

MODIFIED POLYSTYRENES: EFFECTS OF PENDANT FUNCTIONAL GROUPS ON THERMAL STABILITY

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ABSTRACT

Linear polystyrenes modified with pendant chloromethyl, sulfide, sulfoxide, sulfone and aldehyde functional groups have been prepared and their modes of thermal decomposition studied by thermal analysis in a flowing nitrogen atmosphere. Results are interpreted in terms of the effects of functional groups on polymer stability.

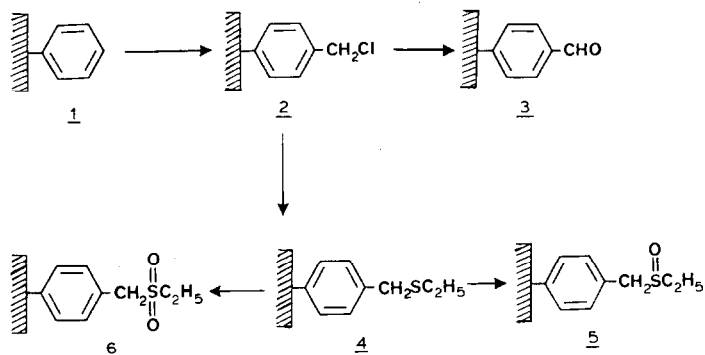
INTRODUCTION

Functionalized organic macromolecules are of current interest as reagents in synthetic organic chemistry [1]. Cross-linked insoluble matrices with pendant functionality have provided the basis for the development of solid-phase synthetic methods [2]. The best-known example of this class of reagent is Merrifield's peptide resin [2,3], typically a 1% cross-linked polystyrene matrix of 200–400 mesh, functionalized with pendant chloromethyl groups to the extent of about one milliequivalent of chlorine per gram of polymer. In a related area, macromolecules functionalized with pendant Lewis base moieties have been employed as support materials for the immobilization of transition metal ions as a means to heterogenize homogeneous catalysts for utilization in catalytic organic syntheses [4,5].

We have recently reported [6] the synthesis of polystyrenes with pendant thioether and sulfoxide functional groups and described some applications in organic synthesis and in transition metal coordination chemistry. The modified polystyrenes were prepared by functional group manipulations on a preformed matrix and the transformations monitored by diffuse reflectance infrared Fourier transform (DRIFT) spectroscopy [7]. The syntheses of these polymers and some related examples are shown in Scheme 1.

Since many reaction systems in which these polymers have the potential to be used operate under extreme conditions [4,5], it is important to understand

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Scheme 1. Preparation of polymers 1-6.

how variations in pendant functionality affect the thermal stability of modified polystyrenes, particularly with regard to the onset of thermal degradation. Accordingly, the modified polystyrenes shown in Scheme 1 have been studied by thermal analysis under a flowing nitrogen atmosphere and the results are described here in terms of the effects of variation in functional group on thermal stability and decomposition.

EXPERIMENTAL

The preparations of polymers 2-6 have been reported previously [6,7]. These polymers were characterized by diffuse reflectance infrared Fourier transform (DRIFT) spectroscopy [7]. Thermogravimetry (TG) and differential scanning calorimetry (DSC) experiments were carried out using a DuPont 1090 thermal analysis system at a heating rate of $10^{\circ}\text{C min}^{-1}$. Both studies were carried out in an atmosphere of flowing nitrogen and 1-8 mg of sample were used. Elemental analyses were performed by Micanal, Arizona and Galbraith labs., Tennessee.

RESULTS AND DISCUSSION

High-purity biological grade (bio-grade) linear polystyrene has been employed as the substrate for the transformations outlined in Scheme 1. The thermal degradation of polystyrene has, of course, been extensively studied (see, for example, refs. 8-10) and two basic processes, depolymerization to monomer and scission to oligomers, appear to dominate the decomposition process which is known to occur by a complex radical chain mechanism [9,10]. As a reference, the thermogram of the polystyrene substrate 1 is shown in Fig. 1. The onset of mass loss at a heating rate of $10^{\circ}\text{C min}^{-1}$ occurs at 270°C and 98.9% of the mass has been lost as volatile products by

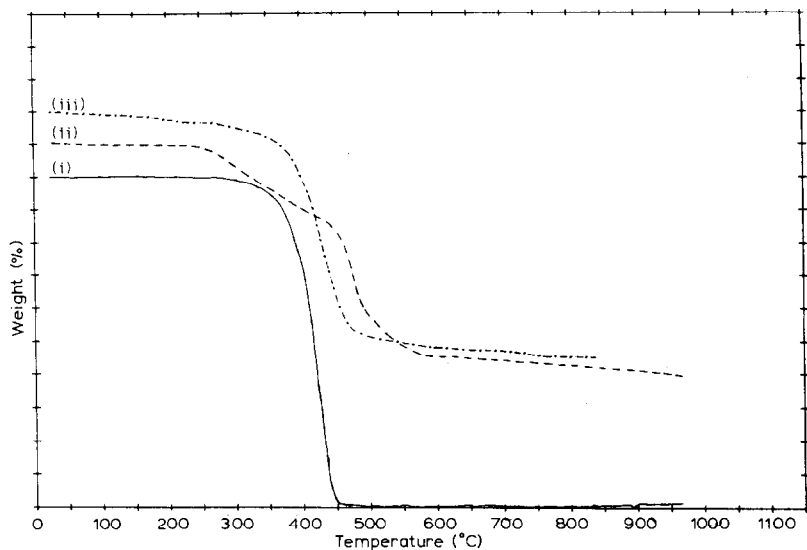


Fig. 1. Thermograms of polymers **1** (i), **2** (ii) and **3** (iii). Each plot begins at 100% on the mass axis, with each division representing a 10% mass loss.

460°C. Only ca. 1% of the mass remains as an involatile residue at 900°C, a feature we have commonly observed in the absence of cross-linking. The DSC plot (Fig. 2) shows a large endotherm at 410°C corresponding to the major mass loss by thermogravimetry and representing the depolymerization/scission process.

Chloromethylation of **1** with chloromethyl methyl ether and anhydrous

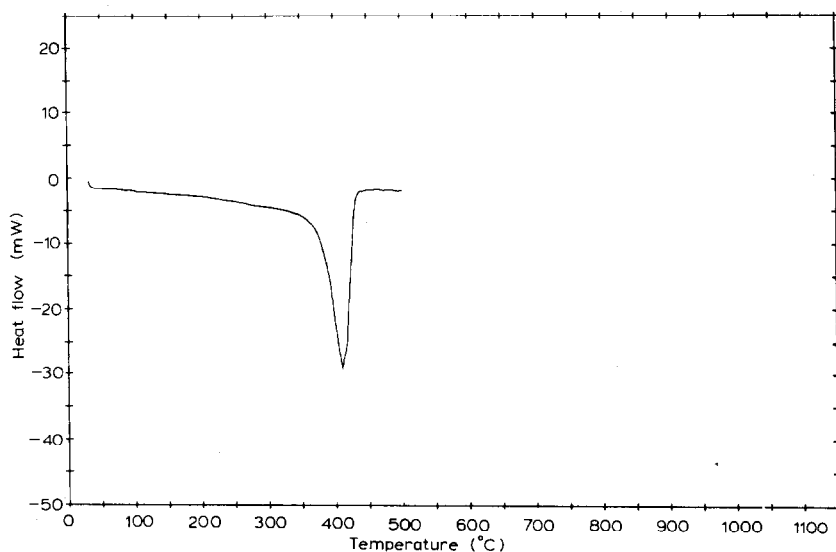
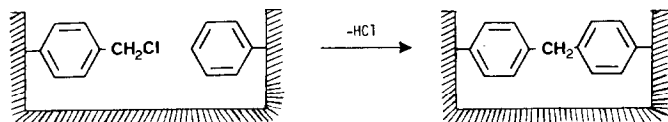
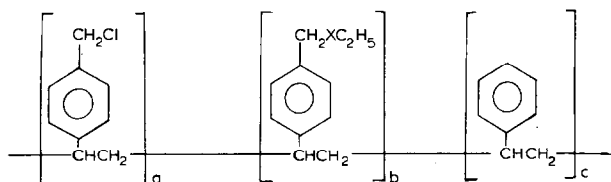


Fig. 2. DSC plot of polymer **1**.

tin(IV) chloride was performed under reaction conditions to minimize cross-linking by dehydrohalogenation [11] (Scheme 2) and the product (2) was



Scheme 2. Dehydrohalogenation of chloromethylated polystyrene (2).



Scheme 3. Composition of polymer samples. 1: $a = 0\%$, $b = 0\%$, $c = 100\%$. 2: $a = 85\%$, $b = 0\%$, $c = 15\%$. Calc. (found): Cl = 20.6% (20.2%). 4: X = S, $a = 1.94\%$, $b = 80.58\%$, $c = 17.48\%$. Calc. (found): S = 15.7% (14.7%), Cl = 0.4% ($\leq 0.4\%$). 5: X = SO. 6: X = SO₂.

characterized by ¹H NMR and DRIFT spectroscopies (Table 1) [7]. Elemental analysis (Scheme 3) indicated that chloromethylation of ca. 85% of the phenyl residues had been achieved [6]. The thermogram of 2 (Fig. 1) indicates that the onset of mass loss occurs at 230°C, at a heating rate of 10°C min⁻¹, and this indicates that no volatile species remain trapped in the polymer matrix after the chloromethylation reaction. Mass loss occurs in two major stages: a 25% mass loss over the range 230–445°C, followed by a more rapid mass loss of 41% over the range 445–580°C. Minor loss occurs up to 960°C, leaving a 29% involatile residue. Chloromethylation thus leads to an increased susceptibility to thermal degradation in comparison to polystyrene itself (230 vs. 270°C under identical conditions). This is not a surprising result since introduction of the chloromethyl groups provides new reactive sites for radical formation. A dehydrohalogenation of the type shown in Scheme 2 is a likely source of the 25% mass loss occurring over the range 230–445°C. Thus, quantitative loss of hydrogen chloride would result in a 21% mass loss, while the accompanying cross-linking would be expected to

TABLE 1
DRIFT data of polymers 1–6

Functional group	Sample	Diagnostic infrared absorbtions (cm ⁻¹)
-H	1	See ref. 7
-CH ₂ Cl	2	$\nu(-\text{CH}_2\text{Cl}) = 1266$, $\nu(\text{C}-\text{Cl}) = 677$
-CHO	3	$\nu(\text{C}=\text{O}) = 1702$, $\nu(\text{C}-\text{H})_{\text{ald}} = 2734$
-CH ₂ SC ₂ H ₅	4	See ref. 7
-CH ₂ S(O)C ₂ H ₅	5	$\nu(\text{S}=\text{O}) = 1049, 1019$
-CH ₂ SO ₂ C ₂ H ₅	6	$\nu(\text{SO}_2) = 1309, 1121$

generate a significant involatile residue, in this case, 29%.

Oxidation of chloromethylated polystyrene (**2**) with dimethylsulfoxide (DMSO) causes conversion to the aldehyde (**3**) [7], as determined by DRIFT spectroscopy (Table 1) [7]. The oxidation reaction is, however, performed at high temperature (110°C) [12] over a long time period (24 h) and so cross-linking by thermal dehydrohalogenation (Scheme 2) is likely. The solubility properties of **3** indicate that cross-linking does indeed occur. The thermogram of sample **3** (Fig. 1) shows a gradual loss of ca. 6% of the total mass on heating at 10°C min⁻¹ up to 340°C, presumably due to trapped DMSO within the polymer network. DMSO is particularly difficult to remove from polymers containing polar functional groups due to its high dielectric constant. A major loss of 67% of the mass occurs over the range 340–500°C, leaving a residue of ca. 26%, involatile up to 850°C. The onset of major mass loss occurs at a higher temperature for the aldehyde-functionalized polymer than for either chloromethylated polystyrene (**2**, 230°C) or for polystyrene itself (**1**, 270°C). Since a significant involatile residue is formed (ca. 26%), cross-linking is either already present (*vide supra*) or a radical-based cross-linking process occurs during decomposition. Oxidation of the chloromethyl groups to aldehyde groups evidently inhibits formation of the benzyl radicals at the pendant sites, which presumably form via carbon–chlorine homolysis in the case of **2**. Since formation of benzyl radicals at the backbone sites is a likely process in the thermal degradation of polystyrene itself [9,10], it seems that this process is also inhibited. The former observation is to be expected on thermodynamic grounds since a benzylic carbon–chlorine bond has a lower bond dissociation energy than a

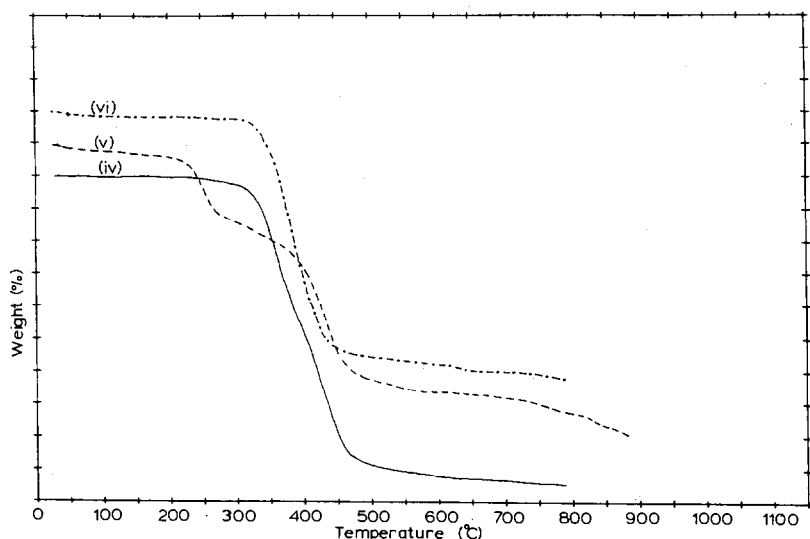


Fig. 3. Thermograms of polymers **4** (iv), **5** (v), and **6** (vi). Each plot begins at 100% on the mass axis, with each division representing a 10% mass loss.

typical aldehydic carbon–hydrogen bond (ca. 70 vs. ca. 86 kcal mol⁻¹) [13], although this does not take the kinetics into consideration. The latter observation is presumably a result of cross-linking already present in the polymer (*vide supra*).

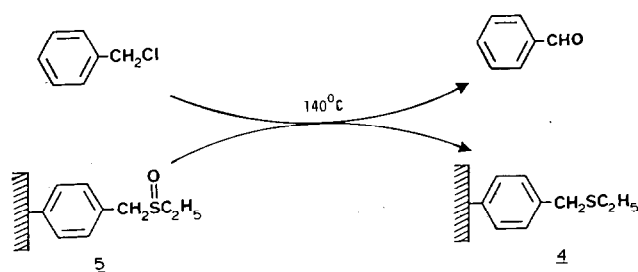
Treatment of the chloromethylated polystyrene (**2**) with the sodium salt of ethanethiol leads to essentially quantitative conversion to the thioether-functionalized polystyrene (**4**) [6], which has been characterized by ¹H NMR, ¹³C NMR and DRIFT spectroscopies (Table 1) [7] and by elemental analysis (Scheme 3). The onset of mass loss for **4** is at 265°C with a heating rate of 10°C min⁻¹ (Fig. 3) and it occurs in two overlapping stages which result in an 88% mass loss up to 500°C. Minor mass loss up to 800°C leaves a 5.5% involatile residue. The initial decomposition temperature is close to that of polystyrene itself (**1**, 270°C) and higher than that of chloromethylated polystyrene (**2**, 230°C). The quantity of involatile residue formed (5.5%) is small and is again closer to the value for polystyrene (ca. 1%) than for chloromethylated polystyrene (29%). There is no evidence for an initial chain stripping process in the thermal degradation of **4** (loss of HSC₂H₅, by analogy with Scheme 2, would represent a ca. 30% mass loss), although this appeared to occur for **2**, both of which have pendant benzylic sites. Indeed, loss of HSC₂H₅ would be an unlikely process since thiols are effective chain transfer reagents [14]. Presumably, sulfur stabilizes α -radicals [15], formed by benzylic C–H cleavage, and so inhibits chain stripping, thus allowing depolymerization/scission to remain dominant processes.

Oxidation of **4** with one equivalent of metachloroperoxybenzoic acid (MCPBA) leads to the formation of the sulfoxide (**5**) [6], characterized by ¹H NMR and DRIFT spectroscopies (Table 1) [7]. Elemental analysis (S and O) proved to be inconclusive for this polymer; not an unexpected result since the presence of S=O groups is known to interfere with combustion analysis [16]. The thermogram of **5** (Fig. 3) shows a 4% mass loss on heating at 10°C min⁻¹ up to 210°C, presumably due to trapped solvent from the oxidation process or due to loss of hydrogen-bonded water. DRIFT spectroscopy [7] indicates that attachment of sulfoxide groups to a polystyrene matrix imparts considerable hydrophilic character to the polymer. This observation may also relate to the problems encountered in combustion analysis. Major mass loss occurs in four distinct stages: rapid loss over the range 210–280°C (19% of mass), gradual loss of 9% mass (280–375°C), rapid loss of 41% mass over the range 375–505°C, and a gradual loss of 17% mass (505–800°C), leaving an involatile residue of ca. 11%.

The onset of mass loss at 210°C is the lowest initial decomposition temperature that we have observed for any of the functionalized polystyrenes studied so far. The individual stages of mass loss do not correlate with the losses calculated for benzylic carbon–sulfur or ethyl carbon–sulfur bond cleavages. The formation of an 11% involatile residue is indicative of radical cross-linking during thermal degradation.

Oxidation of **4** with excess MCPBA leads to sulfone formation (**6**) [7]. The sulfone has been characterized by DRIFT spectroscopy (Table 1) [7]. The thermogram of **6** (Fig. 3) shows negligible mass loss up to 300°C at a heating rate of 10°C min⁻¹, and then a 72% mass loss over the range 300–500°C. Minor mass loss up to 800°C leaves an 18% involatile residue. No low-temperature mass loss, indicative of a distinct chain-stripping process, is observed for **6** and the formation of substantial involatile residue indicates that thermal cross-linking occurs.

Table 2 summarizes the initial decomposition temperatures and percentage involatile residues for the polystyrenes **1–6**. Clearly, modification of polystyrenes with pendant functional groups has a dramatic effect on thermal stability and the variations in percentage residue indicate that a diversity of decomposition pathways is available. This information is important in connection with the reaction chemistry of these functionalized polymers [1–5]. For example, the sulfoxide (**5**) is an effective oxidant for the conversion of alkyl halides to aldehydes [6] (Scheme 4) exhibiting a reactivity



Scheme 4. Oxidation of benzyl chloride to benzaldehyde by the solid-phase oxidant **5**. See ref. 6 for conditions.

which is directly comparable to that of the corresponding model compound, benzyl ethyl sulfoxide [6]. The reaction, however, requires heating at 140°C for an extended period of time (typically in excess of 100 h) [6] and this is

TABLE 2
Thermal analysis data of polymers **1–6**

Functional group	Sample	T_d (°C) ^a	Residue (%) ^b
-CH ₂ S(O)C ₂ H ₅	5	210	11
-CH ₂ Cl	2	230	29
-CH ₂ SC ₂ H ₅	4	265	5.5
-H	1	270	1
-CH ₂ SO ₂ C ₂ H ₅	6	300	18
-CHO	3	340	26

^a Initial decomposition temperature (excluding solvent loss).

^b Involatile at ca. 800°C.

close enough to our observed initial decomposition temperature (210°C at 10°C min⁻¹) to cause concern. Indeed, the DRIFT spectrum of the polymer after reaction indicates that a more complex process than a simple conversion to **4** (Scheme 4) has occurred. A possible solution to this problem is to modify thermally stable lattices, such as silicas, with pendant functional groups and this approach is currently being investigated.

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