Photosensitive Microspheres for Photoresists

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SYNOPSIS

Crosslinked copolymer microspheres of n-butyl methacrylate (BMA) and 2-hydroxyethyl methacrylate (HEMA) having varied diameters and composition were prepared by emulsion polymerization. Photosensitive materials were obtained by reacting hydroxyl pendant groups with cinnamoyl chloride. Photosensitivity and conversion curves were determined after ultraviolet irradiation for different periods of time, and were evaluated as functions of composition and particle size. Minimum irradiation time for insolubilization for each product was also determined, and it has been noted that almost all of the photosensitive microspheres have shown higher performance compared to linear poly(vinyl cinnamate). Synthesized products were characterized by infrared and nuclear magnetic resonance spectroscopies, differential scanning calorimetry, size exclusion chromatography, and transmission electron microscopy. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Polymer microgel spheres have shown to be useful in many technological applications[1,2] as multifunctional crooslinking agents, surface coating modifiers, catalyst support, and cell markers[3] in biological and biomedical systems, because of their permanent spherical shape. This permanent morphology avoids intermolecular entanglement and is responsible for the spheres' low viscosity in concentrated solution even in the very high molecular weight range.[4,5]

The formation of images by photographic processes is essential in microelectronic.[6,7] Line widths of 4 μm are routinely produced in integrated circuits by exposition of photosensitive polymers (photoresists) to ultraviolet (UV) irradiation under photo masks. In many applications, such as photocrosslinking reaction of photoresists, gelation in the case of negative photoresists is far more dependent on molecular weight buildup than on the progress of photodimerization reaction, and the use of higher

molecular weight photosensitive polymer usually introduces to the system great benefit in terms of shorter time to insolubilization. However, higher molecular weight means higher viscosities and also introduces chemical instability in this kind of system. Therefore, the use of another type of high-molecular-weight polymeric support, with permanent shape and lower viscosity in solution, for photosensitive group bonding should mean better response to UV irradiation to insolubilization. Influence of polymer matrix on photodimerization of cinnamate groups in photosensitive polymers has been subject of our previous studies,[8,9] and factors such as glass transition temperature (T_g) of polymer matrix and specific interactions due to hidrogen bonding or ionic interaction modify the domain sizes and also the photoreactivity.

It is the aim of this study to elucidate the possibility of enhancing photosensitivity of polymers by designing a new morphology which maintains the favorable physical properties found in microgel spheres, such as low solution viscosity and low swelling after photocrosslinking. Another objective of this study is to propose a new reactive core–shell type polymer, which retains the original polymer matrix properties in the core part and presents a reactive shell on the surface.

In this study, a two-step reaction procedure was employed for the microgel spheres' preparation. In the first step, permanent spherical copolymer particles bearing varied amounts of reactive hydroxyl groups were obtained by water emulsion copolymerization of different proportions of 2-hydroxyethyl methacrylate (HEMA) and n-butyl methacrylate (BMA), and in a second step, hydroxyl groups were reacted with cinnamoyl chloride to form photosensitive polymers.

EXPERIMENTAL

Materials

Microgel spheres having varied amounts of hydroxyl groups were synthesized by emulsion copolymerization of HEMA and BMA in the presence of small amounts of ethylene glycol dimethacrylate at 60°C under magnetic stirring and nitrogen atmosphere for 22 h. A monomer : aqueous solution ratio of 4 : 75 was established for low gel formation. Lauryl sodium sulfate was used in different concentrations as emulsifier, and potassium persulfate $(8 \times 10^{-3}M)$ and sodium bicarbonate $(1.6 \times 10^{-3}M)$ were employed as free radical initiator and buffer, respectively, in the emulsion polymerization. Complete reaction conditions are described elsewhere.[10] Aqueous solution of the microgel was bluish, slightly opaque, and translucent. The pendant hydroxyl groups in the microspheres were further esterified with cinnamoyl chloride in pyridine at 50°C for 18 h. A molar excess of 4 : 1 cinnamoyl group to hydroxyl group was used to assure a complete conversion of hydroxyl groups. The products were recovered by pouring the resulting solution into an aqueous solution of 10% $NaHCO_3$, and the precipitated product was purified by successive washings with an aqueous solution of 10% $NaHCO_3$ followed by reprecipitation of its chloroform solution into methanol. Complete conversion of hydroxyl groups to cinnamoyl groups was monitored by infrared (IR) spectroscopy and ^{1}H-NMR spectrometry. The photosensitive microgel spheres were dispersed in chloroform and stored in a refrigerator at −10°C. Poly(vinyl cinnamate) (PVC) was synthesized by transesterification of poly(vinyl acetate) $(M_w = 50,000)$ with cinnamoyl chloride in pyridine at 50°C for 18 h.

Characterization

The chemical structures of the products were characterized by using a Perkin-Elmer PE-467 IR spectrometer, Varian Cary-17 UV-VIS spectrophotometer, and Varian CFT-20 ^{1}H-NMR spectrometer. Thermal properties of hydroxylated and cinnamoylated samples were evaluated by differential scanning calorimetry (DSC) using a Perkin-Elmer DSC-2 calorimeter; monitored temperature ranged from −40 to 150°C at a heating rate of 10°C/min. Hydroxylated microspheres' aqueous emulsions were diluted to 0.25% and deionized by mixed bed ion exchanger resin Amberlit MB3 for microscopic observation. Microspheres' particle size was determined by transmission electron microscopy (TEM) using a Jeol 100CX transmission electron microscope; phosphotungstic acid was used for negative contrast, by increasing electron density of the Formvar™ film support on the copper grid. Photosensitive microgel spheres were soluble only in organic solvents and were inadequate for observation on the Formvar™ film support used in TEM. Size exclusion chromatography (SEC) was carried out in order to evaluate the size distribution of the photosensitive microgel spheres having cinnamate groups. A Toyo Soda HLC-803A high-performance liquid chromatograph equipped with UV and RI detectors and a set of poly(styrene divinylbenzene) columns, G-4000H10 (pore size of 10^4 Å) and G2000H6 (pore size of 10^2 Å), was used and analyses were performed in tetrahydrofuran solutions and using monodisperse polystyrene standards.

Evaluation of Photosensitivity

Film specimens were obtained by casting 0.05 to 0.10 mL of chloroform solution containing 0.5–1.0% of sample of microspheres on quartz plates. Films were evaporated at room temperature and then dried at 65°C for 30 min on a thermostatic plate. Films were irradiated at 30°C for a given period of time at a distance of 45 cm from an Ushio Denki Co. 250W ultra high pressure mercury lamp, with a light intensity of 19.5 μWcm^{-2}. A rotating sector was used to reach short exposition times of films to UV irradiation.

The extention of dimerization of cinnamoyl groups, after irradiation by UV light, was monitored by UV spectrometry in the range from 200 to 400 nm. Initial absorbance value was kept under 0.5 in order to achieve uniform light absorption. Photoreactivity of cinnamoyl group in the microgel was estimated by the UV absorption at 270 nm as a function of irradiation time.

Photosensitivity was evaluated on films of the microgel spheres having cinnamoyl groups by using

Table I Composition of Microspheres and Emulsion Copolymerization Conditions

Hydroxylated Copolymer	Cinnamoylated Copolymer	HEMA Mol Fraction in Monomer Feed[a]	NaLS[b] (%)
HB 100-1H	HB 100-1C	1	4.12
HB 80-1H	HB 80-1C	0.8	4.12
HB 80-2H	—	0.8	2.06
HB 80-3H	HB 80-3C	0.8	1.04
HB 80-4H	HB 80-4C	0.8	0.792
HB 80-5H	HB 80-5C	0.8	0.236
HB 50-1H	HB 50-1C	0.5	4.12
HB 20-1H	HB 20-1C	0.2	4.12
HB 20-2H	HB 20-2C	0.2	2.72
HB 20-3H	HB 20-3C	0.2	0.236

[a] Monomer mixture containing 5% w/w of diethylene glycol dimethacrylate.
[b] Sodium lauryl sulfate in total aqueous emulsion of 75 g.

the minimum UV irradiation time to form a complete pattern of the crosslinked film on a quartz plate after immersion of the irradiated film in toluene. The solubilization time in toluene was regulated by an unirradiated film, used as a control of total time for complete dissolution.

RESULTS AND DISCUSSION

Photosensitive Microsphere Preparation

Microgel spheres having various amounts of hydroxyl groups were synthesized by emulsion copolymeriza-
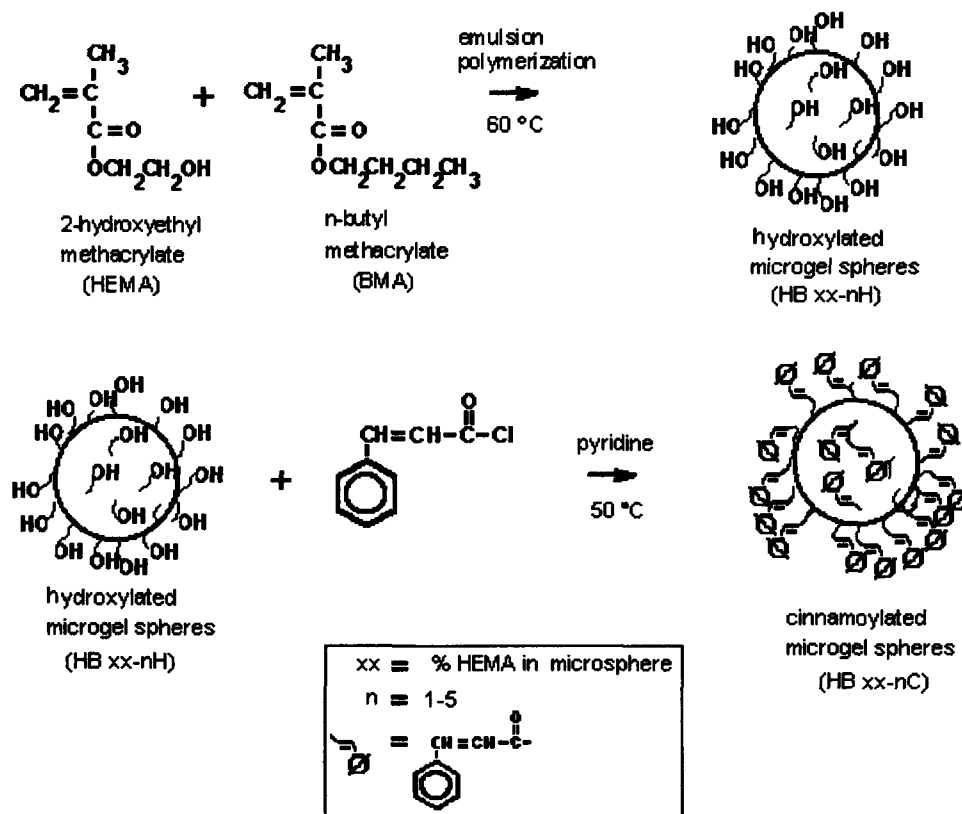

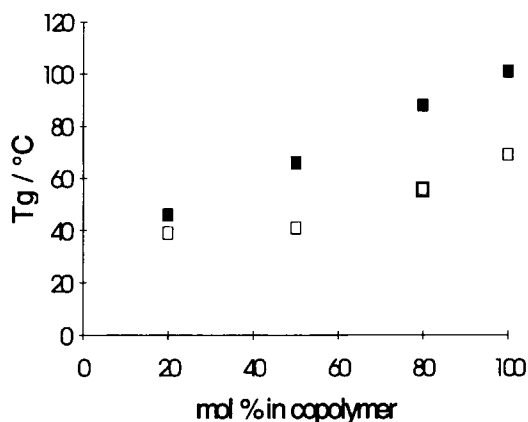**Figure 1** General scheme for photosensitive microsphere preparation.

Figure 2 Dependence of T_g of copolymer microspheres on the composition, in mol %, of hydroxylated comonomer (■) and cinnamoylated comonomer (□).

tion of HEMA and BMA in the presence of small amounts of ethylene glycol dimethacrylate. Aqueous solution of the microgel after polymerization was bluish, slightly opaque, and translucent. The emulsion polymerization conditions and the microsphere samples prepared are shown in Table I.

Hydroxylated microspheres were esterified by cinnamoyl chloride in order to obtain photosensitive microspheres. The whole reaction scheme is presented in Figure 1.

Characteristics of Microgel Spheres

Samples of microgel spheres bearing hydroxyl groups showed one T_g in the DSC curve. The T_g of the hydroxylated microsphere sample increased steadily with the increasing of the HEMA units present in the copolymer, as shown in Figure 2. Therefore, HEMA and BMA units could be considered to be dispersed randomly in the microgel spheres with no preferential location, in spite of the solubility of HEMA in water. The solubility of HEMA in water should introduce a complex distribution of concentration between micelles and intermicellar fluid, and this equilibrium can affect the size and symmetry of the micelle.[11,12] The dependence of T_g on the composition of these copolymers indicates a complete miscibility of the two comonomers. By this polymerization procedure, core–shell type polymers, which keep determined polymer matrix properties in the core part and present a reactive shell on the surfaces, were not produced. Aqueous solution of the microgel was bluish and translucent.

After the reaction of hydroxylated copolymer microspheres with cinnamoyl chloride, the IR and nu-

clear magnetic resonance spectra of the microgel spheres showed conversion of all the hydroxyl groups to cinnamate under the conditions of esterification employed in this work: molar excess of acid chloride, low temperature, and long reaction time. The T_g of the esterified microgel spheres decreased in comparison with the T_g of the corresponding spheres having hydroxyl groups (Fig. 2). This behavior should be explained by higher intra- and intermolecular interaction due to hydrogen bonding observed in the hydroxylated samples, increasing the energy required for main-chain segmental motion. Another possibility should be the increase of the free volume by introduction of the bulk cinnamate groups.

Figure 3 shows some electron micrographs of the microspheres before esterification. The size of the microspheres ranged from 40 to 50 nm for HB 20-1H, HB 50-1H, and HB 80-1H. Larger and irregular particles were observed for HB 20-3H, HB 20-2H, HB 80-4H, and HB 80-3H in the range from 50 to 90 nm, however these microspheres were not uniform and their irregular shape was due to aggregation of smaller microspheres. Dependence of microsphere size on reaction conditions is better observed in Figure 4.

Chloroform solution of the microgel spheres esterified with cinnamoyl chloride had a dull red color. Because its solubility is limited to organic solvents, electron micrographic work on these microgel spheres was hard, as support film on the copper grid was Formvar™. Therefore, sizes of these microgel spheres were investigated by using SEC. Figure 5 shows the SEC results, where HB 20-3C, HB 20-2C, HB 20-1C, HB 50-1C, and HB 80-5C, were shown to be formed of smaller microspheres than the corresponding microspheres bearing hydroxyl groups, observed by TEM. These samples presented polymodal SEC curves or wide polydispersity, which should be attributed to sample formation from different species of nucleation. Monomodal and narrower particle size distributions were observed for HB 100-1C, HB 80-1C, HB 80-4C, and HB 80-3C, where combination of higher HEMA and emulsifier concentrations allowed preferential radical nucleation inside micelles.

For monomodal distributions found by SEC, it was possible to classify microsphere samples in the following order of decreasing size: HB 100-1C > HB 80-1C > HB 80-4C > HB 80-3C.

These results indicate a coemulsifier action of poly(HEMA) by stabilizing increased amounts of monomers inside micelles and allowing larger par-
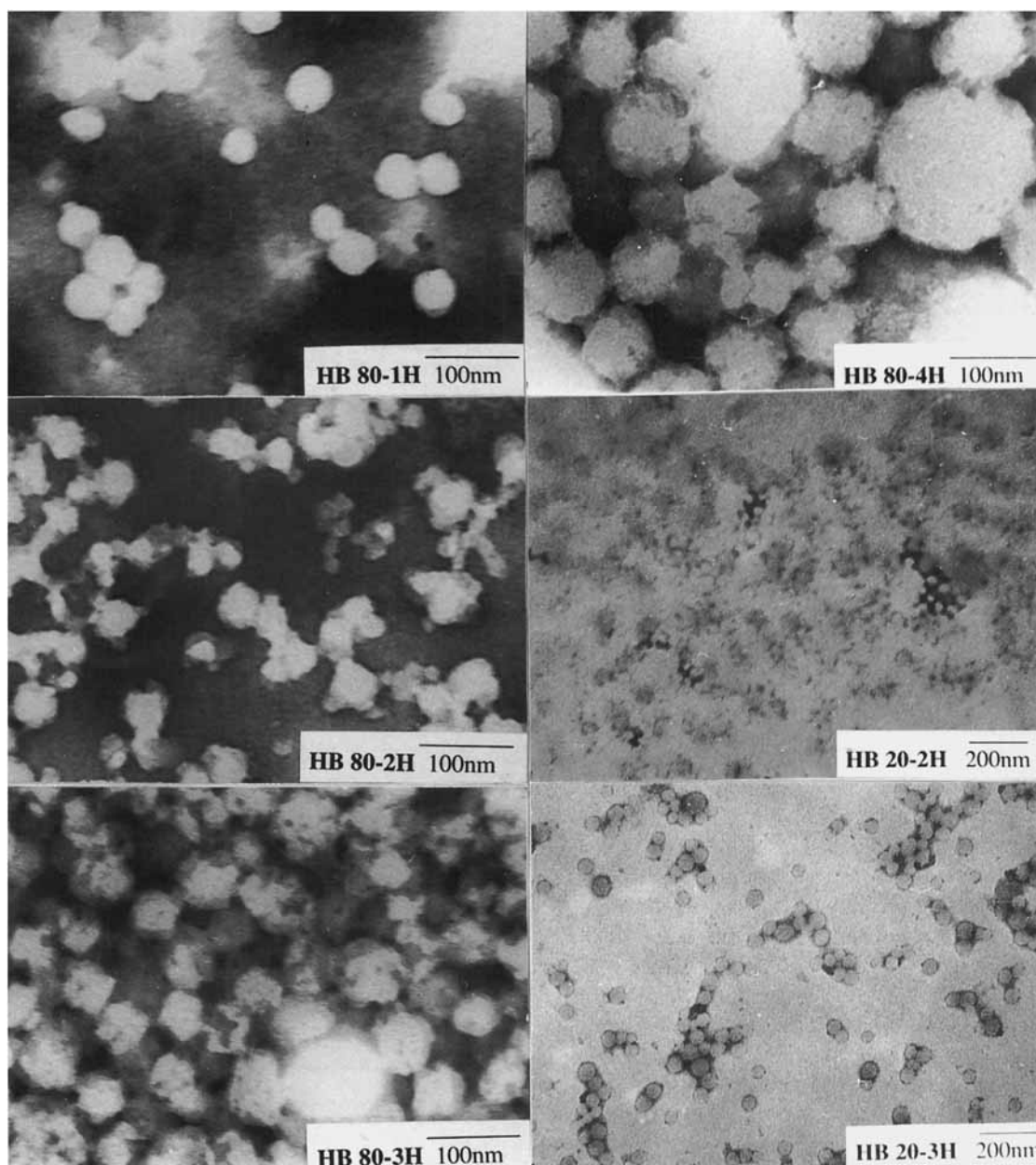
Figure 3 Transmission electron micrographs of polymeric microspheres bearing hydroxyl groups.

ticle formation in aqueous emulsion systems containing a polar component[13] and a higher concentration of emulsifier.

As expected, smaller particles and polidispersed particle sizes due to agglomeration were observed under lower concentrations of emulsifier, where nucleation occurred inside micelles and also in the aqueous media. The presence of fine particles aggregated on the surface of larger particles and/or dispersed among the larger particles was observed in most of the micrographs; in these cases the evaluation of particle size by TEM was inaccurate, so the size data presented in Figure 4 and Table II concern the medium particle diameter and disregard those fine particles. It is believed that in this case the distribution of particle size is better understood by SEC. By this technique, samples should be fractionated by size before detection, with differentiation of physically aggregated particles from chemically bonded particles.
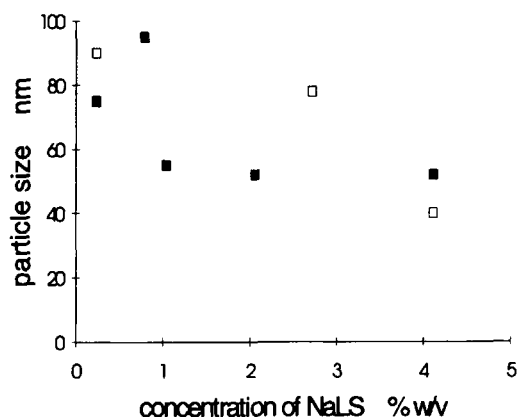
Figure 4 Dependence of microsphere size on emulsifier concentration and copolymer composition, series HB 80 (■) and HB 20 (□).

Films of the microgel spheres esterified with cinnamoyl chloride were very soluble in toluene. However, films of HB 100-1C and HB 20-3C were unstable to heat and became insoluble in organic solvents. These samples were not tested for photoinsolubilization by UV irradiation.

Photosensitivity

Photodimerization reaction of cinnamoyl groups takes place preferentialy in the solid state.[14] The concerted mechanism of this reaction is strongly dependent on the local geometry of the reactive groups, due to the low energy of the surroundings and to the short life time of the active species.[15–17] In polymers, the presence of flexible side-linking groups increases the mobility and reactivity of the cinnamoyl groups and the photoreactivity is strongly dependent on the T_g.[8,9] The photoreactivity of cinnamoyl groups in the microgel spheres are shown in Figures 6 and 7. The photoreactivity of the samples was dependent on the concentration of cinnamoyl groups. Higher conversion curves were found for linear PVC and HB 80-1C compared with HB 100-1C, HB 50-1C, and HB 20-1C. Copolymer with 50 mol % of HEMA showed the same reactivity as samples containing 20 mol %. The lower reactivity of HB 100-1C should be attributed to its thermal instability, which would decrease the mobility of reactive groups.

Figure 7 shows the influence of the particle size on the photoreactivity of the cinnamoyl groups in the microgel spheres. HB 80-1C and HB 80-4C or HB 20-1C and HB 20-2C, which are combinations of different sizes of microgel spheres, showed the same photoreactivity for cinnamoyl groups, respec-

tively, and two distinct conversion curves could be observed. These results showed the photoreactivity of cinnamoyl groups to be independent of particle size of microspheres and conversion rate increased with concentration of photosensitive groups.

Table II summarizes physico-chemical properties of microgel spheres: particle size determined by TEM and SEC, thermal properties determined by DSC, and the photosensitivity concerning photoinsolubilization.

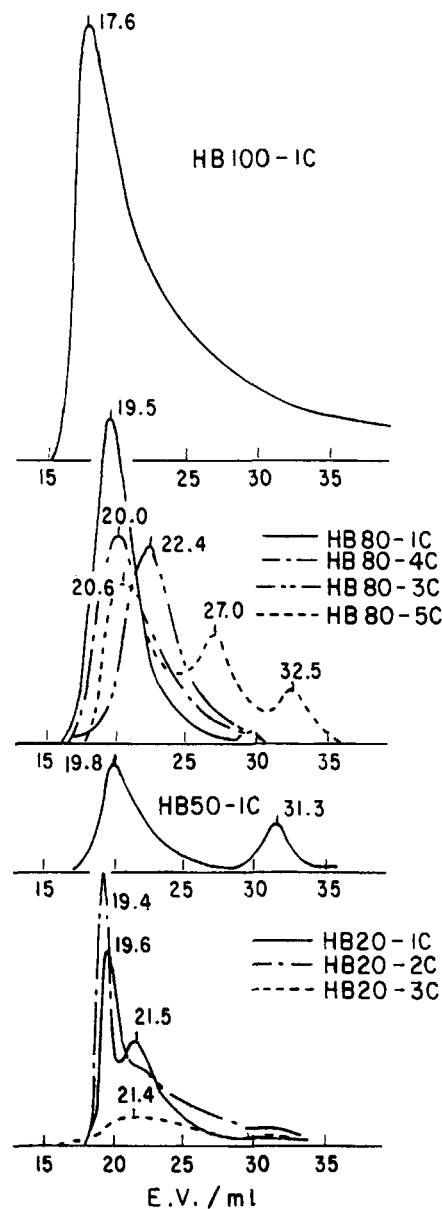The photoinsolubilization rate was found to increase drastically with increasing the amount of

Figure 5 Size exclusion chromatography curves of cinnamoylated microspheres observed with a UV detector.

Table II Properties of Microgel Spheres

	Hydroxylated Microspheres			Cinnamoylated Microspheres			Photosensitivity	
Sample	T_g (°C)	Particle Size (nm)	Sample	T_g (°C)	SEC[a] EV (mL)		Time (s)[b]	RS[c]
HB 100-1H	101	—	HB 100-1C	69	23.6		—[d]	—
HB 80-1H	88	50 (45–55)	HB 80-1C	56	19.5		0.016	47
HB 80-3H	85	55 (50–55)	HB 80-3C	57	22.4		0.064	12
HB 80-4H	88	95 (85–100)	HB 80-4C	56	20.0		0.064	12
HB 80-5H	88	75 (70–80)	HB 80-5C	56	20.6 27.0	32.5	1.504	0.5
HB 50-1H	66	40 (35–45)	HB 50-1C	41	19.8	31.3	0.094	8
HB 20-1H	46	40 (35–45)	HB 20-1C	39	19.6 21.6		0.376	2
HB 20-2H	45	75 (70–85)	HB 20-2C	37	19.4 21.5		0.128	6
HB 20-3H	46	90 (80–100)	HB 20-3C	39	17.0 21.4		—[d]	—
			PVC[e]	14	23.6		0.75	1

[a] Elution volume at peak of SEC curve.
[b] Minimum irradiation time to insolubilization in toluene.
[c] Relative photosensitivity calculated with that of PVC as unity.
[d] Thermally crosslinked after solvent evaporation.
[e] Poly(vinyl cinnamate).

cinnamoyl groups and the size of the microgel spheres. In spite of the minor photoreactivity of cinnamoyl groups in HB 80-1C in comparison with that of PVC, the relative photosensitivity of HB 80-1C was about 50 times higher than that of PVC.

In this work, photoreactive groups could not be introduced only onto the surface of the microgel spheres in order to increase intermolecular photo-

dimerization at the expense of intramolecular reaction. However, photoreactivity to insolubilization enhancement was observed in comparison with linear PVC and this effect is believed to be due to the higher molecular weight of microspheres, which was responsible for shorter irradiation time to gel point. Also, a negative influence on the performance was
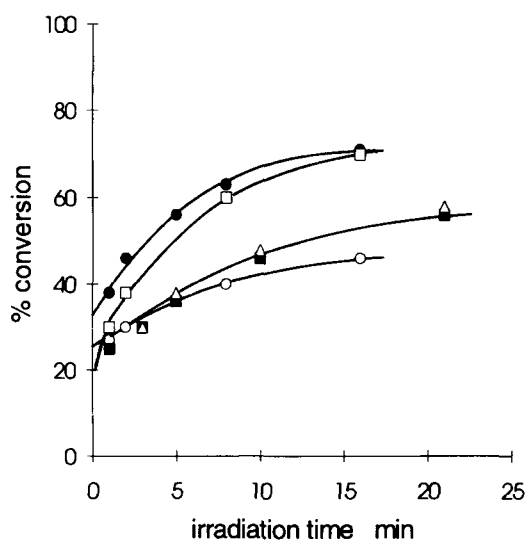

Figure 6 Time conversion curves of cinnamoyl groups by UV irradiation, in microgel spheres with different amounts of cinnamoyl groups: PVC (●); HB 100-1C (■); HB 80-1C (□); HB 50-1C (△); HB 20-1C (○).
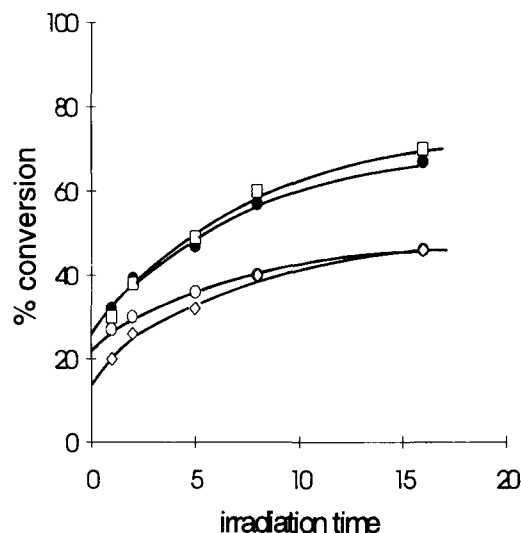

Figure 7 Influence of particle size on the photoreactivity of cinnamoyl groups by UV irradiation, in microgel spheres of different composition: with 80 mol %, HB 80-1C (□) and HB 80-4C (○); and with 20 mol %, HB 20-1C (○) and HB 20-2C (◇).

observed in the presence of smaller particles, as observed by SEC. Those particles seemed to retard the gel point because of their lower molecular weight.

CONCLUSIONS

Photosensitive copolymers for photoresist applications were synthesized with permanent spherical shape by two-step reaction. In the first step, emulsion copolymerization of HEMA and BMA allowed preparation of microgel spheres having varied amounts of reactive hydroxyl groups; and in the second step, hydroxyl groups were reacted with cinnamoyl chloride to form photosensitive polymers. Mild reaction conditions were used in the synthesis in order to preserve the photoreactive cinnamoyl groups.

In spite of the solubility of HEMA in water, reactive polymers of core–shell type, which keeps determined polymer matrix properties in the core part and presents a reactive shell on the surface, were not obtained by this polymerization procedure.

UV irradiation of cinnamoyl groups observed by UV spectrometry showed higher reactivity for microspheres containing larger amounts of cinnamoyl groups, and linear PVC was more reactive than those microspheres containing 80 mol % of photosensitive groups, HB 80-1C, which was more reactive than the corresponding 50 mol % and 20 mol %, HB 50-1C and HB 20-1C, respectively. It was also observed that the dimerization rate of cinnamate groups was dependent on concentration regardless of particle size of microgel spheres.

Photoinsolubilizations by UV irradiation have shown a better performance for monomodal distributed samples, as observed by SEC, and larger particles, corresponding to lower elution volume, were responsible for shorter irradiation time to gel point. The presence of smaller particles in the polymodal distributed samples shifted the gel point to longer irradiation times. Most of the microspheres tested in this study presented shorter gel times compared to linear PVC. And the relative photosensitivity of HB 80-1C was about 50 times higher than that of PVC.

REFERENCES

1. W. Straehle and W. Funke, *Makromol. Chem.,* **76,** 259 (1979).
2. W. Funke, *J. Oil Col. Chem. Assoc.,* **60,** 438 (1977).
3. A. Rembaum, *Pure and Appl. Chem.,* **52,** 1275 (1980).
4. M. Hoffman, *Makromol. Chem.,* **175,** 613 (1974).
5. K. S. Kim, S. H. Cho, and J. S. Shin, *Polym. J.,* **27,** 508 (1995).
6. R. A. Colclaser, *Microelectronics: Processing and Device Design,* John Wiley and Sons, New York, 1980, Chap. 1.
7. C. E. Hoyle, *Am. Paint and Coat. J.,* **May 14,** 42 (1984).
8. C. Azuma, K. Sanui, and N. Ogata, *J. Appl. Polym. Sci.,* **27,** 2065 (1982).
9. C. Azuma, N. Hashizume, K. Sanui, and N. Ogata, *J. Appl. Polym. Sci.,* **28,** 543 (1983).
10. S. H. Wang, *Síntese de Microesferas para Aplicação como Fotorresistes,* M.Sc. Thesis, IMA/Universidade Federal do Rio de Janeiro, Brazil, 1986.
11. P. Mukerjee, *Pure and Appl. Chem.,* **52,** 1317 (1980).
12. N. J. Turro, B. H. Baretz, and P-L. Kuo, *Macromolecules,* **17,** 1321 (1984).
13. A. Rembaum, S. P. Yen, E. Cheovy, S. Wallace, R. S. Molday, and I. L. Gordon, *Macromolecules,* **9,** 328 (1976).
14. P. L. Egerton, E. M. Hyde, J. Trigg, A. Payne, P. Beynon, M. V. Mijovic, and A. Reiser, *J. Am. Chem. Soc.,* **103,** 3859 (1981).
15. M. D. Cohen, *Angew. Chem.,* **14,** 386 (1975).
16. H. I. Bernstein and W. C. Quinby, *J. Am. Chem. Soc.,* **65,** 1845 (1943).
17. G. M. J. Schmidt, *Pure and Appl. Chem.,* **27,** 647 (1971).