Two-photon Chemistry: Facile Synthesis of Naphthalene- and Anthracene-labelled Polystyrene by Photolysis of Aromatic Esters

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Photolysis of 9-anthrylmethyl 9-anthrylacetate and 1-naphthylmethyl 1-naphthylacetate in the presence of polystyrene yields polymers which are labelled with the fluorescent groups of anthrylmethyl and naphthylmethyl, respectively; this novel technique for the fluorescent labelling of polystyrene is believed to involve two-photon excitation.

Two-photon chemistry can lead to reaction pathways which are quite different from those observed in conventional photochemistry.[1] However, because of the need for high-intensity excitation (*e.g.*, pulsed lasers) and a poor understanding of two-photon processes, two-photon chemistry has yet to be proved to be a useful tool in synthetic organic chemistry. This paper reports preliminary studies of two-photon chemistry using steady-state excitation, namely, the photoaddition of naphthylmethyl and anthrylmethyl groups to polystyrene (PS) by steady-state photolysis of 1-naphthylmethyl 1-naphthylacetate (NMNA) and 9-anthrylmethyl 9-anthrylacetate (AMAA).

The synthesis and photolysis of NMNA and AMAA have been described previously.[2] Photolysis of NMNA and AMAA results in decarboxylation and the formation of naphthylmethyl and anthrylmethyl radicals, respectively.[2,3] These radicals are resonance stabilized and thus have low reactivity. For example, they do not initiate free radical polymerization of vinyl monomers. Upon irradiation of solutions of these compounds in the presence of preformed polymers, the resultant polymers such as PS fluoresce strongly at wavelengths where they previously did not.

The molecular weight, $\bar{M}_n$, of the PS sample was 1.6×10^5, the polydispersity index was 2.9, the concentration of polymer in benzene was 80 g l^{-1}, and the concentrations of NMNA and AMAA were 6×10^{-3} and 4×10^{-3} mol dm^{-3}, respectively. Samples (20 μl) were irradiated with a narrowly focused beam from a 500 W Hg–Xe lamp (Optical Associates), through a 280 nm cut-off filter (I_0 = 13 mW cm^{-2}), or a 100 W Hg lamp (Photon Technology) where the focused beam was passed through a 334 broadband filter (I_0 = 115 mW cm^{-2}, sample size, 4 ml). The solution was mixed continuously with a magnetic stirrer.

The fluorescence excitation and emission spectra of PS following irradiation in the presence of AMAA were characteristic of emission by anthracene. Since blank experiments in

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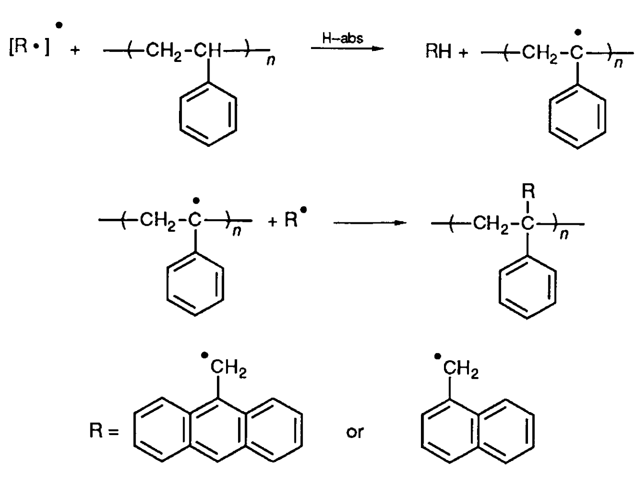

Scheme 1

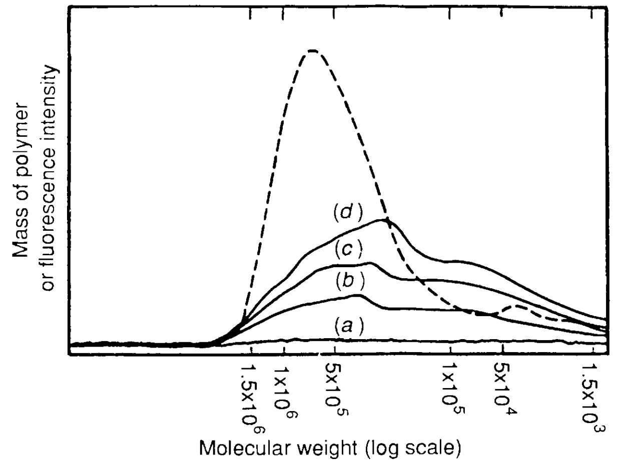

Fig. 1 Molecular weight distribution and fluorescence intensity curves for polystyrene following steady-state irradiation in the presence of AMAA. (---) Molecular weight. (——) Normalized fluorescence. Irradiation time/min: (*a*) 0, (*b*) 3, (*c*) 40, (*d*) 130. λ_{ex} = 366 nm, $\lambda_{em} \geq$ 389 nm.

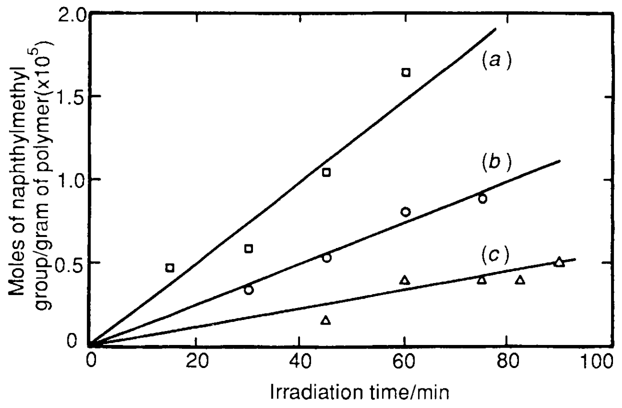

Fig. 2 Moles of naphthylmethyl groups per gram of polymer plotted against irradiation time: irradiation intensity (*a*) I_0; (*b*) 0.73 I_0; (*c*) 0.49 I_0. Irradiation through a 334 nm broad band filter, I_0 = 115 mW cm^{-2}.

Table 1 Degree of photolabelling of polystyrene with anthrylmethyl[a] and naphthylmethyl[b] groups as a function of irradiation time

Irradiation time/min	(Fluorophore/polymer)/(mol g^{-1}) × 10^{6c}	Fluorophores per polymer chain
Fluorophore = anthrylmethyl		
0	0	0
3	0.15	0.024
20	0.29	0.047
40	0.34	0.054
70	0.37	0.059
130	0.41	0.066
Fluorophore = naphthylmethyl		
0	0	0
15	4.6	1.1
30	5.8	1.4
45	10.4	2.6
60	16.4	4.1

[a] λ > 280 nm, I = 13 mW cm^{-2}. [b] 334 nm broad band filter, I = 115 mW cm^{-2}. [c] Determined by GPC.

the absence of polymer showed no fluorescent products in the polymeric region, the anthracene must be chemically bound to the polymer chain.

The polymers were analysed by gel permeation chromatography (GPC). The use of a GPC system equipped with both a fluorescence detector and a differential refractometer enabled the simultaneous measurement of polymer molecular weight, polymer mass and fluorescence intensity. Fig. 1 shows the molecular weight distribution curves and corresponding fluorescence intensities, normalized with respect to polymer mass, for PS samples irradiated in the presence of AMAA. The ratio of fluorescence intensity against polymer mass increases with time of irradiation, as shown quantitatively in Table 1.

Similarly, solutions of PS and NMNA in benzene were irradiated, and the resultant polymers were characterized by GPC and fluorescence spectroscopy. The fluorescence emission spectrum of the purified polymer indicated the presence of the naphthalene moiety. GPC analysis showed that the ratio of the fluorescence intensity to mass of polymer increased with irradiation time. The number of naphthylmethyl units per polymer chain and per gram of polymer are shown in Table 1.

Previous pulsed-laser studies of photolabelling indicate that photoaddition occurs *via* a two-photon process.[4] Additional evidence for this is provided by plots of the number of moles of labelled-fluorescent groups per gram of polymer *vs.* irradiation time for three different irradiation intensities (Fig. 2). The gradients of the plots, normalized to I_0 are 1, 0.48 and 0.23 for intensities of I_0, 0.73 I_0 and 0.49 I_0, respectively. These compare to theoretical values of 1, 0.53 and 0.23 for a squared dependence of photolabelling on irradiation intensity. A log–log plot of the degree of photolabelling *vs.* irradiation intensity yielded a straight line of gradient 2.0 ± 0.1. Thus, the degree of fluorescent-labelling is proportional to the square of the intensity, which is indicative of a two-photon process.

Excited state naphthylmethyl and anthrylmethyl radicals are the most likely reactive species in the photolabelling process. These might be produced by either a photolytic cleavage of the original ester and subsequent excitation of the ground state radical or formation of the triplet state of the original compound, followed by triplet–triplet absorption and photodecarboxylation from the second triplet state.

The α-C–H bond is the least stable bond for PS; thus the mechanism of H-abstraction and radical–radical coupling in Scheme 1 can be inferred.

Two-photon-induced addition of naphthylmethyl and anthrylmethyl fluorophores illustrates the potential usefulness of two-photon chemistry in organic synthesis. For the preparation of fluorescence-labelled polymers, this technique obviates the synthesis and copolymerization of fluorophoric monomers, and should favour random labelling. Photolabelling studies with poly(methyl methacrylate) have already demonstrated the versatility of the method.

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