Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting Information

Recyclable Sulfone-Containing Polymers via Ring-Opening Polymerization of Macroheterocyclic Siloxane Monomers: Synthesis, Properties and Recyclability

Mengdong Guo, Yue Huang, Jinfeng Cao, Guibao Sun, Xia Zhao, Jie zhang* and Shengyu Feng*

E-mail: fsy@sdu.edu.cn

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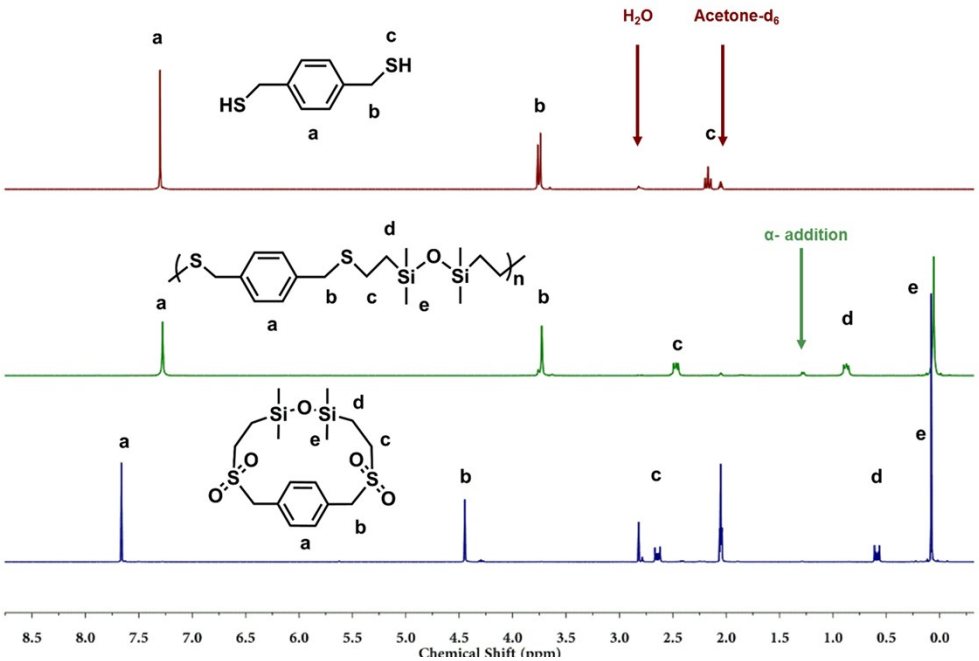

Fig. S1 ^{1}H NMR spectrum of R1 and P1 and P1OX

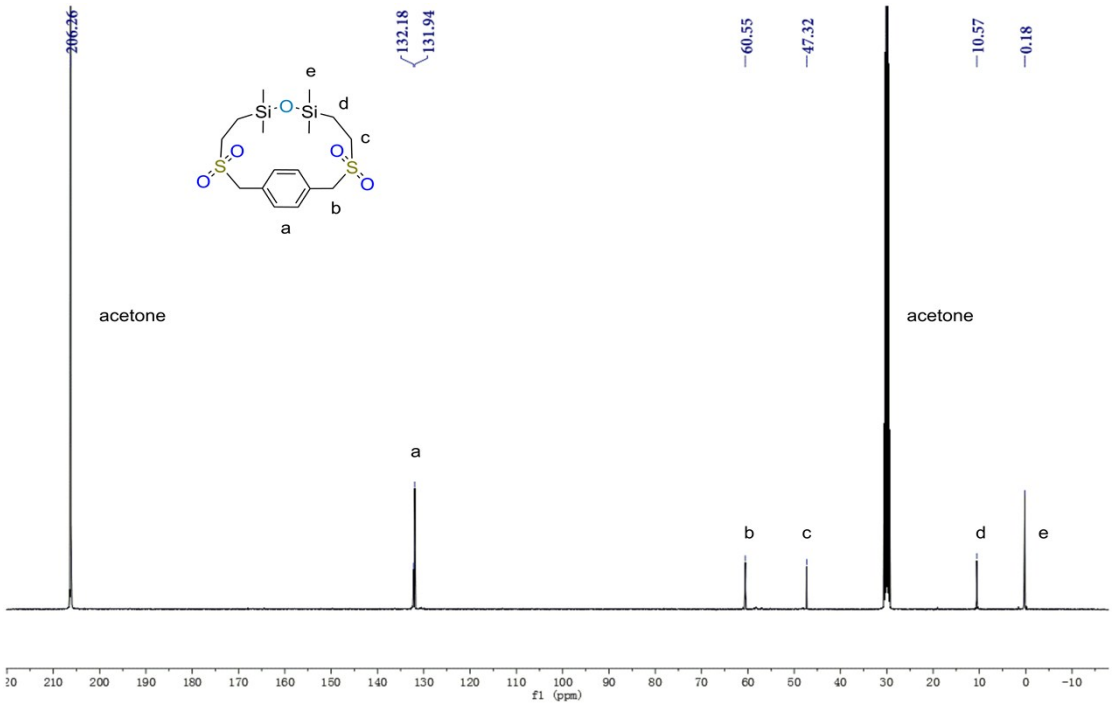

Fig. S2 ^{13}C NMR spectrum of P1OX

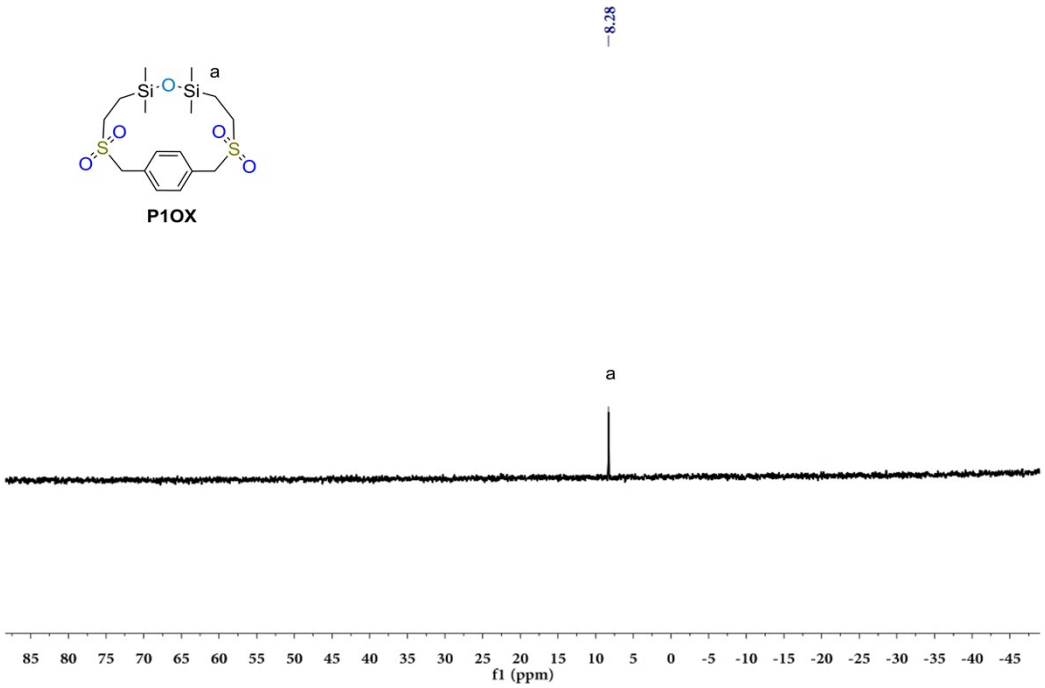

Fig. S3 ^{29}Si NMR spectrum of P1OX

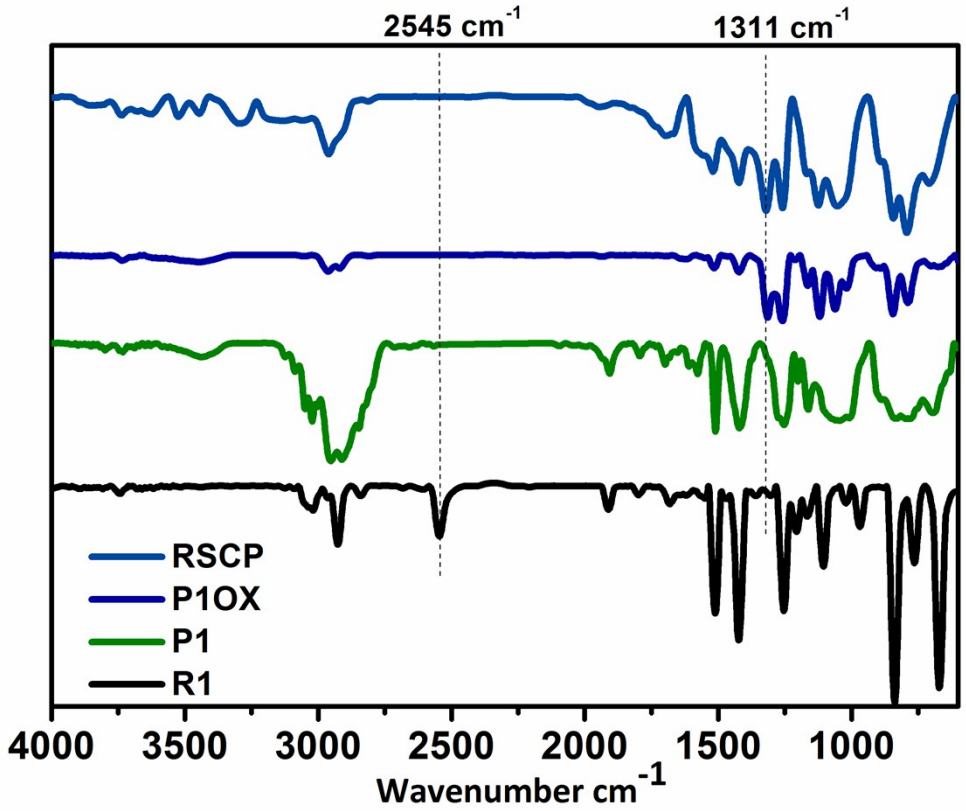

Fig. S4 Infrared spectra of R1 and P1 and P1OX and RSCP

Crystal Structure Determination.

Single crystals of P1OX suitable for X-ray structural analysis were obtained by diffusing H_2O into its DMSO solution. The data was collected on a Bruker Apex II single crystal diffractometer, employing a Mo Kα radiation (λ = 0.71073 Å) and a CCD area detector. The raw frame data were processed using SAINT and SADABS to yield the reflection data file.[1] The structure was solved using the charge-flipping algorithm, as implemented in the program *SUPERFLIP*[2] and refined by full-matrix least-squares techniques against F_o^2 using the SHELXL program[3] through the OLEX2 interface.[4] Hydrogen atoms at carbon were placed in calculated positions and refined isotropically by using a riding model. Selected bonds (Å) and angles (°) for P1OX are given in **Table S1**. Crystal data and processing parameters for P1OX are given in **Table S2.**

The CCDC number is 1888686.

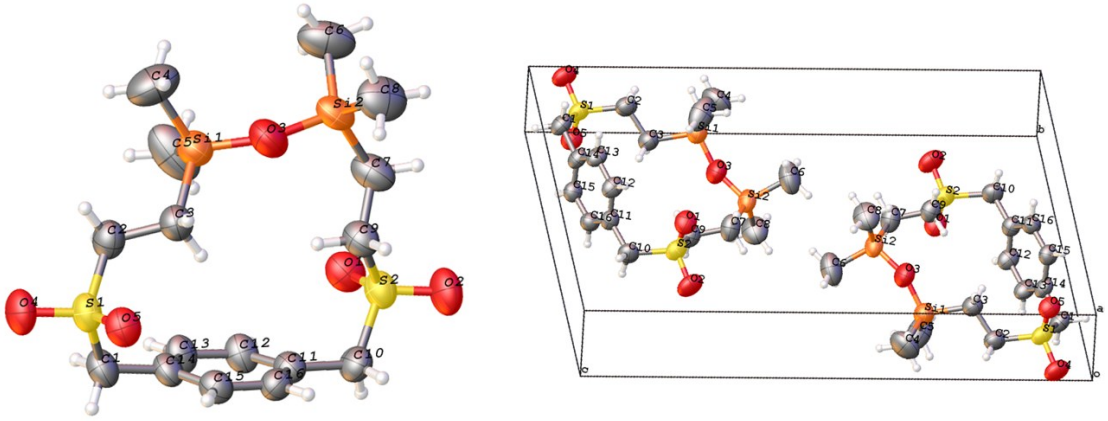

Table S1 Selected bonds (Å) and angles (°) for P1OX

Selected Bonds					
Atom	Atom	Length/Å	Atom	Atom	Length/Å
O1	S2	1.441(4)	C6	Si2	1.865(6)
O2	S2	1.432(3)	C7	Si2	1.863(6)
O3	Si1	1.621(4)	C7	C9	1.523(7)
O3	Si2	1.629(4)	C8	Si2	1.834(6)
O4	S1	1.445(3)	C9	S2	1.784(5)
O5	S1	1.438(3)	C10	S2	1.781(5)
C1	S1	1.792(5)	C10	C11	1.509(6)
C1	C14	1.505(6)	C11	C12	1.388(6)
C2	S1	1.773(5)	C11	C16	1.380(6)
C2	C3	1.516(6)	C12	C13	1.382(6)
C3	Si1	1.863(5)	C13	C14	1.383(6)
C4	Si1	1.842(7)	C14	C15	1.388(6)
C5	Si1	1.833(7)	C15	C16	1.383(6)

Selected Angles							
Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
Si1	O3	Si2	152.5(3)	C5	Si1	C3	109.3(3)
O1	S2	C9	107.9(2)	C5	Si1	C4	110.2(4)
O1	S2	C10	108.6(2)	C7	Si2	C6	109.7(3)
O2	S2	O1	116.6(2)	C7	C9	S2	110.7(3)
O2	S2	C9	109.7(2)	C8	Si2	C6	109.8(3)
O2	S2	C10	107.7(2)	C8	Si2	C7	110.2(3)
O3	Si1	C3	106.1(2)	C9	C7	Si2	115.6(4)
O3	Si1	C4	109.4(3)	C10	S2	C9	105.8(2)
O3	Si1	C5	111.7(3)	C11	C10	S2	114.6(3)
O3	Si2	C6	110.3(3)	C11	C16	C15	121.1(4)
O3	Si2	C7	109.2(2)	C12	C11	C10	121.1(4)
O3	Si2	C8	107.8(3)	C12	C13	C14	120.7(4)
O4	S1	C1	106.1(2)	C13	C12	C11	120.3(4)
O4	S1	C2	107.5(2)	C13	C14	C1	119.5(4)
O5	S1	O4	116.9(2)	C13	C14	C15	119.0(4)
O5	S1	C1	108.8(2)	C14	C1	S1	115.1(3)
O5	S1	C2	109.8(2)	C15	C14	C1	121.5(4)
C2	S1	C1	107.2(2)	C16	C11	C10	120.2(4)
C2	C3	Si1	112.6(3)	C16	C11	C12	118.8(4)
C3	C2	S1	116.5(3)	C16	C15	C14	119.9(4)
C4	Si1	C3	110.1(3)				

Table S2 Crystal data and structure refinement for P1OX.

Complex	**P1OX**
Empirical formula	$C_{16}H_{28}O_5S_2Si_2$
Formula weight	420.68
Temperature / K	293
Crystal system	Triclinic
Space group	P1
a / Å, b/ Å, c/ Å	6.2499(2), 9.4654(3), 19.2084(5)
α / °, β / °, γ / °	78.460(3), 84.048(3), 78.306(3)
Volume / Å^3	1087.90(6)
Z	2
ρ_{calc} mg / mm^3	1.284
μ / mm^{-1}	3.467
F(000)	448
Crystal size / mm^3	0.05 × 0.02 × 0.01
Theta range for data collection	4.991 to 67.077°
Index ranges	$-7 \le h \le 6$, $-11 \le k \le 10$, $-22 \le l \le 22$
Reflections collected	10149
Independent reflections	3858 [R(int) = 0.0668]
Data/restraints/parameters	3858/0/230
Goodness-of-fit on F^2	1.185
Final R indexes [I>2σ (I)]	R_1 = 0.0613, wR_2 = 0.1863
Final R indexes [all data]	R_1 = 0.0772, wR_2 = 0.2026
Largest diff. peak/hole / e Å^{-3}	0.368/-0.388

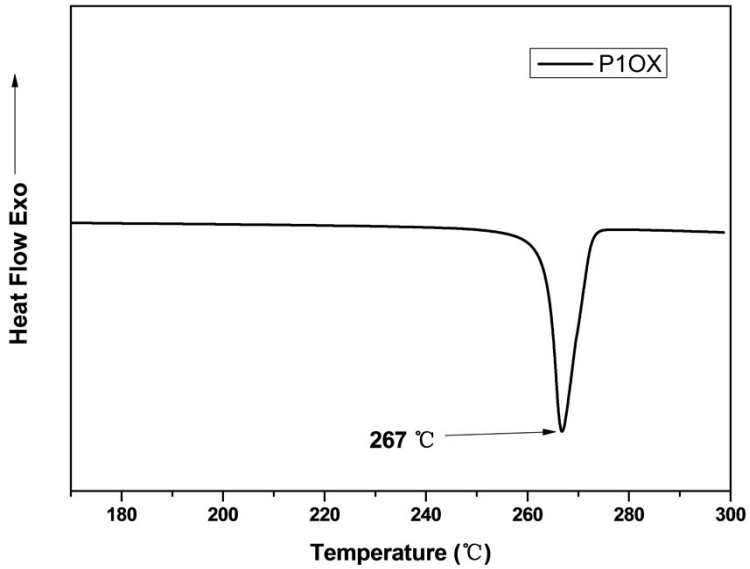

Fig. S5 The melting point (T_m) of P1OX measured by DSC.

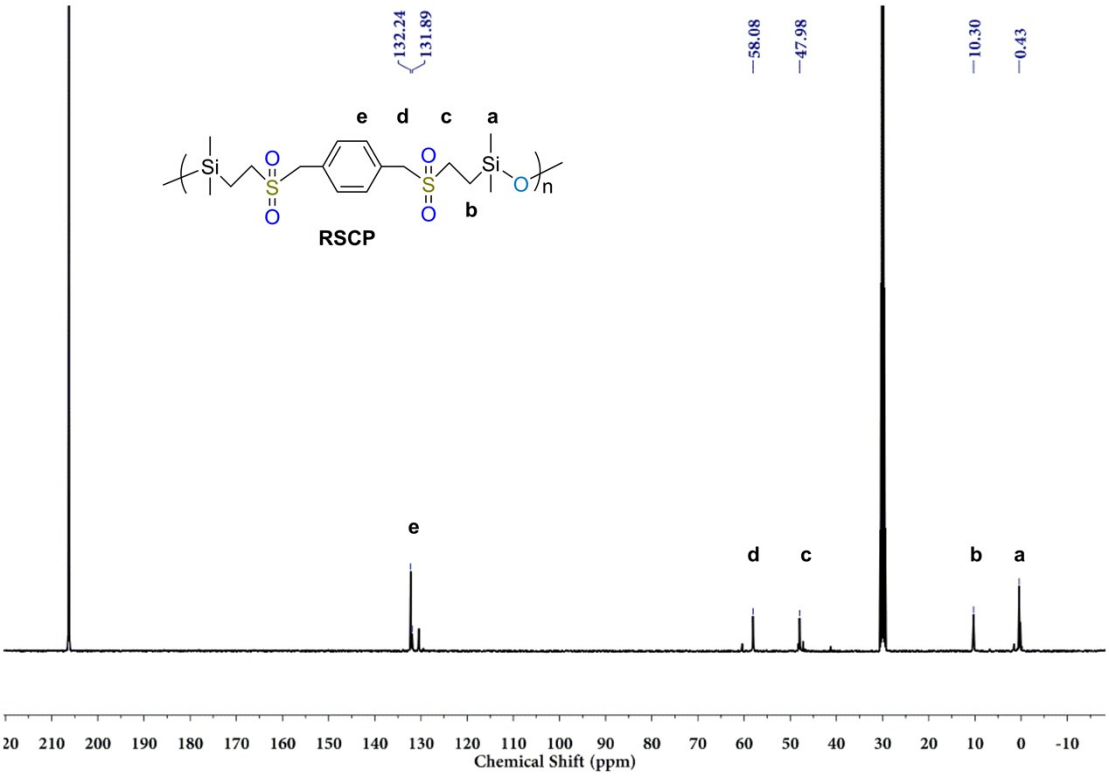

Fig. S6 ^{13}C NMR spectrum of RSCP.

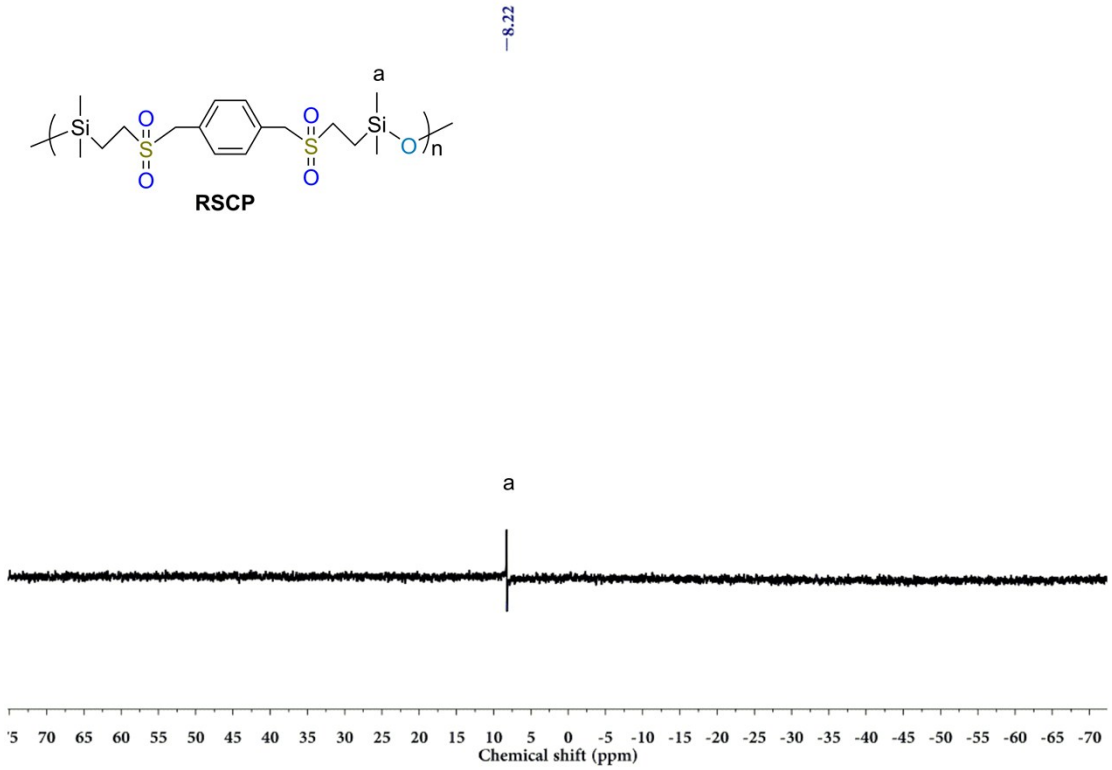

Fig. S7 ^{29}Si NMR spectrum of RSCP.

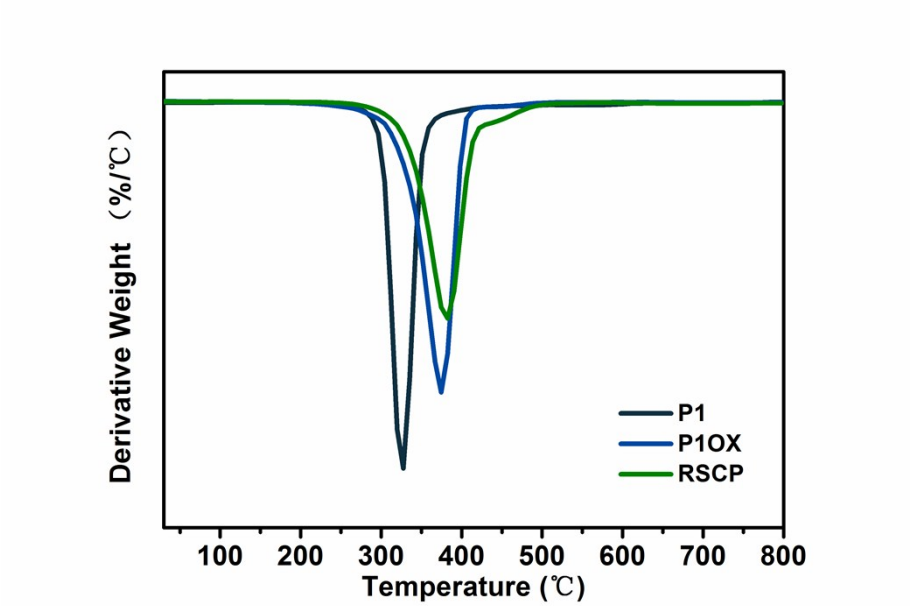

Fig. S8 Overlays of derivative thermogravimetry (DTG) curves of P1 and P1OX and RSCP.

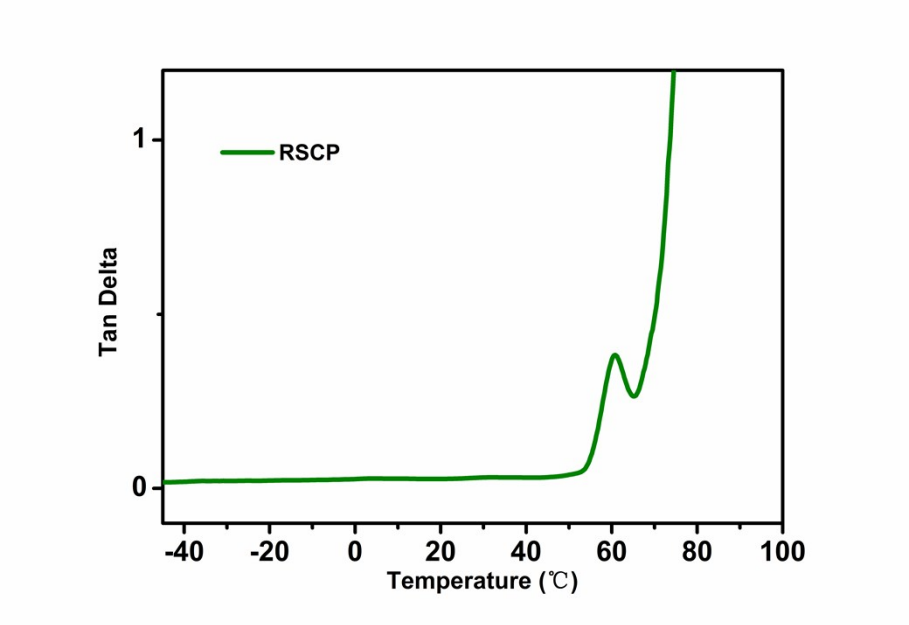

Fig. S9 Overlay of tan δ of RSCP determined by DMA.

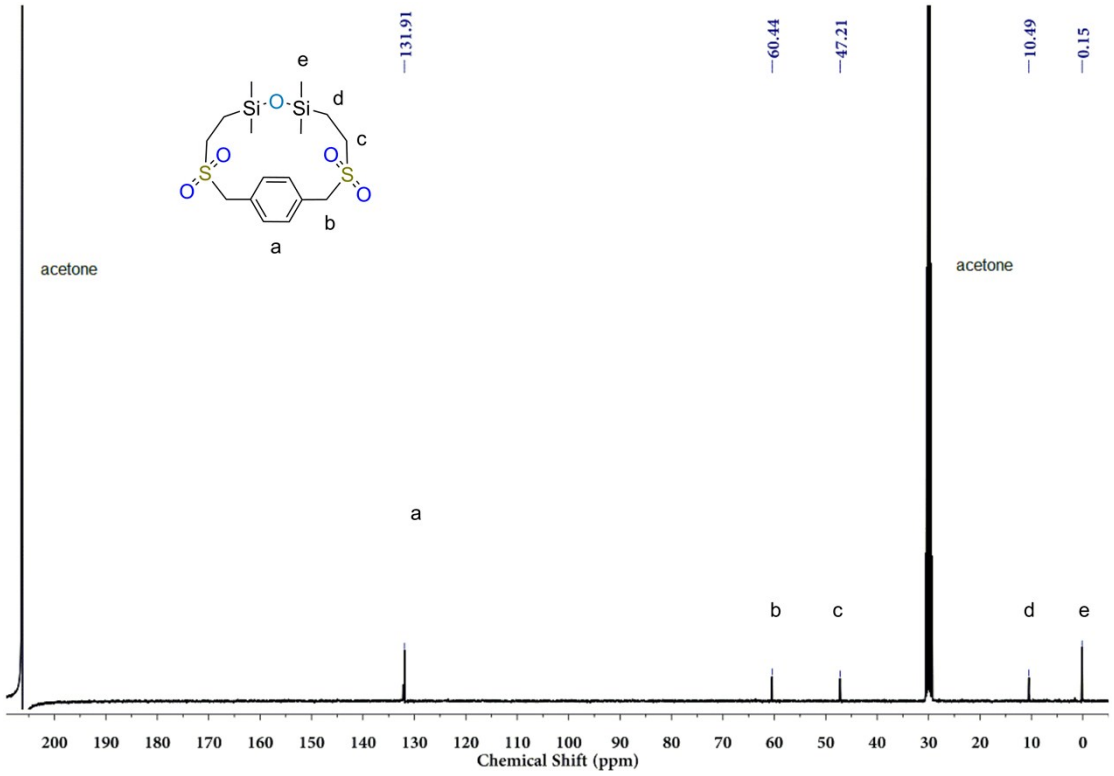

Fig. S10 ^{13}C NMR spectrum of r-P1OX.

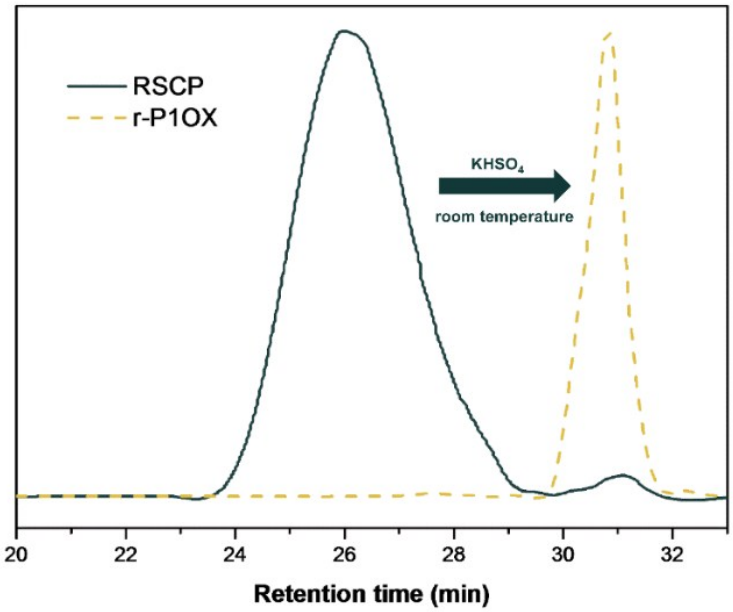

Fig. S11 GPC traces of depolymerisation of RSCP (Mn = 5.8 kg/mol, catalyzed by KOH)

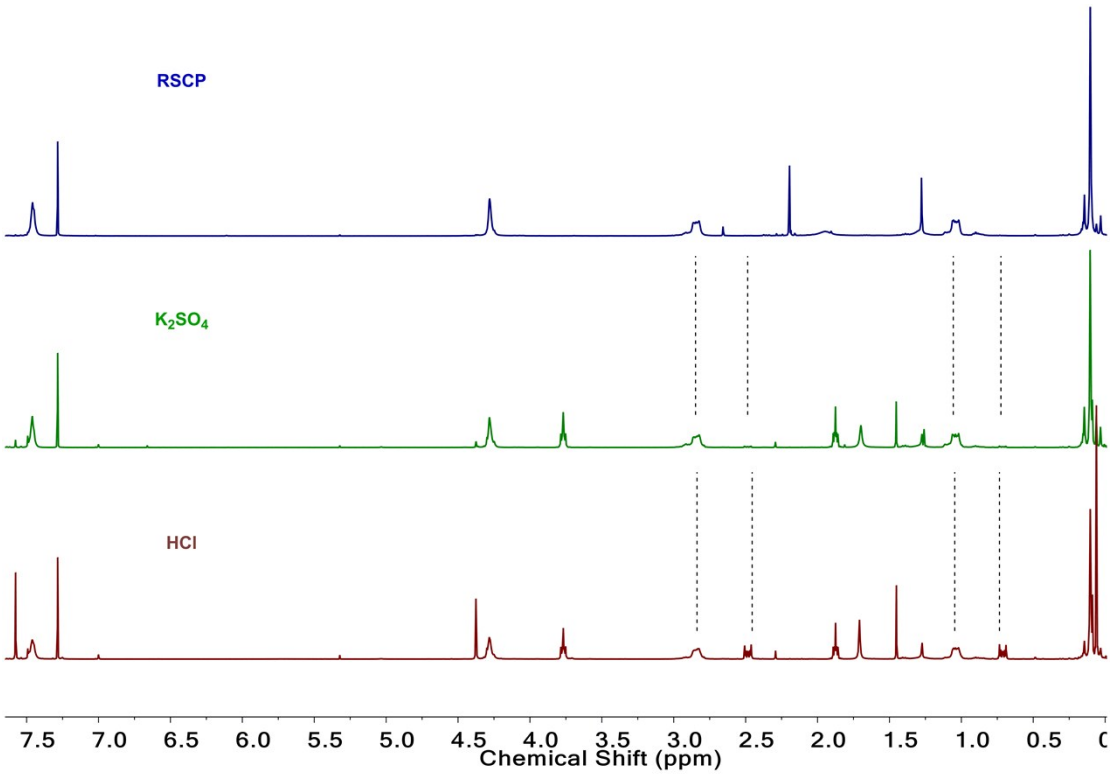

Fig. S12 ^{1}H NMR spectrum of the depolymerization of RSCP with K_2SO_4 and HCl.

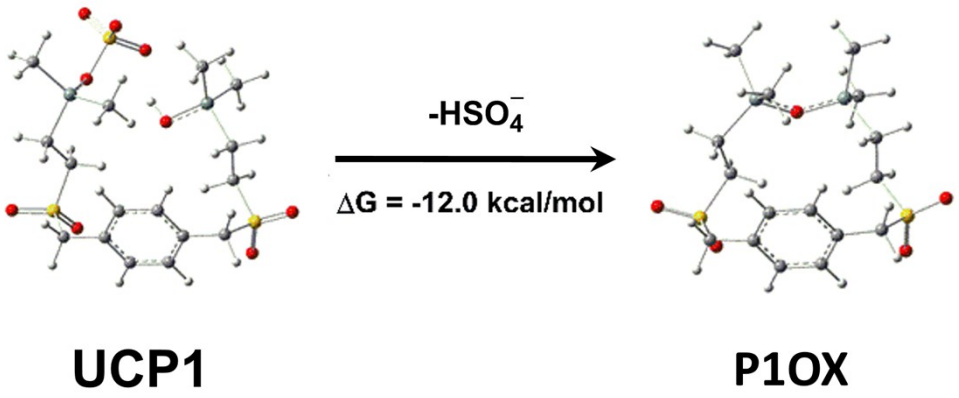

Fig. S13 Optimized structures of P1OX and uncyclization P1OX (UCP1) by DFT calculation..

Table S3 Gibbs free energies (G) and relative Gibbs energies (ΔG) of the structures by DFT calculation.

structure	G(hartree)	ΔG (kcal/mol)
UCP1	-3077.142702	0
HSO- 4	-699.7742523	
P1OX	-2377.387505	-12.0

[a] M06/6-31G(d)/gas-phase.
[b] M06/6-311++G(d,p)/PCM(Tetrahydrofuran).

Table S4 Cartesian coordinates of the structures

HSO_4^-

S	-0.14215500	-0.02784600	0.04987700
O	0.37271400	-0.64735300	1.28634900
O	-0.85683100	1.23749400	0.22873200
O	-0.76780500	-0.96444700	-0.88903500
O	1.29221900	0.43374600	-0.70460100

H	1.95210500	-0.02999000	-0.16958800

UCP1

C	-1.02535500	1.81929200	1.68850700
C	-2.11508300	0.96954800	1.82157600
C	-3.27257900	1.17739700	1.07120600
C	-3.31078400	2.24980600	0.17419000
C	-2.21436900	3.08595100	0.02942200
C	-1.05832100	2.88407300	0.78908700
H	-0.12458400	1.63782300	2.27770300
H	-2.05929500	0.12743100	2.51375500
H	-4.20082400	2.39814700	-0.43611600
H	-2.23769600	3.89769400	-0.69619900
C	0.13535500	3.75840300	0.60540200
C	-4.43148800	0.24055300	1.19413700
H	-0.12594700	4.81134500	0.43300400
H	0.82880000	3.71721600	1.45483200
H	-5.38738200	0.75738600	1.35982500
H	-4.29620500	-0.49244000	1.99781700
C	1.68412800	1.68286500	-0.60416500
C	-3.18426100	-1.35892900	-0.81794600
H	0.78349600	1.10540800	-0.34384900
H	2.01114000	1.31751300	-1.58656000
H	-3.37748900	-1.81831400	-1.79762400
H	-2.54763100	-0.47882500	-0.98520900
C	2.80246200	1.60132200	0.41701000
C	-2.58676000	-2.32862100	0.17814800
H	3.70309900	2.07589900	0.00479500
H	2.54519600	2.17451800	1.32671000
H	-3.17083800	-3.25856700	0.21181400
H	-2.62762100	-1.90371000	1.19461500
Si	3.25748900	-0.12464000	1.05759400
Si	-0.73919400	-2.64985400	-0.13676100
C	-0.45034600	-3.64277400	-1.69540100
C	-0.11837500	-3.56137400	1.37657400
O	-0.14994200	-1.10680100	-0.30312800
H	0.70722000	-1.08863100	-0.79392000
H	-0.65339700	-4.51301100	1.50592700
H	0.95370800	-3.76444800	1.26942900
H	-0.26965400	-2.96072700	2.28476800
H	-0.83640500	-4.66706400	-1.60741500
H	-0.91532200	-3.17037800	-2.57075000
H	0.63273800	-3.69242400	-1.87067700
C	4.95699300	-0.01294500	1.83659000
C	1.95257600	-0.71024000	2.26928800
S	3.42034000	-1.59144400	-0.57277500
H	5.69113800	0.23484800	1.06018600
H	4.99698200	0.75345900	2.62270200
H	5.24879700	-0.97914800	2.26385000
H	2.14782000	-1.74960500	2.56113600
H	1.94592700	-0.08375400	3.17333700

H	0.96043800	-0.68032900	1.79672200
O	2.62821200	-2.82839500	-0.16449200
O	2.28023900	-1.10038300	-1.60171800
O	4.18770300	-0.62358200	-1.63620700
O	4.83481500	-2.20668800	-0.43513200
S	1.12490300	3.36921300	-0.88014800
O	2.26430300	4.28974800	-0.84109100
O	0.21119800	3.38740900	-2.02373700
S	-4.78668700	-0.71515600	-0.31879500
O	-5.66475600	-1.81638000	0.08521000
O	-5.24465600	0.23634400	-1.33631000

P1OX

C	-0.96018600	-1.52010500	1.86658200
C	0.42205100	-1.49094100	1.99171400
C	1.22805800	-2.25957800	1.15131100
C	0.61803300	-3.08643500	0.20229100
C	-0.76319000	-3.10191900	0.06690900
C	-1.56863600	-2.30464900	0.88547900
H	-1.57560500	-0.91249300	2.53239100
H	0.88462300	-0.86369300	2.75551100
H	1.24027700	-3.68687800	-0.46007200
H	-1.22683900	-3.71379200	-0.70523700
C	-3.04037200	-2.21034000	0.65349700
C	2.71571600	-2.13948000	1.23687700
H	-3.51736600	-3.18393100	0.47672500
H	-3.57093100	-1.70978400	1.47184400
H	3.22330800	-3.10443200	1.37604400
H	3.03713200	-1.46421300	2.03873600
C	-2.39362900	0.15948900	-0.82972800
C	2.46525600	-0.13178700	-0.82105600
H	-1.36376100	-0.21920800	-0.80481600
H	-2.54043600	0.61736500	-1.81703200
H	2.86668600	0.07583600	-1.82370000
H	1.44590100	-0.52221800	-0.95156900
C	-2.71581000	1.10572600	0.30974000
C	2.53067000	1.07617500	0.08877200
H	-3.69699700	1.57003500	0.13784600
H	-2.81380800	0.54575800	1.25251700
H	3.57645000	1.39604000	0.20770900
H	2.15729700	0.82964600	1.09680900
Si	-1.39363300	2.43583600	0.59702700
Si	1.48256300	2.50598000	-0.56383700
C	1.81302000	2.77227400	-2.38292200
C	1.89293000	4.04191600	0.42836200
O	-0.11030100	2.07191000	-0.38596300
H	2.93408000	4.33761400	0.24063800
H	1.25846400	4.89510200	0.15502900
H	1.79260400	3.87370300	1.50877500
H	2.88760700	2.88994000	-2.57783100

H	1.45197500	1.92706800	-2.98260100
H	1.30746200	3.67470200	-2.74844800
C	-2.06993800	4.12839200	0.17314400
C	-0.84455200	2.37452700	2.39035900
H	-2.38334300	4.18217400	-0.87713200
H	-2.94405500	4.36717700	0.79368800
H	-1.32192700	4.91465000	0.34103600
H	-0.20702600	3.22874700	2.65347600
H	-1.70573600	2.38502400	3.07230900
H	-0.27445200	1.45469800	2.58713400
S	-3.45307200	-1.29795300	-0.87729400
O	-4.84957700	-0.88245900	-0.75969600
O	-3.01305800	-2.12057800	-2.00388700
S	3.48388000	-1.52629200	-0.29529200
O	4.80993000	-1.02833000	0.06584200
O	3.33349900	-2.57325800	-1.30642700

References:

[1] *APEX2*, *SAINT* and *SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA, 2008.

[2] Palatinus, L.; Chapuis, G. *J. Appl. Crystallogr.* 2007, **40**, 786.

[3] Sheldrick, G. M. *Acta. Crystallogr., Sect.* C 2015, **71**, 3.

[4] Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H. *J. Appl. Crystallogr.* 2009, **42**,339.