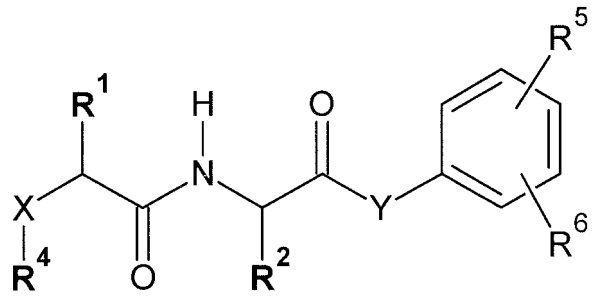
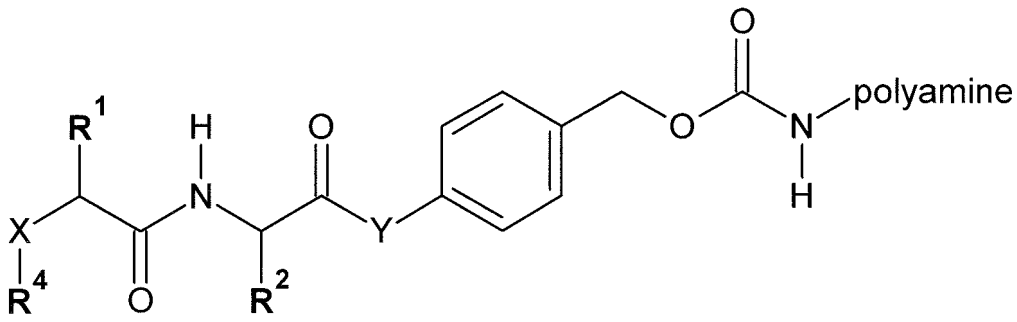
A.



Dipeptide masking agent

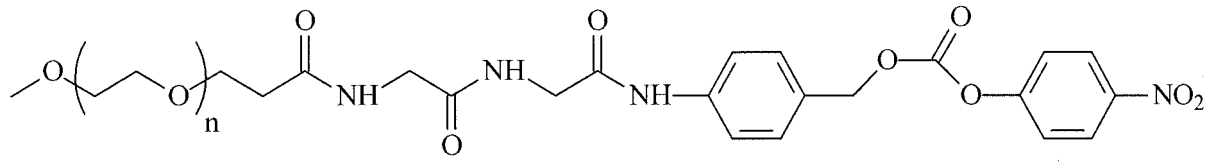
B.



Dipeptide masking agent linked to a polyamine.

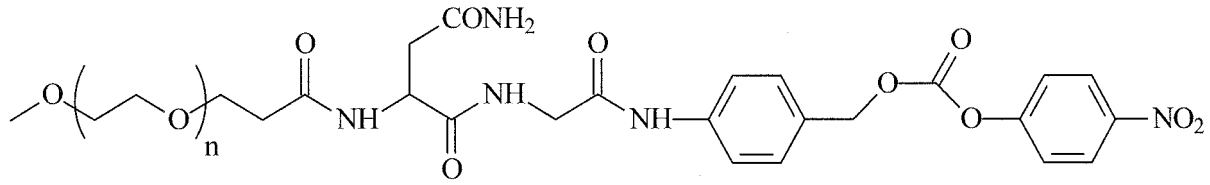
FIG. 1

A.



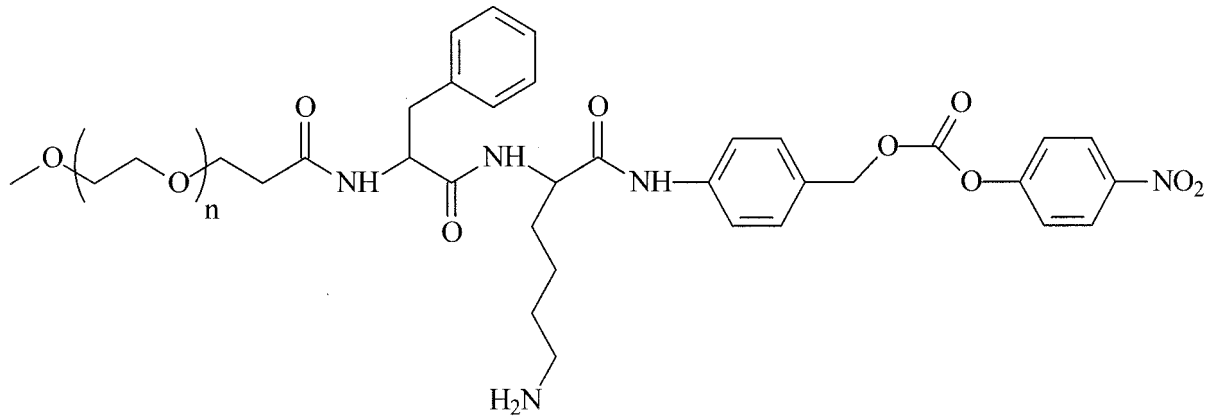
PEG-GlyGly-PABC-PNP

B.



PEG-AsnGly-PABC-PNP

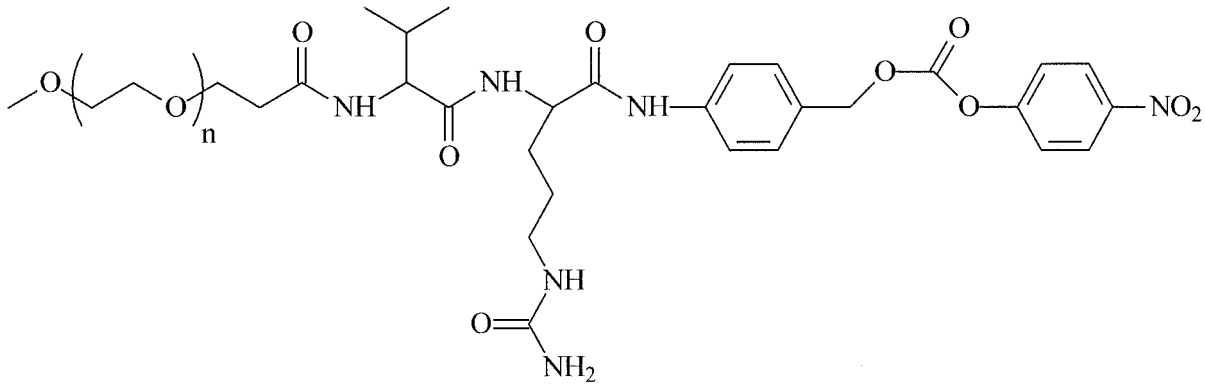
C.



PEG-PheLys-PABC-PNP

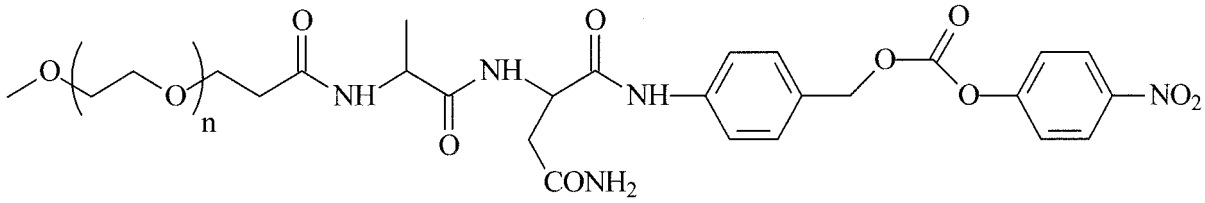
FIG. 2

D.



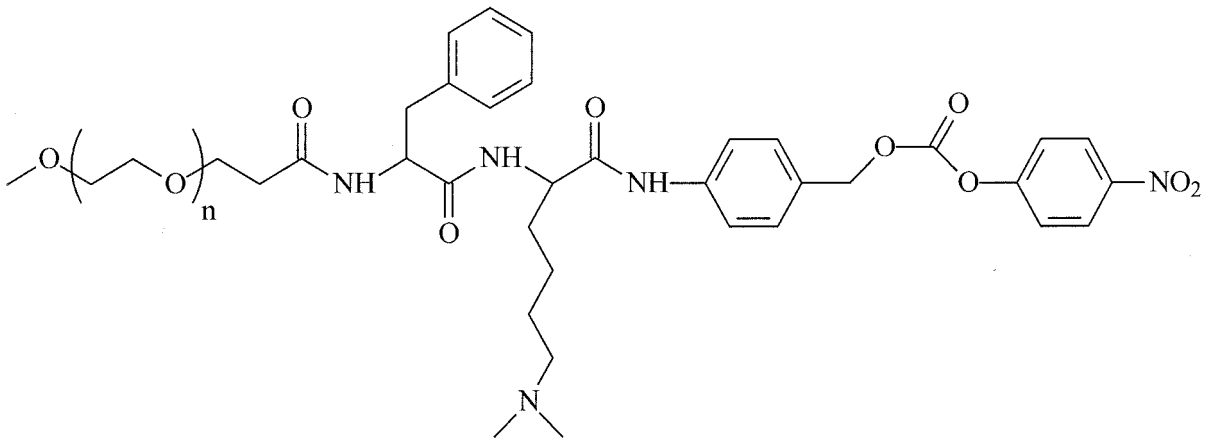
PEG-ValCit-PABC-PNP

E.



PEG-AlaAsn-PABC-PNP

F.



PEG-PheLys$(CH_3)_2$-PABC-PNP

FIG. 2 cont.

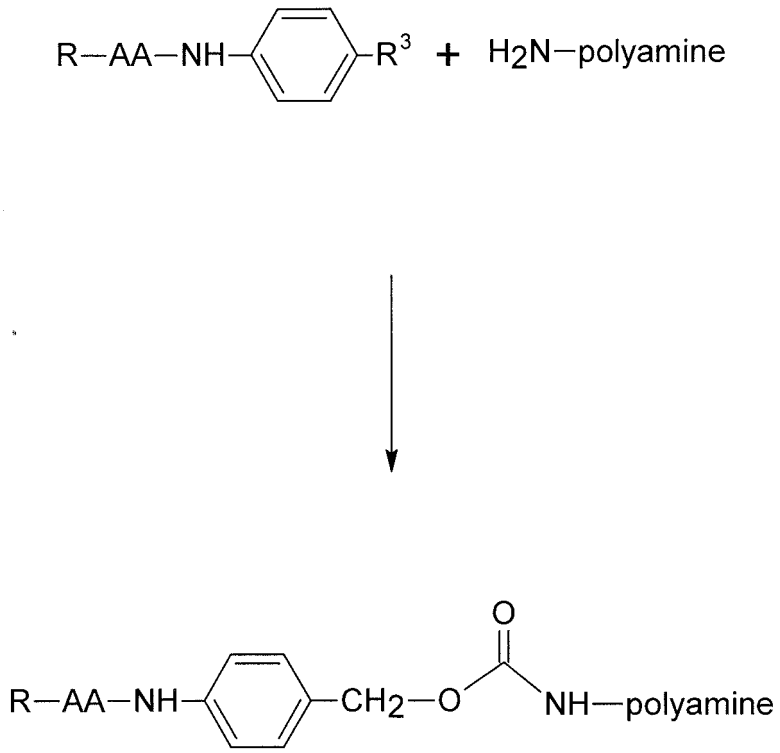


FIG. 3

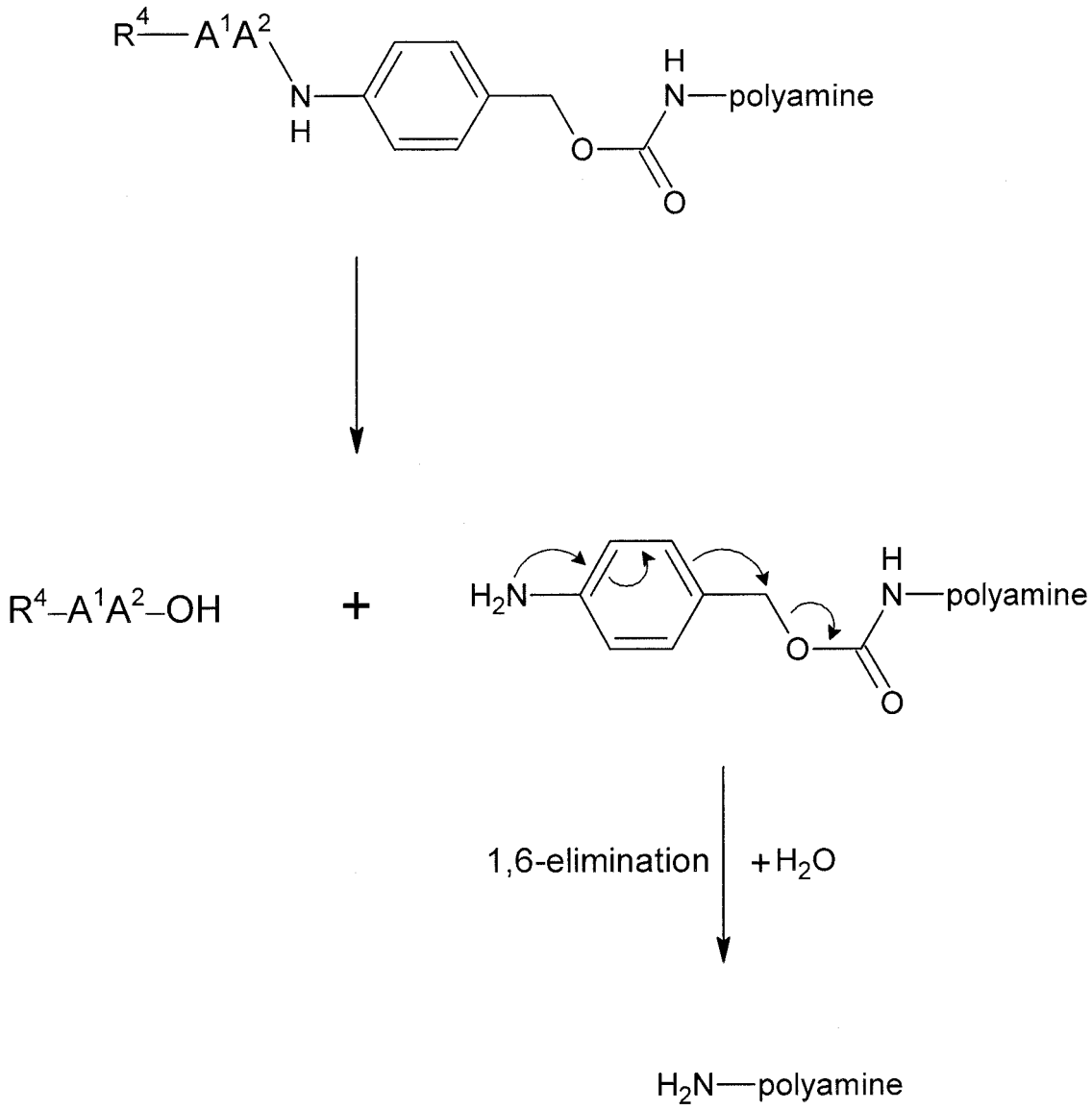

R4—A1A2
N
H
H
N—polyamine
O
O
R4–A1A2–OH
+
H2N
H
N—polyamine
O
O
1,6-elimination
+H2O
H2N—polyamine

FIG. 4

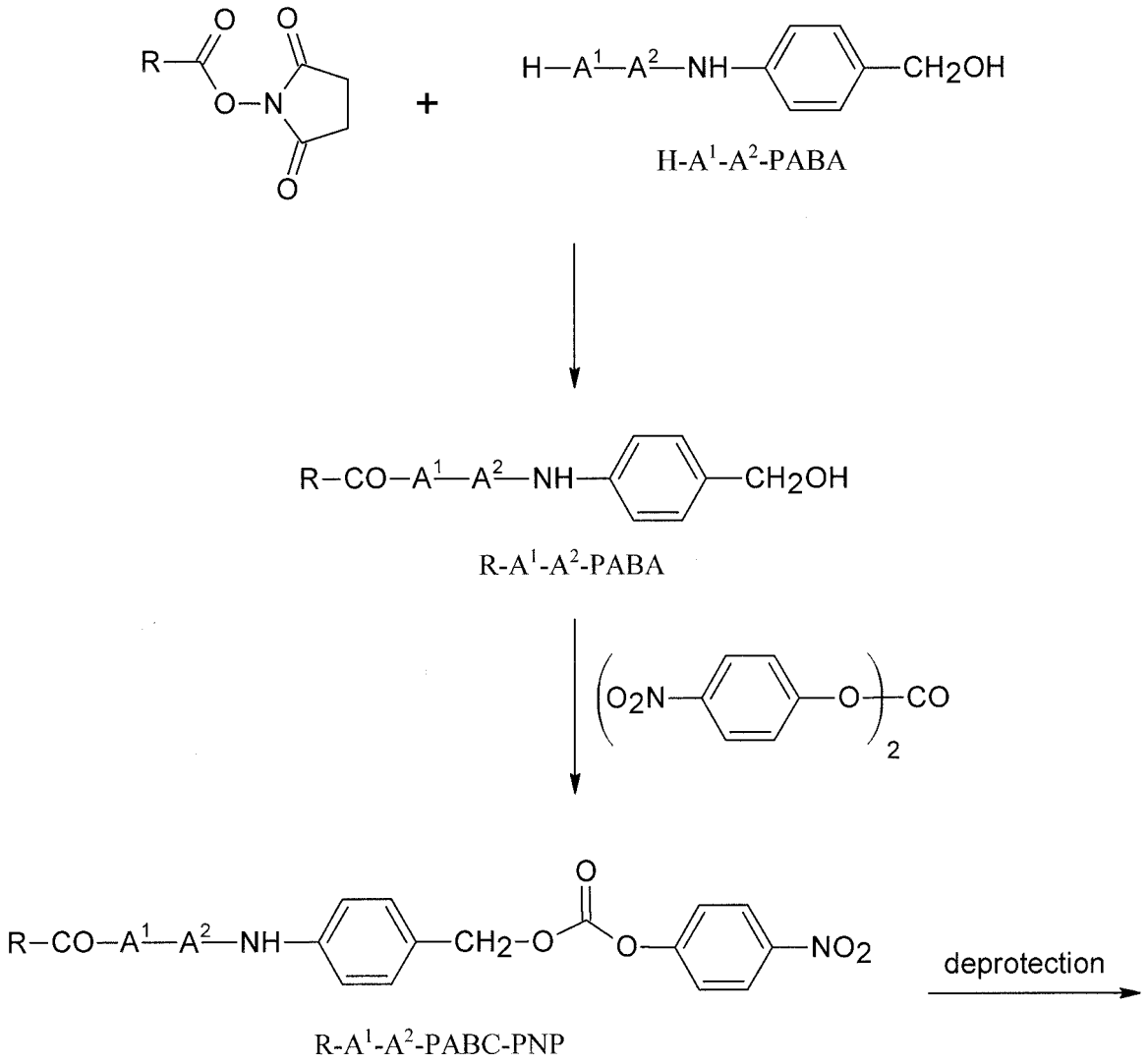
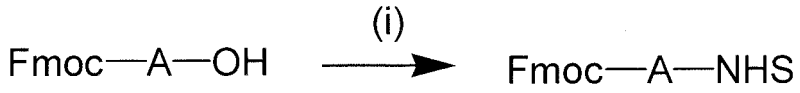


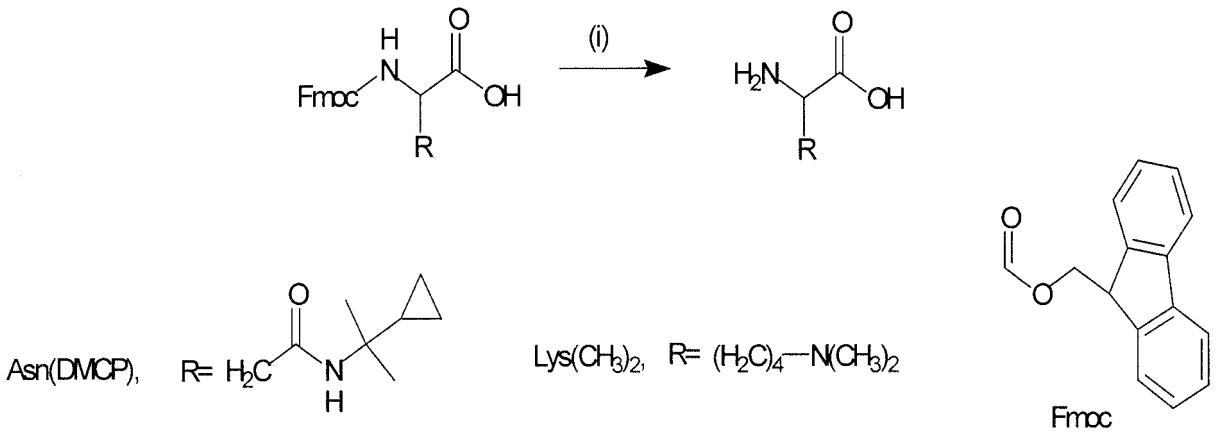
FIG. 5

A.



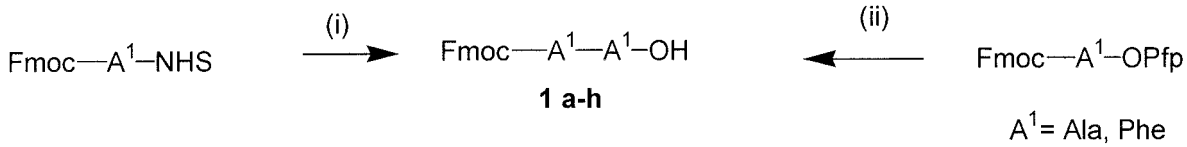
(i) N-hydroxysuccinimide (NHS), N-N'-dicyclohexylcarbodiimide (DCC), 0-20°C.

B.



(i) Triethylamine (Et_3N) in dimethylformamide (DMF).

C.



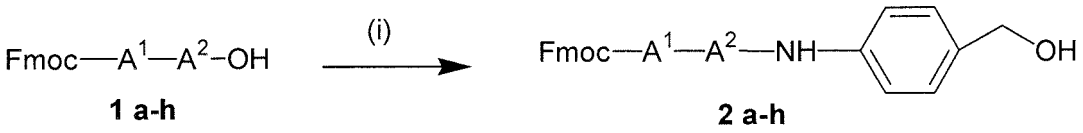
A^1= Gly, Glu(2PhiPr), Asn(DMCP), Phe, Ala, Val.

A^2=Gly, Lys(MMT), Cit, Asn(DMCP), $Lys(CH_3)_2$.

(i) H-A_2-OH, $NaHCO_3$, mixture of dimethoxyethane (DME), tetrahydrofurane (THF) and H_2O. (ii) H-A_2-OH, $NaHCO_3$, DME/THF/H_2O. (iii) H-Cit-OH, $NaHCO_3$, THF in H_2O.

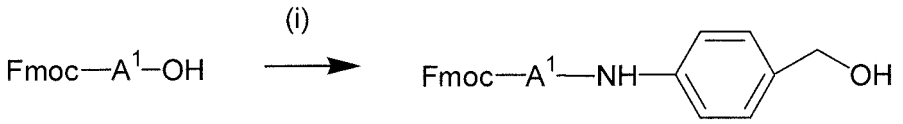
FIG. 6

A.



1 a-h **2 a-h**

A^1= Gly, Glu(2PhiPr), Asn(DMCP), Phe, Ala, Val.
A^2=Gly, Lys(MMT), Cit, Asn(DMCP), $Lys(CH_3)_2$

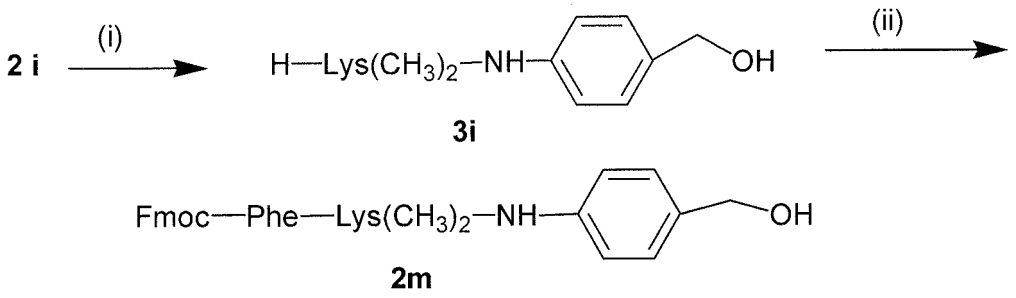


1 i-l **2 i-l**

A^1=$Lys(CH_3)_2$, Leu, Asn(DMCP), Cit

(i) PABA, EEDQ, THF

B.



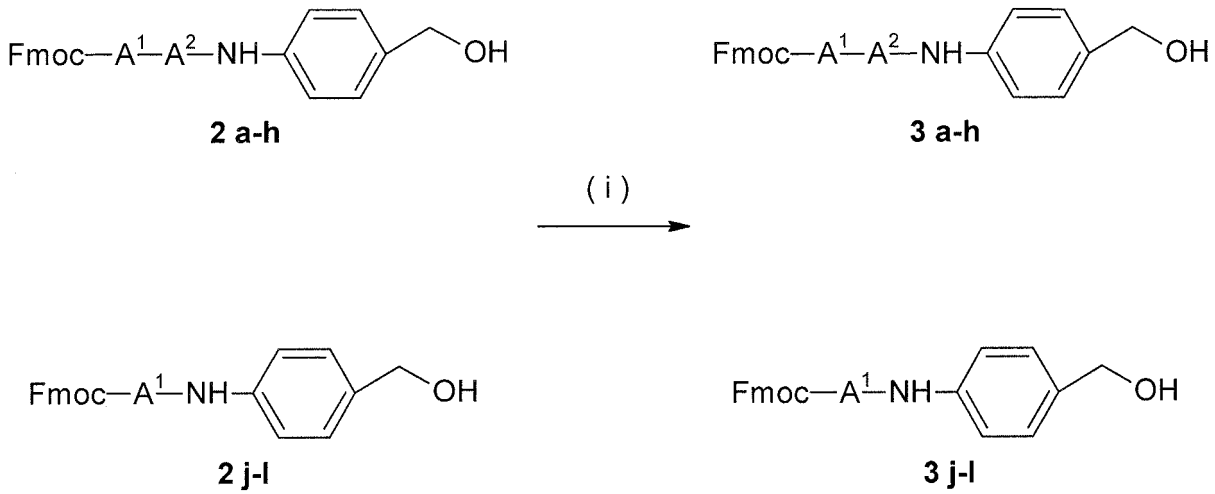
3i

2m

(i) Triethylamine (Et_3N) in DMF, 10h.

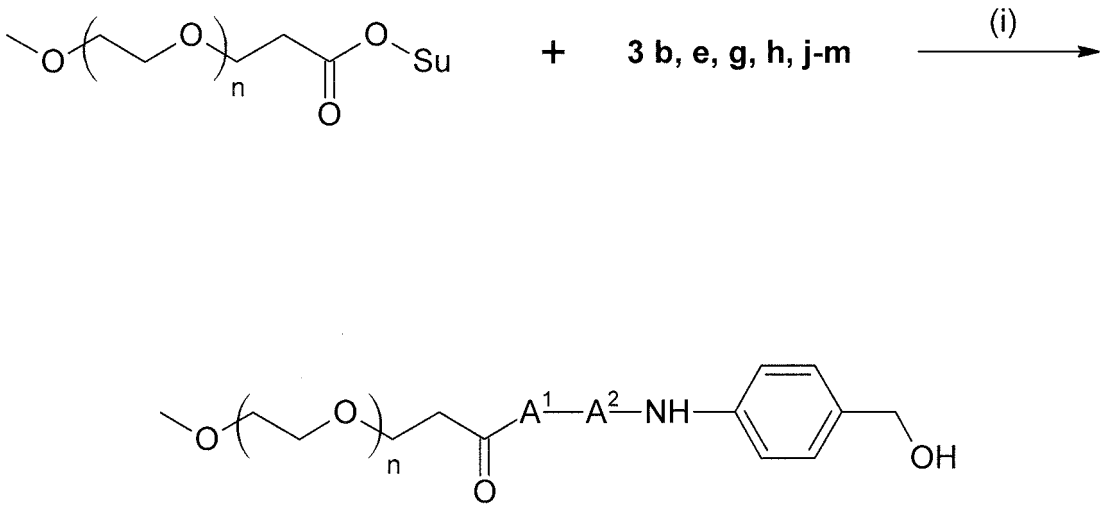
(ii) Fmoc-Phe-NHS, disopropylethylamine (DIEA), DMF.

FIG. 7



(i) Et_3N in DMF, 10h.

FIG. 8



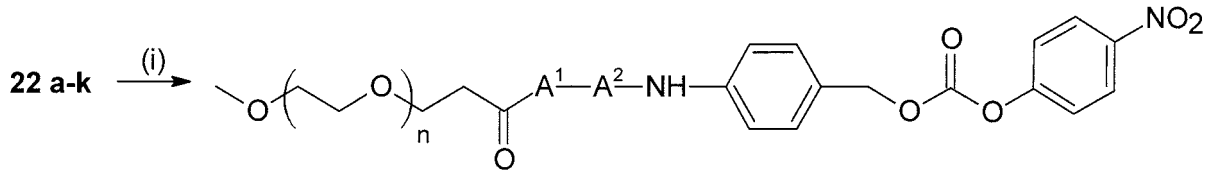
PEG–A^1A^2–PABA

22 a-k

(i) DIEA, DMF, 5-10h.

FIG. 9

A.

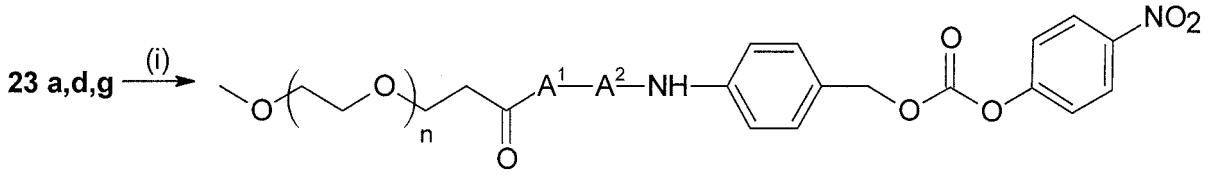


PEG–A^1A^2–PABC–PNP

23 a-k

(i) $(PNP)_2CO$, dioxane or THF, 40-60°C, 10h.

B.

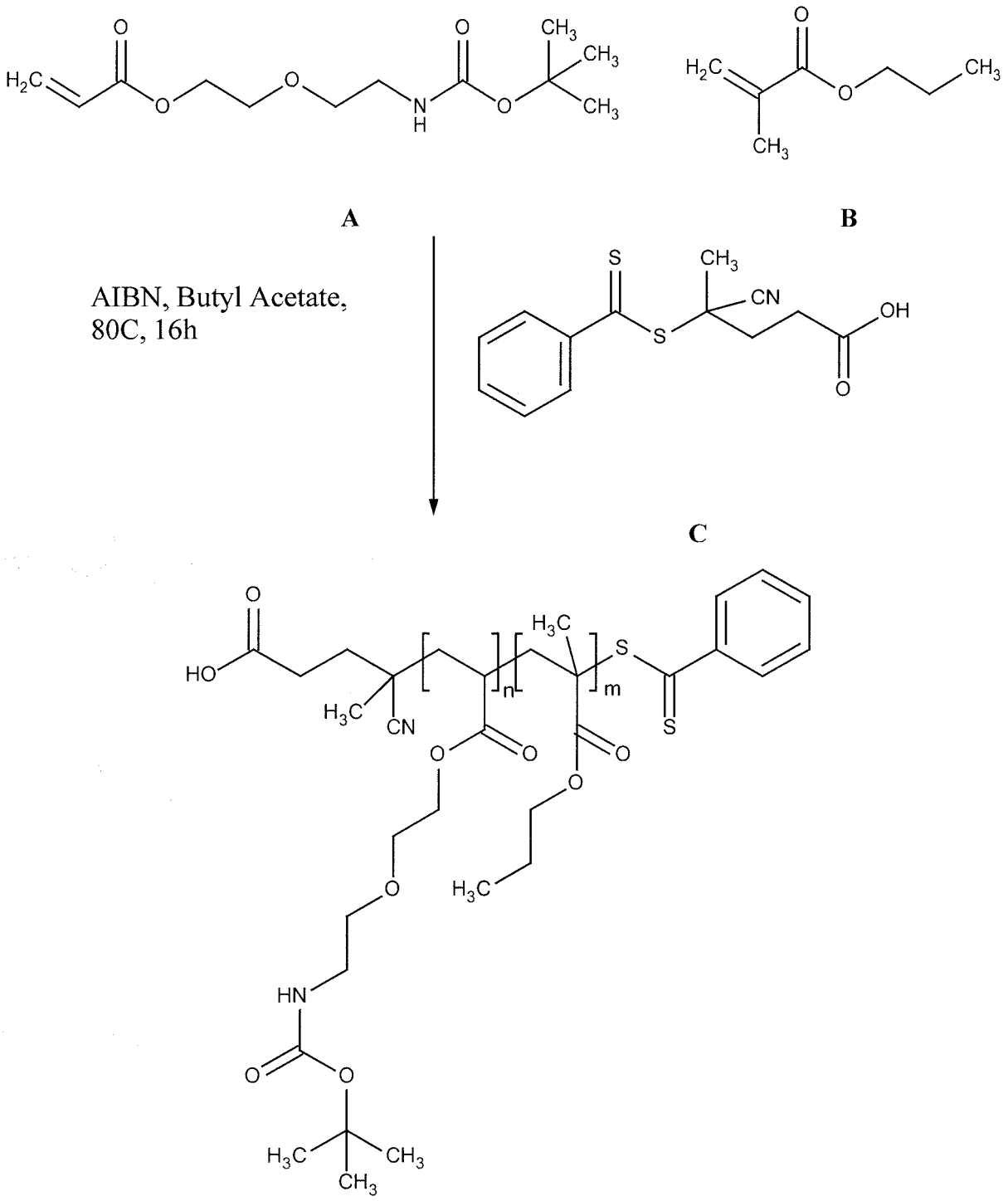


PEG–A^1A^2–PABC–PNP

24 a-c

(i) TFA/H_2O=3:1, 5°C, 2-3h.

FIG. 10



A is a boc protected ethyl-ethoxy amino acrylate

B is a propyl methacrylate

C is a RAFT agent CPCPA (4-Cyano-4-(phenylcarbonothioylthio) pentanoic acid)

n and m are integers.

Removal of the boc protecting group after synthesis yields the amine monomers.

FIG. 11

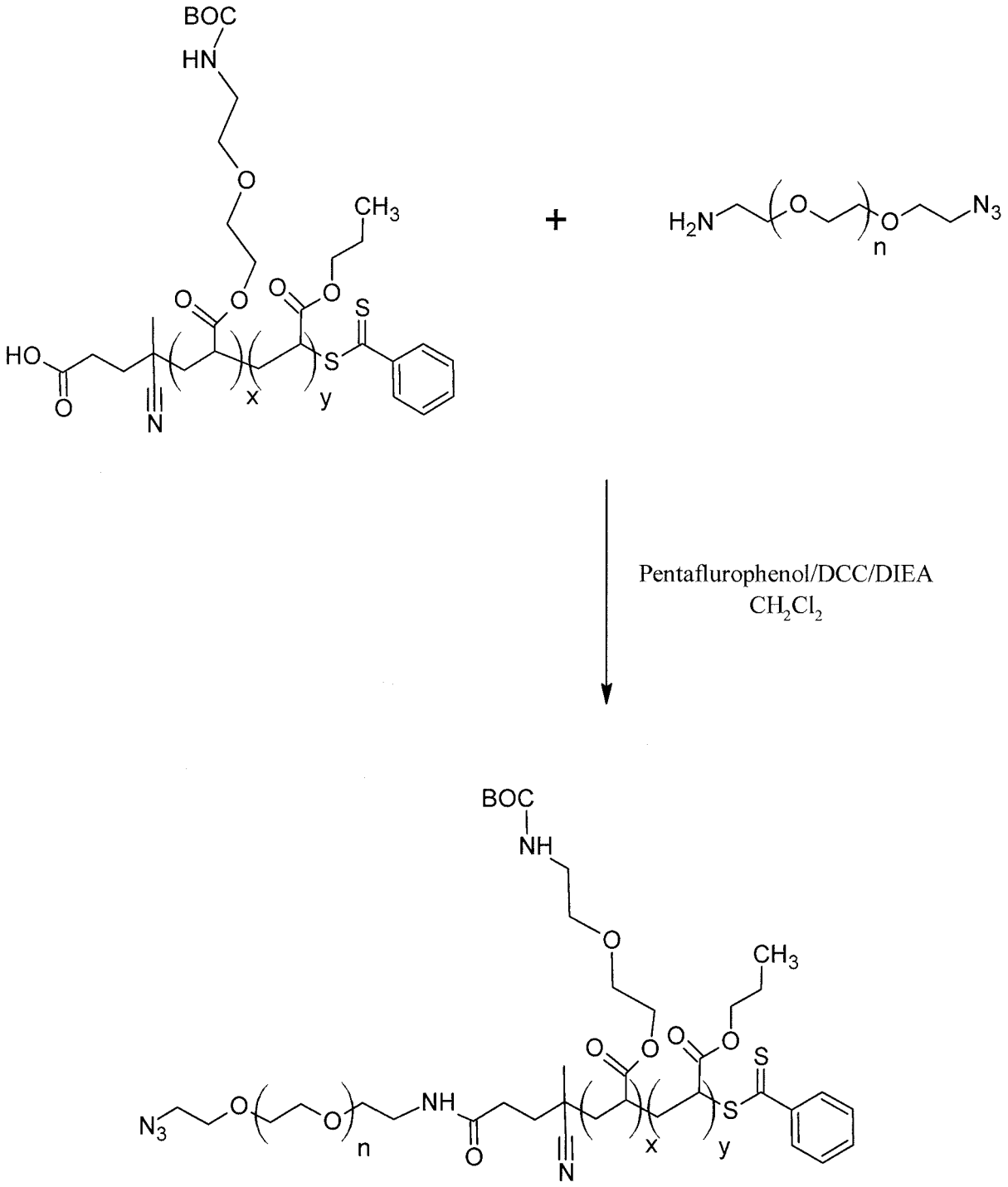

BOC
HN
O
CH3
O
O
O
O
S
HO
O
N
x
y
S
+
H2N
O
n
O
N3
Pentaflurophenol/DCC/DIEA
CH2Cl2
BOC
NH
O
CH3
O
O
O
O
S
N3
O
n
O
NH
O
N
x
y
S

FIG. 12

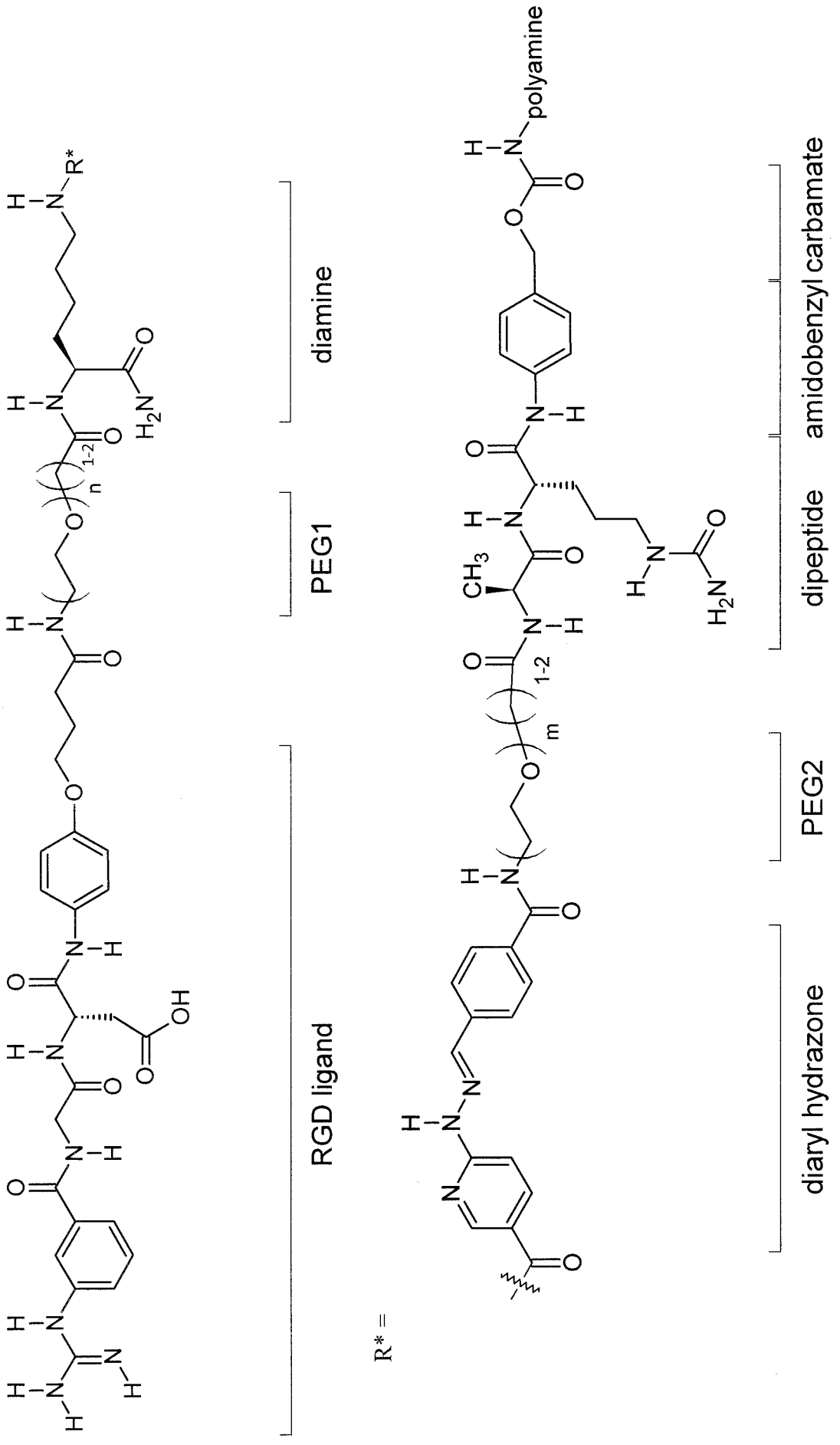

RGD ligand
diamine
PEG1
dipeptide
amidobenzyl carbamate
polyamine
PEG2
diaryl hydrazone
R* =

FIG. 13