

## Polymers | Hot Paper |

# Phosphorus-Containing Block Copolymers from the Sequential Living Anionic Copolymerization of a Phosphaalkene with Methyl Methacrylate

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**Abstract:** Although living polymerization methods are widely applicable to organic monomers, their application to inorganic monomers is rare. For the first time, we show that the living poly(methylenephosphine) ( $\text{PMP}_n^-$ ) anion can function as a macroinitiator for olefins. Specifically, the phosphaalkene,  $\text{MesP}=\text{CPh}_2$  (**PA**), and methyl methacrylate (**MMA**) can be sequentially copolymerized using the  $\text{BnLi-TMEDA}$  initiator system in toluene. A series of  $\text{PMP}_n\text{-}b\text{-PMMA}_m$  copolymers with narrow dispersities are accessible ( $D=1.05\text{--}1.10$ ).

Analysis of the block copolymers provided evidence for  $-\text{P-CPh}_2\text{-CH}_2\text{-CMe}(\text{CO}_2\text{Me})-$  switching groups. Importantly, this indicates that the  $-\text{P-CPh}_2^-$  anion directly initiates the anionic polymerization of **MMA** and stands in stark contrast to the isomerization mechanism followed for the homopolymerization of **PA**. For the first time, the glass transition of a  $\text{PMP}_n$  homopolymer has been measured ( $T_g=45.1^\circ\text{C}$ ,  $n=20$ ). The  $\text{PMP}_n\text{-}b\text{-PMMA}_m$  copolymers do not phase separate and show a single  $T_g$  which increases with higher **PMMA** content.

## Introduction

The incorporation of *p*-block elements into polymers is a rapidly growing area of macromolecular science due to the fascinating properties and potential applications imparted by the presence of inorganic functionalities that possess unique coordination numbers, reactivity, oxidation states, and magnetic properties.<sup>[1]</sup> The dearth of efficient and predictable transformations to incorporate *p*-block elements into long chains stands as the principal barrier to the widespread growth of inorganic polymer science. Despite these challenges, there has been considerable recent growth in the discovery of new and sophisticated synthetic methods to access macromolecular structures featuring inorganic functionalities.<sup>[2]</sup>

Of the known methods to synthesize macromolecules, living polymerization provides the most powerful method to access tailor made block copolymers with controlled size, architecture and properties.<sup>[3]</sup> Although living polymerization techniques have been widely applied to organic monomers, the successful application of these methods to inorganic element-containing monomers is quite rare. Examples are limited to the anionic polymerization of silicon- or phosphorus-bridged [1]-ferroceno-

phanes,<sup>[4]</sup> silacyclobutanes,<sup>[5]</sup> and “masked” disilenes.<sup>[6]</sup> The fascinating cationic polymerization of phosphoranimes is a rare example of a condensation polymerization that follows a living mechanism.<sup>[7]</sup>

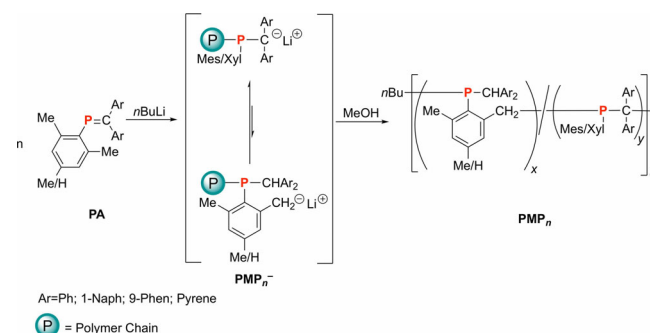
We have successfully accomplished the living anionic polymerization of phosphaalkenes,  $\text{P}=\text{C}$  analogues of olefins, to afford homo- and block co-polymers with controlled architectures and unique chemical functionality.<sup>[8]</sup> For instance, polystyrene-*block*-poly(methylenephosphine) ( $\text{PS}_n\text{-}b\text{-PMP}_m$ ) and polyisoprene-*block*-poly(methylenephosphine) ( $\text{PI}_n\text{-}b\text{-PMP}_m$ ) are accessible using the  $n\text{BuLi}$ -initiated polymerization of styrene or isoprene followed by **PA**.<sup>[8d, f]</sup> The polymerization of **PA** follows an unprecedented addition-isomerization mechanism (Scheme 1) which, until the present work, has prevented the application of living  $\text{PMP}_n^-$  as a macroinitiator for olefins.<sup>[9]</sup>

Herein, we report the first block copolymers derived from the living anionic sequential polymerization of a phosphaalkene (**PA**) and methyl methacrylate (**MMA**). The  $-\text{P}(\text{Mes})\text{-CPh}_2\text{-CH}_2\text{-CMe}(\text{CO}_2\text{Me})-$  switching group was elucidated from multi-

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Scheme 1. Anionic polymerization of  $\text{RP}=\text{CAr}_2$  ( $\text{R} = \text{Mes}$  or  $o\text{-Xyl}$ ).

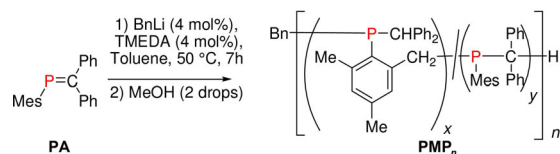
nuclear NMR spectroscopic experiments. In addition, a preliminary examination of the physical properties of these novel polymers is reported, including the measurement of their glass transition temperatures.

## Results and Discussion

Acrylate-containing block copolymers have attracted attention for their self-assembly and biocompatibility characteristics with applications ranging from drug delivery to self-healing.<sup>[10]</sup> The living anionic polymerization of acrylates is synthetically challenging due, in part, to side-reactions involving the ester functionality that compete with initiation and propagation.<sup>[11]</sup> Thus, the living anionic polymerization of acrylates such as methyl methacrylate (MMA) requires low temperatures and bulky  $\pi$ -stabilized diphenylalkyllithium initiators.<sup>[12]</sup> Given the similarity of the  $-P-CPh_2^-$  end of living  $PMP_n$  to the  $nBuCH_2-CPh_2^-$  initiator used for MMA,<sup>[13]</sup> we hypothesized that the sequential living anionic polymerization of **PA** and MMA might be possible.

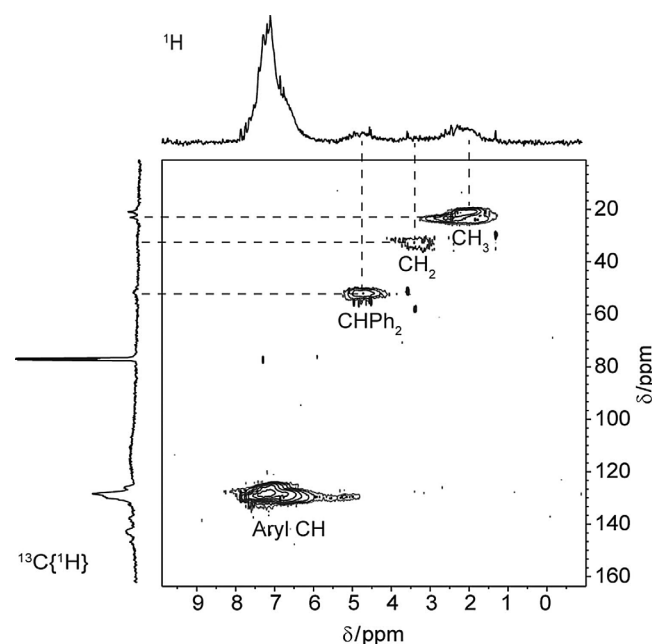
Our previous studies of the  $nBuLi$ -initiated living anionic polymerization of phosphalkenes were performed in polar solvents (THF or glyme) at room temperature in order to achieve acceptable rates of polymerization.<sup>[8e,f]</sup> However, such conditions are not compatible with those employed for living acrylate polymerizations. Therefore, we explored the homopolymerization of **PA** using the milder  $BnLi$  ( $Bn = benzyl$ ) initiator in toluene. Our initial attempts to activate the  $P=C$  bond of **PA** in toluene with  $BnLi$  (4 mol%) initiator at 50 °C were unsuccessful. The reaction was monitored by  $^{31}P$  NMR spectroscopy and no evidence for polymerization was observed after four days.

A common approach to increase the reactivity of organolithium reagents involves adding a chelating agent such as TMEDA to the reaction mixture to bind  $Li^+$  and increase ion separation.<sup>[14]</sup> When the polymerization was repeated in the presence of TMEDA (4 mol%), under otherwise identical conditions, monomer **PA** was quantitatively converted to poly(methylenephosphine)  $PMP_n$  (Scheme 2). Polymerization progress was conveniently monitored using  $^{31}P\{^1H\}$  NMR spectroscopy. After 7 h, the signal corresponding to phosphalkene ( $\delta = 234$ ) was completely replaced by a broad resonance at  $-9$  ppm that was assigned to  $PMP_n$ . Treatment of the deep red solution, characteristic of living  $PMP$ , with MeOH (2 drops) resulted in a color change to pale yellow, indicative of termination of the propagating anion. Polymer  $PMP_n$  was isolated as a colorless solid by concentrating the reaction solution and precipitating with methanol ( $\times 2$ ).



**Scheme 2.** Living anionic polymerization of phosphalkene (**PA**) to afford poly(methylenephosphine) ( $PMP_n$ ,  $n = 25$ ).

The isolated homopolymer,  $PMP_n$ , was analyzed by using one- and two-dimensional  $^1H$ ,  $^{13}C$  and  $^{31}P$  NMR spectroscopy. The  $^1H$ - $^{13}C$  HSQC NMR spectrum (Figure 1) was particularly informative showing clear cross correlations assigned to  $CH_3$



**Figure 1.**  $^1H$ - $^{13}C$  HSQC NMR spectrum (400 MHz for  $^1H$ ,  $CDCl_3$ , 298 K) of  $PMP_{25}$ . The ordinate shows the  $^{13}C\{^1H\}$  NMR spectrum and the abscissa shows the  $^1H$  NMR spectrum.

( $^{13}C$ :  $\delta = 21.1$ ,  $^1H$ :  $\delta = 2.0$ ),  $CHPh_2$  ( $^{13}C$ :  $\delta = 52.0$ ,  $^1H$ :  $\delta = 4.7$ ),  $CH_2$  ( $^{13}C$ :  $\delta = 32.5$ ,  $^1H$ :  $\delta = 3.4$ ) and the aryl moiety ( $^{13}C$ :  $\delta = 128.3$ ,  $^1H$ :  $\delta = 7.1$ ). These signals are consistent with a polymer of microstructure  $PMP_n$  ( $x \gg y$ ). This microstructure has previously been observed in the radical-initiated polymerization of **PA**<sup>[9b]</sup> and our studies into its formation by anionic methods have recently been reported.<sup>[9b]</sup> The isolated  $PMP_n$  was analyzed by GPC with a multi-angle light-scattering (MALS) detector that revealed that the polymer had a molecular weight of  $8000 \text{ g mol}^{-1}$ . This value is close to that predicted by the monomer to initiator used for the polymerization [ $M_n(\text{calcd}) = 7992 \text{ g mol}^{-1}$ ;  $n = 25$ ]. The dispersity of the polymer was also narrow ( $D = 1.12$ ) and consistent with a living mechanism.

The polymerization reaction followed a pseudo-first order rate law to ca. 60% conversion. Measuring the rate constants at six temperatures (range: 50–75 °C) permitted the determination of the activation energy ( $E_a = 16.7 \pm 0.7 \text{ kcal mol}^{-1}$ ; see Figure S4). As expected, this was slightly higher than that found for the  $nBuLi$  initiated polymerization in the more polar glyme ( $E_a = 14.0 \pm 0.9 \text{ kcal mol}^{-1}$ ).<sup>[8e]</sup> It should be noted that above ca. 60% conversion, significant deviations from pseudo-first order kinetics were observed that were highly temperature dependent. Such deviations have been noted previously and may indicate a change in mechanism at high conversion. Studies of this unusual addition-isomerization mechanism are ongoing but are beyond the scope of the present investigation.

The prospect to utilize the  $\text{-CPh}_2^-$  anion of living  $\text{PMP}_n$  as an initiator for methyl methacrylate was intriguing since we have previously been unable to initiate olefinic monomers such as styrene and isoprene using this hindered carbanion. To explore this possibility, a red toluene solution of living  $\text{PMP}_{25}$  was prepared from  $\text{PA}$  and  $\text{BnLi}$  ( $M_1:I=25:1$ ) in the presence of TMEDA as described above. Following a typical procedure for the living anionic polymerization of acrylates,<sup>[12a,15]</sup> a 20 mol% solution of  $\text{LiCl}$  in THF ( $[\text{LiCl}]:[I]=600:1$ ) was added and the reaction mixture was cooled to  $-78^\circ\text{C}$  prior to adding MMA. The lithium salt is believed to stabilize the active ion pair and shift the classical equilibrium between free ions and ion pairs.<sup>[12a]</sup> Subsequently, a solution of methyl methacrylate (100 equiv) in THF was added and the color of solution immediately changed from deep red to light yellow. The reaction mixture was slowly warmed to room temperature over several hours. Subsequently, the polymerization was terminated by the addition of degassed methanol (2 drops). The yellow color of the reaction mixture became much paler, towards colorless, consistent with quenching of the active chain ends. The reaction mixture was concentrated and was added to a vigorously stirred degassed methanol solution, from which the polymer precipitated as a white solid. The material was purified by two additional precipitations and dried in vacuo. GPC-MALS analysis revealed a narrow molecular weight distribution ( $M_n=18000\text{ g mol}^{-1}$ ;  $\mathcal{D}=1.09$ ) with the molecular weight being close to that predicted for  $\text{PMP}_{25}\text{-}b\text{-PMMA}_{100}$  [ $M_n(\text{calcd})=17992\text{ g mol}^{-1}$ ].

By following analogous procedures to those described above, a series of block copolymers,  $\text{PMP}_n\text{-}b\text{-PMMA}_m$ , were prepared with a range of PMP block lengths ( $n=10\text{--}30$ ) and PMMA block lengths ( $m=10\text{--}100$ ). The results are summarized in Table 1. Each copolymer, and the  $\text{PMP}_n$  from which was generated, was analyzed by GPC-MALS. The chromatograms (RI trace) are shown in Figure 2. In each case, the experimentally determined number average molecular weight was within 4% of the calculated value except for  $\text{PMP}_{20}\text{-}b\text{-PMMA}_{20}$  which displays 15% deviation. Overall, the living copolymerization reactions were highly successful as judged by the narrow dispersi-

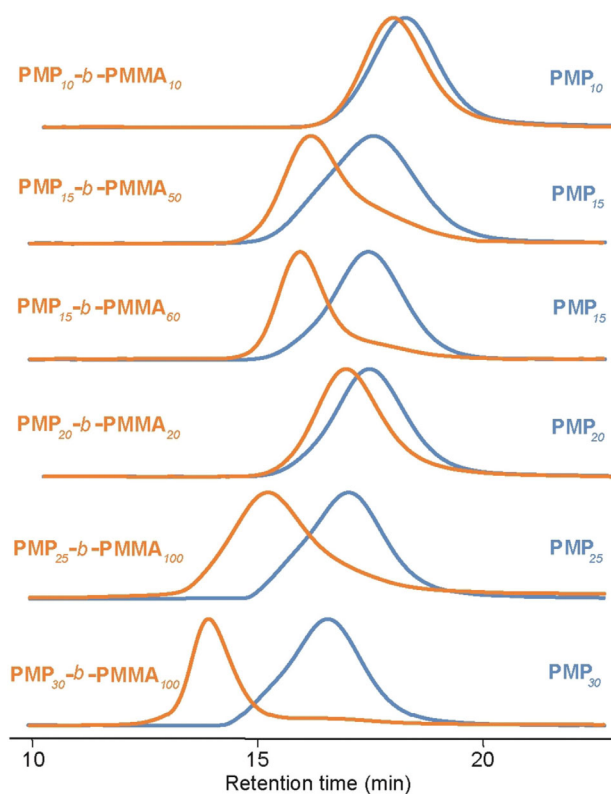


Figure 2. GPC chromatograms (refractive index traces) collected for homo-polymer  $\text{PMP}_n$  (blue trace) and block copolymer  $\text{PMP}_n\text{-}b\text{-PMMA}_m$  (orange trace) for each copolymerization.

ties being observed ( $\mathcal{D}=1.05\text{--}1.10$ ) and the fact that the traces suggest minimal amounts of the homo- $\text{PMP}_n$  in each copolymer.

To gain additional insight into the microstructure of these new block copolymers,  $^1\text{H}$  and  $^{13}\text{C}\{^1\text{H}\}$  NMR spectra were recorded for each along with various two-dimensional spectra. The  $^1\text{H}$  NMR spectra of purified block copolymers (e.g.  $\text{PMP}_{10}\text{-}b\text{-PMMA}_{10}$ ) show the expected signals for the PMP block ( $\delta=2.0$  to  $\text{CH}_3$ ;  $\delta=3.4$  to  $\text{CH}_2$ ;  $\delta=4.7$  to  $\text{CHPh}_2$ ;  $\delta=7.1$  to aryl pro-

Table 1. Tabulated results from the living anionic block copolymerization of  $\text{PA}$  ( $M_1$ ) with  $\text{MMA}$  ( $M_2$ ) initiated with  $\text{BnLi}$  ( $I$ ) in Toluene/THF solution in the presence of  $\text{LiCl}$ .

Entry <sup>[a]</sup>	$M_1/I/M_2$ <sup>[b]</sup>	$M_n(\text{calcd})$ [ $\text{g mol}^{-1}$ ] <sup>[c]</sup>	$\text{PMP}_n$			$\text{PMP}_n\text{-}b\text{-PMMA}_m$			Tacticity PMMA block		
			$M_n(\text{obsd})$ [ $\text{g mol}^{-1}$ ] <sup>[d]</sup>	$\mathcal{D}$ <sup>[d]</sup>	$M_n(\text{calcd})$ [ $\text{g mol}^{-1}$ ] <sup>[c]</sup>	$M_n(\text{obsd})$ [ $\text{g mol}^{-1}$ ] <sup>[d]</sup>	$\mathcal{D}$ <sup>[d]</sup>	$dn/dc$ <sup>[e]</sup>	<i>mm</i>	<i>mr</i>	<i>rr</i>
1	10:1:10	3252	3400	1.06	4252	4300	1.07	0.190	24%	21%	55%
2	15:1:50	4832	4800	1.13	9832	10100	1.06	0.137	2%	21%	77%
3	15:1:60	4832	5100	1.16	10832	10900	1.09	0.128	5%	24%	71%
4	20:1:20	6412	5500	1.08	8412	7100	1.06	0.190	14%	27%	59%
5	25:1:100	7992	7100	1.13	17992	18000	1.09	0.130	2%	27%	71%
6	30:1:100	9572	9000	1.08	19572	19800	1.05	0.137	6%	22%	72%
7	1:1:400				40408	42300	1.10	0.045	1%	23%	76%

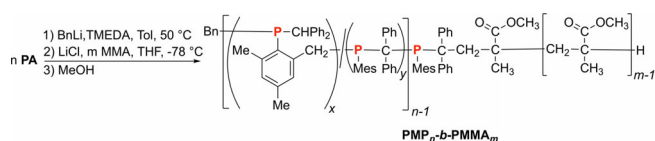
[a] Procedure:  $M_1$  in Tol with TMEDA at  $50^\circ\text{C}$ . Upon complete consumption of  $M_1$ , half of the reaction solution was quenched with  $\text{MeOH}$  affording  $\text{PMP}_n$ . The other half was cooled to  $-78^\circ\text{C}$ ,  $\text{LiCl}$  was added ( $[\text{LiCl}]:[I]=600:1$ ), followed by  $M_2$ . At completion, the reaction mixture was quenched with  $\text{MeOH}$  giving  $\text{PMP}_n\text{-}b\text{-PMMA}_m$ . [b]  $M_1 = \text{PA}$ ,  $I = \text{BnLi}$ ,  $M_2 = \text{MMA}$ . [c]  $M_n(\text{calcd}) = (\text{FW of } M_1 \text{ or } M_2) \times [M_1]:[I] \text{ ratio} + (M_n \text{ of initiator fragment}) + (M_n \text{ of terminator fragment})$ . [d] Evaluated by triple detection MALS-GPC.<sup>[e]</sup> The  $dn/dc$  of  $\text{PMP}_{20}\text{-}b\text{-PMMA}_{20}$  was determined from RI measurements (see: Figure S5 in the Supporting Information). This was used in conjunction with the previously determined  $dn/dc$  of  $\text{PMP}$ <sup>[8e]</sup> to calculate the  $dn/dc$  of the other polymers [Eq. (1)]. These values were similar to those determined using the 100% mass recovery method.

tons) along with signals attributed to the PMMA segment ( $\delta = 0.9, 1.0, 1.2$  to  $\text{CH}_3$ ,  $\delta = 1.8$  to  $\text{CH}_2$ ,  $\delta = 3.6$  to  $\text{OCH}_3$ ). As expected, the three signals at approximately 0.9, 1.0 and 1.1 ppm ( $^1\text{H}$  NMR) were observed for the  $-\text{CH}_3$  moieties of the acrylate repeating unit which are assigned to the *rr*, *mr*, *mm* triads, respectively.<sup>[16]</sup> Based on the integration of these three resonances (Figure S8), we conclude that the PMMA block in **PMP<sub>n</sub>-b-PMMA<sub>m</sub>** adopts a primarily syndiotactic microstructure (55%–77%; see Table 1). Interestingly, shorter MMA block lengths appear to display higher *m* contents which presumably results from influence of the bulky PMP-initiator.

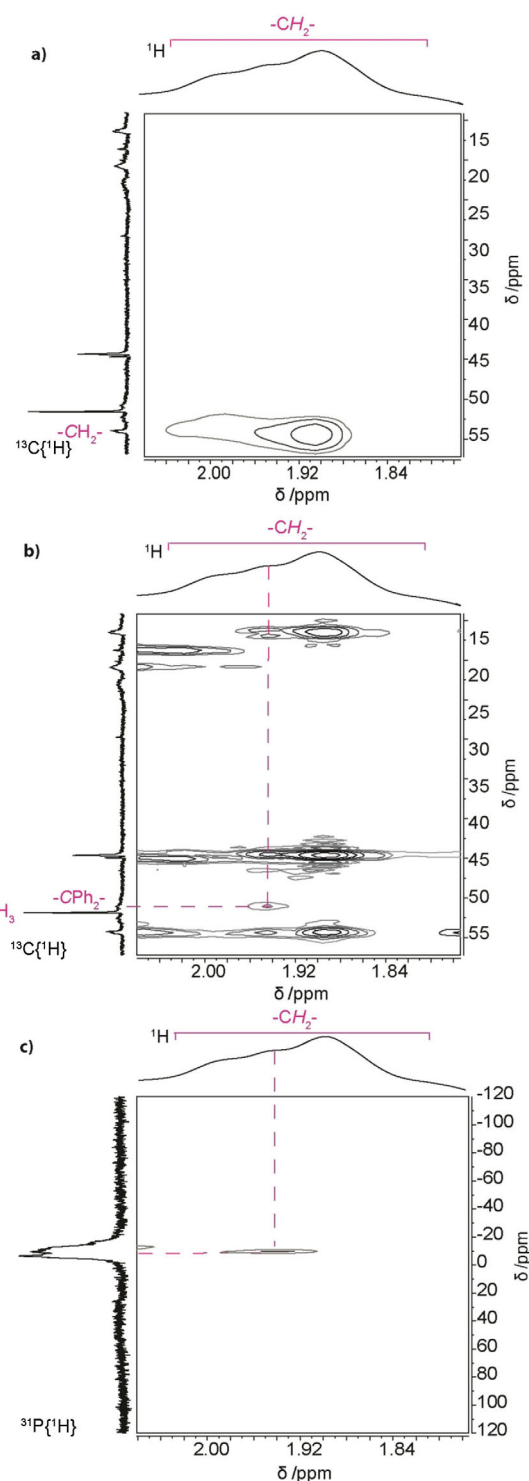
The  $^1\text{H}$ - $^{13}\text{C}$  HSQC, HMBC and  $^1\text{H}$ - $^{31}\text{P}$  HMBC NMR spectra further aided in the elucidation of the microstructure for these new block copolymers. The  $^1\text{H}$ - $^{13}\text{C}$  HSQC spectrum [Figure 3(a)] showed a cross correlation between the broad  $^1\text{H}$  signals between 2.1–1.8 ppm and the  $^{13}\text{C}$  signal at 54.4 ppm. Resonances in this region are commonly assigned to the  $-\text{CH}_2-$  moieties of the PMMA backbone.<sup>[17]</sup> Next, the  $^1\text{H}$ - $^{13}\text{C}$  HMBC NMR spectrum was closely examined and a weak cross correlation was noted between the  $^1\text{H}$  signal of at 1.94 ppm and the  $^{13}\text{C}$  signal at 51.0 ppm [Figure 3(b)]. We tentatively assigned the  $^{13}\text{C}$  signal at 51.0 ppm to the  $-\text{CPh}_2-$  of the switching group from the **PMP<sub>n</sub>** block. Remarkably, these data suggest a  $\text{P-CPh}_2\text{-CH}_2\text{-CMe}(\text{CO}_2\text{Me})-$  connection. Consistent with this above assignment, the  $^1\text{H}$ - $^{13}\text{C}$  HSQC spectrum shows no  $^1\text{H}$  correlations to the  $^{13}\text{C}$  signal at 51.0 ppm. In other words, this  $-\text{CPh}_2-$  moiety does not have a C–H bond. Additional evidence for a  $\text{P-CPh}_2\text{-CH}_2\text{-CMe}(\text{CO}_2\text{Me})-$  connection was provided by the  $^1\text{H}$ - $^{31}\text{P}$  HMBC NMR spectrum [Figure 3(c)]. Specifically, a cross correlation was observed between the  $^1\text{H}$  signal at 1.94 ppm ( $-\text{CH}_2-$  of acrylate) and the broad  $^{31}\text{P}$  signal at ca.  $-10$  ppm (P of PMP).

Taken together, the GPC, NMR spectroscopic data confirm that the desired di-block copolymers with the assigned structure **PMP<sub>n</sub>-b-PMMA<sub>m</sub>** (Scheme 3) were formed successfully. The remarkable identification of the  $\text{P-CPh}_2\text{-CH}_2\text{-CMe}(\text{CO}_2\text{Me})$ -switching group in **PMP<sub>10</sub>-b-PMMA<sub>10</sub>** is very important as it provides clear evidence that the living  $-\text{CPh}_2^-$  anion of the **PMP<sub>n</sub>** block initiates the polymerization of MMA. There is no evidence for the involvement of the isomerized benzylic anion of the Mes moiety which is the main propagating species in the homopolymerization of **PA**. Presumably, the absence of benzylic-PMMA switching groups is a consequence of the extremely small amount of benzylic anion that is present in equilibrium with the  $-\text{CPh}_2^-$  (see Scheme 1).

The physical properties of block copolymer **PMP<sub>n</sub>-b-PMMA<sub>m</sub>** are also of interest. Analysis of **PMP<sub>n</sub>-b-PMMA<sub>m</sub>** samples by powder X-ray diffraction was consistent with a primarily amorphous polymer (Figure S6). Consistent with these results, DSC



**Scheme 3.** Synthetic methodology to afford block copolymers, **PMP<sub>n</sub>-b-PMMA<sub>m</sub>**, using sequential anionic polymerization of **PA** ( $M_1$ ) and **MMA** ( $M_2$ ) initiated by **BnLi** (I).



**Figure 3.** Selected two-dimensional NMR spectra of **PMP<sub>10</sub>-b-PMMA<sub>10</sub>** (400 MHz for  $^1\text{H}$ ,  $\text{CDCl}_3$ , 298 K): (a)  $^1\text{H}$ - $^{13}\text{C}$  HSQC, (b)  $^1\text{H}$ - $^{13}\text{C}$  HMBC and (c)  $^1\text{H}$ - $^{31}\text{P}$  HMBC. The proposed microstructure of **PMP<sub>n</sub>-b-PMMA<sub>m</sub>** is shown in Scheme 3).

analysis of the new block copolymers show no melt transitions ( $T_m$ ) and each possess a single glass transition temperature ( $T_g$ ) estimated from the midpoint of the second heating cycle. The results are tabulated in Table 2 and the DSC traces are shown in Figure 4. For the first time, the  $T_g$  of a PMP homopolymer

Composition	$T_{g \text{ midpoint}}$ [ $^{\circ}\text{C}$ ] <sup>[a]</sup>	PMMA [% wt] <sup>[b]</sup>
<b>PMP<sub>20</sub></b>	45.1	0
<b>PMP<sub>10</sub>-<i>b</i>-PMMA<sub>10</sub></b>	103.7	24
<b>PMP<sub>20</sub>-<i>b</i>-PMMA<sub>20</sub></b>	103.7	24
<b>PMP<sub>30</sub>-<i>b</i>-PMMA<sub>100</sub></b>	114.0	51
<b>PMP<sub>25</sub>-<i>b</i>-PMMA<sub>100</sub></b>	120.4	55
<b>PMP<sub>15</sub>-<i>b</i>-PMMA<sub>60</sub></b>	120.9	55
<b>PMP<sub>1</sub>-PMMA<sub>400</sub></b>	134.2	99
Blend <b>PMP<sub>20</sub>/PMMA<sub>400</sub></b>	85.2	37
Blend <b>PMP<sub>20</sub>/PMMA<sub>400</sub></b>	90.2	50
Blend <b>PMP<sub>20</sub>/PMMA<sub>400</sub></b>	109.4	90

[a] Evaluated by DSC using the second heating scan (heating rate: 10  $^{\circ}\text{C min}^{-1}$ ). [b] %wt PMMA =  $1 - [M_n(\text{calcd}) \text{ of PMP}_n] / [M_n(\text{calcd}) \text{ of PMP}_n - b\text{-PMMA}_m]$  from Table 1.

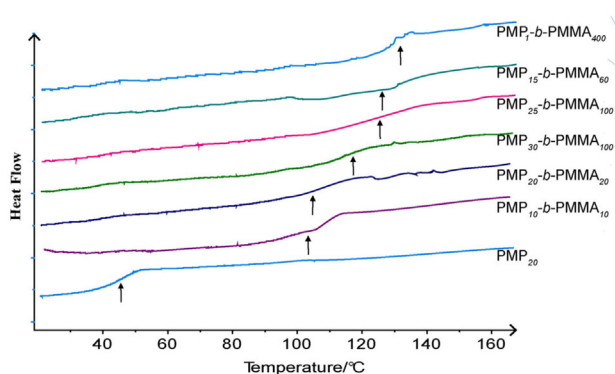


Figure 4. DSC traces of homopolymer **PMP<sub>20</sub>** and block copolymers **PMP<sub>10</sub>-*b*-PMMA<sub>10</sub>**, **PMP<sub>20</sub>-*b*-PMMA<sub>20</sub>**, **PMP<sub>30</sub>-*b*-PMMA<sub>100</sub>**, **PMP<sub>25</sub>-*b*-PMMA<sub>100</sub>**, **PMP<sub>15</sub>-*b*-PMMA<sub>60</sub>**, **PMP<sub>1</sub>-PMMA<sub>400</sub>**. The arrow indicates the midpoint of the  $T_g$ .

was determined ( $T_g = 45.1^{\circ}\text{C}$  for **PMP<sub>20</sub>**). It must be noted that this  $T_g$  will likely be dependent on chain length for this low molecular weight polymer. Significantly, a single glass transition temperature was observed for each block copolymer. Since the  $T_g$  behaviors of block copolymers are mainly affected by the compatibility of their components, this suggests that the **PMP<sub>n</sub>-*b*-PMMA<sub>m</sub>** copolymers in this molecular weight range do not readily phase separate. For comparison, a 50 wt% blend of homopolymers **PMP<sub>20</sub>** with **PMMA<sub>400</sub>** also exhibited a single glass transition also suggestive of no phase separation.

As expected, the block copolymers showed  $T_g$  values that increased with the increasing degree of PMMA incorporation ( $T_g = 134.2^{\circ}\text{C}$ ). However, the trend in  $T_g$  does not correspond to weighted average of the  $T_g$  values of pure **PMP<sub>20</sub>** and **PMMA<sub>400</sub>**. We speculate that this deviation may be due to the fact that the  $T_g$  of a low molecular weight **PMP<sub>n</sub>-*b*-PMMA<sub>m</sub>** is dependent on both the weight fraction of each segment as well as the chain length of each block. In contrast the  $T_g$  values of blends of **PMP<sub>20</sub>** and **PMMA<sub>400</sub>** follow the expected weight fraction dependence.

## Conclusions

The first **PMP<sub>n</sub>-*b*-PMMA<sub>m</sub>** block copolymers, have been prepared using the sequential living anionic polymerization of **PA** and **MMA**. The microstructure of the poly(methylenephosphine) block was determined and suggests that an addition-isomerization mechanism of propagation is predominant for the living anionic polymerization of **PA**. Importantly, two-dimensional NMR spectroscopic studies also provided evidence for the  $-\text{PMes-CPh}_2\text{-CH}_2\text{-CMe(CO}_2\text{Me)-}$  switching groups of the block copolymer. We have also successfully measured the glass transition of PMP-containing homo- and co-polymers for the first time. The  $T_g$  values are dependent on the relative size of each block and suggest that the blocks do not phase separate. Future work will build on these results and will explore the possibility to utilize the techniques developed herein to access a variety of P-containing block copolymers and to explore their unique chemical reactivity and physical properties

## Experimental Section

### General procedures

All experiments were performed under nitrogen using standard Schlenk technique or in an MBraun (LabMaster) glovebox. Toluene (Fisher, GR grade) was deoxygenated with nitrogen and dried by passing through a column containing activated alumina. Subsequently, it was further dried over sodium/benzophenone ketyl and distilled under reduced pressure and stored over activated 4 Å molecular sieves. THF (Fisher, GR grade) was dried over sodium/benzophenone ketyl, distilled and stored in activated 4 Å molecular sieves. Methanol was degassed prior to use.  $\text{CDCl}_3$  was purchased from Cambridge Isotope Laboratories Inc. and dried over 4 Å molecular sieves. *sec*-Butyllithium (*s*BuLi, Sigma Aldrich, 1.4 M in cyclohexane) was titrated prior to use to determine concentration.<sup>[18]</sup> Lithium chloride (LiCl, Alfa Aesar, 99.995%) was dried at 200  $^{\circ}\text{C}$  under reduced pressure for 2 d prior to use. *N,N,N',N'*-tetramethylethylenediamine (TMEDA, Alfa Aesar, 99%) was refluxed with KOH, and distilled under nitrogen atmosphere. Methyl methacrylate (MMA, Sigma Aldrich, 99%) was dried over  $\text{CaH}_2$  overnight and distilled under reduced pressure, followed by distillation over  $\text{AlEt}_3$  (Sigma Aldrich, 1.0 M in hexanes) under reduced pressure immediately prior to use. **PA** was prepared following literature procedure.<sup>[19]</sup>

Polymer molecular weights ( $M_n$ ) were determined by triple detection gel permeation chromatography (GPC-LLS) using an Agilent chromatograph equipped with an Agilent Technologies 1260 series standard autosampler, Phenomenex Phenogel 5 mm narrow bore columns 515 (4.6  $\times$  300 mm) 10<sup>4</sup> Å (5000–500 000  $\text{g mol}^{-1}$ ) 500 Å (1000–15 000  $\text{g mol}^{-1}$ ), and 10<sup>3</sup> Å (1000–75 000  $\text{g mol}^{-1}$ ), Wyatt Optilab T-rEx differential refractometer ( $\lambda = 658 \text{ nm}$ , 40  $^{\circ}\text{C}$ ), Wyatt mini-DAWN TREOS laser light scattering detector ( $\lambda = 690 \text{ nm}$ ), and a Wyatt Viscostar-viscometer. A flow-rate of 0.5  $\text{mL min}^{-1}$  was used and samples were dissolved in THF (ca. 1  $\text{mg mL}^{-1}$ ). HPLC grade THF was used for GPC.  $^1\text{H}$ ,  $^{13}\text{C}\{^1\text{H}\}$ , and  $^{31}\text{P}$  NMR spectra were recorded at 298 K on Bruker Avance 300 or 400 MHz spectrometers.  $\text{H}_3\text{PO}_4$  (85%) was used as an external reference ( $\delta = 0.0 \text{ ppm}$ ) for  $^{31}\text{P}$  NMR.  $^1\text{H}$  NMR spectra were referenced to residual  $\text{CHCl}_3$  ( $\delta = 7.26 \text{ ppm}$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR spectra were referenced to the carbon signal of the deuterated solvent  $\text{CDCl}_3$  ( $\delta = 77.2 \text{ ppm}$ ).

Differential scanning calorimetry (DSC) data were collected with a Netzsch DSC 214 Polyma between temperatures of 0 °C and 300 °C under nitrogen atmosphere. The first cycle involved heating samples to 300 °C followed by rapid cooling to 0 °C before the second and third cycles conducted with a heating rate 10 °C min<sup>-1</sup>. The second heating cycle was used to determine the glass temperature ( $T_g$ ), taken at the middle point of the heat capacity change.

### Preparation of PhCH<sub>2</sub>Li initiator

To a stirred solution of TMEDA (0.84 mL, 0.65 g, 5.6 mmol) in toluene (100 mL) was added sBuLi solution in cyclohexane (3.12 mL, 1.4 M, 4.37 mmol). The red orange solution was heated to 50 °C for 1 h. Subsequently, the solution was cooled to room temperature and the solvent was removed in vacuo. Addition of 50 mL hexanes followed by cooling to -78 °C, resulted in the precipitation of PhCH<sub>2</sub>Li. The product was isolated as a yellow powder after filtration, washing with hexanes (2 × 10 mL at -78 °C) and drying in vacuo. Following a modification of the reported procedure to titrate *n*BuLi,<sup>[18]</sup> the yellow PhCH<sub>2</sub>Li (0.289 g, 2.95 mmol) was dissolved in THF (5 mL) to afford dark red solution. This solution is titrated against *N*-benzylbenzamide requiring (0.623 g, 2.95 mmol) to equivalence. Therefore, the concentration of the PhCH<sub>2</sub>Li solution was 0.059 M.

General procedure for kinetic study of the anionic polymerization of PA: To a stirred solution of PA (0.1 g, 0.32 mmol) in toluene (1 mL) was added a solution of sBuLi (10.40 μL, 14.56 μmol) in toluene (1 mL) with TMEDA (1 drop, ca 0.003 mL, 0.020 mmol) in the glovebox. The reaction mixture was transferred to an NMR tube after stirring for 1 min. The sample was transferred to Bruker Avance 400dir NMR spectrometer which was maintained at the desired temperature (i.e. 323.15 K, 328.15 K, 333.15 K, 338.15 K, 343.15 K, 348.15 K). <sup>31</sup>P NMR spectra were recorded in every 15 min interval with 72 scans for each spectrum until the polymerization was complete. The delay time (*d*<sub>1</sub>) for PMP was set to 10 s. The accuracy of integration in the <sup>31</sup>P NMR spectra was controlled by integrating the same region (between 220–240 ppm) for the PA and the PMP<sub>*n*</sub> (between +10 and -40 ppm). Two drops of degassed methanol were added to the reaction mixture to terminate the living polymer. After precipitation from concentrated solution mixture with dry hexanes (2 × 50 mL), the white polymer solid was isolated by filtration and dried in vacuo. The isolated yields are between 40% to 50%. The reproducibility of the kinetic study was confirmed by repeating every experiment twice at each temperature. *M<sub>n</sub>*, *D* were estimated by triple detection gel permeation chromatography (GPC-LLS).

### Refractive index increments of PMP<sub>*n*</sub>-*b*-PMMA<sub>*m*</sub> block copolymers

The refractive index increment of a copolymer is a linear function of its composition according to equation 1<sup>[20]</sup> where (dn/dc)<sub>A</sub>, (dn/dc)<sub>B</sub> are the refractive index increments of PMP<sub>*n*</sub>, PMMA<sub>*m*</sub> homopolymer, respectively and *W<sub>A</sub>*, *W<sub>B</sub>* are the weight fractions of PMP, PMMA components. The values of (dn/dc)<sub>A</sub> = 0.2387 and (dn/dc)<sub>B</sub> = 0.0445 were determined from Cauchy plot. The measurements of Cauchy plots of the polymer solutions were performed by using a Wyatt Optilab T-rEx differential refractometer at λ<sub>0</sub> = 658 nm [Eq. (1)]:

$$\frac{dn}{dc} = W_A \left( \frac{dn}{dc} \right)_A + W_B \left( \frac{dn}{dc} \right)_B \quad (1)$$

### Preparation of poly(methylenephosphine) homopolymers (PMPs)

In a glove box, benzyl lithium initiator was prepared by adding sBuLi (1.4 M in cyclohexane) dropwise to a stirred solution of TMEDA dissolved in toluene for 30 mins at 50 °C. The color of solution was orange. The concentration of benzyl lithium initiator was subsequently determined by titration following previously reported procedure.<sup>[18]</sup> To the stirred benzyl lithium initiator solution at 50 °C was added dropwise PA in toluene. The color of solution was changing from orange to deep red. Polymerization progress was monitored by <sup>31</sup>P NMR. Upon complete consumption of the PA monomer half of the reaction mixture were withdrawn and quenched by degassed MeOH (2 drops). The deep red color of the reaction mixture became pale yellow. The solvent was removed in vacuo leaving a yellow residue. To the residue was added degassed methanol (3 × 50 mL) and the suspension was filtered, and the solvent removed in vacuo leaving white solid product.

**PMP<sub>10</sub>**: Toluene (1 mL), TMEDA (2 drops, ca. 0.009 mL, 0.060 mmol), sBuLi (in 1.4 M cyclohexane solution) (31.21 μL, 43.69 μmol)/PA (0.100 g, 0.316 mmol) in toluene (1 mL). Yield = 33.1%.

**PMP<sub>15</sub>**: Toluene (1 mL), TMEDA (2 drops, ca. 0.009 mL, 0.060 mmol), sBuLi (in 1.4 M cyclohexane solution) (31.21 μL, 43.69 μmol)/PA (0.150 g, 0.474 mmol) in toluene (1 mL). Yield = 31.7%.

**PMP<sub>20</sub>**: Toluene (1 mL), TMEDA (2 drops, ca. 0.009 mL, 0.060 mmol), sBuLi (in 1.4 M cyclohexane solution) (31.21 μL, 43.69 μmol)/PA (0.200 g, 0.632 mmol) in toluene (1 mL). Yield = 34.1%.

**PMP<sub>25</sub>**: Toluene (1 mL), TMEDA (2 drops, ca. 0.009 mL, 0.060 mmol), sBuLi (in 1.4 M cyclohexane solution) (31.21 μL, 43.69 μmol)/PA (0.250 g, 0.791 mmol) in toluene (1 mL). Yield = 45.2%.

**PMP<sub>30</sub>**: Toluene (1 mL), TMEDA (2 drops, ca. 0.009 mL, 0.060 mmol), sBuLi (in 1.4 M cyclohexane solution) (31.21 μL, 43.69 μmol)/PA (0.300 g, 0.949 mmol) in toluene (1 mL). Yield = 40.1%.

<sup>31</sup>P NMR (161.9 MHz, CDCl<sub>3</sub>, 298 K): δ = -7.10 (br). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 298 K): δ = 7.11 (br, 12 H, aryl H), 4.74 (br, 1 H, -CHPh<sub>2</sub>), 3.41 (br, 2 H, *o*-CH<sub>2</sub>), 2.02 (br, 6 H, *o*, *p*-CH<sub>3</sub>), <sup>13</sup>C{<sup>1</sup>H} NMR (100.6 MHz, CDCl<sub>3</sub>, 298 K): δ = 146.7 (br, Mes-C), 143.1 (br, Mes-C), 138.5 (br, Mes-C), 135.2–125.1 (br, Ph-C), 52.0 (br, -CHPh<sub>2</sub>), 32.5 (br, -CH<sub>2</sub>-), 23.5 (br, -CH<sub>3</sub>), 21.1 (br, -CH<sub>3</sub>). The *M<sub>n</sub>* and *D* for PMP<sub>*n*</sub> are given in Table 1.

### Preparation of poly(methylenephosphine)-*block*-poly(methylmethacrylate)s (PMP<sub>*n*</sub>-*b*-PMMA<sub>*m*</sub>)

The other half of the deep red solution of PMP carbanion was cooled at -78 °C for 10 mins and LiCl solution in THF was slowly added to the reaction mixture followed by the second monomer, MMA, dissolved in THF. After 1 min, the color of solution was from deep red to light yellow. The reaction mixture was stirred at -78 °C then slowly warmed up to room temperature. 2 drops of degassed MeOH were used to quench the polymerization. The yellow color of the reaction mixture became much paler, towards colorless. The solvent was removed in vacuo leaving a pale yellow residue. To the residue was added degassed MeOH (3 × 50 mL) with vigorous stirring and the suspension was filtered and the solvent removed in vacuo leaving white solid product.

**Bn-PMP<sub>1</sub>-PMMA<sub>400</sub>**: Toluene (1 mL), TMEDA (2 drops, ca. 0.009 mL, 0.06 mmol), sBuLi (in 1.4 M cyclohexane solution) (31.21 μL, 43.69 μmol)/PA (0.010 mg, 0.032 mmol) in toluene (1 mL)/LiCl (0.012 g, 0.28 mmol) in THF (1 mL)/MMA (0.10 mL, 0.10 g, 1.00 mmol) in THF (1 mL). Yield = 59.1%.

<sup>31</sup>P NMR (161.9 MHz, CDCl<sub>3</sub>, 298 K): δ = -0.001 (s); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 298 K): δ = 3.62 (br, -OCH<sub>3</sub> of PMMA), 1.94 (br, -CH<sub>2</sub>- of PMMA), 1.19 (br, -CH<sub>3</sub> of PMMA), 1.04 (br, -CH<sub>3</sub> of PMMA), 0.88 (br, -CH<sub>3</sub> of PMMA), <sup>13</sup>C{<sup>1</sup>H} NMR (100.6 MHz, CDCl<sub>3</sub>, 298 K): δ = 177.8 (br, C=O of PMMA), 54.6 (br, -CH<sub>2</sub>- of PMMA), 51.8 (br, -OCH<sub>3</sub> of PMMA), 44.6 (br, -C- of PMMA), 18.7 (br, -CH<sub>3</sub> of PMMA), 16.6 (br, -CH<sub>3</sub> of PMMA). The *M<sub>n</sub>* and Đ for **Bn-PMP<sub>7</sub>-PMMA<sub>400</sub>** is given in Table 1.

**PMP<sub>10</sub>-b-PMMA<sub>10</sub>**: Toluene (1 mL), TMEDA (2 drops, ca. 0.009 mL, 0.06 mmol), sBuLi (in 1.4 M cyclohexane solution) (31.21 μL, 43.69 μmol)/PA (0.100 g, 0.316 mmol) in toluene (1 mL)/LiCl (0.012 g, 0.28 mmol) in THF (1 mL)/MMA (21.28 μL, 0.02000 g, 0.1998 mmol) in THF (1 mL). Yield = 35.8%.

**PMP<sub>15</sub>-b-PMMA<sub>50</sub>**: Toluene (1 mL), TMEDA (2 drops, ca. 0.009 mL, 0.06 mmol), sBuLi (in 1.4 M cyclohexane solution) (31.21 μL, 43.69 μmol)/PA (0.150 g, 0.474 mmol) in toluene (1 mL)/LiCl (0.012 g, 0.28 mmol) in THF (1 mL)/MMA (0.11 mL, 100.0 mg, 1.0 mmol) in THF (1 mL). Yield = 49.6%.

**PMP<sub>15</sub>-b-PMMA<sub>60</sub>**: Toluene (1 mL), TMEDA (2 drops, ca. 0.009 mL, 0.06 mmol), sBuLi (in 1.4 M cyclohexane solution) (31.21 μL, 43.69 μmol)/PA (0.150 g, 0.506 mmol) in toluene (1 mL)/LiCl (0.012 g, 0.28 mmol) in THF (1 mL)/MMA (0.13 mL, 120.0 mg, 1.2 mmol) in THF (1 mL). Yield = 56.1%.

**PMP<sub>20</sub>-b-PMMA<sub>20</sub>**: Toluene (1 mL), TMEDA (2 drops, ca. 0.009 mL, 0.06 mmol), sBuLi (in 1.4 M cyclohexane solution) (31.21 μL, 43.69 μmol)/PA (0.200 g, 0.632 mmol) in toluene (1 mL)/LiCl (0.012 g, 0.28 mmol) in THF (1 mL)/MMA (42.55 μL, 40.00 mg, 0.4 mmol) in THF (1 mL). Yield = 39.7%.

**PMP<sub>25</sub>-b-PMMA<sub>100</sub>**: Toluene (1 mL), TMEDA (2 drops, ca. 0.009 mL, 0.06 mmol), sBuLi (in 1.4 M cyclohexane solution) (31.21 μL, 43.69 μmol)/PA (0.250 g, 0.791 mmol) in toluene (1 mL)/LiCl (0.012 g, 0.28 mmol) in THF (1 mL)/MMA (0.22 mL, 200.0 mg, 2.0 mmol) in THF (1 mL). Yield = 48.2%.

**PMP<sub>30</sub>-b-PMMA<sub>100</sub>**: Toluene (1 mL), TMEDA (2 drops, ca. 0.009 mL, 0.06 mmol), sBuLi (in 1.4 M cyclohexane solution) (31.21 μL, 43.69 μmol)/PA (0.300 g, 0.949 mmol) in toluene (1 mL)/LiCl (0.012 g, 0.28 mmol) in THF (1 mL)/MMA (0.22 mL, 200.0 mg, 2.0 mmol) in THF (1 mL). Yield = 63.4%.

<sup>31</sup>P NMR (161.9 MHz, CDCl<sub>3</sub>, δ): -7.10 (br). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, δ): 7.11 (br, aryl H of PMP), 4.74 (br, -CHPh<sub>2</sub> of PMP), 3.67 (br, -OCH<sub>3</sub> of PMMA), 3.41 (br, *o*-CH<sub>2</sub> of PMP), 2.02 (br, *o*, *p*-CH<sub>3</sub> of PMP), 1.94 (br, -CH<sub>2</sub>- of PMMA), 1.19 (br, -CH<sub>3</sub> of PMMA), 1.10 (br, -CH<sub>3</sub> of PMMA), 0.93 (br, -CH<sub>3</sub> of PMMA), <sup>13</sup>C{<sup>1</sup>H} NMR (100.6 MHz, CDCl<sub>3</sub>, δ): 178.1 (br, C=O of PMMA), 148.1–123.7 (br, aryl C), 54.4 (br, -CH<sub>2</sub>- of PMMA), 51.9 (br, -OCH<sub>3</sub> of PMMA and -CHPh<sub>2</sub> of PMP), 51.0 (br, -CPh<sub>2</sub>- of PMP), 44.7 (br, -C- of PMMA), 30.8 (br, -CH<sub>2</sub>- of PMP), 23.2 (br, -CH<sub>3</sub> of PMP), 20.9 (br, -CH<sub>3</sub> of PMP), 18.8 (br, -CH<sub>3</sub> of PMMA), 16.6 (br, -CH<sub>3</sub> of PMMA). The *M<sub>n</sub>* and Đ for each **PMP<sub>n</sub>-b-PMMA<sub>m</sub>** are given in Table 1.

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## Conflict of interest

The authors declare no conflict of interest.

**Keywords:** block copolymers · inorganic polymers · living polymerization · phosphalkenes · phosphorus

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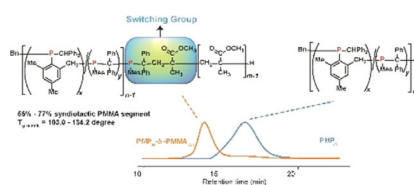
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## FULL PAPER

The  $\text{BnLi}$ -initiated polymerization of  $\text{MesP}=\text{CPh}_2$  in toluene in the presence of TMEDA affords a macroinitiator for the polymerization of methyl methacrylate (MMA) to afford a series of block copolymers. Importantly, the  $-\text{PMes}-\text{CPh}_2-\text{CH}_2-\text{CMe}(\text{COOMe})-$  switching group has been detected and the  $T_g$  of these unprecedented P-containing homo- and co-polymers has been measured for the first time.



### Polymers

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Phosphorus-Containing Block Copolymers from the Sequential Living Anionic Copolymerization of a Phosphaalkene with Methyl Methacrylate

