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CROSS-LINKING OF POLYVINYLIDENE FLUORIDE BY GAMMA RADIATION

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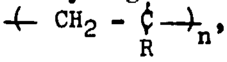
It has been generally observed (1-5) that vinylidene type addition polymers, i.e., 1,1-disubstituted polymers undergo predominantely chain scission on exposure to high energy ionizing radiation. Wall[2] has related this behavior to the heats of polymerization of several addition polymers and has found that in all cases where the heat of polymerization is less than about 16 kilocalories/mol, main chain scission resulted from exposure to high energy ionizing radiation; a low heat of polymerization is associated with high residual steric strain along the chain.

This principle has been found to apply even in those cases where one of the substituents contains a highly effective protective group such as an aromatic ring, e.g., in poly(α-methyl styrene[2]) and polyphenyl methacrylate. Miller, Lawton, and Balwit[3] have concluded that an α-hydrogen atom is necessary for cross-linking since the radical formed,  $\left(\mathrm{CH_2}-\underset{\mathrm{R}}{\dot{\mathrm{C}}}-\right)_n$, would be stabilized by resonance with the R group, whereas the vinylidene group would not form such a radical. Up to now there have been reported no exceptions to the rule that vinylidene type polymers undergo chain scission.

If this behavior is largely due to sterically-induced main chain strain, then there should be very few vinylidene polymers which have both substituents sufficiently small to eliminate the main chain strain. Calculations for vinyl type polymers show that the unstrained polymer can exist as a coplanar zig-zag chain only when the substituent is the size of the OH group or smaller; chains with pendant groups larger than OH, e.g., CH_3, would be required to coil in order to reduce the interaction of substituents. Since fluorine has a covalent radius of .64Å, it meets these requirements, and hence one might expect that polyvinylidene fluoride would have steric strain reduced to such a level as to contribute little to radiation-induced main chain rupture.

Furthermore, the heat of polymerization of polyvinylidene fluoride is 41.2 kilocalories/mol[3a], which is considerably larger than many polymers known to cross-link.[2] A series of experiments was conducted with the object of determining the effect of high energy ionizing radiation on polyvinylidene fluoride.

EXPERIMENTAL

Ten-gram tensile specimens cut from 1-mil polyvinylidene fluoride film (Pennsalt Chemicals Corp.) were placed in Pyrex tubes and degassed for 3 days at 50°C and 10^{-6} Torr. After degassing the tubes were sealed at 10^{-6} Torr and irradiated in a Cobalt-60 Gammacell-220 irradiation facility. The dose rate was 1.5 Mrad/hr. and the temperature of irradiation was 47°C.

Following irradiation the sealed samples were annealed at 85°C for 16 hours. Intrinsic viscosity measurements were made on .3 to 1.% solutions in dimethyl acetamide at 25°C using Ubbelohde viscosimeters. Gel determinations were made by extracting the irradiated polymer for 16 hours at 90°C. Following extraction, aliquot portions of the solution were vacuum dried at 80°C to constant weight, and the percent gel was determined from the weight of the residue.

In the interest of safety, it should be noted that exposure to polyvinylidene fluoride and other fluorocarbon polymers to high doses of radiation produces high pressures (10 to 100 atmospheres), because of the generation of HF, among other gases. Because of weakening of the Pyrex tubes by the HF, in addition to the high pressure generated, violet explosions have been noted when sealed tubes containing about 30 grams of the polymer received in excess of 5,000 MR of gamma radiation. It is recommended that irradiated polyvinylidene fluoride samples in sealed tubes be handled with face and hand protection and that samples not receive more than 1,000 MR unless special safety precautions are followed to releave excess pressure.

RESULTS AND DISCUSSION

Results of the measurement of tensile properties are shown in Table 1 and in Figure 1.

Table 1

TENSILE PROPERTIES AS A FUNCTION OF GAMMA DOSE
FOR POLYVINYLIDENE FLUORIDE

Dose	Yield Strength, psi	Tensile Strength, psi	Tangent Modulus, psi	Elongation, percent
Control	4,200	6,600	21.4×10^4	13
93.0	5,500	8,900	26.3	10
184	4,900	7,600	24.0	9
587	4,400	6,000	21.8	8
966	4,000	5,800	20.8	7

Figure 1 reveals that there is an initial increase in tensile strength as the polymer is irradiated, a behavior typical of polymers which undergo cross-linking; similar behavior was noted for electron radiation by Timmerman and Greyson.[6] After this rise, the curve levels off at a tensile strength of about 85% of its original value, where it remains constant out to doses as high as 1,000 MR. As shown by the other curve in Figure 1, the elongation starts decreasing from the beginning, as the polymer chains are bonded together into a more coherent structure which is less extensible.

The solubility behavior as a function of dose is shown in Table 2 and Figure 2. Even at a dose as low as 2MR, solubility is only 74% (26% gel), and the solubility falls rapidly until it is only 4% after a dose of 590 MR.

This solubility behavior, indicating cross-linking, is consistent with the tensile strength and elongation behavior already discussed. As the radiation bonds the polymer chains together into a three-dimensional network, the tensile strength naturally increases because there are more bonds to be broken, but the simultaneous limitation of movement of the chain segments results in a decrease in elongation.

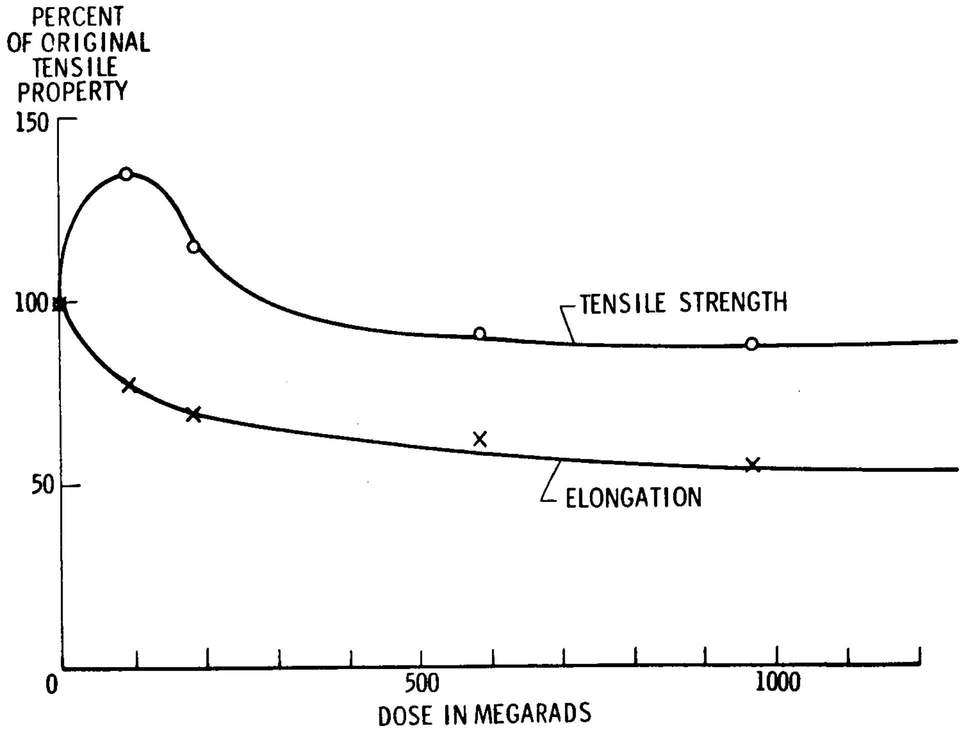


Figure 1. - Tensile properties as a function of gamma dose for polyvinylidene fluoride.

Table 2

SOLUBILITY OF POLYVINYLIDENE FLUORIDE IN DMAC

Sample Number	Dose, MR	Solubility, %	$[\eta]$ dl/g.
Control	0	98.8	1.20
1	.46	86.6	.65
	.46	86.7	.67
2	1.83	73.8	---
	1.83	74.4	
3	4.58	47.8	---
	4.58	49.2	
4	10.0	29.6	
	10.0	30.4	
5	22.8	20.5	
	22.8	21.5	
6	42.3	16.2	
	42.3	15.0	
7	67.6	13.8	
	67.6	14.1	
8	93.0	11.4	
	93.0	12.8	
9	184	9.4	
10	587	4.0	
11	966	2.0	

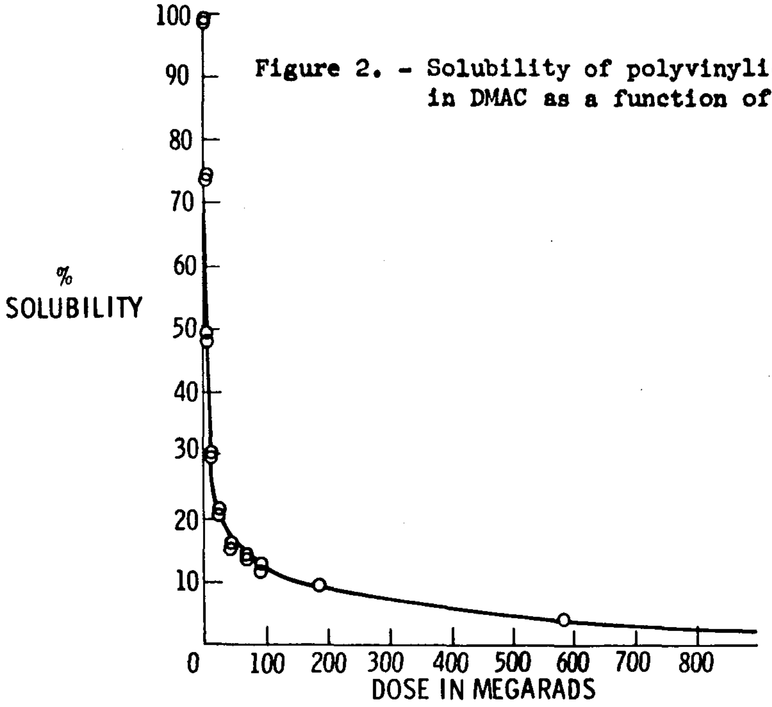


Figure 2. - Solubility of polyvinylidene fluoride in DMAC as a function of dose.

Figure 3 shows a plot of $S + \sqrt{S}$ against $1/R$[1], where S is the fraction of the irradiated polymer soluble in dimethylacetamide and R is the dose in megarads. Extrapolation of the curve to $1/R = 0$ gives the value of .47 for p_o/q_o, the ratio of degradation to cross-linking.

The atypical response of polyvinylidene fluoride to radiation, namely cross-linking instead of the expected chain scission, is associated with the small size of the fluorine atom. Whereas analogous polymers such as polyvinylidene chloride[7] on irradiation undergo chain cleavage because the crowding together of the large chlorine atoms produces strain, the small fluorine groups are not crowded, produce no strain, and hence cross-linking occurs instead of chain rupture.

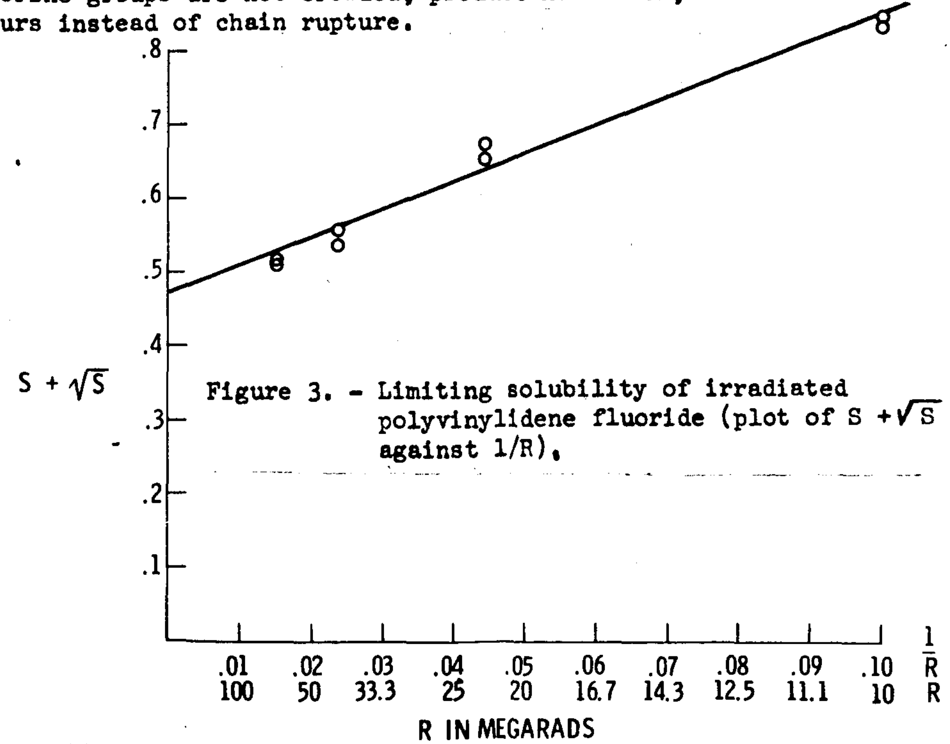


Figure 3. - Limiting solubility of irradiated polyvinylidene fluoride (plot of $S + \sqrt{S}$ against $1/R$).

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