Addition Reaction of Living Polyisobutylene to "Double" Diphenylethylenes. Synthesis of 1,1-Diphenylethylene-Functionalized Polyisobutylene Macromonomers

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Received August 4, 1998
Revised Manuscript Received October 10, 1998

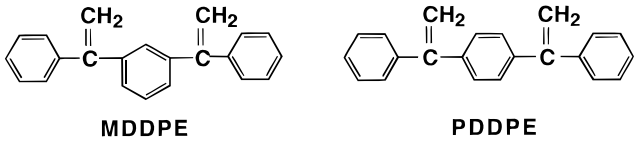
Introduction

Macromonomers with a terminal non(homo)polymerizable vinylidene group, such as 1,1-diphenylethylene (DPE), have gained much attention in recent years.[1−5] One of the most unique and appealing applications of these types of macromonomers is that they can be used as precursor polymers for a variety of block copolymers with controlled architectures such as ABC-type star-block[1−5] or comb-type graft copolymers.[4] Three approaches have been reported to date for the synthesis of DPE-functionalized macromonomers exclusively using anionic polymerization techniques. The first method involves ring-opening polymerizations of heterocyclic monomers with DPE-functionalized initiators yielding α-DPE-functionalized macromonomers.[1,2] *ω*-DPE-functionalized macromonomers can also be prepared by the addition reaction of living anionic polymers to "double" diphenylethylenes (DDPEs, Chart 1), such as 1,3-bis(1-phenylethenyl)benzene (or meta-double diphenylethylene, MDDPE) or 1,4-bis(1-phenylethenyl)benzene (or para-double diphenylethylene, PDDPE), taking advantage of the monoaddition reaction of living anionic polymers to MDDPE or PDDPE in the presence of polar additives.[3,4] Termination of DPE-capped poly(styryl)-lithium with an electrophile containing DPE moiety was also reported to yield *ω*-DPE-functionalized polystyrene macromonomer.[5]

During the study of the "living" coupling reaction of living polyisobutylene (PIB) using bis(DPE) compounds for the synthesis of A_2B_2 star-block copolymers,[6,7] it was found that, for the quantitative coupling reaction of living PIB, two DPE moieties of a coupling agent should be separated by a spacer group which provides independent reactivity of two double bonds toward living PIB. When MDDPE was employed as a potential coupling agent, the coupling reaction of living PIB was not observed, indicating that the second double bond is far less reactive than the first one. Upon monoaddition, the reactivity of the second double bond is reduced presumably due to the electron-deficient α-substituent, arising from the delocalization of positive charge over the two phenyl rings adjacent to the carbenium ion.

Although MDDPE exhibited limitations as a living coupling agent for the synthesis of A_2B_2 star-block copolymers,[6] potential applications of the monoaddition reaction of living PIB to MDDPE were prominent, and the synthetic scheme for DPE-functionalized PIB macromonomer (PIB-DPE macromonomer) was proposed.[8] In this study, we carried out a more detailed investigation on the addition reaction of living PIB to DDPEs, such as MDDPE or PDDPE, for the ultimate goal of the synthesis of PIB-DPE macromonomers. Herein we report a general methodology for the synthesis of DPE-functionalized macromonomers using a living cationic polymerization technique for the first time.

Chart 1. Structures of "Double" Diphenylethylenes (DDPEs)



Experimental Section

Materials. MDDPE was prepared by the Wittig olefination of 3-benzoylbenzophenone according to the procedure reported by Schulz and Hocker.[9] Purification of MDDPE was carried out by column chromatography followed by vacuum distillation just before use, and it was obtained as a supercooled liquid. ^{1}H NMR (250 MHz, $CDCl_3$, δ): 7.3 (m, Ar H, 14H), 5.5−5.4 (AB q, $J = 1.2$ Hz, $\Delta\nu = 4.2$ Hz, $=CH_2$, 2H); ^{13}C NMR (63 MHz, $CDCl_3$, δ): 150.4 ($C{=}CH_2$), 142.0 and 141.8 (Ar quaternary C), 128.7−128.2 (Ar methine C), 114.9 ($C{=}CH_2$). PDDPE was prepared by the Grignard reaction of 4-benzoylbenzophenone[10] with methylmagnesium chloride followed by dehydration: mp 137.5 °C (lit.[11] 137 °C); ^{1}H NMR (250 MHz, $CDCl_3$, δ): 7.3 (m, Ar H, 14H), 5.5−5.4 (AB q, $J = 1.2$ Hz, $\Delta\nu = 11.4$ Hz, $=CH_2$, 4H); ^{13}C NMR (63 MHz, $CDCl_3$, δ): 150.0 ($C{=}CH_2$), 141.7 and 140.1 (Ar quaternary C), 128.5−128.0 (Ar methine C), 114.5 ($C{=}CH_2$). All other chemicals and solvents were purified as described previously[6,7,12] or used as received.

Living Cationic Polymerization and Functionalization. The living cationic polymerization of isobutylene (IB) was carried out using the 2-chloro-2,4,4-trimethylpentane (TMPCl)/$TiCl_4$/hexane:CH_3Cl (60:40, v:v)/−80 °C system in the presence of 2,6-di-*tert*-butylpyridine (DTBP) as reported previously.[6,12] At ∼100% conversion of the IB polymerization, aliquots of living PIB solution were transferred into 75 mL test tubes, and one of the tubes was quenched with prechilled methanol for the characterization of the original PIB. The addition reaction of living PIB to MDDPE or PDDPE was started by adding 5 mL of 0.02 M MDDPE or PDDPE solution in CH_2Cl_2 to 25 mL of living PIB solution ([MDDPE] or [PDDPE]/[living PIB] = 2). At predetermined time intervals, the reaction mixtures were quenched with prechilled methanol inside the glovebox and poured over excess 10% ammoniacal methanol outside of the glovebox. After the evaporation of solvents, the crude product was dissolved in hexane, and inorganics were removed by a simple filtration. The polymer solution in hexane was again poured over an equal volume of methanol, and the hexane layer was slowly evaporated to precipitate PIB on the methanol layer. The remaining methanol was decanted, and the recovered product was again dissolved in hexane to repeat this procedure three times. When MDDPE was used, methanol containing 10 vol % acetone was used to remove unreacted MDDPE.

Characterization and Instrumentation. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker 250 MHz/52MM spectrometer. Thin-layer chromatography (TLC) was carried out on silica gel plates (Merck, Kieselgel $60F_{254}$) with fluorescent indicator (254 nm). Visible spectra were recorded in situ using a fiber-optic UV/vis spectrometer integrated with a quartz immersion probe (666.000-QX, Hellma), a tungsten halogen light source (LS-1, Ocean Optics Inc.), and a photodiode array detector (MMS 256, Zeiss). Spectroscopic data were collected on a PC through an interface (Tec5, Zeiss) and processed using commercial software (Aspect Plus, Zeiss). Determination of molecular weight and its distribution was carried out using a Waters HPLC system equipped with a

10.1021/ma981231h CCC: $15.00
Published on Web 12/04/1998

Table 1. Results in the Addition Reaction of Living PIB to MDDPE[a]

no.	reaction time, min	M_n	M_w/M_n	PIB-DPE, %[b]
1[c]		2100	1.06	
2	5	2400	1.06	29
3	20	2400	1.06	65
4	60	2600	1.08	85
5	150	2700	1.14	91

[a] IB polymerization conditions: [TMPCl] = 0.002 M, [DTBP] = 0.003 M, [$TiCl_4$] = 0.036 M, [IB] = 0.075 M in hexane/CH_3Cl (60/40, v/v) solvent mixture at −80 °C. Addition reaction conditions: 5 mL of 0.02 M MDDPE solution in CH_2Cl_2 was added to 25 mL of living PIB solution ([MDDPE]/[living PIB] = 2). [b] By ^{1}H NMR spectroscopy. [c] Original PIB.

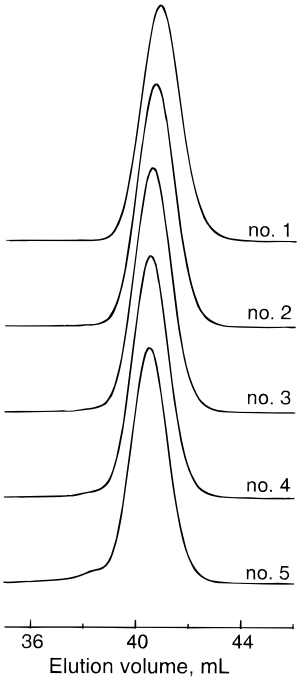


Figure 1. GPC RI traces of PIBs before (no. 1) and after addition reaction of living PIB to MDDPE (no. 2−5).

model 510 HPLC pump, a model 712 sample processor, a model 486 tunable UV/vis detector, and a model 250 dual detector (refractometer/viscometer, Viscotek). Five Ultrastyragel columns (Waters) were connected in the following series: 500, 10^3, 10^4, 10^5, and 100 Å. THF was used as a carrier solvent at a flow rate of 1 mL/min.

Results and Discussion

Addition Reaction of Living PIB to MDDPE. In a previous paper, we reported that the addition reaction of living PIB to MDDPE yields monoadduct due to the reduced reactivity of the second double bond.[6] When the ratio of [MDDPE]/[living PIB] = 0.5 was used for the coupling reaction of living PIB with MDDPE, a mixture of monoadduct and unreacted PIB was obtained. No evidence was observed from GPC for the formation of the coupled product (or diadduct), indicating that the reaction results predominantly in the monoaddition of living PIB to MDDPE. In this study, taking advantage of this monoaddition reaction, the synthesis of PIB-DPE macromonomer was attempted using 2 equiv of MDDPE. A summary of results is listed in Table 1, and corresponding GPC RI traces of samples 1−5 are shown in Figure 1. The original PIB (no. 1 in Table 1) exhibited a targeted M_n and a narrow molecular weight distribution (M_w/M_n = 1.06). Contrary to the previous report, however, negligible but detectable amounts of the coupled product were observed from GPC traces when the reaction was carried out at a prolonged reaction time as can be seen from both the M_w/M_n and the GPC trace of sample 5. A small hump at a lower elution volume (M_p = 6100) is attributed to the coupled product, and using peak analysis software (PeakFit, Jandel Scientific), the amount of the coupled product was calculated to be ∼3%. These contradictory results are most likely due to the relatively broad molecular weight distribution of the original PIB (M_w/M_n = 1.2) in a previous report, which might have hampered the resolution of the monoadduct and the diadduct from GPC traces.

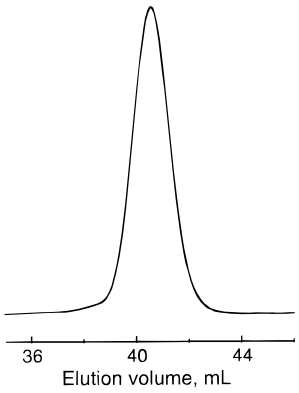


Figure 2. GPC RI trace of PIB-DPE with M_n = 2600 and M_w/M_n = 1.07. Addition reaction conditions: [MDDPE]/[living PIB] = 4 and for 150 min.

The progress of the addition reaction was also studied using ^{1}H NMR spectroscopy by comparison of resonance signals for methylene protons next to a terminal chloro group (−C***H***$_2$(CH_3)$_2$Cl, δ = 1.96 ppm) of the unreacted PIB (PIB-Cl) and methoxy protons (−CH_2(CH_3)$_2$-CH_2-C(Ph)$_2$OC***H***$_3$, δ = 3.0 ppm) of the monoadduct or the diadduct. As listed in Table 1, the conversion of the addition reaction increased rapidly in the early stage, but it leveled off after 150 min to reach a maximum conversion at 91%. Although it was reported that the addition reaction of living PIB to DPE is an equilibrium reaction, this observation was quite unexpected since the addition reaction of living PIB to DPE was reported to reach ∼100% conversion within 75 min under similar conditions.[13] Whereas the steep increase in conversion in the early stage can be explained by the fact that MDDPE has two DPE moieties, the limiting conversion can be accounted for only by a lower equilibrium constant in the addition reaction of living PIB to MDDPE.

To force the addition reaction to completion and to reduce the formation of the coupled product at the same time, a large excess of MDDPE (4 equiv) was employed in the subsequent addition reaction under otherwise same conditions. Figure 2 shows the GPC RI trace of the final product, and it can be seen that the formation of the coupled product is virtually absent from the GPC trace. As shown in Figure 3, the ^{1}H NMR spectrum of the product clearly proves the virtual absence of the coupled product as well as unreacted PIB. For example, the ratio of integration areas of peaks d, e, and f was almost identical to the theoretical ratio (observed 1:1.47:1), indicating the virtual absence of the coupled product. The concomitant absence of unreacted PIB is also supported by the virtual absence of characteristic resonance signals for the chloro-terminated PIB (PIB-Cl), i.e., methylene and methyl protons next to chloro

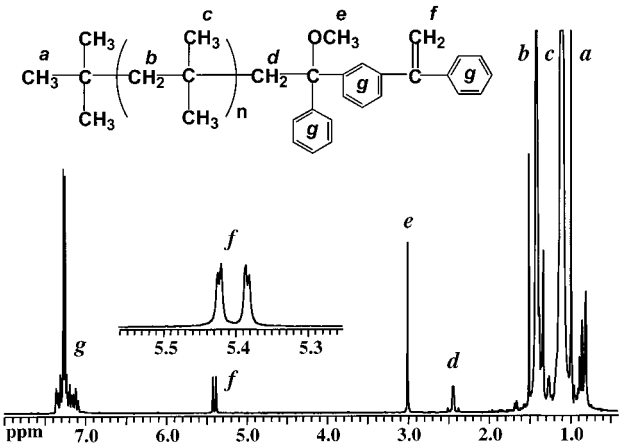


Figure 3. The 250 MHz ^{1}H NMR spectrum of PIB-DPE macromonomer prepared using 4 equiv of MDDPE.

group ($-C\boldsymbol{H}_2C(C\boldsymbol{H}_3)_2Cl$) at δ = 1.96 and 1.67 ppm, respectively. Although reported as chemical shift equivalent,[14] geminal protons of double bonds in MDDPE are diastereotopic, and their resonance signals form an AB system (J = 1.2 Hz and $\Delta\nu$ = 4.1 Hz). Two geminal protons of the DPE moiety in the macromonomer exhibit an upfield shift (δ = 5.46−5.35 ppm) as well as a large increase in $\Delta\nu$ (=9.7 Hz) after the addition of the PIB segment.

Since MDDPE is soluble in hexane and exhibits poor solubility in methanol, it was troublesome to remove unreacted MDDPE by the usual workup, that is, dissolution of the crude product in hexane followed by precipitation onto methanol during the evaporation of hexane. Therefore, after the routine workup, the crude product (containing unreacted MDDPE) was further precipitated onto a methanol/acetone (9/1 v/v) solvent mixture, and the progress of the purification was monitored by TLC using a hexane/THF (98/2 v/v) solvent mixture as eluent. Before this additional purification, the crude product exhibited two spots on the TLC plate (R_f = 0.9 for PIB-DPE macromonomer and R_f = 0.7 for MDDPE). After three times of precipitation in methanol/acetone solvent mixture, the product exhibited only one spot (R_f = 0.9) and methanol/acetone extracts also exhibited one spot (R_f = 0.7), proving the effectiveness of this purification method to remove unreacted MDDPE.

Addition Reaction of Living PIB to PDDPE. Although a clean synthesis of PIB-DPE macromonomer is readily available using MDDPE, a large excess of MDDPE should be used to avoid the coupled product. This may impose difficulties on the isolation of the pure macromonomer, free from unreacted MDDPE. It has been reported that, in the addition reaction of poly(styryl)lithium to DDPEs, the amount of the coupled polystyrene is decreased or minimized when PDDPE, in which the two double bonds are conjugated, is employed.[3] Since electron-deficient α,α-disubstituents are formed in the second double bond upon monoaddition of living PIB to PDDPE, it is readily conceivable that PDDPE might be a better candidate for the synthesis of PIB-DPE macromonomer without using a large excess. It was also expected that the rate as well as the equilibrium constant in the addition reaction of living PIB to PDDPE would be higher than to MDDPE.

Using the same conditions as listed in Table 1, the addition reaction of living PIB to PDDPE was studied using 2 equiv of PDDPE. As summarized in Table 2,

Table 2. Results in the Addition Reaction of Living PIB to PDDPE[a]

no.	reaction time, min	M_n	M_w/M_n	PIB-DPE, %[b]
1[c]		2300	1.06	
2	5	2700	1.05	44
3	10	3100	1.07	62
4	20	2900	1.05	73
5	40	2700	1.07	83
6	75	2700	1.05	∼100
7	130	2900	1.05	∼100
8	240	3000	1.05	∼100

[a] IB polymerization conditions: same as in Table 1. Addition reaction conditions: 5 mL of 0.02 M PDDPE solution in CH_2Cl_2 was added to 25 mL of living PIB solution ([PDDPE]/[living PIB] = 2). [b] By ^{1}H NMR spectroscopy. [c] Original PIB.

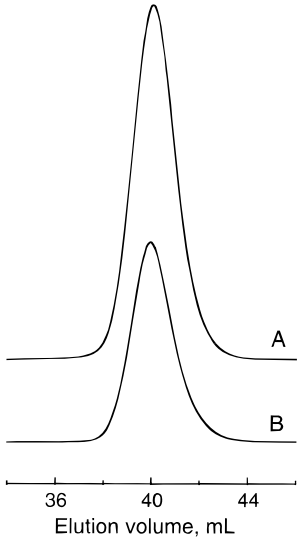


Figure 4. GPC RI (A) and UV (B) traces of PIB-DPE macromonomer prepared using PDDPE (no. 7 in Table 2).

the addition reaction of living PIB to PDDPE was much faster than to MDDPE, and ∼100% functionalization was achieved in 75 min. GPC traces of the products exhibited narrow molecular weight distributions throughout the addition reaction. Moreover, no evidence was observed for the formation of the coupled product from GPC traces as shown in Figure 4. By comparison of ^{1}H and ^{13}C NMR spectra of the products quenched before and after the addition reaction, it was further confirmed that the addition reaction of living PIB to PDDPE goes to completion using only 2 equiv of PDDPE. As shown in Figure 5, resonance signals corresponding to PIB-Cl are not observed from both ^{1}H and ^{13}C NMR spectra of the PIB-DPE macromonomer. For example, the ^{13}C NMR spectrum of PIB-Cl exhibits characteristic resonance signals at δ = 71.9 and 35.6 ppm for the quaternary carbon attached to the terminal chloro group ($-CH_2\boldsymbol{C}(CH_3)_2Cl$) and geminal methyl carbons of this quaternary carbon ($-CH_2C(\boldsymbol{C}H_3)_2Cl$), respectively.[15] From the ^{13}C NMR spectrum of the macromonomer, these two characteristic resonance signals are completely absent, and new resonance signals corresponding to PIB-DPE macromonomer are observed as assigned in Figure 5.

By comparison of ^{1}H and ^{13}C NMR spectra of the macromonomer and PDDPE, it is also proved that excess PDDPE can easily be removed from the macromonomer by a simple purification procedure. Whereas PDDPE exhibits two different resonance signals for aromatic quaternary carbons at δ = 141.7 and 140.1

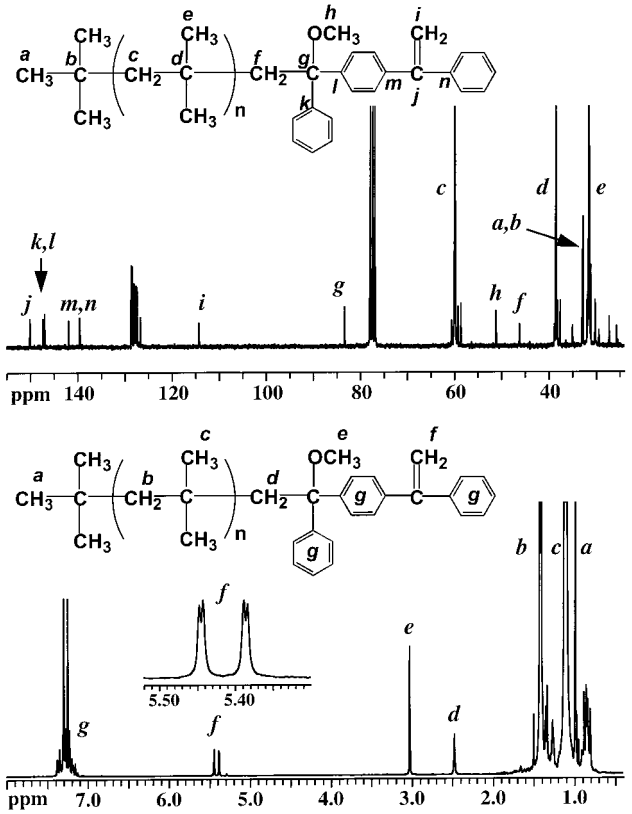


Figure 5. The 250 MHz ^{13}C (top) and ^{1}H (bottom) NMR spectra of PIB-DPE macromonomer prepared using PDDPE.

ppm, four different resonance signals for aromatic quaternary carbons (peaks k, l, m, and n) are observed from PIB-DPE macromonomer at δ = 147.4, 147.1, 142.0, and 139.6 ppm, indicating the absence of unreacted PDDPE from the final product. The compositional integrity of the macromonomer is further demonstrated in the expanded ^{1}H NMR spectrum in Figure 5. Similar to those in MDDPE, geminal protons of the double bond in PDDPE form an AB system (J = 1.2 Hz and $\Delta\nu$ = 11.4 Hz). After the addition of the PIB segment, two geminal protons of the DPE moiety in the macromonomer (peak f) exhibit an upfield shift as well as an increase in $\Delta\nu$ (=13.5 Hz). From the expanded ^{1}H NMR spectrum, no evidence is observed for the presence of unreacted PDDPE in the macromonomer.

Kinetic Studies of Addition Reaction Using a Fiber-Optic Visible Spectrometer. Since diphenylalkylcarbenium ions exhibit a high-intensity absorption ($\epsilon_{max} > 10^4$) in the visible range,[16−19] the kinetics of the addition reaction was further studied in situ using a fiber-optic visible spectrometer. The visible spectra recorded during the addition reaction of living PIB to an excess (4 equiv) of MDDPE are shown in Figure 6A, and the absorbance at λ_{max} (A_{max}) versus time plot is shown in Figure 6B. The carbenium ion of the monoadduct of living PIB to MDDPE (PIB-MDDPE$^+$) exhibits a maximum absorption at λ_{max} = 440 nm, and the molar absorptivity (ϵ_{max}) was calculated to be ~ 30 000 L mol^{-1} cm^{-1}, assuming the quantitative formation of PIB-MDDPE$^+$. For the monoadduct carbenium ion of living PIB to PDDPE (PIB−PDDPE$^+$), a maximum absorption was observed at λ_{max} = 518 nm with ϵ_{max} ~ 34 000 L mol^{-1} cm^{-1} under otherwise identical conditions. It is interesting to note that PIB-MDDPE$^+$ exhibits similar λ_{max} and ϵ_{max} to those of diphenylalkylcarbenium ions.[16−18] It appears that the electronic structure of PIB-MDDPE$^+$ is very similar to those of diphenylalkylcarbenium ions, and the contribution of the *meta*-substituted phenylethenyl group to the stabilization of the resulting carbenium ion is negligible.

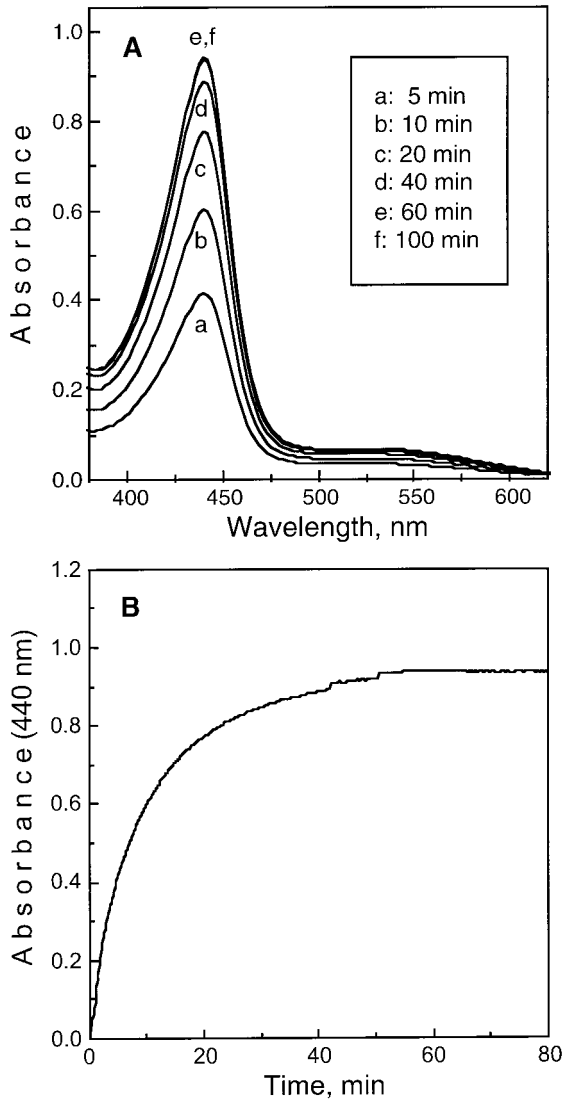


Figure 6. Visible spectra recorded during the addition reaction of living PIB to MDDPE (A) and absorbance at λ_{max} = 440 nm as a function of time (B). Reaction conditions: [MDDPE]/[living PIB] = 4 and other conditions are the same as in Table 1.

Using a similar kinetic equation that was developed for the capping reaction of living PIB with DPE,[19] the apparent rate constants (k_{app}'s) in the addition reaction of living PIB to DDPEs can be calculated from the initial slope in the A_{max} versus time plot (Figure 6B). The k_{app} values obtained using the initial slopes in the A_{max} versus time plots are listed in Table 3. Two different k_{app} values obtained with PDDPE are mainly due to the slight difference in ϵ_{max} values obtained with different PDDPE concentrations. This corresponds to less than 5% difference in the initiator concentration, and therefore, those values are considered to be the same within experimental error. On the basis of k_{app} values, it is concluded that PDDPE is ~2.5 times more reactive than MDDPE toward living PIB. Although direct comparison is not possible due to the slight difference in solvent polarity, it is also notable that the DPE moiety in MDDPE exhibits a similar reactivity as DPE (k_{app} = 170 M^{-3} s^{-1}).[19] When 4 equiv of PDDPE was employed in

Table 3. Kinetic Results in the Addition Reaction of Living PIB to DDPEs[a]

no.	DDPE	[DDPE]/[living PIB]	k_{app}, M^{-3} s^{-1} [b]	$10^{-4}\epsilon_{max}$
1[c]	MDDPE	4	370	3.0
2	PDDPE	2	920	3.3
3[c]	PDDPE	4	940	3.4

[a] IB polymerization and addition reaction conditions: same as in Table 1. [b] Calculated using the initial concentrations of [DDPE], [$TiCl_4$], and [TMPCl] (=[PIBCl]). [c] 0.04 M DDPE solution was used.

the addition reaction, the half-life ($t_{1/2}$) of the addition reaction was calculated to be 2 min from the A_{max} versus time plot, and a plateau in this plot was reached within 20 min.

Conclusions

A facile route for the synthesis of PIB-DPE macromonomers has been developed, taking advantage of the monoaddition reaction of living PIB to DDPEs under given conditions. On the basis of spectroscopic as well as chromatographic results, it is concluded that PDDPE is a better candidate than MDDPE for the synthesis of the macromonomer. When PDDPE was employed, the formation of the coupled product was not detected, and it was found that PDDPE is ~2.5 times more reactive than MDDPE toward living PIB. Syntheses of ABC star-block copolymers or H-shaped block copolymers are under progress using ω- or α,ω-DPE-functionalized PIB, respectively.

Acknowledgment. Financial support from the National Science Foundation (DMR-9806418 and DMR-9502777) is gratefully acknowledged.

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MA981231H