

ELECTRONIC SUPPLEMENTARY INFORMATION

Synthesis and Application of a Novel Bio-based Polyol for Preparation of Polyurethane Foams

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Synthesis and characterization of α -amino- ϵ -caprolactam (ACL)

A stirred mixture of L-lysine hydrochloride (110 g, 600 mmol) and NaOH (24 g, 600 mmol) in hexanol (2.4 L) was heated to reflux with a Dean-Stark trap used to remove H₂O. The suspension was refluxed for 8 hours until all starting material was consumed (which was determined by TLC). The suspension was then cooled and filtered to remove byproduct NaCl. The filtrate was concentrated and the resulting crude α -amino- ϵ -caprolactam was dissolved in water. After acidification to pH 6 with addition of concentrated HCl and partial concentration, crystal was formed at room temperature to afford ACL hydrochloride (74 g) in 75 % yield. The ACL hydrochloride was dissolved in methanol and NaOH (18 g, 450 mmol) was added.

After stir for 2 h, the suspension was then filtered and the filtrate was evaporated under reduced pressure conditions to afford ACL (57 g) as a white solid. Mp: 97 - 101 °C. Elemental analysis (%) found: C: 56.36, H: 9.50, N: 21.71; C₆H₁₂N₂O; C: 56.22, H: 9.44, N: 21.86. HRMS: found $m/z = 129.1046$ ($[M + H]^+$), calculated 129.1028. ¹H-NMR (500 MHz, CD₃OD): δ (ppm) = 7.19 (br s, 2 H), 5.12 (d, $J = 11.1$ Hz, 1 H), 3.58 (s, 1 H), 3.15 (m, 2 H), 1.49-1.14 (m, 6 H). ¹³C-NMR (125 MHz, CD₃OD): δ (ppm) = 178.26, 52.82, 41.01, 33.72, 28.17, 27.94.

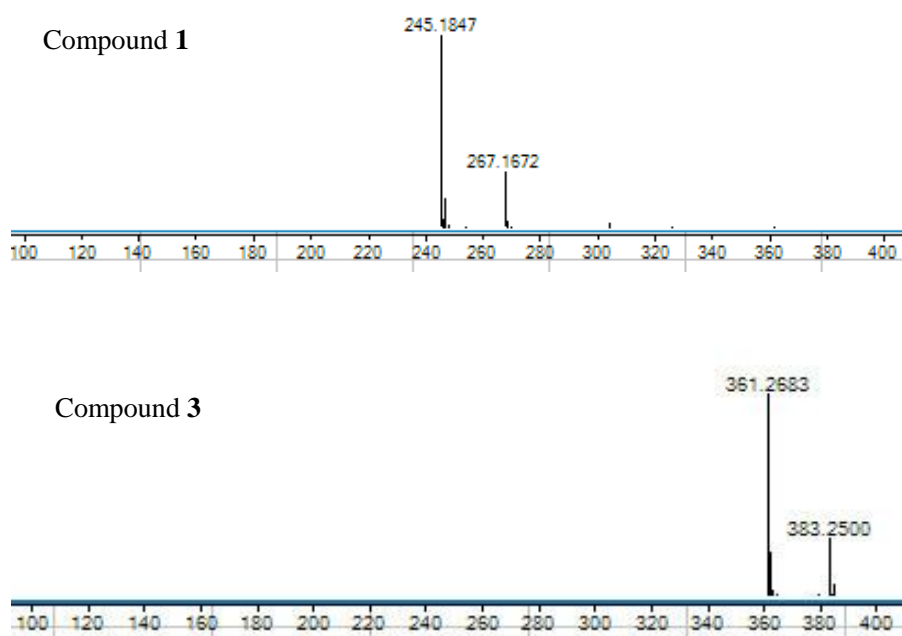


Figure S11. The mass of the structures **1** and **3**.

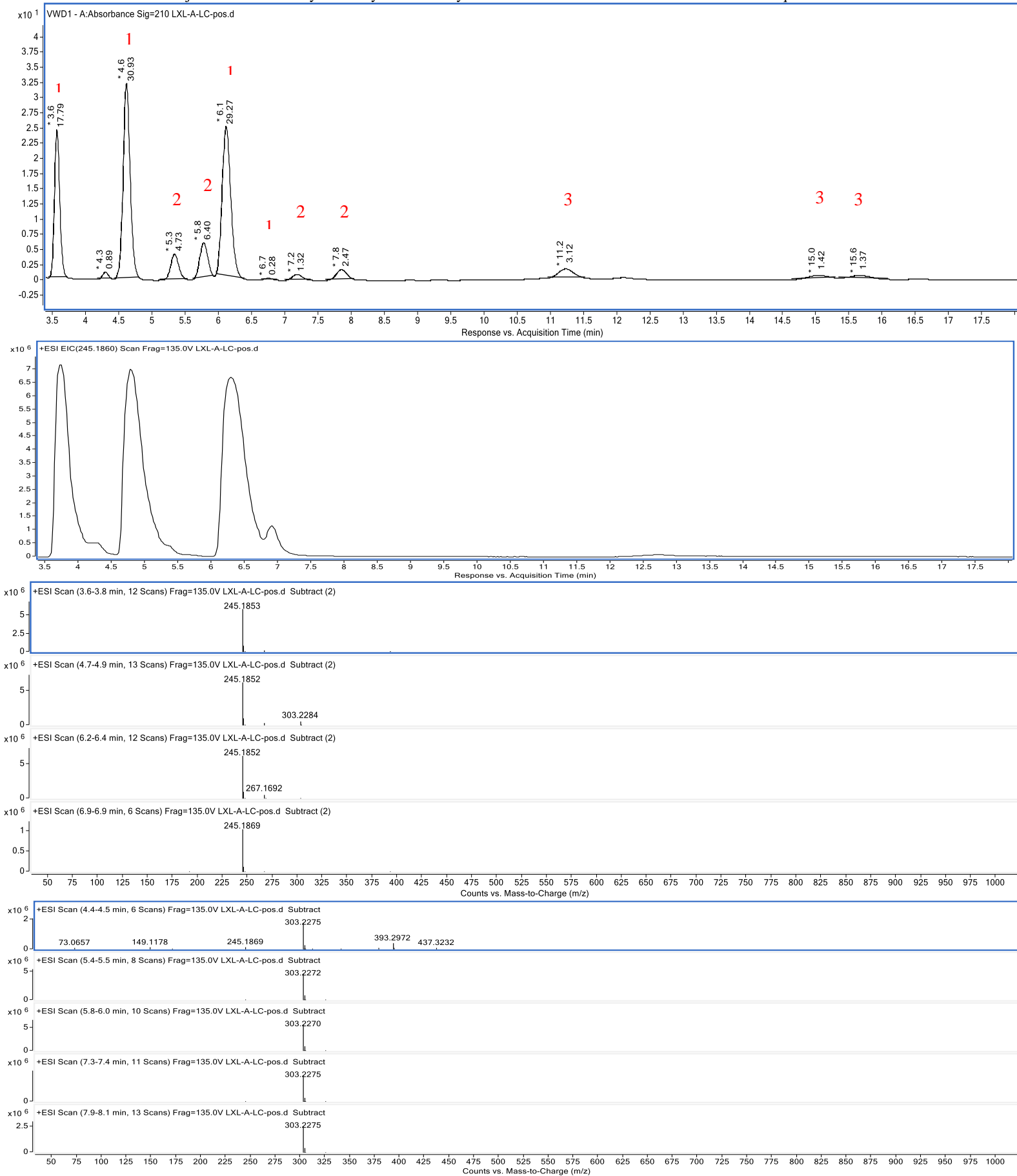


Figure S12. The LC-MS of the ACL-OL at 22 h.

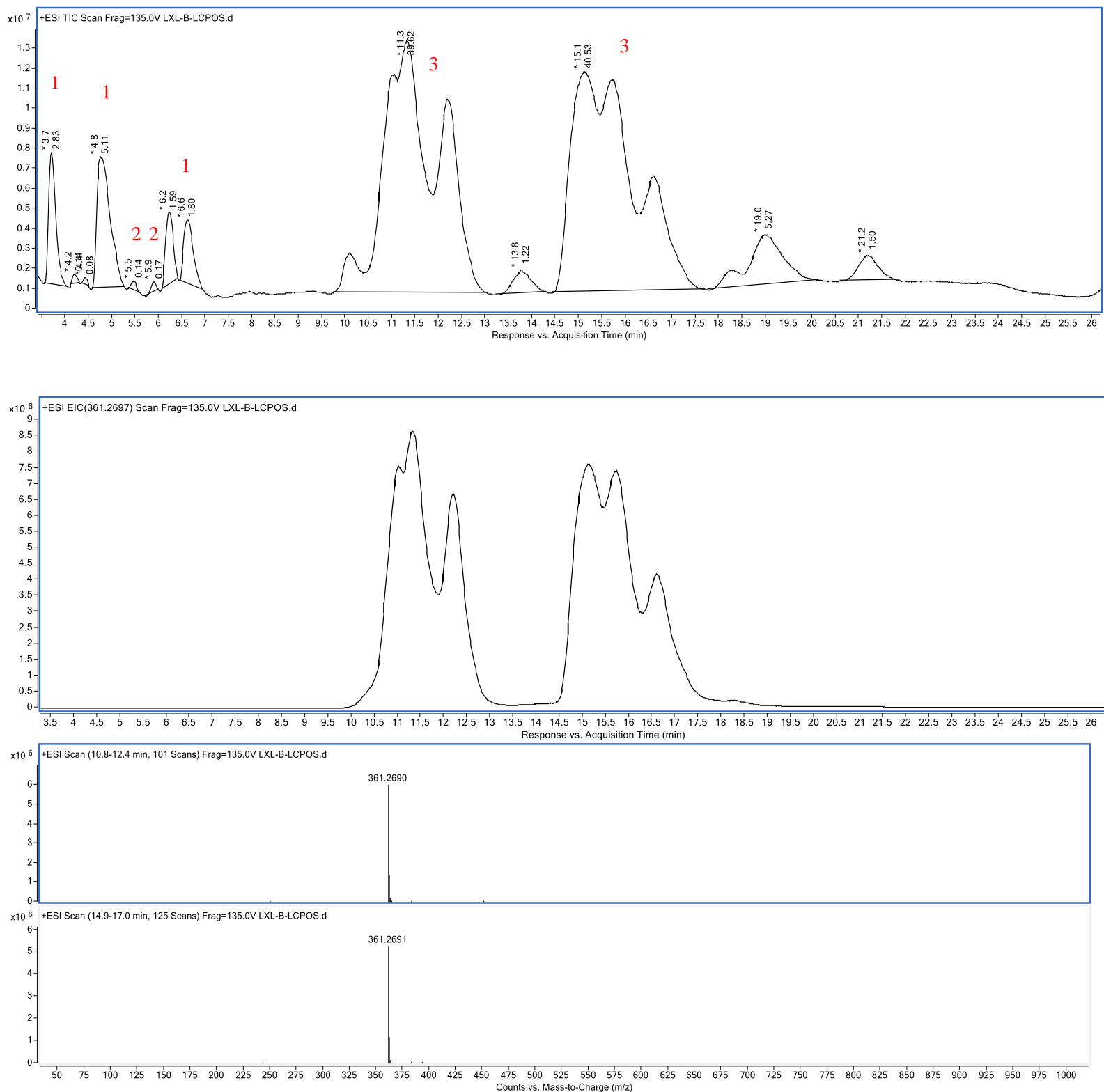


Figure SI3. The LC-MS of the ACL-OL at 72 h. For the different position of $-NH_2$ attacking the PO, the compounds 1, 2 and 3 have several different configuration. We do not talk about it in this article.

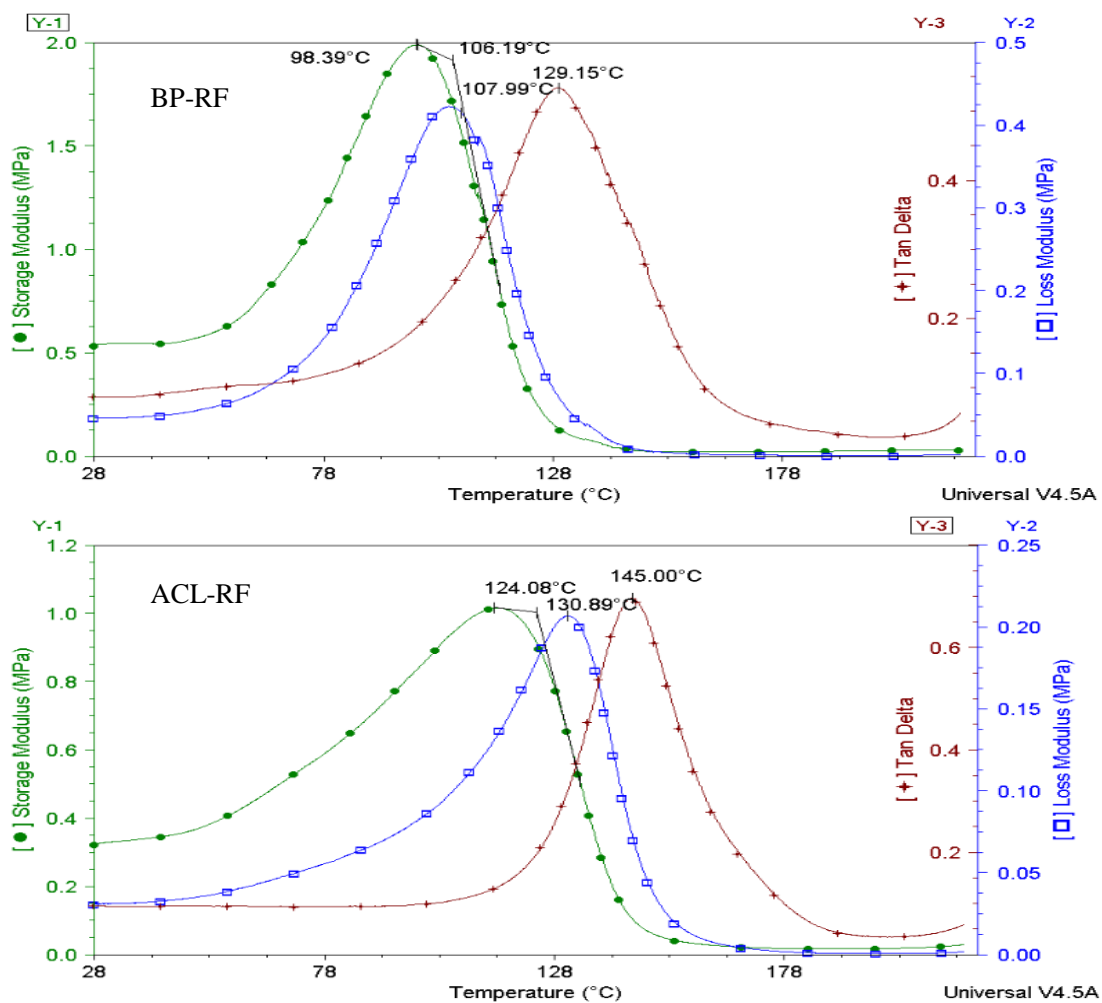


Figure S14. DMTA data of foams showing the thermostability. (Y-1 is storage modulus; Y-2 is loss modulus; Y-3 is $\tan \delta$)

Details about DMTA experiment: sample dimensions, cylinders of $\Phi 15 \times 10$ mm; frequency, 0.01~200 Hz; force, 0.0001~18 N; compression mode, $10^3 \sim 3 \times 10^{12}$ Pa; temperature, -150~600 °C. T_g was determined by the maximum peak at $\tan \delta$.

Module: TG/DTA
Data Name: ACL-RF
Measurement Date: 2013-7-3
Sample Name: ACL-RF
Sample Weight: 2.031 mg
Reference Name:
Reference Weight: 0.000 mg

Temperature Program:
N2 40 200 5 10 0.5

Comment:
Operator: cf
Gas1: 200
Gas2: 200
Pan: ceramics

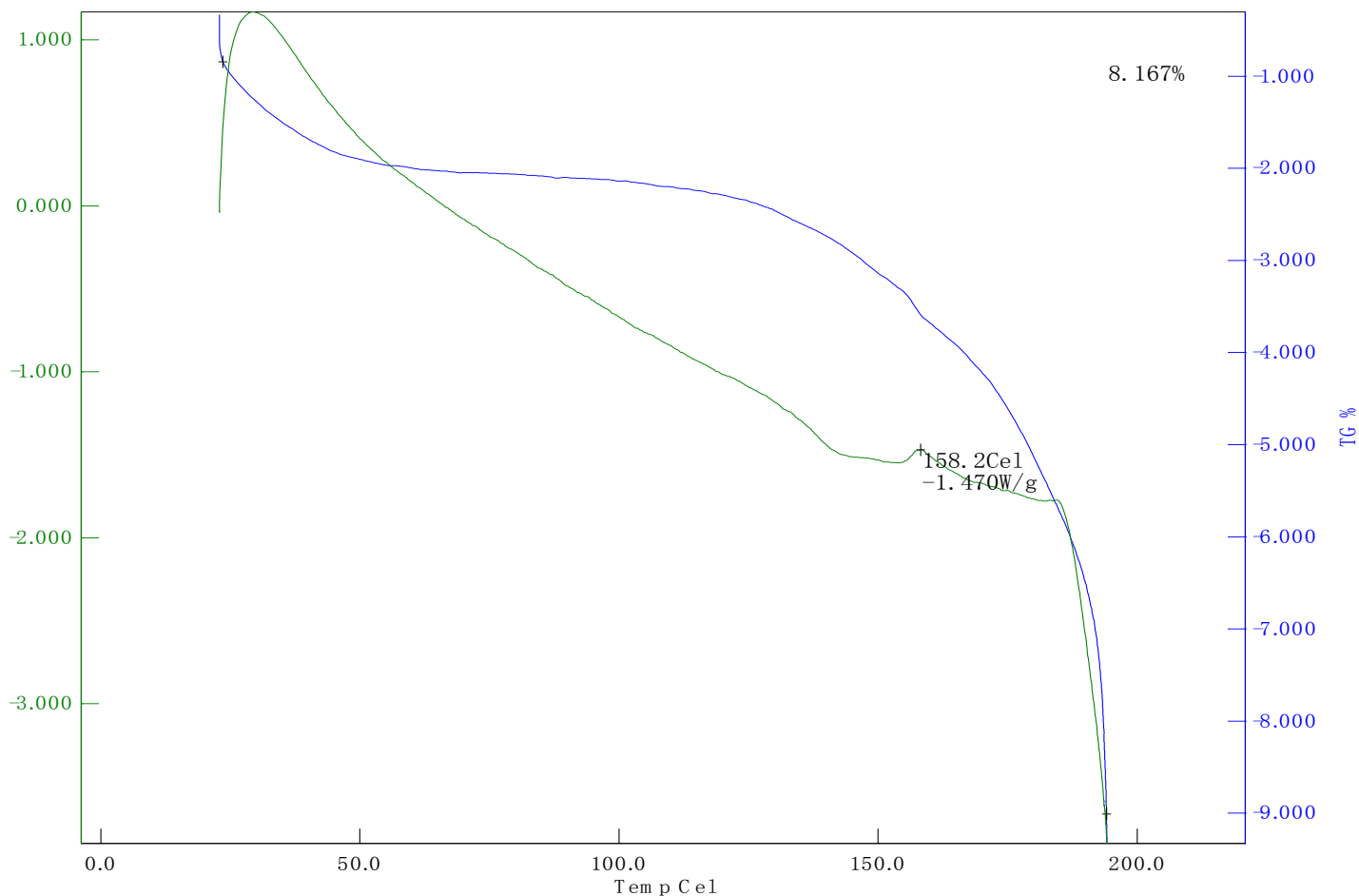


Figure SI5. DSC date of ACL-RF

Module: TG/DTA
Data Name: PB-RF
Measurement Date: 2013-7-3
Sample Name: PB-RF
Sample Weight: 2.678 mg
Reference Name:
Reference Weight: 0.000 mg

Temperature Program:
Cel Cel Cel/min min s
N2 40 150 5 10 0.5

Comment:
Operator: cf
Gas1: 200
Gas2: 200
Pan: ceramics

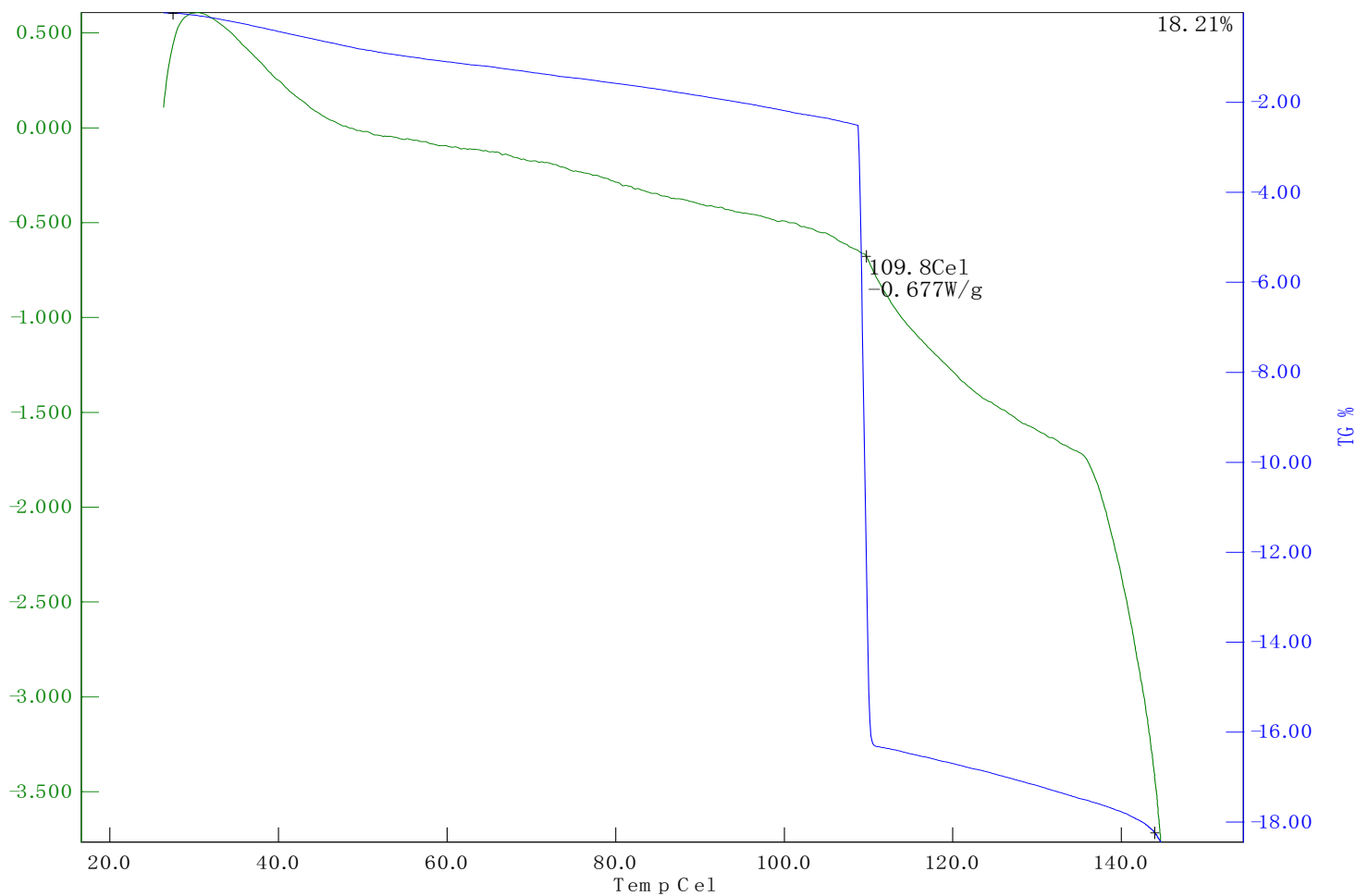


Figure SI6. DSC date of PB-RF.