

Chemoselective and Living/Controlled Polymerization of Alkenyl Methacrylates by the Phosphonium Ylide/Organoaluminum Lewis Pairs

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 Electronic Supplementary Information

Abstract Chemoselective, living/controlled polymerizations of allyl methacrylate (AMA) and vinyl methacrylate (VMA) with/without methyl methacrylate (MMA) by using the phosphonium ylide/organoaluminum based Lewis pairs (LPs) have been realized. The P-ylide-**2**/AIme(BHT)₂ (P-ylide-**2** = Ph₃P=CHMe and BHT = 2,6-*i*Bu₂-4-MeC₆H₂O) was demonstrated to be superior by which homopolymers PAMAs ($M_n=27.6-111.5$ kg/mol and $\bar{D}=1.14-1.25$) and PVMAAs ($M_n=28.4-78.4$ kg/mol and $\bar{D}=1.12-1.18$) and block copolymers PMMA-*b*-PAMA, PAMA-*b*-PVMA, PAMA-*b*-PMMA, PMMA-*b*-PAMA-*b*-PMMA, PAMA-*b*-PMMA-*b*-PAMA, and PAMA-*b*-PVMA-*b*-PAMA were synthesized. In the polymerizations, all of the monomers were reacted by the conjugated ester vinyl groups leaving intactly the nonconjugated acryloxy groups. The pendant acryloxy groups attached to the main chain enable further to post-functionalization by the AIBN-induced radical “thiol-ene” reaction using PhCH₂SH. The thioether side group-containing polymers PAMA-SCH₂Ph and PAMA-SCH₂Ph-*b*-PMMA-*b*-PAMA-SCH₂Ph were thus prepared.

Keywords Phosphonium ylide; Alkenyl methacrylate; Chemoselectivity; Living/controlled polymerization; Post-functionalization

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INTRODUCTION

Alkenyl methacrylates are one of the most important polar divinyl monomers, which have been intensively utilized to synthesize the polymers with the pendant vinyl group attached to the main chain after the polymerization. The pendant vinyl groups are capable of the post-functionalization to produce unusual materials such as crosslinked gels, hyperbranched polymers, functional polymers, and so on.^[1–9] The success of the polymerization of these monomers is based on a large reactivity difference of the two vinyls existed inherently from between the conjugated ester and nonconjugated methacryloyl groups of the alkenyl methacrylates, prior to reaction chemoselectively on the ester vinyl group due to the higher competitive reaction rate, either estimated on the basis of the (Q,e) values from Alfrey-Price theory or determined by the experimentals.^[10]

Nonetheless, earlier studies showed that the radical poly-

merization of these monomers still could not maintain this chemoselectivity throughout the entire reaction process, and in the stage sooner or later additions to the pendant nonconjugated methacryloyl vinyls also took place, resulting in gelation due to formation of the polymers with the cross-linked network structures.^[11–13] While anionic polymerization of the alkenyl methacrylates showed such a high chemoselectivity dependant on the reaction temperature (low to –78 °C) and/or the monomer(s) selected,^[14,15] the silyl ketene acetals (SKA)-mediated group transfer polymerization (GTP) achieved a good chemoselectivity only for allyl methacrylate (AMA), producing polymers with low molecular weight (<2×10⁴ g/mol).^[16,17] Only in recent years, the perfect chemoselective polymerization of the alkenyl methacrylates as AMA, vinyl methacrylate (VMA), and 4-vinylbenzyl methacrylate (VBMA) was realized under mild condition at room temperature by Eugene and coworkers, where the unique zirconocene ester enolate catalyst was employed to perform an intramolecular coordination-addition polymerization.^[18] Meanwhile, Lu and coworkers discovered the organorare-earth metal catalyst that conducted well the highly reactive, chemoselective polymerization of AMA at similar condition following the similar polymerization mechanism.^[19]

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The complete chemoselective polymerization of the alkenyl methacrylates is significantly developed by means of the Lewis pair (LP) initiation method at current time. The Lewis base (LB) acts as a nucleophile while the Lewis acid (LA) an electrophile, which cooperatively work on the events by monomer activation and chain initiation, chain propagation and chain termination or transfer, forming an elusive way that enables the production of the well-defined polymers with customized molecular weight and narrow distribution.^[20–32] This way is now termed as Lewis pair polymerization (LPP), a type of reaction as the Michael enolate addition polymerization.^[33–35] Utilizing the *N*-heterocyclic carbene (NHC), *N*-heterocyclic carbene olefin (NHO), and trisubstituted phosphorus based LPs consisting of NHO (NHC, or PR₃)/Al(C₆F₅)₃ (R = Ph or *t*Bu), monomers AMA, VMA, and VBMA were successfully polymerized at room temperature giving PVMA, PAMA, and PVBMA, respectively, all with the unreacted methacryloyl vinyl as the side group.^[36] The NHC/E(C₆F₅)₃ (E = Al, B) was also workable for similar chemoselective polymerization of the divinyls as γ -vinyl- γ -methyl- α -methylene- γ -butyrolactone (γ VMMBL) and γ -allyl- γ -methyl- α -methylene- γ -butyrolactone (γ AMMBL), respectively.^[37] By the PR₃/(R'O)₃RE (RE = Sc, Y, Sm, La; R' = 2,6-*t*Bu₂C₆H₃; R'' = Cy, Et, Me) LP system, the PVMA, PAMA, and PVBMA were readily synthesized as well with the respective pendant methacryloyl vinyls, allyls, and styrels linked at the chain.^[38]

It is anticipated that the polymers with the pendant methacryloyl vinyl groups at the main chain would then find an expansion into the space-adjustable post-functionalization materials if insertion of the other alkyl (meth)acrylate block polymer (or oligomer) separators is realizable. This would be a new entry into the interesting polymer material and science.^[18,19] Following the most recent advance of the living/controlled manner of the LPP of the alkyl (meth)acrylates, block copolymers with the topology/morphology structures were readily available.^[39–43] As such, groups by Zhang and Lu realized preparation of several copolymers using AMA, VMA, and VBMA with/without methyl methacrylate (MMA), both by the NHO/AlMe(BHT)₂ (BHT = 2,6-*t*Bu₂-4-MeC₆H₂O) LP system.^[44,45] Clearly, the chemoselective and living/controlled polymerization of alkenyl methacrylates with/without alkyl methacrylates is now a route contentedly to approach to the space-adjustable polymers with the methacryloyl vinyl-containing side groups. However, such initiator system is, to our scope, limited. It was also envisioned that the initiation property could change and the polymers produced often varied with respect to the characters such as molecular weight, narrow distribution, and topology/morphology structures when changing the LP initiators. More recently, we reported on the phosphonium ylide/organoaluminum-based LPs for the highly efficient living/controlled polymerization of alkyl (meth)acrylates.^[46] Herein, we further investigate this LP system on the chemoselective, living/controlled polymerization using AMA and VMA with/without MMA. The phosphonium ylides as Ph₃P=CR¹R² (R¹, R² = H, H (P-ylide-**1**), H, Me (P-ylide-**2**), H, Et (P-ylide-**3**), H, Ph (P-ylide-**4**), Me, Me (P-ylide-**5**))^[47,48] were utilized together with the Al-based LAs as Al(C₆F₅)₃, AlR(BHT)₂ (R = Me, Et, *i*Bu), and Al*i*Bu₂(BHT) (Scheme 1).^[49–51] The post-functionalization us-

ing the polymers representative as PAMA and PAMA-*b*-PMMA-*b*-PAMA synthesized is investigated furthermore by means of the thiol–ene “click” reaction.

EXPERIMENTAL

Materials, Reagents and Methods

All manipulations were carried out under a dry argon or nitrogen atmosphere using Schlenk line and glovebox techniques. Solvents toluene, diethyl ether, tetrahydrofuran and *n*-hexane were dried by refluxing with sodium/potassium benzophenone under N₂ prior to use. C₆D₆ was dried over sodium/potassium benzophenone and CDCl₃ done with CaH₂ both under N₂ prior to use. The NMR (¹H and ³¹P) spectra were recorded on Bruker Avance II 400 or 500 MHz spectrometer.

Monomers as methyl methacrylate (MMA), allyl methacrylate (AMA), and vinyl methacrylate (VMA) were purchased from Energy Chemical, which were all dried over CaH₂ for 12 h, followed by vacuum distillation and then storing at –30 °C each in a brown bottle prior to use. Chemicals as [Ph₃PMe]Br, [Ph₃PEt]Br, [Ph₃P*n*Pr]Br, [Ph₃P*i*Pr]I, [Ph₃PBn]Br, and NaN(SiMe₃)₂ were purchased from Energy Chemical and used as received. Chemical reagents as AlMe₃, AlEt₃, Al*i*Bu₃, and 4-Me-2,6-*t*Bu₂C₆H₂OH ((BHT)H) were purchased from J&K and used as received. Phosphonium ylides Ph₃PCH₂ (P-ylide-**1**), Ph₃PCHMe (P-ylide-**2**), Ph₃PCHEt (P-ylide-**3**), Ph₃PCHPh (P-ylide-**4**), and Ph₃PCMe₂ (P-ylide-**5**) were synthesized according to procedures or by modified ones reported in literatures.^[47,48] Compounds B(C₆F₅)₃, Al(C₆F₅)₃, AlMe(BHT)₂, AlEt(BHT)₂, Al*i*Bu(BHT)₂, Al*i*Bu₂(BHT), were prepared according to literature procedures.^[49–51]

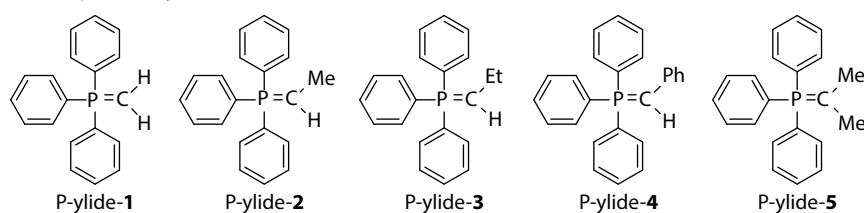
General Polymerization Procedures

Polymerization tests were performed typically using a 25 mL glass reactor kept at room temperature (25 °C). For the polymerization involving one monomer, sequence is by addition of a solution of the LA compound in solvent, monomer, and then a solution of the LB compound in solvent, under vigorous stirring. For monomer conversion study, each aliquot (0.2 mL) was picked out from the reaction mixture *via* pipet at the time interval settled, which was quickly quenched using undried “wet” CDCl₃ (0.6 mL, stabilized with BHT-H (250 ppm)) and was subsequently subject to the ¹H-NMR analysis. For the polymerization containing several monomers, time-traced ¹H-NMR spectral measurement was followed. After complete consumption of the first monomer as detected from the ¹H-NMR data, the second monomer was added, so it was with the other monomers. After the polymerization, the reaction mixture was quenched by addition of HCl (5%)-acidified methanol (50 mL). The polymers produced were collected by filtration and dried in a vacuum oven at 50 °C to a constant weight (typically for 12 h).

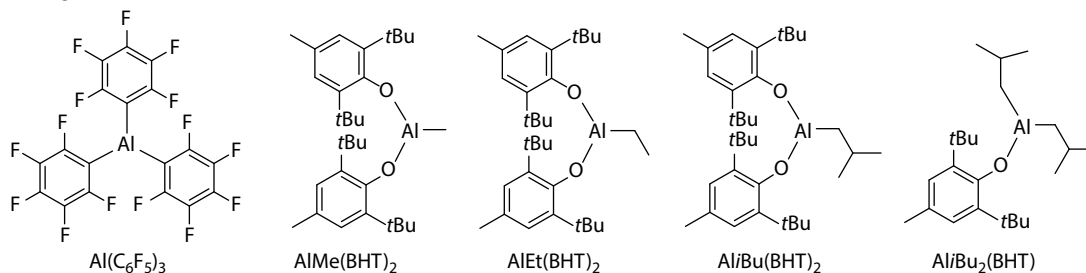
Polymer Characterizations

Number-average molecular weight (*M_n*) and molecular weight distributions (*D* = *M_w*/*M_n*) of the polymers were measured by gel permeation chromatography (GPC) at 35 °C, where THF (HPLC grade) was used as an eluent with a flow rate of 1 mL/min, on a Waters 1515 instrument equipped with 2707 Autosampler, 1515 Isocratic HPLC pump, and 2414 refractive index detector using three combined 7.8×300 mm columns (WAT044237,

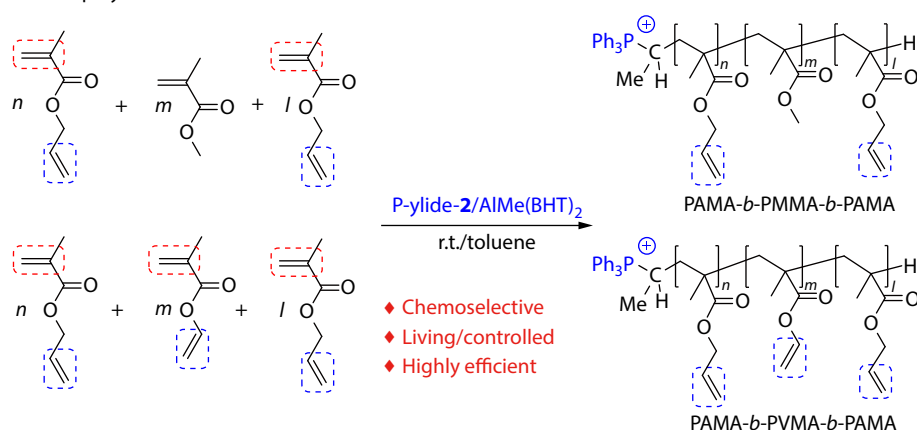
a Phosphonium ylides Lewis bases:



b Organoaluminum Lewis acids:



c Block copolymerizations:



Scheme 1 Phosphonium ylide Lewis bases, organoaluminum Lewis acids, and chemoselective, living/controlled block copolymerizations of AMA/MMA and AMA/VMA initiated by the P-ylide-2/AlMe(BHT)₂ LP system.

WAT054468 and WAT044225). The instrument was calibrated with 10 PMMA standards (Polymer Laboratories, linear range of molecular weight are from 2380 Dalton to 1.12×10⁶ Dalton). The chromatograms were processed with Empower software.

Polymer samples with low-MW were analyzed by matrix-assisted laser desorption/ionization time-of-flight mass spectroscopy (MALDI-TOF MS). The experiment was performed on a Bruker Autoflex speed TOF/TOF mass spectrometer in linear, positive ion, reflector mode using a Nd:YAG laser at 355 nm and 25 KV accelerating voltage. The sample was prepared by a deposition of a thin layer of CF₃COONa (1%) solution in THF on the target plate, followed with a mixture solution of polymer and matrix substrate *trans*-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propylidene]malonitrile (DCTB) (0.8 μL, 20 mg/mL) in THF. The raw data were processed using the Flex Analysis software.

The glass transition temperature (T_g) of the polymer was analyzed by differential scanning calorimeter (DSC, NETZSCH 204 F1). The polymer sample (5–10 mg) was weighed and the lid was compacted in a special aluminum crucible before being placed in the instrument. During the test, the required

temperature range was adjusted according to different polymers, and the temperature change rate was 10 °C/min. The method of liquid nitrogen cooling was adopted, and the test was carried out through the heating-cooling-heating-cooling cycle was tested.

Post-Functionalization

A typical procedure was started with the ratio of reagents [C=C]/[benzyl mercaptan]/[AIBN]=1/40/0.4. Thiol-ene click reaction between PAMAs or PAMA-*b*-PMMA-*b*-PAMAs and benzyl mercaptan was conducted in a 50 mL Schlenk flask under nitrogen atmosphere with 15 mL of THF as solvent and AIBN as initiator. The reaction mixture was allowed to stir for 36 h at 70 °C. After filtration, the solvent was removed by rotary evaporation. The product was dissolved into THF and precipitated in methanol. The product was reprecipitated for several times and dried by vacuum.

RESULTS AND DISCUSSION

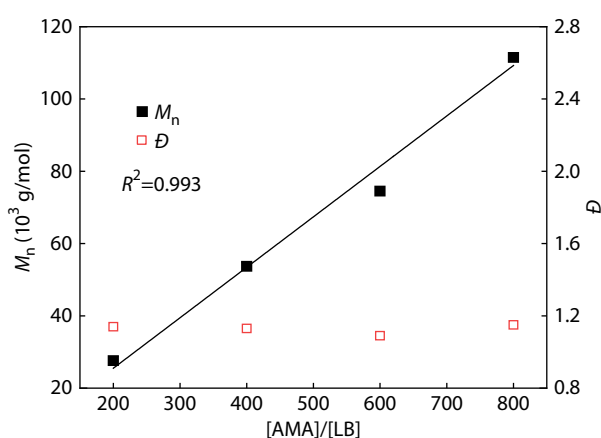
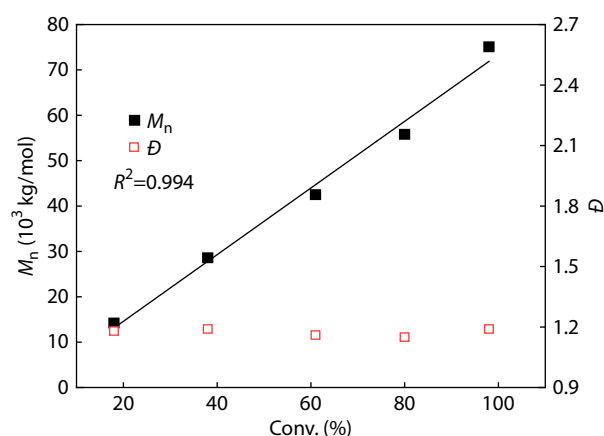
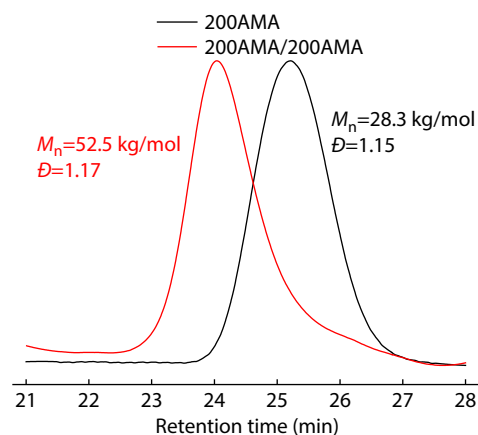
Our previous studies had shown that, by screening on the five LBs as P-ylide-1–P-ylide-5 in connection with the five LAs like

Table 2 The VMA and AMA polymerization results by using P-ylide-2/AIme(BHT)₂ initiator system.^a

Run	LB	LA	M	t (min)	Conv. ^b (%)	M_n^c (kg/mol)	\mathcal{D}^c	I^d (%)
1	P-ylide-2	AIme(BHT) ₂	200AMA	1	100	27.6	1.14	92
2	P-ylide-2	AIme(BHT) ₂	400AMA	5	100	53.7	1.13	94
3	P-ylide-2	AIme(BHT) ₂	600AMA	10	100	74.5	1.09	102
4	P-ylide-2	AIme(BHT) ₂	800AMA	30	100	111.5	1.15	91
5	P-ylide-2	AIme(BHT) ₂	200VMA	10	100	28.4	1.17	80
6	P-ylide-2	AIme(BHT) ₂	400VMA	20	100	50.2	1.18	90
7	P-ylide-2	AIme(BHT) ₂	600VMA	30	100	78.4	1.12	86

^a Conditions: Polymerization was carried in toluene at room temperature, where $[M]_0=0.92$ mol/L; ^b Monomer conversions (%) are measured by ¹H-NMR; ^c M_n and \mathcal{D} are determined by GPC relative to PMMA standards in THF; ^d Initiator efficiency (I^d) = $M_n(\text{calcd.})/M_n(\text{exptl.})$, where $M_n(\text{calcd.}) = [\text{MW}(\text{M})][([M]_0/[I]_0)(\text{conversion}) + \text{MW of chain-end groups}]$.

1, 5, 10, and finally to 30 min. Moreover, the GPC tests show that the M_n values of the PAMAs generated increase linearly ($R^2=0.993$) with the increasingly added AMA amounts while the narrow molecular weight distributions ($\mathcal{D}=1.09\text{--}1.15$) were retained (Fig. 2). Calculations indicate a keeping of the high to quantitative I^d (91%–102%) as well. Secondly, the time-traced monomer conversion detection was accomplished by selecting the 1/2/600 [P-ylide-2]₀/[AIme(BHT)₂]₀/[AMA]₀ reaction system, and a straight line ($R^2=0.994$) plot of the PAMA M_n values versus monomer conversions, coupling with $\mathcal{D}=1.15\text{--}1.18$, was clearly exhibited (Fig. 3). Thirdly, chain extension experiments were also performed by this LP. In one pot, first addition of the 200 equiv. of AMA resulted in the production of the PAMAs with $M_n=28.3$ kg/mol and $\mathcal{D}=1.15$ and the second addition of the 200 equiv. of PAMAs with $M_n=52.5$ kg/mol and $\mathcal{D}=1.17$ as anticipated (Table S1 in ESI and Fig. 4). Finally, block copolymerizations were done involving sequential additions of 200 equiv. of MMA and 200 equiv. of AMA, and well-regulated AB-type diblock copolymers PMMA-*b*-PAMA were readily formed having $M_n=45.4$ kg/mol and $\mathcal{D}=1.17$ (run 1, Table S2 in ESI and Fig. 5a, red). Furthermore, well-defined ABA triblock copolymers PMMA-*b*-PAMA-*b*-PMMA ($M_n=80.7$ kg/mol and $\mathcal{D}=1.25$, run 2, Table S2 in ESI and Fig. 5a, blue) were also successfully synthesized, so it was with the AB diblock PAMA-*b*-PMMA ($M_n=50.4$ kg/mol and $\mathcal{D}=1.21$, run 3, Table S2 in ESI) and PAMA-*b*-PVMA ($M_n=53.5$ kg/mol and $\mathcal{D}=1.18$, run 5, Table S2 in ESI) (Figs. 5b and 5c, red) and ABA triblock PAMA-*b*-PMMA-*b*-PAMA ($M_n=76.4$ kg/mol and

**Fig. 2** Plots of M_n and \mathcal{D} for the PAMA versus $[\text{AMA}]_0/[\text{P-ylide-2}]_0$ ratio.**Fig. 3** Plots of M_n and \mathcal{D} of PAMA versus AMA conversion catalyzed by P-ylide-2/AIme(BHT)₂ at RT. Conditions: $[\text{AMA}]_0/[\text{P-ylide-2}]_0/[\text{AIme(BHT)}_2]_0=600/1/2$.**Fig. 4** The GPC traces of PAMA samples obtained from chain extension experiments in toluene at RT.

$\mathcal{D}=1.26$, run 4, Table S2 in ESI) and PAMA-*b*-PVMA-*b*-PAMA ($M_n=81.2$ kg/mol and $\mathcal{D}=1.21$, run 6, Table S2 in ESI) (Figs. 5b and 5c, blue). All of these results prove the living/controlled AMA polymerization initiated by the P-ylide-2/AIme(BHT)₂ LP.

Next, we selected the PAMA obtained at run 3 in Table 2 and performed the ¹H-NMR spectral study. It is clearly shown that the resonances at $\delta_{\text{=CH}_2}$ 6.13 and 5.58 ppm (\blacktriangle) assigned to the ester vinyl protons of the AMA disappeared after polymerization. Instead, broad resonances at δ 2.00 (5%*mm*), 1.94 (21%*mr*) and 1.85 (74%*rr*) ppm were found corresponding to

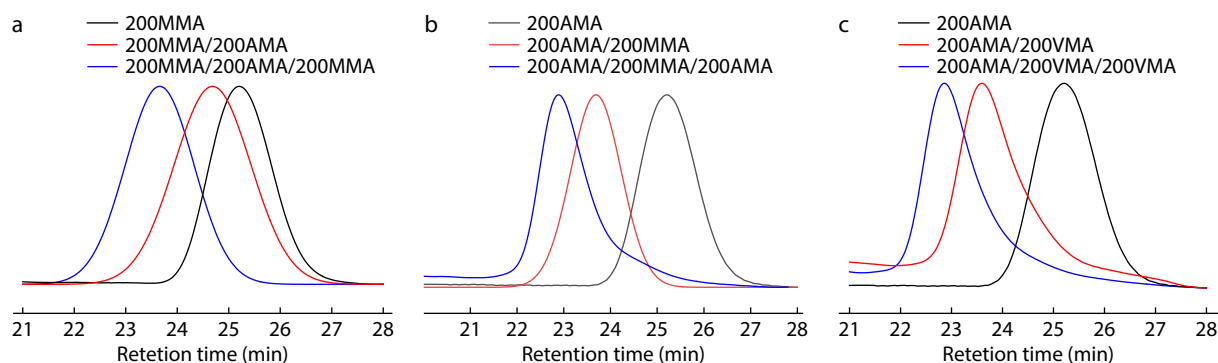


Fig. 5 GPC traces of the homopolymers (black), diblock copolymers (red), and ABA triblock copolymers (blue) produced from the sequential block copolymerization using P-ylide-2/AlMe(BHT)₂ in toluene at RT. Homopolymer, diblock and triblock copolymers produced from the sequential block copolymerization using (a) MMA and AMA, (b) AMA and MMA, and (c) AMA and VMA.

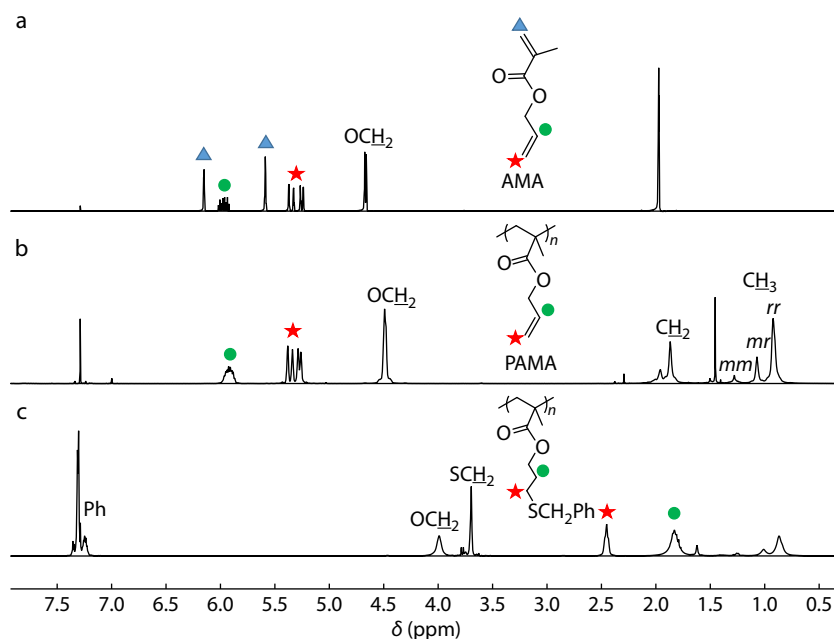


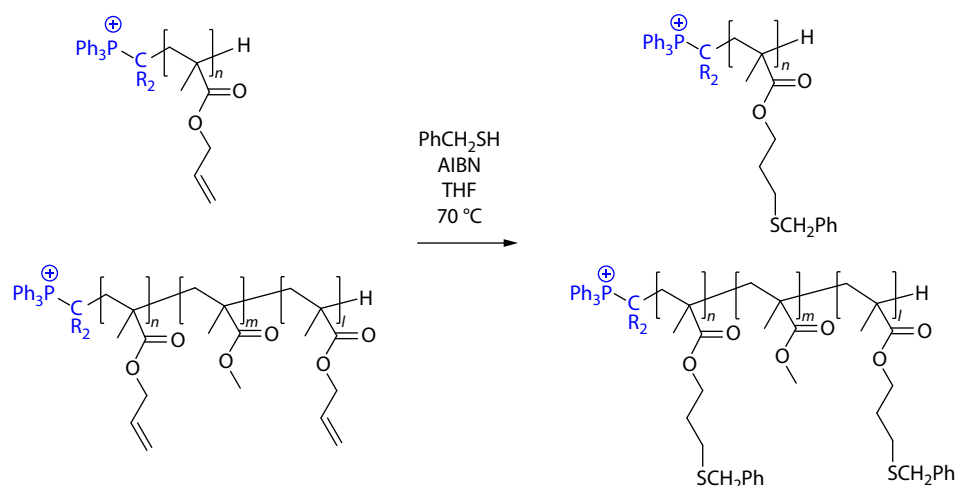
Fig. 6 ¹H-NMR spectra of (a) AMA, (b) PAMA, and (c) PAMA-SCH₂Ph.

the methylene group formed in the main chain of the PAMA.^[52] In comparison, the methacryloyl vinyl protons resonate at δ 5.94 (CHCH₂, ●) and 5.23 (CHCH₂, ★) ppm for the AMA while at δ 5.91 (CHCH₂, ●) and 5.30 (CHCH₂, ★) ppm for the PAMAs (Figs. 6a and 6b). The AMA polymerization occurs substantially at the ester vinyl rather than the methacryloyl vinyl, being indeed chemoselective.

The P-ylide-2/AlMe(BHT)₂ LP system was also proved to work well on the chemoselective, living/controlled polymerization of the VMA with the high f^* of 80%–90% (runs 5–7 in Table 2 and Figs. S2 and S3 in ESI). The as-produced PVMA have low \bar{D} of 1.12–1.18. As mentioned above, well-defined AB diblock PAMA-*b*-PVMA and ABA triblock PAMA-*b*-PVMA-*b*-PAMA have both been successfully synthesized.

We were interested in the post-functionalization of the polymers with the pendant vinyl groups attached to the main chain. As such, the PAMA obtained from run 6 in Table 2 and PAMA-*b*-PMMA-*b*-PAMA from run 4 in Table S2 (in ESI) were selected for the “thiol-ene” reaction. By using AIBN as an initiator, the radical reaction with PhCH₂SH was carried out in THF

at 70 °C for ca. 36 h,^[9] readily affording the thiolated polymers as PAMA-SCH₂Ph and PAMA-SCH₂Ph-*b*-PMMA-*b*-PAMA-SCH₂Ph (Scheme 2). These polymers were characterized by the ¹H-NMR spectroscopy and the GPC analysis. As shown in Fig. 6(c), resonances at δ 5.94 (CHCH₂, ●) and 5.23 (CHCH₂, ★) for the methacryloyl vinyl protons of the PAMA completely vanished after thiolation, and instead the resonances at δ 2.43 (SCH₂CH₂, ★) and 1.81 (SCH₂CH₂, ●) appeared, assignable to the CH₂CH₂ group newly formed in the PAMA-SCH₂Ph. Similar ¹H-NMR data variation was also displayed owing to the PhCH₂SH-function into the PAMA-SCH₂Ph-*b*-PMMA-*b*-PAMA-SCH₂Ph (Fig. S4 in ESI). The GPC analysis showed the M_n of 74.5 kg/mol for the selected PAMA and then increased M_n of 147.2 kg/mol for the PAMA-SCH₂Ph, where the \bar{D} was kept at a narrow value from 1.09 to 1.18 (Fig. S5a in ESI). Notably, the increased molecular weight (72.7 kg/mol) appears very close to that of the consumed PhCH₂SH (74.5 kg/mol). Again, the GPC data exhibit the M_n of 76.4 kg/mol for the original PAMA-*b*-PMMA-*b*-PAMA and of 123.0 kg/mol for the PAMA-SCH₂Ph-



Scheme 2 Post-functionalization by “thiol-ene” reaction using PAMA and PAMA-*b*-PMMA-*b*-PAMA with PhCH₂SH in presence of AIBN.

b-PMMA-*b*-PAMA-SCH₂Ph with the respective *D* of 1.26 and 1.28 (Fig. S5b in ESI), and the increased molecular weight (46.6 kg/mol) is close to the reacted PhCH₂SH amount (49.7 kg/mol). These indicate that the PhCH₂SH added were almost reacted towards the pendant methacryloyl vinyl groups attached to the main chain. Finally, such two polymers PAMA and PAMA-*b*-PMMA-*b*-PAMA and their “thiol-ene” reaction products PAMA-SCH₂Ph and PAMA-SCH₂Ph-*b*-PMMA-*b*-PAMA-SCH₂Ph were subject to the glass-transition temperature (*T*_g) measurement through the differential scanning calorimetry (DSC). The parent two polymers display the *T*_g of 66 and 87 °C while the thiolated two ones exhibit the *T*_g of 63 and 71 °C, respectively (Fig. S6 in ESI). The post-functionalization changes the thermal property of the original polymers prepared.

CONCLUSIONS

In summary, by crossing tests over the five phosphonium ylides, P-ylide-1 to P-ylide-5, as the LB in connection with the five organoaluminums Al(C₆F₅)₃, AlR(BHT)₂ (R = Me, Et, *i*Bu), and Al*i*Bu₂(BHT) as the LA, the P-ylide-2/AlMe(BHT)₂ LP system is demonstrated to be superior to initiate the chemoselective, living/controlled polymerization of the polar divinyl monomers as AMA and VMA both at the ester C=C bond. Especially, the well-defined polymers PAMA and PAMA-*b*-PMMA-*b*-PAMA as-prepared both feature the pendant acryloxy groups attached to the main chains, and these vinyl groups have been successfully post-functionalized by the AIBN-induced radical “thiol-ene” reaction to produce polymers PAMA-SCH₂Ph and PAMA-SCH₂Ph-*b*-PMMA-*b*-PAMA-SCH₂Ph, respectively. The latter is the thioether side group-containing polymer having the block non-thiolation PMMA space separator. Preparation of crosslinked gels and hyperbranched polymers using this method is in progress.

Conflict of Interests

The authors declare no interest conflict.

Electronic Supplementary Information

Electronic supplementary information (ESI) is available free of charge in the online version of this article at <http://doi.org/10.1007/s10118-023-3039-7>.

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