Supporting information

Synergistic Molecular Design of Key Components to Address the Performance trade-off Challenge in Bio-Based Polyurethanes

Jun Du[a,b], Zhe Mei[a,b], Xinyi Shen[a,b], Qingcheng Du[a,b], Liwei Liao[a,b], Shijing Yan [a,b], Liying Liang [a,b*]

[a] School of Materials and Environment, Guangxi Minzu University, Nanning 530105, P. R. China.

[b] Guangxi Key Laboratory of Advanced Structural Materials and Carbon Neutralization, Guangxi Minzu University, Nanning 530105, China.

*Corresponding author:

A. Prof. Dr. Liying Liang, Email: 20210011@gxmzu.edu.cn

Table of contents

1. Materials and Experimental Methods

Materials:

All chemicals were used as received without further purification. Castor oil (CO, reagent grade), polycaprolactone diol (PCL, Mn = 2000 g·mol^{-1}), isosorbide (ISO, $C_6H_{10}O_4$, 97% purity, CAS: 652-67-5, Lot: C14345485). Commercial isosorbide is a mixture of the endo and the exo hydroxyl stereoisomers, with an exo to endo ratio of approximately 55:45 as reported in the literature [1], isophorone diisocyanate (IPDI, $C_{12}H_{18}N_2O_2$, 99% purity), dibutyltin dilaurate (DBTDL, $C_{32}H_{64}O_4Sn$, 95% purity), hexahydro-1,3,5-tris(hydroxyethyl)-s-triazine (HT, $C_9H_{21}N_3O_3$, 75% purity), and (3-aminopropyl)triethoxysilane (APTES, $C_9H_{23}NO_3Si$, 99% purity) were purchased from Macklin Biochemical Technology Co., Ltd. (Shanghai, China).

N,N-Dimethylformamide (DMF, C_3H_7NO, 99.8% purity) was supplied by Adamas Reagent Co., Ltd. (Shanghai, China). Ethanol (EtOH, CH_3CH_2OH, analytical grade, water content ≤ 0.3%) and phosphoric acid (H_3PO_4, analytical grade, ≥ 85 wt% in H_2O) were obtained from Aladdin Biochemical Technology Co., Ltd. (Shanghai, China). Sodium hydroxide (NaOH, pellets, 97%) was sourced from Zesheng Technology Co., Ltd. (Anhui, China).

Instrumentation:

Fourier transform infrared (FTIR) spectroscopy using an IRAffinity-1S spectrophotometer (Shimadzu Corporation, Japan) equipped with an ATR accessory. Spectra were recorded at room temperature in the wavenumber range of 400 to 4000 cm^{-1} with a resolution of 4 cm^{-1}, accumulating 32 scans per spectrum.

Thermogravimetric analysis (TGA) of the bio-based polyurethanes was performed using a STA-6000 synchronous thermal analyzer (PerkinElmer, USA). Approximately 3 mg of the sample was placed in a ceramic crucible and heated from 30 to 600 ℃ at a constant rate of 10 ℃/min under a nitrogen flow of 25 mL/min.

X-ray diffraction (XRD) patterns were acquired on an Ultima IV diffractometer (Rigaku, Japan) using Cu Kα radiation. The measurements were performed at room

temperature under operating conditions of 40 kV and 40 mA, with a scan range of 2θ from 10° to 60°.

Tensile tests were conducted at room temperature using a UTM4503S universal testing machine (Sansi Zongheng Technology Co., Ltd., Shenzhen, China) equipped with a 5 kN load cell. The system was operated at a sampling rate of 1000/5000 Hz, and deformation was monitored using a YSJ50/25-ZC extensometer. Dumbbell-shaped specimens with a gauge length of 35 mm were stretched at a crosshead speed of 20 mm/min, with an initial grip separation of 20 mm.

Methods:

FTIR spectra in the carbonyl region were deconvoluted to quantitatively analyze the hydrogen-bonding states. To ensure objectivity and reproducibility, all deconvolution procedures followed a standardized protocol: (1) initial peak positions were determined from second-derivative spectra to avoid subjective bias; (2) curve fitting was performed using Voigt functions (a Gaussian-Lorentzian convolution), which are widely recognized as the standard for accurately representing overlapping carbonyl bands in polymers such as polyurethanes and polyamides; (3) fitting convergence was strictly monitored, with the correlation coefficient (R^2)

The degradation behavior of the materials was evaluated via chemical degradation testing. Specifically, 0.05 g of each sample was placed in a 20 mL vial containing 5 mL of either H_3PO_4, 2.5 mol/L NaOH, or 1.5 mol/L NaOH solution. To aid dissolution, 5 mL of ethanol (EtOH) was added to each vial. The mixtures were then stirred at 320 rpm under ambient temperature until the films were completely dissolved, and the time required for complete dissolution being recorded.

All molecular dynamics (MD) calculations were performed using the Materials Studio software package. The COMPASS II force field was utilized in all simulations. Prior to the MD production runs, the system underwent energy minimization. During the simulations, temperature and pressure were maintained constant using the Berendsen thermostat and barostat, respectively. Van der Waals interactions were accounted for using the Ewald summation method with a cutoff radius of 1.2 nm.

Coulombic interactions were handled using the Particle Mesh Ewald (PME) method, with a grid spacing of 0.10 nm and a Fourier transform accuracy of 1.0×10^{-5}.

2. Comprehensive table of raw material feed ratios for three different types of synthesized bio-based polyurethanes

Table S1. Designation and formulation of the CO-BPU samples.

Samples	CO(g)	PCL(g)	ISO(g)	IPDI(g)	HT(g)	APTES(g)
CO-BPU	3	3	0	2.6	0.6	0

Table S2. Designation and formulation of the ISO-BPU samples.

Samples	CO(g)	PCL(g)	ISO(g)	IPDI(g)	HT(g)	APTES(g)
ISO-BPU-1	3	3	0.2	3	0.6	0
ISO-BPU-2	3	3	0.45	3.46	0.6	0
ISO-BPU-3	3	3	0.9	4.34	0.6	0
ISO-BPU-4	3	3	1.35	5.21	0.6	0

Table S3. Designation and formulation of the APTES-BPU samples.

Samples	CO(g)	PCL(g)	ISO(g)	IPDI(g)	HT(g)	APTES(g)
APTES-BPU-1	3	3	0.45	3.54	0.6	0.11
APTES-BPU-2	3	3	0.45	3.76	0.6	0.44
APTES-BPU-3	3	3	0.45	4.05	0.6	0.89
APTES-BPU-4	3	3	0.45	4.34	0.6	1.34

3. FTIR spectrum of bio-based polyurethane in the C=O stretching vibration region

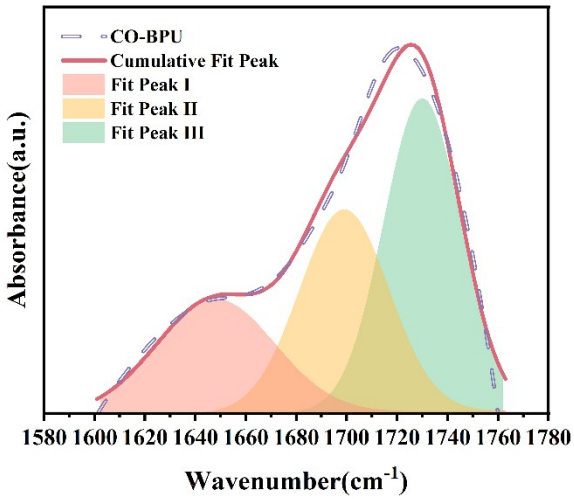

Fig. S1. FTIR spectra of the prepared CO-BPU samples in the C=O stretching vibration region.

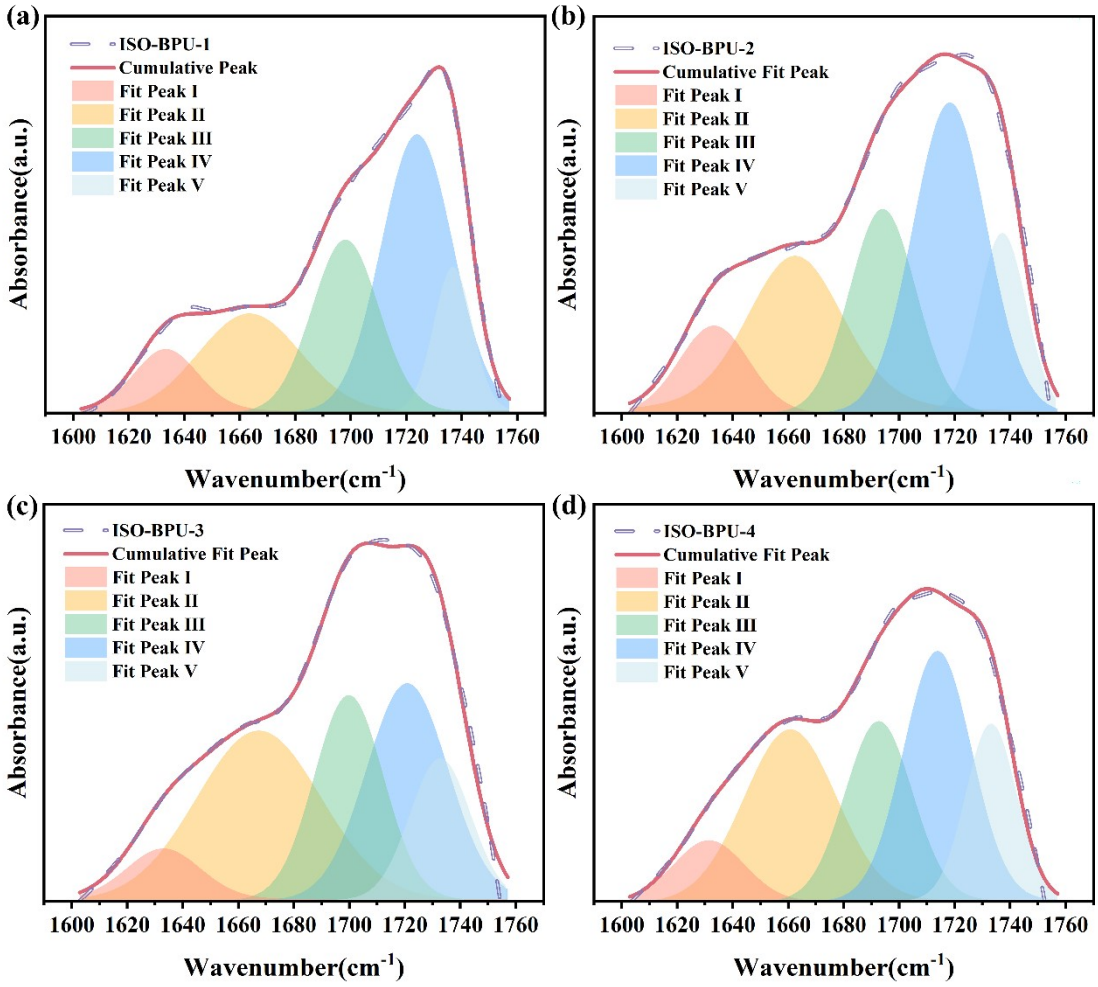

Fig. S2. FTIR spectra of the prepared ISO-BPU samples in the C=O stretching vibration region.

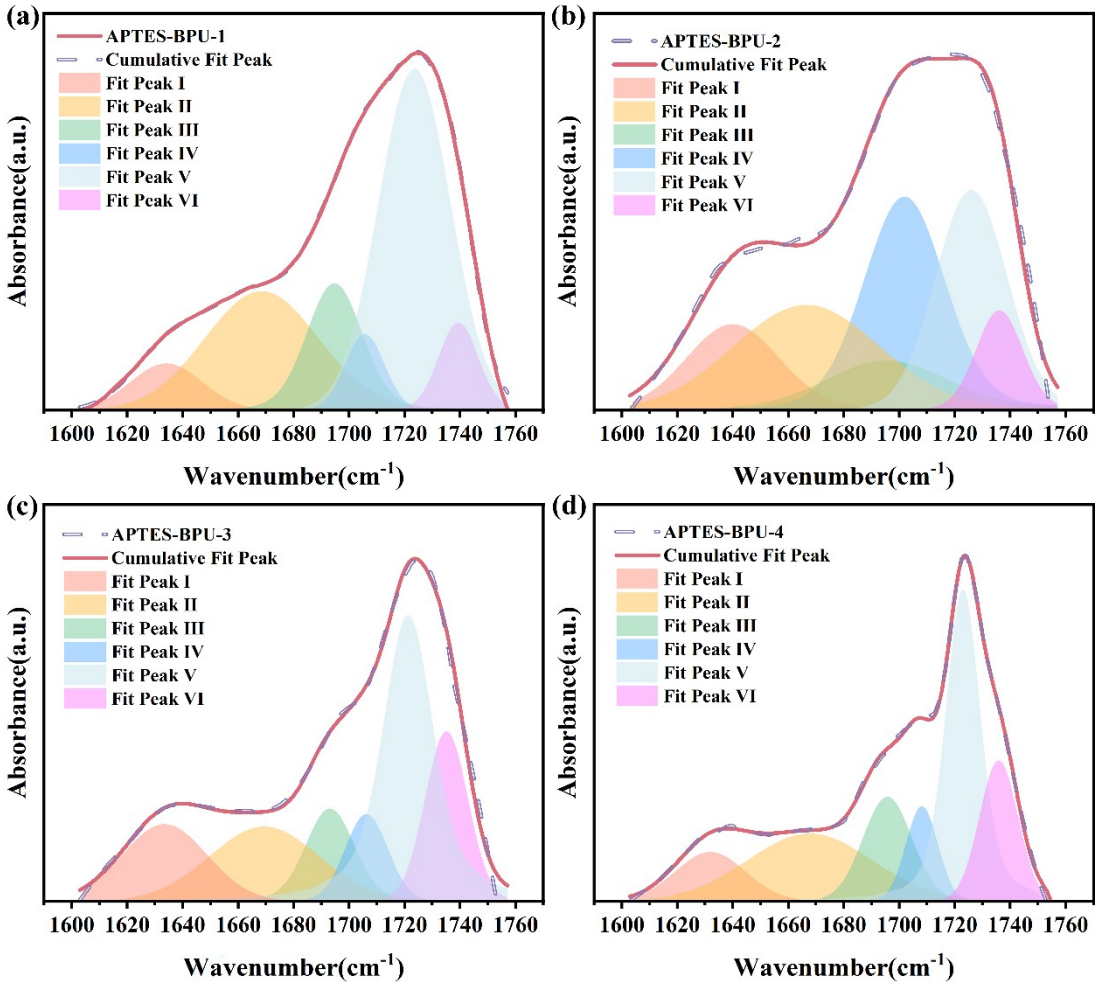

Fig. S3. FTIR spectra of the prepared APTES-BPU samples in the C=O stretching vibration region.

4. Summary table of subpeak assignments for C=O stretching vibration absorption peaks in FTIR spectra

Table S4. Fitting quality parameters (R^2) for the deconvolution of C=O stretching vibration region in FTIR spectra of all samples.

Quality Parameters	CO-BPU	ISO-BPU				APTES-BPU			
		1	2	3	4	1	2	3	4
R^2	0.979	0.997	0.989	0.990	0.985	0.999	0.987	0.984	0.999

Table S5. Summary of the Assignments of Deconvoluted Subpeaks for the C=O Stretching Vibration Absorption Band in the FTIR Spectrum of CO-BPU.

Assignment		Subpeak	Wavenumber(cm^{-1})	Area(%)
υ(C=O) urea amide	**H-bonded (Ordered)**	**I**	1648	24.0
	Free	**II**	1699	32.8
υ(C=O) ester urethane amide	**Free**	**III**	1730	43.2
Total degree of H-bonded				24.0

Table S6. Summary of the Assignments of Deconvoluted Subpeaks for the C=O Stretching Vibration Absorption Band in the FTIR Spectrum of ISO-BPU.

Assignment		Subpeak	Wavenumber(cm^{-1})				Area(%)			
			ISO				ISO			
			1	2	3	4	1	2	3	4
υ(C=O) urea amide	H-bonded (Ordered)	I	1633	1633	1633	1631	8.6	9.0	6.2	7.5
	H-bonded (Disordered)	II	1663	1662	1667	1660	19.8	24.2	32.2	27.3
	Free	III	1698	1694	1699	1692	22.4	20.2	21.7	20.7
υ(C=O) ester urethane amide	H-bonded (Ordered)	IV	1723	1718	1720	1713	38.4	33.9	26.9	29.2
	Free	V	1736	1737	1732	1733	10.8	12.6	13.0	15.3
Total degree of H-bonded							66.8	67.1	65.3	64.0

Table S7. Summary of the Assignments of Deconvoluted Subpeaks for the C=O Stretching Vibration Absorption Band in the FTIR Spectrum of APTES-BPU.

Assignment		Subpeak	Wavenumber(cm^{-1}) APTES				Area(%) APTES			
			1	2	3	4	1	2	3	4
υ(C=O) urea amide	H-bonded (Ordered)	I	1634	1639	1633	1631	6.1	11.9	13.6	9.1
	H-bonded (Disordered)	II	1668	1666	1669	1667	24.5	22.6	17.3	22.3
	Free	III	1694	1695	1693	1690	13.3	9.1	10.1	13.6
υ(C=O) ester urethane amide	H-bonded (Disordered)	IV	1705	1701	1706	1702	5.4	26.5	7.9	8.0
	H-bonded (Ordered)	V	1723	1725	1721	1721	44.5	23.1	35.7	32.8
	Free	VI	1739	1736	1735	1735	6.2	6.7	15.4	14.3
Total degree of H-bonded							80.5	84.1	74.5	72.2

Table S8. FTIR Phase Separation Table of the Prepared Bio-based Polyurethane in the Wavenumber Range of 1760–1600 cm^{-1}.

Symbol	A_b(%)	A_f(%)	R	DPS(%)	DPM(%)
CO-BPU	24.0	76.0	0.32	24.0	76.0
ISO-BPU-1	66.8	33.2	2.01	66.8	33.2
ISO-BPU-2	67.1	32.9	2.04	67.1	32.9
ISO-BPU-3	65.3	34.7	1.88	65.3	34.7
ISO-BPU-4	64.0	36.2	1.78	64.0	36.0
APTES-BPU-1	80.5	19.5	4.13	80.5	19.5
APTES-BPU-2	84.1	15.9	5.29	84.1	15.9
APTES-BPU-3	74.5	25.5	2.92	74.5	25.5
APTES-BPU-4	72.2	27.8	2.60	72.2	27.8

5. Normalized Analysis of Comprehensive Properties for the Prepared BPU Samples

Table S9. Normalized Performance Comparison of the Samples Relative to CO-BPU

	CO-BPU	**ISO-BPU-2**	**APTES-BPU-2**
Thermal Stability (℃)	1	1.01	1.02
Mechanical Strength (MPa)	1	3.11	7.02
Acidic Degradation (h)	1	2.74	2.87
Alkaline Degradation(h)	1	2.5	3.45

6. Degradation profiles of three different types of bio-based polyurethanes

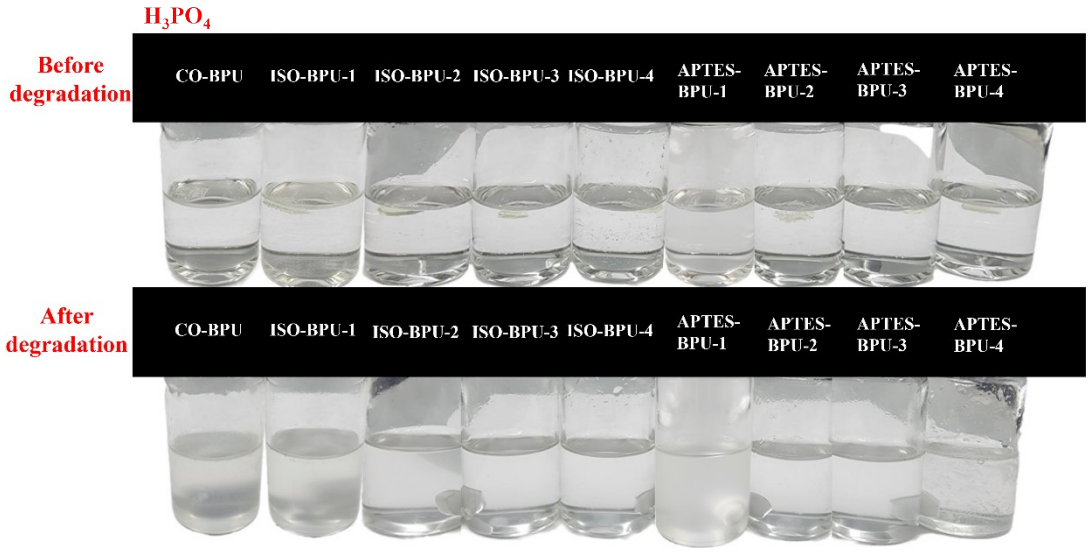

Fig. S4. Degradation process of the synthesized BPU sample in a 1:1 (v/v) mixture of H_3PO_4 (≥85 wt%) and ethanol.

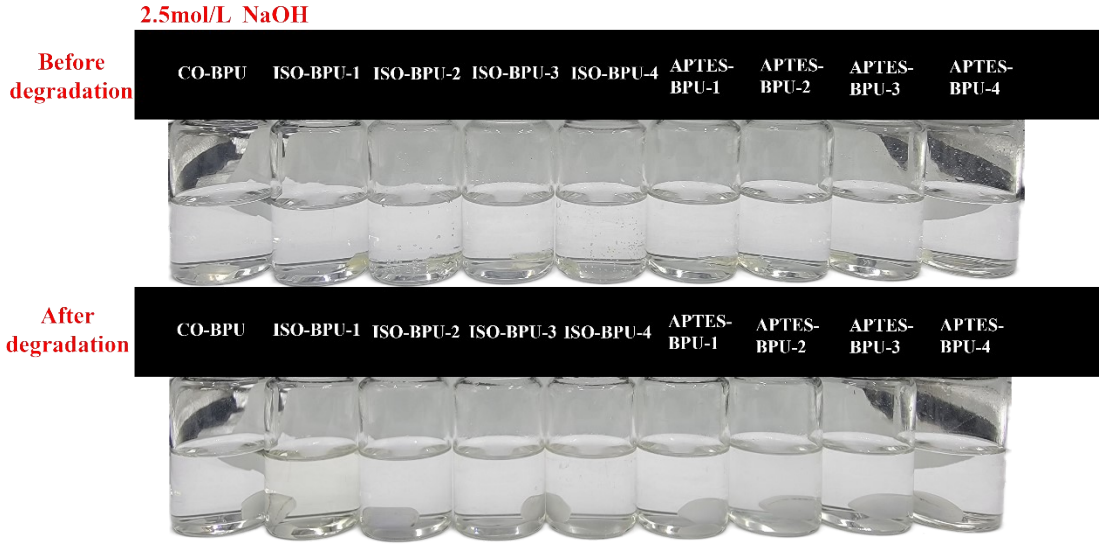

Fig. S5. Degradation process of the synthesized BPU sample in a 1:1 (v/v) mixture of NaOH (2.5 mol/L) and ethanol.

Fig. S6. Degradation process of the synthesized BPU sample in a 1:1 (v/v) mixture of NaOH (1.5 mol/L) and ethanol.

7. Degradation simulation

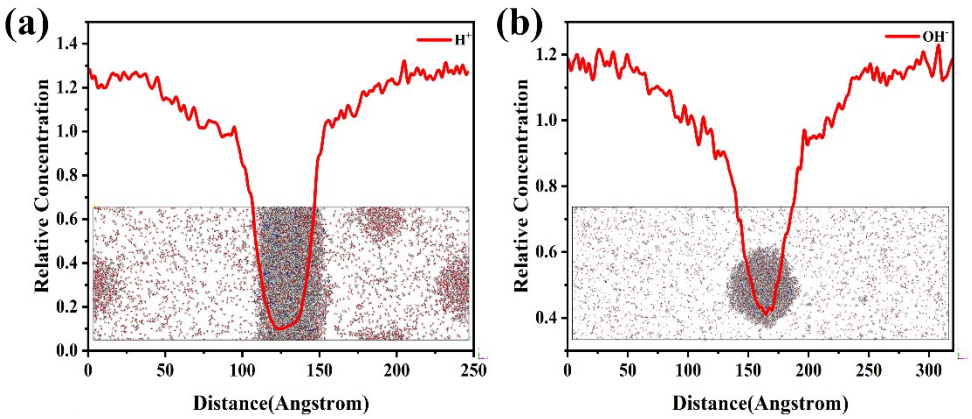

Fig. S7. Simulation of the degradation process for APTES-BPU: (a) degradation kinetic profile in an acidic environment; (b) degradation kinetic profile in an alkaline environment.

8. References

[1] S. Nica, S. Ionescu, A. Hanganu, M. Duldner, S. Iancu, A. Sarbu, P. Filip, E. Bartha, Mechanistic investigations of the organocatalytic depolymerization of PET waste with isosorbide, Rev. Chim. 69 (2018) 1319–1326. https://doi.org/10.37358/RC.18.6.6318.