

RSC Advances

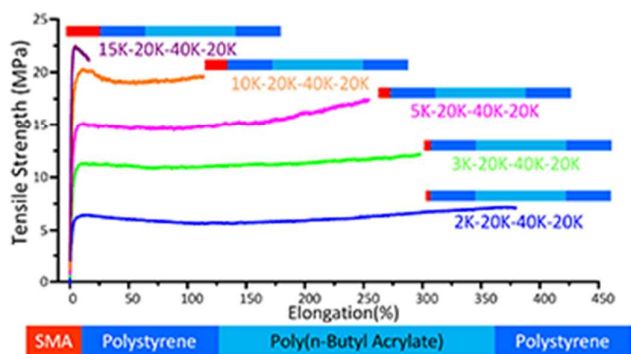


This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. This *Accepted Manuscript* will be replaced by the edited, formatted and paginated article as soon as this is available.

You can find more information about *Accepted Manuscripts* in the [Information for Authors](#).

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard [Terms & Conditions](#) and the [Ethical guidelines](#) still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.



A series of well-defined poly[styrene-*alt*-(maleic anhydride)]-block-polystyrene-block-poly(*n*-butyl acrylate)-block-polystyrene tetrablock copolymers (SMA-PSt-PnBA-PSt) were synthesized via RAFT miniemulsion polymerization. The increasing fractions of hydrophilic SMA in tetrablock copolymers led to sea-island or wormlike morphology in elastomeric matrix and higher T_g , simultaneously increasing ultimate tensile strength and elastic modulus, while lowering elongation at break.

ARTICLE

Microstructure and Mechanical Properties of Amphiphilic Tetrablock Copolymer Elastomers via RAFT Miniemulsion Polymerization: Influence of Poly[Styrene-*alt*-(Maleic Anhydride)] Segments

Cite this: DOI: 10.1039/x0xx00000x

Received 00th January 2012,
Accepted 00th January 2012

DOI: 10.1039/x0xx00000x

www.rsc.org/

Xiaoli Zhan,^a Ren He^a and Qinghua Zhang^{*a}, Fengqiu Chen^a

A series of well-defined poly[styrene-*alt*-(maleic anhydride)]-block-polystyrene-block-poly(*n*-butyl acrylate)-block-polystyrene tetrablock copolymers (SMA-PSt-PnBA-PSt) were synthesized via RAFT miniemulsion polymerization. The precursors were amphiphilic macroRAFT agent (poly[styrene-*alt*-(maleic anhydride)]-RAFT, SMA-RAFT) with different chain lengths. The structure of the copolymers was characterized by ¹H NMR, GPC, and DSC analysis. The influence of hydrophilic SMA block on the microphase separation and mechanical properties of the copolymers was illustrated by TEM observation and tensile test. The results showed that the increasing fractions of SMA in tetrablock copolymers led to sea-island or wormlike morphology in elastomeric matrix and higher *T*_g, simultaneously increasing ultimate tensile strength and lowering elongation at break. With its moderate amount of compatibility groups and typical elasticity, synthesized tetrablock copolymer SMA_{5K}-PSt_{20K}-PnBA_{40K}-PSt_{20K} could be a potential candidate for toughness modification.

Introduction

Block copolymer elastomers composed of soft and hard segments have been shown to be highly effective at improving mechanical properties of thermoplastics, such as polyvinyl chloride, polyamides and epoxy resins.¹⁻⁵ In practical applications, to improve miscibility in polymer blends, reactive or compatible groups were introduced to these elastomers.⁴⁻⁹ Meanwhile, the introduction of reactive groups by means of anionic polymerization was also by definition difficult because of undesirable terminations. Nonetheless, graft copolymerization was an effective way to improve the miscibility in blends. For example, one of the most widely-used commercial elastomeric modifiers for polyamide, styrene-*b*-ethylene/butylene-*b*-styrene triblock copolymer grafted with maleic anhydride (SEBS-*g*-MA), was prepared by melt-grafting MA to SEBS triblock copolymer.¹⁰ MA grafted copolymer elastomers applied in toughness modification has been of interest for a long time.^{6, 11-13}

However, it's very difficult to control the graft yield and the sequential structure in graft copolymerization. Recent years, the

^a Department of Chemical and Biological Engineering, Zhejiang University, Hangzhou 310027, P.R. China. E-mail: qhzhang@zju.edu.cn

[†] Footnotes.

functional block copolymer elastomers can be synthesized by controlled radical copolymerization (CRP), which have already been widely used to prepare multiblock copolymers with tailor-made structures.¹⁴⁻¹⁸ Up to now, some reactive amphiphilic block copolymers designed for toughness modification have been synthesized in this way.^{3, 19, 20} Reactive multiblock copolymers were synthesized because a di- or tri-block copolymer may not meet the demand of forming specific morphology and creating high performance blends.

Not long ago, CRP techniques, including nitroxide mediated polymerization (NMP),²¹ atom transfer radical polymerization (ATRP),²² and reversible addition-fragmentation chain transfer radical (RAFT) polymerization,²³ opened a new era in the domain of polymer chemistry. In these CRP techniques, RAFT polymerization can be applicable to a wide range of monomers at facile temperature.^{24, 25} And RAFT process can proceed in homogeneous and heterogeneous systems without side reactions²⁶. RAFT miniemulsion

polymerization is environmental friendly, energy saving and high efficiency, which is considered to be one of the most prominent CRP processes for both industrial and commercial applications.²⁷⁻²⁹ Luo reported the synthesis of triblock copolymer elastomer PSt-PnBA-PSt via RAFT emulsion polymerization.³⁰

In general, mechanical performance of elastomers is intimately tied to the sequential structure and supramolecular interactions in traditional block copolymers due to the incompatibility of these two blocks.^{31,32} It was widely believed that the hard segments exhibit a tendency toward crystallization and the soft segments impart flexibility to the block copolymers.³³ The elastomeric and thermoplastic behaviour of the functionalized amphiphilic block copolymer elastomers could be influenced by introducing hydrophilic segments with hydrogen-bonding motifs into the backbone.

In our prior works, synthesis and structure of SMA-PSt-PnBA triblock copolymer have been studied, regarding ammonolysis poly[styrene-*alt*-(maleic anhydride)] (SMA) as macroRAFT agent and surfactant in stabilizing miniemulsion system.³⁴ These block copolymers may show interesting phase segregation structure and mechanical performance caused by immiscibility between PS, PnBA and SMA blocks.³⁵ The SMA segments in these copolymers, acting as macroRAFT reagents, also play an important role as compatilizer in the final product. As a result, these multi-block copolymers functionalized with SMA blocks may be adapted to potential application as impact modifiers.³⁶ The mechanical properties of block copolymers containing SMA functional groups in backbone were scarcely reported in literatures. The distinct morphologies and elastomeric properties should be influenced by introducing SMA segments with different molecular weights. Tetrablock copolymers synthesized via RAFT polymerization gave us enough flexibility and freedom to investigate the relationship between copolymer structures and morphologies in blends. Consequently, for both fundamental research and commercial applications, it is important to explore the preparation of amphiphilic tetrablock copolymer elastomers SMA-PSt-PnBA-PSt and to the influences of SMA segments on the microphase structure and mechanical properties.

In this study, we disclose the synthesis and mechanical properties of tetrablock copolymers SMA-PSt-PnBA-PSt by RAFT miniemulsion polymerization comprising SMA units as the reactive and compatibility motif in backbone. Amphiphilic macroRAFT agent (SMA-RAFT) was selected for self-emulsified surfactant and functional group. The copolymers were characterized by ¹H NMR and GPC analysis. Thermal and mechanical properties were investigated using differential scanning calorimetry (DSC) and tensile testing. The self-assembled morphology of the amphiphilic tetrablock copolymers was characterized by TEM. The main emphasis of our research lies in the influence of SMA chain length on the microphase separation and mechanical properties of the block copolymer elastomers. The results of this work would likely provide theoretical basis for potential application of these

amphiphilic multiblock copolymers in modifications of engineering plastics.

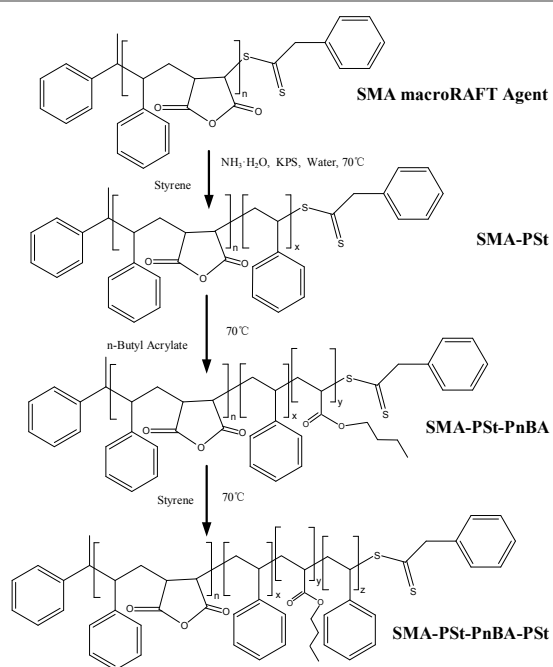
Experimental

Materials

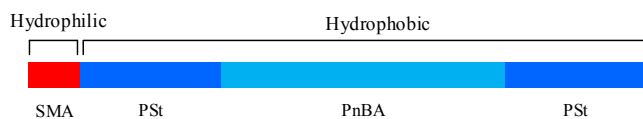
Styrene (St, monomer) was distilled under reduced pressure before use. n-Butyl acrylate (nBA, monomer) was washed with sodium hydroxide aqueous solution (5wt%) to remove the inhibitor. 2,2'-Azobisisobutyronitrile (AIBN, initiator) was recrystallized twice from methanol. Maleic anhydride (MAh, monomer), Potassium persulfate (KPS, initiator), Acetone and Ammonia solution (25wt% in water) were used without further purification. RAFT agent, 1-phenylethyl phenyldithioacetate (PEPDTA), was synthesized and purified as described in ref³⁷.

Synthesis of SMA-PSt-PnBA-PSt Tetrablock Copolymer via Miniemulsion Polymerization Mediated by SMA-RAFT MacroRAFT Agent.

The SMA macro-RAFT agent was synthesized according to ref³³. Molecular weight (Mn) and polydispersity index (PDI) of SMA were showed in Table 1. Scheme 1 presented the synthesis route of the tetrablock copolymers. Take exp1 as example, typically, 2×10^{-4} mol of the SMA-RAFT and 0.038 mol of styrene was dissolved in excess amount of acetone. Then, 20g of deionized water and $\text{NH}_3 \cdot \text{H}_2\text{O}$ were added in the organic styrene solution under stirring. The obtained emulsion was ultrasonicated for 15 min to miniemulsion and then transferred to a flask. The resulting stable miniemulsion was deoxygenated by N_2 purge for 20 min. The initiator KPS (4×10^{-5} mol) dissolved in water was added to start polymerization when the temperature reached to 70°C. 120 min later, 0.063 mol of n-butyl acrylate as the second monomer was added. After 60 min, 0.038 mol of styrene as the third monomer was added and the polymerization proceeded for 90 min. Samples were taken at regular time for analysis the conversion gravimetrically, the molecular weight and the chemical structure by GPC. The test results were showed in Table 1.



Scheme 1 Synthetic route of the amphiphilic tetrablock copolymers via RAFT miniemulsion polymerization mediated by SMA-RAFT macroRAFT agent.



Scheme 2. Molecular chain structure of amphiphilic SMA-PSt-PnBA-PSt tetrablock copolymer, hydrophilic SMA and hydrophobic PSt-PnBA-PSt were linked together by covalent bond.

Analysis and Characterization

Molecular weights and PDIs were measured by GPC (Waters 1525 Binary HPLC Pump, Waters 717 Autosampler, Waters 2414 Refractive Index Detector, Waters 2487 Dual λ Absorbance Detector for UV 311 signals). The samples were dried in an oven at 100°C for 3h and then dissolved in tetrahydrofuran (THF). The eluent was THF with a flow rate of 1.0 mL/min and the testing temperature was 35°C . The molecular weights and PDIs were derived from a calibration curve based on narrow polystyrene standards with molecular weight from 1,200 to 3,940,000 g/mol.

NMR analyses were performed on a Bruker DMX-500 nuclear resonance instrument with Acetone- d_6 as solvent and tetramethylsilane (TMS) as internal standard at ambient temperature. Since styrene and maleic anhydride tend to form comonomer pairs, which lead to the formation of alternating copolymer SMA.^{38, 39} The synthesized SMA_{2k}-macroRAFT agent contained 8 styrene units and 8 maleic anhydride units, they were of almost the same number, proved the alternating structure of the copolymer. ^1H NMR signal of SMA_{2k}-macroRAFT agent were shown in Figure 1 and assigned as follows (in ppm): 1.79(3H, $-\text{CH}_3$ of $-\text{CH}(\text{CH}_3)\text{Ph}$ chain moiety), 7.28(50H, $-\text{Ph}-\text{H}$ of PSt chain and two end group

contain $-\text{Ph}-\text{H}$), 2.10-3.80(43H, $-\text{CH}-\text{CH}_2-$ in PSt chain, $-\text{CH}-\text{CH}-$ in PMAh chain, $-\text{CH}_2-$ and $-\text{CH}-$ in end group), 2.06(H of impurities of acetone). The M_n of SMA_{2k}-macroRAFT agent by ^1H NMR was 1,888g/mol. This molecular weight calculated according to NMR data agreed with GPC measurements (1,752g/mol).

Differential scanning calorimetry (DSC) was measured by TA Q200 instrument. The glass transition temperature (T_g) was reported at the inflection point of the heat capacity jump with a heating rate of $10^\circ\text{C}/\text{min}$.

For tensile measurements, the films were prepared by solvent casting method. The solvent (10wt % copolymer in THF) was

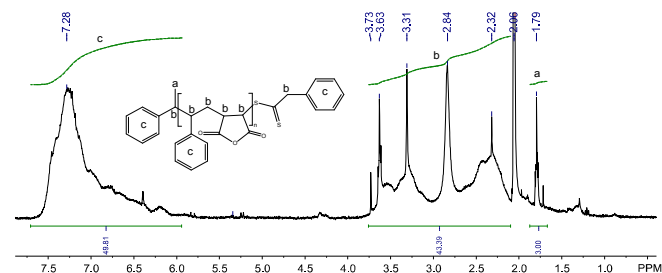


Figure 1. Chemical Structure and ^1H NMR Spectrum of SMA_{2k}-MacroRAFT Agent.

evaporated over a week at room temperature, then dried under vacuum at 80°C for 20h. Room temperature ($23 \pm 0.5^\circ\text{C}$) tensile properties were measured by Zwick/Roell Z020 universal material tester at a crosshead speed 50mm/min with 1N preload. The test method is ASTM D638-10. Standard dumbbell-shaped test specimens (D638, Type IV) were die cut from the casted films ($\sim 1.2\text{mm}$ in thickness). Each measurement was repeated at least 5 times.

To study the microphase separation of these amphiphilic copolymers, ultrathin sections were slowly ($0.2\text{mm}/\text{s}$) sliced off at about -40°C from the surface of SMA-PSt-PnBA-PSt sample (solvent-casted for tensile tests) using a diamond knife in a Reichert Ultracut E microtome, and ultrathin sections (ca. 70 nm in thickness) were collected on a copper grid. The transmission electron microscopy (JEOL JEMACRO-1200) was used to observe the phase morphology of sample at the operating voltage of 80 kV.

Results and Discussion

Synthesis of SMA-PSt-PnBA-PSt Tetralock Copolymer via Miniemulsion Polymerization Mediated by SMA-RAFT MacroRAFT Agent.

The macroRAFT agents used in this paper were designed as listed in Table 1. The molecular weights of the synthesized macroRAFT agents were in gradient distribution from 2,000 to 15,000. The tetrablock copolymers SMA-PSt-PnBA-PSt were synthesized by sequential addition of specific monomers. In each stage, the conversion of monomer was more than 95%. The PDI of the final copolymers were around 2.5 to 3.75. From

Table 1, the PDI of diblock copolymers SMA-PSt were below 1.6. After chain extension, the PDIs of block copolymers increased rapidly. The reason for this phenomenon will be discussed later in this article. The dead chain fractions in SMA-PSt-PnBA-PSt tetrablock copolymers samples were calculated according to ref³⁰ and listed in Table 2. For PSt-PnBA-PSt triblock copolymer thermoplastic elastomers, according to the previous report, if the polymerisation reaction kept “living” characters and the synthesized copolymers were hard-soft-hard sequential structures with few dead chains (all lower than 10% at each stage) the relatively higher PDI had no obvious impacts on their mechanical behaviours.

The formation of the target tetrablock copolymer could be confirmed from ¹H NMR spectrum.

Table 1 Molecular weights and PDIs of SMA-PSt-PnBA-PSt Tetrablock Copolymers via Miniemulsion Polymerization Mediated by SMA-RAFT MacroRAFT Agent

exp		1	2	3	4	5
Stage	Sample	2K-20K-40K-20K	3K-20K-40K-20K	5K-20K-40K-20K	10K-20K-40K-20K	15K-20K-40K-20K
SMA	M _{n,th} (g/mol)	2,090	2,898	4,918	9,362	14,412
	M _{n,exp} (g/mol)	1,752	2,812	4,503	8,973	14,202
	PDI	1.05	1.12	1.18	1.45	1.57
SMA-PSt	M _{n,th} (g/mol)	21,500	23,200	25,200	30,800	34,800
	M _{n,exp} (g/mol)	19,900	21,200	23,500	25,900	30,200
	PDI	1.08	1.18	1.09	1.54	1.85
SMA-PSt-PnBA	M _{n,th} (g/mol)	62,200	62,700	65,400	69,900	73,800
	M _{n,exp} (g/mol)	60,800	66,000	64,200	68,500	70,100
	PDI	2.41	2.46	2.68	2.83	2.61
SMA-PSt-PnBA-PSt	M _{n,th} (g/mol)	81,800	82,600	84,200	89,600	94,800
	M _{n,exp} (g/mol)	80,700	85,400	91,400	93,500	96,900
	PDI	2.49	2.65	3.04	3.19	3.74

Table 2 Dead chain fractions of SMA-PSt-PnBA-PSt Tetrablock Copolymer in Miniemulsion Polymerization Mediated by SMA-RAFT MacroRAFT Agent

Sample	dead chain percentage ^a		
	SMA-PSt (mol %)	SMA-PSt-PnBA (mol %)	SMA-PSt-PnBA-PSt (mol %)
2K-20K-40K-20K	3.7	1.6	4.3
3K-20K-40K-20K	4.0	2.0	5.4
5K-20K-40K-20K	5.0	2.5	6.2
10K-20K-40K-20K	6.5	3.2	7.1
15K-20K-40K-20K	7.8	3.8	8.6

a. The dead chain percentage are calculated according to ref³⁰.

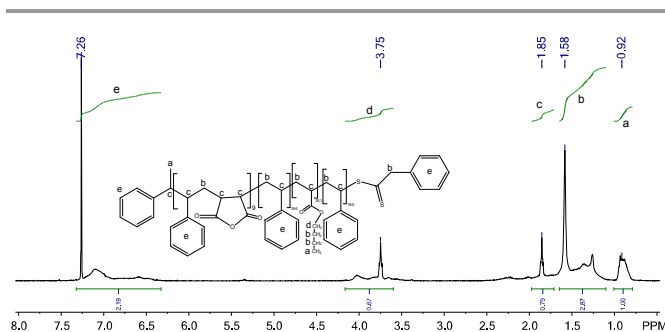


Figure 2 showed the chemical structure and ¹H NMR spectrum of SMA-PSt-PnBA-PSt tetrablock copolymer. The chemical shifts of ¹H were assigned as follows (in ppm): 0.92(–900H, –CH₃ of –CH₃ in PnBA), 1.10-1.60(–2600H, –CH₂ in backbone and in PnBA), 1.85(–700H, –CH in backbone), 3.75-4.10(–600H, –OCH₂ in PnBA), 6.50-7.26(–Ph-H of PSt), and few other impurities. The calculated molecular weight of sample 2K-20K-40K-20K (exp 1) by ¹H NMR was 80,200g/mol, and it was very close to molecular weight obtained from GPC (80,700g/mol).

Figure 2 Chemical Structure and ¹H NMR Spectrum of SMA-PSt-PnBA-PSt tetrablock Copolymer (2K-20K-40K-20K).

The “living” polymerization characteristics of the copolymers were determined by the increasing molecular weight with reaction time. Table 1 showed the Mn and PDI of each segments in the copolymers. As shown in Figure 3, the each block GPC curves of exp1 and exp5 were monitored. In exp 1, the SMA with 2,000 of Mn was used as macro-RAFT agent, the GPC peaks of each intermediate product shifted toward the region of higher molecular weight and all peaks were in unimodal distribution during the copolymerization progress. Meanwhile, as shown in exp 5, small shoulder peak

existed in the chain extension procedure, which indicated that few dead chains might be generated. But the majority of macromolecular chains did not have dead chains, retained living polymerization characteristics. Meanwhile, their molecular weight kept growing gradually.

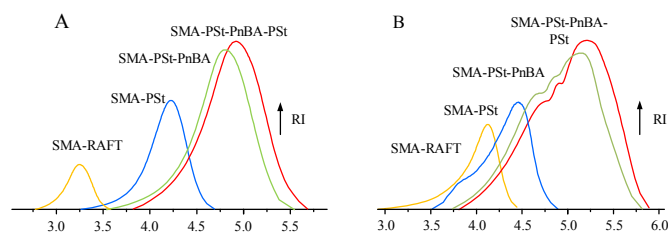


Figure 3 GPC chromatogram variations of before and after chain extensions during the synthesis of sample 2K-20K-40K-20K (A: exp1) and sample 15K-20K-40K-20K (B: exp5).

Furthermore, Figure 4 showed M_n and PDI of the copolymers variation with the total conversions of the monomers. The number-average molecular weight increased linearly over time and agrees with theoretical molecular weight, which confirmed the distinct living character of the polymerization. During the polymerization process, PDI of the copolymers increased gradually in the stages of chain extension with nBA (total conversion higher than 30%), and the PDI of final product was 2.49 (sample 2K-20K-40K-20K). For the exp 5, the PDI of the final product increased from original 1.57 to 3.74 (sample 15K-20K-40K-20K). Compare the results displayed in Table 1, a corresponding growth of PDI of the copolymers could be seen while SMA content increased. The reason might be that longer SMA segments, embedded the dithiocarboxylic esters function group, decreased the transfer constant. On the other hand, the viscosity of the copolymer solution inside the latex increased during miniemulsion polymerization, and the mobility of the copolymer chains were dramatically reduced. So the chain transfer process in RAFT polymerization slowed down and resulted in relatively higher PDI.

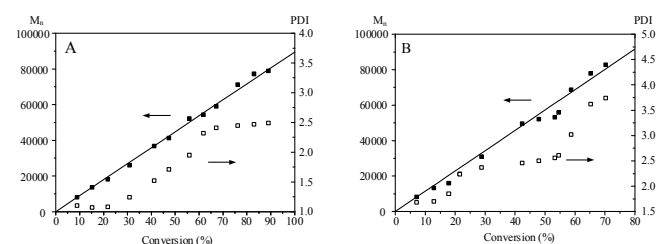


Figure 4 M_n (relative to polystyrene narrow standards) and PDI variation with the total conversions of styrene and n-butyl acrylate during the synthesis of sample 2K-20K-40K-20K (A, exp1) and sample 15K-20K-40K-20K (B, exp 5).

Glass Transition Temperatures of SMA-PSt-PnBA-PSt Tetrablock Copolymer.

DSC curves of the SMA-PSt-PnBA-PSt tetrablock copolymer were shown in Figure 5. All of the copolymers presented two

distinct T_g s, -50°C for PnBA segment and 95°C for PSt segment. DSC traces of altered copolymer (SMA_{5K}) and diblock copolymer (SMA_{5K}-PSt_{20K}) were also listed in Figure 3. T_g of SMA approximately located at 150°C , but for the diblock copolymers, such as SMA_{5K}-PSt_{20K}, the glass transition temperatures was about 100°C close to PSt segments. Because SMA was an alternating copolymer of styrene and maleic anhydride, which was considered to be miscible with PSt chain. On the other hand, the volume fraction of SMA in the copolymers was relatively low. So the glass transition of SMA merged with that of PSt in DSC curves, especial in tetrablock copolymer samples. Meanwhile, the glass transition temperatures of PnBA block at -50°C became more unobvious with longer SMA segment. The main reason for this behaviour could be attributed to the hydrogen bonding interactions between maleic acid residues and acrylate ester groups.

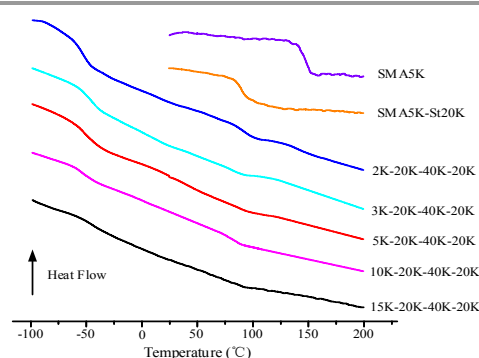


Figure 5 DSC heating traces of SMA-PSt-PnBA-PSt tetrablock copolymers in Table 1. The digital numbers in the sample names, represent the digital molecular weight of each block are listed next to the curves.

Phase Separation morphology of SMA-PSt-PnBA-PSt Tetrablock Copolymer.

The morphology of the block copolymer samples observed by TEM was shown in Figure 6. When the molecular weight of SMA was lower than 5,000 in copolymer samples, microphase structure of the copolymer films seemed to be continuous and homogeneous. As M_n of SMA was below 5,000, the weaker phase separation with island structure was observed on film surfaces. The reason could be that the short SMA chain cannot form state of aggregation as dispersed phase. For sample 10K-20K-40K-20K, the microphase separation became more obvious and transformed to typical incompatible sea-island biphasic structure as molecular weight of SMA increased to 10,000. In sample 15K-20K-40K-20K, the scale of the microphase separation increased and the self-assembly structures transformed from sea-island to wormlike morphology. In these two self-assembled phase structures, the amphiphilic domain SMA formed nanocapsule packed with PSt-PnBA-PSt segments with weak polarity or nonpolar. From TEM micrographs, it could be found that relatively longer amphiphilic segments dramatically influenced self-assembly structure of the copolymer films. Higher content of SMA with hydrophilic property in block copolymers would improve

the incompatibility between SMA segment and PSt-PnBA-PSt backbone. The multiblock copolymer similar to symmetric PSt-PnBA-PSt gradually transformed to asymmetric SMA-PSt-PnBA-PSt. These reasons contributed to the distinct nanostructures of samples having different content of SMA. By calculating the quantitative contents of amphiphilic block SMA in the tetrablock copolymers, it could be found that almost no microphase segregation caused by intramolecular immiscibility when the weight content of amphiphilic block in the final copolymers was not more than 6%.

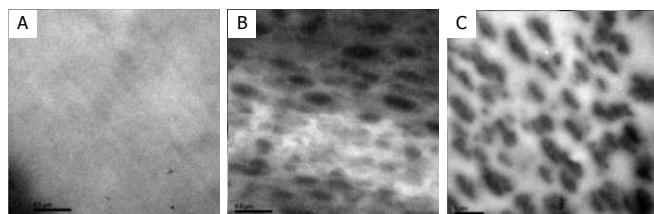


Figure 6 TEM micrographs for microphase separation of sample 5K-20K-40K-20K (A) (scale bar 500nm), sample 10K-20K-40K-20K (B) (scale bar 500nm) and sample 15K-20K-40K-20K (C) (scale bar 1000nm) casted from THF. All samples were stained by RuO₄.

Mechanical Properties of SMA-PSt-PnBA-PSt Tetrablock Copolymer.

Figure 7 showed the stress-strain curves for the synthesized SMA-PSt-PnBA-PSt tetrablock copolymers with different SMA contents. All samples except 15K-20K-40K-20K exhibited typical thermoplastic elastomer mechanical behavior, linear strain response followed by softening and then hardening.⁴⁰ When the contents of SMA in copolymers were below 6%, the tetrablock copolymer exhibited obvious elastomer properties with high elongation at break at 254–380%. The sample 5K-20K-40K-20K with no obvious macrophase separation showed comprehensive performance prior to those samples with high SMA content and distinct phase separation. When the Mn of SMA in copolymers was more than 10,000, the introduction of amphiphilic segments broke the symmetry of the copolymer sequential chain structure and brings in meso or macro scale phase separation then led to poor mechanical performance.

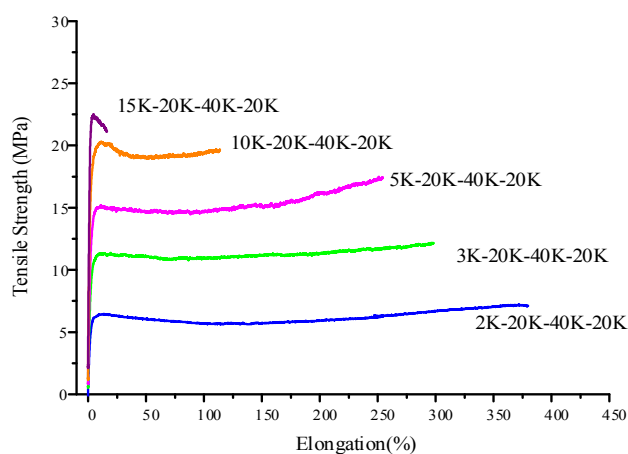


Figure 7 Stress-strain curve of SMA-PSt-PnBA-PSt tetrablock copolymers with different SMA volume fraction and similar PSt-PnBA-PSt block formation.

The mechanical properties of the tetrablock copolymer elastomers were summarized in Table 3. Though the copolymers exhibited specific properties of elastomers, the highest ultimate tensile strength (sample 15K-20K-40K-20K) was about 21 MPa and the highest elongation at break (sample 2K-20K-40K-20K) was about 380%. These values were still lower than the ones of typical SBS with 30 MPa ultimate tensile strength and 800% elongation at break.⁴⁰ This could be attributed to the different entanglement molecular weights (M_e) for between poly (n-butyl acrylate) and polybutadiene. On the other hand, the introduction of incompatible SMA chain and the microphase segregation would likely affect the mechanical performance of the tetrablock copolymer elastomers.

Table 3 Mechanical Properties of SMA-PSt-PnBA-PSt tetrablock copolymers

sample	ultimate tensile strength (MPa)	elongation at break (%)	elastic modulus (MPa) ^a
2K-20K-40K-20K	7.1±0.9	380±34	304±16
3K-20K-40K-20K	11.6±2.1	298±10	396±24
5K-20K-40K-20K	17.4±2.2	254±8	491±37
10K-20K-40K-20K	19.7±1.8	114±6	746±38
15K-20K-40K-20K	21.1±2.0	16±4	1023±43

^a The elastic modulus was calculated from the stress-strain data at <10% low elongation.

As seen in Table 3, with the contents of SMA in copolymers increased from 2.44 to 15.78%, the ultimate tensile strength increased from 7.11 to 21.12 MPa. The introduction of hard segment SMA and decrease in relative amount of PnBA, a higher T_g were likely to make the material more like a plastic and performed to have a higher ultimate tensile strength. Molecular chain movements were limited by both SMA polar group interactions and domain segregation, thus more tension coexisted in samples demonstrated by increased elastic modulus. From ref³⁰ and ref⁴¹, 15% increasing in relative amount of PnBA in PSt-PnBA-PSt triblock copolymer resulted in 5 MPa additional ultimate

tensile strength or 240% more elongation at break. And 6% increasing of PnBA soft segment content in PMMA-PnBA-PMMA triblock copolymers led to 13% additional ultimate tensile strength and 25% drop in elongation at break. It could be inferred from these results, 7% change to the relative amount of PnBA (49% in sample 2K-20K-40K-20K and 42% in sample 15K-20K-40K-20K) in each system did not necessarily led to this huge difference to mechanical properties of block copolymers containing PnBA as central block. Considering 7% decreased amount of soft block PnBA may not necessarily bring about multiplied tensile strength and greatly decreased elongation at break,^{30, 41} it seemed obvious that phase separation of the tetrablock copolymer caused by incompatibility of the different blocks could be the major factor influencing mechanical behaviour. From sample 2K-20K-40K-20K to sample 5K-20K-40K-20K, no significant microphase segregation appeared. The mechanical performance was mainly affected by viscoelastic characters of block copolymers. However, for the sample 10K-20K-40K-20K and 15K-20K-40K-20K, the distinct phase segregation with sea-island or wormlike structure brought the material much less elongation at break. While the macrophase separation destroyed the continuity of the matrix, made the casted samples macroscopic defective, ultimate tensile strength were decreased as well. Consequently, difference in T_g (with more SMA volume fraction and less PnBA content) and various morphologies influenced the mechanical performance of this tetrablock copolymers.

Conclusions

A series of SMA-PSt-PnBA-PSt tetrablock copolymer with designed chain structure were synthesized via miniemulsion polymerization using macroRAFT agent as surfactant and chain transfer agent. The living polymerization characteristics of the reaction and the microstructure of the amphiphilic tetrablock copolymers were determined. The synthesized copolymer exhibited typical mechanical properties of thermoplastic elastomers with SMA content less than 6%. As SMA content kept increasing, phase segregation morphology with sea-island or wormlike structure appeared, which caused the mechanical properties of copolymers changed dramatically. The ultimate tensile strength increased and elongation at break decreased with longer SMA segment due to combination effect of higher T_g and macrophase separation. However, incorporated with multi-functional end-groups and improved compatibility, the copolymers could be applied to many strict areas such as impact modifier, biocompatible layers and multi-functional membranes. And controlled/living radical miniemulsion polymerization holds good promise for synthesis of multifunctional thermoplastic elastomer materials.

Acknowledgements

The authors would like to thank the National Science Foundation of China (NSFC) for Award No. 21176212, 21276224, 21476195 and

Zhejiang Provincial National Science Foundation of China Y14B060038 for supporting this research.

Notes and references

References:

1. S. C. Wong and Y. Mai, *Polymer*, 2000, 41, 5471-5483.
2. P. A. Delgado and M. A. Hillmyer, *RSC Adv.*, 2014, 4, 13266-13273.
3. V. Rebizant, V. Abetz, F. Tournilhac, F. Court and L. Leibler, *Macromolecules*, 2003, 36, 9889-9896.
4. S. Ritzenthaler, F. Court, L. David, E. Girard-Reydet, L. Leibler and J. P. Pascault, *Macromolecules*, 2002, 35, 6245-6254.
5. S. Ritzenthaler, F. Court, E. Girard-Reydet, L. Leibler and J. P. Pascault, *Macromolecules*, 2002, 36, 118-126.
6. Z. Liu, Y. Deng, Y. Han, M. Chen, S. Sun, C. Cao, C. Zhou and H. Zhang, *Ind. Eng. Chem. Res.*, 2012, 51, 9235-9240.
7. L. Corté, V. Rebizant, G. Hochstetter, F. Tournilhac and L. Leibler, *Macromolecules*, 2006, 39, 9365-9374.
8. M. A. Hillmyer, P. M. Lipic, D. A. Hajduk, K. Almdal and F. S. Bates, *J. Am. Chem. Soc.*, 1997, 119, 2749-2750.
9. W. Fan, L. Wang and S. Zheng, *Macromolecules*, 2008, 42, 327-336.
10. S. B. Brown, *Springer*, 2003, pp. 339-415.
11. H. Yu, Y. Zhang, W. Ren, M. Hoch and S. Guo, *J. Appl. Polym. Sci.*, 2011, 121, 3340-3346.
12. S. Sun, Y. He, X. Wang and D. Wu, *J. Appl. Polym. Sci.*, 2011, 121, 541-553.
13. V. Das, V. Kumar, A. Singh, S. S. Gautam and A. K. Pandey, *Polym. Plast. Technol. Eng.*, 2012, 51, 446-454.
14. H. Datta, A. K. Bhowmick and N. K. Singha, *Polymer*, 2009, 50, 3259-3268.
15. Y. Luo, Y. Guo, X. Gao, B. Li and T. Xie, *Adv. Mater.*, 2013, 25, 743-748.
16. P. Froimowicz, B. van Heukelum, C. Scholten, K. Greiner, O. Araujo and K. Landfester, *J. Polym. Sci. Part A: Polym. Chem.*, 2014, n/a-n/a.
17. G. Gody, T. Maschmeyer, P. B. Zetterlund and S. Perrier, *Macromolecules*, 2014.
18. A. E. Smith, X. Xu and C. L. McCormick, *Prog. Polym. Sci.*, 2010, 35, 45-93.
19. V. Rebizant, A. Venet, F. Tournilhac, E. Girard-Reydet, C. Navarro, J. Pascault and L. Leibler, *Macromolecules*, 2004, 37, 8017-8027.
20. R. B. Grubbs, J. M. Dean and F. S. Bates, *Macromolecules*, 2001, 34, 8593-8595.
21. C. J. Hawker, A. W. Bosman and E. Harth, *Chem. Rev.*, 2001, 101, 3661-3688.
22. K. Matyjaszewski and J. Xia, *Chem. Rev.*, 2001, 101, 2921-2990.
23. J. Chiefari, Y. K. Chong, F. Ercole, J. Krstina, J. Jeffery, T. P. Le, R. T. Mayadunne, G. F. Meijs, C. L. Moad and G. Moad, *Macromolecules*, 1998, 31, 5559-5562.
24. J. Chen, M. Liu, C. Gao, S. Lü, X. Zhang and Z. Liu, *RSC Adv.*, 2013, 3, 15085-15093.

Paper

25. X. Liu, R. Zhao, T. Zhao, C. Liu, S. Yang and E. Chen, *RSC Adv.*, 2014, 4, 18431-18441.
26. L. Yang, Y. Luo, X. Liu and B. Li, *Polymer*, 2009, 50, 4334-4342.
27. C. J. Ferguson, R. J. Hughes, B. T. Pham, B. S. Hawke, R. G. Gilbert, A. K. Serelis and C. H. Such, *Macromolecules*, 2002, 35, 9243-9245.
28. C. N. Urbani and M. J. Monteiro, *Aust. J. Chem.*, 2009, 62, 1528-1532.
29. N. Yeole, S. N. R. Kutcherlapati and T. Jana, *RSC Adv.*, 2014, 4, 2382-2388.
30. Y. Luo, X. Wang, Y. Zhu, B. Li and S. Zhu, *Macromolecules*, 2010, 43, 7472-7481.
31. J. S. Noh, *RSC Adv.*, 2014, 4, 1857-1863.
32. C. Creton, G. Hu, F. Deplace, L. Morgret and K. R. Shull, *Macromolecules*, 2009, 42, 7605-7615.
33. D. P. Chatterjee and B. M. Mandal, *Macromolecules*, 2006, 39, 9192-9200.
34. Y. Yu, Q. Zhang, Z. Wang, X. Zhan, R. He, W. Zhang and F. Chen, *J. Macromol. Sci., Pure Appl. Chem.*, 2011, 49, 60-66.
35. R. Ma, R. Ma, L. Feng, L. Fan, Y. Liu, B. Xing, Y. Hou and F. Bao, *Colloids Surf., A*, 2009, 346, 184-194.
36. G. Liang, J. Meng and L. Zhao, *Polym. Int.*, 2003, 52, 966-972.
37. J. F. Quinn, E. Rizzardo and T. P. Davis, *Chem. Commun.*, 2001, 1044-1045.
38. S. Harrison and K. L. Wooley, *Chem. Commun.*, 2005, 3259-3261.
39. F. Du, M. Zhu, H. Guo, Z. Li, F. Li, M. Kamachi and A. Kajiura, *Macromolecules*, 2002, 35, 6739-6741.
40. G. Holden, H. R. Kricheldorf and R. P. Quirk, *Thermoplastic elastomers*, Hanser Munich, 1996.
41. J. D. Tong and R. Jerome, *Polymer*, 2000, 41, 2499-2510.