

Supporting Information for:

End-capping ROMP Polymers with Vinyl Lactones

Stefan Hilf[†], Robert H. Grubbs[§] and Andreas F.M. Kilbinger^{†}*

[†] Institut für Organische Chemie, Johannes Gutenberg-Universität Mainz,
Duesbergweg 10-14, D-55099 Mainz, Germany

[§] Arnold and Mabel Beckman Laboratories of Chemical Synthesis, Division of
Chemistry and Chemical Engineering, California Institute of Technology, Pasadena,
California 91125 (USA)

akilbing@uni-mainz.de

Experimental Section

¹H-NMR data for functionalized poly(PNI):

For poly(PNI)-CHO:

¹H-NMR (400MHz, CDCl₃) δ[ppm]: 1.5-1.8, 2.1-2.3 (m, 2H, CH₂-bridge); 2.8-3.0 (m, 2H, C₃CH); 3.1-3.3 (m, 2H, C(O)CH); 5.5-5.9 (m, 2H, double bonds polymer); 6.2-6.4 (m, 1H, Ph-CH=CH end); 6.5-6.7 (m, 1H, Ph-CH=CH end); 7.2-7.6 (m, 5H, Ph); 9.6 (s, 1H, Aldehyde endgroup).

For poly(PNI)-COOH:

¹H-NMR (400MHz, CDCl₃) δ[ppm]: 1.5-1.8, 2.1-2.3 (m, 2H, CH₂-bridge); 2.8-3.0 (m, 2H, C₃CH); 3.1-3.3 (m, 2H, C(O)CH); 5.5-5.9 (m, 2H, double bonds polymer); 6.2-6.4 (m, 1H, Ph-CH=CH end); 6.5-6.7 (m, 1H, Ph-CH=CH end); 7.2-7.6 (m, 5H, Ph); 11.3(s (br), 1H, COOH endgroup).

General procedure for the synthesis of 2,4-dinitrophenylhydrazones of CHO-functionalized polynorbornenes: 100mg of the aldehyde-functionalized polymer were dissolved in 5mL chloroform. 1mL acetic acid and 50mg 2,4-dinitrophenyl hydrazine (50% slurry in water) were added. The mixture was refluxed for 4 h, precipitated in hot ethanol and collected. The resulting polymer was redissolved in chloroform and precipitated in hot ethanol until the supernatant solution remained colorless. Vacuum drying afforded 60-85% of a yellow polymer material.

Exemplary characterization for poly(PNI):

$^1\text{H-NMR}$ (400MHz, CDCl_3) δ [ppm]: 1.5-1.8, 2.1-2.3 (m, 2H, CH_2 -bridge); 2.8-3.0 (m, 2H, C_3CH); 3.1-3.3 (m, 2H, $\text{C}(\text{O})\text{CH}$); 5.5-5.9 (m, 2H, double bonds polymer); 6.2-6.4 (m, 1H, Ph-CH=CH end); 6.5-6.7 (m, 1H, Ph-CH=CH end); 7.2-7.6 (m, 5H, Ph); 7.91 (d, 1H, 5-(NO_2 -Ph)); 8.28 (d, 1H, 6-(NO_2 -Ph)); 9.10 (s, 1H, 3-(NO_2 -Ph)); 11.06 (s, 1H, N-H).

General procedure for the synthesis of 2,2,2-trichloromethyl ester of COOH-functionalized polynobornenes: 100mg polymer, 50mg dicyclohexyl carbodiimide and 100mg *N,N*-dimethylamino pyridine were dissolved in 5mL dry dichloromethane. 0.1 mL 2,2,2-trichloroethanol were added and the mixture was stirred at r.t. for 14h before the polymer was precipitated in methanol, collected, redissolved in chloroform and reprecipitated in methanol. The resulting polymer was dried in vacuo to give a brownish polymer material in good yields (>80% typically).

Exemplary characterization for poly(**PNI**):

$^1\text{H-NMR}$ (400MHz, CDCl_3) δ [ppm]: 1.5-1.8, 2.1-2.3 (m, 2H, CH_2 -bridge); 2.8-3.0 (m, 2H, C_3CH); 3.1-3.3 (m, 2H, $\text{C}(\text{O})\text{CH}$); 4.75 (m, 2H, $\text{CH}_2\text{-C-Cl}_3$ endgroup); 6.2-6.4 (m, 1H, Ph-CH=CH end); 6.5-6.7 (m, 1H, Ph-CH=CH end); 7.2-7.6 (m, 5H, Ph).

*Synthesis of N-(2-hydroxy-ethoxy)-ethyl-2,3-norbornene dicarboximide (**HEENI**):* 32g (0.2 mol) *exo*-norbornene-2,3-dicarboxanhydride were added 21g (0.2 mol) 2-aminoethoxy-ethanol. The mixture was allowed to stand for 30 min before 150mL toluene were added and the resulting slurry was refluxed under dean-stark conditions until all solids had dissolved and 3.2mL water had been collected (ca. 5 h). The solvent was then evaporated under reduces pressure and the resulting oil was passed through a silica column (eluent: chloroform: methanol 9:1 v:v, R_f =0.85) to give a colorless oil in good yield (42g, 82%).

$^1\text{H-NMR}$ (300MHz, CDCl_3) δ [ppm]: 1.37 (dd, 2H, CH_2 -bridge; $^2J=60\text{Hz}$, $^3J=10\text{Hz}$); 2.65 (s, 2H, C_3CH); 3.23 (s, 2H, $\text{C}(\text{O})\text{CH}$); 3.5-3.7 (m, 8H, $\text{CH}_2\text{-O} + \text{CH}_2\text{-N}$) 6.24 (s, 2H, $\text{C}=\text{CH}$).

Synthesis of poly(HEENI)-CHO and the hydrazone derivative: To a stirred solution of 49mg (56 μmol) catalyst (in 3mL dichloromethane) **C1** was added a solution of 300mg **HEENI** in 12mL dichloromethane. After 1h, a large excess (200 μL) of **VC** was added and stirring was continued over 8h. In order to terminate all residual living chains, a large excess of ethyl vinyl ether was added (0.5mL) and stirring was continued for another 2h. The polymer was precipitated in methanol, collected, re-dissolved in chloroform and re-precipitated in methanol, collected and dried under vacuum over night to give 240mg (80%) of a slightly brown solid. The formation of the 2,4-dinitrophenyl-hydrazone was carried out following the general procedure.

$^1\text{H-NMR}$ (400MHz, CDCl_3) δ [ppm]: 1.6-1.7, 2.0-2.2 (m, 2H, CH_2 -bridge); 2.6-2.8 (m, 2H, C_3CH); 2.9-3.1 (m, 2H, $\text{C}(\text{O})\text{CH}$); 3.5-3.8 (m, 8H, $\text{CH}_2\text{-N}$ and $\text{CH}_2\text{-O}$); 5.5-5.8 (m, 2H, double bonds polymer); 6.2-6.4 (m, 1H, Ph-CH=CH end); 6.5-6.7 (m, 1H, Ph-CH=CH end); 7.2-7.5 (m, 5H, Ph-endgroup); 7.91 (d, 1H, 5-($\text{NO}_2\text{-Ph}$)); 8.31 (d, 1H, 6-($\text{NO}_2\text{-Ph}$)); 9.12 (s, 1H, 3-($\text{NO}_2\text{-Ph}$)); 11.10 (s, 1H, N-H).

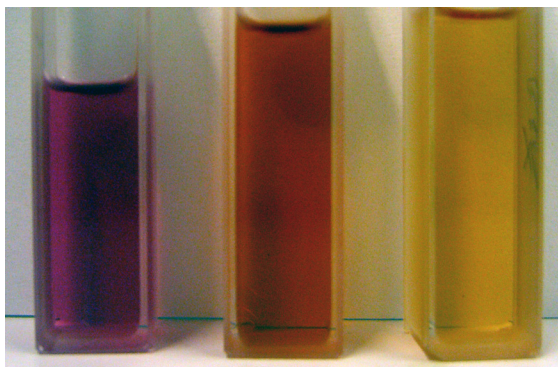
Synthesis of poly(norbornene-aldehyde)-COOH and the trichloroethyl ester: To a stirred solution of 52mg (56 μmol) catalyst (in 3mL dichloromethane) **C3** was added a solution of 300mg 5-norbornene-carbaldehyde (endo/exo-mixture) in 12mL dichloromethane. After 45min, an excess (200 μL) of **3HF** was added and stirring was

continued over 8h. In order to terminate all residual living chains, a large excess of ethyl vinyl ether was added (0.5mL) and stirring was continued for another 2h. The polymer was precipitated in methanol, collected, re-dissolved in chloroform and re-precipitated in methanol, collected and dried under vacuum over night to give 265mg (85%) of a brown solid. The formation of the trichloroethyl ester was carried out following the general procedure.

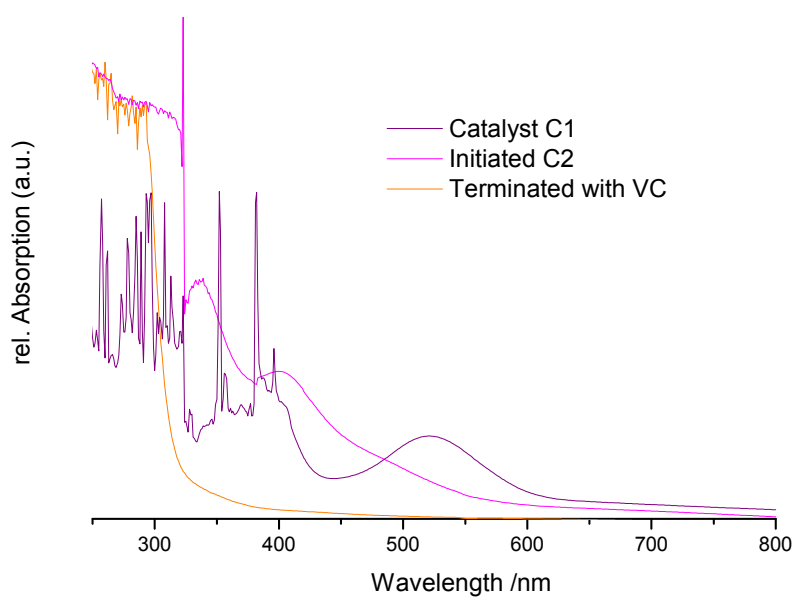
$^1\text{H-NMR}$ (400MHz, CDCl_3) δ [ppm]: 1.2-1.3 (m, 2H, $\text{CH}_2\text{-CH-CHO}$); 1.6-2.2 (m, 2H, $\text{CH}_2\text{-bridge}$); 2.5-3.4 (m, 3H, $\text{C}_3\text{CH} + \text{CH-CHO}$); 5.3-5.5 (m, 2H, double bonds polymer); 6.2-6.3 (m, 1H, Ph-CH=CH end); 6.5-6.6 (m, 1H, Ph-CH=CH end); 7.2-7.5 (m, 5H, Ph-endgroup); 9.6-9.7 (m, 1H, CHO).

Synthesis of poly(PNI)-CONH-CH₂-pyrene: 50mg of poly(PNI) ($M_n=4400$, $\text{PDI}=1.13$ (RI-detection); 11.4 μmol), 20mg (84 μmol) of 1-pyrenemethylamine hydrochloride, 50mg (242 μmol) dicyclohexylcarbodiimide and 50mg (409 μmol) of 4-dimethylaminopyridine were weighed into a 50mL Schlenk-flask, degassed and dissolved in 10mL dry dichloromethane. After stirring at r.t. for 14h, the turbid mixture was concentrated at the rotary evaporator, taken up with a small amount of chloroform and precipitated in methanol. The resulting solids were collected and dried in vacuo yielding 40mg (ca. 80%) of a colorless material.

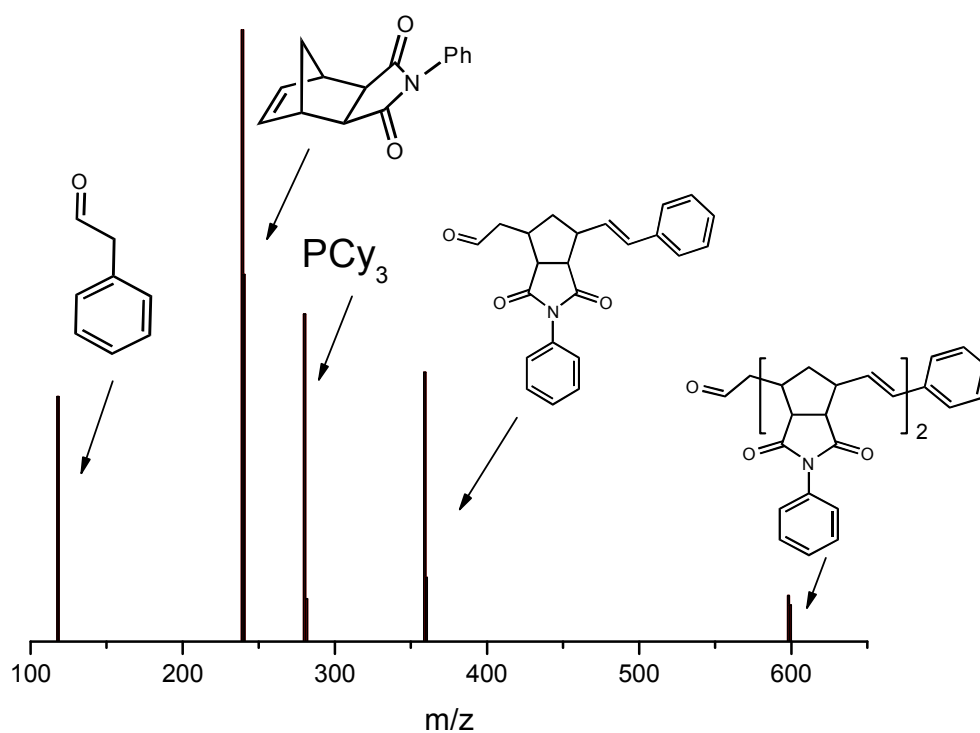
GPC: $M_n=4200$, $\text{PDI}=1.13$ (RI-detection).



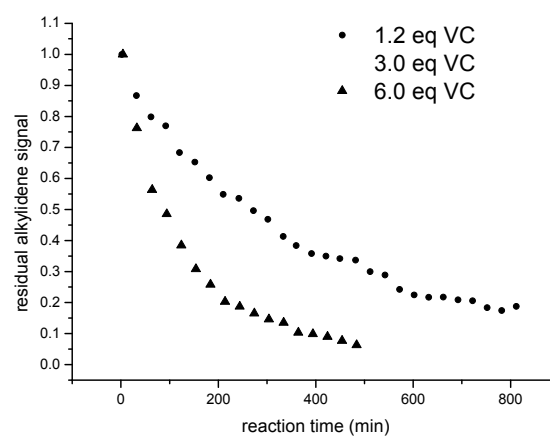
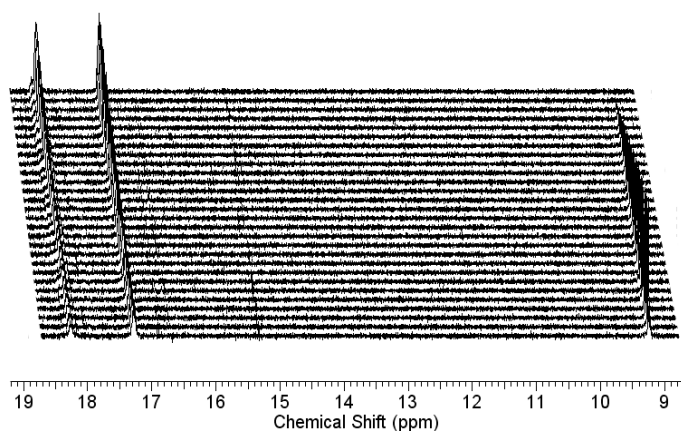
S-1: *Left:* Catalyst **C1** in dichloromethane *Middle:* Catalyst **C2** initiated with 15 equivalents of **PNI** *Right:* After termination with excess **VC**.



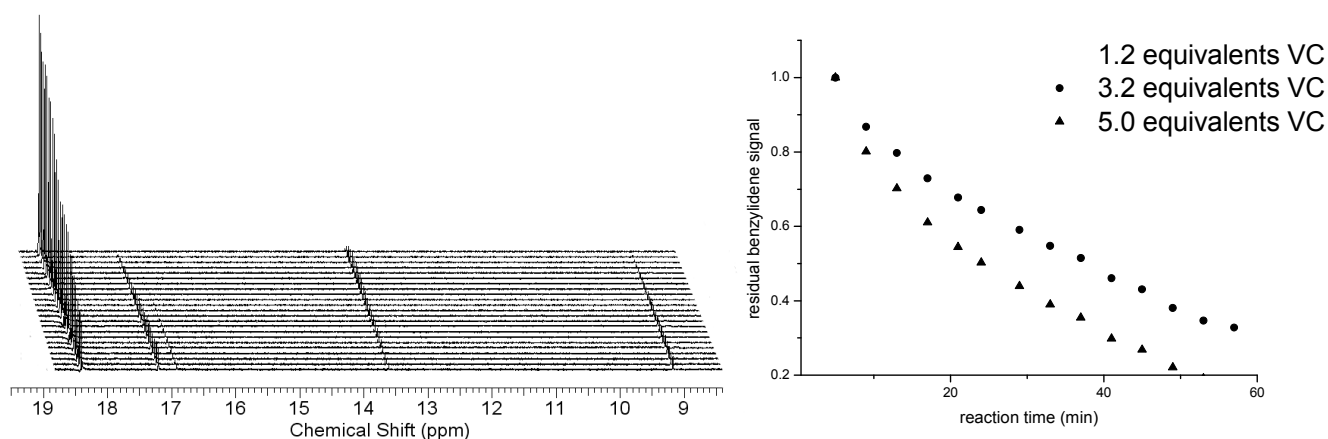
S-2: UV/vis spectra of the above mentioned (see **S-1**) solutions.



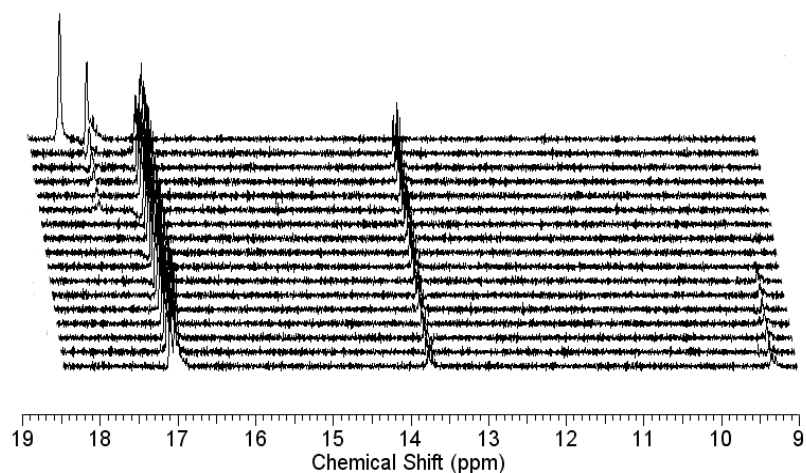
S-3: FD-MS of VC-terminated oligomer solution.



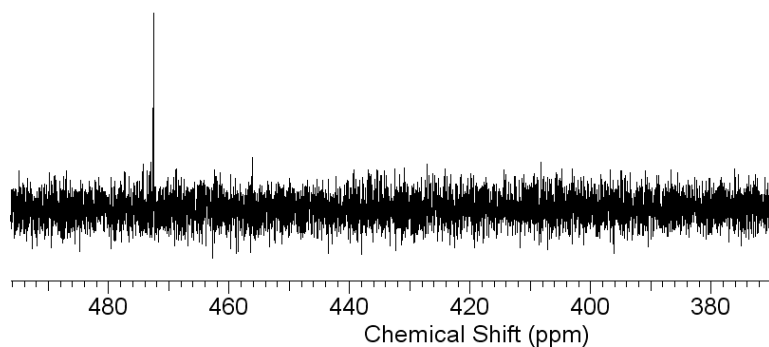
S-4: Reaction between initiated ruthenium benzylidene catalyst **C2** (15 eq. **PNI**) and vinylene carbonate (**VC**). The time resolved disappearance of the benzylidene signal is shown. (30 min between spectra)



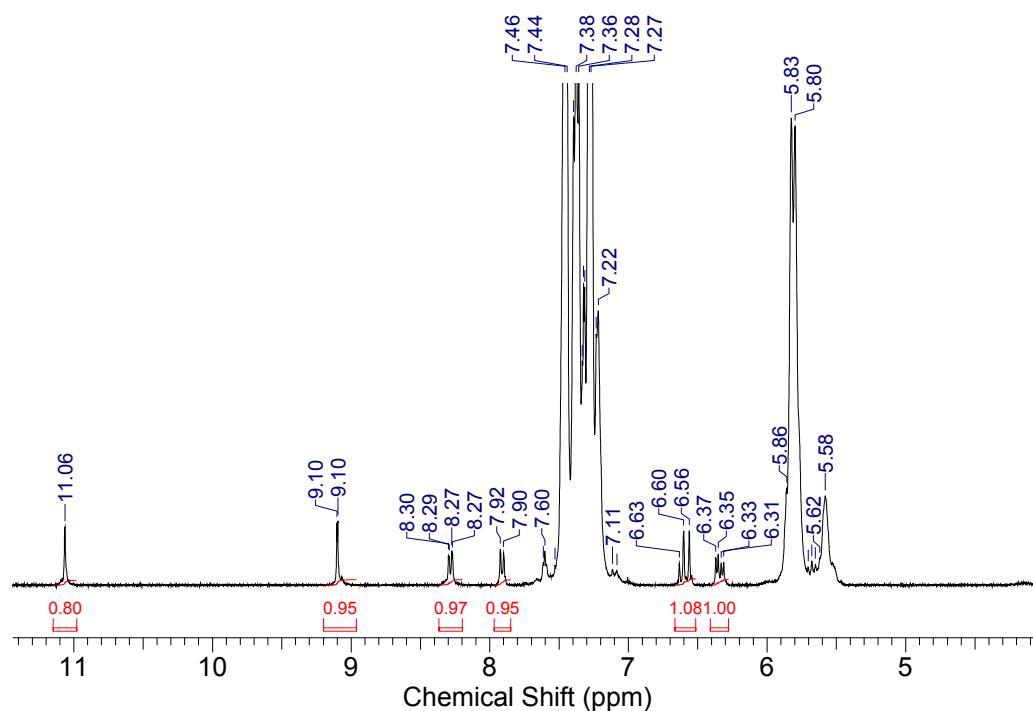
S-5: Reaction between ruthenium benzylidene catalyst **C3** and vinylene carbonate (VC). The time resolved disappearance of the benzylidene signal is shown. (90s between spectra)



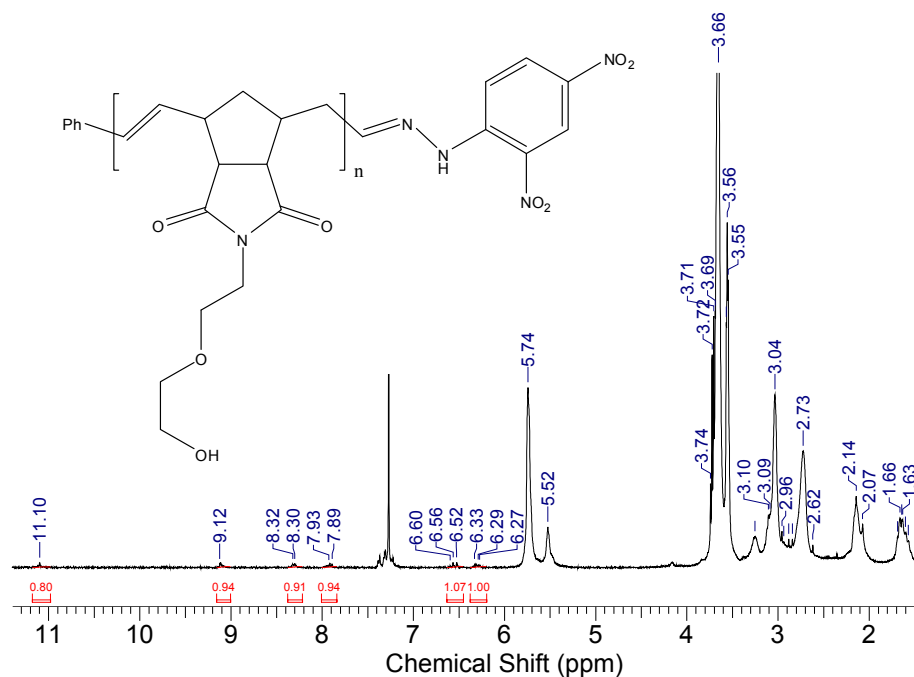
S-6: Reaction between initiated ruthenium benzylidene catalyst **C3** (15 eq. **PNI**) and vinylene carbonate (VC). (60s between spectra)



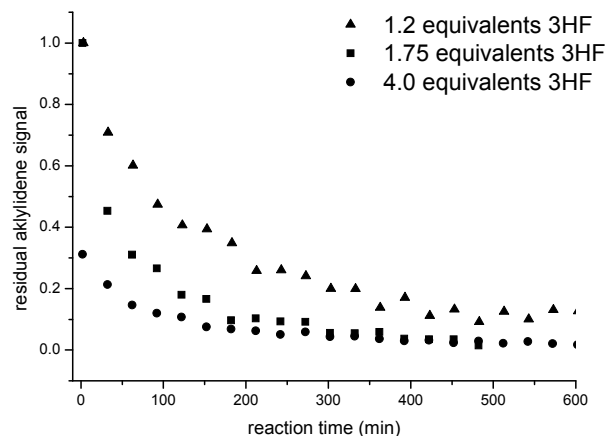
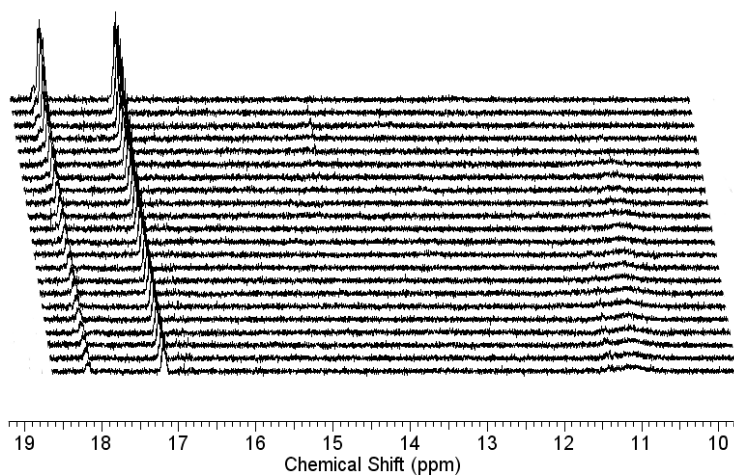
S-7: ^{13}C -NMR spectrum (CD_2Cl_2) of catalyst **C1** initiated with **PNI**, terminated with **VC**.



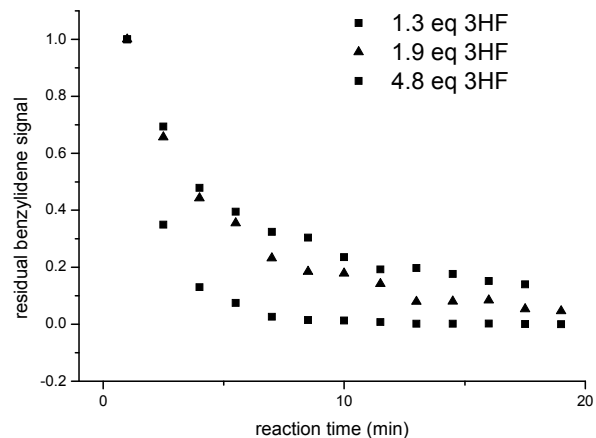
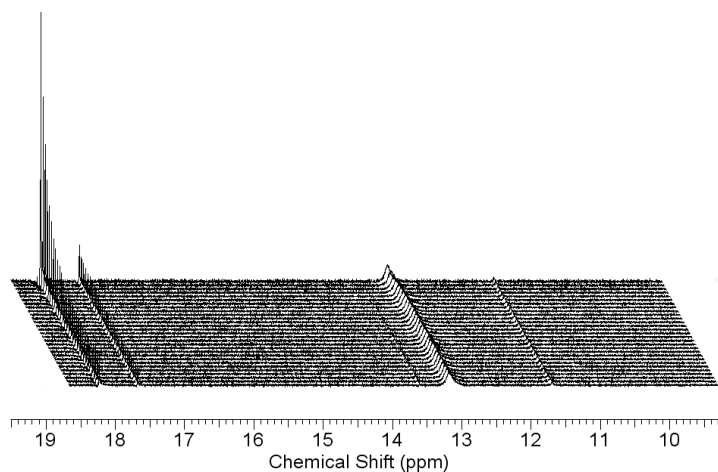
S-8: ^1H -NMR of 2,4-dinitrophenylhydrazone of poly(**PNI**)-CHO for estimation of the total degree of functionalization.



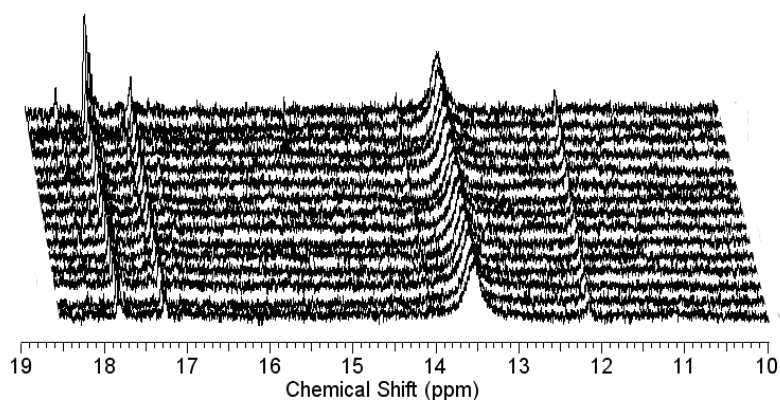
S-9: ^1H -NMR of 2,4-dinitrophenylhydrazone of poly(**HEENI**)-CHO.



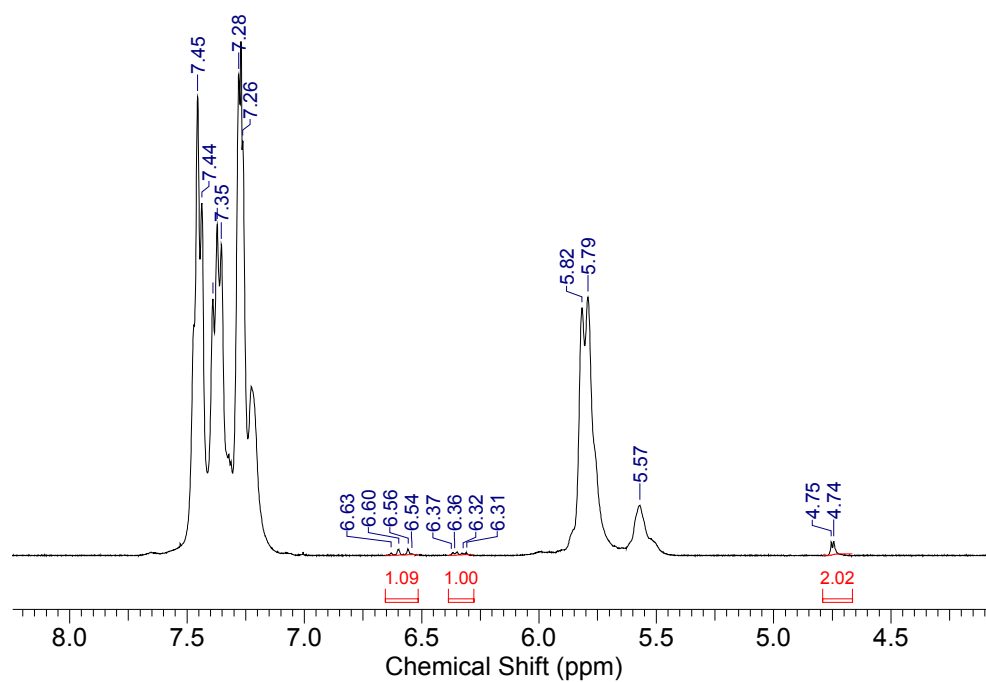
S-10: Reaction between initiated ruthenium benzylidene catalyst **C2** (15 eq. PNI) and 3H-furanone (**3HF**). The time resolved disappearance of the benzylidene signal is shown. (20 min between spectra)



S-11: Reaction between ruthenium benzylidene catalyst **C3** and vinylene carbonate (**VC**). The time resolved disappearance of the benzylidene signal is shown. (90s between spectra)



S-12: Reaction between initiated ruthenium benzylidene catalyst **C3** (15 eq. **PNI**) and vinylene carbonate (**VC**). (60s between spectra)



S-13: ^1H -NMR of 2,2,2-trichloroethyl ester of poly(**PNI**)-COOH for estimation of the total degree of functionalization.

