



Synthesis and Characterization of Random and Block-Random Diblock Silylated Terpolymers *via* RAFT Polymerization

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Well-defined random and block-random diblock terpolymers consisting of methyl methacrylate (MMA), butyl acrylate (BA) and *tert*-butyldimethylsilyl methacrylate (*t*-BDMSMA) were successfully synthesized by reversible addition-fragmentation chain transfer (RAFT) polymerization using 2-cyanoprop-2-yl-dithiobenzoate (CPDB) as RAFT agent. ¹H NMR and GPC analyses indicated the formation of random terpolymers [P(MMA-*co*-BA-*co*-*t*-BDMSMA)] and block-random diblock terpolymers [(PMMA-*b*-P(BA-*co*-*t*-BDMSMA) and Pt-BDMSMA-*b*-P(BA-*co*-MMA)] with good control of terpolymer composition, molecular weights and molecular weight distributions ($\bar{D} < 1.20$). Thermal analysis results showed that the random terpolymers exhibited only one glass transition temperature (T_g) which depends on the terpolymer composition. The (PMMA-*b*-P(BA-*co*-*t*-BDMSMA) block-random diblock terpolymer showed two T_g that can be attributed to two blocks of terpolymer. Meanwhile, Pt-BDMSMA-*b*-P(BA-*co*-MMA) block-random diblock terpolymer exhibited only one T_g value, which is probably due to a low proportion of Pt-BDMSMA block present in the terpolymer.

Keywords: RAFT polymerization, Terpolymer, Trialkylsilyl methacrylate, Silylated polymer.

INTRODUCTION

Located in the tropical zone, Vietnam has a hot and humid climate that fosters a strong development of marine micro- and macro-organisms like diatoms, protozoa, bryozoa, algae, barnacles, oysters, hydroids, tubeworms, *etc.* Thus antifouling protection for vessels and submersed structures is a vital concern for the country having a long coastline and large number of boats. Self-polishing antifouling (AF) paints based on organotin compounds (OTC) have been widely used during the last decades of 20th century due to their high antifouling performance [1,2]. However, because of high toxicity of organotin compounds toward not only biofouling but also other marine species as well as its long persistence in sediments. The presence of antifouling paints containing organotin compounds on ships have been totally prohibited since the 1st January 2008 after adoption of the International Convention AFS/CONF/26 on 5 October 2001 [3]. The convention has officially entered into force for Vietnam since 27 February 2016.

In our previous works [4-6], we indicated that a replacement of tin in organotin compounds-based self-polishing copolymers by silicon, a more eco-friendly element, still maintained

their hydrolyzability and self-polishing properties. Copolymers based on hydrolysable poly(*tert*-butyldimethylsilyl methacrylate), Pt-BDMSMA and poly(methyl methacrylate) (PMMA) were synthesized and studied to show that they can be used as polymer binders in self-polishing antifouling coatings. Nevertheless, a major drawback of the paint films made from these copolymers is that they are quite brittle due to their high glass transition temperatures (T_g , PMMA = 100-105 °C, T_g , Pt-BDMSMA = 135-142 °C) [5,6]. This causes an additional utilization of plasticizers, which results in cost increases and deterioration of certain physico-mechanical properties of paint films.

In this study, our approach consists in incorporating into the structure of polymer binders a much more flexible component such as poly(butyl acrylate) (PBA), whose glass transition temperatures is much lower (T_g , PBA ~ -50 °C) in order to plasticize the paint films, improve their adhesion ability and physico-mechanical properties without plasticizer requirement.

To synthesize copolymers, we used a modern radical copolymerization method which is reversible addition-fragmentation transfer (RAFT) [7-9]. Control in RAFT polymerization is achieved by using a chain transfer agent (CTA), also called RAFT agent, in order to establish a fast equilibrium between

dormant and active chains. This equilibrium decreases the relative proportion of propagating radicals and allows them to reversibly deactivate rather than permanently terminate. Therefore, this controlled polymerization process allows synthesizing simple or complex polymers and copolymers such as homopolymers and random/block copolymers with controlled molecular weight and narrow molecular weight distribution [10,11]. This article presents the controlled synthesis and characterization of random and block-random terpolymers based on methyl methacrylate (MMA), butyl acrylate (BA) and *tert*-butyldimethylsilyl methacrylate (*t*-BDMSMA) by RAFT process. The effect of butyl acrylate proportion on thermal properties of resulting terpolymers is also investigated.

EXPERIMENTAL

Methyl methacrylate (MMA), butyl acrylate (BA) monomers were purchased from Aldrich and purified by distillation under reduced pressure. *tert*-Butyldimethylsilyl methacrylate (*t*-BDMSMA) monomer was prepared from methyl methacrylate and *tert*-butyldimethylchlorosilane following a procedure described earlier [12]. 2-Cyanoprop-2-yl-dithiobenzoate (CPDB, 98 %) was used as received from Aldrich without further purification. 2,2'-Azobis(2-methylpropionitrile) (AIBN, 98 %) was purified by recrystallization from methanol and dried under vacuum. CPDB and AIBN were kept at 4 °C under nitrogen atmosphere.

¹H NMR spectra were recorded on a Bruker Avance 500 MHz spectrometer using CDCl₃ as deuterated solvent at ambient temperature. The number-average and weight-average molecular weights (M_n and M_w) and molecular weight distribution ($\bar{D}$) of polymers were determined by gel permeation chromatography (GPC). Measurements were conducted on a Triple Detection Viscotek TD-SEC Instrument using tetrahydrofuran as eluent at a flow rate of 1.0 mL min⁻¹. PMMA standards (from Polymer Laboratories) with M_p range of 620–3.6 × 10⁵ g mol⁻¹ were used as calibration standards. The glass transition temperatures (T_g) of polymers were measured by differential scanning calorimetry (DSC) using a TA Instruments Q100 differential scanning calorimeter. Analyses were performed in a temperature range from -70 °C to 150 °C at heating rate of 10 °C min⁻¹.

Polymerization procedure: Polymerization reactions were conducted in a 100 mL round-bottom flask equipped with a magnetic stir bar and connected to a nitrogen bubbler system. The reaction mixtures were prepared in volumetric flasks by adding toluene, monomers (MMA, *t*-BDMSMA and BA) and AIBN. The total concentration of three monomers is fixed at 1.5 mol L⁻¹. For RAFT process, a chain transfer agent (CPDB) was added with a [CPDB]/[AIBN] proportion equal to 5. The so-prepared solution was then transferred into the reaction flask

and purged with nitrogen gas for 45 min to eliminate any oxygen trace. The above-setup was placed in a thermostatic bath previously regulated at 70 °C to start polymerization. Resulting copolymers were precipitated from the solution with a methanol/pentane mixture (90/10 v/v), filtered and dried under vacuum at 30 °C for 48 h. Detailed conditions of each particular polymerization reaction were described below.

Synthesis of random terpolymers: An example of quantities used for synthesis of P(MMA-*co*-BA-*co*-*t*-BDMSMA) 50/20/30 (No. 3 in Table-1) is as follows: *t*-BDMSMA (1.80 g, 9 × 10⁻³ mol), MMA (1.50 g, 1.50 × 10⁻² mol), BA (0.77 g, 6.0 × 10⁻³ mol), CPDB (30.0 mg, 1.36 × 10⁻⁴ mol) and AIBN (4.44 mg, 2.71 × 10⁻⁵ mol) were introduced to a 20 mL volumetric flask. Toluene was added to the 20 mL mark. Random terpolymers with other proportion of BA are described in Table-1. For the free radical polymerization reaction, the same quantities of monomers, AIBN and toluene were used except CPDB.

Synthesis of block-random diblock terpolymers

PMMA-SC(=S)Ph: Methyl methacrylate (15.05 g, 1.50 × 10⁻¹ mol), AIBN (35.6 mg, 2.15 × 10⁻⁴ mol), CPDB (0.239 g, 1.08 × 10⁻³ mol) and toluene (40.0 mL) were added to a 100 mL round-bottomed flask equipped with a magnetic stir bar. The degassing and polymerization procedure were the same as described above. In this case, the polymerization was stopped when the monomer conversion reaches about 70 % (the latter is monitored by ¹H NMR spectroscopy). The polymer was then precipitated into *n*-pentane, filtered and dried under vacuum for 24 h at room temperature.

Pt-BDMSMA-SC(=S)Ph: *t*-BDMSMA (10.00 g, 5.0 × 10⁻² mol), AIBN (21.9 mg, 1.33 × 10⁻⁴ mol), CPDB (0.148 g, 6.67 × 10⁻³ mol) and toluene (30.0 mL) were added to a 100 mL round-bottomed flask equipped with a magnetic stir bar. The degassing and polymerization procedure were the same as PMMA synthesis, except the polymer was precipitated into methanol.

PMMA-*b*-P(BA-*co*-*t*-BDMSMA) or Pt-BDMSMA-*b*-P(BA-*co*-MMA): To a 100 mL round-bottomed flask equipped with a magnetic stir bar were added macro-CTA (PMMA-SC(=S)Ph or Pt-BDMSMA-SC(=S)Ph), AIBN as initiator with a [macro-CTA]/[AIBN] ratio close to 5, and toluene as solvent. The degassing and polymerization procedures were the same as described earlier and the polymerization time is 36 h. Block copolymers were precipitated into a mixture methanol/pentane (90/10 v/v), filtered and dried under vacuum for 48 h.

RESULTS AND DISCUSSION

Random terpolymers: Random terpolymers P(MMA-*co*-BA-*co*-*t*-BDMSMA) were synthesized in toluene solution

TABLE-1
RAFT SYNTHESIS OF RANDOM TERPOLYMERS P(MMA-*co*-BA-*co*-*t*-BDMSMA)

CTA	Conv. (%)	[MMA]/[BA]/[<i>t</i> -BDMSMA] molar ratio		$M_{n,cal.}$ (g mol ⁻¹)	$M_{n,exp.}$ (g mol ⁻¹)	$\bar{D}$	$T_{g,th}$ (°C)	T_g (°C)
		Initial	Final					
–	94	50/20/30	52/18/30	–	102 500	1.76	75.0	86.1
CPDB	93	55/15/30	58/10/32	27 700	30 400	1.18	93.9	110.9
CPDB	91	50/20/30	54/17/29	26 800	28 400	1.19	76.5	82.6
CPDB	93	40/30/30	42/28/30	28 500	34 550	1.15	55.8	54.9

[Monomer] = 1.5 mol L⁻¹ in toluene; temperature = 70 °C; time = 36 h; Conv. = monomer conversion; $M_{n,cal.}$ = ([Monomer]/[CPDB]) × Conv. × $M_{monomer}$; $T_{g,th}$ is calculated by Fox equation (eqn. 2)

at 70 °C by free radical polymerization using AIBN as initiator and by RAFT polymerization using 2-cyanoprop-2-yl dithiobenzoate as a chain transfer agent (**Scheme-I**). ^1H NMR spectra of purified polymer products (Fig. 1) indicate the incorporation of all three monomer units through the appearance of characteristic signals for the protons of $-\text{OCH}_3$ (MMA), $-\text{OCH}_2-$ (BA) and $-\text{Si}(\text{CH}_3)_2-$ (*t*-BDMSMA) groups at 3.59, 3.99 and 0.22 ppm, respectively. The molar composition of terpolymers was determined via ^1H NMR spectra based on integrals of these characteristic peaks (I_a , I_b , I_c) using eqn 1 and presented in Table-1. Terpolymers P(MMA-*co*-BA-*co*-*t*-BDMSMA) were obtained with high conversion (> 90 %) and their molar compositions are slightly different from the initial ones due to incomplete monomer conversions.

$$[\text{MMA}]:[\text{BA}]:[\text{t-BDMSMA}] = \frac{I_a/3}{I_t} : \frac{I_b/2}{I_t} : \frac{I_c/6}{I_t} \quad (1)$$

$$\text{with } I_t = \frac{I_a}{3} + \frac{I_b}{2} + \frac{I_c}{6}$$

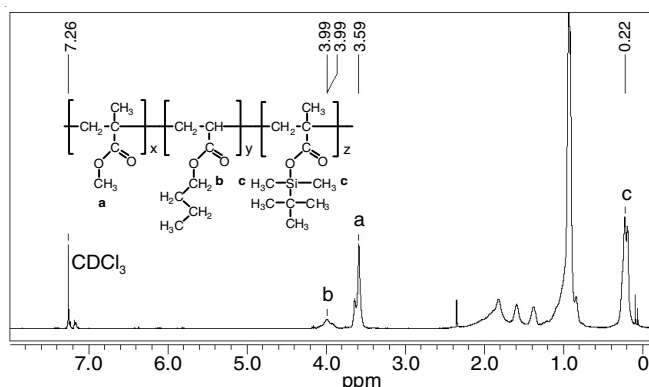


Fig. 1. ^1H NMR spectrum of P(MMA-*co*-BA-*co*-*t*-BDMSMA)

Fig. 2 shows GPC curves of purified products obtained by FRP and RAFT processes. It can be clearly seen that only one peak is observed for both polymerization methods. This observation confirms that the resulting product is a terpolymer rather than a mixture of homopolymers. When no RAFT agent was used (*i.e.* free radical polymerization), a terpolymer with broad molecular weight distribution ($\bar{D} = 1.76$) was obtained. Contrarily, when the RAFT polymerization was performed in the presence of CPDB as RAFT agent, a terpolymer with low dispersity ($\bar{D} = 1.18$) was obtained. In addition, the experimental molecular weight determined by GPC is close to the calculated one which means that CPDB has ability to control the copolymerization effectively.

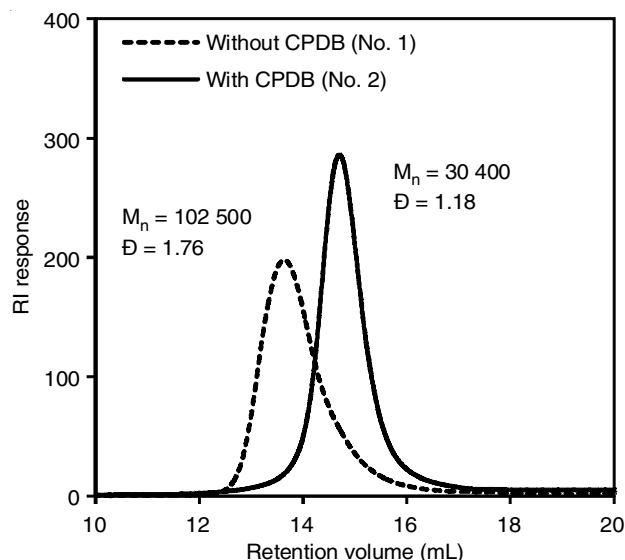
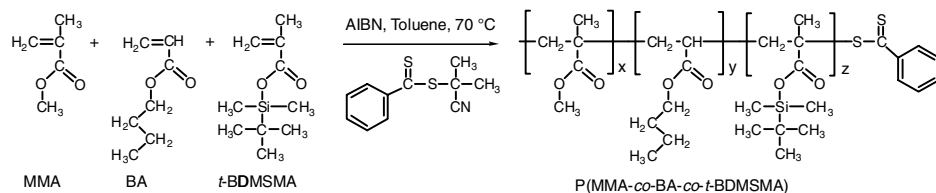
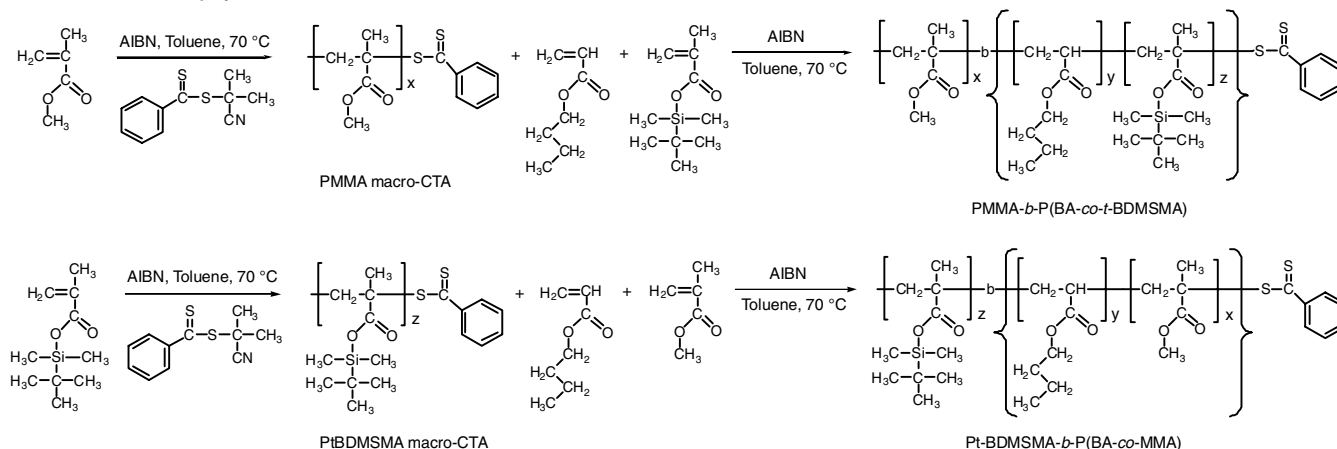


Fig. 2. SEC chromatograms of P(MMA-*co*-BA-*co*-*t*-BDMSMA)

Random terpolymers



Block-random diblock terpolymers



Scheme-I: Synthetic procedures of random and block-random diblock terpolymers containing MMA, BA and *t*-BDMSMA by RAFT process

The glass transition temperatures of random terpolymers were investigated by DSC analysis. The results are presented in Table-2 and Fig. 3. The theoretical $T_{g,th}$ of random polymers can be estimated using Fox equation [13]:

$$\frac{1}{T_{g,th}} = \frac{w_1}{T_{g,1}} + \frac{w_2}{T_{g,2}} + \frac{w_3}{T_{g,3}} \quad (2)$$

where w_i is the weight fraction of the monomer unit i in the copolymer and $T_{g,i}$ is the T_g of a homopolymer of monomer i . In this study, T_g of pure homopolymer is 100.7 °C for PMMA, -52.1 °C for PBA and 142.0 °C for Pt-BDMSMA. Each of the random terpolymers exhibited a single T_g as listed in Table-2. These experimental T_g values are relatively close to the theoretical ones calculated using the Fox equation. As the molar proportion of *t*-BDMSMA was about 30 % for all products, it is clear that the higher butyl acrylate monomer proportion will lower T_g of terpolymer. By varying butyl acrylate monomer proportion, it is possible to modulate the glass transition temperatures of terpolymers.

Block-random diblock terpolymers: The ability to prepare block copolymers is one of the features that distinguish

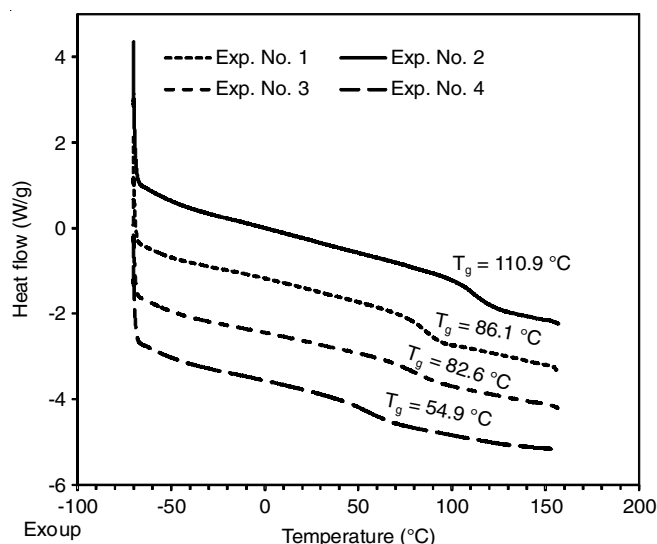


Fig. 3. DSC thermograms of random terpolymers P(MMA-co-BA-co-*t*-BDMSMA)

RAFT polymerization from conventional free-radical polymerization. In the main equilibrium (**Scheme-II**), $S=C(Ph)S-$ moiety is transferred between growing and dormant chains ensuring the living character of the polymerization. When the second monomer is added, the polymerization can be continued producing a block copolymer. In general, the leaving group ability of propagating radicals P_A should be comparable or higher than that of the propagating radicals P_B to achieve a well-controlled polymerization of monomer B [14,15].

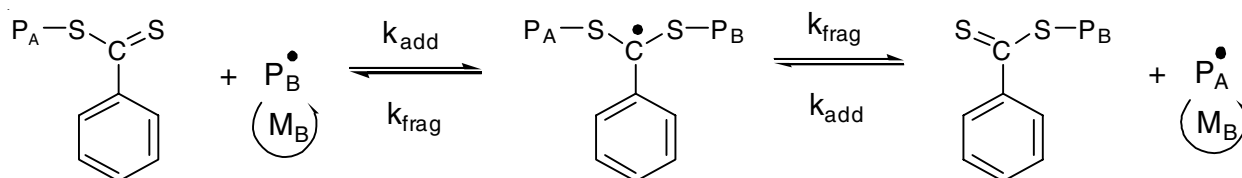
In this study, second block is a random copolymer instead of homopolymer. As PMMA and Pt-BDMSMA are both methacrylates, two types of macro-CTAs, PMMA- $SC(=S)Ph$ (macro-CTA1) and Pt-BDMSMA- $SC(=S)Ph$ (macro-CTA2) were investigated regarding their activity in the formation of two block random diblock terpolymers, PMMA-*b*-P(BA-co-*t*-BDMSMA) and Pt-BDMSMA-*b*-P(BA-co-MMA) (**Scheme-I**). These terpolymers were synthesized using two-step RAFT polymerization process. The first step concerns CPDB-mediated RAFT polymerization of MMA (or *t*-BDMSMA) to obtain homopolymers which could be used as macro-CTA. The reactions were stopped at a monomer conversion of about 70 % to avoid irreversible terminations and consequently ensure the high living character of resulting polymers. In these conditions, good molecular weight control and low dispersity were achieved for both macro-CTA (macro-CTA1: $M_n = 10\,200\text{ g mol}^{-1}$; $\bar{D} = 1.13$, and macro-CTA2: $M_n = 9\,900\text{ g mol}^{-1}$; $\bar{D} = 1.06$). The experimental M_n was close to theoretical M_n . In the second step, macro-CTA1 (or macro-CTA2) was used to control the copolymerization of BA/*t*-BDMSMA (or BA/MMA) monomer mixtures. The results of these syntheses are summarized in Table-2.

Fig. 4 shows the overlay of GPC of macro-CTA and block-random diblock terpolymers. Chain extensions attributed to the formation of diblock terpolymers are confirmed by a shift of GPC peak towards shorter elution times. The macro-CTA1 and macro-CTA2 are both good transfer agents, resulting narrow block-random diblock terpolymers ($\bar{D} < 1.15$). However, after 48 h of reaction, the monomer conversion was about 85 %, lower than that obtained in the random copolymerization as described above. In addition, molar proportion of MMA in PMMA-*b*-P(BA-co-*t*-BDMSMA) or of *t*-BDMSMA in Pt-BDMSMA-*b*-P(MMA-co-BA) is lower than the theoretical one. Actually,

TABLE-2
RAFT SYNTHESIS OF BLOCK-RANDOM DIBLOCK TERPOLYMERS

Terpolymer	Conv. (%)	[MMA]/[BA]/[<i>t</i> -BDMSMA] molar ratio		$M_{n,cal.}$ (g mol^{-1})	$M_{n,exp.}$ (g mol^{-1})	$\bar{D}$	T_g (°C)
		Initial	Final				
PMMA- <i>b</i> -P(BA-co- <i>t</i> -BDMSMA)	87	50/20/30	48/21/31	46 100	54 100	1.15	38.2 and 88.0
Pt-BDMSMA- <i>b</i> -P(MMA-co-BA)	85	50/20/30	58/17/25	31 400	44 500	1.11	68.7

[Monomer] = 1.5 M in toluene; temperature = 70 °C; time = 48 h; Conv. = monomer conversion; $M_{n,cal.} = M_{n,macro-CTA} + ([Monomer]/[macro-CTA]) \times \text{Conv.} \times M_{monomer}$



Scheme-II: Main equilibrium of the RAFT copolymerization using a macro-CTA

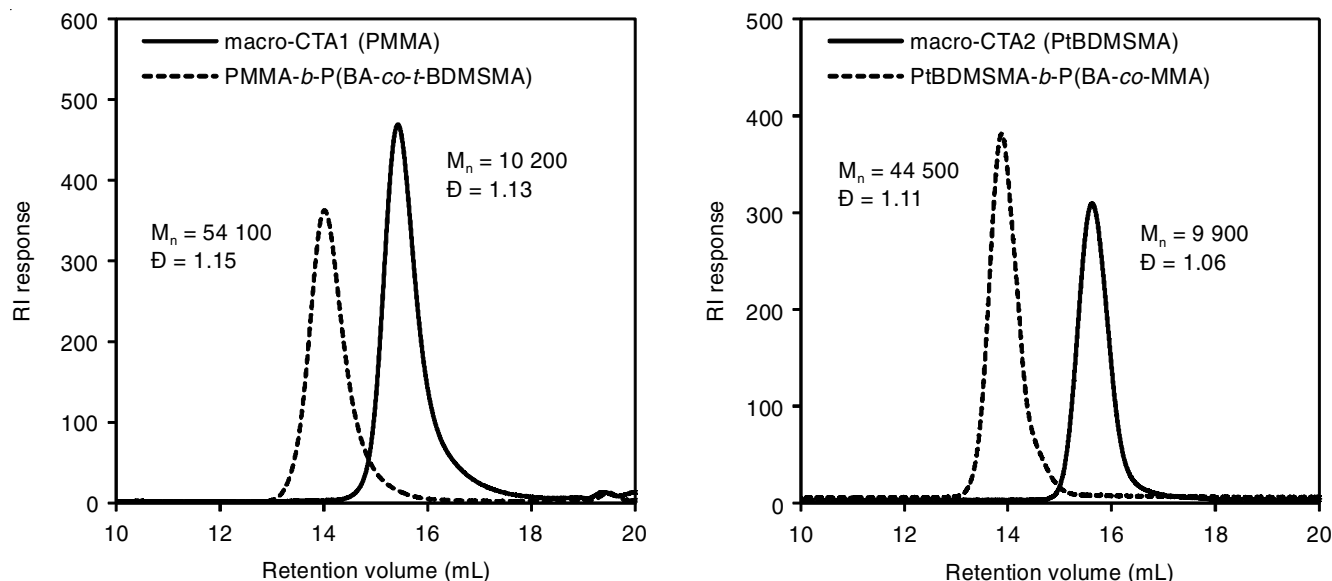


Fig. 4. SEC chromatograms of block-random diblock terpolymers PMMA-*b*-P(BA-*co*-*t*-BDMSMA) and Pt-BDMSMA-*b*-P(BA-*co*-MMA)

it is possible that a part of macro-CTA was not efficient and removed during the purification step. Consequently, the concentration of efficient macro-CTA in the polymerization medium was lower than expected and the experimental number-average molecular weights of resulting diblock terpolymers were higher than the calculated ones (Table-2).

The DSC thermograms for block-random diblock terpolymers are shown in Fig. 5. Two glass transitions at 38.2 °C and 88.0 °C were detected for PMMA-*b*-P(BA-*co*-*t*-BDMSMA). The T_g at 88.0 °C is attributed to the first block PMMA while T_g at 38.2 °C is attributed to the second block P(BA-*co*-*t*-BDMSMA). The presence of two glass transition temperatures indicates that the blocks are partially immiscible. However, the immiscibility is not total because the experimental T_g values do not correspond to the T_g values of pure blocks. For Pt-BDMSMA-*b*-P(MMA-*co*-BA), only one T_g at 68.7 °C was found. We doubt the possibility of a complete miscibility between two blocks but our suggestion was that a low proportion and molecular weight of first block Pt-BDMSMA could prevent the detection of its T_g .

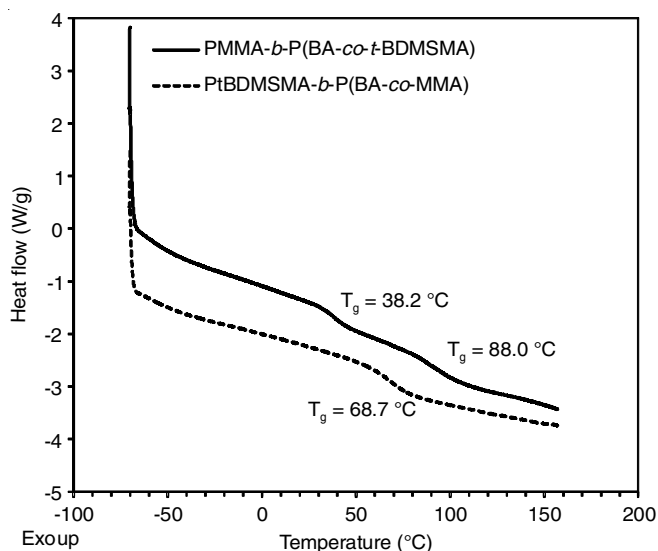


Fig. 5. DSC thermograms of block-random diblock terpolymers

Conclusion

Well-defined random and block-random diblock terpolymers bearing silylated ester groups as hydrolyzable pendant groups were successfully synthesized *via* RAFT process. Narrow random terpolymers P(MMA-*co*-BA-*co*-*t*-BDMSMA) with variation of butyl acrylate proportion were prepared by RAFT copolymerization of methyl methacrylate (MMA), butyl acrylate (BA) and *t*-BDMSMA using CPDB as RAFT agent. It has been demonstrated that well-defined block-random diblock terpolymers PMMA-*b*-P(BA-*co*-*t*-BDMSMA) or Pt-BDMSMA-*b*-P(BA-*co*-MMA) can be prepared using the two-step strategies. It is also possible to control the glass transition temperature of terpolymers (*i.e.* mechanical property) by varying the molar proportion of butyl acrylate (BA) monomer. This result is significant as the resulting terpolymers are more flexible than diblock copolymers PMMA-*b*-Pt-BDMSMA and consequently, it is more easily to use them as potential erodible binders for anti-fouling paints.

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