Chemically modified polystyrene containing pendant vinyl groups: a photosensitive polymer exhibiting chemical amplification

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Soluble polystyrene, modified to contain pendant vinyl groups, was prepared in high functional yield from PSt–CH_2Cl or Pst–CHO *via* Wittig reactions. The polymer was used to prepare a negative-working photosensitive resist in which absorbed light initiated a free radical crosslinking chain reaction.

Keywords Chemical modification; photosensitive polystyrene; chemical amplification

INTRODUCTION

The production of images by exposure to light is an extremely important process; photography, lithography, offset printing, photocopying and the manufacture of microelectronic circuits all depend on photosensitive materials for their operation. Considerable interest has been shown in the development of photoreactive polymer systems for these and other applications[1].

Image production in polymer systems basically results from a change in the solubility properties of a photosensitive layer on exposure to light, either by degradation (increased solubility) or crosslinking (decreased solubility) of the polymer chains. The sensitivity of the polymer depends on the number of chain scissions or crosslinks produced per absorbed photon. The quantum yield of the light absorbing process cannot exceed one, but if the primary event sets off a chain reaction, a sizeable chemical amplification can be achieved.

At present most photocrosslinkable polymer systems are based on the 2 + 2 cycloaddition reactions of polymers containing groups such as cinnamate or on the photodecomposition of azido-containing polymers[2,3], processes which allow no chemical amplification, yielding at most one crosslink per absorbed photon. In this paper we describe a photocrosslinkable polymer system, consisting of a soluble polystyrene containing pendant vinyl groups and a photoactive free radical initiator, which is capable of chemical amplification *via* a chain reaction.

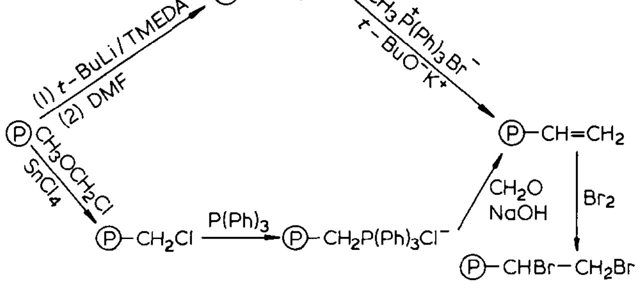
Preparation of the polymer

Polystyrenes containing pendant vinyl groups have previously been prepared by the copolymerization of styrene and divinylbenzene to give highly crosslinked networks containing some unreacted double bonds[4], or by the phase transfer catalysed Wittig reaction of insoluble PSt–CH_2Cl with formaldehyde in 13% functional yield[5]. We obtained soluble PSt–$CH=CH_2$ in high functional yields via two routes (*Scheme 1*). In the first, soluble polystyrene was lithiated by *t*-BuLi/TMEDA[6] and then converted to the aldehyde by reaction with dimethylformamide[7]. Reaction with methyl triphenylphosphonium bromide and potassium *t*-butoxide under anhydrous conditions resulted in a 91% functional yield of PSt–$CH=CH_2$ (*Table 1*).

The second route involves a modification of the procedure of Broos and Anteunis[8]. A polymeric phosphonium salt, prepared from soluble chloromethylated polystyrene, was reacted with aqueous flrmaldehyde and NaOH to give PSt–$CH=CH_2$ in greater than 85% yield (*Table 1*). This route offers the advantages of reduced cost and simplified experimental technique as lithiated reagents and anhydrous conditions are not necessary, and the amount of substitution is easily controlled. However, preparation of PSt–CH_2Cl requires the use of the highly carcinogenic chloromethyl methyl ether, which makes this method less than ideal.

Photocrosslinking of the polymer

The photocrosslinking of the polymer was studied by the adhesion method. The polymer and varying amounts of benzoyl peroxide initiator were dissolved in THF to give a 4% solution which was filtered to remove any insoluble matter and spread on microscope slides. After evaporation of the solvent, polymer films ranging in weight from 5–8 mg were obtained. The films were



Scheme 1 Preparation of ○–$CH=CH_2$

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Table 1 Preparation of PSt–$CH=CH_2$

Starting polymer	Capacity (mequiv. g^{-1})	*DF*	PSt–$CH=CH_2$ (mequiv. g^{-1})	*DF*	Functional yield (%)
PSt–CHO	2.80[a]	0.32	2.63[c]	0.29	91
PSt–CH_2Cl	1.20[b]	0.13	1.15[c]	0.12	92
PSt–CH_2Cl	3.40[b]	0.42	3.18[c]	0.36	86

[a] Determined by conversion to oxime and N analysis
[b] Determined by Cl analysis
[c] Determined by conversion to dibromide and Br analysis

Table 2 Insolublization of Pst–$CH=CH_2$ on exposure to u.v. radiation[a]

Entry #	Benzoyl peroxide initiator % (W/W)	Time in darkness (h)	% Insolublization[b,c] U.v. exposure time (min) 1	2	5	10	20
1	0	0	6	18	36	78	79
2	10	0	12	32	60	77	81
3	18	0	20	48	59	76	79
4	0	18	8	19	60	80	80
5	10	18	15	46	71	81	80
6	18	18	52	64	70	80	80

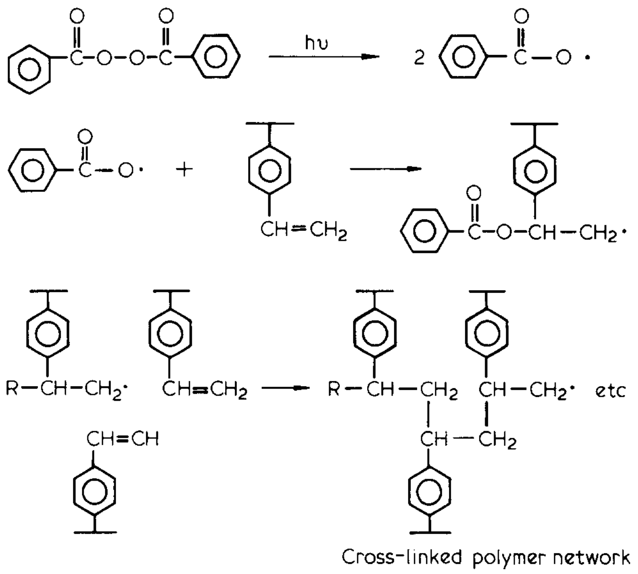
[a] Standard procedure: a 4% solution of polymer (2.6 mequiv. g^{-1}) containing varying amounts of initiator in THF was filtered and spread on pre-weighed glass plates. The solvent was evaporated under vacuum at room temperature for 2 h and the films weights were determined (5–8 mg). After exposure the films were developed in THF for 10 min, dried at 60° for 1 h, and the slides reweighed
[b] Results were reproducible within ±3%
[c] Unexposed films were completely soluble in THF

irradiated for varying lengths of time using a 275 Watt General Electric sunlamp at a distance of 15 cm and then either developed immediately with THF for 10 min or kept in the dark for 18 h before development. The ratio of the weight of polymer adhering to the glass plate to the original weight of the film gave the % insolublization (*Table 2*).

As can be seen, the polymer films reached a maximum of 80% insolublization after 10 min, even without added initiator, and additional exposure did not increase the amount of crosslinking. However, at lower exposure times, addition of benzoyl peroxide did increase the amount of crosslinking, especially if the plate was allowed to cure in darkness for 18 h. Thus only 8% of the film containing no initiator adhered to the plate after 1 min exposure and 18 h in darkness, while a film containing 18% w/w benzoyl peroxide was 52% insolublized under the same conditions. After 2 min exposure, the values were 19% and 64% respectively (*Table 2*). This indicates that chemical amplification has indeed been achieved, and the free radicals generated by the initial absorption of light initiate a chain reaction which produces numerous crosslinks in the polymer in darkness (*Scheme 2*).

EXPERIMENTAL

Soluble polystyrene (*MW* 20 000) was obtained from Polysciences, Inc. Elemental analyses were done in this laboratory (Br, Cl) or by Canadian Microanalytical Service Ltd. (N). Polymer films were exposed using an unfiltered General Electric 275 Watt sunlamp at a distance of 15 cm (intensity ≃ 5 000 μW cm^{-2}).



Scheme 2 Chemical amplification in the insolublization of PSt–$CH=CH_2$

Preparation of PSt–CHO[7]

Polystyrene (*MW* 20 000, 30.0 g) was dissolved in anhydrous cyclohexane (600 ml) under N_2 at room temperature. Tetramethylethylenediamine (TMEDA, 35 ml) was added, followed by *t*-BuLi (2 N, 120 ml). After 1 h, addition of dimethylformamide (DMF, 120 ml) resulted in decolourization of the dark red solution. The reaction mixture was allowed to stand overnight and then poured into methanol. The precipitate was collected, dissolved in CH_2Cl_2, filtered and reprecipitated in methanol to give 22.0 g of polymer. The *DF* was determined by conversion to the oxime[7].

N analysis: 2.7 mequiv. g^{-1}: $DF = 0.32$.

Preparation of PSt–CH_2Cl[9]

Polystyrene (*MW* 20 000, 15.0 g) was dissolved in $CHCl_3$ (80 ml) and chloromethyl methyl ether (40 ml). Stannic chloride (1.5 ml) was added and the solution was stirred at room temperature for 3 h. Overreaction results in the production of an insoluble gel. The dark violet coloured solution was poured into a large volume of methanol containing NaOH (1 g). The precipitate was collected, dissolved in CH_2Cl_2, filtered and reprecipitated in methanol to give 14.3 g of polymer containing 3.40 mequiv. g^{-1} of Cl ($DF = 0.42$). Polymers with lower *DF*'s can be obtained by increasing the amount of inert solvent or by decreasing the reaction time.

Preparation of PSt–$CH_2P^+(Ph)_3Cl^-$ (ref. 10)

PSt–CH_2Cl (3.40 mequiv. g^{-1}, 5.0 ·g) and triphenylphosphine (8.0 g) were dissolved in $CHCl_3$ (150 ml) and heated to reflux for 2 days. The reaction mixture was then cooled and poured into ether. The precipitate was collected, washed well with ether and dried to give 8.9 g of white polymer.

Preparation of PSt–CH = CH$_2$

(a) From PSt–CHO: Methyl triphenylphosphonium bromide (7.25 g) was suspended in anhydrous THF (50 ml) under N_2 at room temperature and, after addition of potassium *t*-butoxide (2.25 g), the reaction mixture was stirred for 15 min. A solution of PSt–CHO ($DF = 0.32$, 5.0 g) in anhydrous THF (50 ml) was added dropwise. After 1.5 h, the reaction mixture was poured into H_2O, and the precipitate was collected, dissolved in THF, filtered and reprecipitated in methanol to give 3.4 g of polymer. A small fraction of the polymer was dissolved in CCl_4 and treated with an excess of Br_2 in the dark to give PSt–$CHBrCH_2Br$.

Br analysis: 3.70 mequiv. g^{-1}; $DF = 0.29$.

(b) from PSt–$CH_2P^+(Ph)_3C.^-$: PSt–$CH_2P(Ph)_3Cl^-$ ($DF = 0.42$, 5.0 g) prepared as described above was dissolved in methanol (150 ml) and aqueous formaldehyde (37%, 80 ml) was added slowly to prevent precipitation of the polymer. Aqueous NaOH (1.2 g in 5 ml H_2O) was added dropwise and the reaction mixture was stirred overnight. The precipitate was dissolved in THF, filtered and reprecipitated in methanol to give 1.4 g of white polymer containing less than 0.2 mequiv. g^{-1} of residual Cl. The polymer contained 3.18 mequiv. g^{-1} of vinyl groups as determined by conversion to the dibromide.

Br analysis: 4.21 mequiv. g^{-1}; $DF = 0.36$.

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