Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

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To cite this Article Takács, Anikó and Faust, Rudolf(1996) 'Synthesis of Poly(Methyl Methacrylate-*graft*-Isobutylene) Copolymers by the Combination of Living Carbocationic and Group Transfer Polymerization', Journal of Macromolecular Science, Part A, 33: 2, 117 — 131
To link to this Article: DOI: 10.1080/10601329608010858
URL: http://dx.doi.org/10.1080/10601329608010858

J.M.S.—PURE APPL. CHEM., A33(2), pp. 117–131 (1996)

SYNTHESIS OF POLY(METHYL METHACRYLATE-*graft*-ISOBUTYLENE) COPOLYMERS BY THE COMBINATION OF LIVING CARBOCATIONIC AND GROUP TRANSFER POLYMERIZATION

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ABSTRACT

The synthesis of poly(methyl methacrylate-*graft*-isobutylene), p(MMA-*g*-IB) copolymers was accomplished by group transfer copolymerization (GTP) of MMA and polyisobutenyl methacrylate (PIBMA). The PIBMA macromer was obtained by living carbocationic polymerization (LC^+P) of IB using a novel functional initiator 3,3,5-trimethyl-5-chloro-1-hexyl methacrylate. Well-defined macromers with perfect functionalities were obtained in the molecular weight range of 2000 to 50,000. The PIBMA macromers were copolymerized with MMA using GTP. The structure and the properties of the resulting p(MMA-*g*-IB) copolymers were determined by the [MMA]/[I] and [MMA]/[PIBMA] ratios. The homopolymerization of the macromer resulted in a mixture of dimers and unreacted macromer.

INTRODUCTION

Since the development of living polymerizations, research has been focused on the synthesis of well-defined block and graft copolymers using living processes. The macromer technique [1] is the most elegant method to obtain "tailor-made" graft copolymers. The first synthesis of poly(methyl methacrylate-*graft*-isobutylene)

[p(MMA-*g*-IB)] by the macromer technique was published by Kennedy and Hiza [2]. Chloro functional PIB, obtained by polymerizing IB with the cumyl chloride/BCl_3 initiating system, was dehydrochlorinated with *tert*-BuOK in THF. Subsequent hydroboration/oxidation and esterification with methacryloyl chloride resulted in the desired macromer. It was homopolymerized in bulk with azobisisobutyronitrile (AIBN) yielding a mixture of unreacted PIBMA and a comblike polymer in the $M_n = 10^5$ to 10^6 range. Copolymerization with MMA by radical initiators has shown nearly ideal behavior, although the macromer exhibited somewhat lower reactivity compared to MMA, especially at higher conversions. The molecular weight distributions of the obtained graft copolymers were quite broad, as expected in radical polymerizations.

Kitayama and coworkers investigated the living anionic homopolymerization of PIBMA synthesized as above [3]. Various anionic initiators were studied including *tert*-C_4H_9MgBr, *tert*-$C_4H_9Li/(C_2H_5)_3Al$, and 1,1-dipenylhexyllithium using toluene or THF as solvent at temperatures between -60 and -100°C. Up to 95% conversion of the macromer was obtained with $DP_n \approx 9$. Copolymerization with MMA was not reported.

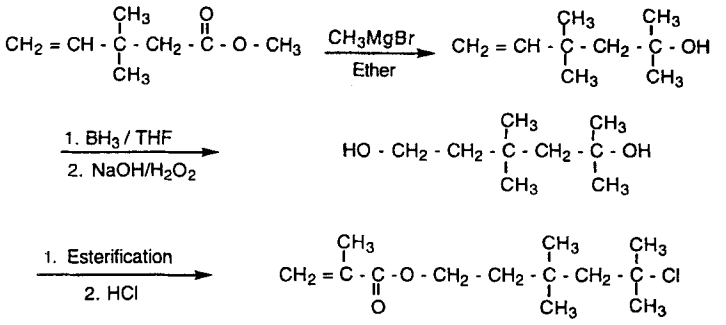
Group transfer copolymerization (GTP) [4] of polystyryl methacrylate (PStMA) was investigated by Asami et al. [5]. PStMA macromers were obtained by reacting polystyryl lithium with methacryloyl chloride. GTP of PStMA did not proceed at ambient temperature and was uncontrolled at 0°C. However at -78°C oligo-PStMA ($DP_n = 5.3$) was obtained with 99% conversion in 24 hours. GTP of PStMA with MMA at 0°C resulted in well-defined graft copolymers of narrow molecular weight distribution with 96% conversion of the macromers. Copolymerization at ambient temperature was not reported.

Macromers may be obtained by postpolymerization reactions or by using functional initiators carrying the desired polymerizable groups. The preparation of macromers using a functional initiator eliminates the need for laborious postpolymerization functionalizations, and macromers can be prepared in a one-pot process by living polymerization. We have recently reported the synthesis of 3,3,5-trimethyl-5-chloro-1-hexyl methacrylate [6]. Living polymerization of IB with this initiator resulted in PIBs carrying methacryloyl functions polymerizable by radical, anionic, and group transfer polymerization. In the present publication the homo- and copolymerization of PIBMA macromers with MMA by GTP and the characterization of the resulting graft copolymers will be discussed.

EXPERIMENTAL

Materials

CH_3MgBr (3 M solution in diethyl ether), methyl-(3,3-dimethyl-1-pentenoate), borane–tetrahydrofuran complex (1 M solution in THF), dimethylaminopyridine, $ZnCl_2$ (99.99%), and anhydrous, acetone-free diethyl ether were used as received from Aldrich. Methacrylic anhydride was freshly distilled under vacuum, benzene was distilled from sodium dispersion prior to use under nitrogen. All other materials have been described elsewhere [4, 7]. The synthesis of 3,3,5-trimethyl-5-chloro-1-hexyl methacrylate functional initiator (Scheme 1) was previously described [6]. Details will be presented below.



SCHEME 1.

Synthesis of 3,3,5-Trimethyl-5-chloro-1-hexyl Methacrylate

3,3,5-Trimethyl-1-hexene-5-ol

The Grignard reaction of methyl-(3,3-dimethyl-1-pentenoate) and CH_3MgBr in ether resulted in 3,3,5-trimethyl-1-hexene-5-ol. Standard techniques for moisture-sensitive reactions were applied: Solvents and the reagents were transferred via canula, positive nitrogen pressure was applied throughout the reaction, and glassware and equipment were dried at 120°C or at room temperature under vacuum prior to use. A colorless liquid was obtained in 60–70% yield. No further purification was necessary after the extraction step.

^{1}H-NMR spectroscopy: δ 1.13 (s, 6H, $-CH_3$); δ 1.22 (s, 6H, $-CH_3$); δ 1.67 (s, 2H, $-CH_2-$); δ 1.88 (s, 1H, $-OH$); δ 5.0 (q, 2H, $=CH_2$); δ 6.05 (q, 1H, $=CH-$).

3,3,5-Trimethyl-1,5-dihydroxy Hexane

The hydroboration of 3,3,5-trimethyl-1-hexene-5-ol was carried out with BH_3/THF in THF at 0°C for 6 hours [8]. Standard anhydrous techniques were utilized as described above. The oxidation step was modified by adding NaOH first while keeping the temperature below 15°C. The reaction mixture was stirred overnight at room temperature followed by the addition of H_2O_2 solution and stirred for additional 2 hours. (Longer reaction time with the peroxide and temperatures exceeding 15°C during the addition resulted in side reactions.) The mixture was salted out with K_2CO_3. The aqueous layer was washed with diethyl ether and after drying the combined organic layers the solvent was removed by Rotavap. The yellow, crude product was dissolved in hexane (Hex) and extracted with distilled water. The organic phase was discharged with the nonpolar impurities. The aqueous phase containing the product was further extracted with diethyl ether to remove polar impurities. After drying and removing the solvent, a viscous, colorless liquid was obtained in 50–60% yield. Bp: 120°C/5 mmHg, $n_D^{25} = 1.4550$.

^{1}H-NMR spectrocopy: δ 1.04 (s, 6H, $-CH_3$); δ 1.30 (s, 6H, $-CH_3$); δ 1.56 (s, 2H, $-CH_2-$); δ 1.70 (t, 2H, $-CH_2-$); δ 3.75 (t, 2H, $-CH_2-O-$).

3,3,5-Trimethyl-5-hydroxy-1-hexyl Methacrylate

3,3,5-Trimethyl-1,5-dihydroxy hexane was dissolved in previously distilled benzene (0.1 m in 800 mL) and then evaporated to half of its volume to remove traces of water. Equimolar dimethylaminopyridine was added to this solution and cooled to 0°C. Methacrylic anhydride was added dropwise, and the reaction mixture was stirred for 2 hours at room temperature. After the reaction was complete, the mixture was extracted with 1% aq HCl, 10% aq $NaHCO_3$, and distilled water. The solution was dried and the solvent was evaporated on a Rotavap. The crude product was purified by column chromatography. The pure ester was eluted with purified hexane, and the fractions were monitored by TLC. (The compound could not be purified by vacuum distillation because of decomposition.) The yield was about 50% after the chromatography step ($n_D^{25} = 1.4606$).

^{1}H-NMR spectroscopy: δ 1.05 (s, 6H, $-CH_3$); δ 1.30 (s, 6H, $-CH_3$); δ 1.56 (s, 2H, $-CH_2-$); δ 1.79 (t, 2H, $-CH_2-$); δ 1.95 (s, 3H, $CH_3-C=$); δ 4.23 (t, 2H, $-CH_2-O-$); δ 5.52 (s, 1H, $=CH_2$); δ 6.08 (s, 1H, $=CH_2$).

3,3,5-Trimethyl-5-chloro-1-hexyl Methacrylate

Hydrochlorination was performed by dissolving the monoester in purified hexane. $ZnCl_2$ and anhydrous $CaCl_2$ were added in excess, then dry HCl gas was bubbled through the mixture at 0°C for 1 hour while stirring. (By the end of the reaction, yellow discoloration of the $ZnCl_2$ was observed.) The stirred solution was allowed to warm up to room temperature. After filtration the solvent was evaporated. The product was pure 3,3,5-trimethyl-5-chloro-1-hexyl methacrylate ($n_D^{25} = 1.4642$).

^{1}H-NMR spectroscopy: δ 1.12 (s, 6H, $-CH_3$); δ 1.67 (s, 6H, $-CH_3$); δ 1.80 (t, 2H, $-CH_2-$); δ 1.85 (s, 2H, $-CH_2-$); δ 1.92 (s, 3H, $CH_3-C=$); δ 4.20 (t, 2H, $-CH_2-O-$); δ 5.55 (s, 1H, $=CH_2$); δ 6.10 (s, 1H, $=CH_2$).

Macromer Synthesis

The synthesis of PIBMA was accomplished using the 3,3,5-trimethyl-5-chloro-1-hexyl methacrylate/$TiCl_4$/IB/Hex:CH_3Cl 60:40 v:v/DTBP/-80°C system. The experimental details were identical to published procedures for the living carbocationic polymerization of isobutylene [7]. A large excess of $(CH_3)_3Al$ in CH_3Cl was added at ~100% IB conversion to convert the chloro to a methyl endgroup, followed by quenching with methanol. The macromer was purified by passing it through a column containing neutral alumina (activity II–III) using purified, olefin-free hexane as eluent. The polymers were dissolved in benzene (distilled from sodium dispersion), and the solvent was evaporated in vacuum to remove traces of water prior to GTP.

Copolymerizations

GTP of MMA and copolymerization of PIBMA with MMA was performed according to Webster et al. [4] using tetrabutyl ammonium biacetate (TBAbiAc) as catalyst in 0.1–0.2 mol% to the silyl ketene acetal initiator in a glove box under dry N_2 atmosphere. The conversion of the monomer was 100% within experimental

error, while some macromer retained unreacted. The macromer conversion did not change after 4 hours reaction time.

Purification of the Graft Copolymers

To remove homopolymer impurities the graft copolymers were extracted with pentane and acetone for 12 hours using a Soxhlet extractor. This method was satisfactory for graft copolymers containing a relatively long PMMA backbone (M_n > 10,000) and a small number of PIB side chains (1-2). Polymers having >2 side chains and a relatively short backbone (M_n = 5000) completely dissolved in pentane and were insoluble in acetone. To obtain pure graft copolymers of the more rubbery materials, the crude products were purified by dissolving in hexane at 60°C. Acetone was added until turbidity was observed. After cooling, the precipitated fraction was used for further characterizations.

Characterizations

The functionality of the macromers was determined by FT-IR measurements on a Mattson Instruments, 2020 Galaxy Series FT-IR spectrometer. A calibration curve was made by using the carbonyl absorbance of 3,3,5-trimethyl-5-chloro-1-hexyl methacrylate at 1711.0 cm^{-1} to determine functionality.

Molecular weights and molecular weight distributions were determined using a Waters HPLC system equipped with Model 510 HPLC pump, Model 410 differential refractometer, Model 486 tunable UV/Vis detector (the UV traces were recorded at 254 or 230 nm against a solvent-filled reference cell), 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 1.0 mL/min. PMMA 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 based on the *dn/dc* values calculated from the composition or assuming 100% mass recovery.

NMR spectroscopy was carried out on a Bruker 270 MHz instrument. The glass transition temperatures of the copolymers were determined by DSC using a Du Pont Instruments Thermal Analyst 2000 instrument with DSC 2910 differential scanning calorimeter. The morphology of copolymers was studied by transmission electron microscopy (Phillips Electronic Instrument Co.). Thin films (<500 Å) were cast on carbon-coated TEM grids from THF solution. Films were imaged with 120 kV electrons.

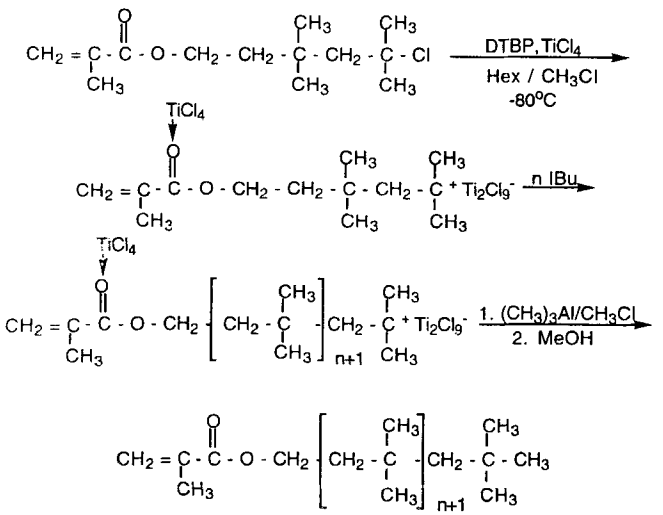
RESULTS AND DISCUSSION

The Synthesis of PIBMA Macromers

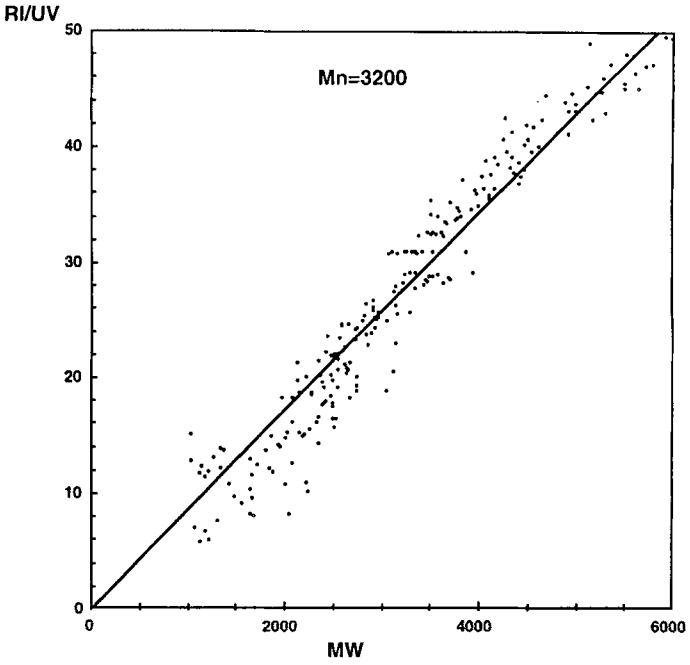
The most commonly used initiators in LC^+P are tertiary esters, ethers, or chlorides. Since primary esters do not ionize to initiate the LC^+P of IB, the use of an initiator having a tertiary ester, ether, or chloride function and another primary ester group should lead to polymers containing an ester head group [6]. The reaction

between the initiator 3,3,5-trimethyl-5-chloro-1-hexyl methacrylate and $TiCl_4$ was investigated at the absence of monomer. The primary ester group remained unreacted upon quenching with methanol. The polymerization mechanism is shown on Scheme 2.

The molecular weight and molecular weight distribution of the PIBs were determined by GPC measurements with RI and UV detection. UV activity in the polymer molecule can be related exclusively to the double bond of the methacryloyl group. A straight line starting from the origin was obtained by plotting RI/UV traces against molecular weight, demonstrating uniform distribution of the chromophores on the polymer chains, i.e., the number of chromophores per chain is constant, independent of the molecular weight (Fig. 1.). The results of the polymerization of IB at various monomer to initiator ratios are summarized in Table 1. The all monomer in (AMI) technique [9], where all the monomer was added at once, was used to obtain the polymers presented in the table. The molecular weights were close to but somewhat lower than theoretical values, thus the chloro initiator can be used to prepare well-defined functional polymers in a one step process. Most importantly, the functionalities were found to be close to theoretical methacrylate functionality, ($F_n \approx 1$), indicating polymerization only from the initiator. To gain more information about the polymerization, kinetic experiments were carried out by the incremental monomer addition (IMA) technique [10]. The absence of chain transfer to the monomer in living polymerizations with fast initiation, can be diagnosed by a linear molecular weight versus conversion plot starting at the origin. The molecular weight versus conversion plot obtained by the polymerization of IB with 3,3,5-trimethyl-5-chloro-1-hexyl methacrylate is shown in Fig. 2. The plot exhibits an upward curvature approaching the theoretical line at high conversions. The increasing number of active sites with conversion suggests $R_i < R_p$. Plotting $-\ln(1 - I_{eff}) - I_{eff}$ versus conversion (Fig. 3) yields a straight line without intercept, which is diagnostic for polymerization with slow initiation where cationation is the rate-



SCHEME 2.



Hex.:CH_3Cl 60:40 v:v; $[TiCl_4]/[I]$= 16; [DTBP]= 2.5×10^{-3} M; [IB]= 1.3 M; -80°C.

FIG. 1. RI/UV traces vs M_n obtained from GPC measurement of PIBMA.

determining step and chain transfer is absent [11]. Macromers of different molecular weights were synthesized and characterized. Table 2 summarizes the data obtained with macromers having $M_n \sim 3000$, ~ 7000, and $\sim 10{,}000$.

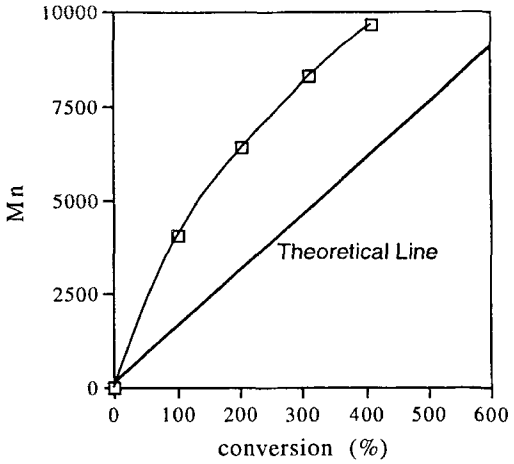
Synthesis of Graft Copolymers

Methanol quenching of living PIBMA results in asymmetric telechelic, α-primary ester, ω-tertiary chloro functional PIBs (PIBMA-Cl) [12]. The copolymerization of MMA with PIBMA-Cl by GTP was unsuccessful. The conversion of MMA

TABLE 1. Polymerization of IB with 3,3,5-Trimethyl-5-chloro-1-hexyl Methacrylate

M_n theoretical	M_n GPC calculated curve	MWD	I_{eff}	F_n
2,400	3,600	1.5	0.67	1.04
4,600	5,500	1.5	0.84	1.01
8,900	9,700	1.3	0.92	1.01
21,900	26,500	1.3	0.83	1.17

[a]Hex:CH_3Cl 60:40 v:v; $[TiCl_4]/[I] = 16$; [DTBP] $= 2.5 \times 10^{-3}$ M; [IB] = 1.3 M; −80°C; AMI.



Hex.:CH_3Cl 60:40 v:v; Concentrations: [I]= 1.3×10^{-2} M; [$TiCl_4$]= 6.6×10^{-2} M; [DTBP]= 4.0×10^{-3} M; $[IB]_o$= 0.3 M; -80°C

FIG. 2. Molecular weight vs conversion plot of IB polymerization with 3,3,5-trimethyl-5-chloro-1-hexyl methacrylate.

was less than 10%, and the macromer remained unreacted. This observation suggested that reactive chloro groups are incompatible with GTP. The chloro endgroup can be converted to unreactive $-CH_3$ by adding $(CH_3)_3Al$ before methanol quenching [13]. The copolymerization of MMA with PIBMA (unreactive endgroup) resulted in well-defined graft copolymers.

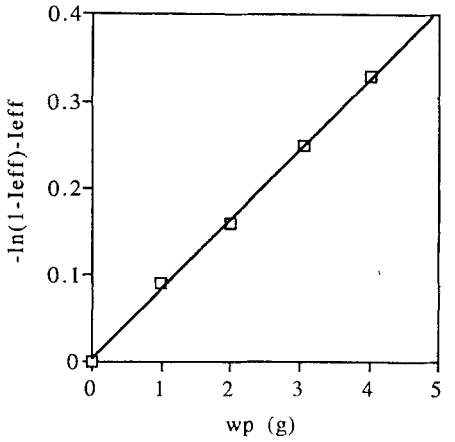


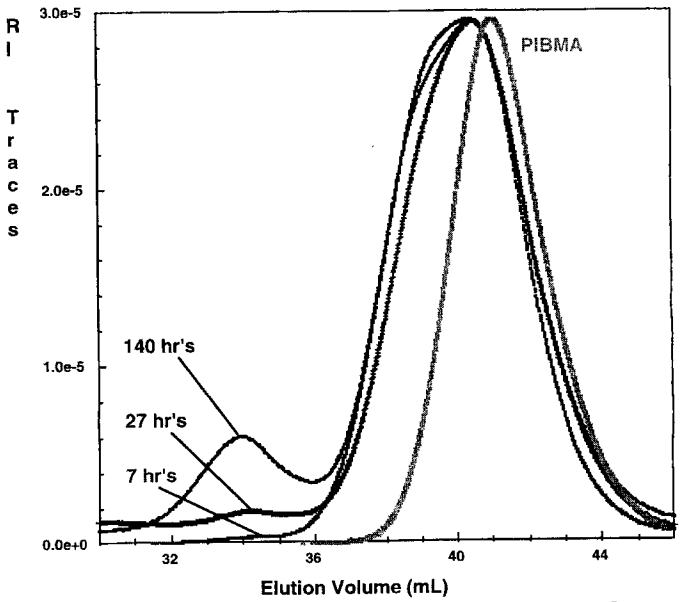
FIG. 3. $-\ln(1 - I_{eff}) - I_{eff}$ vs wp curve obtained by the polymerization of isobutylene with 3,3,5-trimethyl-5-chloro-1-hexyl methacrylate.

TABLE 2. Characteristics of PIBMA Macromers Used in Copolymerizations with MMA by GTP[a]

M_n (LS)	MWD	F_n
2,620	1.3	1.05
3,220	1.4	1.01
7,739	1.2	1.10
11,100	1.2	1.17

[a]Hex:CH_3Cl 60:40 v:v; $[TiCl_4]/[I] = 16$; $[DTBP] = 2.5 \times 10^{-3}$ M; [IB] = 1.3 M; −80°C.

Homopolymerizations of macromers results in high molecular weight polymers of comblike topology exhibiting unusual properties. However, the polymerization of macromers is expected to be quite hindered due to the bulky pendant group. The homopolymerization of PIBMA was investigated by GTP. The theoretical DP_n of 100 was not achieved, and the GPC traces (Fig. 4) indicate only dimer formation even after 140 hours reaction time. This suggests that the reactivity of the macromer is much lower than that of MMA in GTP at ambient temperature. This low homo-



M_nPIBMA= 4,770; M_n= 8,000; M_nTAIL~ 2x10^5.
THF; [I]= 2.5x10^{-4} M; [TBAbiAc.]= 2.7x10^{-7} M; [PIBMA]= 2.5x10^{-2} M.

FIG. 4. RI traces of PIBMA and the result of homopolymerization of PIBMA.

polymerization reactivity can be related to the hindered reactive sites. The half-life of living centers prepared by GTP is ~1.5 hours in the presence of catalyst at 25°C [14]. Thus, the active center becomes deactivated before a third macromer unit would add to the chain end. The slowly increasing peak at 34 mL elution volume ($M_n \approx 10^5$, Fig. 4.) is probably due to radical homopolymerization, as it coincides with GPC traces of aged macromer samples.

The copolymerization of PIBMA with MMA by GTP was investigated using the samples presented in Table 2. The ^{1}H-NMR spectra of these macromers confirmed the absence of peaks related to the chloro ends, and the methacryloyl functionalities were close to 1. However, macromers having 7000 and 10,000 molecular weights did not copolymerize in a controlled manner; less than 10% monomer conversion was obtained. The results of the copolymerizations of PIBMA (M_n = 3,200) with MMA are summarized in Table 3. The conversion of MMA was 100% within experimental error in all cases. The conversion of PIBMA was 80–90% as indicated in Table 3. Incomplete macromer conversion might be related to the decreased diffusion of the macromer to the growing PMMA center at higher conversions and to the decreased macromer concentration at the active sites due to unfavorable solvation of the growing PMMA by PIB.

The M_ns determined by MALLS are also shown in Table 3. There is a good agreement between the theoretical and observed M_ns of the graft copolymers. The actual number of grafts was determined by ^{1}H-NMR spectroscopy. Control homopolymerization experiments of MMA in the absence of macromer but otherwise identical conditions to copolymerizations provide information about the length of the PMMA backbone. The GPC traces of the graft copolymers, the starting macromer, and PMMA controls are shown in Figs. 5–8.

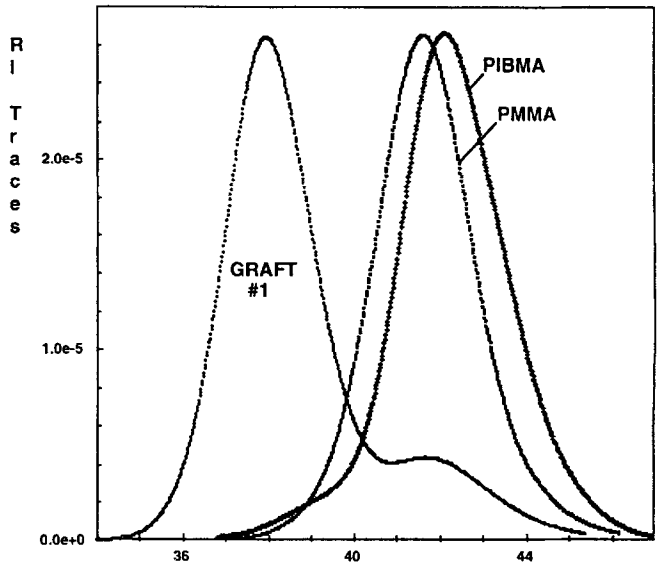
Characterization of the Graft Copolymers

The solubility of the copolymers varied depending on their composition. Table 4 summarizes the solubilities in pentane and acetone. As expected, Sample #1 exhibited the most rubbery characteristics. The polymer fully dissolved in pentane, and it was found to be insoluble in acetone. Twenty percent of the crude graft copolymer was precipitated after adding acetone to the 60°C hexane solution. The molecular weight of the precipitated polymer was 25,000. ^{1}H-NMR measurements indicated

TABLE 3. Results Obtained from the Copolymerization of PIBMA M_n = 3200 with MMA by GTP (20 hours reaction time)

	M_n theoretical	Number of grafts (in feed)	Number of grafts (NMR)	M_n graft (MALLS)	PIBMA in feed, mol%	PIBMA conversion,[a] %
1	16,100	3.3	3.3	17,000	7.2	82
2	9,200	1.4	1.3	9,400	2.9	88
3	17,700	2.8	3.4	22,000	4.2	80
4	14,500	1.5	1.4	17,000	1.5	82

[a]Calculated by mathematical resolution of GPC peaks.



M_nPIBMA= 3,200; M_nPMMA= 5,000; M_nGRAFT= 10,600.
THF; [I]= 1.1×10^{-2} M; [TBAbiAc.]= 2.2×10^{-5} M; [PIBMA]= 3.8×10^{-2} M; [MMA]= 0.48 M.

FIG. 5. RI traces of PIBMA, PMMA control, and Graft Copolymer #1.

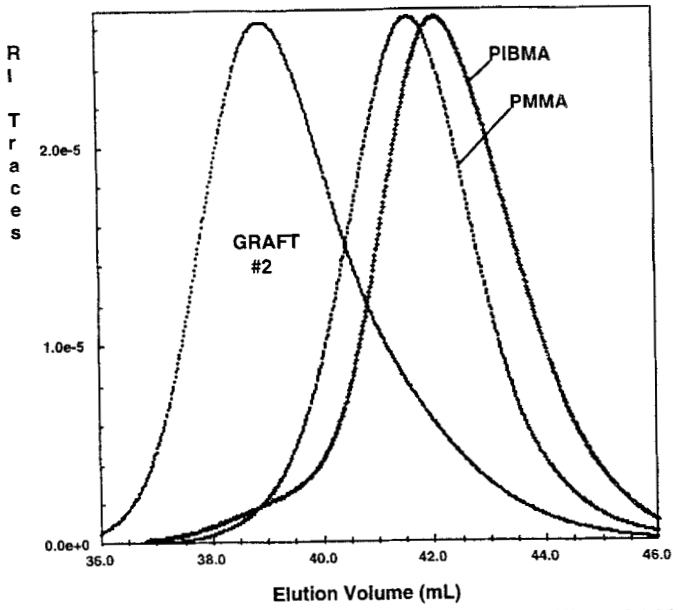
the presence of 5.7 grafts per PMMA backbone. The precipitated polymer was used for DSC and TEM measurements.

Using a similar [MMA]/[I] ratio but twice the [MMA]/[PIBMA] ratio of Sample #1, Copolymer #2 was a white powder. Pure graft copolymer was only obtained in the pentane-insoluble fraction; all other fractions were a mixture of graft copolymer and macromer (Table 4). DSC and TEM measurements were carried out using the pentane-insoluble fraction.

Similarly to Sample #1, Entry #3 was a rubbery material. Both [MMA]/[I] and [MMA]/[PIBMA] ratios were about twice the values of Sample #1, resulting in a longer PMMA backbone ($M_n \approx$ 10,000). Table 4 contains the molecular weights and composition of the extracted fractions. Since pentane extraction did not separate the unreacted macromer from the graft copolymer, the purification of the copolymer was carried out by precipitation in acetone, similarly to Entry #1.

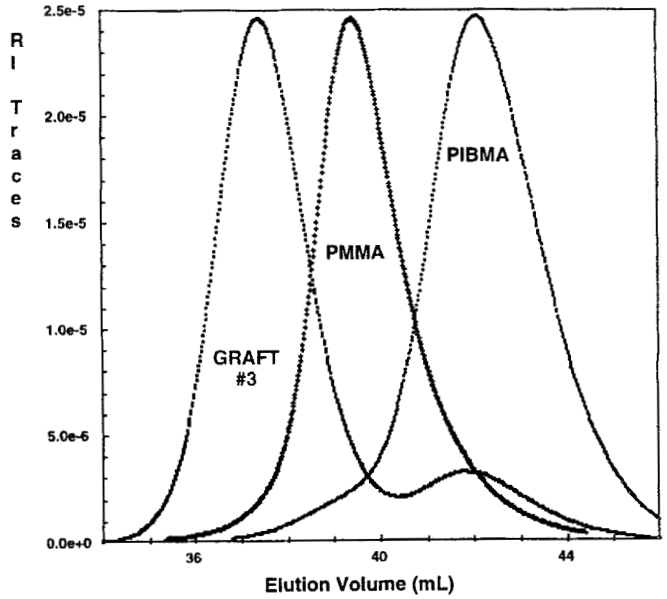
Graft Copolymer #4, a white powder, exhibited glassy characteristics. About 6 wt% of the polymer was soluble in pentane, which was found to be unreacted macromer. The remainder fully dissolved in acetone. Pentane extraction resulted in a pure graft copolymer.

Microphase separation can be detected by DSC measurements; it displays two distinctive glass transition temperatures if homopolymer contamination is absent. The properties of the purified graft copolymers are summarized in Table 5. All except Sample #2 exhibited two glass transition temperatures, suggesting phase separation (Table 5). The absence of a low T_g corresponding to the PIB domain



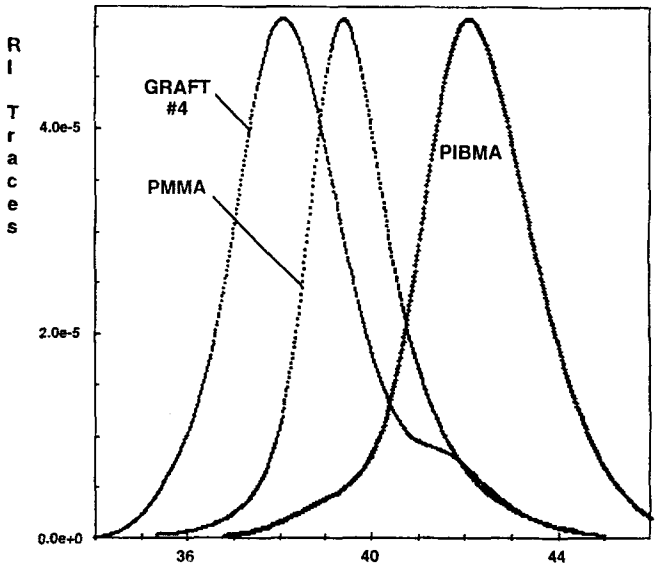
M_nPIBMA= 3,200; M_nPMMA= 5,000; M_nGRAFT= 8,700.
THF; [I]= 1.5×10^{-2} M; [TBAbiAc.]= 3.0×10^{-5} M; [PIBMA]= 2.1×10^{-2} M; [MMA]= 0.71 M.

FIG. 6. RI traces of PIBMA, PMMA control, and Graft Copolymer #2.



M_nPIBMA= 3,200; M_nPMMA= 12,000; M_nGRAFT= 16,700.
THF; [I]= 6.0×10^{-3} M; [TBAbiAc.]= 1.2×10^{-5} M; [PIBMA]= 2.5×10^{-2} M; [MMA]= 0.58 M.

FIG. 7. RI traces of PIBMA, PMMA control, and Graft Copolymer #3.



M_nPIBMA= 3,100; M_nPMMA= 12,000; M_nGRAFT= 17,000. THF; [I]= 9.3×10^{-3} M; [TBAbiAc.]= 1.4×10^{-5} M; [PIBMA]= 1.4×10^{-2} M; [MMA]= 0.87 M.

FIG. 8. RI traces of PIBMA, PMMA control, and Graft Copolymer #4.

TABLE 4. Extraction Results of Graft Copolymers

	Solubility		Amount,		
	Pentane	Acetone	w/w%	M_n (MALLS)	Number of grafts
1	+	−	100	17,000	3.3
2	+	+	17	7,000	1.0
	+	−	18	12,000	2.6
	−	+	65	9,400	1.3
3	+	−	63	21,000	4.1
	−	+	37	12,000	1.7
4	−	+	94	17,000	1.4

TABLE 5. Glass Transition Temperatures and Properties of the Purified Graft Copolymers

	Pentane	Acetone	Amount, w/w%	M_n (MALLS)	Number of grafts	Low T_g, °C	High T_g, °C
1	[a]	–	20	25,000	5.7	−64	100
2	–	+	65	12,000	1.5	–	95
3	[a]	–	15	29,000	5.5	−69	96
4	–	+	94	17,000	1.4	−68	111

[a]Precipitated from pentane with acetone.

cannot be explained for Sample #2 since ^{1}H-NMR and FT-IR measurements confirmed the presence of PIB.

To gain more information about the microstructure of the polymers, TEM measurements were performed using the purified copolymers. Microphase separation was observed with Samples #1, #3, and #4, in good agreement with the DSC results. The transmission electron micrograph of Sample #1 is displayed in Fig. 9.

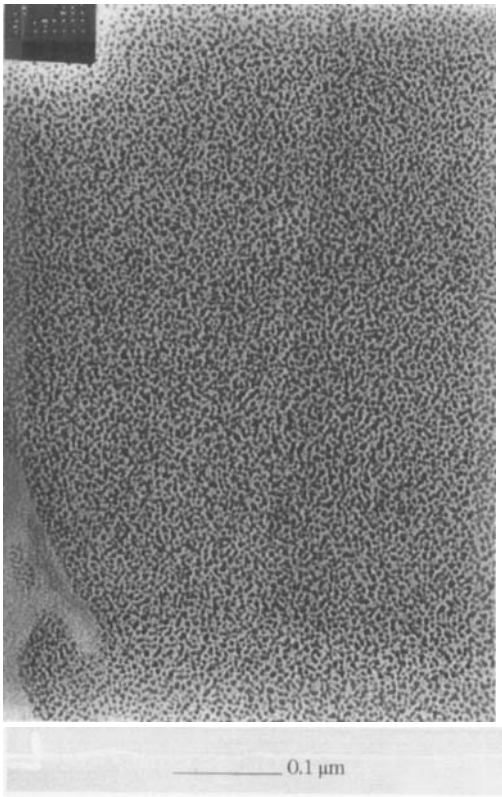


FIG. 9. Transmission electron micrograph of Graft Copolymer #1.

CONCLUSION

Well-defined macromers were prepared in a one-pot process by living polymerization of IB using a functional initiator 3,3,5-trimethyl-5-chloro-1-hexyl methacrylate. The chloro endgroup was converted to $-CH_3$ by the addition of $(CH_3)_3Al$ in CH_3Cl at 100% IB conversion. The resulting PIBMA macromers were copolymerized with MMA by GTP. Homopolymerization of the macromers by GTP at ambient temperature was unsuccessful due to the decreased reactivity of the macromers compared to MMA. The physical properties of the graft copolymers can be fine-tuned by varying [MMA]/[I] and [MMA]/[PIBMA] ratios.

ACKNOWLEDGMENTS

Acknowledgment is made to the Donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research. We wish to thank Prof. Sung of the Center for Advanced Materials of the University of Massachusetts for the transmission electron microscopy.

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Received May 17, 1995