

Spontaneous shape changes in polymersomes

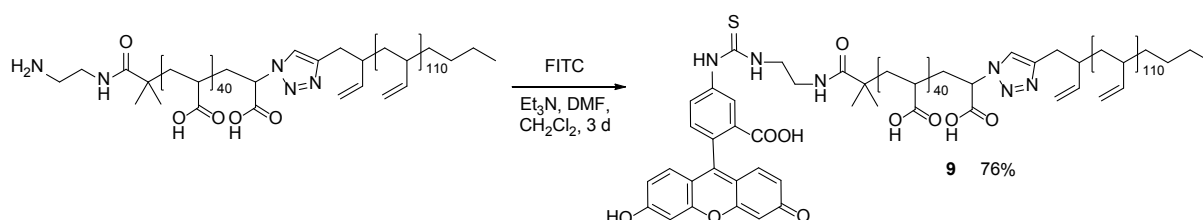
via polymer/polymer phase separation

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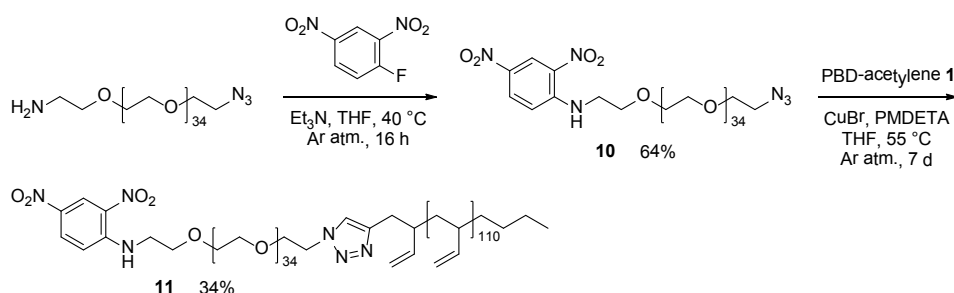
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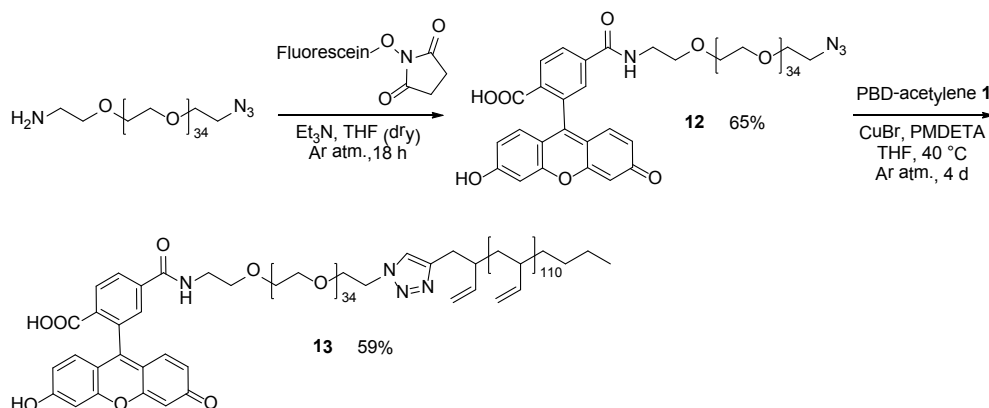
I. Synthesis schemes



Scheme S1. Synthesis of FI-PAA-*b*-PBD **9** by coupling FITC to H₂N-PAA-*b*-PBD **8**.



Scheme S2. Synthesis of block copolymer DNB-PEG-PBD **11** by “clicking” PBD **1** to DNB-PEG-N₃, which was derived from a reaction between fluoro-DNB with H₂N-PEG-N₃.



Scheme S3. Synthesis of block copolymer FI-PEG₃₅-*b*-PBD₁₁₀ **13** by clicking FITC-labelled PEG-N₃ to PBD **1**.

II. Polymer characteristics

Table S1. Molecular characteristics of the polymers **1-3**, **5-6** and **8-11**.

Entry	PDI (SEC) ^a	<i>m/z</i> (MALDI) ^b	DP _n (MALDI) ^c	DP _n (¹ H NMR) ^d	DP _n estimated ^e
	<i>M_w</i> / <i>M_n</i>	(10 ³ Da)			
Acetylene-PBD ₁₁₀ (1)	1.05	5.8	106	108	110
MeO-PEG ₄₄ -N ₃ (2)	1.13	2.143	44	44	44
MeO-PEG ₄₄ - <i>b</i> -PBD ₁₁₀ (3)	1.07	8.4	44, 114 ^f	44, 118	44, 110
BocNH-PtBA ₄₀ -Br (5)	1.13	4.9	36	54	40
BocNH-PtBA ₄₀ -N ₃ (6)	1.10	4.9	36	54	40
H ₂ N-PAA ₄₀ - <i>b</i> -PDB ₁₁₀ (8)	n/a	n/a	n/a	44, 105	40, 110
FI-PAA ₄₀ - <i>b</i> -PBD ₁₁₀ (9)	n/a	8.7	36, 110	45, 112	40, 110
DNB-PEG ₃₅ -N ₃ (10)	1.00	1.815 ^f	35	35	35
DNB-PEG ₃₄ - <i>b</i> -PBD ₁₁₀ (11)	1.05	7.6	35, 106	PEG: 35, PBD: 110	35, 110
FI-PEG ₃₅ -N ₃ (12)	1.00	1.986 ^f	35	35	35, 110
FI-PEG ₃₅ - <i>b</i> -PBD ₁₁₀ (13)	1.04	n/a	n/a	PEG: 35, PBD: 110	35, 110

^aThe PDI was calculated by the quotient of *M_w* and *M_n* obtained by SEC measurements; ^bMolecular weights determined with MALDI-ToF mass spectrometry; ^cCalculated number average degree of polymerisation of PEG, PtBA/PAA and PBD derived from the molecular weight obtained by MALDI-ToF analysis; ^dCalculated number average degree of polymerisation of PEG, PtBA/PAA and PBD derived from ¹H NMR spectra; ^eThe DP_n derived from MALDI-ToF and ¹H NMR analysis were combined into an estimated DP_n, which was rounded up to five; ^fWhen two numbers are given in one cell, their order corresponds to the given order of the accompanying block copolymer segments. ^fMolecular weight was determined with LRMS instead of MALDI.