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Synthesis and application of fluorescently labeled phthalic anhydride (PA) functionalized polymers by ATRP

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Abstract

Fluorescent PMMAs containing a phthalic anhydride (PA) group at the chain ends were prepared using the newly developed initiator **7** by atom transfer radical polymerization and subsequent pyrolysis. These polymers allowed for the detection of inter-macromolecular reaction in reactive polymer blends at a low concentration by the use of fluorescence-gel permeation chromatography. The PA–amine coupling reaction proved to be efficient in reactive blending studies for the compatibilization of PS–PMMA blends at low concentration ($\leq 8\%$) giving a morphology where the average PMMA drop size is 0.6 μm. With 7-nitrobenz-2-oxa-1,3-diazole (NBD) groups as the fluorescent label, the blend morphologies could be visualized in three dimensions by laser confocal microscopy. © 2002 Published by Elsevier Science Ltd.

Keywords: Atom transfer radical polymerization; Fluorescent reactive polymers; Phthalic anhydride functionalized polymers

1. Introduction

In our continuing studies on reactive polymer blending, the correlation between blend morphology and the amount and formation rate of the in situ generated diblock copolymer has been one of the main interests. Gel permeation chromatography (GPC) and transmission electron microscopy (TEM) have been the primary tools to study this subject [1–3]. Quantification of the in situ generated diblock copolymer by GPC generally requires the use of reasonably narrowly polydispersed reactive polymers and proper selection of a polymer pair, one of which can be selectively detected by conventional detectors such as ultraviolet (UV) and refractive index (RI) detectors. However, in the case where the pair of reactive polymers is diluted with non-reactive polymers, detection of the reaction progress by GPC becomes more difficult due to dilution and overlap of the peaks. In order to circumvent this problem, a new technique employing fluorescently labeled reactive polymers and fluorescence-coupled GPC was developed in this lab, which allows for detection of inter-macromolecular reactions at low concentrations [4]. In this previous study, the key fluorescent reactive polymers were prepared by anionic polymerization. Although this methodology proved to be useful in exploring the polymer–polymer coupling events in a quantitative manner, preparations of the desired fluorescent polymers were rather challenging and impractical due to difficulty in finding fluorescent monomers that can survive anionic polymerization conditions. Another limitation may be the thermal pyrolysis (>220 °C, several hours) of the di-*tert*-butyl succinate group used to generate succinic anhydride at the chain ends.

To overcome these limitations, we recently developed a new strategy involving atom transfer radical polymerization (ATRP) [5,6] using an ATRP initiator (**7**, in Scheme 2) containing a di-*t*-butyl phthalate (DTBP) group in place of di-*t*-butyl succinate group that can be pyrolyzed to the corresponding phthalic anhydride group under milder conditions after polymerization [7]. The DTBP moiety in the polymer chains could be transformed to a phthalic anhydride (PA) group cleanly by milder thermal pyrolysis (210 °C, 1 h). The functionalities of these polymers could be determined in a straightforward and accurate manner by conventional ^{1}H NMR spectroscopy. Reactivity of these polymers was superior to the corresponding aliphatic anhydride functional polymers. Since ATRP conditions permit greater chemical tolerance of the monomers or

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functional groups to be used [8], choice of a fluorescent group can be more flexible. Several groups have reported the preparations of fluorescently labeled polymers by ATRP so far [9–11], but to our knowledge, no synthesis of fluorescent polymers with an end-terminal functional group has been reported.

In this paper, we describe our studies to extend this synthetic strategy to prepare fluorescently labeled PA-functionalized polymers and demonstrate the use of these for investigation of reactive blending processes in which low concentrations of reactive polymers were employed. We show that fluorescence-coupled GPC provides useful information about the kinetics of the reactions between PA-functionalized polymers and amine-functionalized polymers under dilute conditions. In addition, with a 7-nitrobenz-2-oxa-1,3-diazole (NBD) group as the fluorescent label, the morphologies of the resulting blends could be visualized by laser confocal fluorescence microscopy [12,13], a simpler microscopic technique than TEM, which can also provide three-dimensional (3D) morphological information.

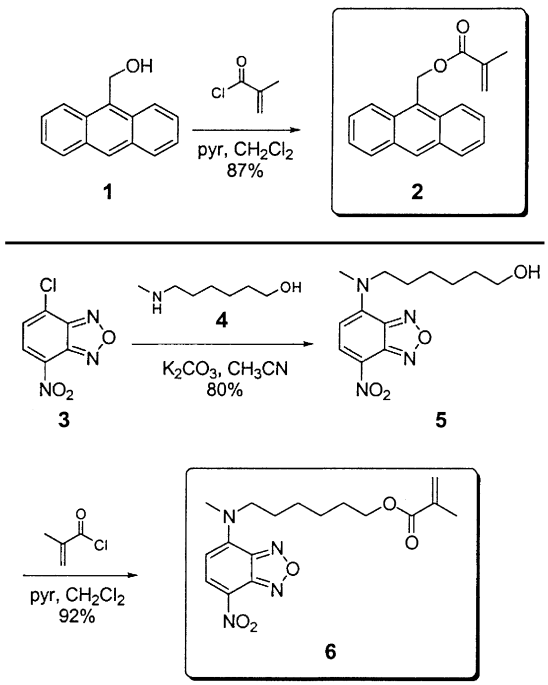
2. Results and discussion

2.1. Synthesis of fluorescent PMMA-PA

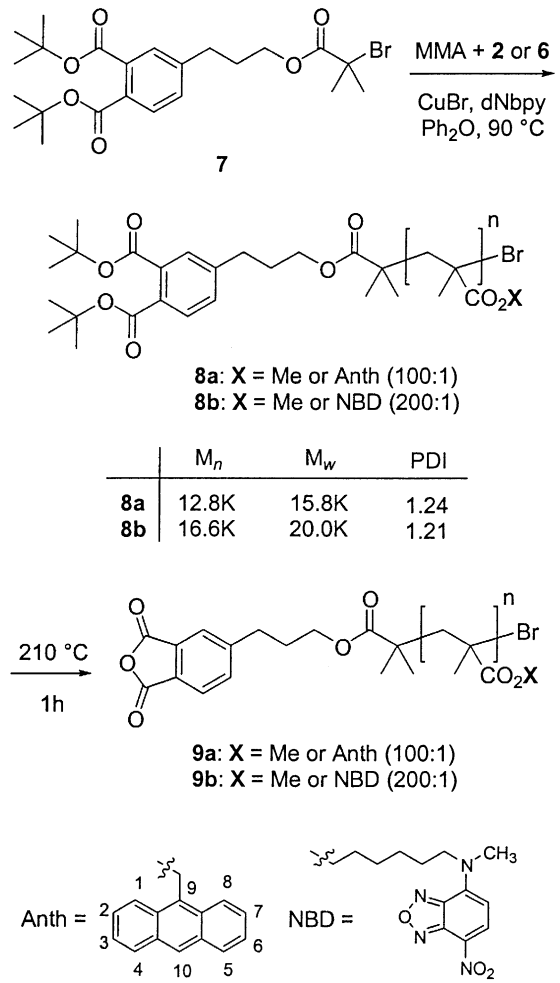
In order to incorporate fluorescence groups into PMMA polymer chains, two different fluorescent methacrylate monomers, **2** and **6**, were prepared in short synthetic pathways as shown in Scheme 1. Anthracenylmethyl methacrylate **2** was prepared by derivatization of commercially available 9-anthracenemethanol (**1**) with methacryloyl chloride in the presence of pyridine in high yield (87%). To obtain a longer wavelength fluorophore, commercially available NBD chloride (**3**) was reacted with 6-(*N*-methylamino)hexan-1-ol (**4**) under basic conditions (K_2CO_3, CH_3CN, rt, 24 h) to provide the corresponding NBD alcohol **5** in 80% yield. Further derivatization of alcohol **5** with methacryloyl chloride gave the desired NBD monomer **6** in 92% yield after isolation. A similar fluorescent monomer having a shorter alkyl linker (2-methylamino alcohol) has been synthesized and used previously by the Winnik group to prepare fluorescent PMMA [14,15]. We chose the longer alkyl chain to enhance the solubility of the monomer in non-polar organic media and to prevent thermal fragmentation that may occur by internal attack of the ester group by the dialkyl amino group at high temperature.

Having these two fluorescent monomers in our hands, two di-*t*-butyl phthalate functionalized fluorescent PMMAs (anth-PMMA-DTBP **8a**, and NBD-PMMA-DTBP **8b**) were prepared by ATRP as described in Scheme 2.

Methyl methacrylate (MMA) monomer was premixed with the fluorescent monomer **2** (1 mol%) and initiator **7** (0.5 mol%), and the resulting mixture was subjected to



Scheme 1.



Scheme 2.

standard ATRP conditions for PMMA (1 equiv. CuBr, 2 equiv. dNbpy to initiator, Ph_2O, 90 °C) [16]. After 11 h the conversion was determined to be 52% by ^{1}H NMR spectroscopy of the crude sample, and the desired anth-PMMA-DTBP **8a** was obtained. Isolation yield was 32% after elution through an alumina column (THF) and two precipitations. The number average molecular weight (M_n) of this polymer was determined to be 12,800 g/mol by GPC and this value matched reasonably well with the theoretical one ($M_{n,cal} = 0.52 \times [\text{monomer}]_0/[\text{initiator}]_0 \times \text{MW}_{\text{monomer}} = 10,400$ g/mol). Polydispersity (M_w/M_n) was 1.24. Each ploymer chain contains about one anthracene group on average. ^{1}H NMR spectroscopy of this sample indicated the presence of both DTBP and anthracene groups in about a 1:1 ratio as shown in Fig. 1 (spectrum (a)). The resonances at δ 8.54 (anth-H_{10}), 8.38 (anth-H_1 and -H_8), 8.06 (anth-H_4 and -H_5), 7.60 (anth-H_2 and -H_7), and 7.47 (anth-H_3 and -H_6) were assigned for the anthracene ring. The broad peak at δ 6.05 designates the 9-methylene group connected to the anthracene ring. The DTBP initiator moiety could also be identified without difficulty. Aromatic protons (δ 7.60 (doublet), 7.39 (singlet), and 7.16 (singlet)), methylene protons (δ 4.03 (multiplet)), benzylic protons (δ 2.72 (triplet)), and *t*-butyl groups (δ 1.64 and 1.65) were easily located. In addition to these peaks, unidentifiable broad peaks at δ 7.22, 5.20, 4.42 and 4.25 existed. These impurities could not be removed even after three precipitations of the polymer in hexanes. We speculate that 9-anthracenylmethyl methacrylate monomer (**2**) reacted with methyl methacrylate monomer or with itself via a Diels–Alder reaction under the conditions of the ATRP reaction. Fortunately, these impurities could be removed in the next step under the pyrolysis conditions (vide infra).

The pyrolysis of anth-PMMA-DTBP **8a** proceeded smoothly under our standard conditions (210 °C, 1 h under vacuum) [7] to give anth-PMMA-PA **9a** (Scheme 2). The ^{1}H NMR spectrum of this polymer indicated that the conversion was complete under the conditions as shown in Fig. 1 (spectrum (b)). The resonances for aromatic protons in the DTBP group have shifted to δ 7.98 (doublet), 7.87 (singlet), and 7.75 (doublet), respectively, which showed that the DTBP group was transformed to PA [7]. Another diagnostic change is the shift of the benzylic methylene peak (δ 2.72, triplet, for anth-PMMA-DTBP **8a**) to a new triplet at δ 2.93 that is the benzylic group of the phthalic anhydride in anth-PMMA-PA **9a**. The impurity peaks mentioned earlier have disappeared over the course of pyrolysis. During the pyrolysis under high vacuum, it was observed that yellow solid material had formed on the top portion of the reactor.

The GPC profile of anth-PMMA-PA **9a** after the pyrolysis was identical with that of precursor anth-PMMA-DTBP **8a**. Degradation of the phthalate functional group and the fluorescent group did not seem to occur since the integration ratio of the polymer backbone peaks to functional group peaks in their ^{1}H NMR spectra remained unchanged during the pyrolysis process.

As for the synthesis of NBD group labeled PMMA-DTBP, NBD group-containing methacrylate monomer **6** was premixed with initiator **7** and methyl methacrylate (MMA) in a 1:1:200 molar ratio and the resulting mixture was subjected to the ATRP conditions (CuBr, dNbpy, Ph_2O, 90 °C) for 21 h. The ^{1}H NMR spectrum of the crude mixture indicated that 74% of MMA monomer had been consumed during the reaction. Purification of the polymer by filtration through alumina and repetitive precipitation gave yellow colored polymer **8b** in 58% isolated yield. The number average molecular weight (M_n) of this polymer was determined to be 16,600 g/mol, which is close to the calculated number average molecular weight, $M_{n,cal}$ (15,800 g/mol). Polydispersity (M_w/M_n) was 1.21, which is slightly narrower than that of the anthracene labeled polymer **8a** ($M_w/M_n = 1.26$). ^{1}H NMR analysis of the purified sample verified that NBD groups are incorporated in the polymer chains (spectrum (a) in Fig. 2). The resonances at δ 8.50 and 6.15 are attributed to the two aromatic protons from the NBD moiety. The peak for *N*-methyl group ($\delta = \sim 3.47$) is hidden underneath the huge

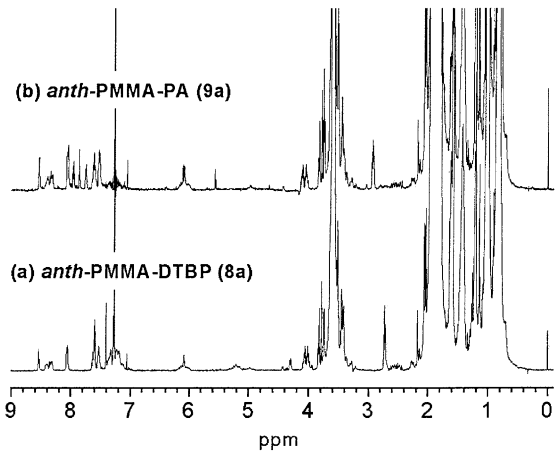


Fig. 1. ^{1}H NMR spectra (500 MHz) of (a) anth-PMMA-DTBP (**8a**) and (b) anth-PMMA-PA (**9a**).

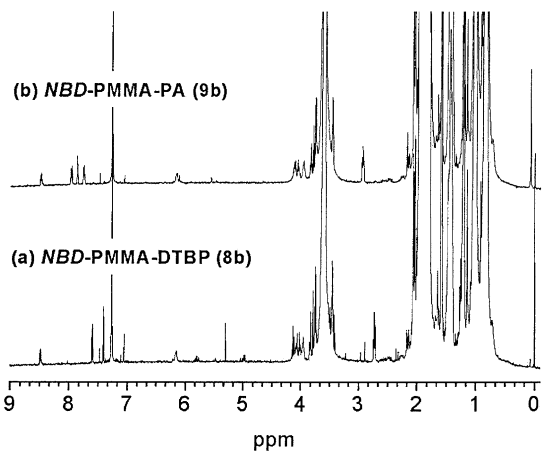


Fig. 2. ^{1}H NMR spectra (500 MHz) of (a) NBD-PMMA-DTBP (**8b**) and (b) NBD-PMMA-PA (**9b**).

methyl ester peak from the polymer backbone, but the *N*-methylene group can be found at δ 4.00.

Pyrolysis of this polymer also was straightforward and gave NBD-PMMA-PA **9b** under the standard conditions (210 °C under vacuum, 1 h) without losing NBD groups (spectrum (b) in Fig. 2). This proves that the NBD groups should survive the polymer blending conditions (180 °C) as well. Functionality of this polymer could be easily checked by reacting with excess PS-NH_2 ($M_n = 15,000$ g/mol, 4 molar equiv.) in solution ($CDCl_3$, rt, 12 h) followed by GPC of the solution with a fluorescence detector. After the reaction, the resulting higher molecular weight and monomodal fluorescence GPC trace proved that all the fluorescent PMMA chains had been reacted with the PS-NH_2 to form the corresponding NBD-PMMA-*b*-PS block copolymer.

2.2. Diluted reactive polymer blend with fluorescent PMMA-PA

Having fluorescently labeled PMMA-PA polymers **9a** and **9b** in hand, we performed a dilute reactive polymer blending experiment and detected the in situ formed diblock copolymer by fluorescence-coupled GPC.

PS-NH_2[2] [17] ($M_n = 15,000$ g/mol, PDI = 1.01, $f = 0.99$) and anth-PMMA-PA **9a** ($M_n = 12,800$ g/mol, PDI = 1.24, $f = 0.99$) each were diluted in non-functional homopolymers to 10 and 8.3 wt%, respectively. Molecular weights of the homopolymers were 100,000 and 21,000 g/mol for PS and PMMA, respectively. A blending experiment of PS/PMMA (70/30) was performed with this mixture using a MiniMAX mixer with three stainless steel balls [18] at 180 °C and 320 rpm mixing speed. Blend samples were taken at 0.5, 1.0, 2, 4, 6, and 10 min, and each sample was checked by GPC with triple detectors (RI, UV and fluorescence).

A representative GPC trace of the blend sample at 0.1 min with the triple detection is shown in Fig. 3. The RI signal shows two separate peaks corresponding to 100K and ~20K molecular weights in an approximately 70:30 ratio. The second peak most likely contains PMMA (21K), PS-NH_2 (15K), and anth-PMMA-PA **9a** (13K). Since PMMA is not very sensitive to UV detection, the UV trace in this chromatogram represents the polystyrene distribution, which is ~90% of 100K PS and ~10% 15K PS-NH_2. In contrast, the fluorescence signal shows only the fluorescent species, that is, anth-PMMA-PA **9a** and the in situ formed diblock copolymer anth-PMMA-*b*-PS. It should be noted that neither the 100K polystyrene nor 21K PMMA was detected at all by fluorescence even though they comprise over 90% of the mixture.

The fluorescence GPC traces over time are presented in Fig. 4. The peak separation was not sufficiently good to obtain the integration of each peak by Gaussian peak deconvolution because the molecular weight distribution of the anth-PMMA-PA **9a** was rather broad ($M_w/M_n = 1.24$) and unsymmetric. However, since the fluorescence intensities from both anth-PMMA-PA **9a** and the resulting diblock copolymer can be safely assumed to be identical on a per-chain basis, the diblock copolymer peak could be deconvoluted by simple subtraction of the pure anth-PMMA-PA peak from the bimodal peaks to give a smooth monomodal diblock copolymer peak [19]. The pure anth-PMMA-PA peak was multiplied by a weighting factor before subtraction, and the procedure was iterated until it left a smooth peak for the diblock product. With this procedure, the two peaks were deconvoluted and the % conversion was obtained from the ratios of product area to total area.

Now the conversion data could be obtained after peak deconvolution as described above and plotted over blending

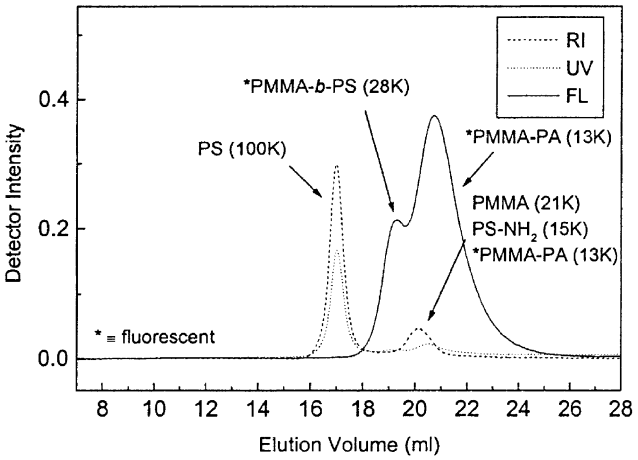


Fig. 3. GPC trace of the blend sample after 0.1 min with triple detection (RI, UV, and fluorescence). Fluorescence detects only anth-PMMA-PA **9a** and the anth-PMMA-*b*-PS copolymer that has been formed in situ. '*' represents the fluorescent species.

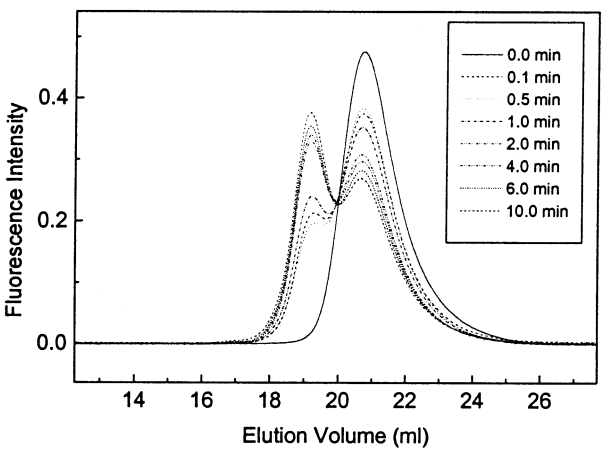


Fig. 4. Fluorescence GPC traces of the diluted reactive blend (PS/PMMA = 70:30) over time. Reactive polymers, PS-NH_2 and anth-PMMA-PA **9a**, were present in each phase in the amounts of 10 and 8.3 wt%, respectively.

[2] This polymer was prepared by Jeffrey T. Cernohous by anionic polymerization. The functionality was determined by the PEG-NPC derivatization method [17] and by $HClO_4$ titration.

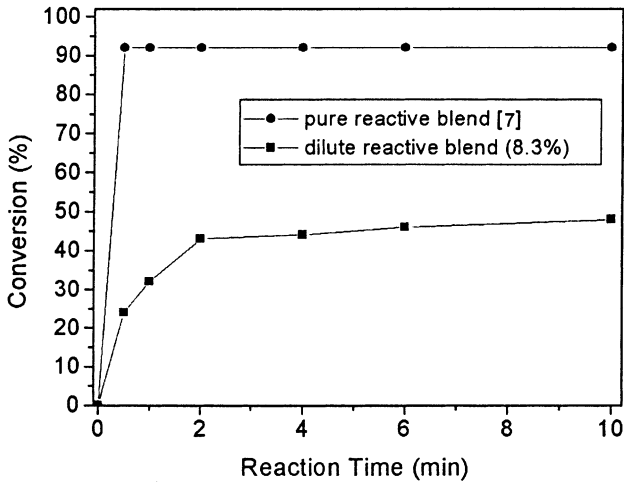


Fig. 5. Conversion of anth-PMMA-PA **9a** vs. time in blends of diluted reactive polymers (8.3%) based on fluorescence GPC trace. For comparison, conversion of an undiluted reactive blend from Ref. [7] is shown, obtained using a non-fluorescent PMMA-PA ($M_n = 21,000$ g/mol) with the same PS-NH2 ($M_n = 15,000$ g/mol) in a 38:62 ratio.

time as shown in Fig. 5. The polymer coupling reaction appears to have occurred very fast (24% conversion at 0.5 min) even at these dilute conditions. After 2 min (43% conversion), the rate slowed, but the conversion still grew by several percent until 10 min (48%). TEM analysis of the 10 min sample showed that submicron PMMA drops are dispersed in PS matrix without forming micelles. For comparison, the conversion data from Ref. 7 for an undiluted blend were included in Fig. 5. Nearly all (92%) of the PMMA-PA reacted within 30 s in this case. These results are consistent with Orr et al. [3,20]. They found very rapid formation of block copolymers and complete conversion for PS-NH2 reacting with anhydride terminal polyisoprene at high concentration. When their reactive polymers were diluted to less than 15%, the morphology of the blend switched to a drop morphology.

In order to get an average particle size, the sample at 10 min was taken and the matrix PS domain was selectively dissolved in cyclohexane and the remaining suspension of PMMA particles was subjected to the particle size analyzer. The volume average particle size of this sample was determined to be 0.61 ± 0.25 μm. With this number, the surface coverage (Σ) of the diblock copolymer in the blend was calculated to be 0.22 chain/nm^2 according to the following equation [1,19]

$$\Sigma = \frac{1}{6}\frac{\phi_w f_{bcp} N_{av} \rho_{PMMA} D_i}{M_n} \quad (1)$$

where ϕ_w is the weight fraction of anth-PMMA-PA in the PMMA phase (0.083), f_{bcp} is the conversion from GPC (0.48), N_{av} is the Avogadro's number (6.02×10^{23} mol^{-1}), ρ_{PMMA} is the density of PMMA (1.15 g/cm^3), D_i is the volume average particle diameter (0.61 μm), and M_n is the number average molecular weight of anth-PMMA-PA.

Maximum coverage (Σ_{max}) was also calculated according to the following equation [21]:

$$\Sigma_{max} = \frac{N_{av}(\lambda/2)}{M_n/\rho} \quad (2)$$

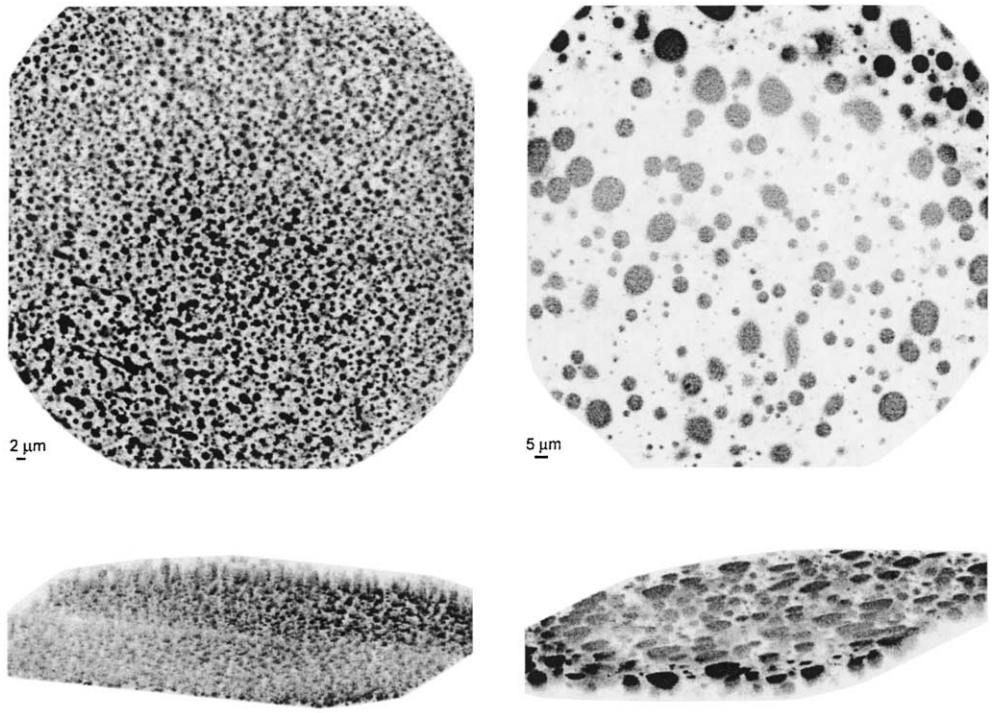
where M_n is the number average molecular weight of diblock copolymer, ρ is the bulk diblock density, N_{av} is Avogadro's number, and λ is the thickness of a dense interfacial layer of block copolymer. The value for λ was rescaled by using the scaling of $\lambda \sim M_n^{2/3}$ [22] and $\lambda =$ 39.8 nm for deuterated PS–PMMA diblock copolymer (dPS-*b*-PMMA) with $M_n = 100,900$ g/mol [23]. λ was 16.9 nm for a (12,800-*b*-15,000) g/mol PS–PMMA block copolymer. This gave a value of 0.18 chain/nm^2 for Σ_{max}. The fact that the experimental surface coverage ($\Sigma =$ 0.22 chain/nm^2) is similar to the maximum surface coverage ($\Sigma_{max} = 0.18$ chain/nm^2) supports that the interface has been saturated with diblock copolymers.

2.3. Imaging of polymer blends by laser confocal fluorescence microscopy

NBD group labeled PMMA-PA **9b** was subjected to the same reactive polymer blending conditions [PS/PMMA (70:30) + 10% PS-NH$_2$/8% NBD-PMMA-PA, MiniMAX, 180 °C, 320 rpm]. The blend sample was collected at 10 min (~5 mg), melted between two cover glasses and the morphology was investigated by laser confocal microscopy (Fig. 6(a)). It was observed that the PMMA particles were dispersed in the PS matrix in submicron sizes under these conditions.

One of the nice features of laser confocal microscopy is that one can get depth profiles of the sample due to the fact that only light from the focal plane reaches the detector in this technique. Each two-dimensional (2D) image from each depth profile can be collected and reconstructed to give a 3D image. The 3D image of this blend sample is shown under the top view image in Fig. 6(a). It is rather blurred due to the small particles whose sizes are comparable or smaller than the inherent depth resolution (~0.5 μm) of this technique. In addition, fluorescence intensity decrease along the depth was observed due to photobleaching of the fluorescent dye because multiple screening was required to get 3D images.

In order to obtain a larger particle size, another diluted reactive blending sample at a lower concentration [PS/PMMA (70:30) + 4% PS-NH$_2$/4% NBD-PMMA-PA, MiniMAX, 180 °C, 320 rpm] was prepared in the same way. A sample was collected after 20 min, annealed at 200 °C for 5 h, and its morphology was checked (Fig. 6(b)). Now the particle sizes are much larger (0.5–12 μm) than those in the case of 8% NBD-PMMA-PA diluted blend, larger than the resolution limit of confocal laser microscopy.



(a) 10% PS-NH_2/8% NBD-PMMA-PA, after 10 min. (b) 4% PS-NH_2/4% NBD-PMMA-PA, after 20 min.

Fig. 6. Laser confocal microscopy images of PS/PMMA (70:30) blends (180 °C, MiniMAX) with diluted reactive polymers. (a) 10% PS-NH_2/8% NBD-PMMA-PA **9b**, after 10 min, (b) 4% PS-NH_2/4% NBD-PMMA-PA **9b**, after 20 min. Black domains represent the PMMA phase (30%) made visible by the fluorescent reactive NBD-PMMA-PA **9b**.

3. Experimental

3.1. Materials

Methylene chloride was dried by passing through a basic alumina column under inert atmosphere. THF was distilled from sodium-benzophenone. Methanol was used as received. Methyl methacrylate and diphenyl ether were purified by filtration through basic alumina (Brockmann I, Aldrich) prior to use. 9-Anthracenemethanol, 4,4′-dinonyl-2,2′-bipyridine, CuBr (99.999%) and NBD chloride were purchased from Aldrich and used without any further purification. DTBP initiator **7** was synthesized as described in Ref. [7]. Non-functional polystyrene and poly(methyl methacrylate) were anionically synthesized. Polystyrene-amine was prepared by Jeffrey J. Cernohous by anionic polymerization. If not specified, all the chemicals were purchased from Aldrich and used as received.

3.2. Polymer characterization

Polymer molecular weights were determined using a Waters GPC system equipped with a Waters 590 HPLC pump. a Waters 717 plus autosampler, three Phenogel columns (ID 7.8 mm; 5 μm particle size; 500, 10^3, and 10^4 Å pore sizes), and three detectors (UV (Spectra-Physics), RI (Waters 410), and fluorescence (Hitachi F1050)). The fluorescence detector was set at 358 nm for excitation and 405 nm for emission wavelength for anthracene-labeled polymers, and at 466 nm for excitation and 539 nm for emission for NBD-labeled polymers. The bandwidth of the fluorescence detector was fixed at 15 nm. The dimensions of the flow cell for the fluorescence detector were 1.3 mm × 1.3 mm × 12 mm (12 μl). Ten standard polystyrenes were used for the calibration: 380; 156; 96.0; 49.9; 22.0; 11.6; 5.05; 2.95; 1.32 and 0.58 × 10^3 g/mol. The GPC was run at ambient temperature using THF as the eluent. GPC samples were prepared by dissolving 1 mg of polymer per 1 ml of THF, and 100 μl of the solution was injected for each run. Amine functionalized polymers were pretreated with phenyl isocyanate (~5 μl of phenyl isocyanate for 1 ml of THF solution followed by 1 h standing at room temperature) prior to injection in order to prevent adsorption of amine functional groups to the column stationary phase. In the case of fluorescent polymers, higher dilution (1 μg–0.1 mg of polymer per 1 ml of THF) was required to avoid detector saturation. ^{1}H NMR spectra were recorded on either a Varian 500 or 300 MHz spectrometer.

3.3. Laser confocal fluorescence microscopy

Polymer samples (~5 mg) were mounted on a glass cover slide (2 cm × 2 cm) while heating the slide on a hot plate at 180 °C. As soon as the polymer melted it was

covered with another glass slide and pressed until the polymer layer thickness is ca. 10–20 μm. Images were scanned at room temperature using an epifluorescence microscope (Nikon Diaphot) linked to the MultiProbe 2000 confocal scanning laser system. Samples were excited with the 488 nm line of an argon ion laser. A 540 DF 30 (Molecular Dynamics) filter was used for filtering emitted light at 540 nm. Depth resolution for this particular excitation wavelength was estimated to be ~0.5 μm. Three-dimensional images were obtained using Image Space software, version 3.1 (Molecular Dynamics).

3.4. Particle size analyzer

A low angle laser light scattering particle size analyzer (LS232, Coulter) was used. The PS matrix in PMMA/PS blend samples (~15 mg) was selectively dissolved in cyclohexane (~5 ml) and diluted further with ~150 ml of cyclohexane.

3.5. Synthesis of (9-anthryl)methyl 2-methyl-2-propenoate (**2**)

9-Anthracenemethanol (**1**, 500 mg, 2.40 mmol), 4-dimethylaminopyridine (DMAP, ~2 mg), and a stir bar were placed in a culture tube (25 ml). After capping the tube with an open-top screw cap and a Teflon lined silicon rubber septum, dry methylene chloride (5 ml), pyridine (284 mg, 3.60 mmol), and toluene were sequentially added. After cooling the tube in a water bath, methacryloyl chloride (276 mg, 2.64 mmol) was added dropwise via syringe. After complete addition the suspension turned to a homogeneous yellow solution. It was allowed to stir for 30 min. The reaction mixture was transferred to a round bottom flask and most of the solvent was removed by rotary evaporation. The residue was loaded on a silica gel column and eluted with hexanes/EtOAc (3:1) to fractionate the product **2**. After concentration of the fractions containing the product, a white solid **2** was obtained (574 mg, 87%).

^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.53 (s, 1H, anth-H_{10}), 8.38 (d, 2H, $J = 9.0$ Hz, anth-$H_{1,8}$), 8.05 (d, 2H, $J = 8.0$ Hz, anth-$H_{4,5}$), 7.58 (ddd, 2H, $J = 9.0$, 6.0 and 1.0 Hz, anth-$H_{2,7}$), 7.50 (t, 2H, $J = 8.0$ Hz, anth-$H_{3,6}$), 6.23 (s, 2H, CH_2O), 6.06 (s, 1H, CH_tH$_c$=C), 5.51 (t, 1H, $J = 1.5$ Hz, CH$_t$H$_c$=C), and 1.92 (s, 3H, CH_3).

3.6. Synthesis of 6-(methylamino)-hexan-1-ol (**4**)

A mixture of $MeNH_2$ (40% aqueous solution, 30 g, 0.397 mol), 6-chloro-1-hexanol (10.6 g, 77.6 mmol), and tetrabutyl ammonium iodide (TBAI, 1 g, 2.7 mmol) was heated at 70 °C for 36 h. After cooling most water was removed by rotary evaporation and 10% NaOH (~15 ml) was added. The mixture was extracted with ether (3 ×). The combined organic layers were washed with brine, dried over Na_2SO_4, filtered. The filtrate was concentrated and the residue was distilled under vacuum (~1 mmHg). The fraction collected at 87 °C (head temperature) provided the desired 6-(methylamino)-hexan-1-ol (**4**) (2.5 g, 25% yield) as a colorless oil.

^{1}H NMR ($CDCl_3$, 300 MHz): δ 3.58 (t, 2H, $J = 6.6$ Hz, CH_2OH), 2.53 (t, 2H, $J = 7.2$ Hz, CH_2N), 2.39 (s, 3H, NCH_3), 2.10 (br, 1H, NH), and 1.62–1.30 (m, 8H, $(CH_2)_4$).

^{13}C NMR ($CDCl_3$, 75 MHz): δ 62.30, 51.92, 36.38, 32.68, 29.67, 26.98, and 25.63.

3.7. Synthesis of 4-[N-methyl-N-(6-hydroxyhexyl)] amino-7-nitrobenz-2-oxa-1,3-diazole (**5**)

To a suspension of NBD chloride (**3**, 500 mg, 2.51 mmol) and K_2CO_3 (693 mg, 5.02 mmol) in CH_3CN (5 ml) was dropwise added 6-(*N*-methylamino)-hexan-l-ol (**4**, 345 mg, 2.63 mmol) at 0 °C. After stirring overnight 10% NaOH solution (10 ml) was added and the mixture was extracted with CH_2Cl_2 (3 ×). The combined organic layer was washed with brine, dried over Na_2SO_4, filtered and the residue was purified by flash column chromatography (Hex/EtOAc = 1:3 + 8% MeOH) to give pure product **5** (592 mg, 80%) as a dark orange solid.

TLC: $R_f = 0.55$ (1:3 Hex/EtOAc + MeOH).

^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.43 (d, 1H, $J = 9.0$ Hz, ArH), 6.09 (d, 1H, $J = 9.0$ Hz, ArH), 4.07 (br s, 2H, CH_3NCH_2), 3.67 (t, 2H, $J = 6.3$ Hz, CH_2OH, 3.49 (br s, 3H, CH_3N), 1.79 (m, 2H, CH_2CH$_2$OH), 1.60 (m, 2H, NCH$_2$CH_2), and 1.46 (m, 4H, $(CH_2)_2$).

^{13}C NMR ($CDCl_3$, 125 MHz): δ 145.43, 144.70, 144.31, 135.44, 135.40, 121.44, 101.07, 100.96, 62.48, 55.92 (br), 32.37, 27.47 (br), 26.35, and 25.37.

IR (neat): 3379 (br, m, OH), 2932 (m), 2859 (m), 1610 (m), 1563 (s), 1557(s), 1553 (s), 1535 (m), 1365 (w), 1282 (s), 1212 (m), 1103 (w), 1036 (w), 1000 (w), 915 (w), 804 (w), and 739 (w) cm^{-1}.

GC/LRMS (EI): *m/z* 294 (M^+, 9), 277 (2), 217 (3), 208 (12), 207 (100), 177 (6), 161 (4), 131 (36), 117 (3), 70 (3), 57 (3), and 55 (9).

3.8. Synthesis of 2-[methyl(7-nitro-2,1,3-benzoxadiazol-4-yl)amino]hexyl 2-methyl-2-propenoate (**6**)

To a solution of alcohol **5** (121 mg, 0.411 mmol) and DMAP (1 mg) in dry CH_2Cl_2 (3 ml) was added pyridine (81 mg, 1.0 mmol) and methacryloyl chloride (64 mg, 0.61 mmol) at 0 °C. The resulting solution was allowed to stir for 1 h and quenched by adding three drops of water. The mixture was loaded on a silica gel column and eluted with Hex/EtOAc (1:3 + 8% MeOH). Collection of the orange colored band and concentration gave the methacrylate **6** (134 mg, 92%) as an orange colored gum.

TLC: $R_f = 0.70$ (1:3 Hex/EtOAc + MeOH).

^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.39 (d, 1H, $J = 9.5$ Hz, ArH), 6.08 (dq, 1H, $J = 1.5$ and 1.0 Hz, C=CH$_{trans}$), 6.07 (d, 1H, $J = 9.5$ Hz, ArH), 5.55 (dq, $J = 1.5$ and 1.5 Hz,

C=CH_{cis}), 4.15 (t, 2H, $J = 6.0$ Hz, CH_2OC=O), 4.07 (br s, 2H, CH_3NCH_2), 3.47 (br s, 3H, CH_3N), 1.93 (s, 3H, O=CCCH_3), 1.80 (m, 2H, CH_2CH_2O), 1.70 (m, 2H, NCH_2CH_2), and 1.46 (m, 4H, $(CH_2)_2$).

^{13}C NMR ($CDCl_3$, 125 MHz): δ 167.45, 145.34, 144.79, 144.40, 136.37, 135.35, 125.33, 125.28, 122.04, 100.98, 100.90, 64.37, 55.86 (br), 41.35 (br), 28.44, 27.60 (br), 26.27, and 25.70.

IR (neat): 3106 (w), 2938 (m), 2861 (w), 1716 (s), 1636 (w), 1611 (m), 1551 (m), 1535 (m), 1497 (m), 1424 (m), 1364 (w), 1288 (vs), 1211 (s), 1167 (s), 1095 (m), 1035 (w), 1000 (w), 928 (w), 801 (w), and 721 (w) cm^{-1}.

GC/LRMS (EI): *m/z* 362 (M^+, 4), 332 (2), 316 (24), 262 (4), 246 (3), 208 (11), 207 (100), 191 (2), 186 (2), 177 (8), 161 (3), 147 (2), 131 (31), 104 (2), 86 (4), 77 (2), 73 (2), 70 (5), 69 (14), 61 (5), 57 (13), 56 (9), and 55 (6).

3.9. Synthesis of anth-PMMA-DTBP (*8a*)

CuBr (10.9 mg, 0.076 mmol), 4,4′-dinonyl-2,2′-bipyridine (62.1 mg, 0.152 mmol), and a stir bar were placed in a pyrex culture tube. After capping the tube with an open-top screw cap and a Teflon lined silicon rubber septum, it was evacuated and back-filled with argon (3 ×). DTBP initiator **7** (73.5 mg, 0.151 mmol) and 9-anthracenylmethyl methacrylate (**2**, 83.4 mg, 0.30 mmol) were dissolved in inhibitor free methyl methacrylate (3.02 g, 30.2 mmol) and diphenyl ether (3.0 g) in a separate round bottom flask (10 ml). The flask was capped with a rubber septum and the mixture was sparged with argon through a needle for 15 min while venting with an extra needle, to remove any oxygen present. The monomer–initiator mixture was then transferred to the culture tube via a syringe through the septum, and the resulting mixture was heated at 90 °C for 11 h. The solution kept a dark brown color and became viscous during the reaction. The tube was removed from the oil bath and cooled in a water bath. An aliquot of the mixture (~10 mg) was taken and checked by ^{1}H NMR spectroscopy to determine the monomer conversion. It was determined to be 52% by comparing the polymer backbone at δ 3.61 (br s) and monomer peak at 3.70 (s). The mixture was then diluted with 20 ml of THF and filtered through a short alumina column (~5 cm). The column was washed with THF three times (15 ml × 3). The resulting colorless filtrate was dripped into hexanes (300 ml) to precipitate the polymer. Precipitation was repeated three times. The white precipitate was filtered and dried under vacuum to provide white polymer **8a** (0.97 g, 32%). Calculated $M_n = 10,400$ g/mol

GPC: $M_w = 15{,}800$ g/mol, $M_n = 12{,}800$ g/mol, PDI = 1.24.

^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.54 (s, 1H, anth-H_{10}), 8.43–8.30 (br m, 2H, anth-$H_{1,8}$), 8.06 (d, 2H, $J = 8.0$ Hz, anth-$H_{4,5}$), 7.60 (m, 2H, anth-$H_{2,7}$), 7.59 (d, 1H, DTBP-Ar*H*), 7.53 (br s, 2H, anth-$H_{3,6}$), 7.41 (s, 1H, DTBP-Ar*H*), 7.16 (s, 1H, DTBP-Ar*H*), 6.23–5.97 (br, 2H, 9-anth-CH_2O) 4.03 (m, 2H, DTBP-CH_2OC=O), 2.73 (t, 2H, DTBP-ArCH_2), 1.65 (s, 9H, *t*-Bu), and 1.64 (s, 9H, *t*-Bu).

3.10. Synthesis of anth-PMMA-PA (*9a*)

Anth-PMMA-DTBP **8a** (0.5 g) was placed in a Schlenk flask. After capping the flask, it was connected to a vacuum line (~0.5 mm Hg) and heated in an oil bath at 210 °C for 1 h. The polymer melted and generated bubbles (isobutene) during the pyrolysis. After heating the stopcock of the flask was closed and the flask was removed from the oil bath. The flask was immediately cooled in a cold water bath followed by cooling in a liquid nitrogen bath. It was warmed to room temperature in a water bath. This cooling–warming procedure was repeated two or three times. After this, the polymer could be easily detached from the flask and broken by an awl. Light brown colored polymer **9a** (468 mg, 94%) was recovered.

3.11. Synthesis of NBD-PMMA-DTBP (*8b*)

CuBr (18 mg, 0.126 mmol), 4,4′-dinonyl-2,2′-bipyridine (103 mg, 0.249 mmol), DTBP initiator **7** (121 mg, 0.249 mmol), NBD methacrylate (**6**, 91 mg, 0.25 mmol), methyl methacrylate (5.3 g, 53 mmol), and diphenyl ether (5 ml) were used for the synthesis of this polymer, following the same procedures for polymer **8a**. The reaction was allowed to run for 21 h. ^{1}H NMR spectroscopy of an aliquot (~10 mg) after this reaction time indicated that 74% of the monomer was consumed. After the routine procedure of polymer purification as described in the procedure for polymer **8a**, yellow polymer **8b** (3.1 g, 58%) was obtained. Calculated $M_n = 15,800$ g/mol.

GPC: $M_w = 20{,}000$ g/mol, $M_n = 16{,}600$ g/mol, PDI = 1.21.

^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.48 (d, 1/2H, NBD-H_6), 7.59 (d, 1H, DTBP-Ar*H*), 7.41 (s, 1H, DTBP-Ar*H*), 7.16 (s, 1H, DTBP-Ar*H*), 6.15 (br, 1/2H, NBD-H_5), 4.03 (m, 2H, DTBP-CH_2OC=O), 3.96 (m, 2/2H, NBD-CH_2O), 2.73 (t, 2H, DTBP-ArCH_2), 1.65 (s, 9H, *t*-Bu), and 1.64 (s, 9H, *t*-Bu).

3.12. Synthesis of NBD-PMMA-PA (*9b*)

NBD-PMMA-DTBP **8b** (0.8 g) was subjected to the pyrolysis conditions described in the synthesis of polymer **9a**. Orange colored polymer **9b** (770 mg, 96%) was collected after this procedure.

4. Conclusions

Two fluorescently labeled PA functionalized PMMAs **9a** and **9b** have been prepared by ATRP and subsequent pyrolysis with high functionality. Anthracene and NBD groups have been used as the fluorophores for polymer **9a**

and **9b**, respectively. Both polymers could be detected with high selectivity and sensitivity by GPC with fluorescence detection. Diluted reactive blends were performed with these reactive polymers and the conversion could be accurately measured by fluorescence GPC. Morphologies of the reactive blends employing NBD-PMMA-PA **9b** could be visualized by laser confocal fluorescence microscopy, which provides 3D images of the blends.

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