Preparation, Morphology, and Physical Properties of Transparent PSt Hybrid Materials Containing Silicone Macromonomer

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ABSTRACT: The aim of this study was to prepare transparent polystyrene (PSt) hybrid materials containing silicone macromonomer. Silicone urethane methacrylate (SiUMA) was synthesized by the reaction between the hydroxyl end groups of a silicone macromonomer and the isocyanate group of 2-methacryloyloxyethyl isocyanate (MOI), and copolymers with different weight proportions were prepared by copolymerization of styrene (St), SiUMA and ethyleneglycol dimethacrylate (EGDMA). Though the prepared P(St-*co*-SiUMA) copolymers which had not introduced EGDMA were opaque, the prepared P(St-*co*-SiUMA-*co*-EGDMA) copolymers were transparent, similarly to pure PSt. DSC and ^{1}H-NMR measurements were carried out to investigate the factors in this transparency in detail. From these measurement results, it was confirmed that the reactivity of the copolymerization had a significant influence on the transparency of the product. In addition, the contact angle of P(St-*co*-SiUMA-*co*-EGDMA) with 10 wt % SiUMA was greater than 90°, which was a 10° improvement compared to pure PSt. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 108: 362–369, 2008

Key words: silicones; polystyrene; copolymerization; phase separation; morphology

INTRODUCTION

High-performance organic–inorganic hybrid materials have recently been the subject of much investigation.[1–5] In particular, the development of polymer polydimethylsiloxane (PDMS) materials has attracted attention.[6–8] Pure PDMS and PDMS copolymer have various useful properties such as water resistance, weatherability, heat resistance, and electrical insulation and gas transmission abilities, and are mainly used in paints and coating agents.[9,10] Further developments in this field include the preparation of novel polymer materials by polymer blending. Novel polymer blend materials are expected to have additional physical properties, but it has been reported that adhesion at the interface is unsatisfactory due to differences in the solubility parameters of the homopolymers.[11,12] Polymer blending with techniques such as interpenetrating polymer networks (IPN) is expected to result in improved adhesion at the interface.[13–15]

Block copolymers and graft copolymers, in which multiple polymers are combined by covalent bonding, are also attracting attention as composite materials. These copolymers form microphase-separated structures according to the segregation of each component. Moreover, the different homopolymers exist in the same molecular chain, and each segment shows independent behavior severally. Therefore, using this technique, it is expected that we will be able to prepare novel materials which combine seemingly contradictory properties.

The morphology and properties of polymer blends, block copolymers, and graft copolymers containing PDMS have been investigated in previous research.[16–20] Zhang et al. prepared polymethylmethacrylate (PMMA)-PDMS and polystyrene (PSt)-PDMS by free radical polymerization followed by a reaction between a silane coupling agent and the hydroxyl group of PDMS.[21,22] Moreover, the mechanical properties were improved by using a sol–gel method to form crosslinked structures. Ohata et al. reported that coating films of various acryl-silicone block copolymers were obtained by free radical polymerization using macro azo initiators containing silicone.[23] It was confirmed by TEM observation that the acryl-silicone copolymers formed a microphase-separated structure which consisted of silicone domains of about 12 nm in diameter. McGrath et al. prepared thin films of PMMA-*g*-PDMS, and the domain size of PDMS in the polymer matrix was found to increase with increasing PDMS content or molecular weight.[24] When the water contact angle of two copolymers containing PMDA with molecular
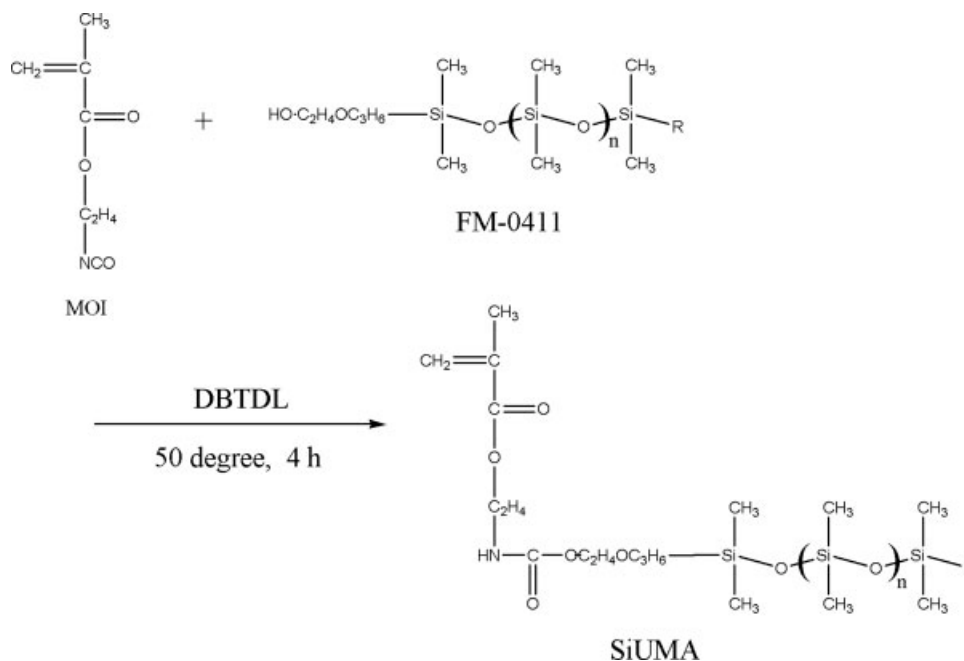
Scheme 1 Synthesis scheme of SiUMA.

weights of 1000 and 20,000 were compared, that of the copolymer containing 20,000 MW PDMS was improved by 10° compared to the other copolymer.

However, the physical properties and morphologies of copolymers or blend polymers containing PDMS have mainly been examined in thin films, and there have been few reports of investigation of the surface properties or microphase-separated structure of bulk materials containing PDMS. It should also be noted that the solubility parameter of silicone differs considerably from those of other polymers, and silicone containing materials prepared by bulk polymerization are opaque.

The aim of this study was to prepare transparent PSt hybrid materials containing silicone macromonomer. We investigated the effect of introducing silicone to pure PSt, since pure PSt has excellent transparency and water repellency. Silicone urethane methacrylate (SiUMA) was synthesized by a reaction between the hydroxyl end groups of the silicone macromonomer and the isocyanate group of 2-methacryloyloxyethyl isocyanate (MOI). Transparent hybrid materials were obtained by bulk polymerization with St, ethyleneglycol dimethacrylate (EGDMA), and SiUMA. The silicone domain size was evaluated by scanning electron microscopy (SEM), and the factors relating to the production of transparent materials were investigated based on the reaction kinetics and ^{1}H-NMR and DSC measurements. In addition, the transparency, surface properties, and mechanical properties of the resulting hybrid materials were evaluated by UV–vis, water contact angle, and surface free energy measurement and by a three-point bending test.

EXPERIMENTAL

Materials

Reactive silicone macromonomers (FM-0411, M_n = 1280) was provided from CHISSO Co. (Japan) MOI was supplied from the Showa Denko K.K (Japan). All other reagents were purchased from Nacalai Tesuque (Japan) and used without further purification.

Sample preparation

Synthesis of SiUMA

The synthesis scheme for SiUMA is shown in Scheme 1. The silicone macromonomer was synthesized by a reaction between the hydroxyl group of FM-0411 and the isocyanate group of MOI. Di-*n*-butyltin dilaurate (DBTDL) was used as a catalyst, and MOI was added in an equimolar amount to introduce the polymerizable group to FM-0411. The reaction was carried out at 50°C for 4 h, and SiUMA was obtained. The occurrence of the reaction was confirmed by the disappearance of the FTIR peak of the isocyanate group (2270 cm^{-1}).

Preparation of P(St-*co*-SiUMA-*co*-EGDMA) copolymers

The composition of each copolymer is shown in Table I, and the preparation scheme for the copolymers is shown in Scheme 2.

Set amounts of St, SiUMA, and EGDMA were mixed at room temperature for 1 h, and then copolymerization was carried out using benzoyl peroxide

TABLE I
Detailed Composition of Each Sample

Sample code	St (g)	SiUMA (g)	EGDMA (g)	BPO (g)
Pure PSt	10	0	0	0.03
P(St-SiUMA)	7	3	0	0.03
P(St-EGDMA-SiUMA10)	8	1	1	0.03
P(St-EGDMA-SiUMA20)	7	2	1	0.03
P(St-EGDMA-SiUMA30)	6	3	1	0.03
P(St-EGDMA-SiUMA40)	5	4	1	0.03

(BPO) as an initiator at 80°C for 12 h. All samples were 2-mm thick.

Analysis

The occurrence of the reaction was confirmed by FTIR (Nicolet AVATAR 320 spectrophotometer, Japan). FTIR spectra were measured in the region of 4000–400 cm^{-1} using a liquid film method with a KRS cell and an ATR method. The transparency of the prepared copolymers was measured in the region of 400–700 nm by visible spectrometry (Hitachi High-Technologies Co. (Japan) U-3310 spectrophotometer).

Field emission type scanning electron microscopy (FE-SEM) (Hitachi, Japan, S-4500) was carried out to investigate phase separation on the sample surface. FE-SEM images were acquired at ambient temperature with 5-nm-thick gold sputtering and an operating voltage of 15 kV.

The exothermic peak arising from polymerization was observed by differential scanning calorimetry (DSC) (Perkin–Elmer, Pyris DSC-type calorimeter, Japan), and differences in the polymerization rates of each sample were evaluated. Measurements were carried out using the following program: (1) holding at 30°C for 30 min; (2) raising the temperature to 80°C at 10°C/min; (3) holding at 80°C for 720 min. Measurements were conducted during holding at 80°C.
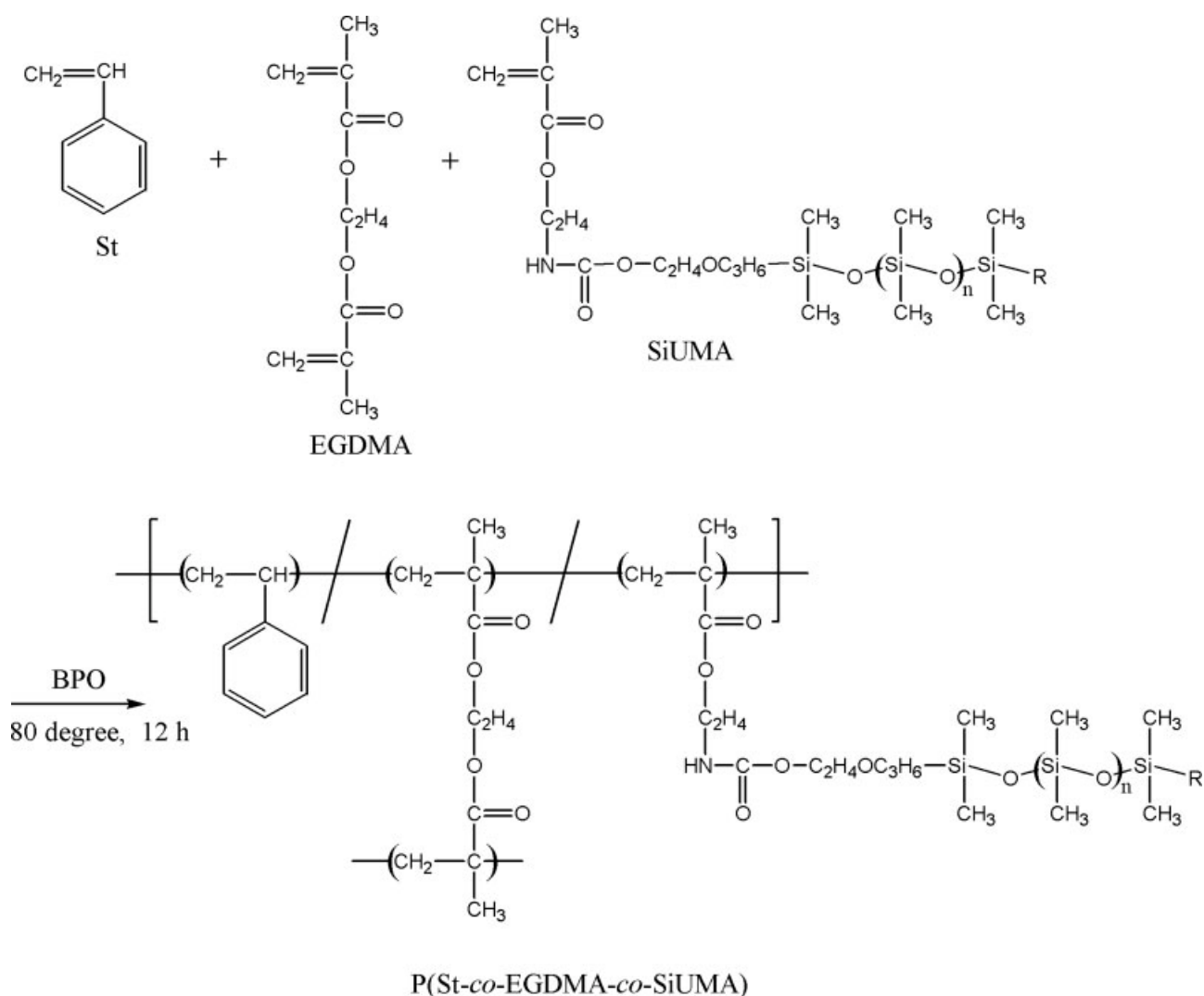
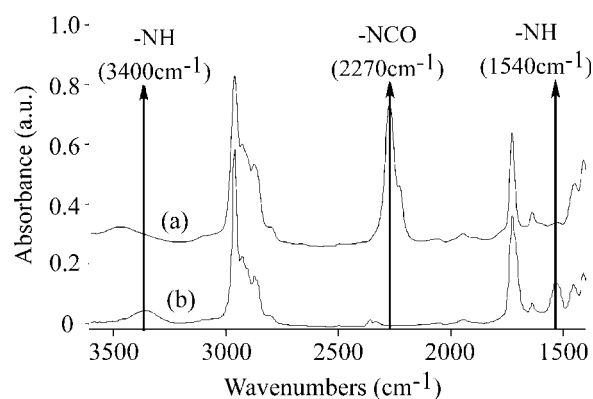Scheme 2 Preparation scheme of P(St-co-EGDMA-co-SiUMA) copolymer.

Figure 1 IR spectra of the preparation of SiUMA: (a) before the reaction; (b) after the reaction.

The reactivity of each monomer was evaluated by ^{1}H-NMR measurement (Bruker AVANCE 200 FT-NMR spectrometer) in CDCl$_3$. After the fixed time had passed starting the polymerization, the little sample was pulled out. And then, it was quenched in the ice bath, and the soluble and insoluble division was divided in CDCl$_3$. The soluble division was evaluated by ^{1}H-NMR measurement with CDCl$_3$. Reactivity was calculated based on the integral ratio of the St **CH$_2$** = peak (5.24 ppm and 5.74 ppm), the EGDMA —OC$_2$H$_4$O— peak (4.39 ppm), and the SiUMA —COOC$_2$H$_4$— peak (4.22 ppm) at fixed quantities, and CDCl$_3$ was used as a primary standard. However, the peak of CDCl$_3$ and the peak of the St benzene ring overlapped between 7.20 and 7.44 ppm; therefore, the integrated value of the peak at 6.12 ppm, which is attributed to the **CH$_2$** = of EGDMA and **CH$_2$** = of SiUMA was defined as 3, and the integrated value of the peak between 7.20 ppm and 7.44 ppm minus 5 (5H of the St benzene ring), was considered to be the integrated value of CDCl$_3$.

Contact angle measurement was carried out under dry conditions to evaluate the surface properties of the prepared samples. The measuring device was a Drop Master 300 (Kyowa Interface Co., Japan), and the contact angle of each sample was obtained by a drop method using distilled water and methylene iodide as a solvent. The surface free energy was calculated using the Owens and Wendt method. The surface free energy of a solid surface (γ) consists of a variance component (γ^d) and a polar component (γ^p). A liquid whose surface free energy (γ_L) is already known is measured to evaluate cos θ, and surface free energy of solid surface (γ_S) may then be calculated using the following two formulae:

$$\gamma_L(1 + \cos\theta) = 2(\gamma_S^d \cdot \gamma_L^d)^{1/2} + 2(\gamma_S^p \cdot \gamma_L^p)^{1/2} \quad (1)$$

$$\gamma_S = \gamma_S^d + \gamma_S^p \quad (2)$$

The physical properties of the prepared materials were evaluated by a three-point bending test using a Tensilon mechanical tester (ORIENTEC Co., Japan, RTC-1250A). The monomer density (ρ_m) was obtained using a pycnometer, and the polymer density (ρ_p) was measured by the Archimedes method using a Mettler Toledo solid density measuring instrument. The volume contraction (V. C.) was calculated using the following formula:

$$V.C. (\%) = 100 \times (1 - \rho_m/\rho_p) \quad (3)$$

RESULTS AND DISCUSSION

Confirmation of synthesis, and transparency of the prepared hybrid materials

The IR results to confirm the synthesis of SiUMA are shown in Figure 1. Comparison of Figure 1(a,b) confirms the disappearance of the isocyanate peak of MOI (2270 cm^{-1}), the appearance of an —NH deformation vibration peak (1540 cm^{-1}), and the appearance of an —NH stretching vibration peak (3400 cm^{-1}) for the urethane bond, which confirms that a reaction occurred between MOI and FM-0411, and thus that SiUMA was prepared. The copolymerization was also confirmed by IR measurement. The disappearance of the peak due to the unsaturated double bond (1640 cm^{-1}) showed that copolymerization had progressed satisfactorily.

The transmittance values (λ = 600 nm) of pure PSt and the prepared PSt hybrid materials are shown in Table II. Pure PSt shows excellent transparency; however, the transparency was dramatically reduced when SiUMA with a PDMS skeleton was introduced into pure PSt. The solubility parameters of PSt and PDMS are, respectively, 9.1 and 7.3 cal$^{1/2}$ cm$^{-3/2}$; the difference between these solubility parameters is sufficiently large to produce segregation in the component interchain between the principal chain and the side chain, resulting in the silicone domain in the microphase-separated structure expanding in size. This is considered to be the reason why the prepared copolymers became opaque. Moreover, when P(St-co-SiUMA-co-EGDMA) copolymers with various silicone contents were prepared, all of the

TABLE II
Transmittance Values of Pure Pst and Pst Hybrid Materials

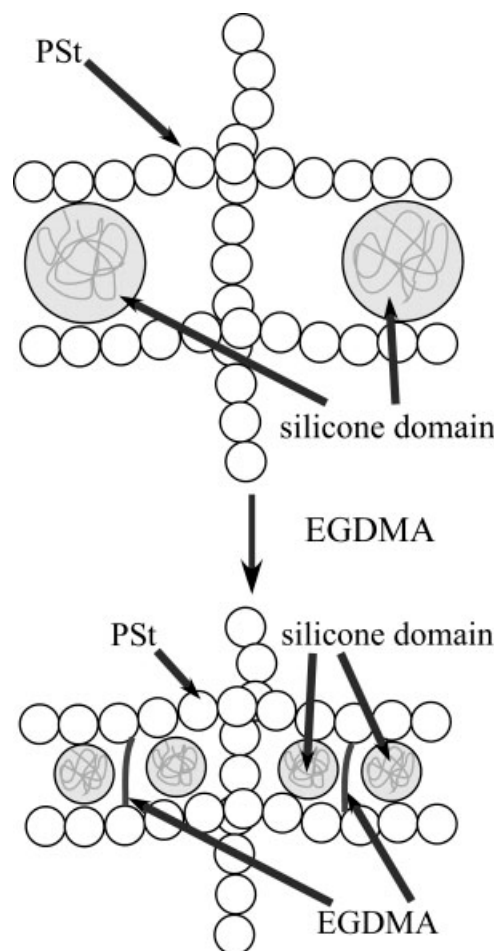| Sample code	Transmittance (%)
Pure PSt	83
P(St-SiUMA)	65
P(St-EGDMA-SiUMA10)	87
P(St-EGDMA-SiUMA20)	88
P(St-EGDMA-SiUMA30)	86
P(St-EGDMA-SiUMA40)	89

Figure 2 Illustration of the effect obtained by addition of EGDMA.

copolymers were transparent; the addition of EGDMA is thought to result in reduction of the microphase separation of the silicone domains (see Fig. 2).

Morphology of the prepared hybrid materials

The silicone domains were evaluated by FE-SEM, and the results are shown in Figure 3. The SEM photograph of P(St-*co*-SiUMA) shown in Figure 3(a) confirms the presence of a distinct phase separation structure of micrometer order. However, in the transparent P(St-*co*-SiUMA-*co*-EGDMA) copolymer with 30 wt % silicone, phase separation structures of more than several hundred nanometers were not observed [Fig. 3(b)]. Based on these results, it was concluded that the addition of EGDMA resulted in a reduction in the size of the silicone domains to a few nanometers.

Next, we investigated the factors influencing the production of transparent PSt hybrid materials. DSC curves for St, SiUMA, EGDMA, St/SiUMA/EGDMA = 60 : 30 : 10 (weight ratio), and St/SiUMA = 70 :
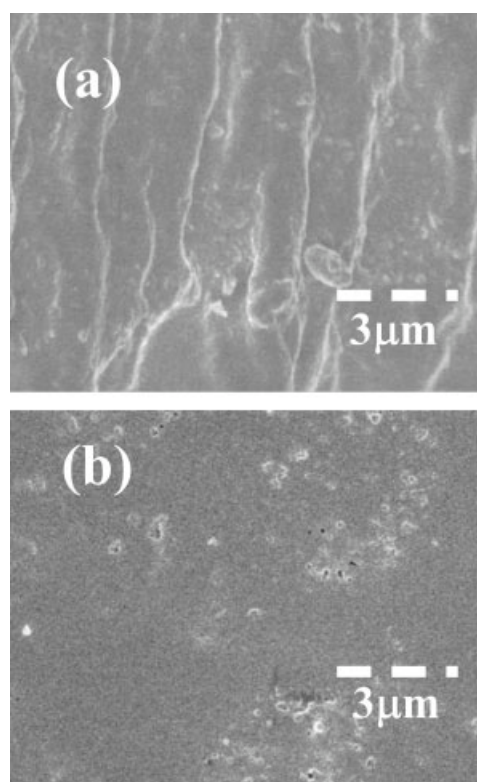

Figure 3 SEM photographs of the hybrid materials. (a) P(St-*co*-SiUMA) and (b) P(St-*co*-EGDMA-*co*-SiUMA30).

30 are shown in Figure 4. A distinct exothermic peak indicating radical polymerization was not observed for St, and the curve tended to drop with the passage of the time. Sharp exothermic peaks were observed for SiUMA and EGDMA from 30 to 50 min and from 20 to 60 min, respectively. A small exothermic peak was observed for St/SiUMA from 350 to 500 min, but it was quite broad. Considering the existence of an early peak only for SiUMA, it is likely that copolymerization between St and SiUMA progresses with difficulty. In fact, the copolymerization ability of St and SiUMA did appear to be low. From these results, it may be concluded that the predominant species is the homopolymer of PSt, and that a
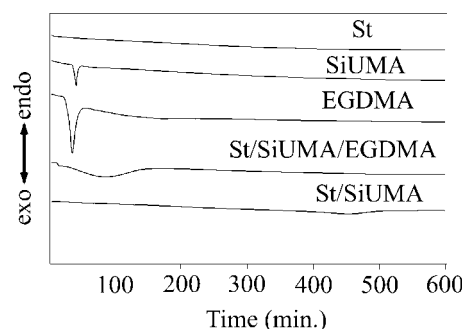

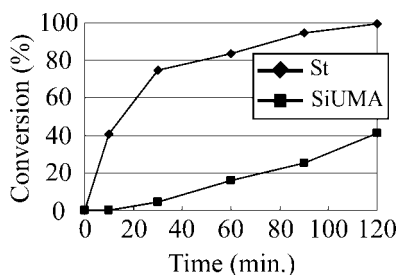**Figure 4** DSC curves of St/SiUMA, St/EGDMA/SiUMA, and each monomer.

Figure 5 Rate of the reaction for St and SiUMA.

Figure 7 Results of ATR-IR measurement of P(St-*co*-EGDMA-*co*-SiUMA) copolymers with various SiUMA contents.

copolymer with high block properties is formed. This results in aggregation of the silicone components, and thus the prepared P(St-*co*-SiUMA) copolymer is opaque.

Next, we examined the DSC curve of St/SiUMA/EGDMA = 60 : 30 : 10, which was the composition at which a transparent sample was formed. Addition of EGDMA resulted in the appearance of a distinct exothermic peak from 30 to 160 min. Thus, the reactivity of SiUMA was promoted by the addition of EGDMA, thereby improving the copolymerization ability of St and SiUMA. As a result, P(St-*co*-SiUMA-*co*-EGDMA) copolymers were readily formed, and the size of the silicone domains was kept to a few nanometers.

^{1}H-NMR measurements were carried out to determine the reaction rate and thus carry out more detailed examination. The reaction rate of each monomer, obtained by ^{1}H-NMR measurement of St/SiUMA = 70 : 30, is shown in Figure 5. In comparison with that of St monomer, it can be seen that the reaction rate of SiUMA monomer was extremely slow. In other words, at the point at which St monomer achieved 100% polymerization, most of the SiUMA was still unreacted. From this result, it was concluded that large amounts of PSt homopolymer were present early in the reaction, after which time the slowly reacting SiUMA was copolymerized with St monomer. This resulted in the formation of silicone domains of micrometer order, so that the prepared P(St-*co*-SiUMA) was opaque. The reaction rate
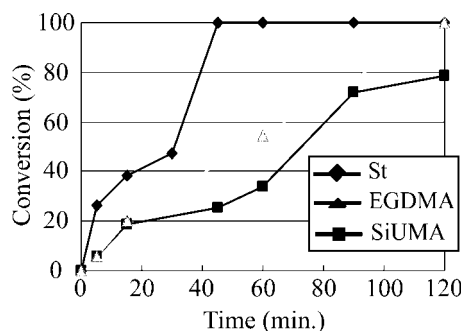
of St/SiUMA/EGDMA = 60 : 30 : 10 is shown in Figure 6. In comparison with the rate shown in Figure 5, the reaction rate of SiUMA was increased by addition of EGDMA. From this result, it was confirmed that copolymerization of St and SiUMA was stimulated by the introduction of EGDMA. Because the addition of EGDMA caused an improvement in the copolymerization ability of St and SiUMA, aggregation of silicone was suppressed, resulting in the formation of transparent and colorless P(St-*co*-SiUMA-*co*-EGDMA) copolymer.

Physical properties of the prepared hybrid materials

The surface state of the prepared PSt hybrid materials was analyzed by FTIR ATR measurement. The variation in the intensity ratio of two peaks-the CH deformation vibration in the benzene ring (760 cm^{-1}) and the Si—CH$_3$ stretching vibration in PDMS (805 cm^{-1}) is shown in Figure 7. It can be seen that the intensity ratio of the Si—CH$_3$ stretching vibration increased with increasing SiUMA content. This shows that the silicone showed an increasing tendency to exist on the sample surface with increasing SiUMA content.

Contact angle measurements were carried out, and water contact angles and surface free energies of pure PSt and the prepared PSt hybrid materials are summarized in Table III. One of the features of silicone is low surface energy. Therefore, the surface free energy of the P(St-*co*-SiUMA-*co*-EGDMA) copolymers decreased with increasing SiUMA content. This result was in agreement with the results of FTIR measurement. Furthermore, the water contact angle increased with increasing SiUMA content; the water contact angle of P(St-*co*-SiUMA-*co*-EGDMA) copolymer with 40 wt % silicone was about 100°, which was an increase of 20° compared with that of pure PSt. Since the silicone, which shows excellent

Figure 6 Rate of the reaction for St, SiUMA and EGDMA.

TABLE III
Physical Properties of Pure Pst and Pst Hybrid Materials

Sample code	Deflection (mm)	Strength (MPa)	Elastic modulus (GPa)	Water contact angle (°)	Surface free energy (erg/cm^2)
Pure PSt	1.5	82	2.9	78	46.2
P(St-SiUMA)	5.4	37	1.3	93	33.4
P(St-EGDMA-SiUMA10)	4.4	101	2.4	91	34.5
P(St-EGDMA-SiUMA20)	6.0	85	2.0	93	33.6
P(St-EGDMA-SiUMA30)	15<	58	1.4	95	29.0
P(St-EGDMA-SiUMA40)	15<	36	0.8	97	29.7

water-repellent properties, mainly exists on the material surface, the water repellent properties of the prepared PSt hybrid materials were improved. Additionally, it can be concluded that the effect of silicone can be seen, because the water contact angle of pure silicone is about 100°. From these results, it can be seen that the prepared PSt hybrid materials have excellent water-repellent properties.

Next, three-point bending tests were conducted for pure PSt and the prepared PSt hybrid materials; the results are shown in Table III. It was anticipated that because of its flexible properties, the addition of silicone would result in a reduction in strength and elastic modulus. In comparison with pure PSt, the elastic modulus of the prepared PSt hybrid materials decreased and their deflection increased with increasing SiUMA content. However, the addition of EGDMA as a crosslinking agent resulted in a strength equivalent to that of pure PSt up to 20 wt % SiUMA.

The monomer densities, polymer densities, and volume contraction of the prepared materials are shown in Table IV. Comparison of the monomer densities of St, SiUMA, and EGDMA gives the order EGDMA > SiUMA > St. Therefore, mixing of EGDMA and SiUMA in the St monomer resulted in an increase in monomer density. In addition, because unsaturated double-bonds groups such as vinyl and methacryloyl are connected via single bonds by free radical polymerization, the polymer density increases, becoming greater than the monomer density. However, the polymer density of P(St-co-SiUMA-co-EGDMA) copolymers was found to decrease with increasing SiUMA content, since SiUMA, which is a macromonomer, contains a high-molecular-weight component which is not used for polymerization. Moreover, the volume contraction rate was found to decrease with increasing SiUMA content due to the decrease in the difference between monomer density and polymer density. In comparison with the dimensional stability of pure PSt, that of P(St-co-SiUMA-co-EGDMA) copolymers was improved by addition of SiUMA.

CONCLUSIONS

P(St-co-SiUMA) copolymer which was prepared by copolymerization of St and SiUMA was opaque; however, P(St-co-SiUMA-co-EGDMA) copolymers, in which EGDMA was introduced, were transparent. The factors influencing the transparency of the resulting copolymer were investigated in detail using FE-SEM, DSC, and ^{1}H-NMR measurements. The presence of silicone domains of micrometer order was confirmed from the SEM photograph of P(St-co-SiUMA), but for P(St-co-SiUMA-co-EGDMA), phase separation structures were not observed over several hundred nanometers. DSC and ^{1}H-NMR measurements were carried out to investigate the reactivity of each monomer. From these results, it was shown that the reactivity of the copolymerization between St and SiUMA was low. However, this property was improved by addition of EGDMA, and

TABLE IV
Monomer Density, Polymer Density, and Volume Contraction for Each Sample

Sample code	Monomer (g/cm^3)	Polymer (g/cm^3)	Volume contraction (%)
Pure PSt	0.90	1.042	13.4
P(St-EGDMA-SiUMA10)	0.92	1.064	13.4
P(St-EGDMA-SiUMA20)	0.93	1.064	12.8
P(St-EGDMA-SiUMA30)	0.93	1.061	11.9
P(St-EGDMA-SiUMA40)	0.94	1.050	10.2
PEGDMA	1.04	1.264	18.1
PSiUMA	0.97	0.994	2.1

aggregation of silicone was inhibited. In fact, the reactivity of the copolymerization between the monomers significantly influences the possibility of obtaining a transparent sample containing silicone. Therefore, the formation of the crosslinked structure and the reactivity of the copolymerization would be important to obtain the transparent PSt hybrid materials containing silicone macromonomer. Moreover, comparison of the contact angle and dimensional stability of pure PSt with those of the prepared P(St-*co*-SiUMA-*co*-EGDMA) copolymers showed that the latter were improved.

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