Poly(ethylene terephthalate) as an Insoluble Electron Transfer Photosensitizer

Angelo Albini and Silvia Spreti
Dipartimento di Chimica Organica dell'Università, V. Taramelli 10, 27100 Pavia, Italy

Poly(ethylene terephthalate) functions as an efficient electron transfer photosensitizer in the cyclodimerization of phenyl vinyl ether.

The use of an immobilized sensitizer for carrying out preparative photosensitized reactions offers clear advantages.[1,2] Thus the sensitizer can be used in relatively high amounts in order to ensure high light absorption and is then easily eliminated at the end of the reaction by filtration. Furthermore, the choice of experimental conditions can be extended to solvents in which the corresponding 'molecular' sensitizer is not sufficiently soluble.

Apart from silica gel adsorbed sensitizers, polymers containing the appropriate chromophore have been shown to

Table 1. Products from the irradiation of phenyl vinyl ether.[a]

No.	Sensitizer[b]	Products (Weight/mg)		Ratio (**1**) : (**2**)
1	DMT, 1 g	(**1**), 185	(**2**), 135	1.37
2	None	None		
3	PET, 1 g	(**1**), 120	(**2**), 100	1.2
4	PET[c]	(**1**), 40	(**2**), 30	1.33
5	PET[d]	(**1**), 15	(**2**), 10	1.5

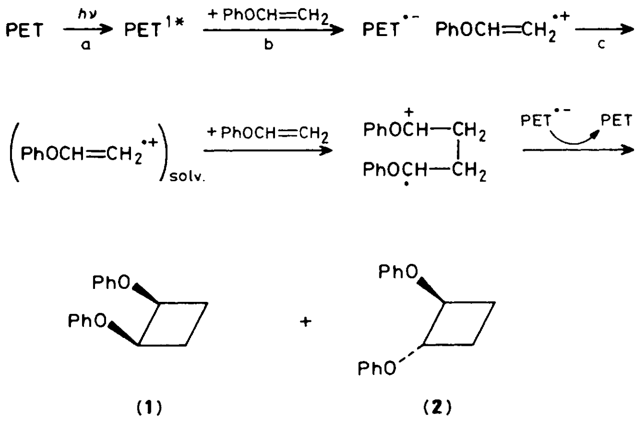
[a] A solution of the ether (3 g) in acetonitrile (75 ml) was degassed and irradiated by means of a high pressure mercury arc through Pyrex for 15 h. Products were separated by column chromatography. [b] See text. [c] Re-using the sensitizer from run 3. [d] Re-using the sensitizer from runs 3 and 4.

function as energy transfer sensitizers, *e.g.* acetylated or benzoylated polystyrene derivatives for sensitizing triplet state photoreactions[3] or polymers containing covalently bound rosebengal for sensitizing singlet oxygen photo-oxidations.[4] To our knowledge, no immobilized photosensitizer working through electron transfer has been reported, despite the increasing importance of this kind of reaction. We reasoned that, as aromatic esters are known to sensitize some of these reactions, the simplest choice would be to use an aromatic polyester and now report some experiments using poly(ethylene terephthalate) (PET).†

The cyclodimerization of phenyl vinyl ether, first reported by Shigemitsu and coworkers[6] appeared a useful test, as this is an unambiguous example of a reaction proceeding through photochemically formed radical ions.‡ The results are reported in Table 1 and lead to the following conclusions. The polymer is an effective sensitizer, causing almost the same amount of dimerization as does the same weight of *dissolved* dimethyl terephthalate (DMT). Both with PET and with DMT the only process consuming the substrate is dimerization to the *cis*- and *trans*-cyclobutanes (**1**) and (**2**), which are obtained in virtually the same ratio.§ Thus, we surmise that the mechanism is the same in the two cases.

Excited terephthalic chromophores at the surface of the polymer accept an electron from phenyl vinyl ether and the radical cation of the latter is stabilized by solvation and diffuses away from $PET^{\cdot-}$ (see Scheme 1). The following chemistry, including final reduction of the dimeric radical cation by the polymer radical anion is analogous to that observed with molecular sensitizers. The exact molecular weight distribution of the polymer is not known, but intervention of lower oligomers is excluded as the material was repeatedly washed with chloroform and acetonitrile before use.

The polymer is filtered out after reaction, washed and re-used. Its effectiveness (Table 1) decreases strongly after each run. This is attributed to irreversible reaction of the terephthalic chromophore at the surface of the polymer, as expected with polyesters;[10] on the other hand monomeric esters are also consumed through side reactions when used as electron transfer sensitizers. This is an important limitation, however, soluble products arising from polymer decomposition are not found in detectable amounts and from the preparative point of view PET is a satisfactory sensitizer as it does not cause contamination of the products from the desired photochemical reaction. The fact that PET and DMT show comparable efficiency is evidence that, while steps a and b in Scheme 1 (light absorption and electron transfer) might be disfavoured, step c (radical ion separation) is favoured when using a polymeric rather than a low molecular weight sensitizer. This is another point of interest as competition between separation and back electron transfer is crucial in determining the overall efficiency of this kind of reaction.



Scheme 1

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† The polymer prepared according to ref. 5 was finely ground and repeatedly washed with chloroform and acetonitrile.

‡ In the original paper the intermediacy of a charge-transfer exciplex between dimethyl terephthalate and the ether was invoked. Since ΔG for electron transfer to the singlet state of the sensitizer is negative by more than 5 kcal dm^3 mol^{-1} (1 cal = 4.184 J) as calculated from the Weller equation, we can safely assume that full electron transfer is occurring under these conditions. For the sensitisation of the reaction by aromatic nitriles, quinones, and metal complexes, see refs. 7—9.

§ Conversion of the starting material was limited to less than 10% since the cyclodimer ratio might otherwise be altered, compare ref. 7.

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