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RADIOLUMINESCENT POLYMER LIGHTS

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INTRODUCTION

Available radioluminescent lights use "gas tube technology"; a single glass tube (or annular tube), coated with a phosphor on the tubing interior, and filled with tritium gas. The tritium gas emits a beta particle (electron) during decay exciting the phosphor; causing the phosphor to emit light (photons). The gas tube technology has been able to produce lights having intensities of 1 to 1.3 ft-Lambert. A standard television set emits approximately 2 ft-Lamberts of light.

An alternative to glass tube technology that has the potential to produce higher light intensities is the use of a tritiated polymer. Such a polymer must be chemically stable with the attached tritium and remain transparent to the light emission from the contained phosphor. Aromatic materials (compounds containing benzene rings), for example polystyrene, have generally been sought as a non-radium source for luminescent paints (Fischer, E. and A. Kaltenhauser, 1966, Rosenberg, J., 1967).

Several attempts to prepare high-intensity, polymer lights have been made by industry. Most involved tritiation of phenylacetylene, followed by polymerization of the substituted styrene; or polymerization of a monomer such as methyl methacrylate or ethylene in the presence of tritium gas (Fischer, E. and A. Kaltenhauser, 1966, Rosenberg, J., 1967). The polymers produced by these and similar reactions, have not been stable due to the placement of tritium in the backbone (ethylene portion) of the polymer. Polystyrene, itself, is quite stable to radiation due to the pendant aromatic rings of its structure. Substitution of tritium for one to five of the hydrogen atoms on the aromatic rings of polystyrene provides a more stable placement for the isotope and should lead to a long-lived product (Cacace, 1975). Substituted polystyrene has the potential to emit greater than 5 ft-Lambert of visible light if a phosphor transparent to its own light emission can be found.

Research at the Pacific Northwest Laboratory (PNL) has confirmed that all five hydrogens of the pendant aromatic rings of polystyrene can be substituted using deuterium as a stand-in for tritium. During the PNL experiments, all five hydrogen atoms in the aryl-ring of the polystyrene were replaced by deuterium with essentially no crosslinking. Experiments using tritium were then completed in cooperation with Mound Laboratories where we demonstrated that tritiated polystyrene can be produced using this procedure. The product was not optimized and became highly crosslinked making it insoluble in typical polystyrene solvents. Homogeneous mixing with zinc sulfide phosphor was impossible; however, light was produced in the polymer-zinc sulfide blend. Due to very short reaction times, less than 0.5 tritium atoms per monomer unit were incorporated into the polymer. This suggests that considerable improvement in light output can be made with a tritiated polymer using appropriate inorganic or organic phosphors that mix well with the polymer.

TESTS CONDUCTED AND RESULTS

Acid-catalyzed tritium exchange has been performed with polystyrene (Burfield, D.R. and C.M. Savariar, 1984). The exchange was attained by combining polystyrene, dissolved in dichloromethane, with tritiated water and P_2O_5 or $AlCl_3$. Although 50% incorporation of tritium was claimed with the $AlCl_3$ catalyst, our experience with deuterated water was considerably less favorable. Cross-linking of the polystyrene, in the presence of $AlCl_3$, was observed by us. Friedel-Crafts reaction conditions using tritium chloride (Satchell, D.P.N., 1960) suggested an alternative to the T_2O/P_2O_5 procedure. We further sought to use a homogeneous catalyst for this process; in this case our choice was $TiCl_4$. Most of our work was performed with deuterium reagents to eliminate the radiation safety requirements of working with tritium.

Rather than generate DCl <u>in situ</u>, by the reaction of $TiCl_4$ with D_2O, we used commercially available DCl for our initial experiments. A typical experiment involved the dissolution of expanded polystyrene (packing material) or Dow 666u polystyrene (1.0 g, 0.01 mole) in 50 mL of dichloromethane in a 75 mL stainless steel pressure vessel. To this was added 1.86 g (0.01 mole) of $TiCl_4$. The vessel was sealed after adding 50 psi of DCl. The solution was magnetically stirred for 24 h at 25°C. The vessel was vented, and the contents were poured into 200 mL of methanol. The precipitated polymer was redissolved in dichloromethane and precipitated in methanol three times. After vacuum drying, a sample of the polymer was pyrolyzed at about 400°C and 0.5 torr. Typically, 70% of the aromatic rings contained one deuterium (predominantly <u>para</u>-position) and 12% of the rings contained two deuterium atoms. Although cross-linking did not occur under these conditions, it could be readily detected by the presence of products such as ß-methylstyrene and propylbenzene. Lesser amounts of $TiCl_4$ (0.0004 mole and 0.002 mole) in the reaction yielded fewer deuterium substituted products. When the vessel was pressurized with DCl to 100 psi, deuterium substitution was enhanced such that 13% of the aromatic rings contained five deuterium atoms with greater amounts of the lesser substituted products; only 11% of the aromatic rings were not substituted to some degree. Increasing the time of reaction to 48 h enhanced the deuteration, but not significantly. We also observed that $SnCl_4$ produced similar results.

Since tritium chloride is not commercially available, we had to establish a procedure for TCl generation using T_2O. Our initial work was again performed with deuterium isotopes. Although DCl can be obtained from $AlCl_3$ and $TiCL_4$, a cleaner and better controlled reaction was found with $SOCl_2$ (Freeman, J.H. and C.E.C. Richards, 1958). However, the DCl contained SO_2 and residual amounts of $SOCl_2$. These latter components apparently contributed to cross-linked polystyrene in our reactions. Thus, the product gas, generated after addition of the D_2O to $SOCl_2$, was passed through a dry ice/dichloromethane trap to remove the sulfur components. The cleaned DCl was cryogenically distilled into the pressure vessel which contained the polymer, solvent, and $TiCl_4$. The deuterium substitution was quite similar to that previously obtained with commercial DCl. That is, it was dependent upon the DCl pressure. The transfer lines must be kept quite short during the trapping and distillation operations to ensure complete passage of DCl.

Tritium chloride was produced using $SOCl_2$ and T_2O in a similar manner. Due to safety constraints, the pressure (reaction) vessel and transfer lines were modified to reduce uncontrolled pressure increases. TCl pressures of way less than 50 psi were attained in the vessel due to poor cryogenic transfer. Of the three experiments performed, the best substitution (31 Ci) was obtained at 23 psi after 16 hours. $SOCl_2$ was apparently carried into the reaction vessel since the polymer cross-linked. The polystyrene was combined with 50 wt% zinc sulfide (GTE 1260), but intimate mixing was not obtained because of the low solubility of the polymer in methylene chloride. Nevertheless, the composite mixture luminesced having very bright streaks (estimated at greater than 3 ft Lamberts) where the tritiated polymer was in contact with the phosphor and dark areas where no phosphor was present. The authors estimate that less than 5% of the tritiated polymer was sufficiently mixed with the phosphor to allow the beta particle to intercept phosphor particles and produce light. The average light output was determined to be approximately 0.01 ft-Lambert.

TRITIUM IN POLYMERIC MATERIALS

Tritium in the backbone of polystyrene should be expected to provide a polymer with slightly more stability than that of tritiated polyethylene. This is because the aromatic rings confer some stability to polystyrene tritiated in the vinyl backbone. Only 10% of the activity was lost annually in polystyrene tritiated in the vinyl backbone (about double the tritium decay rate) (Rosenberg, J., 1967). Cacace (1975) demonstrated that the aromatic ring in essentially not damaged by the beta decay of the tritium. Our assumption is that decay of the tritium to $^3He^+$ with the emission of beta-particle (and an antineutrino) would not result in substantial structural damage to the polymer if the tritium is attached to the aryl-ring in polystyrene or a similar aromatic material. The helium ion is active enough to produce an arenium ion (Speranza, M. 1980, 1983); in the process it becomes an excited helium, and, by collision, eventually returns to the ground state. The electron (beta-particle) may be captured by an unsaturated carbon, such as those in an aryl-ring, forming a free radical. Also much of the energy from the electrons emitted will be absorbed by the phosphor and used for light generation if the phosphor is highly loaded in the polymer, reducing the effects of the radiation exposure.

SUMMARY

The preparation of radioluminescent light sources where the tritium is located on the aryl-ring in a polymer has been demonstrated with deuterium/tritium substitution. Additional research is required with the tritium substitution system. The following sections amplify on this conclusion and identify applications for tritiated polymers that may be developed in the future.

Conclusions and Future Research The aromatic ring in polymers can be tritiated and when mixed with an appropriate phosphor will produce light. These polymers need to be optimized and thoroughly evaluated to determine their stability. A minimum number of experiments are necessary to confirm that near maximum tritium substitution on the aromatic ring in the polymer can be achieved as has been demonstrated with deuterium. As a part of this work, optimum temperature and pressure conditions will be identified for achieving maximum tritium substitution. These polymers would then be mixed with ZnS phosphor and examined for light emission and polymer stability. If the system

is promising, we would investigate alternative inorganic or organic phosphors in the visible and infrared (IR) wave-lengths.

Equipment design indicates that the reaction vessel must be as small and compact as possible, with very short transfer lines to ensure that the all of the tritium chloride reaches the polystyrene reactant. Tritium chloride is currently generated from tritiated water (T_2O) by the action of thionyl chloride with tritium oxide followed by an SO_2 scrubbing step. We would prefer a TCl generation process using tritium gas over a metal chloride.

Possible Applications This research will provide a light-emitting film that requires no power source. Example applications include instrument back-lighting (aircraft and computer), safety striping for emergency egress systems, runway landing lights for remote areas, map overlay back-lighting, and decoy light sources. By using an infra-red emitting phosphor, a range of applications can be considered: invisible route guides, airfield landing lights having no IR signature, and thermal decoys.

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