

# Anionic Polymerization of MMA Initiated by Organolithium/Cuprum Diphenylphosphide ( $\text{Ph}_2\text{PCu}$ ) and Synthesis of Its Block Copolymer

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**ABSTRACT:** Organolithium/cuprum diphenylphosphide ( $\text{Ph}_2\text{PCu}$ ) was used as a novel initiator to polymerize methyl methacrylate (MMA) and styrene in tetrahydrofuran (THF) at  $-50$  to  $-10^\circ\text{C}$ . The polymerizations initiated by  $n\text{-BuLi}/\text{Ph}_2\text{PCu}$ ,  $\text{Ph}_2\text{PCu}/\text{Li}(\text{Ip})_{3-6}$ , and  $\text{PSLi}/\text{Ph}_2\text{PCu}$  were studied in detail. The polymerization of alkyl methacrylate initiated by  $n\text{-BuLi}/\text{Ph}_2\text{PCu}$  showed a narrow molecular weight distribution (MWD) (1.08–1.25) and 100% initiation efficiency. The experimental number average molecular weight increased linearly with increasing  $[\text{MMA}]/[n\text{-BuLi}/\text{Ph}_2\text{PCu}]$ . After the second monomer addition, the molecular weight increased proportionally while the MWD remained

constantly narrow. These results reveal partial living characteristics.  $\text{Ph}_2\text{PCu}/\text{Li}(\text{Ip})_{3-6}$  showed a similar behavior and was used to prepare PGMA-*b*-PBMA-*b*-PMMA-*b*-PBMA-*b*-PGMA successfully. The initiation efficiency of  $n\text{-BuLi}/\text{Ph}_2\text{PCu}$  for styrene was low. The macromolecular initiator  $\text{PSLi}/\text{Ph}_2\text{PCu}$  was prepared and PS-*b*-PMMA with a narrow distribution was synthesized. © 2012 Wiley Periodicals, Inc. *J Appl Polym Sci* 125: 2085–2091, 2012

**Key words:** organolithium/cuprum diphenylphosphide; methyl methacrylate; anionic living polymerization; block copolymer

## INTRODUCTION

The living anionic polymerization of styrene and diene is one of the greatest successes in polymer synthesis.<sup>1</sup> The synthesis of poly(alkyl methacrylate) with a well-defined structure has attracted the attention of both academic and industrial polymer chemists. However, the ideal anionic living polymerization of alkyl methacrylate has not yet been developed because of the inherent side reactions of the polar ester group.<sup>2</sup> All the reactions during both initiation and propagation have been investigated in detail and many methods have been attempted to suppress the side reactions.<sup>2–15</sup> The breakthroughs achieved thus far include group transfer polymerization (GTP) of silyl ketene acetal and metal-free anionic polymerization (MFA), which were developed in the 1980s.<sup>16–18</sup> In addition to GTP and MFA, classical anionic polymerization can also show living

characteristics with ligands capable of coordinating with enolate ion pairs.<sup>19–34</sup> However, the use of ligands has several disadvantages, such as high cost, complex initiator composition, and severe reaction conditions.

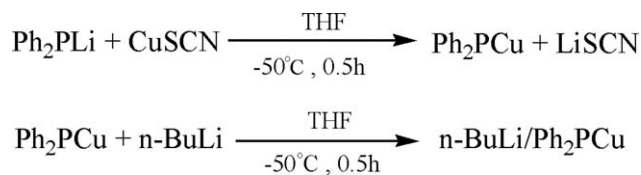
Given the possibility of living polymerization of alkyl (meth)acrylate under mild conditions, lithium organocuprates ( $[\text{R}_2\text{Cu}]^-\text{Li}^+$ ), also known as Gilman reagents, have been used as anionic initiators<sup>35–39</sup> because they favor 1,4-addition reactions and behave with high regio- and stereoselectivity when reacted with various  $\alpha,\beta$ -unsaturated esters and ketones. Gregonis was the first to prepare stereoregular poly(hydroxyethyl methacrylate) with  $\text{Bu}_2\text{CuLi}$  in toluene.<sup>35</sup> Han synthesized stereoregular poly(methyl methacrylate)(PMMA) using the same initiator.<sup>36</sup> Kawaguchi prepared poly(tert-butyl methacrylate) (PTBMA) and PTBMA-*b*-PMMA with  $\text{Me}_2\text{CuLi}$ <sup>39</sup> and polymerization was proven to be partially living.<sup>37,39</sup> However, these lithium homocuprates were easily thermally decomposed and had low initiation efficiencies ( $<10\%$ ), and the resulting polymer showed broad molecular weight distributions (MWDs) (1.2–2.0).<sup>37–39</sup>

Posner<sup>40</sup> was the first to introduce lithium heterocuprates  $[\text{RCuA}]^-\text{Li}^+$ , where A represents  $\text{PhS}$ —,  $\text{PhO}$ —,  $\text{R}_2\text{N}$ —,  $\text{Ph}_2\text{P}$ —, etc. Lithium heterocuprates contain a nontransferable group and exhibit remarkable thermal stability<sup>41</sup> and good reactivity. To determine

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Scheme 1 Synthesis of *n*-BuLi/Ph<sub>2</sub>PCu.

whether or not this type of cuprate reagents could be a better initiator for the polymerization of alkyl methacrylate and to inspire new strategies for the synthesis of block copolymers, the polymerization of MMA initiated by various lithium heterocuprates is investigated in this work in detail. Lithium heterocuprates studied include *n*-BuLi/CuSCN, *n*-BuLi/PhOCu, *n*-BuLi/(Et)<sub>2</sub>NCu, *n*-BuLi/Cy<sub>2</sub>NCu (dicyclohexylamidocopper), and *n*-BuLi/(Ph)<sub>2</sub>PCu.<sup>42–45</sup> The results show that the two latter initiators have good thermal stability, high efficiency, narrow MWD, and high conversion. The polymerization of MMA with RLi/Ph<sub>2</sub>PCu (R = *n*-Bu, PI, PS) as an initiator in tetrahydrofuran (THF) is discussed in the current article, and its block copolymers with glycidyl methacrylate, butyl acrylate, and styrene are prepared.

## EXPERIMENTAL

### Materials

MMA was purchased from Beijing YiLi Fine Chemistry Company. After refluxing, the MMA was vacuum distilled from CaH<sub>2</sub>, stored under a N<sub>2</sub> atmosphere below –12°C, mixed with a triethyl aluminum/hexane solution until a persistent yellowish green color emerged,<sup>46</sup> and then vacuum redistilled just prior to polymerization. Butyl methacrylate (BMA) was purified in the same way. Glycidyl methacrylate (GMA) was distilled twice over CaH<sub>2</sub> powder and redistilled in the presence of a small amount of *n*-BuLi to quench the impurities. THF was purified by refluxing over fresh sodium-naphthalene complex and was further distilled under dry N<sub>2</sub> just prior to use. BMA, GMA, and THF were provided by Beijing Chemical Reagent Company. Isoprene and styrene, which were purchased from the Beijing YiLi Fine Chemistry Company, were degassed over freshly crushed CaH<sub>2</sub>, stored over *n*,*sec*-dibutylmagnesium, and distilled just prior to use. CuSCN and *n*-BuLi were laboratory-made based on conventional methods. Other reagents, including pentamethyl diethylene triamine (PMDETA), LiCl, 2,2'-bipyridine, CuCl, CuBr·Me<sub>2</sub>S, and CuI were purchased from Beijing

TABLE I  
Effect of the Temperature on Polymerization of MMA Initiated by *n*-BuLi/Ph<sub>2</sub>PCu<sup>a</sup>

Entry	T/°C	$\bar{M}_{n,\text{expt}}$	MWD	Conv./%	eff/%	Triad tacticity/%		
						mm	rr	mr
1	–50	2800	1.08	100	100	–	–	–
2	–50	3200	1.09	100	100	70	6	24
3	–30	2700	1.14	100	100	–	–	–
4	–30	2500	1.20	100	92	64	11	25
5	–10	2700	1.25	100	85	65	7	28
6 <sup>b</sup>	–50	3500	1.07	100	50	–	–	–

<sup>a</sup> [MMA] = 0.47 mol/L, initiation efficiency =  $(\bar{M}_{n,\text{thero}}/\bar{M}_{n,\text{expt}}) \times 100$ .

<sup>b</sup> initiated only by Ph<sub>2</sub>PLi.

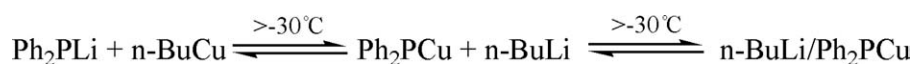
Chemical Reagent Company and purified prior to use. Diphenylphosphide lithium (Ph<sub>2</sub>PLi) was prepared according to Augiar's method.<sup>47</sup> The *n*-BuLi concentration was determined via the double titration method.<sup>48</sup> All reagents were of A.R. grade.

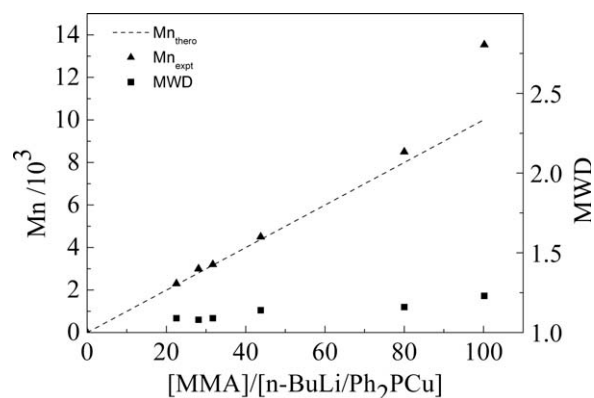
### Initiators

The initiator systems were prepared under an N<sub>2</sub> atmosphere as follows. First, 30 mL of THF was placed in a 50 mL three-necked glass reactor, after which the temperature was lowered to –50°C. Then, equivalent moles of brick red Ph<sub>2</sub>PLi and purified CuSCN were added to the reactor and stirred for 0.5 h. Finally, equivalent moles of the alkyl lithium or living polymer were added into the yellow Ph<sub>2</sub>PCu solution. A homogenous orange-yellow RLi/Ph<sub>2</sub>PCu complex was prepared after stirring for 30 min. In the method used, the alkyl lithium was *n*-BuLi and the living polymers were composed of either polystyryl lithium (PSLi) or the dilithium of the isoprene oligomer (Li-(Ip)<sub>3–6</sub>-Li).<sup>49,50</sup> The synthetic reactions of *n*-BuLi /Ph<sub>2</sub>PCu are shown in Scheme 1.

### Polymerization

The polymerization of MMA was performed in a 50 mL flame-dried three-necked round-bottom glass flask under a N<sub>2</sub> atmosphere at –50 to –10°C. The solvent (THF), initiator, and monomer were added using a syringe. The reaction was terminated by adding a small amount of methanol that had been previously degassed under a vacuum to the flask. The polymer solution was precipitated with hexane and vacuum dried to constant weight at 50°C. PS-*b*-PMMA and PGMA-*b*-PBMA-*b*-PMMA-*b*-PBMA-*b*-PGMA copolymers were

Scheme 2 The reversible decomposition of *n*-BuLi/Ph<sub>2</sub>PCu above –30°C.

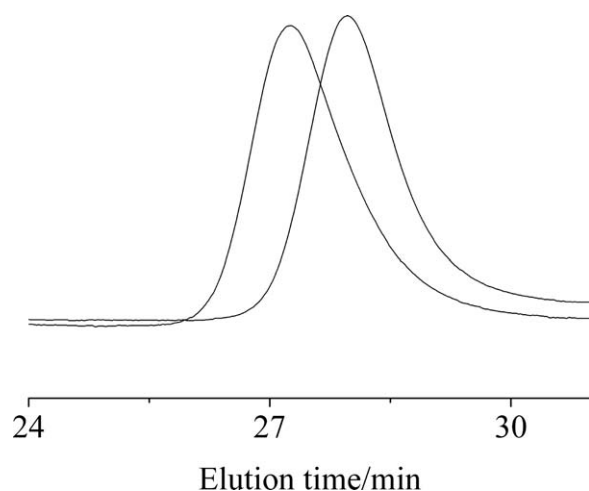


**Figure 1** Plots of  $\overline{M}_{n,expt}$  ( $\blacktriangle$ ) and MWD ( $\blacksquare$ ) versus the mole ratio of  $[MMA]/[n\text{-BuLi}/Ph_2PCu]$  for the polymerization of MMA in THF at  $-50^\circ\text{C}$ .  $\overline{M}_{n,theo/Li}$ ,  $\overline{M}_{n,expt}$ , and MWD are represented by dashed lines, solid triangles, and solid squares, respectively.

synthesized via sequential anionic synthesis in the same way.

### Characterization

The molecular weights and MWDs were determined via gel-permeation chromatography (GPC) using a Waters 150C gel-permeation chromatograph with a 410 differential refractometer as detector. A set of three Styragel columns (HT3, HT4, and HT5) was used. The mobile phase was THF, the flow rate was 1.0 mL/min, and the temperature was  $25^\circ\text{C}$ . The molecular-weight calibration curve was obtained by using polystyrene and PMMA standards for all the block polymers and all the PMMA homopolymers, respectively. The microstructures of the polymers were characterized by nuclear magnetic resonance



**Figure 2** GPC traces of the PMMA prepared via two-step addition with  $n\text{-BuLi}/Ph_2PCu$  as an initiator at  $-50^\circ\text{C}$ . (Curve 1, first addition,  $\overline{M}_{n,expt} = 2000$ , MWD = 1.18; curve 2, second addition,  $\overline{M}_{n,expt} = 2800$ , MWD = 1.21).

**TABLE II**  
Influence of Various Lithium Heterocuprates Initiator on Polymerization of MMA

Initiator	MWD	Conv./%	eff/%
$n\text{-BuLi}/CuSCN$ <sup>41</sup>	1.4–2.8	100	<70
$n\text{-BuLi}/PhOCu$ <sup>42</sup>	1.3–1.7	100	<70
$n\text{-BuLi}/Cy_2NCu$ <sup>44</sup>	1.1–1.3	100	>95
$n\text{-BuLi}/Ph_2PCu$	1.08–1.25	100	>85

(NMR) spectroscopy using a Bruker AV-600 (600 MHz) in  $CDCl_3$  at room temperature. The monomer conversion was determined gravimetrically.

## RESULTS AND DISCUSSION

### MMA polymerization initiated by $n\text{-BuLi}/Ph_2PCu$

The initiation of MMA by  $n\text{-BuLi}/Ph_2PCu$  was very rapid as the orange-yellow disappeared instantaneously after the MMA addition. Moreover, the polymerization was an extremely fast reaction, especially during the first minute. Monomer conversion reached 80% after 1 min and 100% after 15 min. The effect of temperature on the polymerization was investigated to achieve MMA living polymerization in mild conditions. Table I shows that MMA completely polymerized at various temperatures. With the temperature increasing from  $-50$  to  $-10^\circ\text{C}$ , the MWD increased from 1.08 to 1.25, and the initiation efficiency decreased from 100% to 85%. The initiation efficiency began to decrease when the temperature was above  $-30^\circ\text{C}$ . At the same time, when the stored temperature of the initiator was above  $-30^\circ\text{C}$ , a light brick red color appeared in the orange-yellow initiator solution. The  $PPh_2$  group was shown to exist in the terminal via  $^{13}\text{C}$ -NMR, whereas it disappeared at  $-50^\circ\text{C}$ , indicating that a little  $Ph_2PLi$  was formed. The  $n\text{-BuLi}/Ph_2PCu$  complex tended to decompose and a cationic ion exchange exists between Li and Cu above  $-30^\circ\text{C}$ , as shown in Scheme 2. As a product of decomposition,  $Ph_2PLi$  had initiation activity, but its efficiency was only 50% (entry 6). Thus, despite initiating MMA polymerization at  $-50^\circ\text{C}$ , the initiator system consisted of three initiator species with different activities and broadened MWDs, i.e.,  $n\text{-BuLi}/Ph_2PCu$ ,  $n\text{-BuLi}$ , and

**TABLE III**  
Influence of Synthetic Methods of Cuprates of  $n\text{-BuLi}/Ph_2PCu$  Initiator on Polymerization of MMA\*

CuX	$\overline{M}_{n,expt}$	MWD	Conv./%	eff/%
CuSCN	2800	1.08	100	100
CuI	2300	1.20	100	98
CuBr·Me <sub>2</sub> S	2300	1.32	65.4	100
CuCl	8600	1.24	100	53.5

\*  $[MMA] = 0.47$  mol/L, polymerized in THF at  $-50^\circ\text{C}$ .

**TABLE IV**  
Effect of the Additives on Polymerization of MMA Initiated by *n*-BuLi/Ph<sub>2</sub>PCu at  $-10^{\circ}\text{C}^*$

Entry	Additive type	Mole ratio of additive to Cu <sup>+</sup>	$\bar{M}_{n,expt}$	MWD	Conv./%	eff/%
1	No additive	0	2700	1.25	100	85
2	PMDETA	7.6	8300	1.36	100	26.9
3	PMDETA	15.2	11,300	1.44	100	19.9
4	LiCl	1	4600	1.17	100	49.6
5	2,2'-bipyridine	0.5	1300	1.40	100	100
6	2,2'-bipyridine	1	2300	1.25	100	100

\* [MMA] = 0.47 mol/L.

Ph<sub>2</sub>Pli. All evidence indicates that only at temperatures below  $-30^{\circ}\text{C}$  are the monoactive species formed and the coordination of Ph<sub>2</sub>PCu with *n*-BuLi is extremely effective in controlling nucleophilic attacks and eliminating side reactions. Furthermore, syndiotactic PMMA can be prepared by the initiator system, thereby decreasing syndiotacticity to a small extent with increasing temperature. The findings are similar to that of the Bu<sub>2</sub>CuLi initiator.<sup>38</sup>

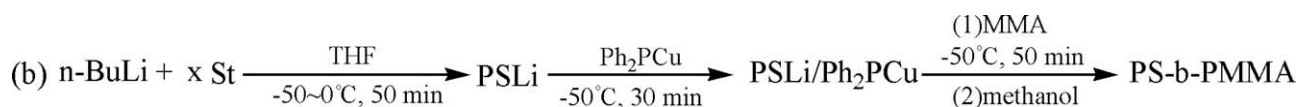
The influence of the mole ratio of MMA to *n*-BuLi/Ph<sub>2</sub>PCu on polymerization was studied to understand the controllability of molecular weight of PMMA at  $-50^{\circ}\text{C}$ . When the designed molecular weight ( $\bar{M}_{n,thero/Li}$ ) was below  $10^4$ , a linear relationship was observed between the experimental number-average molecular weight ( $\bar{M}_{n,expt}$ ) as estimated by GPC and [MMA]/[*n*-BuLi/Ph<sub>2</sub>PCu], while the MWDs remained relatively narrow (1.08–1.32), as illustrated in Figure 1. The linearity indicates the absence of a transfer reaction or slow initiation at  $-50^{\circ}\text{C}$ . As the  $\bar{M}_{n,expt}$  was in agreement with the  $\bar{M}_{n,thero/Li}$  calculated by active lithium, it can be concluded that MMA polymerization at  $-50^{\circ}\text{C}$  is a kind of controlled polymerization.

PMMA was prepared via two-step monomer addition to further investigate whether the polymerization was living or not. The continuous propagation of the living polymer formed after the first monomer addition was confirmed by GPC traces, as shown in Figure 2. After the two-step monomer addition, the resulting PMMA maintained a narrow MWD. However, a slight tail was observed with longer elution times. The observations indicate that some terminations probably existed during the polymerization.

All the above results reveal the partial living characteristics of the anionic polymerization of MMA at  $-50^{\circ}\text{C}$ . The results also indicate that *n*-BuLi/Ph<sub>2</sub>PCu

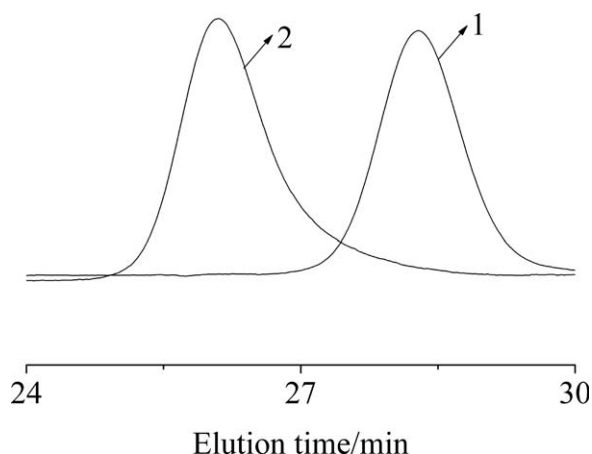
is the key factor to achieve controllable polymerization. In fact, the *n*-BuLi/Ph<sub>2</sub>PCu complex was the best initiator among the various lithium heterocuprates that were studied, as shown in Table II. The MWD of the PMMA initiated by *n*-BuLi/Ph<sub>2</sub>PCu was much lower than those of *n*-BuLi/CuSCN and *n*-BuLi/PhOCu and was approximately equivalent to *n*-BuLi/Cy<sub>2</sub>NCu. The initiation efficiency of *n*-BuLi/Ph<sub>2</sub>PCu was much higher than those of *n*-BuLi/CuSCN and *n*-BuLi/PhOCu and approached that of *n*-BuLi/Cy<sub>2</sub>NCu. These findings mean that N- or P-containing lithium heterocuprates have better thermal stability and reactivity. Compared with S and O, N or P atoms appear to play an important role in forming stable anionic active complexes. Furthermore, the activity appeared to be related to the cuprate synthetic methods. The reactivity was different for cuprates prepared by different methods. Table III shows the effect of the cuprate synthetic method on polymerization. Only *n*-BuLi/Ph<sub>2</sub>PCu prepared by CuSCN simultaneously showed high initiation efficiency and a narrow MWD.

As narrow MWD and high initiation efficiency were only achieved below  $-30^{\circ}\text{C}$ , three additives were introduced to improve the polymerization at higher temperatures. The influences of the kind of additive and their mole ratio to Cu<sup>+</sup> on the polymerization at  $-10^{\circ}\text{C}$  are listed in Table IV. The addition of PMDETA broadened the MWD from 1.25 to 1.44 and decreased the initiation efficiency from 85% to 19.9%. The MWD narrowed down to 1.17 after LiCl introduction despite the low initiation efficiency of 49.6%. This observation indicates that the ligand tends to coordinate with ion pairs to form  $\mu$ -type coordination and enhances the thermal stability of the active center. 2,2'-Bipyridine did not improve the thermal stability of the system, but increased its



**Scheme 3** The synthetic routes of PS-b-PMMA.





**Figure 3** GPC traces of PS-*b*-PMMA prepared by Scheme 3 (curve 1, PS precursor,  $\bar{M}_{n,expt} = 1400$ , MWD = 1.11; curve 2, after MMA addition,  $\bar{M}_{n,expt} = 4600$ , MWD = 1.16).

initiation efficiency to 100%. This finding could be related to the strong complexation and steric effect of 2,2'-bipyridine, by which all the active centers can be disassociated and thus initiate MMA. At present, an appropriate additive is being investigated for ideal living polymerization.

### Synthesis of PS-*b*-PMMA

Based on the aforementioned success in the controlled polymerization of MMA, *n*-BuLi/Ph<sub>2</sub>PCu was further used to initiate the non-polar monomer. Styrene was first initiated in THF at  $-50^{\circ}\text{C}$ . In contrast with the failure of polymerization of the non-polar monomer initiated by lithium homocuprates<sup>36</sup> reported by Han, polystyrene was successfully obtained. Moreover, the molecular weight was high ( $1.1 \times 10^4$ ) and the MWD was narrow (1.26). However, the initiation efficiency (at only 30%) was deficient; this could have been caused by the weak electrophilic reactivity of styrene. For further investigations of its reinitiating ability, MMA was added to PSLi/Ph<sub>2</sub>PCu before the latter was deactivated. A

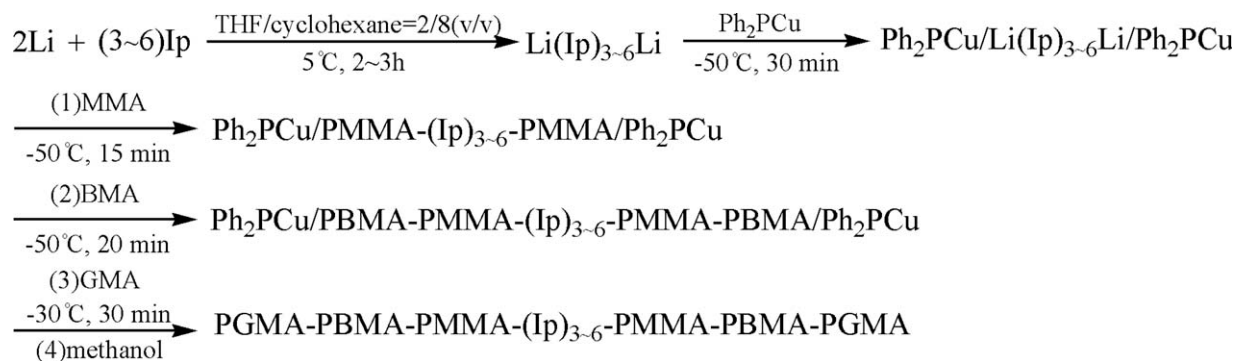
double peak was observed after MMA addition. Only 11.8% of the MMA was successfully block-copolymerized to PSLi according to the calculation of proton integration ratios of PS-PMMA after it was extracted by acetonitrile. In addition, isoprene was initiated as the second non-polar monomer by *n*-BuLi/Ph<sub>2</sub>PCu and the result was negative.

As the synthesis of apolar-polar block copolymers with well-defined structures is significant, another approach in preparing the amphiphilic polymer was sought. A new method was designed by combining traditional anionic polymerization and lithium heterocuprate initiated polymerization, as was shown in Scheme 3. First, the PSLi that was synthesized by traditional anionic polymerization was used to replace *n*-BuLi to prepare the macromolecular initiator PSLi/Ph<sub>2</sub>PCu. MMA was then polymerized. The GPC trace (Fig. 3) shows a narrow peak, and an MWD of was 1.16. These results indicate that a transfer reaction hardly existed between the PSLi/Ph<sub>2</sub>PCu and MMA. However, the monomer conversion was only 67%. In any case, a new route for preparing apolar-polar block copolymers was developed and shall be used in subsequent works.

### Synthesis of block copolymer by Ph<sub>2</sub>PCu/Li(Ip)<sub>3-6</sub>Li/Ph<sub>2</sub>PCu

The aforementioned initiator PSLi/Ph<sub>2</sub>PCu had only a monolithium active center and polymerized in just one direction. It suggests excessive feeding times for the synthesis of segmented copolymer, making it difficult to prepare the symmetrical ABA block copolymer. Thus, dilithium oligomer of isoprene<sup>49,50</sup> was used to prepare dilithium heterocuprates, i.e., Ph<sub>2</sub>PCu/Li(Ip)<sub>3-6</sub>Li/Ph<sub>2</sub>PCu. It initiated MMA to polymerize bidirectionally (Scheme 4). Table V shows that the initiating efficiency was 100% and that the MWD of the resulting polymer was 1.09–1.15.

The living character of the Ph<sub>2</sub>PCu/Li(Ip)<sub>3-6</sub>Li/Ph<sub>2</sub>PCu initiated polymerization was used to prepare the segmented copolymer PGMA-*b*-PBMA-*b*-PMMA-



**Scheme 4** The synthetic route of PGMA-*b*-PBMA-*b*-PMMA-*b*-PBMA-*b*-PGMA.

TABLE V  
Synthesis of PMMA Initiated by  
Ph<sub>2</sub>PCu/Li(Ip)<sub>3-6</sub>Li/Ph<sub>2</sub>PCu\*

Entry	$\bar{M}_{n,expt}$	MWD	Conv./%	eff/%
1	2000	1.15	100	100
2	2300	1.09	100	100
3	2500	1.10	100	100

\* [MMA] = 0.47 mol/L.

b-PBMA-b-PGMA. The synthetic route is illustrated in Scheme 4. Notably, a relatively higher temperature (>−37°C) was required for the effective control of GMA block copolymerization because of the limited solubility of PGMA in THF at low temperatures.

The formation of the pentablock copolymer was confirmed via GPC and <sup>1</sup>H-NMR. GPC traces of the PMMA precursor and the corresponding block copolymers are compared in Figure 4. The triblock copolymer showed a narrow molecule weight distribution and an increase in molecular weight, whereas the MWD (1.38) of the pentablock copolymer was somewhat broad. These results are indicative of possible impurity terminations of the GMA or side reactions of the epoxy group. However, the synthesis of PBMA-b-PMMA-b-PBMA showed partial living characteristics.

The <sup>1</sup>H-NMR spectrum of the pentablock copolymer is shown in Figure 5. The peaks a(a<sub>1</sub>, a<sub>2</sub>: δ = 3.583), b(b<sub>1</sub>, b<sub>2</sub>: δ = 3.922, b<sub>3</sub>, b<sub>4</sub>, b<sub>5</sub>), and c(c<sub>1</sub>, c<sub>2</sub>: δ = 3.797, 4.284, c<sub>3</sub>: δ = 3.460, c<sub>4</sub>: δ = 2.623, 2.830) are assigned to PMMA, PBMA, and PGMA, respectively. By comparing the relative intensities of a<sub>2</sub>, b<sub>2</sub>, and c<sub>2</sub>,

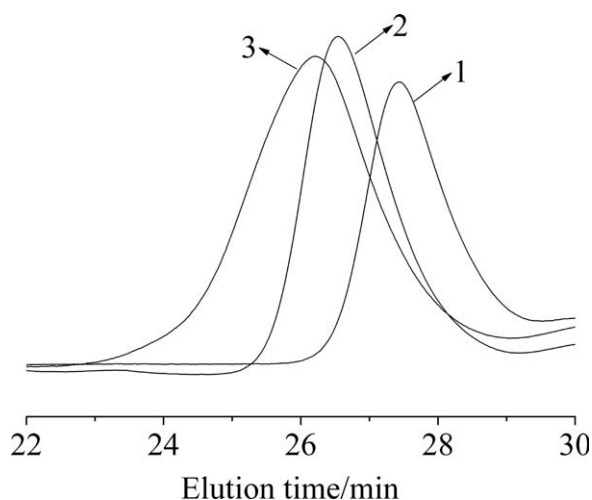


Figure 4 GPC traces of PGMA-b-PBMA-b-PMMA-b-PBMA-b-PGMA initiated by Ph<sub>2</sub>PCu/Li(Ip)<sub>3-6</sub>Li/Ph<sub>2</sub>PCu (curve 1, PMMA:  $\bar{M}_{n,expt}$  = 8100, MWD = 1.13; curve 2, PBMA-b-PMMA-b-PBMA,  $\bar{M}_{n,expt}$  = 11,100, MWD = 1.16; curve 3, PGMA-b-PBMA-b-PMMA-b-PBMA-b-PGMA,  $\bar{M}_{n,expt}$  = 15,300, MWD = 1.38).

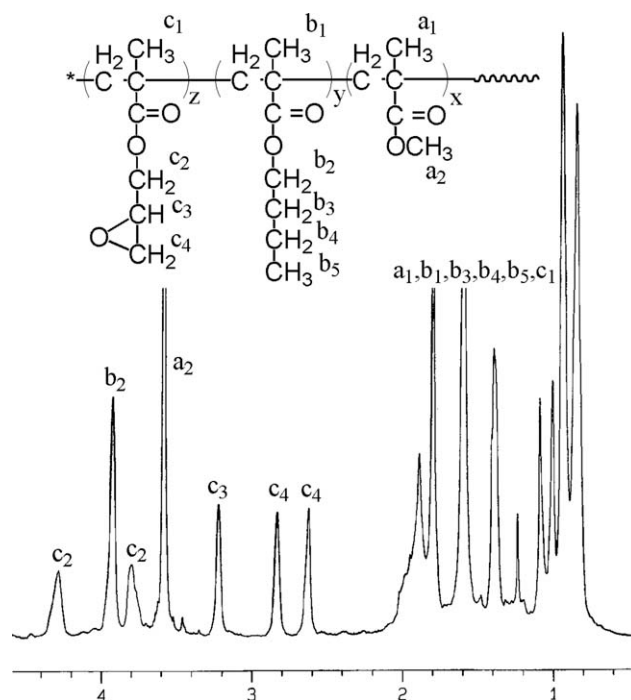


Figure 5 <sup>1</sup>H-NMR of PGMA-b-PBMA-b-PMMA-b-PBMA-b-PGMA initiated by Ph<sub>2</sub>PCu/Li(Ip)<sub>3-6</sub>Li/Ph<sub>2</sub>PCu.

the mole ratio of the monomer units in the block polymer was estimated as 1.14 : 1.04 : 1, which agreed approximately with the monomer mole ratio.

## CONCLUSIONS

Organolithium/cuprum diphenylphosphide (RLi/Ph<sub>2</sub>PCu) complexes have better thermal stability and initiation reactivity than RLi/CuSCN and RLi/PhOCu. Among the three kinds of RLi/Ph<sub>2</sub>Pcu studied, the polymerization of alkyl methacrylate initiated by *n*-BuLi/Ph<sub>2</sub>PCu and Ph<sub>2</sub>PCu/Li(Ip)<sub>3-6</sub>Li/Ph<sub>2</sub>PCu in THF at −50 °C showed partial living characteristics. This finding is demonstrated by the following: (a) the narrow MWD (1.08–1.25), 100% initiation efficiency; (b) the linear relationship between the experimental number average molecular weight and [MMA]/[*n*-BuLi/Ph<sub>2</sub>PCu]; (c) the proportional increase in molecular weight; and (d) the constant narrow distribution after multiple monomer additions. The partial living character of the Ph<sub>2</sub>PCu/Li(Ip)<sub>3-6</sub>Li/Ph<sub>2</sub>PCu initiated polymerization was used to prepare PGMA-b-PBMA-b-PMMA-b-PBMA-b-PGMA. However, the initiation efficiency of *n*-BuLi/Ph<sub>2</sub>PCu for the non-polar monomer was low. The macromolecular initiator PSLi/Ph<sub>2</sub>PCu was prepared to initiate MMA to obtain the apolar-polar block copolymer. PS-b-PMMA was synthesized with a narrow distribution, but the monomer conversion was only 67%.

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