

(3-Aminopropyl)-4-methylpiperazine End-capped Poly(1,4-butanediol diacrylate-co-4-amino-1-butanol)-based Multilayer Films for Gene Delivery

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SUPPORTING INFORMATION

Gel Permeation Chromatography (GPC)

Table 1. Number-averaged (Mn) and weight-averaged (Mw) molecular weight and polydispersity index (PDI) measured by gel permeation chromatography. The average number of subunits per chain was estimated by dividing Mn by the molecular weight of the repeat unit.

Polymer	Mn (Da)	Mw (Da)	PDI	Subunits/chain (average)
B4-S4-E7 (447)	11424	37679	3.30	40
B4-SP (4P)	48698	113421	2.33	120

Nuclear Magnetic Resonance (NMR)

B4-S4-E7 (447):

- 1.45-1.6 (m, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$ and $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$ and t, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{N} < (\text{CH}_2\text{CH}_2)_2 > \text{NCH}_3$)
1.6-1.75 (t, $\text{COOCH}_2\text{CH}_2\text{CH}_2\text{OOC}$)
2.3 (s, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{N} < (\text{CH}_2\text{CH}_2)_2 > \text{NCH}_3$)
2.35-2.6 (t, $\text{COOCH}_2\text{CH}_2\text{NCH}_2\text{CH}_2\text{OOC}$ and t, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$ and m, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{N} < (\text{CH}_2\text{CH}_2)_2 > \text{NCH}_3$)
2.7-2.85 (t, $\text{COOCH}_2\text{CH}_2\text{NCH}_2\text{CH}_2\text{OOC}$)
3.55-3.7 (t, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$)
4.0-4.2 (t, $\text{COOCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{OOC}$)

B4-SP (4P):

- 1.05-1.35 (m, $\text{N} < (\text{CH}_{\text{eq}}\text{H}_{\text{ax}}\text{CH}_{\text{eq}}\text{H}_{\text{ax}})_2 > \text{CHCH}_2\text{CH}_2\text{CH}_2\text{CH} < (\text{CH}_{\text{eq}}\text{H}_{\text{ax}}\text{CH}_{\text{eq}}\text{H}_{\text{ax}})_2 > \text{N}$)
1.55-1.75 (m, $\text{COOCH}_2\text{CH}_2\text{CH}_2\text{OOC}$,
 $\text{N} < (\text{CH}_{\text{eq}}\text{H}_{\text{ax}}\text{CH}_{\text{eq}}\text{H}_{\text{ax}})_2 > \text{CHCH}_2\text{CH}_2\text{CH}_2\text{CH} < (\text{CH}_{\text{eq}}\text{H}_{\text{ax}}\text{CH}_{\text{eq}}\text{H}_{\text{ax}})_2 > \text{N}$)
1.8-2.05 (t, $\text{OOCCH}_2\text{CH}_2\text{N}$)
2.45-2.55 (t, $\text{N} < (\text{CH}_{\text{eq}}\text{H}_{\text{ax}}\text{CH}_{\text{eq}}\text{H}_{\text{ax}})_2 > \text{CHCH}_2\text{CH}_2\text{CH}_2\text{CH} < (\text{CH}_{\text{eq}}\text{H}_{\text{ax}}\text{CH}_{\text{eq}}\text{H}_{\text{ax}})_2 > \text{N}$)
2.6-2.7 (t, $\text{OOCCH}_2\text{CH}_2\text{N}$)
2.8-2.9 (dt, $\text{N} < (\text{CH}_{\text{eq}}\text{H}_{\text{ax}}\text{CH}_{\text{eq}}\text{H}_{\text{ax}})_2 > \text{CHCH}_2\text{CH}_2\text{CH}_2\text{CH} < (\text{CH}_{\text{eq}}\text{H}_{\text{ax}}\text{CH}_{\text{eq}}\text{H}_{\text{ax}})_2 > \text{N}$)
4.05-4.15 (t, $\text{COOCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{OOC}$)
5.75-5.8 (s, $\text{CH}_2\text{OOCCH}=\text{CHH}$)
5.9-5.95 (s, $\text{CH}_2\text{OOCCH}=\text{CHH}$)
6.05-6.1 (s, $\text{CH}_2\text{OOCCH}=\text{CHH}$)

Note: acrylate protons (5.75-6.1) appear very small because they are low in frequency compared to other protons in the backbone. GPC estimates ~120 subunits per polymer chain on average; for example, each acrylate peak is estimated to be >240 times smaller than the backbone peak at 4.05-4.15.

