Electronic Supplementary Material (ESI) for Polymer Chemistry.

Ternary Organic-Inorganic Nanostructured Hybrid Materials by Simultaneous Twin Polymerization

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Supplementary Material

Table of content:

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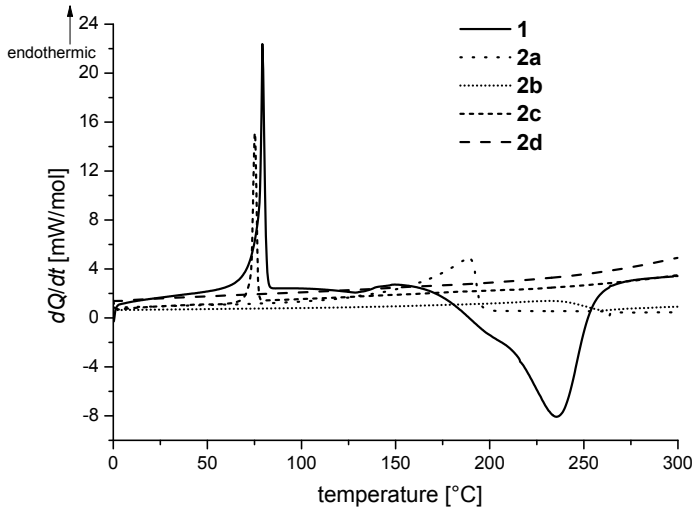
1. Twin polymerization of 2a-d

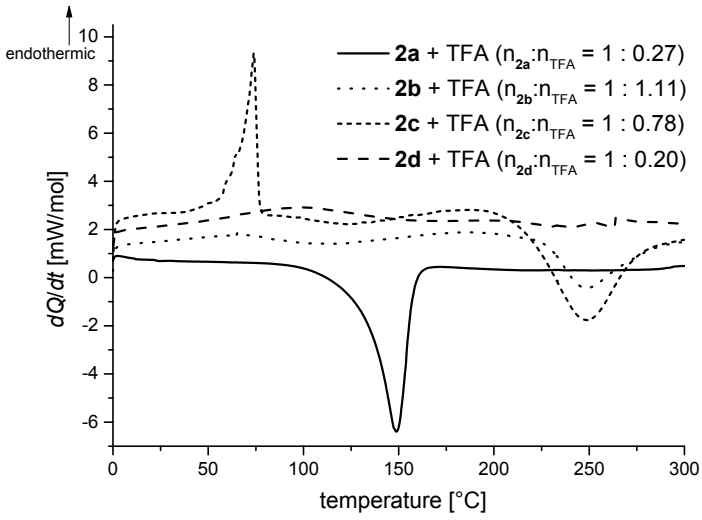
1.1 DSC measurements of the twin monomers with and without catalyst

The thermal behavior of TM´s **2a**–**d** in the presence or absence of catalysts was studied by means of DSC measurements.



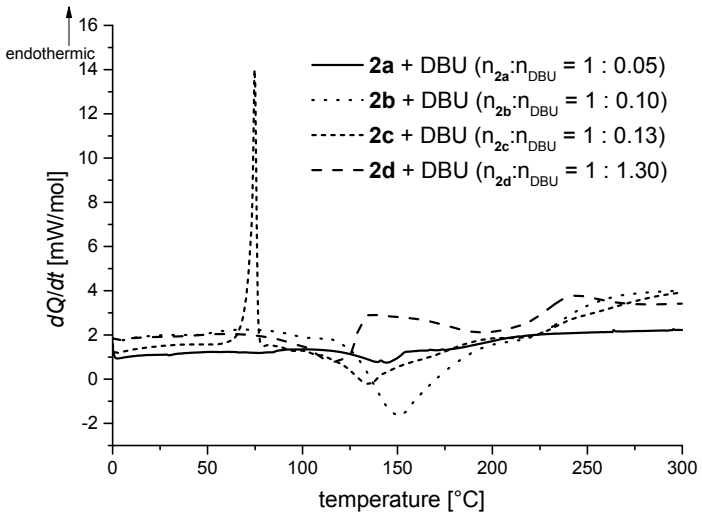
monomer	$T_{onset, endo}$ [°C]	$T_{onset,exo}$ [°C]
1	77	197
2a	147	-
2b	169	-
2c	73	-
2d	-	-

Figure S1 DSC of monomers **1**, **2a**, **2b**, **2c** and **2d**.



experiment	$T_{onset, endo}$ [°C]	$T_{onset,exo}$ [°C]
2a + TFA	-	83
2b + TFA	-	107;226
2c + TFA	66	217
2d + TFA	53	-

Figure S2 DSC of the monomers **2a**, **2b**, **2c** and **2d** using trifluoroacetic acid (TFA) as a catalyst (molar ratio as given in the key).



experiment	$T_{onset, endo}$ [°C]	$T_{onset,exo}$ [°C]
2a + DBU	-	134;202
2b + DBU	46	125
2c + DBU	73	109
2d + DBU	-	93; 128

Figure S3 DSC of the monomers **2a**, **2b**, **2c** and **2d** using 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) as a catalyst (molar ratio as given in the key).

1.2 Twin polymerization experiments of 2a-d and extraction of the hybrid materials

Thermally induced TP was not performed because DSC measurements of **2a**-**d** did not show exothermic peaks which would indicate a polymerization (Figure S1, see insert Table). Acid (trifluoroacetic acid) and base (1,8-diazabicyclo[5.4.0]undec-7-ene) catalyzed TP of **2a–c** and base catalyzed TP of **2d** gave solid and transparent hybrid materials (Table S2). The materials obtained from monomer **2c** with acid and base catalysis are completely soluble in DCM as determined by extraction experiments. Extraction experiments give the possibility to determine amount of conversion and study structure of side reactions and oligomeric products which are removable from the hybrid material. ^{1}H- and ^{13}C-NMR spectra of the extracts show oligomers of phenolic resin and polysiloxane. According to DSC measurements, the polymerization requires higher temperatures (Figure S2 and S3). The other materials also show high extractable contents between 37 to 80 %. However, the polydiarlkyl(aryl) siloxane component in the hybrid material is not completely soluble in DCM which is verified for the DBU catalyzed TP of **2b** by ^{29}Si-{^{1}H}- CP-MAS-NMR (Figure S4).

Table S1. Characteristic trigger temperatures for the thermally induced, DBU and TFA catalyzed TP of monomers **1** and **2a–d** as determined by DSC measurements.

monomer	$T_{onset, exo}$ [°C]		
	thermally induced	DBU	TFA
1	197	130	25
2a	n. o.	134	83
2b	n. o.	125	107
2c	n. o.	109	217
2d	n. o.	94	n. o.

Table S2. Acid and base catalyzed twin polymerization of **2a**–**d** using TFA and DBU, respectively. Extraction experiments were performed with DCM for 30 h.

catalyst	monomer	monomer/ catalyst ratio [n%]	time	tempera-ture	picture	mass loss by extraction	C [%] before extraction	C [%] after extraction
TFA	**2a**	20:1	4 h	85 °C		37 %	64.94	60.48
	2b	20:1	6 h	85 °C		47 %	68.77	71.34
	2c	20:1	6 h	85 °C		100 %	72.96	-
DBU	**2a**	50:1	40 h	140 °C		37 %	62.74	67.23
	2b	50:1	75 h	140 °C		74 %	66.32	67.03
	2c	50:1	123 h	140 °C		100 %	72.44	-
	2d	50:1	200 h	140 °C		80 %	70.89	70.80

1.3 ^{29}Si-{^{1}H} CP-MAS spectra

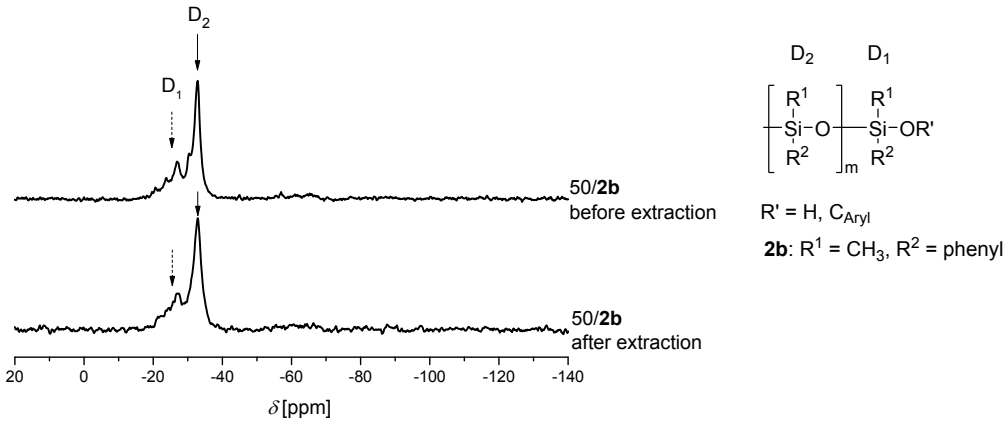


Figure S4 ^{29}Si-{^{1}H} CP-MAS spectra of the hybrid material DBU/**2b**100 before and after extraction with DCM.

1.4 HAADF-STEM

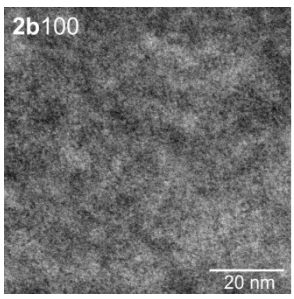
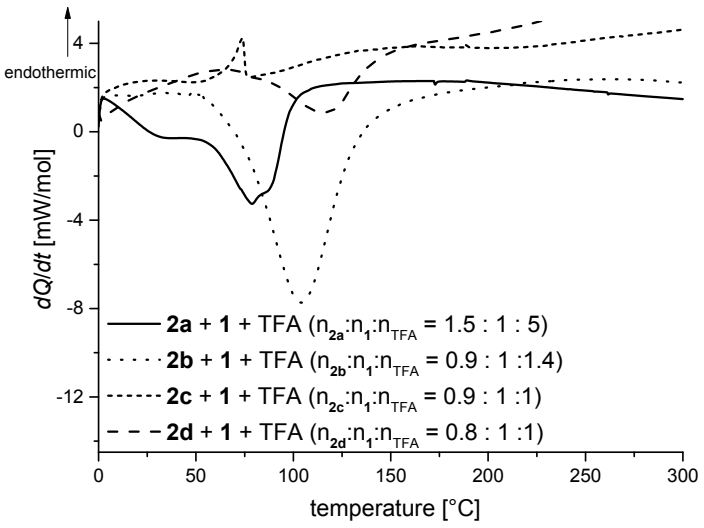


Figure S5 HAADF-STEM of the hybrid material derived from **2b** with TFA as a catalyst.

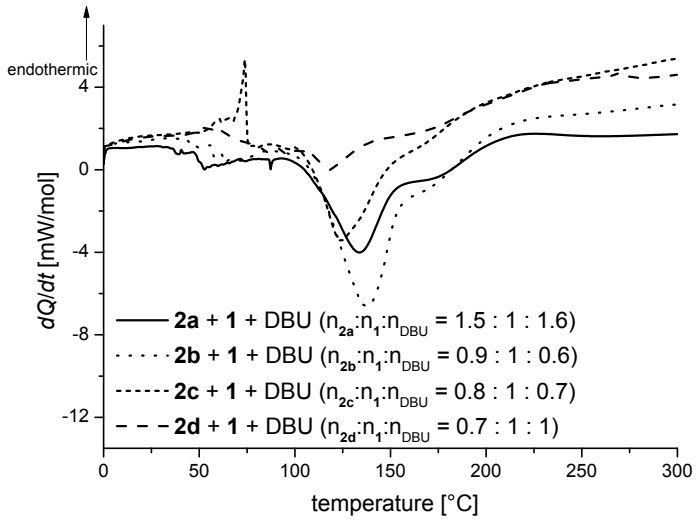
2. Simultaneous twin polymerization of 1 and 2a-d

2.1 DSC measurements



experiment	$T_{onset, endo}$ [°C]	$T_{onset,exo}$ [°C]
2a + **1** +TFA	-	30; 47
2b + **1** +TFA	-	72
2c + **1** +TFA	66; 80	-
2d + **1** +TFA	-	80

Figure S6. Differential scanning calorimetry (DSC) of STP of the monomer mixtures **n** with monomer **1** using TFA as a catalyst (molar ratio as given in the key).



experiment	$T_{onset, endo}$ [°C]	$T_{onset,exo}$ [°C]
2a + **1** +DBU	-	106
2b + **1** +DBU	-	108
2c + **1** +DBU	70	107
2d + **1** +DBU	46	107

Figure S7 DSC of STP of the monomer mixtures **2a**, **2b**, **2c** and **2d** with monomer **1** using DBU as a catalyst (molar ratio as given in the key).

2.2 STP experiments and extraction of the hybrid materials

Table S3 TFA catalysed STP of **1** and **2a–d** at 85 °C for 4 h using a concentration of catalyst of M:I = 20:1 [n%]. The naming of the samples is based on the specific monomer **2** used for the polymerization. The following number indicates the molar ratio of monomer **2** used in the mixture. Extraction experiments of the hybrid materials were performed with DCM for 30 h. The table also shows the appearance of the sample as well as the amount of C determined through elemental analysis before and after extraction.

experiment	sample	mass loss by extraction[%]	C [%] before extraction	C [%] after extraction
2a90*		20	59.12	56.82
2a75		15	58.88	56.93
2a50		10	58.66	57.07
2a25		2	59.17	58.12
2b90		32	67.92	69.98
2b70		21	65.23	65.46
2b50		13	63.86	63.80
2b40		11	61.61	60.24
2b15		6	58.99	58.24
2b10		7	59.28	58.22
2c80		87	70.36	70.55
2c65		76	68.21	66.69
2c50		19	66.19	64.79
2c40		15	64.81	63.54
2c10		9	58.77	-
2d80		100	68.20	-
2d65		73	66.79	55.48
2d50		58	65.12	57.54
2d40		48	64.46	64.47
2d10		12	59.01	61.56

*7h polymerization time

Table S4. DBU catalysed STP of **1** and **2a–d** at monomer ratio of 50:50 n%. The naming of the samples is based on experimental parameters used for the polymerization. The first part of the name represents the molar ratio of monomers to catalyst (M:I) like 50:1 n% is abbreviated as 50. The next part indicates the specific monomer **2** and the molar ratio of that monomer used in the mixture. Extraction experiments of the hybrid materials were performed with DCM for 30 h. The table also shows the appearance of the sample as well as the amount of C determined through elemental analysis before and after extraction.

experiment	sample	mass loss extraction[%]	C [%] before extraction	C [%] after extraction
50/**2a**50		2	60.63	60.89
100/**2a**50		-	59.46	-
300/**2**a50		-	58.59	-
50/**2b**50		14	65.24	64.11
100/**2b**50		25	64.57	63.60
50/**2c**50		23	67.75	65.42
100/**2c**50		28	68.47	67.20
50/**2d**50		62	65.43	55.71

2.2.1 ^{29}Si-{^{1}H} CP-MAS spectra

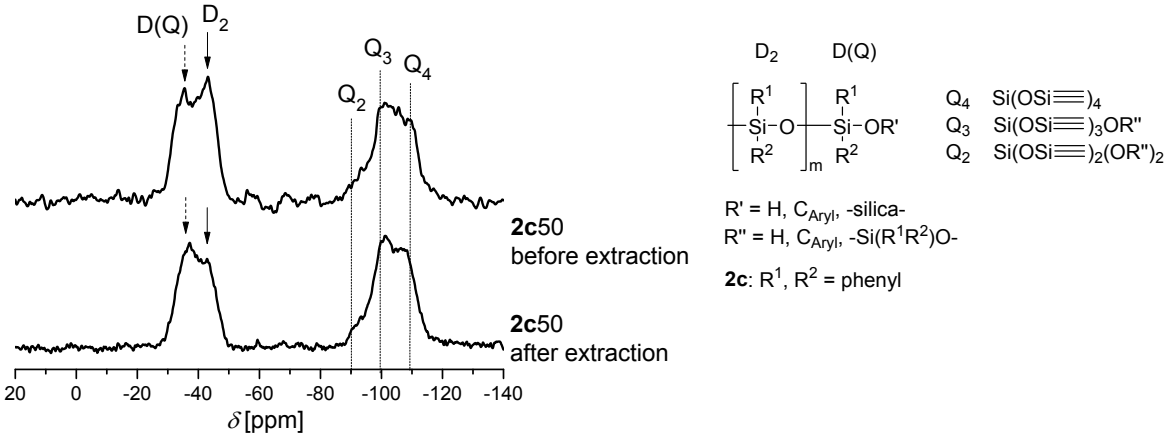


Figure S8 ^{29}Si-{^{1}H} CP-MAS spectra of the hybrid material **2c**50 before and after extraction.

2.3 Post curing

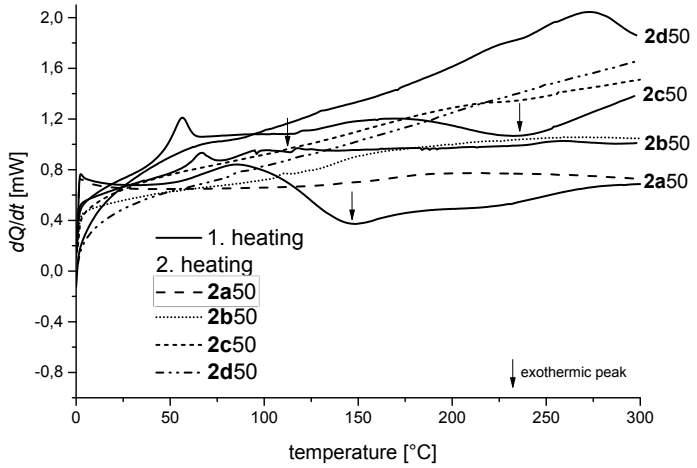


Figure S9. DSC of hybrid materials produced from **1** and **2a–d** at a monomer ratio of 50:50 n% and a concentration of TFA of 20:1 n% (M:I) with two heating steps. Exothermic signals indicate post-curing of the hybrid network.

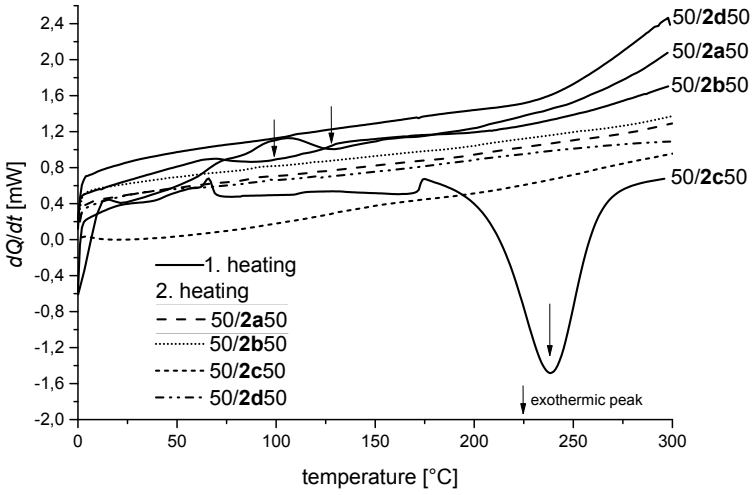


Figure S10. DSC of hybrid materials produced from **1** and **2a–d** at a monomer ratio of 50:50 n% and a concentration of DBU of 50:1 n% (M:I) with two heating steps. Exothermic signals indicate post-curing of the hybrid network.

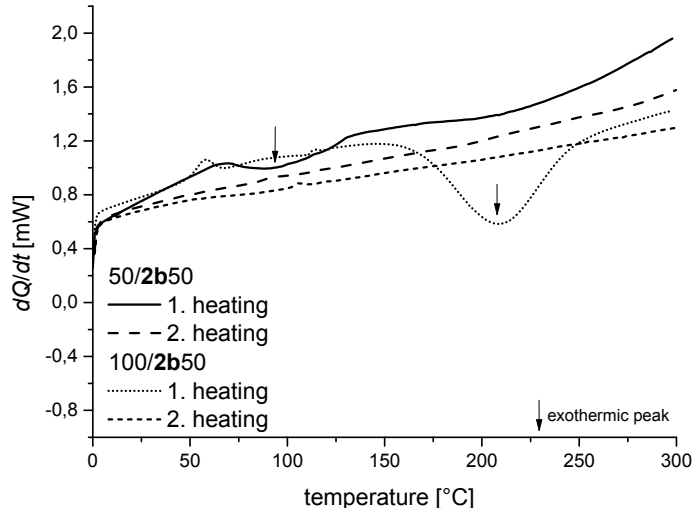


Figure S11. DSC of the hybrid material **1** and **2b** polymerized for 3 h at 110 °C with different concentration of DBU (M:I = 50:1 n%; 100:1 n%). Two heating steps were performed. Exothermic signals indicate post-curing of the hybrid network.

2.4 Mechanical properties – nanoindentation measurements

Table S5. Young's modulus and hardness for the monolithic polymerization products of the STP for monomers **2a** and **2c** at a monomer ratio of 50:50 n% and for different monomer ratios of **1**:**2b** determined through nanoindentation measurements (poisson number estimated at 0.4).

experiment	F [mN]	Young's modulus [GPa]	hardness [MPa]
2a50	5	5.4	296.8
2b90	5	3.6	173.6
2b70	5	4.7	239.7
2b50	5	5.2	254.2
2b40	5	5.4	269.6
2b15	5	6.1	344.0
2b10	5	6.1	339.1
2c50	5	1.3	42.3
2d50	5	-	-

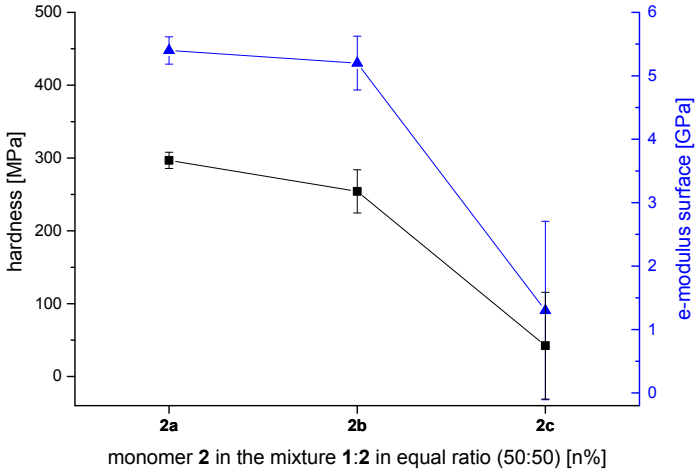


Figure S12. Hardness and elastic modulus as function of the type of monomer **2** in the hybrid material from STP with the composition of **1**:**2** of 50:50 using TFA as catalyst (n= 23-27, error bars cover 3σ).