Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

SYNTHESIS OF POLY(METHYL METHACRYLATE)-SILICA NANO-COMPOSITES. II. POLY[METHYL METHACRYLATE-*block*-(METHYL METHACRYLATE-*co*-2-HYDROXYETHYL METHACRYLATE)]

Reiko Saito[a]; Yasutaka Mori[a]
[a] Department of Organic and Polymeric Materials, Tokyo Institute of Technology, Tokyo, Meguro-ku, Japan

To cite this Article Saito, Reiko and Mori, Yasutaka(2002) 'SYNTHESIS OF POLY(METHYL METHACRYLATE)-SILICA NANO-COMPOSITES. II. POLY[METHYL METHACRYLATE-*block*-(METHYL METHACRYLATE-*co*-2-HYDROXYETHYL METHACRYLATE)]', Journal of Macromolecular Science, Part A, 39: 9, 915 — 934

To link to this Article: DOI: 10.1081/MA-120013571

URL: http://dx.doi.org/10.1081/MA-120013571

MARCEL DEKKER, INC. • 270 MADISON AVENUE • NEW YORK, NY 10016

JOURNAL OF MACROMOLECULAR SCIENCE
Part A—Pure and Applied Chemistry
Vol. A39, No. 9, pp. 915–934, 2002

SYNTHESIS OF POLY(METHYL METHACRYLATE)-SILICA NANO-COMPOSITES. II. POLY[METHYL METHACRYLATE-*block*-(METHYL METHACRYLATE-*co*-2-HYDROXYETHYL METHACRYLATE)]

Reiko Saito* and Yasutaka Mori

Department of Organic and Polymeric Materials,
Tokyo Institute of Technology, 2-12, Ookayama,
Meguro-ku, Tokyo 152-8552, Japan

ABSTRACT

One kind of poly(methyl methacrylate [MMA]-*block*-2-hydroxyethyl methacrylate [HEMA]) block copolymer and two kinds of poly[MMA1-*block*-(MMA-co-HEMA)] block-random copolymers were synthesized by atom transfer radical polymerization. Then, poly(methyl methacrylate) [PMMA]-silica nano composites were synthesized by blending perhydropolysilazane (PHPS: NN-110) and block or block-random copolymers in 1,4-dioxane and casting the blend solutions. All composite films were transparent. Silica and organic domains were microphase separated in the composites. The effects of PHEMA content and blend ratio of PHPS to hydroxyl group on the microphase separation were investigated by transmission electron microscopy (TEM) and scanning electron microscopy (SEM). The thermal properties of the composites were investigated by differential scanning calorimetry (DSC) and thermal gravitic analysis (TGA).

---

*Corresponding author. Fax: +81-3-5734-2888; E-mail: rsaito@polymer.titech.ac.jp

DOI: 10.1081/MA-120013571
1060-1325 (Print); 1520-5738 (Online)

www.dekker.com

Key Words: Nano-composite; PMMA; Silica; Perhydropolysilazane; Block copolymer

INTRODUCTION

Hybridization of organic polymer and silica introduced novel functionality to materials, which were transparency, high mechanical strength, high thermal stability, etc.[1–5] Generally, silica phases of organic-silica nanocomposites are produced by a sol-gel method.[6–12] Because of lattice defects in silica synthesized by the sol-gel method, the properties that are density, transparence, refractive index, etc., of silica synthesized by the sol-gel method are different from silica glass. To remove the lattice defects, the materials should be calcined over 200°C however, most conventional organic polymers decompose during calcination. Thus, it is difficult to synthesize the composite of organic polymer and silica without the lattice defects by the sol-gel method.

Silica can be synthesized from perhydropolysilazane [PHPS] by calcination below 100°C in steam. The physical properties of silica synthesized from PHPS agree with those of silica glass. PHPS dissolves in hydrophobic solvent, and reacts with hydroxyl groups. Therefore, PHPS can be grafted onto the organic polymers that have hydroxyl groups in solution. Block and graft copolymers with incompatible sequences form the microphase separation.[13] Thus, the synthesis of microphase separated composites of the organic polymer and PHPS by blending PHPS and the organic polymer with hydroxyl groups and casting the blend solution is expected. When the decomposition temperature and glass transition temperature of the organic polymer are higher than the calcination temperature of PHPS, 100°C the structure of the microphase separation of the composites will be kept during the calcination. Consequently, the microphase separated composites of the organic polymer and the silica glass will be synthesized (Fig. 1). Based on this concept, the composites of poly(methyl methacrylate) [PMMA] and silica glass was synthesized by blending poly(methyl methacrylate-*co*-2-hydroxyethyl methacrylate) [P(MMA-*co*-HEMA)] random copolymers and PHPS, casting blend solutions, and calcinning composites films at 100°C[14]. When HEMA content was 14.5 mol% and the blend ratio of PHPS to hydroxyl group was 1.5 (mol/mol), nano-composite of PMMA and silica glass with well-ordered lamellae was obtained (Fig. 2).[14] However, it was impossible to control the structure of the microphase separation by changing the HEMA content and the blend ratio of PHPS to hydroxyl group. It was due to the fact that the random copolymers were used.

To develop novel composite, strict control of microphase separation of materials is required. In contrast to the random copolymer, the block copolymer with incompatible sequences forms microphase separation without PHPS. Additionally, microphase separation of block copolymer is well

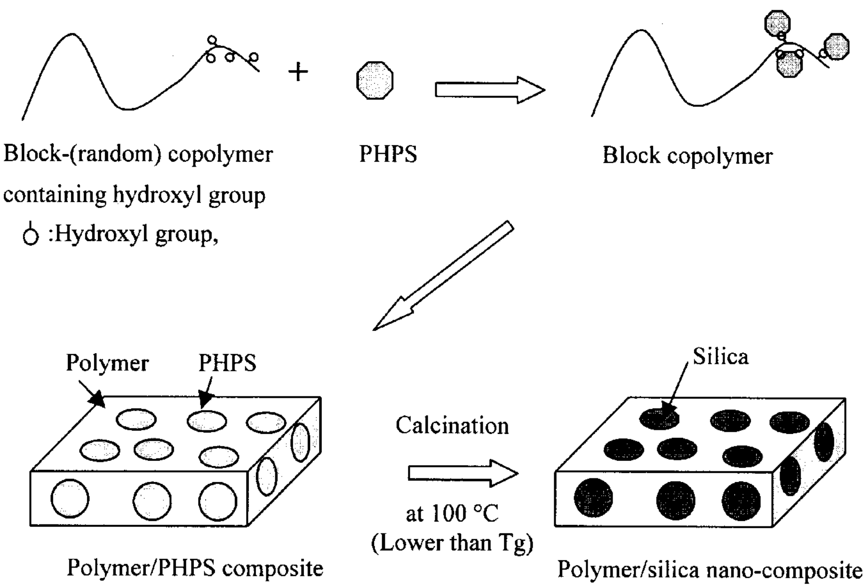

Figure 1. Synthetic concept of nano-composites of PMMA and silica glass by hybridization of PHPS and P[MMA-*block*-(MMA-*co*-HEMA)].

governed by molar content of blocks (Molau's law[13]). Thus, the strict control of the microphase separation of the silica-organic polymer composites is expected for the block copolymer (Fig. 1).

In this work, we aimed to control the microphase separation of PMMA-silica glass nano-composite by hybridization of poly(methyl methacrylate-*block*-2-hydroxyethyl methacrylate), P(MMA-*block*-HEMA), and PHPS,

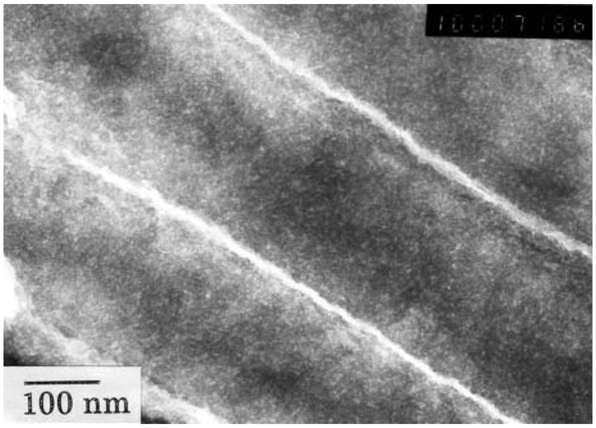

Figure 2. Transmission electron micrograph of cross-section of blend and calcined film of poly(methyl methacrylate-*co*-2-hydroxyethyl methacrylate) and PHPS. (HEMA content: 14.5 mol%, $[PHPS]/[OH]_{Feed}$: 1.5 (mol/mol).)

and to investigate the microphase separation of the composites from a viewpoint of Molau's law.[13] To prevent the macrogelation of the blend solutions, the molar content of PMMA was set to larger than 75 mol%. It was already found that the shorter distance between hydroxyl groups than the average diameter of a PHPS molecule caused the macrogelation of the solutions.[14] Thus, to increase the distance between hydroxyl groups in second sequence, poly[methyl methacrylate-*block*-(methyl methacrylate-*co*-2-hydroxyethyl methacrylate)], P[MMA-*block*-(MMA-*co*-HEMA)], block-random copolymers were also synthesized by atom transfer radical polymerization as precursor organic polymers. The synthetic scheme of the block and block-random copolymers are shown in Fig. 3. The block and block-random copolymers were hybridized with PHPS in 1,4-dioxane. The microphase separation of the copolymers and the composites were investigated by transmission electron microscopy (TEM) and scanning electron

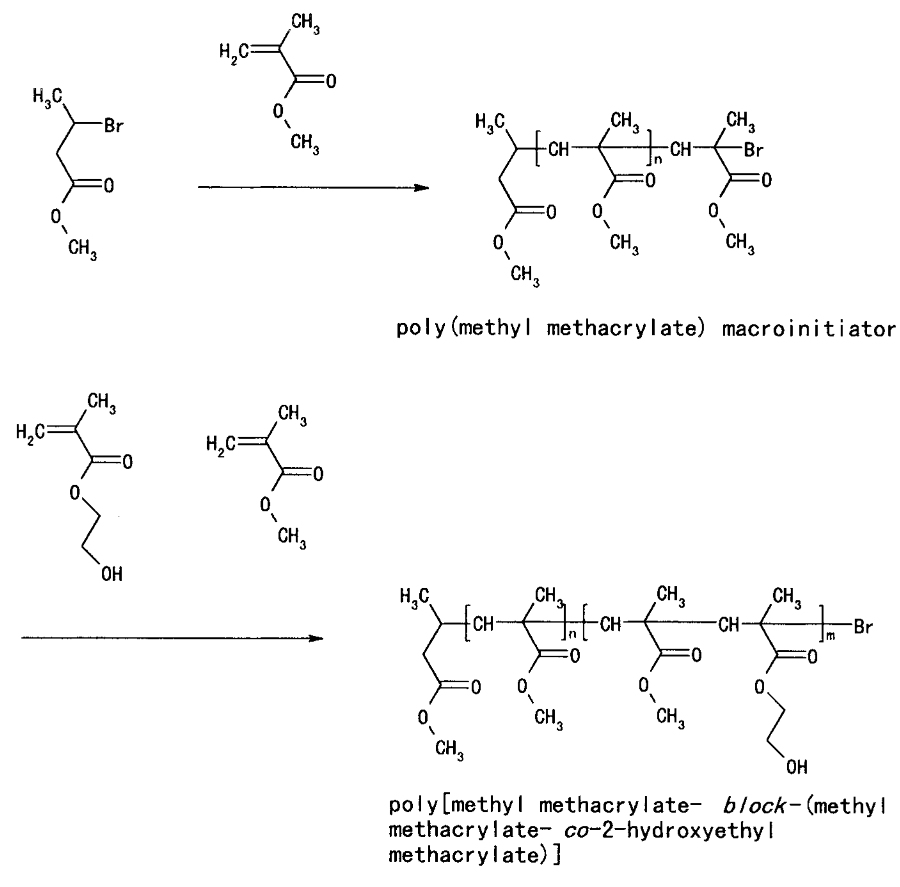

Figure 3. Synthetic scheme of poly[methyl methacrylate-*block*-(methyl methacrylate-*co*-2-hydroxyethyl methacrylate)].

microscopy (SEM). Thermal properties were also investigated by differential scanning calorimetry (DSC) and thermal gavitic analysis (TGA).

EXPERIMENTAL

Materials

Methylmethacrylate (MMA) and 2-hydroxyethyl methacrylate (HEMA) were purified by distillation under vacuum. Benzene, tetrahydrofurane (THF), 1,4-dioxane and n-hexane were dried with sodium metal and distilled under vacuum. Copper (I) chloride (CuCl, Kanto Chemical Co. Inc.), methyl-2-bromopropionate (MBP, Tokyo Chemical Industry Co., Ltd.), 1,1,4,7,10,10-hexamethyltriethylenetetramine (HMTETA, Aldrich), 2-butanon, 1-propanol and perhydro-polysilazane [PHPS]/xylene solution (NN-110, Clariant Japan Co., PHPS concentration: 20 wt%, Mw of PHPS : 700) were used as received.

Synthesis of Organic Polymer

A Poly(Methyl Methacrylate) [PMMA] Macroinitiator

MMA was dissolved in 2-butanon/1-propanol = 7/3 (v/v) mixture with [MMA] = 9.4 [M]. CuCl, HMTETA and MBP were added in the mixture. The solution was sealed in a tube under vacuum and kept for 3 h at 50°C for polymerization. After 3 h polymerization was stopped by cooling the tube. The solution was diluted with THF and precipitated with an excess amount of n-hexane. Polymer was purified by re-precipitation with THF and an excess amount of water, and dried under vacuum.

Poly[Methyl Methacrylate-*block*-(Methyl Methacrylate-*co*-2-Hydroxyethyl Methacrylate)] [P[MMA-*block*-(MMA-*co*-HEMA)]] Copolymers

The PMMA macroinitiator was dissolved in 2-butanon/1-propanol = 7/3 (v/v) mixture with a polymer concentration of PMMA = 32 wt/vol%. Then, MMA, HEMA, CuCl and HMTEMA were added to the solution. The solution was sealed in a tube under vacuum and kept for 15 min at 50°C for polymerization. After 15 min polymerization was stopped by cooling the solution. The solution was dilutes with THF, precipitated with n-hexane. Then, polymer was dried under vacuum, purified by re-precipitation with THF and 1% of aqueous acetic acid, and freeze-dried under vacuum.

Preparation and Calcination of Blend Films of P[MMA-*block*-(MMA-*co*-HEMA)] and PHPS

A certain amount of NN-110 was added to P[MMA-*block*-(MMA-*co*-HEMA)]/1,4-dioxane solution with a polymer concentration = 1 wt/vol%

under nitrogen atmosphere. The solution was stirred for 24 h at 20°C under a nitrogen atmosphere. The polymer solution was cast on a Teflon dish and gradually dried under dried nitrogen atmosphere. The conditions of blending are listed in Table 2. B1 and 0.5 of the code B1-0.5 in Table 2 correspond to the polymer type (B1) and the molar ratio of PHPS to HEMA in feed, $[\mathrm{PHPS}]/[\text{-OH}]_{\mathrm{Feed}} = 0.5$, respectively.

Characterization

The PMMA Macroinitiator and Copolymers

Number-average molecular weight (Mn) and molecular weight distribution index (Mw/Mn) were measured with a Tosoh gel permeation chromatograph HPLC-8020 (Column: Tosoh, TSKgel G-5000HHR) with THF as an eluent at 35°C by using a calibration curve of standard PMMA. The flow rate was $1.0\ \mathrm{mL/min^{-1}}$. Before GPC measurements, hydroxyl group in polymer was previously modified with phenyl isocyanate in THF as follows; Polymer was dissolved in THF at 2.0 wt% of polymer concentration. Phenyl isocyanate was added to the solution. The molar ratio of phenyl isocyanate to hydroxyl group was ca. 10. The solution was stirred overnight at room temperature. Then, the polymer was precipitated with an excess amount of methanol, filtered, and dried under vacuum.

The content of HEMA was measured with a JEOL ^{1}H-NMR GLX-500 (500 MHz, solvent: deuterized chloroform).

Content of PHPS in Modified Copolymers

Modified copolymers with PHPS were precipitated with an excess amount of n-hexane and dried. The content of PHPS in the modified polymer was measured with a Jasco Fourier-transform infrared spectrometer FT/IR-410.

Transmission Electron Microscopy (TEM)

Ultra thin specimens of the polymer films and the composites were microtomed with cryo-microtome (Reichert-Nissei, Ultracut-N) with diamond knives. Structure of the microphase separation was observed with a JEOL transmission electron microscope JEM-200CX with 80 kV. Poly(MMA-*block*-HEMA) and poly[MMA-*block*-(MMA-*co*-HEMA)] were stained with $\mathrm{RuO_4}$. The composites were observed without staining.

Scanning Electron Microscopy (SEM)

A very smooth surface of the composite films was prepared with a microtome (Reichert-Nissei cryo-microtome Ultracut-N) with diamond knives. Then, organic domains on the surface were etched by exposure to fire for a few seconds. The surface was observed with a Hitachi scanning electron microscope S-800 at 15 kV without spattering.

Differential Scanning Calorimetry (DSC)

20 mg of the blend film was sealed in an aluminum pan and measured with a Perkin-Elmer, differential scanning calorimeter Pyris 1 from 50 to 200°C at a heating rate of 20 K/min^{-1}.

Thermogravimetric Analysis (TGA)

TGA was performed with a SEIKO EXSTAR-600TG/DTA6300 up to 600°C at a heating rate of 10 K/min^{-1}.

RESULTS AND DISCUSSION

Synthesis of Block and Block-Random Copolymers

It is possible to synthesize a PMMA macroinitiator with narrow Mw/Mn by copper-mediated atom transfer radical polymerization (ATRP) [15–21]. Conditions and results of polymerization are listed in Table 1. Mw/Mn of the PMMA macroinitiator, 1.23, was sufficiently narrow to form homogeneous microphase separation. Thus, the PMMA macroinitiator was used for the synthesis of block copolymers. One type of P(MMA-*block*-HEMA) block copolymer and two types of P[MMA-*block*-(MMA-*co*-HEMA)] block-random copolymers were synthesized by post-ATRP of MMA and HEMA with the PMMA macroinitiator. Previously, it was found that the decreasing of distance between hydroxyl groups of P(MMA-*co*-HEMA) random copolymers led to the gelation of the mixture by the addition of NN-100 to the polymer solution[14]. It was because several hydroxyl groups were reacted with a perhydropolysilazane molecule. To increase the distance between hydroxyl groups, not only P(MMA-*block*-HEMA) block copolymer, but also two types of P[MMA-*block*-(MMA-*co*-HEMA)] block-random copolymers with different HEMA contents in the second sequence were synthesized. The molar contents of MMA of the first PMMA sequence originated from the macroinitiator to the entire copolymer, φ_{MMA1}, were determined by ^{1}H-NMR with peaks at 3.6 ppm and 3.8 ppm

Table 1. Conditions and Results of ATRP of PMMA Macroinitiator and P[MMA_1-*block*-(MMA_2-*co*-HEMA)] Block Copolymers

Code	Initiator and Macroinitiator	Monomer Concn. [M]		[CuCl]:[Ligand]: [Br]^a:[Monomer]	Mn_{GPC}^{b} ($\times 10^{-4}$)	Mw/Mn^b	Molar Content (mol%)^c			Distance Between Hydroxyl Groups (nm)
		MMA	HEMA				MMA_1^{d}	MMA_2^{d}	HEMA^d	
PMMA macroinitiator	Methyl 2-chloro propyonate	9.42	0.00	0.74:1.0:1:26.9	1.29	1.23	100.0	0.0	0.0	—
B1	PMMA macroinitiator	0.00	8.10	1.1:1.3:1.0:26.6	1.77	1.20	78.4	0.0	21.6	0.8
B2	PMMA macroinitiator	4.08	4.08	1.0:1.6:1.0:288	1.61	1.12	80.5	10.0	9.5	1.6
B3	PMMA macroinitiator	6.09	2.01	1.0:1.6:1.0:295	1.55	1.16	83.7	12.4	3.9	3.3

[a] Molar concentration of bromine group of initiators.

[b] Number-average molecular weight determined by GPC by calibration with linear PMMA standards.

[c] Determined by ^{1}H-NMR.

[d] MMA_1, MMA_2 and HEMA are the sequences of poly[MMA_1-*block*-(MMA_2-*co*-HEMA)], respectively.

originated from hydrogen in methyl ester of MMA and in methylene next to hydroxyl group of HEMA, respectively. The φ_{MMA1} values were in a narrow range from 78.4 to 83.7 mol%. Here, localization of HEMA in the second sequence was neglected, since values of r1 and r2, where monomer 1 = MMA and monomer 2 = HEMA, are 0.29 and 1.054, respectively, at 60°C.[22] The distances between the hydroxyl groups calculated from the HEMA contents are also listed in Table 1. The microphase separation of the block and block-random copolymers is discussed in latter section.

Blending of PHPS with Block and Block-Random Copolymers

Perhydropolysilazane [PHPS] was reacted with P(MMA-*co*-HEMA) or P[MMA-*block*-(MMA-*co*-HEMA)] by blending NN-110 and the organic polymers in 1,4-dioxane. Previously, PHPS was grafted on P(MMA-*co*-HEMA) in benzene.[14] Block copolymer B1, however, formed micelles in benzene, because benzene was a selective solvent, that is a good solvent for PMMA and a poor solvent for PHEMA. Thus, 1,4-dioxane, a good solvent for both PMMA and PHEMA, was used. In this work, no macrogelation of the mixture was observed for all cases.

The reaction of PHPS with the block and block-random copolymers in the solution was estimated by FT-IR. To remove unreacted PHPS from the polymers, the modified polymers were precipitated with an excess amount of n-hexane, which is a good solvent for PHPS, and dried. Figure 4 (a) and (b) shows the FT-IR spectra of B1 and B1-1.0 after purification. New peaks appeared for B1-1.0 at 2277 and 833 cm^{-1} due to the bonds of Si-H and Si-N, respectively, PHPS was reacted with B1. The conversions of PHPS of all polymers were calculated by using FT-IR peaks at 1730 and 833 cm^{-1} due to carboxyl group and PHPS, respectively.

Figure 5 shows the time conversion of PHPS of B1 series as a typical case. The conversion of PHPS increased with the reaction time up to 3 h, and then saturated. Thus, the reaction time in this work, 24 h, was sufficient to the reaction.

Figure 6 shows the molar ratio of introduced PHPS to hydroxyl group at 24 h. The molar ratios of introduced PHPS to hydroxyl group in the modified copolymers, $[PHPS]/[\text{-}OH]_{graft}$, of B2 and B3 were increased with $[PHPS]/[\text{-}OH]_{Feed}$, instead, the values $[PHPS]/[\text{-}OH]_{graft}$ of B1 were independent on $[PHPS]/[\text{-}OH]_{Feed}$. This is explained from a viewpoint of average distances between hydroxyl groups and an average diameter of PHPS molecules. The average distances between hydroxyl groups were 0.8, 1.6 and 3.3 nm for B1, B2 and B3, respectively. The average diameter of PHPS molecules of NN-110 was 0.94 nm. Each PHPS molecule has many reactive sites with hydroxyl group. When the average distance between hydroxyl group was smaller than the average diameter of PHPS molecule, such

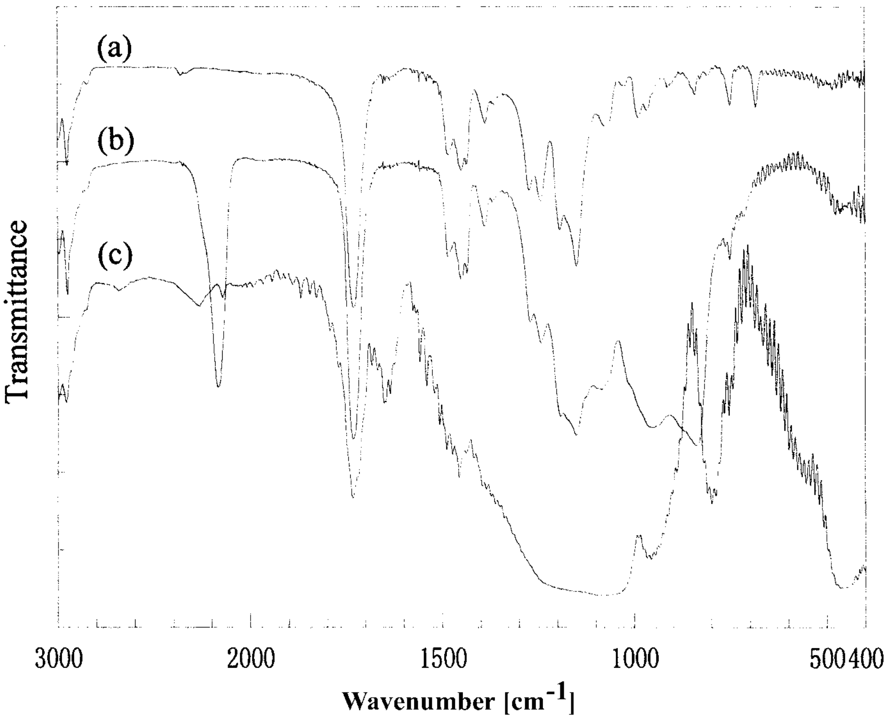

Figure 4. FT-IR spectra of B1 series. Film B1, (a) purified product of B1-1.0; (b) B1-1.0 after casting, (c).

as B1, several hydroxyl groups of B1 would be reacted with the same PHPS molecule. As a result, [PHPS]/[-OH]$_{\mathrm{graft}}$ of B1 was drastically lower than [PHPS]/[-OH]$_{\mathrm{Feed}}$. As well as hybridization with P(MMA-*co*-HEMA), the increasing of distance between hydroxyl group improved the reaction of PHPS with the organic polymer.

Even though the average distances between hydroxyl groups of B2 and B3 were larger than the average diameter of PHPS molecule, the [PHPS]/[-OH]$_{\mathrm{graft}}$ of B2 and B3 did not quantitatively increase by increasing [PHPS]/[-OH]$_{\mathrm{Feed}}$. The diameter of PHPS molecule may have the distribution. Thus, the reaction of PSPS molecules with multi hydroxyl groups was not completely hindered. Consequently, it was possible to qualitatively control the amount of PHPS reacted with the polymer by changing the distance between hydroxyl groups in the polymer and [PHPS]/[-OH]$_{\mathrm{Feed}}$.

Preparation of Composite Films

To prepare composite films, the blend solutions were cast on Teflon sheets in nitrogen atmosphere. Some parts of the purified modified copoly-

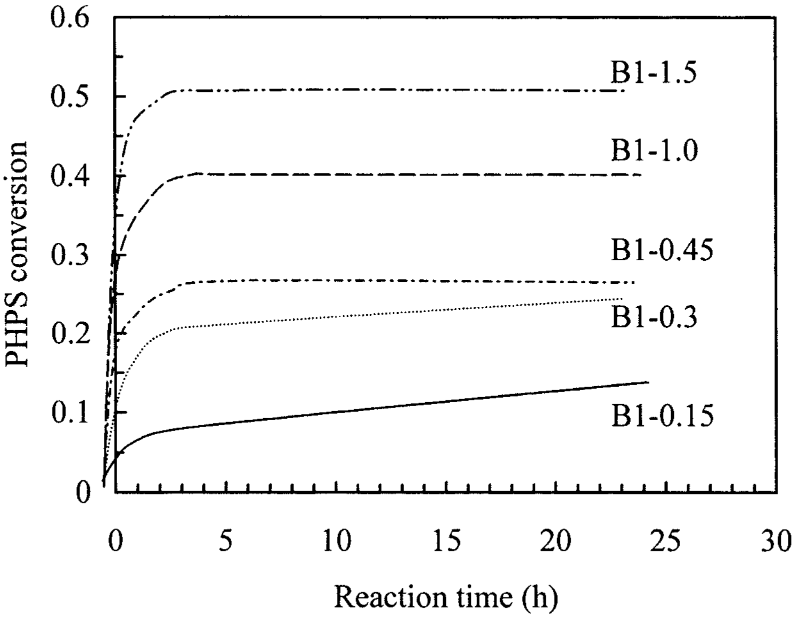

Figure 5. Time conversion of PHPS of B1 series.

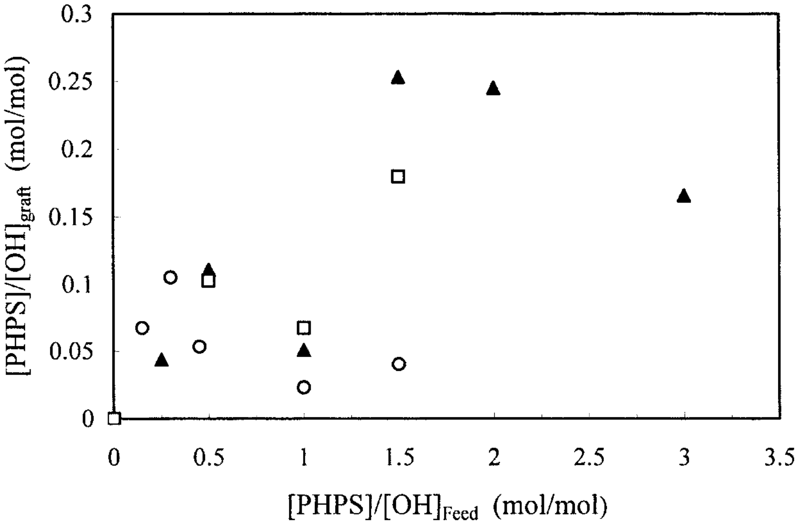

Figure 6. Concentration effect of PHPS in the feed on introduction to block copolymers. (○) B1series, (▲) B2series, (□) B3 series.

mers became insoluble in 1,4-dioxane after drying, because they were highly sensitive against humidity after purification. Thus, the purification of the modified copolymers was not carried out. The composite films were composed with the organic polymer, PHPS and the modified copolymers.

Figure 4 (c) shows the FT-IR spectra of B1-1.0 after casting. The peaks at 2277 and 833 cm^{-1} due to Si-H and N-H, respectively, were drastically decreased, and new broad peaks due to a Si-O bond appeared at 1042 and 460 cm^{-1}. This indicates that PHPS in the composite films was converted to silica during drying. The slow calcination of PHPS cast from NN-110 occurred at room temperature. Thus, it was found that the composites of silica and organic polymer were obtained after drying the hybrid films.

All composite films were transparent. When the size of the phase separation is larger than a few micrometers, the films are not transparent, due to the light scatting of large domains. Thus, the microphase separation of the composite films was expected, although the calcination occurred during the preparation of the composite films.

Phase Separation of Composite Films

The structure of the microphase separation of the composites was investigated by transmission electron microscopy (TEM). Figure 7 shows transmission electron micrographs of B1 and the composites. First, the microphase separation of the organic copolymers was investigated. Figure 7a is a TEM micrograph of B1 stained with RuO_4. The dark regions correspond to HEMA domains. The structure of the microphase separation of B1 was PHEMA spheres with 3.13 nm of an average diameter in a PMMA matrix. Volume fraction of first PMMA sequence, φ_{PMMA1} was 78.4 mol%. The microphase separation of B1 well agreed with Molau's law. For B2 and B3, the microphase separation was not observed, because the second sequences were the random copolymers of HEMA and PMMA.

Then, the microphase separation of composites was observed. Since the silica domains can be observed as dark by TEM without staining, the staining was not carried out for the composites (Fig. 7b to 7h). The clear microphase separation was observed for all composite films. As expected above, the sizes of the phase separation of all composites were less than 80 nm. In particular, the sizes of silica domains of composites with B2 and B3 were less than 10 nm. As described above, all PHPS was not reacted with the organic polymer. Unreacted PHPS increases the size and the size distribution of silica domains in the composites. The conversion of PHPS and the volume fraction of unreacted silica in the composites were calculated with $[PHPS]/[OH]_{Feed}$ and $[PHPS]/[OH]_{graft}$, and are listed in Table 2. The volume fractions of unreacted silica in the composites of the B2 and B3 series were less than 0.13. Thus, the homogeneous structures of the microphase separation were formed

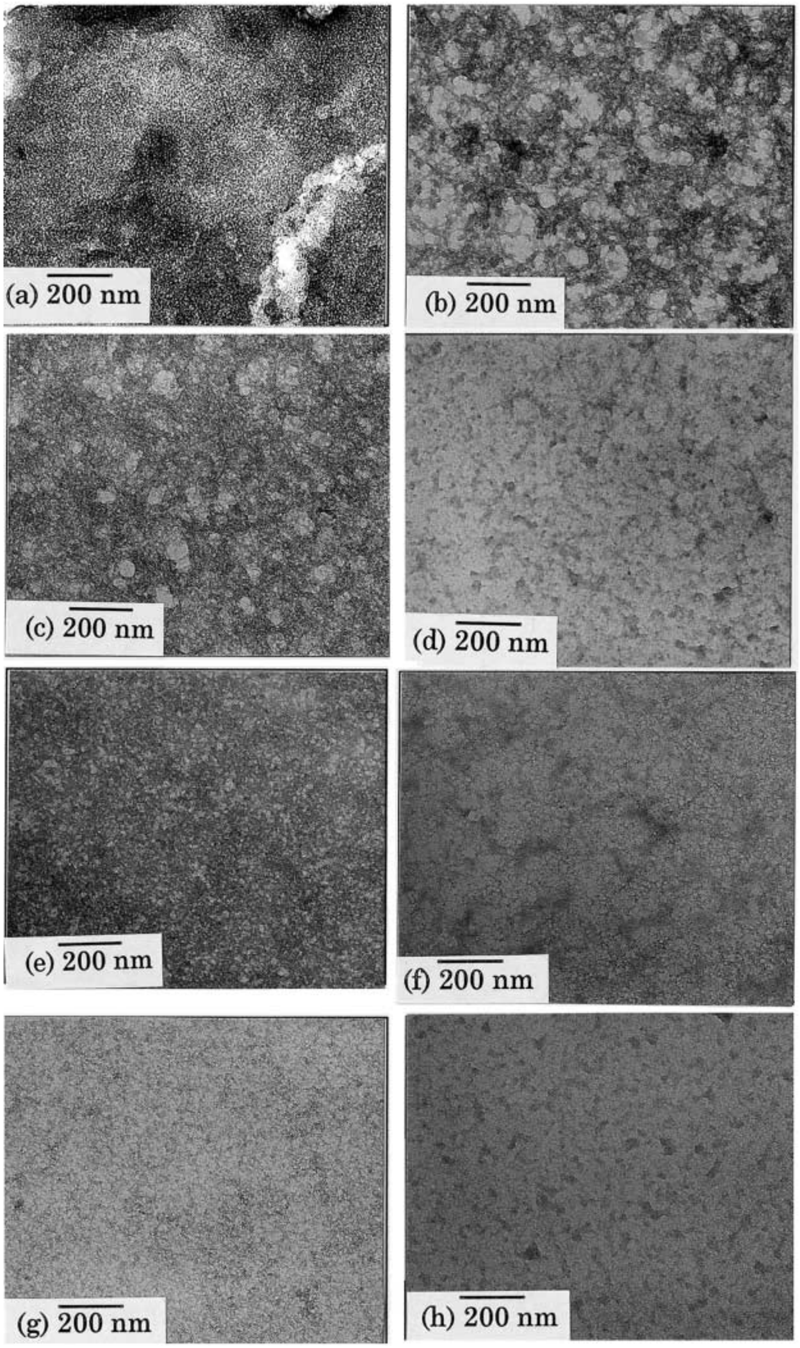

Figure 7. Transmission electron micrographs of block copolymers and the composites: (a) B1 stained with RuO_4; (b) B1-0.25 without staining; (c) B1-1.0 without staining; (d) B2-0.25 without staining; (e) B2-1.0 without staining; (f): B3-0.5 without staining; (g) B3-1.0 without staining; (h) B3-1.5 without staining.

Table 2. Conditions and Results of Blending of PHPS and Block or Block-Random Copolymers.

Code[a]	[PHPS]/ $[OH]_{Feed}$	[PHPS]/ $[OH]_{graft}$	Conversion of PHPS	Volume Fraction of Silica[b]	Volume Fraction of Unreacted Silica[b]	ϕ_{PMA1}[c]
B1	—	—	—	—	—	0.780
B1-0.25	0.25	0.079	0.351	0.092	0.06	0.738
B1-1.0	1.0	0.023	0.023	0.190	0.19	0.690
B1-1.5	1.5	0.040	0.027	0.234	0.23	0.667
B2-0.25	0.25	0.044	0.175	0.025	0.02	0.789
B2-1.0	1.0	0.051	0.051	0.127	0.12	0.727
B3-0.5	0.5	0.103	0.201	0.035	0.03	0.807
B3-1.0	1.0	0.067	0.067	0.055	0.05	0.791
B3-1.5	1.5	0.178	0.120	0.084	0.07	0.767

[a] Code B1-0.25 indicates the type of copolymer, B1, and the molar ratio of PHPS to hydroxyl group in the feed.

[b] Calculated with $[PHPS]/[OH]_{Feed}$ and $[PHPS]/[OH]_{graft}$.

[c] Volume fraction of PMMA1 in the composites.

in the B2 and B3 series. It was concluded that the PMMA-silica glass nano composites were obtained by blending P(MMA-*block*-HEMA) or P[MMA-*block*-(MMA-*co*-HEMA)] with PHPS. It was also found that increasing the distance between hydroxyl groups was important in order to obtain nanocomposite of silica-organic polymer when PHPS was used.

The maximum volume fraction of silica was 0.234 for B1-1.5. Based on the Molau's law, the structure with spherical silica domains in PMMA matrices was expected for all composites. However, the structure with spherical domain of silica was not observed, except for B2-0.25 and B3-1.5. In the case of the B3 series, B3-1.5 formed clear silica spheres with 18 nm of the average diameter. In case of B2 series, the volume fractions of silica were 0.025 and 0.127 for B2-0.25 and B2-1.0, respectively. The structure of the silica domains was changed from sphere to a matrix by increasing of the volume fraction of silica. It was possible to obtain the various structure of the microphase separation by using a block and block-random copolymer instead of a random copolymer, and by changing the HEMA content and $[PHPS]/[OH]_{Feed}$. However, the strict control was not succeeded. This is due to the fact that the calcination occurred during drying the composites.

The structure of the microphase separation of B1-1.0 with silica matrix was also observed by scanning electron microscopy (SEM). SEM micrographs are shown in Fig. 8. By etching the organic domains on the smooth surface of B1-1.0, silica domains were observed to be white. It was found that the structure of the microphase separation observed by SEM (Fig. 8a) agreed with

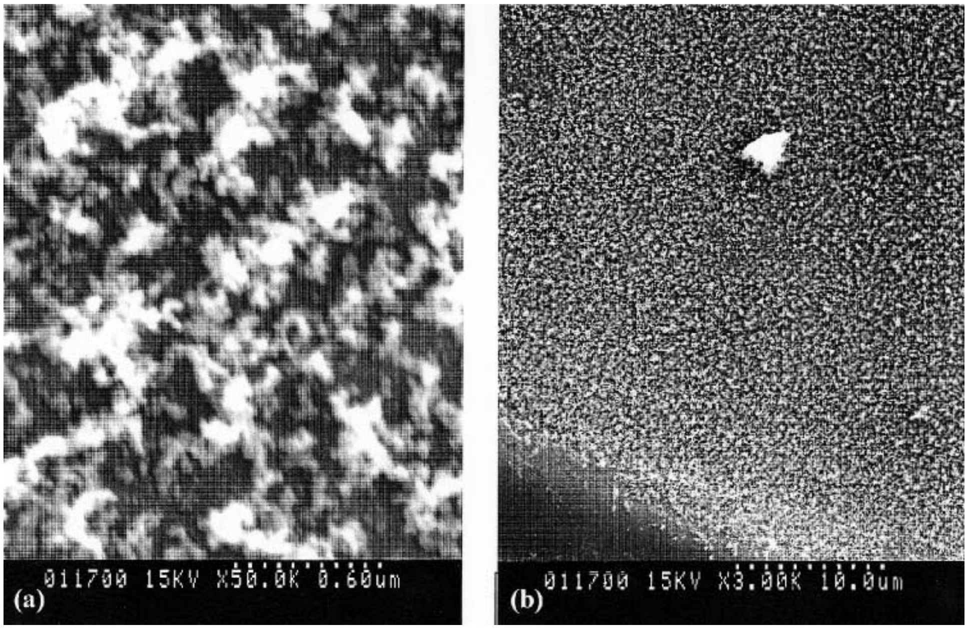

Figure 8. Scanning electron micrograph of etched cross-section of B1-1.0, (a) magnification 50,000; (b) magnification 3,000.

the TEM (Fig. 7c). Additionally, the homogeneous structure of the microphase separation was observed in a wide area of the composite (Fig. 8b).

Thermal Properties of Composite Films

Finally, the thermal properties of the composites were investigated by DSC and TGA measurements. Figure 9 shows the DSC curves of the B1 series. Glass transition temperature, Tg, and Δ Cp determined by DSC are listed in Table 3. For the block and random-block copolymers, clear peaks of Tg due to the first PMMA sequences were observed at 108°C. Two Tg peaks are generally observed for the diblock copolymers when the diblock copolymer forms the microphase separation. The Tg of PHEMA is 118°C[23], however, no Tg peaks were observed at 118°C for the block and block-random copolymers. It was due to the fact that the molecular weight of HEMA of B1 was low, $Mn_{PHEMA} = 3800$, and that the second sequence of B2 and B3 were random copolymer of HEMA and MMA. For the composites, the Tg peaks at 108°C vanished, except for B1-0.25, B1-1.0, and B3-1.0. As shown in Fig. 7, the microphase separation of the composites was not well arranged due to the contamination of unreacted silica. Therefore, the Tg peaks due to PMMA would be vanished by hybridization.

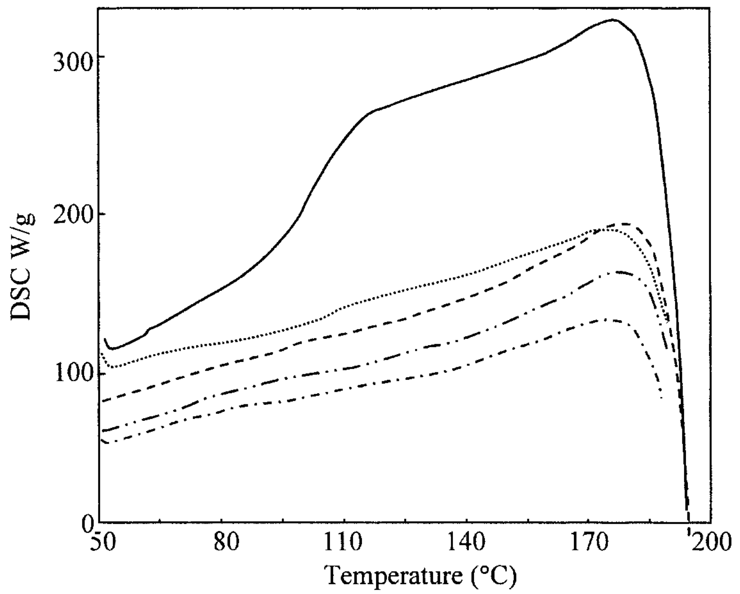

Figure 9. DSC curves of B1 series. (——) B1, (······) B1-0.25, (–––) B1-0.5, (—··—) B1-1.0, (—·—·) B1-1.5.

To investigate the thermal stability of the composites, TGA measurements were carried out under nitrogen. Figure 10 shows the TGA curves of B1 and the composites. The organic copolymer B1 showed a two-step degradation due to the degradation starting at the vinylidene chain end[24] and random initiation by unzipping of the methacrylate

Table 3. Thermal Properties of the Organic Copolymers and the Composites

Sample Code	Weight Fraction of Silica[a]	Tg[b] (°C)	ΔCp[b] (J/gK)	Yc[c]	Peak Temperature (°C)[d]	
					First	Second
B1	0.000	109.5	0.2529	0.938	284.0	389.4
B1-1.0	0.350	—	—	0.369	294.8	421.6
B2-0.5	0.120	116.0	0.0460	0.329	300.6	423.4
B2-1.0	0.250	—	—	0.865	291.2	402.5
B3-1.0	0.118	120.8	0.0247	0.616	296.1	406.8

[a] Calculated from the volume fraction of silica in the composites.
[b] Determined by DSC.
[c] Char residue at 500°C determined by TGA curves.
[d] Determined by DTG curves.

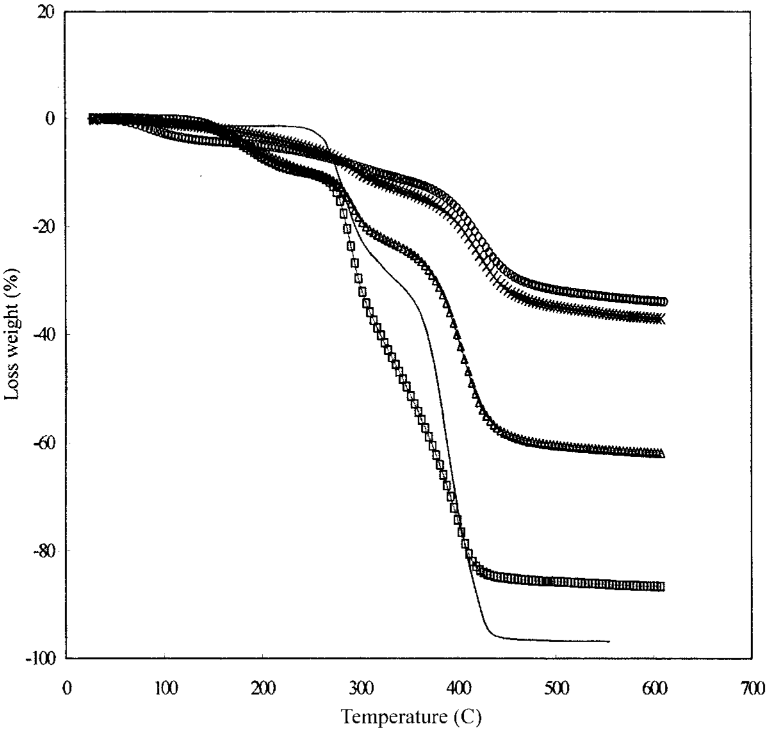

Figure 10. TGA curves of B1 and the composites. (—) B1, (×) B1-1.0, (Δ): B2-1.0, (□) B3-0.5, (○): B3-1.0.

chain[24] observed at ranges of 240–320°C, and 320–440°C, respectively. B2 and B3 showed very similar decomposition behavior to B1. As well as B1, the composites degraded in two steps, except for B2-1.0. Since B1 was destroyed completely at 450°C, the composites did not completely degrade over 500°C. The char residue, Yc, at 600°C and weight fraction of silica of the composites are listed in Table 3. The Yc values and weight fractions of silica were in agreement except for B2-1.0 and B3-1.0

The DTG curves of B1 and the composites are shown in Fig. 11. Figure 11 shows the first and second peak temperature of B1 was 284.0 and 389.4°C, respectively at a heating rate of 10°C/min. It was found that the first and second peak temperature was increased by hybridization of the organic copolymer and PHPS. Especially for B2-1.0, the second peak temperature was increased to 426.4°C by hybridization. Consequently, it was concluded that the thermal stability of the composites was increased by blending PHPS with P(MMA-*block*-HEMA) or P[MMA-*block*-(MMA-*co*-HEMA)].

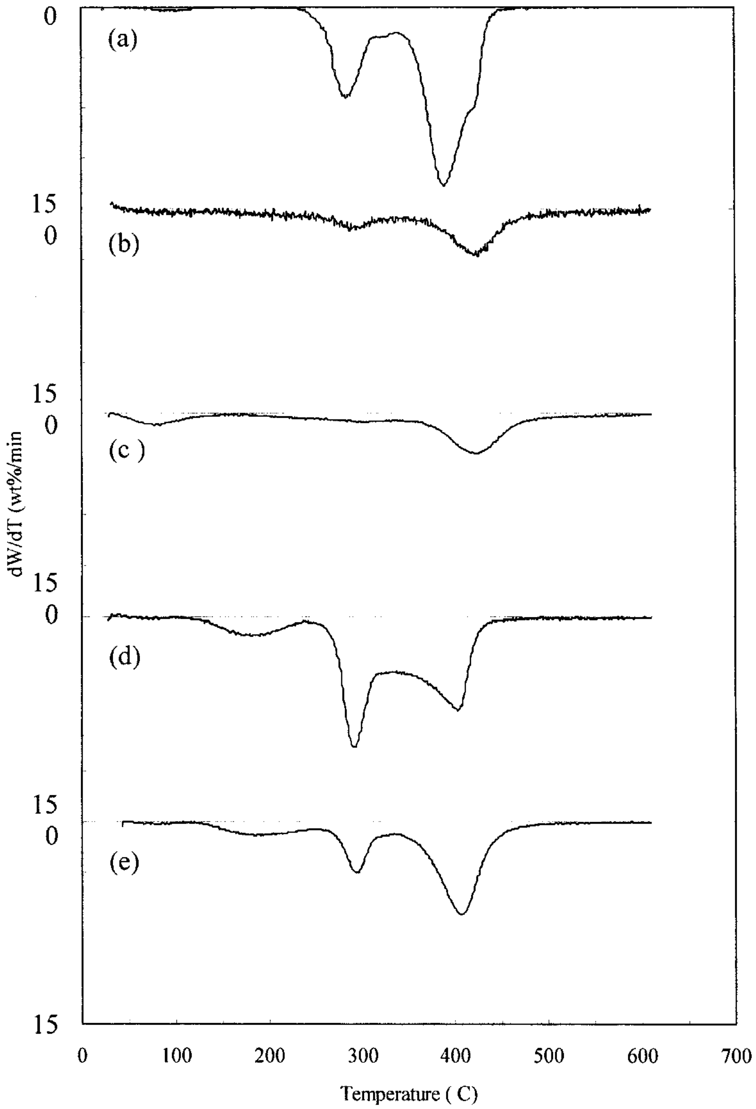

Figure 11. DTG curves of B1 and the composites. (a) B1; (b) B1-1.0; (c) B2-1.0; (d) B3-0.5; (e) B3-1.0.

CONCLUSION

In order to synthesize poly(methyl methacrylate)-silica composites with microphase separation, P(MMA-*block*-HEMA) block copolymer, B1, or MMA-*block*-(MMA-*co*-HEMA) block-random copolymers, B2 and B3 were reacted with perhydropolysilazane [PHPS]. The reaction of PHPS and the block or block-random copolymers was completed up to 3 h. Conversions of

PHPS were lower than the equilibrium values, this was due to the fact that the average diameter of a PHPS molecule was larger than the distance between hydroxyl groups. It was possible to increase the molar ratio of introduced PHPS to hydroxyl group up to 0.18 by decreasing the HEMA content in the second random sequence and increasing the molar ratio of PHPS to hydroxyl groups in the feed. FT-IR results indicated that the calcination of PHPS was completed after drying the composite films. From TEM observation, it was found that the PMMA-silica glass composites with microphase separation were obtained. The microphase separation of the composites was governed not quantitatively but qualitatively by Molau's law. The measurements of DSC and TGA indicated that the thermal stability of the composites was higher than that of the block and block-random copolymers.

REFERENCES

1. Judeinstein, P.; Sanchez, C. Hybrid Organic-Inorganic Materials: a Land of Multidisciplinarity. J. Mater. Chem. **1996**, *6* (4), 511–525.
2. Novak, B.M. Hybrid Nanocomposite Materials- Between Inorganic Glasses and Organic Polymers. Adv. Mater. **1993**, *5* (6), 422–433.
3. Ravaine, D.; Seminel, A.; Charbouillot, Y.; Vincens, M. A New Family of Organically Modified Silicates Prepared From Gels. J. Non-Cryst. Solid. **1986**, *82* (1–3), 210–219.
4. Judeinstein, P.; Titman, J.; Stamm, M.; Schmid, H. Investigation of Ion-Conducting Ormolytes: Structure–property. Chem. Mater. **1994**, *6* (2), 127–134.
5. Brik, M.E.; Titman, J.J.; Bayle, J.P.; Judeinstein, P. Mapping of Motional Heterogeneity in Organic-Inorganic Nanocomposite Gels. J. Polym. Sci., Part B, Polym. Phys. **1996**, *34* (15), 2533–254.
6. Chujo,Y. Organic-Inorganic Hybrid Materials. Curr. Opin. Solid State Mater. Eng. **1996**, *1* (6), 806–811.
7. Brink, C.J.; Scherer, G.W. *Sol-Gel Science: The Physics and Chemistry of Sol-Gel Processing*; Academic Press: SanDiego, 1990.
8. Schmid, H. New Type of Non-Crystalline Solid Between Inorganic and Organic Materials. J. Non-Cryst. Solids, **1985**, *73* (1–3), 681–691.
9. Wen, J.; Wilkes, G.L. Organic/Inorganic Hybrid Network Materials by the Sol-Gel Approaches. Chem. Mater, **1996**, *8* (8), 1667–1681.
10. Schmid, H.; Wolter, H. Organically Modified Ceramics and Their Applications. J. Non-Cryst. Solids, **1990**, *121* (1–3), 428–435.
11. Saegusa, T.; Chujo, Y. Organic/Inorganic Hybrid Polymer. J. Macromol. Sci. Chem. **1990**, A*27* (13–14), 1603–1612.
12. Chujo, Y.; Ihara, E.; Kure, S.; Suzuki, K.; Saegusa, T. Block Copolymer of 2-Methyl-2-oxazoline with Silica Gel: An Organic-Inorganic Hybrid Polymer. Makromol. Chem. Macromol. Symp. **1991**, *42/43* , 303–312.
13. Molau, G.E. *Block Polymers*; Plenum Press: New York, 1970.

14. Saito, R.; Kuwano, K.; Tobe, T. Synthesis of Poly(methyl methacrylate)-Silica Nano-composite. Journal of Macromolecular Science, in press.
15. Xia, J.; Matyjaszewski, K. Controlled/'Living' Radical Polymerization. Atom Transfer Radical Polymerization using Multidentate Amine Ligands. Macromolecules **1997**, *30* (25), 7697–7700.
16. Wang, J.L.; Grimaud, T.; Matyjaszews, K. Kinetic Study of the Homogeneous Atom Transfer Radical Polymerization of Methyl Methacrylate. Macromolecules **1997**, *30* (21), 6507–6512.
17. Shipp, D.A.; Wang, J.L.; Matyjaszewski, K. Synthesis of Acrylate and Methacrylate Block Copolymers using Atom Transfer Radical Polymerization. Macromolecules **1998**, *31* (23), 8005–8008.
18. Wang, X.S.; Luo, N.; Ying, S.K. Controlled Radical Polymerization of Methacrylates at Ambient Temperature and the Synthesis of Block Copolymers Containing Methacrylates. Polymer **1999**, *40* (14), 4157–4161.
19. Beers, K.L.; Boo, S.; Gaynor, S.G.; Matyjaszewski, K. Atom Transfer Radical Polymerization of 2-Hydroxyethyl Methacrylate. Macromolecules **1999**, *32* (18), 5772–5776
20. Reining, B.; Keul, H.; Hoecker, H. Chloro-telechelic Poly(ethylene oxide)s as Initiators for the Atom Transfer Radical Polymerization (ATRP) of Styrene and Methyl Methacrylate; Structural Features that Affect the Initiation Efficiency. Polymer **1999**, *40* (12), 3555–3563.
21. Liou, S.; Rademacher, J.T.; Malaba, D.; Pallack, M.E.; Brittain, W.J. Atom Transfer Radical Polymerization of Methyl Methacrylate with Polyethylene-Functionalized Ligands. Macromolecules **2000**, *33* (12), 4295–4296.
22. Verma, I.K.; Patnaik, S. Copolymerization of 2-Hydroxyethyl Methacrylate with Alkyl Acrylates. Eur. Polym. J. **1976**, *12* (4), 259–261.
23. Sung, Y.K.; Gregonis, D.E.; Rusell, G.A.; Andrade, J.D. Effect of Water and Tacticity on the Glass Transition Temperature of Poly(2-hydroxyethyl methacrylate). Polymer **1978**, *19* (11), 1362–1363.
24. Kashiwagi, T.; Inaba, A.; Brown, J.E.; Hatada, K.; Kitayama, T.; Masuda, E. Effects of Weak Linkages on the Thermal and Oxidative Degradation of Poly(methyl Methacrylates). Macromolecules **1986**, *19* (8), 2160–2168.

Received January 5, 2002
Revision received April 10, 2002