

Identification of the Active Species in the Suppression of Postirradiation Conductivity in Polystyrene Films for Dosimeter Application*

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Synopsis

The resistivity of insulating materials for electrostatic, ion chamber dosimeters must be very high and must remain so after exposure to ionizing radiation. Low dielectric polarization and good fabrication characteristics make hydrocarbon polymers most suitable, but both the conductivity during irradiation and its decay afterward vary greatly even for the same type of polymer, probably depending on impurities. Amorphous, styrene-based polymers and copolymers polymerized in aqueous emulsion and initiated with $K_2S_2O_8$ were found to have much more rapid decay of conductivity after irradiation than pure polystyrene or other nonpolar polymers. The synthesis method incorporates sulfate groups on the polymer chain ends and leaves emulsifier residues distributed throughout the polymer as was demonstrated by various analytical procedures. To identify the trapping species a synthesis program was carried out varying selected ingredients in the polymerization recipe. It was found that the postirradiation conductivity was not dependent on the chemical nature of the emulsifier residues. On the other hand, the decay time of conductivity after irradiation did depend on the polar groups incorporated in the polymer chain. It was concluded that effective charge carrier traps were constituted of a polar second phase highly dispersed through the polymer by association with polar groups incorporated on the polymer chain.

INTRODUCTION

It has been known for some time that the electrical conductivity induced by radiation in different samples of the same polymer can vary widely, both in magnitude and duration.¹⁻³ Although it is apparent that these variations must be caused by impurities or structural differences, very little is known about the characteristics or identity of the entities which determine the electrical properties during and after irradiation. In the interpretation of Fowler,¹ both the magnitude and decay of the induced conductivity were controlled by the distribution of carrier traps, but in our study reported herein, the decay alone was emphasized since this property was of paramount importance in the application toward which this effort was directed—insulation for radiation dosimeters. Hopefully, our characterization of the species determining decay will be relevant also to the behavior of the conductivity during irradiation.

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EXPERIMENTAL RESULTS

The experimental methods and apparatus for the preparation of samples, the irradiation with gamma radiation, and the measurement of conductivity have been described in detail elsewhere.^{4,5} (Applied fields were 4000 V/mm.) The apparent conductivities of some common polymers before and after irradiation are shown in Figures 1 and 2 and tabulated at convenient times after application of voltage or irradiation in Table I. In these high-resistivity materials, dielectric charging persists for many hours, periods comparable to the duration of postirradiation conductivity. Consequently, the dielectric charging was treated as apparent conductivity and no measurement of the unirradiated, equilibrium conductivity was made. The postirradiation conductivity was demonstrated to be electronic (i.e., by electrons or holes) by various techniques (e.g., reversal of polarity, short circuit discharge currents, repeated irradiation and measurement, etc.).^{4,5}

It is apparent from Figure 2 that the styrene- α -methylstyrene copolymer, MRC 250B, is unique in having postirradiation conductivity lower than the other polymers by a factor of 4 or 5. This is a copolymer of about 36 wt-% α -methylstyrene polymerized in aqueous emulsion with alkylaryl sulfonate and initiated with $K_2S_2O_8$. Fractional precipitation and chemical and infrared analyses demonstrated that there were sulfate groups on the chain ends and emulsifier residues in all fractions. Testing of the fractions gave similar electrical prop-

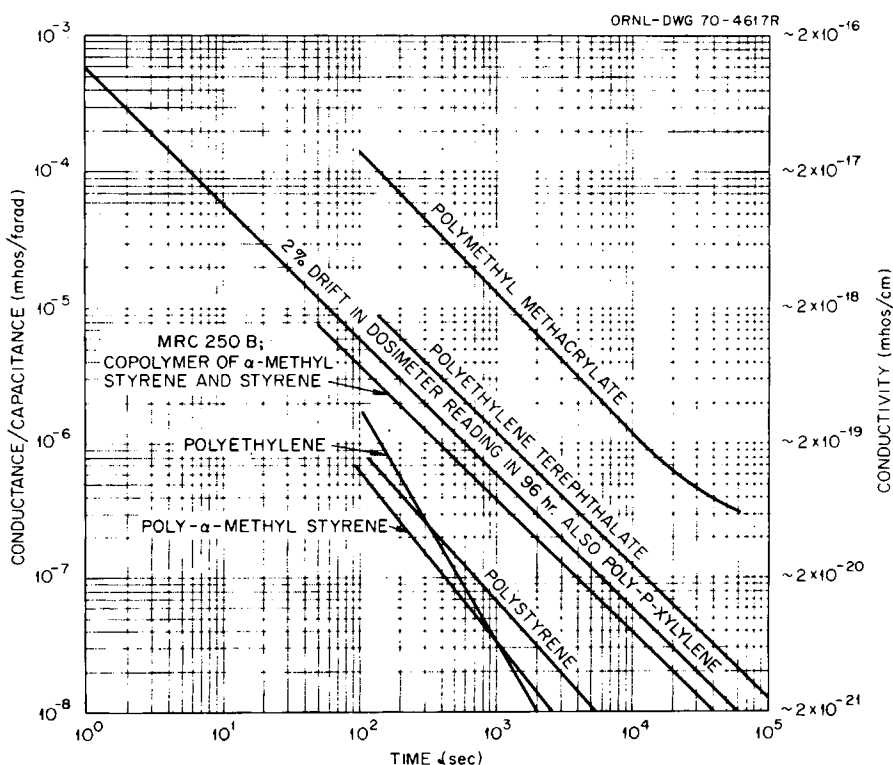


Fig. 1. Apparent conductivities of several common polymeric materials, unirradiated. Drift line represents tolerable leakage in components for radiation dosimeters. It is indicated here as a comparison criterion.

TABLE I
Conductance/Capacitance Ratios of Typical Plastics Before and After Irradiation^a

Specimen	Before irradiation,		After irradiation, ^b		Radiation dose, 10 ³ rad
	mho/F × 10 ⁷		mho/F × 10 ⁷		
	10 ² sec ^c	10 ⁴ sec ^c	10 ³ sec ^d	10 ⁵ sec ^d	
Polyethylene	20	<<0.1	2000	~60	1.8
Polystyrene (pure)	9	<0.1	100	~7	1.8
Poly(α-methylstyrene)	6	<0.1	500	~2	20.0
Styrene-α-methylstyrene	40	0.4	30	0.15	2.0
			150	1.5	20.0
Polycarbonate (Lexan)	100	1.0	40	3	2.0
Poly(ethylene terephthalate)	100	1.0	<100	<1	1.8
Poly(methyl methacrylate)	1000	10.0	<700	~30	20.0
Poly(vinylidene fluoride)	7000	400	too high for irradiation		
Poly(phenylene oxide)	<50	<10	20	8	1.8
Polypropylene			similar to polyethylene		
Poly(methylpentene-1)			similar to polyethylene		
Chlorotrifluoroethylene (KelF)	—	1.0	1000	—	2.0

^a To convert to (ohm-cm)⁻¹ multiply by $\sim 2 \times 10^{-13}$.

^b Electrification began ~ 300 sec after irradiation ceased.

^c Time after electrification.

^d Time after irradiation.

erties, before and after irradiation. Styrene homopolymers polymerized under the same conditions had electrical properties similar to those of the copolymer, both before and after irradiation. Thus, it was demonstrated that the suppression of postirradiation conductivity was neither a function of molecular configuration, nor of copolymer molecular structure.

A synthesis program was carried out to explore the dependence of postirradiation conductivity on polar endgroups and emulsifier residues in the polymer. There was little or no dependence on the nature of the alkali cation for Na⁺, K⁺, and NH₄⁺ ions. Similarly, polystyrenes polymerized in emulsions with aliphatic emulsifiers showed electrical properties no different from those prepared with alkylaryl sulfonate surfactants. Polystyrenes were also prepared by emulsion polymerization using both aliphatic and aromatic emulsifiers and initiated with H₂O₂ to give —OH endgroups. Again, the electrical properties of these polymers were not significantly different from those initiated with K₂S₂O₈ in alkylaryl sulfonate emulsions (Table II).

Since it was evident that polar groups were an essential feature of the electrically active entity, styrene copolymers were prepared with methacrylic acid and maleic anhydride in mass polymerization initiating with ditertiary butyl peroxide to give nonpolar endgroups. The composition of these copolymers ranged up to 1 wt.-% comonomer to encompass the concentration of sulfate end groups in the K₂S₂O₈-initiated polymers. Rather than displaying the rapid decay of postirradiation conductivity characteristic of the emulsion polymers, these copolymers showed long-lived radiation-induced conductivity similar to that of high-purity polystyrene (Table II and Fig. 3).

The effect of detergent or surfactant alone was studied by polymerizing styrene in an aqueous emulsion prepared with alkylaryl sulfonate but thermally initiated to avoid polar groups on the polymer chain itself. These polystyrenes had the

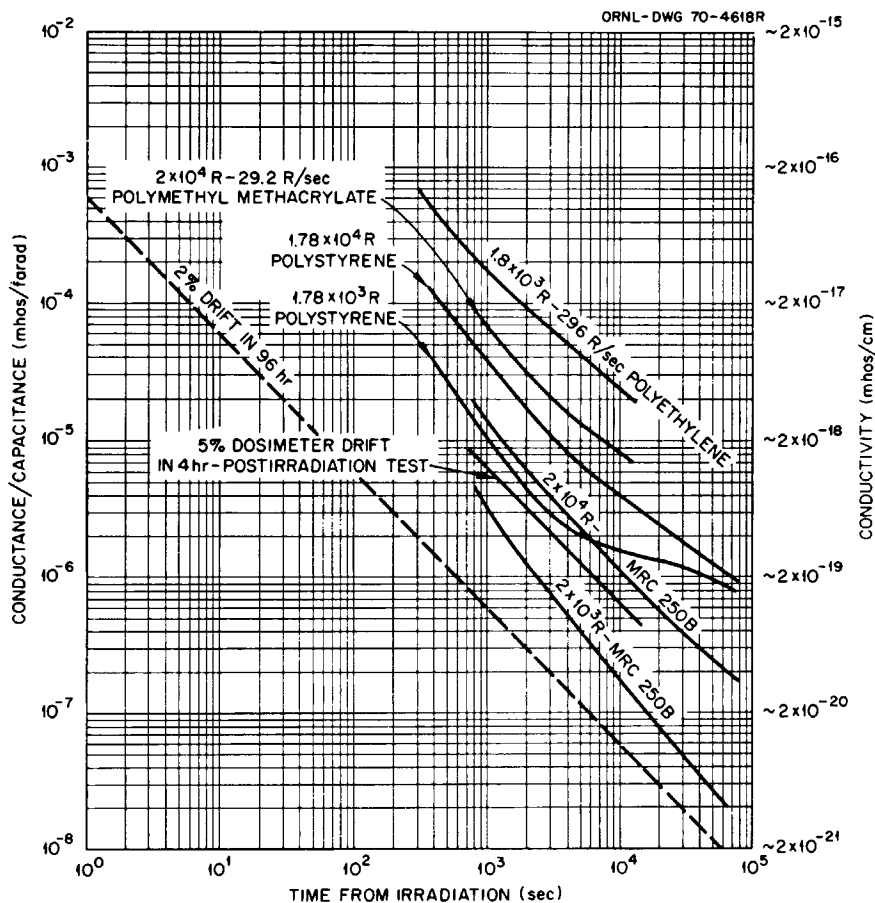


Fig. 2. Apparent conductivities of some polymeric materials after irradiation.

long-lived radiation-induced conductivity of high-purity, mass-polymerized polystyrene.

The evidence for hole or electron conduction suggested that the rapid decay of radiation-induced conductivity was a result of either charge-carrier recombination or trapping in deep traps. For the purposes of this study we refer to both processes as "trapping," recognizing that the active entity could be a recombination center rather than a conventional trap for carriers of a single polarity. Polar groups such as C=O are known to be electron traps in hydrocarbons,⁶ but the failure of the maleic and methacrylic copolymers to demonstrate conductivity suppression indicates that a minimum size or a degree of physical inhomogeneity is required. The absence of suppression in the emulsion-polymerized, thermally initiated polymer probably was due to inadequate dispersal of surfactant residues through the matrix of the relatively nonpolar polystyrene.

To increase the size of polar entities in the polymers and to ensure a high degree of dispersion, benzene solutions of the methacrylic and maleic copolymers were refluxed in water containing sufficient KOH to neutralize the acid groups or in water containing both KOH and alkylbenzene sulfonate at a concentration similar to that of an emulsion polymerization recipe.⁷ Specimens of the co-

TABLE II
Conductance/Capacitance Ratios^a of Specially Synthesized Polystyrenes

Type polymer	Polymerization medium	Polar groups	Treatment	Before irradiation, $\frac{\text{mho/F} \times 10^8}{10^3 \text{ sec}^b}$	Irradiated 2000 rad, $\frac{\text{mho/F} \times 10^8}{10^3 \text{ sec}^c}$
High purity	mass	none	none	10	1500
Persulfate	emulsion	—SO ₄ K	none	40	300
Hydrogen peroxide	emulsion	—OH	none	40	450
Methacrylic copolymer	mass	—CO ₂ H	none	90	2200
Maleic copolymer	mass	=C ₂ O ₃	none	4	600
Methacrylic copolymer	mass	—CO ₂ K	H ₂ O, KOH	100	700
Maleic copolymer	mass	—CO ₂ K	H ₂ O, KOH	210	84

^a To convert to (ohm-cm)⁻¹, multiply by $\sim 2 \times 10^{-13}$.

^b Time after electrification.

^c Time after irradiation.

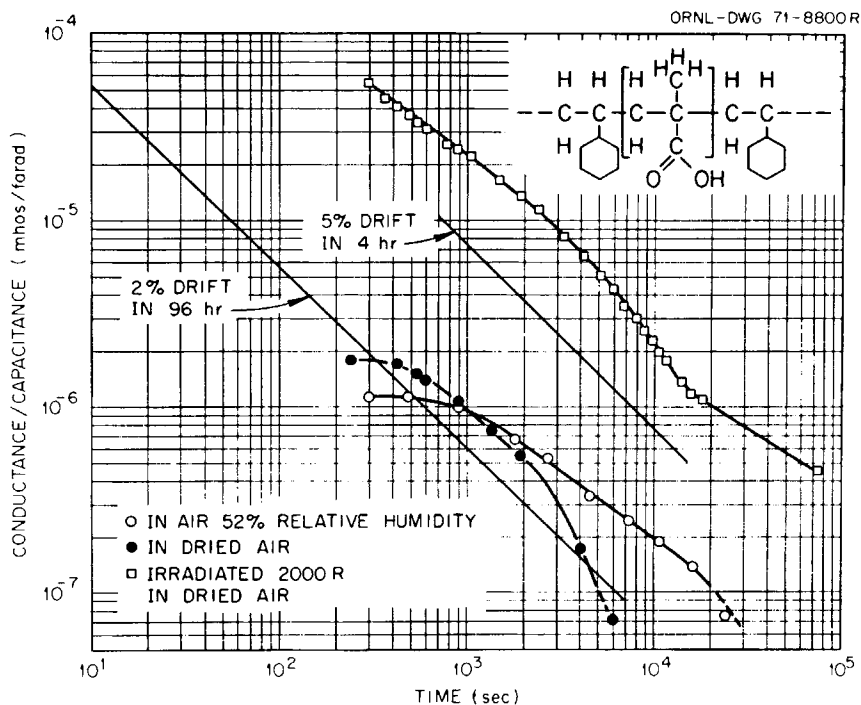


Fig. 3. Apparent conductivity of styrene-methacrylic acid copolymer (1.0 wt-%). Mass polymerized, dibutyl peroxide.

polymers treated in this manner were observed to undergo rapid decay of radiation-induced conductivity similar to the $\text{K}_2\text{S}_2\text{O}_8$ -initiated emulsion polystyrenes (Table II and Fig. 4).

It is evident then that effective trapping requires several features: (a) strongly

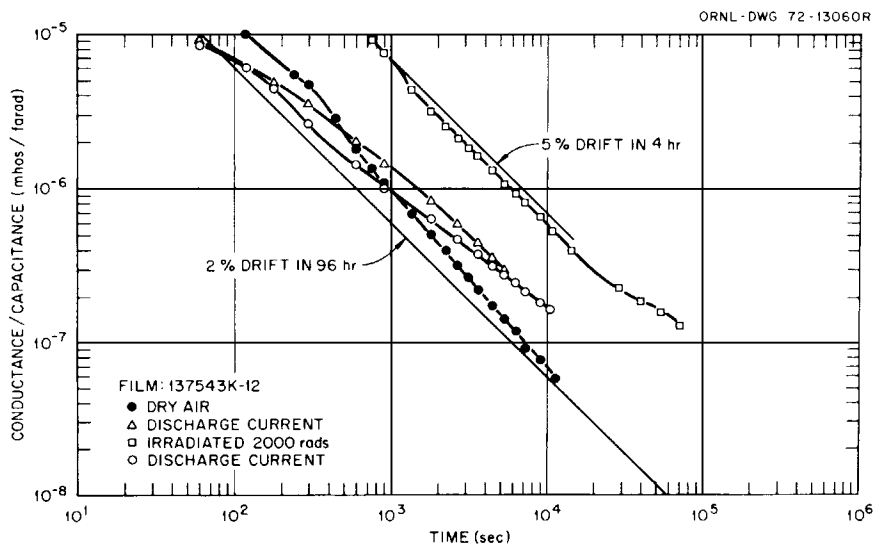


Fig. 4. Apparent conductivity of styrene-methacrylic acid copolymer. Neutralized, KOH, emulsified, H_2O .

polar groups; (b) a minimum volume or aggregation, probably of sufficient size as to constitute a second phase; (c) a high degree of dispersion, practically achievable only by incorporation of polar groups on the polymer chain itself.

Keyser and Williams⁸ noted that a discontinuity in the matrix, probably chain ends, serves as an electron trap in crystalline linear and branched alkane polymers. Partridge⁹ cites evidence for traps at the boundary of the crystalline phase in polyethylene, although the sharpness of this boundary has been under debate for some time. We conclude that the trap or recombination center in the styrene polymers of this investigation is an aggregation of water and surfactant molecules probably of such volume as to constitute an insoluble second phase, associated with polar groups incorporated on the polymer chain itself.

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