1. Materials and Methods

1.1 Materials

Poly(butylene adipate) diol (PBA) (Huakai Resin Co., Ltd., Shandong, China, M_n = 2000 Da) and polycaprolactone diol (PCL) (Merck, Germany, M_n = 2000 Da) were dried in a vacuum for 4 hours at 80 °C. The hydroxyl group content determined by the chemical method [18] was 1.7 wt.%. 2,4-toluene diisocyanate (TDI) and 1,6-hexamethylene diisocyanate (HMDI) from Merck (Germany) were distilled in vacuum at 50-55 °C/12 mm Hg and stored in sealed ampoules. Chain extender 1,4-butanediol (1,4-BD) from Merck (Germany) was distilled over freshly-powdered calcium hydride under reduced pressure. Dibutyltin dilaurate catalyst purchased from Merck (Germany) was used as received.

1.2. Synthesis of multi-block thermoplastic polyurethane (TPU)

Synthesis of multi-block copolymers was carried out by the three-reactor method developed by us earlier [19],[20]. Two crystallizing poly diols were used in different weight ratios PBA/PCL (in wt%) 0/100 for TPU-1(0/100), 50/50 for TPU-2(50/50), 80/20 for TPU-3(80/20), and 100/0 for TPU-4(100/0). Urethane-diol fragments based on aliphatic and aromatic diisocyanates and chain extender BD form the hard segment. In synthesized polymers the PCL and PBA blocks are linked in different combinations with bulky aromatic TDI and more flexible linear HMDI (Table 1). Upon reaching the degree of conversion of NCO groups of ca. 98 %, the reaction mass was poured into a flat Teflon container and dried at 40 °C during a day until constant weight. The control of the reaction was carried out by infrared spectra as complete disappearance of absorption bands of isocyanate (υ_{NCO} = 2272 cm^{-1}) and hydroxyl groups (υ_{OH} = 3623 cm^{-1}).

Table 1. Chemical composition of studied TPUs.

№	Sample	Polymer composition		SS, %		Mass fraction of reagents, %			SS/HS	HS,%
		A	B	A	B	Poly diol	diisocyanate	chain extender		
1	TPU-1(0/100)	-	PCL	0	100	69	23	8	2.2	31
2	TPU-2(50/50)	PBA	PCL	50	50	69	23	8	2.2	31
3	TPU-3(80/20)	PBA	PCL	80	20	69	23	8	2.2	31
4	TPU-4(100/0)	PBA	-	100	0	69	23	8	2.2	31

The hard segment content (HS, %) was calculated as follows:

$$\mathrm{HS}(\%) = \frac{(1+n)\,M(TDI+HMDI) + nM(\mathrm{BD})}{(1+n)\,M(TDI+HMDI) + nM(\mathrm{BD}) + M(poly\ diol)} * 100\%,$$

where *M(poly diol), M(TDI+HMDI)* and *M(BD)* are the molecular weights of PBA and/or PCL; diisocyanate and chain extender, respectively; n is the number of moles of BD.

Wide-angle X-ray scattering (WAXS) analysis of TPUs was performed using the ID02 ESRF, France with a 1.44 Å wavelength (λ). Exposure time was 1 s, the sample-to-detector distance was 120 mm. 2D diffraction patterns were recorded with a Eiger2 detector; the modulus of the scattering vector (s) was calibrated using several diffraction orders of silver behenate and performed in a home-built software environment. Degree of crystallinity (χ_{WAXS}) was calculated according to:

$$\chi_{WAXS} = \frac{\int I_{cr} * s^2 ds}{\int (I_{cr} + I_{amor}) * s^2 ds}$$

where Icr and Iamor – are the areas of all crystalline reflections and amorphous halo on 1D-reduced diffractograms. Crystallite size (D) was calculated using the Scherrer equation:

$$D = \frac{0.9\,\lambda}{\Delta s}$$

where Δs is FWHM of the selected diffraction peak.

Results

In Figure 3, X-ray diffractograms of the studied samples crystallized at 25 and -5°C are presented. Phase composition, d-spacing of the most intense reflections and crystal size are summarized in Table 4. TPU-1(0/100) shows crystalline reflections at s=0.239 and 0.265 Å-1 typical for orthorhombic structure of PCL [26]. The decrease in crystallization temperature from 25 to -5°C results in a significant increase of degree of crystallinity and crystal thickness (Figure 3, blue curves).

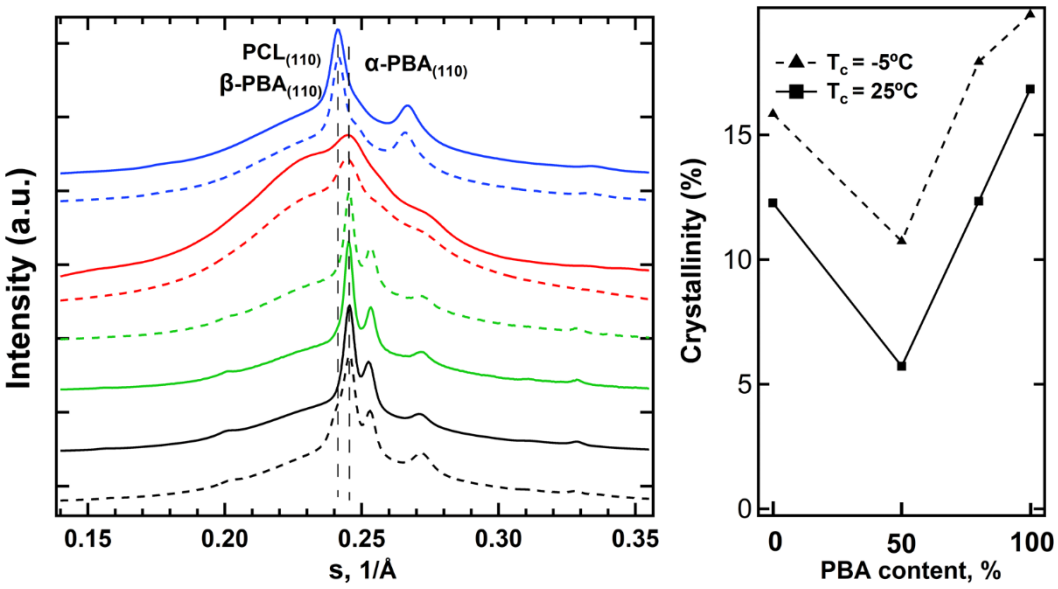
Table 2. Structural parameters of the studied samples obtained by WAXS.

T_c, °C	X_{WAXS}, %	PCL or β-PBA		α-PBA			D, nm
		X, %	d(110), Å	X, %	d(110), Å	d(020), Å	
TPU-1(0/100)							
25	12	12	4.18	-	-	-	14
-5	16	16	4.25	-	-	-	17
TPU-2(50/50)							
25	6	-	-	-	4.01	3.87	-
-5	11	-	-	-	4.03	3.85	-
TPU-3(80/20)							
25	12	-	-	12	4.09	3.96	20
-5	18	2	4.16	16	4.07	3.95	23 (PBA) 24 (PCL)
TPU-4(100/0)							
25	17	-	-	25	4.09	3.97	19
-5	20	5	4.18	15	4.10	3.98	18 (**α**) 13 (**β**)

For the TPU-2(50/50) a broad crystalline peak located at 0.248 $Å^{-1}$ is observed regardless of crystallization conditions. It consists of two overlapped peaks corresponding to the (110) reflections of the α-modifications of PBA and PCL. A small shoulder with d-spacing 3.87 Å related to (020) reflection of α-PBA is an additional evidence of α-PBA crystals formation. Failure to separate the broad peaks does not allow estimation of crystallite size.

For the TPU-3(80/20), α-PBA phase formation at both temperatures is observed. However, after crystallization at -5 °C appearance of a small peak at 0.240 $Å^{-1}$ and a broad peak with maximum at 0.272 $Å^{-1}$ indicates the presence of crystal phase of PCL (Figure 2, green curves).

The diffractogram of TPU-4(100/0) solely based on PBA crystallized at 25°C reveals formation of only α-modification of PBA with high degree of crystallinity (χWAXS = 17%). Crystallization at -5°C shows enhancement of crystallinity due to formation of β-phase with thinner crystals (Figure 3, black curves). In general, decrease of crystallization temperature leads to growth of PCL crystal fraction or formation of β-phase of PBA which is in agreement with the DSC results. The difference in crystallinity measured by DSC and WAXS can be explained by the influence of the adjacent HS on equilibrium melting enthalpy of SS. The dependence of phase composition on crystallization temperature can be associated with a balance between microsegregation of the blocks and nucleation rate. A detailed analysis of the phase separation of SS and HS in TPUs was performed by FTIR technique.



(a) (b)

Figure 2. WAXS diffractograms of TPU-1(0/100) (blue), TPU-2(50/50) (red), TPU-3(80/20) (green) and TPU-4(100/0) (black) crystallized at 25 °C (solid lines) and -5 °C (dashed lines) (a); degree of crystallinity as a function of PBA content of TPU after 24 h of crystallization (b)