Fire and Forget! One-shot Synthesis and Characterization of Block-like Statistical Terpolymers via Living Anionic Polymerization.

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ABSTRACT

Diphenylethylene (DPE) is a monomer which has attracted significant interest from academia and industry both in terms of copolymerization kinetics and for the potential to extend and tune the range of glass transition temperatures accessible for DPE-containing copolymers. DPE can undergo (co)polymerization with a variety of other monomers by living anionic polymerization but is incapable of forming a homopolymer due to steric hindrance. DPE, being a sterically bulky monomer, results in dramatic increases in the glass transition temperature (T_g) of resulting copolymers, with a perfectly alternating copolymer of styrene and DPE having a T_g of approximately 180 °C. Herein we report for the first time, the outcome of the statistical terpolymerization of butadiene, styrene and DPE – a one-pot, one-shot, commercially-scalable reaction using monomers of wide industrial importance. This extremely facile approach produces copolymers with a block-like structure, which undergo microphase separation, possess a high T_g glassy “block” and are virtually indistinguishable from analogous block terpolymers made by the traditional sequential addition of monomers approach.

KEY WORDS: anionic polymerization; monomer sequence distribution; terpolymers; fire and forget

INTRODUCTION

The perfection that Nature is able to exert over the control of monomer sequences in biopolymers such as proteins and nucleic acids has inspired the polymer chemistry community to explore and develop methodologies to influence monomer sequence distribution in synthetic copolymers. The field has grown dramatically in the past decade, prompting a discussion paper[1], authored by key workers, on nomenclature. Progress has been collated in a recently published book[2] edited by Lutz, whose work on the synthesis and characterization of sequence controlled polymers for digital encoding is seminal[3-12]. For brevity, only the most relevant contributions to the field will be mentioned here and specifically those with the aim of controlling monomer sequence distribution in chain growth polymerization where a number of strategies have recently been proposed. These strategies can be crudely divided into either a “template approach” or a “kinetic approach”. The former is in essence 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 high molecular weight templates to control sequence distribution is a major challenge in itself. Various attempts to overcome this challenge include preselecting the monomer sequence through the synthesis of a polymerizable “template” where two or more “monomers” are conjoined prior to polymerization. For example Hillmyer *et al.* reported the synthesis of regioselective terpolymers and quarterpolymers by ring opening metathesis polymerization (ROMP) of multi-substituted cyclooctenes.[13] Sawamoto *et al.* [14-17] employed strategies based on the radical polymerization of conjoined monomers, cyclopolymerization and cleavable linkages to produce polymers with periodic sequences. The use of templating initiators to control the resulting co-monomer sequence has also been proposed. Sawamoto[18,19] designed a template initiator that allows preferential consumption of methacrylic acid over methyl methacrylate and a similar approach[20] utilised a crown ether as a recognition site which specifically recognizes the sodium ion of sodium methacrylate over methacryloxyloxyethyltrimethylammonium chloride. The use of DNA as a template[21] enabled the polymerization of 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 demonstrating a promising approach for future attempts to synthesize sequence controlled copolymers with high molecular weight[22].

Whilst template approaches are both exciting and promising, the (more) facile/scalable approach of exploiting “kinetic control” over co-monomer sequences during polymerization has the advantage of being practically easier and quicker, more economical and hence much more applicable from an industrial perspective. The most basic representation of a perfect copolymer sequence is the alternating copolymer although relatively few examples exist. The best earliest reported[23] example of an alternating copolymer arises via the free radical copolymerization of maleic anhydride and styrene. Lutz[24] exploited the concept of a monomer which is incapable of homopolymerization, with sequential monomer addition, to prepare a multi-block copolymer of polystyrene containing four short alternating styrene-maleimide sequences. There are a number of reported examples of other alternating copolymers prepared by controlled free radical,[25-28] ROMP[29] and cationic polymerization [30-33].

Of particular interest for living anionic copolymerization is the monomer 1,1-diphenylethylene (DPE). DPE is unable to form a homopolymer due to steric bulk although it has been reported[34] that the formation of dimers of DPE can occur following 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 only the monoadduct is formed and homopolymerization does not occur. This property of DPE has been exploited in anionic polymerization for various purposes and DPE (and its derivatives) has been used both to initiate and end-cap polymers prepared by anionic polymerization.[35-39] DPE is particularly useful for the initiation of acrylate and methacrylate monomers where the steric bulk prevents side reactions. DPE has similarly 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.[35,36] Whilst DPE is unable to homopolymerize, it can copolymerize and with a suitable co-monomer, DPE can form alternating copolymers in an analogous fashion to the free-radical copolymerization of maleic anhydride with styrene. Yuki *et al*. explored the copolymerization of DPE with styrene,[40] butadiene,[41] isoprene,[42] 2,3-dimethylbutadiene[43, 44] and methoxystyrene.[45] ^{1}H-NMR analysis suggested the formation of alternating or near-alternating copolymers in all cases when using THF, however, only styrene, 2,3-dimethylbutadiene and *p*-methoxystyrene formed nearly-alternating copolymers with DPE in benzene. A more recent study by ourselves used MALDI-ToF MS to confirm unambiguously the earlier findings of Yuki[46].

A number of studies have used functional derivatives of DPE. 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 and/or the terminus of the chain,[47,48] and at the interface between two blocks[47] Li *et al*. copolymerized 1,1-bis(4-dimethylaminophenyl)ethylene with styrene to prepare a statistical copolymer,[49] and Quirk *et al.* copolymerized 1-(4-dimethylaminophenyl)-1-phenylethylene with styrene.[50] Similarly, DPE derivatives have been used to add phenol groups at either[51,52] or both[46] chain-ends or at the interface between two blocks[51] by living anionic polymerization. Usually, the introduction of functional DPE units is achieved by a sequential approach, however Hutchings *et al.* recently reported the synthesis of telechelic polymers of either butadiene or styrene, end-capped (at both chain ends) with 1,1-bis(4-*tert*-butyldimethylsiloxyphenyl)ethylene (DPE-OSi) in a statistical copolymerization – an example of sequence control via a kinetic approach.[46] However, it has also been shown that the presence of an electron withdrawing (cyano) substituent in the *para* position promotes copolymerization to yield a functional alternating copolymer with styrene[53].

The concept of employing a substituent to modify reactivity ratios with a view to influencing the resulting monomer sequence distribution has also been employed in the statistical copolymerization of more than two monomers. Hutchings *et al.* exploited the deactivated DPE-OSi monomer in a terpolymerization with styrene and DPE to produce a polymer with a pronounced gradient sequence.[54] More recently, Ma *et al.* have described the synthesis and copolymerization/terpolymerization kinetics of styrene with one or more DPE derivatives and their post-polymerization functionalization[55-61]. An analogous approach has also been taken by Frey *et al.* who explored the impact of the protecting group on monomer reactivity in a series of vinyl catechol monomers in anionic copolymerization with styrene[62]. Wurm *et al* was somewhat more ambitious in reporting the simultaneous living anionic polymerization of sulfonamide-activated aziridines for sequence control with up to five competing monomers, resulting in a gradient sequence where monomer consumption was directly correlated to the electron withdrawing effect of the sulfonamide[63].

Herein we describe the simultaneous/statistical terpolymerization of styrene, butadiene and diphenylethylene – three commercially available monomers – by anionic polymerization. The reactivity ratios for each pair of monomers (in non-polar solvents) would suggest that the resulting terpolymers would have a block-like sequence in which one 'block' is predominantly polybutadiene attached to a block of styrene/DPE via a region of tapering composition. Diblock-like terpolymers, initiated by *sec*-butyllithium are reported. A comparison of the sequence controlled statistical copolymers with block copolymers of poly(styrene-*co*-DPE)-*block*-polybutadiene, prepared by the sequential addition of monomers, to investigate the impact of monomer sequence on physical properties was carried out. The results of thermal analysis by DSC and DMA and an investigation of the microphase-separated morphologies by TEM are reported and reveal that the two classes of terpolymer, made by the two different approaches, are almost indistinguishable.

EXPERIMENTAL

Materials. Benzene (Aldrich, HPLC grade > 99.9%), toluene (Fisher, HPLC grade > 99.9%) and styrene (Aldrich, 99%) were dried with calcium hydride (97%, Aldrich) and degassed by a series of freeze-pump-thaw cycles. Butadiene (Aldrich, 99%) was dried and purified by passing the monomer successively through columns of Carbosorb (Aldrich), to remove any inhibitor, and molecular sieves. 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. Methanol (Fisher, AR grade), *sec*-butyllithium (Aldrich, 1.4 M in cyclohexane; Acros, 1.3 M in cyclohexane), 2,6-di-*tert*-butyl-4-methyl phenol (BHT) (Aldrich, 99%) were all used as received.

Measurements. Molecular weight analysis was carried out by size exclusion chromatography (SEC) using a Viscotek TDA 302 with a refractive index, viscosity and light scattering detectors. 2 x 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 with THF as the eluent at a flow rate of 1.0 ml/min at a temperature of 35 °C. Molecular weights were typically obtained by triple detection SEC with light scattering. The calibration was carried out with a single narrow molecular weight polystyrene standard (Polymer Laboratories). A value of 0.185 mL/g (polystyrene) was used as the *dn*/*dc* for all the copolymers produced.

^{1}H NMR spectra were recorded on either a Bruker-400 MHz or a Varian VNMRS-700 MHz spectrometer using $CDCl_3$ as a solvent. Spectra were referenced to the trace of $CHCl_3$ (7.3 ppm) present in $CDCl_3$.

Differential Scanning Calorimetry (DSC) was performed under an inert atmosphere on a TA Q1000 instrument from room temperature to 493 K at 40 K/min. Glass transition temperatures were analyzed using TA instruments Universal Analysis 2000 version 4.5A.

Dynamic Mechanical Analysis (DMA) was performed on a TA Q800 DMA instrument with a 20 mm cantilever using samples with a length of 20.0 mm, width of 10.0 mm and thickness of 1.1 mm. Samples were pressed in a mould using a weight of 10 Kg, degassed, purged with dry nitrogen and put under vacuum. This process was repeated three times before the sample was heated to 220 °C for 24 hours, cooled and raised to atmospheric pressure to ensure no degradation of the polybutadiene block. The samples were then placed in the DMA; equilibrated at 30 °C; cooled to

-150 °C at 5 °C/min; equilibrated at -150 °C and heated to 250 °C at 5 °C/min. The thermal properties were analyzed using TA instruments Universal Analysis 2000 version 4.5A and the glass transition temperatures calculated from the peaks in tan delta.

Samples for Transmission Electron Microscopy (TEM) analysis were prepared by cryo-ultramicrotomy using a Leica EM UC6 Ultramicrotome and Leica EM FC6 cryochamber (Milton Keynes, UK) on a solvent cast film (cast from a 30 wt. % solution in toluene). Cryosections of 50 – 70 nm thickness were cut using a cryo 35° diamond knife (Diatome, Switzerland) at a temperature between -120 °C and -140 °C and then manipulated from the knife edge onto formvar coated grids. Sections were stained for 2 – 4 hours with osmium tetroxide (OsO4) vapour, then viewed with a Hitachi H7600 transmission electron microscope (Hitachi High Technologies Europe) using an accelerating voltage of 100 KV.

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 Poly(Butadiene-*co*-Styrene-*co*-1,1-Diphenylethylene) by the simultaneous (Fire and Forget) approach

All statistical terpolymers in this series were prepared using the same procedure. The (typical) synthesis of PBSD-1 is described. Benzene (80 ml) and styrene (2.42 g, 23 mmol) were distilled, under vacuum, into the reaction apparatus. DPE (2.80 g, 16 mmol) was injected *via* a rubber septum and 6.75 g butadiene (125 mmol) added by distillation. For a target molecular weight of 18,000 g mol^{-1}, *sec*-butyllithium (BuLi) (0.46 ml of 1.4 M solution, 0.65 mmol) was added by injection *via* a rubber septum, resulting in the pale yellow colour indicative of butadienyl lithium.

The solution was stirred at room temperature for 8 hours before a small sample was extracted and terminated by the injection of nitrogen sparged methanol to yield PBSD-1a. The remaining reaction solution was stirred at room temperature for a further 17 hours before a second sample was extracted to yield PBSD-1b and the remaining solution was heated to 50 °C. The pale yellow colour of the reaction mixture began to darken to a red colour, indicative of a mixture of diphenylethyl lithium and styryl lithium, over the next 45 minutes at which point another sample was extracted to yield PBSD-1c. The reaction was then stirred at 50 °C for a further 22.5 hours before being terminated by the injection of nitrogen sparged methanol to yield PBSD-1. The final polymer and intermediate polymer samples were 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*. **PBSD-1** Yield = 78 %. M_n = 36,900 g mol^{-1}; M_w = 39,100 g mol^{-1}; Đ = 1.06 (triple detection SEC with dn/dc = 0.185 mL/g). ^{1}H NMR (700 MHz, CDCl$_3$, ppm): δ = 0.3 – 2.9 (5H $-\mathrm{C}\mathbf{H_2}\mathrm{CPh}\mathbf{H}\text{-}\mathrm{C}\mathbf{H_2}\mathrm{CPh_2}$); (3H $-\mathrm{C}\mathbf{H_2}\mathrm{C}\mathbf{H}\mathrm{CH{=}CH_2}$) and (4H $-\mathrm{C}\mathbf{H_2}\mathrm{CH{=}CHC}\mathbf{H_2}$), 4.9 – 5.0 (2H – $\mathrm{CH_2CHCH{=}C}\mathbf{H_2}$), 5.1 – 5.5 (2H $-\mathrm{CH_2C}\mathbf{H}\mathrm{{=}C}\mathbf{H}\mathrm{CH_2}$), 5.5 – 5.6 (1H – $\mathrm{CH_2CHC}\mathbf{H}\mathrm{{=}CH_2}$), 5.6 – 7.4 (15H $-\mathrm{CH_2C}\mathbf{Ph}\mathrm{H\text{-}CH_2C}\mathbf{Ph_2}$).

PBSD-1a M_n = 13,800 g mol^{-1}; M_w = 14,600 g mol^{-1}; Đ = 1.06

PBSD-1b M_n = 19,300 g mol^{-1}; M_w = 20,400 g mol^{-1}; Đ = 1.06

PBSD-1a and 1b ^{1}H NMR (700 MHz, CDCl$_3$, ppm): δ = 0.8 – 2.9 (5H $-\mathrm{C}\mathbf{H_2}\mathrm{CPh}\mathbf{H}\text{-}\mathrm{C}\mathbf{H_2}\mathrm{CPh_2}$); (3H $-\mathrm{C}\mathbf{H_2}\mathrm{C}\mathbf{H}\mathrm{CH{=}CH_2}$) and (4H $-\mathrm{C}\mathbf{H_2}\mathrm{CH{=}CHC}\mathbf{H_2}$), 4.9 – 5.0 (2H – $\mathrm{CH_2CHCH{=}C}\mathbf{H_2}$), 5.2 – 5.5 (2H $-\mathrm{CH_2C}\mathbf{H}\mathrm{{=}C}\mathbf{H}\mathrm{CH_2}$), 5.5 – 5.6 (1H – $\mathrm{CH_2CHC}\mathbf{H}\mathrm{{=}CH_2}$), 7.0 – 7.4 (15H $-\mathrm{CH_2C}\mathbf{Ph}\mathrm{H\text{-}CH_2C}\mathbf{Ph_2}$).

PBSD-1c M_n = 22,600 g mol^{-1}; M_w = 23,800 g mol^{-1}; Đ = 1.05. ^{1}H NMR (700 MHz, CDCl$_3$, ppm): δ = 0.8 – 2.9 (5H $-\mathrm{C}\mathbf{H_2}\mathrm{CPh}\mathbf{H}\text{-}\mathrm{C}\mathbf{H_2}\mathrm{CPh_2}$); (3H $-\mathrm{C}\mathbf{H_2}\mathrm{C}\mathbf{H}\mathrm{CH{=}CH_2}$) and (4H $-\mathrm{C}\mathbf{H_2}\mathrm{CH{=}CHC}\mathbf{H_2}$), 4.9 – 5.0 (2H – $CH_2CHCH=C\mathbf{H_2}$), 5.2 – 5.5 (2H –$CH_2C\mathbf{H}=C\mathbf{H}CH_2$), 5.5 – 5.6 (1H – $CH_2CHC\mathbf{H}=CH_2$), 6.2 – 7.4 (15H –$CH_2C\mathbf{Ph}H\text{-}CH_2C\mathbf{Ph_2}$).

Synthesis of poly(styrene-*co*-1,1-diphenylethylene)-*block*-polybutadiene by the sequential addition of monomers

All block terpolymers in this series were prepared using the same procedure. The (typical) synthesis of PSD-*b*-B-1 is described. Benzene (90 ml) and styrene (2.36 g, 23 mmol) were distilled, under vacuum, into the reaction apparatus. DPE (2.72 g, 15 mmol) was injected via a rubber septum. For a target block 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 sample was extracted and terminated by the injection of nitrogen sparged methanol. The solution of living polymer was then cooled with an ice-cold water bath and butadiene (5.38 g, 99 mmol) was added by distillation for a target block molecular weight of 8,600 g mol^{-1}. Upon addition of butadiene the red colour indicative of a mixture of diphenylethyl lithium and styryl lithium, dissipated instantly to a pale yellow. The reaction was stirred at room temperature for 22 hours before being terminated by the injection of nitrogen sparged methanol. 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 = 83 %. M_n = 16,800 g mol^{-1}; M_w = 17,800 g mol^{-1}; Đ = 1.06 (triple detection SEC with dn/dc = 0.185). ^{1}H NMR (700 MHz, $CDCl_3$, ppm): δ = 0.2 – 2.4 (5H –$C\mathbf{H_2}CPh\mathbf{H}\text{-}C\mathbf{H_2}CPh_2$); (3H –$C\mathbf{H_2}C\mathbf{H}CH=CH_2$) and (4H –$C\mathbf{H_2}CH=CHC\mathbf{H_2}$), 4.9 – 5.0 (2H – $CH_2CHCH=C\mathbf{H_2}$), 5.1 – 5.5 (2H –$CH_2C\mathbf{H}=C\mathbf{H}CH_2$), 5.5 – 5.6 (1H – $CH_2CHC\mathbf{H}=CH_2$), 5.6 – 7.3 (15H –$CH_2C\mathbf{Ph}H\text{-}CH_2C\mathbf{Ph_2}$).

RESULTS AND DISCUSSION

The anionic copolymerization kinetics of the three pairs of monomers – styrene + butadiene, styrene + DPE and butadiene + DPE are well-known[64] and have recently been revisited by ourselves[46]. Reactivity ratios for each pair of monomers, when benzene is used as the polymerization solvent and butyl lithium as initiator, have been reported by various authors and typical values are shown in Table 1. The comonomer sequence arising from each copolymerization is therefore well understood. Since diphenylethylene (DPE) is unable to homopolymerize, its reactivity ratio in each case is zero. For the copolymerization of DPE with styrene (M1), r_1 is in the region of 0.5 - 0.7 which suggests a preference for styrene to cross-propagate to DPE and we (and others[40]) have shown that if DPE is added in molar excess with respect to styrene, a perfect alternating copolymer results. On the other hand, the copolymerization of butadiene and DPE in benzene yields an almost perfect homopolymer of butadiene, as a result of the very high reactivity ratio, r_1 = 54. Finally, the statistical copolymerization of styrene and butadiene in non-polar solvents is known to produce a tapered block copolymer.[64] Based on our understanding of the copolymerization kinetics of each of the monomer pairs described above, one might hypothesize that a statistical terpolymerization of styrene, butadiene and DPE would result in the initial

Table 1. Monomer reactivity ratios for the anionic copolymerization of styrene/DPE, butadiene/DPE and styrene/butadiene. Polymerization initiated by butyllithium in benzene

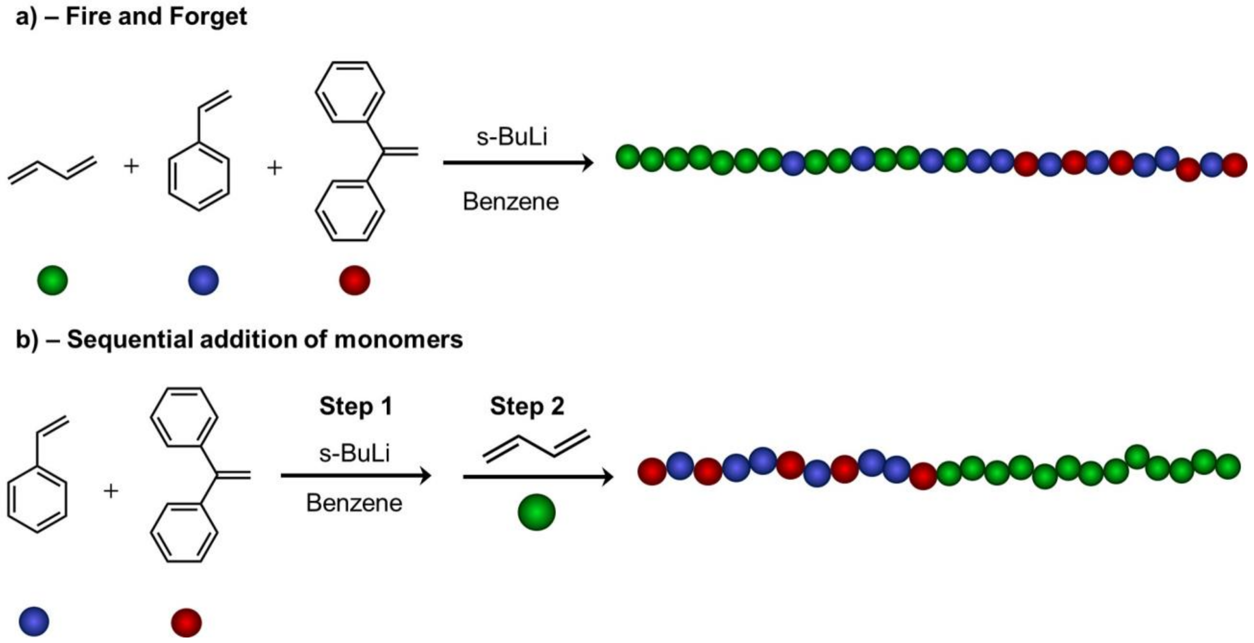
M1	**M2**	**r_1**	**r_2**
Styrene	Diphenylethylene	0.5-0.7	0
Butadiene	Diphenylethylene	54	0
Butadiene	Styrene	10.8	0.04

preferential consumption of butadiene, with the styrene/DPE reacting only when the feed ratio of butadiene is diminished. The principal objective of the current project was to test this hypothesis and to ascertain the comonomer sequence distribution arising from a simultaneous terpolymerization of styrene, butadiene and DPE – a process we shall call "Fire and Forget". In addition, the properties of the resulting statistical terpolymers are compared to analogous block copolymers made by the sequential addition of monomers. The latter approach involves the polymerization of styrene/DPE, to form a statistical block, followed by the addition of butadiene to create a second block, of polybutadiene. This sequential approach has been reported previously for the synthesis of both poly(styrene-*stat*-DPE)-*b*-butadiene[65,66] and poly(styrene-*stat*-DPE)-*b*-isoprene[67] block copolymers but to the best of our knowledge this is the first report of the "Fire and Forget" route to these terpolymers. Herein, a series of diblock-like statistical terpolymers, initiated by *sec*-butyllithium are reported.

Simultaneous Terpolymerization of Styrene, Butadiene and 1,1-Diphenylethylene in Benzene

A series of diblock-like statistical terpolymers, with different molecular weights and compositions were prepared by the simultaneous (Fire and Forget) terpolymerization of styrene, DPE and butadiene, initiated with *sec*-BuLi, in benzene (see Figure 1a)). As a truly living polymerization mechanism, anionic polymerization proceeds in the absence of termination reactions and in each case reaction times were chosen to ensure complete conversion of monomers. The only exception to this situation is where residual DPE remains after complete conversion of styrene and butadiene. In this case the residual DPE is unable to undergo homopolymerization and quantitative conversion of DPE will not occur. The monomer composition of each resulting

Figure 1. Schematic illustration of a) one-shot simultaneous "Fire and Forget" terpolymerisation of butadiene, styrene and DPE leading to statistical 'blocky' terpolymer and b) two step sequential additional of monomer approach to poly(styrene-*co*-DPE)-*block*-(butadiene) copolymer.



terpolymer was estimated by ^{1}H NMR spectroscopy and is reported in Table 2. A detailed discussion of how the terpolymer composition was calculated using NMR data is reported as supporting information. It should be noted that in most cases, deconvolution of the signals arising from the three monomers in the aliphatic region is not possible, and to overcome this issue it is assumed that the mole ratio of styrene : DPE in the terpolymer is the same as that for a poly(styrene-co-DPE) copolymer prepared with the same molar feed ratio of styrene : DPE. Although this assumption introduces a potential error into the composition calculation, given the block-like structure of the resulting terpolymer, in which butadiene is polymerized almost exclusively in the early stages (see later discussion), we believe that the error will be modest and the assumption justified. Thus PBSD-1 was prepared with a molar feed ratio of 1.00 : 0.69 : 5.43 (styrene : DPE : butadiene) and an analogous styrene/DPE copolymer (PSD-1) was synthesized

Table 2. Compositions of poly(butadiene-*co*-styrene-*co*-DPE) copolymers, initiated with *sec*-BuLi, in benzene, using styrene : DPE ratios determined from the previous copolymerizations of styrene and DPE.

Sample	Reaction Temp / °C	Monomer Composition Sty : DPE : Bd (Mol)		% 1,4-PBd
		Feed Ratio	Resulting Copolymer	
PBSD-1	RT to 50[a]	1.00 : 0.69 : 5.43	1.00 : 0.50 : 5.42	90
PBSD-2	50	1.00 : 0.58 : 3.28	1.00 : 0.50 : 3.34	89
PBSD-3	25	1.00 : 1.55 : 1.99	1.00 : 0.85 : 1.92	87
PBSD-4	25	1.00 : 1.55 : 2.71	1.00 : 0.85 : 2.94	90
PBSD-5	25	1.00 : 1.55 : 10.99	1.00 : 0.85 : 13.13	90
PBSD-6	25	1.00 : 1.54 : 10.96	1.00 : 0.85 : 12.60	90
PBSD-7	25	1.00 : 1.60 : 10.04	1.00 : 0.85 : 13.63	90
PBSD-8	25	1.00 : 1.50 : 7.69	1.00 : 0.85 : 9.32	90

a – reaction temperature was raised to 50 °C after 25 hours.

(details previously reported[46]) with an almost identical molar feed ratio of styrene : DPE (1.00 : 0.67) thus allowing the copolymer composition of PSD-1, which was obtained from NMR data as previously reported[46], to be used to obtain the composition of the analogous terpolymer. From the data in Table 2, it is clear that in most cases, the composition of the feed is very similar to the composition of the resulting copolymer. However, closer inspection reveals that in each case the mole fraction of DPE in the final polymer is somewhat lower than that in the feed. This is not unexpected given that DPE is unable to homopolymerize, does not copolymerize with butadiene and even with an excess of DPE with respect to styrene, an alternating copolymer is not assured. Moreover in the case of PBSD 5 - PBSD8, where the mole fraction of butadiene in the feed is high, the mole ratio of butadiene to styrene is even higher in the copolymer than in the feed. This is

Table 3. Molecular weight data (obtained using triple detection SEC with dn/dc = 0.185) of poly(butadiene-*co*-styrene-*co*-DPE) copolymers synthesized in benzene.

Sample	**Target M_n / g mol^{-1}**	**Expt M_n/g mol^{-1}**	**M_w/g mol^{-1}**	**Đ**
PBSD-1	18,000	36,900	39,100	1.06
PBSD-2	10,000	11,100	11,800	1.06
PBSD-3	5,500	4,900	5,400	1.09
PBSD-4	55,000	58,500	62,700	1.07
PBSD-5	60,000	50,700	53,100	1.05
PBSD-6	100,000	111,900	119,600	1.07
PBSD-7	100,000	96,900	99,500	1.03
PBSD-8	100,000	117,100	122,500	1.05

unexpected and is likely due to inaccuracies in the calculation using NMR data, probably arising from the assumption about the styrene/DPE ratio mentioned above. A very high fraction of butadiene in the feed is likely to impact upon the fractions of DPE and styrene incorporated and the assumed styrene: DPE ratio quoted may be slightly in error. However, whilst the ultimate compositions are of interest, the greater interest lies in the relative rate of incorporation of each monomer and thus the resulting monomer sequence distribution. The molecular weight data of each terpolymer was determined by SEC, using the *dn/dc* value for styrene of 0.185 mL/g, and is reported in Table 3. The use of a *dn/dc* value for polystyrene will introduce an error into the molar mass analysis however, the absolute molar mass of the resulting copolymers is of secondary importance to understanding the copolymerization kinetics in this work. That said, the data in table 3 shows a rather good agreement between theoretical (target) molar mass and actual molar mass, with the exception of PBSD-1, where the difference may be due to premature termination from impurities. However, of greater significance is that the Fire and Forget approach can be used to produce narrow dispersity copolymers with no apparent limitation on molar mass, and since experiments PBSD-6, 7 and 8 were all nearly identical, this process shows good reproducibility.

The primary objective of this work is to understand the comonomer sequence arising from a Fire and Forget terpolymerization of styrene, DPE and butadiene. Accurately calculating reactivity ratios for a terpolymerization is an extremely complex and convoluted process so instead, a combination of analyses (NMR, SEC and MALDI) were carried out on samples collected from the terpolymerization at intermediate reaction times, along with (purely qualitative) visual observations of colour changes during the reaction, to explore the order of monomer consumption. Even accepting some of the experimental errors alluded to above, the combined analyses provide compelling evidence to support the original hypothesis. The progress of experiment PBDS-1 was followed by withdrawing samples periodically and subjecting them to both SEC (table 4) and NMR (table 4, figure 2) analysis. Photographs were also taken periodically throughout the duration of the reaction to observe any colour changes – see figure S2 (supporting information). It is well-known that the propagating species polybutadienyllithium is a very pale yellow, whereas that of polystyryllithium is yellow/orange (depending on concentration of end groups) and diphenylethyllithium a deep red. Hence, colour changes can qualitatively indicate the nature of the propagating species at any given point in the reaction. It must be pointed out that the molar mass data in table 4 is only semi-quantitative. All of the molar mass data was obtained using the *dn/dc* value for polystyrene, which is higher than that of polybutadiene and therefore will underestimate the molar mass of the samples. Moreover, the error in SEC analysis will differ for each sample since the comonomer composition will be changing over time. However, whilst it is clear that the

Table 4. Molar mass data and comonomer composition for PBSD-1 and samples collected at the indicated intermediate reaction times.

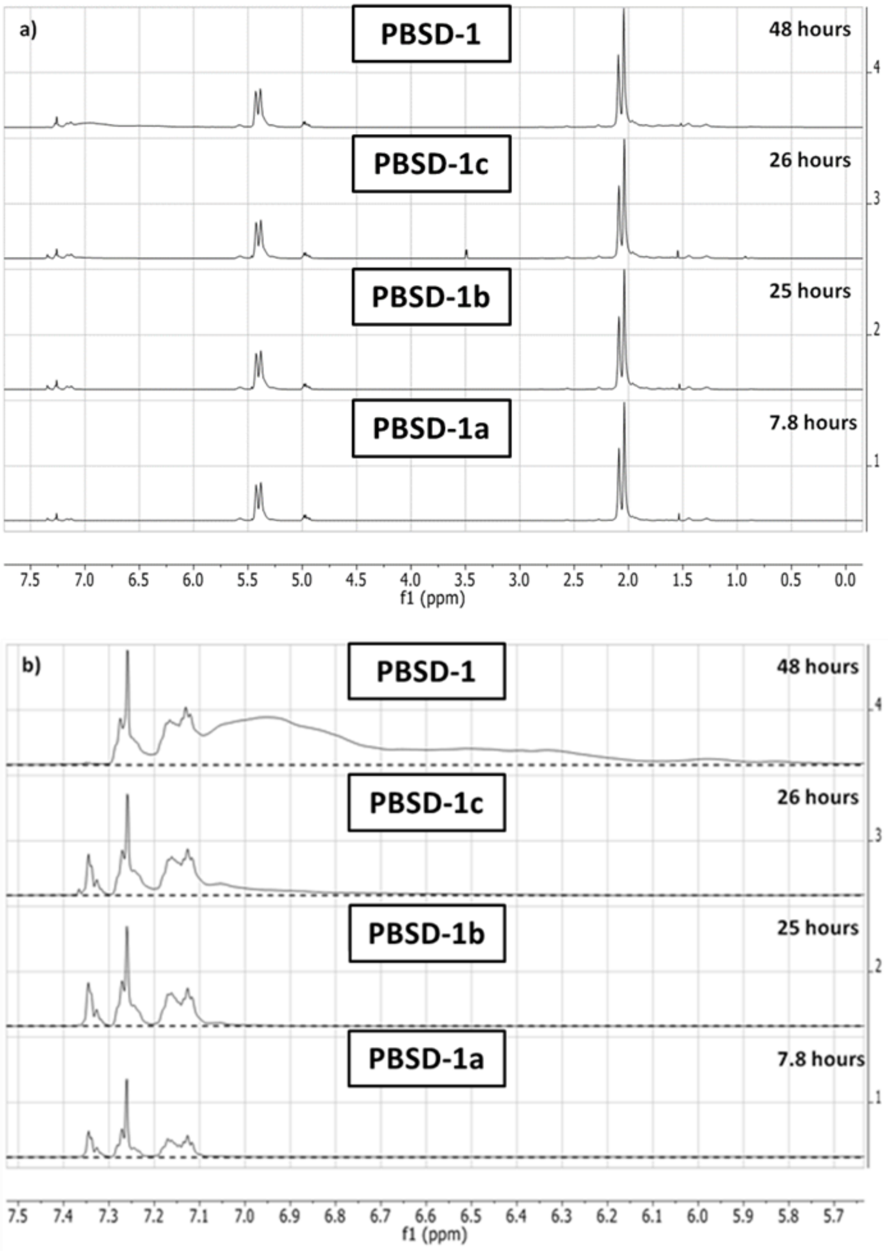
Sample	**Reaction Time/hours**[a]	**M_n/g mol^{-1}**[a]	**Đ**[a]	**Relative Mole Fractions of Sty : DPE : Bd in copolymer**[b]
PBSD-1a	7.8	13,800	1.06	1.00 : 0.50 : 144.44
PBSD-1b	24.9	19,300	1.06	1.00 : 0.50 : 41.94
PBSD-1c	25.7	22,600	1.05	1.00 : 0.50 : 24.76
PBSD-1	48.1	36,900	1.06	1.00 : 0.50 : 5.42

a – SEC data obtained using triple detection SEC with *dn/dc* = 0.185 mL/g

b – Estimated by ^{1}H-NMR analysis using assumed fractions for styrene and DPE.

molar mass is increasing steadily with time, SEC data is not able to provide any direct evidence of chemical composition. However, NMR analysis of the intermediate samples does provide direct evidence of changes in composition as a function of time and the first evidence of the monomer sequence distribution. The NMR data reported in Figure 2a) shows the characteristic signals for polybutadiene at c 2.0 ppm (aliphatic) and 4.9 – 5.6 ppm (alkene) in all samples. Of particular note is that at the shortest reaction time (7.8 hours) there is virtually no signal corresponding to styrene or DPE repeat units. This is particularly evident in Figure 2b), an expansion of the aromatic region of the NMR spectra. For the sample extracted after 7.8 hours, PBSD-1a, there are (very weak) signals in this region, however the peaks at 7.3-7.4 ppm correspond to unreacted DPE monomer and the sharp peak at 7.27 ppm is the trace of $CHCl_3$ in the NMR solvent. The remaining peaks in this aromatic region, may suggest the incorporation of some styrene or DPE but the intensity of these peaks is vanishingly small compared to the polybutadiene signals. Clearly the polymer sample extracted after 7.8 hours is virtually pure homopolybutadiene. This is also evident from the

Figure 2 (a) ^{1}H NMR spectrum (in $CDCl_3$) of PBSD-1 and intermediate samples PBSD-1a-c, synthesized in benzene with a molar feed ratio of 1.00 : 0.67 : 5.37, styrene : DPE : butadiene and (b) expansion of the aromatic region (5.7 – 7.5 ppm).



composition data in table 4 which shows that PBDS-1a is almost pure polybutadiene. If one accepts this to be the case, the molar mass of PBSD-1a can be recalculated by SEC analysis using the *dn/dc* for polybutadiene (0.124 mL/g) to yield a more accurate M_n of 20,700 $gmol^{-1}$. Thus PBDS-1a is polybutadiene which has grown to a degree of polymerization of approximately 380 repeat units during which time styrene and DPE have been almost totally excluded from the reaction. It is only in sample PBDS-1c (figure 2b), extracted after 26 hours and after the reaction temperature had been raised from room temperature to 50 ºC, that we start to see the emergence of signals in the NMR corresponding to a significant fraction of polystyrene/DPE. These peaks are even more evident in the NMR spectra of the final copolymer, PBDS-1. An attempt to quantify/estimate the mole fraction of each monomer has been carried out using the same calculation and assumptions as described above, and whilst we must accept that the reported data in Table 4 may not be perfectly accurate, the data and trends in data are certainly consistent with the original hypothesis and the relative peak intensities shown in the NMR spectra. Thus in the case of PBDS it can be concluded that during the terpolymerization of styrene, butadiene and DPE, butadiene is consumed with a strong preference and initially the monomer sequence is almost purely a sequence of butadiene monomers, with styrene and DPE virtually excluded from the reaction until the majority of butadiene is consumed. It is possible that some styrene is incorporated during the early stages but not to any significant level. As the mole fraction of butadiene in the feed is significantly depleted, the unreacted styrene and DPE monomers will begin to be incorporated and then polymerize statistically until no styrene remains. At this point if any DPE remains unreacted, it will not be consumed due to its inability to homopolymerize. In the case of PBSD-1, the cross over from butadiene to styrenic monomers occurred when the reaction temperature was increased to 50 ºC after 25 hours. The conclusions above are entirely consistent with the colour of the reaction mixture which changes from pale yellow to orange red in the 45 minute period after the temperature was raised (see Figure S2, supporting information). Subsequently, PBSD-2 was polymerized at 50 ºC from the outset and although the general trend in behavior was similar, see Figure S3 and Table S1 (supporting information), the higher temperature accelerated the crossover from butadiene to styrenic monomer and a colour change was observed in less than 2 hours. PBSD-3 was then carried out with two objectives in mind; firstly to decrease the butadiene fraction in the feed and secondly to prepare a low molar mass terpolymer to allow MALDI-TOF-MS analysis of the polymer. Thus a feed ratio of 1.00 : 1.55 : 1.99 (styrene : DPE : butadiene) was used with a target molar mass of 5,500 $gmol^{-1}$. The reaction was carried out at 25 ºC, and samples were collected at various intermediate times and subjected to NMR and SEC analysis as above, see Figure S4 and Table S2 (supporting information). In this case, even though butadiene comprises less than 50 mol% of the total monomer feed, such is the inherent tendency for butadiene to (homo)polymerize in preference to the other monomers, that the overall picture is largely similar to the previous examples. Although the very first sample to be collected, PBSD-3a, did not yield sufficient polymer for analysis, analysis of subsequent fractions shows once again that polymer samples recovered in the initial stages of the terpolymerization are predominantly made up of butadiene units, whilst the styrene and DPE only become incorporated into the chains towards the latter stages of the reaction. This conclusion is supported by MALDI-TOF-MS data for sample PBSD3b, collected after 1 hour 20 minutes – Figure 3. MALDI is an extremely powerful tool in supporting the identification of comonomer compositions[46] and in this case is able to give unambiguous and conclusive evidence that during the early stages of the 'Fire and Forget' terpolymerization, butadiene is almost exclusively consumed to the exclusion of styrene and DPE. Although the mass difference between two butadiene units and one unit of styrene is only 4.03 $gmol^{-1}$, such is the resolution of the peaks in this case, that even isotopic differentiation is possible – see figure 3 inset. It is therefore possible, not only to differentiate between chains comprising of

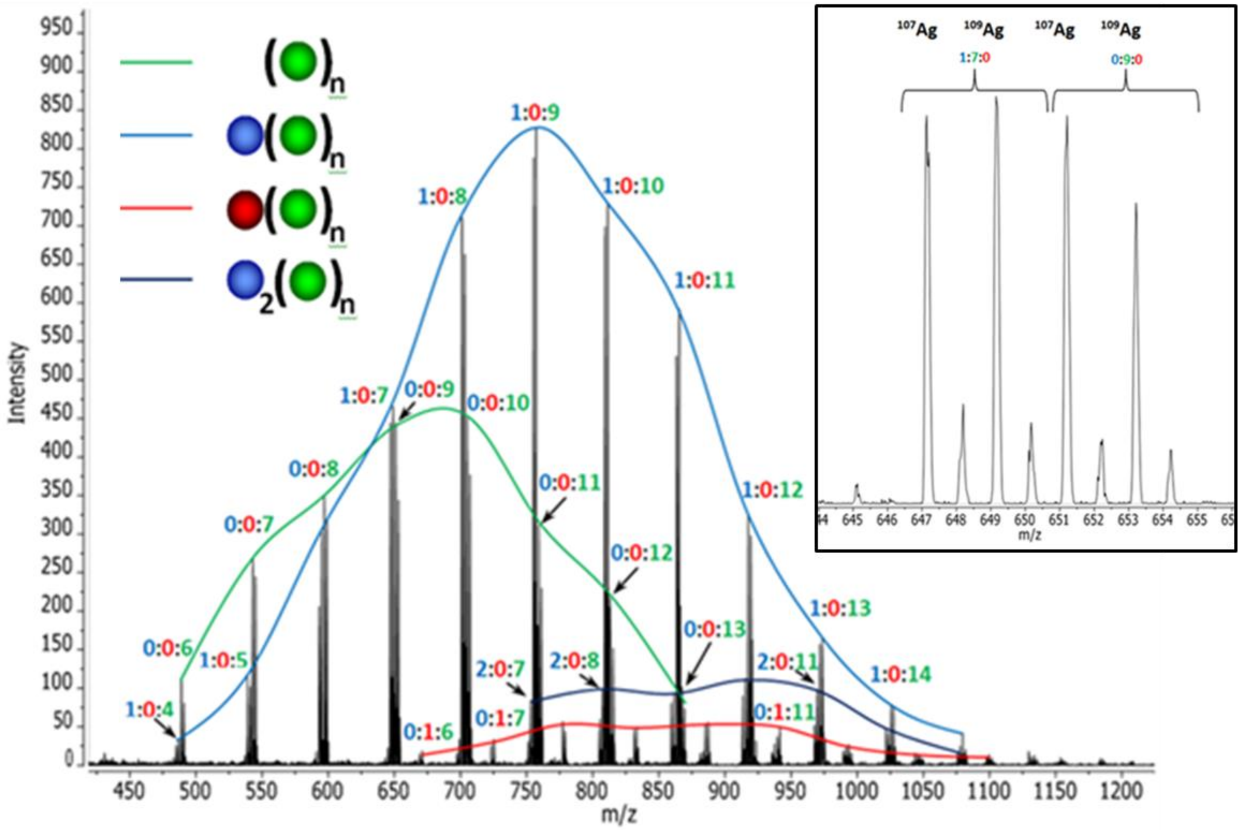


Figure 3. MALDI-ToF mass spectrum for the copolymer PBSD-3b (monomer molar feed ratio of styrene : DPE : butadiene = 1.00 : 1.55 : 1.99) collected after 1.3 hours. The number of repeat units per chain for each monomer is labelled X:Y:Z where X = styrene (blue), Y = DPE (red) and Z = butadiene (green). Inset is an expansion of the range m/z = 645 – 655.

different numbers of styrene and butadiene units, but the inset expanded region shows the splitting pattern of the peaks at approximately 650 g mol^{-1}; the peaks are split due to the isotopes of silver (^{107}Ag and^{109}Ag) and also due to the difference of four protons between one styrene unit and two butadiene units. Thus the peak at m/z = 647 can be assigned to a polymer chain consisting of 1 styrene unit and 7 butadiene units with ^{107}Ag whereas the peak at m/z = 649 has the same monomer composition but with ^{109}Ag. The smaller peak, 1 g mol^{-1} higher in mass, in each case arises from a chain carrying an isotope of either ^{2}H or ^{13}C in the copolymer, given the higher natural abundance of ^{13}C it is likely that ^{13}C will contribute most significantly to these peaks. Looking at the entire spectrum we can observe 4 different distributions of chains, each with a different composition. In figure 3 the peaks associated with each distribution are indicated via a connecting line. Each peak has been assigned a comonomer composition expressed as the number of each monomer X:Y:Z where X = the number of styrene units, Y = number of DPE units and Z = number of butadiene units. Accepting that the relative intensity of peaks in MALDI is rarely accurate, the major distribution comprises peaks corresponding to 'n' butadiene units, a single styrene unit and no DPE units. It is known that the initiator, butyllithium, reacts with styrene in preference to butadiene despite butadiene being the monomer consumed in preference during the copolymerization.[64] Hence, this single unit of styrene is likely to have arisen as a result of the initiation step. This assertion is further supported by the colour changes of the reaction mixture with time (Figure S5 supporting information) whereby, upon initiation, the reaction darkened to an intense yellow colour (Figure S5 b)), indicating the presence of at least some polystyryllithium propagating chain ends, which within seconds faded to very pale yellow colour (Figure S5 d)); a colour more commonly associated with polybutadienyllithium. It is only after 16.3 hours (Figure S5 j)) that the colour of the reaction mixture changes to the orange-red colour associated with a styrene or DPE propagating species. The second most prevalent distribution in the MALDI spectrum, contains exclusively butadiene repeat units with no styrene or DPE, the two minor distributions contain 'n' butadiene units and 2 styrene units and 'n' butadiene units and 1 DPE unit respectively. Samples PBSD-4 to PBSD-8 were prepared in an analogous fashion but without samples collected at intermediate times. The molar mass and composition data of the resulting terpolymers is reported in tables 2 and 3. A series of analogous terpolymers were prepared by the more traditional sequential addition of monomers (Figure 1b)), to allow a comparative investigation into the properties of exemplar terpolymers prepared by each approach. The sequential addition of monomer approach involves the copolymerization of styrene/DPE, to form a statistical block, followed by the addition of butadiene to create a second block, of polybutadiene. Full details of the composition and molar mass of this series of terpolymers is reported in tables S3 and S4 (supporting information).

A Comparison of the Physical Properties of Terpolymers of Styrene, Butadiene and 1,1-Diphenylethylene Prepared by the Sequential Addition of Monomers and the Fire and Forget Approaches.

The physical and mechanical properties of block copolymers very much depend upon the ability of the two blocks to undergo microphase separation. The glass transition temperature of such copolymers is also highly relevant, as T_g correlates mechanical properties to temperature, and therefore the temperature range within which the material possesses desired properties and the temperature required to process the polymer. A pertinent question therefore is, "does the resultant monomer sequence distribution obtained via the Fire and Forget approach, impact upon the microphase separation and thermal properties of the terpolymers"? The monomer sequence in this case is statistical and, although likely to be blocky in nature, there will undoubtedly be some tapering or gradient rather than a clean and abrupt switch from glassy to rubbery blocks. Gradient copolymers are less prone to microphase separation than analogous AB diblocks of similar molar mass and composition and the disordered state can occupy a large area of the phase diagram. Moreover, in some cases gradient copolymers can display a single, broad glass transition temperature, rather than the two distinct glass transitions that would be expected for an AB diblock copolymer[68]. To answer the question posed above, exemplar samples from each series of terpolymers were subjected to both thermal analysis (DSC and DMA), to obtain the glass

Table 5. Molar mass and comonomer composition data for terpolymer samples used in thermal and TEM analysis.

Sample	**Method of Synthesis**	**Sty : DPE : Bd in copolymer**	**M_n (g mol^{-1})**	**M_w (g mol^{-1})**	**Đ**
PSD-*b*-B-3	Sequential	1.00 : 0.85 : 2.28	66,600	71,100	1.07
PBSD-4	Fire and Forget	1.00 : 0.85 : 2.94	58,500	62,700	1.07
PSD-*b*-B-8	Sequential	1.00 : 0.85 : 7.78	135,500	142,200	1.05
PBSD-8	Fire and Forget	1.00 : 0.83 : 9.32	117,100	122,500	1.05

transitions, and transmission electron microscopy (TEM), to investigate the microphase separation and resultant morphologies.

Thermal Analysis. Samples with a reasonably high styrene/DPE content we chosen to allow clear and unambiguous analysis by differential scanning calorimetry (DSC) of the T_g of the glassy block. The T_g of the rubbery block was obtained via dynamic mechanical analysis (DMA). Thus, sample PSD-*b*-B-3, prepared by the sequential addition of monomer approach was analyzed and compared to PBSD-4, prepared by the "Fire and Forget" approach. These two polymers have very similar molecular characteristics and the molar mass and composition of each sample is reported in Table 5. DSC analysis (Figure 4a) and 4b)) of the two samples reveals that each has a nearly identical glass transition temperature at approximately 173 ºC which can be attributed to a styrene/DPE 'block'. Based on previous work[46] this would suggest a nearly alternating sequence of styrene and DPE. DMA analysis of the same two samples also reveals that each has nearly identical thermal properties. PSD-*b*-B-3 (Figure 5a), the block copolymer prepared via the sequential addition of monomers had a T_g of -65.0 °C measured on the heating cycle and -96.2 °C on the cooling cycle

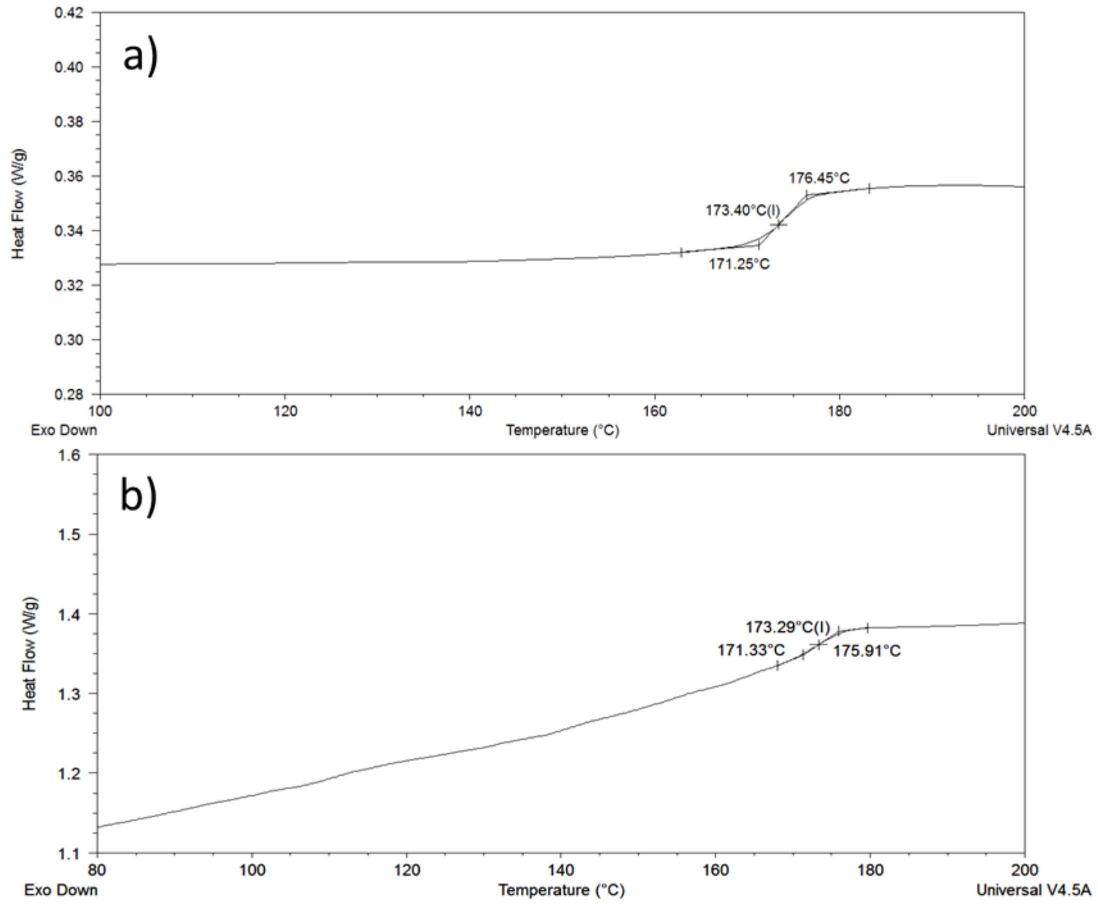


Figure 4. DSC analysis of terpolymers of a) PSD-*b*-B-3 and b) PBSD-4, prepared by the sequential addition of monomer and Fire and Forget approach respectively.

giving an average value of -80.6 °C whereas PBSD-4 (Figure 5b), the statistical (Fire and Forget) terpolymer had a T_g of -57.7 °C on the heating cycle and -92.3 °C on the cooling cycle giving an average value of -75.0 °C. Both samples were also found to have a second T_g for the glassy 'block', at almost identical temperatures; 198.5 °C and 196.4 °C for PSD-*b*-B-3 and PBSD-4 respectively. That the T_g obtained by DMA for the glassy segment in each case is higher than that obtained by DSC, is possibly due to thermal lag, due to the much larger sample size, in the former case.

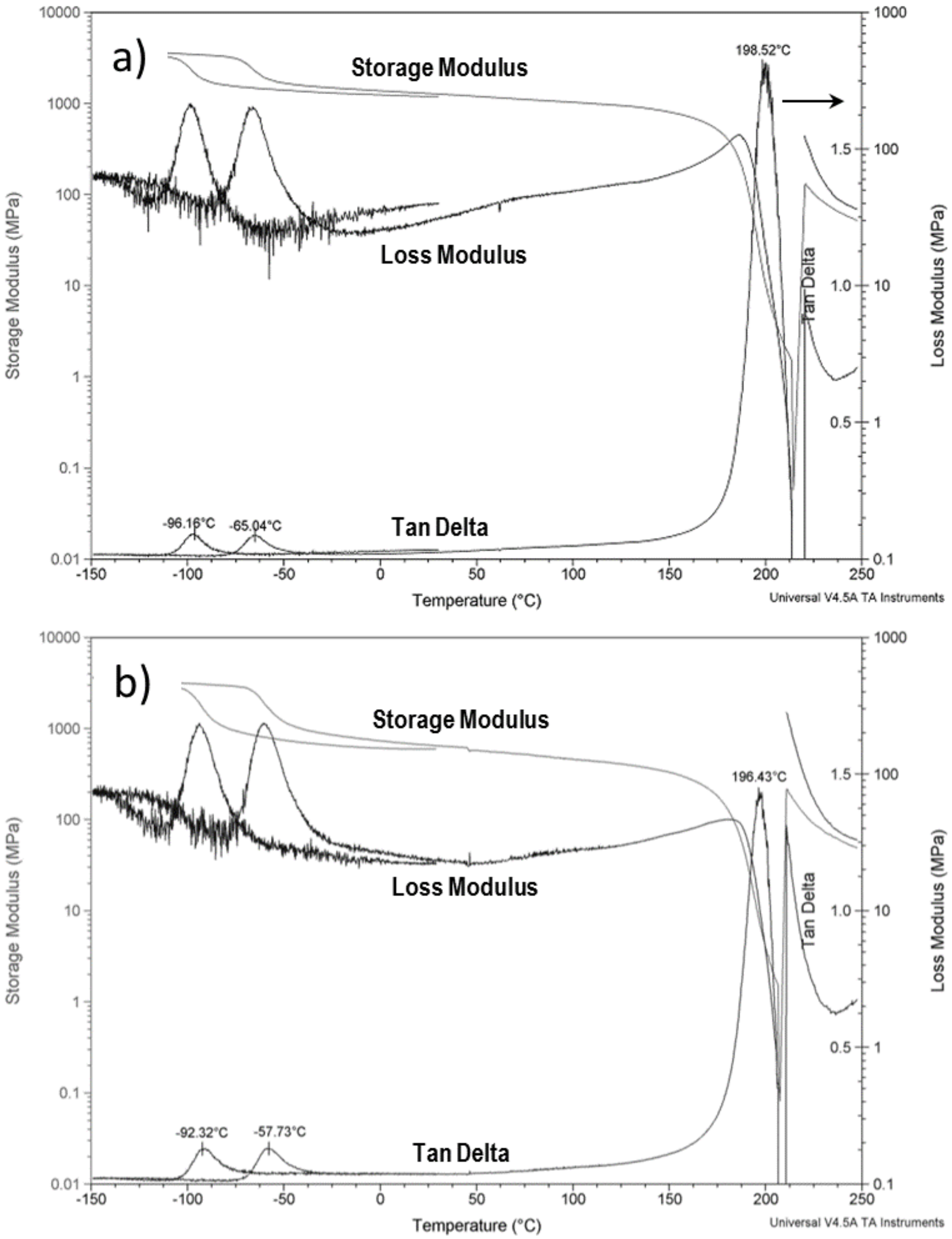


Figure 5. DMA analysis of terpolymers a) PSD-*b*-B-3 and b) PBSD-4, prepared by the sequential addition of monomer and Fire and Forget approach respectively.

However, of primary relevance is the fact the two terpolymers, prepared by the two different approaches have almost identical thermal properties suggesting that the monomer sequence distribution in the statistical terpolymer is very much like a classical block copolymer and any tapering or gradient in monomer composition at the intersect of the glassy and rubbery segments has no significant impact on the resulting glass-transition temperatures.

TEM analysis

There are currently no literature reports (to the best of our knowledge) describing the phase separation and resultant solid state morphology of block copolymers containing DPE. Block copolymers of styrene-isoprene and styrene-butadiene have been widely studied and the relationship between composition and morphology is well-understood. In the present study, the phase-separated morphology of the styrene, DPE and butadiene terpolymers was analyzed by transmission electron microscopy (TEM). It is known[68] that the relevant architectural and molecular parameters that direct self-assembly and phase behavior are the degree of polymerization N, the relative length of each block, and the microstructure of the diene repeat units. Moreover, the distance from the order-disorder transition (ODT) is determined by the degree of segregation, χN where χ is the dimensionless Flory-Huggins interaction parameter. In classic block copolymers, at high values of χN, well-defined microdomains of block A and block B are separated by narrow interfaces. In the current study, terpolymers with a high molecular weight were chosen to ensure that the chosen terpolymers will sit well above the ODT. Furthermore, it was estimated that a block copolymer with a weight fraction of approximately 30-35% of the styrene-DPE block would result in a cylindrical morphology with a continuous rubbery phase. It was therefore decided to use samples PSD-*b*-B-8 (sequential addition/block copolymer) and PBSD-8 (statistical/fire and forget) for TEM analysis, which have a styrene/DPE weight fraction of 0.38 and 0.34 respectively and in each case a molar mass of greater than 100,000 $\mathrm{gmol^{-1}}$. Molar mass and composition data for these samples is reported in Table 5. TEM images for each terpolymer are shown below in Figure 6. In both cases the TEM images reveal clear microphase

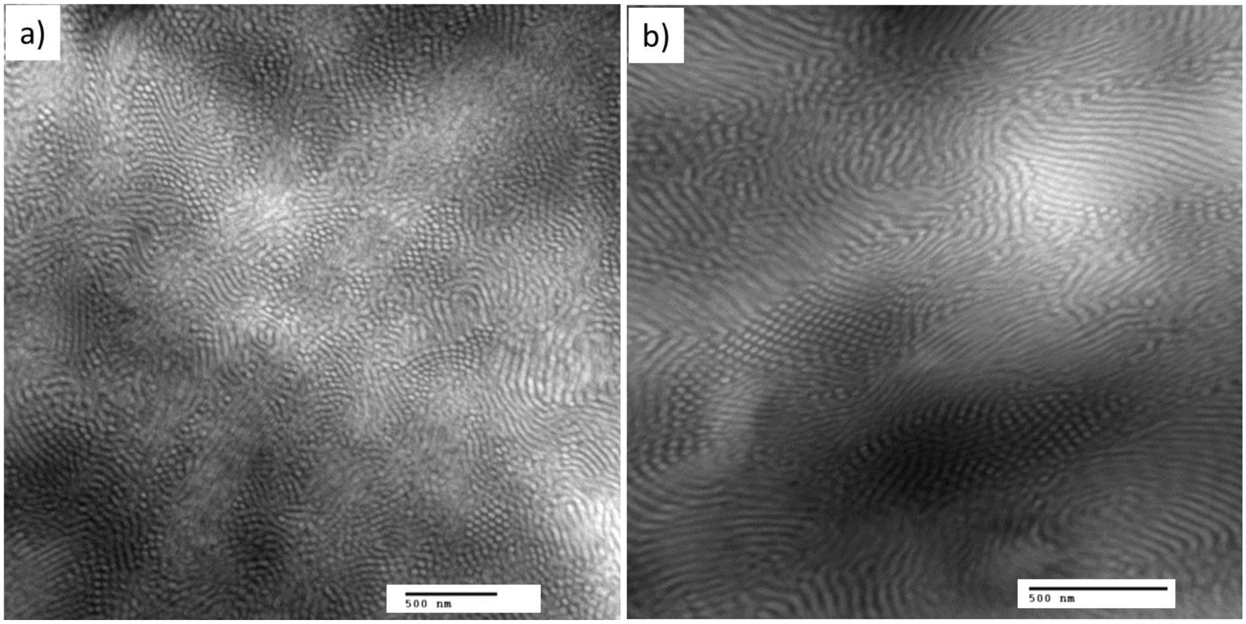


Figure 6 TEM images of terpolymer a) PSD-*b*-B-8 and b) PBSD-8, prepared by the sequential addition of monomer and Fire and Forget approach respectively. The butadiene blocks are stained black with OsO_4.

separation with well-defined microdomains. In the case of PSD-*b*-B-8 (Figure 6a), the block copolymer formed by sequential addition of monomers, the long-range order is not perfect, however there are clear regions of hexagonally packed cylinders. If anything, the microphase separated morphology for PBSD-8, the statistical copolymer prepared by the Fire and Forget approach, shows better long-range order, clearly (also) with a cylindrical morphology, evidenced by regions showing cylinders ‘end-on’ packed hexagonally and other regions showing the cylinders from side. These TEM images further illustrate the fact that the monomer sequence distribution arising from the Fire and Forget approach, and any tapering or gradient in composition, does not appear to inhibit at all, the ability of the statistical terpolymer to undergo microphase separation. This would suggest a rather sharp transition from the polybutadiene “block” to the poly(styrene-*co*-DPE) “block”.

CONCLUSIONS

For the first time a series of statistical terpolymers comprising butadiene, styrene and 1,1-diphenylethylene (DPE) have been prepared in a simultaneous living anionic polymerization, a process we describe as “Fire and Forget”. A knowledge of the reactivity ratios for each pair of monomers suggested a block-like terpolymer would result with a strong preference for the initial consumption of butadiene followed by the incorporation of a nearly alternating ‘block’ of styrene and DPE with a gradient or taper in composition between the two ‘blocks’. ^{1}H-NMR analysis of samples collected at intermediate reaction times supported this hypothesis, which was further evidenced (quantitatively) by MALDI-TOF-MS and qualitatively by the observation of colour changes during the reaction. All analysis (and visual observation) confirm the formation of an almost pure block of polybutadiene at early reaction times with styrene and DPE only incorporated at significant levels at later reaction times. An investigation was also carried out to establish what impact, if any, the resulting comonomer sequence, and the inevitable gradient in composition, would have on the physical properties of the resulting terpolymers and specifically the glass transition temperature(s) and microphase-separated morphology. An analogous series of poly(styrene-*co*-1,1-diphenylethylene)-*block*-polybutadiene terpolymers was prepared by the more commonly used sequential addition of monomers, to allow for a comparison of the physical properties with the statistical terpolymers. A combination of DSC and DMA analysis revealed that samples of each class of terpolymer had two distinct glass transitions, and that the glass transitions for each type of terpolymer were found at almost identical temperatures; approx. -80 ^{o}C for the rubbery block and 173 ^{o}C for the glassy block. Moreover, TEM analysis indicated that both types of terpolymer were able to undergo microphase separation to give clearly defined microdomains with long range order. It would appear therefore as if the extremely facile "Fire and Forget" approach to prepare statistical terpolymers of butadiene, styrene and DPE results in polymers with a highly block-like structure which in turn results in physical properties which are almost indistinguishable from block terpolymers made by the more commonly used sequential addition of monomers.

ACKNOWLEDGEMENTS We acknowledge the financial support of the Department of Chemistry, Durham University and Synthomer for funding the PhD studies of Dr. Paul Brooks.

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