Nonisocyanate Route to 2,5-Bis(hydroxymethyl)furan-based Polyurethanes Crosslinked by Reversible Diels–Alder Reactions

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INTRODUCTION Polyurethane (PU) is a group of polymers that have applications in a diverse range of industries. Current commercial PU products are primarily produced from diisocyanates, which are typically synthesized from highly toxic phosgene. In order to avoid the safety risk associated with the use of phosgene, alternative isocyanate-free routes have been put forward for the production of nonisocyanate PUs (NIPUs) as replacement for conventional PUs.[1] 2,5-Bis(hydroxymethyl)furan (BHMF) is considered to be a promising biobased building block resembling aromatic monomers for polymer productions, and there have been studies using BHMF as a diol for the synthesis of conventional PUs.[2–5] In this work, we demonstrated the feasibility of using BHMF for the production of NIPUs through an isocyanate-free route. A series of NIPUs were obtained from the transurethanization between BHMF and dicarbamates, which were synthesized from the methoxycarbonylation of diamines with dimethyl carbonate (DMC). In addition to BHMF, 1,4-butanediol (BD) was also used to provide the NIPUs with good balance of hardness and flexibility.

One major challenge of using BHMF for NIPU synthesis is that BHMF tends to undergo side reactions at high temperatures (> 140 °C). In our preliminary experiments, the NIPUs synthesized from a one-step heating procedure (at 140 °C for 3 h) were not totally soluble in dimethyl sulfoxide (DMSO) due to the insoluble byproducts generated from BHMF. To solve this problem, transurethanization reactions were firstly carried out at low temperatures (100–130 °C) with excess of dicarbamates being introduced in relation to BHMF, to obtain methoxycarbonyl-terminated prepolymers. The prepolymers were then further reacted with diols at higher temperatures (140–150 °C) to produce NIPUs. Another challenge lies in the volatility of BD, making it difficult to accurately control the BD loadings at stoichiometric proportions. Because of the reversibility of the transurethanization process, it is necessary to remove the methanol generated during the reaction by N_2 flow continuously, in order to allow the reactions to proceed.

On the other hand, significant amounts of BD could also be removed by the N_2 flow. To address this issue, BD was reacted with dicarbamates to obtain hydroxyl-terminated dicarbamates as less volatile diols before being used to react with the methoxycarbonyl-terminated prepolymers. Finally, a series of BHMF-based NIPUs were successfully synthesized from the transurethanization between the previously synthesized methoxycarbonyl-terminated prepolymers and the hydroxyl-terminated dicarbamates. After the furan-bearing NIPUs were obtained, a bismaleimide was used as a crosslinker to produce crosslinked NIPU networks by means of reversible Diels–Alder reaction, providing the NIPU materials with great potentials for developing eco-friendly PU products with recyclable, mendable, and self-healing properties. The overall procedure for the synthesis of the BHMF-based NIPUs is outlined in Figure 1.

Three dicarbamates (Dicarbamate–C2, Dicarbamate–C6, and Dicarbamate–C8) were obtained by reacting three diamines (ethylenediamine, 1,6-hexanediamine, and 1,8-diaminooctane), respectively, with an excess of DMC. Then, BHMF was reacted with the dicarbamates at molar ratios of 1:2 and 1:4, respectively, to prepare a series of methoxycarbonyl-terminated prepolymers. It was found that Dicarbamate–C2 had no reactivity toward BHMF, probably because the low chain flexibility of the two-carbon alkylated dicarbamate gave rise to high viscosity, and thus increased its difficulty to react with BHMF. On the other hand, Dicarbamate–C6 and Dicarbamate–C8 showed similar reactivity toward BHMF, and over 90% of the alcohol groups of BHMF were substituted by the end of the reactions, according to ^{1}H NMR analysis. In the next step, Dicarbamate–C6 and Dicarbamate–C8 were reacted with an excess of BD, respectively, to obtain corresponding hydroxyl-terminated dicarbamates as less volatile diols, and over 99% product purities were obtained after purification according to the ^{1}H NMR analysis.

A series of BHMF-based NIPUs were synthesized from the transurethanization between the previously synthesized
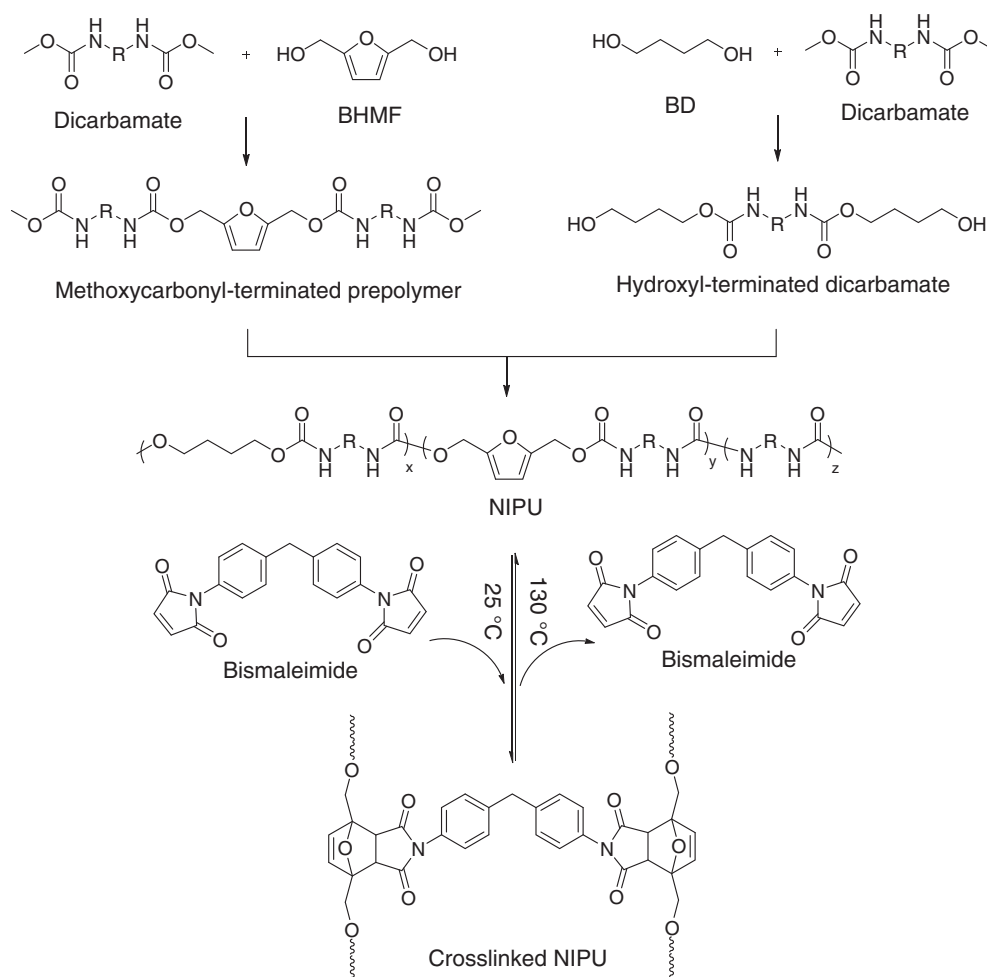
FIGURE 1 Procedure for the synthesis of BHMF-based NIPUs.

methoxycarbonyl-terminated prepolymers (prepared from Dicarbamate–C6 and Dicarbamate–C8) and the hydroxyl-terminated dicarbamates (prepared from Dicarbamate–C6 and Dicarbamate–C8), respectively. In contrast, a series of aliphatic NIPUs were also synthesized from the transurethanization between the methoxycarbonyl- and hydroxyl-terminated dicarbamates (Dicarbamate–C6 and Dicarbamate–C8) without using BHMF. The NIPUs with furan moieties were obtained as brown solids, and those without furan moieties were obtained as white solids at room temperature. All the NIPUs were insoluble in water, chloroform, acetone, acetonitrile, and tetrahydrofuran (THF), slightly soluble in hot methanol, and totally soluble in DMSO and dimethylformamide (DMF).

The NIPUs were characterized by ^{1}H NMR analysis (Fig. 2). The ^{1}H NMR spectra confirmed the occurrence of the transurethanization between the methoxycarbonyl and hydroxyl groups. In addition, urea linkages were also observed presumably due to the transurethanization between two methoxycarbonyl groups.[6] The signals corresponding to the terminal BHMF and BD groups were smaller compared to those of the terminal methoxycarbonyl groups. The inequivalent ratios of the terminal methoxycarbonyl and hydroxyl

groups at the end of the reactions might be attributed to the more or less volatility of the hydroxyl-terminated dicarbamates. Thus, the signal of the remaining terminal methoxycarbonyl groups were used to estimate the NIPU yields. In general, higher BHMF to BD molar ratios led to lower product yields, as a result of the lower reactivity of BHMF toward the methoxycarbonyl groups (Table 1). This lower reactivity could be explained the lower nucleophilicity of the alcohol groups of BHMF, induced by the electron withdrawing effect exerted on its carbonyl group. Besides product yields, the molar contents of urethane, urea, BHMF, and BD repeating units in the polymer chains could also be estimated according to the ^{1}H NMR spectra. It was worth noting that the NIPUs prepared from Dicarbamate–C6 seemed to have higher urea contents, compared to those from Dicarbamate–C8, especially without using BHMF, presumably because the nitrogen of Dicarbamate–C6 had greater nucleophilicity to attack on the carbonyl group of another dicarbamate molecule (Table 1). It was also found that at a 1:6 molar ratio of BHMF to BD, the contents of BHMF incorporated into the polymer chains were consistent with the BHMF loadings in the feed, while at a 1:2 molar ratio, the BHMF contents in the polymer chains were obviously lower than those in the feed (Table 1). The ^{1}H NMR results indicated that significant amounts of furan moieties in the prepolymers were converted back to the
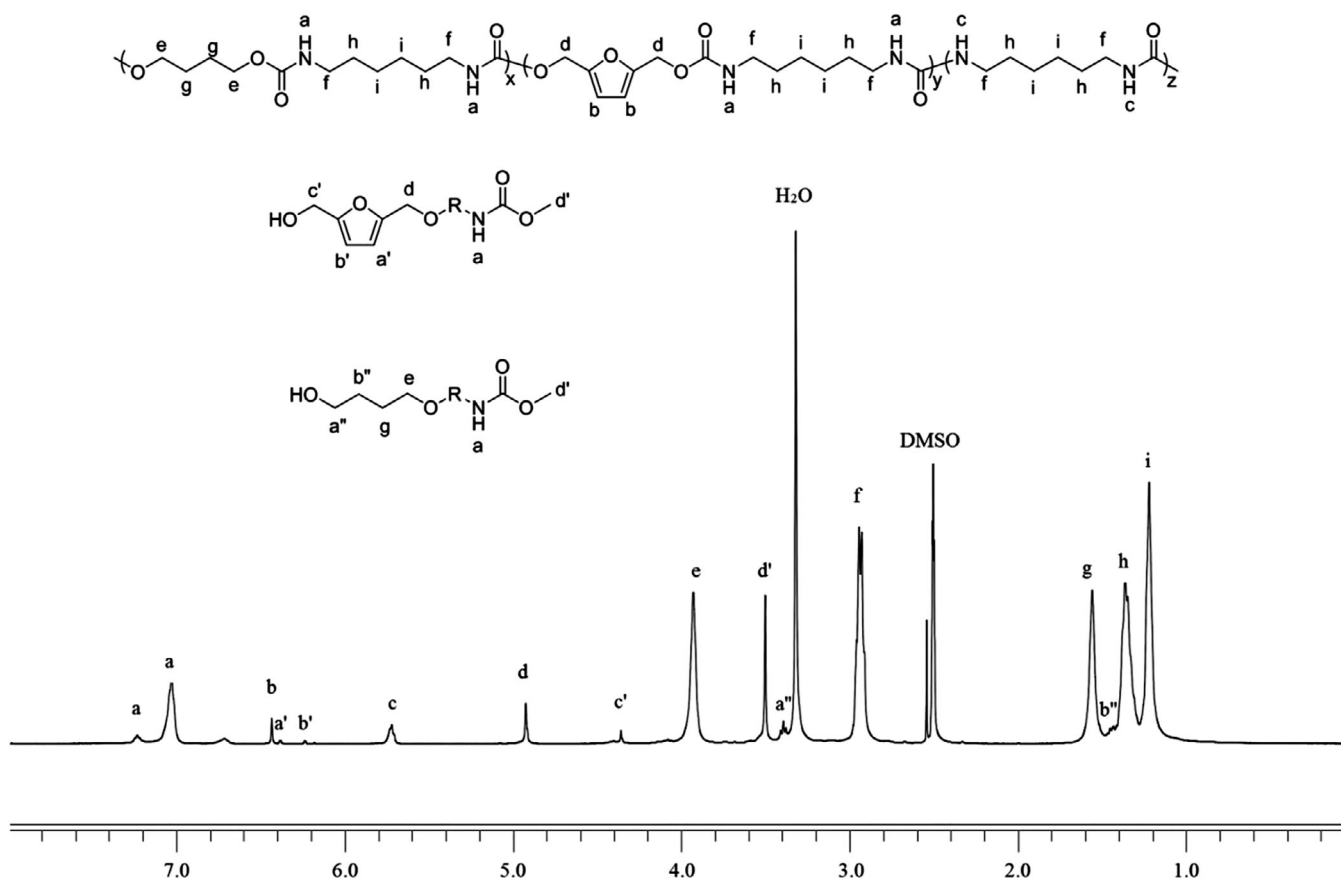
FIGURE 2 ^{1}H NMR spectrum of the NIPU synthesized from Dicarbamate−C6, BHMF, and BD at a molar ratio of 7:1:6.

TABLE 1 Chemical Composition of NIPUs

Sample[a]	Dicarbamate	BHMF:BD (molar ratio)	Yield[b] (%)	$X_{urethane}$[c] (%)	X_{urea}[c] (%)	X_{BHMF}[c] (%)	X_{BD}[c] (%)
NIPU−C6−1/2	Dicarbamate−C6	1:2	85	72	16	22	42
NIPU−C6−1/6	Dicarbamate−C6	1:6	87	76	14	14	67
NIPU−C6−0/1	Dicarbamate−C6	0:1	92	74	24	0	78
NIPU−C8−1/2	Dicarbamate−C8	1:2	71	64	18	14	68
NIPU−C8−1/6	Dicarbamate−C8	1:6	83	82	8	13	59
NIPU−C8−0/1	Dicarbamate−C8	0:1	86	88	6	0	76

[a] Sample was denoted as NIPU−Cx−y, where x is the number of carbons in the alkene chain of the dicarbamate that used, and y is the molar ratio of BHMF to BD in the feed.

[b] Yield is determined based on signal of the methine protons of the terminal methoxycarbonyl groups in the ^{1}H NMR spectra.

[c] $X_{urethane}$, X_{urea}, X_{BHMF}, and X_{BD} represented the molar contents of the urethane, urea, BHMF, and BD repeating units in the NIPU chains calculated based on their characteristic signals in the ^{1}H NMR spectra.

starting BHMF monomer during the polymerization processes at a high BHMF to BD ratio (1:2). Therefore, it was advised to avoid high BHMF to BD ratios for the synthesis of BHMF-based NIPUs using this procedure. The limited solubility of the NIPUs in most solvents, such as THF, makes them difficult to analyze by GPC. However, the ^{1}H NMR results indicated that the number average molecular weight (M_n) might be around 2000–3000 g/mol for the NIPUs prepared at low BHMF to BD ratios (1:6 and 0:1).

DSC analysis was performed to understand the thermal properties of the NIPUs (NIPU−C6−1/6, NIPU−C6−0/1, NIPU−C8−1/6, and NIPU−C8−0/1). In their DSC heating curves, no glass transition temperatures (T_g) were observed, while sharp melting peaks were exhibited, indicating their semicrystalline structures. The melting points (T_m) of these NIPUs appeared to be similar (148–157 °C) in spite of their different chemical structures, whereas their melting enthalpy (ΔH_m) seemed to be related to the number of carbons in the alkene chains in

their monomer units. The NIPUs prepared from Dicarbamate−C8 generally showed higher ΔH_m (51.7–57.3 J/g), compared to those prepared from Dicarbamate−C6 (39.0–42.2 J/g). This could possibly be explained by their higher crystallinity due to the higher flexibility and lower free volume induced by their longer hydrocarbon chains.[7] Next, the thermal stability of these NIPUs was assessed by TGA, and the results showed that all these NIPUs were thermally stable above 200 °C, with decomposition temperatures at 5% weight losses ($T_{5\%}$) ranging from 214 to 224 °C. These $T_{5\%}$ results were similar to those NIPU or conventional PU analogues reported in the previous studies.[8–10] Generally, the BHMF-based NIPUs had relatively lower $T_{5\%}$ (214–215 °C), compared to those prepared without BHMF (220–224 °C). Because of the low reactivity of BHMF toward the methoxycarbonyl groups, it was reasonable for the urethane linkages formed with BHMF to exhibit relatively poor thermal stability.[11] Even so, the $T_{5\%}$ of the BHMF-based NIPUs were still at least 50 °C higher than their T_m, demonstrating their suitability for thermal processing.

The furan moieties within the polymer chains can react with a bismaleimide by the Diels–Alder reaction to give reversible crosslinked NIPUs, and the crosslinking and de-crosslinking of the NIPUs can be seen by their solubility behavior. To observe the change of solubility, NIPU–C6–1/6 and NIPU–C8–1/6 were dissolved in DMSO, respectively, followed by the addition of the bismaleimide. It was observed that the solutions started to gel slowly at room temperature, indicating the formation of crosslinks between their linear NIPU chains. After being heated to 130 °C, the gelled samples went back to solutions immediately, because the Diels–Alder bonds started to open at high temperatures. After being placed at room temperature for a while, the solutions became gels again. In addition, FT − IR analysis also confirmed the occurrence of the Diels −Alder reaction, as well as the presence of some unreacted maleimide groups.

DSC analysis was also performed on the crosslinked NIPUs to further confirm the reversibility of the Diels–Alder reaction (Fig. 3). Sharp endothermic peaks ascribed to the T_m (159 °C) of the crosslinked NIPUs were observed in the first and second heating cycles in the DSC curves. In addition, a broad endothermic peak ranging from 110 to 130 °C was observed in the first heating cycle, but absent in the second one. This broad peak was likely to correspond to the cleavage of the crosslinked bonds through the retro Diels–Alder reaction at high temperatures, and this temperature range was in accordance to those observed in previous literatures.[12–16] The enthalpy of the retro Diels−Alder reaction was measured to be approximately 8–16 J/g with NIPU–C8–1/6 appearing to have a stronger ability to form Diels–Alder crosslinks. Next, TGA was used to investigate the thermal stability of the NIPUs after the formation of crosslinks. The crosslinked NIPUs showed slightly improved $T_{5\%}$ (~8 °C higher) compared to their noncrosslinked counterparts. The final residue contents of the crosslinked NIPUs stabilized at approximately 15%, which was slightly higher than those of their noncrosslinked counterparts (11%), presumably because the bismaleimide generated more char residues.
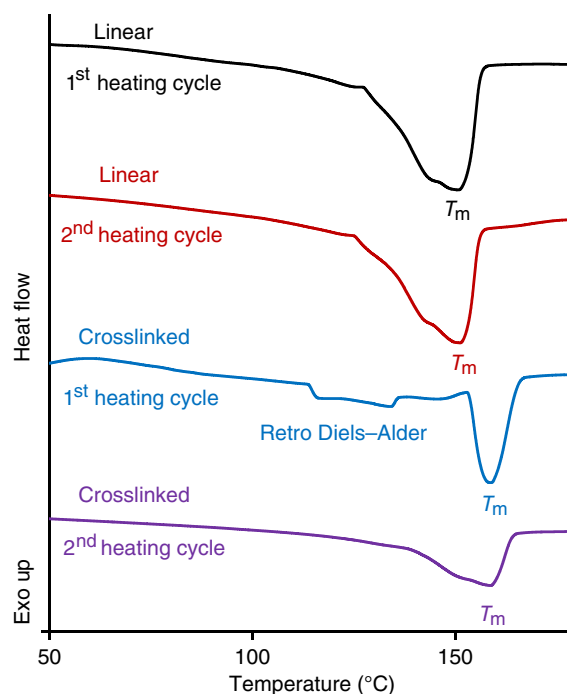

FIGURE 3 DSC thermograms of linear and crosslinked NIPUs (NIPU–C6–1/6) in the first and second heating cycles. [Color figure can be viewed at wileyonlinelibrary.com]

In conclusion, BHMF has been recognized as a promising bio-based building block for the syntheses of various renewable polymers. In this study, a series of NIPUs were synthesized using BHMF, in combination with BD, through transurethanization reactions with dicarbamates. The chemical structures and thermal properties of these BHMF-based NIPUs were characterized by a number of characterization techniques. These furan-bearing NIPUs were then crosslinked using a bismaleimide by means of reversible Diels–Alder reaction, and the thermo-reversibility of these crosslinked NIPUs was demonstrated by their solubility, FT − IR, and DSC analyses. In sum, this study provided an insight into the production of PUs from a biobased furanic platform chemical though a nonisocyanate route, coupled with the benefits of reversible crosslinking. Future application of the BHMF-based NIPUs could be related to the development of eco-friendly PU products with recyclable, mendable, and self-healing properties.

EXPERIMENTAL

Three dicarbamates (Dicarbamate−C2, Dicarbamate−C6, and Dicarbamate−C8) were obtained by reacting three diamines (ethylenediamine, 1,6-hexanediamine, and 1,8-diaminooctane) with an excess of DMC catalyzed by 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD), respectively, according to the work of other researchers.[17,18] Typically, DMC (200 mmol), diamine (20 mmol), and TBD (2 mmol) were loaded into a 250 mL flask and kept stirring at 80 °C for 6 h. After the reaction, the excess of DMC was evaporated to obtain the crude dicarbamate product. Dicarbamate−C6 and Dicarbamate−C8 were purified by washing with water and filtration for several times followed by recrystallization from hot methanol. Dicarbamate−C2 was purified by

washing with cold DMC for several times. The chemical structures and high purities (>99%) of the dicarbamates were confirmed by ^{1}H NMR analysis. The yields of Dicarbamate–C2, Dicarbamate–C6, and Dicarbamate–C8 were 50%, 50%, and 53%, respectively.

BHMF was reacted with the dicarbamates at molar ratios of 1:2 and 1:4, respectively, to prepare a series of methoxycarbonyl-terminated prepolymers. Typically, BHMF (0.25 or 0.5 mmol) and a dicarbamate (1.0 mmol) were introduced into a 50 mL round-bottom flask. K_2CO_3 (0.1 mmol) was added as a catalyst, and a small amount of DMSO (0.4 mL) was added as a solvent to reduce the high viscosity of the reaction mixture. The flask was progressively heated to 100 °C and kept for 3 h, followed by another heating process at 130 °C for 3–6 h. During these two heating processes, the reaction mixture was kept stirring under a N_2 atmosphere.

Dicarbamate–C6 and Dicarbamate–C8 were reacted with an excess of BD, respectively, to obtain hydroxyl-terminated dicarbamates (bis(4-hydroxybutyl) hexane-1,6-diyldicarbamate and bis(4-hydroxybutyl) octane-1,8-diyldicarbamate). Typically, BD (50 mmol), a dicarbamate (5 mmol), and K_2CO_3 (1 mmol) were introduced into a 50 mL round-bottom flask. The flask was progressively heated to 120 °C and kept for 1.5 h. During the heating process, the reaction mixture was kept stirring under a N_2 atmosphere. After the reaction, the hydroxyl-terminated dicarbamate was precipitated in water and then collected via filtration for several times. The chemical structures and high purities (>99%) of the hydroxyl-terminated dicarbamates were confirmed by ^{1}H NMR. The yields of bis(4-hydroxybutyl) hexane-1,6-diyldicarbamate, and bis(4-hydroxybutyl) octane-1,8-diyldicarbamate were 80% and 83%, respectively.

A series of BHMF-based NIPUs were synthesized through the transurethanization between the methoxycarbonyl-terminated prepolymers and hydroxyl-terminated dicarbamates at an equivalent molar ratio of methoxycarbonyl to hydroxyl groups. Typically, a methoxycarbonyl-terminated prepolymer and a hydroxyl-terminated dicarbamate were introduced into a 50 mL round-bottom flask. The flask was progressively heated to 150 °C, and kept for 3 h. During the heating process, the reaction mixture was kept stirring, and N_2 was continuously purged into the reactor to simultaneously remove the methanol generated from the transurethanization reaction. After heating, the NIPU was dried in a vacuum oven at 80 °C for 12 h to remove DMSO. In contrast, a series of aliphatic NIPUs were also synthesized from the transurethanization between the methoxycarbonyl- and hydroxyl-terminated dicarbamates at a molar ratio of 1:1 using the same procedure. The yields of the NIPUs were between 71% and 92%, according to ^{1}H NMR analysis.

The BHMF-based NIPUs (~0.5 g) were dissolved in DMSO (1 mL), respectively, followed by the addition of a crosslinking agent (1,1′-(methylenedi-4,1-phenylene)bismaleimide) at an equivalent molar ratio of furan to maleimide groups. The solutions were kept at 25 °C for 4 h, followed by a Soxhlet extraction in acetone at 60 °C to eliminate DMSO.

All the ^{1}H NMR spectra were recorded with a Bruker ARX −300 spectrometer (Bruker Corporation, Billerica, MA) operating at a frequency of 400 MHz. DMSO-d6 was used as a solvent for ^{1}H NMR analysis. All the FT–IR spectra were recorded with a PerkinElmer Spectrum Two IR spectrometer (PerkinElmer, Waltham, MA). DSC analysis was performed using a TA Q20 differential scanning calorimeter (TA Instruments, New Castle, DE). The samples (~5 mg) were heated from room temperature to 180 °C (first heating scans), and then cooled to −50 °C at a rate of 10 °C/min, followed by second heating scans over the temperature range from −50 to 180 °C at the same rate. T_m and ΔH_m were determined from the DSC thermograms obtained in the second heating scans. TGA was performed using a TA Q50 thermogravimetric analyzer (TA Instruments). The samples (~10 mg) were heated from room temperature to 550 °C at a rate of 10 °C/min in a N_2 atmosphere.

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