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Communications to the Editor

Thermoreversible Polyesters Consisting of Multiple Hydrogen Bonding (MHB)

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Introduction. Multiple hydrogen bonding (MHB) units with extremely high dimerization constants have received significant attention for the creation of new supramolecular structure.[1] In particular, supramolecules containing 2-ureido-4[1*H*]-pyrimidone (UPy) units exhibited polymer-like properties including shear thinning in the melt phase, viscoelastic behavior in the solid state, and a glass transition temperature.[2] The introduction of MHB units is a versatile methodology to improve polymer properties such as melt rheology, phase separation behavior, and thermoreversibility during melt processing.[3] Reversible molecular recognition is attainable through the judicious choice of recognition elements and MHB containing macromolecules.[4]

Our earlier research efforts have involved the synthesis and characterization of well-defined terminal MHB polymers consisting of UPy units and complementary heterocyclic base units such as adenine (6-aminopurine), 2-aminopurine, and thymine. MHB-terminated polymers such as poly(styrene) (PS), poly(isoprene) (PI), and microphase-separated PS-*b*-PI block copolymers were synthesized in a controlled fashion, and the relationship between end group structure and physical properties such as glass transition temperature, melt viscosity, morphology, and dissociation temperature were reported.[5] MHB-terminated polymers formed thermoreversible aggregates in a multiple fashion in the melt state, and complete dissociation was observed at 80−95 °C by varying the structure of the MHB units. In addition, polyacrylates comprising pendant UPy groups exhibited thermoplastic behavior above the dissociation temperature of the MHB units and themoset behavior below the dissociation temperature.[6]

Our current interest is focused on the synthesis of MHB-terminated telechelic engineering plastics to fully understand the nature of MHB containing macromolecules. MHB containing engineering plastics are expected to exhibit good flow characteristics above the dissociation temperature of the MHB units and good mechanical properties in the solid state due to aggregation of the MHB units. This report deals with the synthesis and characterization of novel MHB-terminated telechelic polyesters to fully demonstrate the advantages of MHB containing macromolecules for improvement of mechanical properties and flow characteristics during melt processing.

Experimental Section. a. Synthesis of Hydroxyl-Terminated Telechelic Polyesters (II) (Poly(butylene terephthalate) (PBTOH-1, -2, and -3) and Poly(butylene isophthalate) (PITOH)). As shown in Scheme 1, the synthesis of the MHB-terminated telechelic polyester (**III**) involved a two-step synthesis. Hydroxyl-terminated telechelic polyesters (**II**) were synthesized via polycondensation of dicarboxylic acids and glycols. Terephthalic acid (TPA) (800 g, 4.85 mol), isophthalic acid (IPA) (800 g, 4.85 mol), and a 2.1-fold excess of 1,4-butylene glycol (BG) (900 g, 9.65 mol) compared to the concentration of TPA and IPA were weighed into a three-neck flask fitted with a condenser and stirred at 150 °C in the presence of titanium(IV) butoxide (TBT) (0.42 g, 1.23 mmol). The reaction temperature was raised from 150 °C to 230 °C for 5 h. The molten solution was transferred into a glass tube attached to a mechanical stirrer and torque meter, stirred at 250 °C under nitrogen, and then gradually

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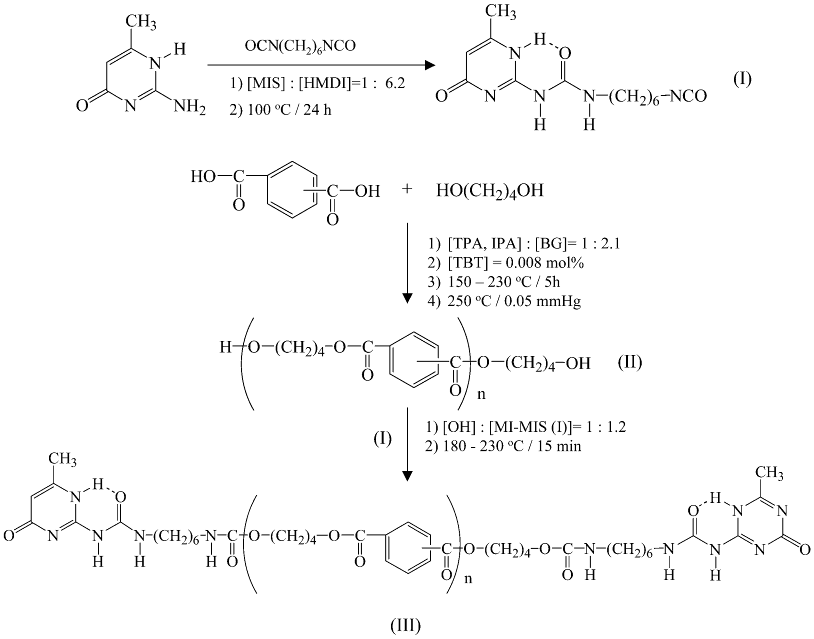
Scheme 1. Synthetic Strategy for MHB-Terminated Telechelic Polyesters



evacuated until the pressure reached 0.05 mmHg for 1 h. The molecular weights of the polymers were controlled by additional polymerization time under 0.05 mmHg. Hydroxyl-terminated telechelic polyesters (PBTOH-1, -2, and -3 and PITOH) were dissolved in 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP) and precipitated into methanol, then washed with methanol three times, and finally dried under reduced pressure (0.5 mmHg) at 80 °C for 24 h. TGA data indicated that hydroxyl-terminated telechelic polyesters exhibited an onset of weight loss at 350 °C.

b. Synthesis of MHB Terminated Telechelic Polyesters (MHB PBT and MHB PIT). MHB PBT and MHB PIT were synthesized by melt mixing 100 g of the corresponding hydroxyl-terminated precursor (PBTOH-1 or PITOH) and a 1.2-fold excess of monoisocyanato methylisocytosine (MI-MIS) (**I**) compared to the concentration of hydroxyl end group in the PBTOH-1 or PITOH. The concentration of hydroxyl end group in the PBTOH-1 and PITOH precursors was estimated from the M_n measured using SEC with MALLS detection and ^{1}H NMR. Melt mixing was performed at 230 °C (PBTOH-1) and 180 °C (PITOH) for 15 min using a TOYOSEKI twin-screw extruder. The products were dissolved in HFIP, precipitated into methanol, then washed with methanol three times, and finally dried under reduced pressure (0.5 mmHg) at 80 °C for 24 h. TGA data indicated MHB-terminated telechelic polyesters exhibited the onset of weight loss at 260 °C due to the elimination of the MHB units.

PBTOH-1. ^{1}H NMR (400 MHz, d_2-HFIP, δ): 8.1 ppm (aromatic protons: 4H × repeating units), 4.4 ppm ($-OCH_2CH_2CH_2CH_2O-$, 4H × repeating units, $-OCH_2CH_2CH_2CH_2OH$, 2H (overlapped)), 2.0 ppm ($-OCH_2CH_2CH_2CH_2O-$, 4H × repeating units). The hydroxyl group ($-OCH_2CH_2CH_2CH_2OH$) was not detected due to proton exchange of the hydroxyl group and d_2-HFIP. Carboxylic acid end groups were not detected by titration due to full termination of carboxylic acid end group during polycondensation in the presence of 2.1-fold excess of BG. Therefore, it was concluded that hydroxyl-terminated telechelic PBTOH-1 was obtained quantitatively.

Table 1. Characterization Data for Hydroxyl Terminated Telechelic Polyesters (II) and MHB Terminated Telechelic Polyesters (III)

sample	yield (%)	SEC MALLS M_n	SEC MALLS M_w/M_n	^{1}H NMR M_n	[COOH] (mmol/kg)	T_g (°C)	T_m (°C)
PBTOH-1	93	5130	2.3	nd[a]	0	nd	222
PBTOH-2	92	13 400	2.4	nd	5	nd	225
PBTOH-3	94	23 400	2.3	nd	3	nd	225
MHB PBT	93	5300	2.2	5100	0	nd	225
PITOH	90	4800	1.8	4700	0	38	nd
MHB PIT	95	5000	1.9	4900	0	38	nd

[a] Not detected.

PBTOH-2 and -3. To fully understand the effect of telechelic MHB units on melt viscosity and mechanical properties, PBTOH-2 and -3 with higher M_n compared to MHB PBT were synthesized using methodologies similar to PBTOH-1. ^{1}H NMR spectra of PBTOH-2 and -3 were similar to that of PBTOH-1. On the basis of the titration values for the concentration of carboxylic acid end groups shown in Table 1, it was presumed that hydroxyl-terminated telechelic PBT was obtained since the titration values were considered to be negligible.

PITOH. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 8.7, 8.2, 7.5 ppm (aromatic protons, 4H × repeating units), 4.6 ppm ($-OCH_2CH_2CH_2CH_2O-$, 4H × repeating units), 4.5 ppm ($-OCH_2CH_2CH_2CH_2OH$, 2H), 2.5 ppm ($-OCH_2CH_2CH_2CH_2OH$, 1H), 2.0 ppm ($-OCH_2CH_2CH_2CH_2O-$, 4H × repeating units). The M_n as estimated from ^{1}H NMR spectrum was in good agreement with the SEC value as shown in Table 1. In addition, carboxylic acid end groups were not detected by titration due to full termination of the carboxylic acid end group during polycondensation in the presence of a 2.1-fold excess of BG. Therefore, hydroxyl-terminated telechelic PITOH was obtained quantitatively.

MHB PBT. ^{1}H NMR (400 MHz, d_2-HFIP, δ): 8.1 ppm (aromatic protons, 4H × repeating units), 5.8 ppm ($-CH{=}C(CH_3)-$, 1H), 4.4 ppm ($-OCH_2CH_2CH_2CH_2O-$, 4H × repeating units, $-OCH_2CH_2CH_2CH_2OH$, 2H (overlapped)), 4.5 ppm ($-NHCH_2(CH_2)_4CH_2NH-$, 4H), 2.3 ppm ($-CH{=}C(CH_3)-$, 3H), 2.0 ppm ($-OCH_2CH_2CH_2CH_2O-$, 4H × repeating units). NH signals ($-NH$-

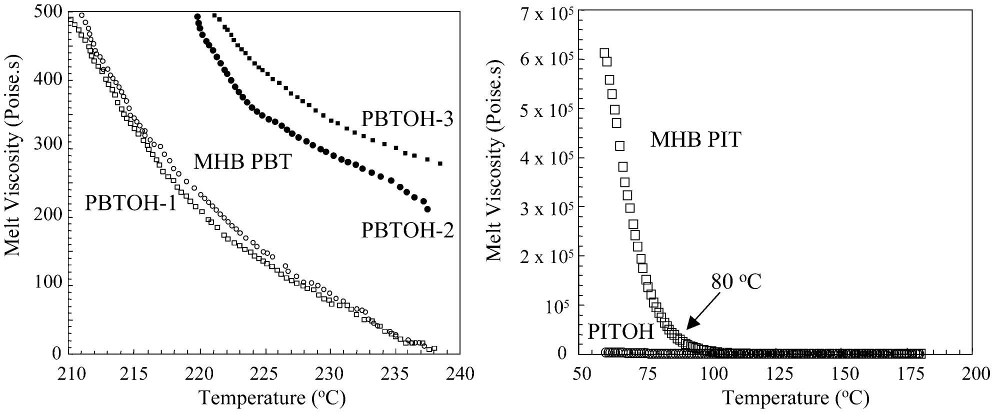


Figure 1. Effect of end group structure and M_n on the melt viscosity of PBT (left) and PIT (right).

$C(CH_3)=$, $-NH\text{-}CO-NH-CH_2-$, $-NH-CO-NH-CH_2-$, $-CH_2NH-COO-$) were not detected due to proton exchange between NH and d_2-HFIP. However, characteristic new resonances assigned to telechelic MHB units, such as $-CH{=}C(CH_3)-$ (5.8 ppm), $-NHCH_2$-$(CH_2)_4CH_2NH-$ (4.5 ppm), $-CH{=}C(CH_3)-$ (2.3 ppm) were observed, and the calculated M_n values were similar to the M_n value measured using ^1H NMR and SEC with MALLS detection. In addition, the M_n using SEC and ^1H NMR for PBTOH-1 and MHB PBT did not appreciably change upon end group modification. Thus, end group modification proceeded quantitatively in the absence of undesirable side reactions. In addition, SEC analysis of MHB PBT suggested that the MHB PBT completely dissociated in the polar HFIP solvent at SEC analysis concentrations (1 mg/1 mL), which was consistent with our earlier reports.[5,6]

MHB PIT. ^1H NMR (400 MHz, $CDCl_3$, δ): 13.0 ppm ($-NH-C(CH_3){=}$, 1H), 11.8 ppm ($-NH-CO-NH-CH_2-$, 1H), 10.0 ppm (overlapped) ($-NH-CO-NH-CH_2-$, $-CH_2NH-COO-$, 2H), 8.7, 8.2, 7.5 ppm (aromatic protons, 4H × repeating units), 5.8 ppm ($-CH{=}C(CH_3)-$, 1H), 4.6 ppm ($-OCH_2CH_2CH_2CH_2O-$, 4H × repeating units), 4.4 ppm ($-NHCH_2(CH_2)_4CH_2NH-$, 4H), 2.3 ppm ($-NH-C(CH_3)-$, 3H). 2.0 ppm ($-OCH_2$-$CH_2CH_2CH_2O-$, 4H × repeating units). A comparison of the ^1H NMR spectra for the precursor (PITOH) and MHB PIT revealed that the resonances of $-OCH_2CH_2$-CH_2CH_2OH (4.5 ppm) and $-OCH_2CH_2CH_2CH_2OH$ (2.5 ppm) disappeared, and characteristic new resonances assigned to telechelic MHB units such as $-NH-C(CH_3){=}$ (13.0 ppm), $-NH-CO-NH-CH_2-$ (11.8 ppm), $-CH{=}C(CH_3)-$ (5.8 ppm), $-NHCH_2(CH_2)_4CH_2NH-$ (4.4 ppm), and $-NH-C(CH_3)-$ (2.3 ppm) were observed. The M_n, as estimated from ^1H NMR spectra, were in good agreement with SEC values as shown in Table 1. In addition, the M_n measured by SEC and ^1H NMR for PITOH and MHB PIT did not appreciably change upon end group modification. Thus, end group modification proceeded quantitatively in the absence of undesirable side reactions. In addition, SEC measurements in HFIP at 40 °C suggested complete dissociation of the telechelic MHB units at typical SEC analysis concentrations (1 mg/1 mL).

Results and Discussion. To understand the dissociation of telechelic MHB units in polyesters, the melt rheological characterization of PBTOH-1, -2, and -3 with various M_n and MHB PBT with an identical M_n to the PBTOH-1 was performed from 210 to 238 °C (Figure 1 (left)). However, the melt viscosity of MHB PBT was comparable to that of PBTOH-1 at nearly identical M_n. It was presumed that the MHB units dissociated below 210 °C. However, melt rheological characterization of PBTOH-1, -2, and -3 and MHB PBT below 210 °C was difficult because these polymers exhibited T_m above 210 °C as shown in Table 1.

To more fully elucidate the dissociation of telechelic MHB units in polyesters, the melt rheological characterization of amorphous PITOH and MHB PIT was performed, since these polyesters have substantially lower T_g and no T_m as shown in Table 1. The melt rheological characterization of PITOH and MHB PIT is depicted in Figure 1 (right). The melt viscosity of MHB PIT was more than 100 times higher than that of PITOH at nearly equivalent number-average molecular M_n. The melt viscosity of MHB PIT decreased dramatically until 80 °C, and then it approached that of PITOH of nearly identical M_n. It is presumed that the MHB PIT formed aggregates in the melt state that completely dissociated at 80 °C, consistent with our earlier reports.[5,6]

PBT is a typical engineering plastic that exhibits superior heat resistance and excellent mechanical properties due to a high degree of crystallinity and high melting temperature. The introduction of thermoreversible MHB units into semicrystalline PBT is an unprecedented methodology to create a new engineering plastic, which combines good flow characteristics during melt processing and excellent mechanical properties in the solid state due to aggregation of the MHB units. To demonstrate the advantages of MHB-terminated telechelic macromolecules, the mechanical properties of PBTOH-1, -2, and -3 and MHB PBT were investigated. Table 2 summarizes the M_n and molecular weight distribution measured using SEC with MALLS detection, the mechanical properties measured under ambient conditions, and the melt viscosity measured at 235 °C for the PBTOH-1, -2, and -3 and MHB PBT. On the basis of a comparison of MHB PBT and PBTOH-1 at nearly identical M_n, the melt viscosity of MHB PBT measured near the typical melt processing temperature (235 °C) was approximately similar to that of PBTOH-1 due to the complete dissociation of the MHB units at 80 °C.

The elongation at break and impact strength, which indicate the toughness of the engineering plastic, drastically increased upon the introduction of telechelic MHB units, while the melt viscosity at 235 °C remained low. The melt viscosity of PBTOH-2 with twice the M_n and PBTOH-3 with four times the M_n were more than 10 times higher than that for MHB PBT. However, the elongation at break and impact strength of the MHB

Table 2. Mechanical Properties of PBTOH-1, -2, and -3 and MHB PBT

properties	PBTOH-1	PBTOH-2	PBTOH-3	MHB PBT
M_n (SEC MALLS)	5130	13 400	23 400	5300
M_w/M_n (SEC MALLS)	2.3	2.4	2.3	2.2
tensile strength (MPa)	54	56	56	55
elongation at break (%)	3	15	16	14
impact strength with noched (J/m)	34	54	54	55
melt viscosity at 235 °C (Pa·s)	20	250	300	27

PBT were comparable to those of the much higher molecular weight and melt viscosity polymers. It was presumed that the MHB units formed multiple aggregates in the solid state. Further elucidation of multiple aggregations of MHB units in the solid state using solid state ^{1}H NMR will be addressed in a future publication.

Conclusions. MHB-terminated telechelic polyesters such as MHB PBT and MHB PIT were synthesized via derivatization of hydroxyl-terminated telechelic polyesters such as PBTOH and PITOH with MI-MIS. The melt viscosity of MHB PIT was higher than that of PITOH of nearly identical M_n at temperatures below 80 °C due to strong aggregation of the MHB units. The complete dissociation of the MHB aggregates was observed at 80 °C, consistent with our earlier studies, and the melt viscosity of the MHB PIT and PITOH were comparable at temperatures above 80 °C.[5,6]

The introduction of telechelic MHB units into PBT demonstrated the advantages of MHB-terminated telechelic macromolecules for improved flow characteristics during melt processing. The melt viscosity of the MHB PBT measured near the typical melt processing temperature (235 °C) was comparable to that of a PBTOH of nearly identical M_n due to the complete dissociation of the MHB units above 80 °C. The elongation at break and impact strength of the MHB PBT were comparable to those of a PBTOH with more than twice the M_n of the MHB PBT possibly due to aggregation of the MHB units in the solid state. While elongation at break and impact strength were comparable, the melt viscosity of the MHB PBT was much lower than that of the PBTOH with more than twice the M_n of the MHB PBT due to the complete dissociation of the MHB units at the melt processing temperature.

In conclusion, MHB-terminated telechelic PBT exhibited good mechanical properties in the solid state and good flow characteristics at the typical melt processing temperature. The introduction of MHB units into an engineering plastic is an unprecedented methodology to improve both the mechanical properties in the solid-state such as elongation at break and impact strength and the flow characteristics during melt processing.

Supporting Information Available: Text giving the experimental details, synthetic strategy for monoisocyanato methylisocytosine (MI-MIS) (Scheme 1S), and ^{1}H NMR spectrum of MI-MIS (Figure 1S) (400 MHz, $CDCl_3$). This material is available free of charge via the Internet at http://pubs.acs.org.

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