Synthesis of Polymeric Nanofiber and Polymeric Nanosphere by Living Free Radical Polymerization

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ABSTRACT: Living free radical polymerizations are employed to synthesize the polystyrene copolymer. The applications of those copolymer in nanomaterials are elucidated in this research. It involves the copolymerization of styrene with 2-hydroxyethyl methacrylate. The copolymers are reacted with cinnamoyl chloride, and then irradiated with UV light. The polymeric nanofibers are formed by solvent splitting. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 101: 3550–3558, 2006

Key words: nanofiber; nanosphere; living free radical polymerization

INTRODUCTION

Polystyrene block copolymers are important materials because they possess several industrial applications. For example, they can be used as compatibilizers for polymer alloys. In this paper, polystyrene block copolymers are synthesized and their nanomaterial applications as nanofibers and nanospheres are elucidated. Nanofibers offer potential applications in nanofiltration and nanocomposites. They[1–5] are also used in some biomedical applications. The preparation of nanofiber has attracted much attention in the past decade since the preparation technique may be modified to construct nanometer-sized electronic and optical devices. Several approaches have been employed to prepare the nanofiber.[4–10] Block copolymer nanopatterning has been[1–10] investigated by several authors. A diblock copolymer, e.g., (A)n-(B)m, in which microdomains of B are uniformly distributed in the matrix of A. The domain structures vary depending on the composition of the relative n and m values. At a volume fraction roughly below 17%, B will exist as spheres dispersed in the continuous A phase. As the B content gradually increases to 60% by volume, the B domain changes its shape from spheres to cylinders, double diamonds, and lamella. In this paper, a diblock copolymer with a crosslinkable B block is synthesized by living free radical polymerization. Then, the cylindrical phase was crosslinked by UV irradiation. The dissolution of the continuous uncrosslinked phase by solvent splitting led to disentanglement of nanofibers.

Although conventional ionic polymerization can be used to prepare the block copolymers, it is tedious and uneconomical because the synthesis[11–13] involves high vaccum and low temperature (−70°C). Therefore, a living free radical polymerization is employed in this research to prepare the nanofibers despite it has broader molecular weight distribution than anionic polymerization. The synthetic scheme involves the solution copolymerization of styrene and 2-hydroxyethyl methacrylate by the living free radical polymerization.

On the other hand, in this research the styrene block copolymers are also used to prepare the star polymers and nanospheres. Star polymers are polymers that consist of more than three linear polymer chains of nearly equal lengths bonded together to a core. The core radius is smaller than the linear polymer chain lengths. On the other hand, if the core radius is larger than the linear polymer chain lengths the particle becomes a nanoparticle.[14] Therefore, the nanoparticle can be regarded as a nanosphere if their dimensions are almost spheric. Star polymers can be processed more easily than linear polymers for industrial applications. They can also be used as melt strength improvers. Recently,[15] it has been shown that the star polymer can be used to exfoliate the montmorillonite in clay nanocomposite. Nanospheres are used in the control release and photonic applications. Traditionally several methods are employed to synthesize star polymer. The first method is to add Silicon tetrachloride to the living anionic polymerization of styrene. This leads to a star polymer with four arms. It has been shown in the literature that the synthetic schemes become more difficult with star polymer

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TABLE I
The Different Mole Ratios of the Bulk Polymerization of Styrene in the Presence of TEMPO and BPO

Sample	Styrene (mL)	TEMPO (mmol/L)	BPO (mmol/L)	TEMPO/BPO
1	12.5	14.95	10.73	
2	6.25	29.9	21.47	
4	3.125	59.8	42.9	1.4
5	2.5	74.75	53.65	
6	2.083	89.70	64.38	

TABLE II
The Molecular Weight of as Sample 1[a] as Determined by GPC

Hours	M_n	M_w
3	38,158	64,406
5.5	42,834	66,520
11	41,475	65,217
16.5	43,167	65,996

[a] Styrene: 12.5 ml; TEMPO: 14.5 mmol/N; BPO: 10.73 mmol/L

TABLE III
The Changes in the Molecular Weight for different Mole Ratios of the Reactants

Sample	(M_w)	(M_n)	M_w/M_n
1	68,946	28,054	2.5
2	41,072	25,023	1.6
4	24,355	16,422	1.5
5	16,032	11,189	1.4
6	13,907	10,396	1.3

TABLE IV
The Mole Ratios of the Reactants for Synthesizing the Copolymer

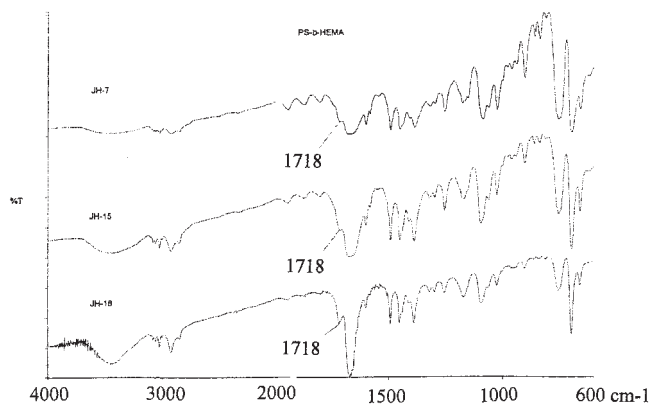| Copolymer	Polystyrene (mol)	HEMA (mol)	Dimethylformamide (as a solvent)
JH-7		0.6×10^{-3}	
JH-15		1.1×10^{-3}	
JH-16		2.1×10^{-3}	
JH-20	3.85×10^{-3}	1.1×10^{-3}	1.6mL
[a]JH-24		1.1×10^{-3}	
[b]JH-1		0.05	
[b]JH-2		0.05	

[a] Heated for 30 min.
[b] Heated for 3 h.

Figure 2 The increase in the intensity of the ester peak with the increasing amount of the HEMA (reaction time is 30 min).
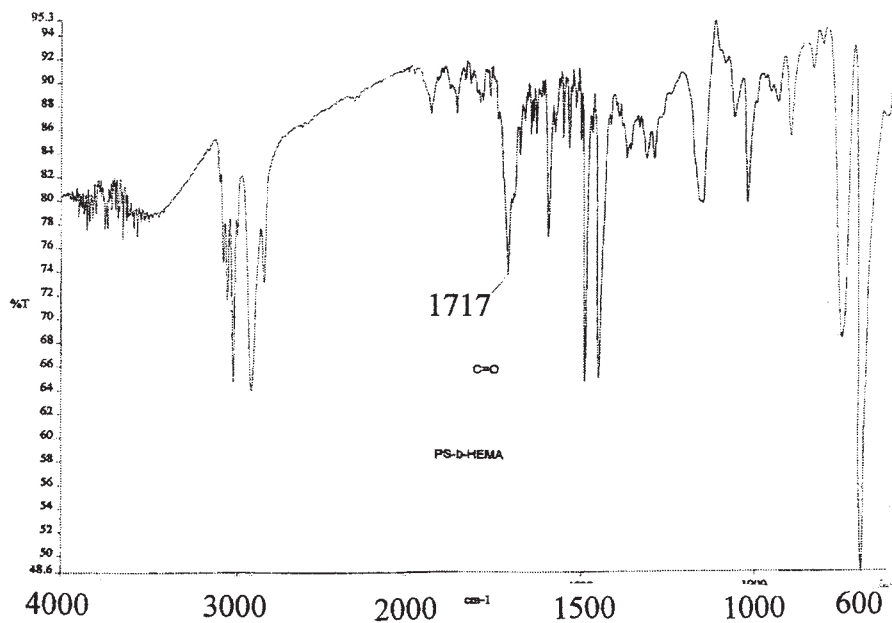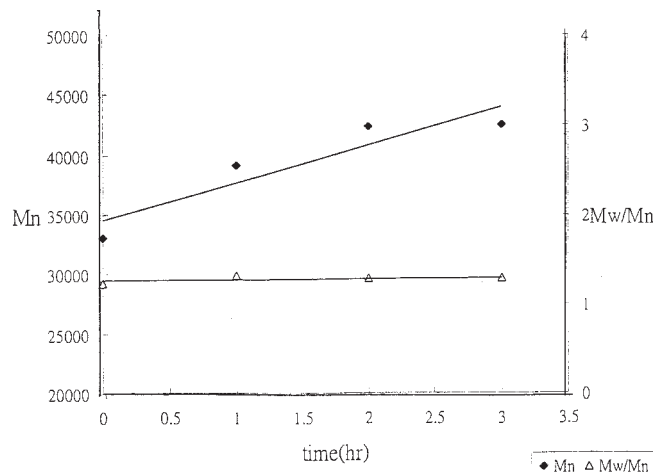

Figure 1 The FTIR spectrum of the copolymer.

Figure 3 The kinetics of the copolymerization. The molecular weights increase linearly with time.

possessing more arms. On the other hand, divinylbenzene is added to the living anionic polymerization of styrene. The divinylbenzene cores are crosslinked with the linear polystyrene as the arms. The shortcoming of the method is the broad f distribution.[14]

Nanospheres have been traditionally prepared by microemulsion polymerization. They are prepared by controlling the polymerization of difunctional and monofunctional monomers. As discussed by Liu and coworkers, the problem is related to a reaction[14] product of gelled polymers, micogels, and linear polymer chains. In this paper, a much easier living free radical polymerization rather than the traditional anionic polymerization is employed to synthesize the block copolymer. Nanospheres or star polymers can be produced by varying the value of m and n in AmBn. The end product is a star polymer for large n/m value. It turns out to be a nanosphere when the n/m is small. The formation of
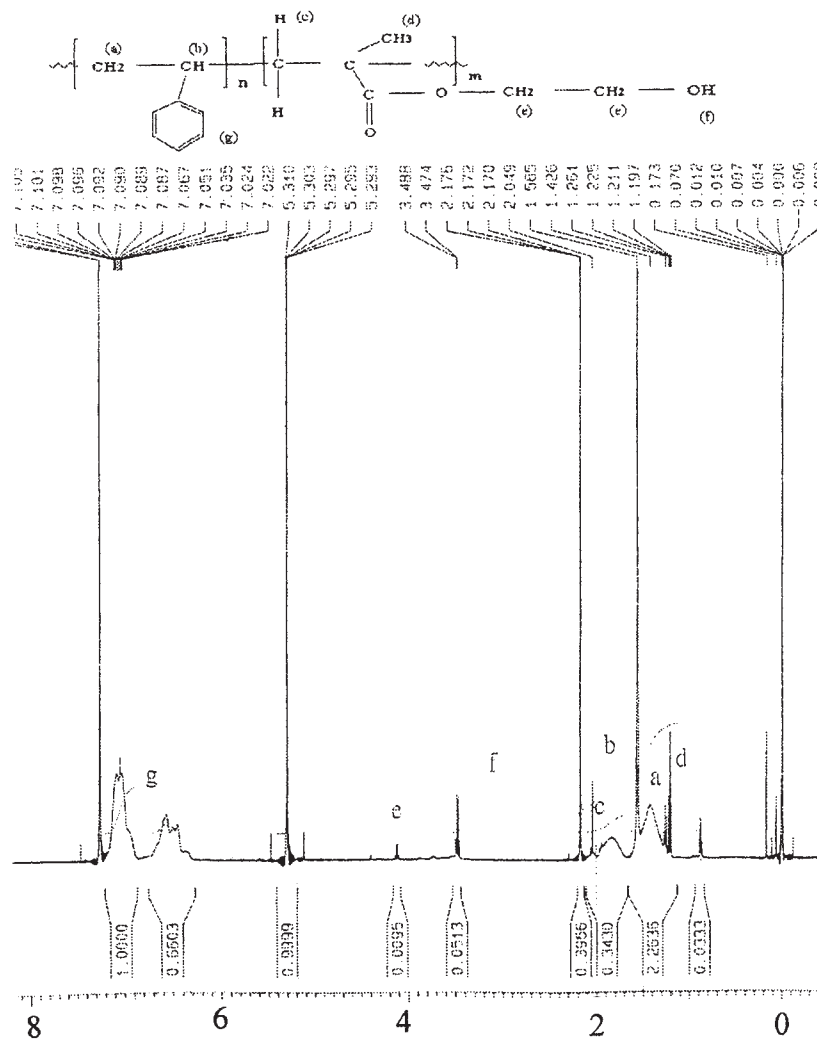
Figure 4 The HNMR of the copolymer.

nanosphere or star polymer is investigated in this paper. The potential applications of those copolymers are also discussed.

Experimental

Materials

Styrene and 2-hydroxy-ethyl methacrylate are form Aldich. Cinnamoyl Chloride and TEMPO (2,2,6,6-tetramethylpiperidin-1-yloxy) are also from Aldrich. Dibenzoylperoxide and Dimethylforamide are from Acros organics.

Synthesis

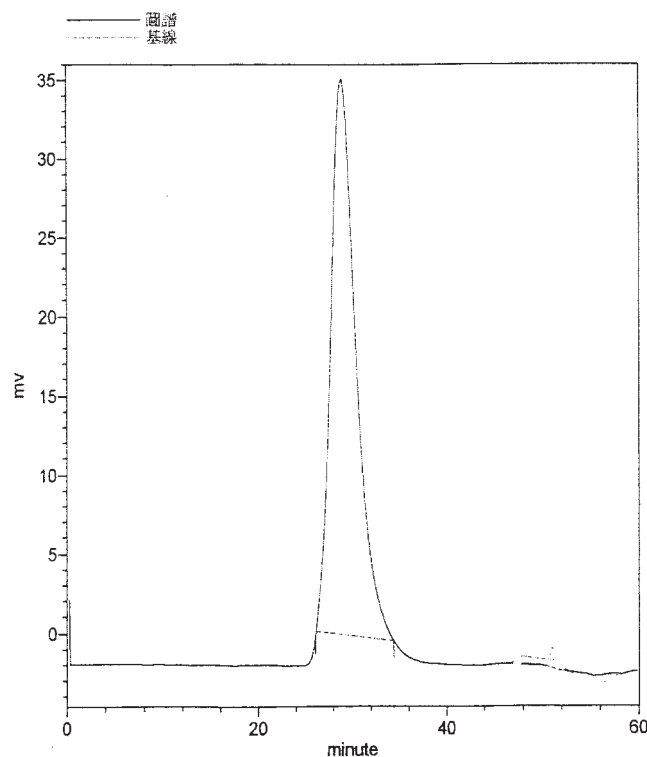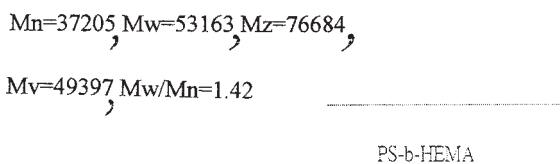The following synthetic schemes are used to synthesize the copolymer.
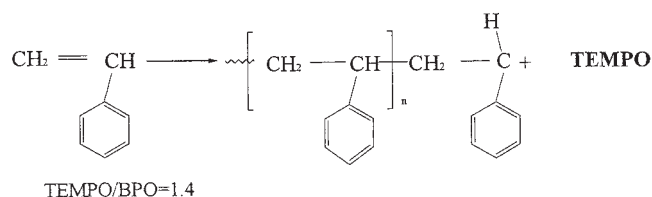*Synthesis of macroinitiators*

Mn=37205, Mw=53163, Mz=76684,

Mv=49397, Mw/Mn=1.42

PS-b-HEMA

Figure 5 The molecular weight distribution for the copolymerization.

TABLE V
The Polydispersity and N/M Values of the Copolymers

| Copolymer	Polydispersity	n/m
JH-7	1.2	3.0
JH-15	1.5	2.6
JH-16	1.5	2.6
JH-20	1.4	2.6
[a]JH-24	1.4	2.9
[b]JH-1	1.6	0.5
[b]JH-2	1.4	0.4

A mixture of styrene, dibenzoylperoxide and 2,2,6,6 tetramethylpiperidin-1-yloxy (TEMPO)(molar ratio of TEMPO/BPO = 1.4), are heated in a glass ampule in an inert atmosphere at 120°C for 17 h. The resulting macroinitiators are precipitated with ethanol from a dichloromethane solution.


Synthesis of the A_nB_m block copolymer
In each experiment, the polystyrene macroinitiator is mixed with 2-hydroxyethyl methacrylate and dimethylforamide (as a solvent), and the solution is heated in a glass ampule in an inert atmosphere at 100°C for 2, 4, 6, and 8 h.
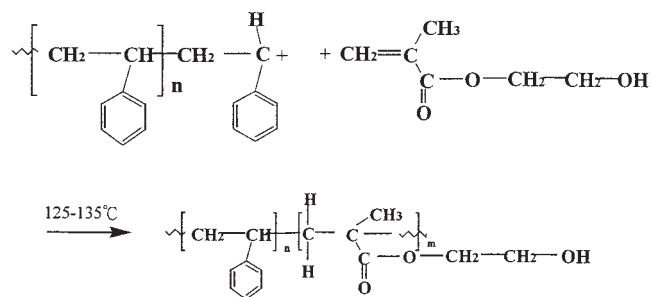
Synthesis of the block copolymer ester
0.1 g of PS-*b*-HEMA and 0.2 g of cinnamoyl chloride are dissolved in 10 mL of pyridine. The solutions are stirred for 24 h at room temperature to complete the esterification.

Pyridine
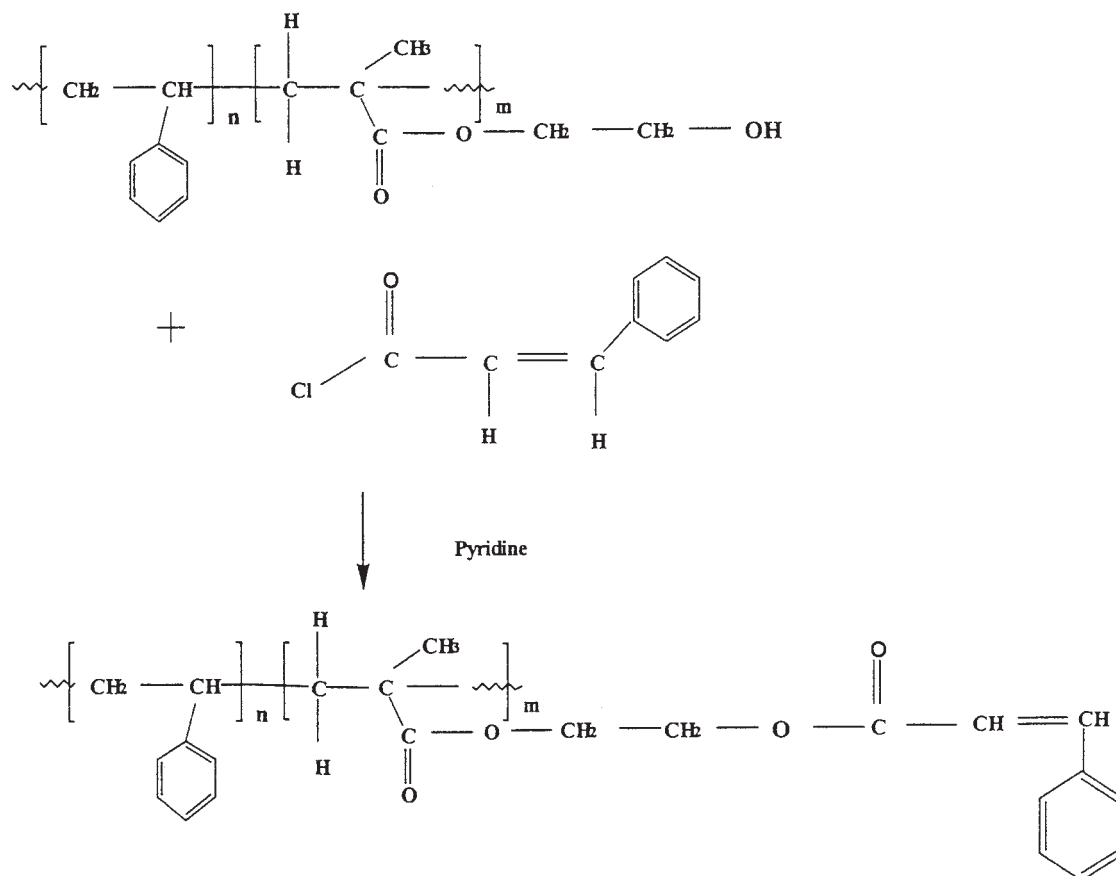
Polymer characterization

Nicolet FTIR (Impact 400) is used to characterize the copolymer. HNMR of the copolymer is characterized by Ruker AC-300 (300MHz) NMR. Polymer molecular weight is determined by Gel Permeation Chromatography (waters).

RESULTS AND DISCUSSION

Synthesizing the macroinitiators

The different mole ratios of the bulk polymerization of styrene in the presence of TEMPO and BPO are shown in Table I. The reaction mixture become gelled after 3 h for sample 1. The conversion is about 70%. Table II shows the molecular weight of sample 1 as determined by GPC. The number average molecular weight increases slightly from 38,518 to 43,168 even after gellation. Table III shows the changes of the molecular weight for different mole ratios of the reactants. Increasing the amount of TEMPO, the molecular weights decrease significantly, and the polydispersity also change to 1.3.

Copolymerization

The mole ratios of the reactants for synthesizing the copolymer are shown in Table IV. Figure 1 is the FTIR spectrum of the copolymer. There is an absorption peak at 1720 cm^{-1} (ester) which shows that the HEMA is copolymerized with the polystyrene macroinitiators. The intensity of the ester peak increases with the increasing amount of the HEMA (Fig. 2), with the reaction times of 30 min. The kinetics of the copolymerization is shown in Figure 3. The molecular weights increase linearly with time. Figure 4 is the HNMR of the copolymer. By integrating the area under the peak, the n/m of the copolymer is determined. Figure 5 shows the molecular weight distribution for the copolymerization. It is very narrow. The polydispersity and n/m value are shown in Table V. The value of n/m reach 2.6 for JH-7, JH-15, and JH-16 after 30 min. On the other hand, the reaction mixtures become gelled after 3 h if the amount of HEMA increases 50 times to that of JH-7.

Esterification of PS-b-HEMA with cinnamoyl chloride

Figure 6 shows the HNMR of the reaction product of PS-b-HEMA and cinnamoyl chloride and its FTIRspectrum is shown in Figure 7. There is an absorption peak at 1634 cm^{-1}, which result from C=C stretching.

Nanofiber formation

Copolymer solution in toluene 15% (by volume) is prepared. Thin films are obtained by casting and evaporating
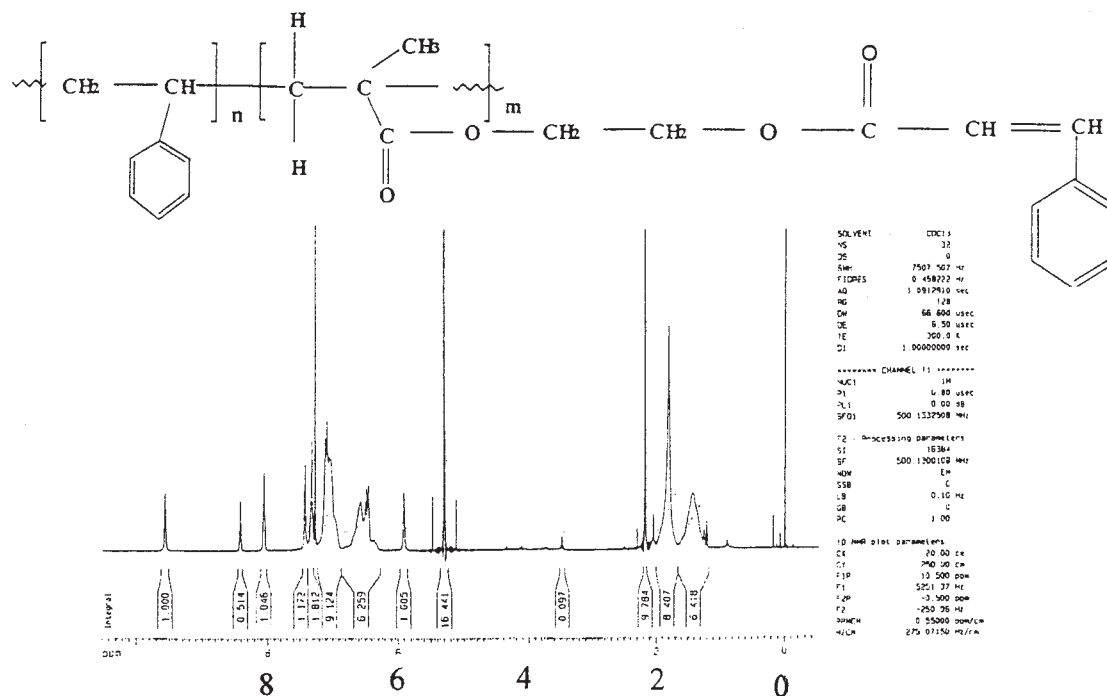
Figure 6 HNMR of the reaction product of PS-*b*-HEMA and cinnamoyl chloride.

them on water. The thin films are annealed under 30 cmHg pressure at 70°C for 3 days and 90°C for 1 week. B blocks in A$_n$B$_m$ copolymer self-assemble on the nanometer scale. After irradiating with UV, 0.02 g of the thin films are stirred in 60 mL of THF for 20 h. Upon centrifugation, a supernatant is separated from precipitate. The 0.1 mL of THF solution are dispensed on water to obtain a thin film. The film is transferred onto a copper grid for viewing through TEM. Their TEM pictures are shown in Figs. 8–10. The diameter is about 20 nm. It is found that the nanofibers are synthesized successfully even with copolymer possessing broad molecular weight distribution than ionic polymerization.
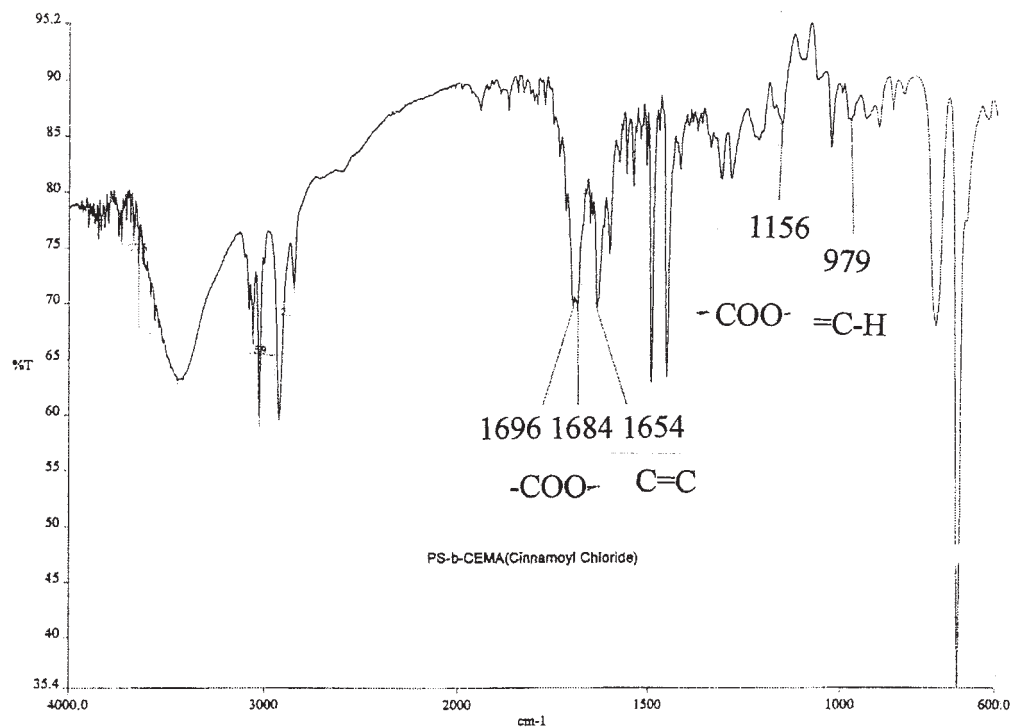

Figure 7 FTIR spectrum of Esterification of PS-*b*-HEMA with cinnamoyl chloride.
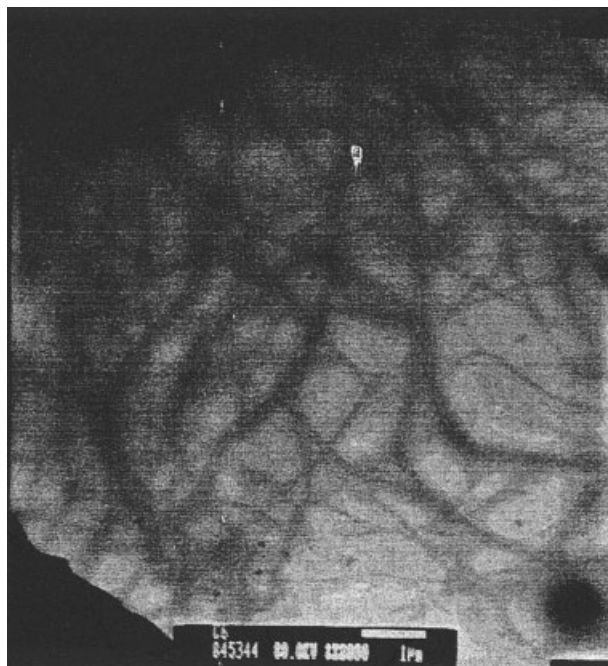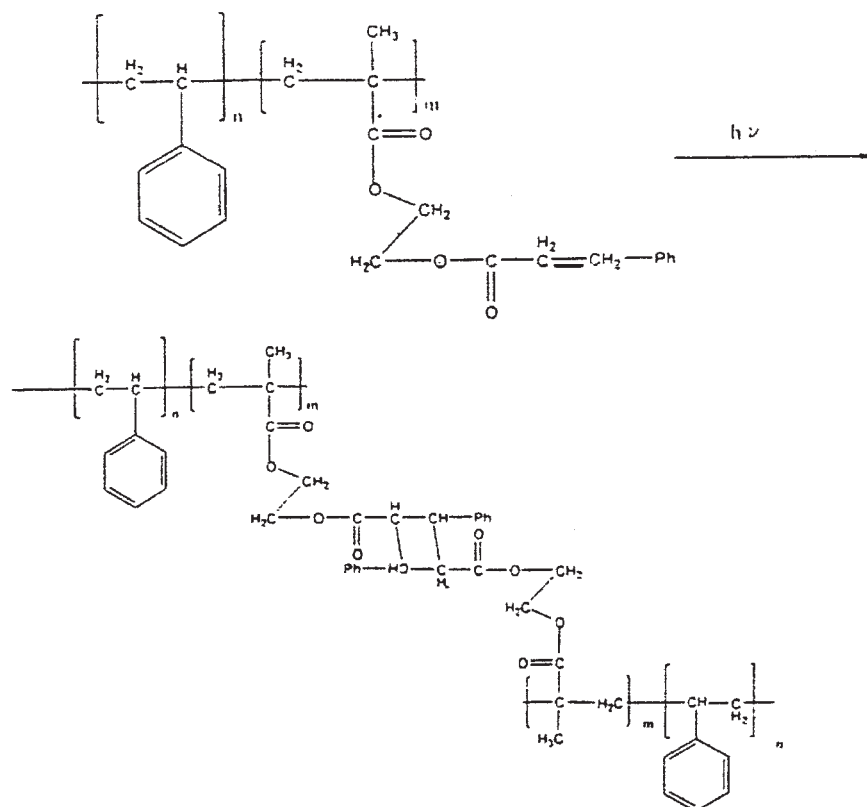
Figure 8   TEM pictures.

Figure 9   TEM picture of the different part of the sample.

Figure 11 shows the FTIR spectrum of the copolymer after UV irradiation. There are vigorous chemical reactions occurred after the UV irradiations as can be seen in Figure 11. It has been shown in the literature that the C=C bond has dimerized after the UV irradiation.
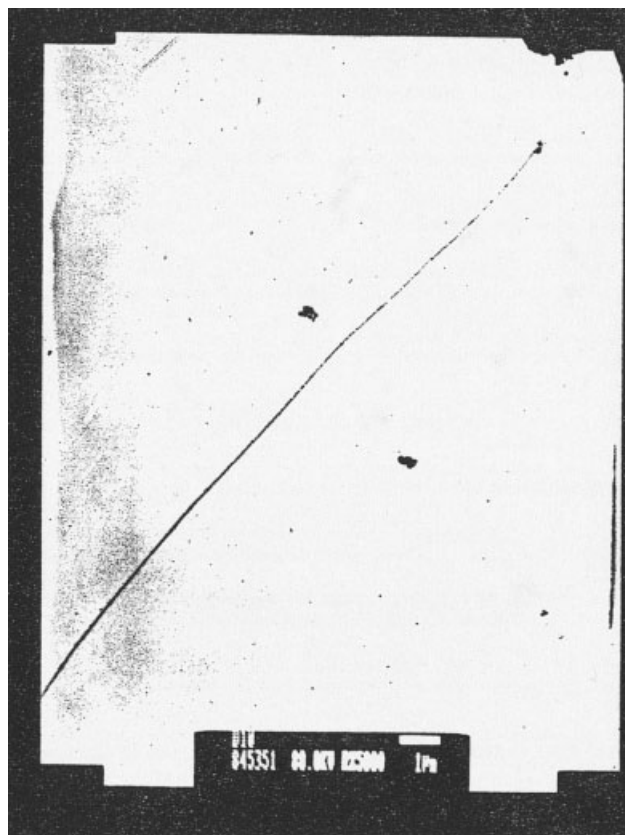
This reaction is shown below[11]

Figure 10 TEM picture of the different part of the sample.

The reaction is also responsible for the application of polyvinylcinnamate as a surface alighment film in liquid crystal industry. Therefore, the copolymer synthesized in this research can also be used in the LCD industry.

Star polymer and nanosphere

About 0.2 g of the copolymer ester (A_nB_m, $n/m = 3$, A = styrene, B = hydroxylethylmethacrylate) is dissolved in 6 mL of THF. 50 mL of cyclohexane are slowly added to the solution. With vigorous stirring, the solution is irradiated with 254 cm^{-1} UV light for
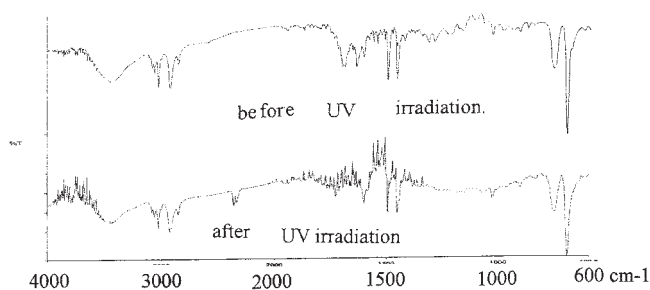

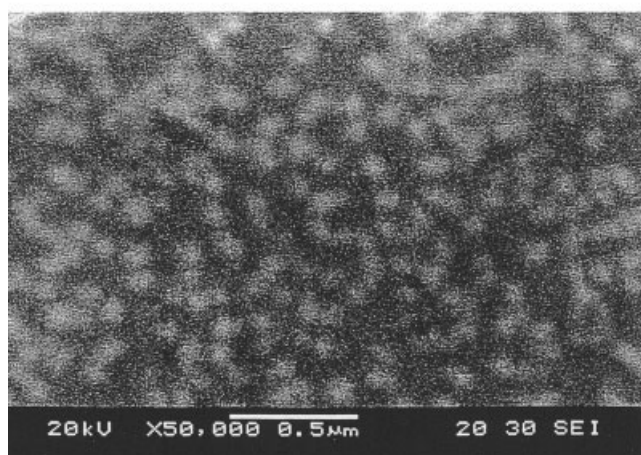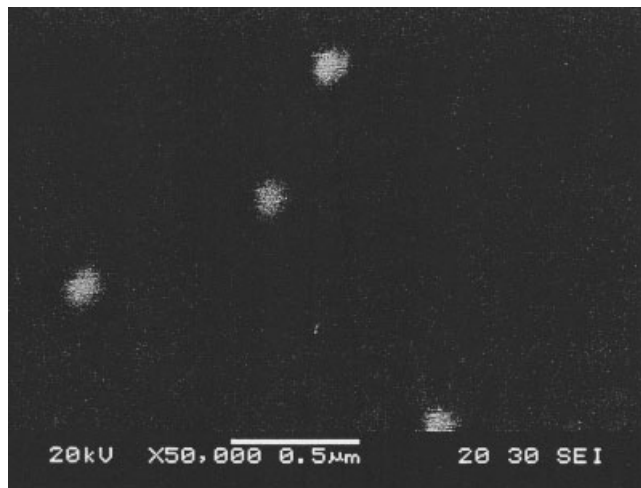**Figure 11** FTIR spectrum of the copolymer after UV irradiation.

Figure 12 SEM of the nanosphere before the UV irradiation.

120 min. The nanospheres are precipitated out by adding methanol. The products are filtered and dried under vacuum. Then, they are investigated using
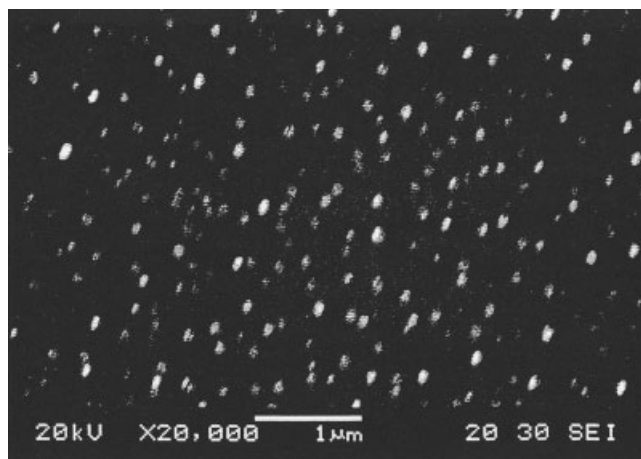

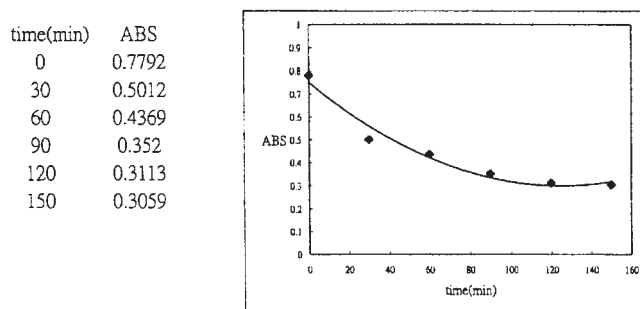**Figure 13** SEM of the nanosphere after the UV irradiation.

time(min)	ABS
0	0.7792
30	0.5012
60	0.4369
90	0.352
120	0.3113
150	0.3059

Figure 14 UV absorption at 274 cm^{-1}.

SEM. THF is a good solvent for both PS and PCEMA. On the other hand, Cyclohexane is a good solvent for PS but not for PCEMA. As discussed by Liu and coworkers,[14] solvated in the mixture of these two solvents, the PCEMA Blocks assemble as a core and the PS blocks become the hairy shell. Figure 12 shows the SEM of the nanosphere before the UV irradiation., while Figure 13 shows the SEM of the nanosphere after the UV irradiation. Figure 14 is the UV absorption at 274 cm^{-1}. The intensity decreases after the UV crosslinking. This proves that the crosslinking reactions occur under UV irradiation.

CONCLUSIONS

1. The nanofibers are successfully synthesized by the living free radical polymerization. Even with a broad molecular weight distribution, nanofibers can be obtained by molecular self-assembly.

2. The copolymer of styrene with HEMA has potential applications since the HEMA can be reacted with other functional groups to impart interesting properties.

3. The block copolymer of this study can be used as liquid crystal alignment film.

4. The star polymers and nanospheres are also successfully synthesized in this paper.

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