Synthesis of Meth(acrylate) Diblock Copolymers Bearing a Fluorescent Dye at the Junction Using A Hydroxyl-Protected Initiator and the Combination of Anionic Polymerization and Controlled Radical Polymerization

Jiang-Dong Tong,[†] Chunlin Zhou, Shaoru Ni, and Mitchell A. Winnik*

Department of Chemistry, University of Toronto, 80 St. George Street,
Toronto, Ontario, Canada M5S 3H6

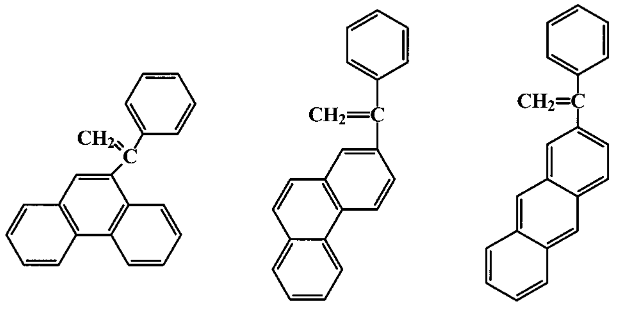
Received May 4, 2000

ABSTRACT: The synthesis of well-defined poly(methyl methacrylate)-*b*-poly(alkyl acrylate) diblock copolymers with a single fluorescent dye molecule (phenanthrene or anthracene) at the junction was investigated. The first block was prepared by the anionic polymerization (AP) of (meth)acrylate in THF at −78 °C, using the 3-(*tert*-butyldimethylsilyloxy)-1-propryllithium/1-aryl-1-phenylethylene (aryl = 2-phenanthryl or 2-anthryl) monoadduct as the initiator. After the end group of the first block was transformed into α-bromoester, the diblock copolymer was formed by the atom transfer radical polymerization (ATRP) of the second methacrylate monomer using the first block as the initiator. The block copolymers were characterized by GPC, UV, and NMR. We found that the synthesis of anthracene-labeled diblock copolymer was perturbed by the reaction of the propagating poly(alkyl acrylate) radical with anthracene. Consequently, this synthesis has to start from the anionic polymerization of *tert*-butyl acrylate, followed by chain extension to poly(methyl methacrylate) by ATRP.

Introduction

Diblock copolymers represent a special case of a system composed of two polymer components attached at a common junction. The degree of phase separation is limited by the covalent bond between the two polymers, resulting in microphases in the bulk state or micelle aggregates in solution. We are particularly interested in characterizing the width of the block copolymer interface, which is one of the key factors influencing polymer properties. We approach this target through the synthesis of pairs of block copolymers containing a single fluorescent dye at the block junction: one polymer contains a donor (e.g., phenanthrene, Phe), and the other polymer contains an acceptor dye (e.g., anthracene, An) for direct nonradiative energy transfer (DET) experiments.[1] In each pair, the polymers have similar molecular weight and composition. In DET experiments, the rate and efficiency of energy transfer depends sensitively on the distance between the donor and acceptor dyes. As a consequence, a fluorescence decay experiment is sensitive to the distribution of junctions across the interface between the two components.[2] Previously, we have synthesized junction labeled polystyrene-*b*-poly(methyl methacrylate)[3] (PS-*b*-PMMA), polyisoprene-*b*-poly(methyl methacrylate)[4] (PI-*b*-PMMA), and PI-*b*-PS[5] using either sequential living anionic polymerization[3,4] or the combination of living anionic polymerization and atom transfer radical polymerization (ATRP).[5] Chart 1 illustrates the three fluorescent dye molecules used in this work. Two of them, 1-(9-phenanthryl)-1-phenylethylene (9-Ph, donor) and 1-(2-anthryl)-1-phenylethylene (2-An, acceptor) have been used previously for labeling and DET analysis of the block copolymers. Our earlier synthesis of junction-labeled block copolymer took advantage of the fact that one can end-cap anionic living polymers (PS and PI) with a single molecule of 1-aryl-1-phenylethylene (APE) to generate a new and less reactive anion. The new active center can be used to initiate the polymerization of methacrylate monomers,[3,4] or it can be transformed into a benzyl bromide group suitable to initiate the ATRP of styrene.[5]

Chart 1



9-Ph 2-Ph 2-An

From a practical point of view, triblock type (meth)-acrylate block copolymers have the potential to serve as novel thermoplastic elastomers,[6,7] whose upper service temperature and oxidation resistance are significantly better than those of their styrene-diene counterparts. Although the synthesis of well-defined polymethacrylate-*b*-polyacrylate is no longer novel, especially in terms of recent achievements in the ligated anionic polymerization[8] and ATRP,[9] the construction of site-specific junction-labeled block copolymer is not straightforward. Living anionic polymerization is usually the preferred technique for the synthesis of polymers with site-specific groups.[10] This type of sequential polymerization (i.e., MMA, APE, and alkyl acrylate) fails for the synthesis of acrylate−methacrylate block copolymers

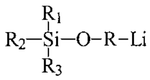
---

* To whom correspondence should be addressed: mwinnik@chem.utoronto.ca.

[†] Current address: 3M Canada, P.O. Box 5757, London, ON, Canada N6A 4T1.

10.1021/ma0007684 CCC: $20.00

Chart 2



$$R_2{-}\overset{R_1}{\underset{R_3}{Si}}{-}O{-}R{-}Li$$

with a dye at the junction because the first living poly(meth)acrylate block cannot react with the APE.

To approach this goal, we considered the combination of anionic polymerization and ATRP, both of which are well-known for the controlled polymerization of (meth)acrylates. The key step in achieving such a combination would be the quantitative preparation of an α-OH terminated dye-labeled poly(meth)acrylate (e.g., HO−dye−PMMA), because the hydroxyl functionality can be quantitatively converted to an α-bromoester end group,[11−13] suitable for ATRP of alkyl acrylates.[14] Anionic preparation of α-OH functionalized PMMA has been reported by Anderson et al.[15] and by Ohata et al.,[16] who utilized either an initiator with an acetaldehyde acetal group[15] or a monoadduct of 1-[4-(2-*tert*-butyldimethylsiloxy)ethyl]phenyl-1-phenylethylene (*t*BDMS-DPE) with *n*-BuLi,[16] followed by the selective hydrolysis of the hydroxyl-protected group on the PMMA chain end. To utilize the 9-Ph and 2-An molecules in the initiation step, we considered using a hydroxyl-protected initiator (HPI). Indeed, in recent years, there has been significant progress in developing HPIs, mostly in industry, to prepare telechelic polyisoprene and polybutadiene elastomers.[17−19] Among the various HPIs, those based on the trialkylsiloxy-protecting group (Chart 2), preferably the *tert*-butyldimethylsiloxy (*t*BDMS) group, show the best results (high initiation efficiency, easy hydrolysis, quantitative functionality and high 1,4-structure for elastomers). Quirk et al.,[20] who recently reviewed these advances,[21] have used several kinds of HPIs to prepare telechelic, heterotelechelic and functionalized star-branched polymers. Zhang and Moore[22] have utilized 6-(*tert*-butyldimethylsilyloxy)-1-hexyllithium to prepare polyethylethylene (hydrogenated 1,2-polybutadiene) with α-hydroxyl and ω-functionalized groups, and then transformed the −OH group to −OK group to initiate the polymerization of ethylene oxide. Unfortunately, there have been few reports on the preparation of α-OH functionalized PMMA using a trialkylsiloxy-protected initiator.

In the present paper, we report the synthesis of fluorescent-dye labeled PMMA-*b*-poly(alkyl acrylate) diblock copolymers utilizing a hydroxyl-protected initiator and the combination of AP and ATRP techniques.

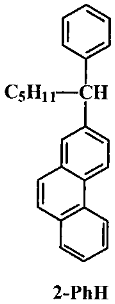
Experimental Section

Materials. All chemicals, except otherwise mentioned, were purchased from Aldrich. THF and toluene were purified by refluxing over the deep purple sodium-benzophenone complex. Methyl methacrylate (MMA), *tert*-butyl acrylate (*t*BA), ethyl acrylate (EA), *n*-butyl acrylate (nBA), and 2-ethylhexyl acrylate (EHA) were purified by distillation from CaH_2. MMA and *t*BA (diluted with 50% toluene) were further distilled over triethyl aluminum (1 M in hexane) prior to anionic polymerization. 3-(*tert*-Butyldimethylsilyloxy)-1-chloropropane (Polymer Source. Inc.), phenylmagnesium bromide (3.0 M), 2-acetylphenanthrene, LiCl (99.99%), CuBr (98%), 4,4′-dimethyl-2,2′-bipyridine, 2-bromopropionyl bromide (BPB), and ethyl 2-bromoisobutyrate (EBIB) were used as received. 4,4′-Di-*n*-heptyl-2,2′-bipyridine (dHbipy)[23] and dye derivatives (9-Ph and 2-An)[3] were synthesized as described in the literature.

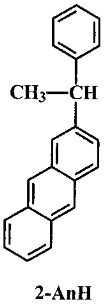
Synthesis of 3-(*tert*-Butyldimethylsilyloxy)-1-propyllithium (*t*BDMSPrLi). A 10-fold excess of lithium dispersion (3.5 g) in mineral oil was charged into a 250 mL three-necked round-bottom flask equipped with a 3-way stopcock, a condenser, a thermometer and stirred magnetically under an argon atmosphere. The lithium was repeatedly washed with hexane under vigorous stirring until the solution became clear, and a silvery metal surface was obtained. The lithium metal was then charged with 150 mL of cyclohexane, and the temperature was raised to 40 °C. A 10 g (0.047 mol) sample of 3-(*tert*-butyldimethylsilyloxy)-1-chloropropane was slowly added to the reaction vessel over 0.5 h. The temperature was then raised to 60 °C, and the reaction was carried out for an additional 2 h. No exotherm was observed. The crude cyclohexane solution was filtered under an argon atmosphere. The alkyllithium concentration, 0.1 M (40% yield), was determined by double titration with benzyl chloride.[24]

Synthesis of 1-(2-Phenanthryl)-1-phenylethylene (2-Ph). To dry toluene (200 mL), 2-acetylphenanthrene (13.0 g, 0.059 mol) was added and warmed until the solution became clear. Then, 3.0 M phenylmagnesium bromide (30 mL) in diethyl ether was added dropwise via a syringe. The reaction mixture was refluxed for 14 h and then poured into crushed ice (400 mL) containing concentrated hydrochloric acid (40 mL). The mixture was stirred with a glass stick until the ice completely melted. After phase separation, the water layer was isolated using a separatory funnel and extracted three times with toluene. The organic layer was dried with anhydrous magnesium sulfate and then filtered. A white powder (the carbinol) was obtained after removing the solvent by rotary evaporation. The crude product was then added to acetic acid (100 mL) containing concentrated sulfuric acid (0.3 mL) and heated until the mixture became a clear yellow-green solution. The solution was allowed to slowly cool for crystallization. The yellow-white crystals obtained were washed with cold acetic acid three times. The product was further purified by recrystallization from methanol. Mp: 103.5−104.5 °C. MS: *m*/*e* 280 (M^+), 265, 202, 176, 91, 77. ^1H NMR ($CDCl_3$): δ (ppm) 8.73−7.27 (m, 14 H, aromatic), 5.67, 5.64 (d, 1 H, $=CH_2$, $J = 1.2$ Hz), 5.60, 5.57 (d, 1 H, $=CH_2$, $J = 1.2$ Hz). ^{13}C NMR ($CDCl_3$, 100.8 MHz): δ (ppm) 149.7−122.5 (aromatic), 131.9 ($=C-$), 114.9 ($=CH_2$);. UV ($CHCl_3$): λ_{max} (nm) at 296, 294.

Synthesis of 1-(2-Phenanthryl)-1-phenylhexane (2-PhH). Dry 2-Ph (1 g, 3.6 mmol) was charged in a flamed-dried glass tube, which was equipped with a 3-way stopcock, a rubber septum and a magnetic stirring bar. After being vacuum-dried for 1 h, the 2-Ph was diluted with dry THF (10 mL) under nitrogen. Then *n*BuLi (2.7 mL, 1.6 M in hexane, 4.3 mmol) was added under stirring. A deep blue color appeared immediately. The reaction was kept at room temperature for 30 min and then quenched by degassed methanol. After extraction with water/chloroform to remove the inorganic salts, the product in chloroform was dried with anhydrous $MgSO_4$. The crude compound was obtained by removing the solvents under reduced pressure. The 2-PhH was finally purified by recrystallization in methanol. ^1H NMR ($CDCl_3$): δ (ppm) 8.70−7.15 (m, 14H, aromatic), 4.12 (t, 1H, 2Ph−C(Ph)H−), 2.18 (m, 2H, $-CH_2-C-Ar$), 1.30 (m, 6H, $-(CH_2)_3-$), 0.85 (t, 3H, $-CH_3$). UV ($CHCl_3$): λ_{max} (nm) at 299, 295. $\epsilon_{299\ nm} = 10\ 070\ M^{-1}\ cm^{-1}$.



2-PhH



2-AnH

Anionic Polymerization of MMA and *t*BA Initiated by *t*BDMSPrLi and APE Adduct. All polymerizations and chemical reactions were carried out under a nitrogen atmosphere in a flamed-dried glass reactor equipped with a three-

Table 1. In Situ Anionic Polymerization Based on *t*BDMSPrLi and Its Derivatives

		yield of 1:1 addition reaction[a]	anionic polymerization[b]				
run	initiator	(%)	monomer	$M_{\mathrm{n\,theor}}$[c]	$M_{\mathrm{n\,GPC}}$	M_w/M_n	f[d] (%)
1	*s*-BuLi/2-An	~100	A, MMA	10 000	9800	1.06	~100[e]
2	*n*-BuLi/9-Ph	~100	B, MMA	10 000	10 200	1.07	~100[e]
3	*t*BDMSPrLi		C, isoprene	4000	4200	1.10	95
4	*t*BDMSPrLi/DPE	37	D, MMA	10 000	49 500	1.15	15[e]
5	*t*BDMSPrLi/2-An	44, 85[f]	E, MMA	2000	9200	1.10	20[e]
6	*t*BDMSPrLi/9-Ph	<6[g]	F, MMA	10 000	32 500	1.16	4[e]
7	*t*BDMSPrLi/2-Ph	84[f]					

[a] The addition reaction of alkyllithium and APE (1:1 molar ratio) was carried out in cyclohexane/THF (1 mL/2 mL) mixture at 20 °C for 15 min. Yield of monoadduct was calculated based on the ^{1}H NMR of the reaction mixtures. [b] All polymerization reactions were carried out in THF at −78 °C (except for the polymerization of isoprene, which was conducted in cyclohexane at 50 °C), using the first anionic polymerization method described in the experimental part. [c] Calculated from [M]/[I]. [d] Initiation efficiency, $f = M_{\mathrm{n\,theor}}/M_{\mathrm{n\,GPC}} \times$ yield $\times$ 100%. [e] Initiators were prepared in situ with [Li]/[APE] = 1:3 for 30 min. [f] Values refer to a reaction time of 30 min. [g] Reactions have been examined for (i) 1:1 addition for 15 min, (ii) 1:1 addition for 30 min, (iii) 1:3 addition for 30 min, and (iv) 1:1 addition in the presence of 1 equiv of tetramethylethylenediamine for 30 min.

Table 2. Anionic Polymerization of MMA and TBA Based on *t*BDMSPrLi/Dye Derivatives

sample	*t*BDMSPrLi/ APE[a]	monomer	M_n theoretical	M_n[b] GPC	M_w/M_n GPC	M_n UV[c]	M_n NMR[d]	initiation efficiency (%)[e]
G	2-An	MMA	10 000	9900	1.04	9400	9500	100
H	2-An	MMA	20 000	22 000	1.03	22 200		91
I	2-Ph	MMA	3000	2980	1.18		3100	100
J	2-Ph	MMA	8000	8400	1.13	7200	8000	95
K	2-Ph	MMA	20 000	18 600	1.03	18 400		100
L	2-An	tBA	10 000	14 500	1.05	12 000	12 500	83[f]

[a] Prepared separately in THF with [Li] = 0.06 M and [APE] = 0.18 M at 20 °C for 30 min. See the second method for anionic polymerization. [b] PMMA standards. [c] $\epsilon = 5000$ (358 nm) for anthracene derivatives, and $\epsilon = 9400$ (300 nm) for phenanthrene derivatives. [d] Determined by the integration ration of Si−C**H**$_3$ (6H, −0.05 ppm), −OC**H**$_3$ (PMMA, 3H, 3.6 ppm) and −C(CO)**H**-C (PtBA, 1H, 2.2 ppm). [e] $M_{\mathrm{n\,theor}}/M_{\mathrm{n\,GPC}} \times$ yield. [f] $M_{\mathrm{n\,theor}}/M_{\mathrm{n\,UV}} \times$ yield.

way stopcock and a rubber septum. A known amount of LiCl was added to a glass reactor that was flamed under vacuum and purged with nitrogen. THF was transferred into the glass reactor through rubber septa using a stainless steel cannula. A 5-fold excess of LiCl was used with respect to *t*BDMSPrLi. The monoadduct initiators were prepared in two ways. The first was an in situ method; APE (3-fold excess with respect to Li) was added to the polymerization solution of THF (~30 mL), followed by *t*BDMSPrLi (the desired amount *t*BDMSPrLi was added after a representative color of THF persisted) at 20 °C for 30 min. This method was used to prepare the polymer samples (A, B, D, E, F) in Table 1. The second method involved reacting *t*BDMSPrLi with APE (mole ratio 1:3) separately in THF, with [Li] = 0.06 M, at room temperature for 30 min. Then the initiator solution was added dropwise to the polymerization flask at 0 °C until a deep color (red for DPE, purple for 2-An, blue for 2-Ph and 9-Ph) persisted, followed by the desired amount of initiator. This method was used to prepare the samples in Table 2. The solution was then cooled to −78 °C, and the required amount of monomer was added. The polymerization was conducted at −78 °C for 1−2 h depending upon the targeted molecular weight. Upon the monomer addition, the deep color of the initiator immediately disappeared. The polymerization product was quenched by the addition of degassed methanol. The final solution was concentrated before being precipitated into an excess of methanol (for PMMA) or methanol/water mixtures (9/1 v/v for P*t*BA) under stirring. The crude polymer (~ 2.0 g) was further purified by silica gel flash chromatography (column size: 20 mm × 300 mm) using hexane/THF (4/1) as solvent (2−3 L).

Hydrolysis of *tert*-Butyldimethylsilyoxyl (*t*BDMS) End Group to a Hydroxyl Group. To a THF solution (20 mL) of PMMA (2 g, 0.21 mmol) with a *t*BDMS end group ($M_n = 9400$) was added concentrated (37%) HCl (0.1 mL, 1 mmol). The solution was refluxed for 2 h. The polymer was recovered by precipitation in methanol. For siloxyl-terminated P*t*BA, tetrabutylammonium fluoride (2 mL, 1.0 M in THF) was added to a THF solution (100 mL) containing the polymer (5.0 g, $M_n = 12\,000$). After 24 h at 20 °C, the reaction mixture was concentrated and then precipitated into cold methanol/water (9/1).

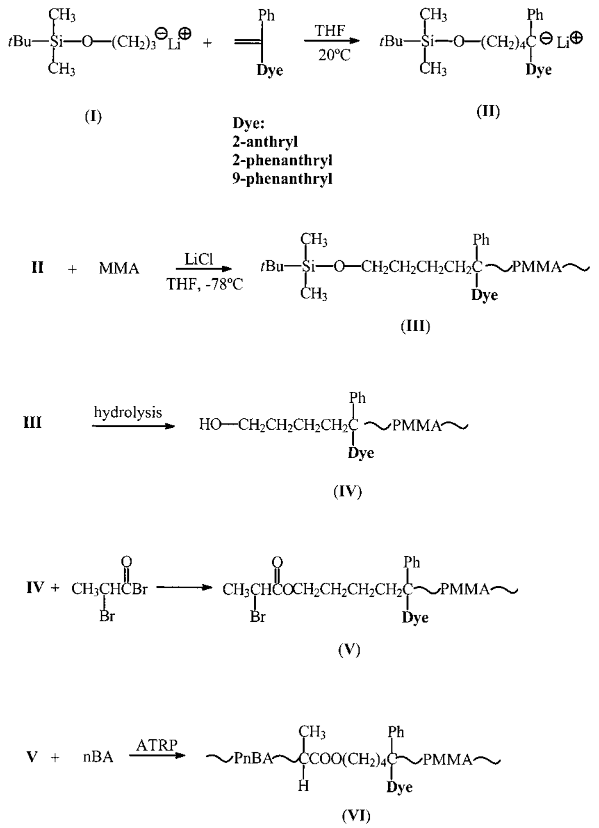
Transformation of the Hydroxyl Group to the $CH_3CHBrCOOCH_2-$ Group. To a cold solution of hydroxyl-terminated PMMA (1.5 g, 0.16 mmol) in dry THF (20 mL) and with triethylamine (81 mg, 0.8 mmol) was added 2-bromopropionyl bromide (173 mg, 0.8 mmol) at 0 °C under N_2. The suspension was stirred at 0 °C for 1 h and then for another 5 h at room temperature. After precipitation in methanol, the crude polymer was vacuum-dried at 60 °C overnight. It was finally purified by flash chromatography through silica gel (hexane/THF, 4/1).

Synthesis of PMMA-2Ph−Poly(alkyl acrylate). Diblock copolymers consisting of PMMA, poly(alkyl acrylate), and the phenanthrene at the junction were synthesized by the ATRP of EHA, *n*BA, or EA, using $CH_3CHBrCOO-$ end-capped PMMA as macroinitiator. In a typical procedure, PMMA (sample I, 0.22 g, $M_n = 3000$, 0.073 mmol), CuBr (10.5 mg, 0.073 mmol), dHbipy (77.4 mg, 0.22 mmol), EHA (2 mL), and toluene (2 mL) were charged into a 50 mL glass tube. The mixtures were immediately degassed by three freeze−thaw cycles, sealed under nitrogen, and finally placed in an oil bath at 90 °C under stirring. The polymerization solution was homogeneous and dark red. At various time intervals, aliquots of the samples were taken out and analyzed by GPC and NMR. At the end of the polymerization, the reaction mixtures were cooled to room temperature, diluted with 4 mL of THF, and passed through an aluminum oxide column (20 mm × 200 mm). The solution was colorless. The block polymer was recovered by precipitation in an excess of methanol.

Synthesis of P*t*BA-2An−PMMA. Diblock copolymers consisting of P*t*BA, PMMA, and the anthracene at the junction were synthesized by the ATRP of MMA, using $(CH_3)_2CBrCOO-$ end-capped P*t*BA as macroinitiator. The polymerization was catalyzed by a somewhat different catalyst system, consisting of $CuCl/CuCl_2$/dHbipy (0.9/0.1/3, mole ratio), to obtain a narrowly distributed PMMA block.[25,26] The polymerization was carried out in toluene (monomer/toluene = 1/1, v/v) at 90 °C under a nitrogen atmosphere in a sealed tube.

Characterization. ^{1}H NMR and ^{13}C NMR spectra were recorded on Varian-300 and Varian-400 spectrometers in $CDCl_3$. Molecular weights (MW) and molecular weight distributions (MWD) were obtained by gel permeation chromatog-

Chart 3



raphy (GPC) from Waters (Water GPC 515 and Waters associates 2690) at 35 °C, using THF as the eluent, monitored with fluorescence (FL) (excitation/emission wavelengths are 300 nm/399 nm for phenanthrene and 350 nm/450 nm for anthracene, respectively), UV (258 nm), and differential refractometer (RI) detectors in tandem. Calibration curves were prepared with PMMA standards. UV spectra were recorded on a PE UV/vis spectrophotometer Lambda 6. The molar extinction coefficients (ϵ) of the model compounds 2-PhH (see above) and 1-(2-anthryl)-1-phenyl-ethane (2-AnH, $\epsilon = 5000$ M^{-1} cm^{-1} at 358 nm),[3] were determined by plotting absorbance vs concentration for solutions in chloroform. With these values, we could assess either the degree of chromophore incorporation or, assuming complete incorporation, calculate M_n(UV) for the samples.

Results and Discussion

This paper describes the synthesis of poly(methyl methacrylate)-*b*-poly(alkyl acrylate) diblock copolymers labeled at the junction with a single fluorescent dye (Chart 3). In the synthesis, *t*BDMSPrLi first is reacted with a 1-aryl-1-phenylethylene, generating an anionic initiator with a dye incorporated and with a protected hydroxyl group (**II**). After the polymerization of MMA to produce **III**, the *t*BDMS end group is hydrolyzed into an OH end group (**IV**), which is then esterified into an α-bromoester end group (**V**). The final block copolymers are synthesized by the ATRP of alkyl acrylates initiated by the PMMA macroinitiator **V**. The design of this synthetic pathway is based on the fact that most alkyl acrylates (except *t*BA) cannot be anionically polymerized in a controlled way, whereas the ATRP of alkyl acrylates proceeds in a living fashion.

Anionic Polymerization of MMA Initiated by *t*BDMSPrLi/APE Monoadduct. In the living anionic polymerization of MMA, one needs a suitable ligand to interact coordinatively with the active alkali metals.[27] One also uses a bulky initiator [i.e. 1,1-diphenyl alkyllithium, usually prepared in situ from the addition reaction of BuLi and 1,1-diphenyl ethylene (DPE)], to avoid side-reactions in the initiation step. Previous reports have shown that the addition reaction between the APE (A = naphthyl[28] or pyrenyl[29]) and an alkyllithium (including polystyryllithium and polyisoprenyllithium) gives only the monoadduct. Table 1 shows that the addition reactions between *n*-BuLi (or *s*-BuLi) and 9-Ph (or 2-An) are quantitative. Anionic polymerization of MMA initiated by these species proceeds in a typical living fashion; i.e., the M_n obtained is in good agreement with the theoretical calculation, and the MWD is monomodal and very narrow. Therefore, 1-(9-phenanthryl)-1-phenyl alkyllithium and 1-(2-anthryl)-1-phenyl alkyllithium can be regarded as ideal anionic initiators for MMA polymerization (samples 1 and 2). Sample 3 (Table 1) demonstrates that *t*BDMSPrLi is a very active and highly efficient initiator in hydrocarbon solvent (e.g., cyclohexane) for the polymerization of isoprene. This result is consistent with those reported for isoprene and butadiene polymerization by this type of initiator.[18−20]

When the HPI initiators for MMA polymerization were prepared in situ, i.e., when *t*BDMSPrLi was added to the THF solution containing the APE at 20 °C before polymerization (samples D−F), the solution color gradually changed to deep red (or purple or blue, depending on the APE used). This slow rate is in striking contrast to what happened in the corresponding reaction of the APE with BuLi, in which the color appeared immediately. After *t*BDMSPrLi and APE reacted for ca. 30 min, the solution was cooled to −78 °C. Upon the addition of MMA, the characteristic deep color disappeared immediately, an indication of fast initiation. However, the initiation efficiencies of these systems were found to be systematically low, ranging from 4% to 20%. It has been reported by Hirao et al.[30] that a side-reaction, such as cleavage of trimethylsilyl group by living anions, can occur in the polymerization of 4-[2-(trimethyl)siloxyethyl]styrene in THF. Hirao et al.[30] overcame this problem by replacing one methyl group with a bulky alkyl group (e.g., *tert*-butyl). Furthermore, Ohata et al. did not observe any notable side-reaction in the *t*BDMS-DPE/*n*-BuLi system for MMA polymerization in THF.[16] Therefore, the very low initiation efficiencies that we found for samples D−F in Table 1 are more likely to result from the incomplete addition reaction of *t*BDMSPrLi and APE than from a side-reaction at the *t*BDMS group. To clarify this issue, we investigated the 1:1 (molar) addition reactions of *t*BDMSPrLi and APE. Both the [Li] and [APE] concentrations for these reactions were around 0.03 M, ca. 10 and 3 times higher, respectively, than those used in the in situ polymerization reactions. As can be seen in Table 1, the addition reaction yields were ca. 37−44% (runs 4 and 5) at 15 min and 85% (run 5) at 30 min in the case of DPE and 2-An. In the case of 9-Ph (run 6), the addition reaction yields (<6%) were much lower than those for the DPE and 2-An counterparts, no matter what method was used to promote the reaction (longer time, high 9-Ph concentration and polar additive). We thus concluded that the addition reaction between *t*BDMSPrLi and the APE was relatively slow compared to that of BuLi system, possibly due to the influence of the *t*BDMS group. Furthermore, the 9-substituted-

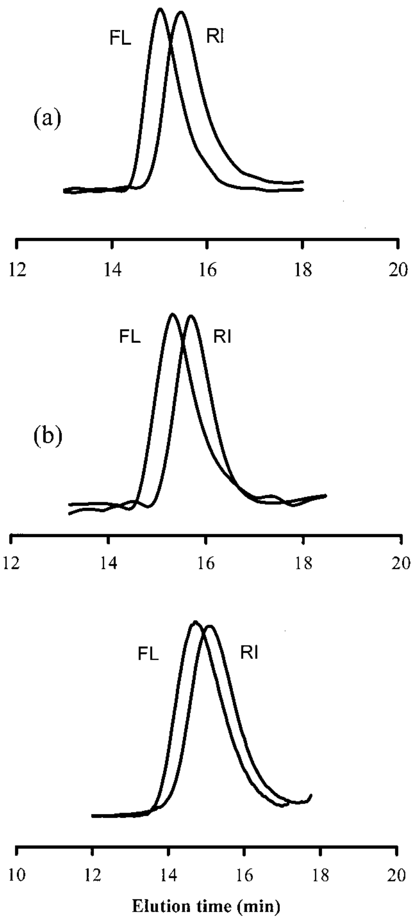


Figure 1. GPC traces of PMMA and P*t*BA initiated by the hydroxyl-protected initiator *t*BDMSPrLi: (a) sample G; (b) sample J; (c) sample L.

phenanthrene derivative might have an additional steric effect to slow the reaction kinetics.

As a result, we synthesized 1-(2-phenanthryl)-1-phenylethylene (2-Ph), which has a similar structure to 2-An. This APE reacts with *t*BDMSPrLi in a relatively high yield (84%, run 7). Samples G−L were therefore synthesized via a different method, in which the initiating species (2-An and 2-Ph derivatives) were prepared separately in THF at high concentration (Table 2). Figure 1 illustrates the GPC traces for samples G, J, and L, representing the three types of polymerization with different dyes and monomers. The molecular weights determined by GPC and NMR are close to those calculated from the ratio of monomer to initiator. In addition, the MWDs are monomodal and very narrow, and the initiation efficiencies are essentially quantitative, in line with those of typical living anionic polymerization reactions. The incorporation of fluorescent dye molecules is clearly demonstrated by the FL signals in the GPC traces. The ^{1}H NMR spectrum of sample I, which has the lowest molecular weight ($M_n = 3000$), is shown in Figure 2 (**III**). Besides the clear presence of both *t*BDMS (−0.05 ppm for Si−CH_3 and 0.9 ppm for *t*Bu) and aromatic (7.1−8.7 ppm) signals, the integrations at −0.05 ppm (6H of Si−CH_3) and 8.8 ppm (2H of phenanthryl group) show a ratio of 3:1, indicating that only one dye molecule is attached to each polymer chain. Under the assumption that only one dye molecule is incorporated in one polymer chain, the M_n of the phenanthrene and anthracene labeled polymers can also be determined by UV (M_n(UV)) based on the extinction coefficients of the model compounds, 2-PhH and 2-AnH, respectively. The M_n(UV) values shown in Table 2 indeed confirm those deduced from the GPC and NMR measurements.

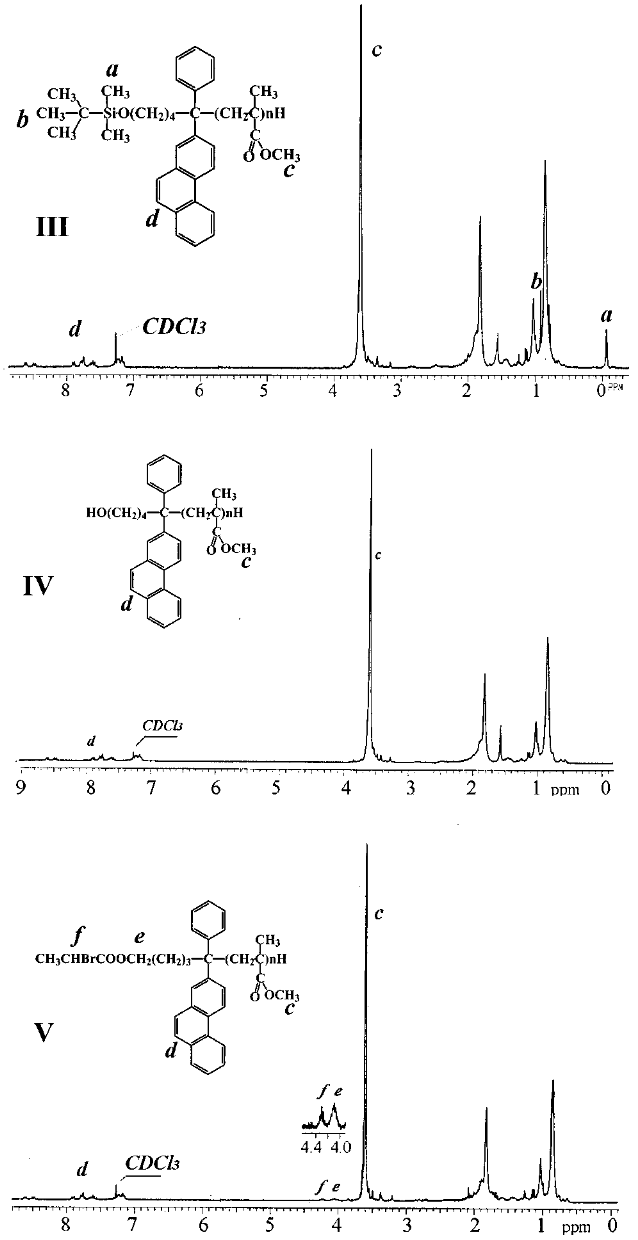
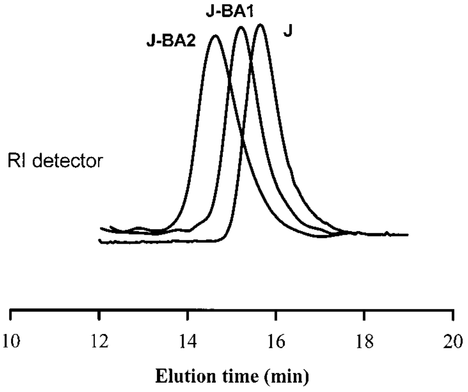
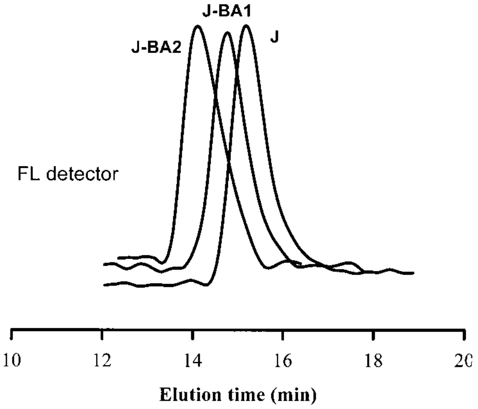


Figure 2. ^{1}H NMR spectra of PMMA−(2-Ph), sample I in Table 2: **III**, with *t*BDMPr end group; **IV**, with OH end group; **V** with bromoester end group. See also Chart 3.

Transformation of tBDMS End Group to α-Bromoester Group. α-Bromoesters are well-known initiators for the ATRP of various monomers.[14] Macroinitiators with an α-bromoester end group can be prepared from a hydroxyl-terminated polymer by reacting the chain end with 2-bromopropionyl bromide.[12] As reported in the literature,[18,19,31] the *t*BDMS-protecting group can be readily removed under mild conditions, forming polymers with a hydroxyl terminal group. For example, samples with a PMMA backbone (G−K, Table 2) can be hydrolyzed by refluxing a PMMA solution in THF with aqueous HCl for 2 h,[20] whereas sample L has to be reacted with tetrabutylammonium fluoride (24 h, room temperature) to prevent the *t*BA groups from being hydrolyzed. The hydrolyzed polymers **IV**, (Chart 3) have



(a)



(b)

Figure 3. GPC traces for PMMA−(2Ph)−P*n*BA prepared from sample J: (a) RI traces; (b) FL traces. PMMA 0.2 g, toluene 2 mL, and alkyl acrylate 2 mL. PMMA/CuBr/dHbipy = 1:1:3 (mole ratio), 90 °C. J−BA1: 4 h, 90 °C. J−BA2: 12 h, 90 °C.

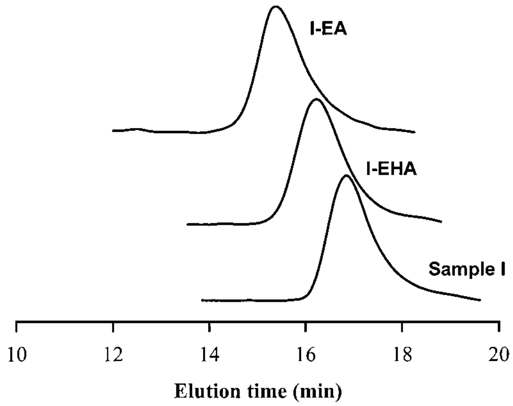


Figure 4. GPC traces (RI) for (a) PMMA-2Ph−Br, prepared from sample I in Table 2, (b) I−EHA, PMMA-2Ph−PEHA, and (c) I−EA, PMMA-2Ph−PEA. Experimental conditions: PMMA 0.2 g, toluene 2 mL, and alkyl acrylate 2 mL. PMMA/CuBr/dHbipy = 1:1:3 (mole ratio), 90 °C.

essentially the same molecular weights (GPC and UV) as those of the precursor **III**, but without the CH_3−Si and *t*Bu signals in the NMR spectrum (Figure 2, **IV**). Figure 2, part **V**, illustrates the ^{1}H NMR spectrum of bromo-esterified PMMA. The two tiny peaks at 4.05 and 4.25 ppm clearly confirm the presence of $CH_3C\mathbf{H}Br$-$COOC\mathbf{H_2}$− group. Furthermore, M_n values determined by NMR [the integration ratio of $c/(e + f)$ peaks] is ca. 2900, which is in very good agreement with that of the parent polymer. The essentially identical M_n values of **V** and **III** by NMR indicate a quantitative reaction not only for esterification, but also for the hydrolysis. Finally, the GPC traces of **V** (such as samples J in Figure 3 and I in Figure 4) are symmetrical and narrow, and are identical with that of the starting material **III**.

ATRP of Alkyl Acrylates Using Dye-Labeled PMMA Macrointiators. ATRP of several alkyl acrylates, EA, nBA, and EHA, by the PMMA macroinitiators (derived from samples G−K) have been carried out in toluene/acrylate monomer mixtures (1:1 v/v) at 90 °C with a homogeneous catalysis system (Initiator/dHbipy/CuBr = 1/3/1). Figure 3 shows the GPC traces of the polymerization of nBA with sample J, the phenanthrene-labeled PMMA. It should be noted that unlike that of RI signal, whose intensity is related to the amount of polymer rather than the number of chains, the intensity of the FL trace depends on the number of dye chromophores and thus the number of polymer chains. Therefore, as a sensor of chain extension from the macroinitiator (PMMA−dye) to diblock copolymer (PMMA−dye−polyacrylate), the FL signal should be more sensitive than the RI signal. In Figure 3, after polymerization, both the RI and FL traces shift to the high molecular region without any noticeable shoulder or tail, indicating a very efficient chain-extension reaction from PMMA to PnBA. The total molecular weight of the block copolymer increases with the polymerization time and the molecular weight distribution remains very narrow, typical characteristics for living polymerization.

The block copolymerization for other alkyl acrylates from phenanthrene-labeled PMMA was also investigated. The GPC (RI) traces (Figure 4) for the block copolymers of PMMA-2Ph−PEA (I−EA) and PMMA-2Ph−PEHA (I−EHA) initiated from sample I (Table 2) are very similar to those observed in Figure 3, confirming the formation of block copolymer free of PMMA macroinitiator. Figure 5 presents the ^{1}H NMR spectrum of PMMA-2Ph−PEHA. The additional signal at 3.9 ppm, compared to the structure of **V** in Figure 2, is an indication of the incorporation of the PEHA block. Finally and most important, the molecular weight of the block copolymers as determined by the UV analysis is in accord with the NMR result (Table 3). For example, sample J−BA2 shows an M_n(UV) of 12 000 and an M_n(NMR) of 13 500. It thus can be concluded that the diblock copolymers consisting of PMMA and poly(alkyl acrylate) with a single phenanthryl molecule labeled at the junction can be synthesized by the combination of living anionic and radical polymerization techniques.

In contrast to the results described above, the synthesis of anthracene-labeled PMMA-poly(alkyl acrylate) does not proceed smoothly. Figure 6 shows the GPC traces (RI, a and b) of block copolymers formed by chain extension from sample G with EHA (G−EHA) and nBA (G−BA) monomers. It seems that the chain extension itself is successful, as indicated by the shift of the RI trace to higher *M*. Under close inspections, problems are detected. First of all, the FL traces of some of the block copolymers prepared in this way, such as PMMA-2An-PnBA (G−BA, Figure 6c), are bimodal with a broad distribution of the retention times. A rough estimate of peak M indicates that the short-time peak has twice the *M* of the second peak. Second, the UV spectra of PMMA-2An (sample G) and PMMA-2An-PnBA (G−BA) are significantly different (Figure 7). The additional absorp-

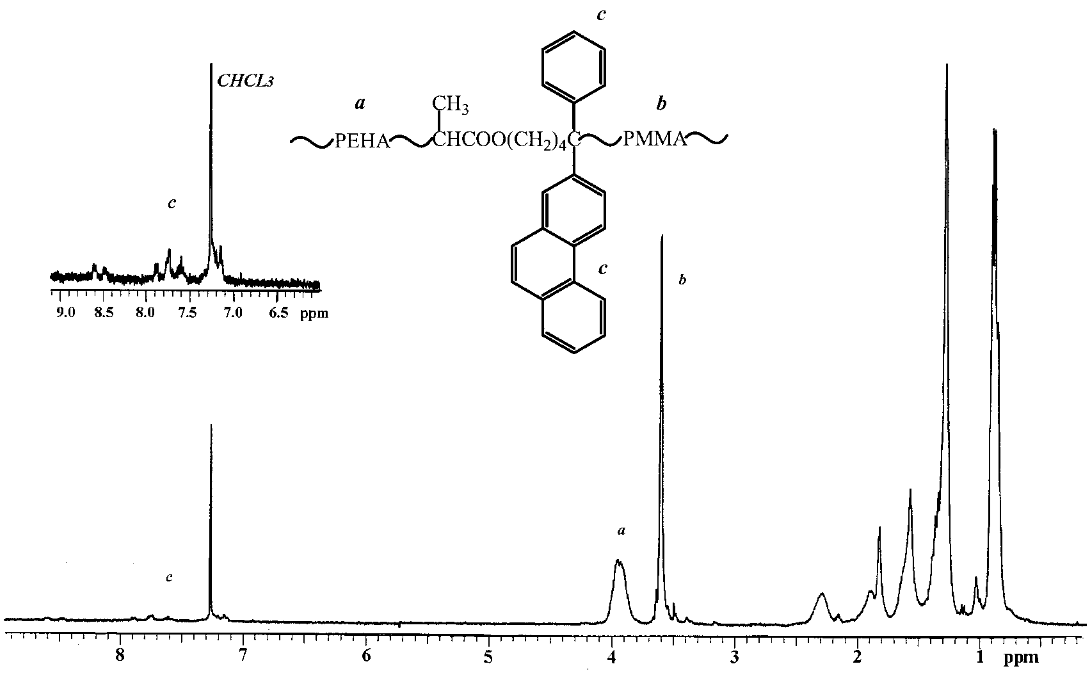


Figure 5. NMR spectrum of I−EHA, prepared from sample I.

Table 3. Meth(acrylate) Diblock Copolymers with Dye Labeled at the Junction[a]

sample[b]	first block[b]	dye	second block	M_n (UV)	M_n (NMR)	M_w/M_n (GPC)
J−BA2	J, PMMA	2-Ph	PBA	12 000	13 500	1.16
I−EHA	I, PMMA	2-Ph	PEHA	not measd	6500	1.18
I−EA	I, PMMA	2-Ph	PEA	9600	11 500	1.20
G−BA	G, PMMA	2-An	PBA	31 000	16 000	1.20
G−EHA2	G, PMMA	2-An	PEHA	29 000	15 000	1.16
L−MMA	L, PtBA	2-An	PMMA	47 000	52 000	1.22

[a] Synthesized by ATRP of meth(acrylate) with PMMA or PtBA as macroinitiators. Reaction conditions are described in figures of GPC traces. [b] The first letter indicates the first block, prepared by anionic polymerization, in Table 2.

tion peaks are not from the dHbipy catalyst (292 nm) but indicate the presence of a new chromophore. Finally, the NMR spectrum of G−BA, which exhibits the characteristic signal of PnBA at 3.9 ppm, gives a much smaller M_n (M_n(NMR) = 16 000) than that determined by UV (358 nm, M_n(UV) = 31 000).

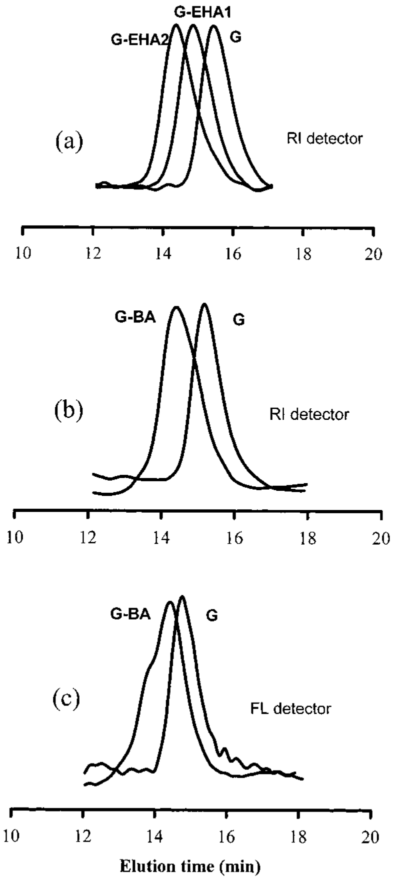


Figure 6. GPC traces of (a) G−EHA, PMMA-2An−PEHA, RI; (b) G−BA, PMMA-2An−PnBA, RI; and (c) G−BA, FL. The PMMA block is from sample G in Table 2. Experimental conditions: PMMA 0.2 g, toluene 2 mL, and alkyl acrylate 2 mL. PMMA/CuBr/dHbipy = 1:1:3 (mole ratio), 90 °C. G−EHA1: 8 h. G−EHA2: 18 h. G−BA: 24 h.

It has long been known that the radical polymerization of 9-vinyl anthracene is perturbed by the competing radical addition to the 10-position of the anthracene, forming an unreactive dibenzylic radical (Chart 4), and resulting in polymers with a low M.[32] Yagci et al. reported recently that the tempo-substituted anthracene derivative, shown in Chart 5, forms a dibenzylic radical. Lacking an R′ group at the 9-position, this radical can initiate styrene polymerization in a living fashion.[33] To examine if the "quenched" anthracene radical could initiate the polymerization of acrylate monomers, we investigate the ATRP of tBA and nBA in the presence of 1 equiv of anthracene (initiator/anthracene = 1:1). The appearance of a UV signal at a similar position to the RI peak in GPC traces of these polymers indicates that the polymerizations of *t*BA and *n*BA are affected by the presence of anthracene. The RI and UV traces are also found to shift to high molecular weight when the polymerization is carried out for an additional time. We therefore believe that during the ATRP of acrylates by anthracene-labeled PMMA, the propagating acrylate type radical adds to the 2-anthryl derivative forming a dibenzylic radical (Chart 6). If the reaction is intermolecular, the MW for the new polymer will be doubled, and the intensity detected by FL will be small. Since

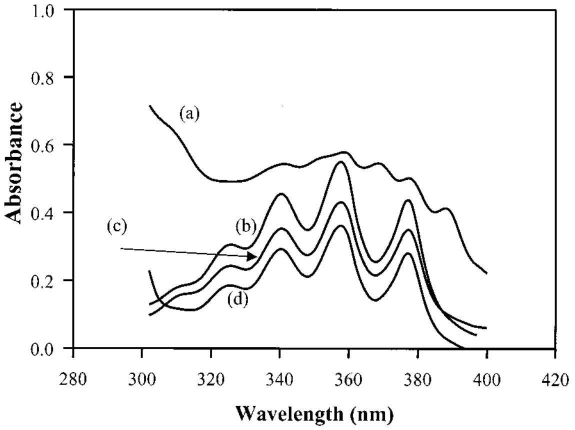


Figure 7. UV spectrum of 2-An labeled polymers: (a) G−BA, PMMA-2An−PnBA, prepared from sample G; (b) PMMA-2An−Br, from sample G; (c) P*t*BA-2An−Br, from sample L; (d) L−MMA, PtBA-2An−PMMA, from sample L.

Chart 4

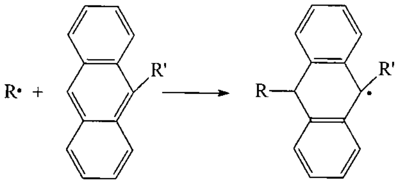


Chart 5

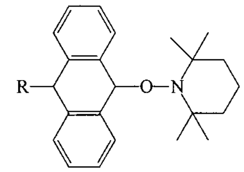
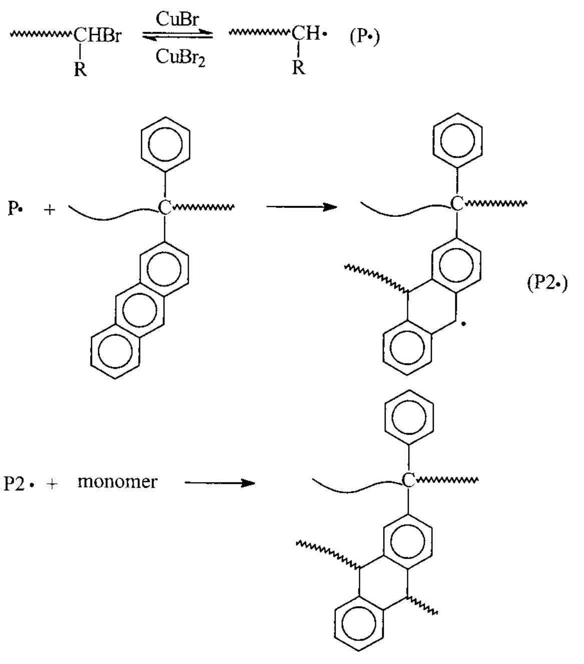


Chart 6



the dibenzylic radical is also an active species for radical polymerization, the anthracene-“quenched” polymer is still living, even in the case of the intramolecular reaction. The polymer chain length will increase with the reaction time (Figure 6a).

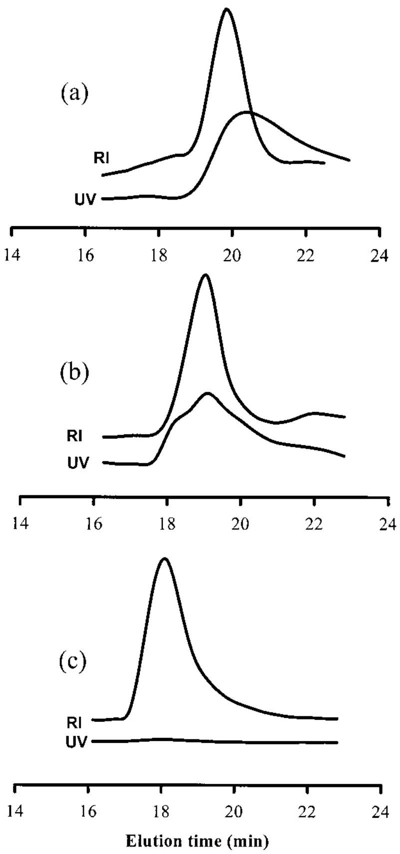


Figure 8. GPC traces of homopolymer initiated with ethyl-2-bromoisobutyrate in the presence of 1 equiv of anthracene: (a) P*t*BA; (b) P*n*BA; (c) PMMA. Experimental conditions: (meth)acrylate 6 mL; EBIB/CuBr/dHbipy = 1:1:3 (molar ratio); 90 °C.

There are two ways being considered in our laboratory to prevent acrylate radicals from reacting with anthracene derivatives. In the first method we introduce substituents at both 9- and 10-positions. This approach is effective at suppressing the radical addition reaction when 9-methylacryloxymethyl-10-methylanthracene or 9-methylacryloxy-10-methylanthracene are copolymerized with alkyl acrylates.[34] To apply this strategy to the synthesis of block copolymers, we would have to synthesize a 9,10-dimethylanthracene derivative analogous to 2-An. We have not yet attempted this synthesis.

An alternative approach, which also works, is to start with the polyacrylate block, and then build the second methacrylate block by ATRP. This strategy is based on the fact that the anthracene molecules do not interfere with the radical polymerization of methacrylate monomers.[35,36] For example, Figure 8, part c, illustrates the GPC traces of an ATRP of MMA in the presence of 1 equivalent anthracene (catalyzed by CuBr/dHbipy).[37] In contrast to what are observed in Figure 8, parts a and b, nearly no UV absorbance is detected for the PMMA, indicating the absence of aromatic moieties in the PMMA backbone.

To proceed with the synthesis, the end group of the P*t*BA sample in Table 2 (sample L) was hydrolyzed and then esterified to the -COC(CH_3)$_2$Br group by reaction with 2-bromoisobutyryl bromide. The end group obtained is similar to the propagating species of the methacrylate polymer, and should not be affected by the anthracene moiety attached to the chains. The peaks in the GPC traces (Figure 9) of the PtBA-2An−PMMA

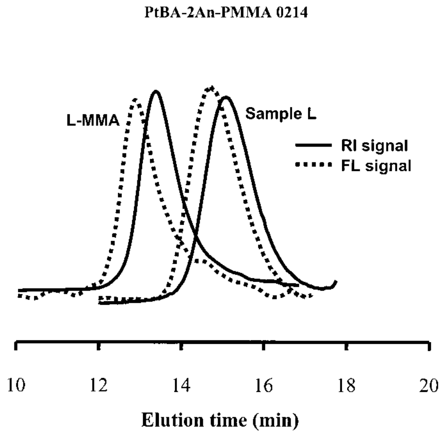


Figure 9. GPC traces of L−MMA (P*t*BA-2An−PMMA), prepared from sample L, catalyzed by CuCl/$CuCl_2$/dHPy: 1:0.1:3 with respect to the sample L.

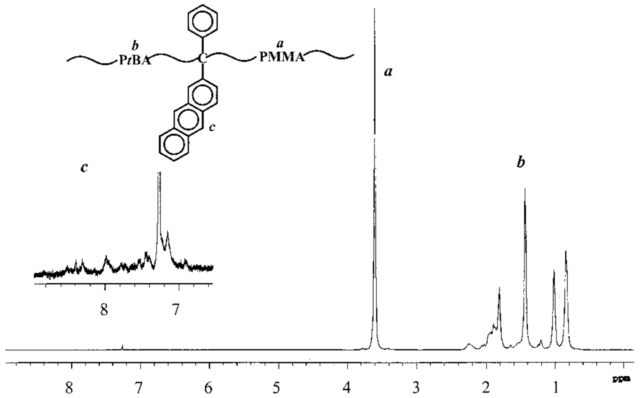


Figure 10. NMR spectrum of L−MMA (P*t*BA-2An−PMMA), prepared from sample L. Peak *a* at 3.6 ppm is the $-OCH_3$ group from PMMA and peak *b* at 1.4 ppm is the *t*Bu group from P*t*BA.

(L−MMA) diblock copolymer are clearly shifted from those of the parent polymer (sample L) and show no tail or shoulder (Figure 9). The UV spectra of samples L and L−MMA are identical (Figure 7, parts c and d). The NMR spectrum (Figure 10) of the L−MMA shows the presence of PMMA moieties (3.6 ppm) and also the presence of the anthracene group; The M_n determined by UV is 47 000, which compares favorably with that detected from the NMR integration (M_n(NMR) = 52 000). As a result, we see that well-defined PtBA−PMMA diblock copolymers, with a single anthracene molecule at the junction, can be synthesized. Finally, it needs to be mentioned that by refluxing these polymers in a primary alcohol solvent (e.g., 1-butanol, 2-ethylhexyl alcohol) under acid catalysis, one can quantitatively (>96%) transform the P*t*BA to other types of poly(alkyl acrylates),[6] providing access to different kinds of anthracene-labeled acrylate−methacrylate diblock copolymers.

Conclusions

This paper reports the synthesis of diblock copolymers consisting of a poly(methyl methacrylate) block and a poly(alkyl acrylate) block, labeled with a single fluorescent dye molecule at the junction. The synthesis proceeds by a combination of anionic polymerization and atom transfer radical polymerization. The in situ anionic polymerization of MMA by the hydroxyl-protected initiator (*t*BDMSPrLi)/1-aryl-1-phenylethylene monoadduct in THF proceeded in low efficiency. The extremely low efficiency for 1-(9-phenanthryl)-1-phenylethylene derivative may be due to the steric effects from both of the *tert*-butyldimethylsilyl and 9-phenanthryl substituents. Using separately prepared initiator and a less hindered 2-Ph derivative, we were able to synthesize dye-labeled PMMA with a hydroxyl-protected end group. Poly(meth)acrylate macroinitiators have been prepared by the selective hydrolysis of the protecting group, followed by the bromo-esterification of the hydroxyl end group. The chain extension, by ATRP, from phenanthrene-labeled PMMA to poly(alkyl acrylate) is highly efficient, leading to the formation of well-defined diblock copolymers with phenanthrene labeled at the junction. The same strategy does not work for the preparation of anthracene-labeled (meth)acrylate diblock copolymers, because the propagating acrylate radical adds to the 10-position of the anthracene chromophore. Anthracene-labeled block copolymer could be obtained through an inverse synthetic pathway, which starts from the PtBA-2An to the PtBA-2An−PMMA diblock, as anthracene does not interfere with the radical polymerization of methacrylate monomers.

Acknowledgment. The authors are grateful to Dr. R. Liu for helpful discussions and NSERC Canada for their support of this work.

References and Notes

(1) (a) Förster, Th. *Discuss. Faraday Soc.* **1959**, *27*, 7. (b) Birks, J. B. *Photophysics of Aromatic Molecules*; Wiley-Interscience: New York, 1970; Chapter 11.
(2) Yekta, A.; Spiro, J. G.; Winnik, M. A. *J. Phys. Chem. B.* **1998**, *102*, 7960.
(3) Ni, S.; Zhang, P.; Wang, Y.; Winnik, M. A. *Macromolecules* **1994**, *27*, 5742.
(4) Tcherkasskaya, O.; Ni, S.; Winnik, M. A. *Macromolecules* **1996**, *29*, 610.
(5) Tong, J. D.; Ni, S.; Winnik, M. A. *Macromolecules* **2000**, 33.
(6) Jerome, R.; Bayard, Ph.; Fayt, R.; Jacobs, Ch.; Varshney, S.; Teyssié, Ph. in *Thermoplastic elastomers*, 2nd ed.; Holden, G., Legge, N. R., Quirk, R., Schroeder, H. E., Eds.; Hanser: Munich, Germany, Vienna, and New York, 1996; p 521.
(7) Tong, J. D.; Jerome, R. *Polymer* **2000**, *41*, 2499−2510.
(8) Teyssié, Ph.; Fayt, R.; Hautekeer, J. P.; Jacobs, C.; Jerome, R.; Leemans, L.; Varshney, S. K. *Makromol. Chem., Macromol. Symp.* **1990**, *32*, 61.
(9) Shipp, D. A.; Wang, J. L.; Matyjaszewski, K. *Macromolecules*, **1998**, *31*, 8005.
(10) Hirao, A.; Hayashi, M. *Acta Polym.* **1999**, *50*, 219.
(11) Ohno, K.; Fujimoto, K.; Tsuji, Y.; Fukuda, T. *Polymer* **1999**, *40*, 759.
(12) Jankova, K.; Kops, J.; Chen, X. Y.; Batsberg, W. *Macromol. Rapid Commun.* **1999**, *20*, 219.
(13) Acar, M. H.; Matyjaszewski, K. *Macromol. Chem. Phys.* **1999**, *200*, 1094.
(14) Patten, T. E.; Matyjaszewski, K. *Adv. Mater.* **1998**, *10*, 901.
(15) Anderson, B. C.; Andrews, G. D.; Arthur, P. Jr.; Jacobson, H. W.; Melby, L. R.; Playtis, A. J.; Sharkey, W. H. *Macromolecules* **1981**, *14*, 1601.
(16) Ohata, M.; Isono, Y. *Polymer* **1993**, *34*, 1546.
(17) Schulz, D. N.; Halasa, A. F.; Oberster, A. E. *J. Polym. Sci., Polym. Chem. Ed.* **1974**, *12*, 153.
(18) Shepherd, N.; Stewart, M. J. U.S. Patent 5,331,058, 1994. U.S. Patent 5,362,699, 1994.
(19) Schwindeman, J. A. U.S. Patent 5,321,148. 1994.
(20) Quirk, R. P.; Jang, S. H.; Yang, H. M.; Lee, Y. *Macromol. Symp.* **1998**, *132*, 281.
(21) Quirk, R. P.; Jang, S. H.; Kim, J. *Rubber Rev., Rubber Chem. Technol.* **1996**, *69*, 444.
(22) Zhang, P.; Moore, J. S. *J. Polym. Sci.: Part A* **2000,** *38*, 207.
(23) Matyjaszewski, K.; Patten T. E.; Xia, J. H. *J. Am. Chem. Soc.* **1997**, *119*, 674.
(24) Gilman, H.; Cartlege, F. K. *J. Organomet. Chem.* **1964**, *2*, 447.

(25) Matyjaszewski, K.; Shipp, D. A.; Wang, J. L.; Grimaud, T.; Patten, T. E. *Macromolecules* **1998**, *31*, 6836.
(26) Moineau, G.; Jerome, R. *Macromol. Chem. Phys.*, in press.
(27) Jerome, R.; Teyssié, Ph.; Vuillemin, B.; Zundel, T.; Zune, C. *J. Polym. Sci. Polym. Chem.* **1999**, *37*, 1.
(28) Al-Takrity, E. T. B.; Jenkins, A. D.; Walton, David. *Makromol. Chem.* **1990**, *191*, 3067.
(29) Quirk, R. P.; Schock, L. E. *Macromolecules* **1991**, *24*, 1237.
(30) Hirao, A.; Yamamoto, A.; Takenaka, K.; Yamaguchi, K.; Nakahama, S. *Polymer* **1987**, *28*, 303.
(31) Handlin, D. L. Jr.; Benning, R. C.; Willis C. L. U.S. Patent 5,376,745. 1994.
(32) Rembaum, A.; Eisenberg, A. *Macromol. Rev.* **1967**, *1*, 57.
(33) Yildirim, T. G.; Hepuzer, Y.; Hizal, G.; Yagci, Y. *Polymer* **1999**, *40*, 3885.
(34) Liu, R. H.; Winnik, M. A.; Di Stefano, F.; Vanketessan, J. *J. Polym. Sci., Part A: Polym. Chem.*, submitted.
(35) Bagdasaryan K. S.; Sinitsyna, A. A. *J. Polym. Sci.* **1961**, *52*, 31.
(36) Stolka, M. *Macromolecules* **1975**, *8*, 8.
(37) The broad MWD of this sample is due to the fact that k_{prop} is much higher than k_{ini} when ATRP of MMA is catalyzed by CuBr, as discussed in ref 25.

MA0007684