

PREPARATION OF ALKOXYSILANE FUNCTIONAL WATER SOLUBLE BLOCK COPOLYMERS VIA RAFT POLYMERIZATION

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Abstract

*Alkoxysilane bearing polymers are hybrid compounds that combine the functionality of a reactive group and the inorganic functionality within an organic macromolecule. However, it may be a challenge to prepare copolymers of vinyl silane monomers due to their low reactivity ratios. Present study describes the synthesis of block copolymers of vinyltriethoxy silane (VTES) with various water soluble acrylic polymers (PAA, PMAA, PAAm) using RAFT polymerization technique with different approaches. The polymerization conditions, control on the molecular weights as well as the characterization of obtained block copolymers were discussed in detailed. The FTIR, H-NMR, GPC and DSC analyses verified the presence of VTES segments on block copolymer structure. It was concluded that PMAA-*b*-PVTES and PAA-*b*-PVTES diblock copolymers can be synthesized successfully under appropriate reaction conditions.*

Key words: RAFT, alkoxysilane, acrylic polymers, block copolymer, VTES

1. INTRODUCTION

Organic/inorganic hybrid materials have considerable attention by researchers due to their potential applications in many fields such as composites, coatings, membranes, catalysis, biology, optoelectronics, etc. The inorganic constituents like silicon alkoxides can react with the oxide framework and link together the organic and inorganic components. Vinyl monomers carrying silane functionality in the monomer unit gives possibility to prepare organic-inorganic hybrid copolymers that are capable of participating directly in the sol–gel-type network formation process in the presence of an appropriate acidic or basic catalyst (Mori et al. 2013). Block copolymers with one block carrying alkoxysilane functionalities would be particularly well suited as reactive building blocks for many applications (Mellon et al. 2005). One way to prepare well-controlled block type copolymers is the use of controlled radical polymerization techniques (CRP) including Reversible Addition Fragmentation Chain Transfer (RAFT), Atom Transfer Radical Polymerization (ATRP), Nitroxide-Mediated Radical Polymerization (NMP).

Among the controlled radical polymerization techniques RAFT polymerization mechanism has advantages in comparison to NMP and ATRP since it is applicable to a wide range of monomers, having no metal contamination and other catalysts but a proper chain transfer agent. Among the monomers; styrene and its derivatives, acrylates, acrylamide, methacrylates, methacrylamide, butadiene, vinyl acetate and several vinyl monomers such as vinyl pyrrolidone have been successfully polymerized via RAFT technique with controlled molecular weights. The technique also provides living type polymers that give possibility for the synthesis of di/tri block copolymers with different architectures.

In RAFT polymerization, the control is provided by a series of complex reactions and formation of intermediary products (Chieffari et al. 2003, Chong et al. 2003). The most important component of RAFT polymerization is the chain transfer agent (CTA). The thio-carbonyl-thio compounds are usually used as chain transfer agents and commonly constitute the family of dithioesters, dithiocarbamates, trithiocarbonates and xanthates. The choice of right CTA for each monomer to be synthesized by RAFT is crucial. The use of improper CTA may cause problems in the control of

reaction, retardation, long reaction times or complete inhibition of the reaction (Mayadunne et al. 1999, Barner-Kowollik et al. 2001, Kwak et al. 2002). The RAFT agents are usually chosen depending on the nature of Z and R groups in their structures (Smith et al. 2010). It is also important to pay attention to some factors such as the concentration and choice of initiators. The RAFT polymerization is usually performed by the conventional radical initiators, most preferably thermal initiators such as azo-based initiators (AIBN, ACVA) or persulfates (i.e. $K_2S_2O_8$). On the other hand it may be advantageous to use an initiator which has the same function with the -R group of CTA (Moad et al. 2005). Therefore, a good control on the polymerization can be achieved with a careful selection of the components and reaction parameters.

Hydrophilic acrylic polymers (poly(meth)acrylic acid –P(M)AA-, polyacrylamide –PAAm-) are polyelectrolytes which are used extensively in various fields such as pharmaceuticals, rheology modifiers, coatings, etc. They are also used in random or block copolymer synthesis for different purposes in combination with other monomers. These ionic block copolymers possess quite unique and attractive properties that can be used in stabilization of colloids, crystal growth modification, induced micelle formation, components of intelligent materials, polyelectrolyte complexing towards novel drug carrier systems (Mori et al. 2003). With the advances in controlled/living polymerization techniques it's possible to prepare such block copolymers. Although there are some problems in NMP and ATRP polymerization of these hydrophilic acrylates regarding the interaction with catalysts or need for specific reaction conditions, RAFT technique seems the most monomer compatible CRP technique and has been extensively used to control the polymerization of water-soluble monomers (Ji et al. 2010, Chaduc et al. 2012).

Present study describes the synthesis of organic-inorganic block copolymers composed of hydrophilic acrylic monomers (methacrylic acid, acrylic acid and acryl amide) and vinyltriethoxysilane via RAFT polymerization. The syntheses were performed either using first block as macro-RAFT agent or one-pot approach by addition of second block subsequent to the first block synthesis. The effect of different CTAs and reaction parameters were discussed to achieve successful control on the polymerizations.

2. MATERIALS AND METHODS

2.1. Materials

Methacrylic acid (MAA, 99%, Sigma-Aldrich), acrylic acid (AA, 99%, Sigma-Aldrich), acrylamide (AAM, 98%, Sigma-Aldrich), vinyl triethoxysilane (VTES, 97%, Sigma-Aldrich) were used as monomers in polymer syntheses. 2-cyano 2-propyldodecylthiocarbonate (CTA-I, 97%, Sigma-Aldrich), 4-cyano 4-dodecyl sulfonyl thiocarbonyl sulfonyl pentanoic acid (CTA-II, 97%, Sigma-Aldrich), 4-cyano 4-phenyl carbonothioylthiopentanoic acid (CTA-III, 97%, Sigma-Aldrich), 2-dodecylthiocarbonothioylthio-2-methyl propionic acid (CTA-IV, 98%, Sigma-Aldrich) were used as chain transfer agents (CTA) in RAFT polymerizations. As the radical initiator 2,2'-azobis 2-methylpropionitrile (AIBN, 98%, Sigma-Aldrich) and 4,4'-azobis 4-cyanovaleric acid (ACVA, 98%, Sigma-Aldrich) were used. Dimethyl sulfoxide (DMSO, $\geq 99.9\%$, Sigma-Aldrich), ethanol (EtOH, $\geq 99.8\%$, Sigma-Aldrich), methanol (MeOH, $\geq 99.9\%$, Sigma-Aldrich), 1,4-dioxane (DO, $\geq 99\%$, Sigma-Aldrich), 2-propanol (2-POH, $\geq 99.8\%$, Merck) solvents were used as the reaction medium in polymerizations. Ethyl acetate (EA, $\geq 99.5\%$, Sigma-Aldrich), diethylether (DEE, $\geq 99.5\%$, Sigma-Aldrich) and n-hexane (Heg, $\geq 99.5\%$, Sigma-Aldrich) were used in purification of polymers after reactions.

The monomers methacrylic acid, acrylic acid and vinyltriethoxysilane were distilled under vacuum to remove the containing inhibitors before the polymerization including copper wire fragments to prevent radical formation. AIBN, ACVA and acrylamide monomer were purified by recrystallization in methanol. All solvents used as the reaction medium were kept over molecular sieves 4A and distilled under vacuum to remove the water content.

2.2. Methods

2.2.1. Synthesis of acrylic Macro-RAFT agent

For the preparation of block copolymers, acrylic homopolymers were synthesized and subsequently used as macro-CTA agent for the synthesis of PVTES. In a typical synthesis the first block was synthesized as follows; 0.85 mL MAA (10 mmol), 35.6 mg CTA-I (0.1 mmol), 4.1 mg AIBN (0.025 mmol), 4.15 mL DMSO were added in a 20 mL reaction tube and mixed. Nitrogen was purged through the tube for 45 min in order to remove the dissolved oxygen from the system. Then the reaction tube was immersed in a pre-heated glycerin bath at 75 °C and reacted for 24 hours. The [Monomer] / [CTA] / [I] molar ratios were selected to be [100] / [1] / [0.25] respectively and the total monomer concentration of the system was adjusted to be 2 M in all experiments. At the end of the reaction, the reaction was terminated by immersing the glass tube in an ice bath. The polymer solution in DMSO was precipitated in ethyl acetate (EA) (10 times in volume), then filtered under vacuum, washed with EA and first block polymer (PMAA-CTA) to be used as macro RAFT agent was obtained after drying in vacuum oven at 60 °C for 24 hours.

2.2.2. Synthesis of block copolymers using Macro-RAFT agent

Previously synthesized acrylic homopolymers were used as Macro-CTA for the polymerization of VTES. In a typical polymerization recipe; 1.1 mL VTES (5.2 mmol), 1.0 g Macro-CTA-PMAA (0.13 mmol, $M_n=7720$ g/mol, PDI=1.26), 9.1 mg ACVA (0.0325 mmol) were mixed in 6 mL DMSO until a homogeneous solution obtained. After purging with N₂ for 45 min the reactor was sealed and immersed in a pre-heated glycerin bath at 75 °C. The reaction was continued for 48 hours. At the end of the reaction, the mixture was cooled in an ice bath and precipitated in cold hexane, filtered and washed. The block copolymer was obtained after drying in vacuum oven at 45 °C for 48 h.

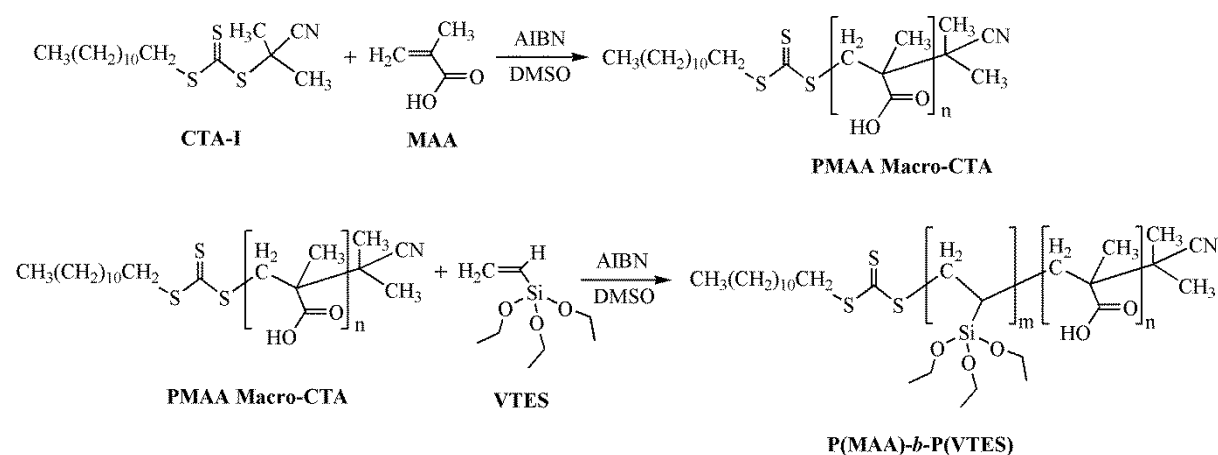
2.2.3. One-pot synthesis of block copolymers

The block copolymers were also synthesized by using a continuous system. For this purpose, the first acrylic block was polymerized until the conversion was above 90 %. Subsequently, the second block monomer was injected to the reaction medium to obtain block copolymers. In a sample polymerization prescription: 1.37 mL AA (20 mmol), 74.4 mg CTA-IV (0.2 mmol), 8.2 mg AIBN (0.05 mmol) were dissolved in 8.6 mL EtOH, N₂ was purged through system for 45 min, then the flask was sealed and reacted at 75 °C for 24 h. In a separate tube, 2.1 mL VTES (10 mmol), 3.3 mg AIBN (0.02 mmol) was dissolved in 3.4 mL EtOH and purged with N₂ for 30 min in an ice bath. The mixture was carefully added to reaction flask containing PAA block. The reaction was continued for another 48 h and terminated by immersion in ice bath. At the end of the reaction, the cooled reaction solution was precipitated in cold hexane, filtered and washed repeatedly. The final block copolymer was obtained after drying in vacuum oven at 45 °C for 48 h.

In both techniques, the theoretical number average molecular weights of block copolymers were determined by using the following equation.

$$M_{n,th} = \frac{[M]_0 \cdot M_{Mw} \cdot \rho}{[Macro-CTA]_0} + Macro-CTA_{Mw} \quad (eq. 1)$$

where $M_{n,th}$ is the theoretical number average molecular weight (g/mol), $[M]_0$ is the mole number of second block monomer (VTES), M_{Mw} is the weight of one mole monomer, ρ is the monomer conversion, $[Macro-CTA]_0$ is the mole number of first block RAFT-polymer, $Macro-CTA_{Mw}$ is the weight of one mole of the first block RAFT-polymer. The route used for the synthesis of block copolymers is summarized in Scheme 1.



Scheme 1. Synthesis route for block copolymer of poly[(meth)acrylic acid]-b-poly [vinyltriethoxysilane]

2.2.4. Polymer characterizations

2.2.4.1. Gel permeation chromatography (GPC) analysis

The average molecular weights and polydispersity indexes of the obtained (co)polymers were determined by aqueous Malvern Gel Permeation Chromatography (GPC). The device consists of one guard column and two ultra-hydrogel columns (10.000 Da and 1.000.000 Da), one refractive index detector with a peristaltic vacuum pump. 0.1 M NaNO₃ and 0.5% NaN₃ aqueous solution were used as the mobile phase with a flow rate of 0.7 mL/min during the measurements. The calibration curve used in the measurements was prepared using 12 different poly(ethylene oxide) standards with peak molecular masses (M_p) ranging from 195 to 610.000 Da. Before the measurement, the polymers in 2 mg/mL concentrations were dissolved in GPC eluent and shaken for at least 6 hours to obtain a complete dissolution. Then, the samples were filtered through 0.45 μ m injector filters and measured for the determination of number average molecular weights (M_n), weight average molecular weight (M_w), molecular weight distributions and polydispersity index (PDI).

2.2.4.2. Fourier transform infrared spectroscopy (FTIR) analysis

The structural analysis of polymers was performed by using Perkin Elmer trademark, Spectrum-100 model FT-IR+ATR spectrometer. The IR spectra of samples in powder form were obtained after 5 scans between 4500 - 600 cm^{-1} using 2 cm^{-1} discriminating power.

2.2.4.3. Proton-nuclear magnetic resonance spectroscopy ($^1\text{H-NMR}$) analysis

The structure analysis of selected samples was also determined by using Liquid MERCURYplus-AS 400 model NMR spectrometer with 400 MHz operating frequency. Polymer samples were analyzed at 10-15 mg/ml concentrations by dissolving in DMSO- d_6 or CDCl_3 solvents.

2.2.4.4. Differential scanning calorimetry (DSC) analysis

The thermal behavior of polymers was determined by using Shimadzu-DSC 60 Plus instrument. The samples weighted between 5-6 mg were transferred to hermetic aluminum pans and sealed. Heat flows were recorded between -100 and 300 $^{\circ}\text{C}$ with heating rate of 10 $^{\circ}\text{C}/\text{min}$ under nitrogen atmosphere.

3. RESULTS

3.1. Synthesis of first block polymers

For the preparation of block copolymers, first block homopolymers were synthesized by using acrylic monomers via RAFT technique. The details of the synthesis of homopolymers used as macro-RAFT agent are summarized in Table 1.

In the experiments, the solvent types, type of chain transfer agent and initiators, molar ratios of monomer/chain transfer agent and other reaction parameters were varied. The molar ratios of the chain transfer agent and initiator were used as [CTA]/[I]:1/0.25 (mmol / mmol). This ratio is widely used in RAFT polymerizations likewise it provides both sufficient chain transfer efficiency and free radical formation necessary to initiate polymerization. In the synthesis of the first hydrophilic blocks, the molar ratios of monomer to the chain transfer agent [M] / [CTA] were chosen to be maximum 100/1 (mmol / mmol) to obtain low molecular weights.

The choice of hydrophilic acrylates to use as first block was due to two reasons: Firstly, the -Z group of CTA having long alkyl chain is positioned at the end of second block, thus the hydrophilic chains of acrylic blocks are not hindered. Secondly, the self-reactivity of VTES monomer is low which makes it difficult to be homopolymerized. On the other hand it can be polymerized in the presence of other monomeric or polymeric radicals as a second block in copolymer synthesis.

Four different chain transfer agents were chosen to provide control on the molecular weights in RAFT polymerizations. Among the RAFT agents CTA-I, CTA-II, CTA-IV were dithiocarbonate-based and CTA-III was dithiobenzoate-based agents. 2,2'-azobis 2-methylpropionitrile (AIBN) and 4,4'-azobis 4-cyanovaleric acid (ACVA) were used as a initiator, due to their good radical activity in organic solvents and their analogous structures of free radicals with -R groups of chain transfer agents. The water-miscible organic solvents were used as the reaction medium in the experiments.

The results of molecular weight and polydispersity index of first block polymers are also given in Table 1. It can be seen that the measured number average molecular weights ranged from 3760-11920 Da regarding to the chosen molar ratios and were close to the theoretical M_n values. The polydispersity indexes were varied from 1.13 to 1.54 showing that a good control was achieved on molecular weights with high monomer conversion.

Experiment No	Monomer	CTA type	[M]/[CTA]/[I]	Solvent	Initiator	T (°C)	Duration (h)	Conversion (%)	$M_{n,th}$ (Da)	$M_{n,GPC}$ (Da)	PDI
H1	MAA	I	100/1/0.25	DO	AIBN	75	24	>99	8950	8790	1.33
H2	MAA	II	100/1/0.25	DO	AIBN	75	24	>99	8950	7720	1.26
H3	MAA	I	100/1/0.25	DMSO	ACVA	75	24	>99	8950	9900	1.15
H4	AAM	IV	100/1/0.25	DMSO	AIBN	80	24	88	6619	5322	1.25
H5	MAA	I	100/1/0.25	2-POH	AIBN	75	24	98	8780	7673	1.22
H6	MAA	III	80/1/0.25	ETOH	ACVA	75	24	89	6407	5415	1.54
H7	MAA	I	100/1/0.25	ETOH	AIBN	75	24	90	8091	6551	1.50
H8	MAA	I	50/1/0.25	DMSO	AIBN	75	12	90	4218	3760	1.33
H9	AA	IV	100/1/0.25	ETOH	AIBN	80	24	>99	7570	11203	1.13
H10	AA	IV	100/1/0.25	ETOH	AIBN	85	24	>99	7570	11920	1.32
H11	AA	I	100/1/0.25	ETOH	ACVA	75	24	95	7210	7660	1.27
H12	AA	II	100/1/0.25	ETOH	ACVA	75	24	95	7210	7530	1.22
H13	AA	IV	83/1/0.25	DMSO	AIBN	75	24	97	6166	6084	1.41
H14	AA	IV	100/1/0.25	ETOH	AIBN	70	24	> 99	7570	9092	1.17
H15	AAM	IV	100/1/0.25	DMSO	AIBN	80	24	82	6193	4853	1.35

Table 1. Experimental details for the synthesis of first block polymers.

The results showed that better control and low PDI values (1.14) were obtained for PMAA synthesis by using DMSO solvent and CTA-I or CTA-II as chain transfer agents. Polymers with high conversion and low polydispersity ($PDI = 1.15$) were obtained in PAA syntheses by using EtOH and CTA-IV. Similarly, polyacrylamide syntheses were also successfully performed by the RAFT technique under given conditions. The type of initiators (AIBN and ACVA) didn't show significant difference on monomer conversion rates and control on the molecular weights and both were used effectively. However, the solvent type used as the reaction medium and the type of chain transfer agent had effect on conversion and control on the molecular weight depending on each monomer type. Overall results showed that the first block acrylic polymers to be used as Macro-RAFT agents were synthesized successfully with controlled low molecular weights.

3.2. Synthesis of diblock copolymers

The experimental details of block copolymerizations are given in Table 2 and GPC curves in Figure 1. In the experiments, the theoretical PVTES block lengths were chosen to be lower than acrylic blocks. During the block copolymer synthesis various conditions such as different solvents (DMSO, MeOH, EtOH and 2-POH), reaction temperatures (70, 75, 80 and 90 °C) and reaction times (12, 24, 48 and 72h) were used. Block copolymerizations were performed using two approaches. In the first approach the first acrylic block were synthesized, purified and used as Macro-RAFT agents for the synthesis of PVTES. In another approach, one-pot synthesis was used where the second block monomer (VTES) was introduced into the reaction medium at the end of first block synthesis.

In the conventional block copolymer synthesis using isolated polyacrylate macro-RAFT agents (B1-B4) the monomer conversion ratios were found to be between 51 and 64 % and the molecular weight distribution curve of first block was shifted to higher molecular weight (Figure 1a). Increases in the molecular weights of the first blocks after synthesis were found to be 2800 Da for B1, 4225 Da for B2 and 627 Da for B4. The PDI values of the block copolymers were also found to be as low as 1.17-1.24 indicating the control on molecular weights. The trial B3 resulted in an insoluble structure possibly due to the self-condensation of silane moieties because of higher reaction temperature.

Experiment No	Monomer	Macro-CTA	$M_{n,Macro-CTA}$ (Da)	[M]/[Macro-CTA]/[I]	Solvent	Initiator	T (°C)	Duration (h)	Conversion (%)	$M_{n,th}$ (Da)	$M_{n,GPC}$ (Da)	PDI
<i>Block copolymerizations with isolated Macro-CTA</i>												
B1	VTES/MAA	H1	8790	32/1/0.25	MeOH	AIBN	80	48	51	11892	11590	1.24
B2	VTES/MAA	H2	7720	40/1/0.25	DMSO	ACVA	80	72	60	12287	11945	1.17
B3	VTES/MAA	H3	9900	50/1/0.25	2-POH	AIBN	90	48	-	-	-	-
B4	VTES/AAm	H4	5322	18/1/0.25	DMSO	ACVA	80	24	64	6140	5949	1.23
<i>One-pot syntheses of block copolymers</i>												
B5	VTES/MAA	H5	7673	50/1/0.25	2-POH	AIBN	70	48	22	9766	8952	1.30
B6	VTES/MAA	H6	5415	50/1/0.25	EtOH	ACVA	75	48	68	11885	11064	1.13
B7	VTES/MAA	H7	6551	30/1/0.25	EtOH	AIBN	90	48	-	-	-	-
B8	VTES/MAA	H8	3760	40/1/0.25	DMSO	AIBN	80	48	76	9545	7693	1.20
B9	VTES/AA	H9	11203	50/1/0.25	EtOH	AIBN	70	12	0	-	10738	1.15
B10	VTES/AA	H10	11920	100/1/0.25	EtOH	AIBN	75	24	26	16867	14072	1.30
B11	VTES/AA	H11	7660	50/1/0.25	EtOH	ACVA	75	24	33	10800	9080	1.18
B12	VTES/AA	H12	7530	50/1/0.25	EtOH	ACVA	75	24	24	9813	8276	1.23
B13	VTES/AA	H13	6084	40/1/0.25	DMSO	AIBN	75	24	30	8367	8361	1.17
B14	VTES/AA	H14	9092	50/1/0.25	EtOH	AIBN	80	48	75	16200	14020	1.13
B15	VTES/AAm	H15	4853	45/1/0.25	DMSO	AIBN	80	48	57	9734	37324	1.10
											5422	1.28

Table 2. Block copolymerization experiments.

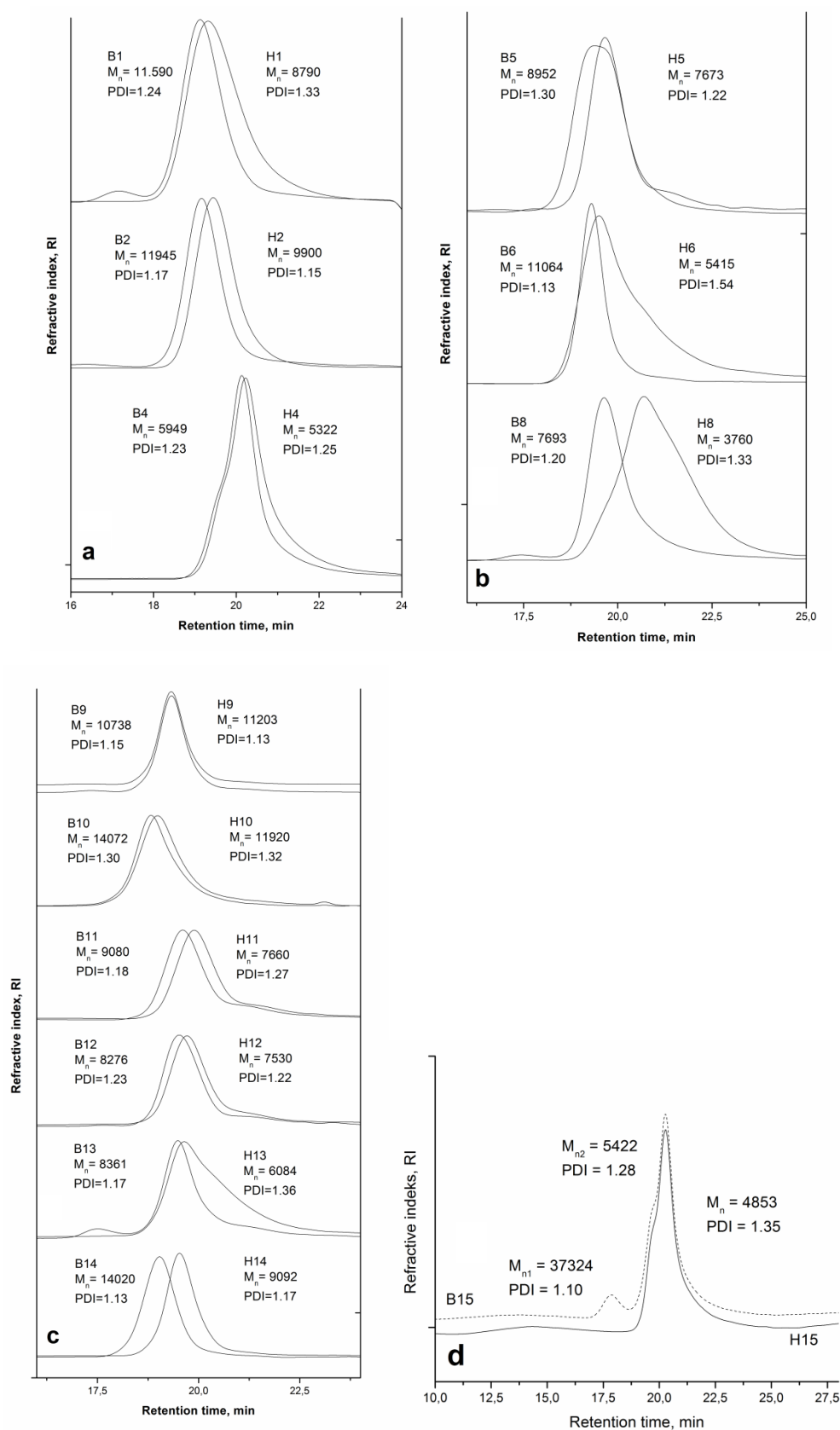


Figure 1. Molecular weight distribution curves of block copolymers synthesized using Macro-RAFT agent (a), PMAA-b-PVTES block copolymers synthesized by the one-pot method (b), PAA-b-PVTES block copolymers synthesized by the one-pot method (c), PAAM-b-PVTES block copolymers synthesized by the one-pot method (d).

In the other block copolymer syntheses using one-pot approach, the monomer conversions were found to be influenced significantly by the reaction temperature and duration. In the case of trial B9 no block formation was observed since the reaction temperature and time were not sufficient for polymerization. Similarly, low monomer conversion ratios were obtained for B10-13 synthesis for 24 hours at 75 °C. However, the copolymers B6, B8 and B14 synthesized at 75 and 80 °C for 48 h, showed higher conversion ratios (68-76%) and significant increase in molecular weights. For instance, the M_n value of B6 increased from 5415 to 11064 Da, for B8 from 3760 to 7693 Da and for B14 from 9092 to 14020 Da. The average molecular weights of the copolymers were close to the theoretical values with low PDIs (1.13-1.30) indicating that a good control on molecular weights were achieved under proper reaction conditions. In the synthesis of PAAm-b-PVTES copolymers no significant block formation was observed. GPC analysis showed that the molecular weight distribution curve of PAAm block remained unchanged, however, a second fraction was formed at higher molecular weight with a low fraction possibly belongs to PVTES homopolymers. It seems that the reactivity between VTES monomers and PAAm radicals was insufficient to give block formation; however, further investigations are necessary.

3.3. IR Spectra of Copolymers

The structures of the synthesized block copolymers were examined by FTIR spectrometry and IR spectra were given in Figure 2. From the spectra of PMAA-b-PVTES copolymers (Figure 2a) the characteristic absorption bands were observed for -COOH groups at 3700-2300 cm^{-1} , -CH stretching of -CH₂ and -CH₃ groups at 2935-2990 cm^{-1} , the carbonyl group stretching at 1692 cm^{-1} , -CH₃ and CH₂ deformation vibrations at 1479-1390 cm^{-1} . The Si-O-C absorption of VTES segments were observed at 1070 cm^{-1} with a significant increase in the intensity. Similarly the spectra of PAA-b-PVTES copolymers showed main absorbance bands at 3700-2200 cm^{-1} , 2990-2930 cm^{-1} , 1696 cm^{-1} , 1449-1376 cm^{-1} which can be attributed to stretching vibrations of -OH (COOH), -CH, C=O and deformation vibrations of -CH₂ and -CH, respectively. Si-O-C stretching vibrations were found around 1070 cm^{-1} which confirms the presence of PVTES segments.

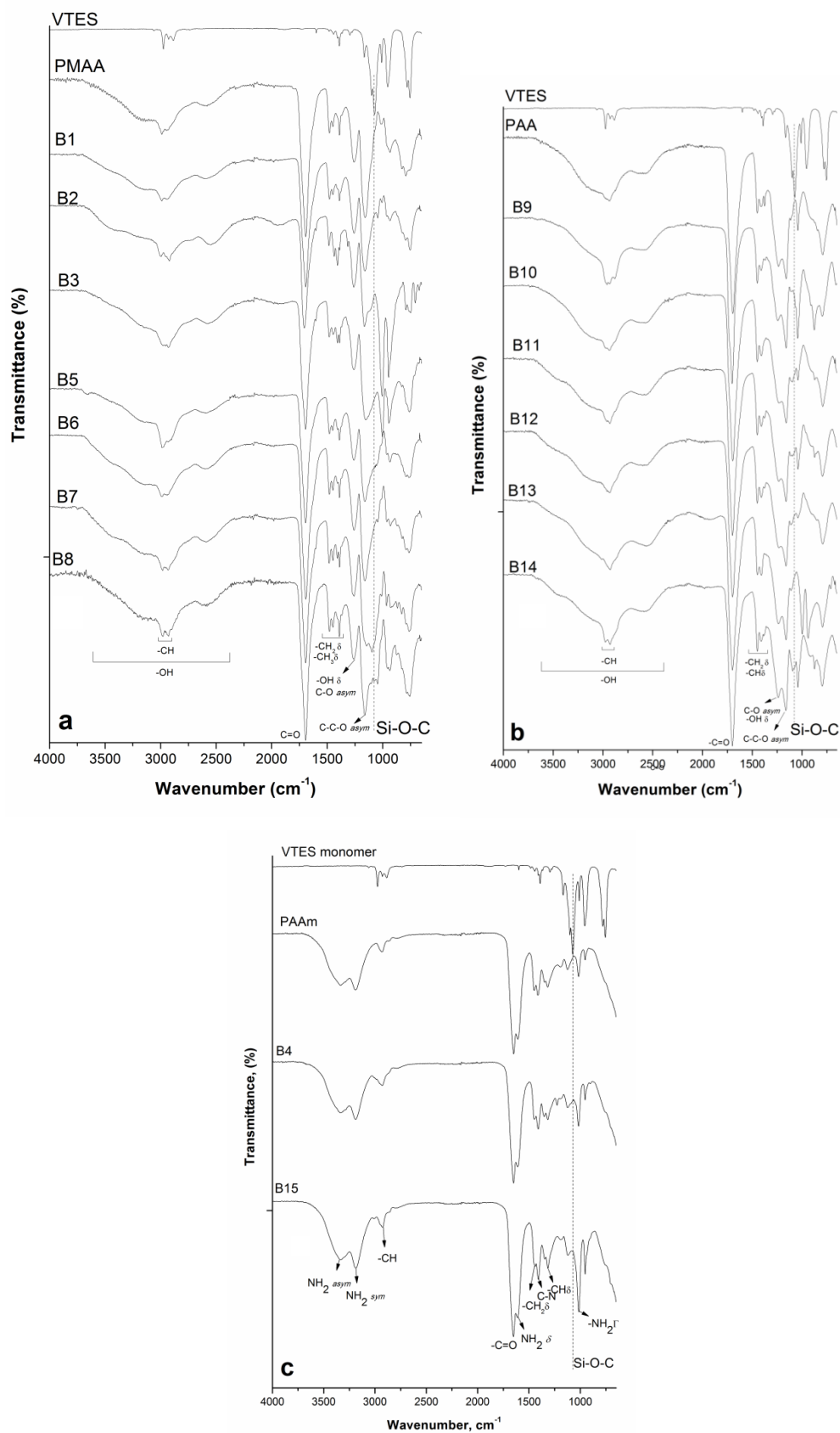


Figure 2. IR spectra of the block copolymers; (a) poly(methacrylic acid)-b-poly(vinyltriethoxysilane), (b) poly(acrylic acid)-b-poly(vinyltriethoxysilane), (c) poly(acrylamide)-b- (polyvinyltriethoxysilane) polymers.

The IR spectra of PAAM-b-PVTES copolymers showed characteristic absorptions peaks of -NH₂ stretching vibrations at 3330 and 3188 cm⁻¹, -CH stretching at 2930-2800 cm⁻¹, C=O stretching at 1651 cm⁻¹ and -NH₂ deformation vibrations at 1607 cm⁻¹. The Si-O-C stretching of PVTES appeared at around 1070 cm⁻¹, however their intensity were low since PVTES content of the copolymers was much lower than PAAm block.

3.4. H-NMR spectra of copolymers

The H-NMR spectra of the homopolymers and representative block copolymers are given in Figures 3 and 4, respectively with the assignation of protons.

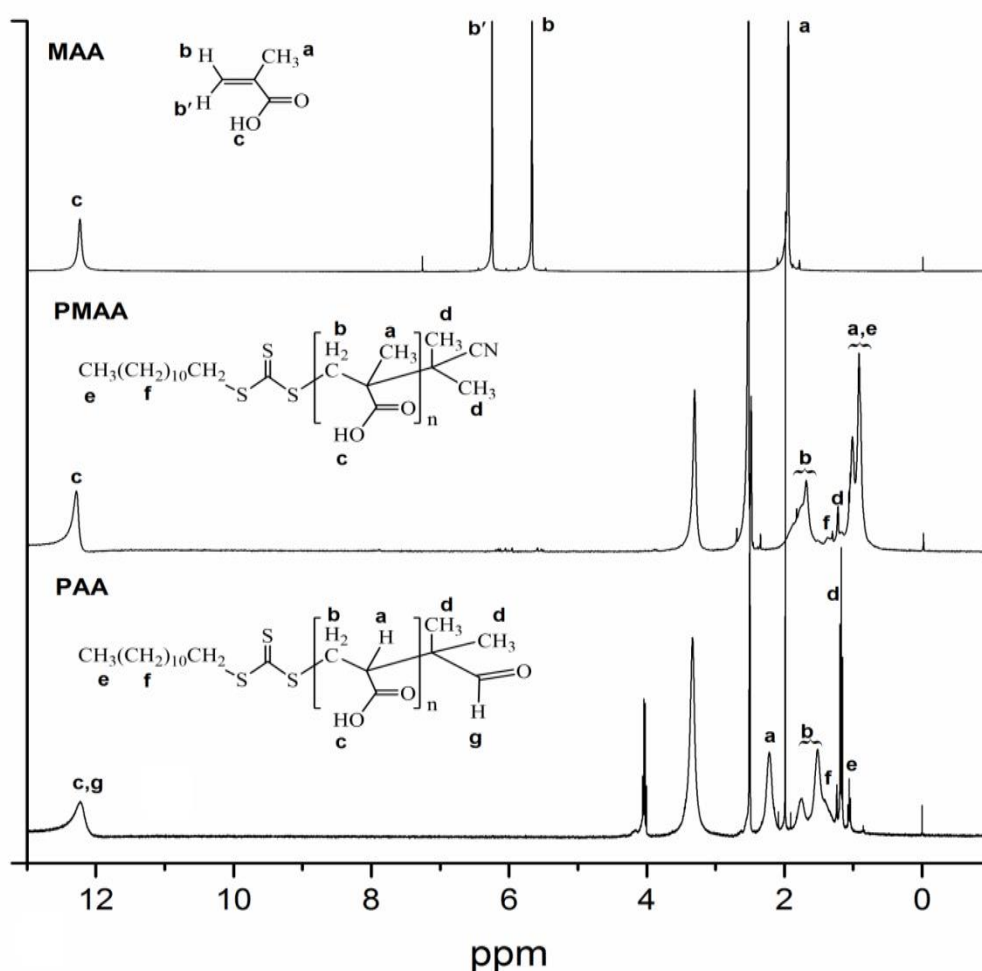


Figure 3. H-NMR spectra of MAA monomer and PMAA, PAA homopolymers.

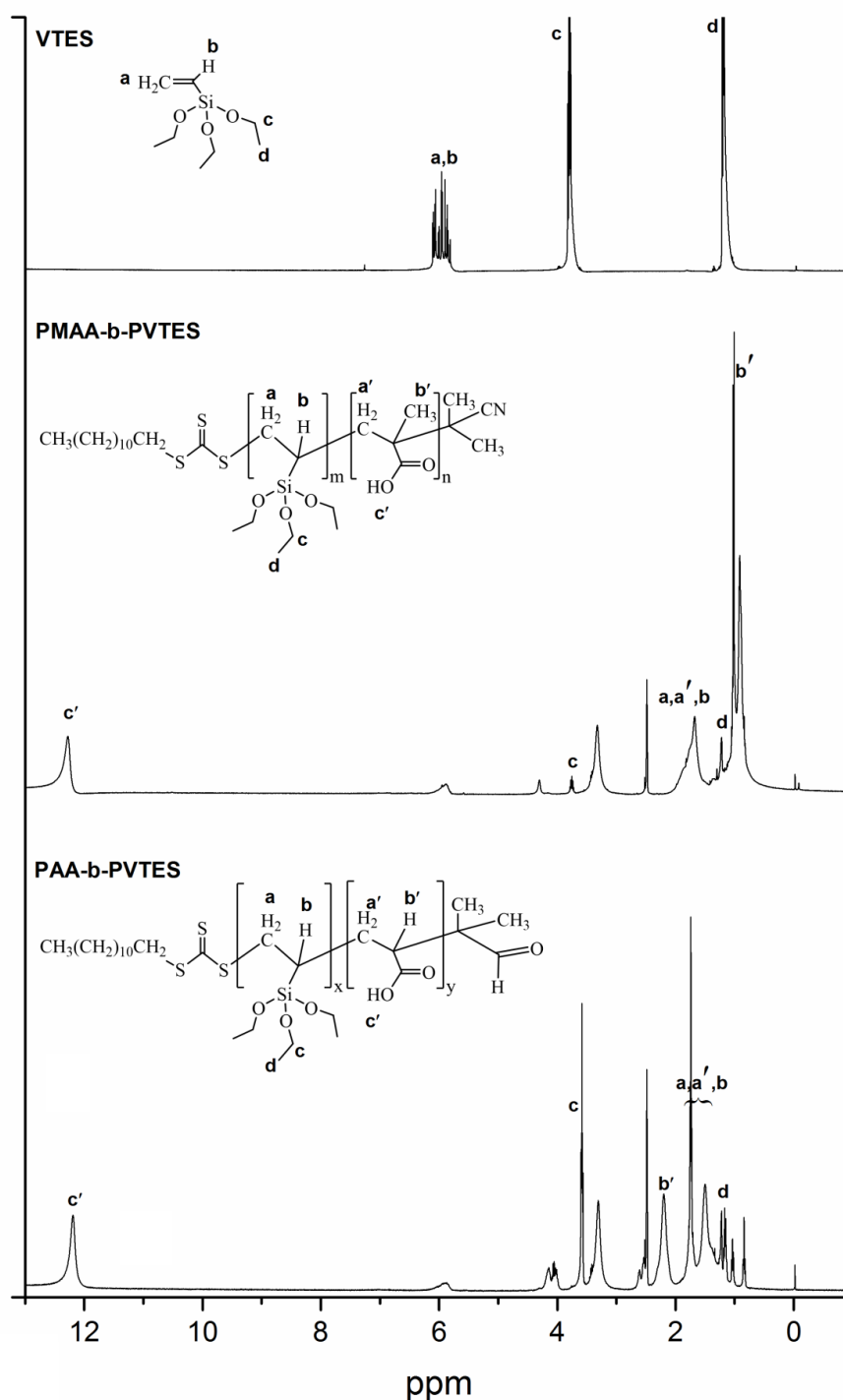


Figure 4. H-NMR spectra of VTES monomer, PMAA-b-PVTES and PAA-b-PVTES copolymers.

In the spectra, $-\text{CH}_2$ and $-\text{CH}$ proton signals of the VTES segments were overlapped with $-\text{CH}_2$ protons of the PMAA and PAA segments. However, the $-\text{CH}_2$ proton signals of the $\text{Si}-\text{O}-\text{CH}_2-\text{CH}_3$ group and the $-\text{CH}_3$ proton signals were observed at 3.60-3.74 ppm and 1.21 ppm, respectively, verifying the presence of PVTES segments in block copolymer structure.

3.5. Thermal behaviors of copolymers

In Figure 5, DSC thermograms of the copolymers are shown. From the results, the glass transition temperature (T_g) value of macro-CTAs was found to be 72 °C for PMAA and 88 °C for PAA. The low T_g values of homopolymers were possibly due to their low molecular weights of 7693 Da (B8) and 14020 Da (B14). The melting temperatures (T_m) were observed at 259 °C and 229 °C for PMAA and PAA, respectively. When the thermograms of block copolymers were examined T_g values of acrylic segments were observed at 69°C and 77°C for PMAA and PAA segments, respectively, which were close to T_g of homopolymers. Despite there was no significant glass transition for PVTES segments, small phase transitions were observed at -93°C (PMAA-b-PVTES) and -91°C (PAA-b-PVTES) which were possibly due to PVTES block since it is known to give flexible and low T_g polymers. Moreover, T_m values of the block copolymers seemed to be shifted to higher values of 290 °C and 253 °C for PMAA-b-PVTES and PAA-b-PVTES. The overall results showed the difference of thermal behavior between the homopolymers and block copolymers which supported the success of syntheses of block copolymers.

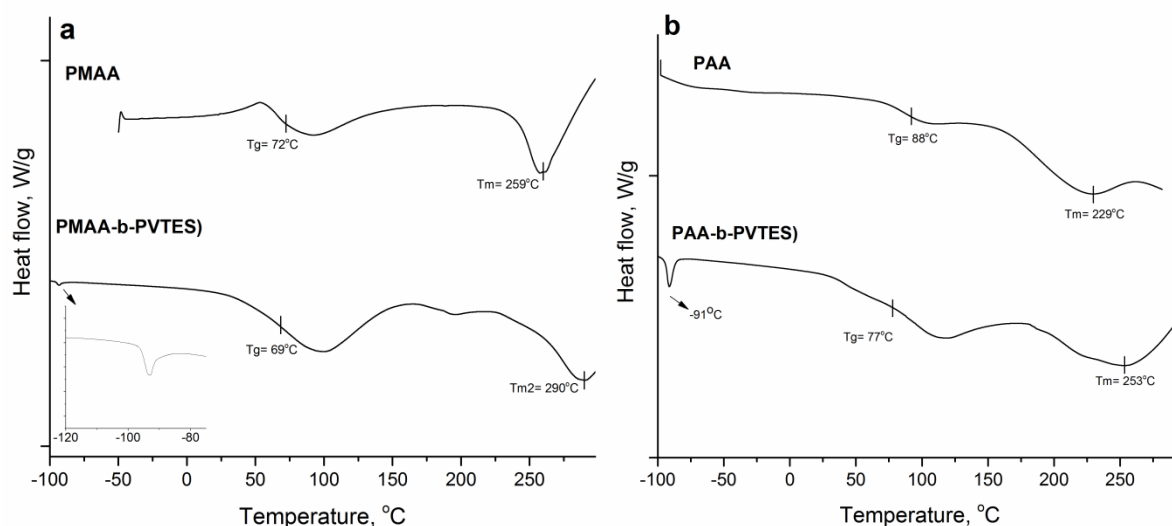


Figure 5. DSC thermograms of PMAA homopolymer and PMAA-b-PVTES block copolymer (a); PAA homopolymer and PAA-b-PVTES block copolymer (b).

4. CONCLUSIONS

PMAA-b-PVTES, PAA-b-PVTES, PAAm-b-PVTES diblock copolymers were synthesized via RAFT polymerization. The trials under different reaction conditions showed that the control on molecular weights, monomer conversion and PDI values were affected by the type of solvent and chain transfer agents as well as the reaction temperature and time. However, with the carefully selected parameters PMAA-b-PVTES and PAA-b-PVTES diblock copolymers were successfully synthesized with controlled molecular weights and low PDI values. The data obtained from GPC, FTIR, H-NMR and DSC measurements verified the success of block copolymer synthesis. This kind of block copolymers can be used in metal surface treatments, as metal chelating agents or water dispersible reactive micelles for different purposes.

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