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## Supplementary Information

# Anionic Polymerization of Phenyl-Substituted Isoprene Derivatives: Polymerization Behaviour and Cyclization-Enabled Fluorescence

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## Instrumentation

### Gel Permeation Chromatography (GPC)

GPC analysis was performed on an Agilent 1260 Infinity II instrument containing a MZ-GEL-DS plus $10^5/10^3/100$ Å column set from MZ-Analysetechnik (Mainz, Germany). All detection were performed by a RI detector (Agilent G1362A). THF was the eluent, and the injection volume was 100 µL. All measurements were measured at 20°C using a flow rate of 1 mL/min. The analysis was calibrated on a toluene standard. The chosen polystyrene and polyisoprene standards are purchased from PSS Polymer Standard Service GmbH (Mainz, Germany).

### Nuclear Magnetic Resonance (NMR) spectroscopy

All NMR spectra ($^1$H, $^{13}$C, $^1$H-$^1$H-COSY, $^1$H-$^{13}$C-HSQC, $^1$H-$^{13}$C-HMBC, and real-time kinetics) were recorded on a Bruker Advance 400 spectrometer equipped with a 5 mm BBFO-SmartProbe with z gradient and ATM as well as a SampleXPress 60 sample changer. Every spectrum was referenced internally to the assigned proton signal of the used deuterated solvent ($CDCl_3$ and $C_6D_{12}$). The measured spectra were evaluated using MestReNova 14.2.0 from Mestrelab Research S.L. (Santiago de Compostela, Spain).

### Differential Scanning Chromatography (DSC)

The thermal analysis was conducted using a DSC 250 from TA instruments with an RCS 90 compressor calibrated with an indium and *n*-octane standard. A minimum of 5 mg polymer was weighed in a pan and subsequently sealed. Firstly, to remove any thermal history the samples were heated before the actual analysis was performed using the second heating ramp using a rate of 10 K/min. All measurements were performed under a nitrogen atmosphere. The different temperature ranges are summarized in the following **Table S1**.

**Table S1**: Temperature ranges of the DSC analysis depending on the polymer entry.

| Entries | $T_{min}$ / °C | $T_{max}$ / °C |
|---|---|---|
| 1-14 | 0 | 120 |
| 15-18 | -90 | 120 |
| 19-20 | 0 | 250 |

**Density functional theory (DFT)** calculations were performed using the ORCA 4.2.1 software on the MOGON II supercomputer, located at the high-performance computing center of Johannes Gutenberg University Mainz. The BXLYP hybrid density functionals were selected due to the availability of the calculation of the analytical Hessian matrix. Additionally, the D3BJ atom-pairwise dispersion correction was applied to the DFT energy, with Becke-Johnson damping. The combination of the Grid6 integration grid and TightSCF convergence criteria

was chosen to ensure accurate single-point energy calculations, while the def2-TZVP valence triple-zeta basis set was employed for all calculations. Geometry optimization was performed using the RIJCOSX approximation and a GridX7 integration grid, providing significant acceleration. Geometrical Counterpoise Correction (gCP) was applied to mitigate artificial overbinding effects. As the experiments involved the use of cyclohexane, with its low dielectric strength ($\varepsilon_r$=2.02), which offers only a negligible solvent effect, solvation effects were not considered. IboView18 was utilized for the visualization of molecular geometries.

**UV/Vis absorption spectra in solution** were recorded on a Jasco V770 spectrometer using 1.0 cm quartz cells. In advance, three solutions were prepared with increasing dilution. 40 mg of the cyclized sample were dissolved in 20 mL dry toluene to obtain a concentration of 2 mg $mL^{-1}$. A dilution series yielded the solutions with concentrations of 0.2 and 0.02 mg $mL^{-1}$.

**Emission spectra (solution samples)** were recorded with an FS5 spectrometer from Edinburgh Instruments equipped with the photomultiplier detector R928P (200-870 nm). A xenon arc lamp (150 W) was used for excitation. The same solutions were used as for the UV/Vis absorption experiments.

**Emission spectra (powder samples)** were recorded with an FLS1000 spectrometer from Edinburgh Instruments equipped with the cooled photomultiplier detector N-G11 PMT-980 (250-980 m). A xenon arc lamp Xe2 (450 W) was used for excitation. Absolute luminescence quantum yields $\Phi$ were determined using an integrating sphere from Edinburgh Instruments. Relative uncertainty of $\Phi$ is estimated to be ±20%. The samples were dried under vaccuo before measurements. The powder was placed on the Teflon sample holder to give an evenly distribution.

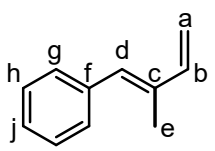
## Experimental section

**Reagents**. Chemicals and solvents were purchased from commercial suppliers (Alfa Aesar, Sigma Aldrich, Carbolution Chemicals GmbH, Acros Organics, TCI and Fisher Scientific). Both Chloroform-d and cyclohexane-d12 were purchased from Deutero GmbH. Cyclohexane and THF were dried prior to use. THF was purified using *sec*-butyl lithium and 1,1-diphenylethylene (DPE) as an indicator. Cyclohexane was dried using sodium and benzophenone as an indicator.

**Monomer synthesis**:

Both monomers were synthesized *via* Wittig-reaction starting from the respective carbonyl moiety.

*Synthesis of E-(2-Methylbuta-1,3-dien-1-yl) benzene (1-Phenyl isoprene, 1PhI)*: In a flame dried 1 L-Schlenk flask methyltriphenylphosphonium bromide (128 g, 0.36 mol, 1.2 eq) was suspended in dry THF (600 mL). 40 g (0.36 mol, 1.2 eq) potassium *tert*-butoxide was added slowly to the solution to form the corresponding ylide. After 1 hour, the carbonyl reagent (44 g, 0.3 mol, 1 eq) was added and the solution was stirred for 14 hours at room temperature. After completion, the reaction mixture, first diluted with 50 mL *n*-pentane, was concentrated under reduced pressure. The precipitated byproducts were removed from the solution *via* centrifugation. Subsequently, the solvents were removed by distillation under reduced pressure. First, the crude product crude product was removed from the TPPO by distillation in high vacuum ($1.0 \times 10^{-3}$ mbar, 150 °C oil bath temperature). Subsequently, a fractionated distillation was performed to obtain the pure diene under high vacuum ($1.0 \times 10^{-3}$ mbar, $T_b$ = 36°C).



1PhI

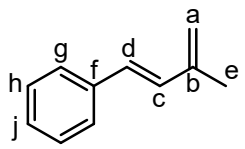
**$^1$H NMR** (400 MHz, $CDCl_3$) δ(ppm) = 7.46 – 7.28 (m, H-g,h, 4H), 7.34 – 7.24 (m, H-j, 1H), 6.69 – 6.53 (m, H-b,d, 2H), 5.43 – 5.20 (m, H-a, 2H), 2.07 (d, H-e, 3H).

**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ(ppm) = 141.94 (H-D), 137.79 (H-F), 136.03 (H-C), 131.71 (H-B), 129.27 (H-H), 128.18 (H-G), 126.67 (H-J), 113.02 (H-A), 13.22 (H-E).

$\boldsymbol{T_b}$ = 104°C (40 mbar)

*Synthesis of (E)-(3-methylbuta-1,3-dien-1-yl) benzene (4-Phenyl isoprene, 4PhI)*: In a flame dried 1 L-Schlenk flask methyltriphenylphosphonium bromide (128 g, 0.36 mol, 1.2 eq) was suspended in dry THF (600 mL). 196 mL of a 2 M solution of sodium hexamethyldisiloxyamine (NaHMDS) in THF was added slowly to the solution to form the corresponding ylide. After 1 hour, the carbonyl reagent (44 g, 0.3 mol, 1 eq) was added and the solution was stirred for 14

hours at 50 °C. After completion, the reaction mixture, first diluted with 50 mL *n*-pentane, was concentrated under reduced pressure. The precipitated byproducts were removed from the solution *via* centrifugation. Subsequently, the solvents were removed by distillation under reduced pressure. First, the crude product was removed from the TPPO by distillation in high vacuum ($1.0 \times 10^{-3}$ mbar, 150°C oil bath temperature). Subsequently, a fractionated distillation was performed to obtain the pure diene under high vacuum ($1.0 \times 10^{-3}$ mbar, $T_b$ = 36°C).




4PhI

**$^1$H NMR** (400 MHz, $CDCl_3$) δ (ppm) = 7.56 – 7.49 (m, H-g, 2H), 7.46 – 7.37 (m, H-h, 2H), 7.36 – 7.26 (m, H-j, 1H), 6.99 (d, J = 16.1 Hz, H-d, 1H), 6.64 (d, J = 16.1 Hz, H-c, 1H), 5.25 – 5.15 (m, H-a, 2H), 2.08 (dd, J = 1.5, 0.8 Hz, H-e, 3H).

**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ(ppm) = 142.12 (H-B), 137.48 (H-F), 131.76 (H-D), 128.74 (H-C,H), 127.51 (H-J), 126.57 (H-G), 117.45 (H-A), 18.68 (H-E).

$T_m$ = 33°C $T_b$ = 47°C ($1 \times 10^{-3}$ mbar)

**General procedure for the carbanionic polymer synthesis:**

*Homopolymerization in CHx:* Residual protonic traces of all monomers were eliminated by drying over calcium hydride and trioctylaluminium. Subsequently, the monomers were distilled into an anionic flask. In an argon-flooded glove box the monomers and solvents were volumetrically added into the reaction vessel. Due to the crystalline nature of 4PhI this monomer was measured gravimetrically. The polymerizations were initiated by the addition of *sec*-butyl lithium into the vigorous stirred solution. After stirring overnight, the polymerizations were terminated outside of the glove box by addition of degassed methanol. Precipitation of the polymer solution was performed in a 50:50 solution of methanol and 2-propanol. After drying under reduced pressure, the samples were stored in the absence of light and air at -20°C.

*Homopolymerization in THF:* Deviating from the procedure described above, the prepared solution were dissolved in an anionic flask and later transferred outside the glove box. In a liquid $N_2$/ethanol cooling bath, the reaction flask was cooled to -78°C. Under argon, the polymerization was initiated via *sec*-butyl lithium using a syringe. After 4 hours, the termination was performed by addition of methanol. The polymer was precipitated into a 50:50 solution of methanol and 2-propanol. The polymers were dried in vacuo and stored in the absence of light and air at -20°C.

## NMR Analysis

NMR characterization of monomers 1PhI and 4PhI

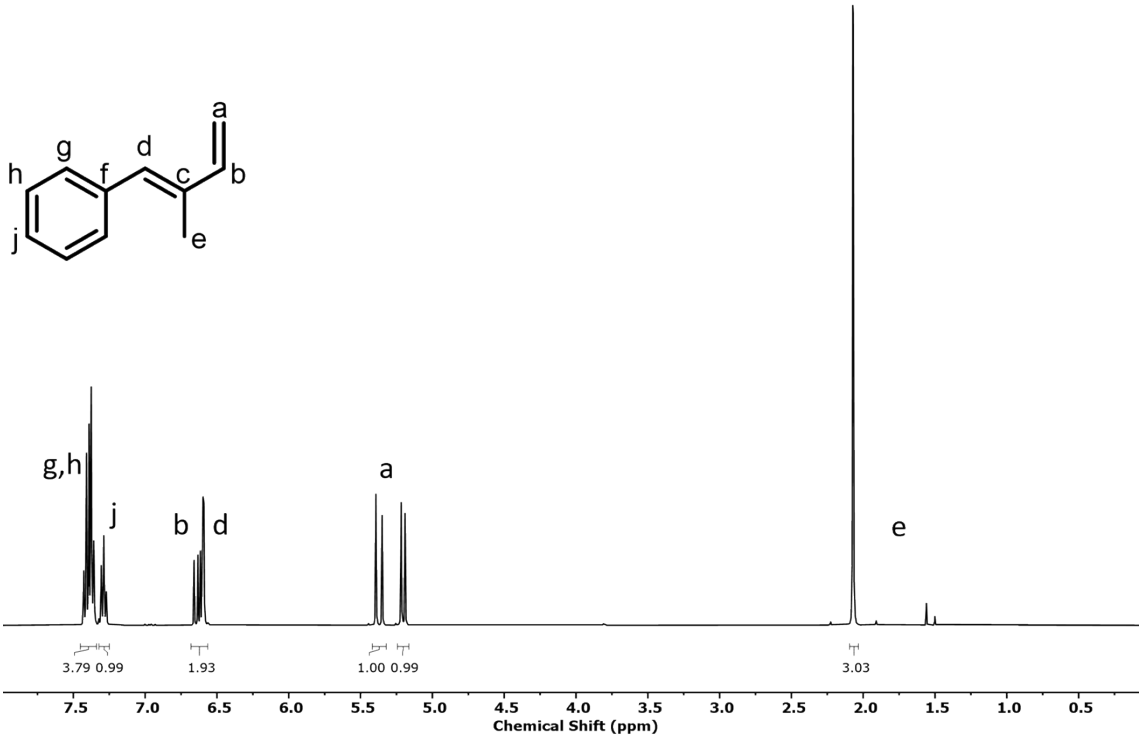



**Figure S1**: $^{1}$H NMR spectrum (400 MHz, $CDCl_3$) of 1PhI

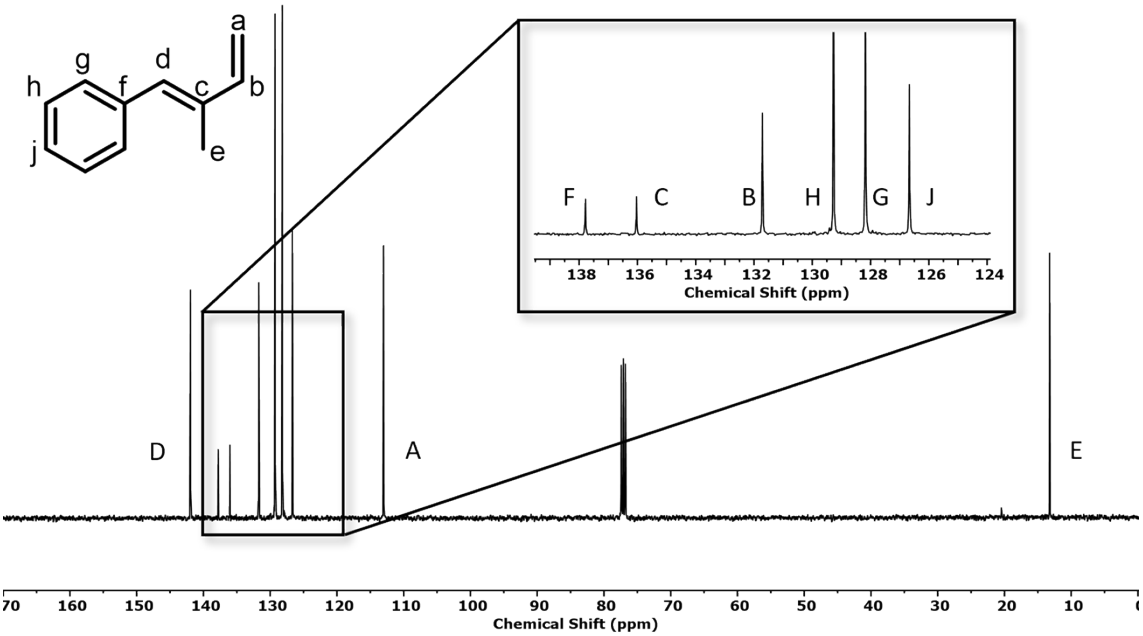



**Figure S2**: $^{13}$C NMR spectrum (103 MHz, $CDCl_3$) of 1PhI.

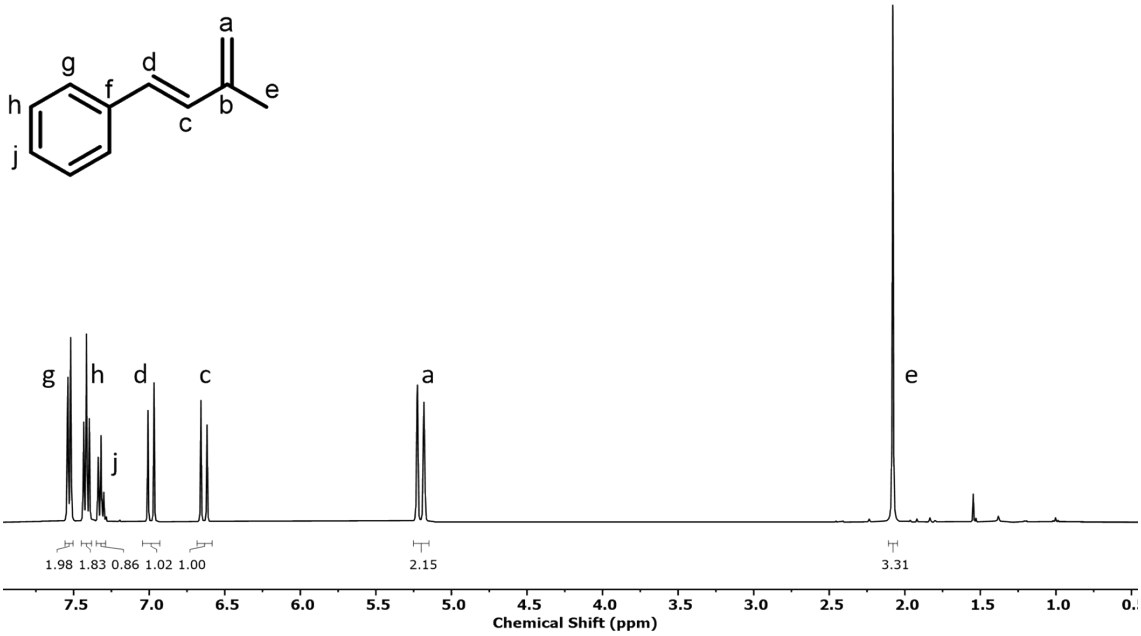



**Figure S3**: $^{1}$H NMR spectrum (400 MHz, $CDCl_3$) of 4PhI

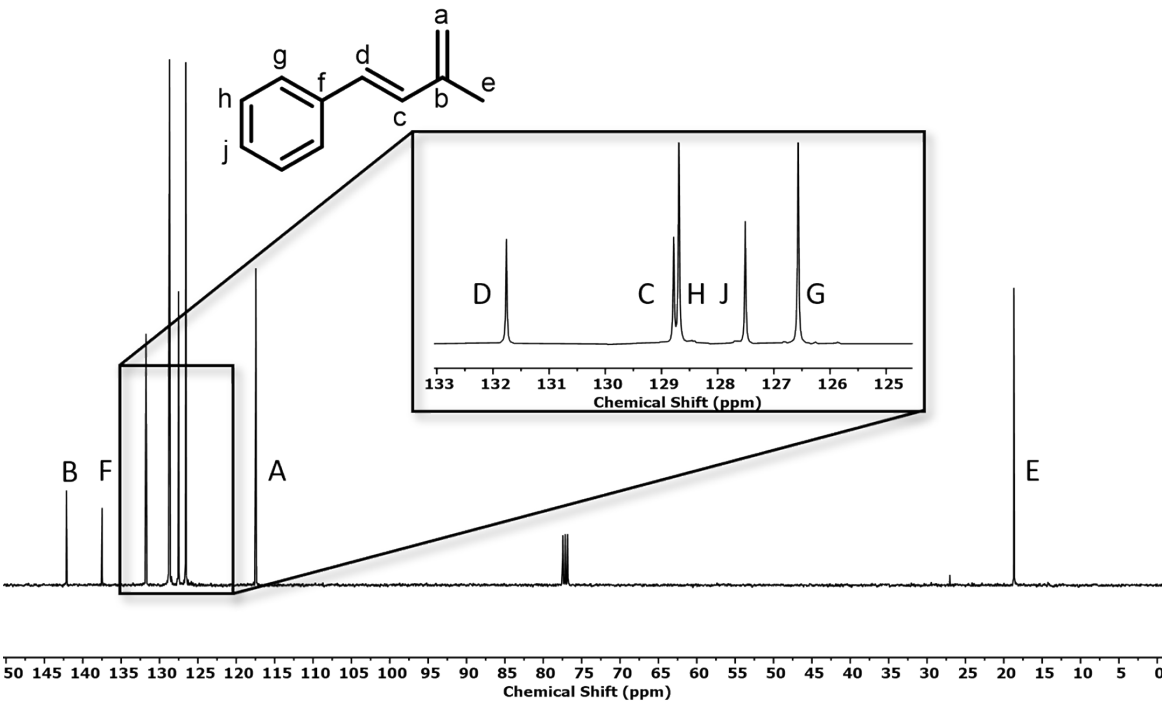



**Figure S4**: $^{13}$C NMR spectrum (103 MHz, $CDCl_3$) of 4PhI.

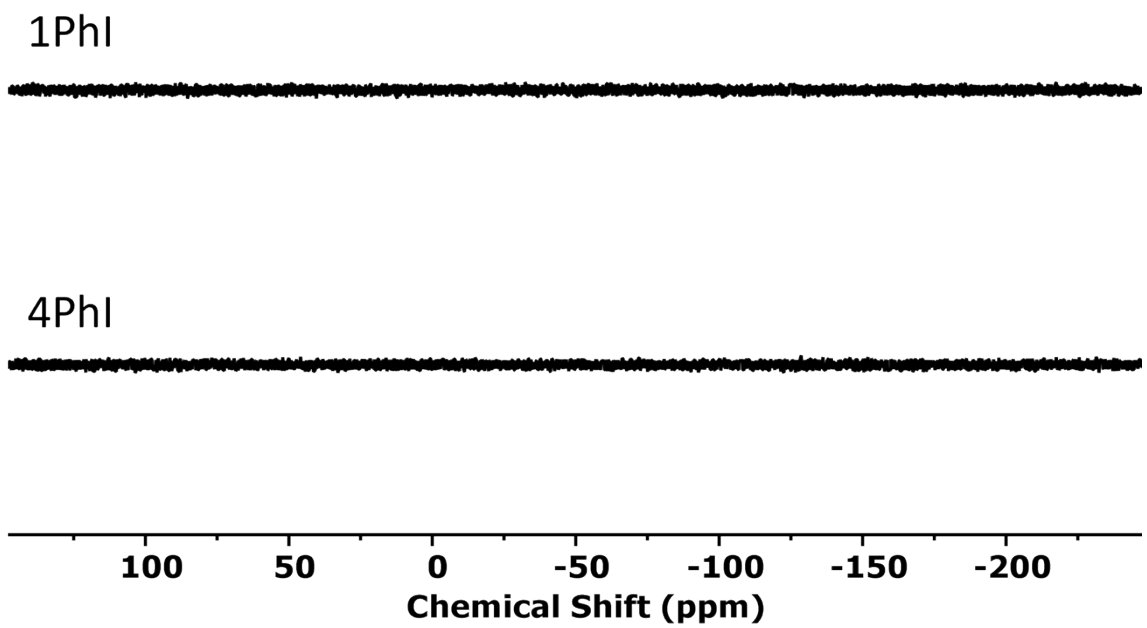



**Figure S5**: $^{31}P$ NMR spectra (162 MHz, $CDCl_3$) of 1PhI and 4PhI.

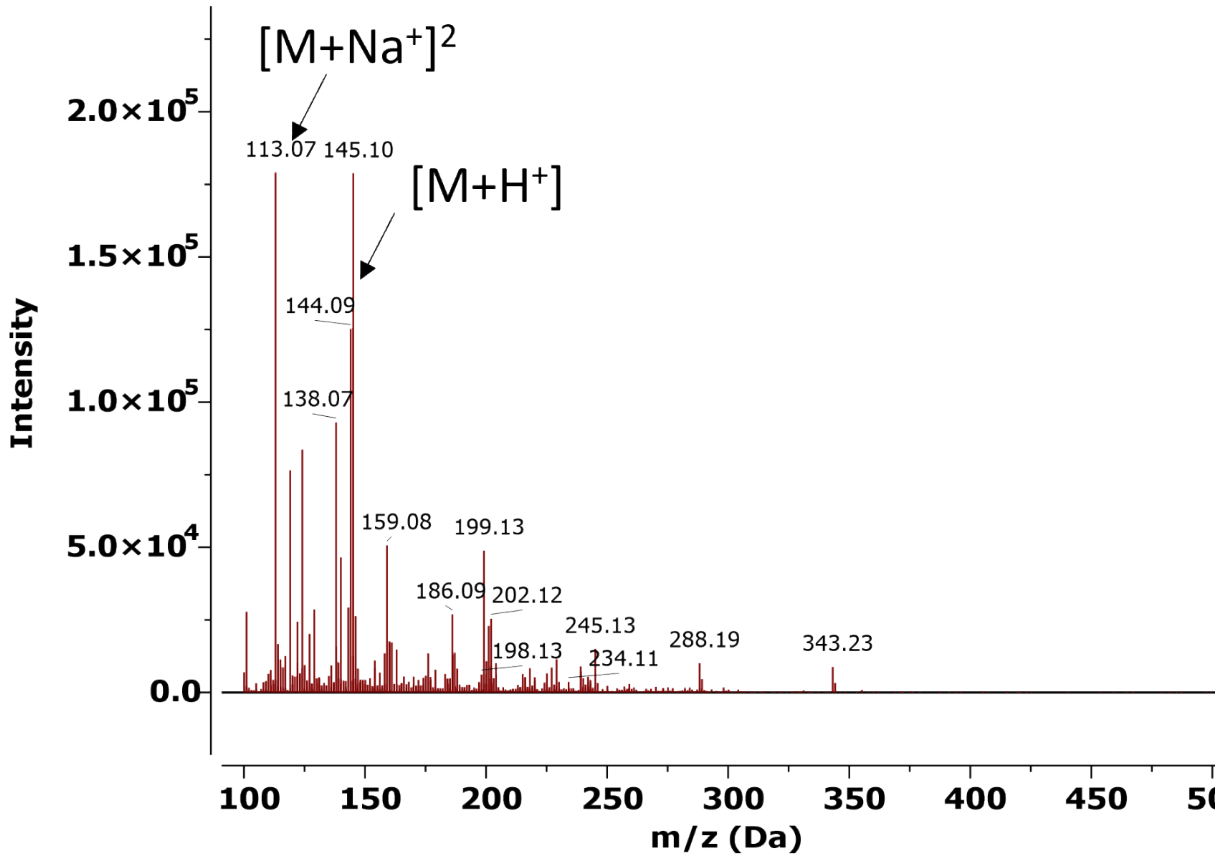



**Figure S6**: Mass spectrum of 1PhI recorded on a G6545A Q-ToF (Agilent GmbH, Waldbronn) *via* atmospheric pressure chemical ionization (APCI). This experiment was repeated twice. Lower purity was traced back to the literature known suppression of adduct ions by acetonitrile.[1]

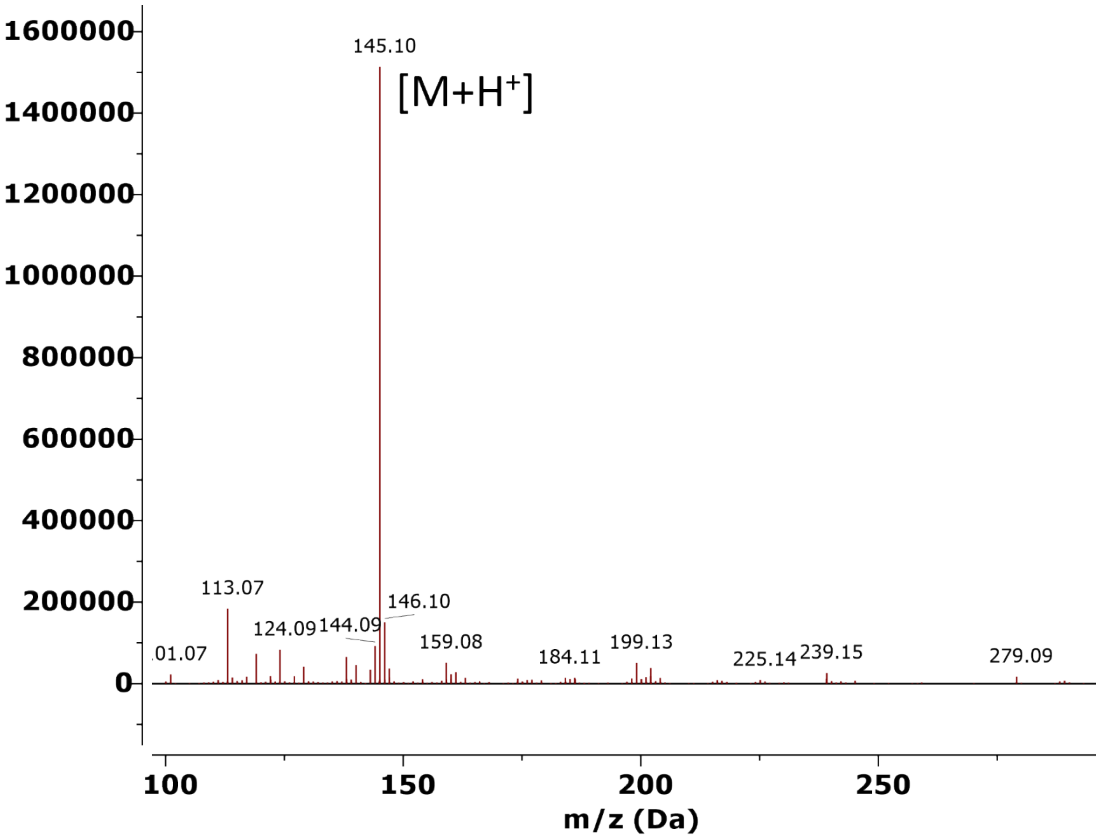



**Figure S7**: Mass spectrum of 4PhI recorded on a G6545A Q-ToF (Agilent GmbH, Waldbronn) *via* atmospheric pressure chemical ionization (APCI).

## NMR characterization of the homopolymers P(1PhI) and P(4PhI)

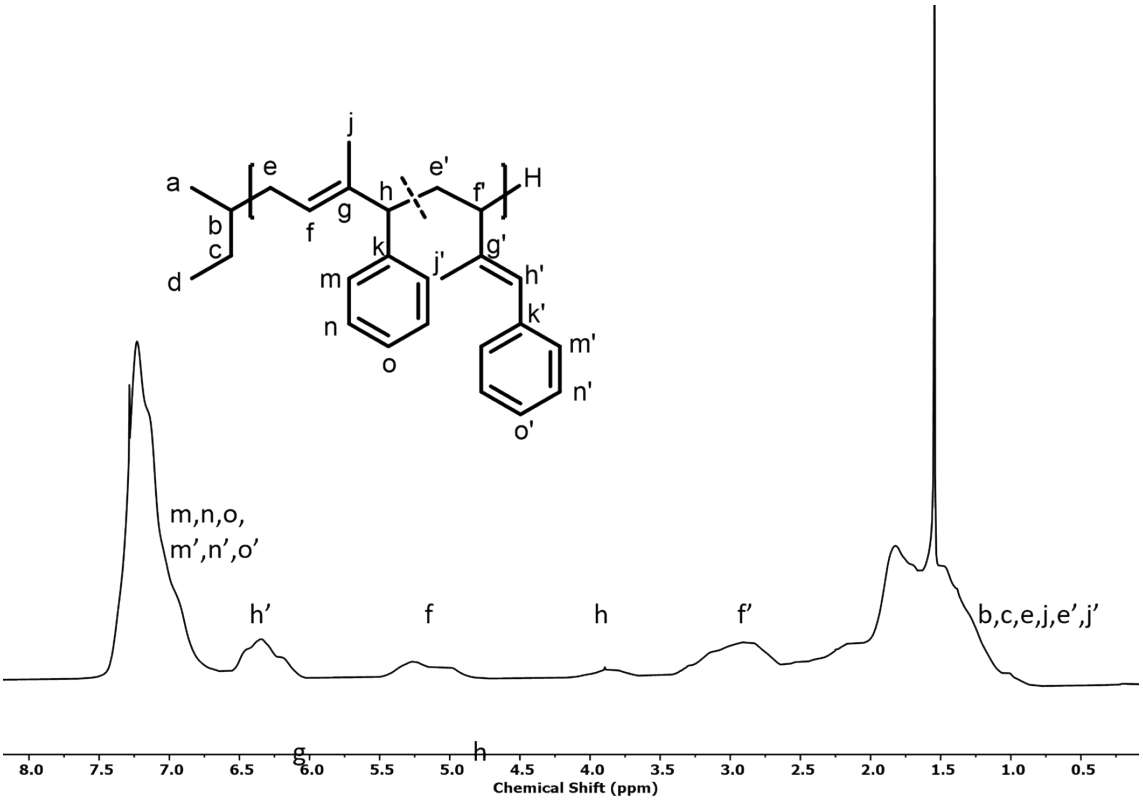



**Figure S8**: $^{1}$H NMR spectrum (400 MHz, $CDCl_3$) of P(1PhI)

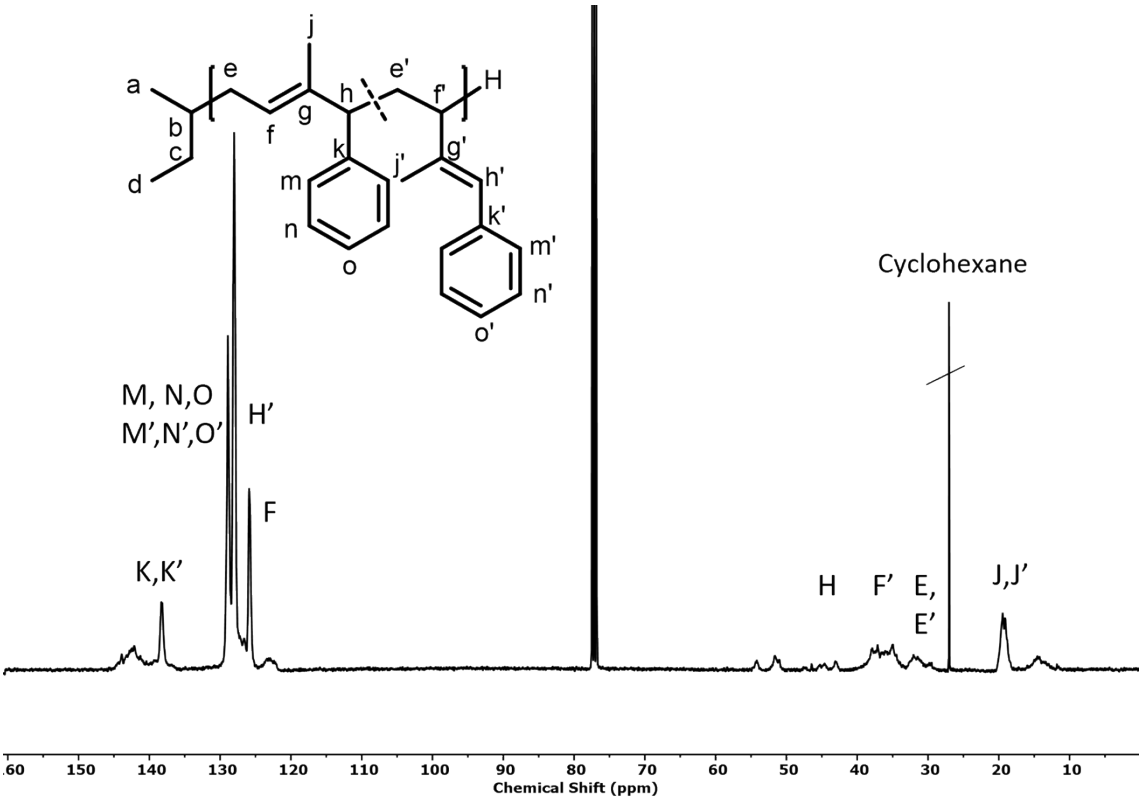



**Figure S9**: $^{13}C$ NMR spectrum (103 MHz, $CDCl_3$) of P(1PhI).

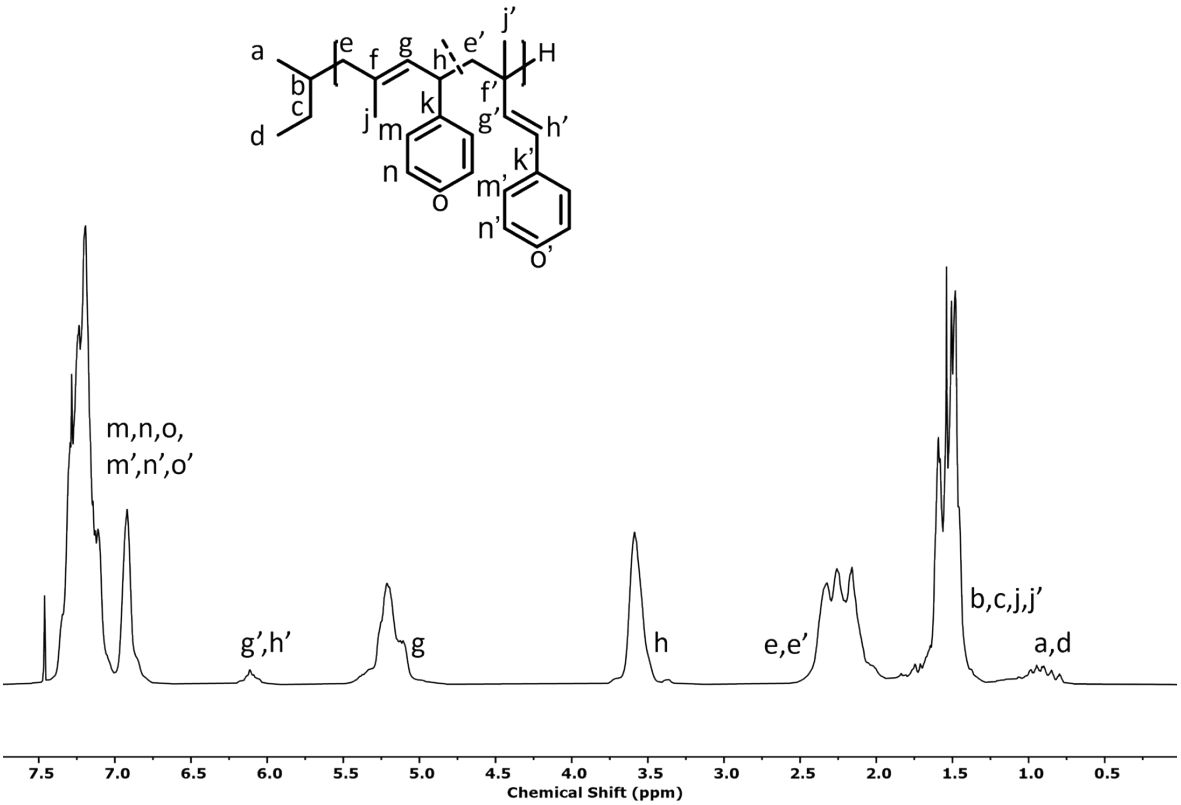



**Figure S10**: $^{1}H$ NMR spectrum (400 MHz, $CDCl_3$) of P(4PhI)

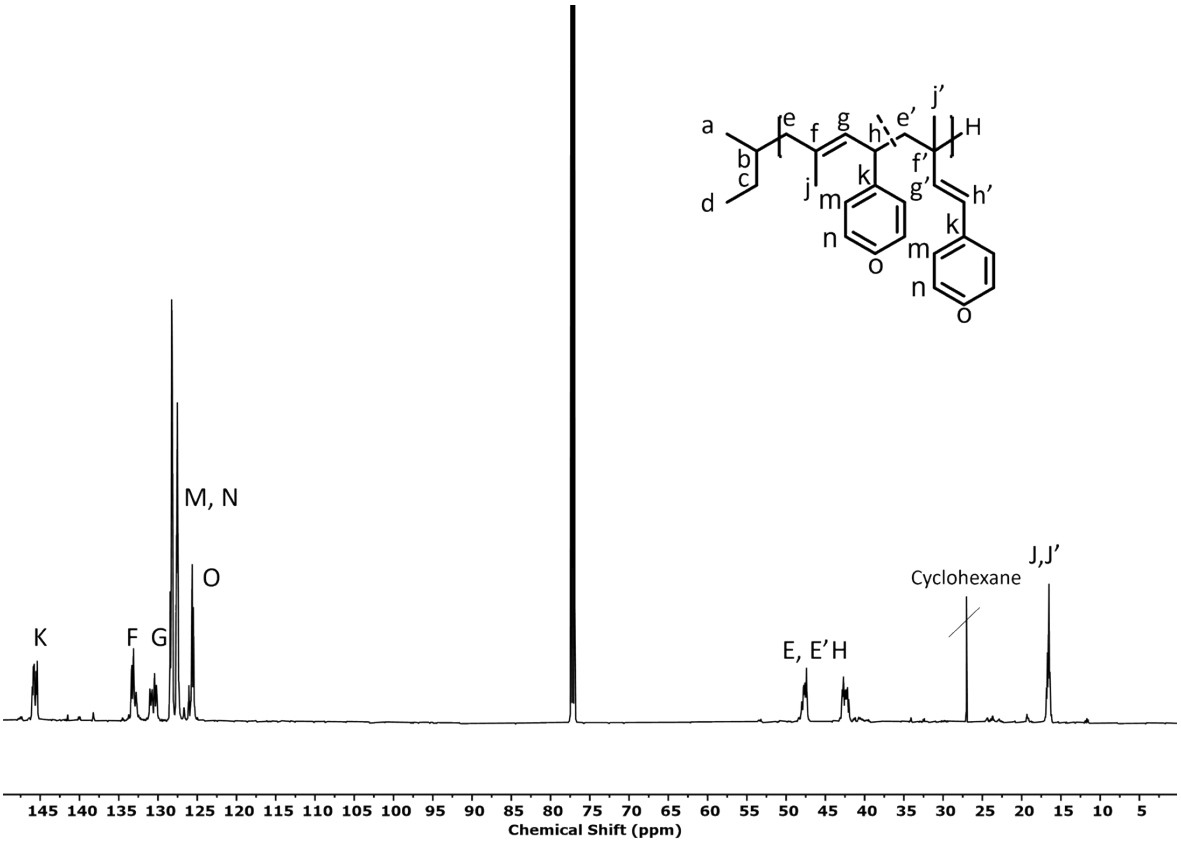



**Figure S11**: $^{13}$C NMR spectrum (103 MHz, $CDCl_3$) of P(4PhI).

## Thermal Analysis of homopolymers

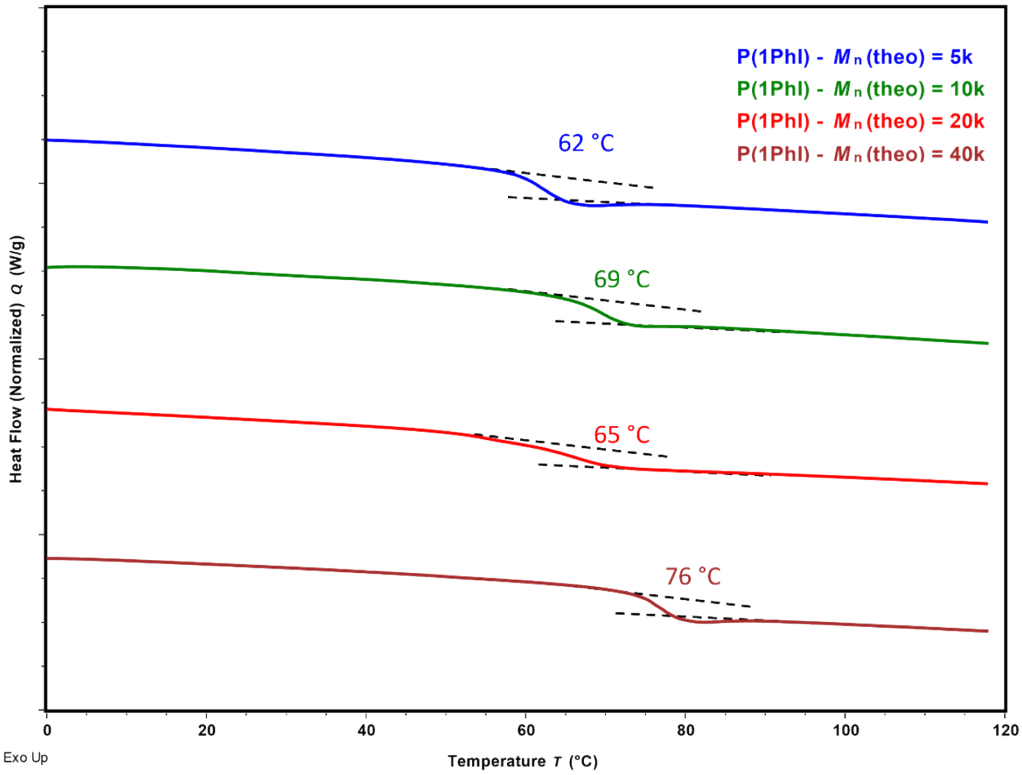



**Figure S12**:DSC curves for the homopolymers P(1PhI) with increasing $M_{n,targ}$ of 5 to 40 kg mol$^{-1}$ (Table 1, entries 1-4).

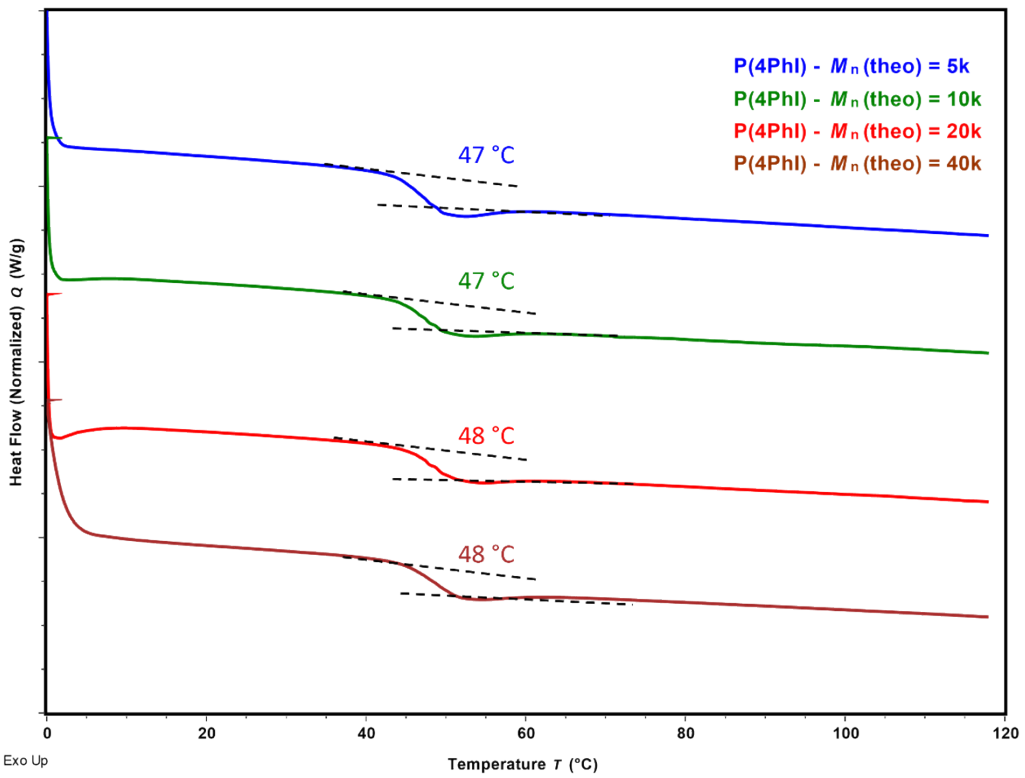



**Figure S13**: DSC curves for the homopolymers P(4PhI) with increasing $M_{n,targ}$ of 5 to 40 kg mol$^{-1}$ (Table 1, entries 5-8).

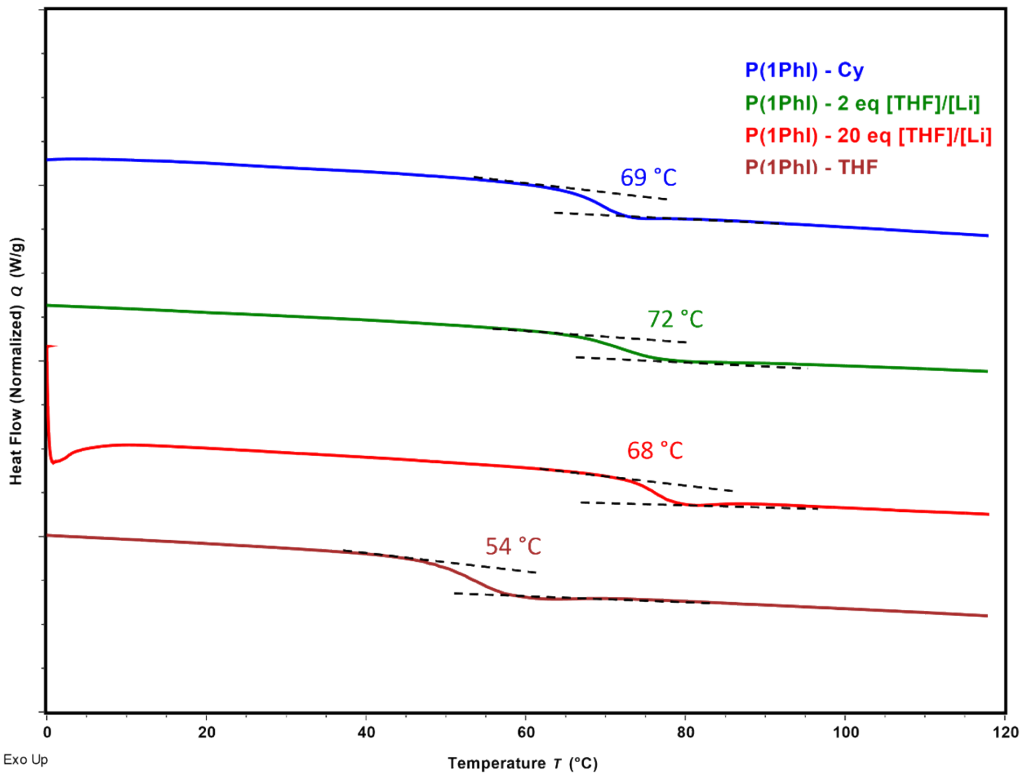



**Figure S14**: DSC curves for the homopolymers P(1PhI) polymerized with different modifier concentration (Table 2, entries 1, 9-11).

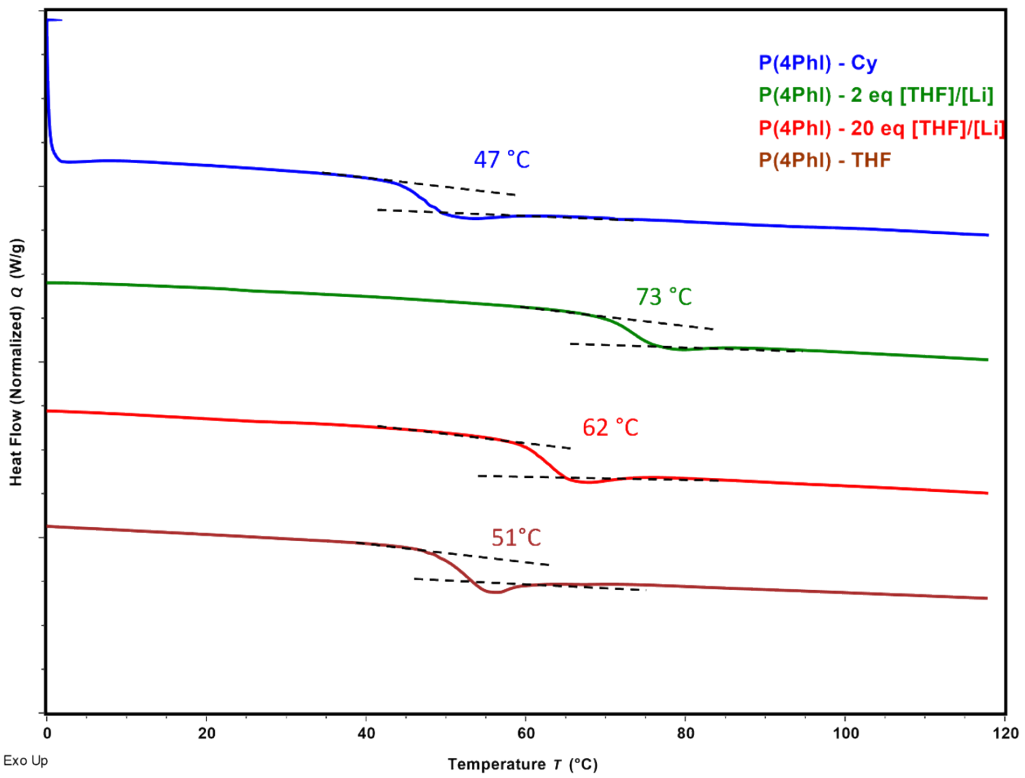



**Figure S15**: DSC curves for the homopolymers P(4PhI) polymerized in with different modifier concentration (Table 2, entries 5,12-14).

## GPC Analysis

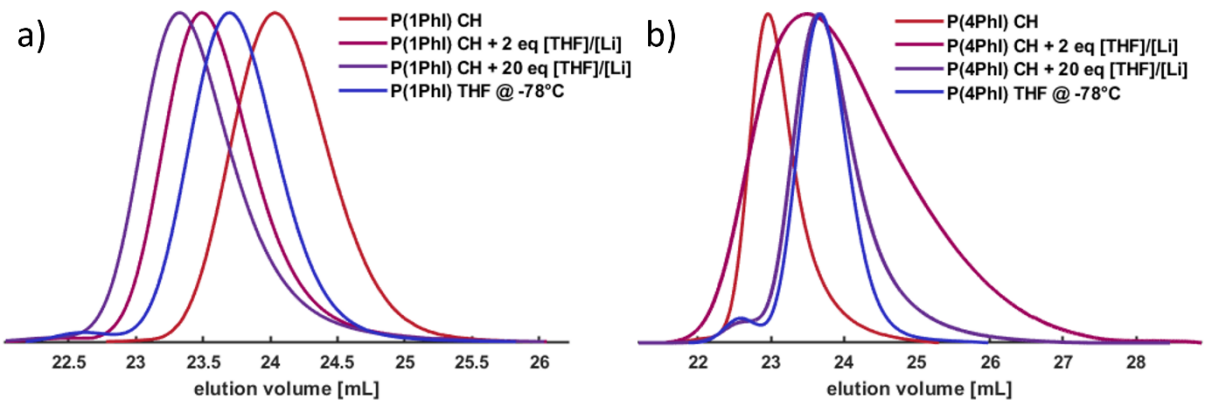



**Figure S16**: GPC traces of the polymerizations of a) 1PhI and b) 4PhI respectively containing increasing amount of THF in the polymerizations.

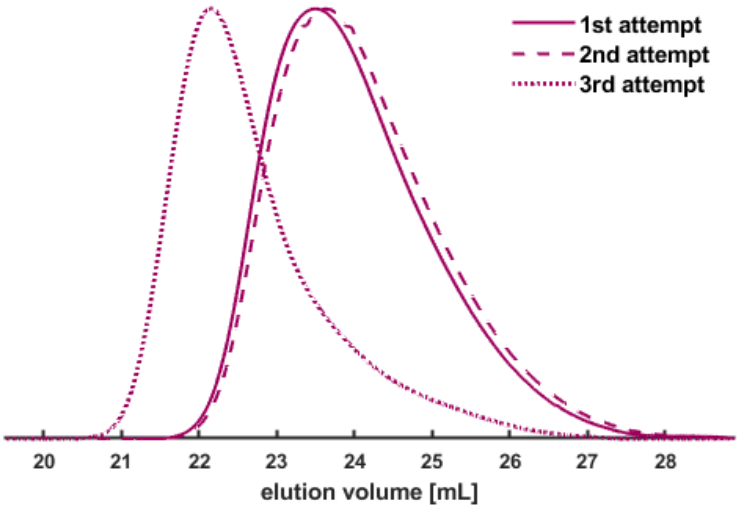



**Figure S17**: Broad GPC traces of all three attempts for the polymerization of 4PhI in the presence of 2 eq [THF]/[Li].

## *In situ* $^1$H NMR kinetics of copolymerisation

**Table S2**: Evaluated reactivity ratios of the copolymerisation of styrene and 1PhI and 4PhI, respectively, using the Meyer-Lowry model.

| Diene | $r_{diene}$ | $r_S$ |
|---|---|---|
| 1-Phenyl isoprene | 2.37 | 0.10 |
| 4-Phenyl isoprene | 9.1 | 0.101 |

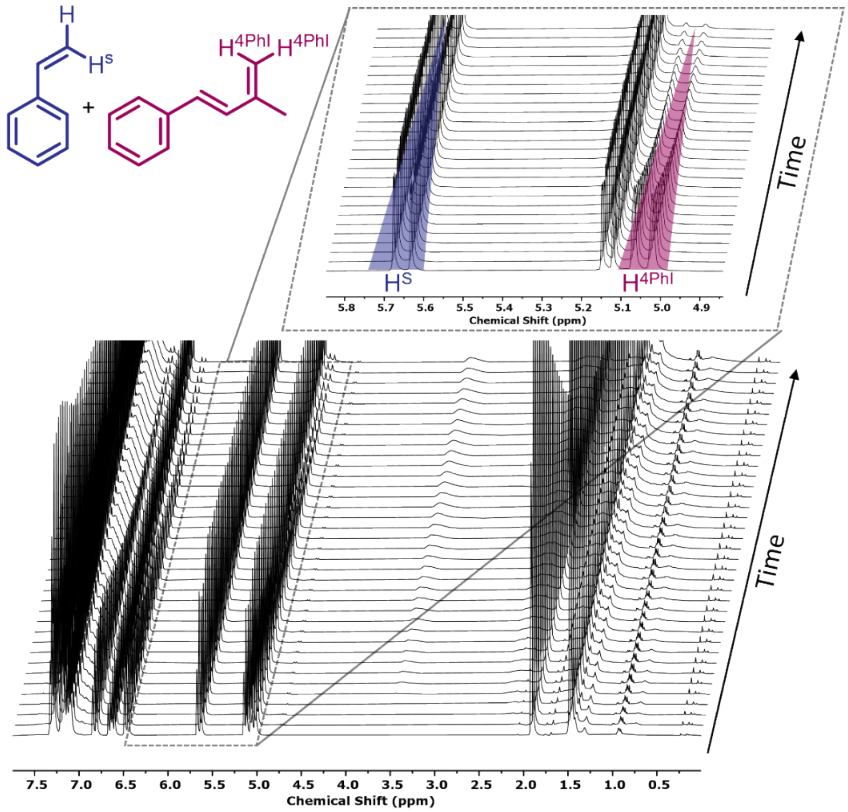



**Figure S18**: Stacked $^{1}$H NMR spectra of the *in situ* kinetics of the statistical copolymerisation of styrene and 4PhI and an expansion of the monomer signals used for determination of the concentration.

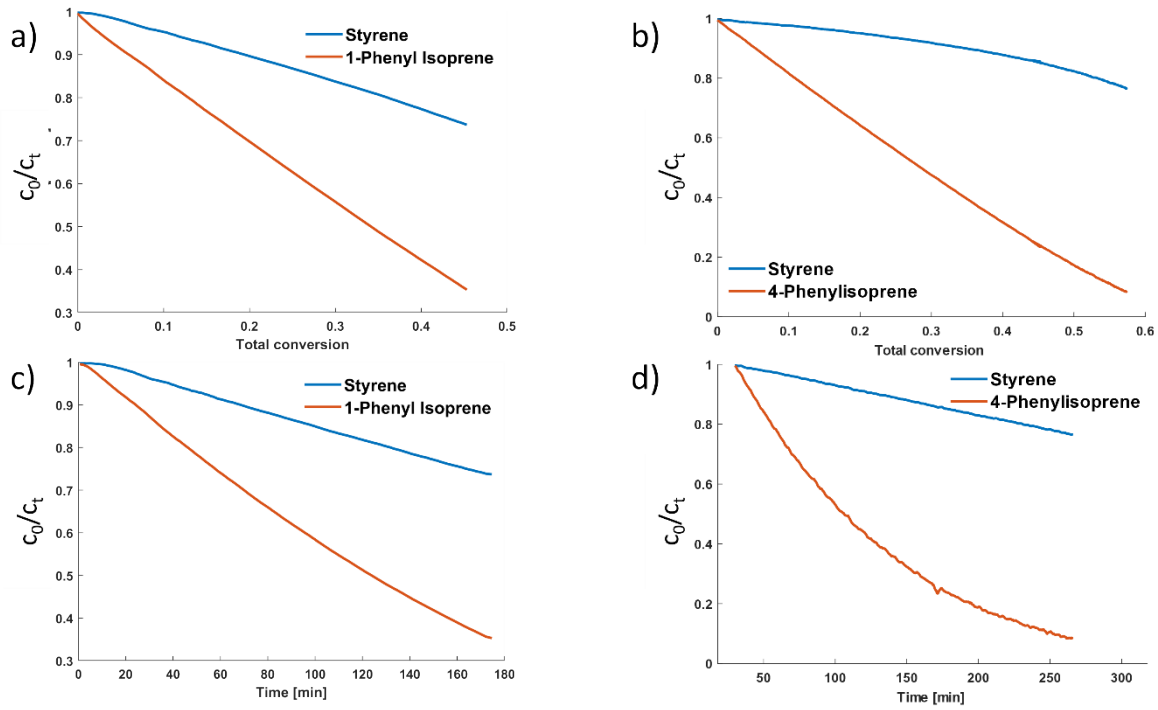



**Figure S19**: Individual monomer conversion of the copolymerisation with styrene and a) 1PhI and b) 4PhI as well as the time-depended monomer conversion of the copolymerisation using c) 1PhI and d) 4PhI.

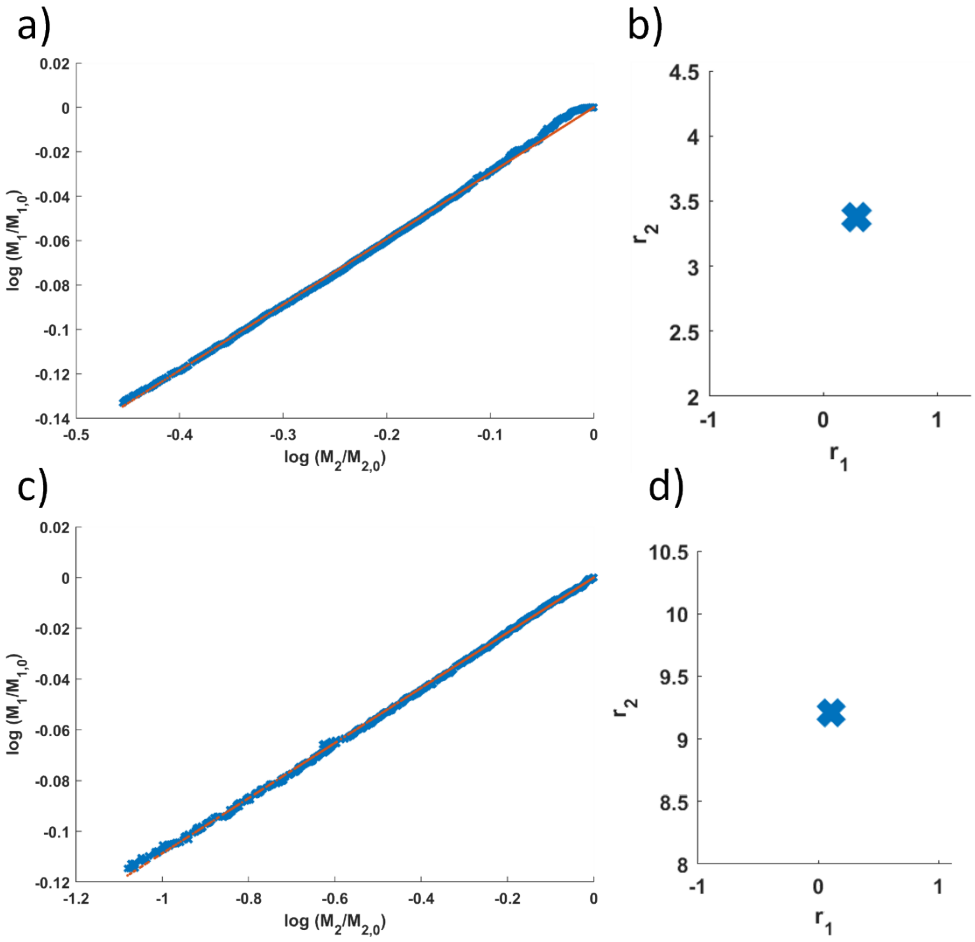



**Figure S20**:Obtained data applied on the Jaacks-Fits for the copolymerisation of styrene with a) 1PhI and b) the given error values for 1PhI + S as well as the copolymerisation with c) 4PhI and the d) corresponding error values.

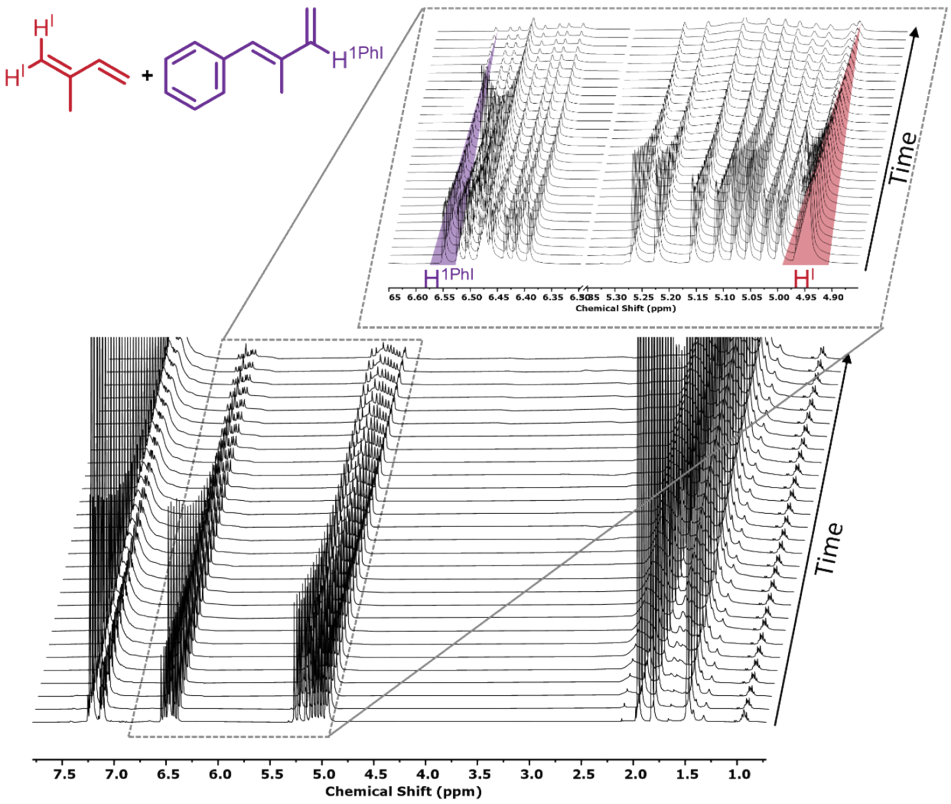



**Figure S21**: Stacked $^{1}$H NMR spectra of the *in situ* kinetics of the copolymerisation of isoprene and 1PhI and an expansion of the monomer signals monitored for evaluation of the monomer concentration.

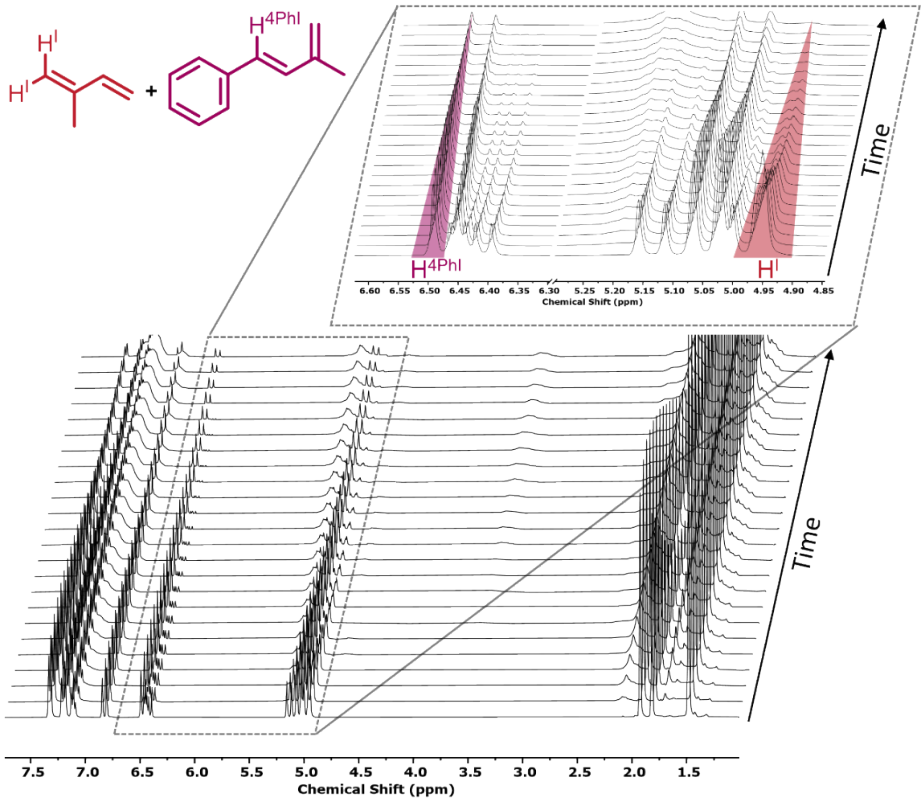



**Figure S22**: Stacked $^{1}$H NMR spectra of the real-time kinetics of isoprene and 4PhI and an expansion of the traced monomer signals.

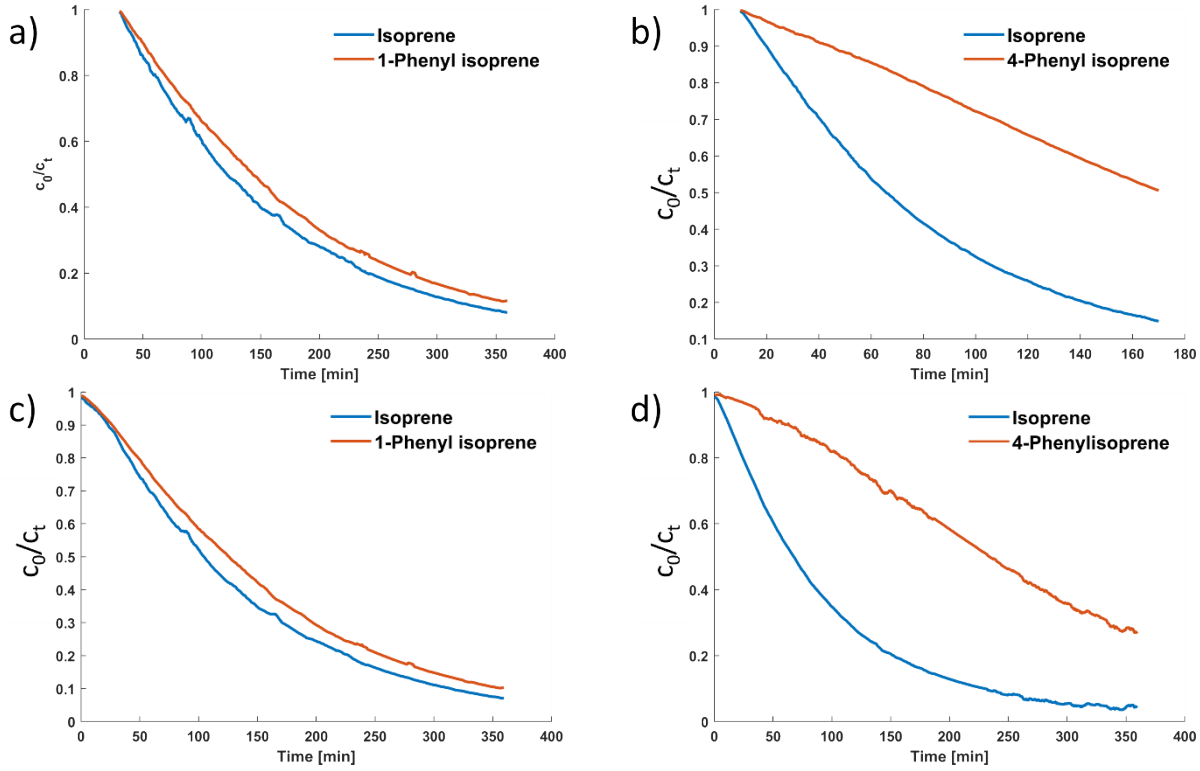



**Figure S23**:Individual monomer conversion of the copolymerisation with isoprene and a) 1PhI and b) 4PhI as well as the time-dependent monomer conversion of the copolymerisation using c) 1PhI and d) 4PhI.

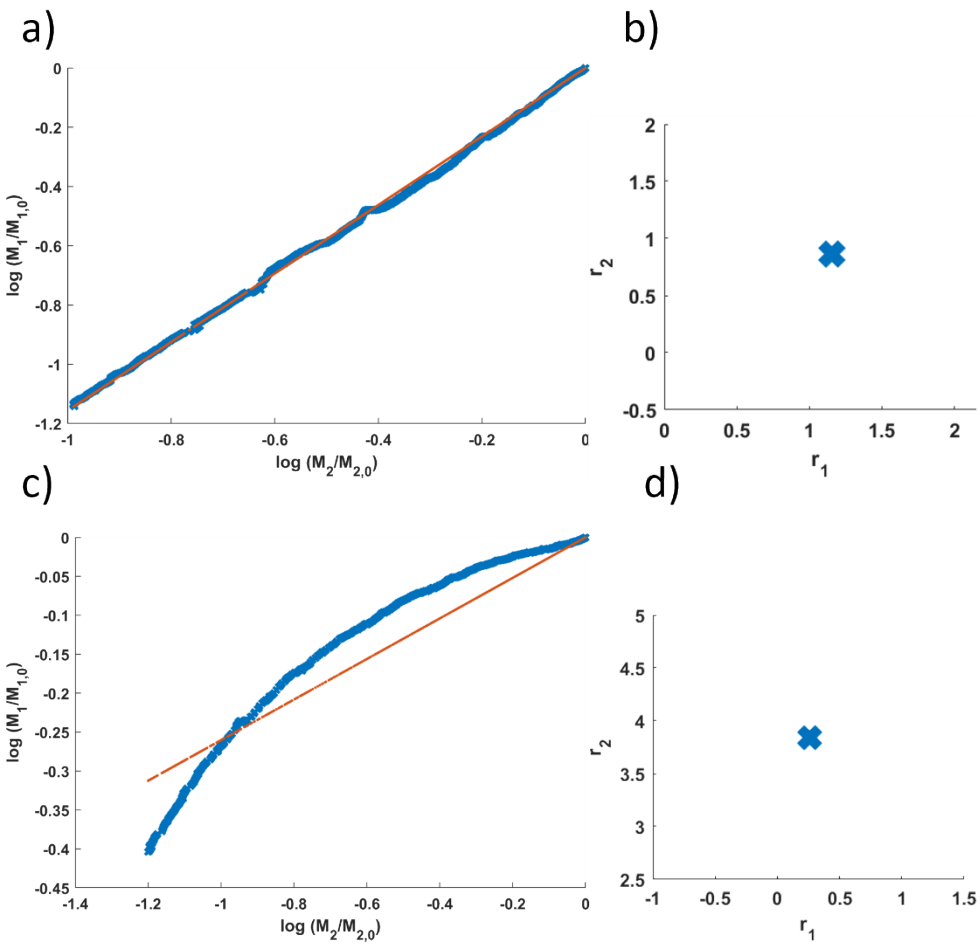



**Figure S24**: Obtained data applied on the Jaacks-Fits for the copolymerisation of isoprene with a) 1PhI and b) the given error values for 1PhI + S as well as the copolymerisation with c) 4PhI and the d) corresponding error values.

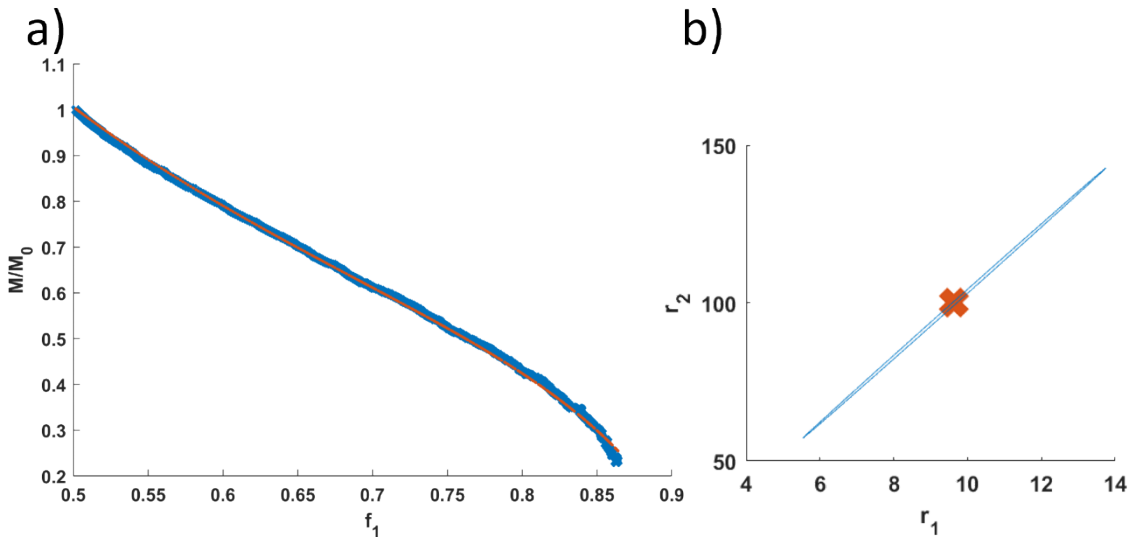



**Figure S25**: Evaluation of the kinetics experiment of 4PhI and I applying the obtained data with the Meyer-Lowry method. a) The fit of the calculation and b) the error values of the obtained reactivity ratios.

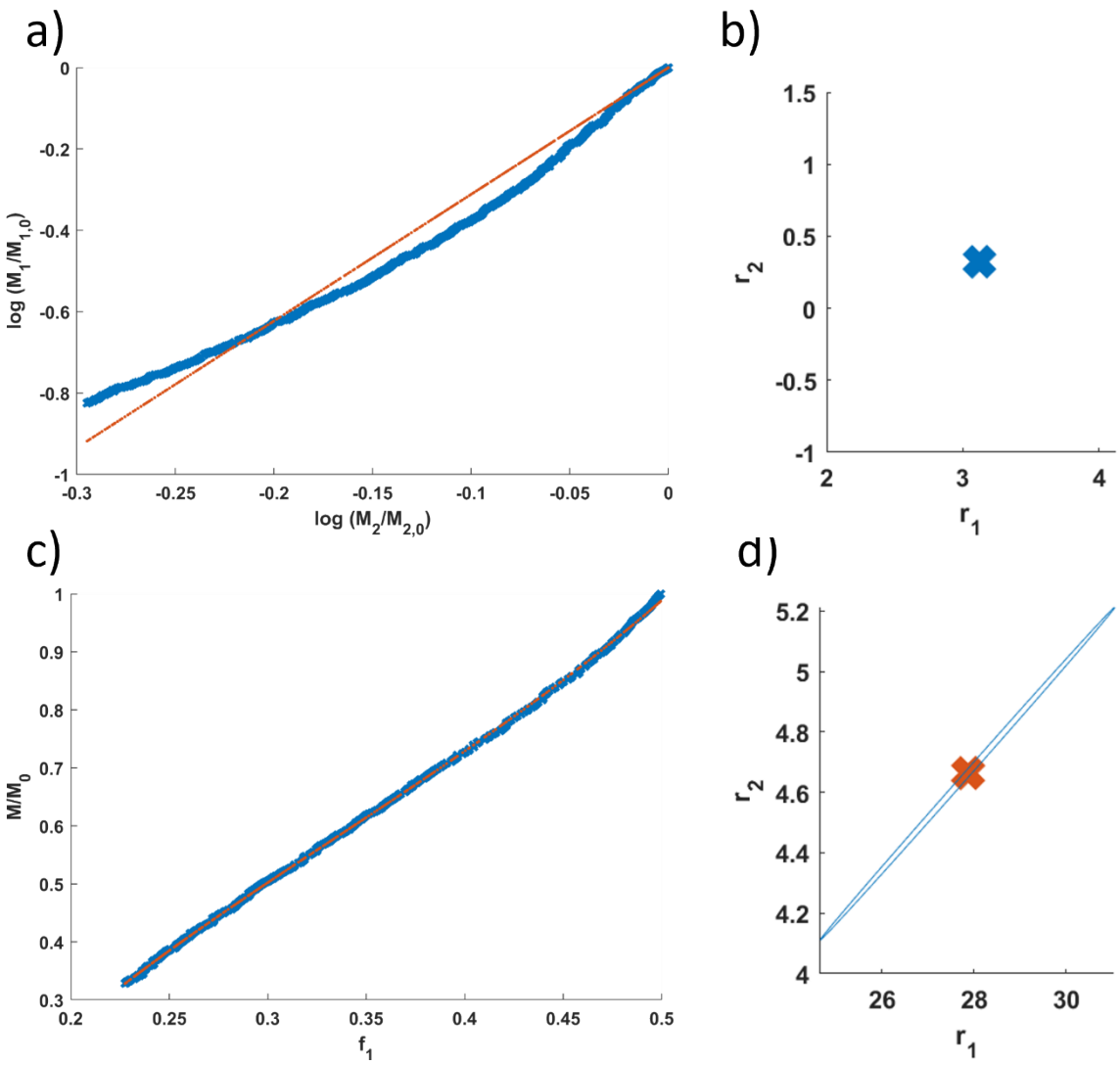



**Figure S26**: Evaluation of the repeated copolymerisation of 4PhI and isoprene at an equimolar ratio using a) the Jaacks fit and b) the corresponding error values as well as c) using the Meyer-Lowry fit and d) the corresponding error values.

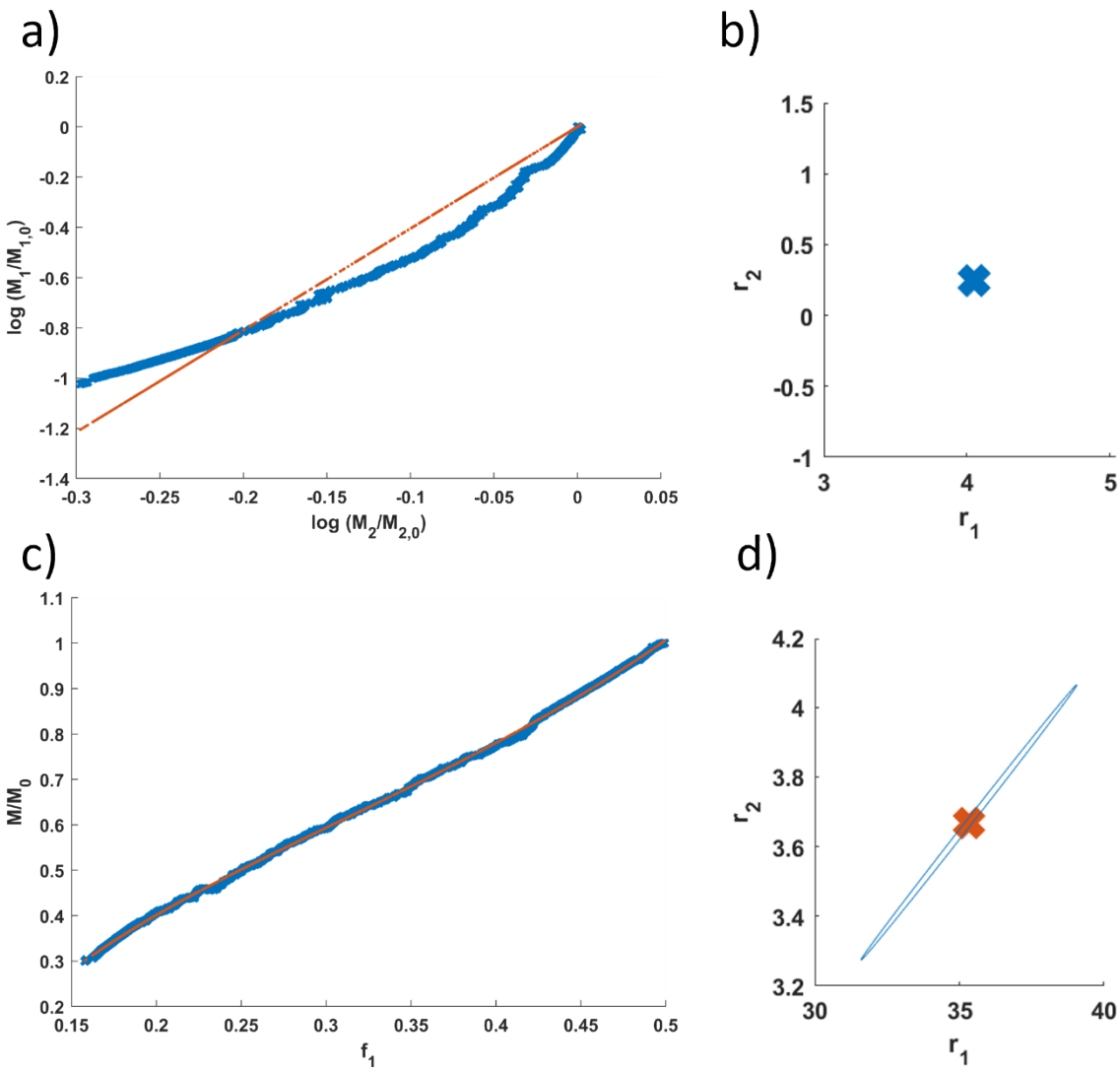



**Figure S27**: Evaluation of the repeated copolymerisation of 4PhI and isoprene with a molar composition of 30 to 70 using a) the Jaacks fit and b) the corresponding error values as well as c) using the Meyer-Lowry fit and d) the corresponding error values.

**Table S3**:Summary of the performed $^{1}$H NMR kinetics of isoprene and 4PhI with different molar ratios. All three attempts were analyzed via the Jaacks fit and the Meyer-Lowry fit representing a non-terminal and a terminal model.

| Attempt | [4PhI]:[I] | $r_I$ [a] | $r_{4PhI}$ [a] | $r_I$ [b] | $r_{4PhI}$ [b] |
|---|---|---|---|---|---|
| 1 | 50:50 | 3.84 | 0.260 | -- | -- |
| 2 | 50:50 | 3.12 | 0.32 | 27 | 4.6 |
| 3 | 30:70 | 4.05 | 0.247 | 35 | 3.7 |

[a] Non-terminal model of the Jaacks fit used for the determination of the reactivity ratios. [b]Terminal model of the Meyer-Lowry fit used for the determination of the reactivity ratios.

## Characterization of the copolymerisations with isoprene and styrene

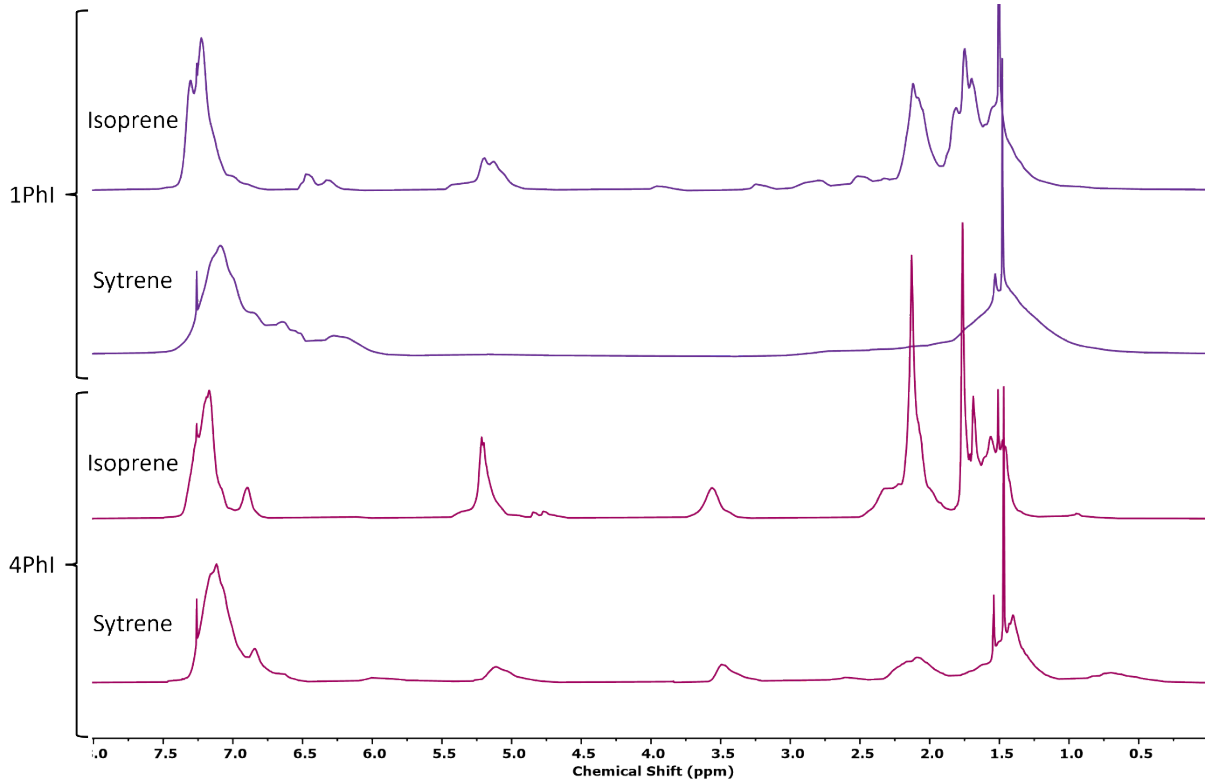



**Figure S28**: Stacked $^1$H NMR spectra (400 MHz, $CDCl_3$) of the copolymers containing 1PhI (dark purple) and 4PhI (light purple) with either isoprene or styrene.

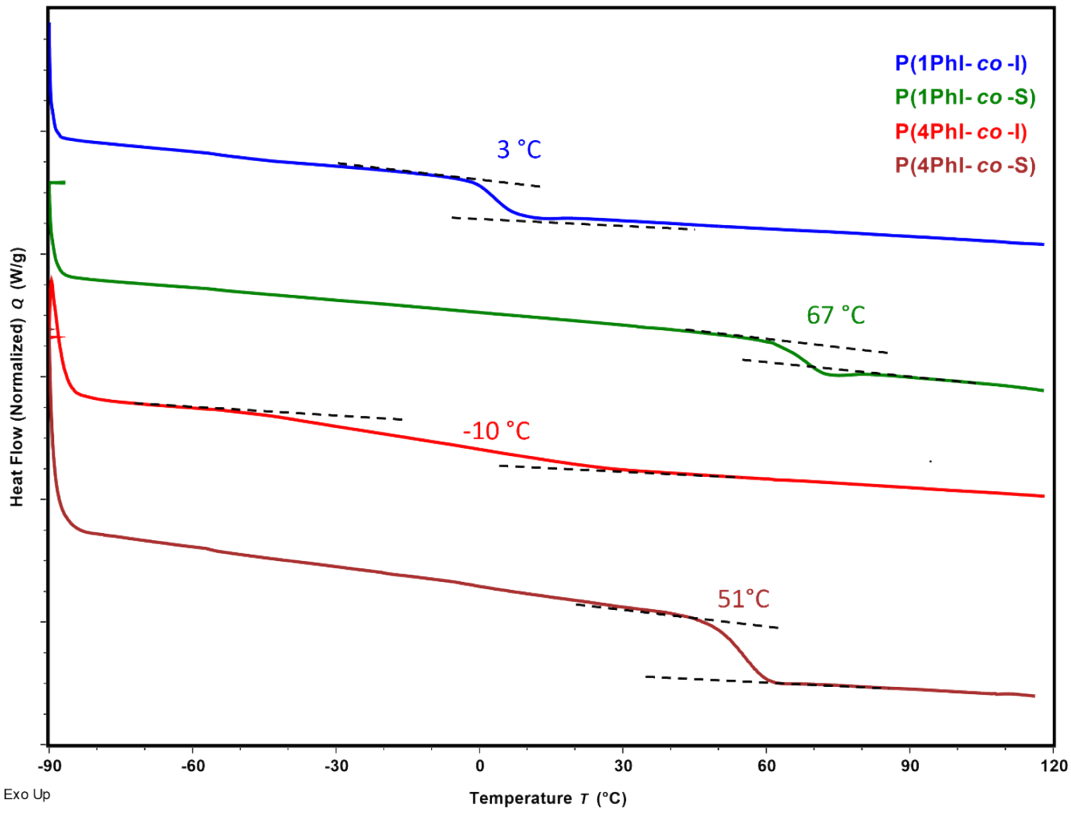



**Figure S29**: DSC curves for the copolymers of 1PhI and 4PhI, respectively, with isoprene or styrene as a comonomer (entries 15-18).

## Characterization of the cyclized structures

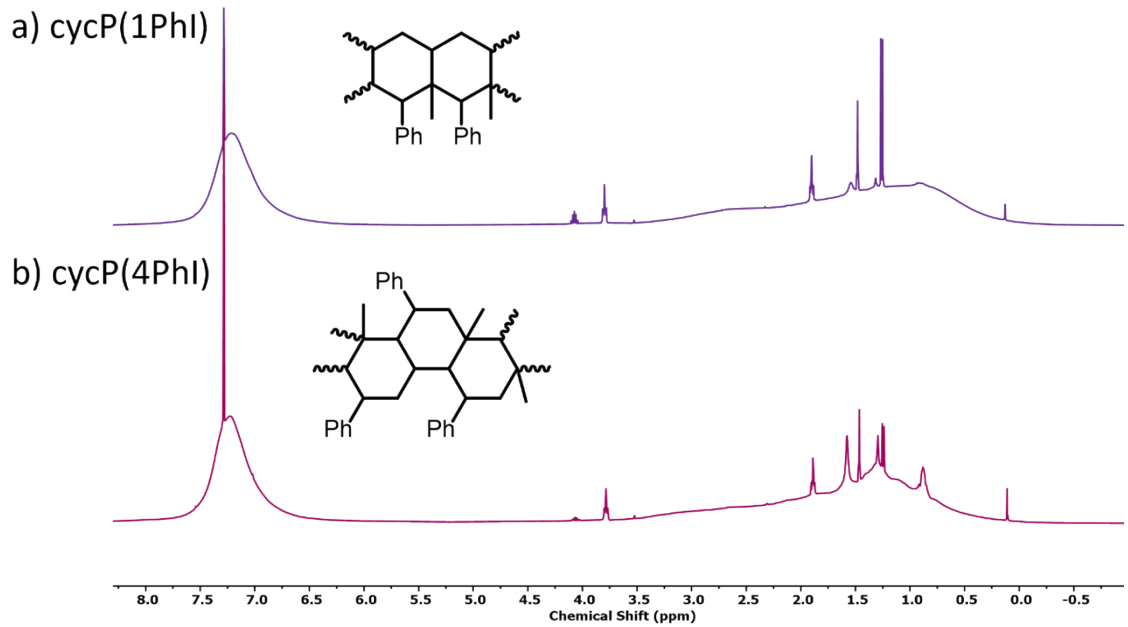



**Figure S30**: Stacked $^{1}$H NMR spectra (400 MHz, $CDCl_3$) of the cyclized polymers containing a) 1PhI (dark purple) and b) 4PhI (light purple).

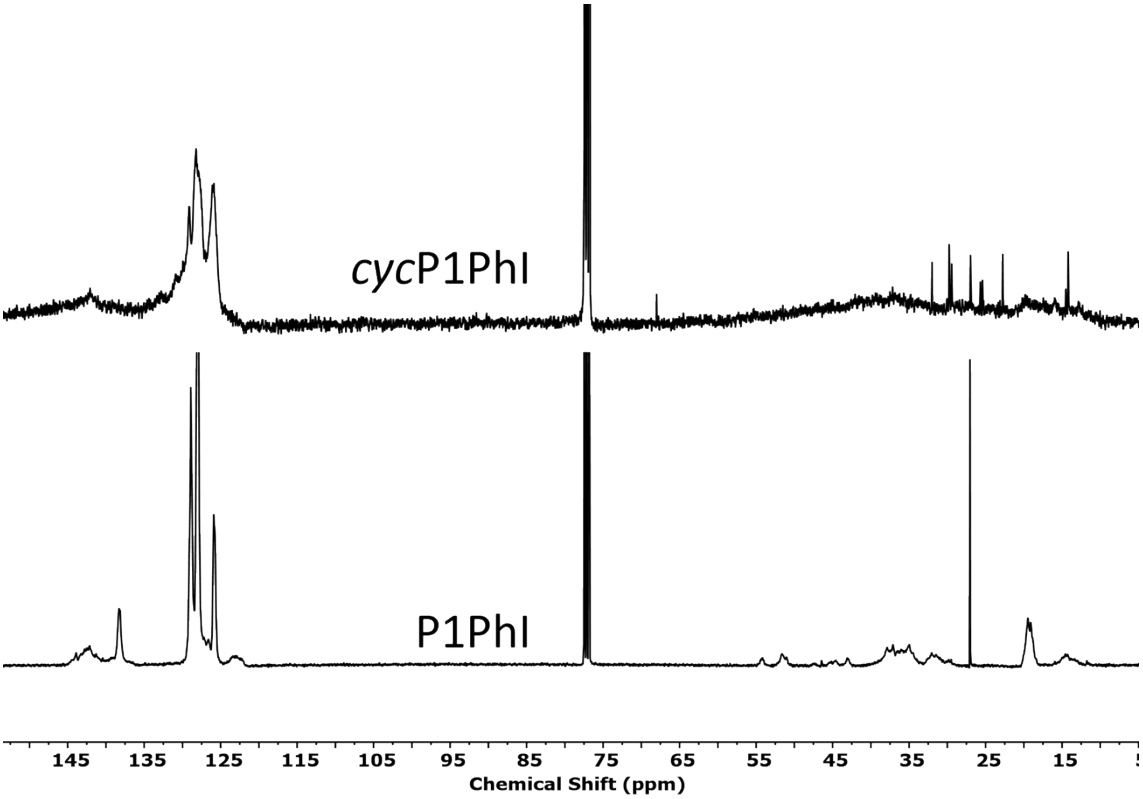



**Figure S31**: Stacked $^{13}$C NMR spectra (103 MHz, $CDCl_3$) of cycP1PhI and P1PhI to identify the disappearing carbon species.

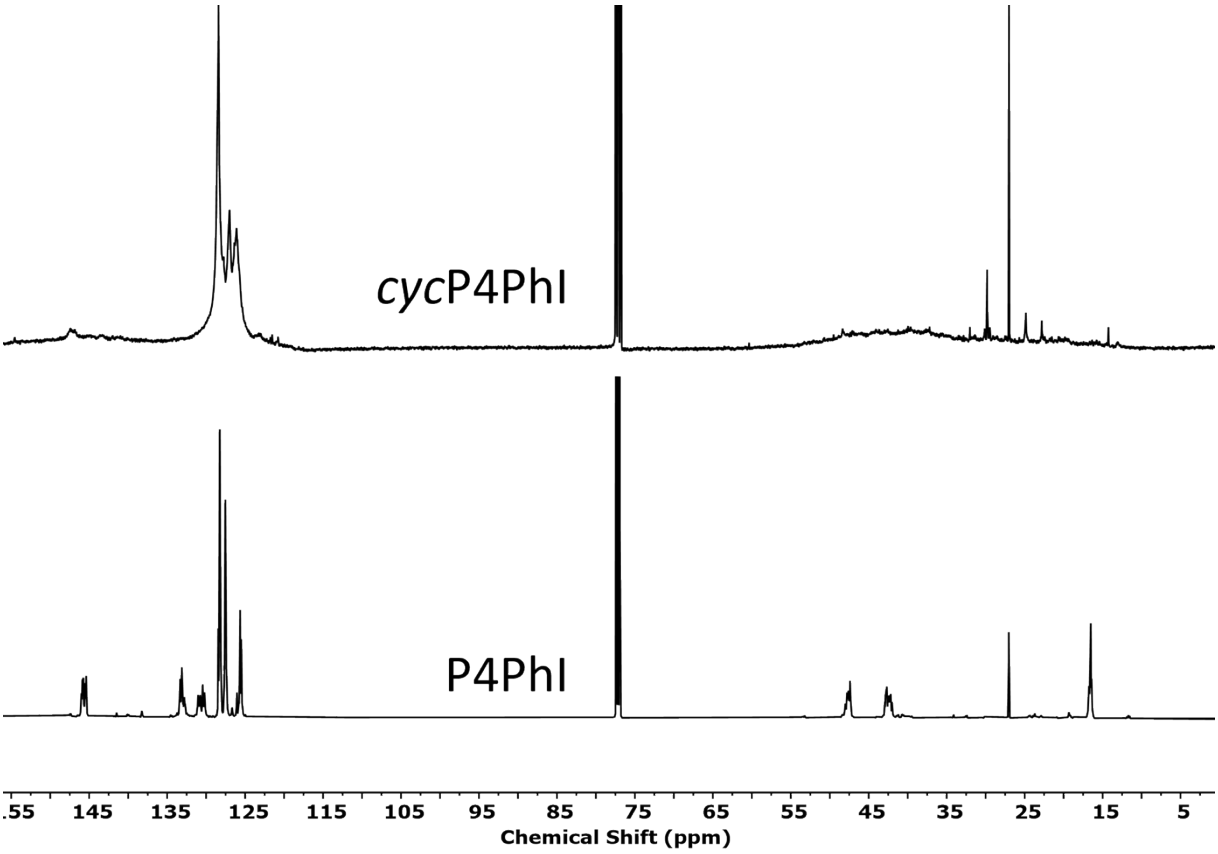



**Figure S32**: Stacked $^{13}C$ NMR spectra (103 MHz, $CDCl_3$) of cycP4PhI and P4PhI to identify the disappearing carbon species.

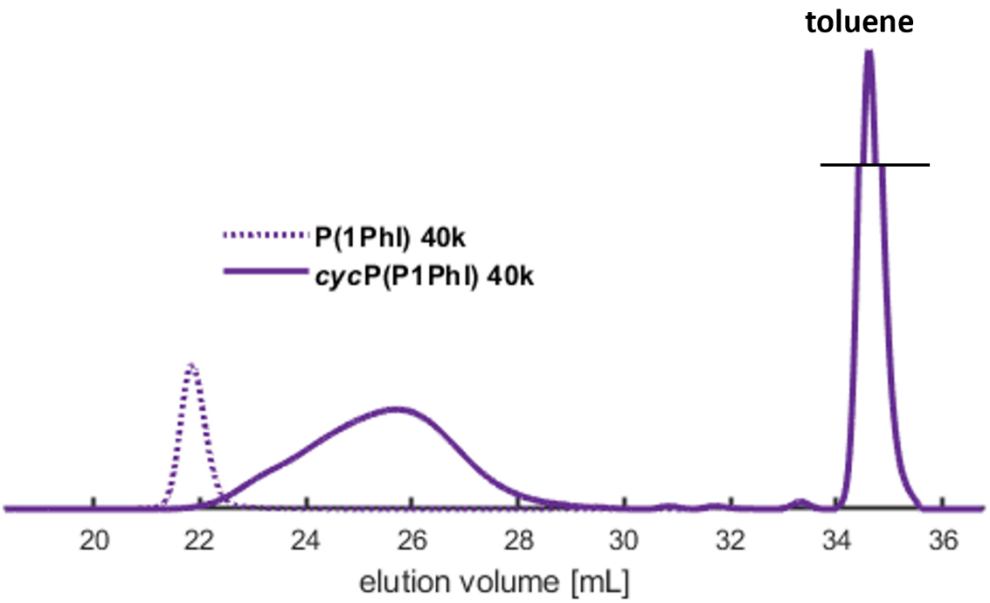



**Figure S33**: SEC traces of the P(1PhI) precursor and the cyclized sample cycP(1PhI). Retention of the internal toluene standard also shown at 34.59 mL.

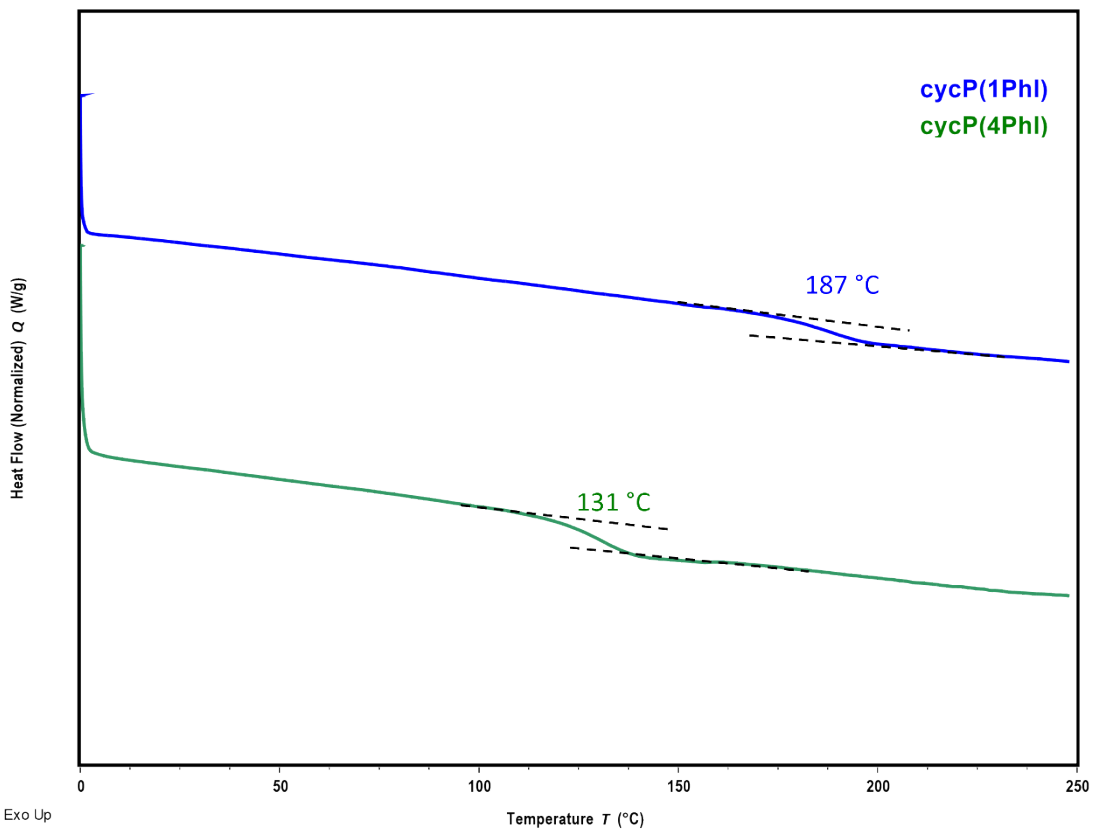



**Figure S34**: DSC curves of the cyclized cycP(1PhI) (blue) and cycP(4PhI) (green).

## Photophysical Analysis of cyclized samples

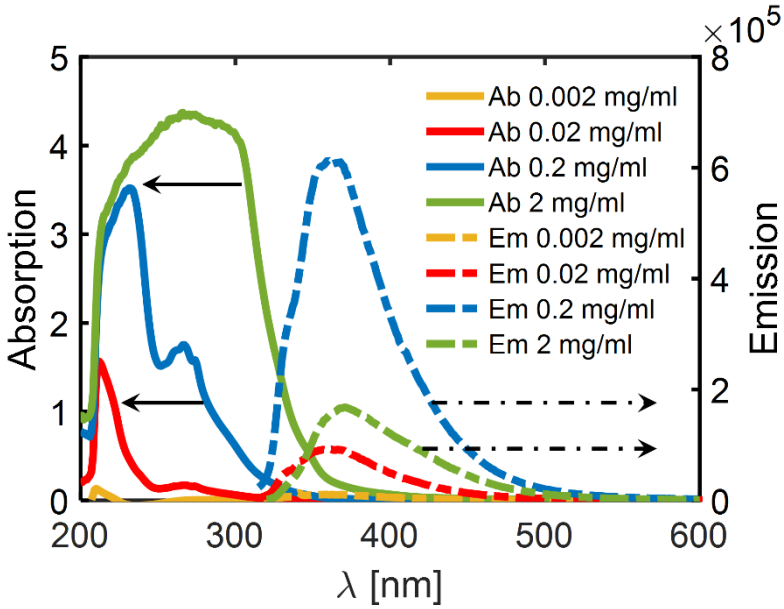



**Figure S35**: Absorption (solid) and emission (dashed) spectra of *cyc*P(1PhI) at different concentrations (0.002 – 2 mg/mL) in toluene ($\lambda_{exc}$ = 310 nm).

**Table S4**: Summary over obtained emission maxima for cycP1PhI and cycP4PhI with increasing concentrations.

| Sample | *c*(*cyc*PPhI) mg mL$^{-1}$ | $\lambda_{em,max}$ nm |
|---|---|---|
| *cyc*P1PhI | 0.02 | 362 |
| | 0.2 | 360 |
| | 2 | 371 |
| *cyc*P1PhI | 0.02 | 375 |
| | 0.2 | 377 |
| | 2 | 395 |

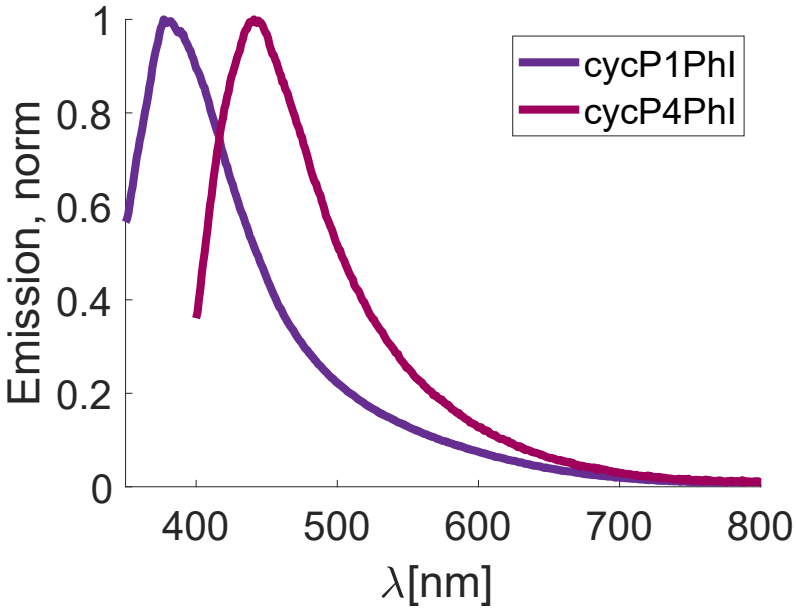



**Figure S36**: Obtained, normed emission spectra of the solid-state quantum yield determination. Worth mention, the conditions of both samples (excitement wavelength [$\lambda_{exc,cycP1PhI}$ = 330 nm; $\lambda_{exc,cycP4PhI}$ = 380 nm], bandwidth etc.) were different in both cases.

## References


1 K. Colizza, K. E. Mahoney, A. V. Yevdokimov, J. L. Smith and J. C. Oxley, *J Am Soc Mass Spectrom*, 2016, **27**, 1796–1804.