

Synthesis of biodegradable PGA-PBC-PGA triblock copolymers and closed-loop recycling via a thermal depolymerization strategy

Yong Wang,^{a, b} Liang Wen,^{*c} Jiajian Liu,^{*a} Chuncheng Li,^{*a} Zijian Zhang,^c Yaonan Xiao,^a Tian Yin,^c Shaohua Wu,^a Zhikui Jiang,^c and Bo Zhang^a

^a Beijing National Laboratory for Molecular Sciences, Key Laboratory of Engineering Plastics, Institute of Chemistry, Chinese Academy of Sciences (ICCAS), Beijing 100190, P. R. China.

^b University of the Chinese Academy of Sciences, Beijing 100049, P. R. China.

^c China Shenhua Coal to Liquid and Chemical Co., Ltd. Beijing 100011, China.

Supplementary Information 1-Further explanation on DMA

As the PGA content decreases, the storage modulus of the triblock copolymer gradually decreases. This indicates a gradual decrease in the stiffness of the copolymers. This is consistent with the high PGA modulus and low PBC modulus. In addition, within the low temperature range (<0 °C), as the PGA content decreases, The T_g of the PBC segments gradually moves towards the high-temperature direction in the loss modulus and ($\tan\delta$). However, the T_g of PGA (40.7 °C by DSC) and the T_m of PBC (52.3 °C by DSC) are too close. Therefore, within the range of 40 °C - 80 °C, there is a transition from glass state to high elastic state in the PGA segments, as well as a transition from high elastic state to viscous flow state in the PBC segments. The T_g of PGA in DMA is affected by the melting of PBC segments, and the results are not accurate. It is difficult to completely distinguish between the two, which affects the accuracy of the T_g of PGA. But within -50 °C - 0 °C, there is only a phase transition of PBC from glass state to high elastic state, so the T_g of PBC is accurate. We can observe the T_g of the PBC chain segments in PGA-PBC-PGA90 in DMA, which is not observed in DSC. It also can be seen that the changes in T_g are consistent with those measured by DSC from the DMA curves.

Table S1 Conversion rate of GL at different times.

Time (min)	15	20	25	30	45	60	90	120	150	180
Conversion (%)	87.9	90.6	93.4	95.7	98.4	98.6	98.7	98.7	98.8	98.8

Table S2 Diffusion coefficients of different characteristic peaks of PGA-PBC-PGA.

Sample	Diffusion coefficient of peak b	Diffusion coefficient of peak c	Diffusion coefficient of peak d
PGA-PBC-PGA40	5.91×10^{-12}	5.50×10^{-12}	5.50×10^{-12}
PGA-PBC-PGA50	4.93×10^{-12}	4.23×10^{-12}	4.23×10^{-12}
PGA-PBC-PGA60	4.42×10^{-12}	3.82×10^{-12}	3.82×10^{-12}
PGA-PBC-PGA70	1.65×10^{-12}	1.19×10^{-12}	1.19×10^{-12}

Table S3 Degradation residual weights of PGA-PBC-PGA in the presence and absence of enzymes.

Samples Conditions	Residue weight (%)							
	PGA	PGA90	PGA80	PGA70	PGA60	PGA50	PGA40	PBC
Enzymatic	3.71	36.56	58.16	65.36	74.80	83.30	86.62	95.84
Without enzymatic	13.97	55.98	66.19	73.90	77.32	89.88	91.34	99.04

Table S4 The structural composition of PGA-PBC-PGA copolymers before degradation, after enzymatic degradation, and after non-enzymatic degradation.

Samples Conditions	PGA90	PGA80	PGA70	PGA60	PGA50	PGA40
	Before degradation	90.0	80.0	70.0	60.0	50.0
Enzymatic catalyzed degradation	79.6	70.2	57.0	51.9	42.7	34.2
Non-enzymatic catalyzed degradation	78.4	69.9	56.7	49.9	42.4	33.3

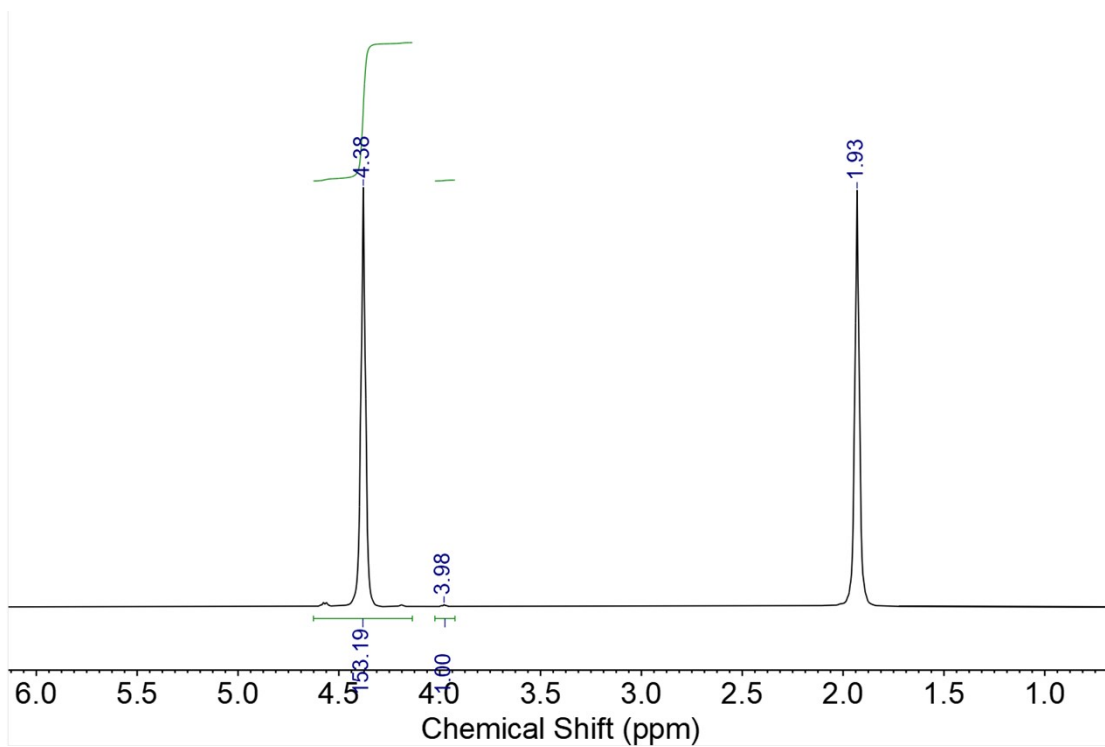


Fig.S1 ¹H NMR spectra of PBC-OH.

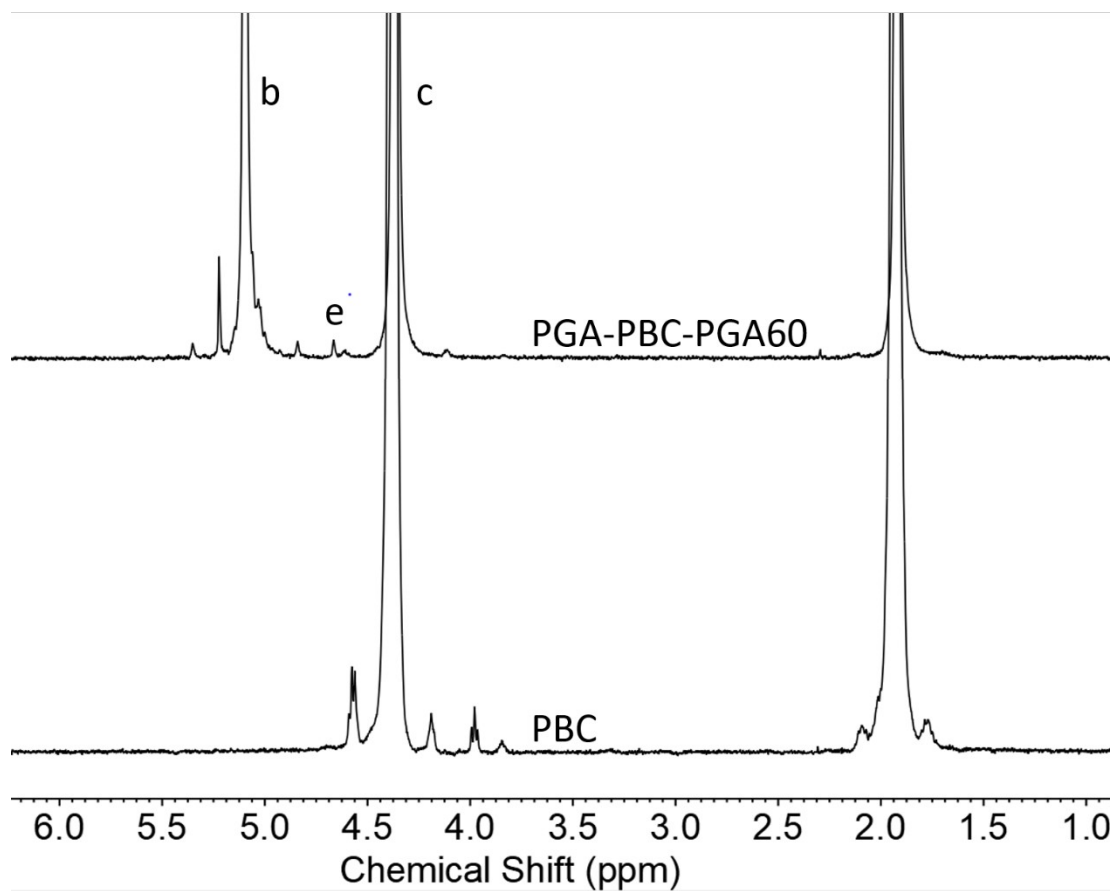


Fig.S2 ¹H NMR spectra of PGA-PBC-PGA60 and PBC-OH.

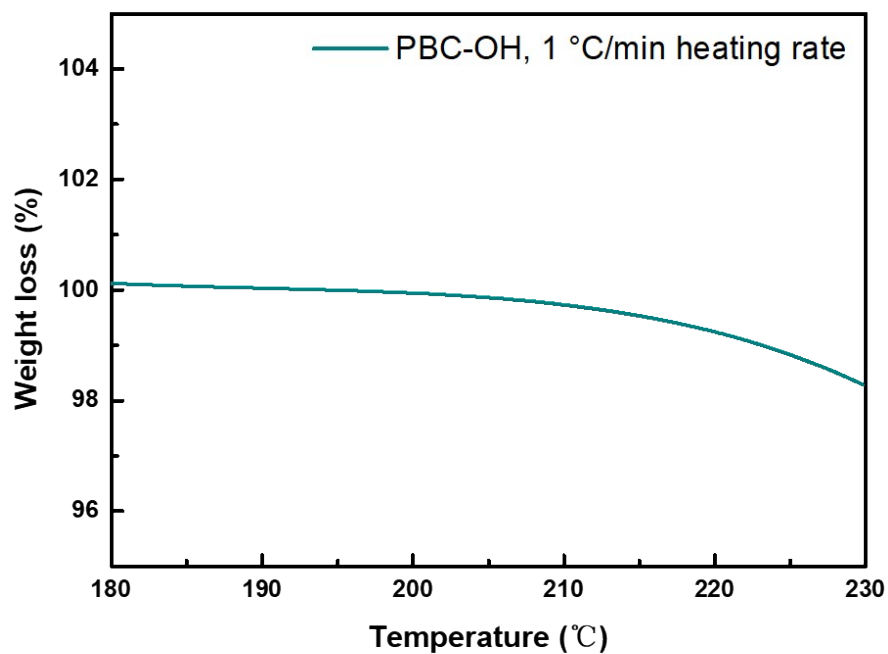


Fig.S3 TGA curve of PBC-OH at a heating rate of 1 °C /min.

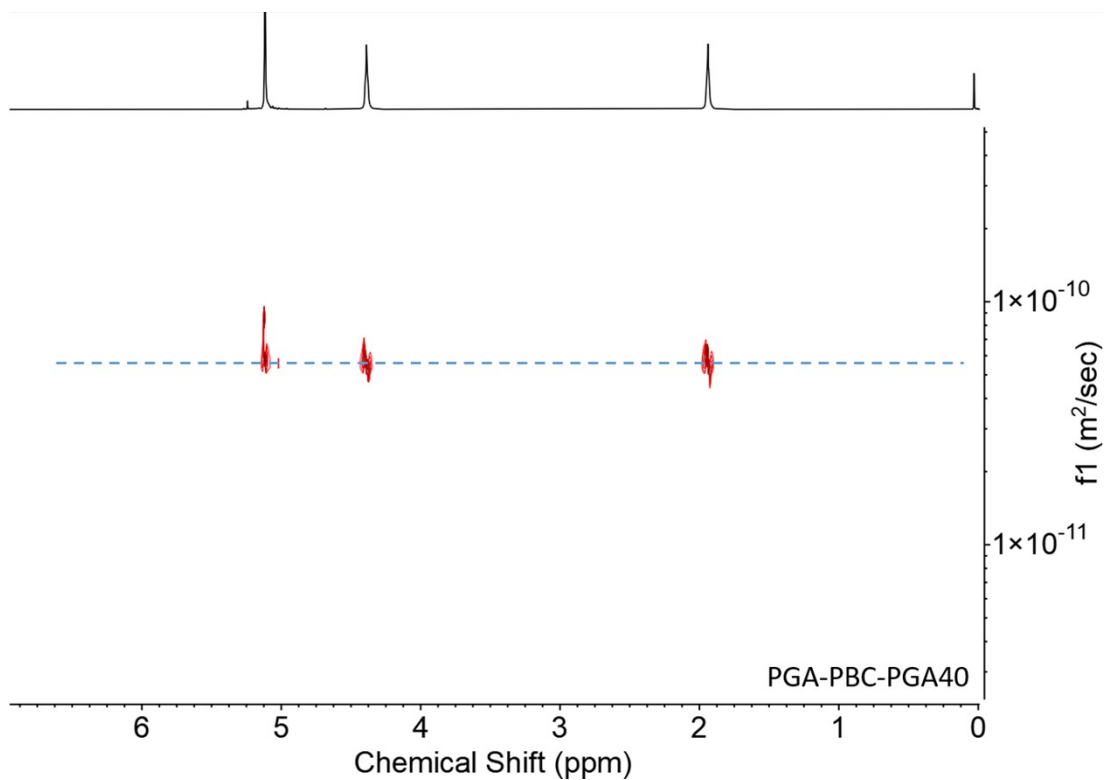


Fig.S4 DOSY spectra of PGA-PBC-PGA40.

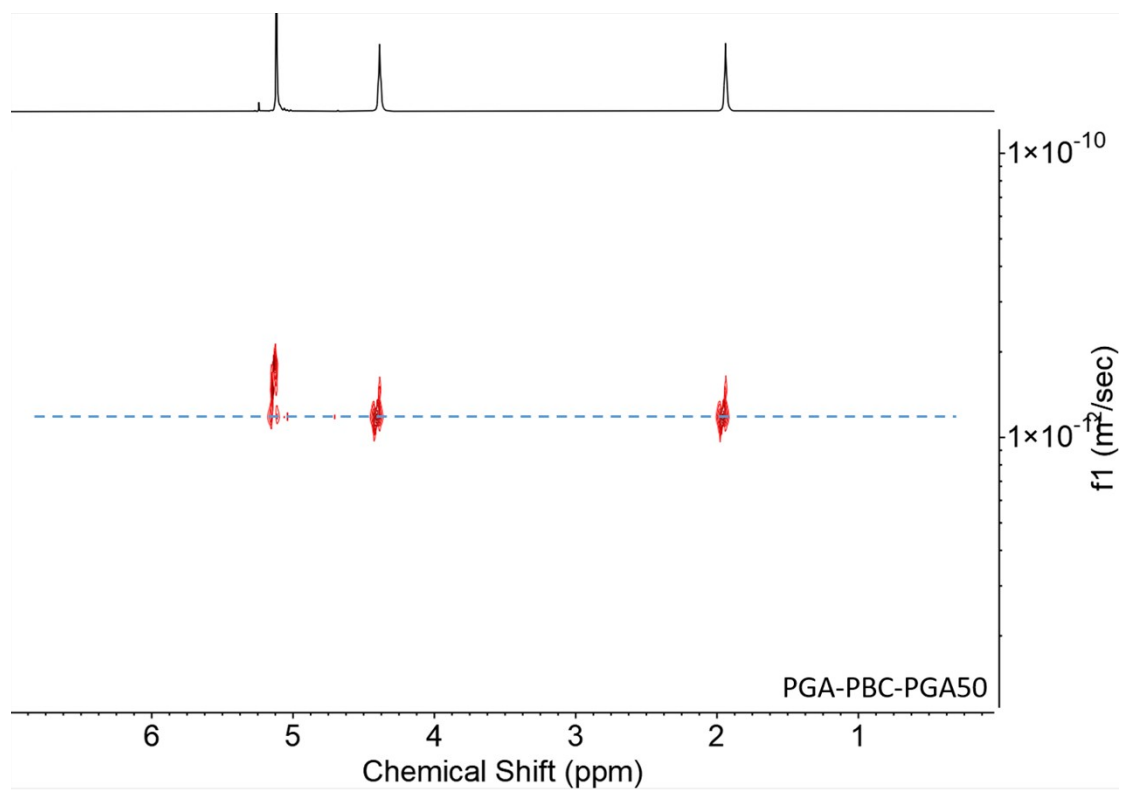


Fig.S5 DOSY spectra of PGA-PBC-PGA50.

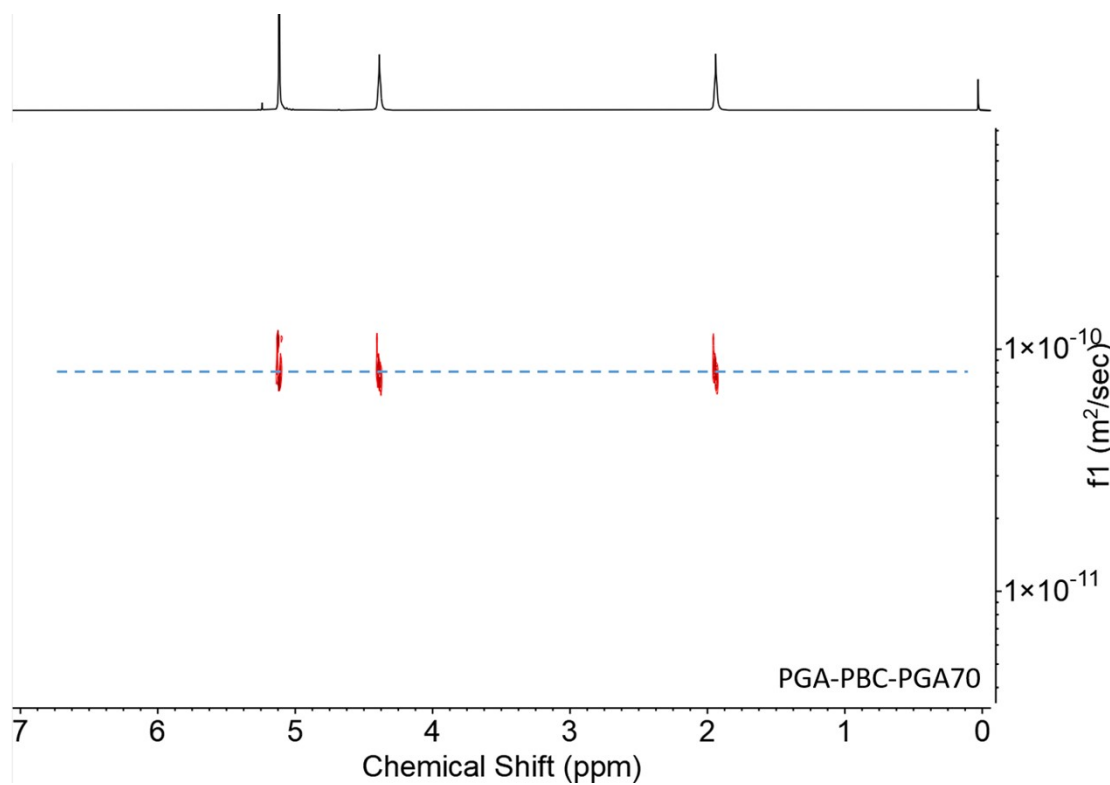
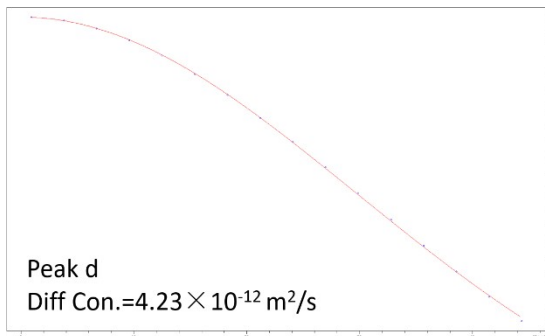
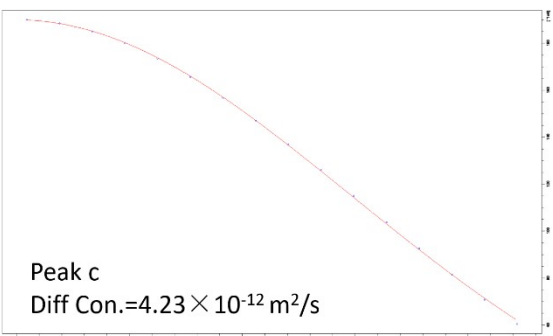
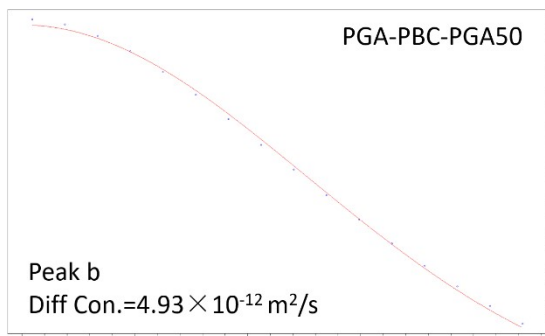
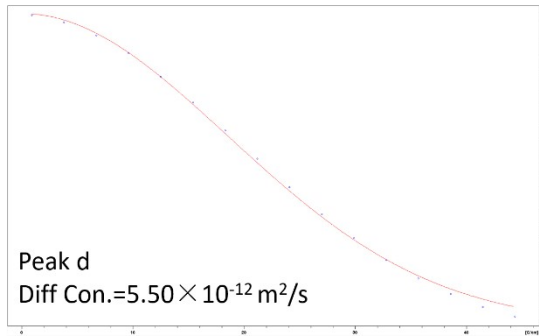
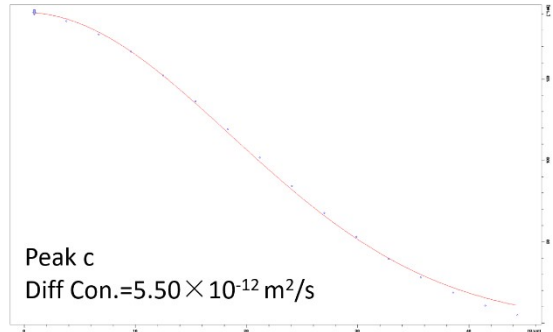
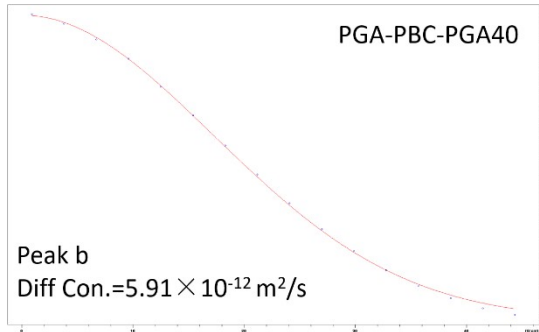


Fig.S6 DOSY spectra of PGA-PBC-PGA70.



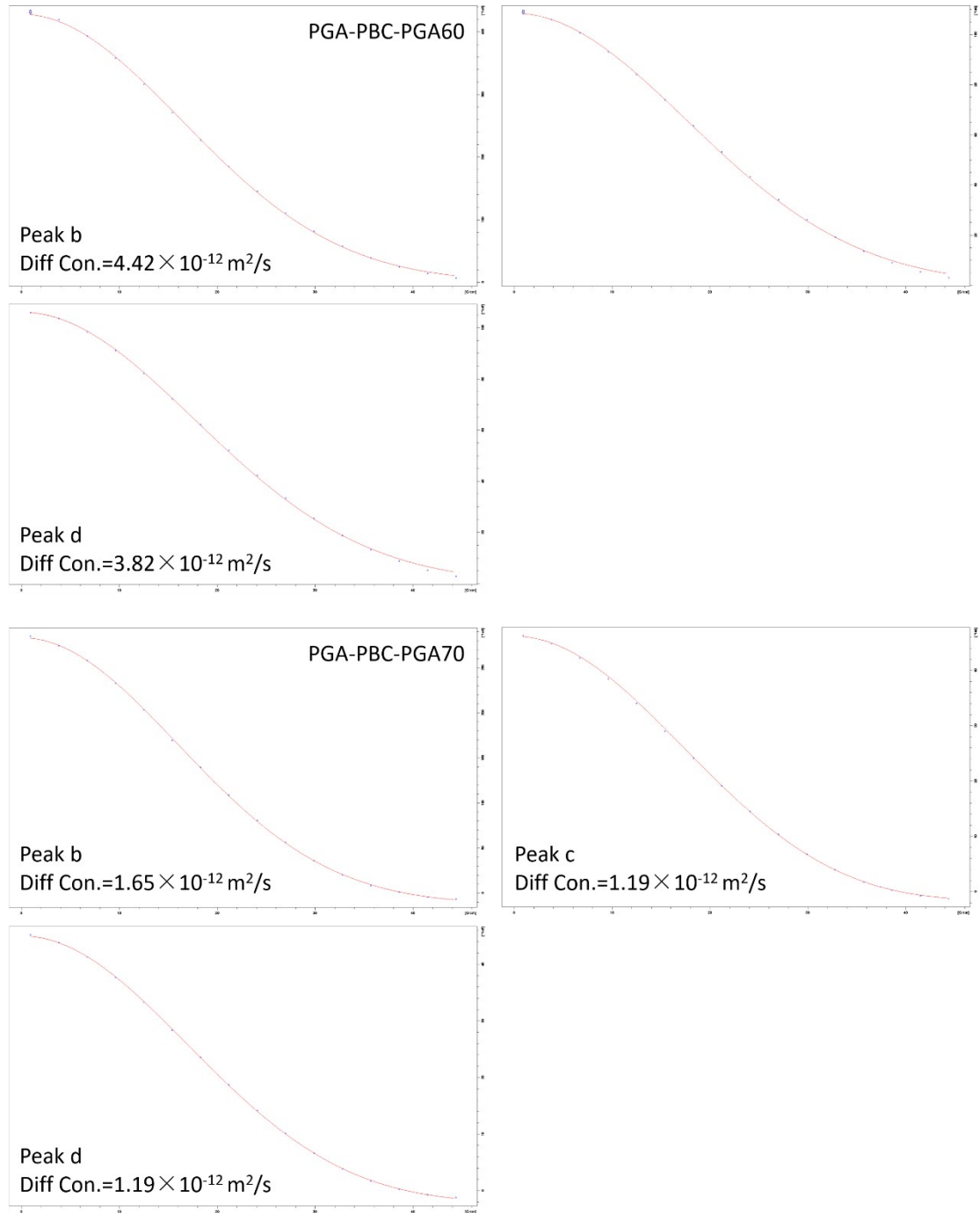


Fig.S7 Fitting curves of diffusion coefficients for different characteristic peaks of PGA-PBC-PGA.

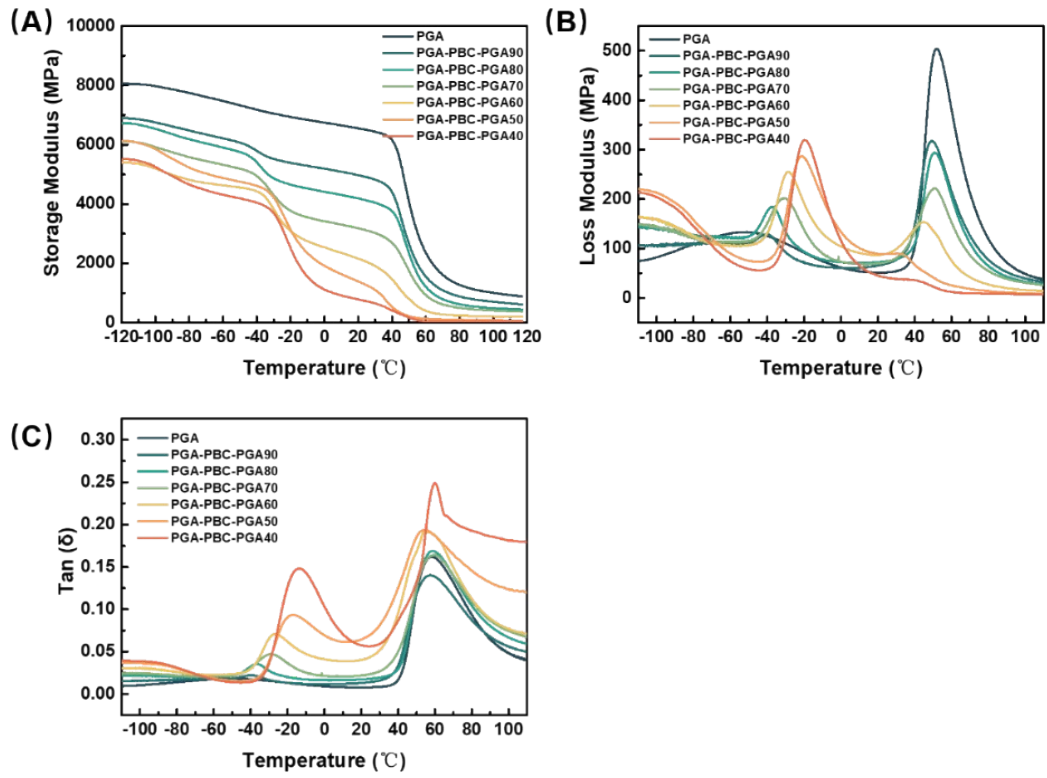


Fig.S8 DMA curves of PGA-PBC-PGA.

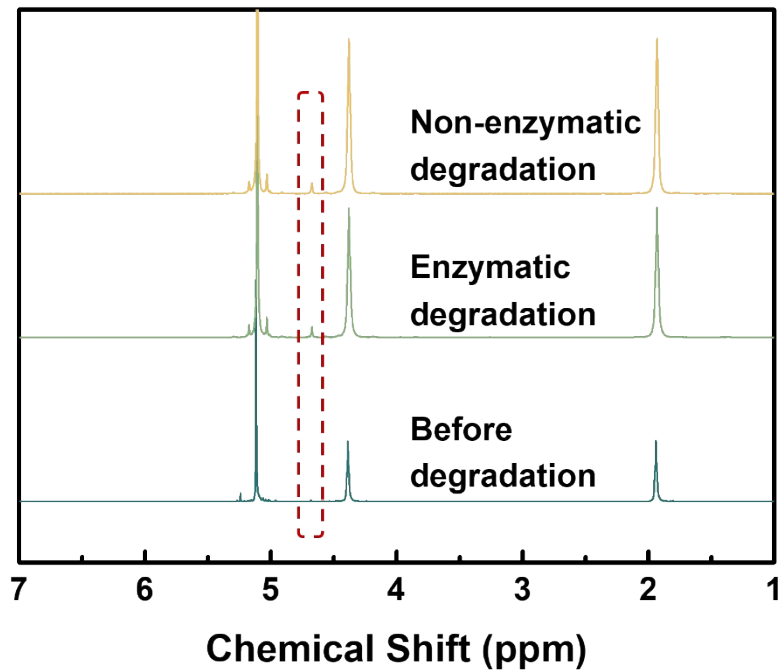
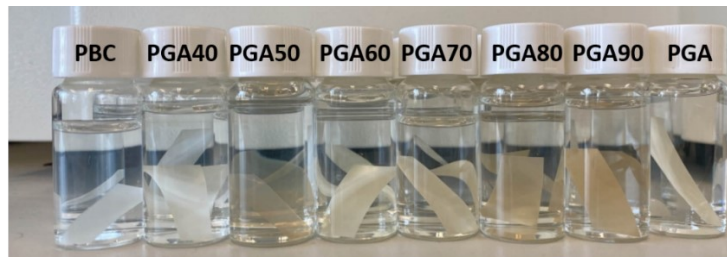
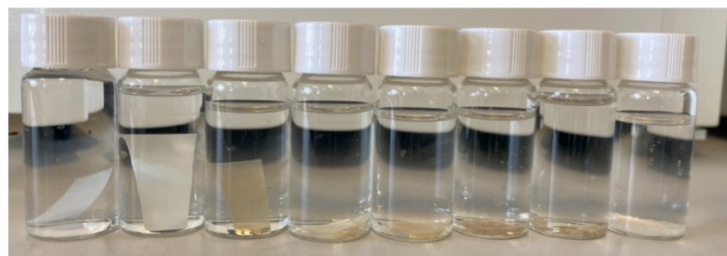


Fig.S9 ¹H NMR spectra of PGA-PBC-PGA60 before degradation, after enzymatic degradation, and after non-enzymatic degradation.

0 day



14 days



28 days



Fig.S10 Pictures of degradation of PGA-PBC-PGA at different times.

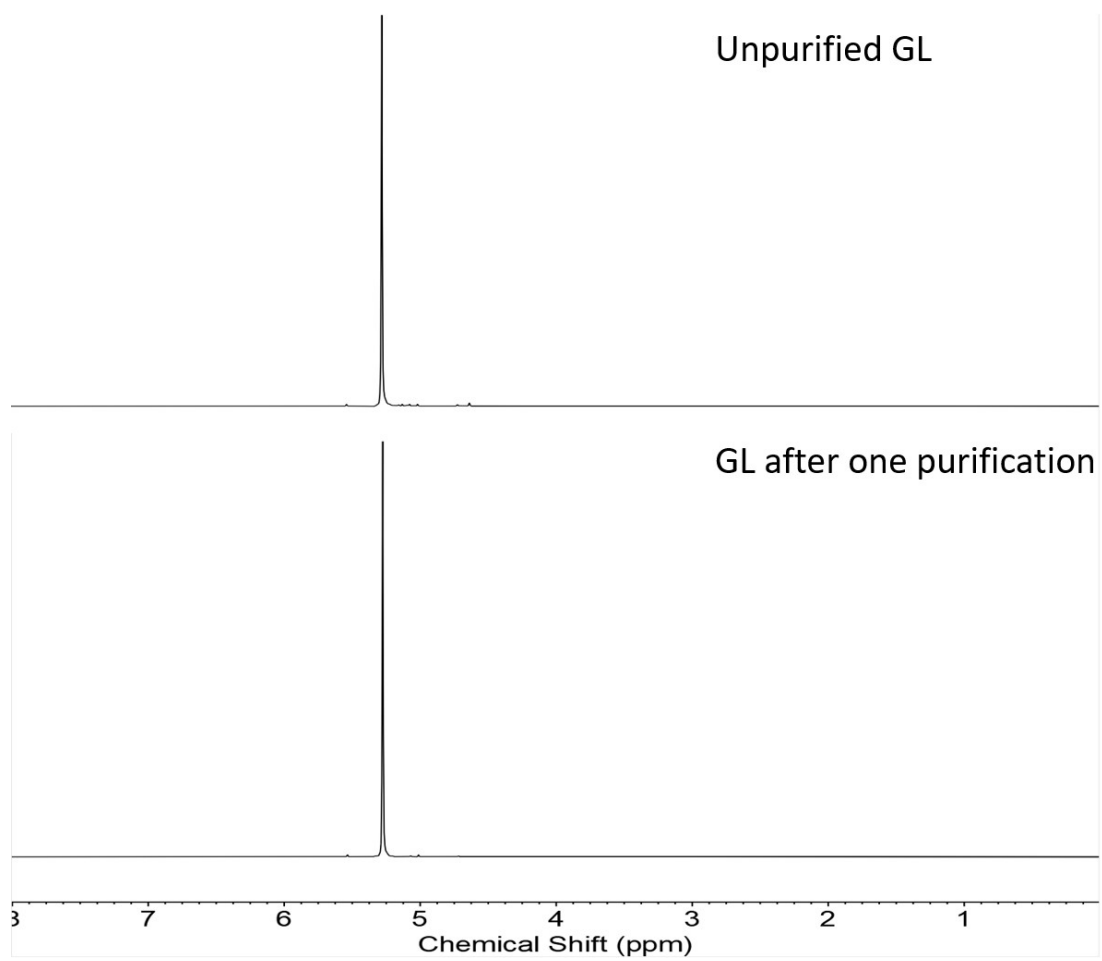


Fig.S11 GL after decomposition of PGA-PBC-PGA60 and after one purification.