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Synthesis of ω-End Group Functionalized Poly(methyl methacrylate)s via RAFT Polymerization

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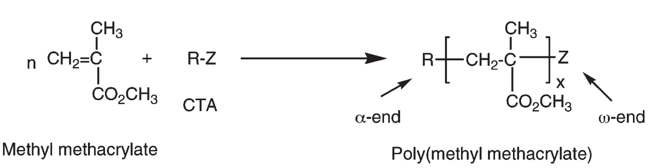
ABSTRACT: "Living" poly(methyl methacrylate) (PMMA), prepared by the RAFT technique, reacted with maleic anhydride to give succinic anhydride-terminated PMMA (SA−PMMA) in very high yield. The ω-terminal anhydride residues react in high yields with primary alcohols, primary amines and aromatic amines. As examples, SA−PMMA reacted with 1*H*,1*H*,2*H*,2*H*-perfluorodecylamine to give a polymer containing 5.78% of fluorine; with Disperse Orange 3 to give a dye-labeled PMMA; with 9-hydroxymethylanthracene to give a fluorescently labeled PMMA; with norephedrine to give a polymer with a biologically active end group; and with 4,4′-diaminophenymethane to give amine-ended PMMA. The latter reacted smoothly with fluorescein isocyanate to give a fluorescently labeled PMMA. In these examples the fraction of polymer chains functionalized were in the range 75−95%. Allowing for the fact the starting PMMAs were up to 96% "living", these loadings correspond to functionalization yields, for the anhydride addition plus the reaction with the nucleophiles, of 81−99%.

Introduction

Reversible addition−fragmentation chain transfer polymerization (RAFT) is a versatile radical polymerization technique that in many cases enables the preparation of polymers with predetermined molecular weights and narrow molecular weight distributions.[1,2] Control is achieved by the use of a chain transfer agent (CTA): see Scheme 1. A wide range of monomers have been successfully polymerized using this technique both in organic solvents and in aqueous conditions.[3−9]

Another valuable feature of RAFT is that it allows the synthesis of telechelic polymers with a variety of α- and ω-end groups.[10] The products may be used, for example, as building blocks for supramolecular systems,[11] or, via the coupling of fluorescent dyes, drugs, peptides, proteins, or targeting moieties, as novel polymeric conjugates.[12−17] Functional α-end groups can be introduced by the incorporation of appropriate R groups in the CTA: see Scheme 1.[16−22] This approach has afforded polymers with α-end groups that include *N*-alkylmorpholine,[18] galactose,[18] biotin,[18] primary alcohol, primary amine,[19] azide,[20] phthalimido,[22] or arylboronic acid residues.[23] The introduction of functional ω-end groups is usually less straightforward and accordingly the range of functionalities that have been introduced at the ω-end is smaller. One synthetic approach is to use functionalized Z groups in the CTA: see Scheme 1. Examples include a novel trithiocarbonate CTA linked, via a short spacer, to a pyridyl disulfide group. Postpolymerization the latter were directly exchanged with thiol-bearing molecules.[24] The disulfide linkages formed are, however, only of moderate chemical stability. In a different approach the sulfur-containing residues remaining from CTAs based on xanthates, dithioesters, dithiocarbamates, and trithiocarbonates can be converted into ω-terminal thiol groups by reaction with either primary amines,[10,25−27] or sodium borohydride.[10,12,13,28] If required the thiol groups can then take part in Michael additions with acrylates[29] or maleimides[30] or additions to isocyanates[31] to give a range of ω-end group functionalities. In some cases both the thiol-forming reaction and the Michael addition have been carried out in one practical step.[32−34] Finally, ω-end group alcohol residues have been obtained by reacting the "living" chain end with oxygen.[35] "Living" chain ends have also been reacted successfully with fullerenes.[36]

Scheme 1. Example of RAFT Polymerization in the Presence of a Generalized Chain Transfer Reagent (CTA)



The work described in the present paper is concerned with another approach to introducing ω-end group functionalities. In this approach, following a RAFT polymerization, the "living" chain end is reacted with an olefin that will add to the chain end easily but will not propagate easily. In the present project "living" poly(methyl methacrylate) (PMMA) is reacted with maleic anhydride.[37] This results in PMMA with reactive anhydride-containing ω−end groups. These can then be reacted with alcohols or amines to attach a wide range of desired functionalities. Related synthetic approaches have been reported before. Thus, Feng and Pan added maleic anhydride to the "living" end of polystyrene prepared using RAFT, and then, in a second RAFT

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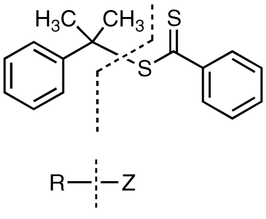
polymerization, they reacted the "living" product with methyl acrylate. Finally the anhydride linking group was reacted with an hydroxyl-terminated oligo(ethylene oxide) to give an ABC star copolymer.[38] More recently Stayton reacted the "living" end of RAFT-prepared methacrylate and acrylamide polymers with a series of N-substituted maleimides.[39] Similar approaches have been used with other types of "living" polymerization, for example, the addition of maleic anhydride to polystyrenes prepared by atom transfer radical polymerization (ATRP)[40] and the addition of 1,1-diarylethylenes in anionic polymerizations.[41]

Results and Discussion

The main aim of the present work was to develop a versatile method for preparing ω-functionalized PMMAs using RAFT. Subsequently the method might be used in combination with appropriate methods for α-end functionalization to give α,ω-end functionalized PMMAs that might have commercial applications.

Synthesis of "Living" PMMA Using RAFT. Bearing in mind potential applications, the initial target was the RAFT-controlled synthesis of PMMA that had a molecular weight of about 3500 g/mol corresponding to a degree of polymerization, DP, of about 35, a polydispersity index (PDI) of < 1.2 and with $> 95\%$ of the chains "living". Since PMMA has no aromatic protons, it was decided to use cumyl dithiobenzoate (CDB) (**1**) as the CTA, and also, where possible for the subsequent reactions of the anhydride end groups with nucleophiles, to use compounds that contain aromatic moieties. In this way the various reactions might be monitored relatively easily by analysis of the aromatic region of the ^{1}H NMR spectra. The CDB (**1**) was prepared by reacting phenylmagnesium bromide with carbon disulfide and then reacting the dithiobenzoic acid produced with α-methylstyrene.[42,43]



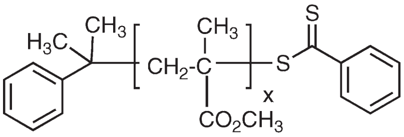
Cumyl dithiobenzoate (CDB) (**1**)

Initially the polymerization was carried out in toluene at 85 °C for 67 h (though a shorter period would almost certainly give similar results) with an initial methyl methacrylate concentration ([M$_0$]) of 4.0 mol/L. Calculation indicated that to obtain the desired DP the required initial mole ratio of methyl methacrylate to CDB ([CDB$_0$]) was 25:1.[44] Benzoyl peroxide (BPO) at an initial concentration ([BPO$_0$]) half that of the initial concentration of the CDB was used to initiate the polymerization. At the end of the reaction the product, polymer **2a**, was isolated by precipitating the reaction mixture into a large excess of methanol at 0−5 °C. As expected the product was a pink powder, so indicating the presence of dithiobenzoate groups. The molecular weights, and hence the PDI, were determined by size exclusion chromatography (SEC). The results are summarized in Table 1, entry 1. The fraction of chains that were "living" was determined by ^{1}H NMR spectroscopy. Thus, the cumyl groups showed characteristic signals at δ 7.0−7.2 while the dithiobenzoate groups showed signals at δ 7.2−7.8. It is evident that the molecular weight and PDI value of polymer **2a** were in the desired region, but that the percentage of "living" chains was too low.

Table 1. Synthesis of "Living" Poly(methyl methacrylate) 2a−2c Using RAFT

polymer	[MMA]$_0$ (mol/L)	[MMA]$_0$/ [CDB]$_0$	[CDB]$_0$/ [BPO]$_0$	convn[a] (%)	M_n[b] (g/mol)	PDI[b]	λ[c]
2a	4.0	25	2	60	3700	1.19	67
2b	2.0	37	10	55	3200	1.16	87
2c	3.0	37	10	48	3100	1.14	96

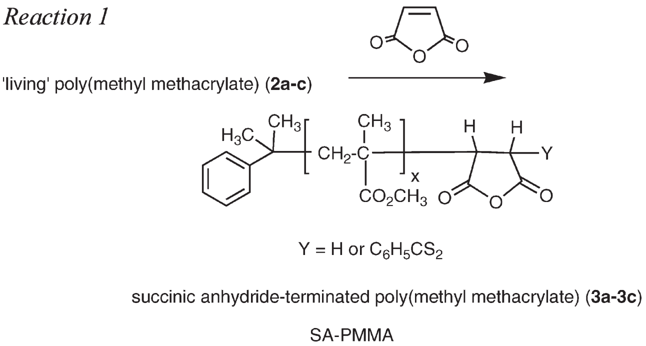
[a] Conversions determined gravimetrically. [b] M_n and PDI determined by SEC. [c] λ determined by ^{1}H NMR spectroscopy.



Two further batches of PMMA were prepared similarly, but with small modifications. To cut back on the usage of CDB, the amount used relative to the monomer was reduced. To reduce the viscosity of the reaction mixtures the initial monomer concentrations were also reduced, in one case to 2.0 mol/L in the other to 3.0 mol/L. Another important parameter is the radical flux. This can be optimized by adjusting the CDB to BPO molar ratio. Since a ratio of 10:1 is often optimal,[45] this ratio was used. The results are summarized in Table 1, entries 2 and 3. Both **2b** and **2c** were pink powders. Product **2b** had a satisfactory Mn, a PDI that was marginally better than that of polymer **2a**, and the percentage of "living" chains improved from 67% to 87%. The latter was probably due mainly to the change in the CDB to BPO ratio. While still not having the desired combination of properties this second batch of PMMA, **2b**, was nevertheless considered suitable for use in the model reactions described below. The third batch of PMMA, polymer **2c**, had a satisfactory Mn value, the best PDI, and the percentage of "living" chains had risen to 96%. The ^{1}H NMR spectrum of polymer **2c** is shown Figure 1. The FT-IR spectrum of the same polymer is shown in Figure 2a. This batch, therefore, had the desired properties and it was used for the more important end group modifications described below.

Addition of Maleic Anhydride to "Living" PMMA.

Reaction 1



The next step in the synthesis of ω-end group functionalized polymers was to react "living" polymers **2a−c** with maleic anhydride to give polymers **3a−c**: see Reaction 1. These products contain succinic anhydride moieties and are conveniently described as SA−PMMA. To achieve reaction 1 polymers **2a−c** in dioxane at 100 °C were separately treated with benzoyl peroxide (mole ratio of peroxide to "living" polymer: 1.0 to 0.33) and a 20-fold excess of maleic anhydride for 16 h. The products were isolated by precipitating the reaction mixtures into dry hexane. The products were pink powders. The results are summarized

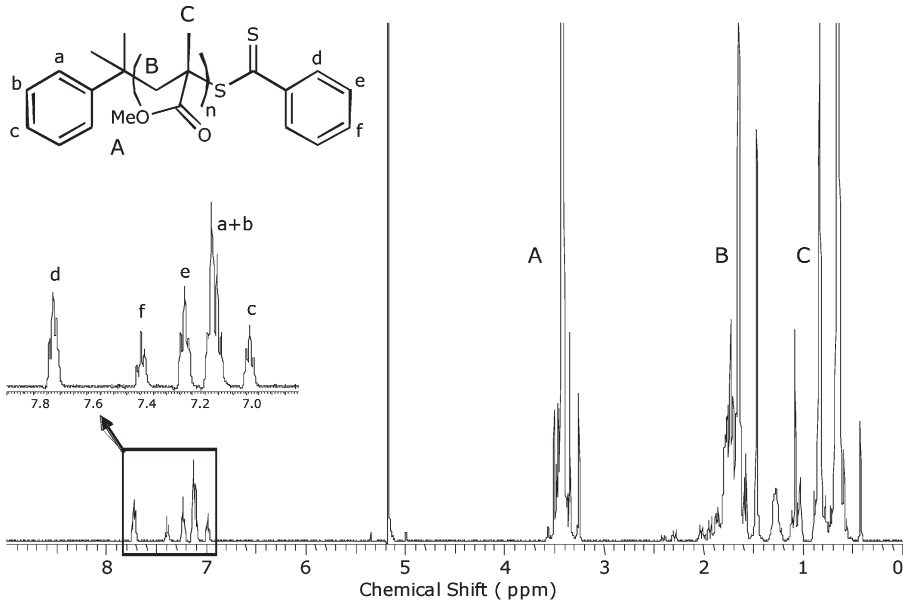


Figure 1. ^{1}H NMR spectrum (CD_2Cl_2, 500 MHz) of "living" PMMA **2c**. Inset shows the aromatic region with assignments.

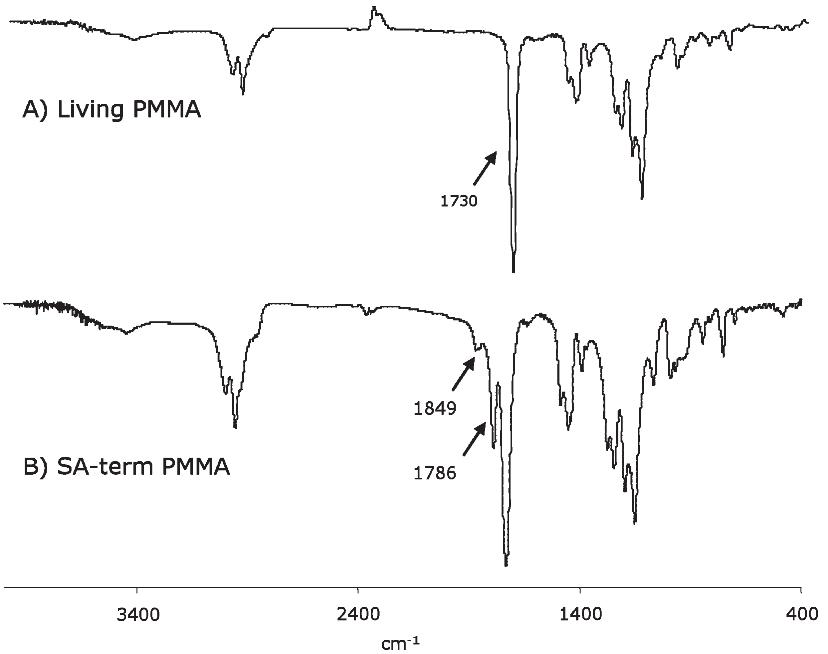


Figure 2. FT-IR spectra (KBr) of (A) "living" PMMA **2c** and (B) SA−PMMA **3c**.

Table 2. Experimental Conditions and Results for the Synthesis of SA-Term PMMAs 3a−c in Dioxane at 100 °C

polymer	concn **2a−c**[a] (mg/mL)	[MAh]$_0$/[**2a−c**]$_0$	[BPO]$_0$/[**2a−c**]$_0$	convn[b] (%)	M_n[c] (g/mol)	PDI[c]	λ[d]
3a	100	5	0.31	86	4200	1.25	n.a.
3b	400	20	0.31	91	3580	1.23	n.a.
3c	400	20	0.31	92	3700	1.21	55

[a] Starting materials for **3a** is PMMA **2a**, for **3b** is PMMA **2b**, and for **3c** is PMMA **2c**. [b] Conversions determined gravimetrically. [c] M_n and PDI determined by GPC. [d] λ determined by ^{1}H NMR spectroscopy.

in Table 2. The FT-IR spectra of the products, **3a−c**, showed carbonyl peaks at 1730 cm^{-1} due to the ester groups, and at, or near, 1786 and 1849 cm^{-1} due to the 5-membered ring anhydride groups.[46] The FT-IR spectra of starting polymer **2c** and product polymer **3c** are shown in Figure 2. The ^{1}H NMR spectra of polymers **3a−c** were similar. That of polymer **3c** is shown in Figure 3. The signals due to the succinic anhydride ring are expected to appear between δ 2 and 3 ppm. Unfortunately in all cases this region of the spectra showed just a broad signal so it was not possible to quantify the efficiency of the anhydride addition. However, the subsequent reactions, discussed below, of the anhydride residues gave the expected products with yields in the range 81−99%. This not only indicates that yields for Reaction 1 were at least this high, but also suggests that with most chains only one maleic anhydride unit was attached. It was not practical to use mass spectrometery to monitor Reaction 1 because the molecular weights of maleic anhydride and

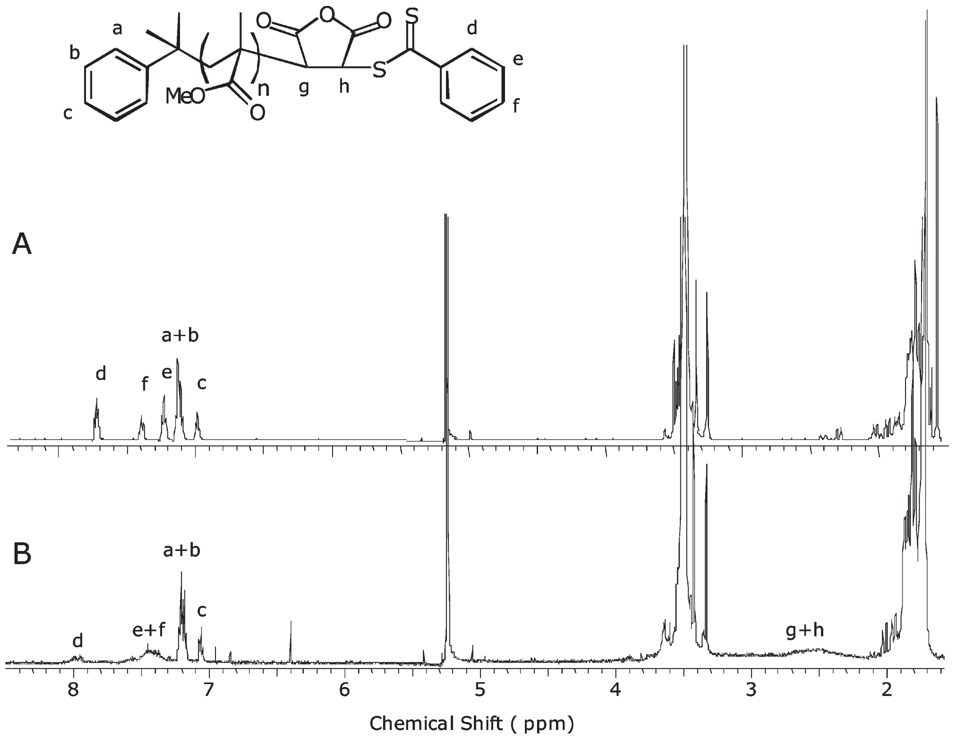
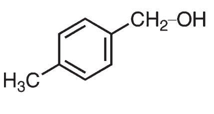


Figure 3. ^{1}H NMR spectrum (CD_2Cl_2, 500 MHz) from δ 1.5−8.5 ppm of (A) "living" PMMA **2c** and (B) SA−PMMA **3c**.

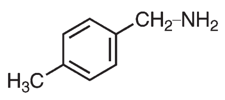
the polymer repeat unit are so similar (98.06 and 100.12, respectively).

The ^{1}H NMR spectrum of polymer **3c** showed that only 55% of the "living" chains of polymer **2c** retained the dithiobenzoate group: see Figure 3b. This was much lower than the yields obtained by Feng and Pan (ca. 95%) in their synthesis of the ABC star polymer.[38] In the present project this was, however, not a problem because, unlike Feng and Pan, it was not proposed to extend the chains by a further RAFT polymerization. It is, nevertheless, interesting to consider why the loss occurred. Feng and Pan carried out the addition of maleic anhydride to the "living" polystyrene chains very efficiently under milder conditions (in THF at 80 °C for 6 h) than we used.[38] It is likely that in the present work the dithiobenzoate groups were lost through thermal decomposition. Since the percentage addition of maleic anhydride was high, most or all of the decomposition must have occurred after the anhydride addition. He et al. studied the thermal decomposition of "living" ends and found that elimination is a major reaction.[47] In the present case this would be expected to result in the formation of terminal maleic anhydride residues. These could be detected by the presence of NMR signals at or near δ 6.70 ppm.[48] Also, after ring-opening to give substituted maleates, signals would be expected at or near δ 6.4−6.7 ppm.[49] However, no significant signals were found in the δ 6.0−7.0 ppm region of the spectra of either the SA−PMMA or the ring-opened products. It may be that the dithiobenzoate−polymer bond is simply cleaved homolytically and the terminal radical on the polymer then abstracts a hydrogen atom from the dioxane solvent. Thus, the end groups would be dithiobenzoate or hydrogen.

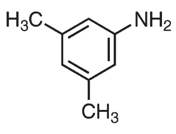
Model reactions of Succinic and 2-Methylsuccinic Anhydrides with Alcohols and Amines. 4-Methylbenzyl alcohol (**4**), 4-methylbenzyl amine (**5**), and 3,5-dimethylaniline (**6**) were selected as initial nucleophiles to react with the anhydride residues. Accordingly a series of model reactions were first carried out with succinic anhydride. These gave, after work up, the half ester acids or half amide acids. The main purpose of these model experiments was to determine the shifts of the methyl groups and aromatic proton signals in the ^{1}H NMR spectra, so assisting characterization of the products obtained by reacting these same nucleophiles with polymers **3a−c**. The analogous reactions were also carried out with 2-methylsuccinic anhydride in order to determine the effect of the methyl group on the regioselectivity. Full details of all these model reactions are given in the Supporting Information.



(**4**)



(**5**)



(**6**)

Aside from knowledge of the ^{1}H NMR shifts, the key points from these model reactions are as follows.

(i) The reaction with 4-methylbenzyl amine is, as expected, much faster than the reaction of 4-methylbenzyl alcohol, but at least two equivalents of the amine are needed as the carboxylic acid formed reacts with the amine to give a salt. This salt must subsequently be converted back to the acid during the work up.

(ii) The reaction with 3,5-dimethylaniline is also more rapid than with the alcohol but it does not form a salt with the carboxylic acid group generated.

(iii) With 2-methylsuccinic anhydride the nucleophiles react almost equally at both carbonyl groups, with just a slight preference for the less hindered one. Thus, with 4-methylbenzyl alcohol (**4**) the ratio was 52:48; with 4-methylbenzyl amine (**5**), 56:44; and with 3,5-dimethylaniline (**6**), 52:48. This suggests that with the anhydride-terminated polymers **3b** and **3c** comparable amounts of reaction would occur at both carbonyls. In the following formulas, for simplicity, only one of the two products is shown.

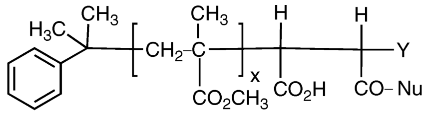
Table 3. Reactions of Anhydride-Terminated PMMA (3) with Various Nucleophiles

			reaction conditions[b]								
entry	SA−PMMA	nucleophile[a]	solvent	temp (°C)	time (h)	polymeric product	convn[c] (%)	$M_n \times 10^{-3}$ /PDI[d]	AFY[e] (%)	RFY[f] (%)	λ[g] (%)
1	**3b**	**4**	THF	66	16	**7**	73	3.22/1.38	75	86	19
2	**3b**	**5**	THF	66	16	**8**	66	3.22/1.28	84	97	0
3	**3b**	**6**	THF	66	16	**9**	74	3.39/1.35	78	90	n.a.
4	**3c**	**10**	THF	20	6[h]	**11**	60	4.90/1.22	94	98	0
5	**3c**	**13**	THF	66	16	**14**	84	4.75/1.24	94	98	n.a.
6	**3c**	**17**	THF	66	16	**18**	76	4.65/1.22	78	81	n.a
7	**3c**	**19**	THF	20	6	**20**	98	4.50/1.25	95	99	0
8	**3c**	**22**	THF	66	16	**23**	62	4.20/1.16	89	93	22

[a] Used in 20-fold excess, except where indicated otherwise. [b] THF = tetrahydrofuran. [c] Weight of product after several precipitations divided by weight of starting polymer. [d] Data obtained on reprecipitated product. [e] Absolute yield of functionalization over RAFT polymerization, maleic anhydride addition and reaction with the nucleophile. [f] Relative yield of functionalization, i.e., the fraction of anhydride residues that reacted with the nucleophile. [g] Fraction of chains that are living. [h] Nucleophile used in 10-fold excess.

Reactions of the Anhydride-Terminated Polymer 3b with the Model Nucleophiles. Polymer **3b** was reacted with nucleophiles **4**−**6** to establish suitable reaction conditions for use with the more complex functionalized nucleophiles. The reaction conditions used and details of the characterization of the products are summarized in Table 3.

A pink solution of polymer **3b** in THF was treated with a 20 equiv of 4-methylbenzyl alcohol (**4**) at 66 °C for 16 h: see Table 3, entry 1. The product was isolated by precipitation into hexane, and further purified by reprecipitation into hexane. The final polymer **7** was obtained as a pale pink powder. By comparing the signals in the ^{1}H NMR spectrum due to the 4-methylbenzyl at δ 7.1 ppm with those due to the terminal cumyl group, it is evident that 75% of the polymer chains had reacted. Since only 87% of the chains in the starting polymer **2b** were "living", this means the overall yield for the anhydride addition plus ring-opening is 86%. Only 19% of the chains were terminated with a dithiobenzoate group.



(**7**): Nu = 4-methylbenzyloxy; Y = dithiobenzoate or H

(**8**): Nu = 4-methylbenzylamino; Y = -SH or H

(**9**): Nu = 3,5-dimethylanilino; Y = dithiobenzoate or H

A pink colored solution of polymer **3b** in THF was treated with a 20 equiv of 4-methylbenzyl amine (**5**) at 66 °C for 16 h: see Table 3, entry 2. Almost immediately after the addition of the amine the color of the solution turned deep yellow. This corresponds to the reaction of the dithiobenzoate groups with the amine. This leaves a thiol group at the end of the polymer chain. At the end of the reaction period the reaction mixture was cooled to 20 °C then treated with hydrochloric acid. The neutralized product **8** was isolated by precipitation into hexane, and further purified by reprecipitation into hexane. The final polymer **8** was obtained as a white powder. By ^{1}H NMR spectroscopy, comparison with the signals due to the aromatic protons of the 4-methylbenzyl group at δ 7.10−7.28 ppm with those of the terminal cumyl group, it is evident that 84% of the polymer chains reacted: see Figure 4. Since only 87% of the chains in polymer **2b** were "living" and so available to react with maleic anhydride, 97% of these chains were converted into the half acid half amide **8**.

A pink solution of polymer **3b** in THF was treated with 20 equiv of 3,5-dimethylaniline (**6**) at 66 °C for 16 h: see Table 3, entry 3. The product was isolated by precipitation into hexane, and further purified by reprecipitation into hexane. The final polymer **9** was obtained as a very pale pink powder indicating that at least some polymer chains were still "living". By ^{1}H NMR spectroscopy, comparison of the signals at δ 6.83 and 6.47 ppm, due to the aromatic protons of the 3,5-dimethyl moiety, with those due to the cumyl group, it is evident that 78% of the polymer chains reacted with the nucleophile. Since only 87% of the chains in the starting polymer **2b** were "living", 90% of these were converted into the anilide.

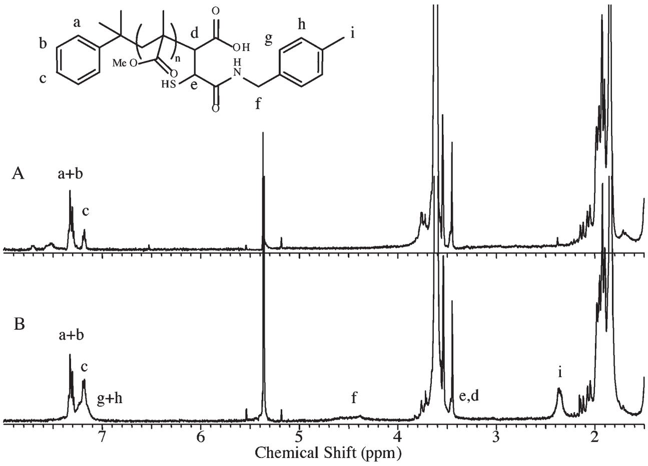


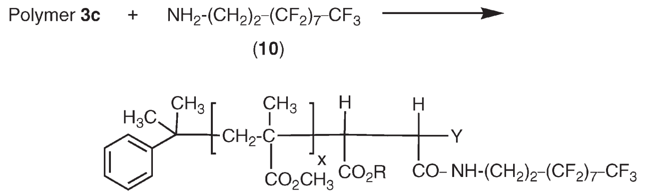
Figure 4. ^{1}H NMR spectra (CD_2Cl_2, 500 MHz) from δ 1.5−7.9 ppm of (A) SA−PMMA **3b** and (B) the product, polymer **8**, formed by reacting SA−PMMA **3b** with 4-methylbenzylamine. Selected signals are assigned.

The above results show that polymer **2b** reacts with maleic anhydride, Reaction 1, to give polymer **3b**, and that the three nucleophiles **7**−**9** then react with the anhydride end groups in polymer **3b** in overall yields of 86−97%. Each of the model reactions was carried out overnight, but satisfactory yields could probably be obtained with shorter reaction times. The Supporting Information includes the SEC traces of polymeric products **7**−**9**. These were very similar and there is, for example, no evidence that the thiol-ended polymer **8**, reacted further.

Reaction of the Anhydride-Terminated Polymer 3c with 1*H*,1*H*,2*H*,2*H*-perfluorodecylamine (10). Block copolymers may contain hydrophilic, lipophilic, and/or fluorophilic blocks.[50] Those which have a significant fluorocarbon block are of interest, for example, as interfacial agents. Thus, suitable PMMA-fluorocarbon blocks may be miscible with PMMA, but tend to migrate to the surface of the blend so modifying the surface properties of the PMMA. In the present project, the aim was to react the

SA−PMMA **3c** with 1*H*,1*H*,2*H*,2*H*-perfluorodecylamine (**10**): see Reaction 2.

Reaction 2



(**11**): R = H; Y = SH or H

(**12**): R = CH_3;Y = SH or H

Polymer **3c**, with terminal anhydride groups, in THF was treated with a 10-fold excess of 1*H*,1*H*,2*H*,2*H*-perfluorodecylamine (**10**) at 20 °C for 6 h: see Table 3, entry 4. As expected, immediately on addition of the amine the color of the solution changed from pink to deep yellow. After the reaction, the mixture was acidified with hydrochloric acid and the product isolated by precipitation into hexane. This gave polymer **11** as a white powder.

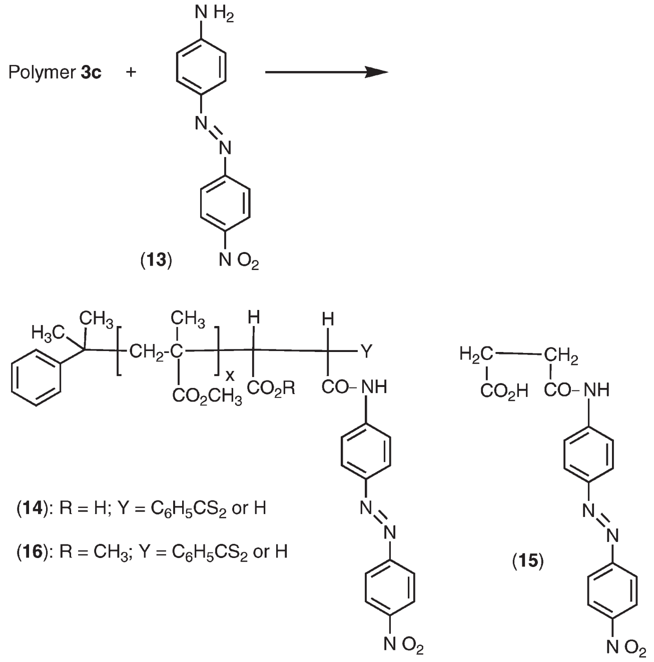
By elemental analysis, polymer **11** contained 5.78% of fluorine. Assuming a molecular weight of 3100 for polymer **2c**, the precursor of **3c**, this corresponds to 93% of the repeat units in **11** having a fluorinated ω-end group. The success of Reaction 2 was supported by FT-IR spectroscopy. Thus, there were no bands present at 1849 and 1786 cm^{-1}, due to a cyclic anhydride, but there was a broad band at 1232−1145 cm^{-1} attributable to C−F bonds.[46] The ^1H NMR spectrum, based on the relative intensities of the signals at δ 2.35 ppm due to the methylene group next to the nitrogen of the fluorinated nucleophile relative to the signals due to the cumyl end group, indicated an absolute functionalization yield of 94%. This agrees well with the yield calculated from the elemental analysis. Since in polymer **2c** 96% of the chains were "living", the functionalization yield of 94% corresponds to an overall yield for Reactions 1 and 2 together of 98%. As expected the ^1H NMR spectrum showed no signals due to dithiobenzoate moieties. Further evidence for the success of Reaction 2 came from the ^{19}F NMR spectrum of polymer **11**, which was very similar to that of the amine **10**.

For some applications the presence of the terminal carboxylic acid group might be a problem. Carboxylic acid groups react very rapidly and cleanly with ethereal diazomethane to give methyl esters.[51] Accordingly polymer **11** was treated with ethereal diazomethane to give polymer **12**. Caution! Note that diazomethane is both poisonous and explosive. Unfortunately it was not possible to prove that methylation occurred as the expected spectroscopic changes were minimal.

In summary, the above results indicate the successful preparation of ω-end fluorinated polymer **11** with a functionalization yield of 98% and a product with a fluorine content of 5.78%. Lebreton and co-workers have reported the synthesis and use of a series of fluorinated chain transfer agents for the RAFT polymerization of styrene, MMA, ethyl acrylate and 1,3-butadiene.[52] The products contained 1−17% of fluorine at the α-end. Perrier et al. have described the use of fluorinated initiators and monomers to synthesize polymers by ATRP that have fluorine contents in the range 3−5%.[53]

Reaction of the Anhydride-Terminated Polymer 3c with Disperse Orange 3 (13). Polymers labeled with dyes or fluorescent moieties have applications in, for example, biological systems. Dye labeled polymers have the advantage that their location can be monitored using standard optical equipment, such as simple microscopes. In the present project, the aim was to react SA−PMMA **3c** with the azo dye Disperse Orange 3 (**13**): see Reaction 3.

Reaction 3



(**14**): R = H; Y = $C_6H_5CS_2$ or H

(**16**): R = CH_3; Y = $C_6H_5CS_2$ or H

SA−PMMA **3c** in THF was treated with Disperse Orange 3 (**13**) at 66 °C for 16 h: see Table 3, entry 5. After the reaction, the product was isolated by precipitation into hexane. This gave polymer **14** as a chocolate-brown powder.

By elemental analysis polymer **14** contained 0.89% of nitrogen. Assuming a molecular weight of 3100 for polymer **2c**, this corresponds to 93% of the repeat units in **12** having an azo dye end group. The success of Reaction 3 was supported by FT-IR spectroscopy in that there were no bands present at 1849 and 1786 cm^{-1}, due to a cyclic anhydride.[46] The ^1H NMR spectrum indicated, by integration of the signal at δ 8.3 ppm due to aromatic protons *ortho* to the nitro group in the dye moiety relative to those due to the cumyl end group, an absolute functionalization yield of 94%. This is in excellent agreement with the value calculated from the elemental analysis. Since in polymer **2c** 96% of the chains were "living", the overall yield for Reactions 1 and 3 was 98%. Because of overlaps of signals, it was not possible to assess whether or not the polymer was still "living". However, it was expected to be so in the light of the results obtained from the experiments with 3,5-dimethylaniline (**7**) discussed above. To assist in understanding the UV−vis spectrum of polymer **14**, model compound **15** was prepared by reacting Disperse Orange 3 (**13**) with succinic anhydride: see the Supporting Information. As expected the UV−vis spectrum of polymer **14** is very similar to that of compound **15**. Treatment of polymer **14** with diazomethane gave polymer **16**.

Reaction of the Anhydride-Terminated Polymer 3c with 9-Hydroxymethylanthracene (17). Fluorescent probes are more sensitive than dye-labeled probes. Polymers containing anthracene units are attractive probes for fluorescence-based imaging techniques, such as confocal laser microscopy,[54] and the studies of the miscibility in polymer blends.[55,56] In the

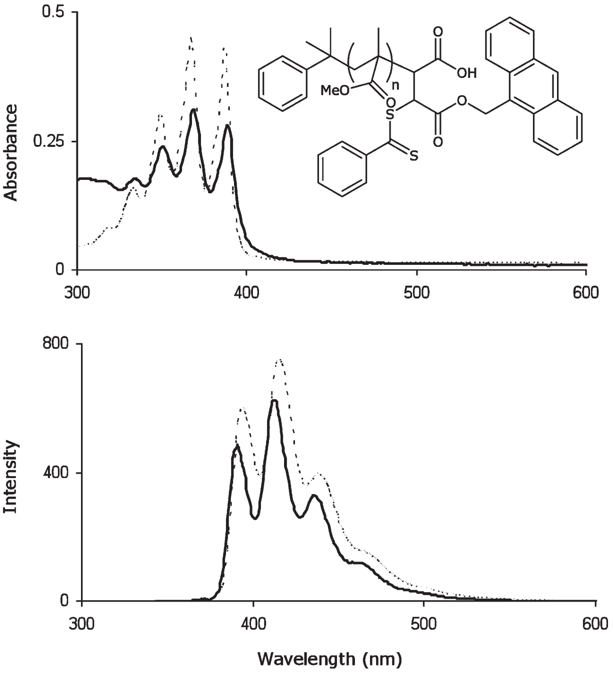
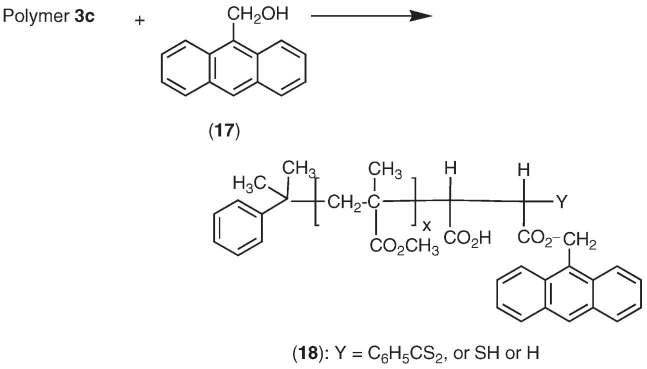


Figure 5. (A) UV−vis spectra of 9-hydroxymethylanthracene (**17**) (dashed line) and polymer **18** (solid line) for solutions in dioxane. (B) Fluorescence spectra for the same compounds as solutions in dichloromethane.

present work the aim was to prepare, using Reaction 4, PMMA with anthracene units in the ω-end group.

Reaction 4



A solution of polymer **3c** in THF was treated with 9-hydroxymethylanthracene (**17**) at 66 °C for 16 h: see Table 3, entry 6. After the reaction the product was isolated by precipitation into hexane. This gave polymer **18** as a pale cream powder.

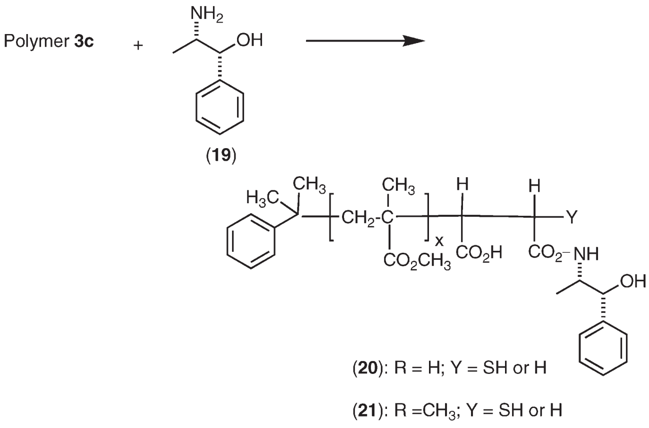
^{1}H NMR spectroscopic analysis showed, by comparing the signal at δ 6.1 ppm due to the benzylic protons next to the anthracene nucleus with those due to the aromatic protons of the cumyl end group, an absolute functionalization yield of 78%. Given that in polymer **2c** 96% of the chains were "living", the overall yield for Reactions 1 and 4 was 81%. Because of overlaps of signals, it was not possible to assess the extent to which the polymer was still "living".

The UV−vis and fluorescence spectra of compound **17** and polymer **18** in dioxane are shown in Figure 5. The UV−vis spectrum of polymer **18** is essentially identical to that of compound **17** in both the shape and the positions of the maxima (304, 334, 350, 369, and 389 nm) so confirming that anthracene moieties are attached to the polymer. The fluorescence maxima of polymer **18** in dichloromethane are at 391, 414, and 437 nm. These are slightly red-shifted relative to those of compound **17**, which has maxima at 395, 416, and 441 nm. This suggests that the environment of the chromophore is slightly modified by being in the polymer. The fluorescence quantum yield for polymer **18** at 20 °C in dichloromethane was determined using anthracene in ethanol as a standard (ϕ_F = 0.27). It was found that for polymer **18**, ϕ_F = 0.11. This lower value can be attributed to fluorescence quenching by residual dithiobenzoate groups at the ω-end of the polymer chains. Many research groups have reported the same effect with dyes attached to polymers prepared by RAFT. Charreyre et al. have attributed the effect to the formation of a CTA−dye complex, which is in equilibrium with the dye in both ground and excited states.[57]

Zhang and co-workers employed ATRP to prepare an PMMA with anthracene moieties at the α-terminus.[58] Rizzardo et al. has described the synthesis of a coumarin-based RAFT agent for α-end functionalization of homopolymers of acenaphthylene and its copolymers with acrylic acid and methacrylate.[59]

Reaction of the Anhydride-Terminated Polymer 3c with Norephedrine (19). The incorporation of biologically active molecules into synthetic polymers gives a class of materials widely used in biotechnology and medicine. The insertion of such a molecule at the ends of the polymer chains offers many advantages: for example it can guide the preferential orientation of the macromolecule toward a surface covered with a complementary unit. Application of bioconjugates in human therapeutics is increasing. In the present work the aim was to prepare, using Reaction 5, a PMMA with norephedrine units at the ω-end group. 1*R*,2*S*-norephedrine (**19**) has proved to be particularly effective at interacting with the receptors involved in the sympathomimetic actions.[60]

Reaction 5



Polymer **3c** in THF was treated with an excess of (1*R*,2*S*)-(−)-norephedrine (**19**) at 20 °C for 6 h: see Table 3, entry 7. As expected, immediately on addition of **19** the color of the solution changed from pink to deep yellow. At the end of the reaction period, the mixture was acidified with dilute hydrochloric acid and left stirring for a further 3 h. The polymer was finally recovered by precipitation of the reaction mixture into hexane and purified by dissolving it in THF and reprecipitating it into hexane several times. This gave polymer **20** as a white powder.

The ^{1}H NMR spectrum of polymer **20** confirmed the absence of dithiobenzoate groups. Comparison of the integral for the aromatic signals, due to the terminal cumyl and norephedrine moieties, with that at δ 4.10 ppm due to the proton nearest the N atom, indicated that 95% of the chains included a norephedrine moiety. Given that in polymer **2c**

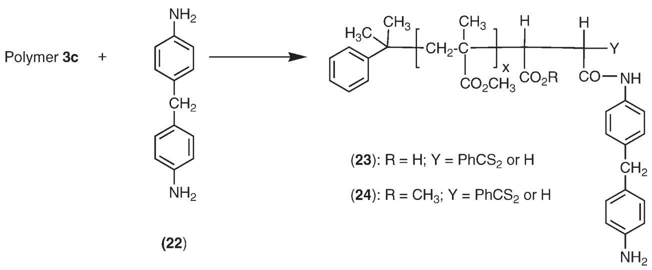
96% of the chains were "living", the overall yield for Reactions 1 plus 5 was 99%.

Treatment of polymer **20** with diazomethane gave polymer **21**.

Other researchers have prepared polymers with end groups that are biologically interesting moieties. Thus, Charreyre et al. have reported the successful application of the RAFT technique to the preparation of α-biofunctionalized poly(*N*-acryloylmorpholine) with carbohydrate and biotine derivatives,[18,61] while van Hest and co-workers have synthesized a *β*-hairpin-containing bifunctional ATRP initiator for the preparation of α-peptide-functionalized triblock copolymers,[62] and Haddleton et al. have used ATRP for the synthesis of several *N*-(hydroxyl)succinimidyl α-ester-terminated glycopolymers.[63]

Reaction of the Anhydride-Terminated Polymer 3c with 4,4′-Diaminodiphenylmethane (22). Polymers with end groups such as an amine are useful because amines react easily to link other groups to the polymer. In the present work the aim was to prepare, using Reaction 6, PMMA with an amine group at the *ω*-terminus. 4,4′-Diaminodiphenylmethane (**22**) was selected as the nucleophile to react with the anhydride groups because, being an aniline derivative, there will be no problems of salt formation between the free amine and the carboxylic acid group generated from the reaction with the anhydride. By using a 20-fold excess of the diamine, it was not necessary to use a protecting group to ensure that one diamine molecule **22** did not, to any significant extent, react with two chains.

Reaction 6



Diamine **22** was reacted with polymer **3c** in THF solution at 66 °C for 16 h: see Table 3, entry 8. The product **23** was recovered by precipitation of the reaction mixture into hexane and purified by dissolving it in an acetone:THF mixture (10:1 v//v) and precipitating it into hexane several times.

The ^{1}H NMR spectrum of polymer **23** showed well-resolved signals at δ 6.89 and 6.54 ppm due to the aromatic protons in the diphenylmethane units: see Figure 6. Comparison of the integrals of these versus those due to the terminal cumyl group indicated that 89% of the polymer chains were terminated with a diphenylmethane moiety. Given that in polymer **2c** 96% of the chains were "living", the overall yield for Reactions 1 plus 7 was 93%. Signals due to dithiobenzoate groups were also present (22% of chains).

Treatment of polymer **23** with diazomethane gave polymer **24**.

Thus, treating SA−PMMA **3c** with diamine **22** affords polymer **23** in which 89% of the chains have an aromatic amine at the *ω*-terminal. As a simple demonstration of the ease with which polymer **23** can be functionalized it was treated in acetone at 20 °C for 16 h with 5 equiv of fluorescein isothiocyanate **25**. This gave PMMA **26**, as a bright yellow solid, labeled at the *ω*-terminus with a strong fluorescer. The ^{1}H NMR spectrum of polymer **26** was too complex in the aromatic region to allow the derivatization yield to be determined. For a solution in ethanol the fluorescence had λ_{max} at 518 nm with $\phi_F = 0.38$ (calibrated using fluorescein in ethanol).

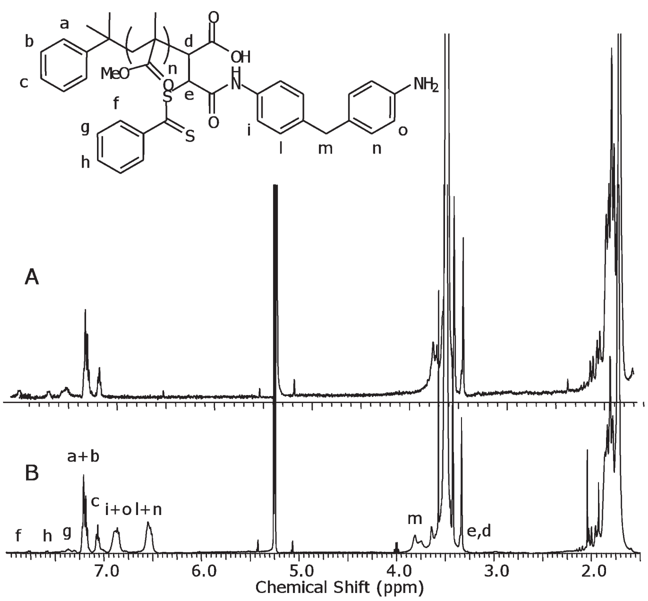
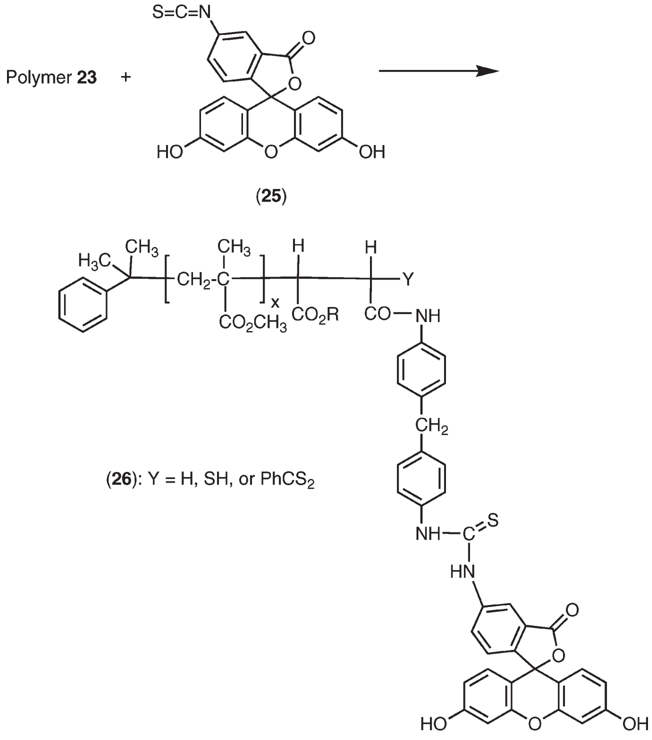


Figure 6. ^{1}H NMR spectra (CD_2Cl_2, 500 MHz) from δ 1.5−8.0 ppm of (A) SA−PMMA **3c** and (B) the product, polymer **23**, formed by reacting SA−PMMA **3c** with 4,4′-diaminodiphenylmethane (**22**). Selected signals are assigned.



Conclusions

"Living" PMMA **2**, prepared by the RAFT technique, reacted with maleic anhydride to give succinic anhydride-terminated PMMAs **3** in very high yield. The *ω*-terminal anhydride residues react in high yields with primary alcohols, primary amines and aromatic amines. As examples, polymer **3** was reacted with 1*H*,1*H*,2*H*,2*H*-perfluorodecylamine (**10**) to give polymer **11** containing 5.78% of fluorine; with Disperse Orange 3 (**13**) to give dye-labeled PMMA **14**; with 9-hydroxymethylanthracene (**17**) to give fluorescently labeled PMMA **18**; with norephedrine

(**19**) to give polymer **20** with a biologically active end group; and with 4,4′-diaminophenymethane (**22**) to give PMMA **23** with an amine end group. The latter reacted smoothly with fluorescein isocyanate (**25**) to give fluorescently labeled PMMA **26**. In these examples the fraction of polymer chains labeled were in the range 75−95%. Allowing for the fact the starting PMMAs were only up to 96% "living", these loadings correspond to ω-terminus functionalization yields, for the anhydride addition plus the reaction with the nucleophiles, of 81−99%.

Experimental Section

Materials and Instrumentation. MMA (Aldrich, 99%) was purified by distillation under reduced pressure. Toluene (Fisher Scientific, AR) was distilled over sodium before use. THF (Fisher Scientific, AR) was distilled over sodium/benzophenone before use. Diazomethane was synthesized from *N*-methyl-*N*-nitroso-*p*-toluenesulfonamide (Diazogen, Molekula) according to the literature.[51] All other reagents and solvents were obtained in the highest purity available from Aldrich Chemical Co. or Avocado and were used without further purification.

Melting points (mp) were recorded using a Gallenkamp hot stage melting point apparatus. Elemental analyses were obtained in house using a Carlo Erba Instruments EA1108 elemental analyzer. FT-IR absorption spectra were measured on an ATI Mattson Genesis series Fourier transform infrared (FTIR) spectrometer. UV/vis spectra were recorded on a Varian Cary 5000 UV−vis−NIR spectrophotometer. Fluorescence spectra were recorded on a Varian Cary Eclipse fluorescence spectrophotometer. ^{1}H NMR spectra were recorded on either a Varian Inova 300 or a Bruker AMX 500 spectrometer. Chemical shifts are quoted on the δ-scale in units of parts per million (ppm). Tetramethylsilane (TMS) was used as internal reference. The quoted splitting patterns are abbreviated to singlet (s), doublet (d), triplet (t), quartet (q), multiplet (m), and broad (b). Coupling constants (J) are reported in hertz.

Analytical SEC measurements were performed with a system equipped with two PL Gel 30 cm 10 mic 2 × Mixed B columns and one PL Gel guard column (500 Å) (Varian) with refractive index detection using THF at a flow rate of 1 mL/min as eluant, unless otherwise stated. Polystyrene standards in the range 200 to 180×10^4 g mol^{-1} were used for calibration. The analyzed samples contained dodecane as the flow marker. PDI = polydispersity index = M_n/M_w.

General RAFT Polymerization of MMA with CDB. The following procedure is typical of that used for the polymerizations summarized in Table 1. The quantities used, yields and the characterization results are as given in the table.

CDB (**1**) and BPO were placed in an oven-dried Schlenk tube. The tube was fitted with a rubber septum, evacuated and flushed with dry nitrogen. MMA (2.14 mL) and toluene were transferred to the reactor via a degassed syringe. The solution was degassed by five freeze−pump−thaw cycles and then placed in a thermostated oil bath at 85 °C for 67 h. After the reaction, the solution was added dropwise, with stirring, to hexane. The pink solid was filtered off and dissolved in a minimum amount of DCM and reprecipitated into hexane two times. Finally, the product was filtered off and dried to constant weight in a vacuum oven at 50 °C for 16 h. Polymer **2** was obtained as a pink solid. ^{1}H NMR ($\mathrm{CD_2Cl_2}$, 500 MHz): δ 0.47−1.40 (m, $\mathrm{CH_3 + C(CH_3)_2Ph}$), 1.50−2.16 (m, $\mathrm{CH_2}$), 3.30−3.68 (m, $\mathrm{OCH_3}$), 7.03−7.10 (m, $\mathrm{ArH}_{para}\mathrm{PhC(CH_3)_2}$), 7.15−7.24 (m, $\mathrm{ArH}_{ortho+meta}\mathit{PhC}\mathrm{(CH_3)_2}$), 7.27−7.34 (m, $\mathrm{ArH}_{meta}\mathrm{PhCS_2}$), 7.43−7.51 (m, $\mathrm{ArH}_{para}\mathrm{PhCS_2}$), 7.77−7.84 (m, $\mathrm{ArH}_{ortho}\mathrm{PhCS_2}$). IR (KBr): ν_{max} 2996, 2952, 1728, 1484, 1449, 1271, 1242, 1193, 1149, 988, 842, 752 cm^{-1}.

General Synthesis of SA−PMMA. The following procedure is typical of that used for the reactions summarized in Table 2. The quantities used, yields and the characterization results are as given in Table 2.

"Living" PMMA (**2**, 400 mg), BPO and maleic anhydride were placed in a Schlenk tube and dissolved in dry dioxane (5.0 mL): see Table 2. The solution was thoroughly deoxygenated by five freeze−pump−thaw cycles. The tube was sealed under vacuum and placed in a thermostated oil bath at 100 °C for 16 h. After the reaction, the polymer was precipitated by dropwise addition of the solution into hexane. After filtration, the pink solid was dissolved in a minimum amount of DCM and reprecipitated into hexane twice. After being dried in a vacuum oven at 50 °C for 16 h, SA-term PMMA (**3**) was obtained as a pink solid. ^{1}H NMR ($\mathrm{CD_2Cl_2}$, 500 MHz): δ 0.47−1.40 (m, $\mathrm{CH_3 + C(CH_3)_2Ph}$), 1.50−2.16 (m, $\mathrm{CH_2}$), 3.30−3.68 (m, $\mathrm{OCH_3}$ + O(CO)CHC), 3.89−4.05 (m, O(CO)CHS), 7.03−7.10 (m, ArH_{para}-$\mathrm{PhC(CH_3)_2}$), 7.15−7.24 (m, $\mathrm{ArH}_{ortho+meta}\mathrm{PhC(CH_3)_2}$), 7.32−7.64 (m, $\mathrm{ArH}_{meta+para}\mathrm{PhCS_2}$), 7.92−8.02 (m, ArH_{ortho} $\mathrm{PhCS_2}$). IR (KBr): ν_{max} 2996, 2952, 1868, 1787, 1731, 1484, 1449, 1272, 1241, 1193, 11450, 988, 844, 751 cm^{-1}.

Reaction of SA−PMMA with 4-Methylbenzyl Alcohol (4). This experiment is summarized in Table 3, entry 1.

SA-term PMMA (**3b**, 250 mg) and 4-methylbenzyl alcohol (**4**, 142 mg, 20-fold excess) were placed into an oven-dried one-neck round-bottom flask. The flask was fitted with a rubber septum and filled with dry nitrogen. Dry THF (4.0 mL) was added to the flask using a degassed syringe, and the resulting solution was gently heated under reflux for 16 h under dry nitrogen. The final polymer was isolated by dropwise addition of the reaction mixture into hexane. After filtration, the powder was redissolved in a minimum amount of DCM and reprecipitated into hexane two times. After being dried in a vacuum oven at 50 °C for 16 h, polymer **7** was obtained as a pale pink-salmon solid. Yield = 183 mg (73%). ^{1}H NMR ($\mathrm{CD_2Cl_2}$, 500 MHz): δ 0.46−1.47 (m, $\mathrm{CH_3 + C(CH_3)_2Ph}$), 1.56−2.14 (m, $\mathrm{CH_2}$), 2.19−2.37 (m, $\mathrm{CH_3Ph}$), 3.20−3.80 (m, $\mathrm{OCH_3}$ + C*H*COOH + CHSCS), 4.85−5.17 (m, $\mathrm{CH_2O}$), 7.00−7.27 (m, $\mathrm{ArHPhC(CH_3)_2 + ArHPhCH_2O}$), 7.31−7.65 (m, $\mathrm{ArH}_{meta+para}\mathrm{PhCS_2}$), 7.85−8.02 (m, $\mathrm{ArH}_{ortho}\mathrm{PhCS_2}$). IR (KBr): ν_{max} 2996, 2952, 1773, 1731, 1481, 1449, 1271, 1243, 1193, 1150, 988, 842, 752 cm^{-1}. SEC: M_n (g/mol) = 3220; PDI = 1.38.

Reaction of SA-Term PMMA with 4-Methylbenzyl Amine (5). This experiment is summarized in Table 3, entry 2.

SA-term PMMA (**3b**, 250 mg) was placed into an oven-dried one-neck round-bottom flask. The flask was fitted with a rubber septum and filled with dry nitrogen. Dry THF (2.0 mL) was added to the flask using a degassed syringe and the resulting pink solution was stirred for 5 min. 4-Methylbenzylamine (**5**) (142 mg) was then added all at once. The color changed rapidly from pink to deep yellow. The reaction mixture was gently heated under reflux for 16 h under dry nitrogen. When the solution was cooled to 20 °C, HCl 1 N was added until pH = 1. An orange jelly-like polymer formed immediately upon addition of the acid. THF was then added to give a transparent yellow solution and the mixture was stirred under nitrogen for 3 h. The final polymer was isolated by dropwise addition of the reaction mixture into hexane. After filtration, the off-white powder was redissolved in a minimum amount of THF/MeOH (2:1) and reprecipitated into hexane two times. After being dried in a vacuum oven at 50 °C for 16 h, polymer **3c** was a white solid. Yield = 165 mg (66%). ^{1}H NMR ($\mathrm{CD_2Cl_2}$, 500 MHz): δ 0.47−1.40 (m, $\mathrm{CH_3 + C(CH_3)_2Ph}$), 1.50−2.16 (m, $\mathrm{CH_2}$), 2.14−2.47 (m, $\mathrm{CH_3Ph}$), 3.30−3.68 (m, $\mathrm{OCH_3}$ + C*H*COOH + C*H*SH), 4.14−4.71 (m, $\mathrm{CH_2NH}$), 6.73−7.14 (m, $\mathrm{ArH}_{para}\mathrm{PhC(CH_3)_2}$ + $\mathrm{ArH}_{ortho+meta}\mathrm{PhCH_2NH}$), 7.15−7.24 (m, $\mathrm{ArH}_{ortho+meta}\mathrm{PhC}$-$\mathrm{(CH_3)_2}$). IR (KBr): ν_{max} 2996, 2951, 1731, 1478, 1449, 1270, 1242, 1193, 1150, 988, 841, 752 cm^{-1}. SEC: M_n (g/mol) = 3200; PDI = 1.28.

Reaction of SA-Term PMMA with 3,5-Dimethylaniline (6). This experiment is summarized in Table 3, entry 3.

SA-term PMMA (**3b**, 250 mg) was placed into an oven-dried one-neck round-bottom flask. The flask was fitted with a rubber septum and filled with dry nitrogen. Dry THF (2.0 mL) was added to the flask using a degassed syringe and the resulting pink solution was stirred for 5 min. 3,5-Dimethylaniline (**6**) (164 mg) was then added all at once and the reaction mixture was heated under gentle reflux for 16 h under dry nitrogen. The final polymer was isolated by dropwise addition of the reaction mixture into hexane. The powder was redissolved in a minimum amount of DCM and reprecipitated into hexane two times. After being dried in a vacuum oven at 50 °C for 16 h, polymer **9** was obtained as a pale pink solid. Yield = 187 mg (74%). ^{1}H NMR (CD_2Cl_2, 500 MHz): δ 0.47−1.40 (m, CH_3 + $C(CH_3)_2$-Ph), 1.50−2.04 (m, CH_2), 2.07−2.36 (m, $(CH_3)_2$Ph), 3.30−3.80 (m, OCH_3 + C*H*COOH + CHSCS), 6.63−6.88 (m, ArH$_{para}$-PhNH), 6.93−7.13 (m, ArH$_{para}$PhC$(CH_3)_2$ + ArH$_{ortho}$PhNH), 7.15−7.23 (m, ArH$_{ortho+meta}$PhC$(CH_3)_2$), 7.24−7.53 (ArH$_{meta+para}$-PhCS$_2$ + NH), 7.77−7.93 (m, ArH$_{ortho}$PhCS$_2$). IR (KBr): ν_{max} 2995, 2951, 1731, 1478, 1449, 1270, 1243, 1193, 1150, 986, 844, 752 cm^{-1}. SEC: M_n (g/mol) = 3390; PDI = 1.35.

Reaction of SA-Term PMMA with 1*H*,1*H*,2*H*,2*H*-Perfluorodecylamine (10). This experiment is summarized in Table 3, entry 4.

SA-term PMMA (**3c**, 100 mg, 29 μmol) was introduced into an oven-dried one-neck round-bottom flask. The flask was fitted with a rubber septum and flushed with dry nitrogen for five min. Dry THF (0.4 mL) was added and the pink-salmon solution was stirred under nitrogen for 3 min. Then, 1H,1H,2H,2H-perfluorodecylamine (**10**, 84 μL, 290 μmol) was added all at once. The color changed rapidly from pink to yellow. The reaction mixture was stirred under dry nitrogen for 6 h at 20 °C. After reaction, hydrochloric acid (1N) was added until pH = 1. An orange jelly-like polymer formed immediately upon addition of the acid. THF was then added to give a transparent yellow solution and the mixture was stirred under nitrogen for 3 h. The final polymer was isolated by dropwise addition of the reaction mixture into hexane (200 mL). After filtration, the off white powder was redissolved in a minimum amount of THF/MeOH/hexafluoro-2-propanol (1:1:1) and reprecipitated into hexane (200 mL) two times. After being dried in a vacuum oven at 50 °C for 16 h, polymer **11** was obtained as a white solid. Yield = 60 mg (60%). ^{1}H NMR (CD_2Cl_2, 500 MHz): δ 0.46−1.47 (m, CH_3 + $C(CH_3)_2$Ph), 1.56−2.14 (m, CH_2 + CH_2CF_2), 2.22−2.61 (m, C*H*$_2$NH), 3.20−3.80 (m, OCH_3 + C*H*COOH + C*H*SH), 7.03−7.10 (m, ArH$_{para}$PhC$(CH_3)_2$), 7.14−7.26 (m, ArH$_{ortho+meta}$PhC$(CH_3)_2$); ^{19}F{^{1}H} NMR (CD_2Cl_2, 400 MHz): δ −84.3 (m, CF_3), −117.4 (bm, CF_2CF_3), −125.3 (bm, −$CF_2CF_2CF_2$−), −126.1 (m, C*F*$_2$$(CF_2)_2CH_2$), −126.9 (m, C*F*$_2$-$CF_2CH_2$), −129.6 (m, CF_2CH_2). IR (KBr): ν_{max} 2996, 2952, 1732, 1481, 1449, 1334, 1232−1145 (broad), 1145, 1073, 989, 840, 705, 659 cm^{-1}. SEC: M_n (g/mol) = 4900; PDI = 1.22. Anal. Found: F, 5.78.

Reaction of SA-Term PMMA with Disperse Orange 3 (13). This experiment is summarized in Table 3, entry 5.

SA-term PMMA (**3c**, 250 mg, 0.07 mmol) and Disperse Orange 3 (**13**) (344 mg, 1.42 mmol) were placed into an oven-dried one-neck round-bottom flask. The flask was fitted with a rubber septum and filled with dry nitrogen. Dry THF (1.0 mL) was added and the resulting dark brown solution was gently heated under reflux for 16 h under dry nitrogen. After cooling to 20 °C, the polymer was isolated by dropwise addition of the reaction mixture into hexane (100 mL). The deep brown powder was purified by Soxhlet extraction with diethyl ether for 8 h. After being air-dried, polymer **14** was obtained as a brown solid. Yield = 210 mg (84%). ^{1}H NMR (CD_2Cl_2, 500 MHz): δ 0.47−1.45 (m, CH_3 + $C(CH_3)_2$Ph), 1.58−2.14 (m, CH_2), 3.25−3.75 (m, OCH_3 + C*H*COOH + CHSCS), 7.02−7.13 (m, ArH$_{para}$PhC$(CH_3)_2$), 7.15−7.23 (m, ArH$_{ortho+meta}$PhC$(CH_3)_2$), 7.30−8.10 (m, ArHPhCS$_2$ + ArHPhNH + ArH$_{meta}$PhNO$_2$), 8.26−8.36 (bm, ArH$_{ortho}$-PhNO$_2$). IR (KBr): ν_{max} 2992, 2950, 1728, 1478, 1448, 1269, 1242, 1194, 1149, 987, 840, 750 cm^{-1}; UV/vis (dioxane): λ_{max} nm (ε M^{-1}cm^{-1}) 368 (35400), 273 (28100). SEC: M_n (g/mol) = 4750; PDI = 1.24. Anal. Found: N, 0.89.

Reaction of SA-Term PMMA with 9-Anthracenemethanol (17). This experiment is summarized in Table 3, entry 6.

SA-term PMMA (**3c**, 250 mg, 0.07 mmol) and 9-anthracenemethanol (**17**) (296 mg, 1.42 mmol) were placed into an oven-dried one-neck round-bottom flask. The flask was fitted with a rubber septum and filled with dry nitrogen. Dry THF (1 mL) was added and the resulting yellow solution was gently heated under reflux for 16 h under dry nitrogen. After cooling to 20 °C, the polymer was isolated by dropwise addition of the solution into hexane (100 mL). The polymer was filtered off and redissolved in a minimum amount of DCM and reprecipitated into hexane (100 mL) two times. After being dried in a vacuum oven at 50 °C for 16 h, polymer **18** was obtained as a pale cream solid. Yield = 190 mg (76%). ^{1}H NMR (CD_2Cl_2, 500 MHz): δ 0.46−1.45 (m, CH_3 + $C(CH_3)_2$Ph), 1.57−2.14 (m, CH_2), 3.31−3.77 (m, OCH_3 + C*H*COOH + CHSCS), 6.00−6.29 (CH_2O), 7.02−7.13 (m, ArH$_{para}$PhC$(CH_3)_2$), 7.15−7.23 (m, ArH$_{ortho+meta}$PhC-$(CH_3)_2$), 7.32−7.68 (H-2,3,6,7$_{anthracene}$ + ArH$_{meta+para}$PhCS$_2$), 7.88−8.11 (H-4,5$_{anthracene}$ + ArH$_{ortho}$PhCS$_2$), 8.16−8.37 (H-1,8$_{anthracene}$), 8.48−8.59 (H-10$_{anthracene}$). IR (KBr): ν_{max} 2992, 2950, 1728, 1478, 1448, 1269, 1242, 1194, 1149, 987, 840, 750 cm^{-1}; UV/vis (dioxane): λ_{max} nm (ε M^{-1} cm^{-1}) = 389 (5300), 369 (5800), 350 (4500), 334 (3300), 304 (3300); Fluorescence (DCM): λ_{max} nm =391, 414, 437. ϕ_F = 0.11 (λ_{ex} = 349 nm, standard: anthracene in ethanol, ϕ_F = 0.27). SEC: M_n (g/mol) = 4650; PDI = 1.22.

Reaction of SA-Term PMMA with (1*R*,2*S*)-(−)-Norephedrine (19). This experiment is summarized in Table 3, entry 7.

SA-term PMMA (**3c**, 100 mg, 29 μmol) and (1*R*,2*S*)-(−)-norephedrine (**19**) (86 mg, 568 μmol) were introduced into an oven-dried one-neck round-bottom flask. The flask was fitted with a rubber septum and flushed with nitrogen for 5 min. Dry THF (0.4 mL) was added and the resulting solution was stirred under dry nitrogen for 6 h at 20 °C. After reaction, hydrochloric acid (1 N) was added until pH = 1. An orange jelly like polymer formed immediately upon addition of the acid. Addition of THF gave a transparent yellow solution. It was stirred under nitrogen for 3 h. The final polymer was isolated by dropwise addition of the reaction mixture to hexane (100 mL). After filtration, the off-white powder was redissolved in a minimum amount of THF and reprecipitated into hexane two times. After being dried in a vacuum oven at 50 °C for 16 h, polymer **20** was obtained as a white solid. Yield = 98 mg (98%). ^{1}H NMR (CD_2Cl_2, 500 MHz): δ 0.45−1.43 (m, CH_3 + $C(CH_3)_2$Ph + C*H*$_3$CNH), 1.58−2.12 (m, CH_2), 3.20−3.80 (m, OCH_3 + C*H*COOH + C*H*SH), 3.92−4.28 (C*H*NH), 4.71−5.02 (C*H*OH), 7.02−7.09 (m, ArH$_{para}$PhC$(CH_3)_2$), 7.10−7.44 ppm (m, ArH$_{ortho+meta}$-PhC$(CH_3)_2$ + ArHPhC(OH)). IR (KBr): ν_{max} 2996, 2950, 1726, 1486, 1451, 1390, 1273, 1243, 1193, 1150, 986, 843, 748, 702 cm^{-1}. SEC: M_n (g/mol) = 4500; PDI = 1.25. Anal. Found: N, 0.23.

Reaction of SA-Term PMMA with 4,4′-Diaminodiphenylmethane (22). This experiment is summarized in Table 3, entry 8.

SA-term PMMA (**3c**, 250 mg, 0.07 mmol) and 4,4′-diaminodiphenylmethane (**22**) (276 mg, 1.40 mmol) were placed into an oven-dried one-neck round-bottom flask. The flask was fitted with a rubber septum and filled with dry nitrogen. Dry THF (1.0 mL) was added and the resulting bright red-orange solution was gently heated under reflux for 16 h under dry nitrogen. After cooling to 20 °C, the polymer was isolated by dropwise addition of the reaction mixture into hexane (100 mL). After filtration, the polymer was purified by dissolving the salmon pink powder in a minimum amount of acetone:THF 10:1 and reprecipitating into hexane (100 mL) five times. After being air-dried, polymer **23** was obtained as a pink solid. Yield = 230 mg (92%). ^{1}H NMR (CD_2Cl_2, 500 MHz): δ 0.46−1.45 (m, CH_3 + $C(CH_3)_2$-Ph), 1.57−2.14 (m, CH_2), 3.31−3.77 (m, OCH_3 + C*H*COOH + CHSCS), 3.71−3.89 ($CH_2(Ph)_2$), 6.44−6.65 (ArH$_{ortho}$PhNH + ArH$_{ortho}$PhNH$_2$), 6.82−6.97 (ArH$_{meta}$PhNH + ArH$_{meta}$Ph-NH$_2$), 7.02−7.13 (m, ArH$_{para}$PhC$(CH_3)_2$), 7.15−7.23 (m, ArH$_{ortho+meta}$PhC$(CH_3)_2$), 7.27−7.55 (ArH$_{meta+para}$PhCS$_2$), 7.65−7.87 (ArH$_{ortho}$PhCS$_2$). IR (KBr): ν_{max} 2992, 2950, 1728, 1478, 1448, 1269, 1242, 1194, 1149, 987, 840, 750 cm^{-1}.SEC: M_n (g/mol) = 4200; PDI = 1.16. Anal. Found: N, 0.97.

Reaction of Amine-Term PMMA (23) with Fluorescein Isothiocyanate (25). Fluorescein isothiocyanate (**25**) (100 μmol) was added to a solution of polymer **23** (85 mg, 20 μmol) in acetone (1.0 mL). The reaction mixture was stirred at 20 °C for 16 h. After removal of solvent the polymer was isolated by dropwise addition of the reaction mixture into hexane (100 mL). After filtration, the off-yellow powder was redissolved in a minimum amount of acetone/ethyl acetate/THF (4:1:0.1) and reprecipitated into hexane (100 mL) seven times. After being dried in a vacuum oven at 50 °C for 16 h, polymer **26** was obtained as a bright yellow solid. Yield = 68 mg (80%). ^{1}H NMR (CD_2Cl_2, 500 MHz): δ 0.46−1.45 (m, CH_3 + $C(CH_3)_2Ph$), 1.57−2.14 (m, CH_2), 3.31−3.77 (m, OCH_3 + C*H*COOH + CHSCS), 3.89−4.06 ($CH_2(Ph)_2$), 6.59−6.88 (m, ArHPhNHCS + $\text{ArH}_{\textit{ortho}}$PhNHCSNH + $\text{ArHPh}_{\textit{ortho+meta}}$-OH), 7.08 + 7.47 (m, $ArHPhC(CH_3)_2$ + $\text{ArH}_{\textit{meta+para}}\text{PhCS}_2$ + ArHPhNHCO+ $\text{ArH}_{\textit{meta+para}}$PhNHCSNH + $\text{ArH}_{\textit{para}}$PhOH), 7.65−7.87 ppm ($\text{ArH}_{\textit{ortho}}\text{PhCS}_2$). IR (KBr): $\nu_{\max}$ 3446, 3000 (broad), 2996, 2951, 1728, 1638, 1610, 1510, 1450, 1387, 1251, 1191, 1154, 992, 847, 750 cm^{-1}; UV/vis (propan-2-ol): $\lambda_{\max}$ nm (ε $\text{M}^{-1}\,\text{cm}^{-1}$) = 447 (5570); Fluorescence (propan-2-ol): $\lambda_{\max}$ nm = 518. $\phi_F = 0.38$ ($\lambda_{ex} = 474$ nm, standard: fluorescein in ethanol, $\phi_F = 0.79$).

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Supporting Information Available: Text describing reactions of succinic and methylsuccinic anhydrides with nucleophiles, with a scheme showing the reactions, text discussing methylations with diazomethane, and figures showing selected SEC traces and structures for **7**−**9**. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Mayadunne, R. T. A.; Rizzardo, E.; Chiefari, J.; Chong, Y. K.; Moad, G.; Thang, S. H. *Macromolecules* **1999**, *32*, 6977–6980.

(2) Chiefari, J.; Chong, B. Y. K.; Ercole, F.; Krstkina, J.; Jeffery, J.; Le, T. P. T.; Maydunne, R. T. A.; Meijs, G. F.; Moad, C. L.; Moad, G.; Rizzardo, E.; Thang, S. H. *Macromolecules* **1998**, *31*, 5559–5562.

(3) Convertine, A. J.; Ayres, N.; Scales, C. W.; Lowe, A. B.; McCormick, C. L. *Biomacromolecules* **2004**, *5*, 1177–1180.

(4) Moad, G.; Rizzardo, E.; Thang, S. H. *Polymer* **2008**, *49*, 1079–1131.

(5) Sumerlin, B. S.; Donovan, M. S.; Mitsukami, Y.; Lowe, A. B.; McCormick, C. L. *Macromolecules* **2001**, *34*, 6561–6544.

(6) Schilli, C.; Lanzendoerfer, M. G.; Muller, A. H. E. *Macromolecules* **2002**, *35*, 6819–6827.

(7) Vasilieva, Y. A.; Thomas, D. B.; Scales, C. W.; McCormick, C. L. *Macromolecules* **2004**, *37*, 2728–2737.

(8) Ganachaud, F.; Monteiro, M. J.; Gilber, R. G.; Dourges, M. A.; Thang, S. H.; Rizzardo, E. *Macromolecules* **2000**, *33*, 6738–6745.

(9) Segui, F.; Qui, X. P.; Winnick, F. M. *J. Polym. Sci., Part A: Polym. Chem.* **2007**, *46*, 314–326.

(10) Moad, G.; Chong, Y. K.; Postma, A.; Rizzardo, E.; Thang, S. H. *Polymer* **2005**, *46*, 8458–8468.

(11) Brunsveld, L.; Folmer, B. J. B.; Meijer, E. W.; Sijbesma, R. P. *Chem. Rev.* **2001**, *101*, 4071–4097.

(12) Lowe, A. B.; Sumerlin, B. S.; Donovan, M. S.; McCormick, C. L. *J. Am. Chem. Soc.* **2002**, *124*, 11562–11563.

(13) Scales, C. W.; Convertine, A. J.; McCormick, C. L. *Biomacromolecules* **2006**, *7*, 1389–1392.

(14) Kulkarni, S.; Schilli, C.; Muller, A. H. E.; Hoffman, A. S.; Stayton, P. S. *Bioconjugate Chem.* **2004**, *15*, 747–753.

(15) Boyer, C.; Bulmus, V.; Liu, J. Q.; Davis, T. P.; Stenzel, M. H.; Barner-Kowollik, C. *J. Am. Chem. Soc.* **2007**, *129*, 7145–7154.

(16) De, P.; Gondi, S. R.; Sumerlin, B. S. *Biomacromolecules* **2008**, *9*, 1064–1070.

(17) Heredia, K. L.; Nguyen, T. H.; Chang, C.; Bulmus, V.; Davis, T. P.; Maynard, H. D. *Chem. Commun.* **2008**, *28*, 3245–3247.

(18) Bathfield, M.; D'Agosto, F.; Spitz, R.; Charreyre, M.-T.; Delair, T. *J. Am. Chem. Soc.* **2006**, *128*, 2546–2547.

(19) Hong, C. Y.; Pan, C. Y. *Macromolecules* **2006**, *39*, 3517–3524.

(20) Gondi, S. R.; Vogt, A. P.; Sumerlin, B. S. *Macromolecules* **2007**, *40*, 474–481.

(21) Ranjan, R.; Brittain, W. J. *Macromolecules* **2007**, *40*, 6217–6223.

(22) Postma, A.; Davis, T. P.; Evans, R. A.; Li, G.; Moad, G.; O'Shea, M. S. *Macromolecules* **2006**, *39*, 5293–5306.

(23) De, P.; Gondi, S. R.; Roy, D.; Sumerlin, B. S. *Macromolecules* **2009**, *42*, 5614–5621.

(24) Liu, J.; Bulmus, V.; Barner-Kowollik, C.; Stenzel, M. H.; Davis, T. P. *Macromol. Rapid Commun.* **2007**, *28*, 305–314.

(25) Patton, D. L.; Mullings, M.; Fulghum, T.; Advincula, R. C. *Macromolecules* **2005**, *38*, 8597–8602.

(26) Deletre, M.; Levesque, G. *Macromolecules* **1990**, *23*, 4733–4741.

(27) Qiu, X.-P.; Winnick, F. M. *Macromolecules* **2007**, *40*, 872–878.

(28) McCormick, C. L.; Lowe, A. B. *Acc. Chem. Res.* **2004**, *37*, 312–325.

(29) Lima, V.; Jiang, X.; Brokken-Zijp, J.; Schoenmakers, P. J.; Klumperman, B.; Van der Linde, R. *J. Polym. Sci., Part A: Polym. Chem.* **2005**, *43*, 959–973.

(30) Li, M.; De, P.; Gondi, S. R.; Sumerlin, B. S. *J. Polym. Sci., Part A: Polym. Chem.* **2008**, *46*, 5093–5100.

(31) Li, H.; Yu, B.; Matsushima, H.; Hoyle, C. E.; Lowe, A. B. *Macromolecules* **2009**, *42*, 6537–6542.

(32) Qiu, X.-P.; Winnik, F. M. *Macromol. Rapid Commun.* **2006**, *27*, 1648–1653.

(33) Spruell, J. M.; Levy, B. A.; Sutherland, A.; Dichtel, W. R.; Cheng, J. Y.; Stoddart, J. F.; Nelson, A. *J. Polym. Sci., Part A: Polym. Chem.* **2009**, *47*, 346–356.

(34) Boyer, C. J.; Granville, A.; Davis, T. P.; Bulmus, V. *J. Polym. Sci., Part A: Polym. Chem.* **2009**, *47*, 3773–3794.

(35) Gruendling, T.; Dietrich, M.; Barner-Kowollik, C. *Aust. J. Chem.* **2009**, *62*, 806–812.

(36) Zhou, G.; He, J.; Harruna, I. I.; Geckeler, K. *J. Mater. Chem.* **2008**, *18*, 5492–5501.

(37) Joshi, R. M. *Makromol. Chem.* **1962**, *53*, 33–45.

(38) Feng, X.-S.; Pan, C.-Y. *Macromolecules* **2002**, *35*, 4888–4893.

(39) Henry, S. M.; Convertine, A. J.; Benoit, D. S. W.; Hoffman, A. S.; Stayton, P. S. *Bioconjugate Chem.* **2009**, *20*, 1122–1128.

(40) Koulouri, E. G.; Kallitsis, J. K.; Hadziioannou, G. *Macromolecules* **1999**, *32*, 6242–6548.

(41) See, for example: (a) Hückstädt, H.; Abetz, V.; Stadler, R. *Macromol. Rapid Commun.* **1996**, *17*, 599–606. (b) Quirk, R. P.; Yoo, T.; Lee, B. *J. Macromol. Sci. Pure Appl. Chem.* **1994**, *A31*, 911–926.

(42) Vosloo, J. J.; De Wet-Roos, D.; Tonge, M. P.; Sanderson, R. D. *Macromolecules* **2002**, *35*, 4894–4902.

(43) Moad, G.; Chiefari, J.; Chong, Y. K.; Krstina, J.; Mayadunne, R. T. A.; Postma, A.; Rizzardo, E.; Thang, S. H. *Polym. Int.* **2000**, *49*, 993–1001.

(44) Moad, G.; Rizzardo, E.; Thang, S. H. *Aust. J. Chem.* **2005**, *58*, 379–410.

(45) Sasso, B. Ph.D. Thesis, University of Manchester, 2008.

(46) Williams, D. H.; Fleming, I. *Spectroscopic Methods in Organic Chemistry*, 5th ed.; McGraw-Hill: London, 1997, Chapter 2.

(47) Xu, J.; He, J.; Fan, D.; Tang, W.; Yang, Y. *Macromolecules* **2006**, *39*, 3753.

(48) Amat, A. M.; Asensio, G.; Miranda, M. A.; Sabater, M. J.; Simon-Fuentes, A. *J. Org. Chem.* **1988**, *53*, 5480.

(49) Jaroszewski, J. W.; Grossen, P.; Mohr, P.; Tamm, C. *Helv. Chim. Acta* **1986**, *69*, 718.

(50) See for example: York, A. W.; Kirkland, S. E.; McCormick, C. L. *Adv. Drug Delivery Rev.* **2008**, *60*, 1018.

(51) Furniss, B. S.; Hannaford, A. J.; Rogers, V.; Smith, P. W. G.; Tatchell, A. R. *Vogel's Textbook of Practical Organic Chemistry*, 4th ed.; Longman Scientific and Technical: Harlow, U.K., 1978, pp 291−292.

(52) Lebreton, P.; Ameduri, B.; Boutevin, B.; Corpart, J.-M. *Macromol. Chem. Phys.* **2002**, *203*, 522–537.

(53) Perrier, S.; Jackson, S. G.; Haddleton, D. M.; Ameduri, B.; Boutevin, B. *Macromolecules* **2003**, *36*, 9042–9049.

(54) Favard, C.; Valisa, P.; Egret-Charlier, M.; Sharonov, S.; Herben, C.; Manfait, M.; Da Silva, E.; Vigny, P. *Biospectroscopy* **1999**, *5*, 101–115.

(55) Danko, M.; Hrdlovic, P.; Borsig, E. *J. Photochem. Photobiol., A* **2003**, *154*, 279–288.

(56) Morawetz, H. *J. Polym. Sci., Part A: Polym. Chem.* **1999**, *37*, 1725–1735.

(57) Farinha, J. P. S.; Relogio, P.; Charreyre, M. T.; Prazeres, T. J. V.; Martinho, J. M. C. *Macromolecules* **2007**, *40*, 4680–4690.

(58) Zhang, M.; Liu, L.; Wu, C.; Fu, G.; Zhao, H.; He, B. *Polymer* **2007**, *48*, 1989–1997.

(59) Chen, M.; Ghiggino, K. P.; Mau, A. W. H.; Rizzardo, E.; Sasse, W. H. F.; Thang, S. H.; Wilson, G. J. *Macromolecules* **2004**, *37*, 5479–5481.

(60) Booth, A. R.; Sherman, W.; Raven, P.; Caffrey, J. L.; Yorio, T.; Forster, M.; Gwirtz, P. PCT Intl. Appl. WO 9948483 A2, 1999.

(61) Bathfield, M.; D'Agosto, F.; Spitz, R.; Ladaviere, C.; Charreyre, M.-T.; Delair, T. *Macromol. Rapid Commun.* **2007**, *28*, 856–862.

(62) Ayres, L.; Hans, P.; Adams, J.; Löwik, D. W. P. M.; van Hest, J. C. M. *J. Polym. Sci., Part A: Polym. Chem.* **2005**, *43*, 6355–6366.

(63) Ladmiral, V.; Monaghan, L.; Mantovani, G.; Haddleton, M. *Polymer* **2005**, *46*, 8536–8545.