Thermoreversible Poly(alkyl acrylates) Consisting of Self-Complementary Multiple Hydrogen Bonding

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ABSTRACT: The synthesis and characterization of novel self-complementary multiple hydrogen-bonded (SCMHB) polymers containing pendant 2-ureido-4[1*H*]-pyrimidone (UPy) units are described. SCMHB pendant polymers, poly(butyl acrylate-*co*-SCMHB methacrylate), were prepared via free radical copolymerization of butyl acrylate (BA) and a novel SCMHB methacrylate (SCMHB MA) monomer, which was synthesized via a quantitative coupling reaction between 2-isocyanatoethyl methacrylate (ICEMA) and methyl isocytosine (MIS) in DMSO. The glass transition temperatures of poly(BA-*co*-SCMHB MA) increased in a linear fashion as the SCMHB MA content increased. Thermogravimetric analysis of the copolymers exhibited an onset of weight loss at 217 °C. Solution viscosity analysis indicated that SCMHB pendant polymers strongly aggregated in nonpolar solvents, such as toluene and $CHCl_3$, and dissociated in polar solvents, such as THF. Based on melt rheological characterization, the melt viscosity of soluble SCMHB pendant polymers was an order of magnitude higher than that of PBA due to strong aggregation in the melt state. SCMHB pendant polymers exhibited thermoreversible characteristics, and complete dissociation in the melt state was observed at 80 °C, which was consistent with our earlier studies involving SCMHB-terminated poly(styrene) (PS), poly(isoprene) (PI), and PS-*b*-PI block copolymers. In addition, SCMHB units completely dissociated at 80 °C in toluene on the basis of ^{1}H NMR measurements. The 90° peel strength values for SCMHB-containing polymers increased as the SCMHB units increased due to the strong interaction of SCMHB units with the glass surface. Thin-layer chromatography indicated that the interaction of SCMHB pendant polymers with silica was more favorable compared to PBA homopolymer.

Introduction

Tailored noncovalent bonding, such as multiple hydrogen and ionic bonding, has recently received renewed attention due to the rapidly evolving field of supramolecular chemistry.[1−20] The future design of advanced macromolecular structures will demand a unique combination of noncovalent and covalent bonding in order to provide both excellent mechanical performance and thermoreversibility during melt processing. Recent research efforts have focused on the design of supramolecular macromolecules consisting of tailored complementary multiple hydrogen bonds with extremely higher dimerization constants. Meijer et al. recently reported the utility of self-complementary multiple hydrogen bonds (SCMHB) between 2-ureido-4[1*H*]-pyrimidone (UPy) units, which self-dimerize strongly through four hydrogen bonds arranged in a donor−donor−acceptor−acceptor fashion.[21−30] In addition, Jean-Marie Lehn et al. have focused on complementary multiple hydrogen bonds in the selective formation of discrete supermolecules from complementary hydrogen bonding (CMHB) pairs, which do not self-dimerize.[31,32] Lehn and coworkers also reported the formation of vesicles containing complementary lipids bearing bartituric acid and triaminopyrimidine units as headgroups.[33,34]

Macromolecules containing pendant multiple hydrogen bonds have resulted in novel thermoplastic elastomers, i.e., thermoplastic behavior above the dissociation temperature of the multiple hydrogen bonds and thermoset behavior below the dissociation temperature.[35−41] Stadler et al. demonstrated that hydrogen-bonding interactions in (4-carboxyphenyl)urazole-substituted poly(1,3-butadiene) significantly influenced the properties of the bulk polymer due to the formation of a thermoreversible network.[39] Stadler also reported DSC, dielectric, and dynamic mechanical analysis of telechelic hydrogen-bonded poly(isobutylene) containing 4-urazoylbenzoic acid.[38] The melting temperature of the ordered aggregates ranged from 380 to 390 K as determined using DSC, and transitions were monitored below the melting temperature using dielectric mechanical measurements. Coates et al. also recently reported the synthesis of elastometric nonpolar poly(1-hexane) possessing pendant SCMHB units (UPy) and their reversible nature in solution.[40] A strong dimerization was observed in nonpolar solvents. Chino et al. reported the synthesis of thermoreversible poly(isoprene) thermosets derived from the subsequent derivatization of a maleic anhydride modified poly(isoprene) with 3-amino-1,2,4-triazole.[41] Interestingly, the SCMHB networks exhibited similar mechanical properties to vulcanized rubber, and thermoreversible dissociation occurred at approximately 185 °C.

Our earlier research efforts have involved the synthesis of well-defined terminal multiple hydrogen-bonded polymers, such as glassy poly(styrene) (PS), rubbery poly(isoprene) (PI), and microphase-separated PS-*b*-PI block copolymers with well-defined molecular weights and narrow molecular weight distributions. The relationship between end-group structure and physical properties, such as the glass transition temperature, melt viscosity, and morphology, were reported.[42−44] Our recent interest has focused on the unprecedented syn-

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thesis and characterization of thermoreversible poly(alkyl acrylates) comprising pendant SCMHB units in order to more fully understand the nature of SCMHB macromolecules. These novel families of acrylic polymers are expected to exhibit interesting rheological, thermal, and adhesive properties.

Experimental Section

Materials. Butyl acrylate (BA) and DMSO were distilled from finely ground calcium hydride at reduced pressure (0.5 mmHg) immediately prior to polymerization. 2-Isocyanatoethyl methacrylate (ICEMA) (Aldrich), 6-methylisocytosine (2-amino-4-hydroxy-6-methylpyrimidone: MIS) (Aldrich) (mp > 300 °C), and 2,2′-azobis(isobutyronitrile) (Aldrich) were used as received.

Synthesis of SCMHB Methacrylate (I) (SCMHB MA). MIS (4 g, 32.0 mmol) was completely dissolved in DMSO with heating at 170 °C, and the flask was then removed from the oil bath. ICEMA (5.5 g, 35.4 mmol) was added immediately to the flask. Addition of ICEMA resulted in a vigorous reaction, which was quickly quenched using a water bath to inhibit polymerization. The precipitated white solid was washed with cyclohexane and dried at reduced pressure (yield 92%). ^{1}H NMR (400 MHz, $CDCl_3$, δ): 13.0 (s, 1H, −N*H*−C(CH_3)═), 11.9 ppm (s, 1H, −N*H*−C═N−), 10.5 ppm (s, 1H, −CH_2N*H*−CO−), 6.2 (s, 1H, C*H*$_{cis}$═C(CH_3)), 5.8 (s, 1H, −NHC(CH_3)═C*H*CO−), 5.5 (s, 1H, C*H*$_{trans}$═C(CH_3)), 4.3 (s, 2H, −COOC*H*$_2$−), 3.6 ppm (s, 2H, −$COOCH_2CH_2$NH−), 2.3 ppm (s, 3H, −NHC(C*H*$_3$)═CH−CO−), 1.9 (s, 3H, CH_2═C(C*H*$_3$)). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 173.3 ppm (−NH*C*ONH−), 167.9 ppm (−*C*OOCH$_2$−), 157.1 ppm (−NH−*C*═N−), 154.7 ppm (−NH*C*-(CH_3)═CH−CO−), 136.3 ppm (CH_2═*C*(CH_3)), 126.0 ppm (*C*H$_2$═C(CH_3)), 106.8 ppm (−NHC(CH_3)═*C*HCO−), 63.3 ppm (−COO*C*H$_2$−), 38.9 ppm (−$COOCH_2CH_2$NH−), 19.2 ppm (−NHC(*C*H$_3$)═CHCO−), 18.4 ppm (CH_2═C(*C*H$_3$)). m/z = 280 (theoretical: 280.26). The monomer was readily soluble in DMSO, dimethylacetamide, DMF, and $CHCl_3$ and insoluble in CH_3OH, acetone, THF, toluene, and water.

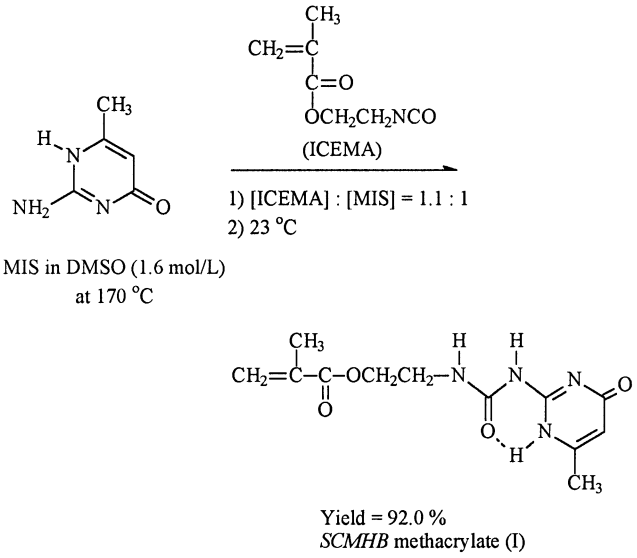
Synthesis of SCMHB Pendant Copolymers (II). All free radical copolymerizations were performed under a nitrogen atmosphere in a 150 mL round-bottomed flask sealed with a rubber septum. Poly(BA-*co*-SCMHB MA) ([SCMHB MA] = 0−10 mol %) (**II**) was synthesized via free radical copolymerization of **I** with BA at 3.3 vol % monomer concentration in DMSO in the presence of 0.5 mol % AIBN. DMSO was successfully used as the polymerization solvent in a similar fashion as reported in the earlier literature.[45−47] The solution was stirred for 24 h at 60 °C, then precipitated into MeOH, redissolved in $CHCl_3$, reprecipitated in MeOH, and dried under vacuum at 60 °C. The SCMHB MA monomer was incorporated in a predictable and quantitative fashion based on ^{1}H NMR analysis. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 12.9−13.2 (s, −N*H*−C(CH_3)═ in SCMHB MA units), 11.8−12.1 (s, −N*H*−C═N− in SCMHB MA units), 10.4−10.7 (s, −CH_2N*H*−CO− in SCMHB MA units), 5.7−6.0 (s, NHC(CH_3)═C*H*CO− in SCMHB MA units), 3.7−4.4 (s, −O*CH*$_2$CH$_2$− in BA), 3.1−3.7 (s, −O*CH*$_2$-CH_2− in SCMHB MA units), 0.6−2.8 (b, −CH_3, −CH_2−, CH in SCMHB MA and BA units)). Poly(BA-*co*-*SCMHB* MA) was soluble in DMSO, dimethylacetamide, DMF, $CHCl_3$, THF, acetone, and toluene and insoluble in CH_3OH and water.

Instrumentation. ^{1}H NMR spectra were recorded in various deuterated solvents using a Varian UNITY 400 spectrometer at 400 MHz. Molecular weights were determined at 40 °C in ACS grade THF at a flow rate of 1.0 mL/min using a Waters SEC (515 pump, 717 autosampler) with an external 410 refractive index detector. Multiangle laser light scattering (MALLS) permitted absolute molecular weight determination using an in-line Wyatt Minidawn. Glass transition temperatures (T_g) were determined under nitrogen using a Pyris Perkin-Elmer DSC at a heating rate of 10 °C/min. All reported glass transition temperatures are reported as the midpoint of the second heat. Thermogravimetric analysis (TGA) was conducted under a nitrogen atmosphere, from 25 to 600 °C at a heating rate of 10 °C using a TA Instruments TGA 295. Rheological measurements were performed at several temperatures <200 °C and a shear rate of 13.16 s^{-1} using a TA Instruments AR 1000. A parallel plate fixture, i.e., plate diameter = 25.0 mm and gap = 1000 μm, was used. The test specimens for the adhesive evaluation were prepared via coating a 10 wt % chloroform solution of a SCMHB pendant polymer on a glass plate (150 × 75 mm) using a film casting knife to control film thickness (0.2 mm). The chloroform was subsequently evaporated at 23 °C under vacuum. Residual solvent and voids were not observed in the thin films. PET film (150 × 75 × 0.020 mm) was placed on top of the SCMHB pendant polymer film. Adhesive strength was measured using a 90° peel test on a LLOYD LR-10K universal testing machine (UTM). The cross-head speed was maintained at 10 mm/min, and five measurements were performed on five different specimens to ensure reproducibility.

Results and Discussion

Synthesis of self-complementary multiple hydrogen-bonded (SCMHB) polymers involved a two-step synthesis as shown in Scheme 1 and Scheme 2. The first step

Scheme 1. Synthetic Scheme for Novel SCMHB Methacrylate Monomer (SCMHB MA)



involved the synthesis of a novel monomer, SCMHB MA, which involved a coupling reaction between ICEMA and MIS in DMSO (Scheme 1). In the second step, butyl acrylate (BA) and the SCMHB MA were copolymerized in the presence of AIBN in DMSO (Scheme 2) at 60 °C.

Synthesis and Characterization of SCMHB Methacrylate (I) (SCMHB MA). The SCMHB MA monomer (**I**) was synthesized via a coupling reaction between MIS and a 1.1 molar excess of ICEMA compared to MIS. The reaction was complete within minutes, and a fine powder was obtained in a quantitative yield (92%). MIS (4.0 g, 32.0 mmol) was readily dissolved in DMSO at 170 °C, and the oil bath was subsequently removed. ICEMA (5.5 g, 35.4 mmol) was added immediately to the flask, and a vigorous reaction, which was quickly cooled using a water bath, resulted. A fine white solid precipitated upon cooling and was washed with excess acetone and dried under vacuum (yield 92%). On the basis of ^{1}H NMR analysis (Figure 1), the SCMHB MA monomer composition was confirmed, and peak integrations of ^{1}H NMR spectra using NMR Utility Transform Software showed good agreement with the proposed

Scheme 2. Synthetic Scheme for Novel SCMHB Pendant Polymers

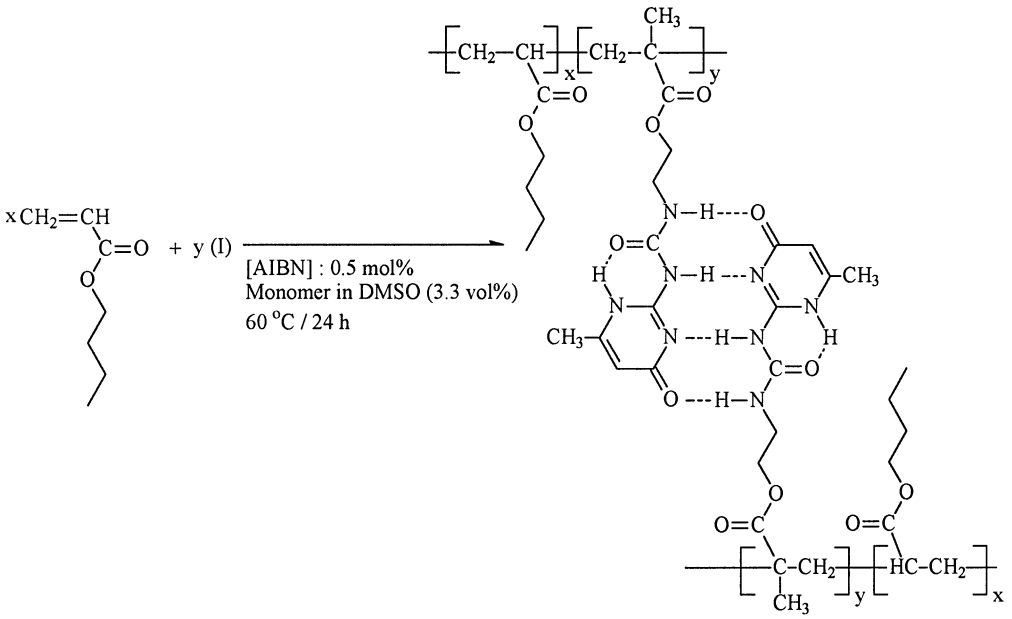


Table 1. Molecular Weight and Molecular Weight Distribution for P(BA-*co*-SCMHB methacrylate)

	monomer feed (mol %)[a]		copolymer composition (%)[b]			SEC MALLS		
sample	BA	SCMHB MA	BA	SCMHB MA	yield (%)	M_n	M_w/M_n	T_g[c] (°C)
PBA	100.0	0.0	100.0	0.0	40.0	37900	2.2	−50
SCMHB-1	99.0	1.0	97.5	2.5	65.0	38300	2.2	−46
SCMHB-2	97.0	3.0	96.7	3.3	70.0	38000	2.1	−43
SCMHB-3	95.0	5.0	92.6	7.4	72.0	55000	2.0	−29
SCMHB-4	90.0	10.0	89.6	10.4	78.0	49600	2.3	−23

[a] 3.3 vol % monomer in DMSO in the presence of 0.5 mol % AIBN at 60 °C for 24 h. [b] Estimated from 400 MHz ^{1}H NMR spectrum. [c] Measured by DSC, midpoint of the second heat.

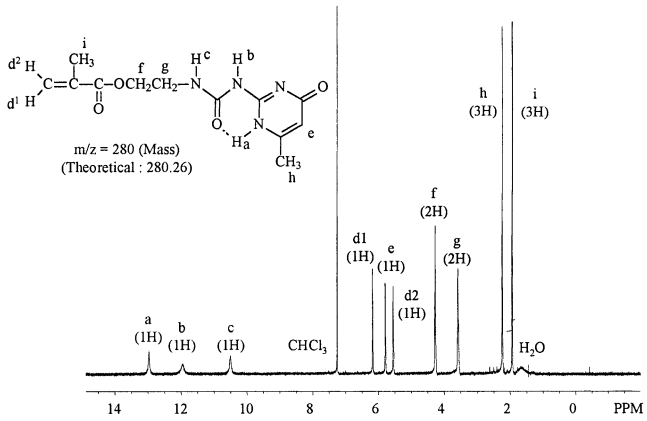


Figure 1. ^{1}H NMR spectrum of the reaction product (SCMHB MA).

structure. In addition, the mass spectrum of the final product exhibited m/z = 280, which agreed well with the theoretical molecular weight (m/z = 280.26). The monomer was soluble in DMSO, dimethylacetamide, DMF, and $CHCl_3$ at 50 °C and insoluble in CH_3OH, acetone, THF, and water.

Synthesis and Characterization of SCMHB Copolymers (II). SCMHB pendant polymers, poly(BA-*co*-*SCMHB* MA), were synthesized via a free radical copolymerization in the presence of AIBN in DMSO under a nitrogen atmosphere at 60 °C. Monomer feed, copolymer composition, molecular weights, and molecular weight distributions are summarized in Table 1. Figure 2 depicts a comparison of ^{1}H NMR spectra for PBA and the copolymer (SCMHB-4). Based on a comparison of ^{1}H NMR spectra, five resonances that were assigned to SCMHB MA units in the copolymer were observed. A well-resolved resonance for PBA that was suitable for quantification was detected between 3.7 and 4.4 ppm (a, $-OCH_2CH_2-$). Overlapping resonances that were assigned to both BA and SCMHB MA units were observed at 0.6−2.8 ppm (b−e, k−m).

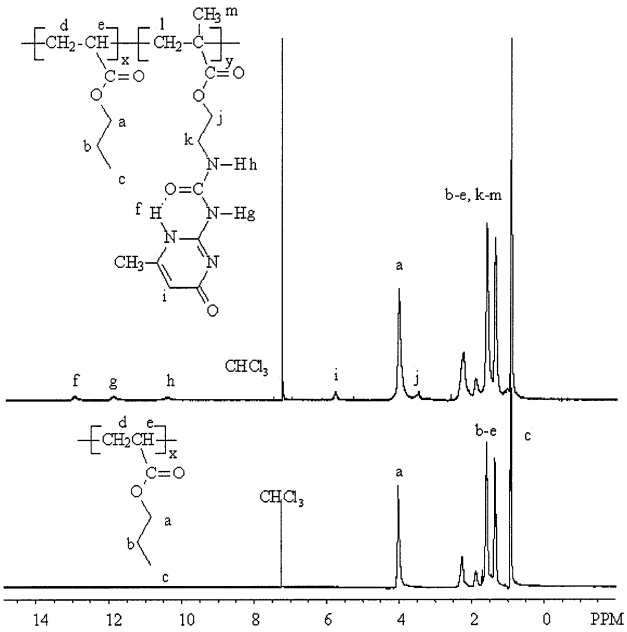


Figure 2. ^{1}H NMR spectra of PBA and SCMHB pendant polymer (SCMHB-4).

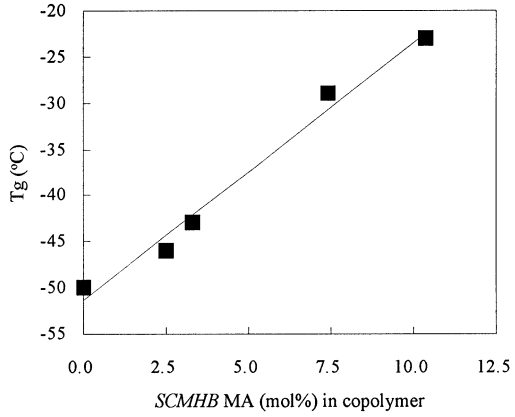


Figure 3. Relationship between SCMHB MA contents in the polymer and T_g (DSC measured from −100 to 180 °C, 10 °C/min).

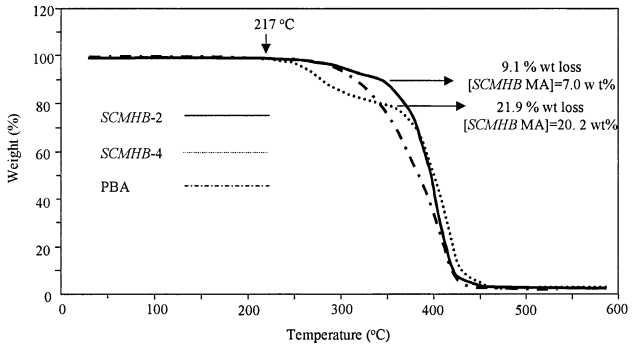


Figure 4. Thermogravimetric analysis of SCMHB pendant polymers and PBA (SCMHB-2 ([BA]:[SCMHB MA] = 96.7:3.3 mol %), SCMHB-4 ([BA]:[SCMHB MA] = 91.6:10.4 mol %)).

Copolymer compositions were determined using integrations associated with the SCMHB MA units such as the ethyl ester (a) in BA with the ethyl ester (j), three NH hydrogen (f, g, h), or methyne hydrogen (i) in the SCMHB MA units. In addition, the vinylic hydrogens in the SCMHB MA monomer, which were observed at 6.2 ppm (d_1: s, 1H, $CH\mathit{H}_{cis}$═C(CH_3), 5.8 ppm (e: s, 1H, −NHC(CH_3)═C*H*CO−), 5.5 ppm (d_2: s, 1H, $CH\mathit{H}_{trans}$═C(CH_3), were not detected. Copolymer compositions as determined using ^{1}H NMR spectroscopy exhibited good agreement with the monomer feed. Thus, the SCMHB MA was incorporated quantitatively into the copolymer based on ^{1}H NMR analysis. The solubility of poly(BA-*co*-SCMHB MA) was similar to that of PBA, and solubility in DMSO, dimethylacetamide, DMF, $CHCl_3$, THF, acetone, and toluene and insolubility in CH_3OH and water were observed.

Thermal Characterization. Figure 3 depicts the relationship between SCMHB MA content in the copolymer and glass transition temperature. As expected, the T_g of SCMHB-containing copolymers increased in a linear fashion with SCMHB MA content due to strong interactions between the SCMHB units. Figure 4 shows the thermogravimetric analysis (TGA) of SCMHB-2 ([BA]:[SCMHB MA] = 96.7:3.3 mol %), SCMHB-4 ([BA]:[SCMHB MA] = 91.6:10.4 mol %), and PBA. TGA data indicated that the SCMHB-containing polymers exhibited an onset of weight loss at 217 °C, which was consistent with our previous efforts on SCMHB-terminated PS.[42−44] The degradation mechanism appeared to involve two steps. The first degradation step corresponded to the elimination of pendant SCMHB units since the weight loss of the first step was similar to the theoretical weight of the SCMHB MA units. The second degradation step corresponded to the degradation of the polymer backbone.

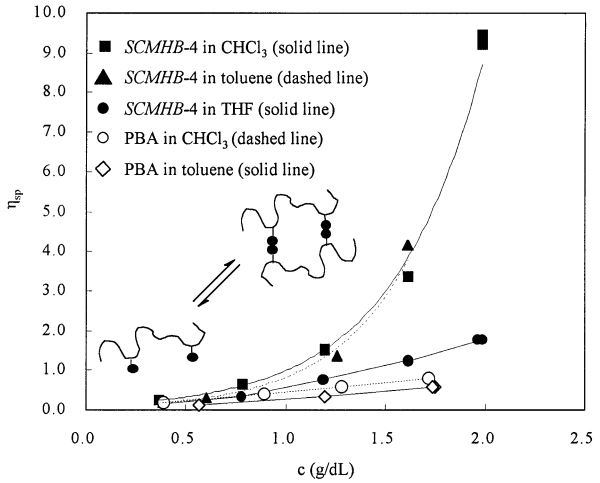


Figure 5. Relationship between the solution concentration and specific viscosity (η_{sp}) of SCMHB pendant polymer and PBA measured in $CHCl_3$ and toluene (SCMHB-4 ([BA]:[SCMHB MA] = 91.6:10.4 mol %)).

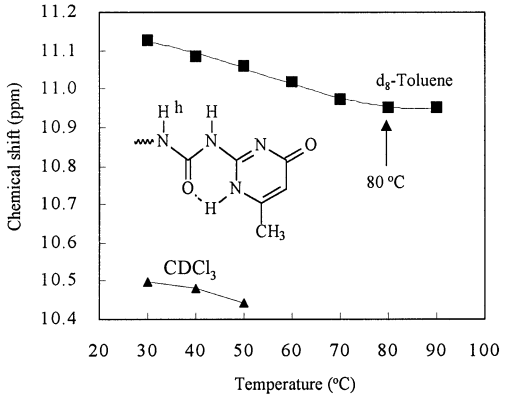


Figure 6. Temperature dependence on the chemical shift of NH hydrogen (h) measured in $CDCl_3$ and d_8-tolunene (SCMHB-4, sample concentration: [SCMHB MA in the polymer] = 8.0×10^{-3} M (10 mg/mL)).

Solution Viscosity Analysis. Figure 5 depicts the relationship between the solution concentration (g/dL) and specific viscosity (η_{sp}) for the SCMHB pendant polymer, SCMHB-4 ([BA]:[SCMHB MA] = 91.6:10.4 mol %) and PBA measured in $CHCl_3$, THF, and toluene. A plot of the solution viscosity of PBA vs concentration was a straight line over the entire concentration range from 0.4 to 2.0 g/dL in both $CHCl_3$ and toluene. However, the solution viscosity for SCMHB-containing polymers increased as the concentration increased in nonpolar solvents such as toluene and chloroform. On the other hand, in polar solvents, such as THF, the plot was approximately linear over the entire 0.4−2.0 g/dL range. This phenomenon indicated that the SCMHB-containing polymers strongly aggregated in nonpolar solvents, such as toluene and $CHCl_3$, as illustrated in Figure 4.

Dissociation Temperature for SCMHB Pendant Polymers. Figure 6 depicts the temperature dependence on the chemical shift of the NH hydrogen (h) in SCMHB-4 measured in $CDCl_3$ and d_8-toluene. In non-hydrogen-bonding solvents, such as $CDCl_3$ and toluene, the peak appreciably shifted to lower field as temperature increased and remained unchanged above 80 °C in toluene. It is presumed that this phenomenon is due

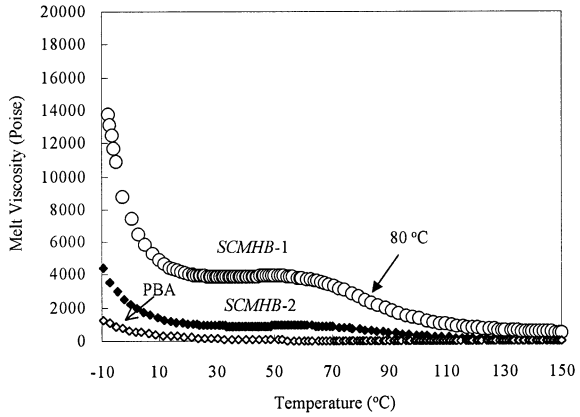


Figure 7. Effect of the SCMHB units on the melt viscosity: Rheological characterization of SCMHB pendant polymer (SCMHB-1, 2) and PBA (temperature: −10 °C to 150 °C, shear rate = 13.16 1/s, a parallel plate fixture with the plate diameter = 25.0 mm, and gap = 1000 μm).

to the dissociation of the SCMHB units, and 80 °C was defined as the dissociation temperature in toluene. Melt rheological characterization of SCMHB pendant polymers such as SCMHB-1 ([BA]:[SCMHB MA] = 97.5:2.5 mol %), SCMHB-2 ([BA]:[SCMHB MA] = 96.7:3.3 mol %), and PBA is shown in Figure 7. The melt viscosity of SCMHB-1 was 10 times higher than PBA having a similar molecular weight. In addition, the melt viscosity of SCMHB-2, which contained a higher concentration of SCMHB MA units compared to SCMHB-1, was more than 100 times higher than PBA. These data suggested that SCMHB pendant polymers formed aggregates in the melt state. The melt viscosity of SCMHB pendant polymers decreased dramatically until 10 °C and then remained relatively constant over the temperature range 10−80 °C. Above 80 °C, the melt viscosity approached PBA of nearly identical weight-average molecular weight. It is presumed that this phenomenon is due to the dissociation of the SCMHB units. Based on TGA analysis as depicted in Figure 4, the copolymers were not stable above approximately 210 °C, and only rheological data below this temperature are reported in Figure 7. The melt viscosity increased at temperatures above 210 °C presumably due to branching and cross-linking via ester−urethane exchange reaction as reported in the earlier literature.[48]

Based on rheological characterization, the dissociation temperature of SCMHB units was estimated at 80 °C, which was similar to our earlier results in SCMHB-terminated PS, PI, and PS-*b*-PI block copolymers.[42−44] In addition, the dissociation temperature that was measured from melt rheological characterization was similar to ^{1}H NMR measurements in d_8-toluene. These data indicated that the aggregation behavior of SCMHB units in the bulk state was similar to behavior in nonpolar solvents such as toluene since the interaction between the SCMHB units and toluene was considered to be negligible.

Adhesive Measurements on SCMHB Copolymers. To more fully understand the adhesive strength of SCMHB pendant polymers, 90° peel testing of SCMHB-1 ([BA]:[SCMHB MA] = 97.5:2.5 mol %), SCMHB-2 ([BA]:[SCMHB MA] = 96.7:3.3 mol %), and PBA was performed using an ASTM-D412-92 standard method. The results are depicted in Figure 8. The peel strength of SCMHB-containing copolymers (SCMHB-1, 2) increased as SCMHB MA content increased.

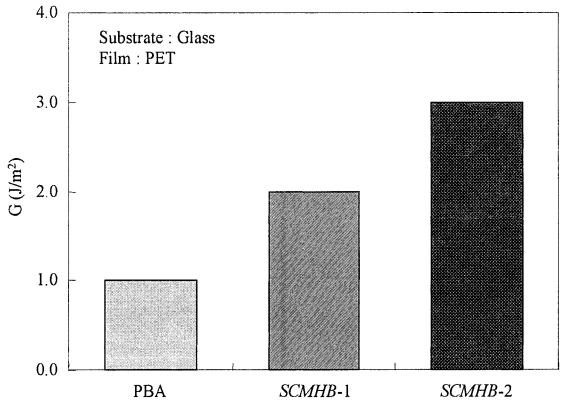


Figure 8. Effect of the SCMHB units on the peel strength: 90°peel test of SCMHB pendant polymer (SCMHB-1, 2) and PBA.

Surprisingly, the peel strength of SCMHB-2 was 3 times higher than that of PBA homopolymer presumably due to a strong association of SCMHB units with the glass surface. TLC was used to examine the interaction of a polymer with silica. In chloroform, PBA transcended to the top of the plate; however, SCMHB pendant polymers (SCMHB-1, 2) did not transcend the TLC plate in chloroform. This observation suggested that the interaction of SCMHB pendant polymers with silica was stronger than PBA in chloroform. In a polar solvent, such as THF or ethyl acetate, all polymers moved to the top of the plate, indicating that SCMHB pendant polymers did not interact with silica in the presence of a polar solvent.

Conclusions

SCMHB pendant polymers, poly(BA-*co*-SCMHB MA) ([SCMHB MA] = 2.5−10.4 mol %), were prepared via a free radical copolymerization of BA and a novel monomer, SCMHB MA, which was synthesized via a coupling reaction between ICEMA and MIS in DMSO. The SCMHB MA was incorporated quantitatively into the copolymer based on ^{1}H NMR analysis. The solubility of poly(BA-*co*-SCMHB MA) was similar to that of PBA, and solubility in DMSO, dimethylacetamide, DMF, $CHCl_3$, THF, acetone, and toluene and insolubility in CH_3OH and water were observed. Solution viscosity analysis indicated that SCMHB-containing polymers strongly aggregated in nonpolar solvents, such as toluene and $CHCl_3$, and dissociated in polar solvents, such as THF. The glass transition temperatures of poly(BA-*co*-SCMHB MA) increased as SCMHB MA content increased. Thermogravimetric analysis of SCMHB pendant polymers exhibited an onset of weight loss at 217 °C, which was consistent with our previous efforts on SCMHB-terminated PS.[42−44] Based on melt rheological characterization, SCMHB-containing polymers exhibited thermoreversibility and SCMHB units completely dissociated at 80 °C, which was consistent with our earlier studies involving SCMHB-terminated PS, PI, and PS-*b*-PI block copolymers.[42−44] In addition, melt viscosity profiles suggested that SCMHB pendant polymers formed aggregates in the melt state. ^{1}H NMR measurements indicated that SCMHB units also completely dissociated at 80 °C in toluene. The peel strength of SCMHB-containing copolymers increased as SCMHB MA content increased, and only 3.3 mol % of SCMHB units increased the peel strength 3 times higher than PBA due to a strong interaction of SCMHB units with

the glass surface. TLC observation suggested that the interaction of SCMHB pendant polymers with silica was stronger than PBA in chloroform. In a polar solvent, such as THF or ethyl acetate, SCMHB pendant polymers did not interact with silica.

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