Supplementary Information

Light-mediated controlled and classical polymerizations of less-activated monomers under high-pressure conditions

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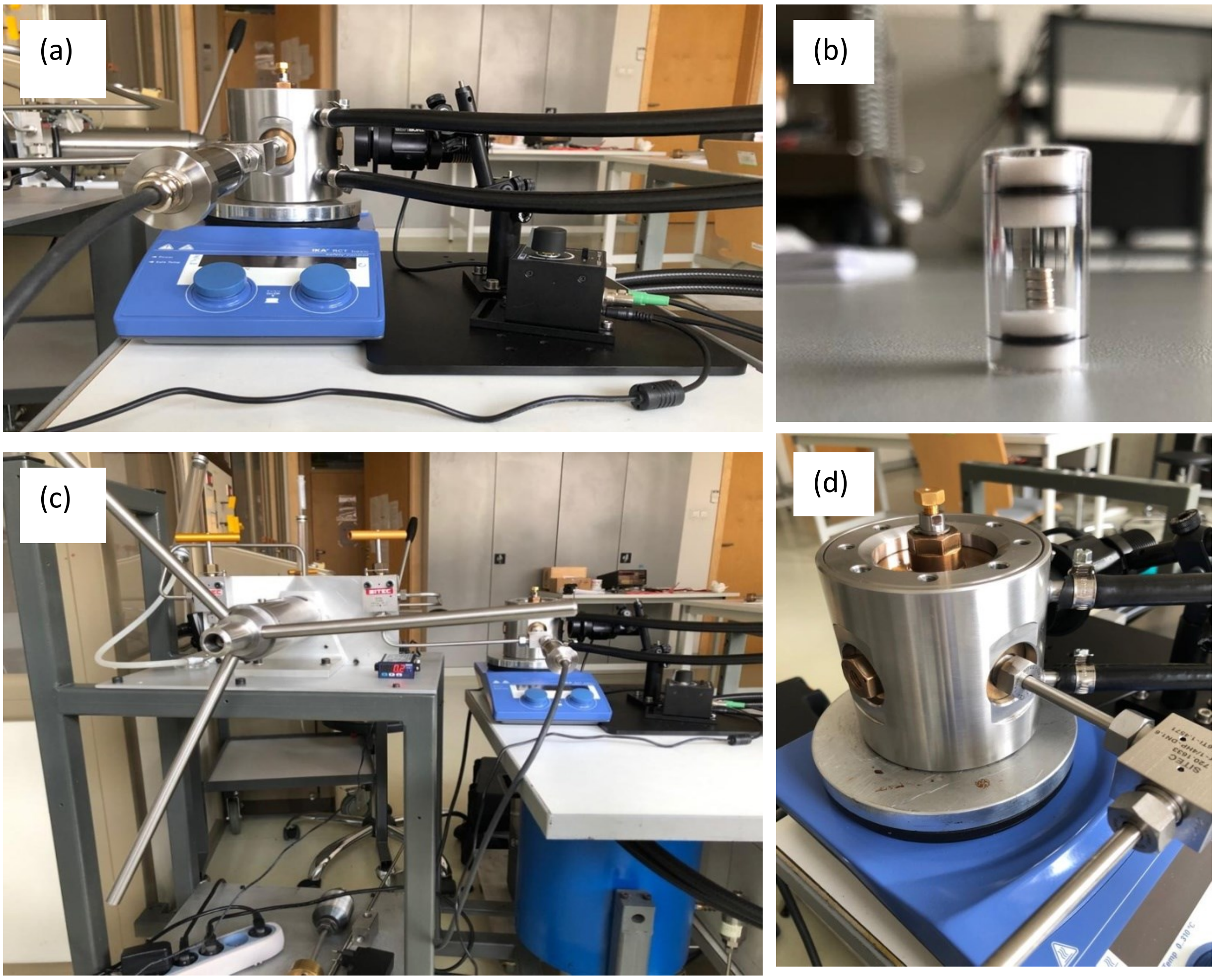


Fig S1. High-pressure equipment, (a) optical pressure chamber and light source, (b) quartz ampule with a stirrer, (c) pressure generator, pressure chamber and light source, (d) optical pressure chamber with Sapphire windows

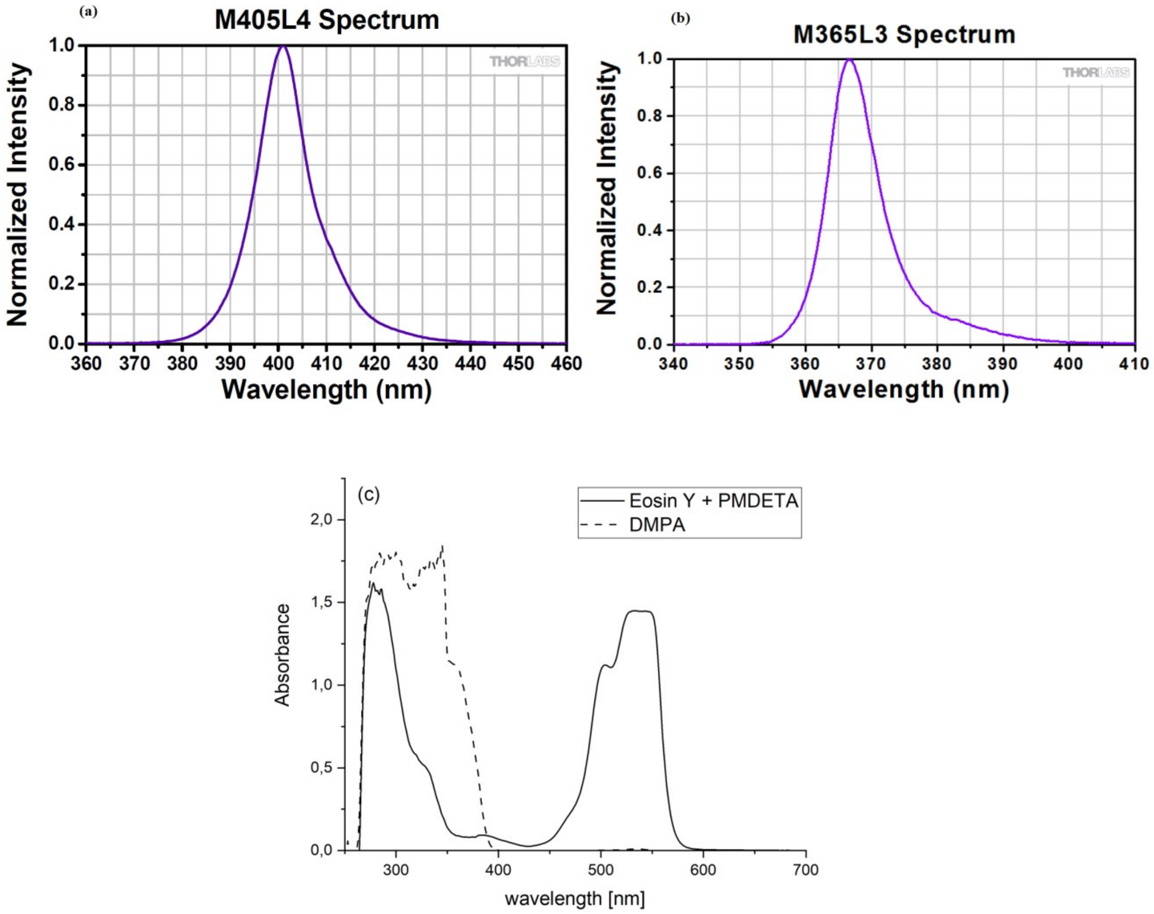
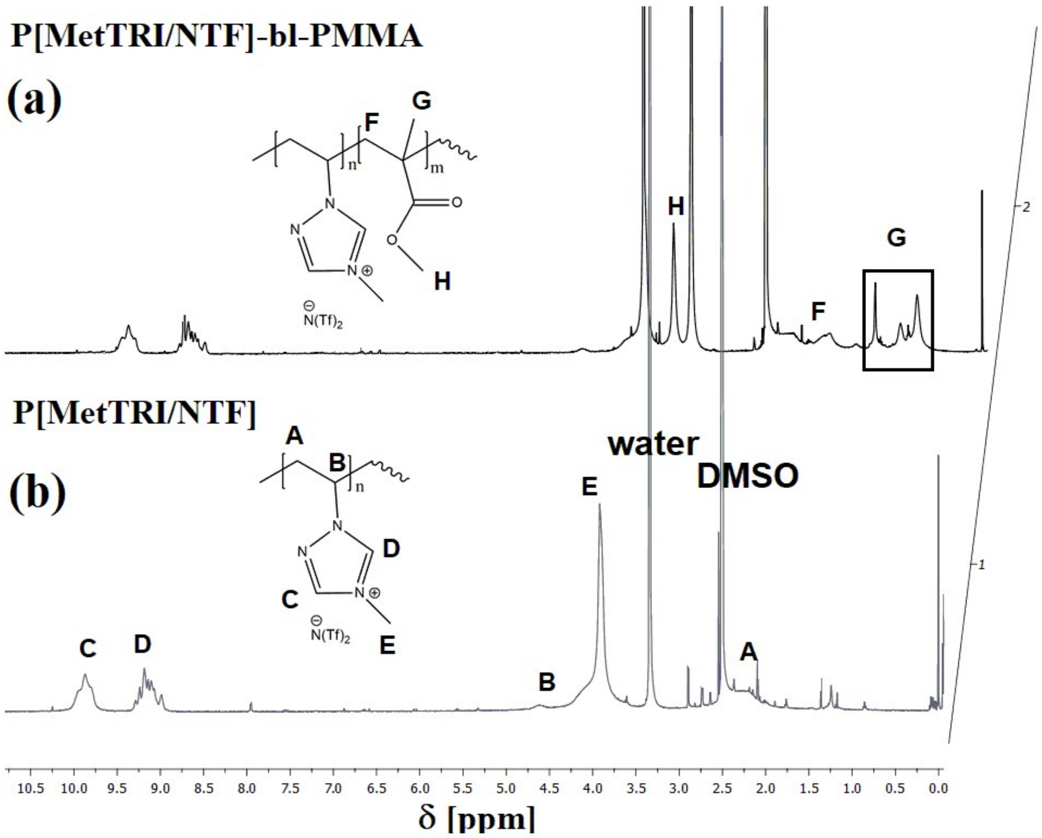
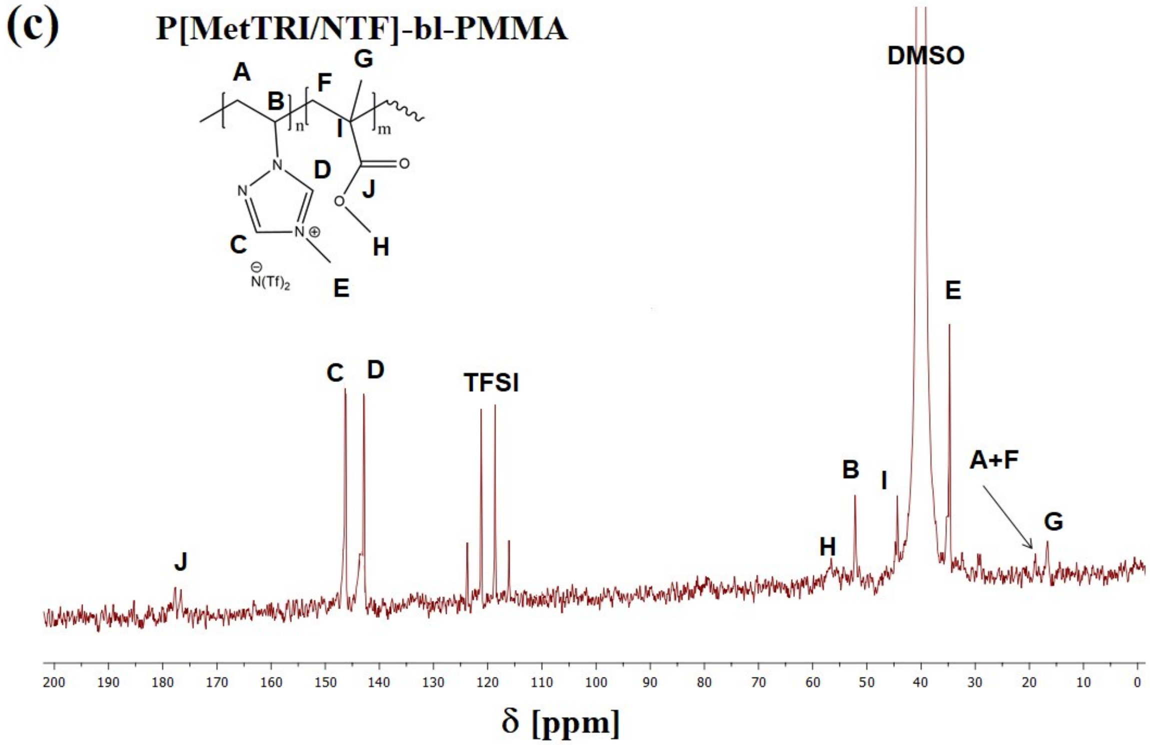


Fig S2. Emission spectrum of the used light sources (a) 405 nm and (b) 365 nm reprinted from the Webpage of the producer https://www.thorlabs.com/locations.cfm; (c) The UV-vis absorption spectra of both studied systems Eosin Y+PMDETA and DMPA (0.01 mmol/ml; DMF)


P[MetTRI/NTF]-bl-PMMA
(a)
F
G
n
m
N
N
N
⊕
O
O
H
⊖
N(Tf)2
H
G
F
2
P[MetTRI/NTF]
(b)
A
B
n
N
N
N
D
C
⊕
⊖
N(Tf)2
E
water
DMSO
E
C
D
B
A
1
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
δ [ppm]


(c)
P[MetTRI/NTF]-bl-PMMA
A
B
F
G
I
n
m
N
N
N
D
⊕
O
O
J
H
C
⊖
N(Tf)2
E
DMSO
E
C
D
TFSI
B
I
A+F
H
G
J
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
δ [ppm]

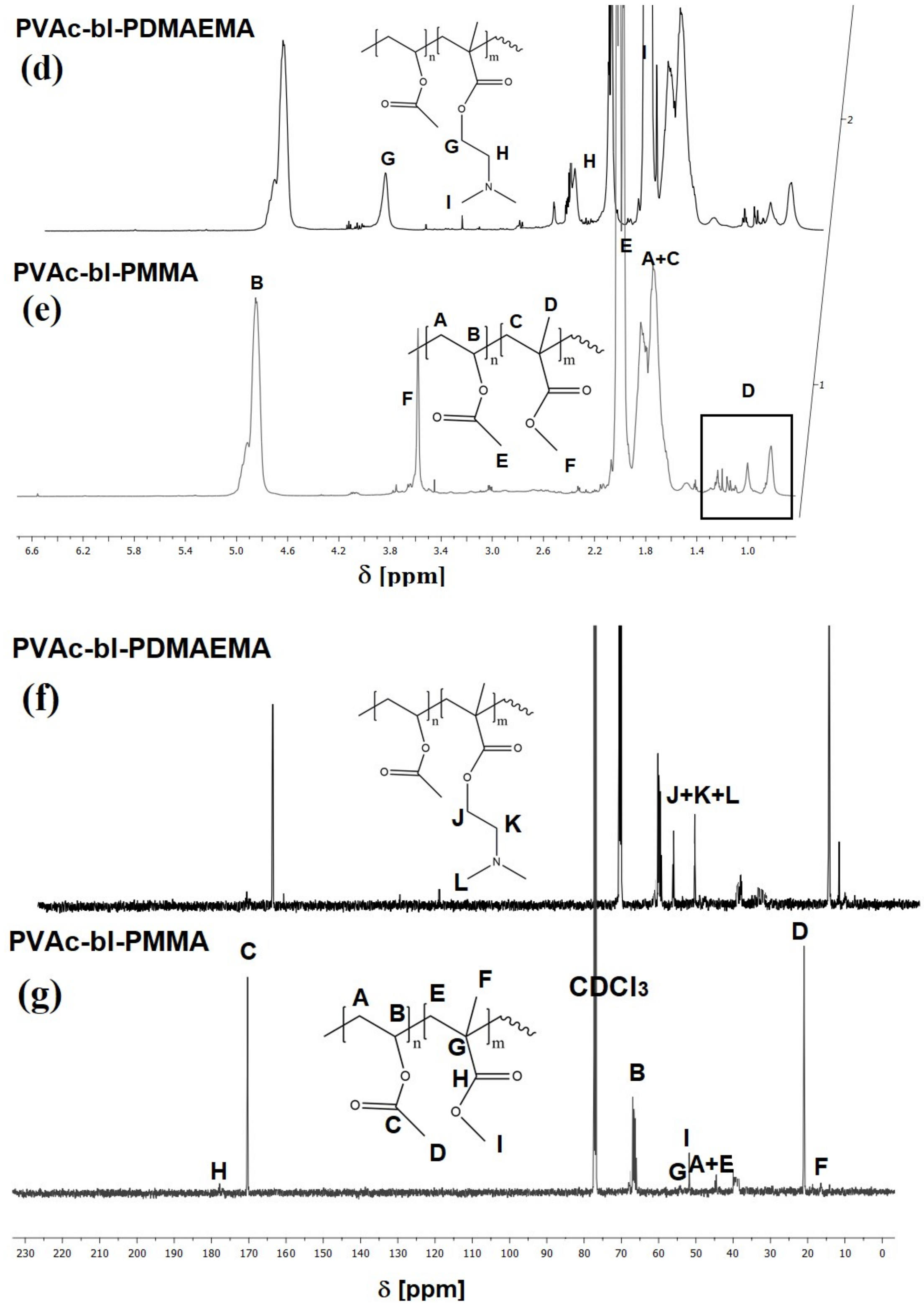
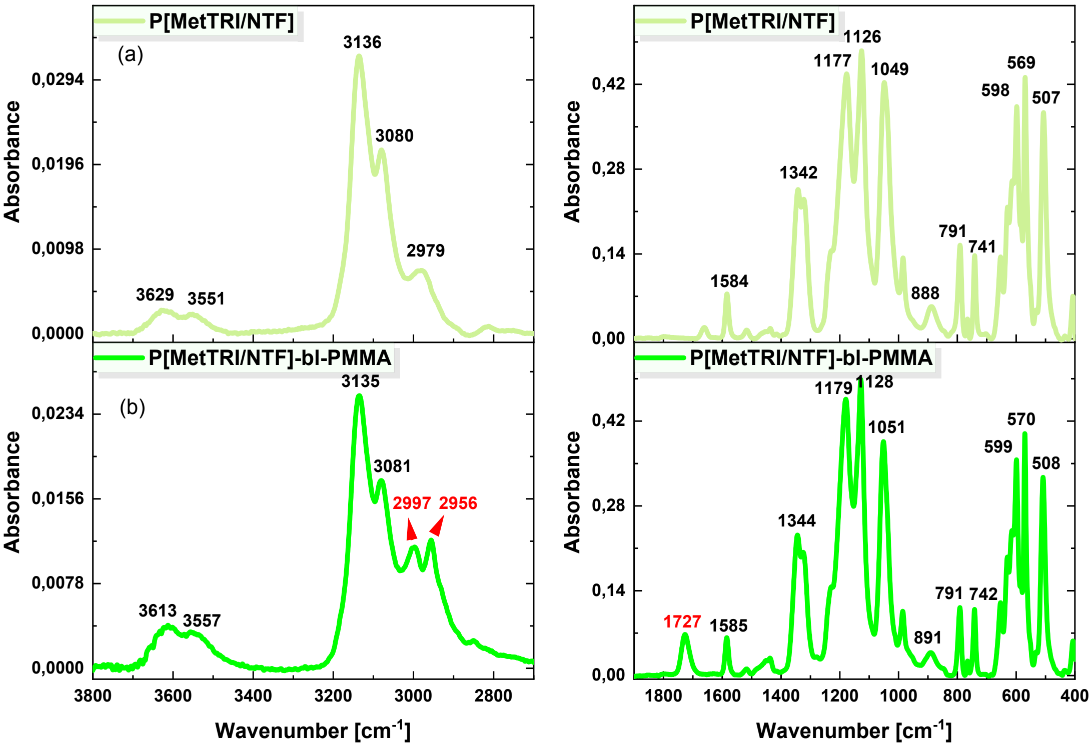
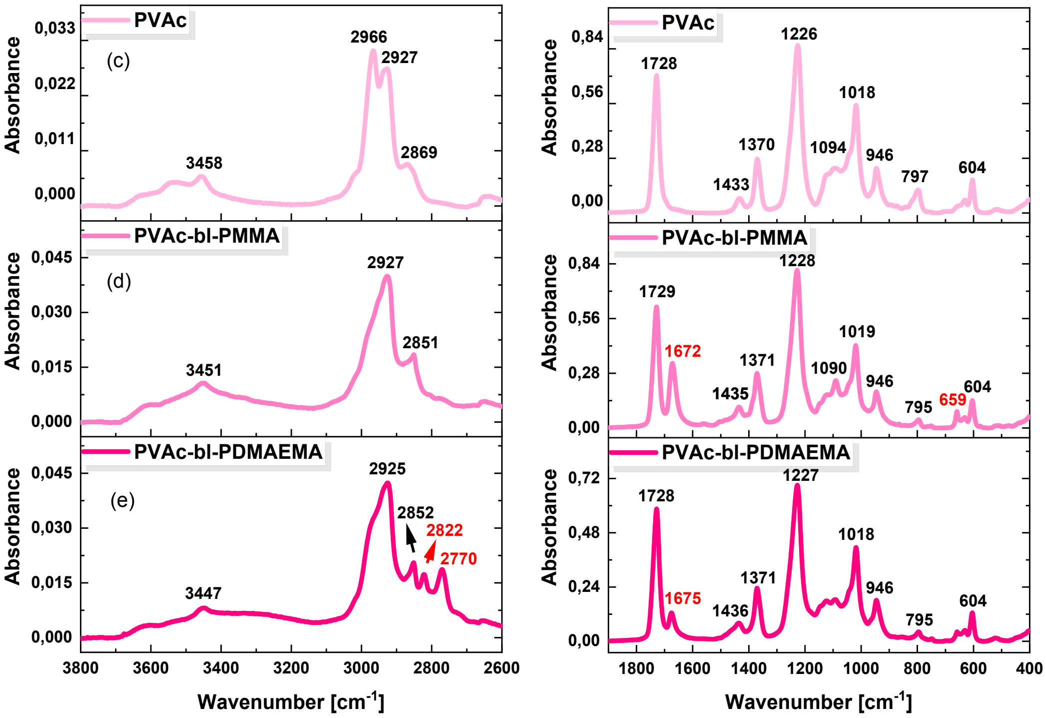


Fig S3. (a) ^{1}H NMR spectrum of P[MetTRI/NTF]-bl-PMMA and (b) their precursor, (c) ^{13}C NMR spectrum of P[MetTRI/NTF]-*bl*-PMMA, (d) ^{1}H NMR spectrum of PVAc-*bl*-PDMAEMA, (e) ^{1}H NMR spectrum of PVAc-*bl*-PMMA, (f) ^{13}C NMR spectrum of PVAc-*bl*-PDMAEMA, (g) ^{13}C NMR spectrum of PVAc-*bl*-PMMA


P[MetTRI/NTF]
(a)
3136
3080
2979
3629
3551
0,0294
0,0196
0,0098
0,0000
Absorbance
P[MetTRI/NTF]-bl-PMMA
(b)
3135
3081
2997
2956
3613
3557
0,0234
0,0156
0,0078
0,0000
3800
3600
3400
3200
3000
2800
Wavenumber [cm^{-1}]
P[MetTRI/NTF]
1126
1177
1049
569
598
507
1342
791
741
1584
888
0,42
0,28
0,14
0,00
P[MetTRI/NTF]-bl-PMMA
1179
1128
1051
570
599
508
1344
791
742
1727
1585
891
1800
1600
1400
1200
1000
800
600
400
Wavenumber [cm^{-1}]


PVAc
(c)
2966
2927
2869
3458
0,033
0,022
0,011
0,000
Absorbance
PVAc-bl-PMMA
(d)
2927
2851
3451
0,045
0,030
0,015
0,000
PVAc-bl-PDMAEMA
(e)
2925
2852
2822
2770
3447
3800
3600
3400
3200
3000
2800
2600
Wavenumber [cm^{-1}]
PVAc
1226
1728
1018
1370
1094
946
1433
797
604
0,84
0,56
0,28
0,00
PVAc-bl-PMMA
1228
1729
1672
1019
1371
1090
946
1435
795
659
604
PVAc-bl-PDMAEMA
1227
1728
1018
1675
1371
946
1436
795
604
0,72
0,48
0,24
0,00
1800
1600
1400
1200
1000
800
600
400
Wavenumber [cm^{-1}]

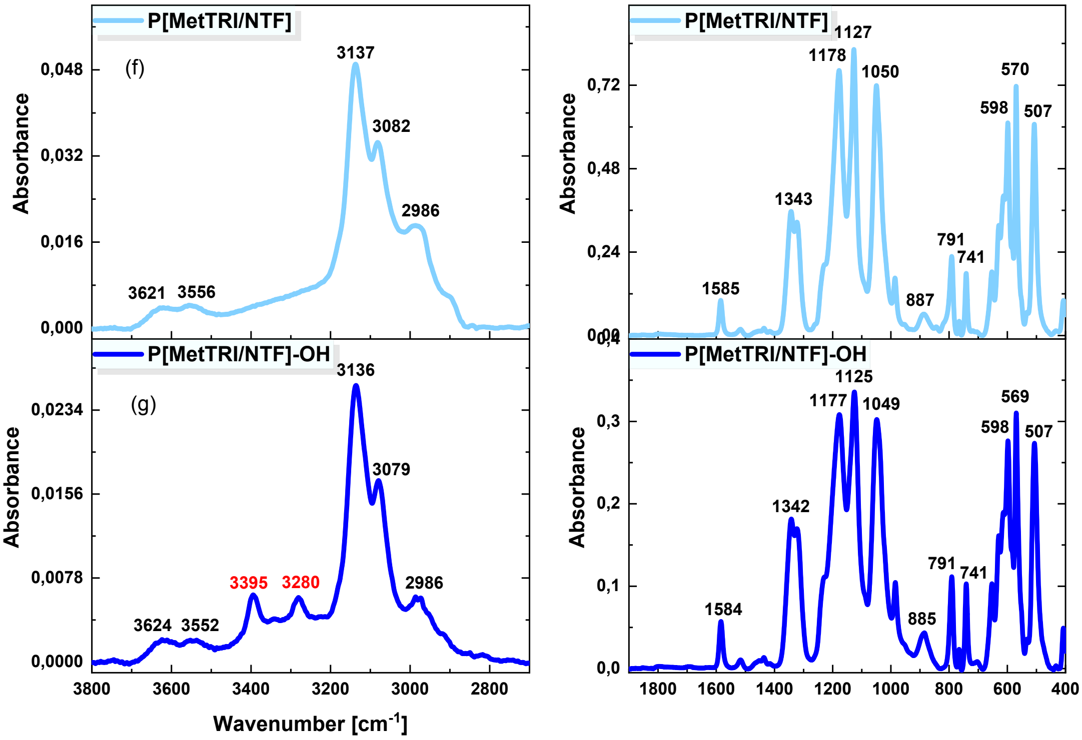


Fig S4. ATR-FTIR spectra of (a) P[MetTRI/NTF] (sample IV) and P[MetTRI/NTF]-*bl*-PMMA presented in two frequency ranges: (left) 3800-2700 cm^{-1} and (right) 1900-400 cm^{-1}; (b) PVAc, PVAc-*bl*-PMMA and PVAc-*bl*-PDMAEMA presented in two frequency ranges: (left) 3800-2600 cm^{-1} and (right) 1900-400 cm^{-1}; (c) P[MetTRI/NTF] (sample XV) and P[MetTRI/NTF]-OH (sample XI) presented in two frequency ranges: (left) 3800-2700 cm^{-1} and (right) 1900-400 cm^{-1}.

A supportive proof of the formation of P[MetTRI/NTF] was provided by FT-IR spectroscopy (Fig. S4a). FTIR spectrum of P[MetTRI/NTF] exhibits the absorption bands characteristic of stretching and bending vibrations of the triazole ring (1585, 1517 cm^{-1} (C=N), 1452, 1436, 1416 cm^{-1} (C—N), 1227 cm^{-1} (N—N), 1050 cm^{-1} (C—H), 653 cm^{-1} (C—N)), and the polymeric chain (3137 cm^{-1}, 3082 (CH), 2986 cm^{-1} (CH_2))[1]. Based on the FTIR data presented in the literature for the NTF anion[2], the assignment of some bands in the FTIR spectra of P[MetTRI/NTF] was done. Thus, four bands of stretching and bending vibrations of $=SO_2$ groups of the NTF anion were observed at 1343 cm^{-1} ($\nu_a SO_2$), 1127 cm^{-1} ($\nu_s SO_2$), 613 cm^{-1} ($\delta_a SO_2$) and 598 cm^{-1} (shoulder $\delta_s SO_2$). Moreover,

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[1] T. G. Ermakova, N. P. Kuznetsova, A. S. Pozdnyakov, L. I. Larina, S. A. Korzhova, I. V. Mazyar, V. S. Shcherbakova, A. V. Ivanov, A. I. Mikhaleva, and G. F. Prozorova, 1-Vinyl-1,2,4-triazole in copolymerization reaction with 1-vinyl-4,5,6,7-tetrahydroindole: synthesis and properties of copolymers, *Russ. Chem. Bull.*, 2016, 65(2):485-489

[2] M. Yahia, S. Mei, A. P. Mathew, and J. Yuan, Linear Main-Chain 1,2,4-Triazolium Poly(ionic liquid)s: Single-Step Synthesis and Stabilization of Cellulose Nanocrystals, *ACS Macro Lett.* 2019, 8, 10, 1372–1377.

three bands occurring at 1178, 741, and 570 cm$^{–1}$ can be attributed to $\nu_a CF_3$, $\delta_s CF_3$, and $\delta_a CF_3$ of the NTF anion, respectively. The symmetric (741 cm$^{–1}$) stretching bands of the S–N–S group and symmetric stretching of C–S (765 cm$^{–1}$) were also observed, confirming the presence of NTF anion in the P[MetTRI/NTF] sample. The presence of new peaks at 2997 and 2956 cm^{-1} in the IR spectrum of P[MetTRI/NTF]-bl-PMMA indicates that these copolymer was successfully prepared/produced.[3] This fact is also confirmed by the occurrence of absorption band at 1727 cm^{-1}, which is associated with the stretching vibrations of carbonyl groups belonging to the PMMA segments.

Based on the FTIR spectroscopy results, the effective incorporation of PMMA or PDMAEMA segments into the PVAc matrix during the polymerization process was confirmed, which was observed by the presence of absorption bands related to the studied polymers. The representative spectra of PVAc homopolymer, PVAc-*bl*-PMMA, and PVAc-*bl*-PDMAEMA copolymers in the high- and low-frequency ranges were presented in Fig. S4b. According to the data reported for PVAc[4,5,6], the bands located between 3100 and 2800 cm^{-1} (2966, 2927, and 2869 cm^{-1}) can be attributed to the asymmetric and symmetric C-H stretching vibrations of CH, CH_3, and CH_2 groups. An intense signal at 1728 cm^{-1} is associated with the stretching vibration of carbonyl moiety (C=O), belonging to the ester group of PVAc polymer. A broad band found at 3458 cm^{-1} is assigned as the first harmonic of the carbonyl vibration (2x C=O). The signals at 1433 cm^{-1} and 1370 cm^{-1} can be attributed to the bending vibrations of the C-H bonds of the CH_2 and CH_3 groups. The intense peak at 1226 cm^{-1} is due to the asymmetric and symmetric C-O-C stretching vibrations. Furthermore, the C-C-O vibrations are observed at 1125 cm^{-1}. The stretching C-C skeletal vibrations occur at 1018 cm^{-1}. A band at 946 cm^{-1} is identified as the in-plane CH_3 rocking vibration. A peak at 797 cm^{-1} can be assigned to the rocking vibrations of CH_2 units. The absorption feature at 604 cm^{-1} is due to the out-of-plane bending vibrations of CH_3COO group. As shown in Fig. S4b, the IR absorption bands of PVAc changed slightly upon copolymerization processes, namely a new band observed in the PVAc modified spectra at 1672 cm^{-1} (PVAc-*bl*-PMMA) and 1675 cm^{-1} (PVAc-*bl*-PDMAEMA) can be attributed to the carbonyl group of PMMA and PDMAEMA segments, respectively[7]. Moreover, the high-frequency component of the C-H band at 2966 cm^{-1} disappears in the spectra of copolymers. The new peaks assigned to aliphatic $N(CH_3)_2$ and CH stretching vibrations of PDMAEMA blocks appeared in the FTIR spectrum of PVAc-*bl*-PDMAEMA copolymer at 2822 and 2770 cm^{-1}, respectively [FTIR5]. Moreover, an increase of the band intensity of the C−N stretching vibrations at

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[3] J. Dybal and S. Krimm, Normal-mode analysis of infrared and Raman spectra of crystalline isotactic poly(methyl methacrylate), *Macromolecules*, 1990, 23, 1301-1308.

[4] J. K. Haken, R. L. Werner. Infrared spectra of polyvinyl acetate and poly-α, α', β-trideuterovinyl acetate. *Brit. Polym. J.*, 1971, 3(4), 157–162

[5] J. K. Haken, R. L. Werner, The low temperature infrared spectrum of polyvinyl acetate. *Brit. Polym. J.*, 1973, 5(6), 451–455.

[6] U. H. Hossain, T. Seidl, W. Ensinger, Combined in situ infrared and mass spectrometric analysis of high-energy heavy ion induced degradation of polyvinyl polymers, *Polym. Chem.*, 2014, 5, 1001-2012

[7] E. A. Elizalde-Peña, N. Flores-Ramirez, G. Luna-Barcenas, S. R. Vásquez-García, G. Arámbula-Villa, B. García-Gaitán, J. González-Hernández. Synthesis and characterization of chitosan-g-glycidyl methacrylate with methyl methacrylate. *Eur. Polym. J.*, 2007, 43(9), 3963–3969.

1110−1160 cm^{-1} is also observed that is related to the PDMAEMA content in the copolymer structure.

FTIR spectrum of P[MetTRI/NTF] prepared via FRP clearly resembles that produced via photo-ATRP (see Fig S4c). In the P[MetTRI/NTF]-OH spectrum, two new signals at 3395 and 3280 cm^{-1}, originating from the stretching vibrations of hydroxyl groups, appeared. It means that the 2-isopropoxyethanol moieties/domains were effectively incorporated into the PIL structure.

Table S1. Control experiments for *O*-ATRP

no	P [MPa]	$[M]_0/[EBiB]_0/[Eosin\ Y]_0/[PMDETA]_0$		
1	0.1	in the dark	400:1:0.1:1	no polymerization
2	150	in the dark	400:1:0.1:1	no polymerization
3	0.1	λ=405 nm	400:0:0.1:1	no polymerization
4	150	λ=405 nm	400:0:0.1:1	no polymerization
5	0.1	λ=405 nm	400:1:0:0	no polymerization
6	150	λ=405 nm	400:1:0:0	no polymerization
7	0.1	λ=405 nm	400:1:0.1:0	no polymerization
8	150	λ=405 nm	400:1:0.1:0	no polymerization
9	0.1	λ=405 nm	400:1:0:1	no polymerization
10	150	λ=405 nm	400:1:0:1	no polymerization

(DMF 1/1 wt%. in respect to monomer); time=300 min

Table S2. Chain extension photo-ATRP experiments performed on produced P[MetTRI]/NTF and PVAc macroinitiators

no	macroinitiator	monomer	Time [h]	Conv. [%]^a	M_{nSEC}^{b} [kg/mol]	Đ^b
1	sample II	MMA	24	20	77.1	1.30
2	sample VI	DMAEMA	24	50	65.7	1.35
3	sample VI	MMA	24	8	56.8	1.31

$[monomer]_0/[MI]_0/[Eosin\ Y]_0/[PMDETA]_0=400/1/0.1/1$ (DMF 1/1 wt%. in respect to monomer); ^{a} determined via NMR, ^{b}SEC (DMF, LiBr as eluent), λ=405 nm

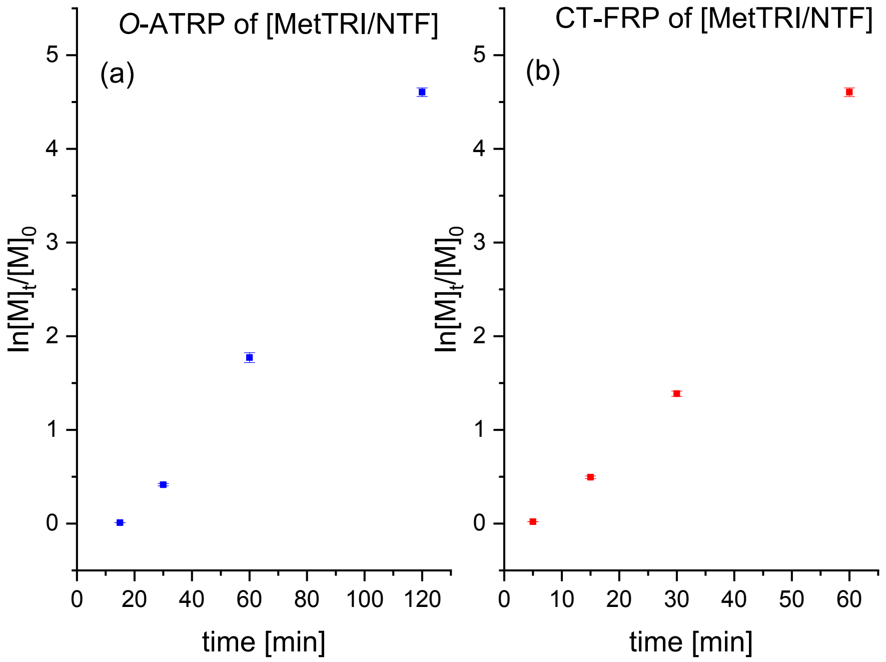

Fig. S5 (a) Pseudo-first-order kinetic plots versus conversion for O-ATRP of MetTRI/NTF under 150 MPa with error bars (b) Pseudo-first-order kinetic plots versus conversion for CT-FRP of MetTRI/NTF under 150 MPa with error bars

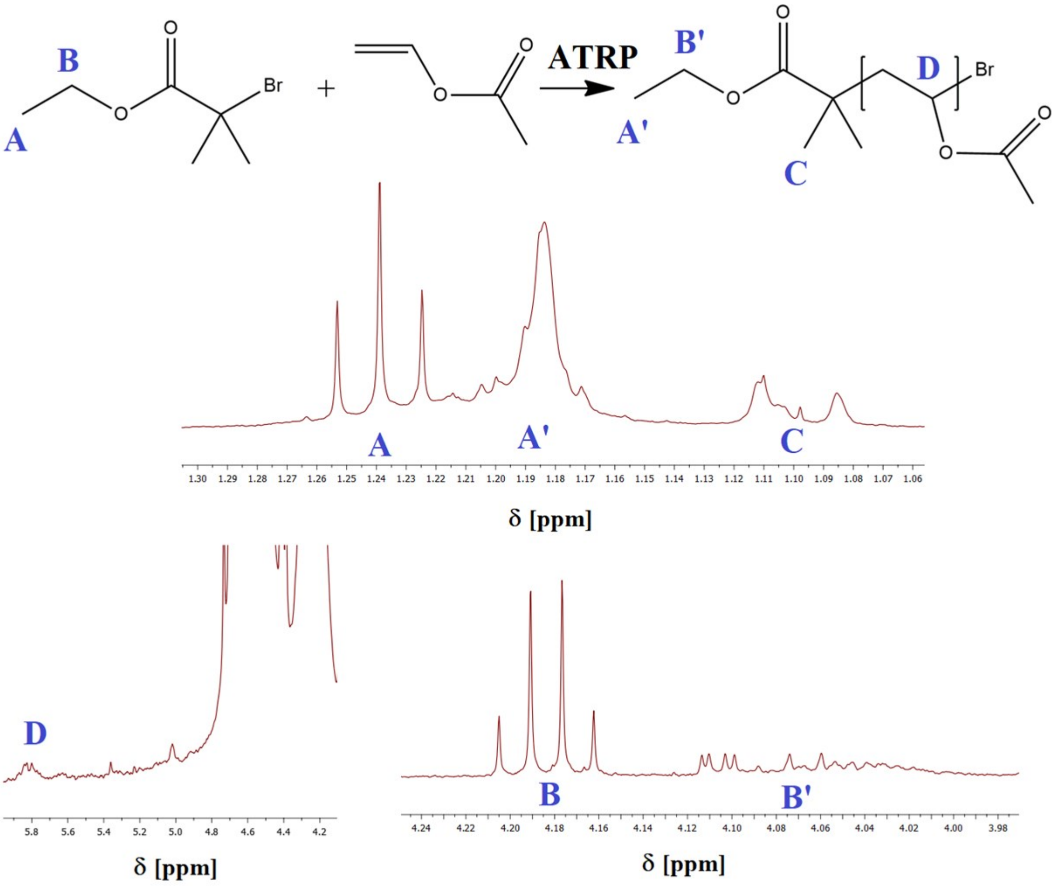

Fig S6. Fragmnets of ^{1}H NMR spectrum taken from the polymerization mixture of VAc *O*-ATRP under high-pressure. Percentage of reacted initiator was calculated using the integrations of methylene protons of the unreacted initiator (sharp triplet at 1.24 ppm), and the integration of the methylene protons corresponding to the consumed initiator (1.19 ppm).

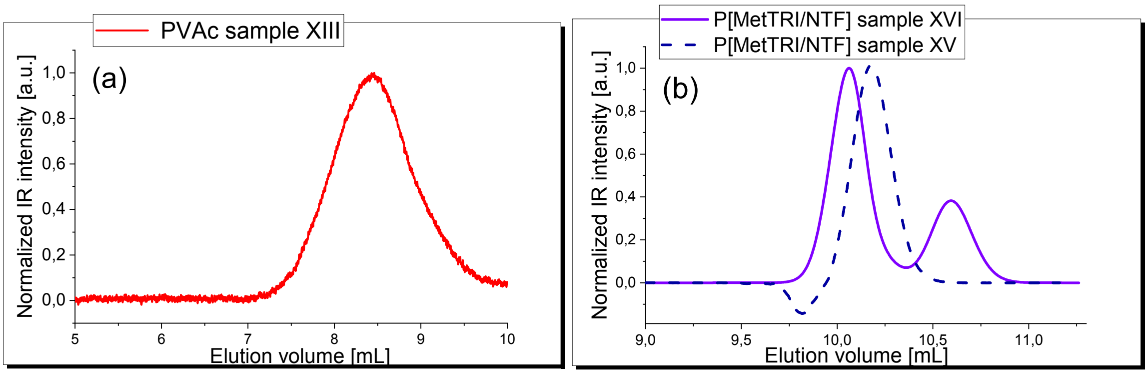

Fig S7. (a) SEC-LALLS trace of PVAc prepared via CT-FRP under p=150 MPa, (b) SEC traces of P[MetTRI/NTF] prepared via FRP under p=0.1 and 150 MPa