

Radioluminescent Polymers: Preparation of Deutero- and Tritopolystyrene

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SYNOPSIS

Deuterium and tritium exchanges were performed on the aromatic groups of polystyrene using DCl or TCl and TiCl_4 . Up to 5 deuterium atoms per monomer unit could be placed on the aromatic groups depending upon time, DCl pressure, and TiCl_4 concentration. Tritiated polystyrene mixed with zinc sulfide phosphor produced 1.06 Cd/m^2 of luminance.

INTRODUCTION

Tritiated polymers, especially polystyrene, have generally been sought as a nonradium source for luminescent paints.^{1,2} Preparation of tritiated polystyrene has been performed by subjecting powdered polystyrene to an electrical discharge in the presence of tritium¹ or more usually by the reduction of phenylacetylene with tritium followed by polymerization.² The highest luminance reported² with a polystyrene system has been $2.5 \times 10^{-3} \text{ fL/Ci}$ ($8.5 \times 10^{-3} \text{ Cd/m}^2/\text{Ci}$). The Wilzbach gas-exposure method has also been used to prepare tritiated polystyrene.³ Polystyrene is a good choice for this type of application since it is relatively resistant to high-energy radiation, and undergoes crosslinking rather than polymer scission at high doses.⁴ However, the presence of tritium in the backbone of polystyrene should be expected to provide a polymer with no more stability than that of tritiated polyethylene. Surprisingly, the aromatic rings do confer stability to polystyrene tritiated in the vinyl backbone since it was shown that only 10% of its activity was lost annually (approximately equal to the tritium decay rate).² Higher tritium substitution might be achieved, with no loss of stability, if tritium can be preferentially attached to the aromatic rings of polystyrene. Acid catalyzed tritium exchange has been performed with polystyrene by combining the dissolved polymer with tritiated water and P_2O_5 or

AlCl_3 .⁵ Tritium incorporation up to 19% was claimed by this route. However, catalytic degradation of polystyrene (mainly β -scission) has been observed in the presence of AlCl_3 at 50°C .⁶

Our major objective during this research was to obtain a much higher tritium substitution with polystyrene, especially on the aromatic ring, than previously reported. We further required mild reaction conditions which would yield a linear (solvent soluble) polymer. Only tritium oxide and tritium gas were available to us as a source of the tritium-bearing reagents. However, prior work with hydrogen isotope exchange on the aryl-group of toluene has shown a first-order relationship with both TCl and stannic chloride.⁷ Thus, Friedel-Crafts conditions using tritium chloride⁷ suggested a procedure which might allow preparation of such a tritiated polystyrene. Most of the research reported here was performed with deuterium reagents to eliminate the radiation safety requirements necessary for tritium usage.

EXPERIMENTAL

Materials

The polystyrene (M_n 20,000), used throughout this research, was obtained from Polysciences Inc. Reagent grade (Aldrich) titanium tetrachloride, stannic chloride, and thionyl chloride were used. Dichloromethane (HPLC grade) and deuterium oxide were also obtained from Aldrich. Deuterium chloride was obtained from MSD Isotopes, Montreal. Tritium oxide (1330 Ci/g) was obtained from

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and used at the EG&G Mound Applied Technologies, Miamisburg, OH.

Deuteration of Polystyrene (Procedure A)

The initial procedure involved dissolution of 1.0 g (0.01 mol) of polystyrene in 50 mL of dichloromethane. This was placed in a 75-mL capacity stainless steel pressure vessel, and 1.82 g (0.01 mol) of titanium tetrachloride was added by pipette. The pressure vessel was connected by stainless steel transfer lines to a lecture bottle containing deuterium chloride. The pressure vessel was sealed after adding 50 psi (0.34 MPa) of DCl. The solution was magnetically stirred for 24 h at 25°C. Following this, the vessel was vented to a caustic solution, and the liquid contents of the vessel were poured into 200 mL of methanol. The precipitated polymer was redissolved in dichloromethane and precipitated in methanol again. After vacuum drying, a sample was pyrolyzed at about 400°C and 0.5 torr. The deuterated styrene was examined by gas chromatography-mass spectrometry (GC/MS) using a 0.25-mm × 30-m capillary column (DB-5). A Hewlett-Packard Model 5890 gas chromatograph with a Series 5970 mass selective detector was used for identifications. Nuclear magnetic resonance spectra (¹H and ²H) were recorded with a Varian FT-80 spectrophotometer.

Dichloromethane had been selected as the solvent in these reactions since it did not hinder the isotope exchange and provided excellent solubility of the polymer. Dichloromethane may potentially enter into the electrophilic substitution and contribute to crosslinked or chloromethylated products. However, no evidence of vinylbenzyl chloride was observed

Table I Deuteration of Polystyrene Using Procedure A for Various Times

Deuterium per Aromatic Ring	Conversion (%) During Time Period (h) ^a			
	24	48	72	144
D ₀	45	13	10	1
D ₁	46	31	25	6
D ₂	8	34	36	21
D ₃	0	16	23	30
D ₄	0	4	6	32
D ₅	0	1	1	10

^a The reaction was performed at 0.34 MPa DCl in dichloromethane with 0.48 M TiCl₄.

Table II Deuteration of Polystyrene Using Procedure A at Different DCl Pressures

Deuterium per Aromatic Ring	Conversion (%) at Pressure (MPa) ^a	
	0.34	0.68
D ₀	10	3
D ₁	25	7
D ₂	36	19
D ₃	23	30
D ₄	6	29
D ₅	0	12

^a The reaction was performed for 72 h in dichloromethane with 0.48 M TiCl₄.

after pyrolysis even with the 144-h polymer. One should note that the solubility of HCl in dichloromethane is rather low, about 4 mol % at 0°C and 1 atm.⁸ Carbon tetrachloride was also examined as a solvent for the exchange, but only three deuterium atoms per ring could be incorporated before cross-linking became evident.

Tables I–III represent the results obtained from various experiments using Procedure A.

Deuteration of Polystyrene (Procedure B)

Since tritium chloride is not commercially available, laboratory procedures were examined for the generation of DCl and, ultimately, TCl. Although DCl can be obtained from AlCl₃, SnCl₄, FeCl₃, or TiCl₄ with deuterium oxide, a cleaner and better controlled reaction was found with D₂O and SOCl₂.⁹ However, DCl formed in this manner contains SO₂ and resid-

Table III Deuteration of Polystyrene Using Modified Procedure A at Various TiCl₄ Concentrations

Deuterium per Aromatic Ring	Conversion (%) at [TiCl ₄] ^a			
	0	0.02 M	0.10 M	0.53 M
D ₀	100	82	52	18
D ₁	0	18	38	33
D ₂	0	0	10	32
D ₃	0	0	0	15
D ₄	0	0	0	2

^a The reaction was performed for 24 h with 0.34 MPa of DCl and 0.25 g [0.5 M] of polystyrene in 5 mL of dichloromethane.

ual amounts of SOCl_2 . These latter components can potentially contribute to crosslinking reactions with polystyrene under our conditions. Thus, the product gas, generated after the addition of 0.071 g (3.6×10^{-3} mol) of D_2O , via a septum, to 0.65 g (5.5×10^{-3} mol) of SOCl_2 , was passed through a dry ice/dichloromethane trap to remove the sulfur components. The scrubbed DCl was cryogenically transferred into a 6-mL capacity stainless steel pressure vessel. Attached to the pressure vessel was a pressure regulator (needle valve) and a diaphragm pressure gauge. The volume of the entire reactor/trap assembly was 23 mL. The transfer lines were kept as short as possible. The pressure vessel contained 0.24 g (2.3×10^{-3} mol) of polystyrene and 0.43 g (2.3×10^{-3} mol) of TiCl_4 dissolved in 3 mL of dichloromethane. Prior to generation of the DCl , the pressure vessel and its contents were cooled in liquid nitrogen and a vacuum was applied to this and the trap assembly for 15 min. This removed most of the air in the reactor/trap assembly and allowed easier cryogenic transfer of the DCl to the pressure vessel. The pressure vessel contents, including DCl , were allowed to reach 25°C . An in-line pressure gauge generally recorded 20 psi (0.14 MPa). The reagents were occasionally shaken during the 24-h reaction period. After this period, the solution was poured into methanol. The precipitated polymer was redissolved in dichloromethane and again precipitated with methanol. The polymer was vacuum dried and pyrolyzed for GC/MS analysis.

Tritiation of Polystyrene (Procedure C)

This synthesis was a modification of Procedure B which was used for the deuteration of polystyrene. It was performed in this matter to meet safety requirements of the host laboratory. The same pressure vessel (6-mL capacity) was used as before. A glass-liner tube was inserted which reduced the interior volume to nearly 5 mL. This vessel was connected to the pressure regulator and gauge by stainless steel transfer lines. The pressure gauge was fitted with an ethylene glycol-filled, stainless steel diaphragm as a dead space reducer/transducer. The volume of the reactor assembly when sealed at the regulator was 6.5 mL. Attached to this assembly were a 100-mL glass volume-regulating device and a coiled assembly which was immersed in a dry ice/dichloromethane bath. These nonreactor assemblies contributed additional volume during the cryogenic transfer of TCl , but were required due to radiation safety considerations. Within the pressure vessel

were placed 0.25 g of polystyrene (2.4×10^{-3} mol) dissolved in 4.9 mL of dichloromethane and 0.4 g (2.3×10^{-3} mol) of TiCl_4 . This solution was frozen in the vessel using liquid nitrogen and the pressure in the reactor/trap assembly was reduced to about 0.5 torr. The reactor/trap assembly was then back flushed with 1 atm of helium. To 0.65 g (5.5×10^{-3} mol) of frozen thionyl chloride in a small glass receiver was introduced 0.078 g (3.5×10^{-3} mol) of tritium oxide through a rubber septum. The TCl and SO_2 formed by this reaction were passed through the dry ice/dichloromethane trap to remove the SO_2 . After cryogenic transfer of the TCl (assumed to be < 15 min), the pressure vessel was sealed, and the temperature was allowed to rise to 25°C . The pressure slowly increased over about 1 h. The vessel was maintained at pressures of 0.03 MPa to 0.29 MPa for periods ranging from 12 h to 11 days. At this point, residual TCl was flushed from the system and the liquid/gel contents were poured into methanol.

Analytical Procedure

In this research, unless otherwise specified, those deuterated polymer products soluble in dichloromethane were assumed to be linear. Pyrolysis of the products at 400°C and 0.5 torr generally gave a 75% recovery of styrene. The remainder of the pyrolyzate was presumed to contain trimers and other small fragments.¹⁰ Crosslinked polystyrene did provide styrene monomer upon pyrolysis, but considerable char remained in the distillation flask, and the gc-ms patterns were distinct. These polymers produced large amounts of β -methylstyrene and propylbenzene together with styrene. The DB-5 capillary column used throughout this work gave excellent separation of the various pyrolyzate products. Due to the 75% recovery of the styrene monomer during pyrolysis, the values given in the tables for deuteroproducts are representative only of the recovered fraction. The deuterium values presented in the tables were calculated using a 6 by 6 matrix (6 equations, 6 unknowns) based upon the abundances of the various molecular ions.

Analysis for tritium was performed by subjecting the polymer to combustion in an oxygen flask. The resulting water was examined by liquid scintillation counting.

Phosphor Incorporation

The zinc sulfide phosphor used in this research was GTE 1260, Fisher size 6.83. Samples of polystyrene

containing 5 wt % through 80 wt % of the phosphor were prepared by mixing the phosphor into dichloromethane solutions of the polystyrene. The mixtures were poured onto a glass plate to allow the solvent to evaporate. The resulting films were examined with an ultraviolet lamp to establish the uniformity of fluorescence. The films were transparent to about 40 wt % and became opaque at about 80 wt %. The useful higher limit of filling was determined to be 75 wt % of phosphor. As a comparison with the results presented herein, a standard television screen emits about 2 fL (6.8 Cd/m²) of luminance. A Minolta SL-100 photometer was used to measure luminance of the tritiated polymers.

RESULTS AND DISCUSSION

Although other research⁵ has shown that AlCl₃ can be used as an effective catalyst for the tritiation of polystyrene, our results with this catalyst in the presence of deuterated water indicated that severe crosslinking can occur. This experiment was followed by one which used AlCl₃ with DCl sparged into the dichloromethane-polymer solution. Although the solvent soluble product contained 1% monodeutero-styrene, removal of the aluminum salts from the polymer was quite difficult. Since it was our desire to prepare a linear deuterated polystyrene, homogeneous catalysts were considered. Prior research⁷ showed that protium-tritium exchange could be achieved with toluene using stannic chloride as a catalyst. We were also interested in the use of TiCl₄ since it produced Ti(OCH₃)₄ which was soluble in methanol after the reaction was quenched with that solvent.¹¹ Most of this research was performed with TiCl₄, but similar results, in a limited number of experiments, were obtained with SnCl₄. However, in the presence of SnCl₄ moderate amounts of gum formation occurred during the precipitation of polystyrene. The initial experiments were performed in the larger pressure vessel (75 mL) using the conditions of Procedure A; that is, 0.34 MPa of DCl with the reagents dissolved in dichloromethane. One additional experiment, performed with AlCl₃, produced considerable insoluble polymer which we attributed to crosslinking. The homogeneous experiments were examined at various times (see Table I).

The results of Table I indicate that more deuterium is exchanged at longer reaction times. However, crosslinking (gel formation) was noted in the product obtained at 144 h. Thus, reaction times longer

than 144 h were not considered suitable for this work.

The product obtained after 24 h was examined by ²H- and ¹H-NMR to determine the position of substitution in the aromatic ring. Since the directing group for the mechanism of electrophilic aromatic substitution in this reaction is the alkyl chain of the polymer, and the *ortho*-positions may be blocked by that chain, it was assumed that most of the isotope exchange occurred in the *para*-position. This, indeed, was confirmed since the *o/p* ratio of exchange products is 1 : 4 in favor of *para*. One should expect a statistical ratio of 2 for *o/p* exchange; however, experience with Freidel-Craft alkylations indicates that the ratio is ≤ 1 for toluene and ethylbenzene.

One of the first reactions performed with this system was a precursor of Procedure A using a slow sparge of DCl into the reagents. This represented 0.10 MPa of DCl accessible to the reaction, but only about 1% deuteration could be achieved. Thus, the higher DCl pressure was adopted for Procedure A. The results with two higher pressures are presented in Table II. Although the results with 0.68 MPa were significantly better, small amounts of gelled polymer were present. This suggests the useful limit of the reaction is less than 72 h at the higher pressure.

During the deuterium exchanges using Procedure A, the TiCl₄ concentration was maintained at 0.48 M, the same as the polystyrene concentration. It was necessary to examine the effect of the TiCl₄ concentration prior to establishing Procedure B, an intermediate step before tritiation. Thus, a pressure vessel of 6-mL volume was used, the same as that of Procedure B, but DCl was provided from a lecture bottle. The variation of "catalyst" concentration is presented in Table III. One should note that the TiCl₄ concentration, in one instance (0.53 M), was close to that used in Procedure A (0.48 M).

There was no detectable exchange of deuterium in the absence of TiCl₄. The substitution occurred more rapidly with higher concentrations of TiCl₄. Larger amounts of TiCl₄ were not used since it was considered impractical for the tritium experiments. Note that the conversion with 0.53 M of TiCl₄ for a 24-h period in the 6-mL vessel is nearly the same as observed for a 48-h period using 0.48 M TiCl₄ in the 75-mL vessel (Table I). Calculations indicate that the DCl concentration in each dichloromethane solution is 0.014 M. The reactivity differences of these two vessels could be due to the lower concentration of polystyrene in the larger vessel (0.19 M) compared to the smaller vessel (0.48 M). However, there would be more exchangeable hydrogen avail-

able in the larger vessel, since it contained 0.01 mol of polystyrene compared to 0.002 mol of polystyrene in the smaller vessel.

Procedure B is a modification of Procedure A using the thionyl chloride-deuterium oxide reaction rather than commercial DCl. To increase the amount of exchange, approximately 10 times the amounts of SOCl_2 and D_2O specified in Procedure B were used with the 75-mL vessel. After warming the cryogenically transferred DCl, pressure to 192 psi (1.32 MPa) was obtained in the vessel. The exchange reaction was performed for 24 h and quenched in methanol. The pyrolyzed polymer provided 31% unsubstituted styrene and deuterated styrene containing 45% D_1 , 23% D_2 , and 1% D_3 . This result is not significantly better than that obtained with 0.34 MPa of commercial DCl for 24 h. It is presumed that not all SO_2 was removed from the gas stream. The air removal from the vessel and lines may not have been as effective as presumed. The solubility of DCl in the scrubbed SO_2 was thought to be sufficient to reduce total transfer of that reagent. However, this may not be a factor since SO_2 is sparingly soluble in liquid HCl.¹² Procedure B, with a 6-mL pressure vessel, was investigated several times. The maximum pressure obtained after DCl generation was 10 psi (0.07 MPa). A soluble polymer was obtained after 24 h, but only 14% of the styrene monomer (pyrolyzate) contained a deuterium substituent.

Tritium chloride was produced using SOCl_2 and T_2O in a manner similar to that described in Procedure B. The volume of the nonreactor assemblies was increased due to safety requirements as noted in Procedure C. Experience from Procedure B suggested that TCl transfer from the generation receiver to the reactor was diminished. The initial experiment of the three performed was maintained at 0.12 MPa TCl for 11 days. This long period was used to test the integrity of the system and the potential corrosion of the transfer lines and reactor. As expected, the quenched product was a dark brown gel which was not soluble in dichloromethane or toluene. However, the solvent washes of the gel were mixed with ZnS phosphor and a visible glow was observed.

The second experiment was performed for 12 h using the same equipment; however, the TCl pressure was maintained at 42.5 psi (0.29 MPa). The clear yellow solution from this reaction was poured into methanol to give a white precipitate. This polymer was not soluble in dichloromethane. The powdered polymer was mixed with 75 wt % phosphor,

but only 0.01 foot-Lambert (fL) or 0.07 Cd/m^2 of luminance was observed. The 0.246-g polymer sample contained 31.3 Ci. This indicated that about 0.5 tritium atoms were present per monomer unit. The third experiment was performed in a manner similar to that of the second, except that only 5.5 psi (0.03 MPa) of TCl was maintained within the reactor for 12 h. The white polymer obtained after quenching was partially soluble in dichloromethane. This polymer was mixed with phosphor, and 0.31 fL (1.06 Cd/m^2) of luminance was observed. The 0.248-g polymer sample contained 3.1 Ci which indicated that only about 0.05 tritium was present per monomer unit. This represents 0.1 fL/Ci which is considerably higher than the .0025 fL/Ci reported by Rosenberg.² It is evident that the polymer must be solvent soluble to obtain good mixing with the phosphor and enhanced luminance. Considerable improvement should be possible since the theoretical maximum exchange of tritium (5 ring hydrogens) can provide 1284 Ci/g of polystyrene.

The results of the tritium exchange experiments indicate that further modification of the procedure is necessary before the tritium exchange can match the results obtained with deuterium. Comparison of the tritium and deuterium exchange results should be made cautiously since the experiments were not performed under identical conditions. It should be noted that Yang and Ingalls³ observed extensive crosslinking with polystyrene exposed to tritium gas. However, calculations of their results with the tritiated polystyrene suggest that only 7×10^{-7} tritium per monomer unit was attained. The higher tritium content and, apparently, lower amount of crosslinking of the polymer obtained by the TiCl_4 -TCl procedure indicate that this technique should be further investigated for direct tritium exchange into aromatic polymers.

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