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# Living Coupling Reaction in Living Cationic Polymerization. 1. Coupling Reaction of Living Polyisobutylene

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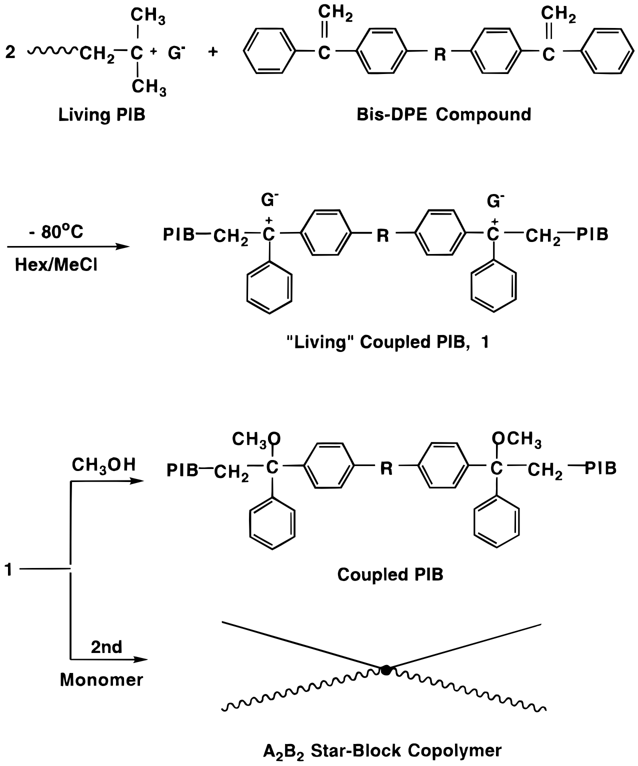
ABSTRACT: The living coupling reaction of living polyisobutylene (PIB), prepared by the 2,4,4-trimethyl-2-chloropentane/$TiCl_4$/hexane:methyl chloride (60:40, v:v)/−80 °C system, has been studied using 1,3-bis(1-phenylethenyl)benzene (MDDPE), 2,2-bis[4-(1-phenylethenyl)phenyl]propane (BDPEP), and 2,2-bis[4-(1-tolylethenyl)phenyl]propane (BDTEP) as coupling agents. The reaction of living PIB with MDDPE yielded the monoadduct, possibly due to delocalization of positive charge over the *meta*-substituted benzene ring upon monoaddition and thereby decreased reactivity of the second double bond. Using BDPEP and BDTEP which have two diphenylethylene (DPE) moieties separated by an electron-donating spacer group, rapid and quantitative coupling was achieved independently of the chain length of the original PIB. The coupled product exhibited doubled molecular weight and narrowed molecular weight distribution. Direct evidence of the quantitative coupling reaction was also obtained by comparison of the $^1H$ NMR spectra of the samples before and after the coupling reaction. Kinetic studies by $^1H$ NMR spectroscopy indicated the coupling reaction of living PIB by BDPEP is a consecutive reaction where the second addition is faster than the first one. By kinetic treatment of the experimental results, it was found that the second addition is about 5 times faster than the first one. As a result, high coupling efficiency was also observed when excess BDPEP was used.

## Introduction

In a series of recent publications, we demonstrated synthetic applications of non(homo)polymerizable monomers such as 1,1-diphenylethylene (DPE) and 1,1-ditolylethylene (DTE) in carbocationic macromolecular engineering.[1−4] These processes involved the intermediate capping reaction of living polyisobutylene (PIB) with DPE or DTE, in the courses of quantitative end-functionalization of PIB,[1] coupling reaction of two homopolymers prepared by different mechanisms,[2] and the clean synthesis of diblock[3] or triblock copolymers.[4] As an extension of our recent efforts on the applications of nonpolymerizable monomers in carbocationic polymerization, it was conceived that bis-DPE compounds could be useful as “living” coupling agents for living PIB. The concept of a living coupling agent was first introduced by Quirk et al.[5] in anionic polymerization. According to the definition, a living coupling agent first must react quantitatively with the living chain ends. Secondly, the coupled product must retain the living centers stoichiometrically. And finally, the living coupled product must be able to reinitiate the second monomer rapidly and stoichiometrically. Living PIB reacts quantitatively with DPE or DTE to yield stoichiometric amounts of diarylalkylcarbenium ions. These resulting stable and fully ionized carbenium ions have been successfully employed for the controlled initiation of the second monomers[3] such as *p*-methylstyrene, α-methylstyrene, isobutyl vinyl ether, and methyl vinyl ether. In this context, it is apparent that bis-DPE compounds are highly qualified as living coupling agents, satisfying all the criteria, as illustrated in Scheme 1.

**Scheme 1. Living Coupling Reaction of Living PIB by Bis-DPE Compound**



The basic example of a living coupling reaction can be found in the work by Tung et al.[6] In pursuit of hydrocarbon-soluble di- or multifunctional organolithium initiators, they investigated coupling reactions of 2 equiv or an excess of *sec*-butyllithium or oligomeric poly(styryl)lithium with bis(1-phenylethenyl) compounds of *m*-phenylene, *p*-phenylene, *p,p′*- biphenyl, or *p,p′*-diphenyl ether. More recently, the full potential of the living coupling reaction in anionic polymerization by 1,3-bis(1-phenylethenyl)benzene (or *meta*-double DPE, MD-DPE) was exploited by Quirk et al. in the preparation of star-block copolymers.[5]

Although several coupling agents for living poly(vinyl ethers) and poly(α-methylstyrene) have been reported

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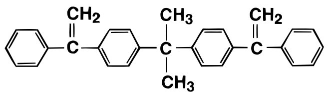
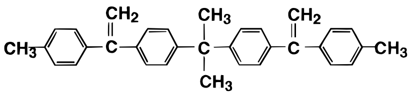
in cationic polymerization,[7] quantitative coupling was limited to the living polymers with low molecular weight ($DP_n \sim 10$). Sodiomalonate anions, which were used as coupling agents for living poly(isobutyl vinyl ether), showed limitation because of their limited solubility in polymerization solvents and thereby low yield in the coupling reaction. Nonionic coupling agents such as bifunctional silyl enol ethers were successfully employed in the coupling of short living chains ($DP_n \sim 10$) of poly(isobutyl vinyl ether), displaying a high coupling efficiency ($>95\%$). With increasing molecular weight ($DP_n \sim 100$), however, the coupling efficiency was drastically reduced ($\sim 74\%$) even after a 24 h coupling reaction. No report has been published on the quantitative coupling reaction of living PIB, and no attempt has been made on the living coupling reaction in carbocationic polymerization. Based on the recent successful applications of non(homo)polymerizable monomers, herein are reported our results toward the living coupling reaction of living PIB using MDDPE as well as bis-DPE compounds such as 2,2-bis[4-(1-phenylethenyl)phenyl]propane (or bis(diphenylethenyl)propane, BDPEP) and 2,2-bis[4-(1-tolylethenyl)phenyl]propane (or bis(ditolylethenyl)propane, BDTEP).



**BDPEP**



**BDTEP**

## Experimental Section

**Materials.** MDDPE was synthesized using procedures analogous to those reported by Schulz and Hocker.[8] Syntheses of BDPEP and BDTEP have been reported elsewhere.[9] All other chemicals and solvents were purified as described previously[1-3] or used as received.

**Polymerization and Coupling Reaction.** Polymerizations were carried out in a three-neck flask equipped with an overhead stirrer at −80 °C under a dry ($[H_2O] < 1.0$ ppm) nitrogen atmosphere in an MBraun 150-M glovebox (Innovative Technology Inc.). A hexane (Hex) stock solution containing 2-chloro-2,4,4-trimethylpentane (TMPCl), as an initiator, and 2,6-di-*tert*-butylpyridine (DTBP), as a proton trap, was prepared and charged to the flask. This was followed by the addition of methyl chloride (MeCl) to reach the ratio of Hex/MeCl = 60/40 (v/v) at −80 °C. Then $TiCl_4$, dissolved in Hex with $TiCl_4$/Hex = 1/3 (v/v), was added. Isobutylene (IB) was introduced to the flask 10 min after the addition of $TiCl_4$. After 1 h of polymerization (~100% conversion), a portion of the reaction mixture was withdrawn from the flask and quenched with prechilled methanol for molecular weight measurement of the original PIB. Coupling reactions were effected by adding a stoichiometric amount of coupling agent dissolved in Hex/MeCl (50/50, v/v) at −80 °C. At predetermined time intervals, aliquots of the reaction mixture were withdrawn and quenched with prechilled methanol inside the glovebox, and poured over excess 10% ammoniacal methanol outside of the glovebox to preserve diarylmethoxy functionality. The purification procedure of the product has already been reported.[1]

**Characterization.** Molecular weights were measured using a Waters HPLC system equipped with Model 510 HPLC pump, Model 410 differential refractometer, Model 486 tunable UV/vis detector, on-line multiangle laser light scattering (MALLS) detector (miniDawn, Wyatt Technology Inc.), Model 712 sample processor, and five Ultrastyragel GPC columns connected in the following series: 500, $10^3$, $10^4$, $10^5$, and 100 Å. The flow rate of THF was l.0 mL/min. $^1H$ NMR spectroscopy for structural analysis was carried out by a Bruker 250 MHz spectrometer.

**Table 1. Reaction of the Living PIB with MDDPE**[a]

| no. | reacn time, min | $10^{-3}\ M_n$ | $M_w/M_n$ | UV activity[c] |
|---|---|---|---|---|
| 1[b] | | 1.3 | 1.2 | no |
| 2 | 30 | 1.5 | 1.2 | yes |
| 3 | 60 | 1.5 | 1.2 | yes |
| 4 | 90 | 1.4 | 1.2 | yes |
| 5 | 120 | 1.4 | 1.2 | yes |

[a] Reaction condition: [MDDPE]/[living PIB] = 0.5. [b] Original PIB; polymerization conditions [TMPCl] = 0.002 M, $[TiCl_4]$ = 0.036 M, [IB] = 0.04 M, and [DTBP] = 0.003 M; in Hex:MeCl (60:40, v:v) at −80 °C. [c] Recorded on a Waters 486 tunable absorbance detector at 254 nm.

## Results and Discussion

**Coupling Reaction of Living PIB by MDDPE.** Our initial interest was focused on MDDPE, since the efficacy of this compound as a living coupling agent in anionic polymerization has already been reported.[5] The coupling reaction of living PIB by MDDPE was carried out by adding a stoichiometric amount ([MDDPE]/[living PIB] = 0.5) of MDDPE to the reactor at ~100% IB conversion. After the addition of MDDPE solution, a dark-red color gradually developed in minutes, indicating slow formation of diarylalkylcarbenium ions. During the reaction, aliquots of the reaction mixture were withdrawn at predetermined time intervals, quenched with prechilled methanol, and analyzed by GPC to monitor the progress of the coupling reaction. A summary of the reaction of living PIB with MDDPE is given in Table 1. Even after a 2 h reaction time (no. 5 in Table 1), there was no appreciable increase in the molecular weight of the product. GPC traces of all products showed monomodal distribution with identical molecular weight distribution reflecting the absence of coupling of living PIB by MDDPE. All products, however, became UV active, indicating monoaddition of living PIB to MDDPE. This monoaddition reaction was also confirmed by comparison of the $^1H$ NMR spectra of the original PIB, which exhibits characteristic proton resonances due to the methylene and methyl group with a *tert*-chlorine end ($\text{PIB-C}\boldsymbol{H}_2\text{C(C}\boldsymbol{H}_3)_2\text{-Cl}$) at $\delta = 1.66$ and 1.92 ppm, respectively, and the resulting PIB. This exhibited characteristic resonance peaks for the terminal diphenylalkylmethoxy protons at $\delta = 3.0$ ppm in addition to those characteristic peaks of the unreacted PIB (PIB−Cl).

This monoaddition of living PIB to MDDPE could be explained in terms of the lower reactivity of the second double bond. Upon monoaddition, the reactivity of the second double bond is reduced due to the electron deficient α-substituent, arising from the delocalization of positive charge over the two phenyl rings adjacent to the carbenium ion. In other words, even though the two double bonds are not conjugated with each other, it is concluded that the reactivity of the second double bond is much lower than that of DPE.

**Coupling Reaction of Living PIB by Bis-DPE Compounds.** In order to enhance our control over the coupling reaction of living PIB using bis-DPE compounds as coupling agents, it behooved us to scrutinize the capping behavior of living PIB with DPE or its derivatives. In line with the result for MDDPE, we found that the reaction of living PIB with DPE is an equilibrium reaction and that this equilibrium is shifted toward the right or to completion by increasing the

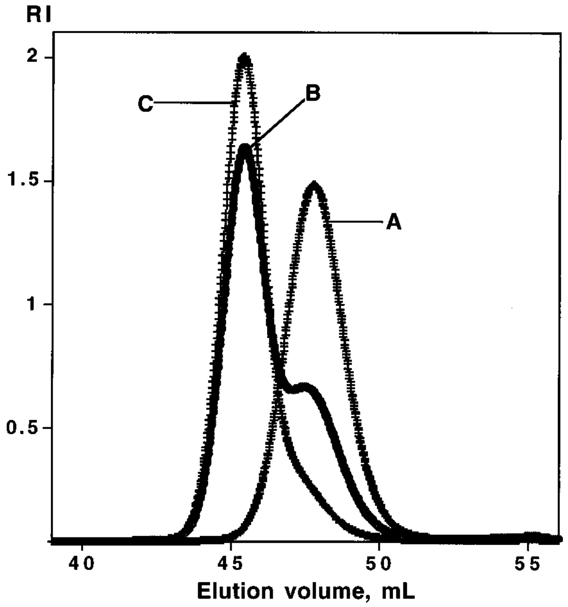


**Figure 1.** GPC RI traces of the original PIB (A) with $M_n$ = $1.6 \times 10^3$ and $M_w/M_n$ = 1.1, the intermediate product (B) quenched after 15 min with $M_n = 2.7 \times 10^3$ and $M_w/M_n = 1.3$, and the coupled product (C) after 180 min with $M_n = 3.5 \times 10^3$ and $M_w/M_n$ <1.1. Polymerization conditions: [TMPCl] = 0.002 M, [$TiCl_4$] = 0.036 M, [DTBP] = 0.003 M and [IB] = 0.04 M; in Hex:MeCl (60:40, v:v) at −80 °C. Coupling reaction condition: [BDPEP]/[living PIB] = 0.5.

Lewis acidity, solvent polarity, electron-donating ability of *para*-substituents, or concentration of reactants such as DPE and Lewis acid or by decreasing the reaction temperature.[10] Without affecting the living system, this can be accomplished by introducing electron-donating substituents over the phenyl rings of bis-DPE compounds as in BDPEP and BDTEP.

In the coupling reaction of living PIB by BDPEP, in which the two DPE moieties are separated by an electron-donating spacer group, the characteristic dark-red color of diarylalkylcarbenium ions developed instantaneously upon addition of BDPEP solution to the reactor at ~100% conversion of IB. The GPC RI traces of the original PIB (A) and the products (B and C) are shown in Figure 1. After 15 min of the coupling reaction, the GPC trace of the intermediate product (B) showed a significant extent of coupling (>50%) with a distinct bimodal distribution representing a mixture of the original PIB and the coupled product. After 3 h of the coupling reaction, the product (C) showed monomodal distribution with doubled molecular weight and narrowed molecular weight distribution. By comparison of the $^1H$ NMR spectra of the original PIB and the product, it was also confirmed that virtually quantitative coupling of living PIB was achieved by BDPEP. In the original PIB (or PIB−Cl, A in Figure 2), the terminal *tert*-chlorine exerts a strong electron-withdrawing effect on the vicinal methyl and methylene groups and shifts the resonances of these groups downfield. The proton resonances of the methyl and methylene groups in the main chain appear at 1.09 (peak b) and 1.40 ppm (peak d), respectively, while those of the terminal repeating unit directly attached to chlorine appear at 1.66 (peak f) and 1.92 ppm (peak g) and those of the penultimate unit appear at 1.16 (peak c) and 1.46 ppm (peak e). Those four characteristic peaks (c, e, f, and g) of the original PIB were completely absent from the product which was quenched after a 3 h coupling reaction (D in Figure 2), whereas new peaks characteristic of PIB capped with DPE units (h, i, j, and k) appeared as assigned.

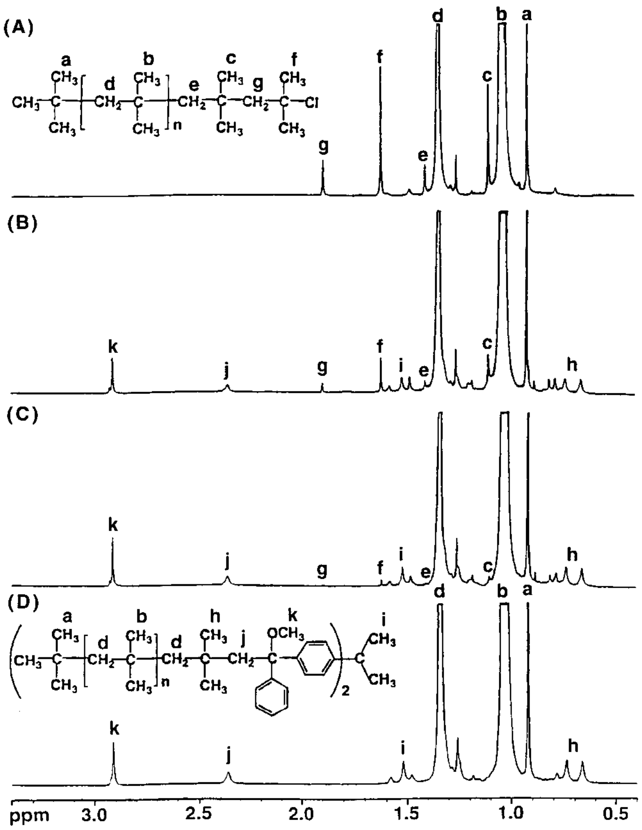


**Figure 2.** $^1H$ NMR spectra ($CDCl_3$) of the original PIB (A) and the products after 15 min (B), 45 min (C) and 180 min (D) of coupling reaction.

Few efforts have been made on the quantitative coupling of living cationic polymers with high molecular weight. Success has been limited to the coupling of low molecular weight polymer ($M_n$ <10 000). Based on the model coupling reaction of low molecular weight PIB, our study was extended to the coupling reaction of high molecular weight PIB ($M_n$ ~50 000) by BDPEP. Characterization results by GPC showed BDPEP is an effective coupling agent for living PIB independently of the chain length. A longer reaction time (6 h) was necessary for the coupling reaction to proceed to completion, however. This could be attributed to the increased viscosity of the reaction medium due to the high molecular weight of the original PIB. Figure 3 illustrates GPC RI traces of the original PIB (A) and the coupled product (B) after a 6 h coupling reaction. The coupled product indicated virtually quantitative coupling, and the product exhibited doubled molecular weight and narrowed molecular weight distribution.

Using BDTEP as a coupling agent, the coupling reaction was more rapid than the corresponding reaction with BDPEP. As can be seen in Figure 4, GPC results indicate the coupling reaction was complete in 1.5 h. It has been known that the addition reaction of living PIB to DPE or its derivatives exhibits extremely large differences in reactivity depending on the aromatic substituents. Under the same solvent and concentration of reactants as the coupling reaction, the capping equilibrium constant ($K_e$) was found to be $8.0 \times 10^2$ $M^{-3}$ in the reaction of living PIB with a stoichiometric amount of DPE at −40 °C. With DTE, this equilibrium constant was almost 3 orders of magnitude ($K_e = 2.9 \times 10^5$ $M^{-3}$) higher, with a simultaneous increase in the

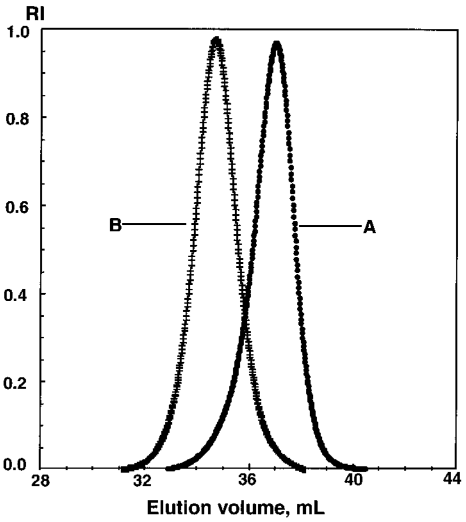


**Figure 3.** GPC RI traces of the original PIB (A) with $M_n$ = 4.67 x $10^4$ and $M_w/M_n$ = 1.14 and the coupled product (B) with $M_n$ = 9.14 x $10^4$ and $M_w/M_n$ = 1.12. Polymerization conditions: [TMPCl] = 0.002 M, [$TiCl_4$] = 0.036 M, [DTBP] = 0.003 M, and [IB] = 1.78 M; in Hex:MeCl (60:40, v:v) at −80 °C. Coupling reaction conditions: [BDPEP]/[living PIB] = 0.5 and 6 h.

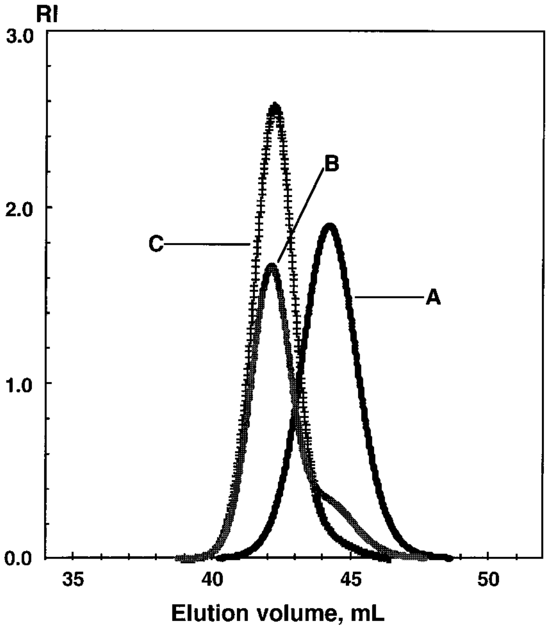


**Figure 4.** GPC RI traces of the original PIB (A) with $M_n$ = 2.4 x $10^3$ and $M_w/M_n$ = 1.1, the intermediate product (B) quenched after 15 min with $M_n$ = 4.9 x $10^3$ and $M_w/M_n$=1.2, and the coupled product (C) after 90 min with $M_n$ = 5.2 x $10^3$ and $M_w/M_n$ <1.1). Polymerization conditions: [TMPCl] = 0.002 M, [$TiCl_4$] = 0.036 M, [DTBP] = 0.003 M, and [IB] = 0.072 M; in Hex:MeCl (60:40, v:v) at −80 °C. Coupling reaction condition: [BDTEP]/[living PIB] = 0.5.

rate of capping, under identical conditions. Thus a significant effect of stabilization of the resulting diarylalkylcarbenium ions by the electron-donating substituent is exhibited. Hence it is not surprising that BDTEP, which yields a more stable carbenium ion in the coupling reaction, is a more efficient coupling agent than BDPEP. Figure 5 shows $^1$H NMR spectra of the original PIB and the coupled product along with peak assignments.

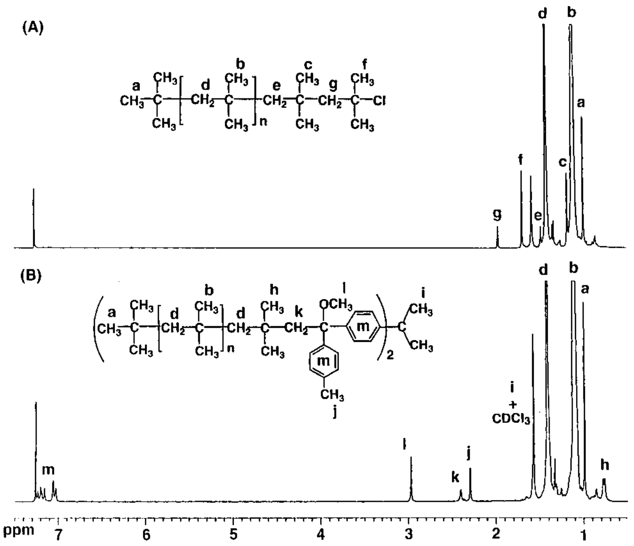


**Figure 5.** $^1$H NMR spectra ($CDCl_3$) of the original PIB (A) and the coupled product (B) after 90 min of the coupling reaction.

**Table 2. Coupling Reaction of Living PIB with BDPEP**[a]

| no. | reacn time, min | $10^{-3}$ Mn $^1$H NMR | $10^{-3}$ Mn GPC | $M_w/M_n$ | coupling efficiency, %[b] | unreacted PIB, %[b] | PIB−DPE,[c] %[b] |
|---|---|---|---|---|---|---|---|
| 1[d] | | 1.6 | 1.6 | 1.1 | | | |
| 2 | 15 | | 2.7 | 1.3 | 50.6 | 46.0 | 3.4 |
| 3 | 45 | | 3.3 | 1.1 | 79.3 | 12.8 | 5.1 |
| 4 | 95 | | 3.6 | 1.1 | >95 | ~0 | <5 |
| 5 | 180 | 3.6 | 3.5 | 1.1 | >98 | ~0 | <2 |

[a] Polymerization and coupling reaction conditions: same as in Figure 1. [b] By $^1$H NMR spectroscopy. [c] PIB−DPE: the monoadduct of PIB to BDPEP. [d] Original PIB.

**Table 3. Coupling Reaction of Living PIB with BDTEP**[a]

| no. | reacn time, min | $10^{-3}$ $M_n$ $^1$H NMR | $10^{-3}$ $M_n$ GPC | $M_w/M_n$ | coupling efficiency, %[b] | unreacted PIB, %[b] | PIB-DTE,[c] %[b] |
|---|---|---|---|---|---|---|---|
| 1[d] | | 2.4 | 2.4 | 1.1 | | | |
| 2 | 15 | | 4.9 | 1.2 | 89 | 11 | |
| 3 | 45 | | 5.2 | 1.1 | 97 | 3 | |
| 4 | 90 | | 5.2 | <1.1 | ~100 | | |
| 5 | 180 | 5.2 | 5.3 | <1.1 | ~100 | | |

[a] Polymerization and coupling reaction conditions: same as in Figure 4. [b] By $^1$H NMR spectroscopy. [c] PIB−DTE: the monoadduct of PIB to BDTEP. [d] Original PIB.

Kinetic studies of the addition of living PIB to a stoichiometric amount of bis-DPE compounds were also paralleled by $^1$H NMR spectroscopy. The results with BDPEP and BDTEP are listed in Tables 2 and 3, respectively. In Table 2, it should be noted that the concentration of the monoadduct remains extremely low throughout the coupling reaction compared to that of unreacted PIB. It is evident that the addition of living PIB to BDPEP is a consecutive reaction where the second addition is faster than the first one. With BDTEP the reaction was too fast to compare the relative amount of the unreacted PIB and the monoadduct, however. In order to prove the faster rate of the second addition, excess BDPEP was employed in the coupling reaction. Supporting our previous experimental results, a high coupling efficiency was also observed when excess BDPEP ([BDPEP]/[living PIB] = 1) was used. Interestingly, the GPC trace of the product was followed by that of unreacted BDPEP at ~53 mL of elution volume (D in Figure 6). Similar results were obtained in the coupling reaction of high molecular weight PIB with excess BDPEP. The coupled products exhibited a gradual decrease in molecular weight with the increasing ratio of [BDPEP]/[living PIB], as shown in Table 4.

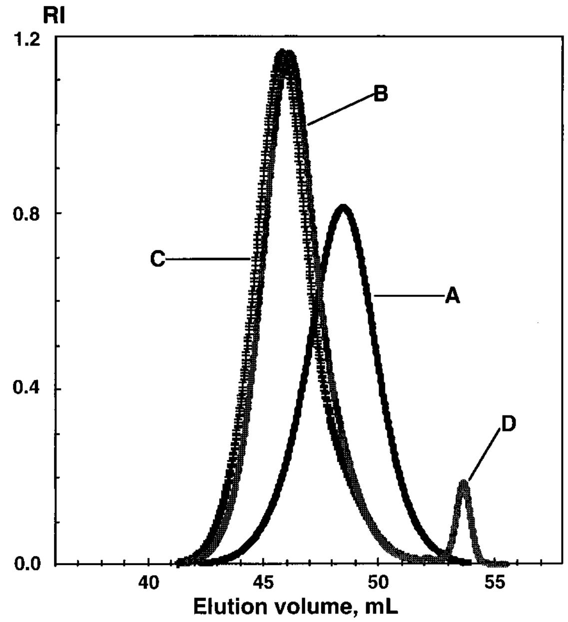


**Figure 6.** GPC RI traces of the original PIB (A) with $M_n = 1.3 \times 10^3$ and $M_w/M_n = 1.3$ and the coupled products (B) with $M_n = 2.8 \times 10^3$ and $M_w/M_n = 1.2$ and (C) with $M_n = 3.0 \times 10^3$ and $M_w/M_n = 1.2$. Coupling reaction conditions: [BDPEP]/[living PIB] = 1.0 (B) and [BDPEP]/[living PIB] = 0.5 (C) for 3 h. Polymerization conditions: [TMPCl] = 0.005 M, [$TiCl_4$] = 0.023 M, [DTBP] = 0.003 M, and [IB] = 0.09 M; in Hex: MeCl (60:40, v:v) at −80 °C.

It is notable that the experimental molecular weights are significantly higher than those calculated assuming the equal reactivity of two double bonds.

For the kinetic evaluation of this coupling reaction, the three most important reactions were taken into consideration:

$$\mathrm{PIBCl} + 2\mathrm{TiCl_4} \overset{K}{\rightleftharpoons} \mathrm{PIB^+Ti_2Cl_9^-} \qquad (1)$$

$$\mathrm{PIB^+Ti_2Cl_9^-} + \mathrm{BDPEP} \xrightarrow{k_1} \mathrm{PIB{-}BDPEP^+Ti_2Cl_9^-} \qquad (2)$$

$$\mathrm{PIB^+Ti_2Cl_9^-} + \mathrm{PIB{-}BDPEP^+Ti_2Cl_9^-} \xrightarrow{k_2} \mathrm{(PIB)_2BDPEP} \qquad (3)$$

We assumed that equilibrium 1 is fast, that reactions 2 and 3 are not equilibrium reactions, and that the concentration of $TiCl_4$ is constant. The corresponding differential equations describing the concentration changes of the different species with time can be written as follows:

$$\mathrm{d}([\mathrm{P}] + [\mathrm{P}^+])/\mathrm{d}t = -k_1[\mathrm{P}^+][\mathrm{D}] - k_2[\mathrm{P}^+][\mathrm{PD}^+] \qquad (4)$$

$$\mathrm{d}[\mathrm{PD}^+]/\mathrm{d}t = k_1[\mathrm{P}^+][\mathrm{D}] - k_2[\mathrm{P}^+][\mathrm{PD}^+] \qquad (5)$$

$$\mathrm{d}[\mathrm{P_2D^{2+}}]/\mathrm{d}t = k_2[\mathrm{P}^+][\mathrm{PD}^+] \qquad (6)$$

where [P], [$P^+$], [D], [$PD^+$], and [$P_2D^{2+}$] represent concentrations of PIBCl, $PIB^+Ti_2Cl_9^-$, BDPEP, the monoadduct, and the coupled product, respectively. Combining eqs 5 and 6, followed by integration of the resulting equation, the relationship between [$PD^+$] and [$P_2D^{2+}$] can be expressed by

**Table 4. Effect of BDPEP Concentration on $M_n$ and $M_w/M_n$ of the Coupled Products**[a]

| no. | [BDPEP]/ [living PIB] | $10^{-4}M_n$ | $M_w/M_n$ | $10^{-4}M_{n,\mathrm{cald}}$[b] |
|---|---|---|---|---|
| 1 | | 4.67 | 1.14 | |
| 2 | 0.5 | 9.14 | 1.12 | 9.34 |
| 3 | 1 | 8.07 | 1.17 | 6.23 |
| 4 | 1.5 | 7.21 | 1.18 | 5.60 |
| 5 | 2 | 6.60 | 1.31 | 5.34 |
| 6 | 3 | 6.06 | 1.30 | 5.09 |

[a] Polymerization and coupling reaction conditions: same as in Figure 3. [b] Calculated by eq 8 assuming α = 2.

$$\frac{[\mathrm{D}]_o - [\mathrm{PD}^+] - [\mathrm{P_2D^{2+}}]}{[\mathrm{D}]_o} = \left[\frac{[\mathrm{D}]_o - [\mathrm{PD}^+]/\alpha - [\mathrm{P_2D^{2+}}]}{[\mathrm{D}]_o}\right]^{\alpha} \qquad (7)$$

where $[D]_o$ is the starting concentration of BDPEP and $\alpha$ is the ratio of the rate constants of the first and second addition ($k_1/k_2$).

If BDPEP is used in excess, i.e., $[D]_o > [P]_o/2$, [P] should be zero after completion of the reaction. In this case, the molecular weight of the product ($M_{n,\infty}$) can be expressed in terms of [$PD^+$], [$P_2D^{2+}$], and the molecular weight of the original PIB ($M_{n,o}$). [$PD^+$] and [$P_2D^{2+}$] of eq 7 can also be expressed in terms of $M_{n,\infty}$, $M_{n,o}$, and $[P]_o$ and eq 7 can be rewritten as

$$1 - \frac{[\mathrm{P}]_o M_{n,o}}{[\mathrm{D}]_o M_{n,\infty}} = \left[1 - \left(\frac{2}{\alpha} - 1\right)\frac{[\mathrm{P}]_o M_{n,o}}{[\mathrm{D}]_o M_{n,\infty}} - \left(1 - \frac{1}{\alpha}\right)\frac{[\mathrm{P}]_o}{[\mathrm{D}]_o}\right]^{\alpha} \qquad (8)$$

Using the experimental data listed in Table 4, α has been calculated by a numerical method after rearrangement of eq 8 and found to be 0.39 ± 0.02, as can be seen in Figure 7. This indicates that the second addition is about 5 times faster than the first one.

A similar observation was reported by McGrath et al.[11] in the coupling reaction of *sec*-butyllithium by MDDPE in cyclohexane, presumably due to chain association in nonpolar solvent. Since viscosity studies indicated that there is no chain end association in cationic polymerization of IB,[12] this mechanism is not applicable to the anomalous addition behavior of living PIB to BDPEP. It would appear to be more germane to consider topological aspects of the bulky gegenion, $Ti_2Cl_9^-$, and the monoadduct of living PIB to BDPEP. The model to explain this hypothesis is shown in Scheme 2. For simplicity the PIB segment has been replaced with the trimethylpentyl group (head group of PIB) and hydrogen atoms have been omitted. Stucky et al. reported the adduct of [$PCl_4$][$Ti_2Cl_9$] in the reaction of $PCl_5$ with $TiCl_4$ in $SOCl_2$ and the face-shared bi-octahedral structure of $Ti_2Cl_9^-$ by X-ray structural analysis.[13] If a similar bulky structure could be applied to $Ti_2Cl_9^-$ in the solution state, we can easily imagine the interaction between the bulky gegenion and the second double bond upon monoaddition. This interaction is expected to increase the electron density of the second double bond. Thereby, the second double bond will be activated, rendering the monoaddition rate-determining step. In order to prove this hypothesis, ab initio or semi-empirical molecular orbital calculations may be necessary.

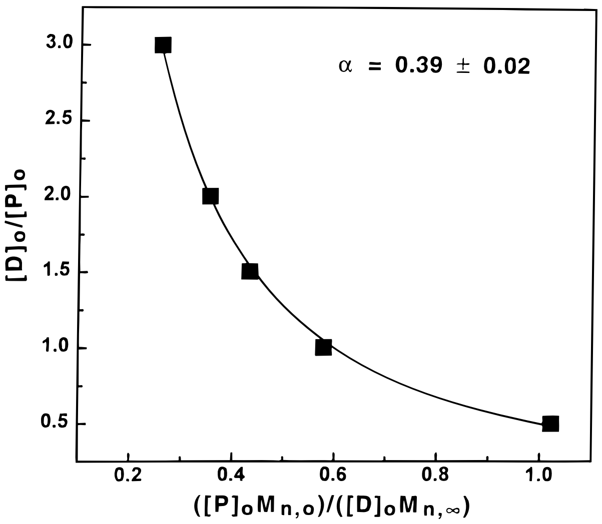
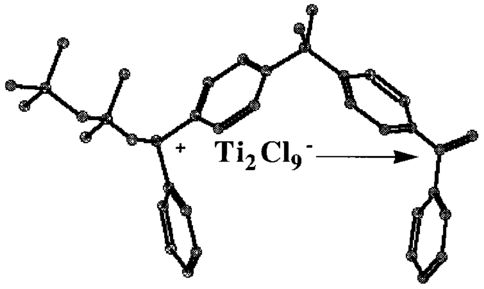


**Figure 7.** Plot of $[D]_o/[P]_o$ versus $([P]_oM_{n,o})/([D]_oM_{n,\infty})$. Filled squares: data from Table 4; Solid line: from eq 8 with $\alpha$ ($=k_1/k_2$) value of 0.39 ± 0.02.

**Scheme 2**



## Conclusions

Quantitative coupling of low as well as high $M_n$ living PIB was accomplished for the first time using BDPEP and BDTEP as coupling agents. The rate of this coupling reaction is dependent on aromatic *para*-substituents of coupling agents; a faster rate was observed when the more stabilized carbenium ions were produced. This process yields the living coupled PIB, useful as an intermediate for the synthesis of $A_2B_2$ star-block copolymers. Synthesis of ABC or $A_2B_2$ type star-block copolymers using anionic and/or cationic living polymers will be the subsequent subjects of this series.

The observed faster rate of the second addition is proposed to involve the activation of the second double bond by the bulky gegenion, $Ti_2Cl_9^-$, upon monoaddition. Further investigation supporting this hypothesis is in progress.

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