

A facile method for synthesis of ABA triblock copolymers with macro-iniferter technique

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Abstract

A facile method for synthesis of well-defined ABA triblock copolymers, such as poly(vinyl acetate-*b*-styrene-*b*-vinyl acetate), was investigated. The polymerization proceeds 'living' radical mechanism realized by macro-iniferter technique. The macro-iniferters were designed and synthesized by 'living' radical polymerization of vinyl monomers utilizing diethyl 2,3-dicyano-2,3-di(*p*-*N,N*-diethyldithiocarbamylmethyl)phenylsuccinate (DDDCS) as a multi-functional iniferter, that is, under heating without ultra-violet (UV) light, DDDCS serve as a thermal iniferter by the reversible cleavage of the hexa-substituted C–C bond, while under UV light irradiation at ambient temperature, it serve as a photoiniferter by the reversible cleavage of the two diethyldithiocarbamyl (DC) functional groups. The polymers prepared via these two processes bearing α - and ω -DC end groups are macro-iniferters. The ABA triblock copolymers with different block components were easily synthesized via 'living' polymerization through these macro-iniferters. The formation of block copolymers were characterized by gel permeation chromatograph, ^1H nuclear magnetic resonance and differential scanning calorimeter analyses. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Living radical polymerization; ABA triblockcopolymer; Macro-iniferter

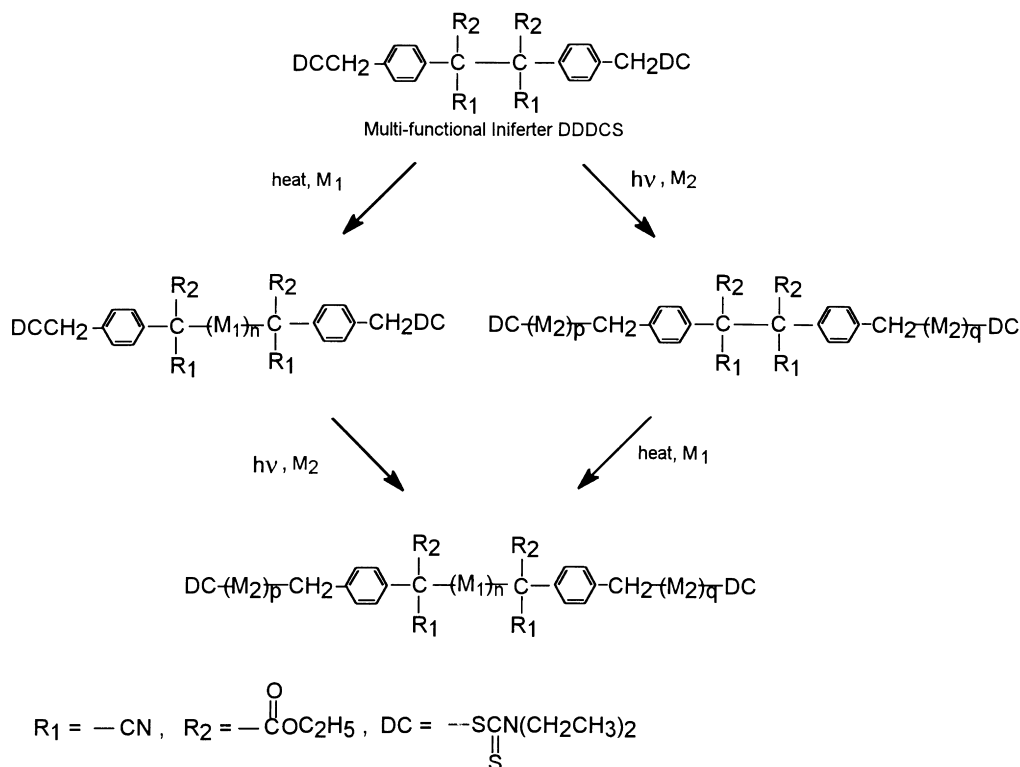
1. Introduction

Block copolymers often provide useful and unique properties which are not attainable in simple homopolymer or random copolymers. This is a result of the thermodynamic incompatibility of the constituent blocks, and leads to microphase separations with various phase morphologies. Therefore, controlling polymer properties through the synthesis of various kinds of block copolymers is a continuing theme in both industry and academic laboratories [1,2]. Polymerizations that are generally used to prepare block copolymers are ionic and coordination polymerizations because of the living nature of the polymer chain end [2]. These techniques are useful not only to control molecular weights and molecular weight distributions of the copolymers but also to control the components of block units in copolymers. Typical diblock copolymers such as polystyrene-*b*-polyisoprene and polystyrene-*b*-polybutadiene were prepared from anionic polymerization processes [3]. However, these materials are synthesized

under rigorous conditions in high vacuum, highly purified monomers and solvents. Furthermore, anionic polymerization is limited in the range of monomers which can be chosen. Free radical polymerization is the preferred process for polymer manufacturing because it possesses a relating economical process, that can tolerance to trace impurities and polymerize a wide range of monomers with various functional groups under mild reaction conditions and using water as reaction media. It has been in many years, the block copolymers are prepared through conventional radical polymerization by the sequential decomposition of difunctional initiators or polyfunctional initiators, such as an initiator having more than two azo or peroxy groups [4], azo and peroxy groups [5], redox and azo groups [6,7], azo and benzoin groups [8,9], and initiators containing azo, peroxy, perester, or diacyl groups [10]. However, these polymerizations generally produce mixtures of block copolymer and homopolymers, and their molecular weight and molecular weight distributions are not controlled. Recently, living free radical polymerizations [11–15] for controlled polymerizations of vinyl monomers have witnessed tremendous growth, and many attempts have been carried out for the synthesis of block copolymers using these techniques. For example, nitroxide-mediated stable free radical

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Scheme 1.

polymerization (SFRP) [12] is a major technique for living free radical polymerization, many styrene (St) and substituted styrenes block copolymers have been effectively synthesized by using 2,2,6,6-tetramethyl-1-piperdinolxy (TEMPO) and substituted TEMPO as stable free radicals [16–18], and some novel nitroxides were synthesized and used for the block copolymerization of a wide variety of monomer families recently [19,20]. Atom transfer radical polymerization (ATRP) [13,14] technique is another attractive route for block copolymers syntheses, and several block copolymers with well-defined structures have been successfully prepared by using this methods [21–23]. So far ATRP has not been successful in polymerization of vinyl acetate (VAc) and 1,3-dienes. More recently, some block copolymers containing butyl acrylate, isoprene (IP), or VAc segments have been synthesized by a sequential conventional/living radical polymerization using functionalized azoinitiators [24–26]. However, the molecular weight distributions and components of block units in copolymers are not well controlled by the processes, since one block is prepared by a conventional free radical polymerization process.

On the other hand, the iniferter technique [11] is a convenient and useful method in ‘living’ radical polymerization. Iniferter can be used for polymerization of various monomers, especially for VAc [27] and IP [28], with some ‘living’ characteristics, yet the molecular weight and the polydispersity are not well controlled. It has been reported that difunctional photoiniferter [29] and macro-iniferters [30–32] are used for the preparation of block copolymers.

In previous articles, we reported the synthesis of a novel compound, diethyl 2,3-dicyano-2,3-di(*p*-*N,N*-diethyldithiocarbamyl)phenylsuccinate (DDDCS) [33], and found that DDDCS can be used as a multi-functional iniferter for ‘living’ radical polymerization of St and methyl methacrylate (MMA) under ultra-violet (UV) light irradiation or under heating [34]. The resulting polymers bearing α - and ω -diethyldithiocarbamyl (DC) end groups are macro-iniferters. In this publication, we report the syntheses and characterization of several ABA triblock copolymers using a facile macro-iniferter technique. The general approach is shown in Scheme 1. One of the objectives of our research is also to prepare PVAc-*b*-PSt-*b*-PVAc copolymers with different block components by sequential polymerization of monomers via ‘living’ radical polymerization process, which is difficult to carry out with other present ‘living’ radical polymerization methods.

2. Experimental

2.1. Materials

Diethyl 2,3-dicyano-2,3-di(*p*-*N,N*-diethyldithiocarbamyl-methyl)phenylsuccinate was prepared according to a previously reported procedure [33]. IP from Fluka Chemical Company was stored over type A4 molecular sieves, other monomers were purified by washing with 5% sodium hydroxide aqueous solution, then with water, and dried over

magnesium sulfate over night. They were then fractionally distilled in vacuum over CaH₂ and stored in a refrigerator. Tetrahydrofuran (THF) and toluene were also distilled over CaH₂. Other reagents and solvents were used as received.

2.2. Preparation of macro-iniferters

The macro-iniferters were prepared by bulk polymerization of vinyl monomers with DDDCS multi-functional iniferter in sealed glass tubes after three freeze–pump–thaw cycles: MMA at 60°C, St at 85°C without UV light and under UV irradiation with a 250 W high pressure Hg lamp from a distance of 20 cm at ambient temperature, respectively. After polymerization for a given time, the resulting products were diluted and dissolved with THF, then poured into a large amount of methanol, the obtained macro-iniferters were purified by reprecipitation from a benzene–methanol system, and then dried in vacuum.

2.3. Synthesis of ABA block copolymers

All the block copolymerizations were carried out using the following procedure: to a glass tube, deaerated monomer (with macroiniferter dissolved, for polymerization) was added via a syringe under nitrogen atmosphere. After three freeze–pump–thaw cycles, the glass tube was sealed under vacuum, and the reaction mixture was heated in a temperature-controlled oil bath or under irradiation with a 250 W UV lamp at a distance of 20 cm at ambient temperature. After preset time periods, the tube was removed from the bath or the UV lamp, and the reaction mixture was dissolved in THF and precipitated into petroleum ether (PIP-*b*-PSt-*b*-PIP was precipitated into methanol). The precipitates were filtered, dried in vacuum, weighted and calculated for the monomer conversion. The separation of the mixture of homopolymers and block copolymer was carried out by solvent extraction. PMMA was extracted with 95% ethanol, PSt with cyclohexane and PVAc with methanol.

2.4. Analyses and characterization

Molecular weights and molecular weight distributions of the polymers were determined on a Waters gel permeation chromatograph (GPC) equipped with a 515 HPLC pump, 2410 refractive index detector, and the following three μ -Styragel columns (HT2 + HT3 + HT4). All samples were run in THF at 35°C at a rate of 1.0 ml/min. Linear polystyrene standards were used for calibration. The data were analyzed on a Waters Millennium 32 system. The number of the *N,N*-diethyldithiocarbamate (Et₂NCSS) end groups of the macroiniferter was determined in THF by UV spectroscopy recorded on a Shimadzu UV-250 instrument (benzyl *N,N*-diethyldithiocarbamate as standard, at 282 nm). ¹H nuclear magnetic resonance (NMR) spectra were recorded at 25°C on a Bruker ARX400 (400 MHz) spectrometer with CDCl₃ and tetramethylsilane (TMS) as solvent and

internal reference, respectively. The glass transition temperature (T_g) was determined with a TA DSC-2010 Differential Scanning Calorimeter (DSC) at a heating rate of 10°C/min, indium and tin were used for temperature calibration.

3. Results and discussion

3.1. Preparation of macro-iniferters

The macro-iniferters were synthesized by the bulk polymerization of MMA or St with DDDCS multi-functional iniferter. When MMA and St polymerizations were carried out at 60 and at 85°C without UV light, respectively, the resultant polymers referred as PMMA–CCDCM and PSt–CCDCM were obtained. CCDCM is the abbreviation of carbethoxy-cyano-*p*-(diethyldithiocarbamylphenyl)methyl end group, which contains a DC group either. When St polymerization was carried out under UV light irradiation at ambient temperature, the product was stamped as PSt–DC. Because the DDDCS can not dissolve in MMA at ambient temperature, only the thermal polymerizations of MMA initiated with DDDCS were performed. In our previous studies on the mechanism of the free radical polymerization of MMA and St with DDDCS by electron paramagnetic resonance revealed that DDDCS under heating acted as a thermal iniferter by the reversible hexa-substituted C–C bond dissociation and under UV light irradiation as a photoiniferter by the reversible C–S bonds dissociation. In both cases, the molecular weights of the resultant polymers increased with time and conversion [34]. Therefore, it is easy to obtain the macro-iniferters with different molecular weights bearing α - and ω -DC groups, and then under UV light irradiation through the polymerization of second monomer with these macro-iniferters, ABA type block copolymers were facily formed as shown in Scheme 1. The polymerization data for syntheses of macro-iniferters are list in Table 1, the well-defined structures of the obtained macro-iniferters, that is, PMMA–CCDCM, PSt–CCDCM and PSt–DC, are shown

Table 1
The data of macro-iniferters preparation

Macro-iniferter	Time (h)	Conversion(%)	M_n	M_w/M_n	N_e^a
PSt–CCDCM ^b	1.0	25.5	32,800	1.44	1.99
	2.0	39.7	41,500	1.59	2.00
PMMA–CCDCM ^c	1.0	21.7	43,200	1.48	1.97
	1.5	17.2	3,900	1.74	2.01

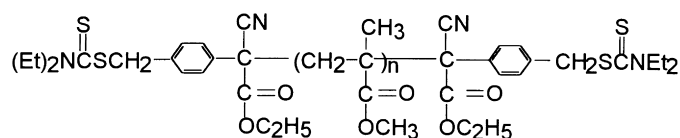
^a Numbers of Et₂NCSS (DC) end group.

^b [St] = 8.7 mol L⁻¹, [DDDCS] = 2.2 × 10⁻² mol L⁻¹, at 85°C without UV light.

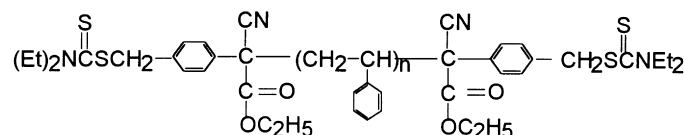
^c [MMA] = 9.4 mol L⁻¹, [DDDCS] = 4.7 × 10⁻² mol L⁻¹, at 60°C without UV light.

^d [St] = 8.7 mol L⁻¹, [DDDCS] = 2.2 × 10⁻² mol L⁻¹, under UV irradiation at ambient temperature.

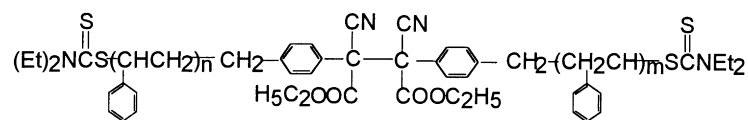
PMMA–CCDCM :



PSt–CCDCM :



PSt–DC :



Scheme 2.

in Scheme 2. From this scheme, we can find that all the macro-iniferters have α - and ω -DC groups, and PSt–DC contains a central hexa-substituted C–C functional group as well.

3.2. Block copolymerization of vinyl monomers with PSt–CCDCM as a macro-photoiniferter

Otsu et al. [29] reported that *p*-xylylene bis(*N,N*-diethyldithiocarbamate) can be used as difunctional photoiniferter for the ‘living’ polymerization of St and MMA. The resultant polymers bearing α - and ω -DC end groups were used as macro-photoiniferter for second monomer including VAc polymerization to prepare ABA block copolymers. Yang and Qiu [30,31] have reported that polyethers with α - and ω -DC groups can be used as macro-photoiniferters for synthesis of ABA type block copolymers. As reported in literature, photoiniferter technique is the unique method for the ‘living’ radical polymerization of VAc [27]. Because PSt–CCDCM has α - and ω -DC end groups, an analogue of *p*-xylylene bis(*N,N*-diethyldithiocarbamate), it can serve as a macro-photoiniferter for the ‘living’ block copolymerization of VAc.

Fig. 1 represents GPC elution curves for the VAc block copolymerization with PSt–CCDCM macro-photoiniferter in different polymerization times. It can be seen that in all of cases, the unimodal peaks are obtained and the peaks move distinctly to high molecular weight (M_n) position with increasing the time. This shows the formation of PVAc-*b*-PSt-*b*-PVAc copolymer with different molecular weights. The conversion of VAc monomer and M_n of the resultant PVAc-*b*-PSt-*b*-PVAc copolymers increase with time, and

the molecular weight distributions (MWDs) are always less than 1.90. The formed block copolymers are also characterized by ^1H NMR and DSC. ^1H NMR data shown in Fig. 2 are drawn with the absorption of the benzene ring protons in PSt as standard, the chemical shifts at 4.9 ppm are assigned to the absorption of the methyl protons in PVAc. From this figure, it is evident that the absorption of PVAc increases with increasing the reaction time from 0 to 20 h (A)–(F), indicating that the contents of VAc block units increase with time and conversion. Typical DSC curves of the block copolymers obtained at different VAc conversion are shown in Fig. 3, the T_g at 42.5°C belongs to the PVAc segments, and the T_g at 105°C belongs to the PSt segments.

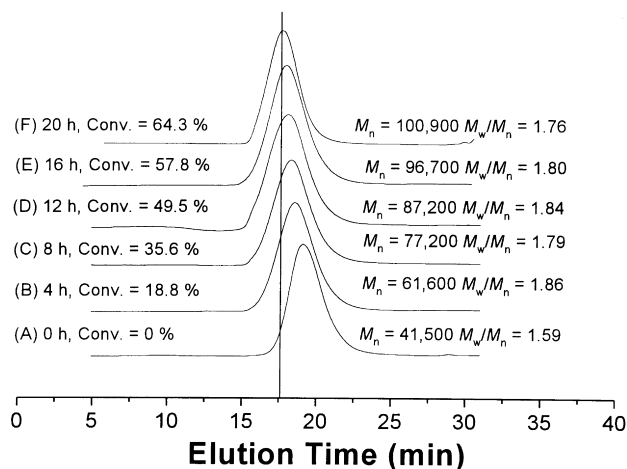


Fig. 1. GPC curves of PSt–CCDCM and PVAc-*b*-PSt-*b*-PVAc copolymers. [VAc] = 10.8 mol L⁻¹, [PSt – CCDCM] = 1.6 × 10⁻³ mol L⁻¹.

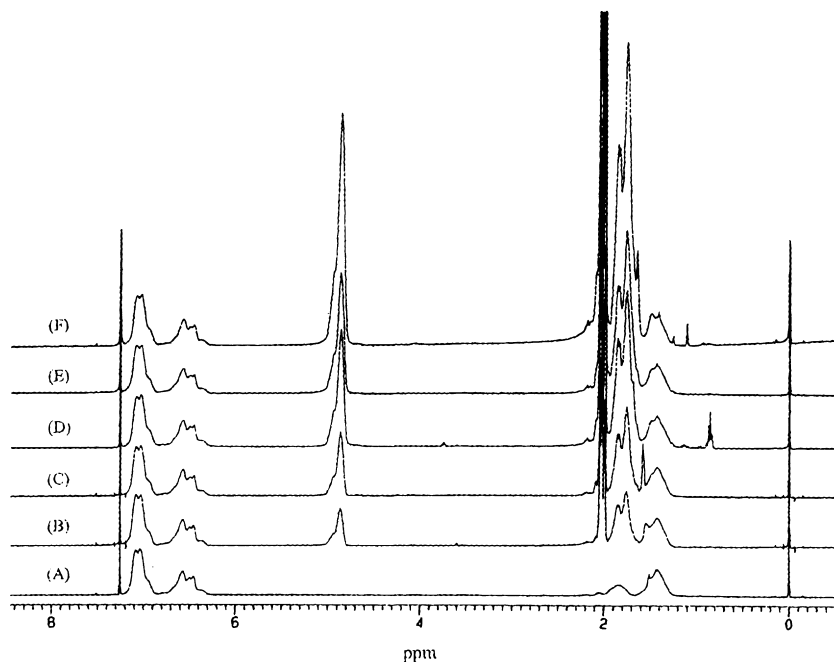


Fig. 2. ^1H NMR spectra of PSt-CCDCM and PVAc-*b*-PSt-*b*-PVAc copolymers. Content of VAc in mol%: (A) 0; (B) 34.7; (C) 43.2; (D) 56.3; (E) 60.1; (F) 72.3. See Fig. 1 for detailed conditions.

At low VAc conversions, the content of PVAc in the block copolymer is less than that of PSt (curve a in Fig. 3), the T_g of PVAc segments is not as distinct as that of PSt. With increasing the content of PVAc and decreasing of PSt in the copolymer, the T_g of PVAc segments becomes more distinctly, while the T_g of PSt segments become gradually disappears at last (curve d in Fig. 3). The DSC data confirm that the PVAc composition increases with increasing conversion. All these results indicate that the photo-induced block copolymerization of VAc with PSt-CCDCM macro-iniferter is a 'living' process, the chain length of PVAc segments can be determined by the VAc conversion. The chain length of PSt segments, on the other

hand, depends on the molecular weight of macro-iniferter used.

Similarly, PMMA-*b*-PSt-*b*-PMMA triblock copolymers are synthesized by using PSt-CCDCM macro-iniferter and the successful formation of triblock copolymers are characterized with GPC, ^1H NMR and DSC analyses. Fig. 4 shows the GPC elution curves, from which the M_n of the obtained block copolymers increases with increasing reaction time. Also, the increasing correlation of M_n with conversion can be obtained. The ^1H NMR spectra shown in Fig. 5 confirms the progressive incorporation of MMA into the block polymerization product with increasing reaction time. The successive increase of

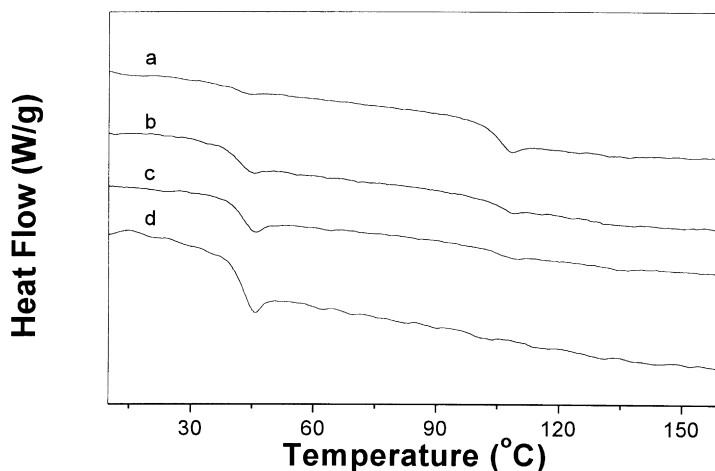


Fig. 3. DSC curves of PVAc-*b*-PSt-*b*-PVAc copolymers. Conversion of VAc (%): (a) 18.8; (b) 49.5; (c) 57.8; (d) 64.3.

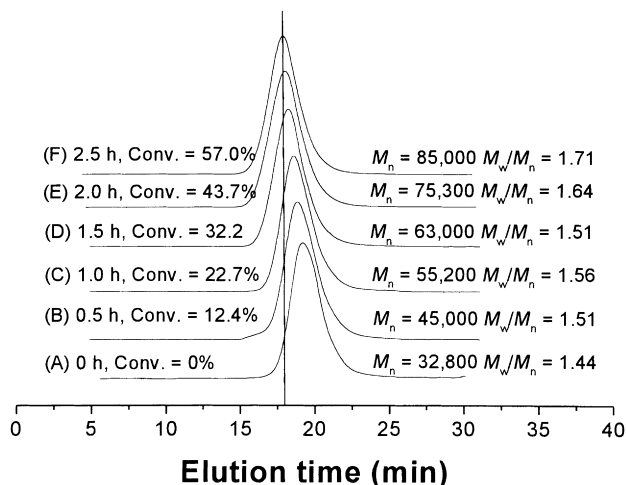


Fig. 4. GPC curves PSSt-CCDCM and PMMA-*b*-PSt-*b*-PMMA copolymers. [MMA] = 9.4 mol L⁻¹, [PSt-CCDCM] = 3.1 × 10⁻³ mol L⁻¹.

PMMA contents with conversion in block copolymers is further supported by DSC analysis as shown in Fig. 6, in which the T_g appears at 107°C is attributed to the PSt blocks, and the T_g at 121°C is from the PMMA blocks. These results indicate that the block copolymerization of MMA with PSt-CCDCM macro-iniferter is a 'living' process. The PSt/PMMA ratio can be controlled by MMA conversion.

Block copolymerizations of other monomers with PSt-CCDCM macro-iniferter are also attempted. The results are compiled in Table 2. It shows that the M_n of the obtained

block copolymers is greater than that of the original PSt-CCDCM macro-iniferter used in all the cases, revealing the feasibility of preparation of these block copolymers using this approach.

3.3. Block copolymerization with PMMA-CCDCM as a macro-photoiniferter

As depicted in Scheme 2, PMMA-CCDCM bears α - and ω -DC end groups, it can be used as a difunctional photoiniferter. The photopolymerization of St in the presence of PMMA-CCDCM under UV light irradiation produces a PSt-*b*-PMMA-*b*-PSt triblock copolymer. The M_n increase with increasing the conversion is found in Fig. 7, indicating that the polymerization has a 'living' characteristic. The ¹H NMR spectra in Fig. 8 show that the absorption of the methyl protons in PMMA is at 0.78–1.11 ppm as standard, the signals at 6.2–7.2 ppm are assigned to the absorption of the benzene ring in PSt. Furthermore, the existence of PMMA and PSt blocks can be clearly identified, and the St amount in the block polymer increase with the reaction time. In addition, increasing PSt blocks with increasing the conversion can also be revealed in DSC curves (Fig. 9). The T_g appeared at 106°C is the transition of PSt blocks, and the T_g at 121°C is attributed to PMMA blocks. A gradually appearance of the T_g at 106°C and slowly diminishing T_g at 121°C can be found in the curves a–d.

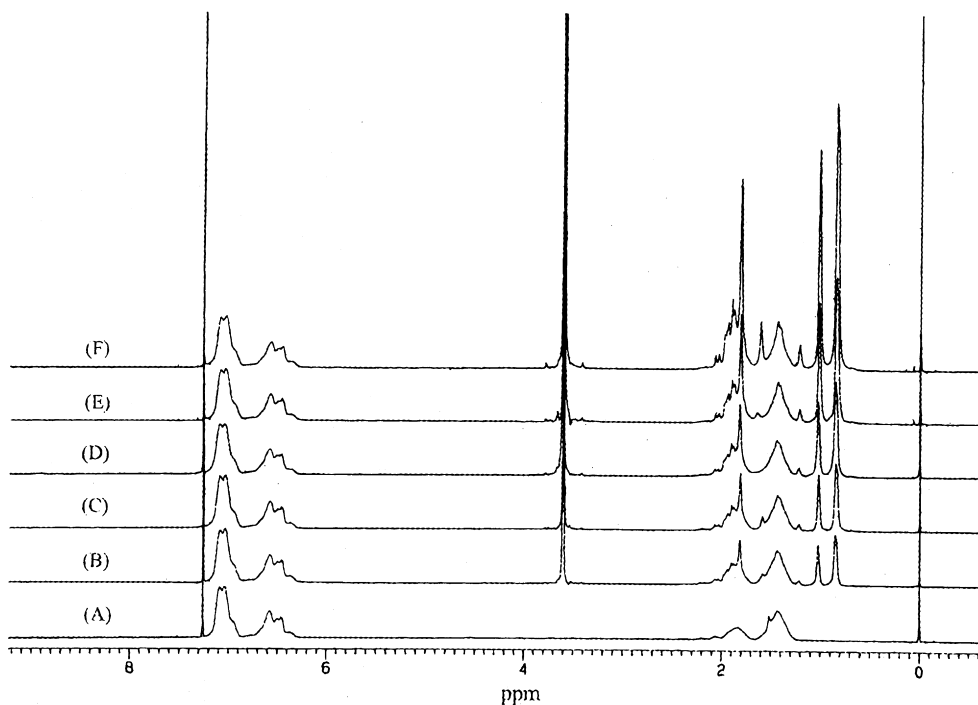


Fig. 5. ¹H NMR spectra of PSSt-CCDCM and PMMA-*b*-PSt-*b*-PMMA copolymers. Content of MMA in mol%: (A) 0; (B) 26.7; (C) 38.6; (D) 49.8; (E) 58.4; (F) 69.2. See Fig. 4 for detailed conditions.

Table 2
Block copolymerization of PSt–CCDCM ($M_n = 32,800$; $M_w/M_n = 1.44$)
with monomers in bulk under UV light for 5 h

Monomers	Conversion (%)	M_n	M_w/M_n
St ^a	11.2	49,200	1.80
BA	84.6	99,500	1.94
EA	82.0	92,200	2.07
MA	78.5	109,800	2.15
IP ^b	46.3	96,500	1.64
AN ^c	34.7	–	–

^a In this case the product is extended PSt.

^b In toluene for 22 h.

^c In DMSO.

3.4. Block copolymerization with PSt–DC as a macro-thermal-iniferter

The PSt–DC contains a central hexa-substituted C–C functional group, which is an analogue of diethyl 2,3-dicyano-2,3-diphenylsuccinate (DCDPS). We have reported that DCDPS can serve as a thermal iniferter for MMA polymerization by a ‘living’ radical mechanism [35]. Therefore, PSt–DC can be used as a macro-thermal-iniferter for MMA polymerization and the resulting polymers should be a PSt-*b*-PMMA-*b*-PSt triblock copolymer according to the Scheme 1. The polymerization is carried out at 70°C in different time periods. In GPC traces (Fig. 10), it can be seen that the peak of PSt–DC decreases as the polymerization progresses and the block copolymers with high M_n are obtained. The M_n of the block copolymers increases with increasing reaction time. This also shows the ‘living’ polymerization character. However, different from the case in above discussed macro-photoiniferter block copolymerization, trace amount of the macro-iniferter remains after 10 h in this thermal-iniferter block copolymerization. This is due to that the reactivity of the central hexa-substituted C–C bond is weaker than that in the case of small molecule DCDPS. Also, in this case the reversible termination group is a macroradical as shown in Scheme 1. It capps the

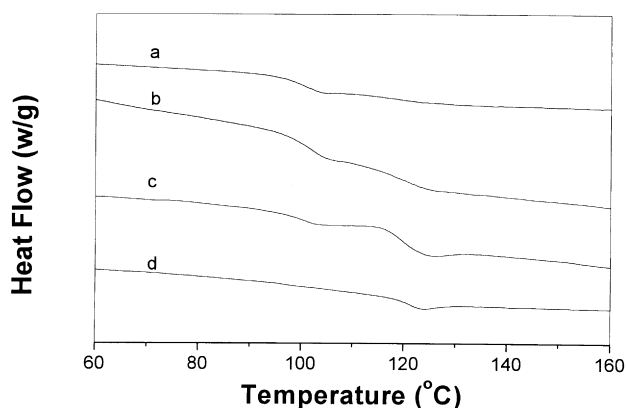


Fig. 6. DSC curves of PMMA-*b*-PSt-*b*-PMMA copolymers. Conversion of MMA (%): (a) 12.4; (b) 22.7; (c) 43.7; (d) 57.0.

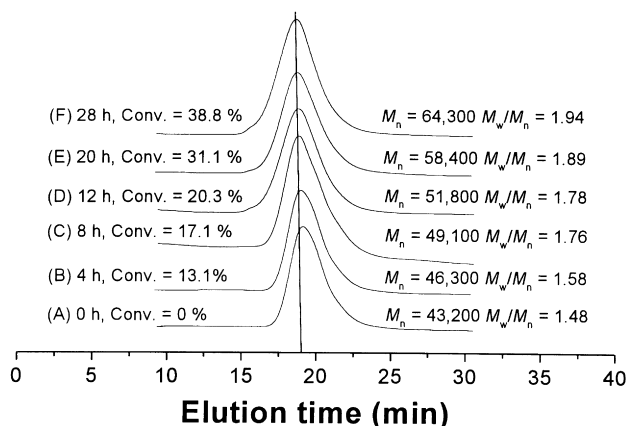


Fig. 7. GPC curves of PMMA–CCDCM and PSt-*b*-PMMA-*b*-PSt copolymers. $[St] = 8.7 \text{ mol L}^{-1}$, $[PMMA - CCDCM] = 2.3 \times 10^{-3} \text{ mol L}^{-1}$.

propagating radical reversibly which may be not as efficient as the DC radical in photopolymerization. Termination of the propagating radicals by irreversible coupling or disproportionation may thus exist in this system. It is concluded that this PSt–DC macro-thermal-iniferter is not as efficient as using PMMA–CCDCM in preparation of PSt-*b*-PMMA-*b*-PSt copolymer.

3.5. Comparison of the yield of block copolymer by using different macro-iniferters

As described in the experimental sections, the weight percentage of block copolymer in the total yield was determined by solvent extraction method, i.e. PMMA was extracted with 95% ethanol, PSt with cyclohexane and PVAc with methanol, respectively. Results of block copolymerizations of vinyl monomers with different macro-iniferters are list in Table 3.

As it can be seen from this table, in all case, the block copolymers were obtained in high yields. When the block copolymers are produced from block copolymerization of VAc by using PSt–CCDCM, the block percentage and the contents of homopolymers are different with VAc conversion, e.g. when the VAc conversion increased from 18.8 to 64.3%, the contents of homoPSt decreased from 6.94 to 1.64%, while homoPVAc increased from 2.75 to 9.42%. This is partly because that the separation of homopolymers from block copolymer is by solvent extraction method, i.e. in low VAc conversion, the chain length of PVAc segments is shorter than that of PSt segments in block copolymers, some of block copolymers containing short PVAc chain are also extracted by cyclohexane. The contrary case is in high VAc conversion.

Comparing the block copolymerization of MMA and St with PSt–CCDCM and PMMA–CCDCM as macro-iniferters, respectively, it can be found that 8.52% homo-PMMA and 2.53% homoPSt were produced during the photopolymerization. The diversity seems to be originated from the photo-dissociation at different sites of C–S bond

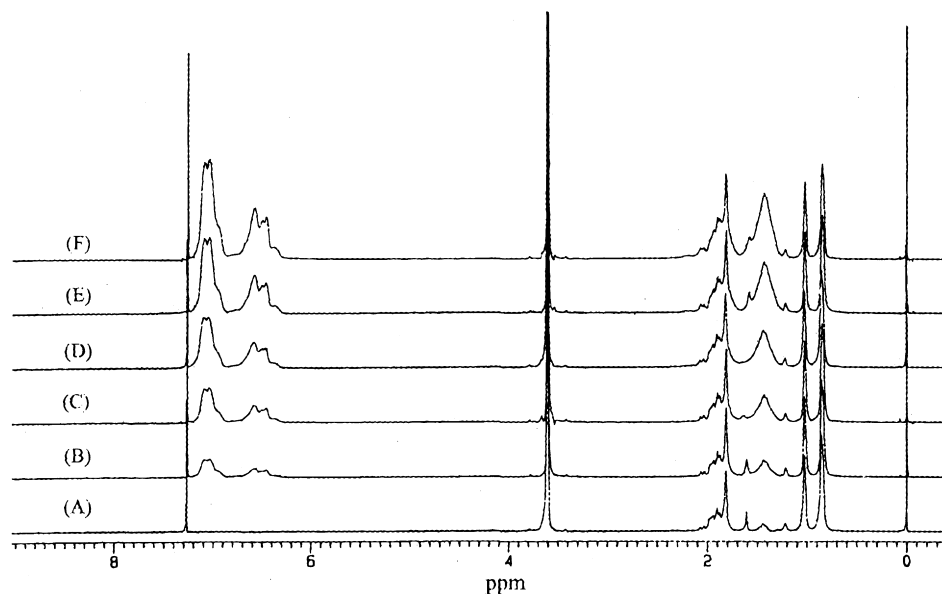


Fig. 8. ^1H NMR spectra of PMMA-CCDCM and PSt-*b*-PMMA-*b*-PSt copolymers. Content of St in mol%: (A) 0; (B) 29.0; (C) 42.6; (D) 51.2; (E) 61.4; (F) 68.7. See Fig. 7 for detailed conditions.

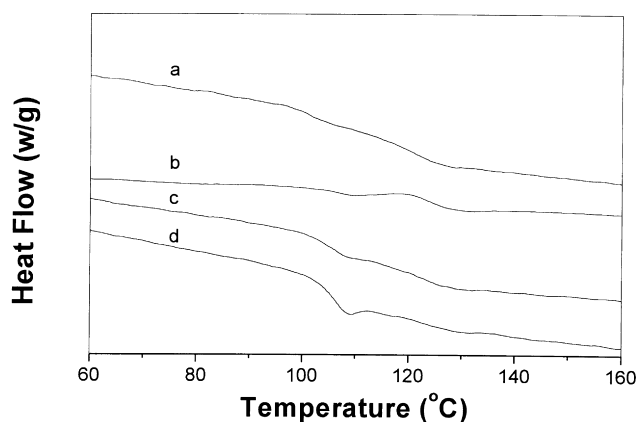


Fig. 9. DSC curves of PSt-*b*-PMMA-*b*-PSt copolymers. Conversion of St (%): (a) 13.1; (b) 17.1; (c) 20.3; (d) 38.8.

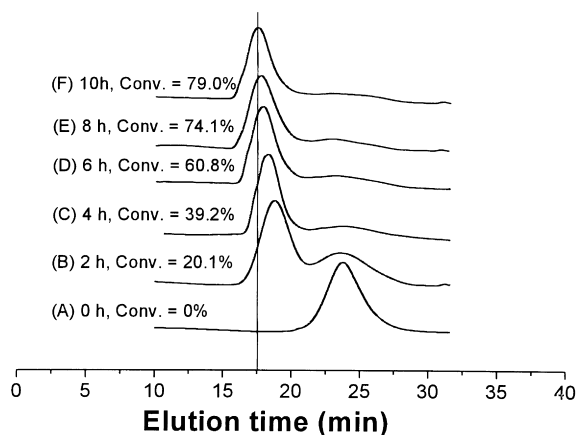


Fig. 10. GPC curves of PSt-DC and PSt-*b*-PMMA-*b*-PSt copolymers. PSt-DC with $M_n = 3,900$, $[\text{MMA}] = 9.4 \text{ mol L}^{-1}$, $[\text{PSt-DC}] = 2.1 \times 10^{-2} \text{ mol L}^{-1}$.

[36] as shown in Scheme 3. In the case of St polymerization initiated with PMMA-CCDCM, there is only one site of C-S bond dissociation, thus the polymerization can proceed with 'living' manner. While in the case of MMA polymerization with PSt-CCDCM, two positions of C-S bonds, *a* and *b*, can be dissociated under UV light irradiation. Although 'living' radical polymerization is performed by successive dissociated at cite *a*, a part of the PMMA end may be dissociated at site *b*, to give an unreactive polymeric thiol radical and a reactive carbon radical which undergoes homopolymerization.

The yields of block copolymers for both methods using PSt-CCDCM and PSt-DC for MMA polymerization were also shown in Table 3. It can be seen that, during the polymerization, little of homoPMMA was produced by using PSt-DC as a thermal iniferter than by using PSt-CCDCM as a photoiniferter, this is due to the different polymerization mechanism as shown in Schemes 1 and 3. While more macro-iniferter was left when using PSt-DC as a thermal iniferter, this may be due to the low reactivity of the central hexa-substituted C-C bond in macro-iniferter chain as discussed above.

4. Conclusion

Several ABA triblock copolymers have been successfully synthesized by 'living' radical polymerization process with macro-iniferter technique. The GPC results show that the molecular weights of the resulting block copolymers increase with increasing reaction times. ^1H NMR and DSC analyses reveal that the contents of the second blocks increase with increasing conversion. The molar ratio of the two compositions in block copolymers may be controlled

Table 3
Results of polymerizations of vinyl monomers with different macro-iniferters

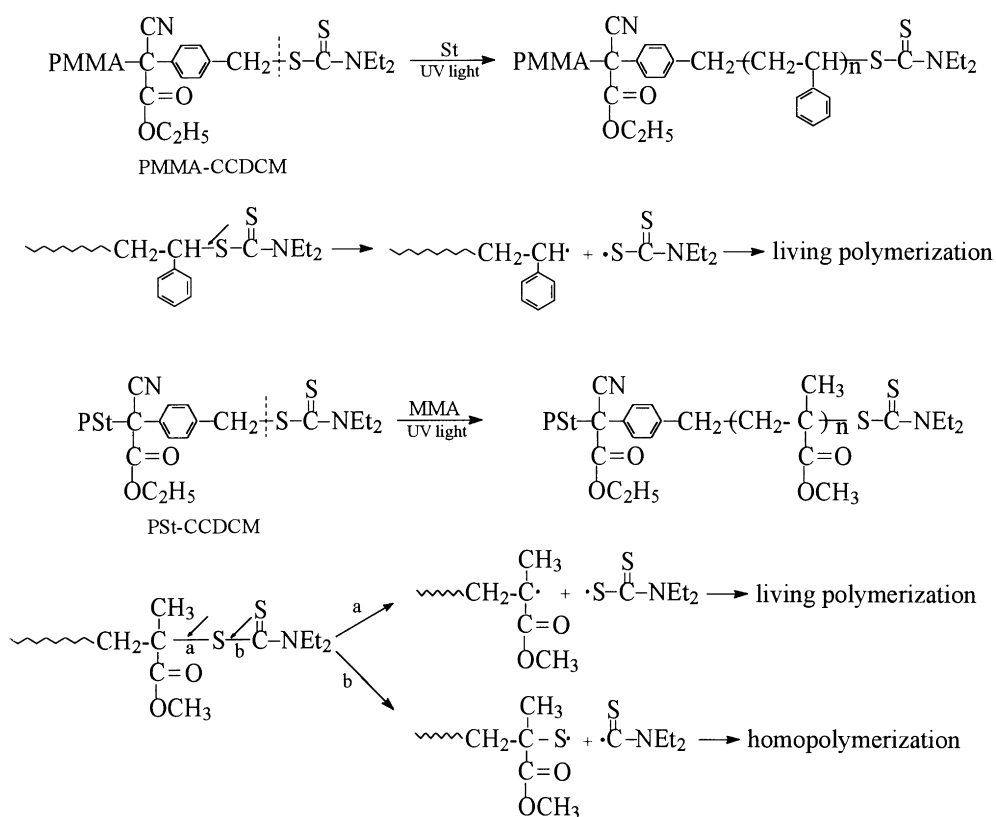
Macro-iniferter	Second monomer	Time (h)	Total yield (g)	Conv. (%)	Fraction isolated (wt%)		
					HomoPM ₁	HomoPM ₂	Block copolymer
PSt-CCDCM ^a	VAc	4	0.363	18.8	6.94	2.75	90.31
PSt-CCDCM ^a	VAc	12	0.791	49.5	2.16	6.10	91.74
PSt-CCDCM ^a	VAc	20	0.997	64.3	1.64	9.42	88.94
PSt-CCDCM ^b	MMA	2.5	0.815	57.0	1.83	8.52	89.65
PMMA-CCDCM ^c	St	28	0.784	38.8	5.49	2.53	91.98
PSt-DC ^d	MMA	6	0.796	60.8	7.16	3.36	89.48

^a See Fig. 1 for detailed conditions.

^b See Fig. 4 for detailed conditions.

^c See Fig. 7 for detailed conditions.

^d See Fig. 10 for detailed conditions.



Scheme 3.

arbitrarily by the molecular weight of the macro-iniferter used and the monomer conversion. It provides a facile way for preparations of ABA triblock copolymers via 'living' radical polymerization technique, especially for those block copolymers of PVAc-*b*-PSt-*b*-PVAc, that can not be synthesized by others 'living' radical polymerization methods.

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