

Termination and side-reactions of polystyryllithium with β -bromostyrene

Norman J. Ward, Howell G.M. Edwards*

Chemical and Forensic Sciences, Interdisciplinary Research Centre for Polymer Science and Technology,
University of Bradford, Bradford, West Yorkshire BD7 1DP, UK

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Abstract

Low molecular weight polystyryllithium was synthesised and terminated with a two-fold molar excess of β -bromostyrene to produce an end-functionalised polymer. 1,3-Diphenylallyl-terminated polystyrene and other reaction products were analysed by FT-Raman spectroscopy. By comparison with model compounds, it can be deduced that β -bromostyrene with a predominantly *trans* configuration gave rise to primarily *cis* conformational unsaturation at the polystyrene chain-end. It was also demonstrated that a polystyrene 'dimer' and 1,4-diphenylbutadiene were produced via side-reactions which are considered to result from metal-halogen exchange in the reagents.
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1. Introduction

Macromolecules such as macromers and telechelics are normally low molecular weight polymers which are able to undergo further reaction by virtue of an available functional group at, or very near to, their chain-end [1–3]. These reactive oligomers are often synthesised by 'living' anionic polymerisation methods in aprotic solvents by introducing an unsaturated electrophile to the polyanions. For example, the addition of *p*-vinylbenzyl chloride to a polystyryllithium solution produces a polystyrene macromer with a styryl end-group [4].

In the current work, polystyrene oligomers are functionalised by the addition of β -bromostyrene to a polystyryllithium solution, producing a polystyrene macromer with a 1,3-diphenylallyl end-group as shown in Scheme 1.

Living polyanions have distinctive absorptions in the UV–vis spectral range leading to characteristic colours [5] which can be used to follow the progress of reactions; the bright orange colour of a polystyryllithium solution reduces in intensity as the polymer is deactivated by β -bromostyrene.

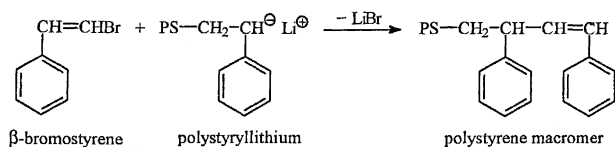
The β -bromostyrene sample employed in the current work comprises a mixture of *cis* and *trans* isomers, predominantly *trans*. It may be expected that the isomeric nature of the resulting polystyrene end-group would reflect the *cis/trans* ratio of the terminating agent employed.

It is known that the wavenumber of a $\nu(\text{C}=\text{C})$ Raman band is dependent upon the environment of the double bond [6] so that, for example, *cis* and *trans* isomers of both β -bromostyrene and 1,3-diphenylallyl-terminated polystyrene, can be identified and discriminated by Raman spectroscopy.

Cornell and Koenig [7] reported that the microstructure of polybutadienes can be quantitatively determined from a peak height determination of the $\nu(\text{C}=\text{C})$ Raman bands of *vinyl*, *cis*-1,4 and *trans*-1,4 units occurring at 1639, 1650 and 1664 cm^{-1} , respectively, since the intensity of Raman scattering is directly proportional to the concentration of the species. However, this method suffers from the inherent disadvantage that derives from the incomplete resolution of the $\nu(\text{C}=\text{C})$ Raman bands arising from these three microstructures, particularly when one or more of the components is in a low species concentration [8]. Also, a prominent aromatic $\nu(\text{C}=\text{C})$ quadrant stretching band for polystyrene [9] appears at 1603 cm^{-1} which is close to the three diene $\nu(\text{C}=\text{C})$ bands in the spectrum, and causes further potential complication in

* Corresponding author.

E-mail address: h.g.m.edwards@bradford.ac.uk (H.G.M. Edwards).



the spectral resolution of the conformations of the microstructural components of the chain-termination process.

2. Experimental

The polymerisations were carried out in specially designed glass vessels evacuated on a high-vacuum-line. The vessels were washed with *sec*-butyllithium solution followed by three aliquots of cyclohexane (May and Baker, h.p.l.c. grade) distilled from *sec*-butyllithium in situ. Freshly distilled solvent was subsequently used as the reaction medium. Styrene (Aldrich, 99+%) monomer, passed through a column of molecular sieve and basic alumina and then stored over calcium hydride, was distilled into the reaction vessel. The ‘living’ anionic polymerisation of styrene was initiated with a calculated amount of *sec*-butyllithium solution (1.3 M in cyclohexane, Aldrich). At completion, a known sample volume of the polystyryllithium solution was retrieved and terminated by a drop of methanol. A calculated excess of β -bromostyrene (Aldrich, 99%) was injected into the remainder of the solution. The colour of the solution changed immediately from bright orange to a very pale-yellow. A few drops of methanol were injected into the solution and the colour did not change further, thus indicating that the β -bromostyrene addition to the polymer chain had reached completion.

The polymers were precipitated by addition of alcohol, filtered, redissolved in tetrahydrofuran, reprecipitated in alcohol, filtered and finally dried in a vacuum oven for

48 h at 40 °C. The β -bromostyrene-terminated polystyrene macromer and the unfunctionalised polystyrene sample were recovered as fine white powders. The reaction medium was collected and subsequently reduced in volume by rotary evaporation in order to recover unreacted β -bromostyrene.

In two separate experiments, the above procedure was initially undertaken employing an approximately 10-fold (Experiment 1) and secondly an approximately 2-fold (Experiment 2) molar excess of β -bromostyrene to polystyryllithium.

2.1. Characterisation

Molecular weight determination of the polystyrene products was made by gel permeation chromatography using a Waters model R410 refractometer and two Polymer Labs 5 g mixed-bed columns (suitable for analysis with polystyrene molecular weights as low as 200 g mol⁻¹) with tetrahydrofuran as the eluant. Approximately 100 μ l of polymer solution (0.25 wt.%) was injected into the columns and analysed with an eluant flow rate of 1 ml/min. The columns were calibrated with polystyrene standards, hence molecular weights of the copolymers quoted in this work are in terms of polystyrene equivalents. The raw data collected were processed via an in-house software package.

The Raman spectra of the diene-terminated polystyrene oligomers were obtained using an FT-Raman instrument using excitation at 1064 nm produced by an ND:YAG laser and recorded using a Bruker IFS 66 with the FRA 106 FT-Raman module attachment for a total of 500 scans at 4 cm⁻¹ spectral resolution. Raman spectral wavenumbers were accurate to better than ± 1 cm⁻¹ for strong, sharp bands.

3. Results and discussion

In Fig. 1, the Raman spectrum of β -bromostyrene between 1500 and 1750 cm⁻¹ is provided. The suppliers (Aldrich) of

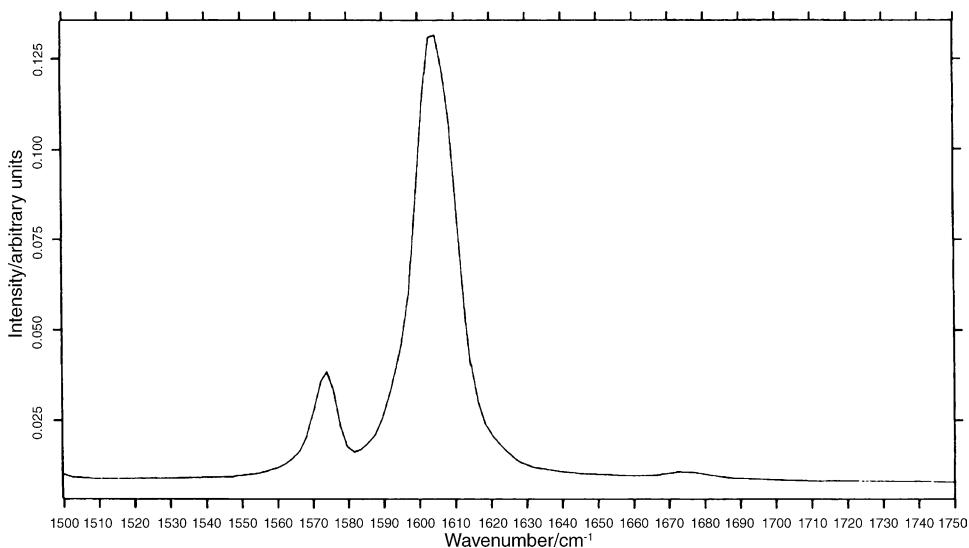


Fig. 1. FT-Raman spectrum of β -bromostyrene; 1064 nm excitation, 2000 scans accumulated at 4 cm⁻¹ spectral resolution.

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