Supplementary Material (ESI) for *Soft Matter*

Supporting Information

Self-organization of gradient copolymers with ligand groups in supercritical CO_2

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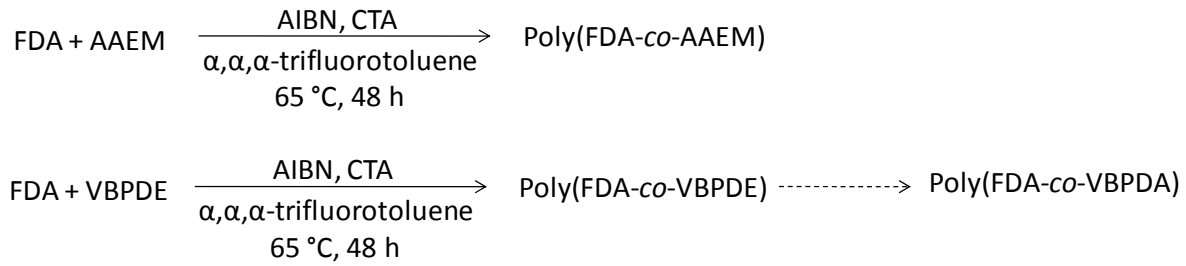
I. Synthesis of gradient polymers

Gradient copolymers poly(FDA-*co*-AAEM) and poly(FDA-*co*-VBPDE) were synthesized by RAFT polymerization in a batch process from FDA (1,1,2,2-tetrahydroperfluorodecyl acrylate) and AAEM (acetoacetoxyethyl methacrylate), and FDA and VBPDE (vinylbenzylphosphonic acid diethylester) monomers, respectively (Scheme S1). Poly(FDA-*co*-VBPDA) gradient copolymer was efficiently obtained by cleavage of the phosphonic ester groups of poly(FDA-*co*-VBPDE).



Scheme S1: Synthesis of the gradient copolymers from FDA, AAEM and VBPDE monomers at 65 °C in α,α,α-trifluorotoluene as a solvent. AIBN (Azobis(isobutyronitrile)) is the initiator and CTA is the chain transfer agent 1-(ethoxycarbonyl)-ethyl dithiobenzoate

1) Kinetic analyses of the copolymerization

In controlled radical polymerization, all chains grow together and have thus the same molecular weight and composition. The architecture of copolymers only depends on the reactivity ratios of the monomers. To prove the gradient structure of our copolymers, we have confirmed experimentally the difference of reactivities of the monomers by performing kinetic analyses of the copolymerizations. Figures S1 and S2 show the faster consumption of AAEM and VBPDE monomers in comparison with FDA monomer. Monomer conversions were followed by on-line ^{1}H NMR

spectroscopy at 65 °C of the crude reaction medium containing C_6D_6 capillaries for locking. A Bruker DRX 400 spectrometer was used and 16 scans were performed for each spectrum.

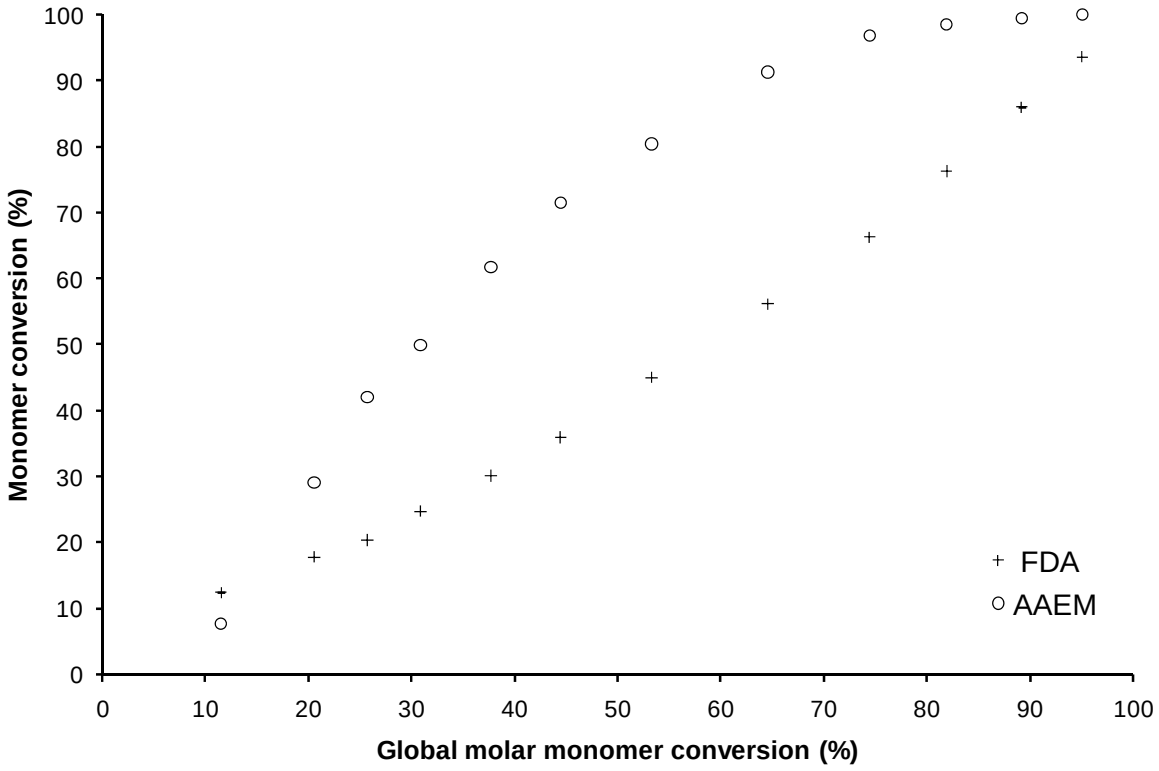


Figure S1: Evolution of individual monomer conversions in the copolymerization of AAEM (○) with FDA (+) as a function of the global molar monomer conversion (initial molar fraction of AAEM: $[AAEM]_0/([AAEM]_0+[FDA]_0)$=25.1 %)

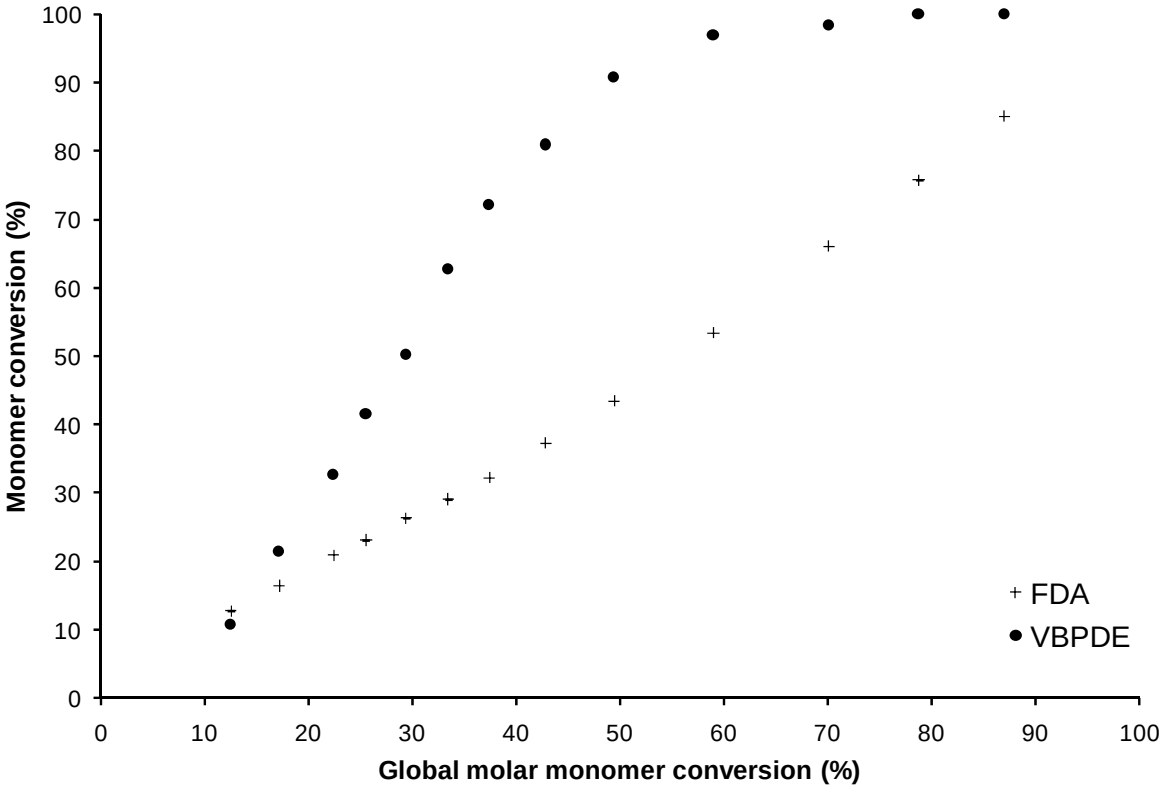


Figure S2: Evolution of individual monomer conversions in the copolymerization of VBPDE (•) with FDA (+) as a function of the global molar monomer conversion (initial molar fraction of VBPDE: $[VBPDE]_0/([VBPDE]_0+[FDA]_0)=14.8$ %)

2) Experimental section

1. Materials

1,1,2,2-tetrahydroperfluorodecylacrylate (FDA, Atofina) and acetoacetoxyethyl methacrylate (AAEM, Eastman, 97 %) were purified by passing through activated basic and neutral aluminum oxide respectively. Azobis(isobutyronitrile) (AIBN) was recrystallized in methanol and dried under vacuum. α,α,α-trifluorotoluene (TFT, Lancaster, 99 %) was distilled before use. VBPDE was synthesized as described in the literature.[1] The chain transfer agent (CTA) 1-(ethoxycarbonyl)-ethyl dithiobenzoate was prepared in 82 % yield with a procedure already described[2] (reaction time of six

hours). 1,1,2 Trichlorotrifluoroethane (F113, Aldrich, 99%), CO_2 (99.99992 %, SFE 5.2, Linde Gas SA, France) and all other chemicals were used as received unless otherwise stated.

2. Synthesis of the homopolymer poly(FDA) and the gradient copolymers poly(FDA-*co*-AAEM) and poly(FDA-*co*-VBPDE)

All polymerizations were carried out with a ratio [AIBN]/[CTA]=0.3 and an initial concentration in monomer of 0.8 g per mL of solvent. In a typical procedure, AIBN, CTA, the monomers and TFT were introduced along with a stir bar in a 100 mL Schlenk flask stopped with a rubber septum. The solution was degassed by freezing in liquid N_2 and thawing under vacuum (26 mmHg) (three cycles), and finally backfilling with argon. The mixture was heated in an oil bath at 65 °C with magnetic stirring for 48 h. Samples were withdrawn from the flask with a glass syringe and stainless steel needle after 24 h and 48 h of reaction and analyzed by ^{1}H NMR. At the end of the polymerization, TFT was evaporated at 45 °C under vacuum, the polymer was washed three times with n-pentane 95 % under magnetic stirring and then dried under vacuum at room temperature.

3. Chemical modification of poly(FDA-*co*-VBPDE) to form poly(FDA-*co*-VBPDA)

In a typical procedure, poly(FDA-*co*-VBPDE) (3 g) were dissolved in TFT (12.6 mL) in a 50 mL Schlenk flask equipped with a magnetic stir bar. Air was removed from the solution by argon bubbling. Trimethylsilyl bromide (0.53 g, 3.46 mmol, 2.8 eq versus VBPDE units) was added dropwise via a syringe and the mixture was stirred at room temperature for 4 days. The cleavage of the phosphonic ester groups was followed with ^{1}H NMR spectroscopy. Then, methanol (2 mL) was added and the mixture was stirred at room temperature for one night. The mixture TFT/methanol was evaporated at 45 °C under vacuum. The polymer was washed three times with acetonitrile under magnetic stirring, and then dried under vacuum at room temperature (yield: 95 %).

II. Physico-chemical properties of gradient copolymers:

Table S1: Characteristics of the gradient copolymers

	Theoretical M_n[a] (g/mol)	M_n (chain-end ^{1}H -NMR analysis)[b] (g/mol)	Theoretical molar fraction of M_2 (theoretical weight fraction)[c] (%)	^{1}H NMR analysis: molar fraction of M_2 (weight fraction)[d] (%)	Cloud point pressures at 4 % wt[e] (bar)	
					40 °C	55 °C
Poly(FDA-*co*-AAEM) 17 % mol AAEM	16000	19000	16.8 (7.7)	14.3 (6.4)	130	177
Poly(FDA-*co*-AAEM) 28 % mol AAEM	16300	22000	27.5 (13.6)	24.2 (11.6)	158	206
Poly(FDA-*co*-VBPDE) 20 % mol VBPDE	14500	16000	20.2 (11.0)	18.9 (10.3)	133	178
Poly(FDA-*co*-VBPDE) 17 % mol VBPDE	34100	42000	16.9 (9.0)	12.9 (6.8)	143	190
Poly(FDA-*co*-VBPDA) 19 % mol VBPDA	12900	11800	18.8 (8.2)	16.3 (6.9)	138	183
Poly(FDA-*co*-VBPDA) 23 % mol VBPDA	11000	15700	23.0 (10.2)	22.5 (10.0)	147	193

[a] Theoretical M_n calculated by:

$$M_n = \frac{m_{FDA} \times conv(FDA) + m_{M_2} \times conv(M_2)}{n_{CTA}} + M(CTA) = \frac{m_{monomers} \times overall\ weight\ conversion}{n_{CTA}} + M(CTA)$$

where m_{FDA} and m_{M2} are respectively the initial masses of FDA and M_2 (AAEM or VBPDE), conv(FDA) and conv(M_2) are the conversions of FDA and M2 given by ^{1}H-NMR analysis of the crude reaction medium, and n_{CTA} and M(CTA) are the number of moles and the molecular weight of the chain transfer agent.

[b] M_n determined by ^{1}H-NMR chain-end analysis (–CH_2-C***H***X-S-C(S)***Ph***) of the purified polymer. For poly(FDA-*co*-AAEM), intensity of a chain-end proton is the average of the intensity of a phenyl proton (δ=7.25-7.9 ppm). For poly(FDA-*co*-VBPDE) and poly(FDA-*co*-VBPDA), intensity of a chain-end proton is the intensity of proton in alpha of the dithiobenzoate group (δ=4.9 ppm).

[c] Molar fraction of M_2 calculated from monomer conversions according to:

$$\frac{n_{M_2} \times conv(M_2)}{n_{FDA} \times conv(FDA) + n_{M2} \times conv(M_2)}$$

[d] Molar fraction of M_2 determined by ^{1}H-NMR of the washed polymer. Weight fraction is given by:

$$\frac{molar\ fraction of\ M_2 \times M(M_2)}{molar\ fraction of\ M_2 \times M(M_2) + molar\ fraction of\ FDA \times M(FDA)}$$

where M(FDA) and M(M_2) are the molecular weights of FDA and M_2 (AAEM or VBPDE).

[e] Concentration of polymer versus CO_2

III. Scattering data

1) Determination of scattering length densities

Scattering length densities of pure CO_2 at the different conditions are given in Table S2.

Table S2: Scattering length densities for CO_2

ρ (CO_2) (10^{10}×cm^{-2})				
T=40°C, P=140 bar	T=40°C, P=155 bar	T=40°C, P=210 bar	T=40°C, P=350 bar	T=55°C, P=210 bar
1.91	1.97	2.12	2.34	1.92

The volumes of one gram of copolymer poly(FDA-*co*-AAEM) (Table S3) have been estimated by using the densities determined at ambient pressure and temperature: d(poly(FDA))=1.70 g/mL[3] and d(poly(AAEM))=1.263 g/mL.[4] In the same way, the volumes of one gram of poly(FDA-*co*-VBPDE) and poly(FDA-*co*-VBPDA) (Table S3) have been calculated with the approximation that d(poly(VBPDE))=d(poly(VBPDA))= d(poly(styrene))=1.05g/mL.[5]

Table S3: Scattering length densities for copolymers

Gradient copolymers	ρ (10^{10}×cm^{-2})
Poly(FDA-*co*-AAEM) 17 % mol AAEM	3.14
Poly(FDA-*co*-AAEM) 28 % mol AAEM	3.00
Poly(FDA-*co*-VBPDE) 20 % mol VBPDE, M_n=14500 g/mol	2.93
Poly(FDA-*co*-VBPDE) 17 % mol VBPDE, M_n=34100 g/mol	2.99
Poly(FDA-*co*-VBPDA) 19 % mol VBPDA	3.07
Poly(FDA-*co*-VBPDA) 23 % mol VBPDA + D_2O	3.11

2) Volumes of the polymer

Table S4: Volumes of one gram of gradient copolymer and dry volume of individual polymer chains V_{pol}

Gradient copolymers	Volume of one gram of copolymer (mL)	Dry volumes of individual polymer chains V_{pol} (nm^3)
Poly(FDA-*co*-AAEM) 17 % mol AAEM	0.616	16.2
Poly(FDA-*co*-AAEM) 28 % mol AAEM	0.604	16.8
Poly(FDA-*co*-VBPDE) 20 % mol VBPDE, M_n=14500 g/mol	0.621	15.5
Poly(FDA-*co*-VBPDE) 17 % mol VBPDE, M_n=34100 g/mol	0.628	35.5
Poly(FDA-*co*-VBPDA) 19 % mol VBPDA	0.604	13.5
Poly(FDA-*co*-VBPDA) 23 % mol VBPDA	0.663	11.8

IV. Intra-chain hydrogen bonding

It can be supposed that the evolution of the self-assembly at fixed CO_2-density is here the effect of the hydrogen bonding on the aggregation. Schlaad et al. proposed the establishment of hydrogen bonding between acetoacetoxy groups in the homopolymer poly(AAEM),[6] cf. Figure S3 below. With increasing temperature, these interactions weaken and may compensate the effect of the decrease of the density of CO_2 which favors aggregation.

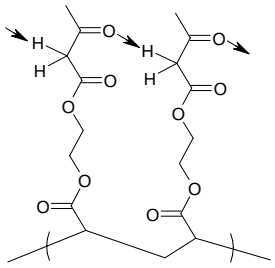


Figure S3: Hypothesis of hydrogen-bonding interactions between aceto acetoxy units of poly(AAEM)[6]

V. Influence of concentration on self-assembly

In Figure S4 SANS data for poly(FDA-*co*-AAEM) gradient copolymer are shown in a reduced representation I(q)/ϕ, where ϕ is the volume fraction. In absence of interactions, concentrations has no effect on I/ϕ if the aggregates do not evolve. This plot thus clearly prooves that the mean aggregation number increases with increasing concentration.

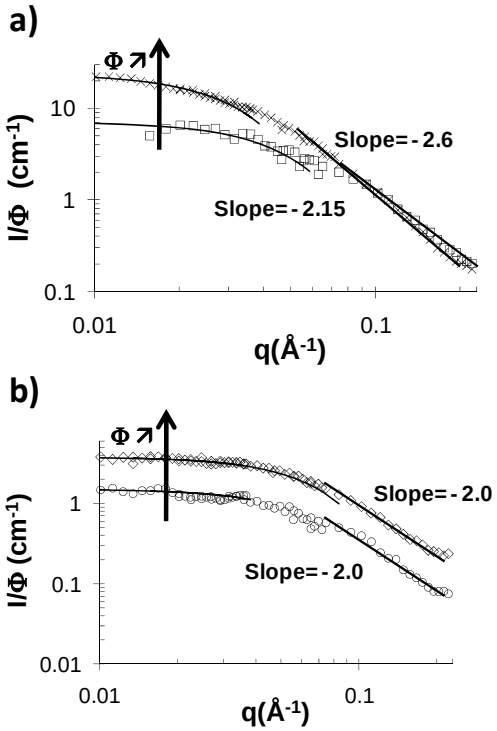


Figure S4: Influence of concentration. SANS data for poly(FDA-*co*-AAEM) gradient copolymer 17 % mol AAEM. a) at T=40 °C, P=140 bar, C=4 % wt (□) and 8 % wt (×) of polymer vs. CO_2; b) at T=40 °C, P=210 bar, C=4 % wt (○) and 8 % wt (◊) of polymer vs. CO_2; corresponding Guinier plots in the domain $qR_g<2$ for readability reasons. The arrows indicate the evolution with increasing volume fraction of polymer.

VI. References

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