Electronic Supplementary Information

Effect of Anethole on the Copolymerization of Vinyl Monomers

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1. Polymerization

Conversions were monitored by ^{1}H NMR spectroscopy. Signals of vinyl protons of monomers were compared to a reference signal (that remain unchanged over the polymerization process): CH_3 adjacent to O of ANE for the system St : ANE ; CH_3 adjacent to O of ANE + CHX adjacent to O of ester side group for the systems MMA : ANE and 2EHA : ANE ; 1,3,5-trioxane was introduced in the batch for the system AA : ANE. Figure S1 shows NMR spectra of different systems during the polymerization process.

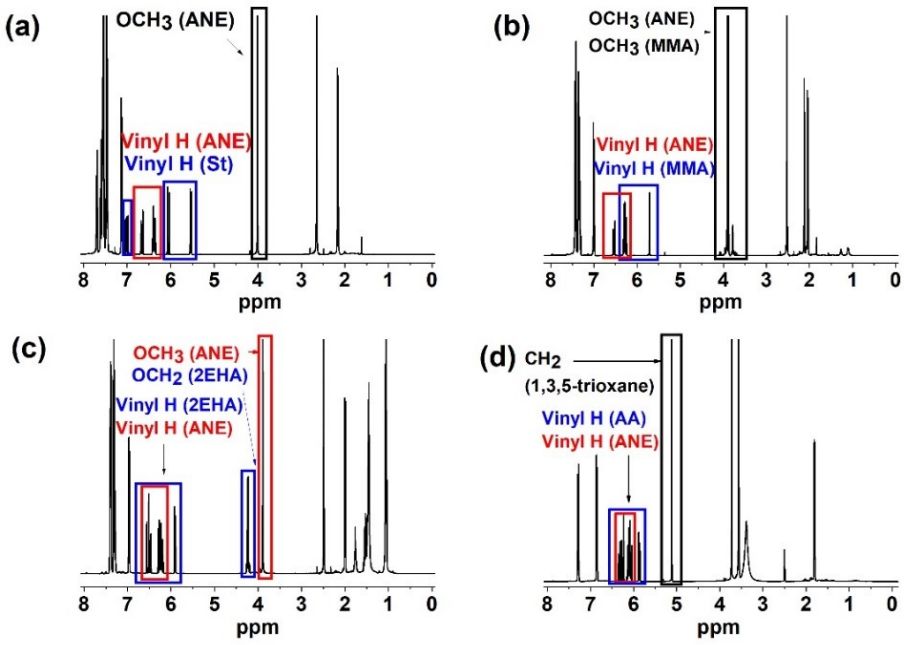


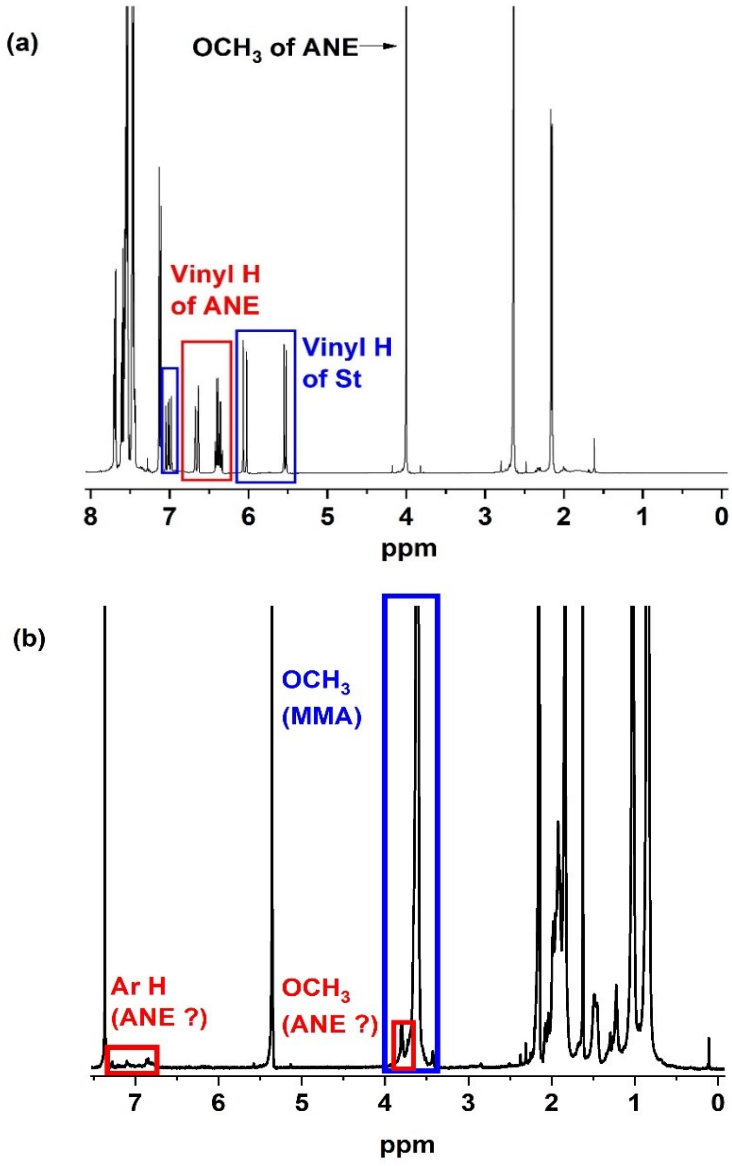
Figure S1: ^{1}H NMR spectra of polymerization medium after 1 h of reaction for preparation of (a) P(St-co-ANE) (polymer 3), (b) P(MMA-co-ANE) (polymer 14), (c) P(2EHA-co-ANE) (polymer 21), (d) P(AA-co-ANE) (polymer 36)

Conversions were calculated as follows:

$$X\,(t) = 1 - \frac{I(vinyl\ H)_t}{I(vinyl\ H)_{t=0}} \quad \text{(S1)}$$

For homopolymerization of St, MMA and 2EHA, the vinyl protons signals were to the NH2 signal of an internal standard : dimethylformamide (DMF), as in (1). For AA homopolymerization, conversions were determined as in (2).

Copolymer compositions were also determined by ^{1}H NMR spectroscopy. Pure P(St-co-ANE), P(MMA-co-ANE), P(2EHA-co-ANE) were analyzed in CD_2Cl_2. Composition of P(AA-co-ANE)s were determined before purification in MeOD. In this solvent, we managed to isolate a signal of protons of ANE (monomer) and separate the water signal to the massif containing alkaline protons of AA and ANE units. ^{1}H NMR analyses of purified polymers from MMA : ANE copolymerization cannot confirm the presence of ANE units in chains. Details are below.


(a)
OCH3 of ANE
Vinyl H
of ANE
Vinyl H
of St
8
7
6
5
4
3
2
1
0
ppm
(b)
OCH3
(MMA)
Ar H
(ANE ?)
OCH3
(ANE ?)
7
6
5
4
3
2
1
0
ppm

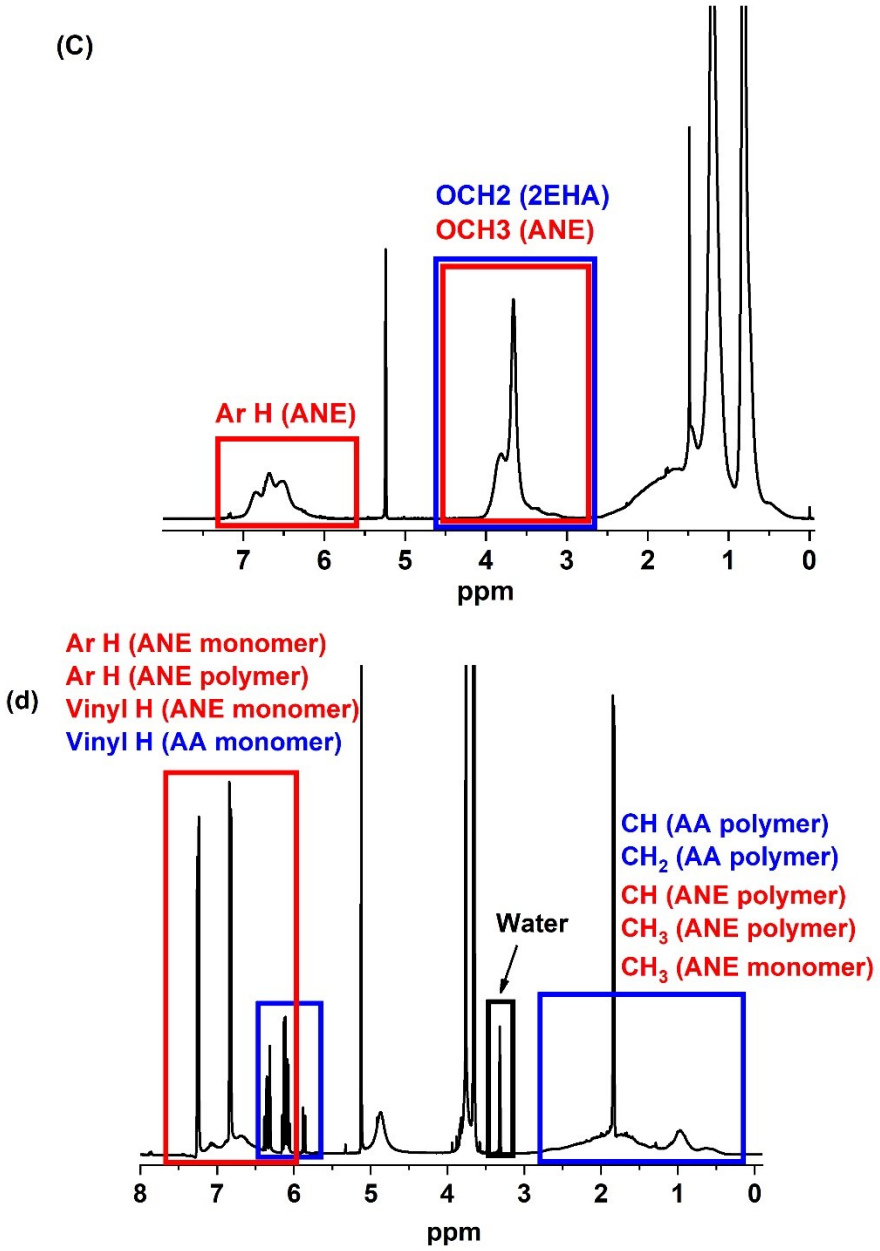


Figure S2: ^{1}H NMR spectra of (a) Purified P(St-co-ANE) (polymer 3), (b) Purified P(MMA-co-ANE) (polymer 14), (c) Purified P(2EHA-co-ANE) (polymer 21), (d) Non purified P(AA-co-ANE) (polymer 36).

Copolymers compositions are determined as follows:

Table S1: Equations used to determine the copolymers composition

Polymer	Equation to determine F_{ANE}
P(St-co-ANE)	$F_{ANE} = \dfrac{\dfrac{I(OCH_3\,(ANE))}{3}}{I\,(Ar\,H) - \dfrac{4 \times I(OCH_3\,(ANE))}{3}}{5}$ $(S2)$
P(MMA-co-ANE)	$F_{ANE} = \dfrac{\dfrac{I(Ar\,H)}{4}}{I\left(OCH_3\,(MMA + ANE\right) - \dfrac{3 \times I\,(Ar\,H)}{4}}{3}$ $(S3)$
P(2EHA-co-ANE)	$F_{ANE} = \dfrac{\dfrac{I(Ar\,H)}{4}}{I\left(OCH_x\,(MMA + ANE\right) - \dfrac{3 \times I\,(Ar\,H)}{4}}{2}$ $(S4)$
P(AA-co-ANE)	$A = \dfrac{I(Ar\,H) - \dfrac{6 \times I\,Ar\,(ANE\ monomer)}{2} - 3 \times I\,(vinyl\,H\,(AA\ monomer))}{4}$ $(S5)$ $F_{ANE} = \dfrac{A}{A + \dfrac{I\,(massif\,(0-3\,ppm) - 3 \times A - 3 \times \dfrac{I\,(Ar\ monomer)}{2}}{3}}$ $(S6)$

2. Kinetics of polymerization

The details of the kinetic of polymerization of polymers 1, 3, 11, 13, 14, 15, 19, 21, 31, 34 and 36 is presented in tables S2 to S12.

Table S2: Kinetic of St homopolymerization (polymer 1)

Time (min)	Monomer conversion
0	0
60	0.19
120	0.44
180	0.56
240	0.72

Table S3: Kinetic of St and ANE copolymerization (polymer 3)

Time (min)	St conversion	ANE conversion	Overall conversion	f_{St}	f_{ANE}
0	0	0	0	0.50	0.50
30	0.06	0	0.03	0.48	0.52
60	0.15	0.01	0.08	0.46	0.54
90	0.21	0.01	0.11	0.44	0.56
120	0.28	0.03	0.15	0.42	0.58
180	0.37	0.03	0.20	0.39	0.61
240	0.44	0.04	0.24	0.36	0.64
300	0.55	0.08	0.31	0.33	0.67

360	0.59	0.08	0.34	0.30	0.70
1350	0.81	0.09	0.45	0.17	0.83

Table S4: Kinetic of St and ANE copolymerization (polymer 11)

Time (min)	St conv.	St inst conv.	ANE conv.	Overall conv	Overall inst conv	f_{St}	f_{st}, inst.	f_{ANE}
0	0	0	0	0	0	0.50	0.03	0.50
60	0.01	0.11	0.01	0.01	0.02	0.50	0.04	0.50
120	0.01	0.09	0.01	0.01	0.02	0.50	0.06	0.50
180	0.02	0.09	0.01	0.01	0.03	0.50	0.08	0.50
240	0.03	0.14	0.03	0.03	0.05	0.50	0.09	0.50
300	0.05	0.19	0.05	0.05	0.08	0.50	0.11	0.50
360	0.05	0.18	0.04	0.04	0.07	0.50	0.13	0.50
1440	0.58	0.58	0.12	0.36	0.36	0.32	0.32	0.68
1470	0.60	0.60	0.12	0.36	0.36	0.32	0.32	0.68

Table S5: Kinetic of MMA homopolymerization (polymer 13)

Time (min)	Monomer conversion
0	0
60	0.65
120	0.90
180	0.98

Table S6: Kinetic of MMA homopolymerization (polymer 15)

Time (min)	Monomer conversion

0	0
60	0.65
120	0.86
180	0.92
240	0.96

Table S7: Kinetic of MMA and ANE copolymerization (polymer 14)

Time (min)	MMA conversion	ANE conversion	Overall conversion	f_{MMA}	f_{ANE}
0	0	0	0	0.48	0.52
30	0.17	0	0.09	0.44	0.56
60	0.28	0	0.13	0.39	0.61
90	0.40	0	0.19	0.36	0.64
120	0.45	0	0.22	0.34	0.66
150	0.53	0	0.25	0.31	0.69
180	0.60	0.03	0.31	0.28	0.72
240	0.66	0.01	0.32	0.24	0.76
300	0.72	0.02	0.36	0.21	0.79
360	0.78	0.03	0.39	0.18	0.82
1380	0.95	0.04	0.48	0.04	0.96

Table S8: Kinetic of 2EHA homopolymerization (polymer 19)

Time (min)	Monomer conversion
0	0
30	0.95
60	0.97
120	0.99

Table S9: Kinetic of 2EHA and ANE copolymerization (polymer 21)

Time (min)	2EHA conversion	ANE conversion	Overall conversion	f_{2EHA}	f_{ANE}
0	0	0	0	0.54	0.46
30	0.06	0	0.03	0.52	0.48
90	0.19	0.03	0.12	0.49	0.51
120	0.25	0.06	0.16	0.48	0.52
180	0.34	0.07	0.22	0.45	0.55
240	0.40	0.13	0.28	0.44	0.56
300	0.49	0.17	0.34	0.41	0.59
360	0.52	0.17	0.36	0.40	0.60
1290	0.75	0.31	0.55	0.30	0.70

Table S10: Kinetic of 2EHA and ANE copolymerization (polymer 31)

Time (min)	2EHA conversion	2EHA inst conversion	ANE conversion	Overall conversion	Overall inst conversion	f_{2EHA}	f_{2EHA}, inst.	f_{ANE}
0	0	0	0	0	0	0.53	0	0.47
60	0.01	0.33	0	0.01	0.02	0.53	0.01	0.47
120	0*	0*	0.09*	0.04*	0.08*	0.55*	0.05*	0.45*
180	0.01	0.11	0.03	0.02	0.04	0.53	0.06	0.47
240	0	0	0.03	0.01	0.03	0.54	0.09	0.46
1470	0.53	0.53	0.28	0.41	0.41	0.43	0.53	0.57

*outliers

Table S11: Kinetic of AA homopolymerization (polymer 34)

Time (min)	Monomer conversion
0	0
30	0.93

Table S12: Kinetic of AA and ANE copolymerization (polymer 35)

Time (min)	AA conversion	ANE conversion	Overall conversion	f_{AA}	f_{ANE}
0	0	0	0	0.50	0.50
30	0.06	0.01	0.04	0.49	0.51
60	0.14	0.04	0.09	0.47	0.53
90	0.22	0.09	0.16	0.46	0.54
120	0.28	0.10	0.19	0.45	0.55
180	0.44	0.22	0.33	0.42	0.58
240	0.47	0.21	0.34	0.40	0.60
300	0.54	0.23	0.38	0.37	0.63
360	0.58	0.24	0.41	0.36	0.64
1330	0.83	0.31	0.57	0.20	0.80

3. Reactivity ratios

Table S13: Results obtained with CONTOUR from the kinetic of vinyl : ANE copolymerizations with 1 : 1 as monomer ratio on batch.

System vinyl : ANE	r_{vinyl} roughly estimated from the kinetic of copolymerization	r_{ANE} roughly estimated from the kinetic of copolymerization	Experiments predicted by CONTOUR to minimize the error	Experiments carried out
St : ANE	r_{St} = 16.196 (-5.778, +178.890)	r_{ANE} = 0.025 (-0.207, +6.479)	f_{ANEt}=0.99 f_{ANE}=0.90	f_{ANE}=0.90 f_{ANE}=0.80
2EHA :	r_{2EHA}≈2.00*	r_{ANE}≈0*	f_{ANEt}=0.99	f_{ANE}=0.90

ANE			f_{ANE}=0.65	f_{ANE}=0.65
AA : ANE	R_{AA}≈2.00*	r_{ANE}≈0*	f_{ANEt}=0.90 f_{ANE}=0.55	f_{ANE}=0.80 f_{ANE}=0.55

*: CONTOUR was unable to find a solution with the set of data obtain. We looked manualy for the estimation.

As using 99 % of ANE in the batch would have led to (i) a very slow polymerization, (ii) a spoil of ANE, (iii) the use of too much ant solvent for polymer precipitation, we decided to not carry out experiments with a fraction of ANE in batch not above 90 %.

Table S14: Polymerization time, fraction of ANE at the start and end of the polymerization, and fraction of ANE in the copolymers, for each experiments carried out to determine r_{St} and r_{ANE}.

Experiment	Polymerization time (min)	f_{ANE} (t=0)	f_{ANE} (end)	F_{ANE}
Polymer 4	30	0.91	0.92	0.31
Polymer 5	30	0.90	0.91	0.31
Polymer 6	30	0.91	0.91	0.29
Polymer 7	30	0.80	0.82	0.18
Polymer 8	30	0.81	0.82	0.18
Polymer 9	30	0.81	0.82	0.18

Table S15: Polymerization time, fraction of ANE at the start and end of the polymerization, and fraction of ANE in the copolymers, for each experiments carried out to determine r_{2EHA} and r_{ANE}.

Experiment	Polymerization time (min)	f_{ANE} (t=0)	f_{ANE} (end)	F_{ANE}
Polymer 22	30	0.90	0.90	0.48
Polymer 23	30	0.90	0.90	0.43
Polymer 24	30	0.90	0.90	0.45
Polymer 25	30	0.90	0.90	0.50
Polymer 26	80	0.64	0.68	0.35
Polymer 27	60	0.61	0.68	0.34
Polymer 28	60	0.61	0.64	0.34
Polymer 29	60	0.60	0.63	0.33

Table S16: Polymerization time, fraction of ANE at the start and end of the polymerization, and fraction of ANE in the copolymers, for each experiments carried out to determine r_{2EHA} and r_{ANE}.

Experiment	Polymerization	f_{ANE} (t=0)	f_{ANE} (end)	F_{ANE}

	time (min)			
Polymer 37	30	0.57	0.54	0.26
Polymer 38	30	0.55	0.55	0.28
Polymer 39	30	0.55	0.55	0.26
Polymer 40	90	0.81	0.82	0.38
Polymer 41	90	0.81	0.81	0.35
Polymer 42	90	0.81	0.81	0.37

4. Optimal addition feeding profiles obtained with MAP

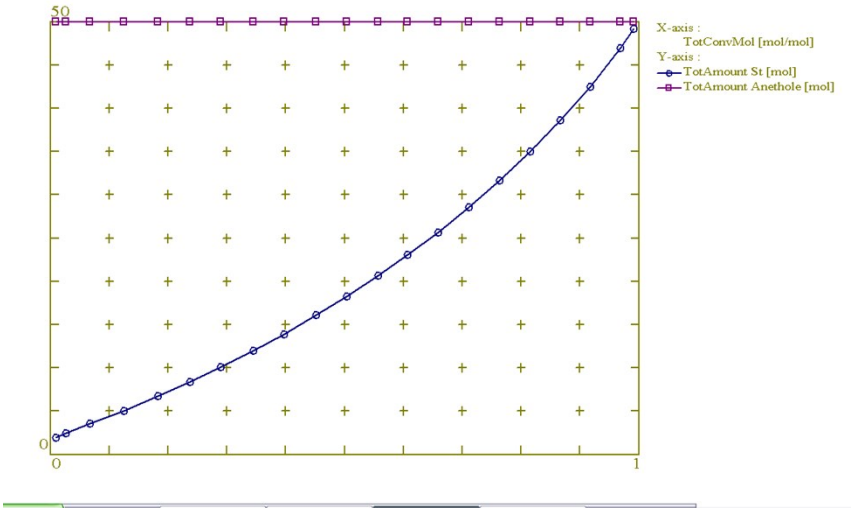


Figure S3: Optimal feeding addition profiles for a St:ANE copolymerization system using 2EHA:ANE = 1:1. The number of mol of monomer in the batch is shown on the Y axis while X axis shows the monomer conversion. Blue and purple lines represent St and ANE monomers respectively.

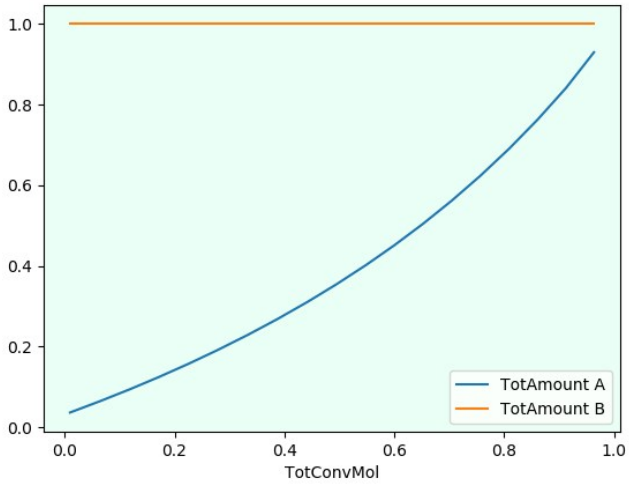


Figure S4: Optimal feeding addition profiles for a St:ANE copolymerization system using 2EHA:ANE = 1:1. The number of mol of monomer in the batch is shown on the Y axis while X axis shows the monomer conversion. Blue and orange lines represent 2EHA and ANE monomers respectively.

5. Determination of the transfer constant C_T

When a chain transfer agent (CTA) is present in the polymerization medium, the degree of polymerization depend on the monomer concentration, the CTA concentration, and the transfer constant C_T according to the Equation S7.

$$\frac{1}{\bar{DP}_n} = \frac{1}{\bar{DP}_n^0} + C_T\frac{[CTA]}{[M]}, C_T = \frac{k_{tr}}{k_p} \qquad (S7)$$

The method of Mayo consists in plotting $1/DP_n$ versus [CTA]/[M] and so the value of the slope correspond to C_T (3).

Here, experiments used to determine reactivity ratios were used to calculate the C_T. One extra measurement was added at a different value of [CTA]/[M]. When several experiments with the same [CTA]/[M] were carried out, an average of all the DP_n corresponding to that [CTA]/[M] was used. For the transfer from MMA to ANE, experiments were designed specifically for the C_T calculation. DP_n was calculated as follows:

$$M_{average} = F_{ANE} \times M(ANE) + F_{vinyl} \times M(vinyl) \qquad (S8)$$

$$\bar{DP}_n = \frac{M_n(GPC)}{M_{average}} \qquad (S9)$$

The effect of end groups was neglected.

Results are presented in tables S17 and S18.

Table S17: [CTA]/[M], DP_n, and $1/DP_n$ for the C_T determination of transfer from St, MMA, and 2EHA to ANE.

Transfer from St to ANE			Transfer from MMA to ANE			Transfer from 2EHA to ANE		
[CTA]/[M]	DP_n	$1/DP$n	[CTA]/[M]	DP_n	$1/DP$n	[CTA]/[M]	DP_n	$1/DP$n
9	29.5	0.0339	0.25	738.1	0.00136	9	48.5	0.0206
4	41.83	0.0228	1	601.4	0.00166	1.86	73.0	0.0137
1	84.62	0.0118	2	411.5	0.00243	1	102.2	0.00979

Table S18: [CTA]/[M], DP_n, and $1/DP_n$ for the C_T determination of transfer from AA to ANE.

Transfer from AA to ANE at T = 90 °C			Transfer from AA to ANE at T = 70 °C		
[CTA]/[M]	DP_n	$1/DP$n	[CTA]/[M]	DP_n	$1/DP$n
1.22	93.33	0.01071	1.22	109.64	0.01107
4	31.38	0.03187	4	29.74	0.03362
9	16.05*	0.06231	9	16.33	0.06123

*: F_{ANE} was not determined by ^{1}H NMR due to the presence of impurities on the spectrum F_{ANE}=0.47 was chosen according to the reactivity ratio values.

6. Branching and β-scission

Branching and β-scission were detected in P2EHA and PAA (see figure S5). The quaternary carbon $\mathbf{C_q}$ at a branching point is not visible in P(2EHA-co-ANE) as it overlaps with the C-Ar of a ANE unit. Consequently, branching were quantified using $\mathbf{I_b}$. Results are in table S18.

Table S19: $DB_{Acrylate}$ and DβS and their relative standard deviation (RSD) for some PAA, P(AA-co-ANE), P2EHA, and P(2EHA-co-ANE)

Polymer	Nature	F_{ANE}	$DB_{Acrylate}$ (%)	*RSD*	*DβS* (%)	*RSD*
Polymer 19	P2EHA	0	6.46	0.28	1.16	0.09
Polymer 20	P(2EHA-co-ANE)	0.15	1.67	0.18	0	0
Polymer 21	P(2EHA-co-ANE)	0.31	0	0	0	0

Bibliography

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