RSC Advances

PAPER

A controlled synthesis method of polystyrene-b-polyisoprene-b-poly(methyl methacrylate) copolymer via anionic polymerization with trace amounts of THF having potential of a commercial scale

Zheng Li, Jianding Chen, Ling Su, Bin Zou, Pengfei Zhan, Yong Guan* and Anna Zheng*

A controlled synthesis method for the polystyrene-b-polyisoprene-b-poly(methyl methacrylate) (PS-b-PI-b-PMMA) tri-block copolymer using the anionic copolymerization was innovated, in which being differ from previous researches for the anionic polymerization of polar monomers, nonpolar cyclohexane was used as solvent and only trace amounts tetrahydrofuran (THF) was adopted as a polar regulator. The sequential anionic copolymerization could be smoothly conducted at 0 °C and the conversion of all monomers reached 100%. The copolymer was characterized by gel permeation chromatography (GPC), proton nuclear magnetic resonance (^{1}H-MNR), dynamic mechanical analysis (DMA) and differential scanning calorimetry (DSC). It was found that the number average molecular weights (M_n) of PS, PI and PMMA were 12 760, 26 340 and 13 600 respectively. The 1,4-addition structure in PI block occupied 93% and its forming mechanism was explained. Furthermore, the produce of tri-block copolymers with PMMA block of different lengths confirmed this synthesis method controlled for definite structures, fewer side reactions and a appropriate temperature. Based on these results, the anionic block copolymerization containing polar monomer MMA at a commercial scale starts to become possible.

Introduction

Research on living anionic polymerization has never been interrupted since the polymerization mechanism was demonstrated by Scwarc in 1956,[1-6] due to its remarkable advantages such as fast initiation and propagation, almost no termination, controllable molecular weight, narrow molecular weight distribution (MWD), and definite molecular structure.

Decades of researches have realized the application of anionic polymerization in the industry, and products such as polystyrene-b-polyisoprene/polybutadiene-b-polystyrene (SIS/SBS) and the hydrogenation products of SBS and SIS (SEBS and SEPS) have been proposed subsequently.[7-12] Y. Duan et al. synthesised a kind of tetrafunctional multigraft polystrene–polyisoprine copolymers by means of anionic polymerization and researched the morphology and deformation mechanism and tensile properties of the copolymers.[13]

However, to date, there is almost no one polar monomer, which could be used as the monomer in the anionic

polymerization in industrial scale, also including the commonly used methyl methacrylate (MMA). Due to too more side reactions are likely to occur during the anionic polymerization of MMA.[14]

In order to overcome these side reactions, extremely low reaction temperature and addition of some inhibiting ligand have been adopted in recent years. Kim et al.[15] used a plug flow reactor to synthesize the polystyrene and poly(methyl methacrylate) di-block copolymer (PS-b-PMMA) with high molecular weight in tetrahydrofuran (THF) at −78 °C. Lee et al.[16] synthesized the polystyrene, polyisoprene and poly(methyl methacrylate) tri-block copolymer (PS-b-PI-b-PMMA) by anionic polymerization, in which the PS-b-PI di-block copolymer polymerized in toluene at room temperature at first. Then the PS-b-PI chains end-capped with DPE and the reactor was cooled down to −78 °C. After that, a certain amount of the solution of LiCl in THF was added in, for a while, the anionic polymerization of MMA was carried out. In this study, multimodal size exclusion chromatography (SEC) peak was observed, which might be caused by the inadvertent termination reaction of PS-b-PI living anions for the impurities secondly added in with THF solvent and MMA monomer. Unfortunately, in the synthesis method the extra-low temperature (−78 °C) was infaust to the industry realization. Similarly to the polymerization above, a well-defined novel block polymerization containing PMMA

Key Laboratory of Special Functional Polymeric Materials and Related Technology of the Ministry of Education, School of Materials Science and Engineering, East China University of Science and Technology, Shanghai 200237, P. R. China. E-mail: yguan@ecust.edu.cn; zan@ecust.edu.cn

block was synthesized under the existence of potassium *tert*-butoxide (*t*-BuOK) by Shunsuke Tanaka *et al.*[17] D. Baskaran researched the living anionic polymerization of MMA at −40 °C in THF and −78 °C in toluene/THF (9/1 v/v) using (1,1-diphenylhexyl) lithium as the initiator in the presence of lithium perchlorate (LiClO₄) as the additive.[18] However, the polymerization was conducted at −78 °C which could not be realized in industrialized conditions either.

Zheng *et al.*[19,20] synthesized a compound named "P-Complex" which was used as an effective inhibitor to control the side reactions in the anionic polymerization of MMA and its copolymers at 0 °C. However, "P-Complex" cannot be dissolved in nonpolar solvent.

Group transfer polymerization (GTP)[21,22] and metal-free anionic polymerization[23,24] could synthesize PMMA under mild conditions, however, these methods cannot be applied in the industry because there exist some issues such as high cost, inherent termination reaction, incomplete initiation efficiency, *etc.*

As a fact that copolymers containing PMMA block have extensive potential applications.[25–27] PS-*b*-PB-*b*-PMMA, for example, can be used as an excellent compatibilizer of PVC and SBS.[28] Furthermore, a thermoplastic elastomer PS-*b*-PI-*b*-PMMA may be a new and excellent transparent toughening agent for PMMA, a widely used material only with brittleness weakness.

A series of thermoplastic elastomers consisted of unpolar monomers has been synthesized by living anionic polymerization in hydrocarbon solvent at room temperature by Wang *et al.*[29] As mentioned above, the impurities in the polar solvents or monomers may a main factor to affect the side reactions during the anionic polymerization of polar monomers.

For example, there existed some effects of THF on the anionic polymerization initiated by organic lithium initiator, in which the reaction of THF with *n*-BuLi could generate and form the lithium enolate of acetaldehyde (CH₂=CHOLi).[30,31] Lee *et al.* supported this idea, however, they adopted the *s*-BuLi as the initiator.[32] It is regrettable in these researches that the reaction of THF with organic lithium is related to some impurities or not, such as water and alcohols. On the other hand, Chen[20] and Su[33] synthesized PMMA through the anionic polymerization with *n*-BuLi as the initiator at about room temperature with 100% conversion of MMA.

Therefore, in this work, a new method to synthesize a tri-block copolymer of PS-*b*-PI-*b*-PMMA was initiated, in which three monomers (St, Ip, MMA) were sequentially added in the polymerization system with *n*-BuLi in nonpolar cyclohexane (CH) solvent as the initiator. This is for decreasing the impurities accompanied by the polar solvents in the polymerization system by means of nonpolar CH. Furthermore, only trace amounts of THF was adopted as the polar regulator. By doing this, not only the polymerization rate could be greatly increased, but also the conformation of polyisoprene (PI) was unlikely changed.

Experimental

Materials

Styrene (St, Sinopharm Chemical Reagent Co., Ltd., China) and methyl methacrylate (MMA, Lingfeng Chemical Reagent Co.,

LTD., China) were purified by distillation in a vacuum system at 50 °C and 20 °C after stirring with calcium hydride for 48 h, and soaked with 4 Å molecular sieves for more than 24 h before use. Isoprene (Ip) was dried with calcium hydride for 48 h and distilled under normal atmosphere at 40 °C, and soaked with 4 Å molecular sieves as well before use. Cyclohexane (CH, Sinopharm Chemical Reagent Co., Ltd., China) used as solvent was refluxed with sodium at 81 °C for 24 h, distilled and soaked with 4 Å molecular sieves for more than 24 h. Tetrahydrofuran (THF, Sinopharm Chemical Reagent Co., Ltd., China) used as solvent was refluxed with sodium at 66 °C for 24 h, distilled and soaked with sodium. *n*-Butyl-lithium (*n*-BuLi, 2.4 mol L⁻¹, in *n*-hexane, J&K Chemical Co., Ltd, Shanghai, China) was used as received. Argon (Ar, 99.99999%) was purified by flowing through two connected towers filled with 4 Å molecular sieves. 1,1-Diphenylethylene (DPE) (98%, TCI, Japan) was used as received.

Characterization methods

The molecular weight and its distribution (M_w/M_n) was determined by multi-detector gel permeation chromatography (Water 1515 system; Waters corporation, America), equipped with an 18 angles laser scattering detector (LS signal) and a refractive detector (RI signal), using THF as the eluent at a flow rate of 1.0 mL min⁻¹ at 25 °C.

¹H-NMR spectra were measured by a BRUKER AV400 spectrometer with CDCl₃ as solvent and tetramethylsilane (TMS) as the internal reference.

Dynamic mechanical spectrometer (Q800, TA Co., USA) was used to study the dynamic mechanical properties of the copolymer. The samples were made into rectangular strips with size of 20 × 5 × 2 mm, tested with single cantilever bending mode and heated from −100 to 125 °C, at heating rate of 5 °C min⁻¹ and frequency of 1 Hz in a nitrogen atmosphere.

The glass transition temperature of tri-block copolymers was also performed to on a differential scanning calorimetry (DSC)-SP thermal analyzer (Netzsch STA 409, Germany). The sample was heated from −80 °C to 125 °C at a heating rate of 10 °C min⁻¹ under a steady flow of a nitrogen atmosphere.
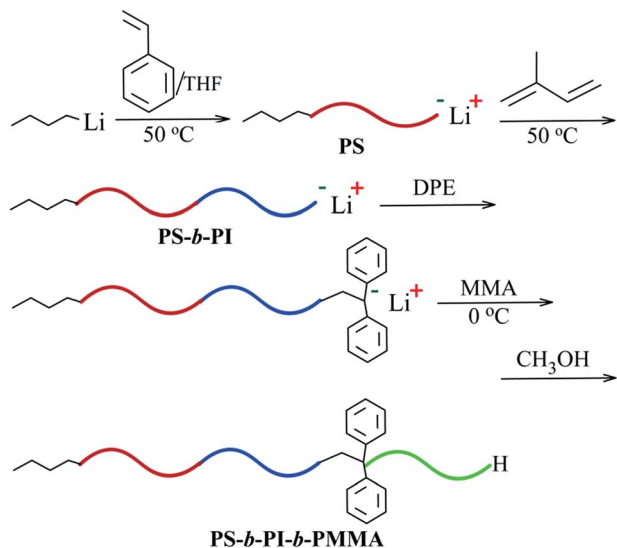
Synthesis of PI

All the polymerization and reactions were carried out under Ar atmosphere and all the flasks were inflated by Ar after baked. The anionic homo-polymerization of Ip (20 mL) was performed in a three-necked flask at 50 °C with *n*-BuLi (2.4 mmol) as an initiator and CH (150 mL) as a solvent. Different amounts of THF (0, 0.48, 0.24, 0.096, 0.048 mmol, respectively) was added as the polar regulator before reaction. Along with the polymerization proceeding, a small quantity of polymeric sample was drawn out by an injector at the reaction time of 5, 10, 15, 20, 30 and 40 minutes, respectively, and terminated by methanol immediately. At last, all the polymers were obtained by drying in the vacuum oven at 50 °C for 12 h.

Synthesis of PS-*b*-PI-*b*-PMMA

The reaction was conducted in a 500 mL reaction kettle, whose gas tight test and removing impurities should be done before

Scheme 1 Synthesis mechanism of PS-*b*-PI-*b*-PMMA.

Fig. 1 Time-conversion curves of the polymerization of PI with different molar ratios of THF/*n*-BuLi (*r*) at 50 °C.
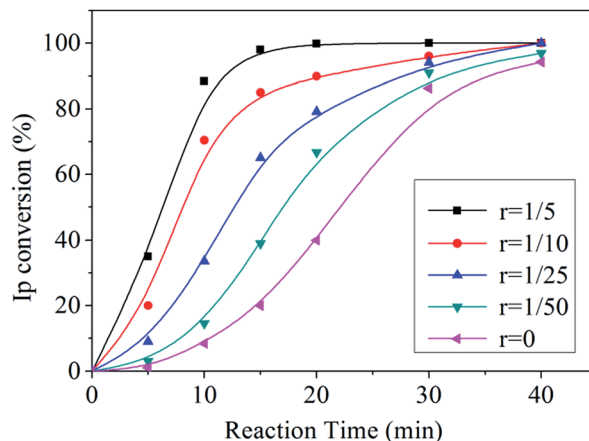
the polymerization as commonly introduced in the anionic polymerization. The purified CH solvent (400 mL) and *n*-BuLi (5 mL) were injected into the kettle and kept stirring for 2 hours in order to eliminate the impurities further. Afterward, the solution in the kettle was drawn out. Then, another purified CH (400 mL) and the trace amounts of THF ($n_{THF}/n_{n\text{-BuLi}} = 1 : 10$) were injected in the kettle and stirred. The polymerization of St (15 mL) in this kettle was initiated by *n*-BuLi in CH (0.5 mL) mentioned above at 50 °C. After 30 minutes, Ip (40 mL) was added in and the polymerization was carried out for another 1 hour, then DPE (0.5 mL) was added subsequently. MMA (15 mL) was injected in after the solution was cooled down to 0 °C. The polymerization of MMA was carried out for 45 minutes and terminated by methanol (Scheme 1). The final polymer was precipitated out with methanol and dried in vacuum oven at 50 °C for 24 h. A series of experiments were conducted in the same steps with injecting different amounts of monomers.

Results and discussion

The effect of THF in the anionic polymerization of PI

THF is a common polar regulator in anionic polymerization, which can be utilized to accelerate the reaction process. Its effect on the reaction rate in the polymerization of Ip is shown in Fig. 1, where the *r* means the molar ratio of THF/*n*-BuLi. It was revealed that comparing with the polymerization without THF, even quite a little THF could bring remarkable acceleration in the polymerization of Ip and it became more remarkable after 10 minutes. At 50 °C, the polymerization conversion of PI without THF was around 8%, in contrast, a high conversion of 88% was observed in the polymerization with 0.48 mmol THF ($n_{THF}/n_{n\text{-BuLi}} = 1/5$) at 10 min. Furthermore, the complete conversion time was shortened from more than 40 minutes (*r* = 0) to 20 minutes (*r* = 1/5).

THF as the polar regulator has another effect on the microstructure of conjugated diolefine formed during anionic polymerization. For example, the content of 1,4-addition structure will be decreased following the increasing of THF during the anionic polymerization of PI. The ^{1}H-NMR spectra of the polymers produced in the anionic polymerization adding THF were shown in Fig. 2.

There are three types of microstructure in PI: 1,4-, 1,2- and 3,4-addition microstructure, respectively. The peak (a) at δ 4.95–5.14 indicates the existence of –CH=C– in 1,4-addition microstructure and the peak (b) at δ 4.56–4.71 corresponds to the protons of –C=CH$_2$ in 3,4-addition microstructure. Based on the ^{1}H-NMR spectra, the compositions of PI were concluded in
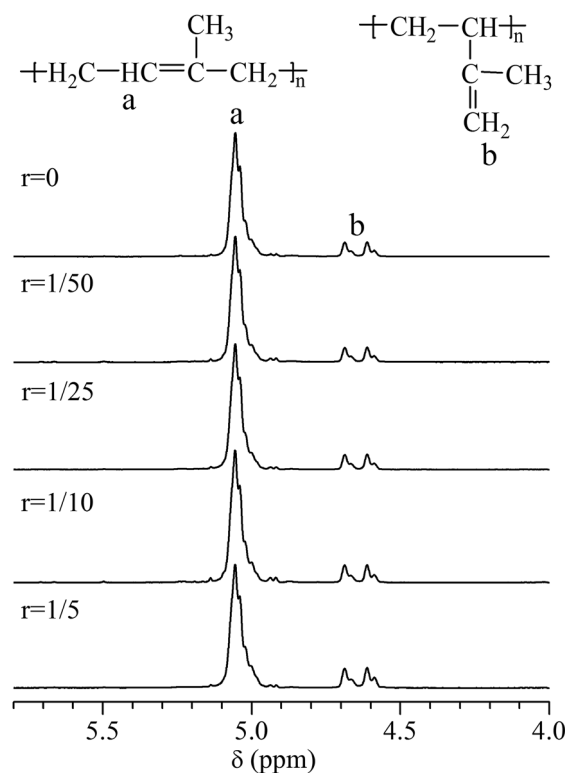

Fig. 2 ^{1}H-NMR spectra of PI.

Table 1 through calculating the integral area ratio of relevant characteristic peaks. It was confirmed that with increasing of added THF, there was a growing trend in the content percentage of 3,4-addition structure. The percentage of 1,4-addition structure, in contrast, reduced slightly and there was a mutation between 1/10 and 1/5 of "r". Furthermore, there was no 1,2-addition structure all the way.

The formation of 1,2-addition structure, as stated by Cheng's work,[34] might be unable to occur until the value of "r" reached to 25.

Our laboratory's previous studies[35] proposed a new explanation about the formation mechanism of different microstructures in PI, called "Ion Pair Channel Idea". It stated that when n-BuLi is used as the initiator, the polymerization rate and molecular structure of the products are determined by the channel space between the ion pairs. Naturally, when the channel space is smaller than the requirement for the monomers to insert in, the polymerization cannot occur. However, in contrast, when the channel space is much larger than that for the monomers to insert in, the polymerization also is not easy to occur, because the too large channel space between the ion pairs is unfavorable for the electric charge on the inserted monomers to migrate. Therefore, when the channel space is compatible with the requirement for the certain conformation of monomers to insert in, the polymerization rate of the configuration formed from this conformation would be maximum. The THF molecules could associate with Li$^+$ due to electronegative oxygen atom, as a result, the channel between the ion pairs was blocked partly (see Fig. 3). For this reason, the

increase of 3,4-structure and the decrease of 1,4-structure are very natural. Li *et al.* primely explained the reason of formed microstructure of PI in the anionic polymerization process with the "Ion Pair Channel Idea".[35] However, they didn't adopt THF but the lithium phenolate.

In order to make PS-*b*-PI-*b*-PMMA become a kind of ideal thermoplastic elastomer, high content of 1,4-addition PI is expected. Meanwhile, for shorting the reaction time of first two blocks, trace amounts of THF could be added with little effect to the structure of PI blocks. Therefore, adding trace amounts of THF ($n_{\text{THF}}/n_{n\text{-BuLi}} = 1 : 10$) into polymerization system was appropriate.

Polymerization and characterizations of PS-*b*-PI-*b*-PMMA

PMMA is a kind of polar polymer which is insoluble in nonpolar solvent, therefore, the polymerization of PMMA in CH is a precipitation polymerization. That is why polar solvent or nonpolar/polar mixed solvent was used in almost every previous study of anionic polymerization of copolymer contain PMMA block. However, the polar solvents may contain more impurities which is unfavourable to anionic polymerization, thus the side reactions caused by the carbonyl in PMMA are more likely to occur in polar solvent.

In our work, the anionic polymerization of MMA was conducted in a nonpolar solvent CH at 0 °C. The usage of nonpolar solvent is different from others' studies. Therefore, the mild conditions enable the polymerization to carry out in the industry conditions. Because of the good solubility of long chains of PS-*b*-PI in CH, the chains of PS-*b*-PI-*b*-PMMA formed after addition of MMA can be almost completely dissolved as well. Furthermore, the electromagnetic stirring made the MMA monomers homogeneously disperse in CH and the narrow MWD copolymer was obtained. Fortunately, because CH was utilized instead of any other polar solvent, the side reactions of MMA could be controlled even the reaction temperature was elevated to 0 °C. On the other hand, the trace amounts of THF helped to accelerate the polymerization.

The results of polymerization of PS-*b*-PI-*b*-PMMA were summarized in Table 2. The MWD of the final tri-block copolymer extended to 1.21 was slightly higher than that of the PS-*b*-PI copolymer before MMA added (1.03). However, considering that the polymerization does not need any ligand for stable and

Table 1 The microstructure in PI with different amounts of THF

r^b	Microstructure composition of PI^a		
	1,4-Addition (%)	3,4-Addition (%)	1,2-Addition (%)
0	93.90	6.10	0
1/50	93.46	6.54	0
1/25	93.46	6.54	0
1/10	93.02	6.98	0
1/5	91.30	8.70	0

^{a} Initiated by n-BuLi with different amounts of THF. ^{b} $r = n_{\text{THF}}/n_{n\text{-BuLi}}$.
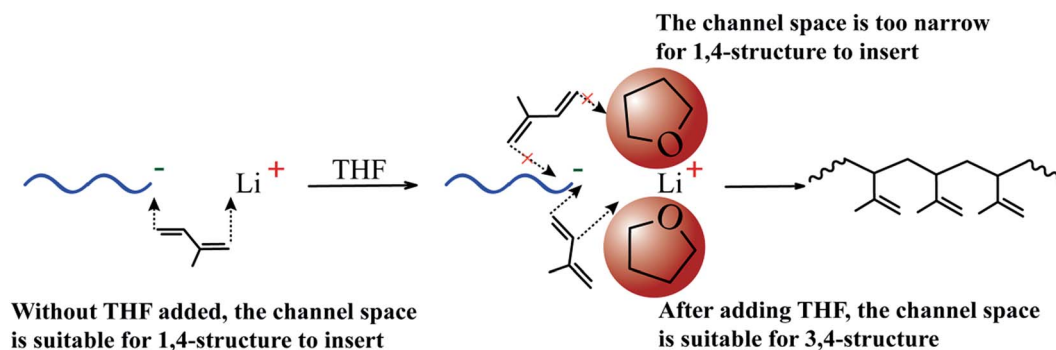

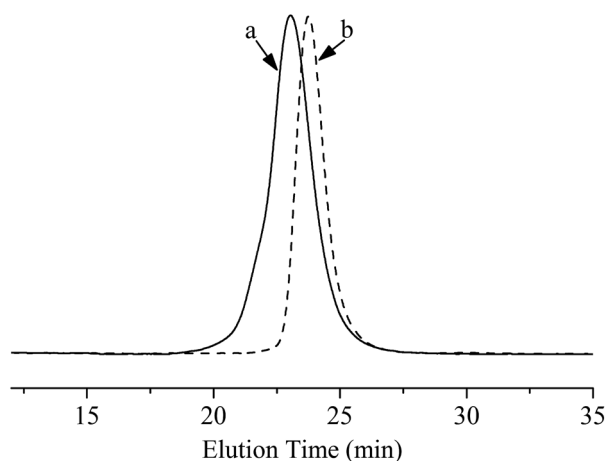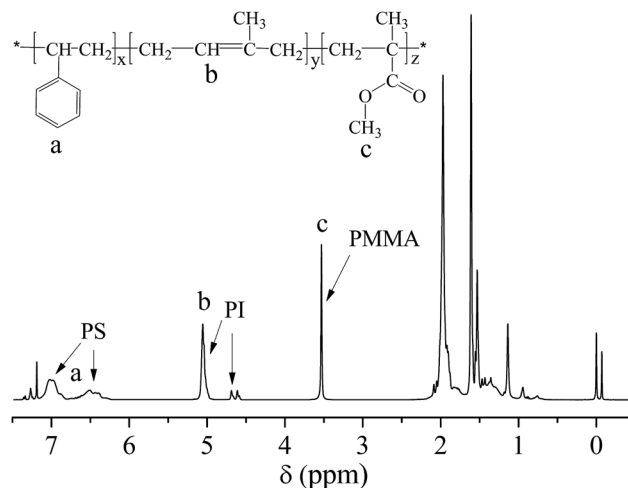**Fig. 3** "Ion Pair Channel Idea" in the interaction mechanism of THF and ion pairs.

Table 2 Anionic polymerization of PS-PI-PMMA and its precursor[a]

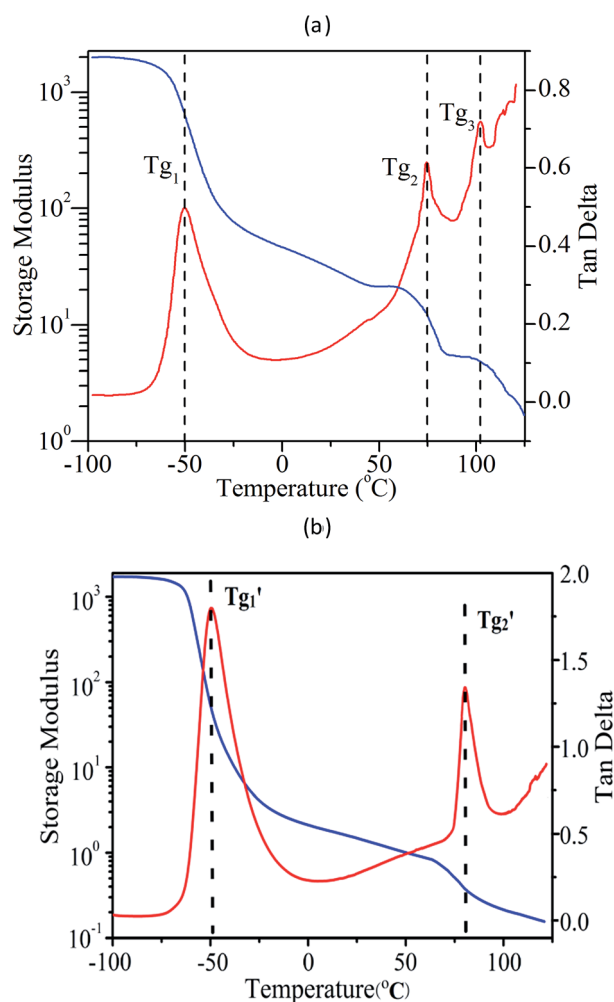| Sample | $M_n/\times 10^{-4}$ | | | Yield | Eff[c] (%) |
	Obsed[b]	Calcd	MWD[b]		
PS-b-PI	3.91	3.40	1.03	~100%	87.0
PS-b-PI-b-PMMA	5.27	4.58	1.21	~100%	86.9

[a] Synthesized by anionic polymerization with trace amount of THF ($n_{THF}/n_{n\text{-BuLi}} = 1 : 10$). [b] Determined by GPC in THF elusion. [c] Initiator efficiency (I^*) = M_n(calcd)/M_n(obsed), where M_n(calcd) = MW(monomer) × [monomer]/[initiator] × conversion% + MW of chain end groups.

the reaction temperature could be raised up to 0 °C, the MWD of PS-b-PI-b-PMMA was rather narrow. The M_n of copolymer from GPC was rather close to the calculated ones and a special note is that the yield reached up to 100%, which could not be achieved in many previous researches in the area of anionic polymerization of MMA at the 0 °C. Furthermore, it was clearly indicated from Table 2 that the M_n of PMMA block was about 13 600. On the other hand, the reason why the M_n of final copolymer was a little higher than the calculated, one was that there still existed the trace impurities derived from the solvent and the after added monomers, which could kill the reactive species in the system, even though all reaction agents were purified strictly. The initiation efficiency of 86.9% can be figured out. According to the GPC traces in Fig. 4, the MWDs of both PS-b-PI-b-PMMA and its precursor PS-b-PI were in the good narrow distribution. The results indicated that the side reactions of MMA were well inhibited and a homogeneous and ideal PS-b-PI-b-PMMA was obtained.

^{1}H-NMR of PS-b-PI-b-PMMA was revealed in Fig. 5, in which there were a broad signal at δ 6.3–7.1 (a) corresponding to the aromatic protons (C$_6$H$_5$–), some peaks at δ 5.13 and δ 4.6–4.8 (b) assigned to the olefinic protons of 1,4-addition (–CH=C–) and 3,4-addition (–C=CH$_2$) of PI, and a signal at δ 3.6 (c) attributing to the protons of the methyl connected with the ester group in PMMA (–O–CH$_3$). Calculating the ratio of the integral areas of these characteristic peaks, we figured out the mole ratio of St, Ip

Fig. 5 ^{1}H-NMR spectrum of PS-b-PI-b-PMMA.

and MMA ($n_{St} : n_{Ip} : n_{MMA}$) is 19 : 60 : 21, which is very approximate to the theoretical value (19.5 : 59.5 : 21). The result confirmed almost no side reaction existed during the process of

Fig. 6 Dynamic mechanical curves of PS-b-PI-b-PMMA (a) and PS-b-PI (b).

Fig. 4 GPC traces of copolymers: (a) PS-b-PI-b-PMMA; (b) PS-b-PI.

anionic polymerization of MMA and the conversion of St, Ip and MMA monomers were complete. Based on $n_{St} : n_{Ip} = 19 : 60$, the M_n of PS block is about 12 760 while M_n of PI block is about 26 340. Obviously, the M_n of PMMA block (13 600) is larger than that of PS block.

Fig. 6(a) depicted the dynamic mechanical behaviour of the synthesized PS-b-PI-b-PMMA tri-block copolymer. The storage modulus and loss tangent clearly indicated three glass transitions. Of course, T_{g_1} (−50 °C) was referred to the glass transition temperature of PI block. Furthermore, because the T_g of PS equals approximately to that of PMMA and is close to T_{g_3}, T_g (103 °C) may belong either to PS block or to PMMA block. However, the glass transition temperature of polymers follows the eqn (1):

$$T_g = T_{g_\infty} - \frac{K}{M_n} \quad (1)$$

where T_{g_∞} is the glass transition temperature of the polymers while n being high enough and the K is the effect parameter of the T_g on n. Considering that PMMA is a polar polymer and PS is not, the K of PMMA should be smaller than that of PS. Furthermore, the n of PMMA block (13 600) is larger than that of PS block (12 760), so that T_{g_2} (75 °C) should belong to PS block and T_{g_3} (103 °C) to the PMMA block. To discriminate the two different T_gs further, the di-block copolymers PS-b-PI was

synthesized in exactly the same conditions as the PS-b-PI-b-PMMA mentioned above before adding of MMA monomer. Its DMA results were shown in Fig. 6(b), two glass transition temperatures ($T'_{g_1} = -49.3$ °C; $T'_{g_2} = 81.2$ °C) were clear indicated. By comparison of the DMA results of PS-b-PI-b-PMMA and PS-b-PI, it is obvious that the T_{g_2} belonged to PS block and T_{g_3} was the glass transition temperature of PMMA block.

These results not only clearly demonstrated the micro-phase separation existing in PS-b-PI-b-PMMA, but also suggested that the molecular weight of PMMA block was large enough to surpass the length of segment and to possess the properties of PMMA.

The thermodynamics properties of PS-b-PI-b-PMMA tri-block copolymers was also studied by DSC showed in Fig. 7. Heat flow was legible and negative value during the rise processing of temperatures, which means the change being heat-absorbing. Since DSC measurements showed three glass transition temperatures ($T_{g_1} = -57.7$ °C; $T_{g_2} = 80.2$ °C; $T_{g_3} = 105.4$ °C) which were corresponded to the results of DMA, it suggested the presences of different phases in tri-block copolymers. Combined with the DMA measurements, we were clear that the length of PMMA block has ensured the PMMA properties to exist in copolymers according to the appearance of T_{g_3} (105.4 °C) which belonged to PMMA block.

To confirm the synthesis method are controlled, we varied the last PMMA block lengths and a series of tri-block copolymers were shown in Table 3. The MWDs were stable at 1.2–1.3 and yields nearly hit 100% until the contents of PMMA block came to 30%. Meanwhile, the MWDs increased a little along with the ratio of PMMA however the ratios of three blocks calculated by ^{1}H-NMR spectra were still corresponded to the designed ones. The broaden of MWDs may be caused by two aspects: the side reactions of MMA and the raise of temperature which were both attributed to the increase of MMA monomers. We compared the GPC traces of 5 samples (Fig. 8) to analyse the effect of MMA's amount in anionic polymerization and found out that those two tri-block copolymers were all in the good narrow distribution. However, a small peak found in the left of the spectra of sample 5 showed that the high molecular weight polymer was product in the tri-block copolymerization.

Speculated on the mechanism of side reactions, the formation of that polymer which we inferred was shown in Fig. 9. Indeed, this part polymer was too rare to affect the properties of tri-block copolymers and that was why we would ignore it.
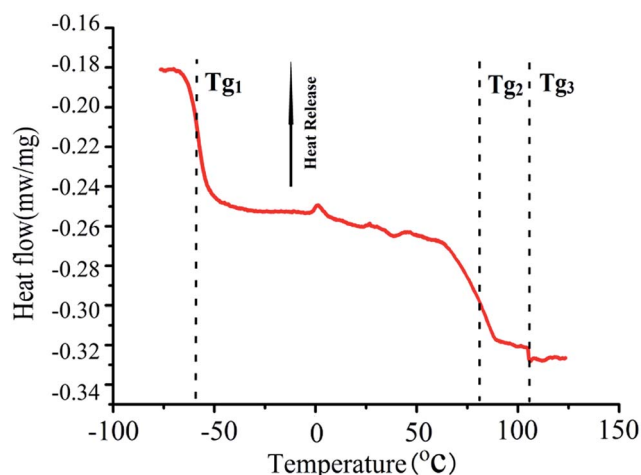

Fig. 7 DSC curves of PS-b-PI-b-PMMA.

Table 3 Anionic polymerization of PS-PI-PMMA containing PMMA block of different lengths[a]

| Sample | Ratio (wt%) | Conversion of MMA (%) | MWD[b] | $M_n/\times 10^{-4b}$ | Wt$_{St}$: wt$_{Ip}$: wt$_{MMA}$ | |
					Calcd	Obsed[c]
1	16	~100	1.22	4.11	15 : 70 : 15	15 : 70 : 15
2	20	~100	1.21	6.32	20 : 60 : 20	19.5 : 60 : 20.5
3	25.5	~100	1.21	5.27	25.5 : 49 : 25.5	25 : 49.5 : 25.5
4	28	~100	1.26	5.85	27 : 45 : 28	27 : 45.5 : 27.5
5	30	~100	1.28	6.23	29 : 41 : 30	29 : 41.5 : 29.5

[a] Synthesized in the same way with trace amounts of THF ($n_{THF}/n_{n\text{-}BuLi} = 1 : 10$). [b] Determined by GPC in THF elusion. [c] Calculated by ^{1}H-NMR spectra.
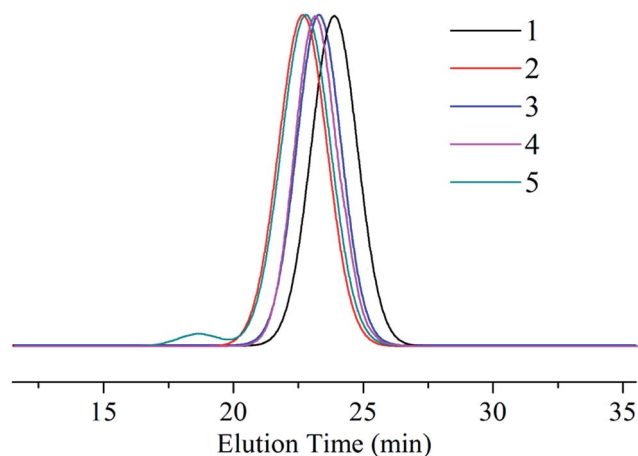
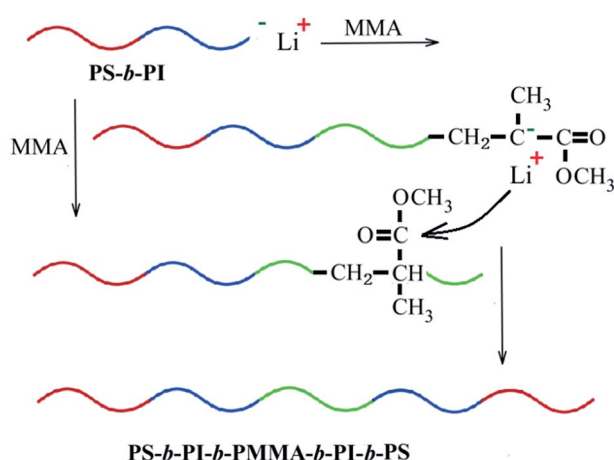**Fig. 8** GPC traces of tri-block copolymers.

Fig. 9 Formation of high molecular weight polymers.

Conclusions

In summary, the anionic polymerization of well-defined PS-*b*-PI-*b*-PMMA tri-block copolymer was conducted in CH solvent with trace amounts of THF as a polar regulator, and the reaction temperature of MMA was elevated to 0 °C. The measurement results demonstrated that a homogeneous and ideal PS-*b*-PI-*b*-PMMA tri-block copolymer was obtained. Specifically, GPC data and ^{1}H-MNR spectra revealed that the MWD of the final copolymer was rather narrow and M_n of PS, PI and PMMA were 12 760, 26 340 and 13 600 respectively, which was approximate to the calculated values. After adding trace amounts of THF, the reaction rate was remarkably accelerated and meanwhile high content of 1,4-addition structure of PI was guaranteed, herein, the "Ion Pair Channel Idea" can be used to explain the microstructure forming mechanism of PI. Furthermore, determined by DMA and DSC, the micro-phase separation clearly existed in synthesized PS-*b*-PI-*b*-PMMA and it was figured out that the M_n of PMMA block was large enough to possess the properties of PMMA. Varying the lengths of last PMMA blocks, we confirmed that until the content of PMMA block raised up to 30%, the

structure of tri-block copolymers was well-defined. Accordingly, this new method with appropriate temperature rather than −78 °C, a faster reaction rate, fewer side reactions and a definite structure provides the possibility to realize the anionic polymerization of copolymers containing polar PMMA block at a commercial scale.

Acknowledgements

References

1 D. Baskaran and A. H. E. Müller, *Prog. Polym. Sci.*, 2007, **2**, 173–219.

2 Y. Ren, Q. Gao, C. Zhou, Z. Wei, Y. Zhang and Y. Li, *RSC Adv.*, 2015, **35**, 27421–27430.

3 A. Mavroudis and N. Hadjichristidis, *Macromolecules*, 2006, **39**(2), 535–540.

4 S. Ito, R. Goseki, I. Manners, T. Ishizone and A. Hirao, *Macromol. Chem. Phys.*, 2015, **14**, 1523–1533.

5 H. F. Fei, W. Xie, Q. Wang, X. Gao, T. Hu, Z. Zhang and Z. Xie, *RSC Adv.*, 2014, **99**, 56279–56287.

6 Y. Matsuo, R. Konno, T. Ishizone, R. Goseki and A. Hirao, *Polymers*, 2013, **3**, 1012–1040.

7 Y. Deng, *Chem. Ind. Eng. Prog.*, 2005, **2**, 212–215.

8 K. Knoll and N. Niessner, *Macromol. Symp.*, 1998, **132**, 231–243.

9 J. Wang, D. Shan, W. Liu and A. Zheng, *Polym. Mater. Sci. Eng.*, 2015, **10**, 99–104.

10 X. Yuan, J. Wang, D. Shan and A. Zheng, *Polym. Mater. Sci. Eng.*, 2014, **8**, 1–6.

11 D. Shan, L. Yang, J. Wang and A. Zheng, *Chemical Journal of Chinese Universities*, 2014, **12**, 2698–2705.

12 J. Wang, B. Chen, S. Tang and A. Zheng, *Chin. J. Polym. Sci.*, 2015, **8**, 1096–1103.

13 Y. Duan, M. Thunga, R. Schlegel, K. Schneider, E. Rettler, R. Weidisch, H. W. Siesler, M. Stamm, J. W. Mays and N. Hadjichristidis, *Macromolecules*, 2009, **42**(12), 4155–4164.

14 D. Baskaran, *Prog. Polym. Sci.*, 2003, **28**, 521–581.

15 J. S. Kim, J. O. Kweon, J. H. Lee and S. T. Noh, *Macromol. Res.*, 2015, **1**, 100–110.

16 S. Y. Lee and T. Y. Chang, *Eur. Polym. J.*, 2011, **47**, 800–804.

17 S. Tanaka, R. Goseki, T. Ishizone and A. Hirao, *Macromolecules*, 2014, **47**, 2333–2339.

18 D. Baskaran and S. Sivaram, *Macromolecules*, 1997, **30**, 1550–1555.

19 A. Zheng, J. Zhang, Y. Guan, F. Hu, D. Wei and S. Wang, 8546503 B2, USA, 2013.

20 B. Chen, J. Wang, M. Shu, B. Zou and A. Zheng, *Chinese Journal of Chemistry*, 2014, **32**, 1128–1134.

21 R. Zhuang and A. H. E. Müller, *Macromolecules*, 1995, **28**, 8035–8042.

22 O. W. Webster, W. R. Hertler, D. Y. Sogah, W. B. Farnham and T. V. RajanBabu, *J. Am. Chem. Soc.*, 1983, **105**, 5706–5708.

23 F. Bandermann, D. Beckelmann, D. Broska, A. Fieberg, T. Roloff and D. Wolters, *Macromol. Chem. Phys.*, 1995, **196**, 2335–2347.

24 M. T. Reetz and R. Ostarek, *J. Chem. Soc., Chem. Commun.*, 1988, 213–215.

25 L. Yi, X. Zhan, F. Chen, B. Jiang and B. Chen, *Chemical Journal of Chinese Universities*, 2007, **28**(12), 2393–2397.

26 H. Ruckdäschel, J. K. W. Sandler, V. Altstädt, C. Rettig, H. Schmalz and V. Abetz, *Polymer*, 2006, **47**, 2772–2790.

27 C. Auschra and R. Stadler, *Macromolecules*, 1993, **26**, 6364–6377.

28 X. Lv, G. Jin, Q. Liu and X. Yang, *J. Beijing Univ. Chem. Technol.*, 2000, **27**(3), 29–32.

29 W. Wang, R. Schlegel, B. T. White and K. Williams, *Macromolecules*, 2016, **49**(7), 2646–2655.

30 M. Schlosser, *Organometallics in Organic Synthesis*, Wiley, New York, 1994, p. 172.

31 H. Iatrou, J. W. Mays and N. Hadjichristidis, *Macromolecules*, 1998, **31**, 6697–6701.

32 Y. Lee, C. Chang and C. Kao, *Langmuir*, 2010, **26**(6), 4196–4206.

33 M. Su, B. Chen, B. Zou, F. Chen, A. Zheng and Y. Guan, *Acta Polym. Sin.*, 2015, 7, 835–844.

34 J. Cheng, C. He and G. Jin, *China Elastomerics*, 1998, **2**, 12–16.

35 T. Li, B. Chen, S. Wu, Y. Guan and A. Zheng, *Acta Polym. Sin.*, 2014, **9**, 1204–1211.