The polymorphic microstructure of MDI/BD-blocked polyurethane determined by temperature-sensitive conformation variation

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260 °C 3min

50 °C/min

130/140/150/160
170/180/190°C for 30min

a

260 °C 3min

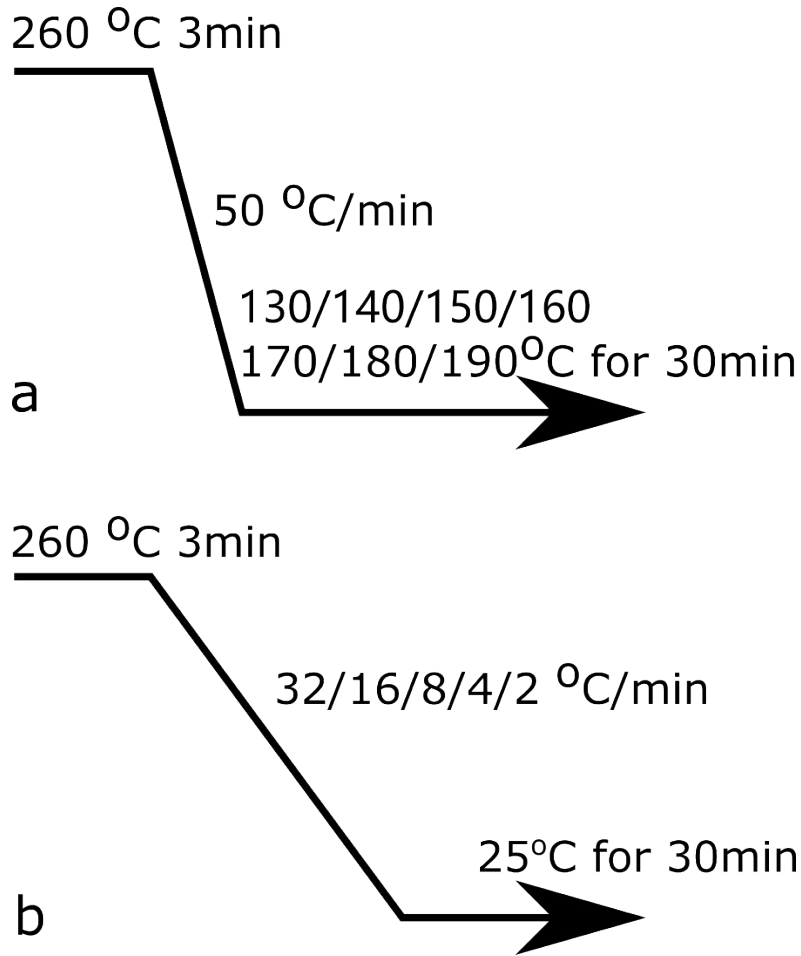32/16/8/4/2 °C/min

25°C for 30min

b

Figure S1. The protocol of isothermal crystallization and different cooling rates. (a) The TPU melt at 260 °C for 3min was cooled to different isothermal crystallization temperature at the rate of 50 °C and kept for 30 mins. (b) The TPU melt at 260 °C for 3min was cooled at different rates and kept at 25 °C for 30 mins.

Crystallinity index determined from WAXS. $I_{WAXS}(s)$ obtained from azimuthal averaging of 2D WAXS pattern has to be separated into the contribution from the crystallite and the amorphous phases, $I_{WAXS}(s) = I_{WAXS,cr}(s) + I_{WAXS,am}(s)$. Herein, $s = (2/\lambda)\sin\theta$ is the scattering vector with scattering angle 2θ and wavelength λ. Crystallinity index can be calculated with the integral ratio of scattering from the crystallites and all the matter, $X_c = \int I_{WAXS,cr}(s)ds / \int I_{WAXS}(s)ds$, in which the integral range is from low s to high s[34,37]. Determination of the low crystallinity index of form I

using peak fitting is unreliable in this work as the peaks cannot fit well. Thus, we developed a manual algorithm to separate the contribution of crystallites and amorphous parts. Both form I and form II are calculated using the manual algorithm to compare. The process is described in Figure S2.
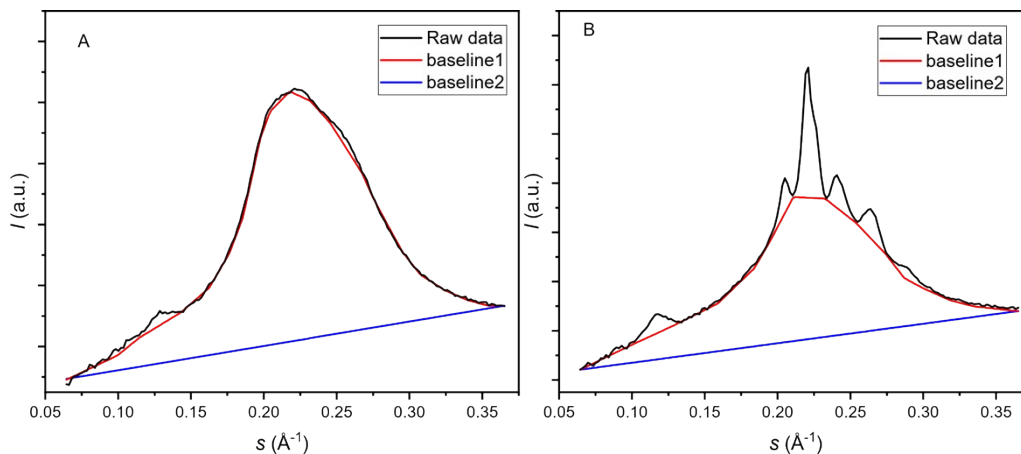

Figure S2. A manual separation of the scattering contribution from crystallites and amorphous part of form I (A) and form II (B). The baseline2 is the incoherent background scattering. The incoherent background contribution is subtracted firstly and the. The baseline1 is the contribution from the amorphous part. The crystallinity index is calculated using the ratio of the area between Raw data and baseline1 and the area between baseline2 and Raw data.
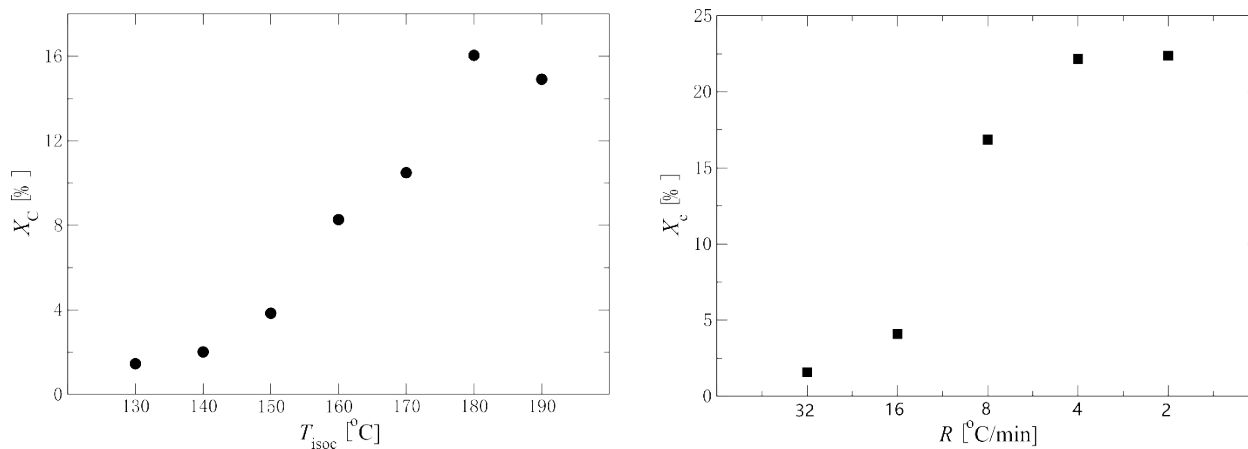

Figure S3. The crystallinity index calculated from Figure 4 in the method described above.

The integrated crystallization and melting enthalpy H_m during heating and cooling scan are shown in the tables below.
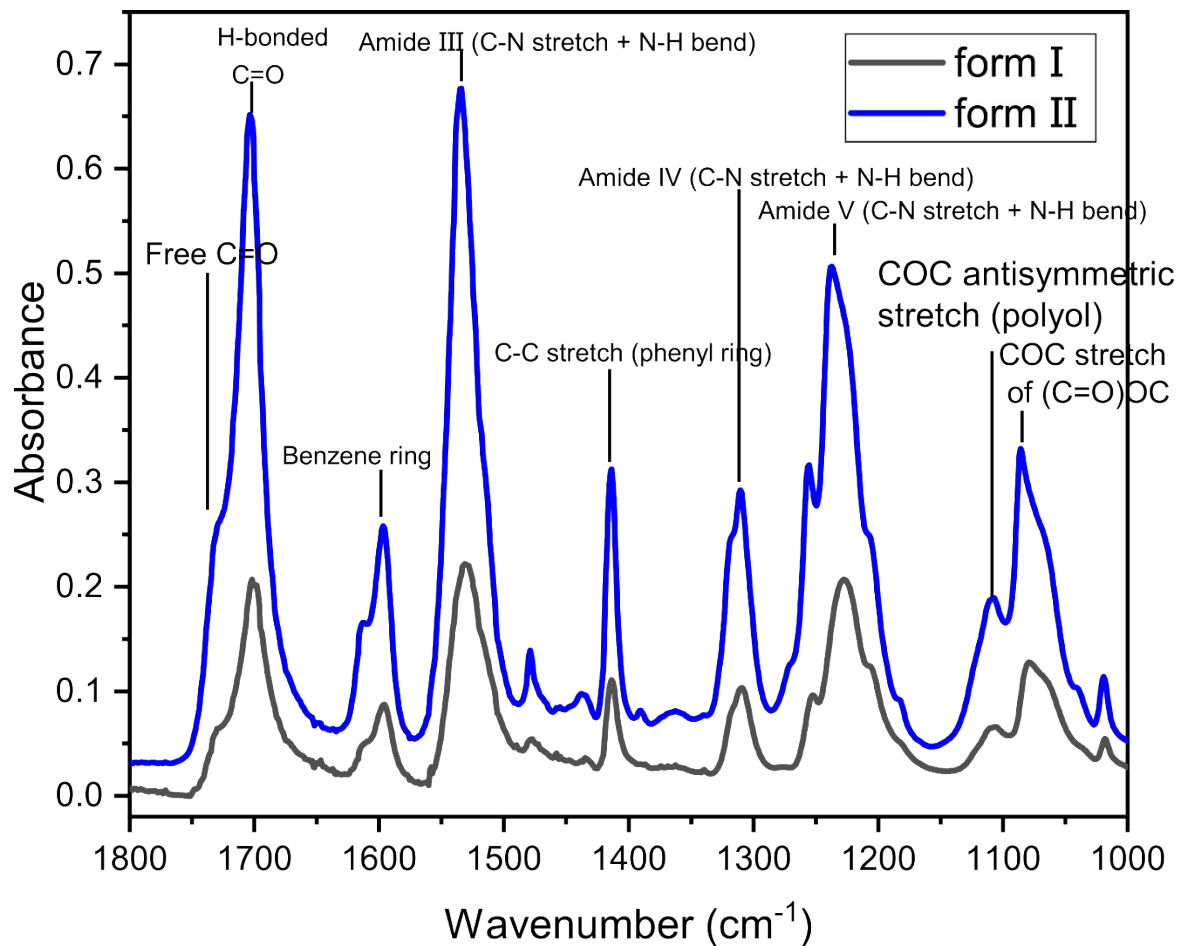
Figure S4. The normalized FTIR spectroscopy in the region of 1800-1000 cm⁻¹.

Table S1. Melting enthalpy H_m during heat scan of H75 as shown in Figure 4a. Unit: J/g.

T_{isoc}	H_{m1}	H_{m2}	H_{m3}	H_{m4}	$H_{m2}+ H_{m4}$
190	-	3.4	-	4.0	7.4
180	-	16.0	-	10.5	26.5
170	-	18.5	-	3.8	22.3
160	-	20.5	-	2.2	22.7
150	-	23.2	-	1.6	24.8

| 140 | 15.0 | 1.1 | 7.4 | - | - |
| 130 | 16.5 | 1.5 | 8.0 | - | - |

Table S2. The integrated intensity of diffraction peak at the smallest angle and the area ratio of form II with respect to the sum of form I and form II at different cooling rates.

$R_{cooling}$	I_{formII}	I_{formI}	$I_{formII}/ (I_{formI}+ I_{formII})$
32	0.11	0.40	21.6%
16	0.34	0.23	59.6%
8	0.82	0.18	82.0%
4	0.78	0.10	88.6%
2	0.70	0.04	94.6%

Table S3. The wavenumber difference of form I and form II and their assignment.

wavenumber (cm^{-1})		Vibrational assignment
Form I	Form II	
1701	1703	Carbonyl stretch (H-bonded)
1533	1534	Amide.III (C-N stretch + N-H bend)
1318	1320	Amide IV (C-N stretch + N-H bend)
1253	1256	Amide V (C-N stretch + N-H bend)
1082	1086	COC stretch of (C=O)OC

1018	1019	In-plane CH bend (phenyl ring)

The effects of variations of the dihedral angle of urethane and phenyl and opening of phenyl-CH_2-phenyl on the repeat period along c-axis of crystalline structure was performed based on the assumption. Setting of bond length and bond angle refers to Blackwell and Nagarajan's paper [1].

Table S4. The variation of repeat period with increasing the phenyl-CH2-phenyl angle β. The ψ_1 and ψ_2 is set as 90°, respectively.

bond angle β [°]	repeat period [Å]
109	33.43
110	33.65
111	33.87
112	34.08
113	34.30
114	34.50
115	34.71
116	34.91
117	35.11
118	35.31
119	35.51
120	35.70

Table S5. The variation of repeat period with rotating the dihedral angle ψ_1 and ψ_2. The phenyl-CH$_2$-phenyl bond angle is set as 109°, respectively.

ψ_1 [°]	ψ_2 [°]	repeat period [Å]
90	-90	33.43
80	-100	34.15
70	-110	34.73
60	-120	35.17
50	-130	35.36
40	-140	35.60
30	-150	35.62
20	-160	35.53
10	-170	35.39
0	-180	35.20

Table S6. The variation of repeat period with rotating the dihedral angle ψ_1 and ψ_2. The phenyl-CH$_2$-phenyl bond angle is set as 120°, respectively.

ψ_1 [°]	ψ_2 [°]	repeat period [Å]
90	-90	35.70
80	-100	36.35
70	-110	36.85

60	-120	37.22
50	-130	37.42
40	-140	37.48
30	-150	37.41
20	-160	37.25
10	-170	37.04
0	-180	36.81

[1]   J. Blackwell, M.R. Nagarajan, Conformational analysis of poly(MDI-butandiol) hard segment in polyurethane elastomers, Polymer. 22 (1981) 202–208. https://doi.org/10.1016/0032-3861(81)90199-3.