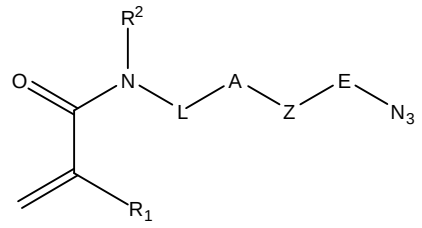
CLAIMS

1. A compound of formula (I)



(I)

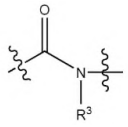
wherein

R^1 is H or C_{1-4} alkyl;

R^2 is H or C_{1-4} alkyl;

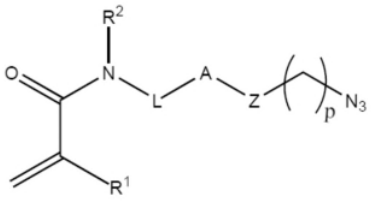
L is a linker comprising a linear chain having 2 to 20 atoms selected from the group consisting of carbon, oxygen, and nitrogen and optional substituents on the carbon and any nitrogen atoms in the chain;

E is a C_{1-4} alkylene;

A is an N substituted amide having formula , wherein R^3 is H or C_{1-4} alkyl; and

Z is a nitrogen containing heterocycle.

2. A compound according to claim 1, wherein the compound is of formula (Ia)



(Ia)

wherein p is 1, 2, 3 or 4.

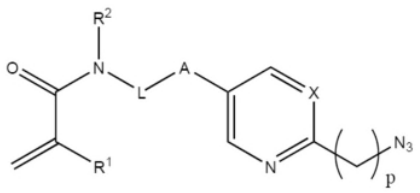
3. A compound according to claim 1 or claim 2, wherein the nitrogen containing heterocycle:

i) comprises a 6 membered ring, optionally wherein A and E are bonded at positions 2 and 5 of the 6 membered ring, or a 5 membered ring; and/or

ii) is aromatic or saturated.

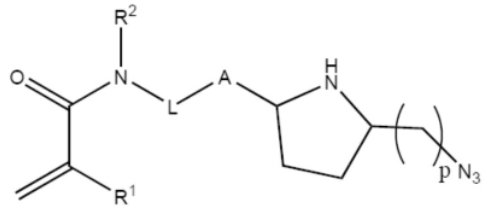
4. A compound according to claim 1 or claim 2, wherein the compound is:

i) of formula (Ib)



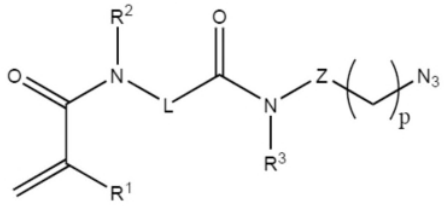
(Ib)
wherein X is CH or N; or

ii) of formula (Ic)



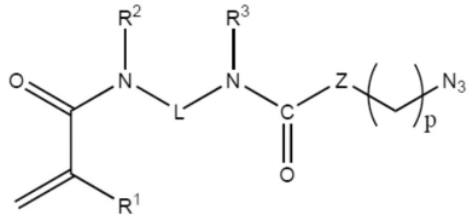
(Ic); or

iii) of formula (Id)



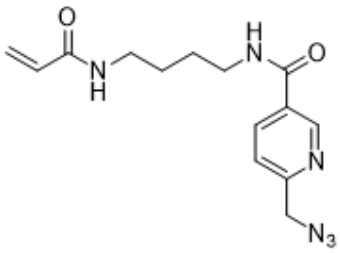
(Id); or

iv) of formula (Ie)



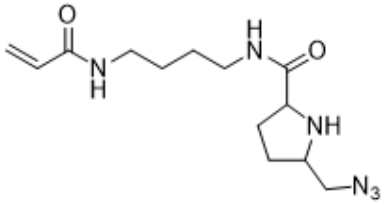
(Ie); or

v) of formula (If)



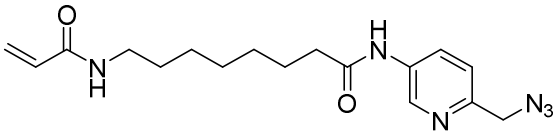
(If); or

vi) of formula (Ig)



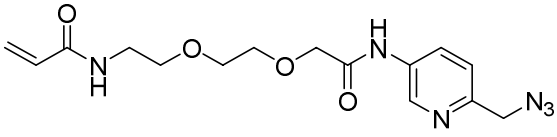
(Ig); or

vii) of formula (Ih)



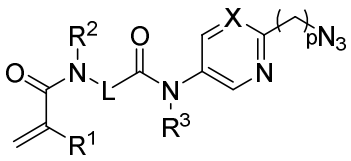
(Ih); or

viii) of formula (Ij)



(Ij); or

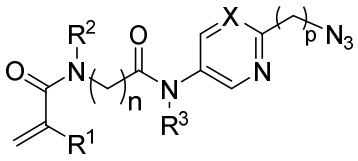
ix) of formula (Ik):



(Ik)

wherein X is CH or N; or

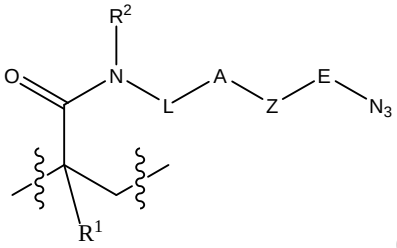
x) of Formula (Im):



(Im)

wherein n is an integer from 2 to 20.

5. A copolymer comprising a recurring monomer unit of formula (II):



(II)

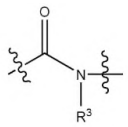
wherein

R^1 is H or C_{1-4} alkyl;

R^2 is H or C_{1-4} alkyl;

L is a linker comprising a linear chain having 2 to 20 atoms selected from the group consisting of carbon, oxygen, and nitrogen and optional substituents on the carbon and any nitrogen atoms in the chain;

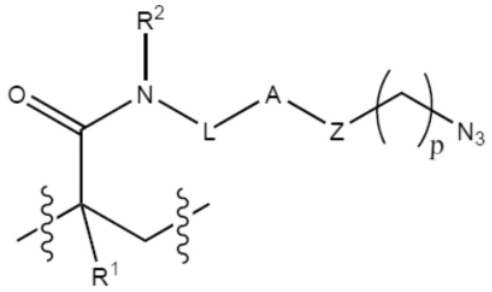
E is a C_{1-4} alkylene;

A is an N substituted amide having formula , wherein R^3 is H or C_{1-4} alkyl; and

Z is a nitrogen containing heterocycle; and

at least one other recurring monomer unit.

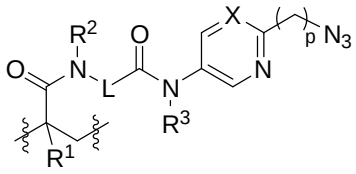
6. A copolymer according to claim 5, wherein the recurring monomer unit of formula (II) is a recurring monomer unit of formula (IIa)



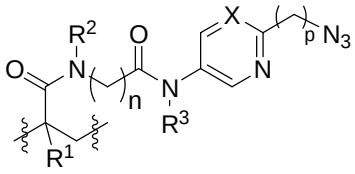
(IIa)

where p is 1, 2, 3, or 4;

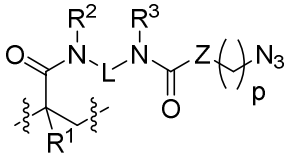
optionally wherein the recurring monomer unit of Formula (IIa) is a compound of Formula (IIb), Formula (IIc), Formula (IId), or Formula (IIe):



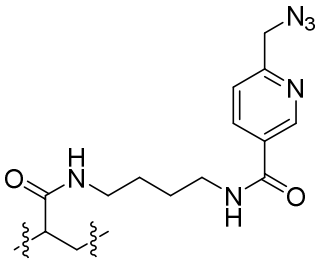
(IIb)



(IIc)



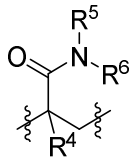
(IId)



(IIe)

wherein n in Formula (IIc) is an integer from 2 to 20.

7. The copolymer of claim 5 to 6, wherein the at least one other recurring monomer unit is a compound of Formula (III):



(III)

wherein

R^4 is H or $C_{1\text{-}4}$alkyl;

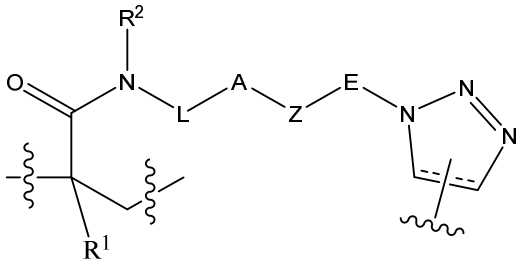
R^5 is H or $C_{1\text{-}4}$alkyl; and

R^6 is H or $C_{1\text{-}4}$alkyl;

optionally wherein the copolymer comprises a recurring monomer unit of Formula (IIb), (IIc), (IId), or (IIe), a recurring monomer unit of Formula (III), and at least one other recurring monomer unit.

8. A substrate-copolymer product formed from reaction of the copolymer according to claim 6 or claim 7 with a substrate; optionally wherein the substrate copolymer product is formed by reaction of the azido group of the copolymer with an alkenyl- or alkynyl-containing group on a surface of the substrate.

9. A structure comprising a copolymer covalently bound to the substrate, wherein the substrate-bound copolymer comprises a recurring monomer unit that is covalently bound to the substrate, wherein the recurring, covalently-bound, monomer unit is a compound of Formula (IV):



(IV)

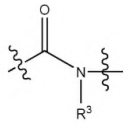
wherein

R^1 is H or $C_{1\text{-}4}$ alkyl;

R^2 is H or C_{1-4} alkyl;

L is a linker comprising a linear chain consisting of 2 to 20 atoms selected from the group consisting of carbon, oxygen, and nitrogen and optional substituents on the carbon and any nitrogen atoms in the chain;

E is a C_{1-4} alkylene;

A is an N substituted amide having formula , wherein R^3 is H or C_{1-4} alkyl;

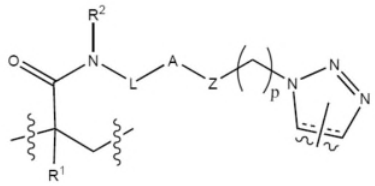
Z is a nitrogen containing heterocycle;

 is a single or double bond; and

the triazole or triazoline is covalently bound, directly or indirectly through a linker, through one or both triazole/triazoline ring carbon atoms to the substrate.

10. The structure of claim 9, wherein the recurring, covalently-bound monomer unit is:

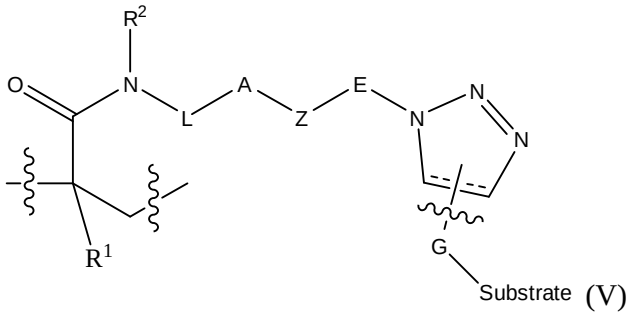
i) a compound of formula (IVa):



(IVa)

wherein p is 1, 2, 3, or 4;

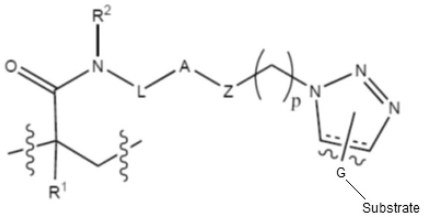
optionally wherein the recurring, covalently-bound monomer unit is a compound of Formula (V):



(V)

(V)

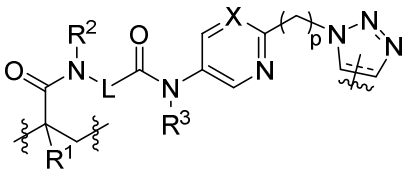
wherein G is a linker between the triazole/triazoline ring and the substrate; further optionally wherein the recurring covalently-bound monomer unit is a compound of formula (Va):



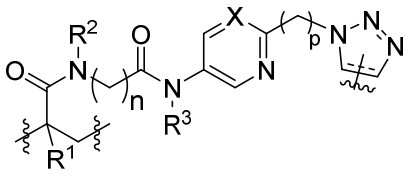
(Va)

wherein p is 1, 2, 3, or 4; or

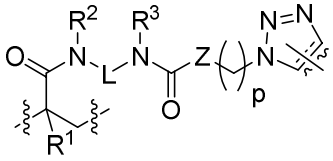
ii) a compound of Formula (IVb), Formula (IVc), Formula (IVd), or Formula (IVe):



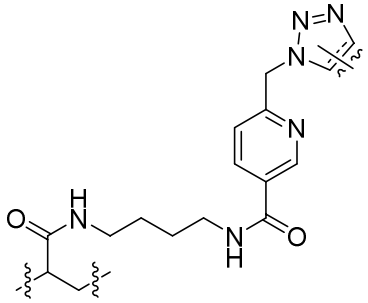
(IVb)



(IVc)



(IVd)



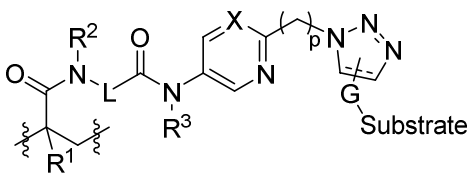
(IVe)

wherein

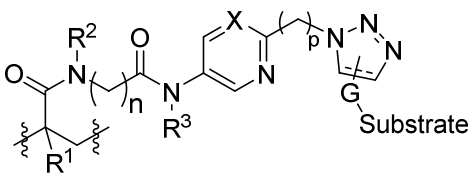
X is CH or N; and

n in formula (IVc) is an integer from 2 to 20.

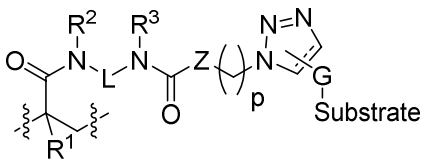
11. The structure of claim 9 or claim 10, wherein the recurring, covalently-bound monomer unit is a compound of Formula (Vb), Formula (Vc), Formula (Vd), or Formula (Ve):



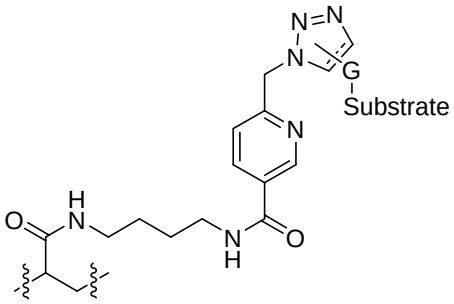
(Vb)



(Vc)



(Vd)



(Ve)

wherein G is a linker between the triazole/triazoline ring and the substrate.

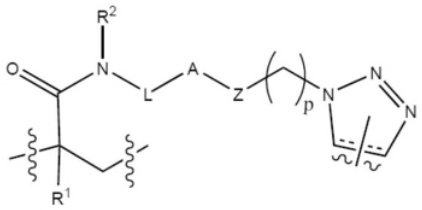
12. A copolymer-oligonucleotide product formed from reaction between the copolymer of any one of claims 5 to 7 and one or more oligonucleotides; optionally wherein the copolymer oligonucleotide product is formed from reaction of the azido group of the copolymer and an alkene- or alkyne-functionalized oligonucleotide.

13. An oligonucleotide bound copolymer, comprising an oligonucleotide bound recurring monomer unit of Formula (IV) as defined in claim 9

; and

the copolymer is covalently bound, directly or indirectly through a linker, through one or both triazole/triazoline ring carbon atoms to the oligonucleotide.

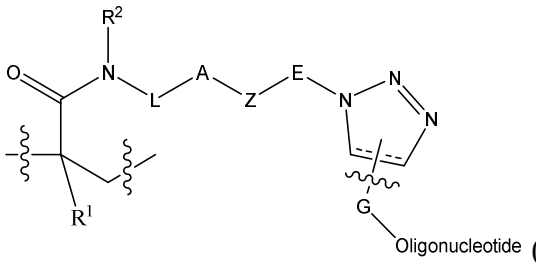
14. The oligonucleotide bound copolymer of claim 13, wherein the oligonucleotide bound recurring monomer unit is of formula (IVa):



(IVa)

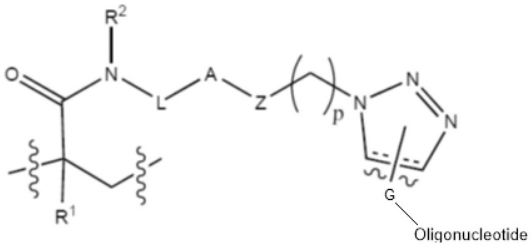
wherein p is 1, 2, 3 or 4;

optionally wherein the oligonucleotide-bound recurring monomer unit is of Formula (VI):



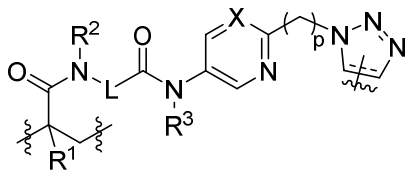
(VI)

further optionally wherein the oligonucleotide-bound recurring monomer unit is of Formula (VIa):

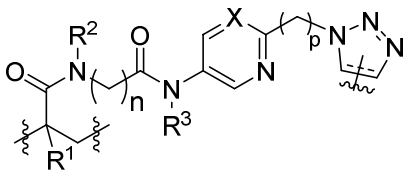


(VIa)

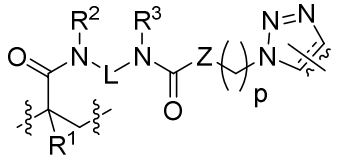
wherein p is 1, 2, 3, or 4, of Formula (IVb), Formula (IVc), Formula (IVd), or Formula (IVe):



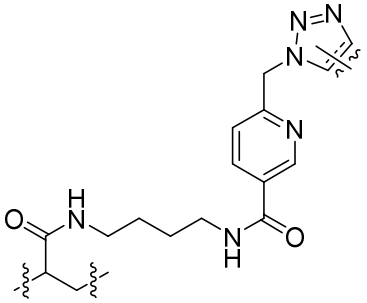
(IVb)



(IVc)



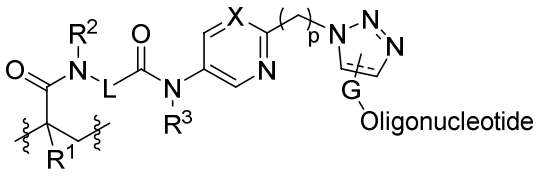
(IVd)



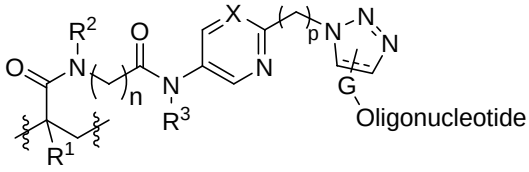
(IVe)

wherein X is CH or N; p is 1, 2, 3, or 4; and n in formula (IVc) is an integer from 2 to 20.

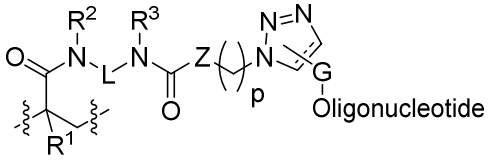
15. The oligonucleotide bound copolymer of claim 13 or claim 14, wherein the oligonucleotide-bound recurring monomer unit is of Formula (VIb), Formula (VIc), Formula (VId), or Formula (VIe):



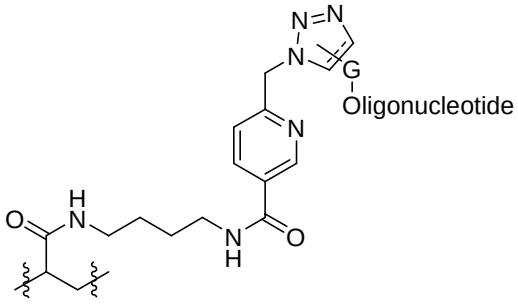
(VIb)



(VIc)



(VId)



(VIe)

wherein X is CH or N; and n in formula (IVc) is an integer from 2 to 20.

16. A copolymer-substrate-oligonucleotide product formed by reaction of the copolymer according to any one of claims 5 to 7 with a substrate and one or more oligonucleotides.

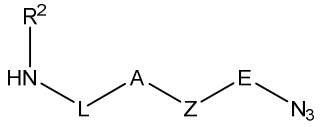
17. A method of immobilizing a copolymer according to any one of claims 5 to 7 to a substrate, comprising reacting azido groups of the copolymer with a plurality of alkenyl- or alkynyl-containing functional groups on a surface of the substrate to form covalent bonds between the copolymer and the surface.

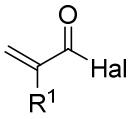
18. A method of grafting a plurality of oligonucleotides to a copolymer according to any one of claims 5 to 7, comprising reacting azido groups of the copolymer with the plurality of oligonucleotides;

optionally wherein the plurality of oligonucleotides comprise alkenyl or alkynyl groups, and the reaction occurs between the azido groups of the copolymer and the alkenyl or alkynyl groups of the oligonucleotides.

19. A method of making a compound of formula (I) as defined in claim 1

comprising reacting a compound of Formula (X) with an acrylate of Formula (XI):





(X) (XI)

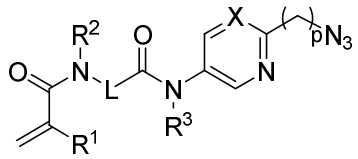
wherein

Hal is Cl or F

to form the compound of Formula (I).

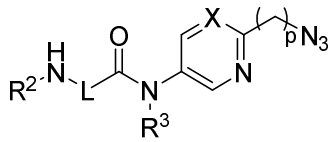
20. A method as claimed in claim 19 of making a compound of:

i) Formula (Ik):



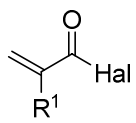
(Ik)

comprising reacting a compound of Formula (Xa):



(Xa)

with an acrylate of Formula (XI):



(XI)

wherein

R^1 is H or C_{1-4} alkyl;

R^2 is H or C_{1-4} alkyl;

L is a linker comprising a linear chain consisting of 2 to 20 atoms selected from the group consisting of carbon, oxygen, and nitrogen and optional substituents on the carbon and any nitrogen atoms in the chain;

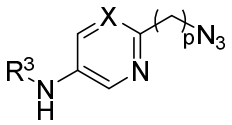
p is 1, 2, 3 or 4;

X is CH or N; and

Hal is Cl or F

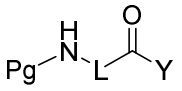
to form a compound of Formula (Ik),

optionally further comprising reacting a compound of Formula (XII):



(XII)

with a compound of Formula (XIII):



(XIII)

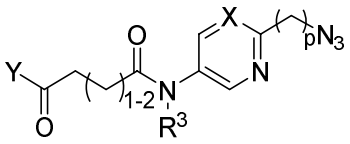
wherein

Pg is H or an amino protecting group; and

Y is -OH or -Cl;

to form the compound of Formula (Xa); or

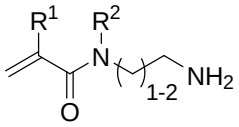
ii) of Formula (Ik) comprising reacting a compound of Formula (XIV):



(XIV)

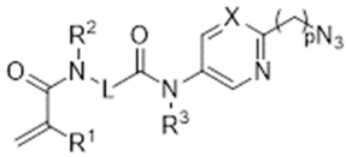
wherein Y is -OH or -Cl;

with a compound of Formula (XV):



(XV)

to form the compound of Formula (Ik)



(Ik)

wherein

R^1 is H or C_{1-4} alkyl;

R^2 is H or C_{1-4} alkyl;

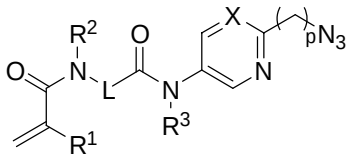
L is a linker comprising a linear chain consisting of 6 to 8 atoms selected from the group consisting of carbon, oxygen, and nitrogen and optional substituents on the carbon and any nitrogen atoms in the chain;

p is 1, 2, 3 or 4; and

X is CH or N,

optionally further comprising reacting a compound of Formula (XII) with a cyclic anhydride to form the compound of Formula (XIV).

21. A compound as claimed in claim 4 of Formula (Ik):



(Ik)

wherein

R^1 is H or C_{1-4}alkyl;

R^2 is H or C_{1-4}alkyl;

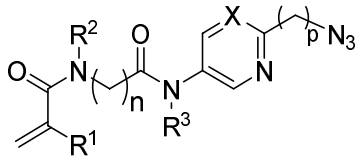
R^3 is H or C_{1-4}alkyl;

X is CH or N;

p is 1, 2, 3, or 4; and

L is a linker with a linear chain consisting of 2 to 20 atoms selected from the group consisting of carbon, oxygen, and nitrogen and optional substituents on the carbon and nitrogen atoms in the chain.

22. The compound of claim 21, wherein the compound of Formula (Ik) is a compound of Formula (Im):



(Im)

wherein

R^1 is H or $C_{1\text{-}4}$alkyl;

R^2 is H or $C_{1\text{-}4}$alkyl;

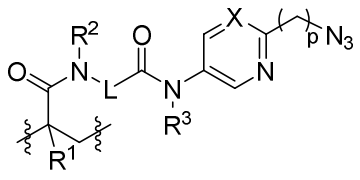
R^3 is H or $C_{1\text{-}4}$alkyl;

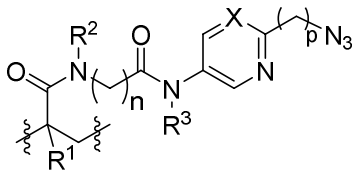
X is CH or N;

p is 1, 2, 3, or 4; and

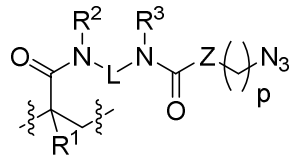
n is an integer from 2 to 20.

23. A copolymer as claimed in claim 5, comprising a recurring monomer unit of Formula (IIb), Formula (IIc), Formula (IId), or Formula (IIe):

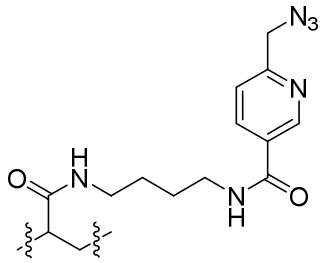




(IIb)



(IIc)



(IId)

(IIe)

wherein

R^1 is H or $C_{1\text{-}4}$alkyl;

R^2 is H or $C_{1\text{-}4}$alkyl;

R^3 is H or $C_{1\text{-}4}$alkyl;

X is CH or N;

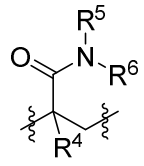
p is 1, 2, 3, or 4;

L in Formula (IIb) is a linker with a linear chain consisting of 2 to 20 atoms selected from the group consisting of carbon, oxygen, and nitrogen and optional substituents on the carbon and nitrogen atoms in the chain; and

n in Formula (IIc) is an integer from 2 to 20;

and at least one other recurring monomer unit;

optionally wherein the copolymer comprises a recurring monomer unit of Formula (IIb), (IIc), (IId), or (IIe) and a recurring monomer unit of Formula (III):



(III)

wherein

R^4 is H or $C_{1\text{-}4}$alkyl;

R^5 is H or $C_{1\text{-}4}$alkyl; and

R^6 is H or $C_{1\text{-}4}$alkyl;

further optionally wherein the copolymer comprises a recurring monomer unit of Formula (IIb), (IIc), (IId), or (IIe), a recurring monomer unit of Formula (III), and at least one other recurring monomer unit.

24. A substrate comprising a copolymer comprising a recurring monomer unit of Formula (IIb), Formula (IIc), Formula (IId), or Formula II(e) as defined in claim 6 and at least one other recurring monomer unit, wherein the copolymer is covalently bound to the substrate;optionally:

i) wherein the covalent attachment is made by reaction of the azido group of a monomer unit of Formula (IIb), Formula (IIc), Formula (IId), or Formula (IIe) as defined in claim 6 with an alkenyl- or alkynyl-containing group on a surface of the substrate; and/or

ii) wherein the substrate-bound copolymer further comprises a recurring monomer unit that is covalently bound to a substrate, wherein the recurring, covalently-bound, monomer unit is represented by Formula (IVb), Formula (IVc), Formula (IVd), or Formula (IVe) as defined in claim 9;

wherein the triazole or triazoline is covalently bound, directly or indirectly through a linker, through one or both triazole/triazoline ring carbon atoms to the substrate; optionally wherein the copolymer comprises a recurring, substrate-bound monomer unit represented by Formula (Vb), (Vc), (Vd), or (Ve) as defined in claim 11.

25. The copolymer of claim 23, wherein:

i) the copolymer is covalently bound to oligonucleotides, optionally wherein the oligonucleotides are covalently bonded to the copolymer through reaction of the azido group of the recurring monomer unit of Formula (IIb), (IIc), (IId), or (IIe) as defined in claim 6 and an alkene- or alkyne-functionalized oligonucleotide, further optionally wherein the oligonucleotide-bound copolymer comprises a recurring monomer unit of Formula (IVb), (IVc), (IVd), or (IVe) as defined in claim 9, wherein the copolymer is covalently bound, directly or indirectly through a linker, through one or both triazole/triazoline ring carbon atoms to the oligonucleotide, yet further optionally wherein the copolymer comprises oligonucleotide-bound recurring monomer units of Formula (VIb), (VIc), (VId), or VI(e) as defined in claim 15

; or

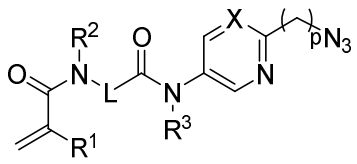
ii) wherein the copolymer is covalently bound to a substrate and is covalently bound to oligonucleotides, optionally wherein the copolymer comprises recurring monomer units of one or more of Formula (VIb), Formula (VIc), Formula (VId), and Formula (VIe).

26. A method of immobilizing a copolymer comprising a recurring monomer unit of Formula (IIb), (IIc), (IId), or (IIe) as defined in claim 6 to a substrate, comprising reacting azido groups

of a copolymer comprising a recurring monomer unit of Formula (IIb), (IIc), (IId), or (IIe) with a plurality of alkenyl- or alkynyl-containing functional groups on a surface of the substrate to form covalent bonds between the copolymer and the surface.

27. A method of grafting a plurality of oligonucleotides to a copolymer comprising a recurring monomer unit of Formula (IIb), (IIc), (IId), or (IIe) as defined in claim 6, comprising reacting azido groups of the copolymer with the oligonucleotides, optionally wherein the oligonucleotides comprise alkenyl or alkynyl groups and the reacting occurs between the azido groups of the copolymer and the oligonucleotides.

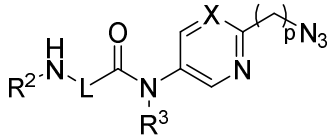
28. A method of making a compound of Formula (Ik):



(Ik)

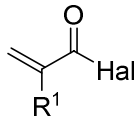
comprising:

i) reacting a compound of Formula (Xa):



(Xa)

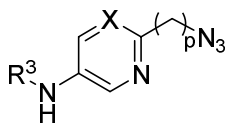
with an acrylate of Formula (XI):



(XI)

wherein Hal is Cl or F,

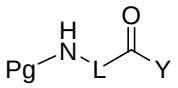
to form a compound of Formula (Ik), optionally further comprising reacting a compound of Formula (XII):



(XII)

wherein p, R^3, and X are as defined in claim 4;

with a compound of Formula (XIII):



(XIII)

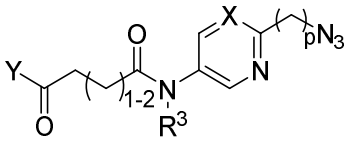
wherein

Pg is H or an amino protecting group; and

Y is -OH or -Cl;

to form the compound of Formula (Xa); or

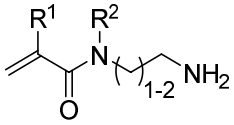
ii) reacting a compound of Formula (XIV):



(XIV)

where Y is -OH or -Cl;

with a compound of Formula (XV):



(XV)

to form the compound of Formula (Ik), optionally further comprising reacting a compound of Formula (XII) with a cyclic anhydride to form the compound of Formula (XIV).

29. A compound as claimed in claim 1; a copolymer as claimed in claim 5 or claim 23; a structure as claimed in claim 9; an oligo-bound copolymer as claimed in claim 13; a copolymer-substrate-oligonucleotide product as claimed in claim 16 when dependent upon claim 5; a method as claimed in claim 17 when dependent upon claim 5 of immobilizing a copolymer; a method as claimed in claim 18 when dependent upon claim 5 of grafting a plurality of oligonucleotides to a copolymer; or a method as claimed in claim 19; wherein E is substituted with one or more substituents independently selected from C_1-C_6 alkyl, C_1-C_6 alkenyl, C_1-C_6 alkynyl, C_1-C_6 heteroalkyl, C_3-C_7 carbocyclyl (optionally substituted with halo, C_1-C_6 alkyl, C_1-C_6 alkoxy, C_1-C_6 haloalkyl, and C_1-C_6 haloalkoxy), C_3-C_7-carbocyclyl-C_1-C_6-alkyl (optionally

substituted with halo, C_1-C_6 alkyl, C_1-C_6 alkoxy, C_1-C_6 haloalkyl, and C_1-C_6 haloalkoxy), 5-10 membered heterocyclyl (optionally substituted with halo, C_1-C_6 alkyl, C_1-C_6 alkoxy, C_1-C_6 haloalkyl, and C_1-C_6 haloalkoxy), 5-10 membered heterocyclyl-C_1-C_6-alkyl (optionally substituted with halo, C_1-C_6 alkyl, C_1-C_6 alkoxy, C_1-C_6 haloalkyl, and C_1-C_6 haloalkoxy), aryl (optionally substituted with halo, C_1-C_6 alkyl, C_1-C_6 alkoxy, C_1-C_6 haloalkyl, and C_1-C_6 haloalkoxy), aryl(C_1-C_6)alkyl (optionally substituted with halo, C_1-C_6 alkyl, C_1-C_6 alkoxy, C_1-C_6 haloalkyl, and C_1-C_6 haloalkoxy), 5-10 membered heteroaryl (optionally substituted with halo, C_1-C_6 alkyl, C_1-C_6 alkoxy, C_1-C_6 haloalkyl, and C_1-C_6 haloalkoxy), 5-10 membered heteroaryl(C_1-C_6)alkyl (optionally substituted with halo, C_1-C_6 alkyl, C_1-C_6 alkoxy, C_1-C_6 haloalkyl, and C_1-C_6 haloalkoxy), halo, cyano, hydroxy, C_1-C_6 alkoxy, C_1-C_6 alkoxy(C_1-C_6)alkyl, ether, aryloxy, sulfhydryl (mercapto), halo(C_1-C_6)alkyl, $–CF_3$, halo(C_1-C_6)alkoxy $–OCF_3$, C_1-C_6 alkylthio, arylthio, amino, amino(C_1-C_6)alkyl, nitro, O-carbamyl, N-carbamyl, O-thiocarbamyl, N-thiocarbamyl, C-amido, N-amido, S-sulfonamido, N-sulfonamido, C-carboxy, O-carboxy, acyl, cyanato, isocyanato, thiocyanato, isothiocyanato, sulfinyl, sulfonyl, and oxo (=O).