Miscibility of Polystyrene with One Hydroxystyrene Chain End into Poly(butyl methacrylate)

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ABSTRACT: To investigate the effect of a single chain-end group on the miscibility of poly(butyl methacrylate) (PBMA)/polystyrene blend, polystyrenes having one hydroxylstyrene unit at the chain end (P-HS) were prepared by reversible addition−fragmentation chain transfer (RAFT) polymerization. The molecular weight of these polystyrenes with one hydroxystyrene unit at the chain end was controlled in a molecular weight range from 2200 to 15 300 g/mol with a narrow polydispersity index of less than 1.14. When miscibility behavior was investigated by differential scanning calorimetry (DSC) measurement, P-HS with molecular weight lower than 8500 g/mol were found to be miscible with PBMA as shown by the existence of a single glass transition, whereas polystyrenes with similar molecular weight were immiscible with PBMA. DSC results suggested that the single hydroxystyrene unit at the chain end effectively operated as a miscibility enhancer.

Introduction

In recent years, considerable efforts have been expended in the development of controlled radical polymerization through such methods as reversible addition−fragmentation chain transfer (RAFT) polymerization[1−4] and atom transfer radical polymerization (ATRP).[5,6] RAFT polymerization, in particular, has been widely used as a method of synthesizing functional polymers. Chen et al. reported a novel method for introducing monomeric units into RAFT agents, and by using this unique RAFT polymerization method, it has been possible to insert various functional monomeric units as terminal units in polymer chains.[7]

Polymer−polymer miscibility can be considerably enhanced by causing specific interactions to occur between component polymers,[8] with hydrogen bonding being one effective way of making miscible polymer blends.[9−15] Poly(hydroxystyrene) and styrene−hydroxystyrene copolymers form miscible blends with various polymers such as an homologous series of poly(alkyl methacrylate)s,[16−27] poly(ε-caprolactone),[28−30] poly(acrylic acid),[31] and polyethers.[32,33] In particular, poly(methyl methacrylate)/poly(hydroxystyrene) and poly(methyl methacrylate)/styrene−hydroxystyrene copolymer blends have been widely studied as polymer blend systems, where hydroxystyrene units in the styrene−hydroxystyrene copolymer function as miscibility enhancers in giving a miscible blend with poly(methyl methacrylate). In these systems, hydrogen bonding plays a contributory role because through hydrogen bonding the carbonyl groups in ester groups interact effectively with the hydroxyl groups in hydroxystyrene units inserted into polystyrene chains so as to render polystyrene miscible with an homologous series of poly(alkyl methacrylate)s.

As mentioned above, the unique RAFT polymerization method permits the introduction of a single monomeric unit at the polymer chain end. In this study, the contribution of the end group on polymer blend miscibility was investigated by preparing polystyrenes with various end groups using the RAFT polymerization method. Scheme 1 depicts the chemical structures of polystyrene with various end groups synthesized in this study. Attention was focused on the effect of a single hydroxystyrene unit at a polystyrene chain end on the miscibility of polystyrene/poly(butyl methacrylate) (PBMA) blend. Influences of thermal treatments and casting solvents on the miscibility in the blend were also discussed. Miscibility/immiscibility behaviors of the modified polystyrene/PBMA blends were investigated by using differential scanning calorimetry.

Experimental Section

Materials. Monomers: styrene (Tokyo Chemical Industry Co., Ltd.) and 4-*tert*-butoxystyrene (Hokko Chemical Industry Co., Ltd.) were purified by washing with a 5% sodium hydroxide aqueous solution and with deionized water until the aqueous phase became totally neutral, followed by drying over anhydrous magnesium sulfate, and finally distilling over CaH_2 under vacuum before use. Butyl methacrylate (Tokyo Chemical Industry Co., Ltd.) was distilled just before use. Solvent: chlorobenzene (Wako Pure Chemical Industries Ltd.) was distilled over CaH_2 with all other solvents being used as received. Initiator: 2,2-azobis(isobutyronitrile) (AIBN, 99%, Wako Pure Chemical Industries Ltd.) was recrystallized from acetone. Chain transfer agent: 2-cyanoprop-2-yl dithiobenzoate (CTA 1) was synthesized from cumyl dithiobenzoate and AIBN in accordance with the procedure outlined in the literature.[1] Poly(butyl methacrylate) (PBMA) was prepared by free radical polymerization of butyl methacrylate with AIBN at 60 °C in toluene. The number- and weight-average molecular weights M_n and M_w of PBMA were estimated, by size exclusion chromatography measurements, to be 82 000 and 170 000 g/mol, respectively.

Synthesis of Chain Transfer Agent 2 (CTA 2). The procedure reported by Chen et al. was applied to produce a chain transfer agent CTA 2 including one unit of *tert*-butoxystyrene (Scheme 2).[7] A mixture of CTA 1 (3.30 g, 14.9 mmol), *tert*-butoxystyrene (2.62 g, 14.9 mmol), AIBN (0.048 g, 0.29 mmol), and chlorobenzene (10 mL) was degassed through three freeze−pump−thaw cycles, sealed under vacuum, and heated in a oil bath at 70 °C for 24 h. The crude product was purified by column chromatography with a silica gel column using a solution of hexane/ethyl acetate (9/1 (v/v)) as an eluent. An orange solid (3.5 g) was obtained as a final product in a 60% yield. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 1.26 (s, 3H, −CH_3), 1.35 (s, 9H, −C(CH_3)$_3$), 1.44 (s, 3H, −CH_3), 2.3−2.5 (m, 2H, −CH_2−), 5.3 (q, 1H, −C*H*(Ar)−), 7.0 (dd, 2H, Ar−*H*), 7.3−7.4 (m, 4H, Ar−*H*), 7.6 (m, 1H, *p*-Ar−*H* of dithiobenzoate), 7.9 (m, 2H, *m*-Ar−*H* of dithiobenzoate). ^{13}C NMR

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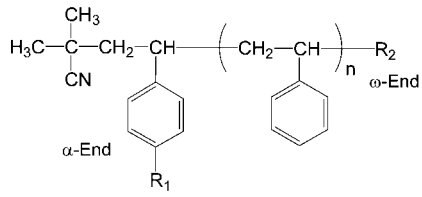
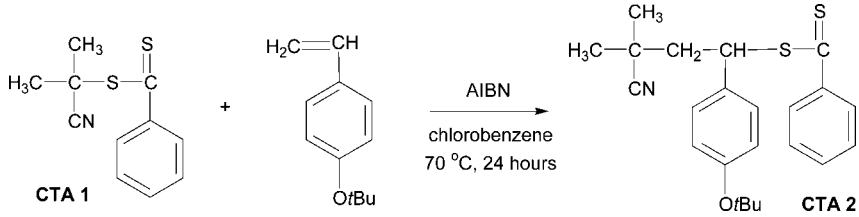
Scheme 1. Polystyrenes with Various α- and ω-Chain End Groups



	α-End Group	ω-End Group
P-BS	$R_1 = OC(CH_3)_3$	$R_2 =$ —S—C(=S)—Ph
P-HS	$R_1 = OH$	$R_2 =$ —S—C(=S)—Ph
P-STS	$R_1 = H$	$R_2 =$ —S—C(=S)—Ph
P-HC	$R_1 = OH$	$R_2 = C(CH_3)_2CN$

Scheme 2. Synthesis of CTA 2



Scheme 3. Synthesis of Polystyrene with a Single Hydroxystyrene α-End Group (P-HS) by RAFT Polymerization of Styrene with CTA 2 and Following Deprotection

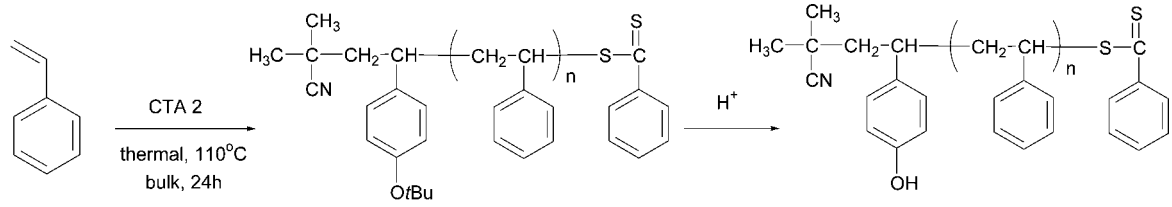


Table 1. Characterization of Polystyrenes Prepared by RAFT Polymerization with CTA 1 or 2

polymer	CTA	$[M]_0/[CTA]_0$	conv (%)	M_n (g/mol)[a]	M_w/M_n[a]	T_g (°C)
P-22BS	2	50/1	46	2200	1.09	84 (88[b])
P-44BS	2	100/1	50	4400	1.09	93 (95[b])
P-67BS	2	150/1	52	6700	1.09	97 (98[b])
P-85BS	2	200/1	50	8500	1.09	99 (99[b])
P-153BS	2	300/1	58	15300	1.14	101 (101[b])
P-25STS	1	50/1	52	2500	1.08	84
P-51STS	1	100/1	57	5100	1.10	94
P-87STS	1	150/1	61	8700	1.10	98
P-130STS	1	200/1	57	13000	1.15	99

[a] Measured by SEC using polystyrene standards in chloroform eluent. [b] Glass transition temperatures after deprotection of *tert*-butyl group.

(100 MHz, $CDCl_3$, ppm); δ 26.8 (CH_3), 28.0 (CH_3), 28.9 (OC-(CH_3)$_3$), 31.8 ($C(CH_3)_2CN$), 45.0 (CCH_2CH), 52.0 (CH−Ar), 79.0 ($OC(CH_3)_3$), 124.0 (CN), 124.6, 127.0, 128.4, 129.2, 132.7, 133.0, 144.8 (Ar), 155.8 (Ar−$COC(CH_3)_3$), 226.2 (C=S). UV−vis (CH_2Cl_2): λ_{max}= 307 and 496 nm. Elem. Anal. Calcd for $C_{23}H_{27}ONS_2$: C, 69.48%; H, 6.85%; N, 3.52%; S, 16.12%. Found: C, 69.47%; H, 6.74%; N, 3.61%; S, 16.07%. Melting point: 69.7 °C.

Synthesis of Polystyrenes with a Single Hydroxystyrene Unit at the α-Chain End. The following procedure (Scheme 3) is a typical method for obtaining polystyrene having a *tert*-butoxystyrene α-end group, which is denoted as P-BS. A mixture of styrene (14 mL, 12.614 g, 121 mmol) and CTA 2 (0.481 g, 1.21 mmol) in a glass ampule was degassed through three freeze−pump−thaw cycles. The ampule was sealed under vacuum and heated at 110 °C for 24 h. The polymerization was quenched by rapid cooling with liquid nitrogen, and the reaction mixture then poured in an excess of methanol to precipitate a polymeric product, which was isolated by filtration and dried under vacuum at 50 °C. The polymer yield was gravimetrically determined from the weight of the methanol-insoluble product.

P-BS was converted to polystyrene with a single hydroxystyrene unit at the α-chain end, which is denoted as P-HS, through hydrolysis of the *tert*-butoxy group. A typical procedure for the reaction is as follows: The P-BS (M_n = 6700 g/mol, 4.9 g, 0.73 mmol) was dissolved in a mixture of toluene/methanol (7/2 (v/v)), and then concentrated sulfuric acid (97%, 0.39 g, 3.9 mmol) was added. The mixture was stirred at 60 °C overnight under a nitrogen atmosphere, and then 50% sodium lactate aqueous solution (3 mL, 15.5 mmol) was added for neutralization. The resulting polymer

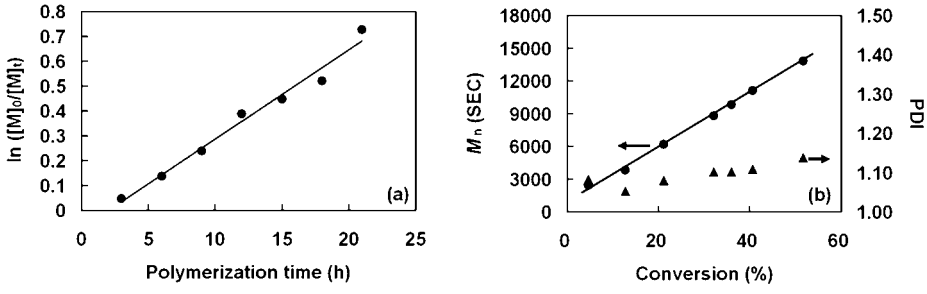


Figure 1. (a) First-order kinetic plot against polymerization time for RAFT polymerization of styrene at 110 °C with $[M]_0/[CTA\ 2]_0$ = 300/1. (b) Number-average molecular weight (circles) and polydispersity index (triangles) as a function of conversion.

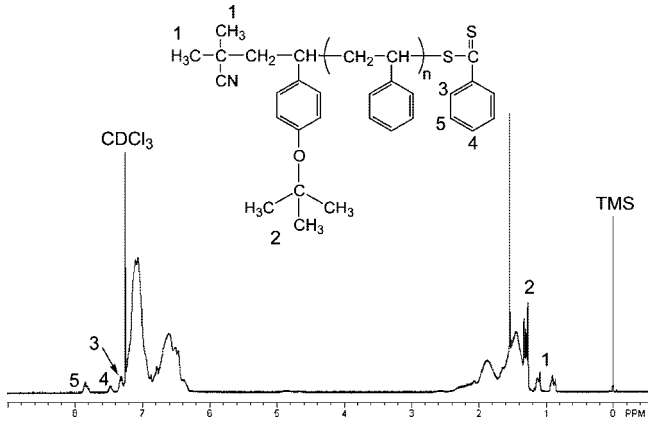


Figure 2. ^{1}H NMR spectrum of polystyrene having M_n(SEC) = 2200 g/mol, a *tert*-butoxystyrene unit as α-chain end group, and a dithiobenzoate group at the ω-chain end, P-22BS.

was purified by three cycles of dissolving in tetrahydrofuran and precipitating with methanol, before being finally dried at 50 °C under vacuum.

Change of Dithiobenzoate to 2-Cyanopropyl Group as the ω-End Group. The dithiobenzoate moieties of polystyrene ω-ends were changed to 2-cyanopropyl groups by a procedure reported by Perrier et al.[34] In a typical experiment, polystyrene with a dithiobenzoate ω-end group (P-85BS, M_n = 8500 g/mol, M_w/M_n = 1.09, 0.9965 g, 0.118 mmol) and AIBN (0.56 g, 3.4 mmol) were dissolved in 10 mL of toluene. The solution was degassed by bubbling through N_2 for 2 h and then heated at 90 °C for 2 h. After the reaction, the solution was cooled, and polymeric products were precipitated into an excess of methanol to obtain a white powder product. From ^{1}H MMR analysis, the product was characterized as a polystyrene having one 2-cyanopropyl ω-end group: Yield: 91%. M_n = 8300 g/mol; M_w/M_n = 1.13.

Preparation of Blend Films. Polymer blend films with various composition ratios (w/w) of modified polystyrene/PBMA were prepared by a conventional solution-casting method with four different solvents: dichloromethane (DCM), toluene, tetrahydrofuran (THF), and methyl ethyl ketone (MEK). The solution containing 5 wt % of a polymer mixture was stirred for 2 h until completely dissolved and then cast onto a glass Petri dish. The solvent was evaporated slowly at room temperature for several days. Resulting cast film was dried under vacuum at 80 °C for 3 days and followed by thermal treatment at 120 °C for 2 days under vacuum in a thermostated vacuum oven.

Characterization Methods. The molecular weight of polymers was measured on a size exclusion chromatograph (SEC) (TOSOH HLC-8220 SEC system) with refractive index (RI) and ultraviolet (UV) detectors, using chloroform as an eluent. The number- and weight-average molecular weights (M_n and M_w) were calculated based on a calibration curve prepared by using polystyrene standards with low polydispersity values. ^{1}H and ^{13}C NMR spectra were recorded on a Varian UNITY INOVA 400 with tetramethylsilane as an internal standard. Differential scanning calorimeter (DSC) measurements were carried out on a Seiko DSC 6200 at a constant heating rate of 10 °C/min in a nitrogen flow of 20 mL/min. A sample sealed in an aluminum pan was quickly cooled from room temperature to −40 °C and then heated from −35 to 140 °C at a constant heating rate of 10 °C/min. The glass transition temperature, T_g, was taken to be the onset point of change of slope in the DSC curve.

Results and Discussion

Preparation of Polystyrenes Having a Single Hydroxylstyrene Unit as the α-Chain End Group. Polystyrenes having one *tert*-butoxystyrene unit at each α-chain end, which are denoted as P-BS, were synthesized by the RAFT polymerization method at 110 °C with a chain transfer agent having a thiocarbonylthio group (CTA 2). Results of the polymerization are summarized in Table 1. The controlled/living nature of this polymerization was kinetically analyzed. Figure 1a shows the typical change for $\ln([M]_0/[M]_t)$ against polymerization time under the condition $[M]_0/[CTA\ 2]_0$ = 300/1, where $[M]_0$ and $[CTA\ 2]_0$ are the initial concentration values of monomer and CTA 2, respectively, and $[M]_t$ is the monomer concentration at time *t*. The plot of $\ln([M]_0/[M]_t)$ was linear and well approximated by a first-order kinetics simulation. The number-average molecular weight, M_n, as estimated by SEC analysis, also increased linearly with increase in the conversion (Figure 1b), consistent with polymerization proceeding in a controlled fashion. Polydispersity index values (PDI), M_w/M_n, were maintained below 1.15 during the polymerization. The ^{1}H NMR spectrum of the obtained P-BS showed typical signals for polystyrene as well as minor signals originating from α and ω-end groups as shown in Figure 2, with these minor signals giving similar M_n values for P-BS to those values obtained in Table 1. P-BS having various molecular weights from 2200 to 15 300 g/mol were prepared by changing the ratio $[M]_0/[CTA\ 2]_0$ in feed. These results indicate that the RAFT polymerization of styrene with CTA 2 as the initiator proceeded well to produce P-BS having one *tert*-butoxystyrene α-chain end unit and one dithiobenzoate ω-chain end group with a low polydispersity index value. Styrene homopolymers having various molecular weights from 2500 to 13 000 g/mol, which are denoted as P-STS, were also synthesized by the RAFT polymerization method with CTA 1 (Table 1).

The *tert*-butoxystyrene unit in the α-chain end group of polystyrene was converted into a hydroxystyrene unit by the deprotection of the *tert*-butyl group at 60 °C under acidic conditions, with the complete elimination of the *tert*-butyl protective group being determined by ^{13}C NMR analysis. Figure 3 shows the ^{13}C NMR spectra before and after the deprotection of P-22BS. A sharp signal at 29 ppm, assigned to the three methyl carbon atoms of the *tert*-butyl group, disappeared after hydrolysis. The deprotection of the *tert*-butyl group in P-BS proceeded quantitatively to produce a P-HS.

Blends of PBMA/Polystyrenes with Different α-Chain Ends. The polystyrenes with different α-chain end groups, P-HS and P-STS (Scheme 1), were blended with PBMA in a 50/50 (w/w) composition ratio using DCM as a solvent. PBMA/P-22HS and PBMA/P-25STS blend films appeared clear and showed single glass transitions at 51 and 55 °C, respectively. The polystyrenes with the lowest M_n values formed miscible mixtures irrespective of the different chemical structures of their α-end group. Blend films of PBMA/P-44HS, PBMA/P-67HS, and PBMA/P-85HS were also transparent; however, only the PBMA/P-153HS blend film appeared opaque. On the other hand, blend films of PBMA/P-51STS, PMMA/P-87STS, and PBMA/P-130STS were cloudy. These preliminary results suggest that the single hydroxystyrene unit at the α-chain end operated effectively as a miscibility enhancer.

Miscibility Analysis by Differential Scanning Calorimeter (DSC). The DSC measurement is a convenient method for determining the miscibility of polymer blends. Generally, when a single glass transition is observed in a blend, the blend is taken as being miscible. Figure 4 shows DSC thermograms of PBMA/P-HS blend films cast from DCM solutions and dried at 80 °C for 3 days under vacuum. A single glass transition at around 50 °C was observed for the blends of PBMA with P-44HS, P-67HS, and P-85HS. These results indicate that the PBMA/P-HS blends are miscible mixtures in this molecular weight range of P-HS. On the other hand, the PBMA/P-153HS blend film, which appeared cloudy, exhibited two glass transitions due to phase separation, suggesting that the P-HS with high molecular weight is immiscible with PBMA even with the

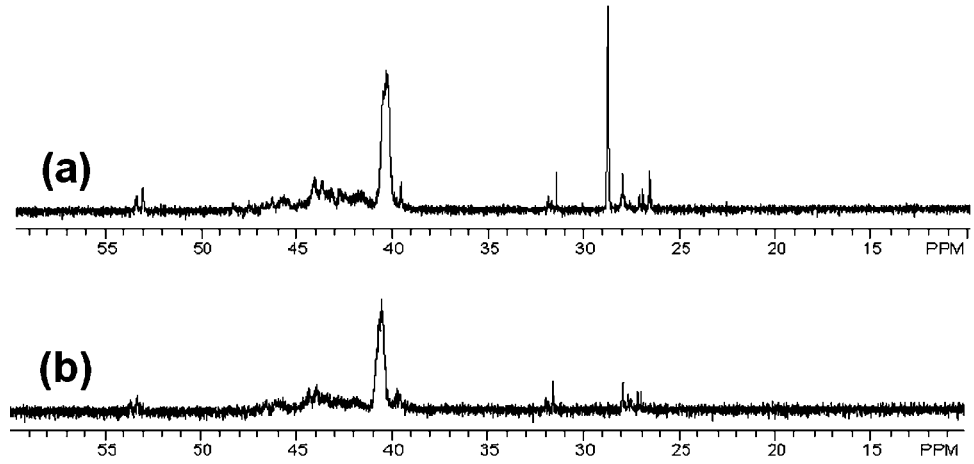


Figure 3. ^{13}C NMR spectra (10−60 ppm, $CDCl_3$) of (a) before and (b) after hydrolysis of P-22BS (M_n = 2200 g/mol).

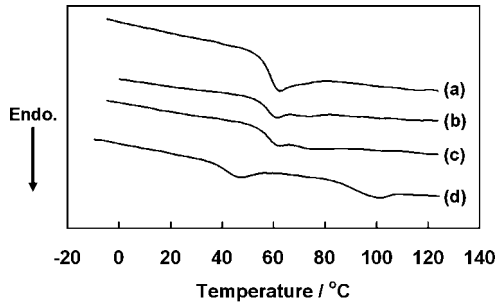


Figure 4. DSC thermograms of PBMA/P-HS blends with different M_n of P-HS. The composition ratio of PBMA to P-HS is 50/50 (w/w). M_n = (a) 4400, (b) 6700, (c) 8500, and (d) 15 300 g/mol. Dichloromethane was used as a solvent.

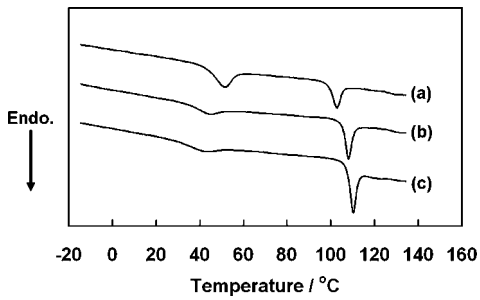


Figure 5. DSC thermograms of PBMA/P-STS blends with different M_n of P-STS. The composition ratio of PBMA to P-STS is 50/50 (w/w). M_n = (a) 5100, (b) 8700, and (c) 13 000 g/mol. Dichloromethane was used as a solvent.

introduction a single hydroxystyrene unit at the polystyrene chain end. This immiscibility is due to the single hydroxystyrene unit content in the blend decreasing with increase in the molecular weight of P-HS. Figure 5 shows DSC thermograms of a series of PBMA/P-STS films cast from DCM solutions and dried at 80 °C for 3 days under vacuum. All PBMA/P-STS blends exhibited two glass transitions, indicating that the P-STSs were immiscible with PBMA. The lower T_g at ca. 40 °C and higher T_g at ca. 100 °C are attributable to the glass transitions of PBMA-rich and P-STS-rich domains, respectively.

When a conventional solvent casting method is used to prepare polymer blend films, some interactions between polymers and solvents influence the miscibility/immiscibility behavior of the blends, tending to induce a nonequilibrium state. To clarify that the miscibility of PBMA/P-HS blends is related to a hydrogen-bonding interaction between the carbonyl group of PBMA and hydroxyl group at the P-HS chain end, thermal

Table 2. Glass Transition Temperatures (°C) of Blends of P-HS or P-STS with PBMA at 50/50 Composition (DCM Cast)

component	dried at 80 °C	treatment at 120 °C
PBMA/P-44HS	55	51
PBMA/P-67HS	54	51
PBMA/P-85HS	54	48
PBMA/P-153HS	36, 84	33, 95
PBMA/P-25STS	55	50
PBMA/P-51STS	43, 99	43, 90
PBMA/P-87STS	35, 105	34, 99
PBMA/P-130STS	32, 107	30, 99

treatment of PBMA/P-HS blends was carried out at 120 °C. The solvent effect of DCM on the miscibility of polymer blend can be removed by thermal treatment at a temperature of 120 °C, which is higher than the T_g values of both the components. Table 2 lists T_g values of PBMA/P-HS and PBMA/P-STS blends after thermal treatment at 120 °C. In the blends of PBMA with P-44HS, P-67HS, and P-85HS, a single glass transition was observed for each blend after thermal treatment. T_g values of the blends treated at 120 °C were almost the same as those of the blends treated at 80 °C. Opaque PBMA/P-153HS blend film also remained cloudy even after thermal treatment at 120 °C, indicative of the two glass transitions. No significant change in the miscibility/immiscibility behavior of the PBMA/P-HS blends was observed upon thermal treatment at 120 °C.

Contrastively, PBMA/P-51STS, PBMA/P-87STS, and PBMA/P-130STS blends showed two glass transitions, indicating that, with the exception of PBMA/P-25STS, all P-STS were immiscible with PBMA upon thermal treatment at 120 °C. These DSC results clearly demonstrate that the contribution of the single hydroxystyrene unit introduced at the polystyrene α-chain end significantly improved the miscibility with PBMA in the molecular weight range of 4400−8500 g/mol of polystyrene.

The PBMA/P-85HS blend film cast from DCM solution showed a single T_g over a wide blend composition range of 0.2/0.8−0.8/0.2 (w/w). The dependence of the T_g value on the composition of PBMA/P-85HS blends is shown in Figure 6. The plot of T_g values was compared with a simulation curve calculated from Wood's equation:[35]

$$T_g = (W_1T_{g1} + kW_2T_{g2})/(W_1 + kW_2) \quad (1)$$

where T_g is the glass transition temperature of the blend, T_{g1} and T_{g2} are the transition temperatures of the original components, k is an adjustable fitting parameter that semiqualitatively describes the strength of intermolecular interaction, and W_1 and W_2 are the weight fraction values of the components. The k value is determined by a curve adjusted to fit the experimental

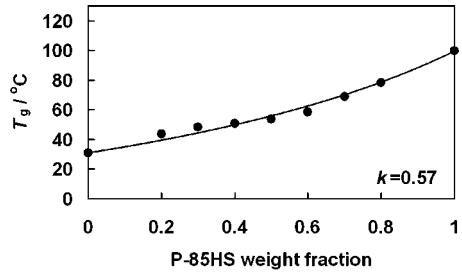


Figure 6. Relationship between the glass transition temperature (T_g) and the composition of PBMA/P-85HS blends (dichloromethane cast). The solid line represents the calculated T_g values based on Wood's equation with k value of 0.57.

Table 3. Glass Transition Temperatures (°C) of PBMA/P-HS Blends at 50/50 (w/w) Composition for Various Solvents

	DCM	toluene	THF		MEK	
component	120 °C	120 °C	80 °C	120 °C	80 °C	120 °C
PBMA/P-67HS	51	51	51	51	41, 96	49
PBMA/P-85HS	48	51	44, 97	50	37, 103	40, 99
PBMA/P-153HS	33, 95	34, 97	31, 99	31, 99	29, 107	32, 101

data according to eq 1. For a k value of 0.57, good agreement between the observed T_g plots with the simulation curve from eq 1 was found as shown in Figure 6, indicating that PBMA and P-85HS are miscible and form a single homogeneous phase.

When the blend films are prepared by casting from solutions, the solvent used for blending is an important factor affecting blend miscibility. Table 3 lists T_g values of PBMA/P-HS blends prepared with different solvents: DCM, toluene, THF, and MEK. The blends of PBMA with P-153HS having highest molecular weight of P-HS were immiscible regardless of the solvents. The blend films of PBMA with P-67HS and P-85HS cast from toluene solutions showed a single T_g value at ca. 50 °C. The miscibility of the blends cast from toluene solutions was similar to those prepared from DCM solutions as listed in Table 3.

PBMA/P-67HS blend films cast from THF solutions exhibited a single T_g regardless of the thermal treatment temperatures, whereas the thermal treatment temperatures did influence the miscibility of PBMA/P-85HS blend film cast from a THF solution. Although the blend film treated at 80 °C exhibited two values of T_g, upon heating at 120 °C, it became visually clear and showed a single T_g at 50 °C. When MEK was used as a casting solvent, blend films of PBMA with P-67HS and P-85HS showed some different features in their miscibility behavior. The PBMA/P-67HS blend film treated at 80 °C was opaque and exhibited two T_gs, but when heated at 120 °C, the blend became clear and showed a single T_g at 49 °C. On the other hand, PBMA/P-85HS blend film cast from a MEK solution was immiscible even after thermal treatment at 120 °C.

The miscibility of PBMA/P-HS blend films cast from THF and MEK was different from that of the films cast from DCM and toluene. According to the Hansen solubility parameter of liquids, THF and MEK have higher δ_h values of 8 and 5.1 $MPa^{1/2}$, respectively.[36] These δ_h values mean that the electronegative oxygens in the solvents draw the sole electron on the hydrogen atom attached to oxygen in the hydroxyl styrene unit to prevent the interaction between the carbonyl group in PBMA and the hydroxyl group in P-HS. Conversely, toluene has a lower δ_h value of 2 $MPa^{1/2}$, so that in the case of toluene casting, the carbonyl and hydroxyl groups easily form hydrogen bonding, resulting in the formation of a miscible mixture. In the case of DCM, which has a high δ_h value of 6.1 $MPa^{1/2}$, the electropositive hydrogens in DCM must form hydrogen bonding with a large number of electronegative carbonyl oxygens in PBMA. Thus, the hydrogen in the single hydroxyl group of the P-HS unit may be able to form hydrogen bonding with residual carbonyl oxygen in PBMA to form a miscible mixture in a similar way to the case of toluene casting.

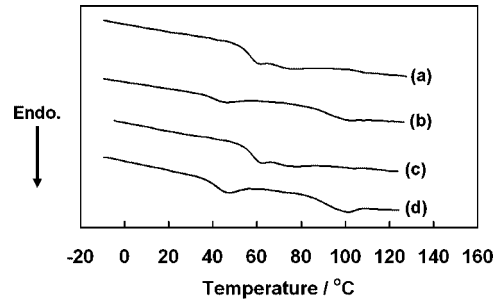


Figure 7. DSC thermograms of blends of (a) PBMA/P-85HC, (b) PBMA/P-153HC, (c) PBMA/P-85HS, and (d) PBMA/P-153HS. The composition ratio of PBMA to P-HC or P-HS is 50/50 (w/w). Dichloromethane was used as a solvent.

Therefore, the difference in the miscibility of PBMA/P-85HS blend films cast from the four kinds of solvents may be explained in terms of the opportunity for hydrogen bonding to occur among PBMA, P-HS, and solvent.

Effect of Dithiobenzoate ω-End Group on Miscibility of the Blends. To examine effect of a single ω-chain end group in the polystyrenes on the miscibility with PBMA, the ω-chain end dithiobenzoate group of P-HS was converted to a cyanopropyl group. The polystyrenes with one cyanopropyl group as the ω-chain end and a hydroxystyrene unit as the α-chain end unit are denoted as P-HC (Scheme 1). Prepared P-HCs were blended with PBMA in a 50/50 (w/w) composition ratio by casting from DCM solutions. Obtained blend films were thermally treated at 80 °C for 3 days under vacuum. Figure 7 shows DSC thermograms of PBMA/P-85HC and PBMA/P-153HC blends. A single T_g was observed at 52 °C in the thermogram of the PBMA/P-85HC blend, and two T_gs were shown at 36 and 88 °C in the thermogram of PBMA/P-153HC blend. DSC thermograms of PBMA blends with P-85HS and P-153HS are also shown in Figure 7. No significant difference in glass transition temperature was observed even after the change in the ω-chain end structure from a dithiobenzoate to a cyanopropyl group. When compared with the effect of the introduction of a single hydroxystyrene unit at the α-chain end, the effect of introducing a single cyanopropyl group at the ω-chain end was not significant in terms of its miscibility with PBMA.

Conclusions

Designed polystyrenes with a single hydroxystyrene unit at the α-chain end (P-HS) were prepared by the RAFT polymerization of styrene using the designed chain transfer agent, CTA 2, followed by the deprotection reaction of the *tert*-butyl group. The controlled/living fashion of the polymerization allowed the designed polystyrenes to be obtained with M_n values in a range from 2200 to 15 300 g/mol and low PDI values (M_w/M_n = 1.09−1.14). The effect of a single hydroxylstyrene α-chain end unit on the miscibility was demonstrated by PBMA/P-HS blends at a 50/50 (w/w) composition ratio. The influences of thermal treatment and casting solvent on miscibility in the blend were also examined. In the PBMA/P-HS blends, the blends in the M_n range of P-HS from 2200 to 8500 g/mol were miscible and exhibited a single T_g. The P-HS having M_n = 15 300 g/mol was immiscible with PBMA. Corresponding P-STSs in the M_n range of 5100−8700 g/mol without the single hydroxylstyrene α-chain end unit were immiscible with PBMA. It was clarified that the single hydroxylstyrene α-chain end unit operated

effectively as a miscibility enhancer in PBMA/polystyrene blends.

References and Notes

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