

Monomer Sequence Control via Living Anionic Copolymerization – Synthesis of Alternating, Statistical and Telechelic Copolymers and Sequence Analysis by MALDI ToF Mass Spectrometry

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ABSTRACT: Diphenylethylene (DPE) is a monomer which has attracted significant interest from both academia and industry. DPE can undergo (co)polymerization by living anionic polymerization but is incapable of forming a homopolymer due to steric hindrance. Herein the copolymerization of DPE and 1,1-bis(4-*tert*-butyldimethylsiloxyphenyl)ethylene (DPE-OSi) with styrene or butadiene is described in order to produce (functional) copolymers with controlled co-monomer sequences – either alternating or telechelic. The copolymer sequences are inherently controlled by relative reactivity ratios, which in turn can be tuned by both monomer structure and by the polarity of the polymerization solvent. The composition of the copolymers prepared in this study were analyzed by ^1H NMR spectroscopy and MALDI ToF

mass spectrometry, the latter offering a unique opportunity to demonstrate perfect alternating sequences and insight into other sequences such as telechelic polymers.

INTRODUCTION: Nature has perfected the control of monomer sequences in natural polymers such as proteins and nucleic acids; using enzymes or RNA to control the sequence. In the case of proteins, the resulting amino acid sequence constitutes the primary structure of the protein, which in turn dictates higher ordered structure, the three dimensional form and ultimately the function of the protein. The possibility of controlling monomer sequences in synthetic polymers might be considered one of the last great challenges in polymer chemistry and offers the opportunity to design new sequences and copolymers with enhanced or entirely new properties. However, until recently the control of co-monomer sequences in synthetic polymers has been almost totally neglected. The polymer molecules of a particular protein are self-similar in both sequence order and chain length but such absolute sequence control is unlikely to be realized in the world of man-made polymers - however, perfect sequence control may not be necessary to produce new and interesting materials. In recent years a growing number of research groups have begun working towards various strategies to impart control over monomer sequence distribution. Step-growth polymerizations involving two monomers which each contain mutually-reactive functional groups, i.e. $AX_2 + BY_2$ allow perfectly alternating copolymers to be formed. The co-monomer sequence control in this case is inherent and does not constitute a synthetic challenge. An extension of the simple step-growth approach was reported by Ueda and Okada who described the preparation of an ABC alternating terpolymer by combining polyaddition with polycondensation reactions and using very specific monomer reactions to control the sequence.¹⁻² By the introduction of protecting groups, step-growth polymerization can be used to create perfect extended monomer sequences – a methodology currently used for the synthesis of

biopolymers such as peptides³ and oligonucleotides⁴ – but each monomer addition requires a number of reaction steps and this can both time-consuming and expensive. The real challenge lies in controlling monomer sequences in chain-growth mechanisms such as radical or ionic polymerizations and a number of strategies to control co-monomer sequence distribution have recently been proposed. One such strategy involves the use of a template to control monomer addition. In essence this is how nature controls sequences in natural polymers, where the template (enzymes, RNA, etc.) ensures that only the desired monomer is available at the active site. However, these templates are usually very complex molecules and the synthesis of templates to control sequence distribution is a major challenge in itself. Hillmyer *et al.* reported a novel approach to prepare regioselective terpolymers and quarterpolymers by ring opening metathesis polymerization (ROMP) of multi-substituted cyclooctenes.⁵ In this case the sequence is built into the monomer which unfolds to create a perfectly ordered copolymer structure with high regio- and stereo-control. However, the synthesis of the multi-functional cyclooctene monomer is non-trivial. A similar strategy was reported by Sawamoto *et al.*^{6,7} in which one unit of methacrylic acid and one unit of acrylic acid were each attached via an ester linkage to the *peri*-position of a naphthalene template. Upon radical polymerization and cleavage of the monomers from the naphthalene “template” by hydrolysis, a perfectly alternating copolymer of methacrylic acid and acrylic acid results. In a similar fashion, the same group used a palladium template coordinated to three monomers (two units of 4-aminomethylstyrene and one unit of 4-vinylpyridine) to prepare a copolymer with repeating ABA monomer sequences. This approach can also be used to prepare ABC and other triad sequences. The use of templating initiators to control the resulting co-monomer sequence has also been proposed. In a proof of concept demonstration Sawamoto^{8,9} designed a template initiator that allows preferential consumption of

methacrylic acid over methyl methacrylate. The template contained an initiating site for metal mediated living radical polymerization and pendent amino groups to enable template controlled monomer insertion in which methacrylic acid was ‘recognized’ and consumed in preference to methyl methacrylate. A similar approach¹⁰ involved the introduction of a crown ether to provide a different type of recognition site into the initiator, which specifically recognizes the sodium ion of sodium methacrylate over methacryloxyloxyethyltrimethylammonium chloride. Moreover, this recognition template promoted reaction of the less reactive monomer; the latter monomer proved more reactive than the former with an analogous template free initiator. The use of DNA as a polymerization template has been reported by O’Reilly¹¹ who polymerized a nucleobase-containing vinyl monomer in the presence of a complementary self-assembled block copolymer to yield a homopolymer with high molecular weight and low dispersity. Although this preliminary homopolymerization does not demonstrate co-monomer sequence control, it is a very promising approach for future attempts to synthesise sequence controlled copolymers with high molecular weight¹².

Whilst template controlled polymerization is a very exciting and promising approach to impact sequence control in polymers, the (more) facile approach of exploiting kinetic control over co-monomer sequences during polymerization has the advantage of being experimentally easier, more economical and hence much more applicable from an industrial perspective. Provided the right monomer pairs are found, it is possible to obtain perfectly controlled alternating sequences. One of the earliest reported¹³ examples of monomer sequence control is the free radical copolymerization of maleic anhydride, which is incapable of homopolymerization, and styrene to form an alternating copolymer.¹⁷ This monomer combination was later exploited by Hawker¹⁴ who used an excess of styrene with maleic anhydride to prepare a block copolymer of

poly(styrene-*co*-maleic anhydride)-*block*-polystyrene by nitroxide-mediated radical polymerization. Lutz¹⁵ expanded on this idea of exploiting a monomer incapable of homopolymerization, with sequential monomer addition to prepare a multi-block copolymer. In this innovative method, an excess of styrene was copolymerized in turn with a selection of substituted maleimide monomers. The controlled radical polymerization of styrene by ATRP was interrupted periodically by the addition of an aliquot of maleimide co-monomer. As a result of the reactivity ratios, a short sequence of alternating styrene-maleimide was introduced until the maleimide derivative was consumed, at which point the homopolymerization of styrene resumed. A second maleimide derivative could be subsequently added and a second short alternating sequence introduced. This procedure was repeated for two more maleimide derivatives to prepare a polystyrene polymer containing four short alternating styrene-maleimide sequences. This elegant approach exploits manual intervention or “intelligent-design” combined with intrinsic kinetic sequence control.

There are a number of reported examples of other alternating copolymers prepared by controlled free radical,¹⁶⁻¹⁹ ROMP,²⁰ cationic,²¹ and living anionic copolymerizations.²²⁻²⁷ Of particular interest for living anionic copolymerizations is the monomer 1,1-diphenylethylene (DPE). DPE is unable to form a homopolymer due to the steric bulk of the monomer although it has been reported²⁸ that the formation of dimers of DPE can occur following the initiation with *n*-butyllithium where there is a large excess of DPE with respect to lithium. That said it is assumed that in most cases the monoadduct is formed, homopolymerization does not occur and DPE has therefore been used to initiate and end-cap polymers prepared by anionic polymerization.²⁹⁻³³ DPE is particularly useful for the initiation of acrylate and methacrylate monomers where the steric bulk prevents side reactions including attack by the carbanion upon

the carbonyl group of the monomer. DPE has also been used to moderate the reactivity of propagating species such as polystyryl lithium before the addition of methyl methacrylate to prepare a polystyrene-block-poly(methyl methacrylate) copolymer.^{29,30} Whilst DPE is unable to homopolymerize, it can copolymerize with other monomers, and with a suitable co-monomer, DPE can be used to prepare alternating copolymers in an analogous fashion to the free-radical copolymerization of maleic anhydride with styrene. Alternating copolymers might be considered the simplest example of a copolymer with perfect sequence control in so much as all polymer chains are self-similar in monomer sequence order (if not in chain length). Yuki *et al.* explored the copolymerization of DPE with styrene,²⁶ butadiene,²⁴ isoprene,²⁵ 2,3-dimethylbutadiene^{23, 27} and methoxystyrene.²² ¹H-NMR analysis suggested the formation of alternating or near-alternating copolymers in all cases when THF was used as reaction solvent, however only styrene, 2,3-dimethylbutadiene and *p*-methoxystyrene formed nearly-alternating copolymers with DPE in benzene. Butadiene, isoprene and *o*-methoxystyrene showed a very strong tendency to homopolymerize in the presence of DPE when using non-polar solvents. The reactivity ratios obtained by Yuki *et al.* are shown in Table S1. Hatada *et al.* investigated the copolymerization of DPE with *m*- and *p*-divinylbenzene (DVB).^{34,35} They found *p*-DVB had a reactivity ratio, $r_1 = 16$ in toluene and 2.5 in THF (if DVB is M1 and DPE is M2), and hence *p*-DVB had a strong tendency to homopolymerize in the presence of DPE. *m*-DVB had a reactivity ratio, $r_1 = 2.5$ in toluene and 1.2 in THF and hence *m*-DVB also has a slight tendency to homopolymerize rather than cross-propagate. In comparison, it was reported that styrene has a reactivity ratio, $r_1 = 0.4$ in toluene and 0.13 in THF (if styrene is M1 and DPE M2). Whilst the incorporation of DPE could be increased by using a large excess of DPE in the monomer feed, it was concluded that *p*-DVB and *m*-DVB are not ideal co-monomers for preparing alternating copolymers.

Functional derivatives of DPE have been used to introduce functionality at various positions along the polymer chain. These functional derivatives usually require the functionality to be masked due to the sensitivity of living anionic polymerization to the presence of functional groups. A number of polymerization studies have involved derivatives of DPE, such as 1-phenyl-1-(1'-pyrenyl)ethylene, as a fluorescent labeling group.³⁶⁻⁴⁰ Amino-derivatives such as 1-(4-dimethylaminophenyl)-1-phenylethylene and 1-(4-(*N,N*-bis(trimethylsilyl)amino)phenyl)-1-phenylethylene have been used to place amino groups at the beginning of the chain,⁴⁰ the terminus of the chain,^{41,42} at the interface between two blocks⁴¹ or to prepare telechelic copolymers by the use of sequential addition of stoichiometric amounts of the functionalized DPE.⁴¹ Li *et al.* copolymerized 1,1-bis(4-dimethylaminophenyl)ethylene with styrene to prepare a statistical copolymer,⁴³ and Quirk *et al.* copolymerized 1-(4-dimethylaminophenyl)-1-phenylethylene with styrene.⁴⁴ Hayashi has reported the synthesis by anionic polymerization of telechelic copolymers of poly(styrene-*co*-butadiene) end-capped at both chain ends with 1,1-bis(4-dimethylaminophenyl)ethylene by two strategies – both involving the introduction of the functional DPE at the α -chain end via the initiation process. The first strategy introduces the second functional DPE via an end-capping reaction subsequent to the complete consumption of monomer and the second strategy involves the simultaneous copolymerization of styrene, butadiene and the functional DPE monomer, relying upon the exclusion of the DPE monomer, due to low reactivity, until the end of the reaction - an approach analogous to that used in the present work and described later. However, the analysis provided in this previously reported work, to support claims that reactivity ratios can be exploited to exclude the DPE monomer from the copolymerization enabling a one-pot, selective, end-capping reaction with the functional DPE are rather qualitative.⁴⁵ Summers *et al.* also used amino-derivatives of DPE to prepare a

variety of telechelic copolymers by ATRP using stoichiometric amounts and sequential addition of the DPE-derivative.⁴⁶⁻⁴⁹ Telechelic copolymers with carboxylic acid groups at each chain end were also synthesized by Summers by both ATRP using 4,5-dihydro-4,4-dimethyl-2-[4-(1-phenylethenyl)phenyl]oxazole⁵⁰ and by living anionic polymerization using *N,N*-diisopropyl-4-(1-phenylethenyl)benzamide⁵¹ and deprotection of the carboxylic acid groups post polymerization. Similarly DPE derivatives have been used to add phenol groups at the chain terminus by both ATRP⁵² and by living anionic polymerization⁵³ or at the interface between two styrene blocks by living anionic polymerization.⁵⁴ 1,1-Bis(4-*tert*-butyldimethylsiloxyphenyl)ethylene (DPE-OSi) has also been used to end-cap polystyrene and the resulting macromonomers used to prepare hierarchically branched polymers and copolymers (HyperMacs and DendriMacs).^{55,56} Hutchings *et al.* have recently reported the synthesis of sequence controlled copolymerizations of styrene and DPE-OSi (a derivative of DPE which is a less reactive monomer than DPE) and the synthesis of alternating oligomers of 4-cyanodiphenylethylene (a derivative of DPE which is a more reactive monomer than DPE) and styrene.^{57,58}

Herein sequence-controlled copolymerizations containing DPE and the synthesis of telechelic copolymers using a DPE derivative in a single one-step copolymerization are investigated. Early examples of alternating copolymers (based upon DPE) prepared by living anionic polymerization were reported nearly half a century ago²²⁻²⁷. In the 1960's NMR was the state-of-the-art analytical technique and was used in combination with infrared spectroscopy and reaction yields to analyze the composition of the resulting copolymers. In the present study MALDI ToF mass spectrometry (MS) data is reported to establish unequivocally the alternating sequence of such copolymers and to provide insight into the composition of other key co-monomer sequences.

EXPERIMENTAL:

Materials. Benzene (Aldrich, HPLC grade >99.9%), toluene (Fisher, HPLC grade >99.9%) and styrene (Aldrich) were dried with calcium hydride (97%, Aldrich) and degassed by a series of freeze-pump-thaw cycles. Tetrahydrofuran (THF) was dried and degassed over sodium (Aldrich) and benzophenone (Aldrich) by freeze-pump-thaw cycles until the solution turned purple, and was freshly distilled prior to use. Butadiene (Aldrich, 99%) was dried and purified by passing the monomer successively through columns of Carbosorb (Aldrich), to remove any inhibitor, and molecular sieves. Methanol (Fisher, AR grade), *sec*-butyllithium (Aldrich, 1.4M in cyclohexane), 2,6-di-*tert*-butyl-4-methyl phenol (BHT) (Aldrich, 99%), and *N, N, N', N'*-tetramethylethylenediamine (TMEDA) (Aldrich, 99.5%) were used as received. 1,1-Diphenylethylene (DPE) (Aldrich, 97%) was degassed by freeze-pump-thaw cycles and purified by the dropwise addition of *sec*-butyllithium until a red colour persisted and freshly distilled prior to use. 1,1-*Bis*(4-*tert*-butyldimethylsiloxyphenyl)ethylene (DPE-OSi) was synthesized according to the procedure of Quirk and Wang.⁵⁴

Measurements. Molecular weight analysis was carried out by size exclusion chromatography (SEC) on a Viscotek TDA 302 with a refractive index, viscosity and light scattering detectors. 2 × 300 mm PLgel 5 μm mixed C-columns (with a linear range of molecular weight from 200 to 2,000,000 g mol⁻¹) were used and THF as the eluent with a flow rate of 1.0 ml/min at a temperature of 35 °C. In all cases the molecular weights were obtained by triple detection SEC with light scattering, using a value of 0.185 for polystyrene and 0.124 for polybutadiene (obtained from Viscotek) for the *dn/dc*. A *dn/dc* value of 0.196 (calculated from a known concentration of PSD-9) was used for the poly(styrene-*co*-DPE) copolymers and a *dn/dc* value of

0.189 (calculated from a known concentration of PBdD-1) was used for the poly(butadiene-*co*-DPE) copolymers.

¹H NMR, ¹³C NMR, HSQCAD and COSY spectra were recorded on either a Bruker-400 MHz or a Varian VNMRS-700 MHz spectrometer using CDCl₃ as a solvent. Spectra were referenced to the trace of CHCl₃ (7.3 ppm) present in CDCl₃.

MALDI ToF MS analysis was carried out on an Autoflex II TOF/TOF mass spectrometer (Bruker Daltonik GmbH). The instrument is equipped with a 337 nm nitrogen laser and a reflectron is used to enhance performance below, typically, *m/z* 10,000. This was calibrated for MS experiments with the sodium adducts of poly(ethylene glycol) 2.0 K. A ground steel target plate was cleaned with methanol and acetone prior to use. Positive ion MSMS experiments using the LIFTTM capability were conducted in the absence of a collision gas at a source pressure of approximately 2.5×10^{-7} mbar. The LIFTTM device accelerates product ions allowing them passage through the reflectron improving sensitivity, resolution and mass accuracy.⁵⁹⁻⁶⁰ Samples were dissolved in a solution of THF or chloroform (~1 mg/ml) and mixed with a matrix solution (~50 mg/ml) in a ratio of 10 : 10 : 1 (sample : matrix : silver solution). 1 μ L of this mixture is spotted on to a metal target and placed into the MALDI ion source. The matrix used was *trans*-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propenylidene]malonitrile (DCTB) and Ag⁺ was used as a dopant.

Differential Scanning Calorimetry (DSC) was performed under an inert atmosphere on a TA Q1000 instrument from room temperature to 493 K at 10 K/min, 20 K/min and 40 K/min; with 5 minute isothermal periods between each temperature ramp. Glass transition temperatures were analysed using TA instruments Universal Analysis 2000 version 4.5A.

Polymer Synthesis. All copolymers were synthesized by living anionic polymerization using standard high vacuum techniques, highly purified (dried and degassed) solvents and monomers and trap to trap distillation.

Synthesis of alternating and statistical copolymers.

Synthesis of poly(styrene-*co*-DPE).

Synthesis of PSD-1. The synthesis of poly(styrene-*co*-DPE) was carried out as follows: benzene (90 ml) and styrene (2.36 g, 23 mmol) were distilled, under vacuum, into the reaction apparatus. DPE (2.72 g, 26 mmol) was injected *via* a rubber septum. For a target molecular weight of 7,500 g mol⁻¹, *sec*-butyllithium (BuLi) (0.45 ml of 1.4 M solution, 0.63 mmol) was added by injection *via* a rubber septum, resulting in the red colour indicative of a mixture of diphenylethyl lithium and styryl lithium. The solution was stirred at room temperature for 21 hours before a small sample was extracted and terminated by the injection of nitrogen-sparged methanol. The red colour of the living polymer solution dissipated instantly. The remaining reaction mixture was used in a subsequent reaction, the results of which will be published elsewhere. The polymer sample was recovered by precipitation into methanol, collected by filtration, washed with further methanol and dried *in vacuo*. ¹H NMR (700 MHz, CDCl₃, ppm): δ = 0.0 – 2.5 (5H –CH₂CPhH-CH₂CPh₂), 4.8 – 7.4 (15H –CH₂CPhH-CH₂CPh₂). $M_n = 9,000 \text{ g mol}^{-1}$; $M_w = 9,900 \text{ g mol}^{-1}$; $\mathcal{D} = 1.10$.

Synthesis of PSD-2. Poly(styrene-*co*-DPE) with a target molecular weight of 14,500 g mol⁻¹, was prepared by the previously described procedure except that 100 ml of benzene, 2.10 g styrene (20 mmol), 3.75 g DPE (21 mmol) and 0.28 ml of 1.4 M BuLi (0.39 mmol) were used and the reaction was stirred at 50 °C for 21 hours before a sample was extracted and terminated.

Again the remaining reaction mixture was used in a subsequent reaction, the results of which will be published elsewhere. ^1H NMR (700 MHz, CDCl_3 , ppm): $\delta = 0.0 - 2.5$ (5H $-\text{CH}_2\text{CPhH}-\text{CH}_2\text{CPh}_2$), 4.8 – 7.4 (15H $-\text{CH}_2\text{CPhH}-\text{CH}_2\text{CPh}_2$). $M_n = 10,700 \text{ g mol}^{-1}$; $M_w = 12,200 \text{ g mol}^{-1}$; $\mathcal{D} = 1.14$.

Synthesis of PSD-3(a-c). Poly(styrene-*co*-DPE) with a target molecular weight of $40,000 \text{ g mol}^{-1}$, was prepared by the previously described procedure except that 50 ml of benzene, 2.38 g styrene (23 mmol), 6.37 g DPE (35 mmol) and 0.12 ml of 1.4 M BuLi (0.17 mmol) were used and the reaction was stirred at $30 \text{ }^\circ\text{C}$ and sampled after 4 hours and after 18 hours to yield PSD-3a and PSD-3b respectively. The remaining reaction mixture was stirred at $30 \text{ }^\circ\text{C}$ for a further 30 hours before being terminated with degassed methanol to yield PSD-3c. Yield = 90 %. ^1H NMR (700 MHz, CDCl_3 , ppm): $\delta = 0.0 - 2.5$ (5H $-\text{CH}_2\text{CPhH}-\text{CH}_2\text{CPh}_2$), 4.8 – 7.4 (15H $-\text{CH}_2\text{CPhH}-\text{CH}_2\text{CPh}_2$). (PSD-3a) $M_n = 24,100 \text{ g mol}^{-1}$; $M_w = 25,600 \text{ g mol}^{-1}$; $\mathcal{D} = 1.06$ (PSD-3b) $M_n = 59,400 \text{ g mol}^{-1}$; $M_w = 66,600 \text{ g mol}^{-1}$; $\mathcal{D} = 1.12$ (PSD-3c) $M_n = 91,800 \text{ g mol}^{-1}$; $M_w = 105,500 \text{ g mol}^{-1}$; $\mathcal{D} = 1.15$.

Synthesis of PSD-4. Poly(styrene-*co*-DPE) with a target molecular weight of $35,600 \text{ g mol}^{-1}$, was prepared by the previously described procedure except that 70 ml of benzene, 2.23 g styrene (21 mmol), 5.97 g DPE (33 mmol) and 0.13 ml of 1.4 M BuLi (0.18 mmol) were used and the reaction was stirred at room temperature for 4 days before a sample was extracted and terminated. The remaining reaction mixture was used in a subsequent reaction, the results of which will be published elsewhere. ^1H NMR (700 MHz, CDCl_3 , ppm): $\delta = 0.0 - 2.5$ (5H $-\text{CH}_2\text{CPhH}-\text{CH}_2\text{CPh}_2$), 4.8 – 7.4 (15H $-\text{CH}_2\text{CPhH}-\text{CH}_2\text{CPh}_2$). $M_n = 40,100 \text{ g mol}^{-1}$; $M_w = 43,800 \text{ g mol}^{-1}$; $\mathcal{D} = 1.09$.

Synthesis of PSD-5. Poly(styrene-*co*-DPE) with a target molecular weight of $1,500 \text{ g mol}^{-1}$, was prepared by the previously described procedure except that 50 ml of benzene, 1.94 g styrene (19 mmol), 3.46 g DPE (19 mol) and 2.5 ml of 1.4 M BuLi (3.5 mmol) were used and the reaction was stirred at $50 \text{ }^{\circ}\text{C}$ for 20.5 hours before a sample was extracted and terminated. Again the remaining reaction mixture was used in a subsequent reaction, the results of which will be published elsewhere. ^1H NMR (700 MHz, CDCl_3 , ppm): $\delta = 0.0 - 2.5$ (5H $-\text{CH}_2\text{CPhH}-\text{CH}_2\text{CPh}_2$), 4.8 – 7.4 (15H $-\text{CH}_2\text{CPhH}-\text{CH}_2\text{CPh}_2$). $M_n = 1,900 \text{ g mol}^{-1}$; $M_w = 2,200 \text{ g mol}^{-1}$; $\mathcal{D} = 1.10$.

Synthesis of PSD-6. Poly(styrene-*co*-DPE) with a target molecular weight of $1,500 \text{ g mol}^{-1}$, was prepared by the previously described procedure except that 65 ml of benzene, 2.22 g styrene (21 mmol), 5.93 g DPE (33 mmol) and 2.9 ml of 1.4 M BuLi (4.1 mmol) were used and the reaction was stirred at $50 \text{ }^{\circ}\text{C}$ for 18 hours before a sample was extracted and terminated. Again the remaining reaction mixture was used in a subsequent reaction, the results of which will be published elsewhere. ^1H NMR (700 MHz, CDCl_3 , ppm): $\delta = 0.0 - 2.5$ (5H $-\text{CH}_2\text{CPhH}-\text{CH}_2\text{CPh}_2$), 4.8 – 7.4 (15H $-\text{CH}_2\text{CPhH}-\text{CH}_2\text{CPh}_2$). $M_n = 1,900 \text{ g mol}^{-1}$; $M_w = 2,100 \text{ g mol}^{-1}$; $\mathcal{D} = 1.11$.

Synthesis of PSD-7. Poly(styrene-*co*-DPE) with a target molecular weight of $50,000 \text{ g mol}^{-1}$, was prepared by the previously described procedure except that toluene (50 ml) was used as the solvent; 2.00 g styrene (19 mmol), 3.65 g DPE (20 mmol) and 0.078 ml of 1.4 M BuLi (0.11 mmol) were used and the reaction was stirred at $25 \text{ }^{\circ}\text{C}$ for 6 days before being terminated with degassed methanol. Yield = 75 %. ^1H NMR (700 MHz, CDCl_3 , ppm): $\delta = 0.0 - 2.5$ (5H –

$\text{CH}_2\text{CPhH-CH}_2\text{CPh}_2$), 4.8 – 7.4 (15H $-\text{CH}_2\text{CPhH-CH}_2\text{CPh}_2$). $M_n = 57,200 \text{ g mol}^{-1}$; $M_w = 62,300 \text{ g mol}^{-1}$; $\mathcal{D} = 1.09$.

Synthesis of PSD-8. Poly(styrene-*co*-DPE) with a target molecular weight of $50,000 \text{ g mol}^{-1}$, was prepared by the previously described procedure except that 55ml of toluene, 1.72 g styrene (17 mmol), 4.70 g DPE (26 mmol) and 65 μl of 1.4 M BuLi (0.091 mmol) were used and the reaction was stirred at $25 \text{ }^\circ\text{C}$ for 5.5 days before being terminated with degassed methanol. Yield = 71 %. $^1\text{H NMR}$ (700 MHz, CDCl_3 , ppm): $\delta = 0.0 - 2.5$ (5H $-\text{CH}_2\text{CPhH-CH}_2\text{CPh}_2$), 4.8 – 7.4 (15H $-\text{CH}_2\text{CPhH-CH}_2\text{CPh}_2$). $M_n = 71,600 \text{ g mol}^{-1}$; $M_w = 84,900 \text{ g mol}^{-1}$; $\mathcal{D} = 1.19$.

Synthesis of PSD-9. Poly(styrene-*co*-DPE) with a target molecular weight of $50,000 \text{ g mol}^{-1}$, was prepared by the previously described procedure except that THF (60 ml) was used as the solvent; 2.51 g styrene (24 mmol), 4.57 g DPE (25 mmol) and 98 μl of 1.4 M BuLi (0.14 mmol) were used and the reaction was stirred at $0 \text{ }^\circ\text{C}$ for 16.3 hours before being terminated with degassed methanol. Yield = 88 %. $^1\text{H NMR}$ (700 MHz, CDCl_3 , ppm): $\delta = 0.0 - 2.5$ (5H $-\text{CH}_2\text{CPhH-CH}_2\text{CPh}_2$), 4.8 – 7.4 (15H $-\text{CH}_2\text{CPhH-CH}_2\text{CPh}_2$). $M_n = 60,000 \text{ g mol}^{-1}$; $M_w = 66,000 \text{ g mol}^{-1}$; $\mathcal{D} = 1.10$.

Synthesis of PSD-10. Poly(styrene-*co*-DPE) with a target molecular weight of $1,500 \text{ g mol}^{-1}$, was prepared by the previously described procedure except that 25 ml of THF, 2.37 g styrene (23 mmol), 4.32 g DPE (24 mmol) and 3.1 ml of 1.4 M BuLi (4.3 mmol) were used and the reaction was stirred at $0 \text{ }^\circ\text{C}$ for 16.6 hours before being terminated with degassed methanol. Yield = 93 %. $^1\text{H NMR}$ (700 MHz, CDCl_3 , ppm): $\delta = 0.0 - 2.5$ (5H $-\text{CH}_2\text{CPhH-CH}_2\text{CPh}_2$), 4.8 – 7.4 (15H $-\text{CH}_2\text{CPhH-CH}_2\text{CPh}_2$). $M_n = 1,800 \text{ g mol}^{-1}$; $M_w = 2,200 \text{ g mol}^{-1}$; $\mathcal{D} = 1.24$.

Synthesis of poly(butadiene-*co*-DPE).

Synthesis of PBdD-1. The synthesis of poly(butadiene-*co*-DPE) was carried out as follows: THF (60 ml) and butadiene (1.89 g, 35 mol) were distilled, under vacuum, into the reaction apparatus. DPE (6.07 g, 34 mol) was injected *via* a rubber septum. The solution was cooled to 0 °C with an ice bath and for a target molecular weight of 50,000 g mol⁻¹, *sec*-butyllithium (0.11 ml of 1.4 M solution, 0.16 mmol) was added by injection *via* a rubber septum, resulting in the red colour indicative of a mixture of diphenylethyl lithium and butadienyl lithium. The solution was stirred at 0 °C for 4 days after which time the reaction was terminated by the injection of nitrogen-sparged methanol. The red colour of the living polymer solution dissipated instantly. The polymer was recovered by precipitation into excess methanol that contained a small amount of antioxidant (BHT), collected by filtration, washed with further methanol and dried *in vacuo*. Yield > 70 %. ¹H NMR (700 MHz, CDCl₃, ppm): δ = 1.0 – 2.9 (2H -CH₂CPh₂); (3H -CH₂CHCH=CH₂) and (4H -CH₂CH=CHCH₂), 3.7 – 5.7 (3H -CH₂CHCH=CH₂) and (2H -CH₂CH=CHCH₂), 6.5 – 7.4 (10H -CH₂CPh₂). $M_n = 40,600 \text{ g mol}^{-1}$; $M_w = 43,400 \text{ g mol}^{-1}$; $\mathcal{D} = 1.07$.

Synthesis of PBdD-2. Poly(butadiene-*co*-DPE) with a target molecular weight of 1,100 g mol⁻¹, was prepared by the previously described procedure except that 50 ml of THF, 1.30 g butadiene (24 mmol), 4.46 g DPE (25 mmol) and 3.6 ml of 1.4 M BuLi (5.0 mmol) were used and the reaction was stirred at 0 °C for 3 days before being terminated with degassed methanol. Yield > 50 %. ¹H NMR (700 MHz, CDCl₃, ppm): δ = 1.0 – 2.9 (2H -CH₂CPh₂); (3H -CH₂CHCH=CH₂) and (4H -CH₂CH=CHCH₂), 3.7 – 5.7 (3H -CH₂CHCH=CH₂) and (2H -CH₂CH=CHCH₂), 6.5 – 7.4 (10H -CH₂CPh₂). $M_n = 2,100 \text{ g mol}^{-1}$; $M_w = 2,300 \text{ g mol}^{-1}$; $\mathcal{D} = 1.11$.

Synthesis of Telechelic Polystyrene using DPE-OSi.

Synthesis of PSD_{OSi}-(a-b). DPE-OSi (0.99 g, 2.3 mmol), a crystalline solid, was added to an ampoule sealed with a Youngs tap, degassed and evacuated overnight. Approximately 20 ml of dry benzene was distilled into the ampoule, dissolving the DPE-OSi. The benzene was then removed from the vessel by distillation and replaced with a further 20 ml of dry benzene. This process was repeated two more times to azeotropically dry the DPE-OSi. Benzene (20 ml) was added by distillation into the ampoule to dissolve the DPE-OSi, and then the ampoule was raised to atmospheric pressure with dry nitrogen. The DPE-OSi/benzene solution was then added to the reaction vessel by injection *via* a rubber septum. Benzene (40 ml) was distilled into the reaction vessel and the mixture was freeze-pump-thawed for further purification. 1.3 M *sec*-butyllithium was added drop wise (to titrate out any residual impurities) until the red colour persisted and a final addition of 0.69 ml *sec*-butyllithium (0.90 mmol) of 1.3 M *sec*-butyllithium was added by injection *via* a rubber septum for a target molecular weight of 3,400 g mol⁻¹. The solution was stirred at room temperature for 1 hour before styrene (2.25 g, 22 mmol) was added by injection into the reaction vessel and the red colour could be seen to turn orange, indicative of polystyryllithium. Within several minutes the orange colour had darkened a little, more closely resembling the red colour of living DPE-OSi. The reaction was allowed to stir at room temperature for one day, at which point part of the reaction mixture was separated into a side flask (PSD_{OSi}-a) and TMEDA (0.269 ml, 1.8 mmol; 2 mole equivalents with respect to *sec*-butyllithium) injected into the main reaction vessel (PSD_{OSi}-b) and allowed to continue reacting. After one more day both solutions were terminated with nitrogen-sparged methanol, precipitated into methanol, collected and dried to constant mass *in vacuo*. (PSD_{OSi}-a and PSD_{OSi}-b) ¹H NMR (400 MHz, CDCl₃, ppm): δ = 0.0 – 2.7 (3H –CH₂CPhH), 0.0 – 0.4 (12H –Si(CH₃)₂C(CH₃)₃), 0.8

– 1.1 (18H –Si(CH₃)₂C(CH₃)₃), 6.0 – 7.5 (5H –CH₂CPhH). (PSD_{OSi-a}) $M_n = 3,100 \text{ g mol}^{-1}$; $M_w = 3,300 \text{ g mol}^{-1}$; $\mathcal{D} = 1.06$ (PSD_{OSi-b}) Yield = 71 %. $M_n = 3,100 \text{ g mol}^{-1}$; $M_w = 3,300 \text{ g mol}^{-1}$; $\mathcal{D} = 1.05$

Synthesis of Telechelic Polybutadiene and DPE-OSi.

Synthesis of PBdD_{OSi}-(a-c). DPE-OSi (1.43 g, 3.2 mmol) was added to an ampoule sealed with a Youngs tap, degassed and dried azeotropically three times using benzene. Benzene (20 ml) was added by distillation into the ampoule to dissolve the DPE-OSi, and then the ampoule was raised to atmospheric pressure with dry nitrogen. The DPE-OSi/benzene solution was then added to the reaction vessel by injection *via* a rubber septum. Benzene (50 ml) was distilled into the reaction vessel and the reaction mixture was freeze-pump-thawed for further purification. 1.4 M *sec*-butyllithium was added dropwise (to titrate out any residual impurities) until the red colour persisted and a final addition of 0.92 ml *sec*-butyllithium (1.3 mmol) of 1.4 M *sec*-butyllithium was added by injection *via* a rubber septum for a target molecular weight of 2,600 g mol⁻¹. The solution was stirred at room temperature for 24 hours before butadiene (2.26 g, 42 mmol) was distilled into the reaction vessel. Upon addition of butadiene the colour of the reaction mixture could be seen to fade to pale orange. The reaction was allowed to stir at room temperature overnight, during which time the colour of the reaction mixture had faded further to dark yellow. After the reaction had proceeded for 3 days, the reaction mixture was sampled (PBdD_{OSi-a}). The remaining reaction mixture was split into two portions. A small portion was separated into a side arm (PBdD_{OSi-b}) and to the remainder was added TMEDA (0.22 ml, 1.5 mmol; 2 mole equivalents with respect to *sec*-butyllithium) (PBdD_{OSi-c}). Within minutes of the addition of TMEDA, the colour of the reaction mixture became red. Both portions of living polymer were stirred at room temperature for a further 6.5 days before being terminated with nitrogen-sparged

methanol. All three samples were then recovered by precipitation into excess methanol that contained a small amount of anti-oxidant (BHT), collected and dried to constant mass *in vacuo*. (PBdD_{Osi}-a, b and c) ¹H NMR (400 MHz, CDCl₃, ppm): δ = 0.0 – 2.9 (2H –CH₂CAr₂) and (3H - CH₂CHCH=CH₂), 0.1 – 0.2 (12H –Si(CH₃)₂C(CH₃)₃), 0.9 – 1.0 (18H –Si(CH₃)₂C(CH₃)₃), 1.8 – 2.2 (4H -CH₂CH=CHCH₂), 4.8 – 5.0 (CH₂CHCH=CH₂), 5.1 – 5.5 (CH₂CH=CHCH₂), 5.5 – 5.7 (CH₂CHCH=CH₂), 6.6 – 7.1 (8H – CH₂CAr₂). (PBdD_{Osi}-a) $M_n = 3,700 \text{ g mol}^{-1}$; $M_w = 3,900 \text{ g mol}^{-1}$; $\mathcal{D} = 1.06$ (PBdD_{Osi}-b) $M_n = 4,200 \text{ g mol}^{-1}$; $M_w = 5,000 \text{ g mol}^{-1}$; $\mathcal{D} = 1.19$ (PBdD_{Osi}-c) Yield = 62 %. $M_n = 4,300 \text{ g mol}^{-1}$; $M_w = 4,600 \text{ g mol}^{-1}$; $\mathcal{D} = 1.08$.

RESULTS AND DISCUSSION

It has long been assumed that diphenylethylene (DPE) cannot homopolymerize by any mechanism due to steric hindrance. However, Yuki *et al.* first reported in 1967 that DPE could be used in an anionic copolymerization with other monomers.²²⁻²⁷ Furthermore, depending on the feed ratio, solvent and co-monomer, apparently perfect alternating copolymers could be prepared provided that the rate constant for cross-propagation to DPE (M_2) is significantly higher than the rate constant for self-propagation of the non-DPE monomer (M_1) i.e. $k_{12} \ll k_{11}$. One such co-monomer is styrene which can form alternating copolymers with DPE but the propensity for alternation is highly dependent upon solvent polarity. Yuki *et al.* used ¹H NMR and mass balance (yield) calculations to estimate the amount of DPE in the copolymer and therefore postulate co-monomer sequences. However, nearly 50 years later, using a combination of high field (700 MHz) NMR spectroscopy and MALDI ToF MS it is possible to distinguish the exact composition of the copolymer and therefore establish whether the monomer sequence in these copolymers is perfectly alternating or not.

Hutchings *et al.* have previously reported that derivatives of DPE can be copolymerized by anionic polymerization with monomers such as styrene to produce sequence controlled functional copolymers.⁵⁷⁻⁵⁸ Herein a detailed investigation into the impact of reaction conditions is described, specifically the impact of solvent polarity upon the copolymerization reactivity ratios for the anionic polymerization of DPE with styrene and butadiene respectively using MALDI ToF MS to identify the resulting monomer sequences. Furthermore, it will also be shown how an informed choice of (functional) co-monomers, feed ratio and reaction conditions can yield telechelic polymers in a one-pot, one-shot reaction, in which the resulting monomer sequence is controlled inherently by reactivity ratios rather than sequential addition of reactants. Again MALDI ToF MS (and NMR) can be used to conclusively prove the resulting sequences and the telechelic structure.

Synthesis of DPE containing alternating and statistical copolymers.

Copolymerization reactions were carried out using DPE and styrene or DPE and butadiene in which the impact of solvent polarity and co-monomer feed ratio upon the resulting composition and co-monomer sequence has been investigated. MALDI ToF MS has proved uniquely useful in identifying monomer sequence distributions.

Styrene/DPE copolymerization in benzene.

A series of poly(styrene-*co*-DPE) copolymers were synthesized and the composition and molecular weight data are shown in Table 1 and Table 2 respectively. The copolymer composition was determined from ¹H NMR spectroscopy as described in the Electronic Supporting Information, however, it was not possible to accurately determine the composition of low molecular weight copolymers of poly(styrene-*co*-DPE) (PSD-5 and PSD-6) due to the contribution of the *sec*-butyl end-groups on the ¹H NMR spectra.

The reactivity ratios for the copolymerization of styrene (M_1) and DPE (M_2), r_1 , (listed in Table 1) were calculated by an iterative process using the following equation,

$$\ln \frac{[M_2]}{[M_2]_0} + \frac{1}{r_1 - 1} \ln \left[\frac{[M_1]_0}{[M_2]_0} (r_1 - 1) + 1 \right] = 0 \quad [1]$$

derived by Yuki *et al.* from the Mayo-Lewis equation, where $[M_2]$ is the final concentration of DPE, $[M_1]_0$ and $[M_2]_0$ are the initial monomer concentrations of styrene and DPE respectively, $r_1 \neq 1$, the reaction must have gone to completion and $[M_2] \neq 0$.²⁶ In order to calculate the reactivity ratio, the instantaneous monomer feed ratios are required. However, as the monomer feed ratios vary throughout the reaction, reactivity ratios are typically calculated at low monomer conversion when the monomer feed ratio is close to the initial monomer feed ratio.⁶¹ However, when DPE is used as a co-monomer it is possible to calculate the reactivity ratio at complete conversion provided there is unreacted DPE monomer present at the end of the reaction. Upon consumption of the non-DPE co-monomer, styrene in this case, the polymerization will end as DPE cannot homopolymerize. One might expect any excess DPE to end cap the living chain but dimerization does not occur when excess DPE is added to living polystyrene chain ends²⁸. At this point it is possible to calculate the final concentration of DPE monomer, determine the final monomer feed ratio and therefore calculate the reactivity ratio. However, if the DPE monomer is consumed first, the co-monomer will continue to homopolymerize regardless and the final composition will inevitably be equal to the molar feed ratio. For this reason the reactivity ratios have only been calculated when the molar feed ratio of DPE was equimolar or in excess of the co-monomer. Furthermore, if the reaction had not reached completion, as in the case of PSD-3a and PSD-3b, then it is also not possible to calculate the reactivity ratio as the concentration of the

non-DPE co-monomer will not be equal to 0 and the instantaneous molar feed ratios cannot be determined.

The values in Table 1 show that for each copolymerization when benzene is the solvent, the reactivity ratio (r_1) is less than 1.0, indicating that styrene has a preference for cross-propagation. However, the values are not so low as to promote perfect alternation – even when DPE is present in excess of styrene. The reactivity ratios obtained for the copolymerization of styrene and DPE in benzene are approximately between 0.5 – 0.6, which are close to the value obtained by Yuki *et al.* who reported a reactivity ratio of 0.7. Reactivity ratios have been reported to vary with temperature; however, in this case there does not appear to be a significant variation in the reactivity ratio obtained from the copolymerization at 30 °C and at 50 °C.

The MALDI ToF MS analysis was performed on low molecular weight copolymers ($M_n \sim 2,000 \text{ g mol}^{-1}$) as it is often difficult to obtain MALDI spectra for high molecular weight polymers⁶² and because at higher molecular weight the mass resolution is insufficient to separate individual chains and results in a continuous distribution.⁶³ Using MALDI ToF MS, the molar mass corresponding to each individual copolymer chain could be found, from which it was possible to calculate the number of styrene and DPE units in a given chain. Since it is not possible for two DPE units to be adjacent to each other, it is possible to establish if the copolymer has a perfectly alternating sequence, as shown in Figure 2. It should be noted that the intensities of individual peaks are not 100 % quantitative, since some copolymer chains may be less prone to ionization.⁶⁴ Regardless, the MALDI ToF mass spectrum in Figure 1 provides an excellent indication of the copolymer composition and suggests that the polymerization of an

Table 1: Monomer Reactivity Ratios, r_1 , for anionic copolymerization of styrene and 1,1-Diphenylethylene.

Sample	Sty : DPE feed ratio	Solvent	Temp/°C	Sty : DPE in copolymer (from ^1H NMR)	r_1
PSD-1	1.00 : 0.67	Benzene	RT	1.00 : 0.50	-
PSD-2	1.00 : 1.03	Benzene	50	1.00 : 0.73	0.60
PSD-3a	1.00 : 1.54	Benzene	30	1.00 : 0.85	-
PSD-3b	1.00 : 1.54	Benzene	30	1.00 : 0.85	-
PSD-3c	1.00 : 1.54	Benzene	30	1.00 : 0.82	0.57
PSD-4	1.00 : 1.54	Benzene	RT	1.00 : 0.85	0.46
PSD-5	1.00 : 1.03	Benzene	50	-	-
PSD-6	1.00 : 1.54	Benzene	50	-	-
PSD-7	1.00 : 1.05	Toluene	25	1.00 : 0.81	0.37
PSD-8	1.00 : 1.59	Toluene	25	1.00 : 0.83	0.54
PSD-9	1.00 : 1.05	THF	0	1.00 : 0.90	0.15
PSD-10	1.00 : 1.05	THF	0	-	-

Table 2: Molecular weight data (obtained using triple detection SEC with $dn/dc = 0.196$) for the anionic copolymerization of styrene and 1,1-diphenylethylene.

Sample	$M_n/\text{g mol}^{-1}$	$M_w/\text{g mol}^{-1}$	\bar{D}
PSD-1	9,000	9,900	1.10
PSD-2	10,700	12,200	1.14
PSD-3a	24,100	25,600	1.06
PSD-3b	59,400	66,600	1.12
PSD-3c	91,800	105,500	1.15
PSD-4	40,100	43,800	1.09
PSD-5	1,900	2,100	1.10
PSD-6	1,900	2,100	1.11
PSD-7	57,200	62,300	1.09
PSD-8	71,600	84,900	1.19
PSD-9	60,000	66,000	1.10
PSD-10	1,800	2,200	1.24

almost equimolar feed ratio in benzene results in a copolymer which is highly but not perfectly alternating. Figure 1 shows that many of the individual chains are perfectly alternating with equal numbers of styrene and DPE units; for example the most intense peak with an m/z of 1587 corresponds to 5 units of styrene ($5 \times 104.06 \text{ u}$) + 5 units of DPE ($5 \times 180.09 \text{ u}$) + the counter ion, Ag (107.87 u) + the *sec*-butyl end-group (57.07 u) + the hydrogen end-group (1.01 u). The difference between this peak and the peak at m/z 1303, labelled 4 : 4, is exactly 284 g mol^{-1} ; corresponding to one styrene + one DPE unit. The majority of the peaks correspond to perfect alternating sequences, comprising equal numbers of styrene and DPE units (blue lines), or ratios of styrene : DPE = $n : n + 1$ (red lines), or $n : n - 1$ (green lines). Importantly, there is no evidence of any peaks corresponding to ratios of styrene : DPE = $n : n + 2$ which one might expect to see as evidence of DPE homopolymerization. The latter two ratios ($n : n + 1$ and $n : n - 1$) represent chains with the same monomer unit at both chain ends (see inset Figure 1). There are also a few, low intensity peaks indicating a low concentration of chains which are not perfectly alternating, highlighted with red circles. Thus the reactivity ratio r_1 is indeed less than 1.0 – indicating that styrene shows a preference for undergoing cross-propagation reactions – but not so low as to avoid any sequence imperfections. It will subsequently be shown that solvent polarity can be used to change the reactivity ratios and promote alternation, but the resulting composition can of course also be controlled by the monomer feed ratio. Thus, by increasing the amount of DPE in the monomer feed to give a feed ratio of 1.00 : 1.54 (styrene : DPE) the likelihood of styrene-DPE cross-propagation can be increased and alternation enhanced. The MALDI ToF mass spectrum in Figure 2 confirms this and shows chains which are predominately alternating copolymers with only a very few imperfections – the peaks corresponding to imperfections being highlighted with red circles. The difference between Figures 1 and 2 clearly

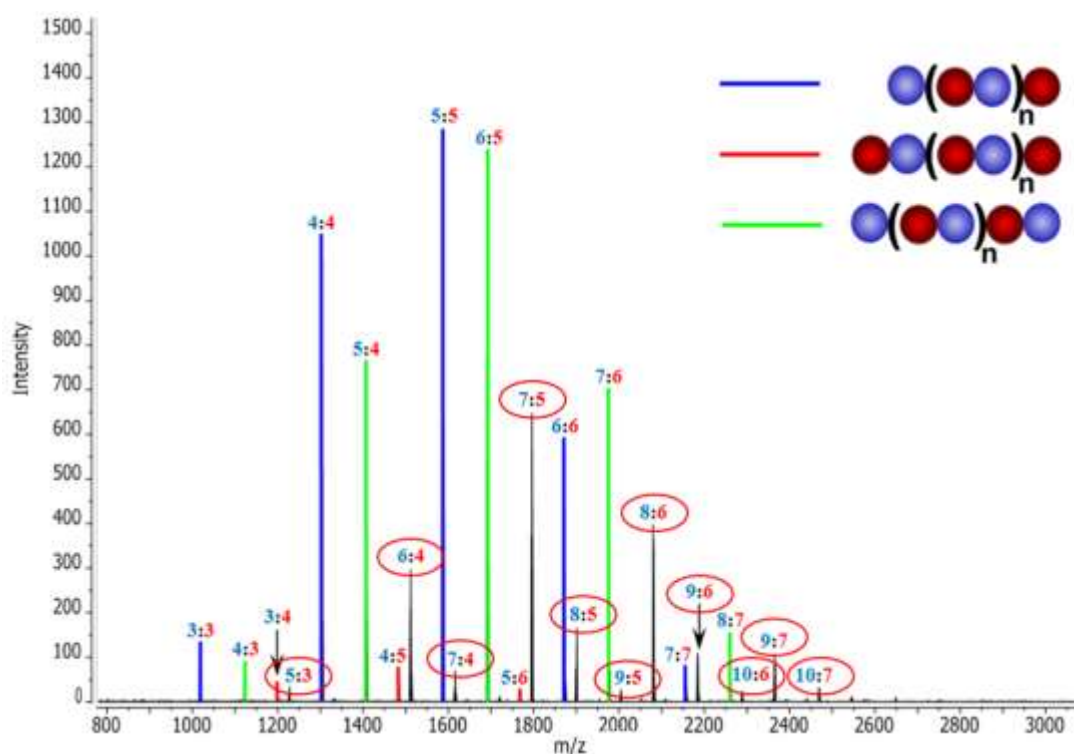


Figure 1: MALDI ToF mass spectrum for the copolymer PSD-5 prepared by the anionic copolymerization (in benzene) of styrene and DPE (monomer molar feed ratio of styrene : DPE = 1.00 : 1.03). The mole ratio of styrene : DPE for any given chain is labelled with styrene in blue and DPE in red.

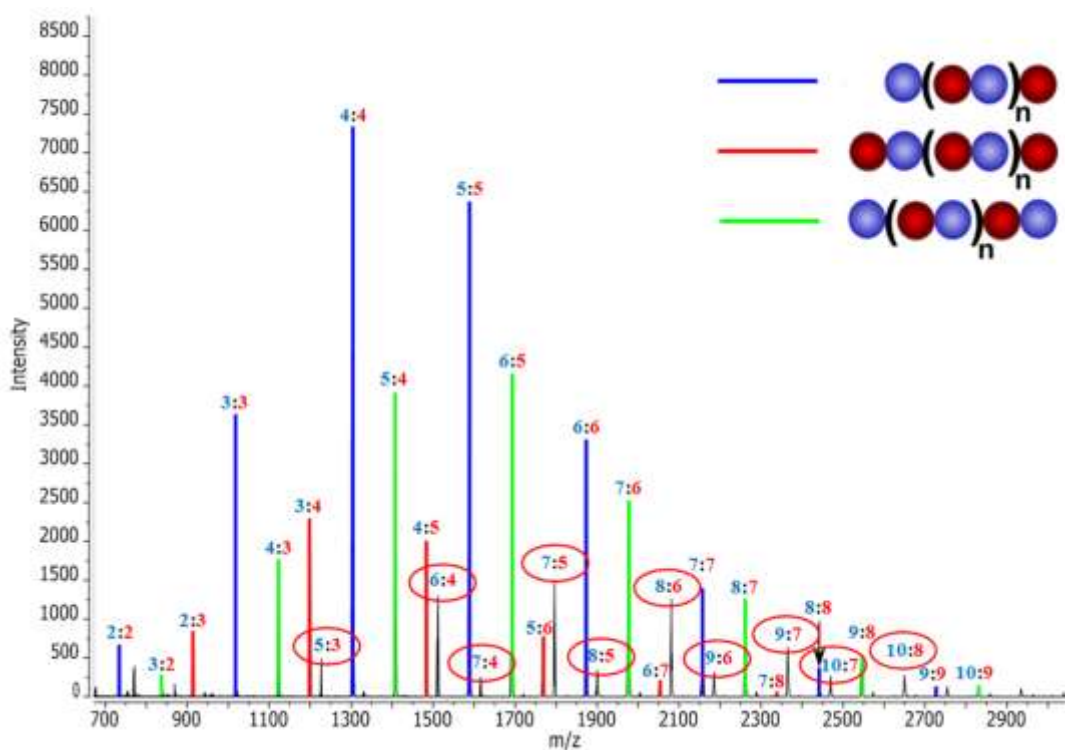


Figure 2: MALDI ToF mass spectrum for the copolymer PSD-6 prepared by the anionic copolymerization (in benzene) of styrene and DPE (monomer molar feed ratio of styrene : DPE = 1.00 : 1.54). The mole ratio of styrene : DPE for any given chain is labelled with styrene in blue and DPE in red.

demonstrates the impact that increasing the feed ratio of DPE has upon the resulting monomer sequence and shows a near-perfect alternating copolymer can be obtained even when the reactivity ratio is not 0.

Impact of Solvent Polarity on Reactivity Ratios. Changing the polarity of the polymerization solvent has been shown to have an impact upon reactivity ratios in living anionic copolymerization²⁶ and in the case of styrene and DPE, increasing polarity reduces the magnitude of the reactivity ratio, r_1 , such that styrene has a stronger propensity for cross-propagation. The copolymerization of styrene and DPE in both toluene and THF was investigated and the resulting polymers analyzed by ¹H NMR (for composition) and DSC (to establish thermal properties – see later). Comparing the copolymerization of styrene and DPE in toluene (PSD-7 and 8) with analogous reactions in benzene indicates that in toluene, the reactivity ratio, r_1 , is between 0.4 – 0.5 whereas in benzene r_1 is observed to be 0.5 – 0.6 and again in excellent agreement with Yuki *et al.* who reported a reactivity ratio $r_1 = 0.44$.²⁶ This indicates that changing the solvent from benzene to toluene may slightly decrease the reactivity ratio but does not have a significant effect.

Switching to the more polar solvent THF, had a much greater effect on the relative reactivities. PSD-9 (Table 1), a copolymerization of (almost) equimolar amounts of DPE and styrene in THF at 0 °C resulted in a copolymer with an (almost) equimolar composition of DPE and styrene and a reactivity ratio $r_1 = 0.15$, much lower than the reactivity ratios calculated for reactions carried out in benzene and toluene and in good agreement with previously reported data by Yuki *et al.* who found a reactivity ratio $r_1 = 0.13$.²⁶

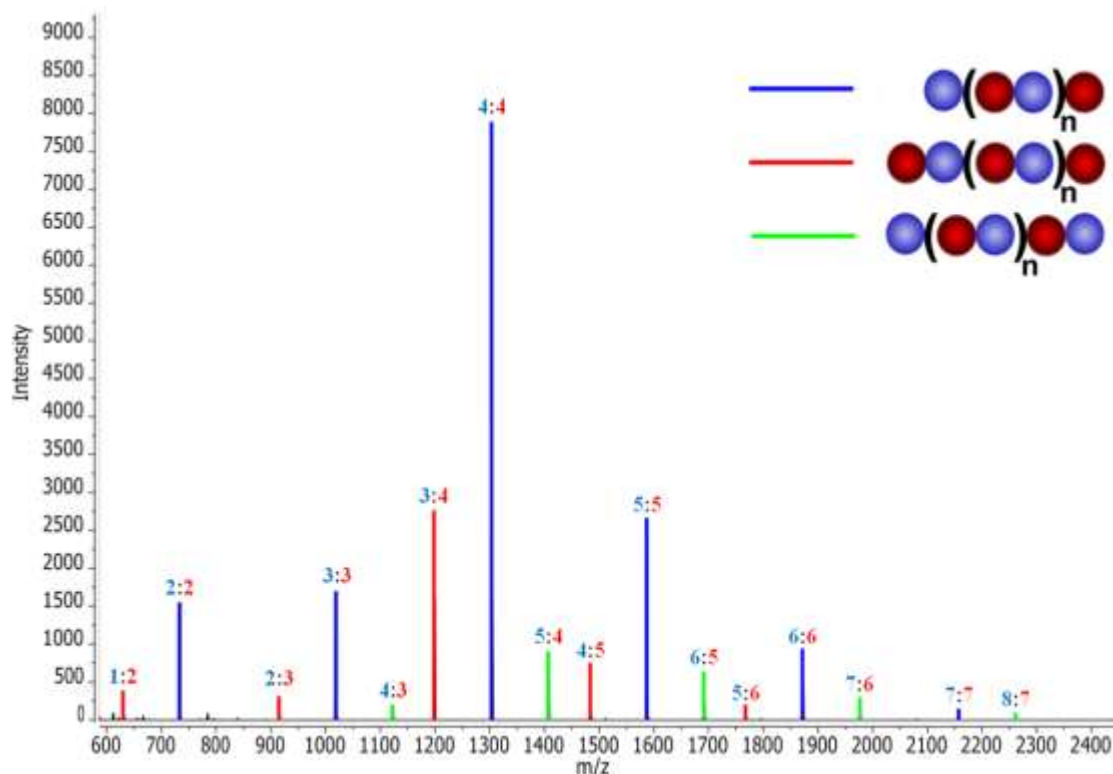


Figure 3: MALDI ToF mass spectrum for the copolymer PSD-10, prepared by the anionic copolymerization (in THF) of styrene and DPE (monomer molar feed ratio of styrene : DPE = 1.00 : 1.05). The mole ratio of styrene : DPE for any given chain is labelled with styrene in blue and DPE in red.

A low molecular weight copolymer of poly(styrene-*co*-DPE) (PSD-10) was prepared in THF and analyzed by MALDI ToF MS (Figure 3). Every visible peak in the MALDI ToF mass spectrum of PSD-10 can be attributed to a perfectly alternating co-monomer sequence. The blue lines indicate alternating copolymers with equal numbers of styrene and DPE units – this is the major distribution present. The second most populous distribution is of alternating chains with one more DPE unit than styrene, indicating alternating copolymers with DPE units at each chain end and finally there is a distribution of chains which are alternating with styrene units at each end of the chain, indicated by the green lines. MALDI ToF MS is unique in being able to reveal this level of detail about not only sequence distribution but also end groups.

Copolymerization of butadiene and DPE in benzene and THF. The co-polymerization of butadiene (M_1) and DPE (M_2) in non-polar solvents, such as benzene, results in a homopolymer

of polybutadiene due to the very high r_1 value (54 in benzene)²⁴ and DPE is almost entirely excluded from the reaction. However, in polar solvents such as THF, the behavior of these monomers is very different. Yuki *et al.* previously reported a reactivity ratio $r_1 = 0.13$ in THF and the formation of an alternating copolymer.²⁴ In the current work a high and low molecular weight copolymer of poly(butadiene-*co*-DPE) were synthesized using THF as the solvent, PBdD-1 and PBdD-2 respectively. The composition and molecular weight data for these copolymers are shown in Tables 3 and 4 respectively. The butadiene : DPE ratio in the copolymer PBdD-1 was determined from ¹H NMR spectroscopy (see Supplementary Information) and the r_1 value was calculated as 0.05 using Equation 1. However, the r_1 value calculated for PBdD-1 used an excess of butadiene which means it is possible that all the DPE monomer had been consumed before the reaction was completed and this value of r_1 may therefore be an overestimate.

Whilst it was not possible to obtain an accurate ratio of styrene : DPE by ¹H NMR spectroscopy for low molecular weight copolymers of poly(styrene-*co*-DPE) due to contributions from the end-groups, in the case of poly(butadiene-*co*-DPE), PBdD-2, the ratio of butadiene : DPE could be calculated from the alkene and aromatic region, and the reactivity ratio, r_1 , was calculated as 0.04.

The MALDI ToF mass spectrum of PBdD-2 indicates a perfectly alternating copolymer (Figure 4) with three distinct distributions of chains, differing only in the nature of the terminal repeat units. In common with the perfectly alternating copolymer of styrene and DPE (Figure 3)

Table 3: Monomer Reactivity Ratios, r_1 , for anionic copolymerization of butadiene and 1,1-diphenylethylene in THF.

Sample	Bd : DPE feed ratio	Solvent	Temp/°C	Bd : DPE in copolymer (from ^1H NMR)	% 1,4-PBd	r_1
PBdD-1	1.00 : 0.96	THF	0	1.00 : 0.95	64	<0.05
PBdD-2	1.00 : 1.03	THF	0	1.00 : 0.97	64 ^a	0.04

^a Assuming the same 1,4-PBd content as PBdD-1

Table 4: Molecular weight data (obtained using triple detection SEC with $dn/dc = 0.189$) for the anionic copolymerization of butadiene and 1,1-diphenylethylene.

Sample	$M_n/\text{g mol}^{-1}$	$M_w/\text{g mol}^{-1}$	\mathcal{D}
PBdD-1	40,600	43,400	1.07
PBdD-2	2,100	2,300	1.11

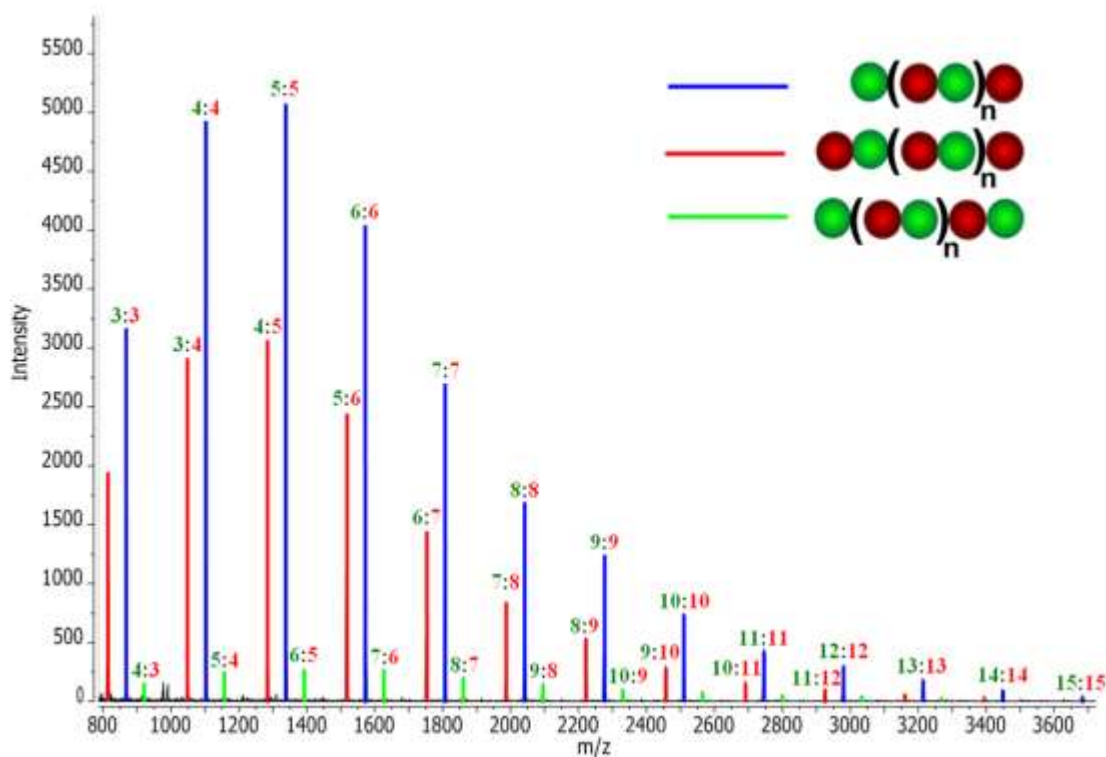


Figure 4: MALDI ToF mass spectrum for the copolymer PBdD-2 prepared by the anionic copolymerization (in THF) of butadiene and DPE (monomer molar feed ratio of butadiene : DPE = 1.00 : 1.03). The mole ratio of butadiene : DPE for any given chain is labelled with butadiene in green and DPE in red.

the MALDI ToF mass spectrum for butadiene and DPE in THF indicates that the most prevalent distribution is that of chains containing equal numbers of butadiene and DPE units (the blue lines), followed by chains with DPE units at either end (the red lines) and finally the least common chains are those with butadiene units at either end (the green lines). Once again there is no evidence to suggest that homopolymerization of DPE occurs. If this were the case we might expect to see peaks in the MALDI ToF mass spectrum corresponding to a ratio of butadiene : DPE equal to $n : n + 2$. Although as described above, there is some evidence²⁸ to support the dimerization of DPE following addition to *n*-butyllithium, dimerization of DPE in the end capping of polystyrene was shown not to occur and there is no published data to suggest that dimerization in the end capping of polybutadienyllithium occurs. Moreover, in the current work the feed ratio of butadiene and DPE is almost stoichiometric and therefore little residual DPE would be expected to remain following consumption of all the butadiene.

A further interesting point is that that the poly(butadiene-*co*-DPE) copolymer prepared in THF contains polybutadiene units with a microstructure comprising 64 % 1,4-PBd whereas when butadiene is homopolymerized in THF, a microstructure with nearly 90 % 1,2-enchainment results.⁶⁴ The anomalously high degree of 1,4 enchainment observed in the nearly alternating poly(butadiene-*co*-DPE) copolymer is likely due to steric crowding caused by the two phenyl groups on DPE when the butadienyl lithium chain end reacts with the incoming DPE monomer. The propagating butadiene chain end can either react via the 2-carbon on the butadiene unit or the 4-carbon. The latter, being a primary carbon will experience considerably less steric crowding and will be favored in spite of the fact that THF usually strongly promotes 1,2 enchainment (Figure 5).

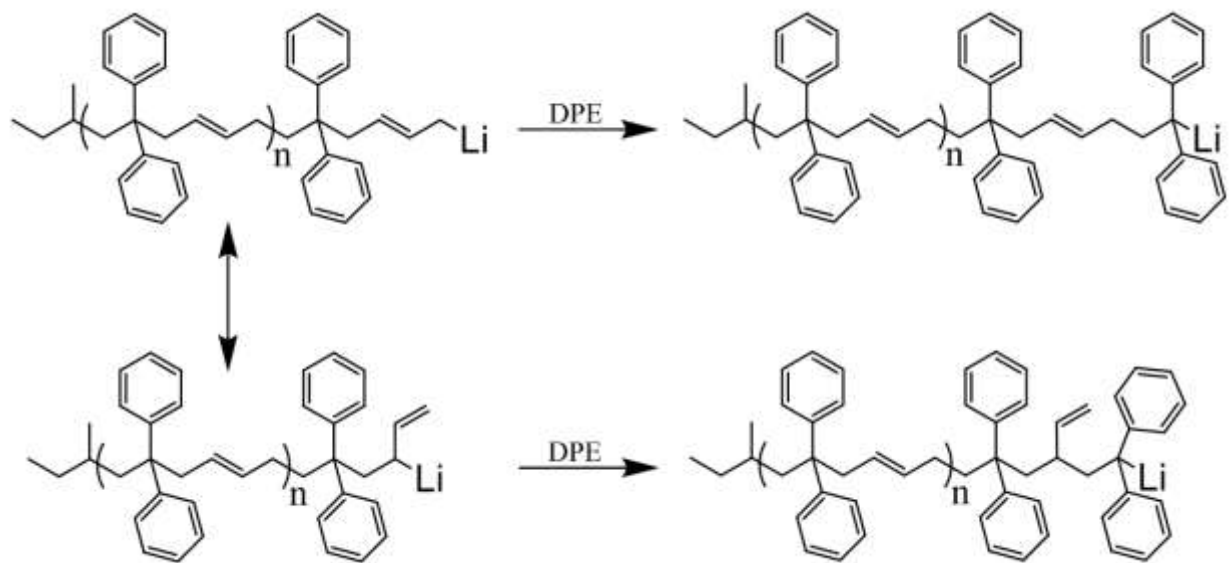


Figure 5: Impact of DPE steric crowding upon microstructure of butadiene units.

Thermal analysis of DPE containing copolymers. As well as being a monomer of interest from the perspective of monomer sequence control, DPE is also interesting in so much that it can dramatically increase the glass transition temperature (T_g) of the resulting copolymers and allow T_g to be tuned as a function of co-monomer composition.⁶⁶⁻⁶⁸ DPE is a bulky monomer and results in reduced chain motion and stiffening of the polymer backbone, in turn leading to polymers with higher values of T_g . Previous studies suggest that a perfectly alternating copolymer of styrene and DPE will have a T_g of approximately 180 °C, substantially higher than polystyrene which has a T_g of about 100 °C.⁶⁹ In the present study T_g values (shown in Table 5) were obtained by differential scanning calorimetry (DSC), which can be correlated with the corresponding copolymer composition: Xu and Bates have previously reported that the T_g of poly(styrene-*co*-DPE) increases by 1.09 °C/wt. % DPE,⁶⁶ whilst Knoll *et al.* found T_g increases by 1.26 °C/wt. % DPE.⁶⁸ Plotting the experimental values of T_g for copolymers of PSD-1 to 4 and PSD-7 to 9 versus wt. % DPE shows that T_g increases linearly by a value of 1.19 °C/wt. % DPE (Figure 6).

Table 5: Copolymer composition and T_g values measured by DSC for the copolymerization of 1,1-diphenylethylene with styrene and 1,1-diphenylethylene with butadiene.

Sample	DPE mole %	DPE wt. %	$T_g/^\circ\text{C}$	$M_n/\text{g mol}^{-1}$
PSD-9	47	61	177	60,000
PSD-3a	46	60	164	24,100
PSD-3b	46	60	171	59,400
PSD-4	46	59	169	40,100
PSD-3c	45	59	170	91,800
PSD-8	45	59	168	71,600
PSD-7	45	58	170	57,200
PSD-2	42	56	158	10,700
PSD-1	33	46	142	9,000
PBdD-1	49	76	117	40,600
PBdD-2	49	76	67	2,100

However, T_g is not independent of molecular weight as shown by the Flory-Fox equation:

$$T_g = T_g^\infty - \frac{K}{M_n} \quad [2]$$

where T_g^∞ is the T_g of a theoretical polymer of infinite molar mass.⁶⁹ K is a constant and an empirical parameter, related to the free volume contribution of chain ends, which for polystyrene is $1.7 \times 10^5 \text{ mol K g}^{-1}$,⁶⁹ and hence T_g decreases rapidly below about $40,000 \text{ g mol}^{-1}$ but is relatively constant above this value. It should be noted that the value of K for poly(styrene-co-DPE) may not be the same as the value of K for polystyrene however due to the similarity in chemical structure it is unlikely that poly(styrene-co-DPE) will have a significantly different value of K from polystyrene and hence it has been assumed that values above $40,000 \text{ g mol}^{-1}$ will have a relatively constant T_g with respect to molecular weight. For this reason copolymers with a

lower molecular weight ($< 40,000 \text{ g mol}^{-1}$) have been excluded from the calculation of the dependence of T_g on the wt. % DPE. The T_g for 0 wt. % DPE (i.e. a homopolymer of polystyrene) has been obtained from literature as $100 \text{ }^\circ\text{C}$ and was set as the intercept.⁶⁹ For comparison, the values obtained by Xu and Bates (shown as crosses) have been included as well as both trend lines representing the correlation of T_g to wt. % DPE found by Xu *et al.* and Knoll *et al.* (shown by dashed lines).

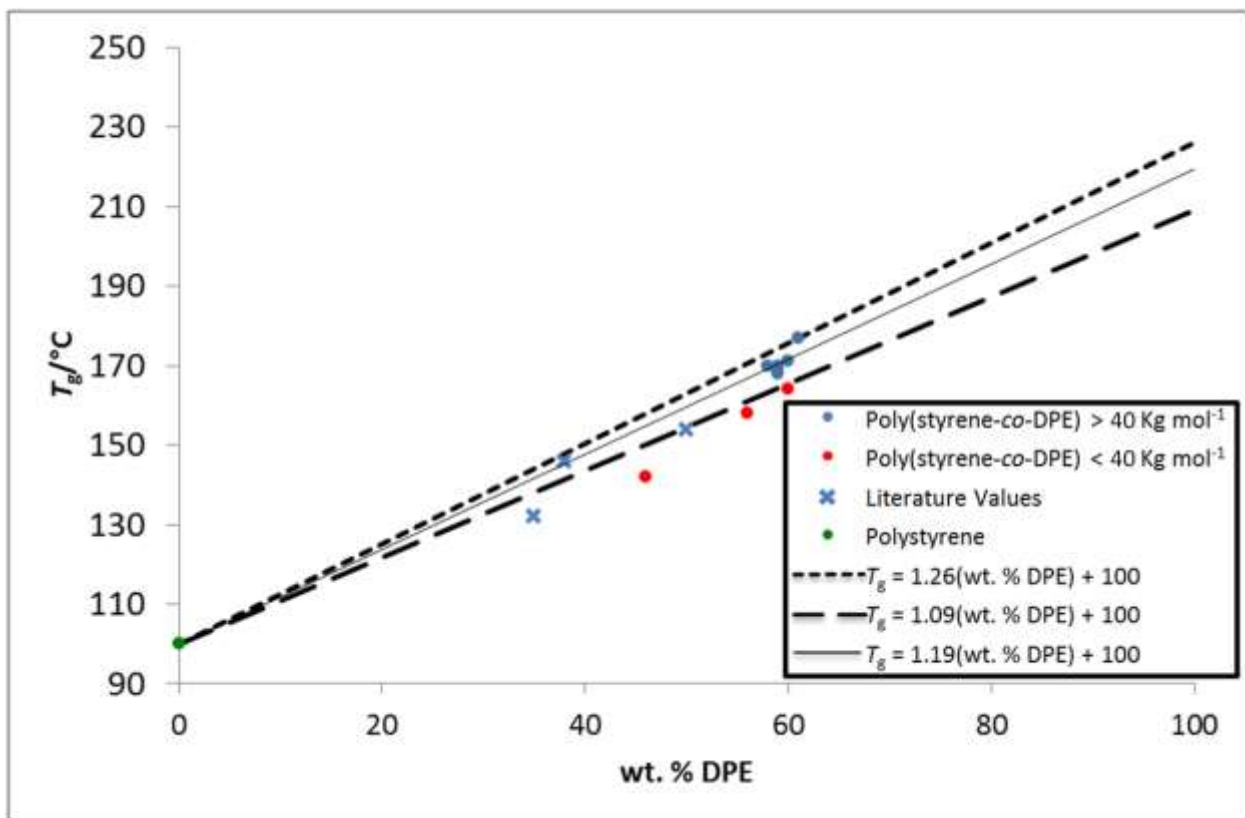


Figure 6: Graph showing the correlation between T_g and wt. % DPE for poly(styrene-co-DPE) copolymers.

This relationship between the wt. % of the co-monomers and T_g is approximately linear and can be approximated by the equation:

$$T_{gco} = T_{gSty} \omega_{Sty} + T_{gDPE} \omega_{DPE} \quad [3]$$

where T_{gco} is the T_g of the copolymer, T_{gSty} and T_{gDPE} are T_g values of the respective homopolymers and ω_{Sty} and ω_{DPE} are the respective weight fractions.⁷⁰ Although it is not possible for DPE to homopolymerize, this equation can be used to calculate the theoretical T_g of poly(1,1-diphenylethylene) as 219 °C which can be seen graphically by extrapolating the values to 100 wt. % DPE in Figure 6. The theoretical maximum T_g can also be determined for a perfectly alternating copolymer of poly(styrene-*alt*-DPE) to be 175 °C (wt. % DPE = 63.4 %). The T_g values obtained herein for the poly(styrene-*co*-DPE) samples are in good agreement with the correlations for wt. % DPE found in literature. Furthermore, due to the high incorporation of DPE, the copolymers obtained herein have very high T_g values (~170 °C) which are higher than any previously reported T_g values for poly(styrene-*co*-DPE) copolymers.

There is no reported comparable equation to estimate the relationship between composition and T_g for a P(Bd-*co*-DPE) copolymer. The T_g for a homopolymer of polybutadiene varies with the microstructure (i.e. 1,4-PBd to 1,2-PBd content) and as the poly(butadiene-*co*-DPE) copolymer PBdD-1 was found to contain 64 % 1,4- and 36 % 1,2-PBd by ¹H NMR spectroscopy. Comparable homopolymers of polybutadiene with a 62 – 66 % 1,4-PBd content have a glass transition temperature of –73 °C calculated by Makhyanov and Temnikova.⁷¹ A T_g value of 117 °C was found for PBdDPE-1, which contained 76 wt. % DPE, significantly higher than polybutadiene homopolymer.

Synthesis of telechelic polymers via monomer sequence control. The reactivity of DPE can be dramatically modified by the addition of electron-withdrawing or donating groups on the para-position of the phenyl rings. The addition of electron-donating groups will increase the electron density in the double bond by conjugation thereby deactivating the DPE to nucleophilic attack by

a propagating carbanion – the same electron donating group will also increase the reactivity of DPE as a propagating species. Conversely, electron-withdrawing groups will increase the reactivity of DPE as a monomer, but decrease the reactivity of DPE as a propagating species.

Hutchings *et al.* reported⁵⁷ that for the copolymerization of 1,1-bis(4-*tert*-butyldimethylsiloxyphenyl)ethylene (DPE-OSi) and styrene in benzene, the reactivity ratio, r_1 , was between 3 and 4 (if styrene is M_1) indicating a strong preference for styrene to undergo self-propagation. Changing the solvent to THF and using diphenylmethyl potassium (DPMK) as the initiator yielded similar results with a reactivity ratio, r_1 , of 6.1. Only by the slow addition of styrene (under starved monomer conditions) was it possible to generate copolymers with a higher incorporation (40 mol. %) of DPE-OSi.

The observation that DPE-OSi *can* copolymerize with styrene and butadiene *but* cross-propagation to the DPE-OSi is highly dis-favoured, suggested the possibility that the relative reactivities might enable the synthesis of telechelic polymers in a one-shot, one-pot reaction – that is, following initiation, the resulting sequence would be controlled solely by reactivity ratios. Hence, the copolymerization of styrene and DPE-OSi in which k_{11} is much higher than k_{12} but k_{12} is not negligible and in which the feed ratio of DPE-OSi is low, should result in the formation of a telechelic polymer with the functional DPE monomer units confined to the chain ends. A further attractive advantage of using DPE-OSi as the co-monomer is that mild acid hydrolysis of this monomer results in cleavage of the silyl groups to produce a telechelic polymer with 4 reactive terminal phenol groups.

Synthesis of telechelic polystyrene by the copolymerization of styrene and DPE-OSi in benzene. Telechelic polymers are effectively homopolymers which are functionalized at each

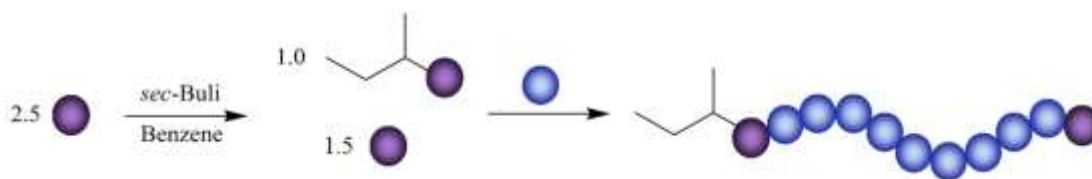


Figure 7: Reaction scheme showing the formation of a telechelic copolymer in a simultaneous copolymerization with styrene (blue) and DPE-OSi (purple).

chain end and as such, in the present work, the successful synthesis of telechelic polystyrene requires only two units of DPE-OSi per chain. Hence, styrene (M_1) and DPE-OSi (M_2) were copolymerized using 2.5 mole equivalents of DPE-OSi with respect to the initiator (*sec*-butyllithium) and a monomer molar feed ratio of styrene : DPE-OSi = 9.6 : 1.0. The hypothesis was that the reaction between *sec*-butyllithium and (2.5 mole equivalents of) DPE-OSi would introduce one DPE-OSi unit at the α -chain end and the excess DPE-OSi would remain unreacted. Based on results discussed above and previously published work²⁸ there was no expectation that homopolymerization of DPE-OSi would occur. Subsequent addition of styrene monomer would result in polymerization but a reactivity ratio r_1 of 3-4,⁵⁷ coupled with a monomer feed ratio containing a very low concentration of DPE-OSi, would result in homopolymerization of styrene and exclusion of the DPE-OSi until all of the styrene is consumed. Only then would the DPE-OSi react, effectively end-capping the polymer (Figure 7).

DPE-OSi was initially allowed to react with *sec*-BuLi to introduce the first DPE-OSi at the α -chain-end before the addition of styrene. Hutchings *et al.* have previously reported the use of DPE-OSi as a functional initiator in the synthesis of PMMA and polybutadiene HyperMacs⁷² and as an end capping monomer for the synthesis of AB₂ macromonomers for the preparation of polystyrene⁷³ and polybutadiene⁷⁴ DendriMacs, polystyrene HyperMacs⁷⁵ and asymmetric stars⁷⁶ and polystyrene-polyisoprene-polystyrene HyperBlocks.⁷² In none of the above cases was

Table 6: DPE-OSi content and molecular weight analysis of P(S-co-DPE-OSi) copolymers.

Sty : DPE-OSi molar feed ratio	Total Reaction Time/ hours	TMEDA	M_n / g mol^{-1}	Modal Molecular Weight/ g mol^{-1} (MALDI ToF)	\bar{D}	Sty : DPE-OSi by ^1H NMR	DPE-OSi per chain
9.6 : 1.0	48	No	3,100	3,300	1.07	11.7 : 1.0	1.9 ± 0.2
9.6 : 1.0	48	Yes	3,100	3,300	1.21	10.0 : 1.0	2.1 ± 0.2

any evidence observed of DPE-OSi dimerization. In hydrocarbon non-polar solvents the rate of end-capping was reportedly slow and tetramethylethylenediamine (TMEDA) was added to enhance the rate of end-capping. In the current work the polymerization of styrene in benzene was initiated by the BuLi-DPE-OSi adduct and in the presence of DPE-OSi monomer with a target molecular weight of $3,400 \text{ g mol}^{-1}$ (PSD_{OSi}). Upon addition of styrene the red colour of the living DPE-OSi was observed to turn orange, indicative of propagating polystyrene. Within several minutes the orange colour darkened a little towards the red colour of living DPE-OSi. This early colour change may suggest that the polystyrene chains have begun to react with DPE-OSi via end-capping. Whilst this is possible as the polymer chains are very short and the time for propagation is short, previous results suggests the end-capping process can take up to 5 days even in the presence of TMEDA.⁵⁵ The reaction was allowed to proceed for 24 hours before the reaction mixture was split into two equal portions ($\text{PSD}_{\text{OSi-a}}$ and $\text{PSD}_{\text{OSi-b}}$). TMEDA (2 moles with respect to the initiator) was added to one portion of polymer ($\text{PSD}_{\text{OSi-a}}$) to promote end-capping and then both portions allowed to react for a further 24 hours. The resulting copolymers were analyzed by ^1H NMR spectroscopy, SEC and MALDI ToF MS (Table 6 and Figures 8 and 9). ^1H NMR spectroscopy enables accurate calculation of the ratio of DPE-OSi : styrene repeat units using the intense signals resulting from the $-\text{Si}(\text{CH}_3)_2$ and $-(\text{CH}_3)_3$ groups on DPE-OSi, from which it was possible to calculate 10.0 and 11.7 units of styrene per unit of DPE-OSi for

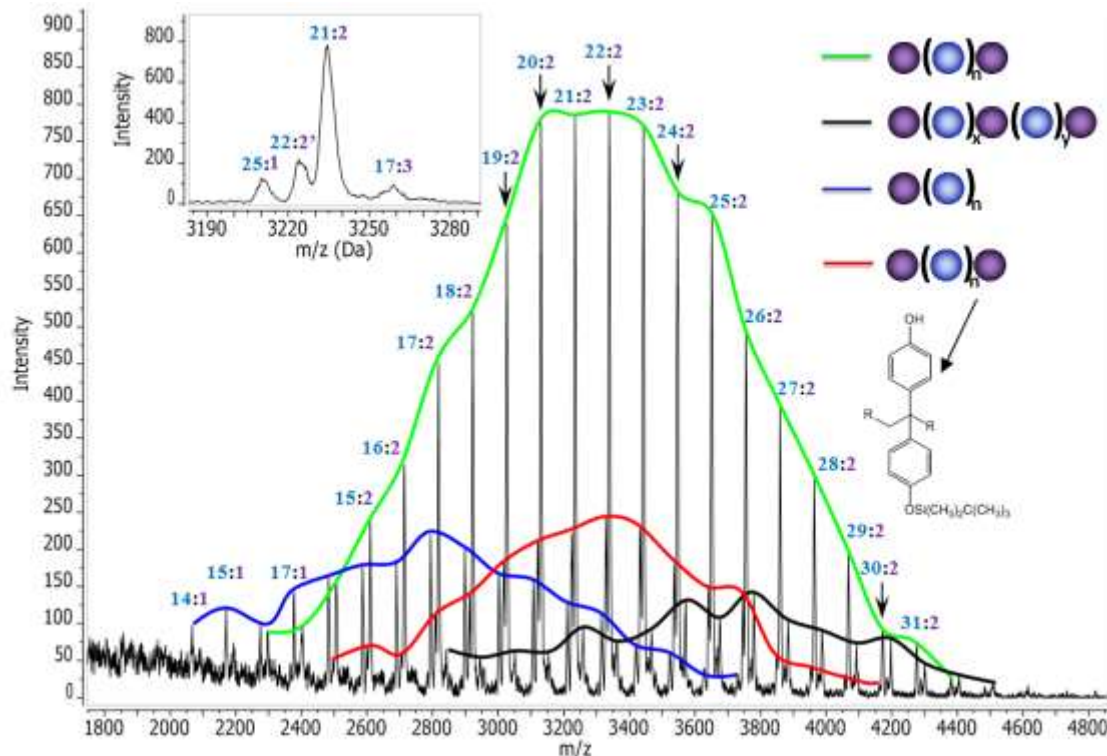


Figure 8: MALDI ToF mass spectrum for the anionic copolymerization (in benzene) of styrene and DPE-OSi (monomer feed ratio of Sty : DPE-OSi = 9.6 : 1.0). The mole ratio of styrene : DPE-OSi for any given chain is labelled with styrene in blue and DPE-OSi in purple.

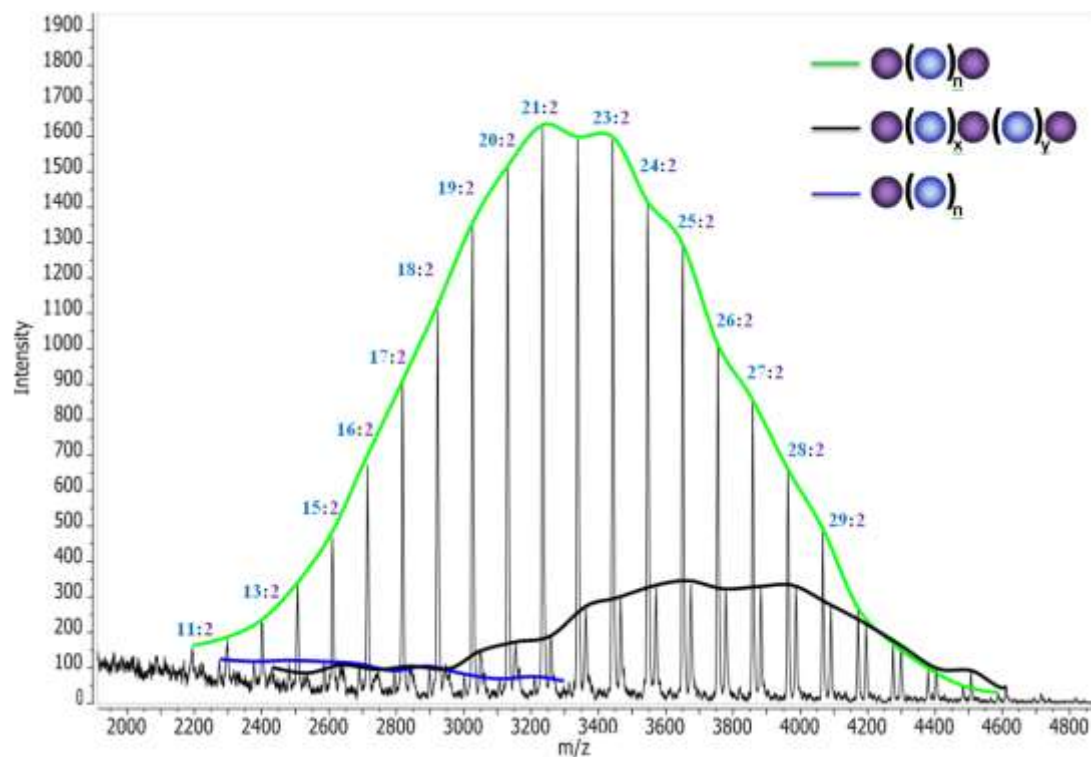


Figure 9: MALDI ToF mass spectrum for the anionic copolymerization (in benzene) of styrene and DPE-OSi (monomer molar feed ratio of Sty : DPE-OSi = 9.6 : 1.0) with TMEDA injected after 24 hours. The mole ratio of styrene : DPE-OSi for any given chain is labelled with styrene in blue and DPE-OSi in purple.

the reaction carried out with and without TMEDA respectively. These values are in good agreement with the styrene : DPE-OSi feed ratio of 9.6 : 1.0. Of course the NMR spectroscopy data can tell us nothing about the co-monomer sequence. MALDI ToF MS analysis of the sample prepared *without* the addition of TMEDA (Figure 8) indicates chain sequences containing some variation in the number of DPE-OSi units. By far the most prevalent distribution of chains is that indicated by the green line in Figure 8 and comprises of chains with ‘*n*’ styrene units and 2 DPE-OSi units. One of these DPE-OSi units was introduced via the initiation step and assuming the hypothesis described above is correct, then this population of chains would be the intended telechelic polymers, further evidence to support this hypothesis is given below. Although this distribution represents the overwhelming majority of chains present, it is also clear from the data in Figure 8 that other types of chains are to be found in the polymer sample. The population of chains indicated by the red line also represents polystyrene chains containing two DPE-OSi units with appropriate *m/z* values – however in this case the value of *m/z* is 115.27 g mol⁻¹ lower than expected and these peaks correspond to chains in which one Si(CH₃)₂C(CH₃)₃ group is missing from the DPE-OSi unit. It cannot be stated with certainty why this group is missing but this population of chains also represents the successful production of telechelic polymers. The chains indicated by the blue line have *m/z* values corresponding to polystyrene chains containing a single DPE-OSi unit (introduced at the α -chain end) and therefore chains which have not been end-capped with a second DPE-OSi unit. In some way the presence of these chains also supports the hypothesis that DPE-OSi units will be *all but* excluded from the polymerization reaction until all the styrene has been consumed and that homopolymerisation of DPE-OSi is not observed. If one considers the sum total of the populations represented by the green, red and blue lines – probably more than 90% of the total number of chains – as being chains where DPE-OSi has

been excluded from the polymerization it would appear that the hypothesis is valid. The remainder and very small minority of chains represented by the black line have m/z values which are consistent with polystyrene chains containing 3 DPE-OSi units – most likely 1 DPE-OSi at each chain end and an additional DPE-OSi unit mid-chain.

Considering the MALDI ToF mass spectrum in Figure 9 for the sample to which TMEDA was added after 24 hours (PSD_{OSi-b}), it can be seen that the situation is slightly different. It is clear that once again, by far the major portion of polystyrene chains contain 2 DPE-OSi units – again represented by the green line. However, it is equally clear that the number of chains containing only a single DPE-OSi unit at the α -chain end is significantly reduced in comparison to Figure 8. This would suggest that the addition of TMEDA after 24 hours does indeed have a positive impact upon reactivity ratios and would appear to have promoted the end-capping of polystyrene chains with DPE-OSi. The same conclusion can be drawn from the fact that the proportion of polystyrene chains containing 3 DPE-OSi units is also more intense in Figure 9 than Figure 8.

The average number of DPE-OSi units per chain, $N_{\text{DPE-OSi}}$, can be calculated using the total number of styrene units relative to DPE-OSi units, Sty/DPE-OSi, (obtained by ¹H NMR analysis) and the average molecular weight of the polymer. Ideally the mean molecular weight would be used, however only the modal molecular weight could be reliably obtained from the MALDI ToF mass spectra. It is possible to use the M_n value from SEC analysis, however, at low molecular weight, SEC is likely to be less accurate as the dn/dc value (used by triple detection SEC) is dependent on both the molecular weight and the nature of the end-groups, and conventional calibration SEC calculates the molecular weight from polystyrene standards. MALDI ToF MS revealed that the modal molecular weight for PSD_{OSi-a} (the sample obtained without the addition of TMEDA), was approximately 3,300 g mol⁻¹, and after subtracting the

average mass for the silver cation (107.0 g mol^{-1}) and the end groups (57.1 g mol^{-1} and 1.0 g mol^{-1} , assuming the first unit of DPE-OSi is a monomer and not an end-group) the modal molecular weight of the copolymer is approximately $3,100 \text{ g mol}^{-1}$. From the modal molecular weight and the average molecular weight of the monomer units (104.2 g mol^{-1} for styrene and 440.8 g mol^{-1} for DPE-OSi) the following equation can be obtained:

$$104.2x + 440.8y = 3100 \pm 300 \quad [4]$$

where $x : y$ is the ratio of styrene : DPE-OSi and assuming up to a 10 % error of the molecular weight. It was calculated from ^1H NMR spectroscopy that $x/y = 11.7$ and the error on this value is likely to be small due to the intense signals arising from the $\text{Si}(\text{CH}_3)_2\text{C}(\text{CH}_3)_3$ groups. Solving Equation 4 gives a value of $N_{\text{DPE-OSi}} = 1.9 \pm 0.2$ which is consistent with the MALDI ToF analysis and indicates that the majority of chains contain 2 units of DPE-OSi. Similar analysis for PSD_{OSi-b} (the sample obtained after the addition of TMEDA), gives a value of $N_{\text{DPE-OSi}} = 2.1 \pm 0.2$ again indicating that the majority of chains contain 2 units of DPE-OSi.

It appears from the MALDI mass spectra (Figures 8 and 9) that the basis for the hypothesis is valid. The reactivity ratios for the copolymerization of styrene and DPE-OSi are such that the DPE-OSi is almost totally excluded from the reaction and the overwhelming majority of chains contain only 2 DPE-OSi units. One of these is at the α -chain end and it is most likely that the other DPE-OSi unit is at the ω -chain end. To provide further evidence that the second DPE-OSi unit is indeed located at the ω -chain end, a positive ion MSMS experiment using LIFTTM was conducted to allow us to more deeply interrogate the monomer sequence of the chains by analysis of the fragmentation of a specific chain. The peak at m/z 3133.0 in Figure 9 corresponding to 20 : 2 (styrene : DPE-OSi) was isolated and fragmented – the fragmentation and MSMS analysis is described in detail by Wesdemiotis *et al.*⁷⁷ Fragmentation of these chains

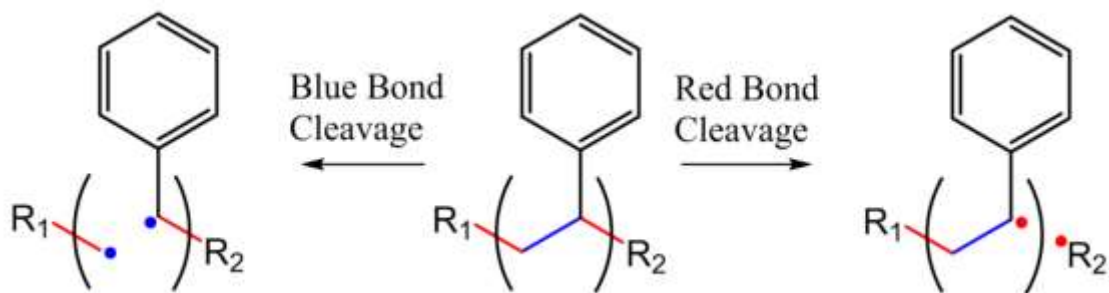


Figure 10: Schematic diagram showing the fragmentation of a styrene unit.

can occur at any position along the polymer backbone, to generate two radical chain fragments of varying length (as shown in Figure 10 and 11a) depending on the site of fragmentation. Fragmentation occurs as a result of cleavage of either one of the two C-C backbone bonds in the polystyrene repeat unit indicated by the red bonds and blue bonds shown in Figure 10 and in Figure 11a where the representative chain is drawn with a DPE-OSi unit at each end of the chain. Following bond cleavage, the resulting fragments can either include the initiating chain end (α -chain end) or the terminating chain end (ω -chain end). Assuming that the chains all contain a DPE-OSi unit at both the α - and the ω - chain end then four possible fragment sequences can arise. Moreover, if the two DPE-OSi units are exclusively located at each chain end (as intended) then no matter where the fragmentation occurs, both of the resulting fragments must contain a DPE-OSi unit. The radical fragment containing the α -chain end resulting from breaking a red bond is denoted α -D₁S_n[•], where n represents the number of styrene units in the fragment. The radical fragment containing the ω -chain end resulting from cleavage of a red bond is denoted ω -D₁S_n[•]. Whereas the radical fragments arising from cleavage of a blue bond are denoted α -D₁S_{n+CH₂}[•] and ω -D₁S_{n-CH₂}[•] for the fragment containing the α -chain end and the ω -chain end respectively, and have therefore either gained or lost a CH₂ group – see Figure 11a. However, if

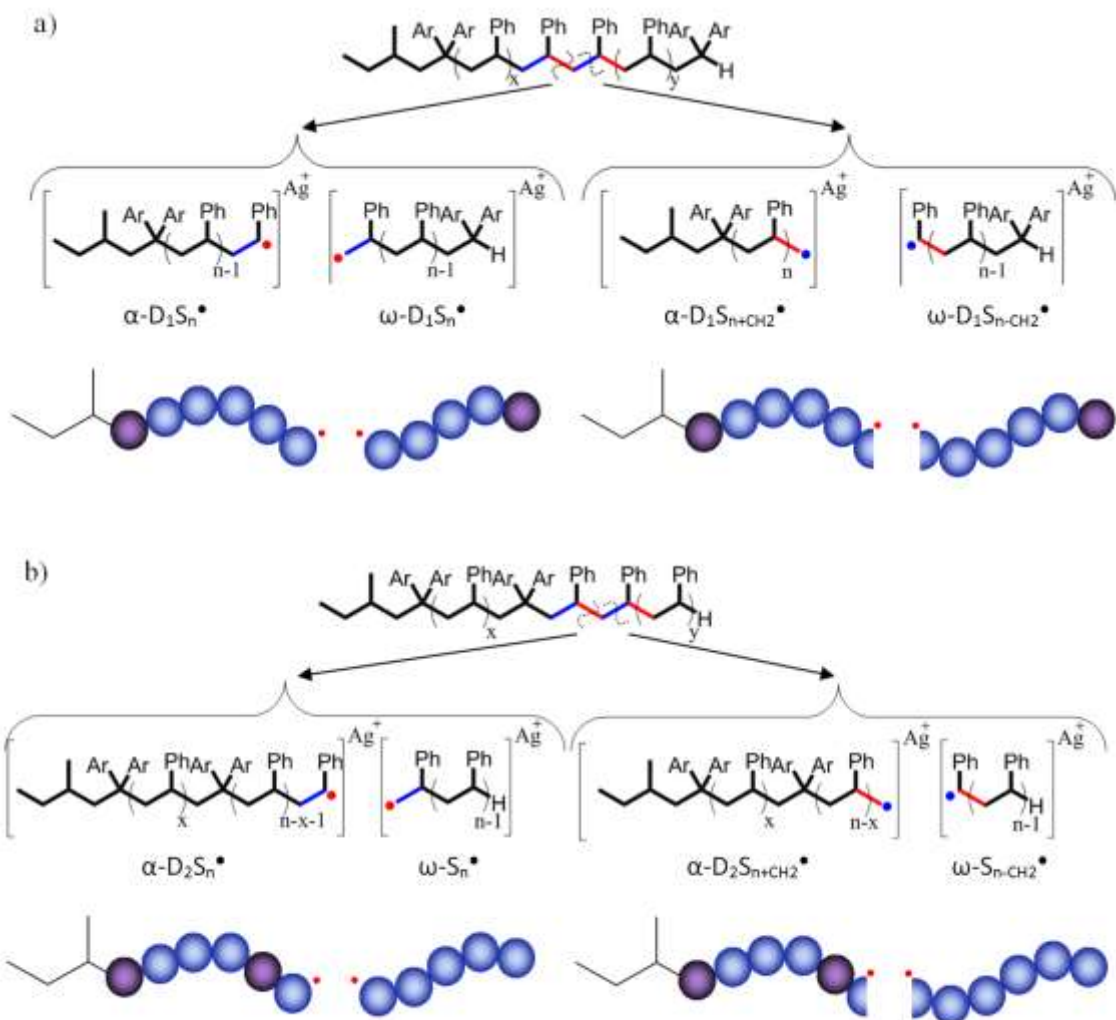


Figure 21: Possible sequences arising from fragmentation of (a) a perfect telechelic copolymer (b) a non-telechelic copolymer.

the second DPE-OSi unit is not located at the ω -chain end but mid-chain, then fragmentation gives rise to a different set of possible fragment sequences as shown in Figure 11b and, depending where fragmentation occurs it is possible that one fragment will contain no DPE-OSi units, denoted $\omega\text{-S}_n^\bullet$ and $\omega\text{S}_{n\text{-CH}_2}^\bullet$ for the breaking of the red and blue bond respectively, and the other fragment will contain two DPE-OSi units, denoted $\alpha\text{-D}_2\text{S}_n^\bullet$ and $\alpha\text{-D}_2\text{S}_{n+\text{CH}_2}^\bullet$ for the breaking of the red and blue bond respectively. The radical fragments, $\alpha\text{-D}_1\text{S}_n^\bullet$, $\omega\text{-D}_1\text{S}_{n\text{-CH}_2}^\bullet$, $\alpha\text{-D}_2\text{S}_n^\bullet$ and $\omega\text{-S}_{n\text{-CH}_2}^\bullet$, can also undergo both a backbiting rearrangement followed by β -scission to

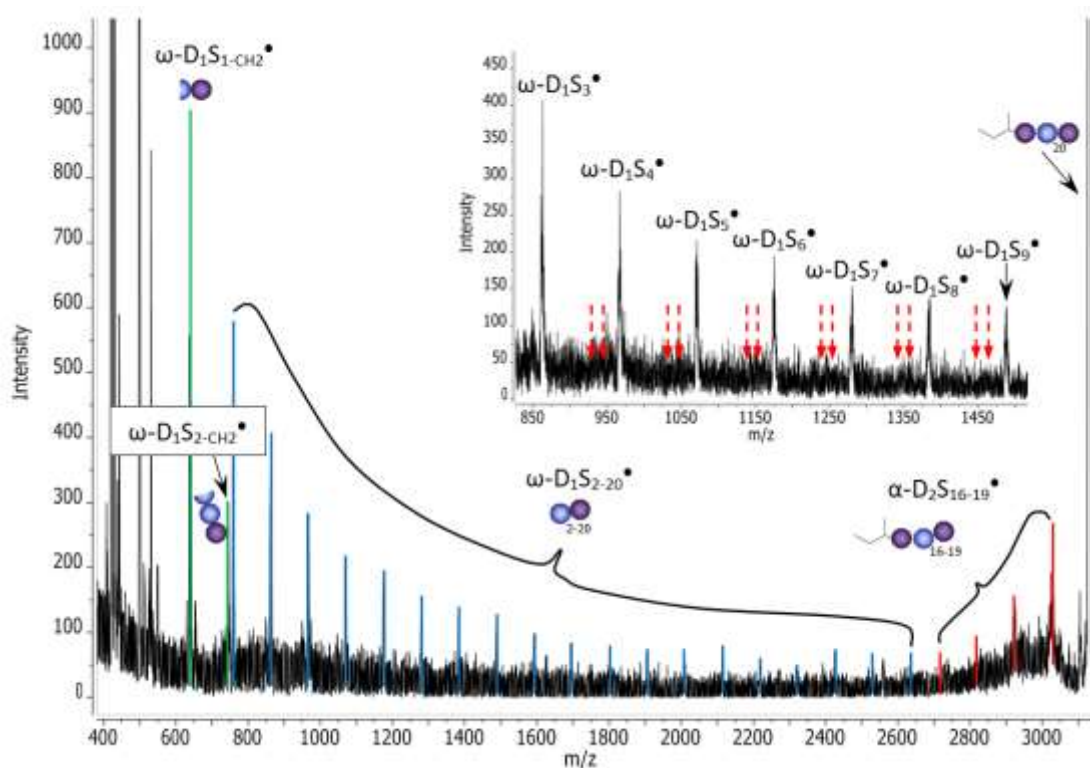


Figure 32: Positive Ion MSMS spectrum with LIFTTM for the anionic copolymerization (in benzene) of styrene and DPE-OSi (monomer molar feed ratio of styrene : DPE-OSi = 9.6 : 1.0) with TMEDA injected after 24 hours with the expansion over the range $m/z = 850 - 1500$. Red arrows indicate where the sequences of $\omega\text{-S}_n^\bullet$ and $\omega\text{-S}_{n\text{-CH}_2}^\bullet$ corresponding to non-telechelic copolymers would appear.

yield common internal fragments which dominate in the lower region of the spectra ($> 500 m/z$).

Other possible sequences arise from β -scission of an H atom on the radical fragments which would differ from their radical counterparts by only the mass of an H atom (1.008 g mol^{-1}); however, these sequences are not observed in this case. It should also be noted that not every sequence is observed, as less stable primary radical atoms could undergo rapid depolymerization.

The results of the fragmentation of the primary polymer chains are shown in Figure 12. In this case only the following sequences were observed: $\omega\text{-D}_1\text{S}_n^\bullet$; $\omega\text{-D}_1\text{S}_{n\text{-CH}_2}^\bullet$ and $\alpha\text{-D}_2\text{S}_n^\bullet$. The sequences of chains corresponding to $\omega\text{-D}_1\text{S}_n^\bullet$ dominate throughout the entire spectrum confirming the hypothesis that the second DPE-OSi unit is indeed predominantly located at the end of the chain. The hypothesis is particularly supported by the signals corresponding to ω -

$D_1S_{1-CH_2}^\bullet$, $\omega-D_1S_{2-CH_2}^\bullet$ and $\omega-D_1S_2^\bullet$ because these signals show that there is still a DPE-OSi unit present when the chain is fragmented near the ω end of the chain. The signals corresponding to $\alpha-D_2S_n^\bullet$ indicate that in some cases DPE-OSi has been incorporated prior to the terminal unit suggesting the formation of telechelic polymers is not perfect. This is not particularly surprising since it is already known that DPE-OSi can be incorporated before the full consumption of styrene. However, these sequences are only observed when there are over 16 units of styrene; showing that the second DPE-OSi does not become incorporated until the later stages of the polymerization. This not only supports the original hypothesis that DPE-OSi is all but excluded from the copolymerization but also confirms the absence of any dimerization of the DPE-OSi at the start of the reaction. Signals corresponding to $\omega-S_3^\bullet$ and $\omega-S_{2-CH_2}^\bullet$ can be seen which are consistent with the presence of $\alpha-D_2S_{17}^\bullet$ and $\alpha-D_2S_{18}^\bullet$ respectively, but these appear in the noisy region at low molecular weight. To further emphasize that the majority of chains are the intended telechelic copolymer, Figure 12 shows an expansion of the m/z 850 – 1,500 region and the red arrows indicate where the sequences corresponding to $\omega-S_n^\bullet$ and $\omega-S_{n-CH_2}^\bullet$ (i.e. signals arising from fragments containing no DPE-OSi units at the ω -chain end) would be expected to appear. It can therefore be concluded that the hypothesis is indeed valid and that the overwhelming majority of chains were the intended telechelic copolymers.

Synthesis of telechelic polybutadiene by the copolymerization of butadiene and DPE-OSi in benzene. Telechelic polybutadiene was prepared by the one-pot copolymerization of butadiene with DPE-OSi in an analogous fashion to that described above for telechelic polystyrene. Previous results suggest that the likelihood of DPE-OSi undergoing copolymerization with butadiene in a non-polar solvent such as benzene is extremely low. The reactivity ratio r_1 is 54

Table 7: DPE-OSi content and molecular weight analysis of P(Bd-co-DPE-OSi) copolymers.

Bd : DPE-OSi feed ratio	Total Reaction Time/ days	TMEDA	M_n / g mol^{-1}	Modal Molecular Weight/ g mol^{-1} (MALDI ToF)	\bar{D}	Bd : DPE-OSi by ^1H NMR	DPE-OSi per chain
13.0 : 1.0	3	No	3,700	3,500	1.06	48 : 1.0	1.1 ± 0.1
13.0 : 1.0	9	No	4,200	3,500	1.19	47 : 1.0	1.1 ± 0.1
13.0 : 1.0	9	Yes	4,300	3,700	1.08	28 : 1.0	1.8 ± 0.2

for the copolymerization in benzene of butadiene (M_1) and unsubstituted DPE (M_2),²⁴ and the effect of the electron donating substituent on the DPE has been shown to deactivate the monomer and will therefore increase the value of r_1 . Hence it was expected that if butadiene and DPE-OSi were copolymerized, DPE-OSi would be completely excluded until complete consumption of butadiene. With this in mind the reaction between butadiene and DPE-OSi (2.5 mole equivalents with respect to the initiator) was carried out. DPE-OSi was initiated with *sec*-butyllithium and allowed to react for 24 hours at room temperature prior to the addition of butadiene. After the reaction had been stirred for 3 days at room temperature a sample was withdrawn (PBdD_{OSi}-a) for characterization and the remaining reaction mixture was separated into two equal portions and TMEDA (2 mole equivalents with respect to lithium) injected into one portion. Both portions were allowed to proceed for a further 6 days before being terminated with degassed methanol. The resulting polymers were analyzed by ^1H NMR spectroscopy, SEC and MALDI ToF MS and characterization data for this experiment are contained in Table 7.

The MALDI ToF MS data for the samples without TMEDA (PBdD_{OSi}-a and PBdD_{OSi}-b) and that with TMEDA (PBdD_{OSi}-c) are shown in Figures 13 – 15. Although determining the sequence using the m/z values is potentially inaccurate (as the difference between 1 unit of DPE-OSi and 8 units of butadiene is only 8.0 g mol^{-1} as shown in Figure 13b), these results indicate in the

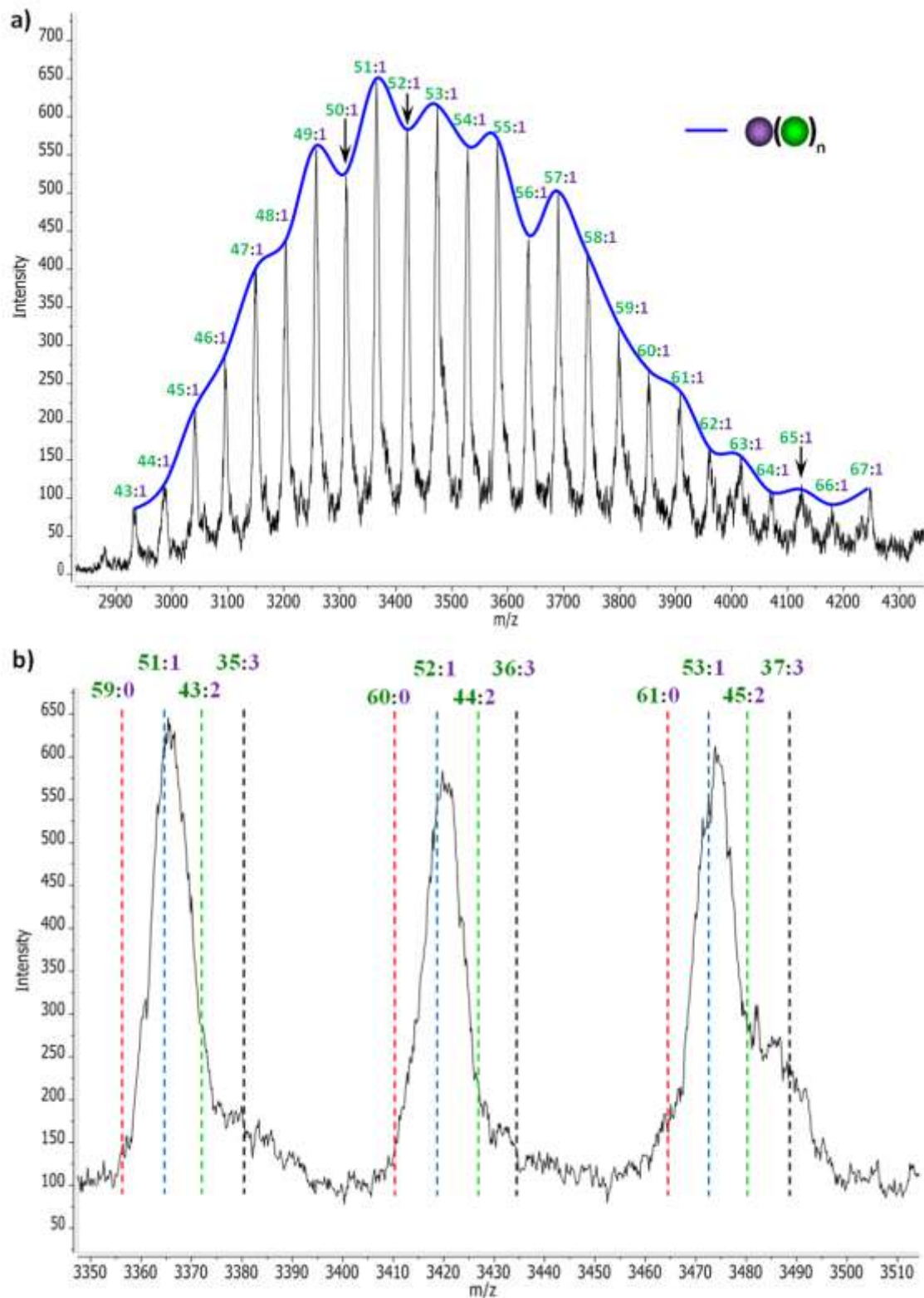


Figure 43: (a) MALDI ToF mass spectrum for the anionic copolymerization (in benzene) of butadiene and DPE-OSi after 3 days, PBdD_{OSi}-a, with a molar feed ratio of butadiene : DPE-OSi = 13.0 : 1.0 and (b) expansion showing the range $m/z = 3,350 - 3,510$ with red, blue and green dashed lines indicating where chains containing 0, 1 and 2 units of DPE-OSi respectively, would be expected to appear. The mole ratio of butadiene : DPE-OSi for any given chain is labelled with butadiene in green and DPE-OSi in purple.

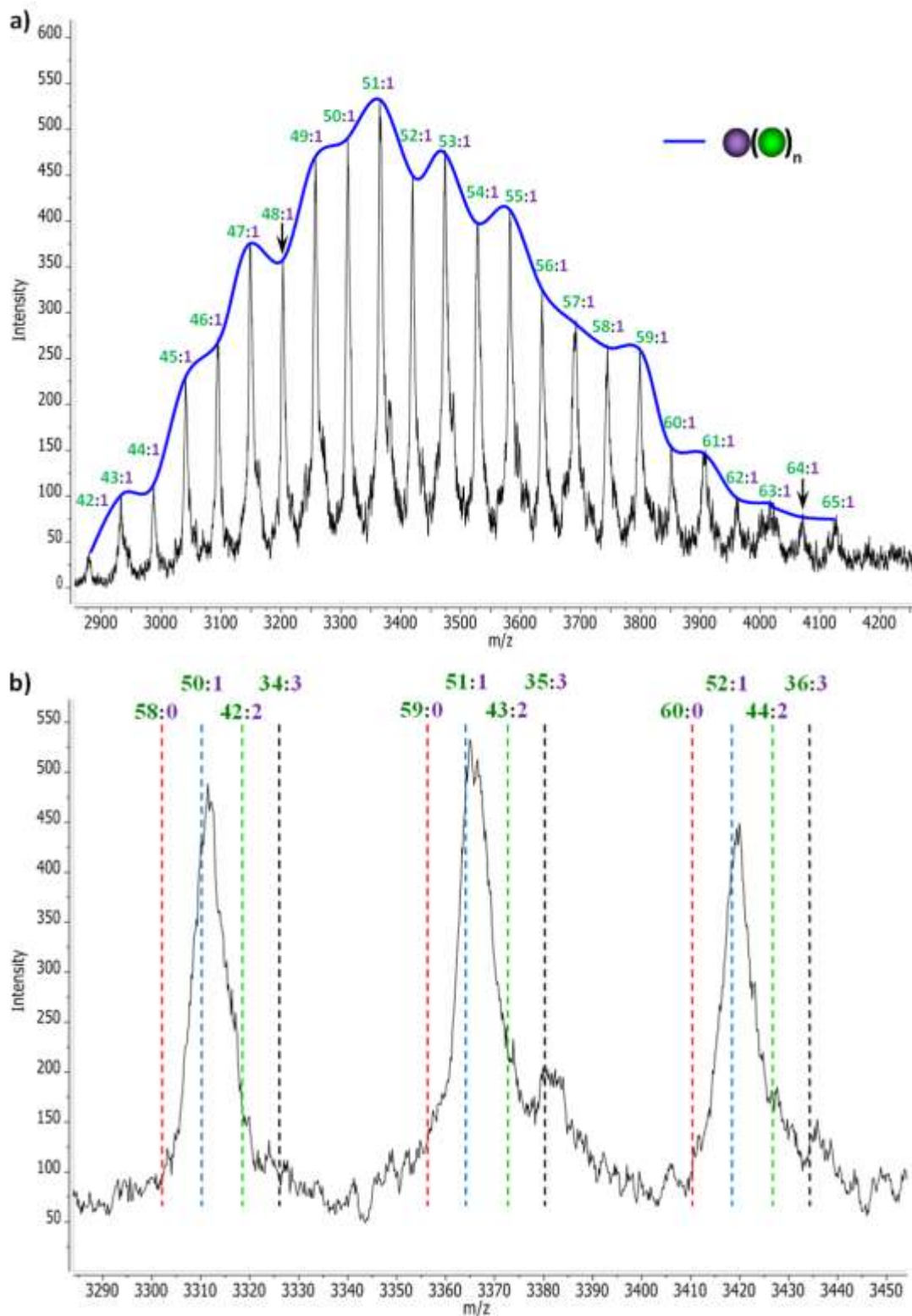


Figure 54: (a) MALDI ToF mass spectrum for the anionic copolymerization (in benzene) of butadiene and DPE-OSi after 9 days, $\text{PBdD}_{\text{OSi-b}}$, with a molar feed ratio of butadiene : DPE-OSi = 13.0 : 1.0 and (b) expansion showing the range $m/z = 3,290 - 3,450$ with red, blue, green and black dashed lines indicating where chains containing 0, 1, 2 and 3 units of DPE-OSi respectively, would be expected to appear. The mole ratio of butadiene : DPE-OSi for any given chain is labelled with butadiene in green and DPE-OSi in purple.

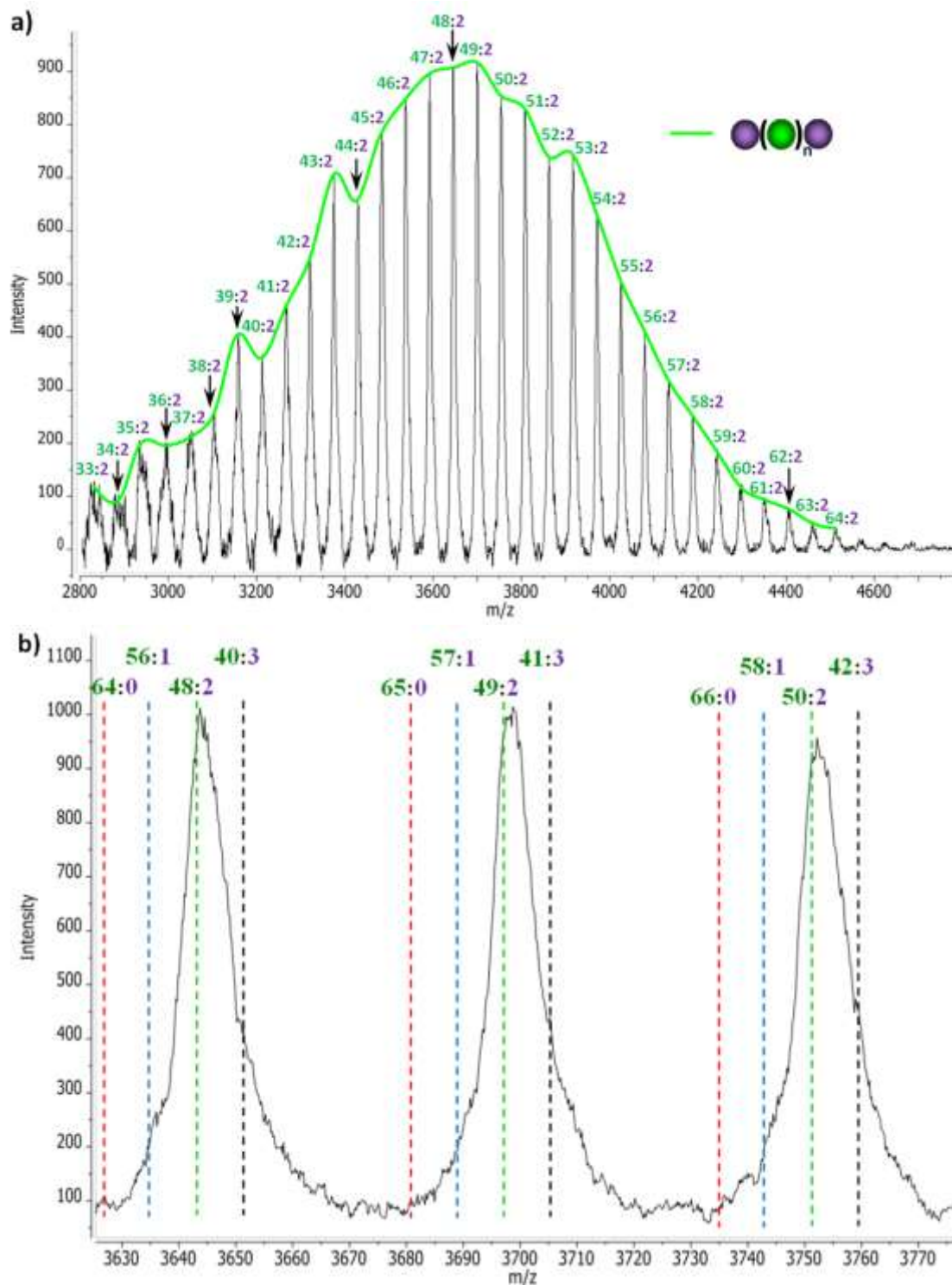


Figure 65: (a) MALDI ToF mass spectrum for the anionic copolymerization (in benzene) of butadiene and DPE-OSi after 3 days without TMEDA and 6 days with TMEDA, PBdD_{OSi}-c, with a molar feed ratio of butadiene : DPE-OSi = 13.0 : 1.0 and (b) expansion showing the range $m/z = 3,630 - 3,770$ with red, blue, green and black dashed lines indicating where chains containing 0, 1, 2 and 3 units of DPE-OSi respectively, would be expected to appear. The mole ratio of butadiene : DPE-OSi for any given chain is labelled with butadiene in green and DPE-OSi in purple.

absence of TMEDA, DPE-OSi is completely excluded from the polymerization, even after 9 days. Furthermore the polymerization of butadiene was complete after 3 days as the degree of polymerization, N_{Bd} , does not increase between 3 and 9 days. From the modal mass (obtained from the MALDI ToF mass spectrum) and the value of butadiene/DPE-OSi (obtained from the 1H NMR spectrum) the average number of DPE-OSi units per chain was calculated as 1.1 ± 0.1 for both samples that were obtained in the absence of TMEDA (PBdD_{OSi}-a and PBdD_{OSi}-b), which is consistent with the signals in the MALDI ToF mass spectrum corresponding to chains containing only 1 unit of DPE-OSi.

The MALDI ToF mass spectrum of the final sample (Figure 15) shows that after 6 days of reaction in the presence of TMEDA, all the peaks correspond to chains with 2 units of DPE-OSi and the average number of DPE-OSi units per chain was calculated as 1.8 ± 0.2 . These results imply that end-capping of butadiene with DPE-OSi either does not occur or is an extremely slow process in the absence of TMEDA; however, this is ideal for preparing telechelic copolymers as this prevents the incorporation of DPE-OSi units into the middle of the chains. Although it was not possible to obtain a signal for these copolymers by MSMS, the fact that both PBdD_{OSi}-a and b only contain 1 unit of DPE-OSi and that there does not appear to be any increase in the number of butadiene units prove that the extra unit of DPE-OSi in PBdD_{OSi}-c must be at the chain end. Hence this shows that it is possible to synthesize perfect telechelic copolymers in a simultaneous copolymerization.

CONCLUSIONS:

The copolymerization of DPE with styrene and butadiene has been carried out under various reaction conditions and the resulting monomer sequences were investigated and analyzed by 1D

and 2D NMR spectroscopy and MALDI ToF MS. It has been demonstrated that MALDI ToF MS is an extremely useful technique for analyzing the resulting sequences of these copolymers. Indeed it was used to unequivocally prove the presence of perfectly alternating sequences. The copolymerization of styrene was found to form nearly perfectly alternating copolymers with DPE in a polar solvent (THF), however, in non-polar solvents, such as benzene or toluene, it was found that the copolymerization of styrene and DPE did not result in an alternating sequence, although a high degree of incorporation of DPE was observed with some level of alternation. The incorporation of DPE (with styrene) was also shown to be enhanced by increasing the molar feed ratio of DPE with respect to styrene, and the extent of DPE incorporation was correlated with the glass transition temperature of the copolymer. The copolymerization of butadiene with DPE in a polar solvent such as THF was also investigated and the resulting monomer sequence was shown by MALDI ToF MS to be perfectly alternating. The glass transition temperature of the resulting poly(butadiene-*co*-DPE) copolymer was found to be 117 °C.

The copolymerization of styrene with the less reactive DPE derivative monomer, 1,1-*bis*(4-*tert*-butyldimethylsiloxyphenyl)ethylene (DPE-OSi), in benzene resulted in the formation of telechelic copolymers, with only a small minority of chains corresponding to sequences containing one or three units of DPE-OSi. The sequence of these copolymers was determined using ¹H NMR spectroscopy, MALDI ToF MS and a positive ion MSMS experiment, and demonstrated that it was possible to prepare telechelic copolymers in a one-step simultaneous copolymerization in which a combination of a low feed ratio of the functional monomer and kinetic control dictate the telechelic sequence. The high prevalence of desired telechelic sequence was demonstrated by MALDI ToF-MS and positive ion MSMS analysis using LIFTTM.

The copolymerization of butadiene with DPE-OSi in a non-polar solvent proceeded with DPE-OSi being completely excluded from the polymerization due to the very low tendency of the functional comonomer to copolymerize. However, the addition of TMEDA promotes the copolymerization/end-capping reaction of polybutadienyllithium with DPE-OSi, showing that polybutadiene can be end-capped to form a perfect telechelic copolymer.

We have therefore shown that DPE is very useful and versatile monomer motif for the synthesis of a wide variety of polymeric materials using anionic polymerization, especially in terms of controlling monomer sequence. Moreover we have shown that MALDI ToF MS is a valuable tool for the analysis of such sequence controlled polymers.

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