Electronic Supplementary Material (ESI) for Polymer Chemistry

Supporting information for

Control of cationic epoxy polymerization by supramolecular initiation

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I. **Materials**

The epoxy resin used is the diglycidylether of bisphenol A (DGEBA), supplied from Dow Chemical. 18-crown-6, boron trifluoride etherate, 4-chloroaniline were supplied from Acros. Tetrafluoroboric acid was supplied from Alfa Aesar. All reagents were used as received.

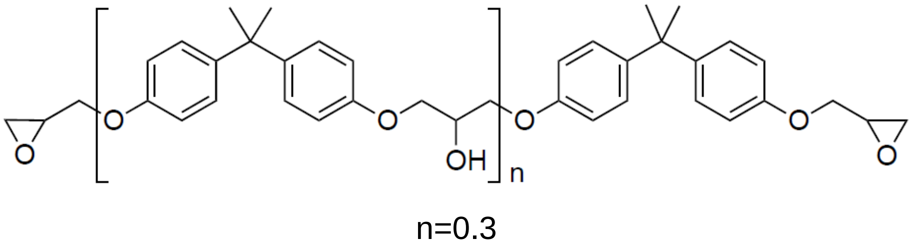
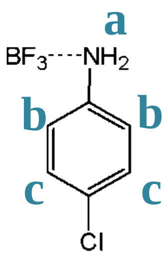


Figure S1 – Molecular formula of the epoxy resin used in the study, DGEBA DER 332

II. **Synthesis** of initiators **BF_3▪4CA, BF_4^-▪4CA$^+$, BF_4^-▪4CA$^+$▪18-crown-6**

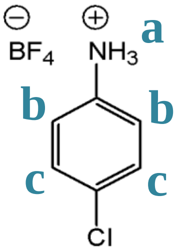
Complex of 4-chloroaniline and boron trifluoride [i], BF_3▪4CA



To a solution of 4-chloroaniline (10 g, 78.4 mmol, 1 eq.) in dichloromethane (70 mL) cooled to 0°C, was added $BF_3.(C_2H_5)_2O$ (solution 48% BF_3 in Et_2O, 9.9 mL, 11.1 g, 78.4 mmol of BF_3, 1éq.) under nitrogen atmosphere and allowed to stir for 3h at room temperature. The resulted beige precipitate was filtered, washed with dichloromethane and dried under vacuum for 5h at 35°C. Yield : 15g, 76.8 mmol, 98%. ^1H NMR (DMSO-d6, in ppm from tetramethylsilane) : 6,10 (s, 2H, Ha), 6.66 (dt, 2H, Hb), 7.09 (dt, 2H, Hc).

Elem. Anal. Calcd for $C_6H_6BF_3NCl$: C, 36,88; H, 3,09; N, 7,17; F,15,84. Found: C, 35,82; H, 2,92; N, 6,79.

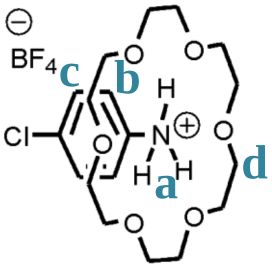
4-chloro-anilinium tetrafluoroborate salt, BF_4^-▪4CA$^+$



To a solution of 4-chloroaniline (4 g, 23.4 mmol, 1 eq.) in MeOH (10 mL), was added HBF_4 (solution 50wt% HBF_4 in H_2O, 3.8 mL, 4,1 g, 23.1 mmol of HBF_4, 0.98éq.) allowed to stir for 30min at room temperature. The solvent was removed under vacuum and the resulted beige solid was recristallized from CH_3CN (6mL, 70°C). The resulted white precipitate was filtered, washed with dichloromethane and dried under vacuum for 15h at 80°C. Yield : 4g, 18.6 mmol, 79%. ^1H NMR (DMSO-d6, in ppm from tetramethylsilane) : 7.27 (dt, 2H, Hb), 7.51 (dt, 2H, Hc). 9.20 (s, 3H, Ha).

Elem. Anal. Calcd for $C_6H_7BF_4NCl$: C, 33,45; H, 3,28; N, 6,50; F,35,28. Found: C, 33,26; H, 3,34; N, 6,67; F, 35,26.

4-chloro-anilinium tetrafluoroborate 18-crown-6, BF_4^-▪4CA$^+$▪18-crown-6



To a solution of 4-chloroaniline (1.5 g, 11.7 mmol, 1 eq.) in MeOH (5 mL), was added HBF_4 (solution 50wt% HBF_4 in H_2O, 1.76 mL, 2.48 g, 14.1 mmol of HBF_4, 1.2éq.) allowed to stir for 50min at room temperature. 18-crown-6 was dissolved in MeOH (2mL) and the mixture was added to the previous solution. The resulted mixture was allowed to stir for 30min at room temperature. The white precipitate was filtered and recristallized from MeOH (50mL, 65°C). The resulted white precipitate was filtered, washed with MeOH and dried under vacuum for 20h at 45°C. Yield : 4.4g, 9.2 mmol, 75%. ^{1}H NMR (DMSO-d6, in ppm from tetramethylsilane): 3.53 (s, 24H, Hd), 7.27 (dt, 2H, Hb), 7.51 (dt, 2H, Hc), 8.91 (s, 3H, Ha). Elem. Anal. Calcd for $C_{18}H_{31}BF_4NO_6Cl$: C, 45,07; H, 6,51; N, 2,91; F,15,84. Found: C, 45,22; H, 6,75; N, 3,01; F, 15,68.

General remarks on initiators solubility

BF_3▪4CA: excellent solubility in Acetone, MeOH and DMSO. Good solubility in resin after solubilisation in Acetone. Poor solubility in CH_2Cl_2 and $CHCl_3$.

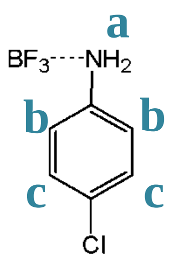
BF_4^-▪4CA$^+$: excellent solubility in Acetone, MeOH and DMSO. Good solubility in resin after solubilisation in Acetone. Poor solubility in CH_2Cl_2 and $CHCl_3$.

BF_4^-▪4CA$^+$▪18-crown-6: Good solubility in CH_2Cl_2, $CHCl_3$, and DMSO. Good solubility in resin after solubilisation in CH_2Cl_2. Poor solubility in MeOH and Acetone.

III. ^{1}**H NMR** of initiators **BF_3▪4CA, BF_4^-▪4CA$^+$, BF_4^-▪4CA$^+$▪18-crown-6**

NMR spectrums were performed on a Brüker (400MHz) instrument. **BF_3▪4CA**, **BF_4^-▪4CA$^+$** and **BF_4^-▪4CA$^+$▪18-crown-6** spectrum were all performed in deuterated dimethylsulfoxide (DMSO-d6) at 1wt%.

Notation for peaks shape: s (singulet), dt (doublet of triplet).



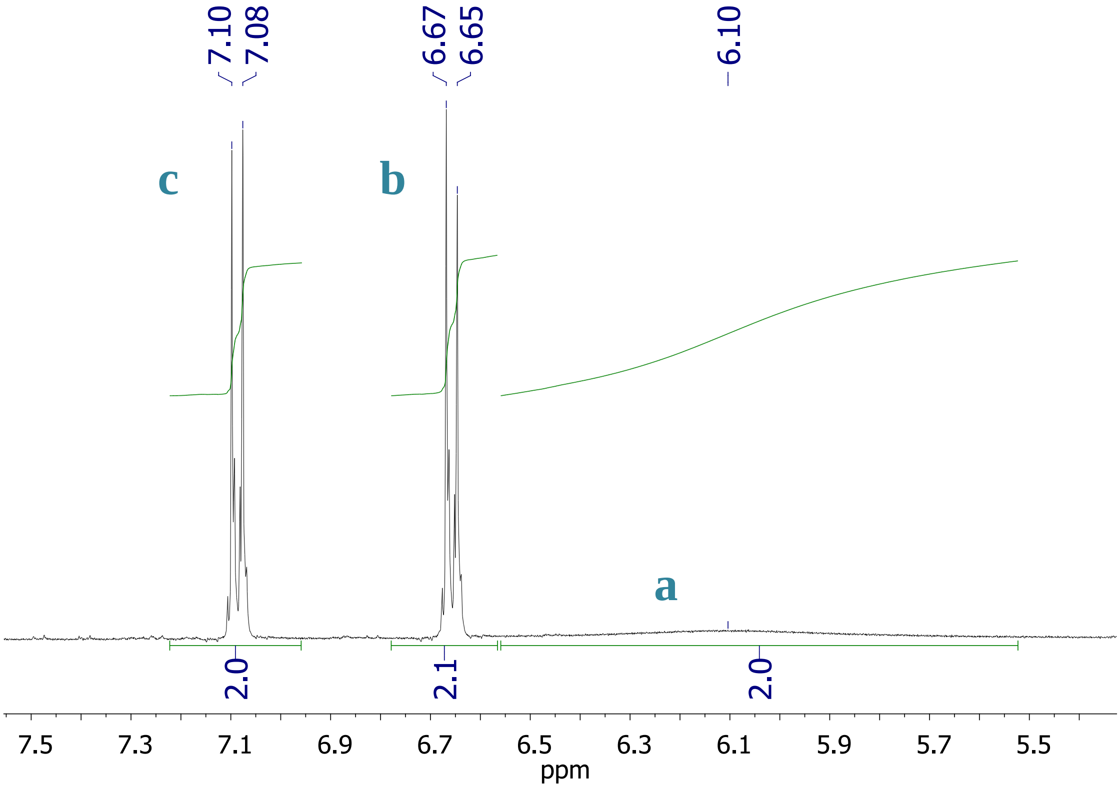


Figure S2 - ^{1}H NMR spectrum in DMSO-d$_6$ of **BF_3▪4CA**.

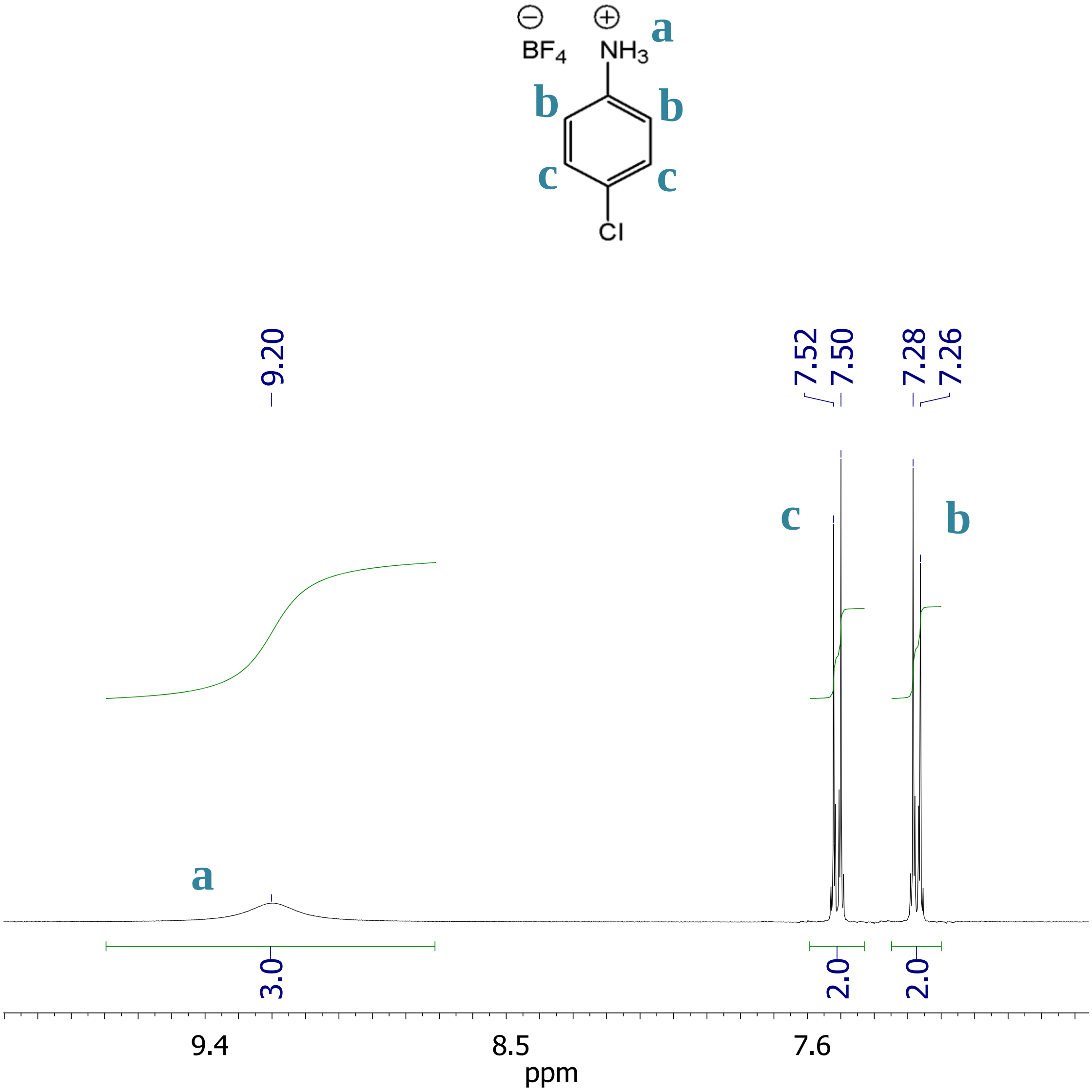


Figure S3 - ^{1}H NMR spectrum in DMSO-d_6 of **BF_4^-▪4CA$^+$**.

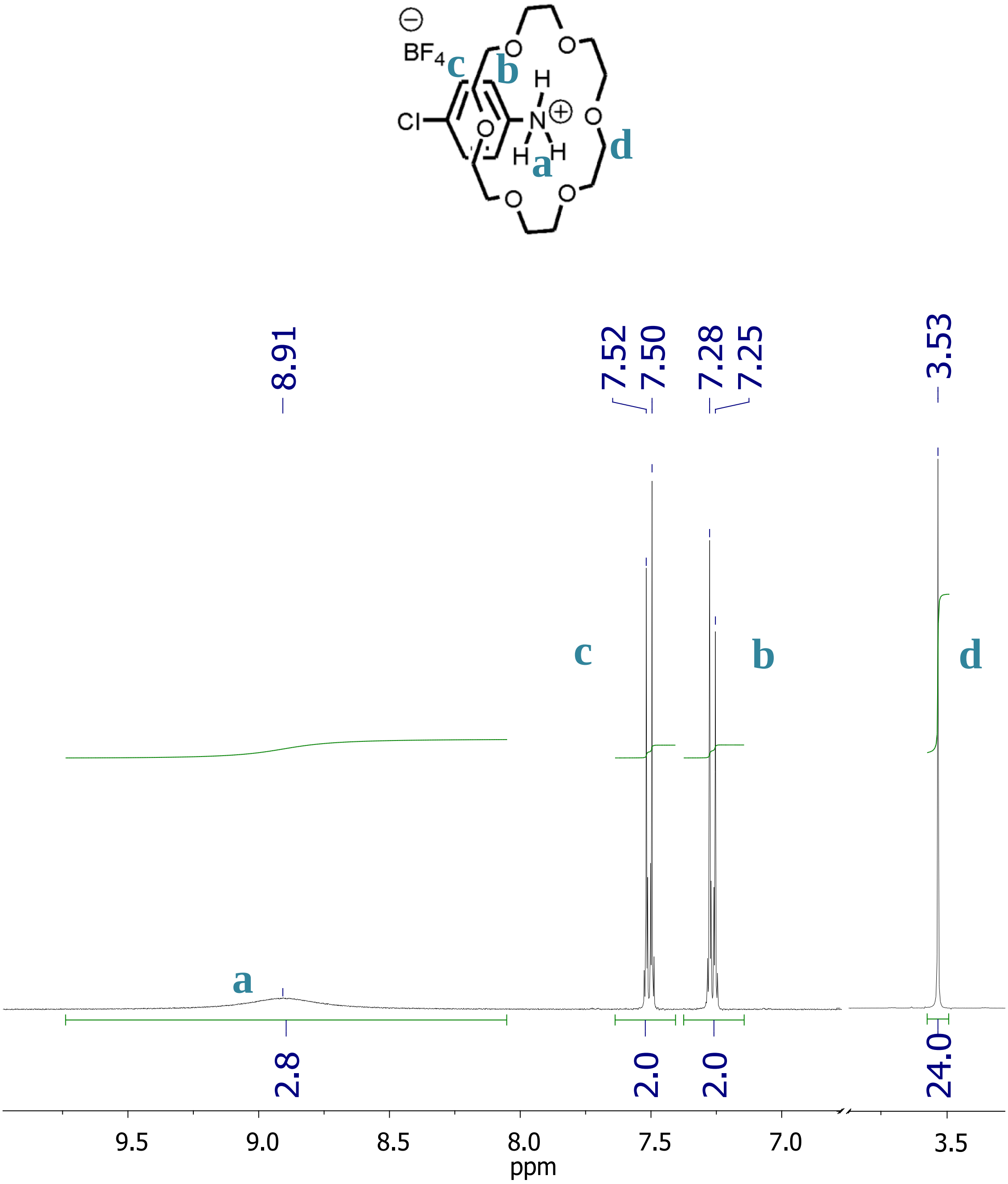


Figure S4 - ^{1}H NMR spectrum in DMSO-d$_6$ of **BF_4^-▪4CA$^+$▪18-crown-6**.

IV. **General procedure for sample preparation** before IR, Rheology and DSC tests.

The reactive mixtures were obtained by melting the epoxy resins DGEBA (2g) at 70°C to give a viscous liquid then cooled at room temperature. The initiator was predissolved in a solvent using acetone (~0.4mL) for **BF_3▪4CA** (59mg, 0,026eq./epoxy) and **BF_4^-▪$4CA^+$** (66mg, 0,026eq./epoxy)**,** and using dichloromethane (~0.4mL) for **BF_4^-▪$4CA^+$▪18-crown-6** (146mg, 0,026eq./epoxy). The solution was then added to the resin. The resulting mixture was vigorously stirred to give a homogeneous and colourless sample placed under vacuum during several minutes to evaporate the solvent used to dissolve the initiator. Blends obtained were then studied through spectroscopic, rheological and Dynamic Scanning Calorimetry experiments.

V. **IR monitoring** of the curing: procedure, spectra and conversion data.

The isothermal curing process was monitored using a Bruker-Tensor 37 with a resolution of 4cm^{-1}, equipped with a thermally controlled SPECAC Goldengate ATR accessory. The disappearance of the 914cm^{-1} absorbance peak (epoxy bending) was monitored to determine the epoxy conversion. The peak at 1605 cm^{-1} (phenyl group) was chosen as an internal standard[ii,iii,iv]. Conversion was determined by the Lambert-Beer law from the normalized change of absorbance at 914cm^{-1}:

$$\alpha_{époxy} = 1 - \left(\frac{\bar{A}_{914}^{t}}{\bar{A}_{914}^{0}}\right)$$

where $\bar{A}_{914}^{0} = A_{914}^{0}/A_{1605}^{0}$ et $\bar{A}_{914}^{t} = A_{914}^{t}/A_{1605}^{t}$ are the normalized absorbance of the epoxy groups before curing and after reaction time t, respectively.

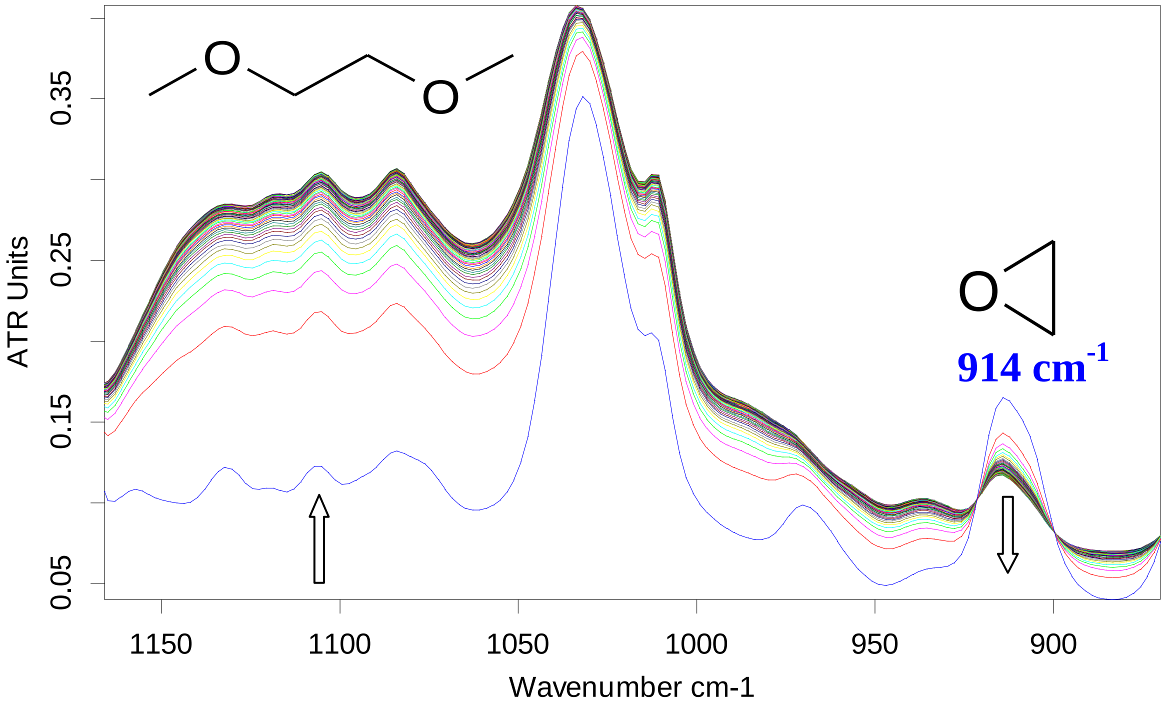


Figure S5 – FTIR spectra of the DGEBA/**BF$_4^-$-4CA$^+$** 0.026eq./epoxy system at 60°C at different curing periods with the decrease of the absorption of the epoxide group at 914cm^{-1} and the increase of the 1,2-polyether absorption peaks between 1050 and 1150 cm^{-1}.

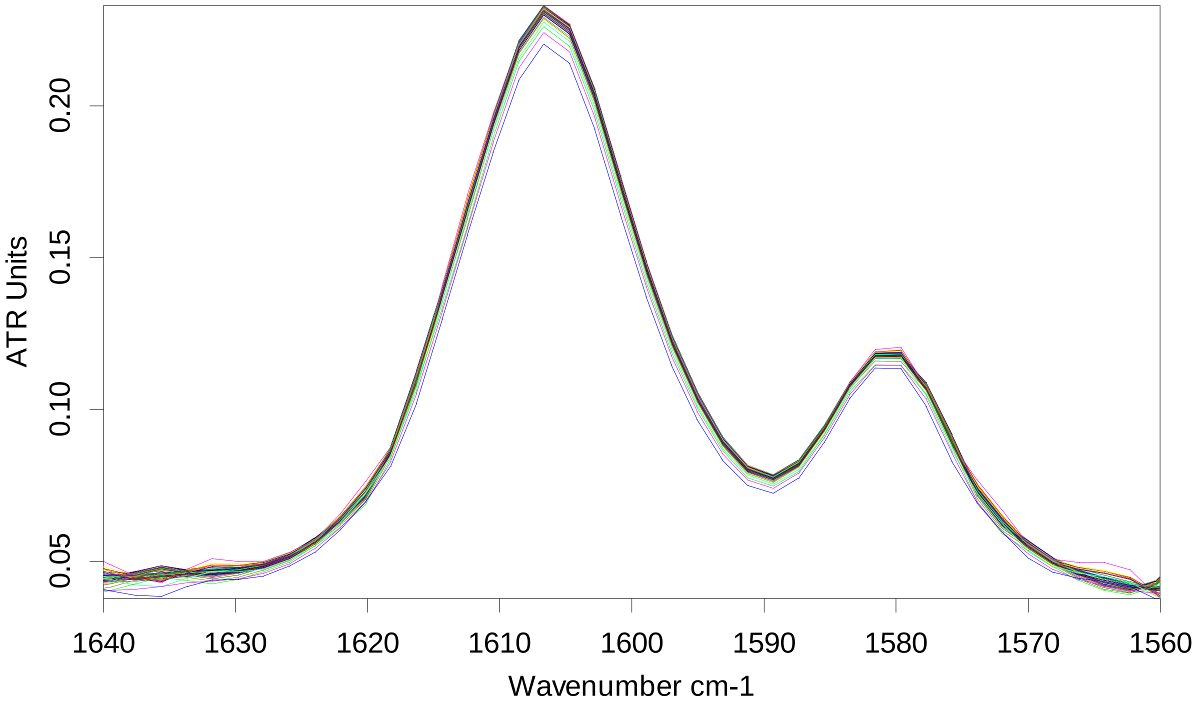


Figure S6 - FTIR spectra of the DGEBA/**BF_4^--4CA$^+$** system at 60°C at different curing periods: reference peak at 1605cm^{-1}.

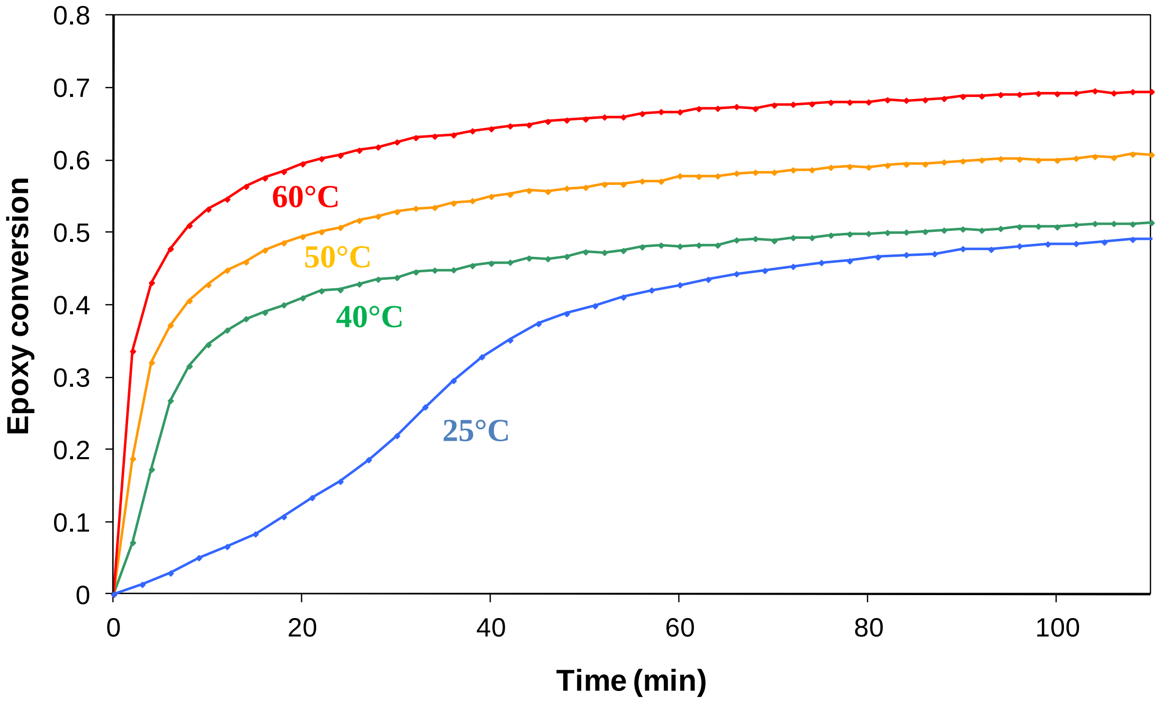


Figure S7 - Plots of epoxy conversion during the cationic polymerization of DGEBA initiated by 0.026eq./epoxy of **BF_4^-▪4CA$^+$** at various temperatures.

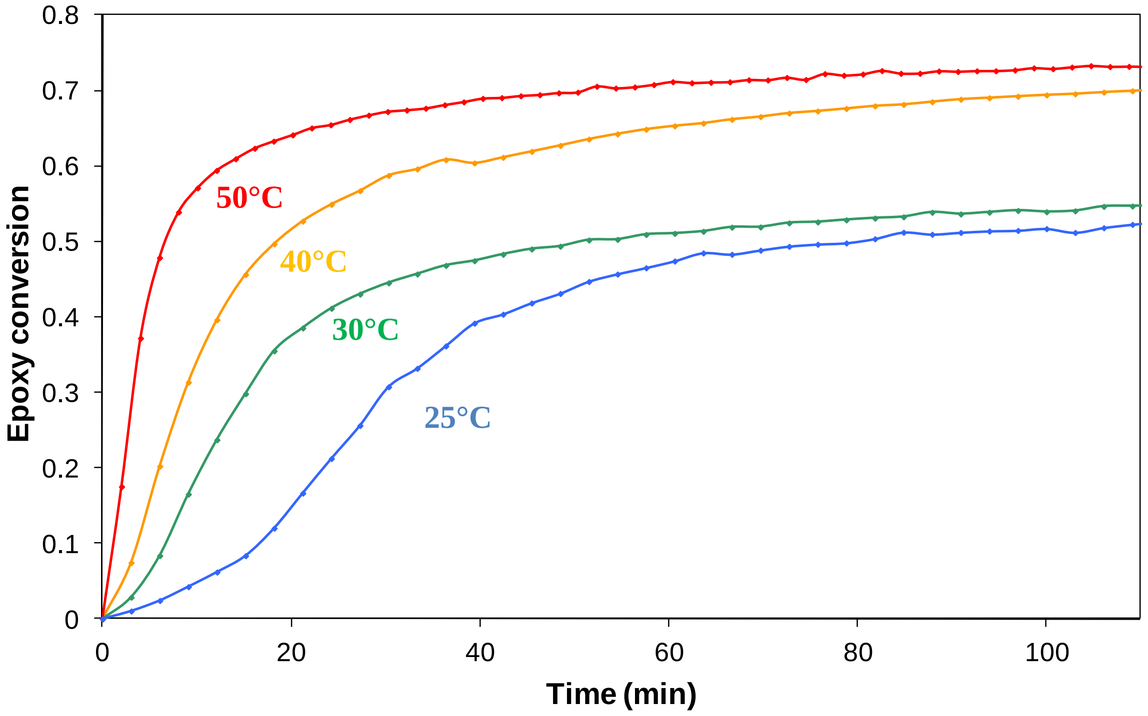


Figure S8 - Plots of epoxy conversion during the cationic polymerization of DGEBA initiated by 0.026eq./epoxy of **BF_3▪4CA** at various temperatures.

VI. **Rheology monitoring** of the curing: procedure and G'/G'' data.

Rheological measurements under isothermal conditions were monitored using an Anton Paar Physica MCR 501 rheometer operating in the parallel plates geometry. The disposable plates were preheated in the rheometer environmental chamber for approximately 10min at the set temperature before loading the samples. The gap between plates was fixed at 1mm, and experiments were performed under oscillations at a frequency of 1rad/s and a shear strain of 1%. In the article, complex viscosity modulus, defined as $|\eta^*| = |G' + iG''/i\omega|$, is reported in the different plots. Here are represented the G' and G'' moduli plots as a function of reaction time for the DGEBA/ **BF_4^-▪4CA$^+$▪18-crown-6** mixtures.

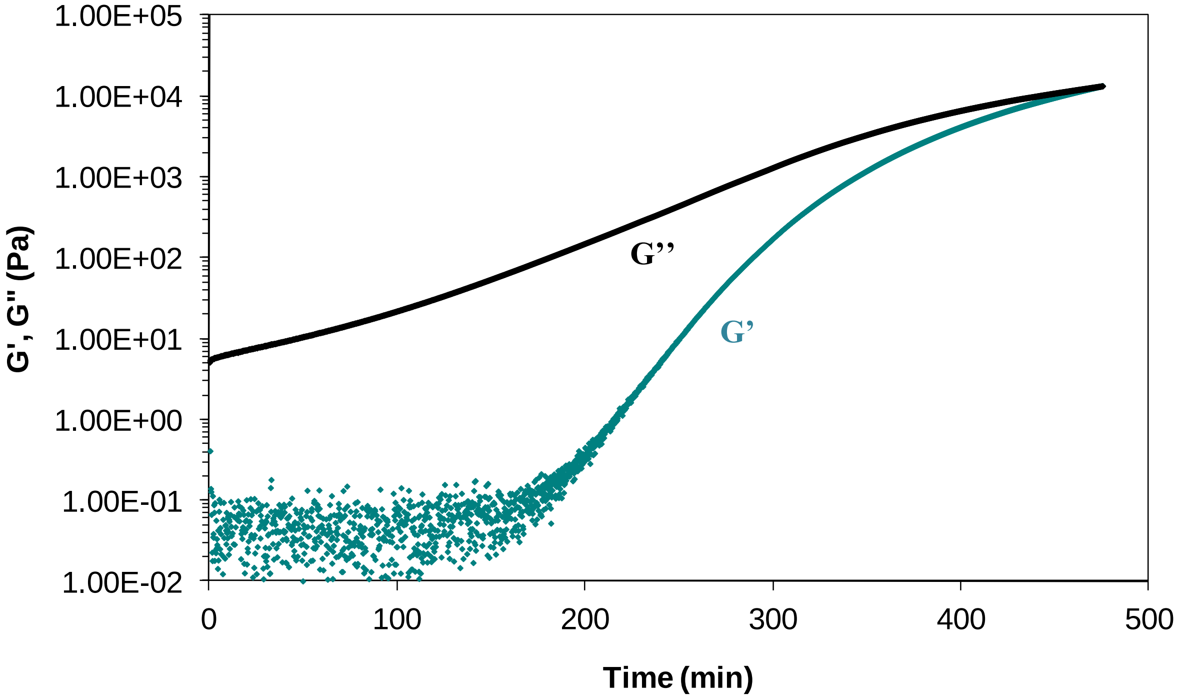


Figure S9 - Plot of G' and G'' moduli as a function of reaction time for the DGEBA/ **BF_4^-▪4CA$^+$▪18-crown-6** 0.026eq./epoxy at 25°C.

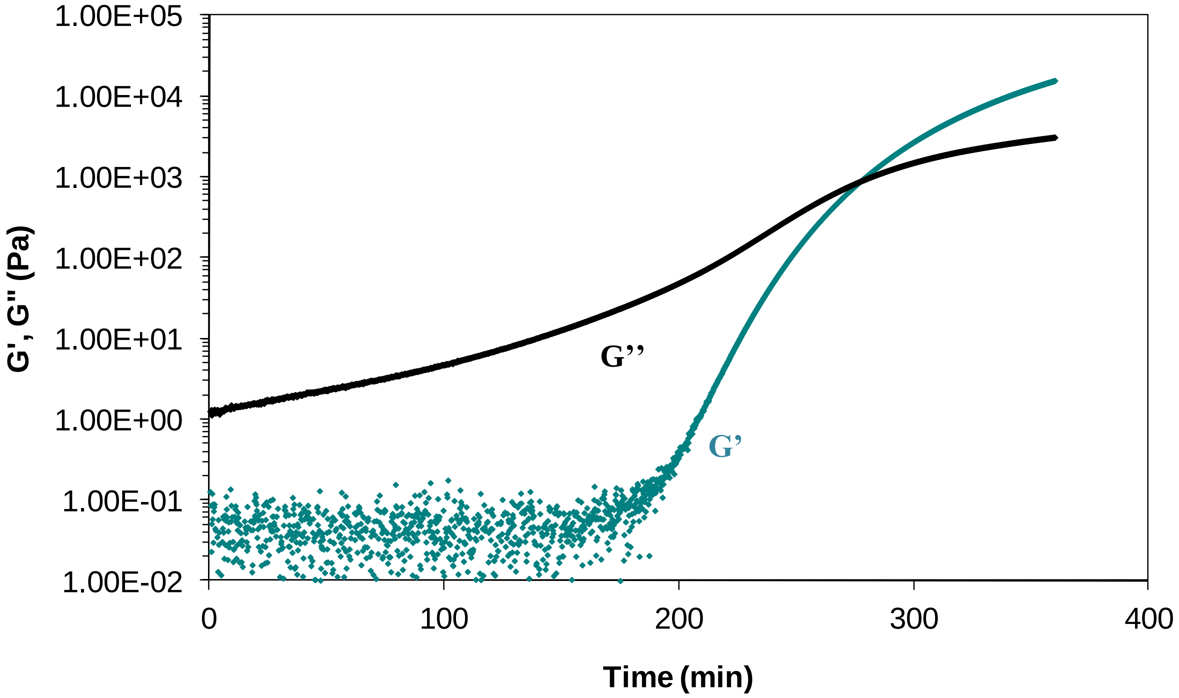


Figure S10 - Plot of G' and G'' moduli as a function of reaction time for the DGEBA/ **BF_4^- ▪4CA$^+$▪18-crown-6** 0.026eq./epoxy at 30°C.

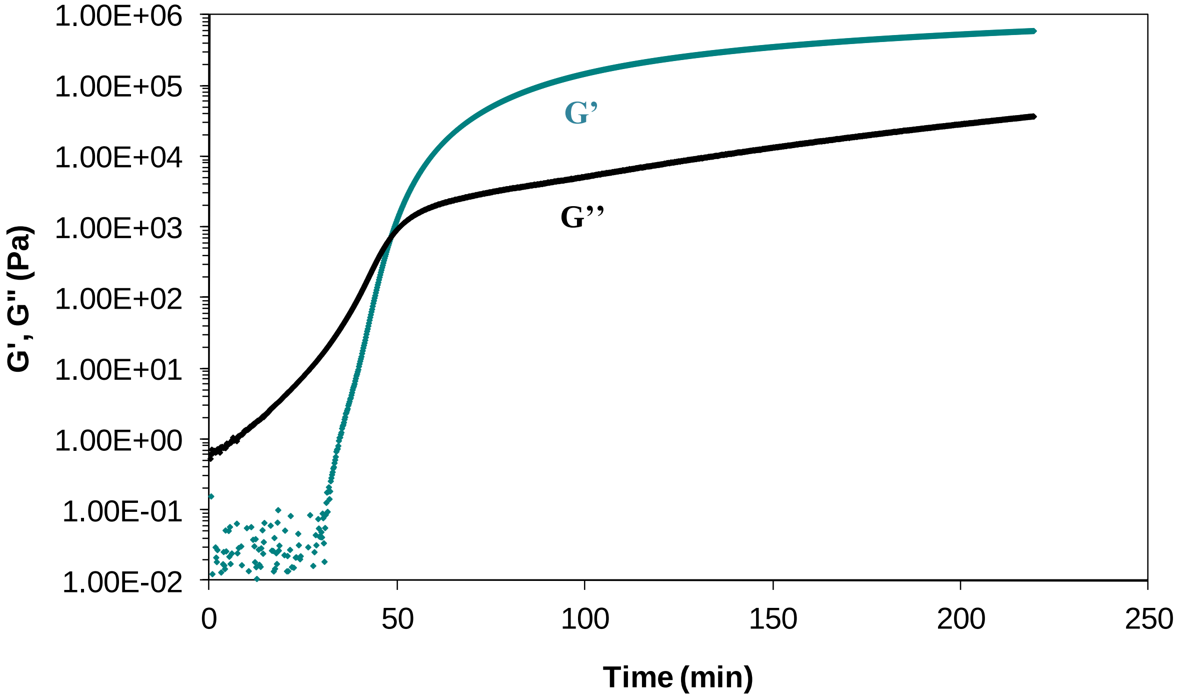


Figure S11 - Plot of G' and G'' moduli as a function of reaction time for the DGEBA/ **BF_4^- ▪4CA$^+$▪18-crown-6** 0.026eq./epoxy at 40°C.

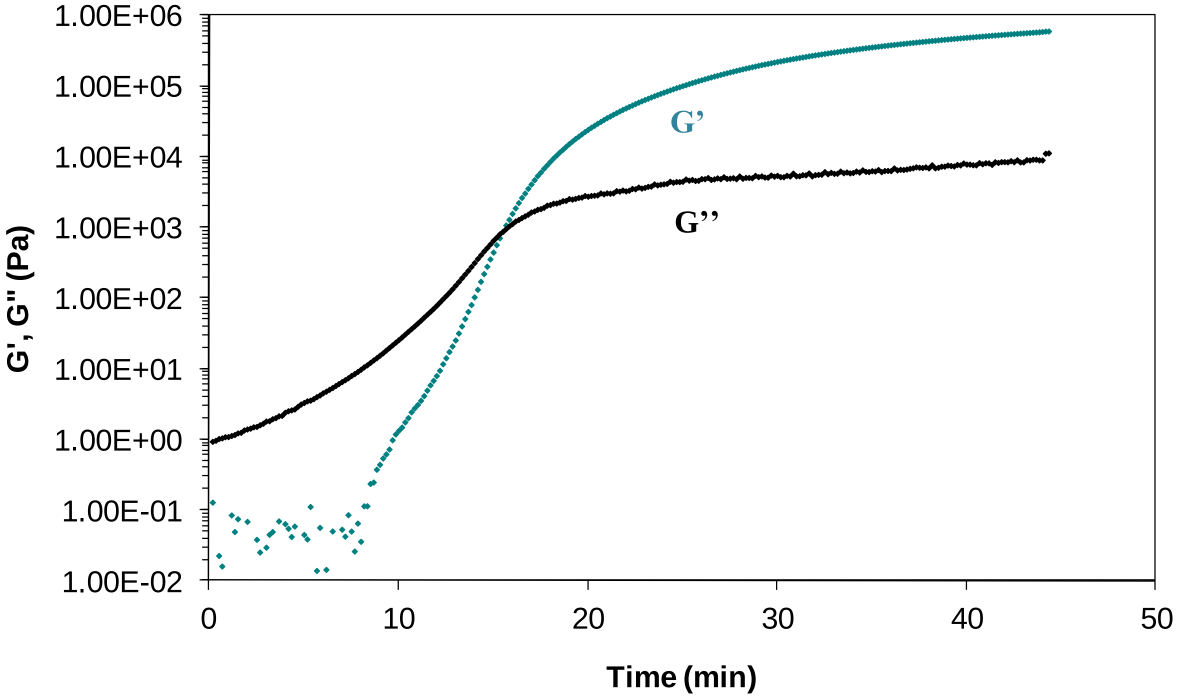


Figure S12 - Plot of G’ and G’’ moduli as a function of reaction time for the DGEBA/ **BF_4^- ▪4CA$^+$▪18-crown-6** 0.026eq./epoxy at 50°C.

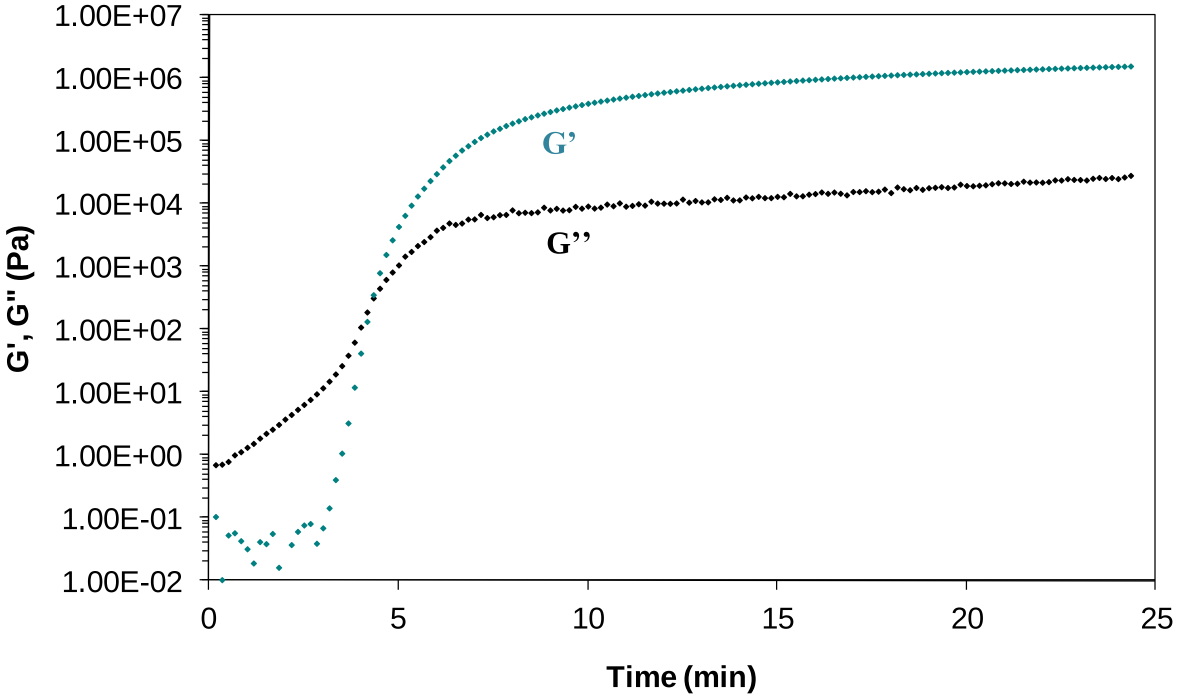


Figure S13 - Plot of G’ and G’’ moduli as a function of reaction time for the DGEBA/ **BF_4^- ▪4CA$^+$▪18-crown-6** 0.026eq./epoxy at 60°C.

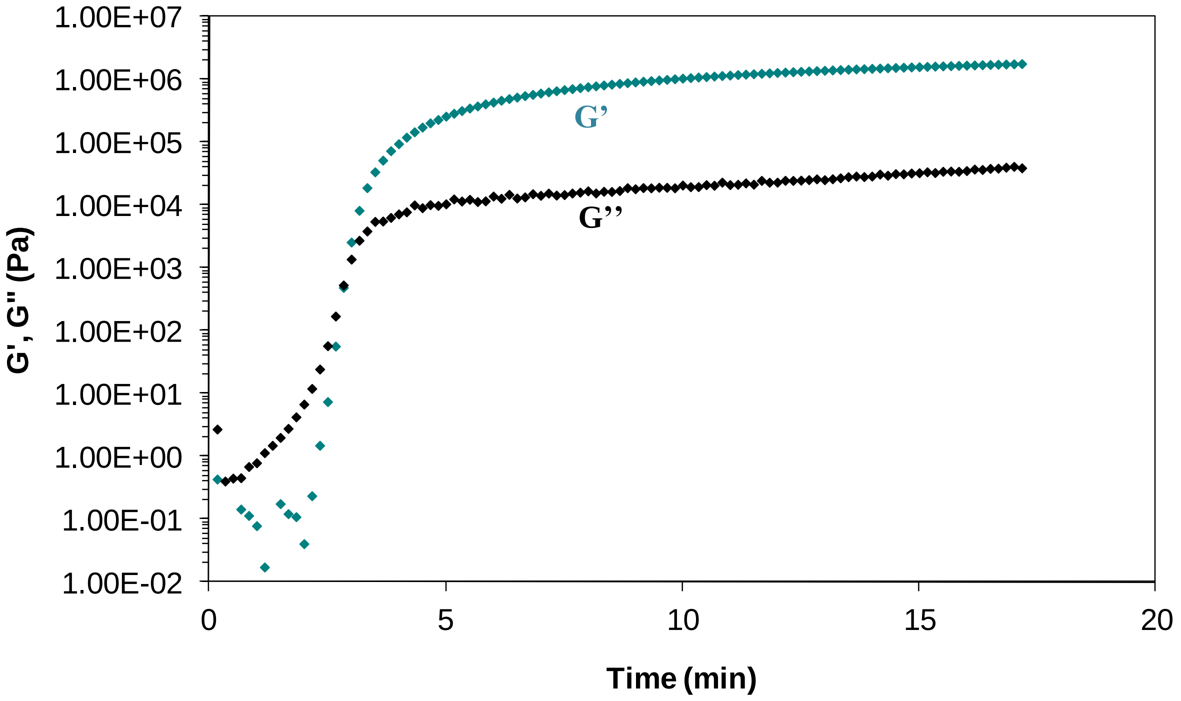


Figure S14 - Plot of G’ and G’’ moduli as a function of reaction time for the DGEBA/ **BF_4^-▪4CA$^+$▪18-crown-6** 0.026eq./epoxy at 70°C.

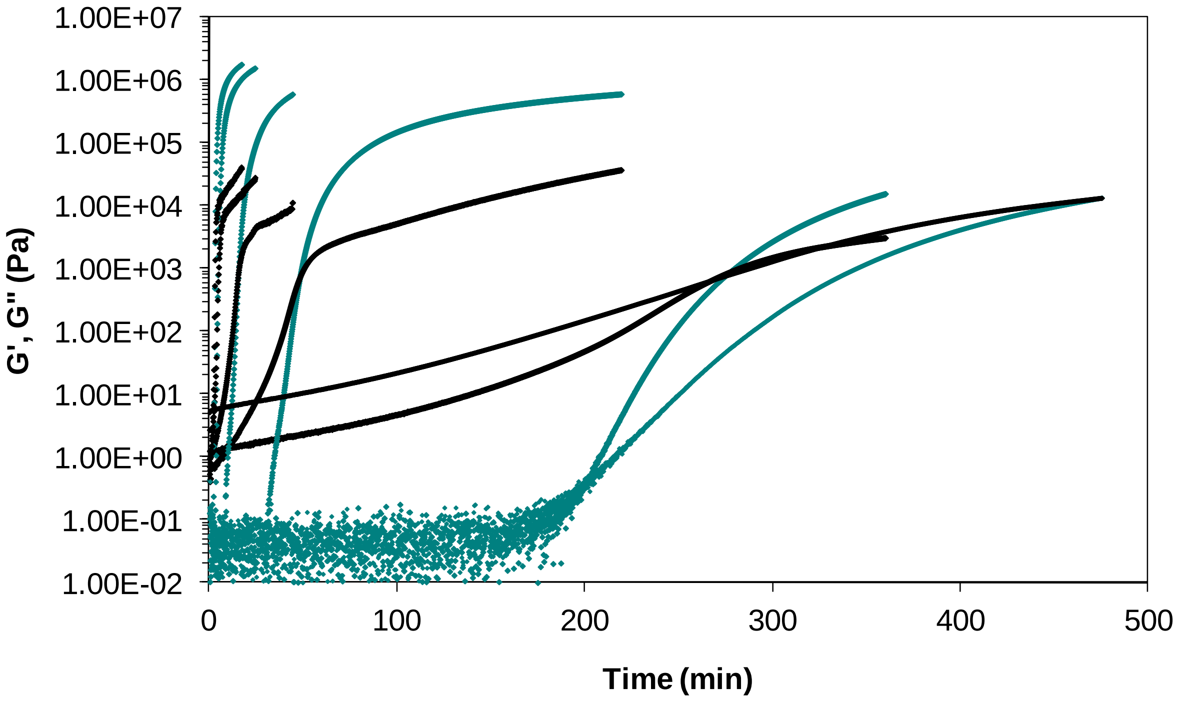


Figure S15 – Supperposition of the plots of G’ and G’’ moduli as a function of reaction time for the DGEBA/ **BF_4^-▪4CA$^+$▪18-crown-6** 0.026eq./epoxy for all the temperature previously reported.

VII. **DSC monitoring** of the curing: Procedure and Thermograms.

Calorimetric measurements were carried out using a TA DSC Q1000 instrument. Samples of 5 to 10 mg (prepared following the procedure previously reported in IV.) were scanned at 2°C.min^{-1} in 40µL aluminum pans under nitrogen atmosphere. Samples were first stabilized at 25°C and then heated to 180°C while monitoring the heat flow.

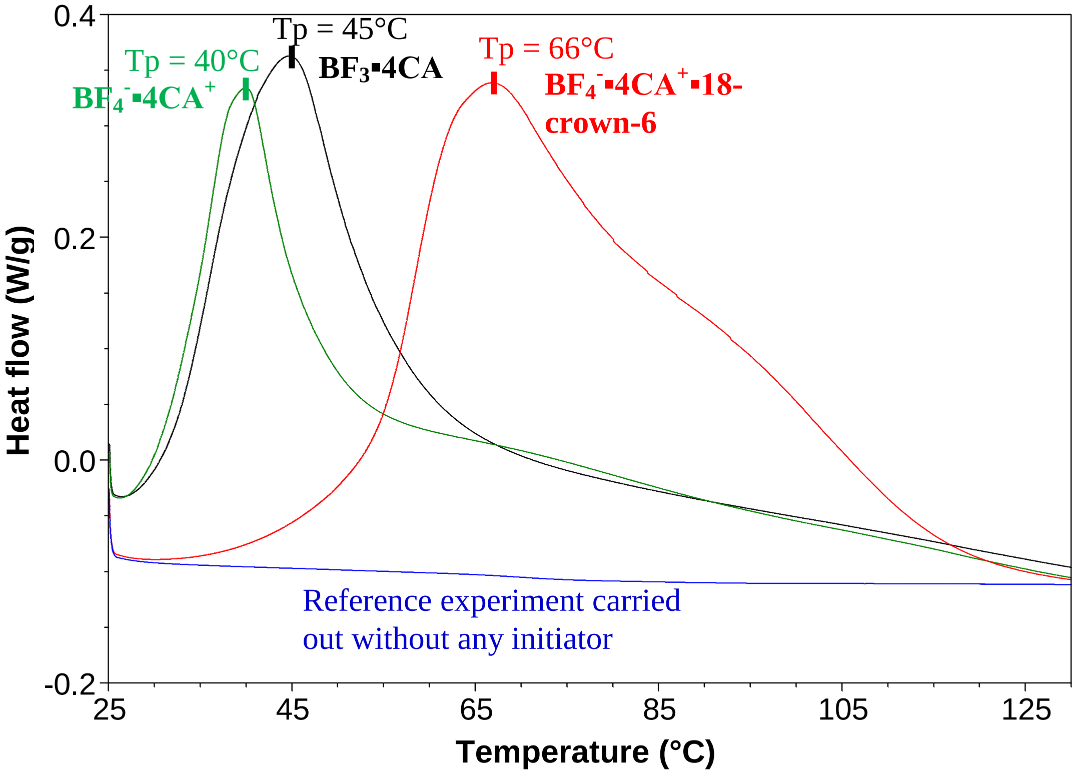


Figure S16 – DSC thermograms of the polymerization of the systems DGEBA/ **BF_4^-▪4CA$^+$** 0.026eq./epoxy, DGEBA/ **BF_3▪4CA** 0.026eq./epoxy and DGEBA/ **BF_4^-▪4CA$^+$▪18-crown-6** 0.026eq./epoxy carried out between 25°C and 180°C at 2°C/min. (Exotherm up)

The same experiments were carried out at different heating rates (5, 10 and 20°C/min) for mixtures of DGEBA with **BF_4^-▪4CA$^+$▪18-crown-6** (0.026eq./epoxy). Prime^{v} has suggested that the apparent cure activation energy (Ea) may be estimated with a very good accuracy through the dependence of the peak exotherm temperature Tp on heating rate according to the following equation:

$$E_a = -\frac{R}{1{,}052}\frac{\Delta \ln \Phi}{\Delta(1/Tp)}$$

where Φ is the heating rate and R the gas constant.

Φ (°C/min)	ln Φ	Tp (°C)	1000/Tp (K^{-1})
2	0.69	66	2.95
5	1.61	73	2.89
10	2.30	79	2.84
20	2.99	88	2.77

Table S1 – Heating rates Φ of the different curing experiment for the system **BF_4^-▪4CA$^+$▪18-crown-6 (**0.026eq./epoxy) and the corresponding peak exotherm temperatures Tp

For each heating rate the value of the peak exotherm temperature is reported in the Table S1. The plot of ln Φ as a function of 1/Tp, given in figure S17, presents a good linear relationship (correlation coefficient of 0.99) from which the apparent activation energy Ea is calculated using the previous equation. A value of **101KJ/mol** was found which is in very good agreement with the value estimated from gel times **100KJ/mol** and presented in the article.

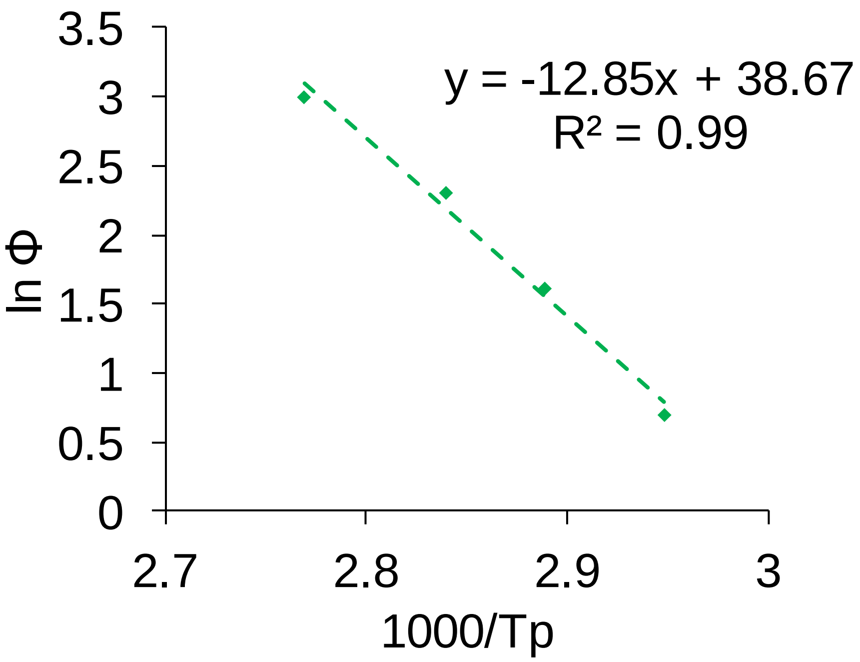


Figure S17 – Plot of ln Φ as a function of 1000/Tp obtained from the different DSC thermograms during the curing experiments of the system DGEBA/**BF_4^-▪4CA$^+$▪18-crown-6** (0.026eq./epoxy)

VIII. **DSC of materials** : glass temperature Tg.

Mixtures, prepared following the procedure previously reported (IV), were cured in a press at 70°C during 10 hours followed by a post curing at 140°C during 4 hours. DSC of the materials were performed using a TA DSC Q1000 instrument. Samples of 5 to 10 mg were scanned at 10°C.min^{-1} in 40µL aluminum pans under nitrogen atmosphere. They were first heated to 200°C to stabilize their geometry and optimize heat transfer and cooled to -20°C. They were then heated a second time to 200°C and Tg was obtained from the inflection point of the curves of the third scan.

Initiator	Tg of materials (°C)
BF$_3$▪4CA	125
BF$_4^-$▪4CA$^+$	142
BF$_4^-$▪4CA$^+$▪18-crown-6	121

Table S2 – Tg of materials DGEBA/ **BF$_4^-$▪4CA$^+$** 0.026eq./epoxy, DGEBA/ **BF$_3$▪4CA** 0.026eq./epoxy and DGEBA/ **BF$_4^-$▪4CA$^+$▪18-crown-6** 0.026eq./epoxy obtained from DSC thermograms carried out at 10°C/min.

IX. **References**.

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[i] J. J. Harris, S. C. Temin, **Proposed Mechanism for the Curing of Epoxy Resins with Amine-Lewis Acid Complexes or Salts**, J. App. Polym. Sci., *Vol. 10*, 523-531, **1966**

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[iii] N. Poisson, G. Lachenal, H. Sautereau, **Near- and mid-infrared spectroscopy studies of an epoxy reactive system, Vibrational spectroscopy**, *12*, 237-247, **1996**

[iv] P. Musto, E. Martuscelli, G. Ragosta, P. Russo, P. Villano, **Tetrafunctional Epoxy Resins : Modeling the Curing Kinetics Based on FTIR Spectroscopy Data**, J. App. Polym. Sci., *Vol. 74*, 532-540, **1999**

[v] B. Prime, in **Thermal Characterization of Polymeric Materials**, Ch. 5, E. A. Turi, ed., Academic Press, New York, **1981**