Emulsion Polymerization of Styrene and DEAEMA with a Core–Shell Structure

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ABSTRACT: Polystyrene–poly(N,N-diethylamino ethyl methacrylate) (PS–PDEAEMA) particles with a core–shell morphology were prepared by seeded emulsion polymerization. Poly(oxyethylene) (POE) ($n = 15$ and 30) nonyl phenol and sodium lauryl sulfate (SLS) were used as emulsifiers. These two emulsifiers were selected in order to study the effect of nonionic and ionic emulsifiers on the reaction because of the basic character of DEAEMA. The core–shell morphology was investigated independently in the presence of water-soluble potassium persulfate (KPS) and of oil-soluble azobisisobutyronitrile (AIBN). The morphologic structure of the particles was studied using scanning electron microscopy and transmission electron microscopy. The latex particles and the polymers were characterized by differential scanning analysis, thermogravimetric analysis, and gel permeation chromatography. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 78: 1977–1985, 2000

Key words: styrene; DEAEMA; emulsion; core–shell

INTRODUCTION

It has been generally assumed that in styrene polymerization, the growing of a monomer–polymer particle was homogeneous throughout the particle. This hypothesis was challenged, however, by Krackeler and Naidus.[1] They suggested that there were some preferred zones with higher concentrations of monomer. This idea was pursued by numerous authors. It was, however, the work of Grancio and Williams[2–3] as well as the work of Keusch et al.,[4–5] Keusch and Williams,[6] and Williams[7] that confirmed this. A core–shell morphology was adopted for the styrene–polystyrene system. They showed that the growing styrene particle has two regions, a core rich in polymer and a shell rich in monomer. The polymerization of the monomer is initiated at the shell, which is rich in monomer; the polymer formed migrates to the center core, making this "core–shell" structure.

This subject opened up a wholly new field of research in which the preparation of particles with a core and shell of different polymeric media was studied. Various kinds of morphologies were found.

These morphologies depend on the properties of the monomers used, such as the hydrophilic and the solubility characteristics and on the polymer preparation method. For the PMMA–PS system we have such peculiar morphologies as confetti or raspberry,[8] or dumbbell for poly(butyl acrylate)–polystyrene systems,[9] as well as mushroomlike,[10] half-moon-like, sandwichlike,[11] and inverse core–shell[12] morphologies.

The way the polymer is prepared is also of great importance. Methods include batch process, successive addition process, a continuous time-controlled addition of the monomer.[13] Considering the special structure of these of particles, they could be considered polymer blends with the same chemical composition. However, these systems should give a better final product as they have a more "intimate" mix. By selecting the proper procedure the outer chemical structure of the particle could be changed more or less at will.

Several applications of this family of polymers have been found for the paint and coatings industries.[14–17] It can also be used as an opacifier,[18] to void particles and impact modifiers,[19–20] as a water absorbent,[21] temperature-dependent tacky films,[22] for binders,[23] for the preparation of SBR,[24] in the preparation of transparent, invisible and weather-resistant film,[25] and as a toner.[26]

The present articles reports our study of the preparation of functional particles with a core–shell morphology, using N,N-diethylamino ethyl methacrylate (DEAEMA) and styrene as monomers. The DEAEMA is a cationic monomer that because of quaternized amino groups will provide a built-in charge in the outer shell of the particle. In our case, however, the DEAEMA was unquaternized. It was not even a salt of an alkyl amine as the reactional medium is basic. Because of its solubility in water, DEAEMA may affect the pH of the emulsion.

EXPERIMENTAL

Materials

The styrene used was supplied by Merck Chemical Co. (Whitehouse Station, NJ), and the DEAEMA was obtained from Polysciences, Inc. (Warrington, PA). They were purified by distillation under vacuum and stored in a dark bottle at −20°C until required. The azobisisobutyronitrile (AIBN) and absolute ethanol were also supplied by Merck Chemical Co. The AIBN was purified by recrystallization and stored at −20°C. The potassium persulfate (KPS), the sodium lauryl sulfate

Table I   Sample Washing Conditions

Ethanol/Water (Volume Ratios)	50/50	25/75	10/90	0/100
Time (mins)	15	15	15	60

Table II   Ethanol Elimination Conditions

Ethanol/Epoxy Resin (Volume ratios)	1/1	1/2	1/3	0/1
Mixing time (hrs)	1	2	6	6

(SLS), and the osmium tetroxide were also obtained from Polysciences, Inc. The epoxide resin used for the scanning electron microscopy analysis was a EPON 812 from Shell Chemical Co. (Houston, TX). The POE ($n = 15$, $n = 30$) nonyl phenol was obtained from BASF (Mt. Olive, NJ) and was used without further purification. Double-distilled water was used in all experiments.

The samples were characterized for particle size by scanning electron microscopy (SEM; Stereoscan 360, Cambridge Instrument, Cambridge, UK), by transmission electron microscopy (TEM, Zeiss 10 c, Thornwood, NJ), by gel permeation chromatography (GPC; Waters Associates, Milford, MA) and by differential scanning calorimeter (DSC, Perkin–Elmer, Wilton, CT). The samples were microtomed using an Ultramicrotom (V 2088 LKB, Pharmacia, Piscataway, NJ).

Sample Preparation

For the SEM analysis, the emulsion samples were diluted in water 1:100 (v/v). A drop of diluted emulsion was placed on the sample holder and dried at room temperature. They were then placed under vacuum, flushed with Ar, evacuated, and coated with powdered gold.

Each of the emulsion samples for the TEM analysis was diluted in water 1:100 (v/v). This diluted emulsion was stained with a 2% aqueous solution of OsO_4. After 1 h, the sample was washed with distilled water and the water was removed according to the schedule given in Table I. The procedure given in Table II was followed in order to eliminate the ethanol before treating the samples with epoxy. The samples were centrifuged for 6 h in epoxy resin and molded for 24 h at 60°C. The molded samples were ultramicrotomed with a 50- to 70-nm-thick glass knife. Each of the sliced samples was analyzed by both TEM and DSC. For TGA analysis the latex was dried under vacuum at room temperature.

Procedure

The reaction conditions are given in Table III. The reactor setup was similar to the one described by Poehlein et al.[27] The required amount

Table III   Experimental Conditions

Experiment	DEAEMA (mol)	Styrene (mol)	Water (g)	SLS (mol)	POE $n = 15$ (mol)	POE $n = 30$ (mol)	KPS (mol)	AIBN (mol)	Reaction Step 1 (h)	Reaction Step 2 (h)
1	5.56×10^{-2}	0.41	450	0.01	—	—	3.0×10^{-3}	—	2.5	—
2	5.56×10^{-2}	0.41	450	0.02	—	—	3.0×10^{-3}	—	2.5	—
3	1.73×10^{-2}	0.45	280	—	6.05×10^{-3}	—	2.1×10^{-3}	—	3.0	4.0
4	3.24×10^{-2}	0.45	280	—	—	1.89×10^{-3}	2.66×10^{-3}	—	5.0	6.0
5	3.24×10^{-2}	0.45	280	—	—	1.51×10^{-3}	2.66×10^{-3}	—	6.0	8.0
6	5.02×10^{-2}	0.22	280	—	—	8.20×10^{-4}	—	2.68×10^{-3}	24.0	12.0

of distilled water was poured into the reactor. The water and the reactor were purged with nitrogen, and a nitrogen blanket was maintained throughout the reaction. A half-moon shape Teflon stirrer was set at 240 rpm. The polymerization was a two-step operation. Initially it started as a batch process in which the emulsifier and the styrene were mixed with the water. After 10 min the initiator was added, after which the system was converted to a semi–batch process as the DEAEMA was added gradually at a rate of 1 mL per min. The water bath was held constant at 70°C. Several experiments were run at other time intervals in order to find the optimum conditions. Because of the absence of protective colloids, some coagulation was observed at the end of polymerization.

RESULTS AND DISCUSSION

The first two experiments were run with both DEAEMA and SLS. The polymerization ran smoothly when only the SLS and the KPS were added to the styrene. However, when the DEAEMA was added, the emulsion coagulated, even in the second experiments when the SLS concentration was doubled. This is probably a result of the poor efficacy of SLS for DEAEMA in the presence of styrene.[28] This problem is solved by changing the emulsifier to POEs.

In the third experiment the SLS was replaced by POE ($n = 15$) nonyl phenol. It has an HLB of 14.4.[29] This partially solved the problem, as no coagulation occurred, but after a few hours the latex sedimented.

The DSC analysis (Fig. 1) indicated a copolymer of styrene with DEAEMA as the T_g of the final product at 51.2°C. The T_g of the two homopolymers would have given a T_g of 100°C for polystyrene and 19–24°C for PDEAEMA.[30]

Figure 2 shows the SEM micrograph of the early part of the reaction as only styrene is present as the monomer. The polystyrene particles formed have a diameter of about 430 nm. At the end of the second step, which can be seen on the next micrograph (Fig. 3), both the growth of primary particles and the formation of secondary particles with smaller diameter with the same glass transition are apparent.

The CMC of POE ($n = 15$) nonyl phenol is 7,9 (10^{-4} mol L^{-1}).[31] As higher concentrations of nonionic emulsifier must be used, we settled for 0.019 mol l^{-1} of emulsifier, which is 24-folds higher than the CMC. This excess of emulsifier would produce secondary micelles and the formation of secondary particles.

In order to solve the stability and aging problem, a POE ($n = 30$) nonyl phenol with an HLB of 17.1[28] was used in the fourth experiment. The concentration was 30 times the CMC. The resulting latex did not show any sedimentation. The DSC diagram (Fig. 4) indicated three distinct regions: one at 24–30°C for the PDEAEMA homopolymer, the second at 56°C for the styrene–DEAEMA copolymer, and the third at 105°C for the styrene homopolymer.

The 5°C deviation of T_g of the polymers with the standard T_g of polystyrene and PDEAEMA results from the calibration of the DSC instrument.

To avoid copolymerization, which occurred in the previous experiments, a fifth experiment was designed. It was run at the same conditions as the fourth experiment, but the time allotted for each step in the polymerization was increased. In order to increase the particle size as compared to the fourth experiment, the emulsifier concentration of the POE ($n = 30$) nonyl phenol was decreased
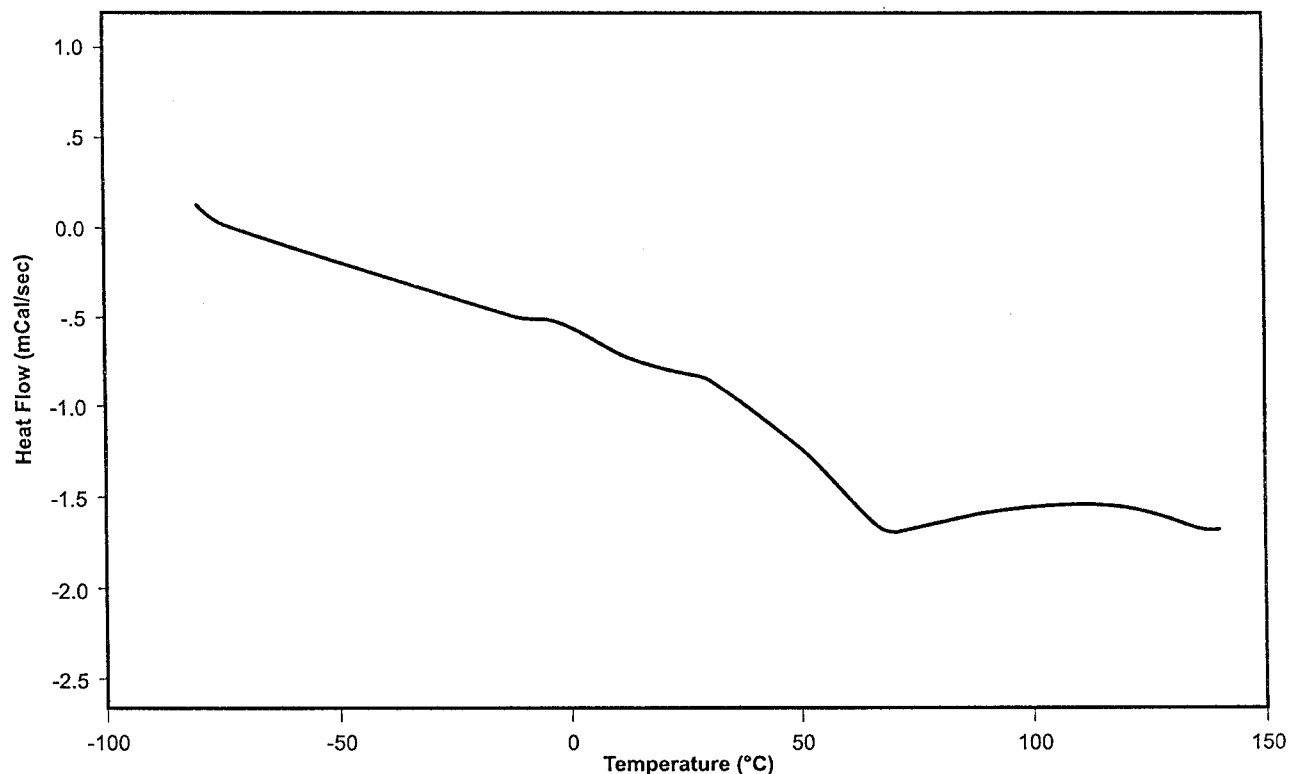
Figure 1   DSC trace of copolymer of styrene and DEAEMA from experiment 3.

to 24 times the CMC. From a comparison of the SEM micrographs of experiment 3 (Fig. 2) and of experiment 5 (Fig. 5), it can be seen that the primary particles (PS) and the secondary particles (PDEAEMA) of experiment 5 are much smaller than the ones obtained in experiment 3. Because of the higher polarity of DEAEMA com-

pared to the styrene, the system requires a higher HLB than for PS emulsions. This is why POE (n = 30), by raising the HLB[32] to 17.1, has a greater efficacy than POE (n = 15). It stabilized the styrene–DEAEMA and at the same time lowered the particles sizes.[33,34]

DSC analysis gives us a good clue. For the core–shell structure, examining the DSC results of the
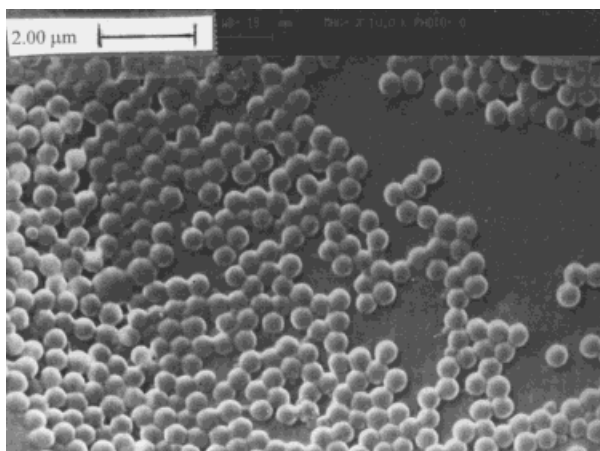
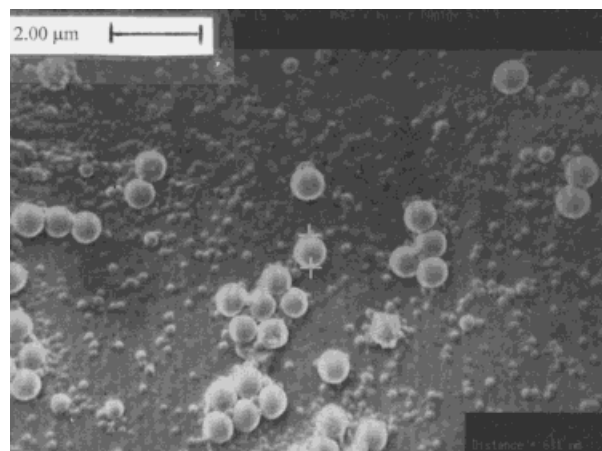**Figure 2**   SEM micrograph of polystyrene from experiment 3, first step.

Figure 3   SEM micrograph of polystyrene with DEAEMA from experiment 3, second step.
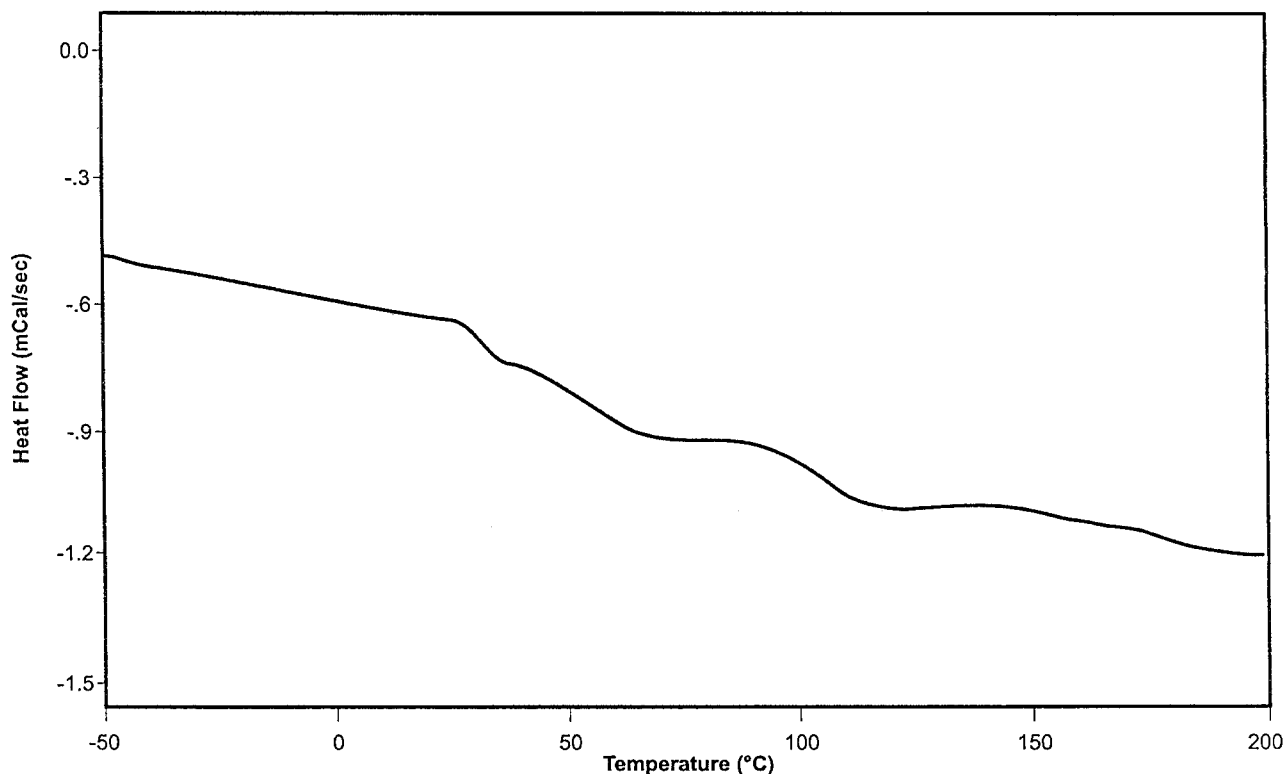
Figure 4 DSC trace of polymer from experiment 4.

third experiment (Fig. 1) shows there was a peak at 51°C, unlike with the last experiment (Fig. 6), in which there were two distinct peaks—one at 105°C (PS) and the other at 30°C (PDEAEMA). This suggests that we do not have a copolymer but particles

Figure 5 SEM micrograph of polymer from experiment 5.

with a core–shell structure, which was confirmed by TEM micrographs (Fig. 7). When stained with OsO₄, there is a PS stained zone and a clear unstained shell of PDEAEMA. The shapeless particles in the TEM micrographs result from the procedure used for the sample preparation. The spherical shape of the particles is confirmed by SEM micrographs (Fig. 8).

GPC analysis of the first and second polymerization steps is shown in Table IV. It is interesting to note the increase of the molecular weight in the fifth experiment between the first and second step. This may be a result of the grafting of the shell polymers to the core polymers.

As noted above, we had some coagulation occurring during the polymerization. This may be because of DEAEMA's low water solubility and the water soluble initiator. In order to solve this problem, an oil-soluble (AIBN) was used (Experiment 6) and it reduced successfully the coagulation.

Nomura et al[35] has shown that oil-soluble radical initiators, such as AIBN, initiate emulsion polymerization in the aqueous phase despite their
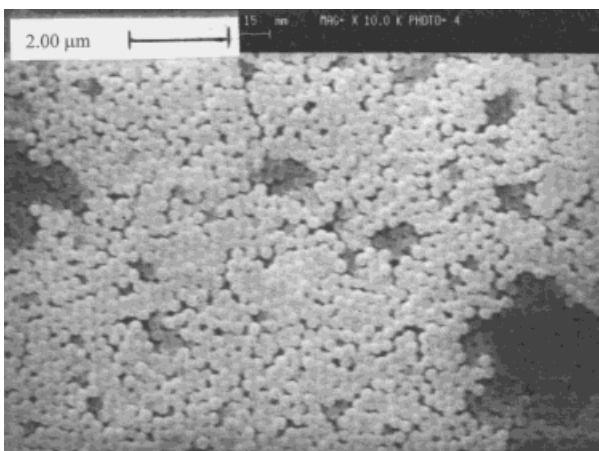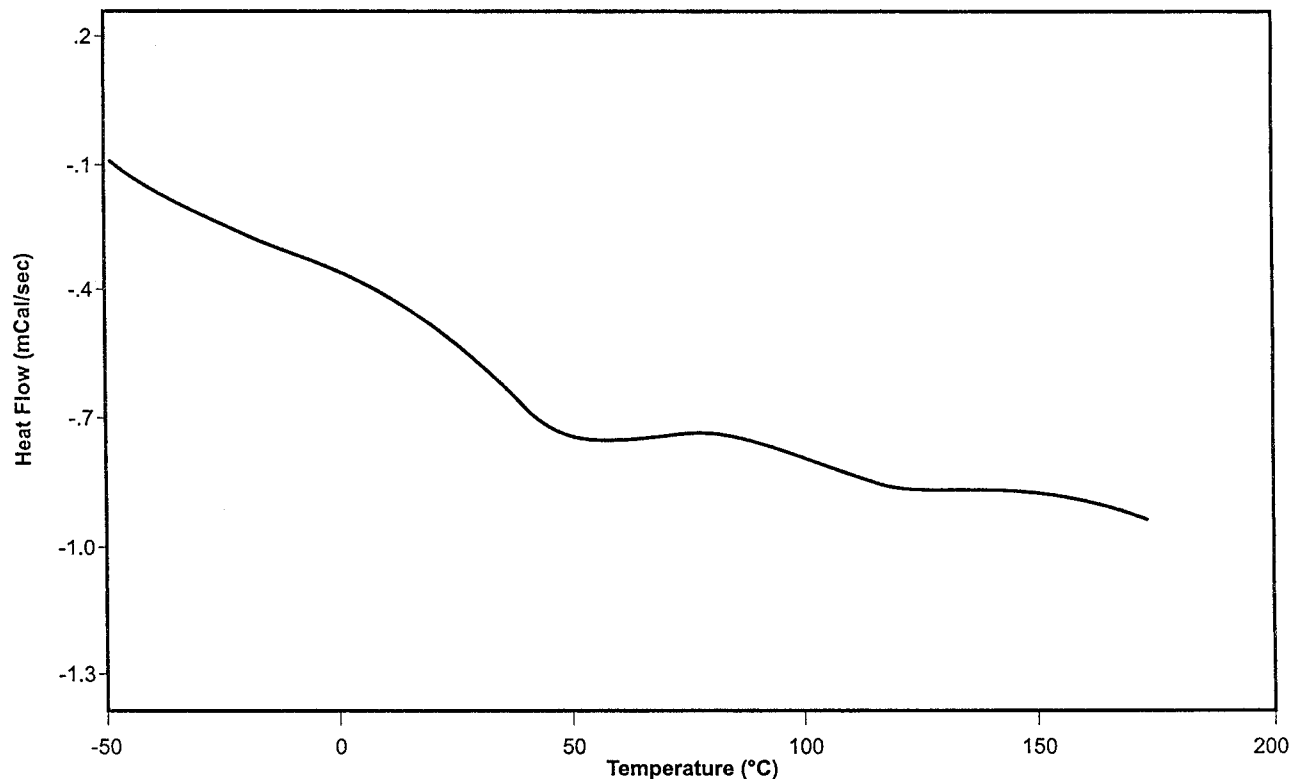
Figure 6 DSC trace of polymer from experiment 5.

solubility in the monomer phase. Because of the absence of polar groups generated by the initiator, the growing polymer molecule is able to diffuse into the primary PS particles and establish internal domains.

External domains are also formed by adsorption of the second monomers such as DEAEMA, which polymerize on the particles surface.

SEM micrographs of this last experiment (Fig. 8) shows that the particles are spherical and the DSC analysis (Fig. 9) give two T_gs, one at 26°C (PDEAEMA) and a second at 102°C (PS), indicating that two homopolymers. The GPC data (Table IV) show a decrease going from the first to the second step of the polymerization. This is because of the homopolymerization of DEAEMA, which produces polymers of low average molecular
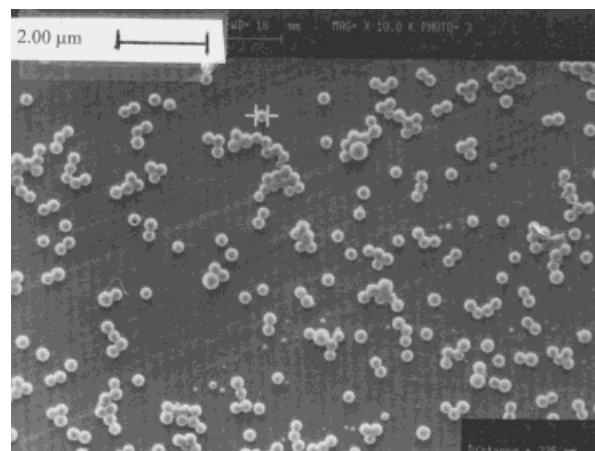

Figure 7 TEM micrograph of polymer from experiment 5.

Figure 8 SEM micrograph of polymer from experiment 6.

Table IV Molecular Weight Determination Results

| Experiment Number	Polymer	Number Average Molecular Weight (M_n)	Weight Average Molecular Weight (M_w)	Polydispersity ($\bar{M}_w/\bar{M}_n$)
3.	PS	13 100	32 500	2.49
	PS-PDEAEMA	40 000	1 456 000	36.40
4.	PS	343 000	1 390 000	4.00
	PS-PDEAEMA	176 000	956 000	5.43
5.	PS	101 000	431 000	4.26
	PS-PDEAEMA	157 000	1 117 000	7.10
6.	PS	113 000	310 000	2.74
	PS-PDEAEMA	97 000	256 000	2.63

weights, causing a drop in the total average molecular weight. Given that we could not find particles on the SEM micrographs (Fig. 8) and that the ratio between the particle size of DEAEMA to styrene used is only 22.8%, the probability of the formation of PDEAEMA particles comparable to PS is remote. Thus, homopolymers of PDEAEMA must be deposited on the primary PS particles.

The TEM micrographs (Fig. 10) confirm the presence of a core–shell structure, although on the laser reproduction it is not clear, instead showing that two domains exist, an internal one and an external one [Fig. 10(a,b)]. The same procedure was used as was used for Figure 7. TGA analysis of the products to determine the composition of the final product according to the weight loss was of little help. The maximum weight loss occurs at about 404°C for photosynthesis, while it occurs for PDEAEMA in the range of 250–500°C.
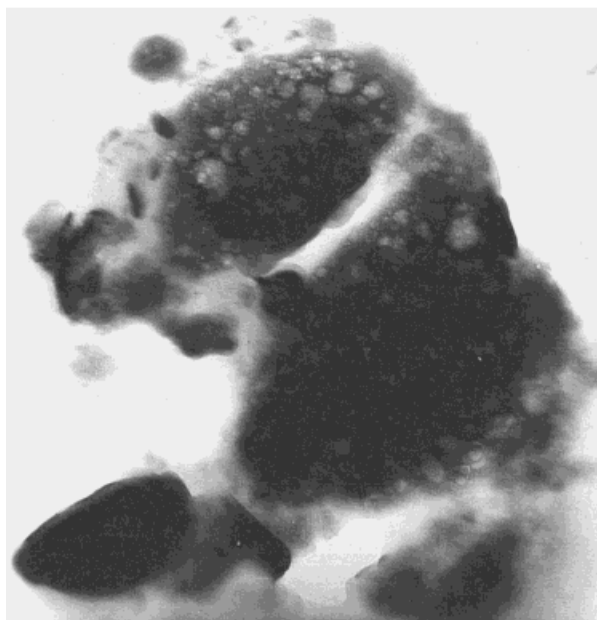
CONCLUSION

A procedure was developed that permitted us to prepare a polymer of styrene and PDEAEMA hav-
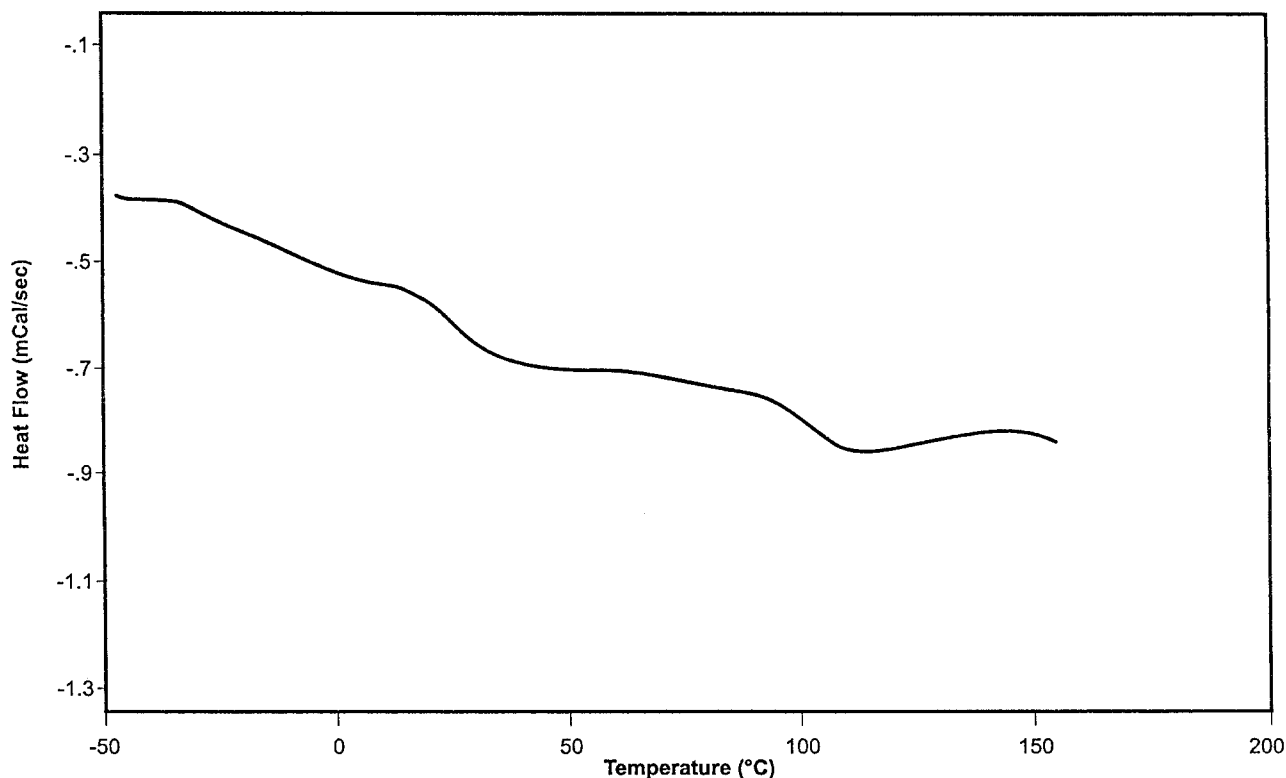
Figure 9 DSC trace of polymer from experiment 6.
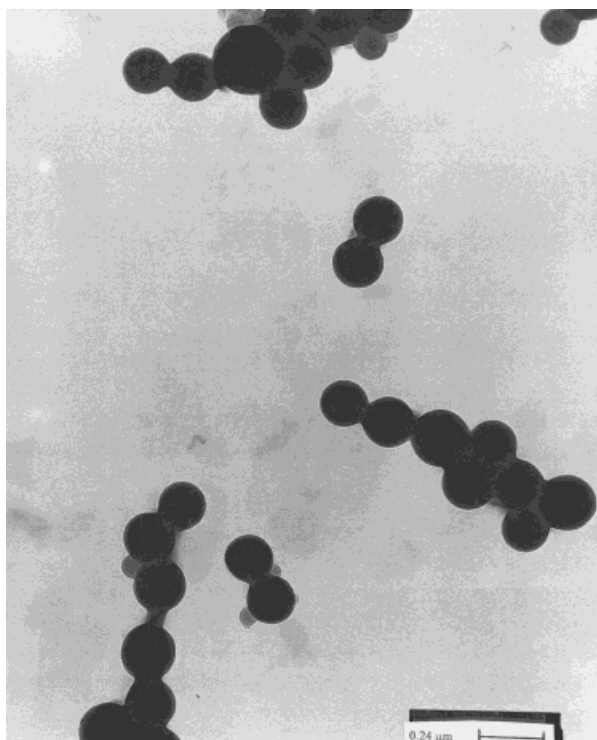
(a)

(b)

Figure 10 (a) TEM micrograph of polymer from experiment 6, (b) TEM micrograph of polymer from experiment 6.

ing a core–shell morphology. Using the right procedure produced different morphologies, one with an external domain composed only of PDEAEMA

and a second one in which DEAEMA is in both the internal and external domains. In order to achieve this, an oil-soluble initiator (AIBN) had to be used in the presence of POE ($n = 30$) nonyl phenol as emulsifier. However, to stabilize the core–shell, a high concentration of emulsifier must be used. If a water-soluble initiator ($K_2S_2O_8$) is used, a copolymer of styrene and DEAEMA is obtained.

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