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Synthesis of segmented polyurethanes based on furazan units

Timur I. Mukhametshin, Dmitry B. Vinogradov, Pavel V. Bulatov, Valery G. Nikitin and Vladimir A. Petrov

The structure of copolymers was confirmed by using a Nicolet iS10 FT-IR spectrometer. ^{1}H and ^{13}C NMR spectra were acquired on a Bruker Avance AM300 instrument at 300 and 100 MHz, respectively, using solvent signals as an internal standard (δ 2.505 ppm for ^{1}H nuclei in DMSO-d6, 39.98 ppm for ^{13}C nuclei in DMSO-d_6). The solvents were purified and dried prior use in accordance with standardized procedures. Elemental analysis was performed using Vario EL III CHN-analyzer. Phase transitions of copolymers were analysed using a MettlerToledo DSC 823e instrument with a heating rate of 10°C/min over the range of -25 to +400 °C. Intrinsic viscosity ([η]) was determined in accordance with a standardized procedure [X. F. Li *et al*., *J. Semicond*, 2021, **42**, *6*, 060501] at 20 °C for solutions of copolymers in cyclohexanone.

Commercial reagents were used: butane-1,4-diol **3** (Acros Organics); cyclohexanone (99%) (Khimmed, Russia), 2,4-diisocyanatotoluene **2** (98%) (Khimmed, Russia).

3,4-Bis(hydroxymethyl)furazane (BHMF) 1 was obtained as reported [I. V. Vigalok, A. V. Ostrovskaya and N. V. Svetlakov, SU Patent 435240 A1, 1974]. M.p. 48.7°C. IR (KBr), ν, cm^{-1}: 3376 (OH), 2108 (CNO), 1635 (C=N cycl.), 895 (NO) (Figure S1). $C_4H_6N_2O_3$. Calcd: C, 36.39; H, 4.65; N, 21.53%. Found: C, 36.44; H, 4.46; N, 21.54%. ^{1}H NMR, δ (*J*, 300.13 MHz, DMSO-d_6) 4.72 (d, *J*=5.9, 2H, HO$\underline{CH_2}$C=N-O), 5.65 (t, *J*=5.9, 1H, $\underline{HO}CH_2$C=N-O) (Figure S2). Prior to use, the compound was recrystallized.

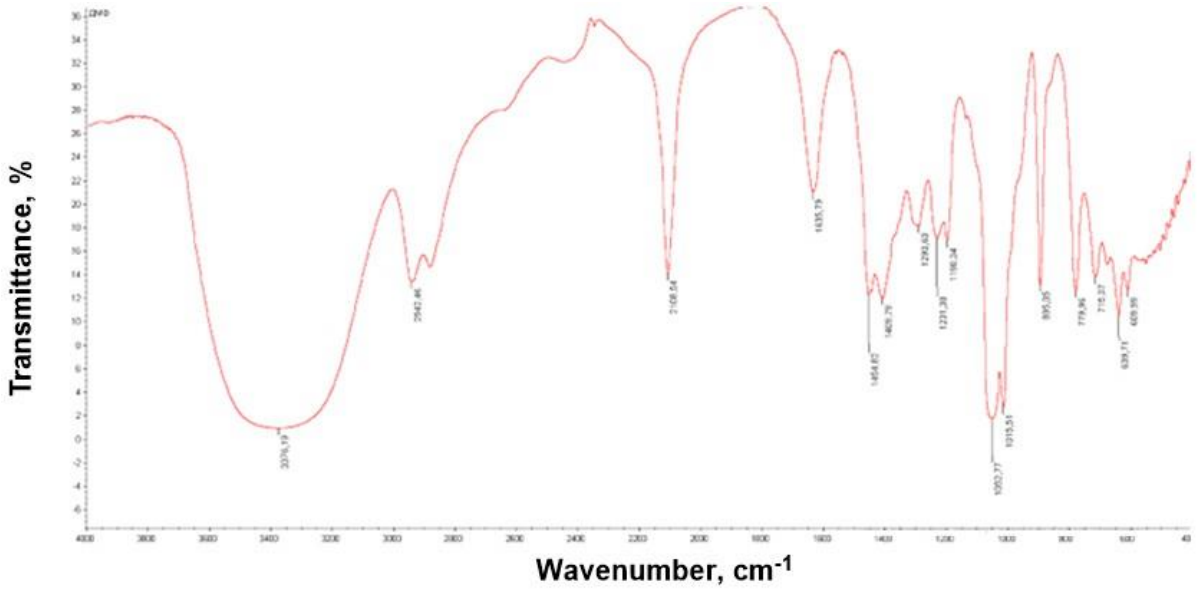

Figure S1. IR spectrum of BHMF **1** in KBr.

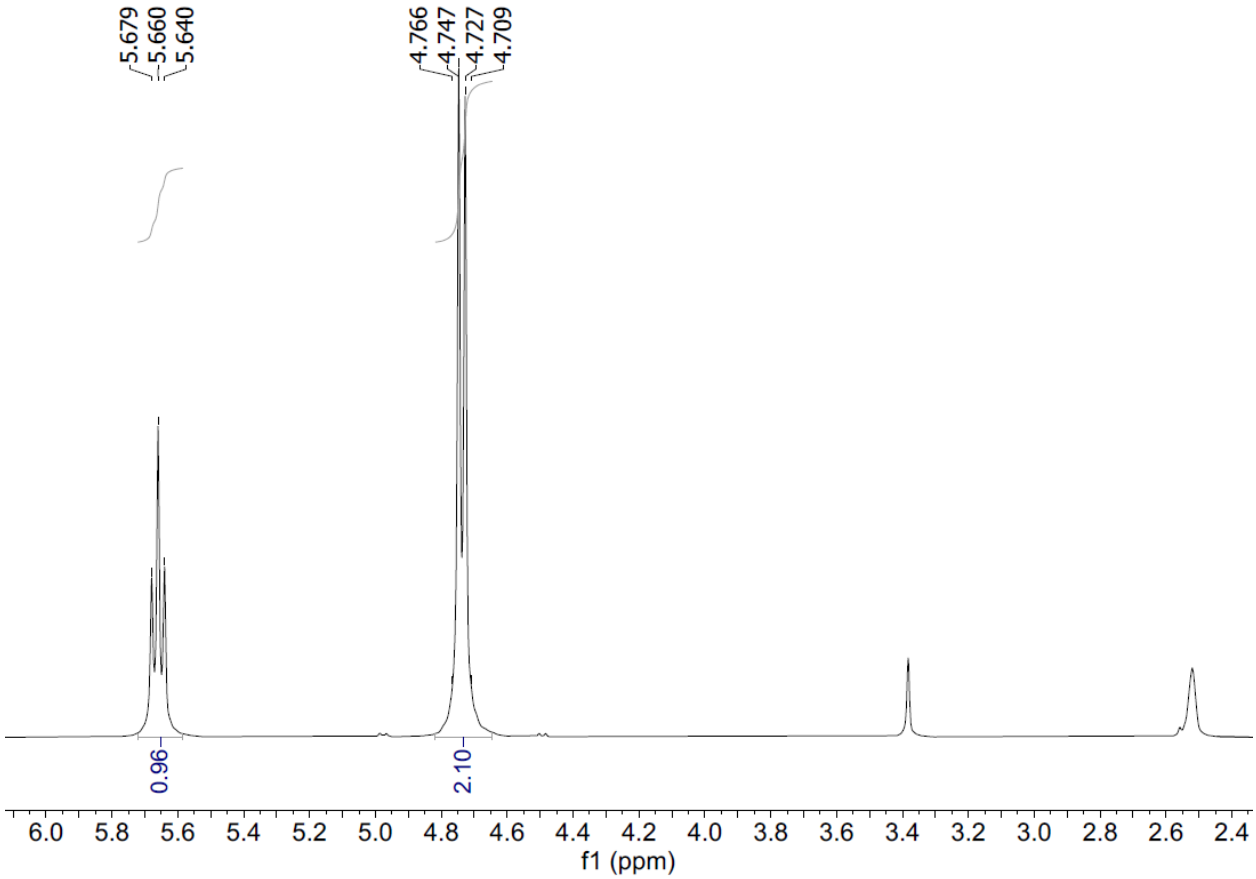

Figure S2. ^{1}H NMR spectrum of BHMF **1** in DMSO-d_6.

Poly(oxy(1,2,5-oxadiazole-3,4-diylbis(methylene)))oxycarbonylimino(4-methylbenzene-1,3-diyl)iminocarbonyl) PU-BHMF-100 **4a**. 3,4-Bis(hydroxymethyl)furazan **1** (0.49 g, 3.8 mmol), and 2,4-diisocyanatotoluene **2** (0.66 g, 3.8 mmol) were loaded into a two-neck round bottom flask (25 ml) equipped with a magnetic stirrer under nitrogen. After completion of the reaction for 1.5 h, the mixture was precipitated by addition in ethanol. The final product was washed 3 times with EtOH and dried under vacuum at 100-105 °C. PU is a rubber-like colorless substance. M. p. 137.8 °C (Figure S15). Intrinsic viscosity 0.191 dl·g^{-1}. Yield 1.13 g (94.2%). $C_{26}H_{24}N_8O_{10}$$^{2\bullet}$(unit) Calculated: C, 51.32; H, 3.98; N, 18.41. Found: C, 51.27; H, 5.17; N, 16.10%.

IR spectrum (KBr), ν, cm^{-1}: 3302 (NH), 1709 (C=O), 1609 (C=N cycl.), 1065 (C-O-C), 887 (NO) (Figure S3). ^{1}H NMR, δ (*J*, 300.13 MHz, DMSO-d_6) 1.25 (t, *J*=7.1, 3H, $\underline{CH_3}CH_2O(CO)NH)$ ^{term}, 2.13 (s, 3H, $\underline{CH_3}Ar$), 4.11 (q, *J*=6.8, 2H, $CH_3\underline{CH_2}O(CO)NH$), 4.77 (dd, *J*=18.1, 5.6, 2H, $HO\underline{CH_2}C$=N-O–) ^{term}, 5.45 (dd, *J*=19.1, 3.1, 2H, $CO\underline{CH_2}C$=N-O–), 5.68 (t, *J*=5.9, 1H, $\underline{HO}CH_2C$=N-O–) ^{term}, 5.80 (t, *J*=5.3, 1H, $\underline{HO}CH_2C$=N-O–) ^{term}, 7.12 (m, 2H, $\underline{CH}CH$(Ar)), 7.52 (s, 1H, $\underline{CH}$(Ar)), 8.78 (d, *J*=6.8, 1H, N$\underline{H}$C(O)O), 8.86 (s, 1H, N$\underline{H}$C(O)O), 9.20 (s, 1H, N$\underline{H}$C(O)O), 9.50 (s, 1H, N$\underline{H}$C(O)O), 9.89 (s, 1H, N$\underline{H}$C(O)O) (Fig. S4). ^{13}C NMR δ (75 MHz, DMSO-d_6) 154.8 =($OCH_2\underline{C}$=NO–), 154.3($OCH_2\underline{C}$=NO–), 153.5 (NH$\underline{C}$(O)O), 152.5(NH$\underline{C}$(O)O), 151.6(NH$\underline{C}$(O)O), 137.2 (NH$\underline{C}$-Ar), 136.6(NH$\underline{C}$-Ar), 136.0(NH$\underline{C}$-Ar), 130.4 ($\underline{C}H_2{}^{Ar}CHCH_3$), 130.3($\underline{C}H_2{}^{Ar}CHCH_3$), 130.2 ($\underline{C}H_2{}^{Ar}CHCH_3$), 125.2 ($\underline{C}^{Ar}CH_3$), 122.3($\underline{C}^{Ar}CH_3$), 115.5 ($CH_2\underline{CH}$=CH), 114.9(NHCH=$\underline{CH}$), 60.1($\underline{CH_2}$C=N-O–), 55.3 ($\underline{CH_2}$C=N-O–), 55.1($\underline{CH_2}$C=N-O–) , 52.7 ($\underline{CH_2}$C=N-O–), 17.1(Ar$\underline{C}H_3$), 14.6 ($\underline{C}H_3CH_2O$) (Figure S5).

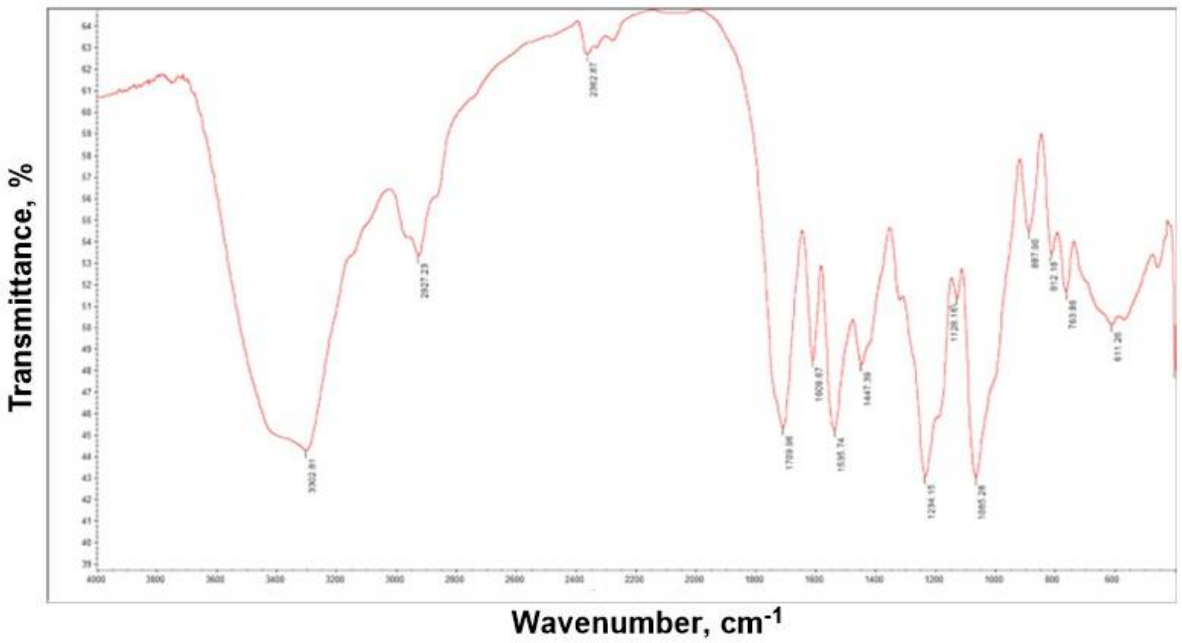

Figure S3. IR spectrum of PU-BHMF-100 **4a** in KBr.

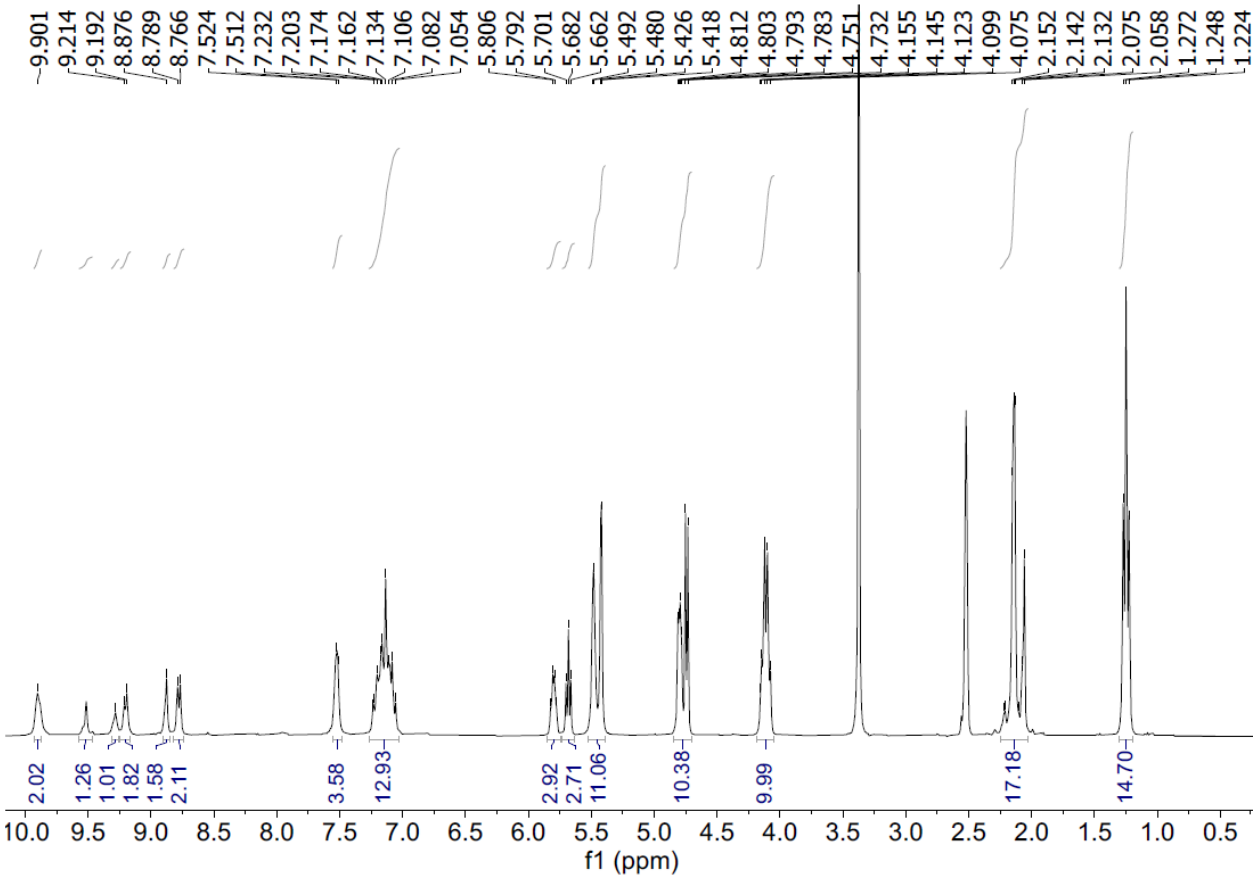

Figure S4. ^{1}H NMR spectrum of PU-BHMF-100 **4a** in DMSO-d_6.

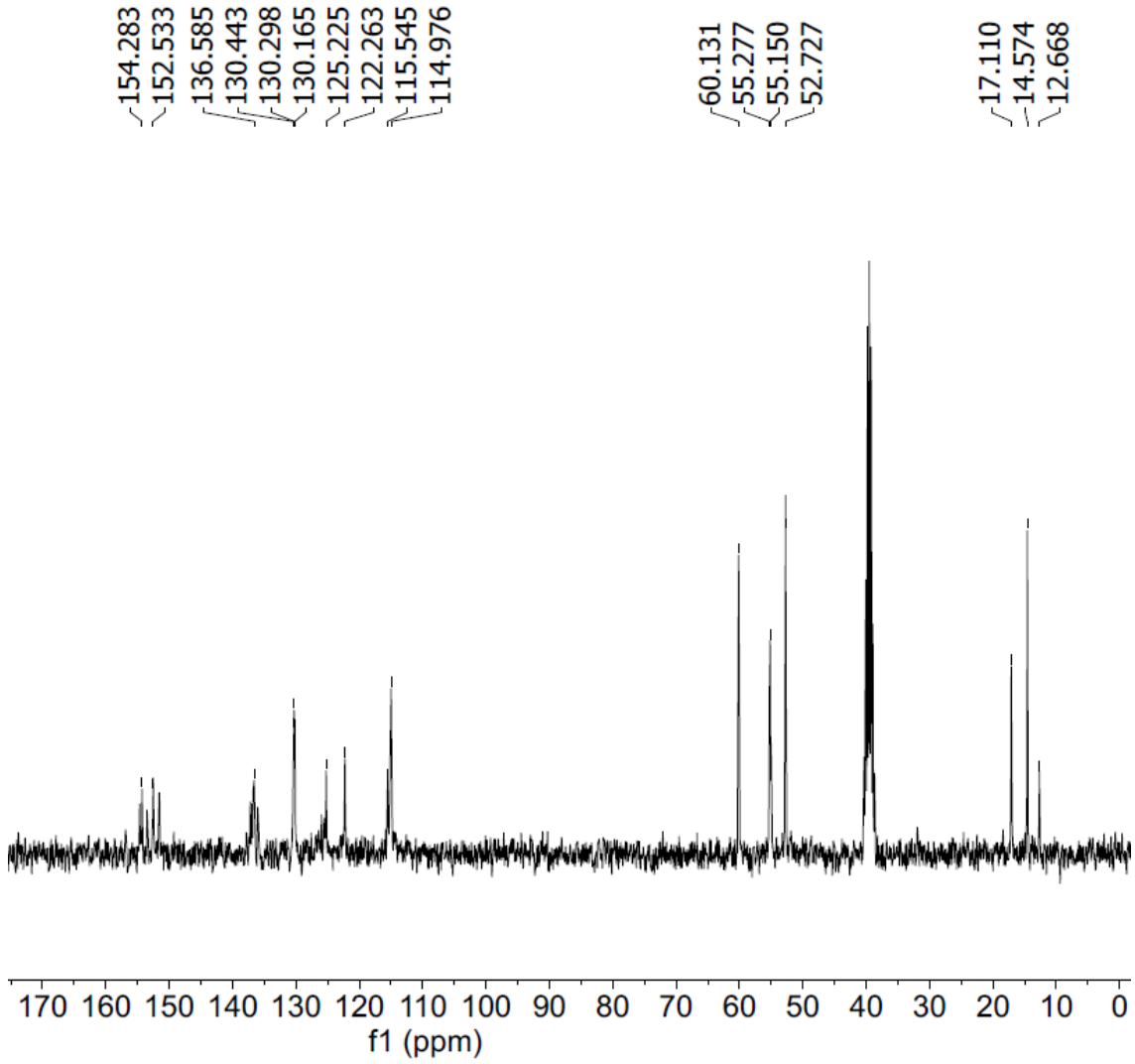

Figure S5. ^{13}C NMR spectrum of PU-BHMF-100 **4a** in DMSO-d_6.

Poly(oxy(1,2,5-oxadiazole-3,4-diylbis(methylene))oxycarbonylimino((4-methylbenzene-1,3-diyl)iminocarbonyl)-co-(oxybutane-1,4-diyloxycarbonylimino(4-methylbenzene-1,3-diyl)iminocarbonyl) PU-BHMF-80 **4b.** After melting BHMF **1** (1.0 g, 7.7 mmol), freshly distilled butanediol **3** (0.17 g, 1.9 mmol) was dosed and stirred at 50°C for 10 min. Next, 2,4-diisocyanatotoluene **2** (1.67 g, 9.60 mmol) was added. After completion of the reaction for 1.5 h, the mixture was precipitated with in ethanol. The final PU was washed 3 times with EtOH and dried under vacuum to remove ethanol at 100-105 °C. Substance **4b** is a white powder. M.p. 66.7 °C (Figure S16). Intrinsic viscosity 0.194 dl·g^{-1}. Yield 2.79 g (98.5%). Yield after flushing 2.56 g (90.5%). $C_{26}H_{25.6}N_{7.2}O_{9.6}^{2\bullet}$ (unit) Calculated: C, 52.70; H, 4.36; N, 17.02. Found: C, 52.26; H, 4.84; N, 16.65%.

IR spectrum (KBr), ν, cm^{-1}: 3321 (NH), 1717 (C=O), 1606 (C=N cycl.), 1069 (C-O-C), 884 (NO) (Figure S6). ^{1}H NMR, δ (*J*, 300.13 MHz, DMSO-d_6) 1.24 (t, *J*=6.9, 3H, $\underline{CH_3}CH_2O(CO)N$), 1.72 (s, 3H,

$OCH_2\underline{CH_2CH_2}CH_2O(CO)N$), 2.13 (s, 3H, $\underline{CH_3}Ar$), 4.11 (s, 2H, $CH_2CH_2CH_2\underline{CH_2}O(CO)N$), 4.79 (s, 2H, $HO\underline{CH_2}C{=}NO–)^{term}$, 5.41 (s, 2H, $CO\underline{CH_2}C{=}N{-}O–$), 5.47 (s, 2H, $CO\underline{CH_2}C{=}N{-}O–$), 5.79 (m, 1H, $\underline{HO}CH_2C{=}N{-}O–)^{term}$, 7.18 (m, 2H, $\underline{CH}CH(Ar)$), 7.51 (s, 1H, $\underline{CH}(Ar)$), 7.96 (d, *J*=4.1, 1H, $CH_2CH_2CH_2CH_2O(CO)N\underline{H}$), 8.22 (d, *J*=6.3, 1H, $CH_2CH_2CH_2CH_2O(CO)N\underline{H}$), .80 (m, 1H, $N\underline{H}C(O)OCH_2C{=}N{-}O–$), 9.19 (s, 1H, $N\underline{H}C(O)OCH_2C{=}N{-}O–$), 9.53 (m, 1H, $N\underline{H}C(O)OCH_2C{=}N{-}O–$), 9.86 (m, 1H, $N\underline{H}C(O)OCH_2C{=}N{-}O–$) (Figure S7). ^{13}C NMR δ (75 MHz, DMSO-d_6) 153.5($OCH_2\underline{C}{=}N{-}O–$), 152.5 ($OCH_2\underline{C}{=}N{-}O–$), 151.5($NH\underline{C}(O)O$), 136.6 ($NH\underline{C}$-Ar), 135.9 ($NH\underline{C}$-Ar), 130.4($\underline{C}H_2{}^{Ar}CHCH_3$), 115.5 ($CH_2\underline{CH}{=}CH$), 115.0($CH_2CH{=}CH$) ($CH_2\underline{CH}{=}CH$), 63.7 ($O\underline{C}H_2CH_2$, $O\underline{C}H_2CH_3$), 55.1($\underline{CH_2}C{=}N{-}O–$), 52.7($\underline{CH_2}C{=}N{-}O–$), 25.2($OCH_2\underline{C}H_2$), 16.9($Ar\underline{C}H_3$), 14.6 ($\underline{C}H_3CH_2O$) (Figure S8).

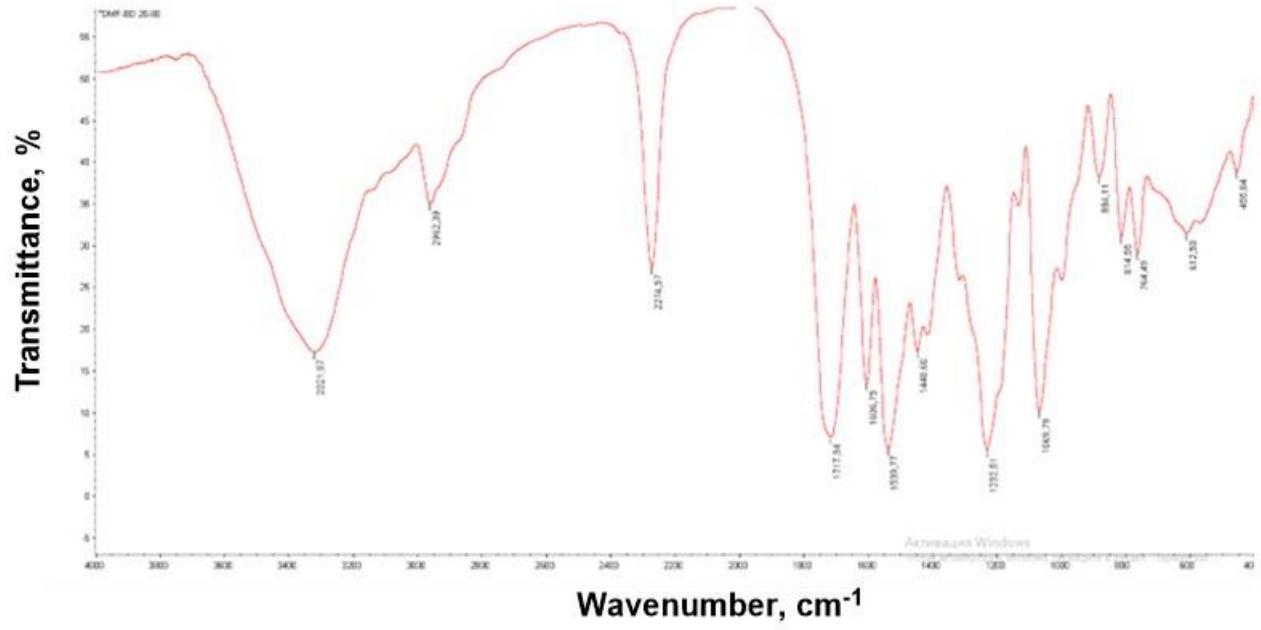

Figure S6. IR spectrum of PU-DGMF-80 **4b** in KBr.

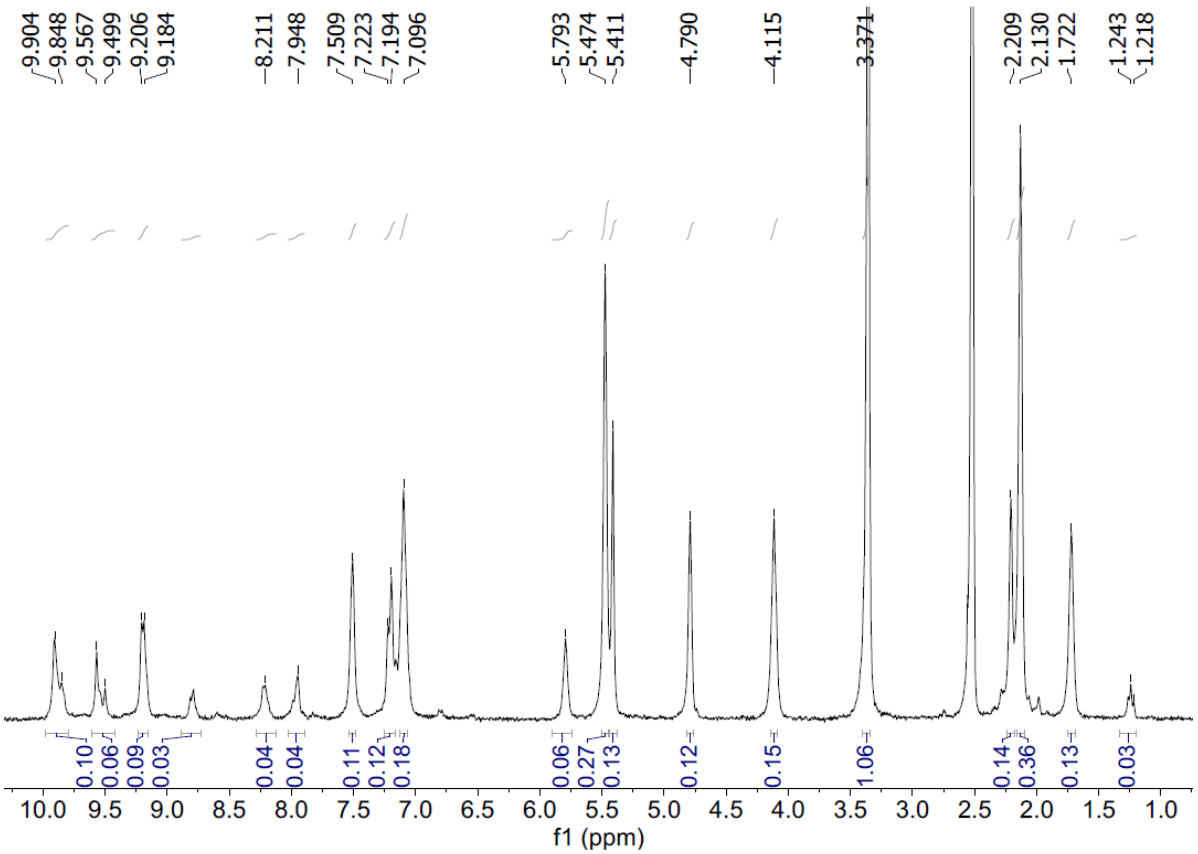

Figure S7.[1]H NMR of PU-DGMF-80 **4b** in DMSO-d_6.

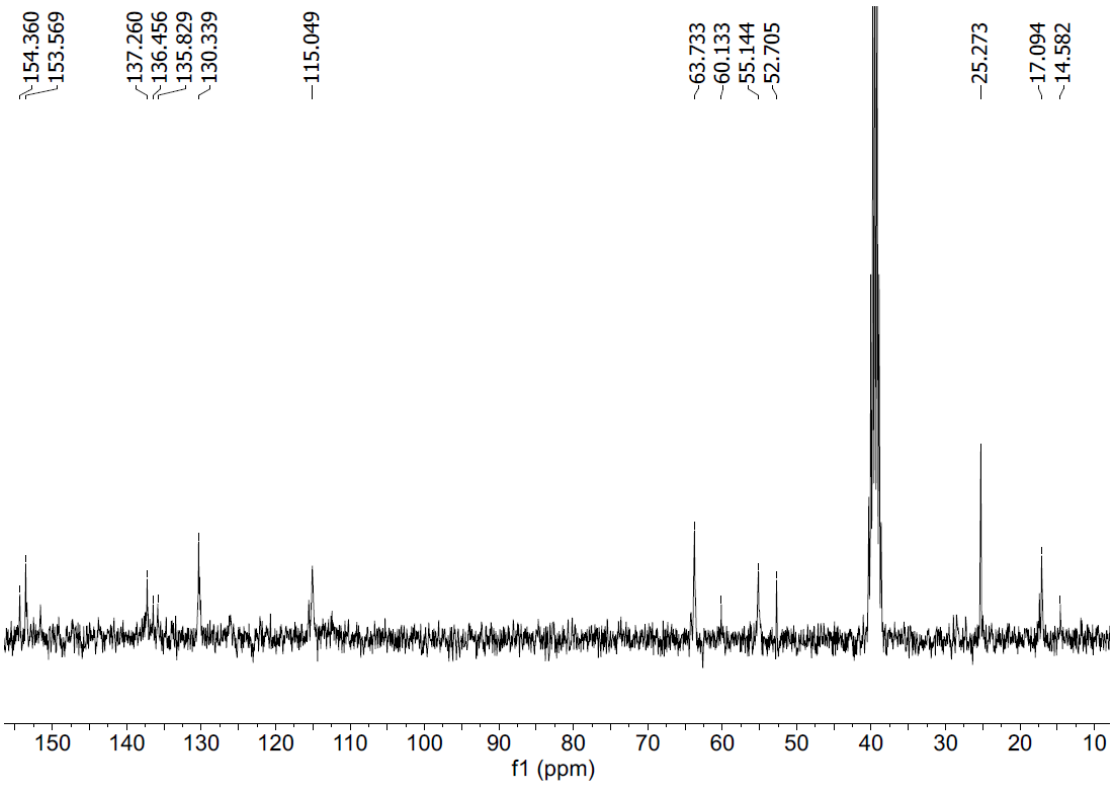

Figure S8.[13]C NMR of PU-DGMF-80 **4b** in DMSO-d_6.

Poly(oxy(1,2,5-oxadiazole-3,4-diylbis(methylene))oxycarbonylimino((4-methylbenzene-1,3-diyl)iminocarbonyl)-co-(oxybutane-1,4-diyloxycarbonylimino(4-methylbenzene-1,3-diyl)iminocarbonyl) PU-BHMF-70 **4c**. After melting BHMF **1** (1.0 g, 7.7 mmol), freshly distilled butanediol **3** (0.29 g, 3.30 mmol) was dosed, and this was stirred at 50 °C for 10 min. 2,4-Diisocyanatotoluene **2** (1.92 g, 11.0 mmol) was added. After completion the reaction for 1.5 h, the product was precipitated by pouring into ethanol. The final PU was washed 3 times with ethanol and dried under vacuum at 100-105 °C. Yield 3.16 g (97.3%). Polyurethane **4c** is a white powder. M.p. 65.7 °C (Figure S17). Intrinsic viscosity 0.186 $dl \cdot g^{-1}$. Yield after flushing 2.75 g (84.9%). $C_{26}H_{26}.4N_{6.8}O_{9.4}^{2\bullet}$ (unit) Calculated: C, 53.42; H, 4.55; N, 16.29. Found: C, 53.56; H, 5.72; N, 15.63%.

IR spectrum (KBr), ν, cm^{-1}: 3324 (NH), 1715 (C=O), 1606 (C=N cycl.), 1068 (C-O-C), 881 (NO) (Figure S9). ^{1}H NMR, δ (*J*, 300.13 MHz, DMSO-d_6) 1.24 (t, *J*=7.1, 3H, $\underline{CH_3}CH_2O(CO)N$), 1.70 (s, 3H, $OCH_2\underline{CH_2}\underline{CH_2}CH_2O(CO)N$), 2.13 (s, 3H, $\underline{CH_3}Ar$), 4.09 (s, 2H, $CH_2CH_2CH_2\underline{CH_2}O(CO)N$), 4.79 (d, *J*=2.9, 2H, $HO\underline{CH_2}C{=}NO–$) ^{term}, 5.39 (s, 2H, $CO\underline{CH_2}C{=}N\text{-}O–$), 5.45 (s, 2H, $CO\underline{CH_2}C{=}N\text{-}O–$), 5.78 (m, 1H, $\underline{HO}CH_2C{=}N\text{-}O–$) ^{term}, 7.14 (m, 2H, $\underline{CH}CH(Ar)$), 7.49 (s, 1H, $\underline{CH}(Ar)$), 7.94 (s, 1H, $CH_2CH_2CH_2CH_2O(CO)N\underline{H}$), 8.21 (m, 1H, $CH_2CH_2CH_2CH_2O(CO)N\underline{H}$), 8.79 (t, *J*=6.6, 1H, $N\underline{H}C(O)OCH_2C{=}N\text{-}O–$), 9.19 (d, *J*=5.4, 1H, $N\underline{H}C(O)OCH_2C{=}N\text{-}O–$), 9.54 (m, 1H, $N\underline{H}C(O)OCH_2C{=}N\text{-}O–$), 9.87 (m, $N\underline{H}C(O)OCH_2C{=}N\text{-}O–$) (Figure S10). ^{13}C NMR δ (75 MHz, DMSO-d_6) 153.5($OCH_2\underline{C}{=}N\text{-}O–$), 153.3 ($OCH_2\underline{C}{=}N\text{-}O–$), 151.5 ($NH\underline{C}(O)O$), 136.9 ($NH\underline{C}$-Ar), 135.9 ($NH\underline{C}$-Ar), 130.1 ($\underline{C}H_2{}^{Ar}CHCH_3$), 115.4 ($CH_2\underline{CH}{=}CH$), 115.0 ($CH_2\underline{CH}{=}CH$), 63.7 ($O\underline{C}H_2CH_2$, $O\underline{C}H_2CH_3$), 55.1($\underline{CH_2}C{=}N\text{-}O–$), 52.7 ($\underline{CH_2}C{=}N\text{-}O–$), 25.2 ($OCH_2\underline{C}H_2$), 16.9 ($Ar\underline{C}H_3$), 14.6 ($\underline{C}H_3CH_2O$) (Figure S11).

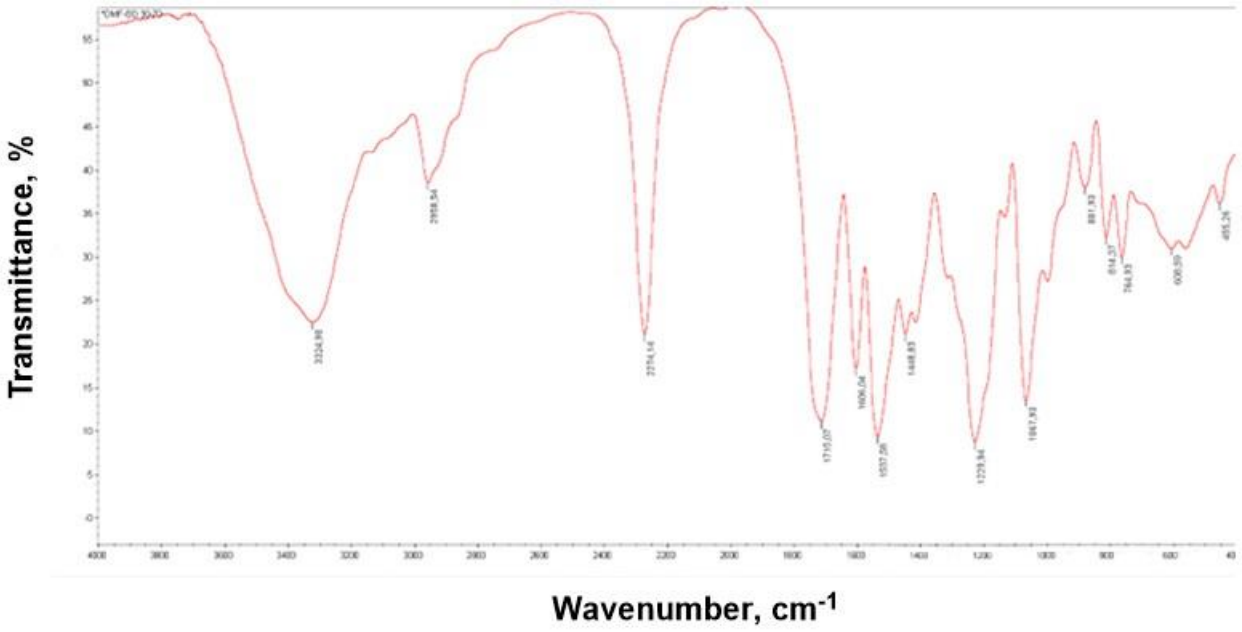

Figure S9. IR spectrum of PU-BHMF-70 **4c** in KBr.

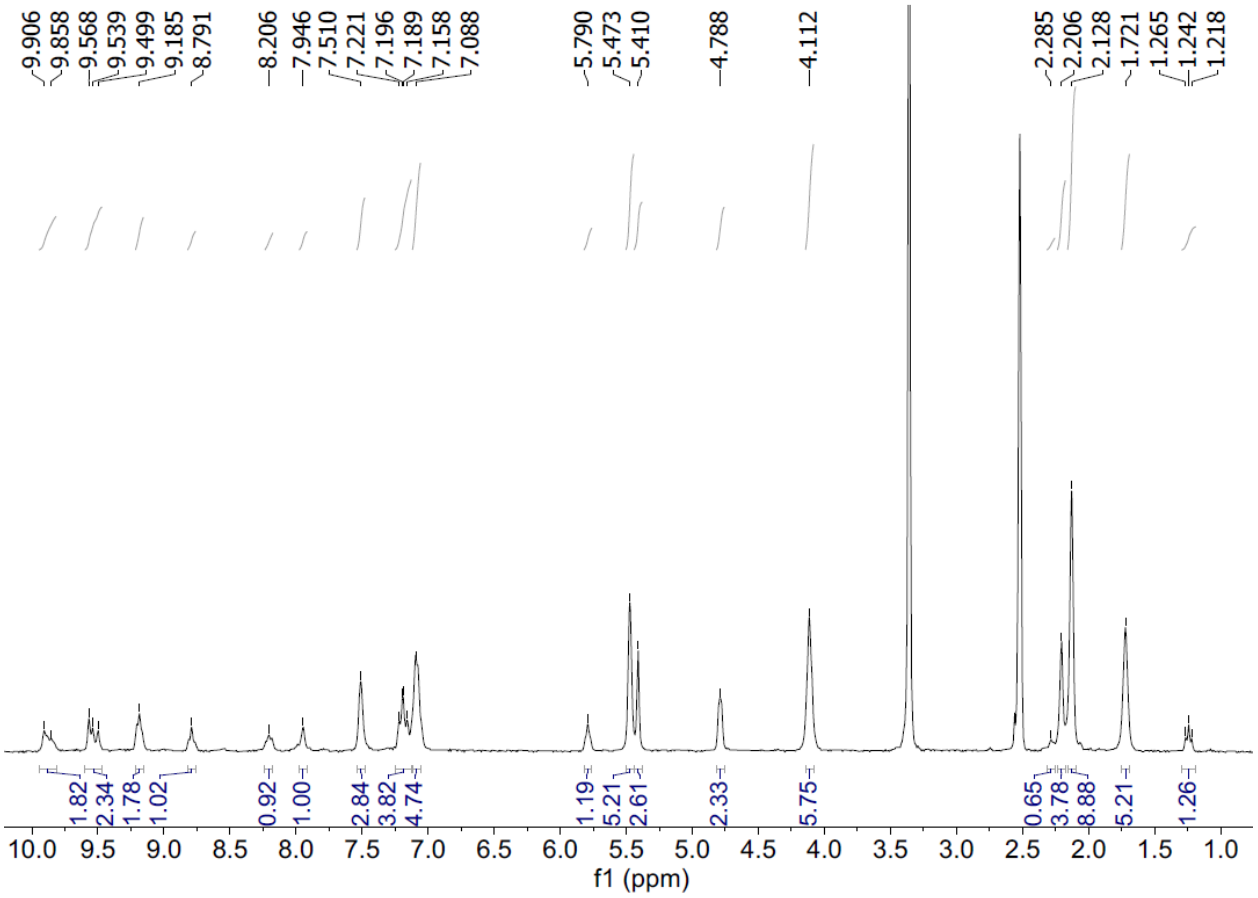

Figure S10. ^{1}H NMR spectrum of PU-BHMF-70 **4c** in DMSO-d_6.

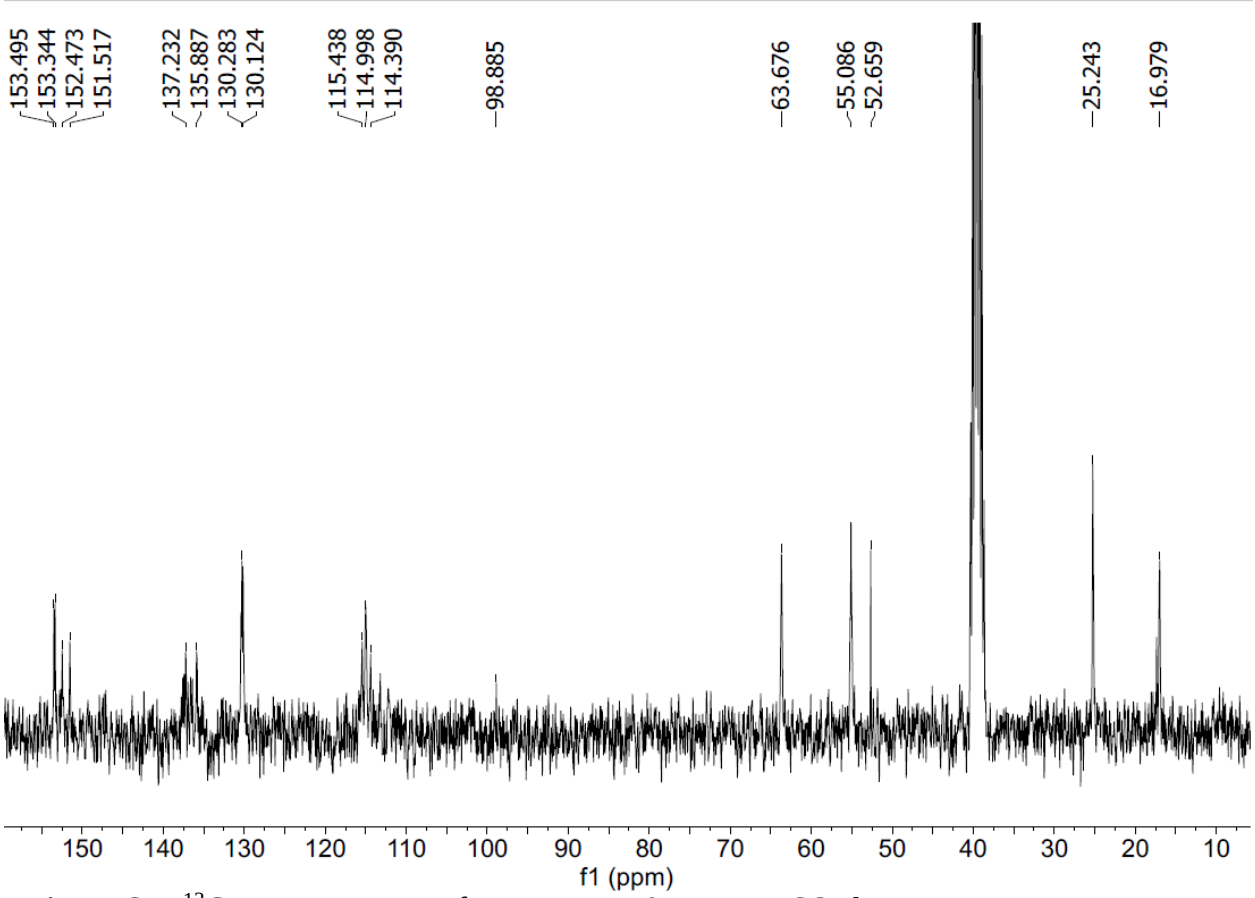

Figure S11. ^{13}C NMR spectrum of PU-BHMF-70 **4c** in DMSO-d_6.

Poly(oxy(1,2,5-oxadiazole-3,4-diylbis(methylene))oxycarbonylimino((4-methylbenzene-1,3-diyl)iminocarbonyl)-co-(oxybutane-1,4-diyloxycarbonylimino(4-methylbenzene-1,3-diyl)iminocarbonyl) PU-BHMF-50 **4d**. After melting BHMF **1** (1.0 g, 7.7 mmol), freshly distilled butanediol **3** (0.69 g, 7.7 mmol) was dosed, and this was stirred at 50 °C for 10 min. 2,4-Diisocyanatotoluene **2** (2.68 g, 15.4 mmol) was added. After completion of the reaction for 1.5 h, the mixture was precipitated by its addition into ethanol. The final product was washed 3 times with ethanol and dried under vacuum at 100-105 °C. Polyurethane **4d** is a white powder. M.p. 66.3 °C (Figure S18). Intrinsic viscosity 0.332 dl·g^{-1}. Yield 4.28 g (97.9%). Yield after flushing 3.67 g (84.1%). $C_{26}H_{28}N_6O_9^{2\bullet}$ (unit) Calculated: C, 54.93; H, 4.96; N, 14.78%. Found: C, 54.88; H, 5.59; N, 14.41%.

IR spectrum (KBr), ν, cm^{-1}: 3336 (NH), 1710 (C=O), 1606 (C=N cycl.), 1065 (C-O-C), 884 (NO) (Figure S12). ^{1}H NMR, δ (*J*, 300.13 MHz, DMSO-d_6) 1.24 (t, *J*=6.9, 3H, $\underline{CH_3}CH_2O(CO)N$), 1.72 (s, 3H, $OCH_2\underline{CH_2}\underline{CH_2}CH_2O(CO)N$), 2.13 (s, 3H, $\underline{CH_3}Ar$), 4.11 (s, 2H, $CH_2CH_2CH_2\underline{CH_2}O(CO)N$), 4.79 (d, *J*=5.5, 2H, $HO\underline{CH_2}C{=}NO–$) ^{term}, 5.41 (s, 2H, $CO\underline{CH_2}C{=}N{-}O–$), 5.47 (s, 2H, $CO\underline{CH_2}C{=}N{-}O–$), 5.79 (t, *J*=5.4, 1H, $\underline{HO}CH_2C{=}N{-}O–$) ^{term}, 7.14 (m, 2H, $\underline{CH}CH(Ar)$), 7.51 (s, 1H, $\underline{CH}(Ar)$), 7.94 (s, 1H,

$CH_2CH_2CH_2CH_2O(CO)N\underline{H}$), 8.19 (d, *J*=5.3, 1H, $CH_2CH_2CH_2CH_2O(CO)N\underline{H}$), 8.79 (t, *J*=7.3, 1H, $N\underline{H}C(O)OCH_2C=N-O-$), 9.17 (d, *J*=6.0, 1H, $N\underline{H}C(O)OCH_2C=N-O-$), 9.53 (m, 1H, $N\underline{H}C(O)OCH_2C=N-O-$), 9.88 (m, 1H, $N\underline{H}C(O)OCH_2C=N-O-$) (Figure S13). ^{13}C NMR δ (75 MHz, DMSO-d_6) 154.4($OCH_2\underline{C}=N-O-$), 153.6 ($OCH_2\underline{C}=N-O-$), 151.6($NH\underline{C}(O)O$), 136.5 ($NH\underline{C}$-Ar), 135.8 ($NH\underline{C}$-Ar), 130.3 ($\underline{C}H_2{}^{Ar}CHCH_3$), 115.4 ($CH_2\underline{C}H=CH$), 115.0($CH_2\underline{C}H=CH$), 63.7 ($O\underline{C}H_2CH_2$, $O\underline{C}H_2CH_3$), 60.1($\underline{C}H_2C=N-O-)^{term}$ 55.1($\underline{C}H_2C=N-O-$), 52.7($\underline{C}H_2C=N-O-$), 25.3($OCH_2\underline{C}H_2$), 17.1($Ar\underline{C}H_3$), 14.6 ($\underline{C}H_3CH_2O$) (Figure S14).

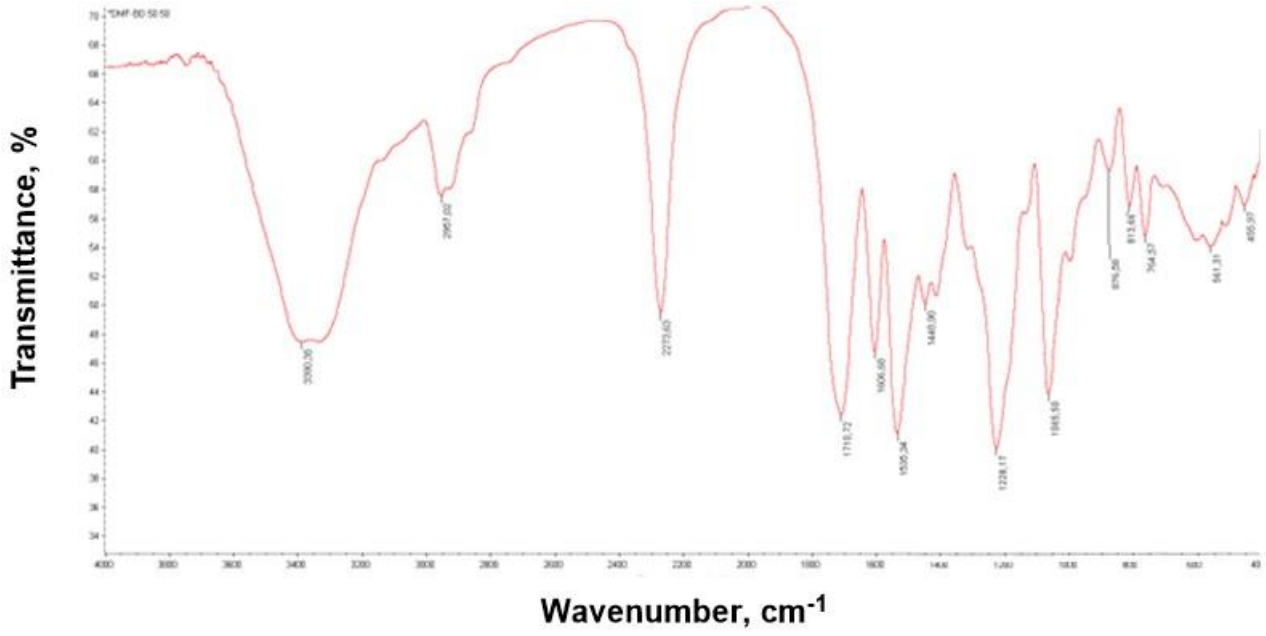

Figure S12. IR spectrum of PU-BHMF-50 **4d** in KBr.

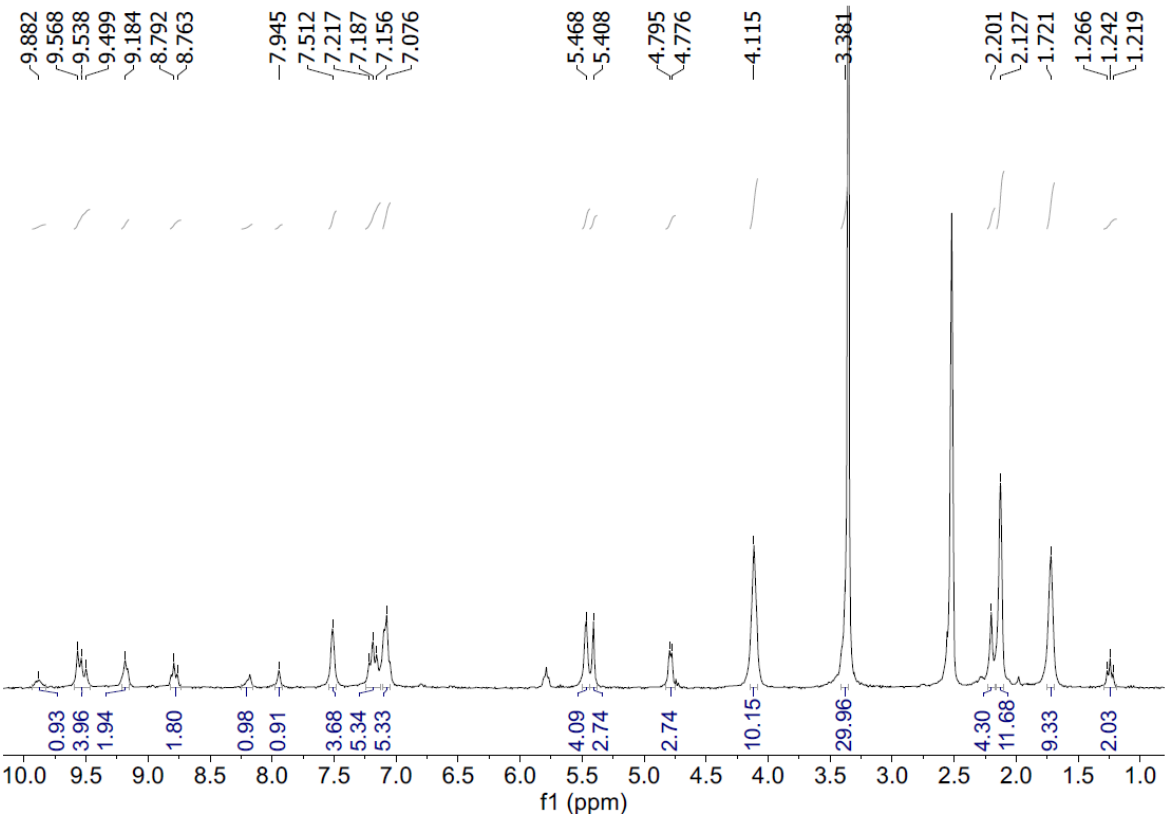

Figure S13.[1]H NMR spectrum of PU-BHMF-50 **4d** in DMSO-d_6.

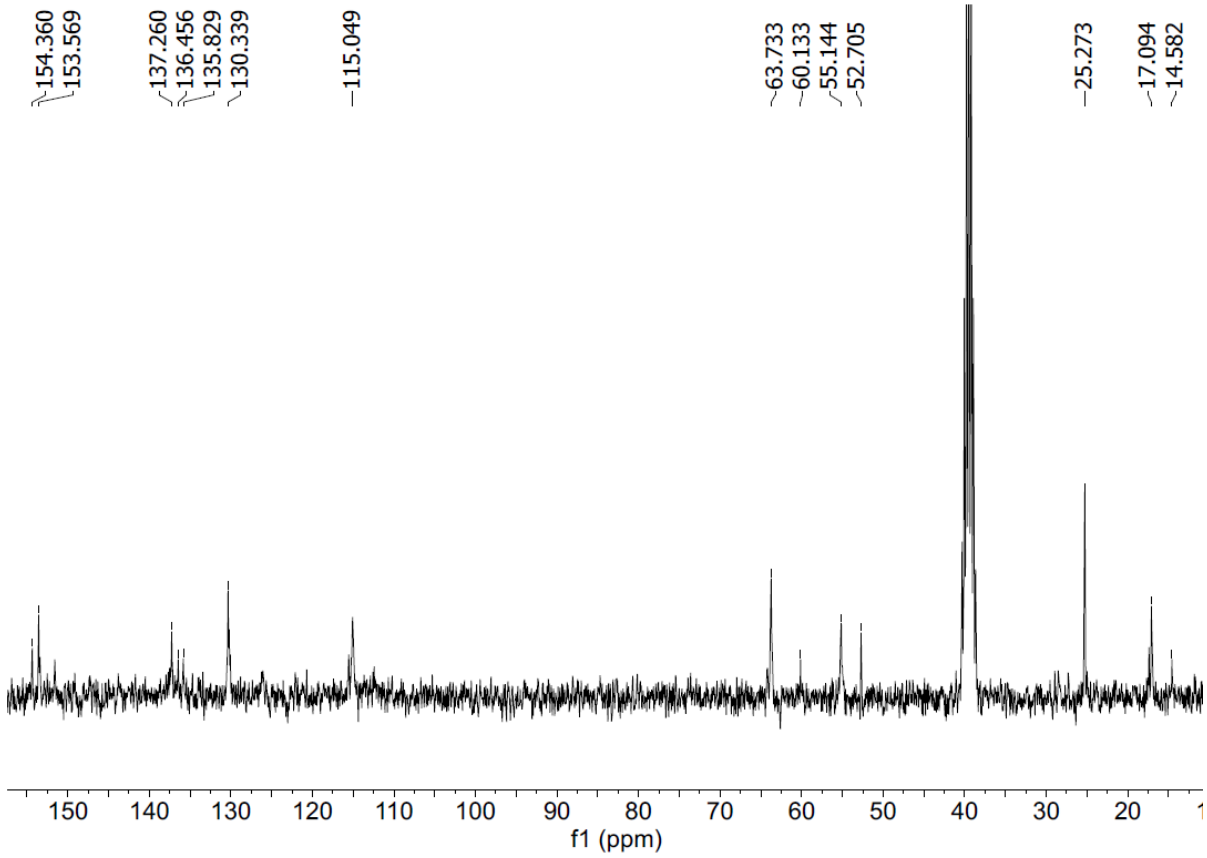

Figure S14.[13]C NMR spectrum of PU-BHMF-50 **4d** in DMSO-d_6.

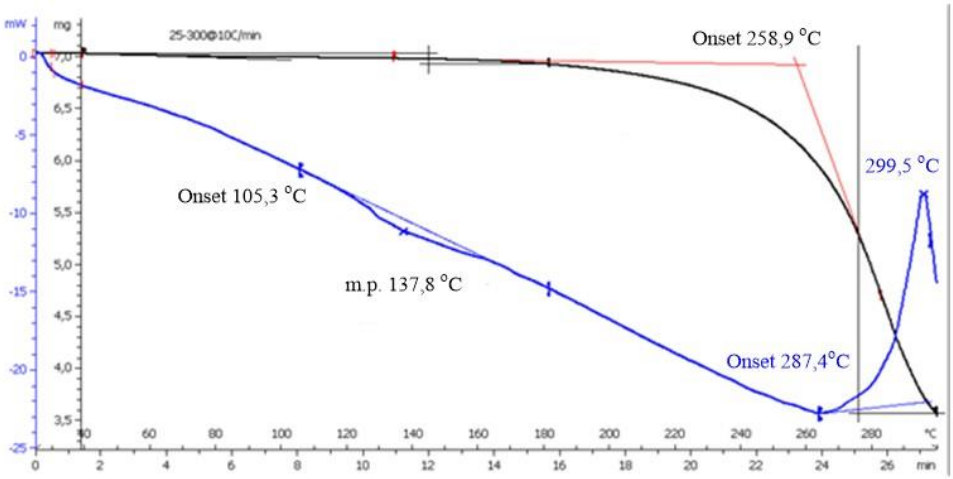

Figure S15. DSC/TGA thermograms of PU-BHMF-100 **4a**.

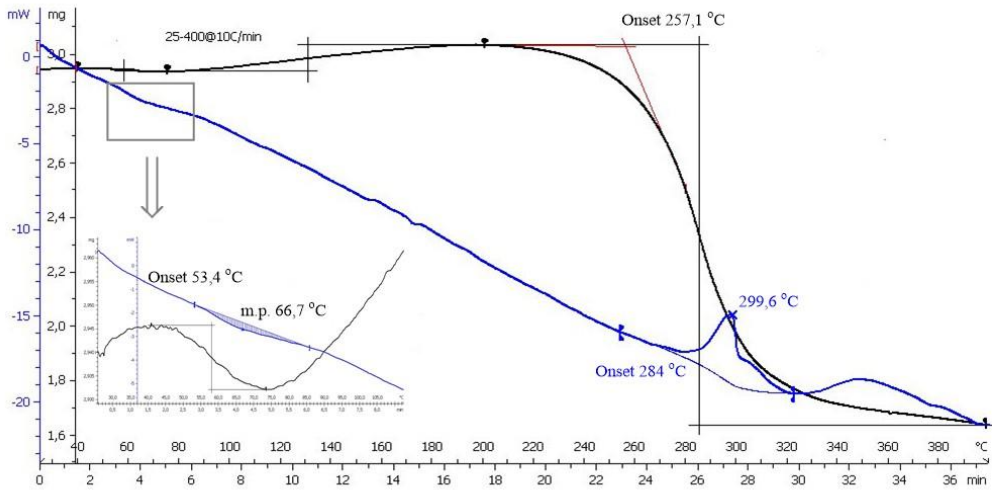

Figure S16. DSC/TGA thermograms of PU-BHMF-80 **4b**.

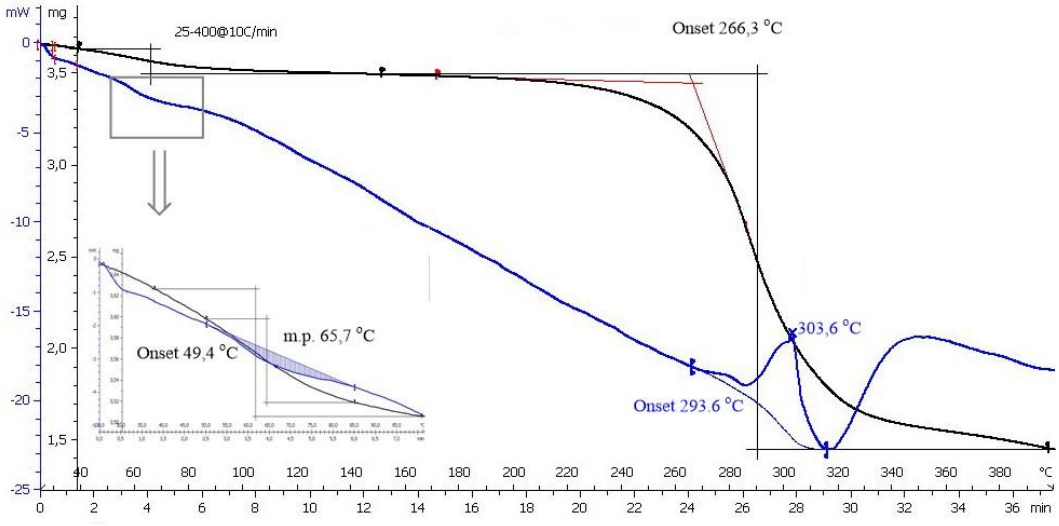

Figure S17. DSC/TGA thermograms of PU-BHMF-70 **4c**.

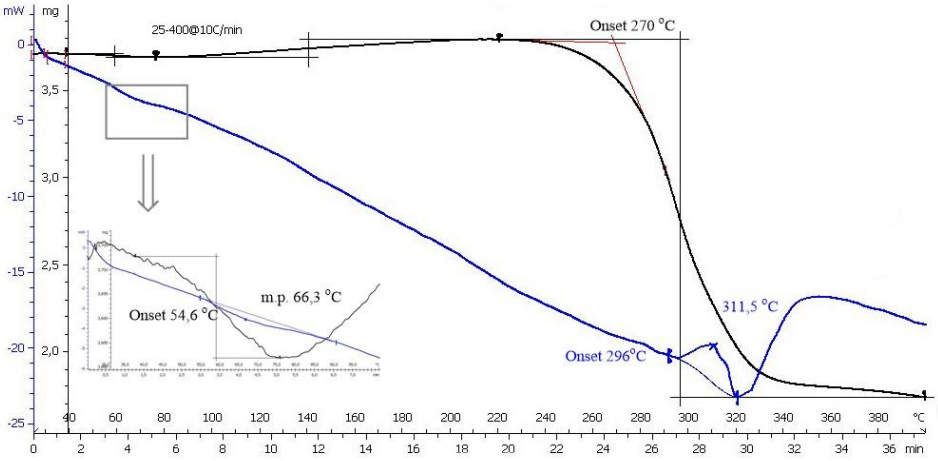

Figure S18. DSC/TGA thermograms of PU-BHMF-50 **4d**.