Pulsed Radiolysis of Model Aromatic Polymers and Epoxy Based Matrix Materials

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Abstract - Models of primary processes leading to deactivation of energy deposited by a pulse of high energy electrons have been derived for epoxy matrix materials and poly[1-vinyl naphthalene]. The basic conclusion is that recombination of initially formed charged states is complete within 1 nanosecond, and subsequent degradation chemistry is controlled by the reactivity of these excited states. Excited states in both systems form complexes with ground state molecules. These excimers or exciplexes have their characteristic emissive and absorptive properties and may decay to form separated pairs of ground state molecules, cross over to the triplet manifold or emit fluorescence. ESR studies and chemical analyses subsequent to pulse radiolysis have been performed in order to estimate bond cleavage probabilities and net reaction rates. The energy deactivation models which have been proposed to interpret these data have led to the development of radiation stabilization criteria for these systems.

Introduction - Reliable prediction of chemical and mechanical stability of large space structures over periods of up to thirty years requires that a fundamental understanding of damage mechanisms be built into models for prediction of long term damage for each candidate material and the corresponding system. Methodology of predictive model development involves adoption of a dual approach in which engineering testing on hardware is complemented by mechanistic modeling of the effect of radiation stresses on the materials and subsequent validation of these models by means of accelerated tests. This material science approach allows better definition of engineering tests and test facilities and may also be used to interpret engineering test data in terms of changes in chemical structure of the material causing a specific failure mode. Development of mechanistic models requires an understanding of the primary processes which occur on impact of the energetic species (in our work, 600-KeV electrons) on the material. These primary processes control the subsequent cascade of energy deactivation paths some of which involve bond cleavage and consequent chemical change. Primary processes can be inferred from an investigation of the net chemical change; however, it is necessary to use time resolved techniques in order to directly observe them and study their mechanisms. In this work, the excitation source is a nanosecond pulsed electron beam, which allows time resolution down to 1-2 nsec. Time and spectrally resolved fluorescence and transient absorption have been recorded on a model aromatic-polymer poly[1-vinyl naphthalene] and a typical epoxy matrix material, namely the tetraglycidyl 4,4'-diaminodiphenyl methane-diaminodiphyenyl sulfone (TGDDM-DDS) system. Chemical analysis has been performed on P1VN subsequent to pulsed excitation and ESR studies have been performed on the epoxy resin as a function of curing and the number of beam pulses incident on the
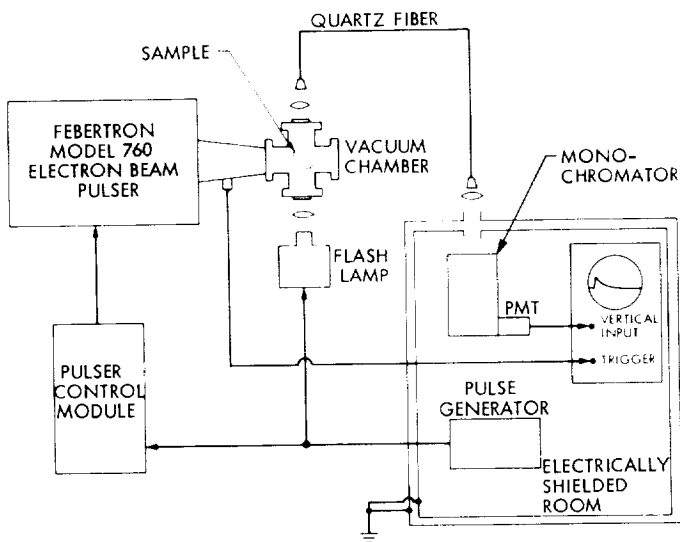
Fig. 1.   Schematic diagram of JPL
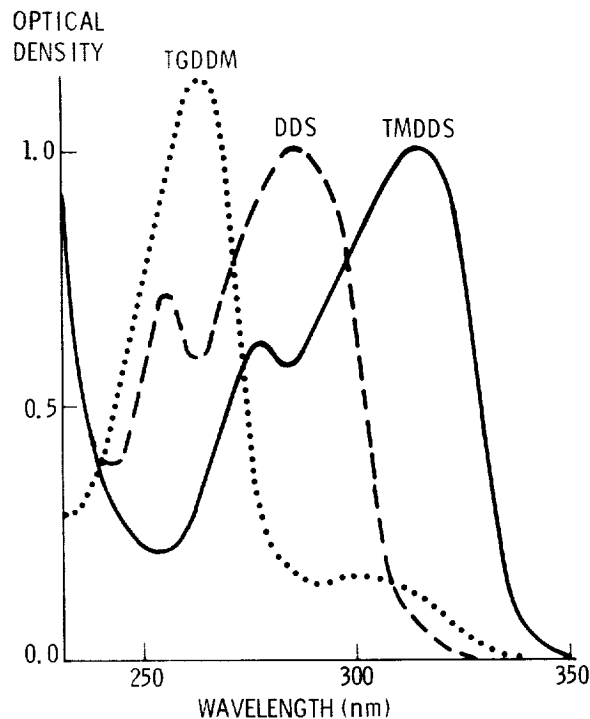   pulse radiolysis laboratory.

Fig. 2.   UV absorption spectra of
           TGDDM (.013g/1), DDS (.013g/1)
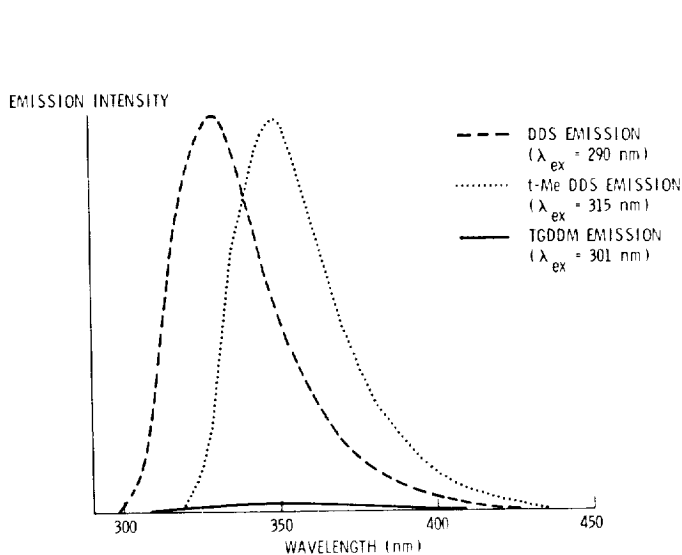   and TMDDS (.011g/1) in CH_2Cl_2.

Fig. 3a.   Photoexcited emission spectra
           of TGDDM (.013g/1), DDS
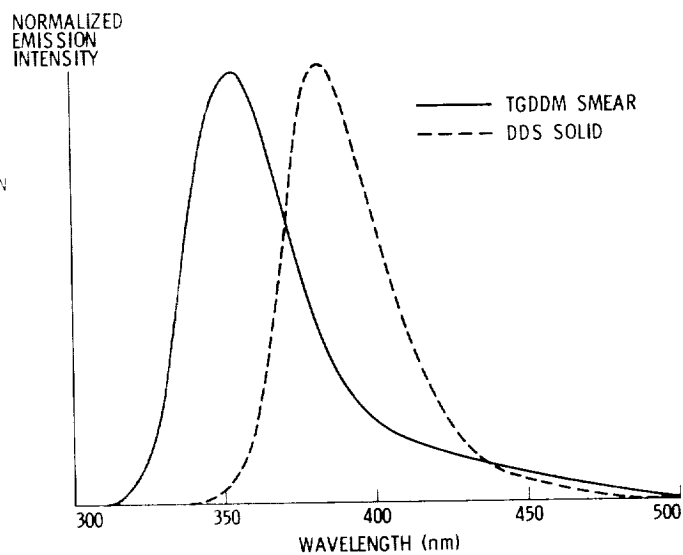   (.013g/1) and TMDDS (.011g/1)
           in CH_2Cl_2.

Fig. 3b.   Photoexcited emission spectra
           of TGDDM smear (λex = 301 nm)
           and solid DDS (λex = 290 nm).

material. In this paper, we report the status of degradation modeling on the epoxy system. An account of the work on P1VN has been published and will not be discussed here.

Experimental Methods and Results - The source of excitation is a Febertron (Hewlett-Packard) which generates 3-ns pulses (FWHM) of 600-KeV electrons with approximately 10 joules per pulse. Solid samples were placed in an evacuated sample chamber. Fluorescence was collected by a quartz lens and was transmitted via a fiber optics assembly to a 1/4-m monochromator. The spectrally resolved emission was then monitored by a 1P-28 phototube, the output of which was displayed on a Tektronix fast-rise scope. Transient absorption measurements were carried out by using a xenon flash lamp (2-μs pulses) as a probe beam incident on the sample approximately 20° to the e-beam. After passing through the e-beam excited volume, the probe beam was collected and transmitted via the fiber optics assembly, spectrally resolved and analyzed as before. Figure 1 shows the experimental set up. Pure (neat) samples of TGDDM, DDS, their mixtures, and cured specimens were studied by this technique. DDS was exhaustively methylated to form NN'tetramethyl diaminodiphenyl sulfone (TMDDS). A recrystallized sample of TMDDS was characterized by IR and NMR spectroscopy and also by elemental analysis. TMDDS may be used as a model for DDS after it has became part of the fully cross-linked network. Under actual conditions a more realistic model will be some weighted statistical mixture of TMDDS, Tri-M DDS and DMDDS, when Tri-M DDS and DMDDS are the trimethylated and dimethylated analogs of TMDDS. Synthesis of these model compound is in progress. To obtain cured specimens, mixtures of TGDDM and DDS in appropriate mole ratios were heated in a vacuum oven at 175°C for five hours, and pumped overnight to remove any volatile matter. Optically excited fluorescence spectra of these samples were recorded on a Perkin-Elmer MPF-3A spectrofluorimeter.

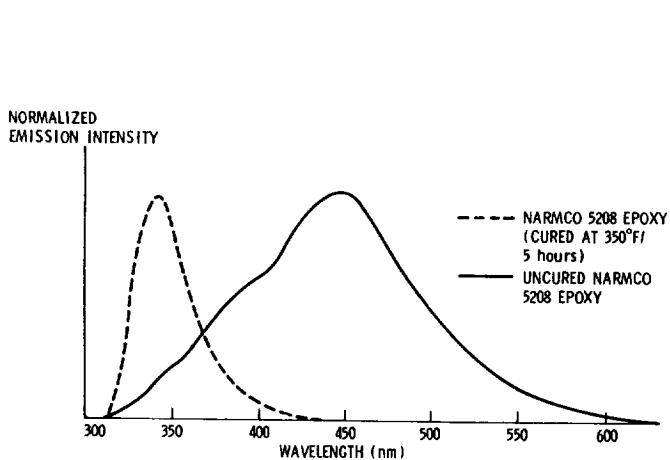Fig. 4.   Photoexcited emission spectra of cured and uncured NARMCO 5208 epoxy formulation (λex = 301 nm).
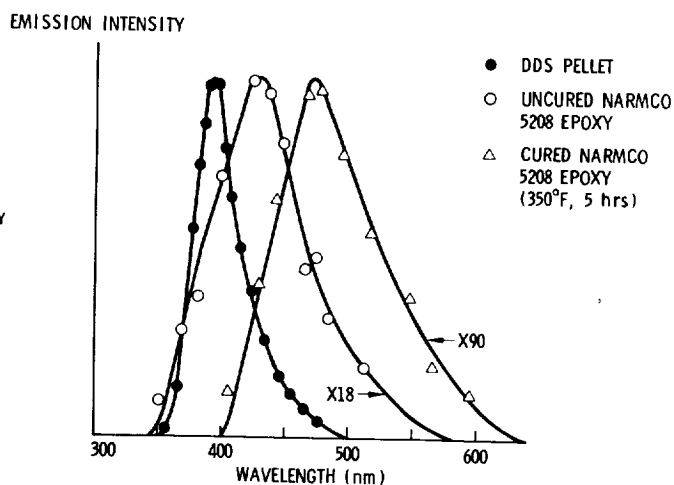
Fig. 5   Prompt emission spectra of solid DDS, cured and uncured NARMCO 5208 epoxy formulation following pulsed electron beam excitation.

Fluorescence spectra were also recorded on dilute solutions of the pure materials and their mixtures in CH_2Cl_2. Figure 2 shows absorption spectra of TGDDM, DDS and TMDDS in dilute solution. Figure 3a shows the emission spectra of DDS, TMDDS and TGDDM in dilute CH_2Cl_2 solution while Figure 3b shows the same spectra taken on TGDDM and DDS in neat form. Figure 4 shows the emission spectra of the uncured mixture and the resin cured at $180^{\circ}C$ (350F) for 5 hours. Figure 5 shows emission spectra taken at 0-5-ns delay following pulsed e-beam excitation on DDS, uncured mixture and the cured resin. Figure 6 shows typical time profiles for the uncured mixture as a function of wavelength. Table 1 gives fluorescence decay lifetimes measured on these systems.

Discussion - Since the emission intensity from TGDDM is 80-150 times weaker than that from DDS or TMDDS, it is expected that the emission of the mixture (cured or uncured) will be dominated by TMDDS or DDS fluorescence. Comparison of emission spectra of DDS in dilute solution with the spectrum of neat DDS shows that it is considerably red shifted in neat DDS. While the same effect is also observed in case of TGDDM, it is not nearly as large. This result has been attributed to formation of excited state complexes or excimers in these systems in which an excited molecule interacts with a neighboring molecule in the ground state in approximate parallel configuration with the excited molecule. Interaction between molecules of the same species forms excimers, while interaction between two different species forms exciplexes. Excimers are not efficiently formed within the excited state lifetime of DDS in dilute solution, since the formation of excimers is a bimolecular process and requires multiple diffusive encounters. Excimer formation is found to be not nearly as important in case of TGDDM as it is for DDS. The uncured mixture should then show evidence of formation of two excimers as well as a heterogeneous complex, the exciplex between DDS and TGDDM. The emission envelope of the uncured mixture (Figure 3b) does indeed have three segments approximately corresponding to emissions

NORMALIZED
EMISSION INTENSITY

a. 340 nm
b. 380 nm
c. 470 nm

0 20 40 60 80 100 120 140 160 180 200
TIME (nsec)
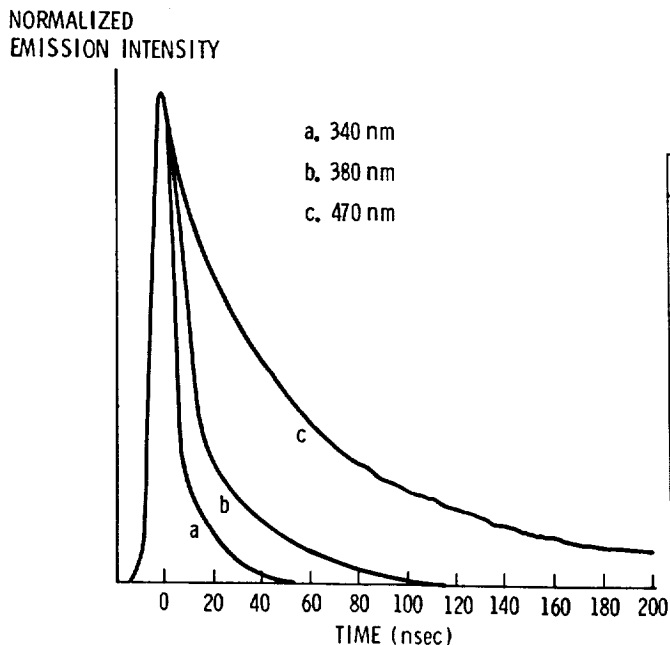
Fig. 6. Time-resolved emission from uncured NARMCO 5208 epoxy formulation following 3-nsec pulsed electron beam excitation.

Table 1. Fluorescence Decay Times Following Pulse Radiolysis

SYSTEM	λ(nm)	τ_{FAST} (nsec)	τ_{SLOW} (nsec)
TGDDM	350	≤ 5	-
	450	-	10-20
DDS	350-450	≤ 5	10-15
UNCURED NARMCO 5208	340	≤ 5	10-20
	470	18-22	85-100
CURED NARMCO 5208 (350°F, 5 hrs)	470	≤ 5	MULTI-EXPONENTIAL

from these three species. However, diffusive encounters of two molecules or substantial, rapid molecular rotation is eliminated on network formation, and hence only a trace amount of excimer formation is expected in cured specimens, when the exciting photon happens to be incident on a methylated DDS molecule in a preformed, configuration position with a TGDDM or another methylated DDS molecule. Hence the emission spectrum of the cured system is blue shifted and largely resembles a combination of emission spectra from methylated DDS molecules. Scheme 1 may be proposed to interpret the optical excitation data,

$$R \xrightarrow{h\nu} R^{1*}$$

$$R^{1*} + R \underset{\longleftarrow}{\longrightarrow} [RR]^{1*}$$

$$R^{1*} \longrightarrow R + h\nu_1 \ (345 \ nm)$$
$$\longrightarrow R + \Delta$$
$$\longrightarrow etc$$

$$[RR]^{1*} \longrightarrow 2R + h\nu_2 \ (360 \ nm)$$
$$\longrightarrow 2R + \Delta$$
$$\longrightarrow etc$$

$$A \xrightarrow{h\nu} A^{1*}$$

$$A^{1*} + A \underset{\longleftarrow}{\longrightarrow} [AA]^{1*}$$

$$A^{1*} \longrightarrow A + h\nu_3 \ (330 \ nm)$$
$$\longrightarrow etc$$

$$[AA]^{1*} \longrightarrow 2A + h\nu_4 \ (385 \ nm)$$
$$\longrightarrow etc$$

$$A^{1*} + R \ or \ R^{1*} + A \longrightarrow [AR]^{1*}$$

$$[AR]^{1*} \longrightarrow A + R + h\nu_5 \ (445 \ nm)$$

$$[AR]^{1*} \longrightarrow A + R + \Delta$$
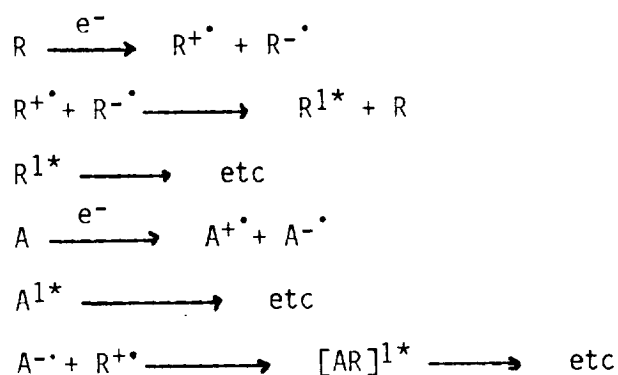$$\longrightarrow etc$$
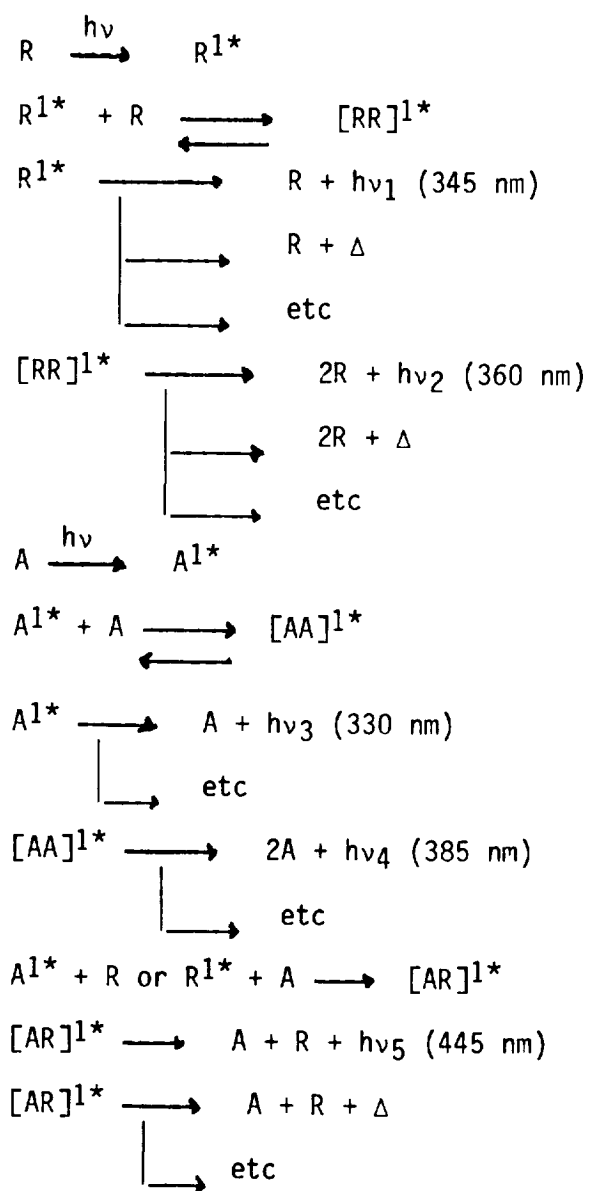
Scheme 1

where A is DDS and R is TGDDM scheme 1. In scheme 1, $[AA]^{1*}$ is the DDS excimer, $[RR]^{1*}$ is the TGDDM excimer, while $[AR]^{1*}$ is the exciplex. These excited state complexes have no ground state counterpart, since there is no ground state complex formation in this system, as determined by monitoring electronic spectra as a function of concentration. In other words, the excimers and the exciplex have potential

of concentration. In other words, the excimers and the exciplex have potential minima in the excited state but no such minimum in the ground electronic state. The nature of electronic interaction leading to stabilization of $[AR]^{1*}$ is not understood clearly, but it seems that there is a considerable degree of charge transfer, allowing mixing of higher excited states of A and R in $[AR]^{1*}$. Under favorable conditions, $[AR]^{1*}$ may be dissociated to form radical cations and anions. This experiment is in progress, and if successful, will produce useful insight into the nature of bonding in $[AR]^{1*}$ and hence its reactivity and lifetime.

The primary products of e-beam excitation are radical cations and anions. Recombination takes place through the back transfer of an electron from the anion to the cation. Within the spur, the ions are nearest neighbors and recombination is ultrafast, being essentially complete in less than 10 ps. Outside of the spur, recombination requires migration or hopping of the electrons from the anion until it encounters a cation. Normally this recombination would lead to the formation of excited states such as R^{1*} or A^{1*}. However in that case, the emission spectra following pulse radiolysis would be identical to that observed on optical excitation, except for perhaps a measurable time delay in the onset of fluorescence following pulse radiolysis. This is found to be the case for TGDDM, DDS and the uncured mixture, but the emission spectrum of the cured resin is considerably red shifted following e-beam excitation. This red shift may be rationalized as being due to direct formation of exciplexes when adjacent ionic species interact and seek to recombine within the rigid network, particularly since the exciplex is expected to incorporate a considerable degree of charge separation. Hence Scheme 2 may be proposed to interpret pulse radiolysis data:

$$R \xrightarrow{\ e^-\ } R^{+\bullet} + R^{-\bullet}$$

$$R^{+\bullet} + R^{-\bullet} \longrightarrow R^{1*} + R$$

$$R^{1*} \longrightarrow \text{etc}$$

$$A \xrightarrow{\ e^-\ } A^{+\bullet} + A^{-\bullet}$$

$$A^{1*} \longrightarrow \text{etc}$$

$$A^{-\bullet} + R^{+\bullet} \longrightarrow [AR]^{1*} \longrightarrow \text{etc}$$

Scheme 2

Fluorescence decay of uncured mixtures is found to have three single exponential decay components (Table 1). The fast component ($\tau \simeq 5$ ns) increases in amplitude at shorter wavelengths (300-390 nm) and is assigned to the TGDDM monomers (R^{1*}). There is a slow component of variable lifetime ($\tau \simeq 70-90$ ns) occuring at longer wavelengths (400-500 nm) which may be assigned to the exciplex (RA^{1*}). A third component having a lifetime of 10-25 ns, occurs at intermediate wavelengths and is tentatively assigned to the DDS excimer AA^{1*}.

The mechanism of excimer and exciplex formation from A^{1*} and R^{1*} as observed on optical excitation or directly from A^- and R^+ as observed on pulse radiolysis on the cured system, requires the postulation of fast migration of excited states and electrons, since diffusive encounter rates even in uncured materials are not sufficiently fast to explain the observed rate of onset of excimer and exciplex fluorescence. Preliminary estimation of these hopping frequencies put them at or above

fluorescence. Preliminary estimation of these hopping requencies put them at or above 10^{10} sec^{-1}. Such fast hopping processes allow the possibility of quenching or trapping the excitation energy as well as charges by placing quenchers or acceptors in the matrix. Less than 2 mole percent of quencher concentration is sufficient. Then the matrix can be depleted of its excitation energy before bond cleavage can take place. In preliminary experiments > 90% quenching of energy in P1VN was demonstrated by using 1 mole percent of anthracene traps. Additives for radiation stabilization may be developed according to these quenching criteria. For the TGDDM-DDS system, the initial additive being tested is TMDDS, which is compatible to the network, does not change its chemistry, and acts as a shallow trap of excitation and electrons.

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