenes (CPE) are formed by a simple chemical substitution reaction of hydrogens in polyethylene (PE) with chlorines. The resultant polymers range widely in properties from elastomers to resins. Some work on the characterization of the polymers has been reported[1,2] by the use of ir. Nambu[1] has interpreted ir data of CPE formed by the CCl_4 solution method at 70° and concluded that $-CH_2CHCl-$ and $-CHClCHCl-$ units are formed, but that the formation of $-CCl_2-$ does not occur during the chlorination of PE up to 68.1 wt % chlorine. Oswald and Kubu[2] have developed the ir investigation of CPE and discussed the concentration of the following three structures, $-CH_2CH_2CH_2-$, $-CH_2CH_2CHCl-$ and $-CHClCH_2CHCl-$, determined from the characteristic absorption bands of the δ (CH_2) mode between 1396 and 1470 cm^{-1}. However, the ir method has some disadvantages in the troublesome preparation of transparent film, KBr disk or solutions in addition to poor resolution of the ir spectra in these regions.

Recently we have characterized the sequence distributions of triads of vinylidene chloride–vinyl chloride copolymers by pyrolysis–gas chromatography (PGC).[3] In the present report a pyrolysis–gas chromatographic study of CPE is presented, and the distributions of chlorine in the chain of the polymers are discussed.

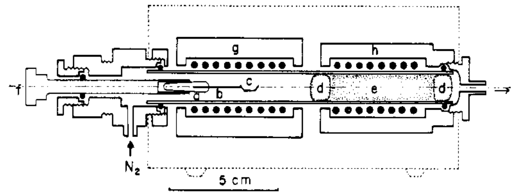

Figure 1. Pyrolyzer: a, glass rod; b, needle; c, sample dish (Ag); d, glass wool; e, NaOH coated on Diasolid H; f, sample charging rod; g, pyrolysis heater; h, precut heater.

Experimental Section

Materials. The series of CPE samples used in this work was obtained by chlorination of low-density PE using the CCl_4 solution method proposed by Campbell and Lyman,[4] and by suspension–chlorination of high-density PE (the latter samples were supplied by Showadenko Co. Ltd.). Chlorine contents of the samples were determined by the usual chemical method and are listed in Table I.

Pyrolysis–Gas Chromatographic Conditions. Figure 1 shows the furnace-type pyrolyzer used in this study. It was directly attached to the inlet port of the Yanagimoto Model GCG-550F gas chromatograph with double flame ionization detectors. The precut column in the pyrolyzer contained 25 wt % NaOH coated on Diasolid H (30–60 mesh) to adsorb hydrogen chloride evolved during the degradation of the polymers.

Samples ranging in size from 0.1 to 0.3 mg were pyrolyzed

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