PMMA-containing ITX Residues and its Initiation for Synthesizing PMMA-b-PSt Copolymer

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In virtue of the reversible coupling and cleaving mechanism involved isopropylthioxanthone (ITX), a precursor of poly(methyl methacrylate) ended with ITX residues (PMMA-ITXH) was firstly synthesized through the photopolymerization of methyl methacrylate (MMA) initiated by a binary system of ITX and ethyl-*p*-dimethyl amino benzoate (EDAB), and secondly, applying this precursor as a macroinitiator, block copolymer of poly(methyl methacrylate) and polystyrene (PMMA-b-PSt) was produced through a thermal activated radical polymerization of styrene (St) at a temperature above 80°C. The content of incorporation of the reduced ITX groups in the precursor was estimated by UV-vis spectrum analysis and the results indicated that it was greatly influenced by the ITX concentration in system. The presence of EDAB could promote the polymerization and result in high monomer conversions and low molecular weight of polymers with wide distributions, but had no evident effect on the incorporation of reduced ITX moieties in polymer. Furthermore, more monomer supplied in system was advantageous for the production of high molecular weight of polymers and provided apparently low content of reduced ITX residues in polymer. Using a selected precursor of PMMA-ITXH with a moderate level of reduced ITX residues, molecular weight and its distribution, the bulk polymerization of St was initiated. FTIR spectrum analysis and GPC measurement confirmed the formation of block copolymer of PMMA-b-PSt.

Keywords: Isopropylthioxanthone, macroinitiator, re-initiation, block copolymer

1 Introduction

Block copolymers have additive and synergistic properties owned by each section, which enable them suitable as dispersants and emulsifier, as thickeners, impact modifiers, phase promoters or adhesives, and make their syntheses to achieve well-defined structure a continuing research theme in polymer chemistry.

It is well known that a number of techniques for the preparation of block copolymers have been developed hitherto (1–6). Among them, the application of sequential free radical initiator, macro-initiators or macro-co-initiators with active functional groups bound on their ends is a simple and favorable alternative to prepare block copolymer under mild conditions. Piirma (7) synthesized a block copolymer of PMMA-b-PSt in two stages by utilizing a unique, sequential initiator di-t-butyl 4,4′-azobis (4-cyanoperoxyvalerate). Borsig (8) and Braun (9–11) observed the formation of block copolymers in the presence

of PMMA precursors containing di-, tri- phenyl or phenoxy terminal groups, which could further initiate free radical polymerization of vinyl monomers. Moreover, a selective and efficient preparation of block copolymers can be accomplished using a bimolecular photoinitiating system. The most recognized and practically used bimolecular free radical initiating system usually comprises an aromatic ketone and a tertiary amine, namely Norrish II initiator system. Huang (12–15) synthesized diblock copolymers of PMMA-b-PVAc (poly(vinyl acetate)) or PSt-b-PVAc by a successive photoinduced polymerization, in which prepolymers with amine end groups were firstly obtained by a polymerization initiated with a binary system composed of aniline and benzophenone (BP), and secondly, using the resultant macro-electron donor for BP, the photopolymerization of vinyl acetate were initiated.

In a bimolecular photoinitiating system, if the electron donor comes from a macromolecular chain of polymer film, the active hydrogen abstraction of electron acceptor such as BP and isopropylthioxanthone (ITX) will produce macroradicals which could further initiate grafting polymerization of vinyl monomers (16–17). The coupling of propagating radicals with diaryl ketyl radicals and the reversible cleaving of the formed weak C—C bond under UV irradiation or thermal treatment suggest the possibility of

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performing living or controlled free radical polymerization. This has been demonstrated by Yang, Bowman and Yamamoto in their researches of photograft polymerization occurred on the surface of polymeric materials (18–20). Furthermore, by employing the above mentioned reversible coupling and cleaving reactions, composite core-shell particles have been synthesized with a commercially available vulcanized acrylonitrile butadiene rubber (NBR) emulsion as model latex (21).

In this paper, in order to further extend the reversible coupling and cleaving mechanism involved BP or ITX to a homogeneous bulk system, a simple approach to prepare block copolymer was proposed. Firstly, a precursor with isopropylthioxanthone residues (ITXH) incorporated onto the end of PMMA chain was synthesized through the photopolymerization of MMA initiated by a binary system of ITX and EDAB (Scheme 1). In this process, the generated isopropylthioxanthyl ketyl radical is a resonance stabilized specie and readily undergoes coupling reactions at 2-, 4-, 5-, 7- and 9-positions (22). Accordingly, it acts more likely as a chain terminator (23, 24). In particular, the coupling reaction occurred between the radical at 9-position and polymer chain radical can bound a reduced ITX residue onto the end of PMMA chain, namely polymer-bound reduced ITX residue, which is capable of re-initiating polymerization under UV irradiation or heat treatment. Secondly, applying the precursor of PMMA-containing ITX residues as a macroinitiator and by the thermal activated radical polymerization of St, block copolymer of PMMA-b-PSt was produced (Scheme 2). The content of incorporation of the reduced ITX residue, a key factor for the generation of block copolymer in the second step, was estimated by UV-Vis spectrum analysis and some parameters influenced the combination of reduced ITX residue were examined. The initiation of this special macroinitiator was demonstrated by FTIR spectrum analysis and GPC measurement.
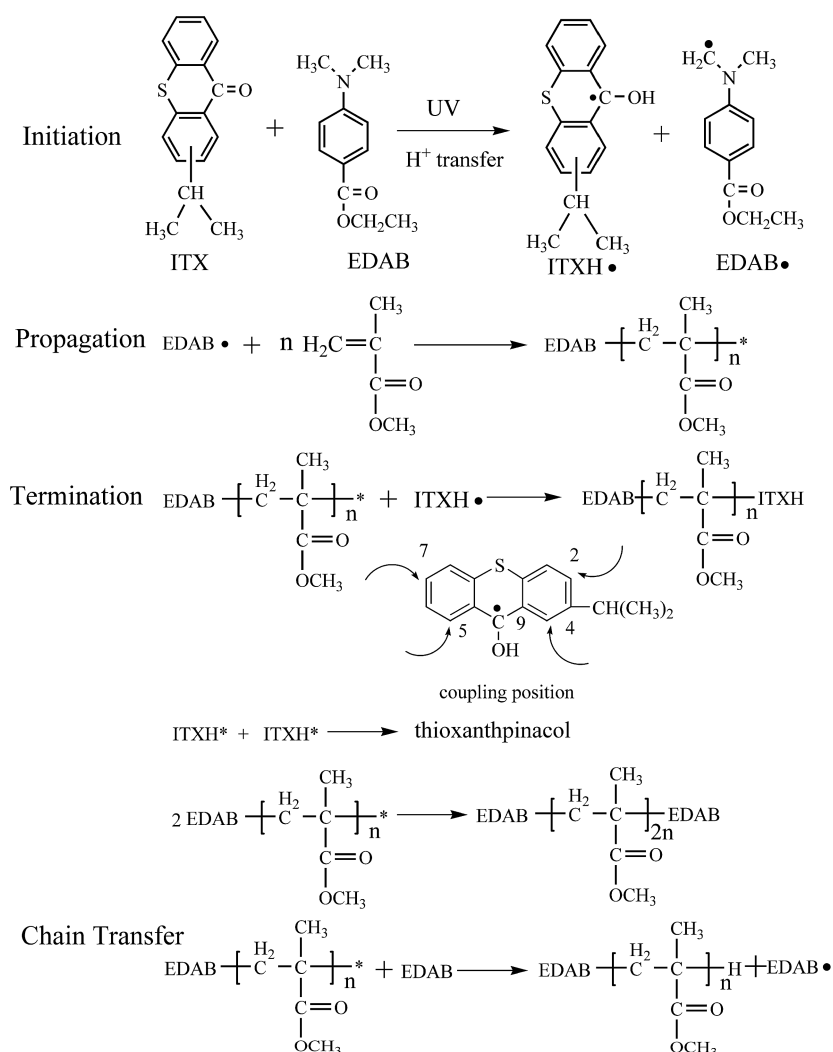
Sch. 1. The process for the formation of PMMA-ITXH in a photo-induced polymerization of MMA using ITX/EDAB as initiator.
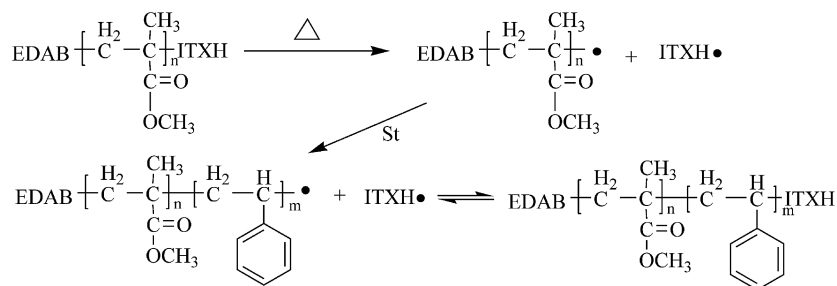
Sch. 2. The thermal activated initiation of PMMA-ITXH to produce PMMA-b-PSt copolymer.

2 Experimental

2.1 Materials

Methyl methacrylate (MMA) and styrene (St) procured from Sinopharm Chemical Reagent Beijing Co., Ltd, China, were distilled under vacuum and stored at 4°C. Isopropylthioxanthone (ITX) and ethyl-p-dimethyl amino benzoate (EDAB) from TH-UNIS Insight Co., Ltd, China, were used as received. Sodium borohydride and solvents such as dichloromethane, methanol, acetonitrile et al. obtained from Sinopharm Chemical Reagent Beijing Co., Ltd, China, were used without further purification.

2.2 Synthesis of PMMA-containing ITX Residues (PMMA-ITXH)

The PMMA with coupled ITXH end-groups (PMMA-ITXH) was synthesized by UV-induced polymerization using ITX/EDAB as a binary initiation system. The photopolymerization was carried out in a cylindrical quartz reactor ($\Phi = 5$ cm, H $= 9$ cm) with a 250 W mercury lamp used as a light source ($\lambda = 250$–450 nm), and kept purging with argon at 25°C. A solution of MMA mixed with ITX and EDAB in CH_2Cl_2 was charged into the quartz reactor. After a determined reaction time, the resultant polymer was precipitated with an excess of methanol, and then filtered, dissolved in acetone. The above treatments were repeated for at least three cycles to ensure the purity of PMMA-ITXH. The residue was dried under vacuum at 40–50°C for at least 24 h, and the conversion of MMA was determined by gravimetry.

In order to ascertain the incorporation of reduced ITX residue onto PMMA chain by UV-Vis spectrum analysis, PMMA with no ITX residues was produced by a control experiment carried out using AIBN as an initiator. Furthermore, free reduced ITX was generated by the reaction of ITX with sodium borohydride: 0.5 g of ITX was placed in a 50 ml Erlenmeyer flask with 10 ml of ethanol added, and then 150 mg of sodium borohydride was charged. The reaction was checked by thin layer chromatography (TLC), using 6:1 hexane/ethyl acetate as a developing solvent. When the reaction was completed, 20 ml of saturated sodium bicarbonate solution was introduced and the mixture was filtered. The obtained solid product was washed with deionized water, dried in a vacuum oven.

2.3 Preparation of PMMA-b-PSt Copolymer

1.0 g of macroinitiator PMMA-ITXH dissolved in 30 ml of styrene was placed in a 100 ml, four neck flask equipped with magnetic stirrer, reflux condenser, argon inset and outlet. Purged with argon for 30 min, the flask was transferred to a water bath at a predetermined temperature. Samples were taken at a certain interval using a syringe, and then dissolved in THF, precipitated with an excess of methanol. The sediments were separated by filtration and dried in a vacuum oven at 50°C for 24 hours. Further purification of copolymers was carried out in a Soxhlet extractor for more than 96 h to remove the residual PMMA (7), using a selective solvent of acetonitrile.
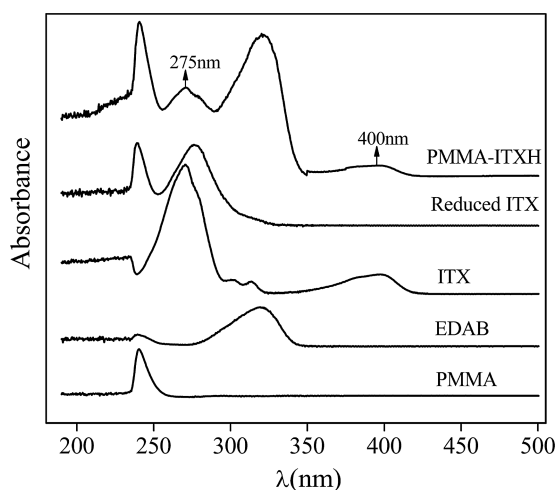
2.4 Characterization

The number- and weight-average molecular weights of the obtained polymers were evaluated by gel permeation chromatography (GPC 515–2410 system from waters) with tetrahydrofuran (THF) as an eluent. Typically, 2 mg of sample was dissolved in 1 ml of solvent and the flow rate was kept at 1 ml/min for analysis. A set of narrow molecular weight polystyrene standard covering a molecular weight range of 350–3,500,000 g/mol was used as GPC standards. All molecular weights were reported as polystyrene equivalents. The molecular weight distribution of polymer was expressed by polydispersity index (PDI). FT-IR spectra (KBr pellets) were collected on a NEXUS 670 (from Nicolet) FTIR spectrometer. UV-vis spectra were collected on a CENTRA 20 (from GBC Company Australia) photodiode array spectrophotometer in the 190–500 nm range with a data interval of 0.427 nm. For a series of given concentrations of free ITX in dichloromethane, 2 calibration curves were built by the absorbance of ITX at 275 nm and 400 nm as a function of its concentration. The absorbance of a diluted PMMA-ITXH solution in dichloromethane was measured at 275 nm and 400 nm, respectively, and the content of reduced ITX bound onto polymer chain was calculated by comparison with the standard curves.
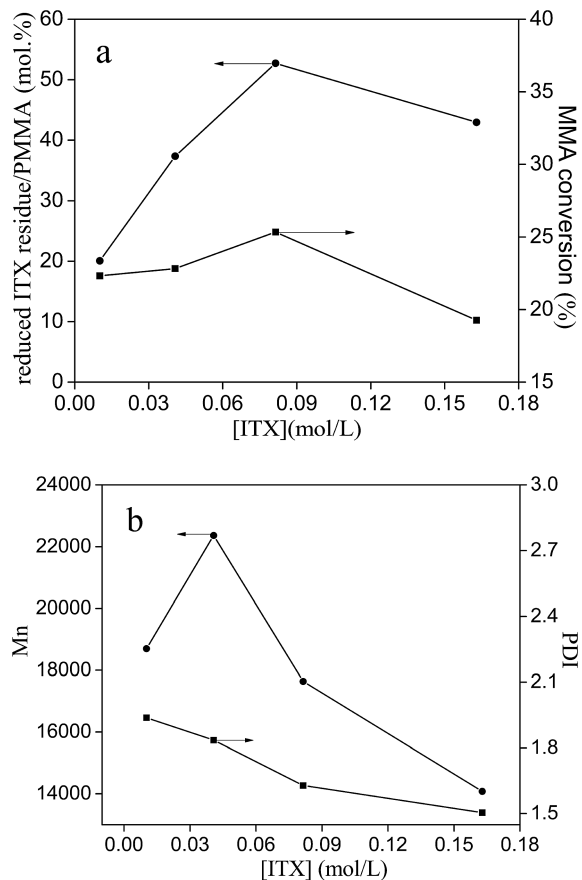
3 Results and Discussion

3.1 Synthesis of PMMA-ITXH

Usually, the photo-reduction of ITX in the presence of tertiary amine leads to the formation of an α-aminoalkyl radical which is preferential to initiate the polymerization of vinyl monomers, and an isopropylthioxanthyl ketyl radical which inclines to terminate propagating radical to produce PMMA with ITXH end group (PMMA-ITXH) (Scheme 1). The presence of PMMA-ITXH was confirmed by UV spectrum analyses (Figure 1). In contrast to the UV spectra of PMMA with no ITX residues, it could be seen that the UV spectra of PMMA-ITXH presented absorptions at 275 nm, 320 nm and 400 nm. The absorption at 320 nm comparable to the UV spectra of EDAB revealed the combination of amine residues. The absorption at 275 nm indicated the incorporation of aromatic species, including polymer-bound reduced and unreduced ITX. The wide absorption of PMMA-ITXH demonstrated at around 400 nm was similar to that of free ITX, but discriminated remarkably from that of free reduced ITX. There was no marked absorption displayed at 400 nm on the spectra of free reduced ITX. Consequently, the absorption of PMMA-ITXH at about 400 nm could be ascribed to the character absorption of carbonyl group in conjugation to aromatic rings, implying the formation of polymer-bound unreduced ITX. By monitoring the absorptions of PMMA-ITXH at 275 nm and 400 nm, and in comparison with the standard calibration curves constructed by the absorptions of given concentrations of ITX at 275 nm and 400 nm, the content of reduced ITX incorporated onto polymer chain can be calculated. This content would dominate the initiation efficiency of thermal activated polymerization in the subsequent step.

Fig. 2. Effect of ITX concentration on (a) the content of reduced ITX residue in PMMA and monomer conversion, (b) molecular weight and its polydispersity ([MMA] = 4.2 mol/L, [EDAB]/[ITX] = 1:1, reaction time = 3 h).

When the concentration of ITX in reaction system was increased, the content of polymer-bound reduced ITX residue in resultant polymer increased firstly, and then at a higher ITX concentration, showed a decline tendency (Figure 2). It is known that the active hydrogen abstraction of ITX from tertiary amine generates a α-aminoalkyl radical probably acting as an initiating radical and an isopropylthioxanthyl ketyl radical primarily acting as a chain terminator. With more ITX introduced, the hydrogen abstraction could also be occurred from the resultant polymer or other hydrogen donors such as monomer in system, leading to the formation of more initiating radicals and terminating radicals. The former accelerated the polymerization and gave rise to the improvement of conversion, while the later brought about more ITX residues, and accordingly more reduced ITX onto the polymer chains. At a higher ITX concentration, the enhanced combination termination between primary initiating radicals and growing radicals could decrease the incorporation of ITX residues and the conversion of monomer. The molecular weight of the obtained PMMA-ITXH presented a peak value in the evolution of monomer conversion as a function of ITX concentration.
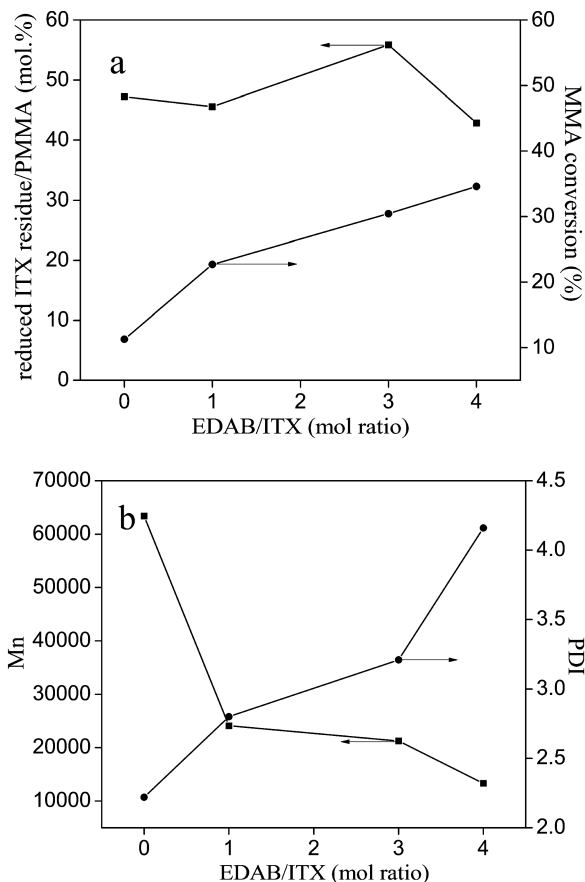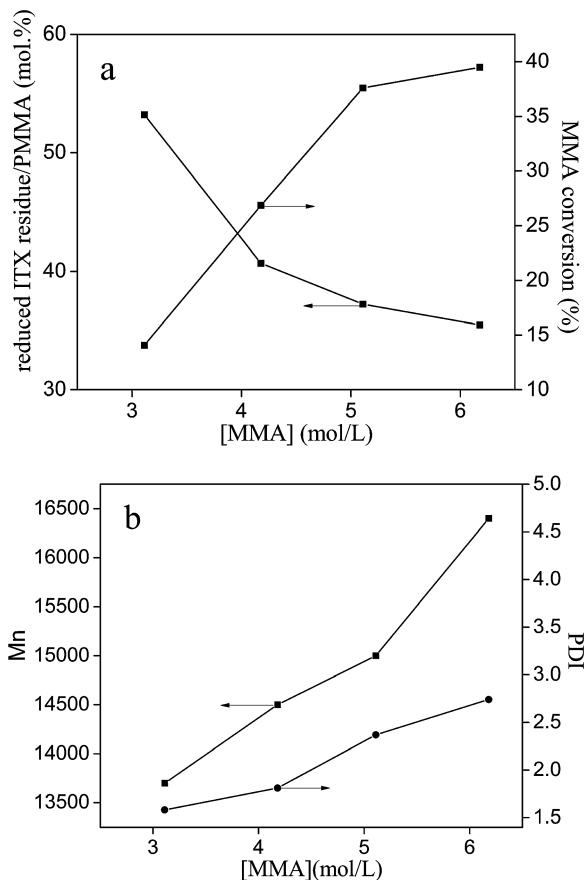

Fig. 1. UV spectra of PMMA-ITXH (its concentration in dichloromethane: 1.279 wt%), ITX (its concentration in dichloromethane: 0.001 wt%), EDAB and PMMA (produced by thermal radical polymerization).

Fig. 3. Effect of EDAB/ITX mol ratio on (a) the content of reduced ITX residue in PMMA and monomer conversion, (b) molecular weight and its polydispersity ([MMA] = 6.33 mol/L, [ITX] = 0.1 mol/L, reaction time = 3 h).


Fig. 4. Effect of MMA concentration on (a) the content of reduced ITX residue in PMMA and monomer conversion, (b) molecular weight and its polydispersity ([ITX] = 0.08 mol/L, [EDAB] = 0.32 mol/L).

The elevated combination termination at higher ITX concentrations could be a handicap for the growing of polymer chains, but it was advantageous for creating polymer with a narrower molecular weight distribution (Figure 2b).

Increasing the EDAB/ITX molar ratio at a fixed concentration of ITX, it is observed that the reduced ITX residue content in resultant polymer remained at an almost same level. The greater concentration of EDAB in reaction system did not evidently change the number of the produced isopropylthioxanthyl ketyl radicals and thus had little effect on the incorporation of ITX moieties onto polymer chains by termination reaction occurred between isopropylthioxanthyl radicals (ITXH•) and propagating radicals. However, it could reduce the extent of oxygen inhibition via the reaction with singlet oxygen and via hydrogen abstraction by radicals generated in system (22). This could give rise to more α-aminoalkyl radicals to promote the polymerization, resulting in higher monomer conversions. Simultaneously, the greater concentration of EDAB could enhance the probability of chain transfer to EDAB and of combination termination of propagating radicals, not only giving a descent tendency of ITXH• coupling with propagating

radicals, but also bringing about lower molecular weight and wider distribution of polymers (Figure 3).

Furthermore, higher molecular weight of polymers obtained by supplying more monomers in reaction system would provide an apparently low content of reduced ITX residue in resultant polymer (Figure 4). Actually, the probable envelopment of ITXH groups, derived mainly from the entanglement of high molecular weight of polymers, may be detrimental to get an effective re-initiation in a subsequent step. Herein, a macroinitiator, polymers contained more residues of reduced ITX and with shorter chain lengths in narrower distributions are favorable in the further thermal activated polymerization of St for achieving block copolymer. So, PMMA with molecular weight of 1.9×10^4, polydispersity index (PDI) of 3.1 and content of reduced ITX residue in PMMA-ITXH of 69.7 mol.% was selected.

## 3.2 Synthesis of PMMA-b-PSt Block Copolymer

In the presence of PMMA-ITXH, the bulk polymerization of St was performed to produce PMMA-b-PSt block copolymer at a temperature above 80°C. The capped
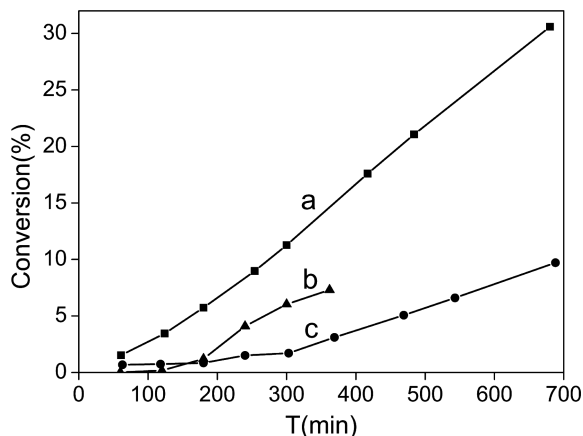
Fig. 5. Styrene conversion against reaction time (a, PMMA-ITXH%/wt = 3.53%, 90°C; b, blank thermal polymerization of St at 90°C; c, PMMA-ITXH%/wt = 3.53%, 80°C).

ITXH terminal groups in PMMA would be divorced from polymer chains by heating, re-generating macroradicals to initiate the bulk polymerization of styrene. The re-produced radical ITXH• could only serve as a terminator (Scheme 2).

The behavior of bulk polymerization initiated by PMMA-ITXH exhibited that an almost linear increase of conversion of St appeared along with reaction time (Figure 5), other than a typical S-shaped curve with an obvious induction period displayed in the self-initiating polymerization of St, even at a higher temperature. This phenomenon not only confirmed the initiation of PMMA-ITXH, but also implied the thermal self-initiating polymerization of styrene might be inhibited because of the pref-
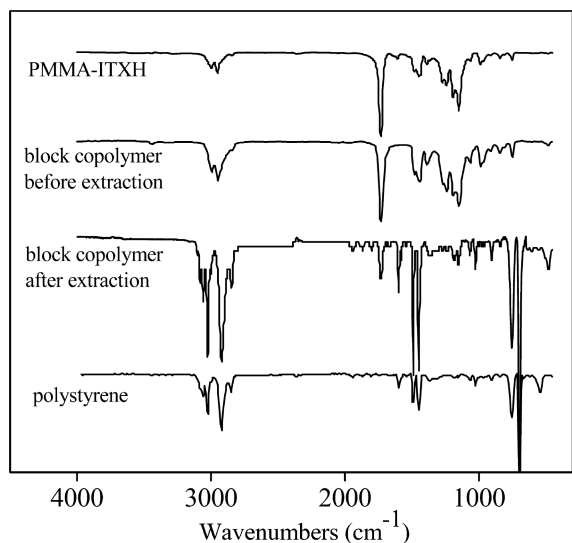
Fig. 6. FT-IR spectra of PMMA-ITXH, block copolymer before and after extraction, and PSt (PMMA-ITXH PMMA: Mn = 1.9×10^4, PDI = 3.1; PMMA-b-PSt, Mn = 8.1×10^4, PDI = 4.3).
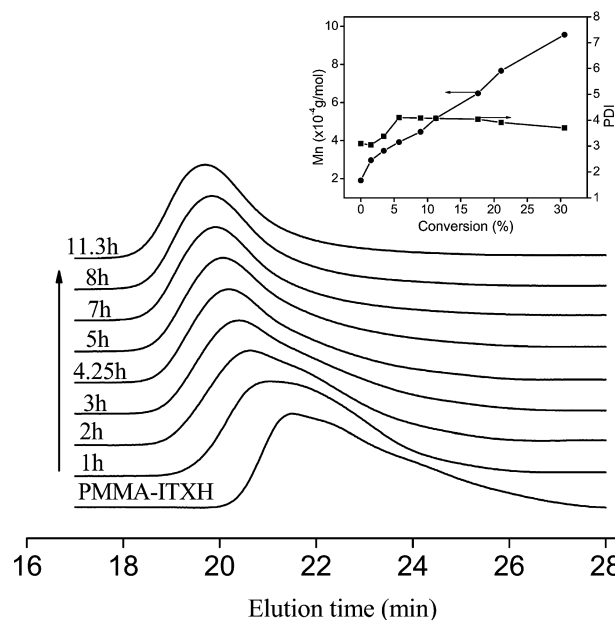
Fig. 7. GPC trace spectra of experiment in Figure 5(a), the arrow indicated the increase of reaction time; insert molecular weight and polydispersities of copolymers by GPC.

erence of initiation of PMMA-ITXH. Moreover, a higher temperature applied in the bulk polymerization of St would permit a remarkable improvement of conversion of St, due to more favored cleavage of weak C-C bond between ITXH group and polymer chain.

FTIR spectrum analysis of PMMA-b-PSt copolymer revealed the characteristic absorptions of PMMA and PSt (Figure 6). Among them, a band at 1,733 cm^{-1} could be attributed to the distinctive carbonyl stretching of PMMA segments. The weak absorption suggested the low concentration of PMMA segments in the copolymer, which could be ascribed to the dramatic improvement of molecular weight of polymer by the polymerization of St.

GPC measurement (Figure 7) showed the peaks of the end products obtained at prolonged reaction times gradually shifted to the positions at shorter elution times, indicating the increase of molecular weights of copolymer. At reaction time of 11.3 h, the molecular weight of end product grew up to 8.1×10^4, much higher than the initial value of 1.9×10^4. This also provided a direct evidence for the formation of block copolymer. On the other hand, the GPC peaks arising from PMMA-ITXH disappeared gradually, demonstrating that all PMMA-containing ITXH got involved in the second polymerization. However, the PDI of products exhibited an increase at first. This suggested that the macroradical's re-generation might be a slow procedure, and the re-initiation of PMMA-ITXH could not be started immediately and simultaneously. With the molecular chains growing to a longer length, the PDI showed a little bit reduction.

4 Conclusions

From the above description, it can be concluded that the block copolymer PMMA-b-PSt could be successfully synthesized through the first capping of ITXH groups on polymer chain ends and the sequential reversible cleaving of ITXH groups from polymer chain to initiate the further polymerization. This two-step method was simple to produce block copolymer only by heating the bulk system incorporated with precursor polymer containing ITXH dormant end groups.

Acknowledgement

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