Synthesis and Characterization of 1,2-Dicarboxyethyl-Terminated Polystyrene

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ABSTRACT: 1,2-Dicarboxyethyl-terminated polystyrenes were synthesized by anionic polymerization of styrene initiated by *sec*-butyllithium, followed by reaction with dimethyl maleate, basic hydrolysis of the ester groups, acidification, and neutralization with sodium hydroxide. The polymers were characterized by size-exclusion chromatography (SEC), Fourier transform infrared spectroscopy (FTIR), nuclear magnetic resonance spectroscopy (NMR), acid–base titration, and light scattering. SEC indicated the absence of undesired coupling reaction as well as the absence of polymerization of dimethyl maleate. FTIR showed that the hydrolysis and the neutralization were complete. The functionality of the polymers was found to be very close to 2 by NMR spectroscopy and acid–base titration. A sodium-neutralized dicarboxylate-terminated polystyrene was found by light scattering measurements to form reverse micelles in cyclohexane, which have an aggregation number of *ca.* 20 and extremely low critical micelle concentration (cmc), by contrast to a monocarboxylate-terminated polystyrene, which gave an aggregation number of *ca.* 12 and a cmc of *ca.* 10^{-5} M. When dimethyl fumarate was used instead of dimethyl maleate, side reactions occurred and only a low functionality was obtained.

Introduction

Low molecular mass amphiphiles are known to form regular micelles in water or reverse micelles in organic solvents. Extensive studies have been done over several decades to explore effects of various parameters on the aggregation number and the critical micelle concentration (cmc).[1-5] More recently, it was found that block ionomers[6-8] and monochelic polymers[9-11] form reverse micelles with an ionic core and a corona of polymer chains which are soluble in a wide range of organic solvents. A block ionomer is a block copolymer with a long nonionic block and a short ionic block, such as polystyrene-*b*-poly(sodium acrylate), while a monochelic polymer is a chain with an ionic group at one chain end, such as monocarboxylate-terminated polystyrene. If the composition of a block ionomer is inverted, one can speak of block polyelectrolytes, which were found to form regular micelles in water.[12-14]

In block ionomer micelles, the number of ionic groups in the block (the ionic block length) is a major factor which determines the aggregation number and the cmc. With increasing ionic block length, the aggregation number increases and the cmc decreases. The change in the cmc with increasing ionic block length is believed to be so steep that under certain conditions it is useful to think of a critical micelle length (cml) for the ionic blocks, above which the block ionomers start to form micelles. A cml of *ca.* 3 was found for polystyrene-*b*-poly(sodium acrylate) block ionomers in tetrahydrofuran (THF) over a wide concentration range.[8]

The block ionomers are composed of polymer chains of different ionic block lengths. It is frequently impossible to determine the detailed molecular weight distribution for these short blocks since they are attached to long nonionic blocks, so various approximations are invoked, e.g., Gaussian distribution. While the anionic polymerization is supposed to yield materials with Poison distribution,[15] it is found experimentally that the distribution is frequently broader. The presence of a molecular weight distribution and uncertainty about the nature of the distribution make the interpretation of the results quite difficult. For examples, micelles formed from such polydisperse block ionomers can be considered as "mixed" micelles, and it is only recently that a micellization model has appeared which takes polydispersity into account.[16]

One way to avoid these complications is to synthesize model compounds in which an identical ionic block is linked to one end of each polymer chain. Monocarboxylate-terminated polystyrene is one example of such a model compound in which the ionic block length is one. In the present work, we go one step further by synthesizing dicarboxylate-terminated polystyrenes. The synthetic method used in this work is to react poly(styryllithium) with dimethyl maleate (or fumarate), which does not polymerize anionically because of steric hindrance. Only one unit is, therefore, added to the polystyrene chain end; the two ester groups can subsequently be hydrolyzed and neutralized to give two ionic carboxylate groups. The synthesis of tri- and tetracarboxylate-terminated polystyrenes will be the subject of a future work.

Another interest in the dicarboxylate-terminated polymers is based on the possibility of using these materials in the synthesis of comblike copolymers consisting of, for example, a polyester or polyamide backbone and pendant polystyrene chains. These could be prepared by reacting a diol or a diamine with the two carboxylic acid groups (or the two acid chloride groups formed by the chlorination of the carboxylic acids) at the chain end of polystyrene. Another possibility is the synthesis of three-arm "star" copolymers by coupling a dicarboxy-terminated polymer and two monofunctionally terminated polymer chains. For instance, a hydroxyl-terminated poly(ethylene oxide) could be coupled with the dicarboxy-terminated polystyrene to give a three-arm copolymer containing one polystyrene branch and two branches of poly(ethylene oxide). If a polymer is terminated with dicarboxy groups at both ends in a way similar to that reported here, it could be used to prepare four-arm copolymers, or well-defined copolymer networks.

In this paper, we present the synthetic procedure for the preparation of 1,2-dicarboxyethyl-terminated polystyrene. The characterization of the materials by size-

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exclusion chromatography (SEC), Fourier transform infrared spectroscopy (FTIR), nuclear magnetic resonance spectroscopy (NMR), and acid–base titration is also discussed. The result of a light scattering run of one sodium-neutralized dicarboxylate-terminated polystyrene illustrates its micellization behavior. A more detailed study of the micellization behaviour of these materials is now underway.

Experimental Section

Reagents and Solvents. Styrene and α-methylstyrene (α-MeS; Aldrich) were dried over calcium hydride (Aldrich) for 24 h, distilled under vacuum, and stored under nitrogen at −20 °C. They were then treated with fluorenyllithium for 15 min and distilled under vacuum just before polymerization. *sec*-Butyllithium (1.3 M) in cyclohexane (Aldrich) was used without further purification. Diphenylethylene (DPE) was treated with the *sec*-butyllithium until it turned red, distilled under vacuum, and sealed in different ampules with break-seals. Dimethyl maleate (Aldrich) was treated with triethylaluminum (Aldrich) until it turned greenish-yellow and was distilled under vacuum just before the reaction. Dimethyl fumarate (Aldrich) was recrystallized in benzene, dried under vacuum, and sealed in different ampules with break-seals. Tetrahydrofuran (THF; BDH) was distilled under nitrogen over a sodium benzophenone complex, which yielded a blue–violet color, indicating a solvent free of oxygen and moisture. Toluene and methanol of analytical reagent grade (from BDH) were used without further purification. Spectroscopic grade cyclohexane (ACP Chemicals Inc.) was dried over molecular sieves for the light scattering measurement.

Polymerization and Functionalization. An example of the styrene polymerization and the functionalization of the DPE end-capped polystyrene with dimethyl fumarate is given here. The reactions were carried out under a nitrogen atmosphere in a previously flamed glass reactor with two break-seal ampules containing respectively DPE and dimethyl fumarate. The DPE was used to end cap the polystyryl anion so that side reactions toward the ester groups of dimethyl fumarate would be avoided. The freshly distilled THF was first transferred into the reactor under nitrogen with a double-ended needle. After the reactor had been cooled to −78 °C in a dry ice/acetone bath, a predetermined volume of *sec*-butyllithium was added with a syringe, whereupon the solution turned yellow. Then a predetermined amount of freshly distilled styrene was added dropwise by means of a stainless steel capillary, accompanied by vigorous stirring. The yellow color of the initiator solution changed quickly to an orange–red color. After 15 min, the DPE was added by breaking the break-seal, and the solution turned quickly dark red. After another 15 min, an aliquot of the reaction medium was withdrawn for SEC characterization of the unfunctionalized polystyrene. In order to functionalize the polystyrene, dimethyl fumarate was introduced to the reactor through the break-seal. The color of the solution changed slowly from dark red to light yellow. A few drops of methanol was added to deactivate the polymer chains. The polymer solution was added dropwise to a 5–10-fold excess of methanol. The precipitated polymer was filtered and dried under vacuum at 70–80 °C for 24 h.

The polymerization and the functionalization with dimethyl maleate of polystyrene chains without end-capping, or end-capped with either α-methylstyrene or DPE, were performed in a way similar to that described above. The process was similar, with the exception that the freshly distilled dimethyl maleate was added with a double-ended needle to the reaction medium to functionalize the chains, whereupon the color of the polymer solution changed instantaneously from red, dark red, or orange-red to light yellow, depending on whether the polystyrene was end-capped with α-methylstyrene or DPE or had no end cap. The α-methylstyrene was added before the styrene polymerization, and it end-capped the polystyrene only when the polymerization was complete.

Saponification, Acidification, and Neutralization. A total of 5–10 g of the polymers obtained as described above was dissolved in 100 mL of toluene, and 30 mL of 2.5 N NaOH in methanol was added. The mixture was heated at 80–90 °C for about 40 h. After cooling to room temperature, the mixture was added dropwise into 700 mL of methanol under magnetic stirring. The precipitated polymer was filtered and washed with methanol.

The polymer was redissolved in 100 mL of THF. A total of 2 mL of concentrated HCl (36.5%) was added to acidify the carboxylate. The polymer was precipitated into methanol/water (7:3, v/v) containing HCl. The polymer was filtered and washed repeatedly with methanol/water (7:3, v/v). It was dried at 80 °C under vacuum for 24 h.

The dried polymers were dissolved in benzene/methanol (95:5, v/v). The acid content was neutralized by adding excess NaOH solution in methanol. The polymer solution was stirred for 30 min, and the methanol was stripped off under vacuum. The material was recovered by freeze-drying. It was subsequently washed with methanol several times to remove any excess base. The polymer was filtered and dried under vacuum at 80 °C for 24 h.

Size-Exclusion Chromatography. The SEC measurements were performed at room temperature on a Varian 5010 liquid chromatography apparatus equipped with a refractive index detector. THF was used as the eluent at a flow rate of 1 mL/min. The columns were progel-TSK G4000 HXL, and 2000 HXL from Supelco, Inc. The system was calibrated with polystyrene standards. The polymer concentration of injected solution was about 2 mg/mL. The solution was filtered through membrane filters (0.5-μm porosity) before injection. The molecular weight and the polydispersity index were calculated using a Varian DS-604 computer with SEC application software.

Titration. The functionality of the polymers was determined by titration with 1.146 M NaOH/MeOH. A known weight of polymer was dissolved in toluene/MeOH (95:5, v/v), and a few drops of a phenolphthalein solution was added as the indicator. The end point was reached when the solution turned from colorless to pink. The functionality was calculated from the obtained acid content and the molecular weight as determined by SEC.

Nuclear Magnetic Resonance Spectroscopy. The ^{1}H NMR spectra were recorded on a Varian XL-300 spectrometer at room temperature. The samples were dissolved in deuterated chloroform. The chemical shift was calibrated against that of the solvent (7.24 ppm). The number of transients for the data acquisition was 64.

Fourier Transform Infrared Spectroscopy. The FTIR spectroscopy was carried out on a Perkin-Elmer 16PC apparatus. The polymers were dissolved in chloroform, and the films were cast on a KBr window. The spectra of the films were recorded by making 16 scans from 4000 to 400 cm^{-1}.

Light Scattering Measurement. The light scattering measurements were performed at 25 °C on a DAWN instrument from Wyatt Technology Corp. The wavelength of the laser beam was 632.8 nm. Fifteen detectors were situated at different angles, ranging from 26.57 to 128.66°. At the beginning of the measurement, the solvent offset was recorded. Cyclohexane was dried with molecular sieves. Toluene and THF were distilled over CaH_2 and a sodium benzophenone complex, respectively. The polymer solution and the solvents were filtered through 0.5-μm Millipore filters. The measurement vials from Kimble Glass Inc. were rinsed three times with filtered methanol and dried under protection from dust. The initial polymer solution was prepared in a 10-mL volumetric flask and diluted in the vial. After the first measurement by light scattering, the solution was further diluted stepwise to a lower concentration. Each dilution was followed by a light scattering measurement. Alternating measurement and dilution were continued until the scattering intensity at 90° was down to 50 mV. The polymer concentration at each measurement was calculated from the previous polymer concentration and the dilution factor as determined by weighing.

Results and Discussion

Size-Exclusion Chromatography. All the unfunctionalized polystyrenes gave a single narrow peak. The calculated molecular weights (in the range of 4200–5100) corresponded to the ratio of the weight of the added monomer per mole of initiator during the synthesis. The polydispersity index varied between 1.10 and 1.13. After

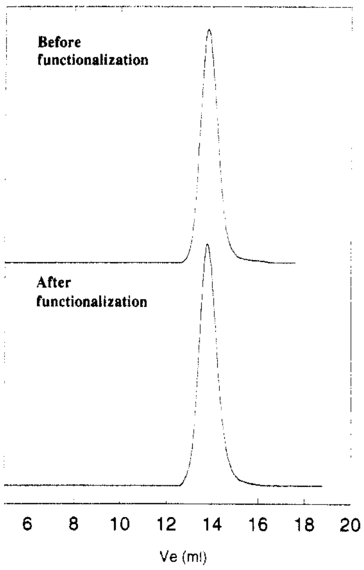


Figure 1. Size-exclusion chromatograms of polystyrene end-capped with α-methylstyrene before and after functionalization with dimethyl maleate.

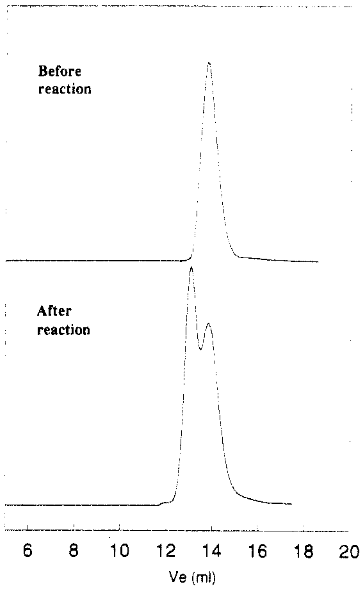


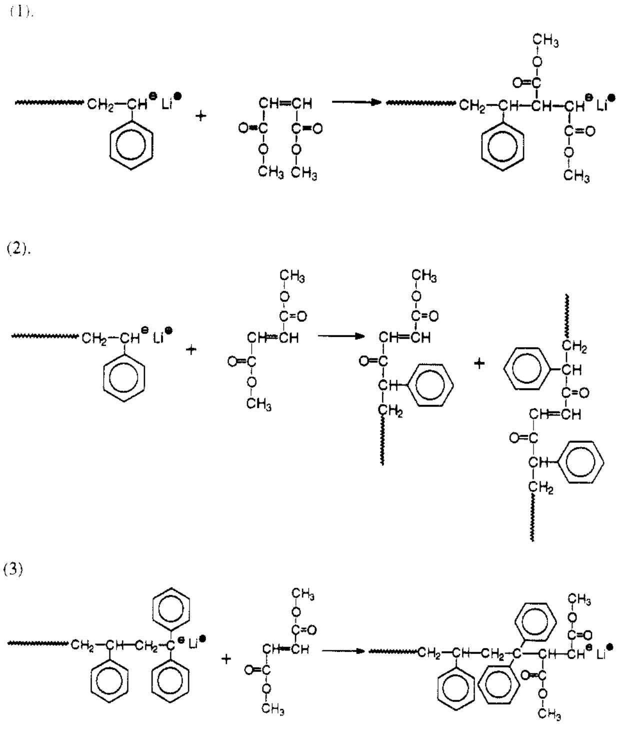
Figure 2. Size-exclusion chromatograms of polystyrene end-capped with α-methylstyrene before and after the reaction with dimethyl fumarate.

the functionalization with dimethyl maleate, the polymer still gave a narrow peak, as shown in Figure 1. Its elution volume was almost the same as that of the unfunctionalized polystyrene, which means that the dimethyl maleate did not copolymerize to increase significantly the molecular weight. This result was expected, since the steric hindrance of the dimethyl maleate prevents it from polymerizing. On the other hand, when dimethyl fumarate was reacted with poly(styryllithium) without end-capping, or end-capped with α-methylstyrene, the resulting polymers gave two peaks. One example is shown in Figure 2. One peak is at the same position as that of the unfunctionalized polystyrene, and the other peak has a lower elution volume, with the number-average molecular weight twice that of the polystyrene. However, when diphenylethylene was used to end-cap the polystyrene before the reaction with dimethyl fumarate, the resulting polymer gave one narrow peak in the same way as that functionalized with dimethyl maleate. The summary of the results for the different experimental conditions is given in the Table 1.

Table 1. Number of SEC Peaks of the Polymers Obtained by the Reaction of Dimethyl Maleate or Dimethyl Fumarate with Poly(styryllithium) without End-Capping or End-Capped with α-Methylstyrene or Diphenylethylene

		end-capped with	
	no end-capping	α-methyl-styrene	diphenyl-ethylene
reaction with dimethyl maleate	1	1	1
reaction with dimethyl fumarate	2	2	1

The difference in reaction selectivity of dimethyl maleate and dimethyl fumarate toward poly(styryllitium) is due to the different relative positions of the two substituents on the two carbons of the ethylene. It seems that the two ester groups of dimethyl maleate in the *cis* position are close enough to protect each other from the attack of poly(styryllithium), while those of dimethyl fumarate in the *trans* position are far apart and allow the polystyryl anion to add to one or both carbonyl groups. In order to avoid this undesired reaction, the end-capping of the polystyryl chain with diphenylethylene is necessary to reduce the reactivity of polymer carbanion and to increase its steric hindrance for that reaction. The normal functionalization and a possible mechanism for the side reaction are given in the following reaction scheme:



Reactions 1 and 3 are normal functionalizations, giving dimethyl ester terminated polystyrene. Reaction 2 is a possible scheme for the undesired addition of polystyrene to the carbonyl of dimethyl fumarate, resulting in a single ester terminated polystyrene and a coupled polystyrene, which give two SEC peaks as shown in Figure 2.

Fourier Transform Infrared Spectroscopy. Since the carbonyl groups have a very strong absorption band in the infrared range, infrared spectroscopy can be used to monitor the ester functionalization of the polystyrene and its subsequent hydrolysis and neutralization if the polymer molecular weight is not very high. Indeed, the molecular weight of the polystyrene in this study was maintained at *ca.* 4000–5000 just for this purpose and for the subsequent titration and NMR characterization.

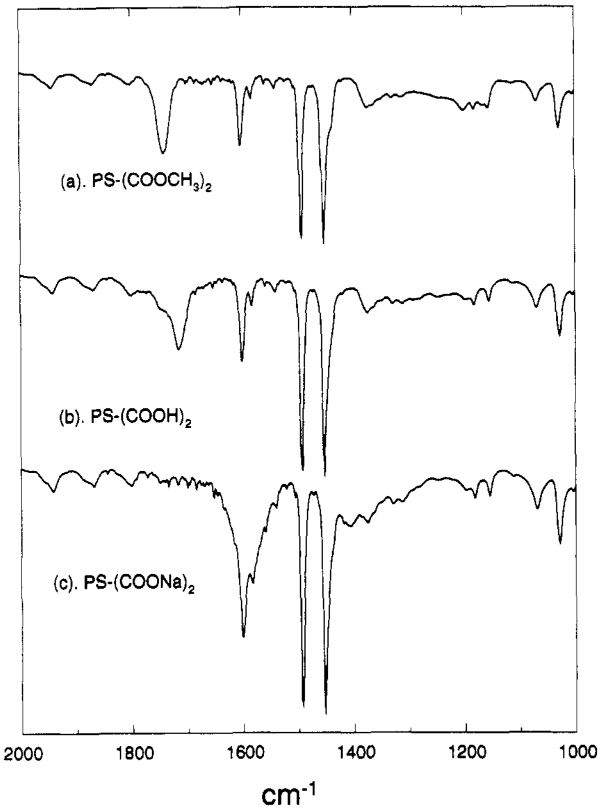


Figure 3. FTIR spectra of a dicarboxyethyl-terminated polystyrene (a), the hydrolyzed polymer (b), and the neutralized polymer (c).

Figure 3 shows the spectra of a dimethyl maleate functionalized polystyrene, the subsequently saponified and acidified polymer, and the neutralized material. It is clear that the dimethyl maleate functionalized polystyrene gives a band at 1740 cm^{-1}, characteristic of the ester carbonyls; after the saponification and acidification, this band is split into two bands at 1714 and 1746 cm^{-1}, attributed to the hydrogen-bonded and free carboxylic acid, respectively. When this polymer is finally neutralized with NaOH, the carbonyl band shifts totally to 1580 cm^{-1}, indicating that the ester groups in the polymer are completely hydrolyzed into carboxylic acids and that all the carboxylic acids are neutralized into sodium carboxylate.

Functionality Determined by Nuclear Magnetic Resonance Spectroscopy and Titration. Figure 4 shows the NMR spectra of a dicarboxyethyl-terminated polystyrene, PS–(COOCH$_3$)$_2$ and the hydrolyzed polymer, PS–(COOH)$_2$. The peak at 0.88 ppm is due to the methyl proton from the *sec*-butyllithium initiator. The two peaks at 1.63 and 2.13 ppm are attributed respectively to the –CH$_2$– and –CH– protons on the polymer backbone. The one at 3.75 ppm is assigned to the methoxy proton of the esters. Those at 6.78 and 7.25 ppm are characteristic of the aromatic protons of polystyrene. After hydrolysis, the peak of the methoxy proton at 3.75 ppm disappears completely. This confirms the complete hydrolysis found by FTIR. It is worth mentioning that the signal to noise ratio in the spectrum of PS–(COOH)$_2$ is higher than that of PS–(COOCH$_3$)$_2$. This is because the concentration of the PS–(COOH)$_2$ solution was made about three times higher in an attempt to see a trace amount of residual methoxy proton. In fact, it was not detectable at that high concentration.

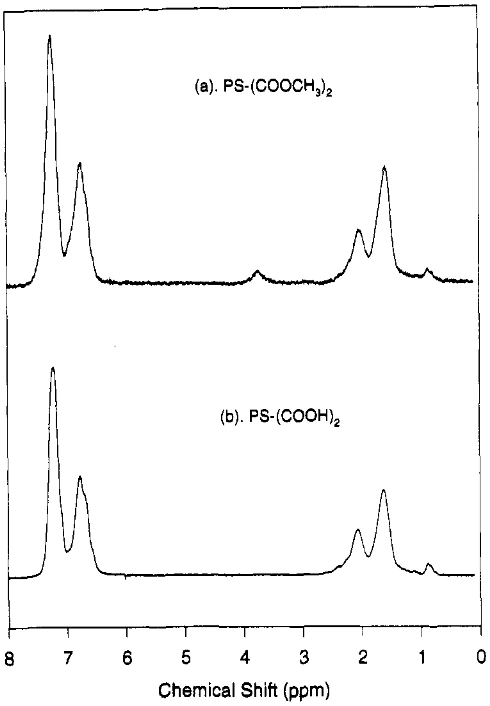


Figure 4. ^{1}H NMR spectra of a dicarboxyethyl-terminated polystyrene (a) and the hydrolyzed polymer (b).

The number of the ester groups per chain or the functionality was calculated from the ratio of the peak areas of the methoxy proton at 3.75 ppm to that of the aromatic protons at 6.78 and 7.25 ppm, combined with the molecular weight as determined by SEC. The functionality was also determined by titration of the acid content in the hydrolyzed polymer. The results from both methods are compared in the Table 2.

The functionalities determined by both methods are in good agreement and close to 2, except for sample D, which was prepared by functionalization with dimethyl fumarate. These results show that functionalization with dimethyl fumarate is less effective than that with dimethyl maleate, even though the polystyrene was end-capped with DPE. The best way to prepare the dicarboxyethyl-terminated polystyrene is to use a dimethyl maleate to functionalize the polystyrene without end-capping or end-capped with α-methylstyrene.

Micellization in Cyclohexane. As discussed in the Introduction section, the dicarboxylate-terminated polystyrenes are expected to form reverse micelles in some organic solvents in a way similar to that of the carboxylate-terminated monochelic polystyrene and that of the block ionomers of polystyrene-*b*-poly(sodium acrylate). Light scattering is a simple technique to study the micellization of these systems by determining the molar mass and the size of the particles in solution. The aggregation number can be calculated from the molar mass of the aggregates determined by light scattering divided by that of the unfunctionalized polystyrenes determined by size-exclusion chromatography.

The results for one dicarboxylate-terminated polystyrene in cyclohexane at 25 °C are presented here in comparison with those of the monocarboxylate-terminal polystyrene. The reduced light scattering intensity $Kc/R(90)$ is plotted as a function of the polymer concentration in Figure 5. The experimental points are fitted with theoretical lines obtained using the phase-separation model as described previously.[11] The aggregation number and the critical micelle concentration (cmc) can be obtained in this way. It was found that the aggregation number increased from 11.8 to 20.9 when the number of carboxylates in the polymer chain end was raised from 1 to 2. The

Table 2. Functionality of the Dicarboxyethyl-Terminated Polystyrene Determined by NMR Spectroscopy and Acid–base Titration

sample	mode of synthesis	number-average mol wt.	polydispersity index	functionality by NMR	functionality by titration
A	no end-capping, functionalization with dimethyl maleate	4300	1.12	2.05	1.97
B	end-capping with α-MeS, functionalization with dimethyl maleate	5100	1.13	1.95	1.98
C	end-capping with DPE, functionalization with dimethyl maleate	4400	1.12	1.83	1.89
D	end-capping with DPE, functionalization with dimethyl fumarate	4200	1.10	1.29	1.60

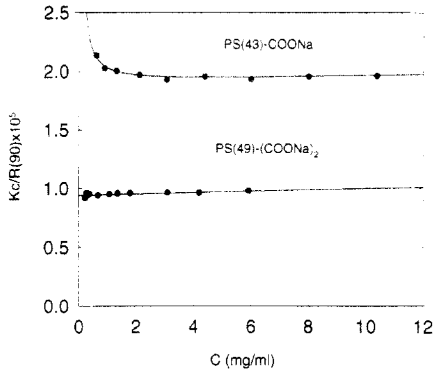


Figure 5. Light scattering of monocarboxylate- and dicarboxylate-terminated polystyrene in cyclohexane at 25 °C. PS(43)–COONa: aggregation number, 11.8; cmc, 1.6×10^{-5} M. PS(49)–(COONa)$_2$: aggregation number, 20.9; cmc, very low.

polystyrene chain lengths were 49 and 43, respectively, for the two materials. On the other hand, the cmc decreased from 1.6×10^{-5} M for the monocarboxylate to such a low value for the dicarboxylate that light scattering was not sensitive enough to determine it.

These effects are understandable since the more ionic groups are present in a polymer chain end, the higher is the free energy of micellization and the lower is the critical micelle concentration. On the other hand, the aggregation number of block copolymer micelles is directly related to the chain length of the insoluble block. In the Helparin model,[17] for example, $f \propto N_B^{4/5}$, where f is the aggregation number and N_B is the chain length of the insoluble block. Although the present systems represent the extreme cases of block copolymer micelles at the low end, it is not unreasonable that the same general relationship might still apply. As a matter of fact, $2^{4/5} = 1.74$, which suggests that the aggregation number for the dicarboxylate should be 20.5 if that of the monocarboxylate is 11.8. The experimental value is 20.9. This agreement is possibly fortuitous, and much more detailed and systematic work is needed to investigate these effects. This is left for future publications.

Conclusion

In the present work, new functionalized polymers, i.e., 1,2-dicarboxyethyl-terminated polystyrenes, were synthesized by anionic polymerization of styrene, followed by reaction with dimethyl maleate. SEC indicated the absence of a chain coupling reaction as well as the absence of the dimethyl maleate polymerization. The ester groups in the polymers were hydrolyzed and neutralized to give polystyrenes with two ionic carboxylate groups at one chain end. FTIR spectroscopy showed that the hydrolysis and the neutralization were complete. The functionality was found to be close to 2 by NMR spectroscopy of the ester-terminated polystyrenes and by acid–base titration of the hydrolyzed polymers. Light scattering of one sodium-neutralized dicarboxylate-terminated polystyrene in cyclohexane showed that it formed reverse micelles with an aggregation number of 20.9 and a very low cmc, compared to a monocarboxylate-terminated polystyrene with an aggregation number of 11.8 and a cmc of 1.6×10^{-5} M. When dimethyl fumarate was used instead of dimethyl maleate, an undesired coupling reaction occurred as shown by SEC. When polystyrene was end-capped with diphenylethylene, the coupling reaction was absent, but the functionality was found to be somewhat lower.

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