Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Electronic Supplementary Information (ESI) for

Conformational changes in the heat-induced crystallization of poly(2-isopropyl-2-oxazoline) in solid state

Shengtong Sun ,*[a,b] and Peiyi Wu*[a]

[a] State Key Laboratory of Molecular Engineering of Polymers, Collaborative Innovation Center of Polymers and Polymer Composite Materials, Department of Macromolecular Science and Laboratory for Advanced Materials, Fudan University, Shanghai 200433, China

[b] State Key Laboratory of Chemical Engineering, East China University of Science and Technology, Meilong Road 130, Shanghai 200237, China.

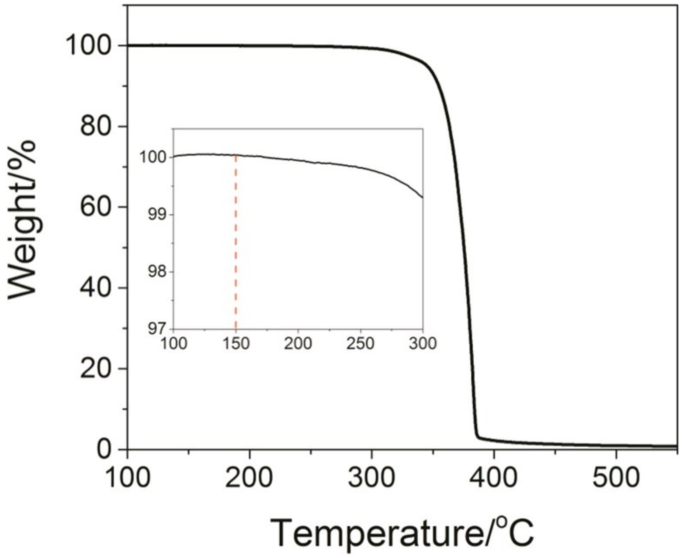

Fig. S1 TGA curve of annealed PIPOZ sample under N_2 at a heating rate of 10 °C·min^{-1}. The inset shows an enlarged view of TGA curve from 100 to 300 °C.

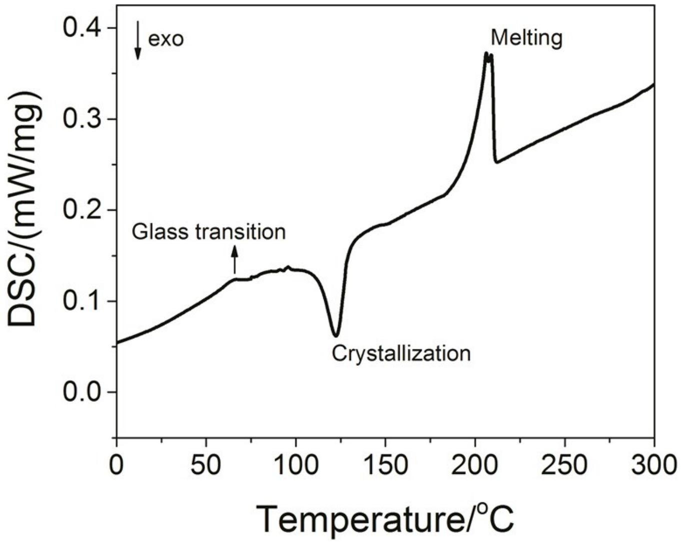

Fig. S2 DSC heating curve of annealed PIPOZ sample at a heating rate of 2 °C·min^{-1}.

Experimental details for molecular dynamics simulation

30 repeat units consisting of 572 atoms were chosen for constructing different PIPOZ chains. Molecular dynamics relaxation of amorphous PIPOZ chain was performed at a NVT (constant particle number, volume and temperature) ensemble at 298.15 K controlled by an Andersen thermostat[1] for 10,000 K steps (1 fs each) applying the Verlet velocity algorithm[2], which was implemented in the Discover module by a compass force field. To sufficiently relax the structure of PIPOZ, the PIPOZ chain was put in vacuum during simulation without a boundary, and energy deviation was controlled within 5000 kcal/mol. A cutoff of 9.5 Å was employed in the evaluation of Ewald sums[3] for non-bonded interactions. The torsion or dihedral angles in all repeat units along the PIPOZ backbone were counted manually by the measuring tools in the software package and the statistical distribution was further plotted, which can help us to evaluate the accessibility of different conformations of different group moieties. Crystalline PIPOZ chain with an all-trans backbone conformation was only slightly structurally optimized. Crystalline PIPOZ chain with a slightly distorted backbone conformation was constructed by structurally relaxing the backbone of the all-trans PIPOZ chain while fixing the conformations of side chains.

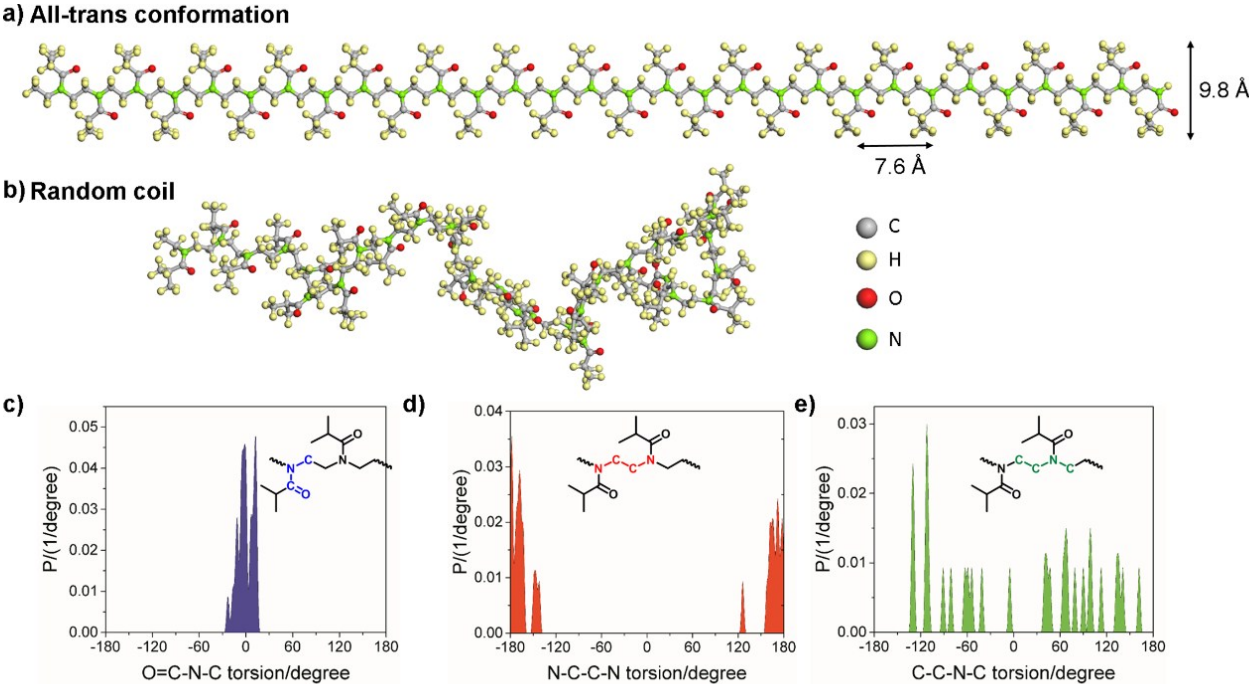

Fig. S3. PIPOZ chains with (a) all trans and (b) random coil conformations (30 repeat units). (c) O=C-N-C, (d) N-C-C-N, (e) C-C-N-C torsion distributions of PIPOZ in the structurally optimized random coil conformation. PIPOZ with all-trans conformation has highly ordered chain alignment with a periodicity along the backbone of ~7.6 Å, which could represent one possible conformation of crystalline PIPOZ chains.

Operation Details of Sequence Order Determination from 2DCOS Results

Noda's rule can be summarized as follows: if the cross-peaks (v_1, v_2, and assume $v_1 > v_2$) in synchronous and asynchronous spectra have the same sign, the change at v_1 may occur prior to that of v_2, and vice versa. Thus, we firstly listed all the signs of cross-peaks in asynchronous spectra, then turned back to list the corresponding signs in synchronous spectra. Multiplication was performed in succession on these two signs of each cross-peak. To each final sign of cross-peaks, two corresponding wavenumbers can be found on the left and bottom respectively. Because all the signs are above the diagonal line ($v_1 = v_2$) in accordance with our spectra-reading habits, the wavenumber on the bottom is affirmatively larger than the one on the left. Therefore, according to Noda's rule, if the sign is positive (+), the larger wavenumber or the bottom wavenumber will respond to external perturbation earlier than the smaller wavenumber or the left wavenumber. Similarly, if the sign is negative (-), the left wavenumber will respond earlier than the bottom one. If the sign is zero (or blank), we cannot make an exact judgment.

The following are final results of multiplication on the signs of each cross-peak in synchronous and asynchronous spectra.

1628	+	+	-	-	-	-	-	+	-	+	-	-	-	
1641	+	+	-	+	-	-	-	+	-	+	-	-		
1657	+	+	-	+	-	-	-	+	-	+	-			
1664	+	+	+	+	-	-	+	+	+	+				
2854	+	+	-	-	-	-	-	+	-					
2868	+	+	+	+	-	-	+	+						
2881		+	-	-	-	-	-							
2910	+	+	+	+	-	-								
2926	+	+	+	+	-									
2939	+	+	+	+										
2962	+	+	-											
2978	+	+												
2991														
3008														
	3008	2991	2978	2962	2939	2926	2910	2881	2868	2854	1664	1657	1641	1628

Thus we have the sequence order as follows:

3008, 2991 cm^{-1} → 2881 cm^{-1} → 2854 cm^{-1} → 1628 cm^{-1} → 2962 cm^{-1} → 1641 cm^{-1} → 1657 cm^{-1} → 2978 cm^{-1} → 2910 cm^{-1} → 2868 cm^{-1} → 1664 cm^{-1} → 2926 cm^{-1} → 2939 cm^{-1}.

References

1. H. C. Andersen, *J. Chem. Phys.*, 1980, 72, 2384-2393.
2. M. P. Allen and D. J. Tildesley, *Computer simulation of liquids*, Oxford university press, 1989.
3. N. Karasawa and W. A. Goddard III, *J. Phys. Chem.*, 1989, 93, 7320-7327.