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Synthesis of Poly(isobutylene-*b*-methyl methacrylate) Copolymers by the Combination of Living Carbocationic and Group Transfer Polymerization

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ABSTRACT: Poly(isobutylene-*b*-methyl methacrylate), p(IB-*b*-MMA), copolymers were synthesized by reacting the two corresponding living homopolymers, obtained by living carbocationic and group transfer polymerization, respectively. IB was polymerized by the 2,4,4-trimethyl-2-chloropentane (TMPCl)/$TiCl_4$/methylcyclohexane:CH_3Cl 60:40 v:v/−80 °C system. When the polymerization was complete, 1,1-diphenylethylene was added to convert PIB-Cl to the corresponding diphenylcarbenium ions. To this solution living PMMA, obtained by group transfer polymerization, isolated and dissolved in CH_3Cl was added, and the reaction mixture was allowed to warm to −40 °C. Depending on the livingness of PMMA, up to 80% coupling efficiency could be obtained. It was found that at −40 °C after reaching a maximum of ~80% the coupling efficiency decreases with time. In a very slow competitive reaction, the formed block copolymers are cleaved by a mechanism suggested to involve the complexation of $TiCl_4$ to the carbonyl oxygen adjacent to the coupling site, followed by anion formation and irreversible termination. This side reaction can be minimized by limiting the reaction time to <4 h at −40 °C and by using a low $[TiCl_4]/[TMPCl] = 4$ ratio.

Introduction

Tailored block copolymers of monomers polymerizable by different mechanisms such as IB and MMA can be prepared by several methods. Among these the site transformation technique and coupling of living polymers have been used most frequently. The synthesis of p(MMA-*b*-IB-*b*-MMA) triblock copolymer using site transformation has been reported by Brittain et al.[1] Cl−PIB−Cl was synthesized by living carbocationic polymerization. The polymer was dehydrochlorinated and subsequent hydroboration−oxidation of the corresponding α,ω-diisopropenyl-PIB yielded HO−PIB−OH. In two more steps the end groups were converted to a bifunctional silylketene acetal macroinitiator. The subsequent group transfer polymerization of MMA by the PIB macroinitiator resulted in p(MMA-*b*-IB-*b*-MMA) triblock copolymer formation although the blocking efficiency was only about 55%. The same block copolymer has been synthesized by Hatada et al.[2] using cationic to anionic site transformation. α,ω-Hydroxyl telechelic PIB, prepared similarly to above, was esterified, resulting in PIB diisobutyrate in 92% yield. Lithiation with an equimolar amount of LDA produced an α,ω-dianion which was used to initiate anionic polymerization of MMA. Triblock copolymers with close to theoretical molecular weights were obtained without diblock contamination.

The coupling reaction of two living homopolymers having antagonist functions is a fast and efficient way to prepare well-defined block copolymers when sequential addition of the monomers is not applicable. The reactivities of the end groups have to be matched and a good solvent has to be found for both homopolymers and copolymer to achieve quantitative coupling. Poly(alkyl vinyl ether, VE-*b*-MMA) block copolymer was obtained in the work of Riffle et al.[3] by coupling the two living homopolymers. The toluene solution of PVE prepared by living carbocationic polymerization was quenched with living PMMA synthesized by group transfer polymerization also using toluene as solvent. The presence of an undetermined, small amount of unreacted homopolymer was observed on the GPC trace of the product.

Living polystyryllithium anions and poly(ethyl vinyl ether) cations were successfully coupled by Jérôme et al.[4] Polystyrene polymerized by *sec*-butyllithium in THF at −78 °C was end-capped with a few units of α-methylstyrene for the observation of quantitative stoichiometry and was used to titrate poly(ethyl vinyl ether), PEVE, obtained with the HI/ZnI_2 initiating system in toluene at −30 °C. P(St-*b*-EVE) block copolymers were obtained without homopolymer contamination.

In-situ functionalization of the living carbocationic chain ends was recently realized in our laboratory using 1,1-diphenylethylene (DPE) capping followed by end-quenching with soft nucleophiles such as silylketene acetals. Close to quantitative functionalization was observed with 1-methoxy-1-(trimethylsiloxy)-2-methyl-1-propene (MTS).[5] Since living PMMA prepared by group transfer polymerization[6] contains the silylketene acetal moiety, it occurred to us that p(IB-*b*-MMA) could be prepared by coupling the corresponding living homopolymers.

In the present study we report on the coupling reaction between living PMMA, prepared by group transfer polymerization, and the polyisobutenyl diphenylcarbenium ions.

Experimental Section

Materials. DPE, BuLi, and hexafluorocumyl alcohol were used as received from Aldrich. Methylcyclohexane (MeChx) and pentane were refluxed for 48 h with concentrated sulfuric acid to remove unsaturated impurities and then were extracted with dilute NaOH and distilled water and kept over $MgSO_4$. After filtration it was refluxed over CaH_2 overnight in a N_2 atmosphere and freshly distilled prior to use. Tetramethylethylenediamine (TMEDA) and $SiCl_4$ were freshly distilled. All other materials have been described elsewhere.[6,7]

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Procedures. The synthesis of the spirosilane catalyst quencher was carried out according to the procedure provided by Farnham.[8]

The model reaction between TMPDPE$^+$Ti$_2$Cl$_9$$^-$ and MTS was carried out in MeChx:CH$_3$Cl 40:60 v:v; ([TMPCl] = 6.1×10^{-2} M; [TiCl$_4$]/[TMPCl] = 3; [DTBP] = 3.6×10^{-3} M; [DPE] = 6.4×10^{-2} M; [MTS] = 6.1×10^{-2} M). The coupling reactions between PIBDPE$^+$Ti$_2$Cl$_9$$^-$ and PMMA were carried out in MChx:CH$_3$Cl 35:65 v:v. The two homopolymers were synthesized simultaneously in separate dryboxes: IB was polymerized by the 2,4,4-trimethyl-2-chloropentane (TMPCl)/TiCl$_4$/MeChx:CH$_3$Cl 60:40 v:v/−80 °C system. When the polymerization was complete, DPE was added to convert PIB−Cl to the corresponding diphenylcarbenium ions (PIBDPE$^+$Ti$_2$Cl$_9$$^-$)[9].

Group transfer polymerization (GTP) of MMA was carried out by a procedure according to Webster,[6] using 1-methoxy-1-(trimethylsiloxy)-2-methyl-1-propene (MTS) as initiator and tetrabutylammonium fluoride trihydrate (TBAF$^-$) or biacetate as catalyst (0.1 mol % to initiator) in THF. Fourty minutes after the exothermic peak of the MMA polymerization, the THF solution of the living PMMA was poured into a threefold volume of olefin-free, dry pentane. The precipitated polymer was vacuum filtered inside the drybox, rinsed with pentane, and dried in the entry port for 10 min. After removing an aliquot for control, the polymer was weighed in a sealed, tared flask and transferred into the drybox containing the cationic living system, where it was dissolved in CH$_3$Cl and cooled to −80 °C. The aliquot was dissolved in THF, and a second increment of MMA was added with a calculated amount of catalyst to investigate the livingness of the precipitated polymer.

The −80 °C solution containing a stoichiometric amount of PMMA was charged into the PIBDPE$^+$Ti$_2$Cl$_9$$^-$ solution while stirring. CH$_3$Cl was added to adjust the MeChx:CH$_3$Cl ratio to ~35:65 v:v to ensure system homogeneity. The reaction system was allowed to warm to −40 °C and stirred for 4 h from the time of the addition.

The block copolymers were quenched with prechilled methanol and then poured over an equal volume of methanol containing 5% (v:v) NH$_4$OH. The solvents were evaporated under the hood, and the dry polymer was dissolved in THF and filtered to remove inorganic salts. THF was removed by vacuum, and the polymer was dried and analyzed.

Characterizations. Molecular weights and molecular weight distributions were determined using a Waters HPLC system equipped with a Model 510 HPLC pump, a Model 410 differential refractometer, a Model 486 tunable UV−vis detector, an on-line multiangle laser light scattering detector (MiniDawn, Wyatt Technology Inc.), a 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 1.0 mL/min. PMMA (narrow MWD standards received from Polysciences Inc.) and PIB calibration curves were used for molecular weight determination of the corresponding homopolymers. The absolute molecular weights of the block copolymers were determined using Astrette software by calculating the d*n*/d*c* values based on composition or assuming 100% mass recovery. NMR spectroscopy was carried out on a Bruker 270 MHz instrument.

Results and Discussion

We recently reported that PIBDPE$^+$Ti$_2$Cl$_9$$^-$ readily reacts with MTS, giving rise to −COOCH$_3$ functional PIB in close to quantitative yields.[5] Since silylketene acetals act as initiators and are the dormant centers in GTP, there is a potential for this reaction to be used as a coupling reaction in block copolymer synthesis.

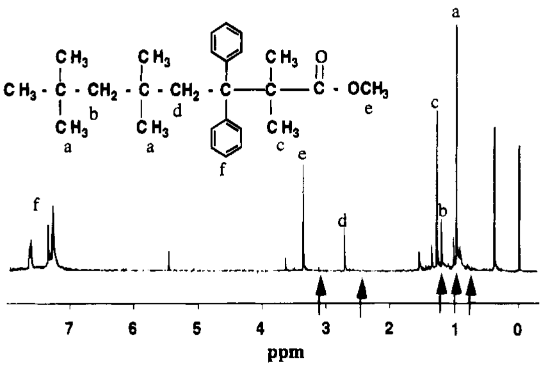
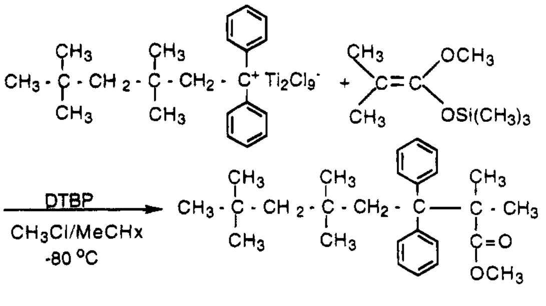


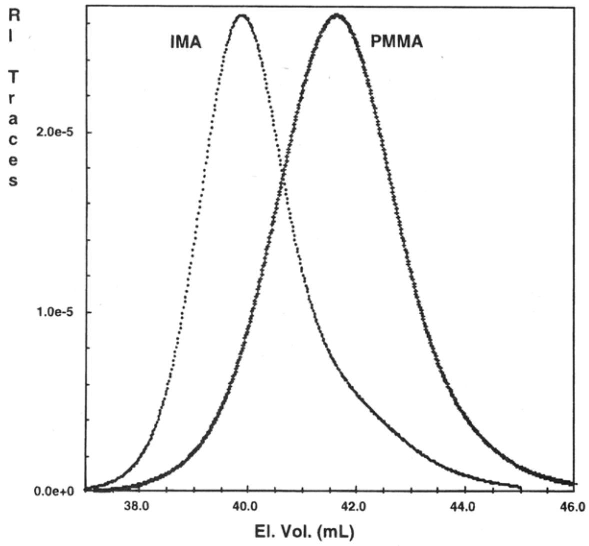
Figure 1. ^{1}H NMR spectrum of crude product obtained in coupling TMPDPE$^+$Ti$_2$Cl$_9$$^-$ and MTS at −80 °C. MChx:CH$_3$Cl 40:60 v:v; [TMPCl] = 6.1×10^{-2} M; [DTBP] = 3.6×10^{-3} M; [DPE] = 6.4×10^{-2} M; [TiCl$_4$] = [Ti(OBu)$_4$] = 1.8×10^{-1} M; [MTS] = 6.1×10^{-2} M.

Scheme 1. Coupling Reaction between TMPDPE$^+$Ti$_2$Cl$_9$$^-$ and MTS



To identify the optimum reaction conditions, model reactions were carried out first between TMPDPE$^+$Ti$_2$Cl$_9$$^-$ (TMPCl capped with DPE) and MTS, and two corresponding small molecules mimicking the polymer chain ends. While in the functionalization reaction a fourfold excess MTS was used,[5] well-defined block copolymers with the absence of homopolymer contaminants can only be obtained when the reaction between the reactive sites in stoichiometric amounts is quantitative. The conditions for the model reaction were chosen to be similar to the conditions of living polymerization of isobutylene.[7,9] To avoid a side reaction between silylketene acetal and TiCl$_4$,[10] the Lewis acidity of TiCl$_4$ can be decreased by the addition of Ti(OR)$_4$, giving rise to TiCl$_n$(OR)$_{4-n}$ determined by the stoichiometry.[9] The effect of the addition of Ti(OBu)$_4$ in different concentrations was studied in regard to the coupling reaction. Scheme 1 demonstrates the synthetic route of the model experiment. The ^{1}H NMR spectrum of the crude products after methanol quenching and extraction with water was recorded to monitor the yield and the nature of the products. The use of TiCl$_4$ alone resulted in the desired product in ~70 % yield, but undesired side reactions prevented quantitative coupling. Due to the presence of overlapping peaks in the ^{1}H NMR spectrum, we were unable to determine the extent of the reaction and the nature of the side products; however, resonances at 1.0 and 3.5 ppm suggest the presence of dimethyl tetramethylsuccinate, the condensation product of MTS catalyzed by TiCl$_4$[10]. Thus, according to the results, the addition of Ti(OBu)$_4$ is necessary for successful coupling at [TiCl$_4$]/[living end] = 3. With the aid of milder Lewis acids such as Ti(OBu)$_4$ using the TiCl$_4$/Ti(OBu)$_4$ = 1 or 2 ratios, the capping reaction was quantitative. The ^{1}H NMR spectrum representing 100% capping is shown in Figure 1. Arrows indicate the position of peaks expected to arise due to TMPDPE−OCH$_3$ (TMPDPE$^+$Ti$_2$Cl$_4$$^-$ quenched with methanol) if coupling is less than quantitative. These resonances are absent, indicating quantitative reaction.

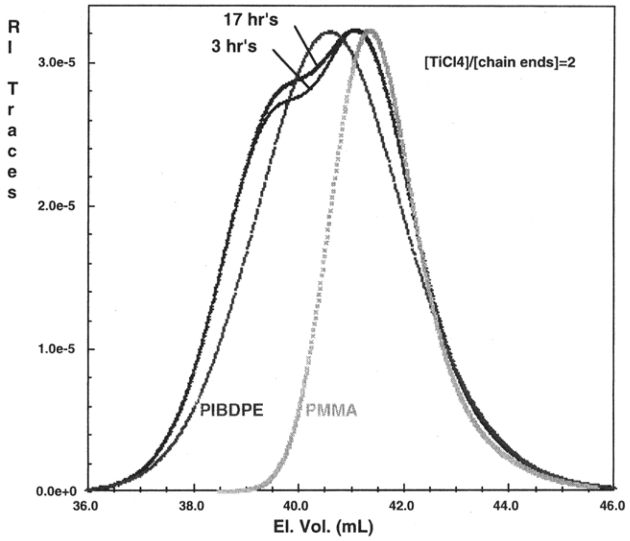
Since the half-life of the active center in GTP is finite,[11] in order to identify the best catalyst, we investigated the livingness of the unquenched PMMA after isolation. Unquenched PMMA, obtained using



M_nPMMA=5100, M_w/M_n = 1.2; M_nIMA=11300 M_w/M_n=1.1.

Figure 2. GPC traces of original and chain-extended PMMA obtained after the addition of a second MMA increment (IMA, incremental monomer addition). PMMA: THF; [MTS] = 1.5 × 10^{-2} M; [TBAF$^-$] = 1.5 × 10^{-5} M; [MMA] = 0.8 M. IMA: THF; [PMMA] = 1.0 × 10^{-2} M; [TBAF$^-$] = 1.8 × $101-^{5}$ M; [MMA] = 0.6 M.

biacetate catalyst, precipitated in pentane (after about 1 h from the exothermic peak) was redissolved in THF, and a new increment of monomer and catalyst was added. The cut and weigh method and mathematical resolution (Peakfit by Jandel Scientific, using exponential Gaussian distribution) of the bimodel GPC trace have shown the presence of about 30% terminated polymer. Similarly to anionic polymerization, spontaneous termination in GTP proceeds by a back-biting mechanism, resulting in a cyclic chain end.[11] High temperature, long time, and high concentration of the catalysts increase the rate of this undesired chain-breaking reaction. Thus slow monomer addition and fast workup are necessary to lower the extent of spontaneous termination. Even more important is the removal of the catalyst by precipitation of the living PMMA in a suitable nonsolvent or deactivation by the use of catalyst quenchers.[12] We have determined that tetrabutylammonium biacetate is insoluble in pentane. Thus it coprecipitates with the polymer and is most probably responsible for the premature termination. It was reported that tetrabutylammonium (TBA) fluoride trihydrate catalyst can be removed by precipitation in pentane.[13] Therefore the livingness of PMMA was also studied using this catalyst. Fourty minutes after the exothermic peak, the polymerization solution was poured into excess pentane followed by rinsing with pentane. It was subsequently redissolved in THF, and a new increment of monomer and catalyst was added. Figure 2 shows the GPC traces of the starting PMMA and the chain-extended PMMA after the addition of another monomer increment. A small tail is still present in the GPC curve of the chain-extended polymer, which was calculated to be equivalent to about 10% terminated polymer. In a separate series of experiments, a catalyst quencher spirosilane[12] was added before precipitation. In agreement with ref 13, the results were identical; i.e., the use of a catalyst quencher is not necessary and precipitation in pentane is sufficient to remove the catalyst. Thus using this system, the coupling efficiency can be expected to be up to 90%.



M_nPIBDPE = 5200; M_nPMMA = 5600; M_nBLOCK = 7700.

Figure 3. GPC traces of p(IB-*b*-MMA) and the corresponding homopolymers. MeChx:CH_3Cl 35:65 v:v; [TMPCl] = 3.8 × 10^{-3} M; [DTBP] = 2.6 × 10^{-3} M; [$TiCl_4$] = 7.6 × 10^{-3} M; [DPE] = 4.8 × 10^{-3} M; [PMMA] = 3.5 × 10^{-3} M, −40 °C.

A series of blocking experiments were conducted at −80 °C, using TBAF as a GTP catalyst by varying the amount of $TiCl_4$ and $Ti(OBu)_4$. While in the absence of $Ti(OBu)_4$ ~50% coupling occurred, in its presence coupling was virtually absent. Substitution of $Ti(OBu)_4$ by $Ti(OiPr)_4$ did not change the results. According to the model reactions between $TMPDPE^+Ti_2Cl_9^-$ and MTS, the use of $TiCl_4$ alone leads to uncontrollable side reactions, preventing a quantitative coupling reaction. The results obtained using the corresponding polymers however suggest that $TiCl_4$ is most likely complexed with the carbonyl groups of the methyl methacrylate repeating unit in PMMA, and therefore the addition of titanium alkoxides does not aid the coupling reaction between the homopolymers. Interesting, in the presence of a large excess of $TiCl_4$ ([$TiCl_4$]/[chain end] = 8) coupling between $PIBDPE^+Ti_2Cl_9^-$ and living PMMA was also negligible.

The effect of temperature, time, and Lewis acidity on the coupling reaction was further investigated. To increase reactivity, the experiments using $TiCl_4$ alone were repeated at −40 °C. Figure 3 shows the GPC traces of polymers obtained at −40 °C using the [$TiCl_4$]/[living end] ratio of 2. The GPC trace of the product has not changed significantly after 4 h and the coupling efficiency remained low. Evidently, the effective $TiCl_4$ concentration was decreased by complexation, resulting in incomplete ionization of the PIBDPE chain ends. Consequently, the amount of $TiCl_4$ in the system seems to be critical. Figure 4 presents the GPC traces of the homopolymers and the products obtained after 4 h of coupling time using a [$TiCl_4$]/[living end] ratio of 4. By increasing the concentration of $TiCl_4$, the extent of coupling after 4 h reached about 80%, determined by mathematical resolution of the GPC peaks (Peakfit by Jandel Scientific, using exponential Gaussian distribution). Solvent extraction to separate the homopolymers from the block copolymer was unsuccessful. About 50% of the crude product dissolved in pentane, while the pentane-insoluble fraction completely dissolved in acetonitrile. However, both fractions were a mixture of block copolymer and homopolymers as indicated by GPC.

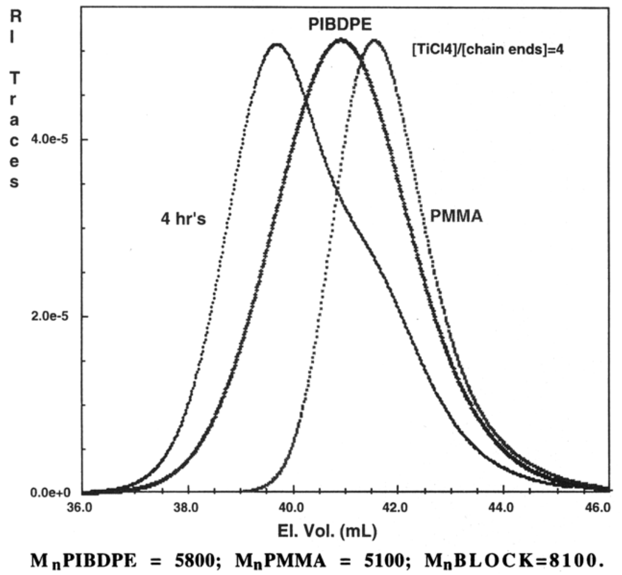


Figure 4. GPC traces of p(IB-*b*-MMA) and the corresponding homopolymers. MeChx:CH_3Cl 35:65 v:v; [TMPCl] = 3.7×10^{-3} M; [DTBP] = 2.6×10^{-3} M; [$TiCl_4$] = 1.5×10^{-2} M; [DPE] = 4.6×10^{-3} M; [PMMA] = 3.5×10^{-3} M, −40 °C.

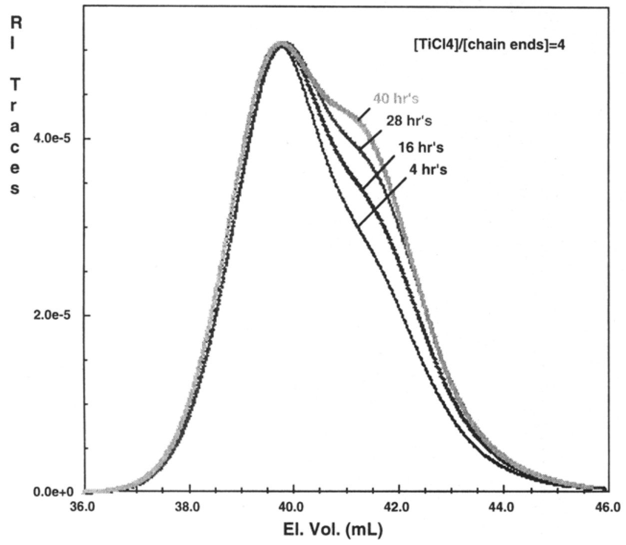


Figure 5. GPC traces of p(IB-*b*-MMA) at different coupling times at −40 °C. MeChx:CH_3Cl 35:65 v:v; [TMPCl] = 3.7×10^{-3} M; [DTBP] = 2.6×10^{-3} M; [$TiCl_4$] = 1.5×10^{-2} M; [DPE] = 4.6×10^{-3} M; [PMMA] = 3.5×10^{-3} M.

Scheme 2. Schematic Diagram of the Cleavage Mechanism Catalyzed by $TiCl_4$

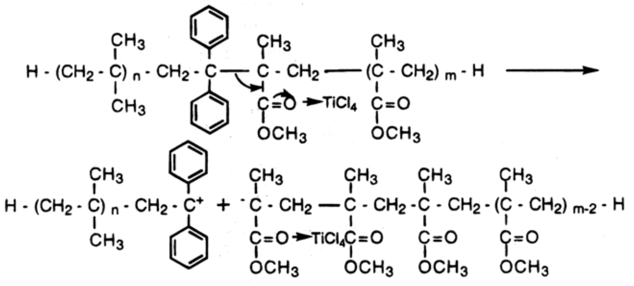


Table 1. Effect of [$TiCl_4$] on the Coupling Reaction between $PIBDPE^+Ti_2Cl_9^-$ and Living PMMA Prepared by GTP

[$TiCl_4$]/ [$PIBDPE^+Ti_2Cl_9^-$]	coupling	decoupling
2	slow	very slow
4	satisfactory	very slow
8	satisfactory	fast

Interestingly, according to Figure 5, longer reaction time not only did not bring about any improvement but resulted in lower coupling efficiencies, suggesting a competing decoupling reaction. Using the [$TiCl_4$]/[living end] = 2 ratio, the extent of the coupling was lower than that obtained with [$TiCl_4$]/[living end] = 4; cleavage was not detected even after 18 h. This suggests that $TiCl_4$ also catalyzes the decoupling process. Our proposed decoupling reaction mechanism is shown in Scheme 2. According to this proposal, $TiCl_4$ reversibly complexes with the carboxyl oxygen of the methacrylate monomer. When the site of this complexation is the methyl methacrylate unit adjacent to the coupling site, an anion formation is promoted, followed by Ti-enolate formation or termination possibly via cyclization. To substantiate our proposition, the following experiment was carried out. Low-M_n (~2000) PIB was prepared and capped with DPE. The chain ends were functionalized by end-quenching with 1-methoxy-1-(trimethylsiloxy)-2-methyl-1-propene. Subsequent analysis of the isolated product indicated quantitative functionalization. The ester functional PIB was dissolved in MeChx:CH_3Cl 35:65 v:v at −40 °C, and $TiCl_4$ was added ([$TiCl_4$]/[chain end] = 8). After 40 h the polymer was isolated and analyzed. According to FTIR analysis, the ester functionality was only 0.23; i.e., 77% of the ester functionality was lost.

The decoupling is quite slow in the case of P(IB-*b*-MMA) copolymer for [$TiCl_4$]/[living end] = 4 due to the low ratio of $TiCl_4$ to the methyl methacrylate repeating unit (1:12 for $M_{n\ PMMA} = 5000$). Thus the probability of complexation of the coupling site is low. Table 1 summarizes the factors which influence block formation in regard to [$TiCl_4$] at −40 °C. To maximize coupling, [$TiCl_4$]/[TMPCl] < 4 would be necessary, but at this $TiCl_4$ concentration coupling is too slow. At high $TiCl_4$ concentration coupling is faster but the rate of decoupling is similarly enhanced. Thus to obtain block copolymers with high coupling efficiency, optimized [$TiCl_4$] and reaction time are necessary.

Conclusions

The synthesis of (MMA-*b*-IB) copolymers was accomplished by reacting living PMMA prepared by the group transfer polymerization with $PIBDPE^+Ti_2Cl_9^-$. The blocking efficiency is dependent upon temperature, reaction time, and [$TiCl_4$].

The observed slow competitive decoupling reaction at higher temperatures and high [$TiCl_4$] is proposed to involve the complexation of $TiCl_4$ to the carbonyl oxygen adjacent to the coupling site, followed by anion formation and irreversible termination. This side reaction is negligible when the reaction time is <4 h at −40 °C and [$TiCl_4$]/[$PIBDPE^+Ti_2Cl_9^-$] = 4.

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