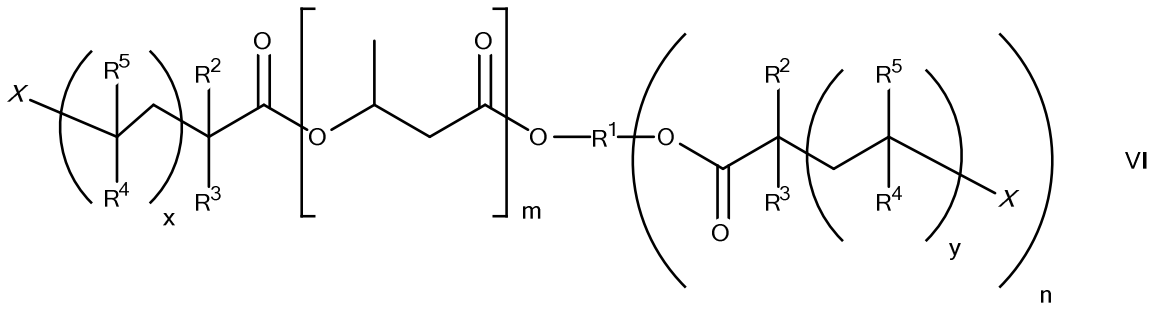
CLAIMS

1. A block copolymer having formula VI:



VI

wherein:

m represents a polymeric repeating unit of a first polymeric component;

R^1 represents a straight-chain or branched C_{1-14} alkyl or a C_{3-10} cycloalkyl that are substituted with n ester groups;

n represents 0 to 8;

X represents Cl, Br and I;

R^2 and R^3 are independently selected from C_{1-6} alkyl;

R^4 represents C_{6-10} aryl, C_{5-10} heteroaryl, $C(O)R^{6a}$, $C(O)OR^{6b}$ and $C(O)NR^{7a}R^{7b}$;

R^5 represents H or straight-chain or branched C_{1-6} alkyl;

R^{6a} and R^{6b} independently represent a straight-chain or branched C_{1-6} alkyl or straight-chain or branched C_{1-6} alkyl substituted by one or more of the substituents selected from OR^8 or NR^9R^{10};

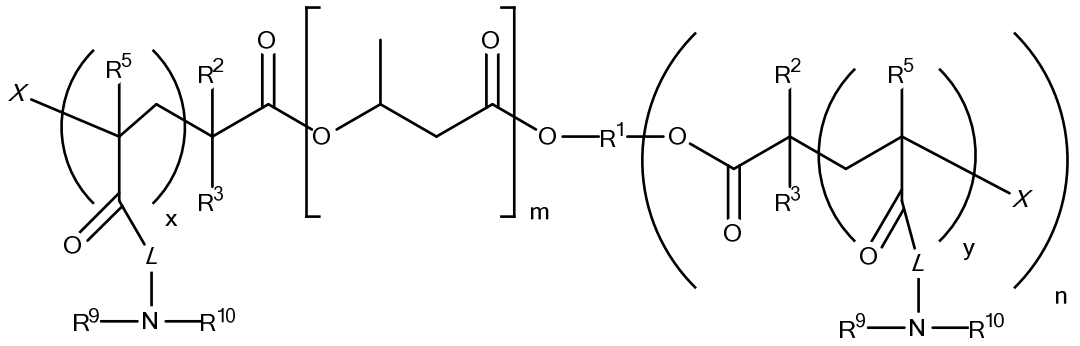
R^{7a}, R^{7b}, R^8, R^9 and R^{10} are independently selected from H or straight-chain or branched C_{1-6} alkyl,

x represents a polymeric repeating unit of a second polymeric component;

y, when present, represents a polymeric repeating unit of a third polymeric component when n is 1 up to a tenth polymeric component when n is 8; and

the number average molecular weight of the block copolymer is from 15,000 to 200,000 Daltons (e.g. from 20,000 to 150,000 Daltons or from 20,000 to 200,000 daltons).

2. The block copolymer of Claim 1 having the structure of formula VIa:



VIa

wherein:

m represents a polymeric repeating unit of a first polymeric component;

R^1 represents a straight-chain or branched C_{1-14} alkyl or a C_{3-10} cycloalkyl that are substituted with n ester groups;

n represents 0 to 8;

X represents Cl, Br and I;

R^2 and R^3 are independently selected from C_{1-6} alkyl;

R^5 represents straight-chain or branched C_{1-6} alkyl;

R^9 and R^{10} are independently selected from straight-chain or branched C_{1-6} alkyl,

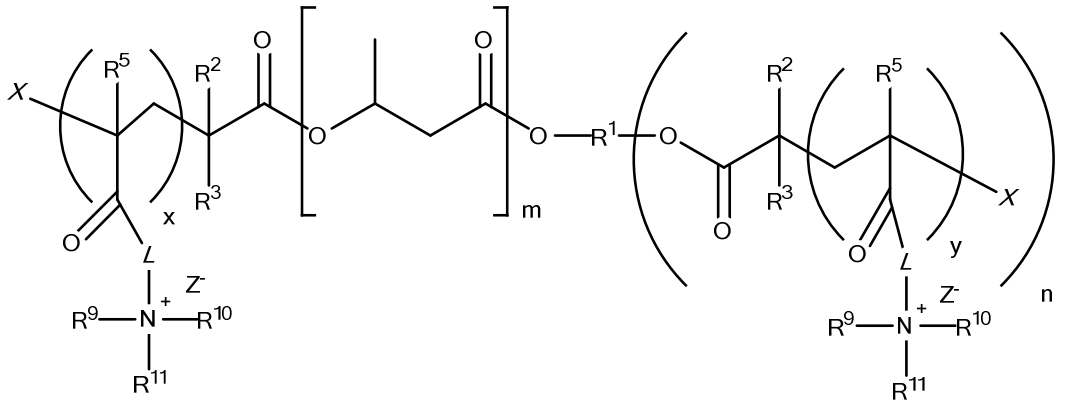
x represents a polymeric repeating unit of a second polymeric component;

y, when present, represents a polymeric repeating unit of a third polymeric component when n is 1 up to a tenth polymeric component when n is 8;

L represents a straight-chain or branched -C_{1-6} alkylene or a straight-chain or branched -O-C_{1-6} alkylene; and

the number average molecular weight of the block copolymer is from 15,000 to 200,000 Daltons (e.g. from 20,000 to 150,000 Daltons or from 20,000 to 200,000 daltons).

3. A block copolymer having formula VIII:



VIII

wherein:

m represents a polymeric repeating unit of a first polymeric component;

R^1 represents a straight-chain or branched C_{1-14} alkyl or a C_{3-10} cycloalkyl that are substituted with n ester groups;

n represents 0 to 8;

X represents Cl, Br and I;

R^2 and R^3 are independently selected from C_{1-6} alkyl;

R^5 represents straight-chain or branched C_{1-6} alkyl;

R^9 and R^{10} are independently selected from straight-chain or branched C_{1-6} alkyl,

R^{11} represents straight-chain or branched C_{1-6} alkyl or straight-chain or branched C_{1-6} alkyl substituted with one or more of C_{6-10} aryl, C_{5-10} heteroaryl and OH;

Z represents Br, Cl or I;

x represents a polymeric repeating unit of a second polymeric component;

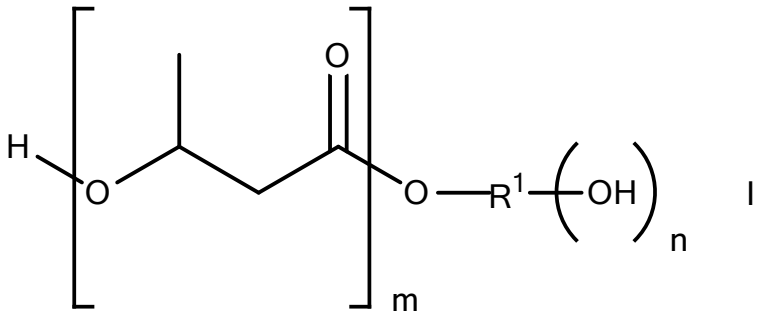
y, when present, represents a polymeric repeating unit of a third polymeric component when n is 1 up to a tenth polymeric component when n is 8;

L represents a straight-chain or branched -C_{1-6} alkylene or a straight-chain or branched -O-C_{1-6} alkylene; and

the number average molecular weight of the block copolymer is from 15,000 to 200,000 Daltons (e.g. from 20,000 to 150,000 Daltons or from 20,000 to 200,000 daltons).

4. A process to provide a block copolymer of formula VI, the process comprising:

(a) reacting a compound of formula I:



I

wherein:

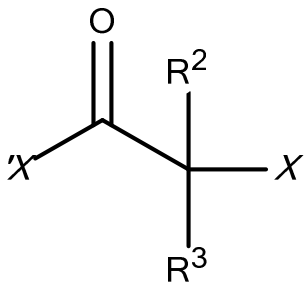
m represents the repeating unit of the polymer;

R^1 represents a straight-chain or branched C_{1-14} alkyl or a C_{3-10} cycloalkyl that are substituted with n hydroxyl groups;

n represents 0 to 8, and wherein

the number average molecular weight of the polymer is from 500 to 80,000 Daltons,

with a sufficient quantity of a suitable atom transfer radical polymerization (ATRP) initiator of formula III:

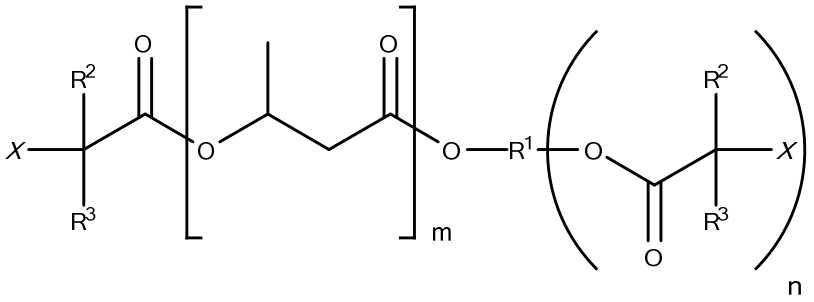


III

where X and ‘X are independently selected from Cl, Br and I; and

R^2 and R^3 are independently selected from C_{1-6} alkyl,

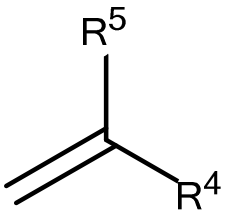
to provide a compound of formula IV:



IV

where X, R^2 and R^3 are as defined for the compound of formula III and R^1, m and n are as defined for the compound of formula I; and

(b) reacting the compound of formula IV under ATRP conditions with a monomer compound of formula V:



V

where:

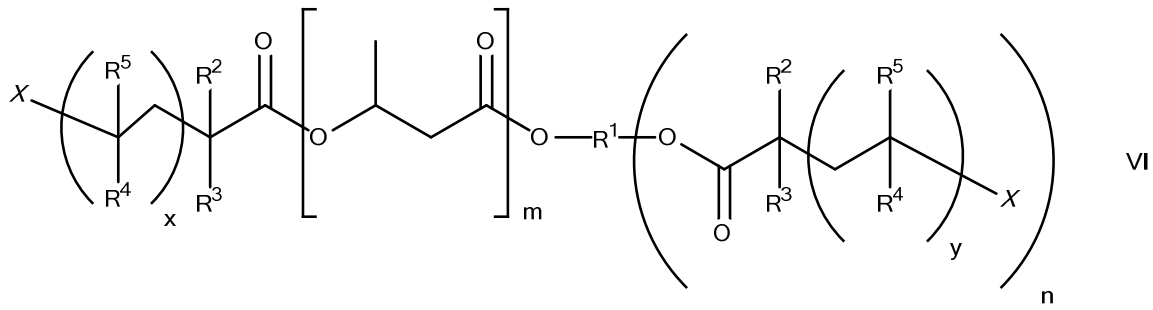
R^4 represents C_{6-10} aryl, C_{5-10} heteroaryl, $C(O)R^{6a}$, $C(O)OR^{6b}$ and $C(O)NR^{7a}R^{7b}$;

R^5 represents H or straight-chain or branched C_{1-6} alkyl;

R^{6a} and R^{6b} independently represent a straight-chain or branched C_{1-6} alkyl or straight-chain or branched C_{1-6} alkyl substituted by one or more of the substituents selected from OR^8 or NR^9R^{10};

R^{7a}, R^{7b}, R^8, R^9 and R^{10} are independently selected from H or straight-chain or branched C_{1-6} alkyl,

to provide a compound of formula VI:



VI

where:

x and y represent a polymeric repeating unit of the monomer of the compound of formula V;

R^4 and R^5 are as defined for the compound of formula V

X, R^2 and R^3 are as defined for the compound of formula III; and

R^1, m and n are as defined for the compound of formula I.

5. A process to functionalise the block copolymer of formula VI as defined in Claim 1, wherein when R^4 represents $C(O)R^{6a}$ or $C(O)OR^{6b}$, where R^{6a} and R^{6b} independently represent a $C_{1\text{-}6}$ straight-chain or branched alkyl substituted by a NR^9R^{10} substituent, the process comprises:

(i) reacting the compound of formula VI as defined in Claim 1 with a compound of formula VII:

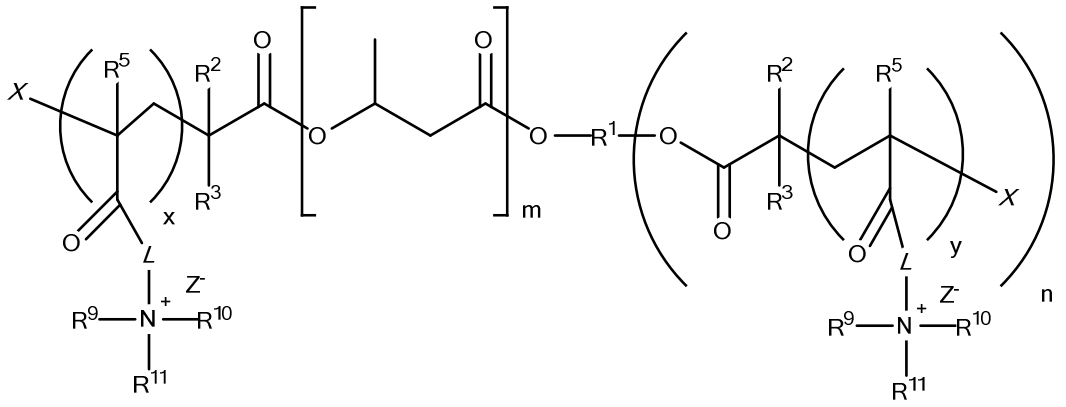
$$R^{11}\text{-}Z \quad \text{VII}$$

where:

R^{11} represents straight-chain or branched $C_{1\text{-}6}$ alkyl or straight-chain or branched $C_{1\text{-}6}$ alkyl substituted with one or more of $C_{6\text{-}10}$ aryl, $C_{5\text{-}10}$ heteroaryl and OH; and

Z represents Br, Cl or I,

to provide a quarternised compound of formula VIII:



VIII

where:

L represents a straight-chain or branched -C_{1-6} alkylene or a straight-chain or branched -O-C_{1-6} alkylene, R^9 and R^{10} are independently selected from straight-chain or branched C_{1-6} alkyl;

R^{11} and Z are as defined for the compound of formula VII;

x and y are as defined for the compound of formula VI in Claim 1;

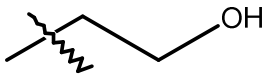
R^4 and R^5 are as defined for the compound of formula V in Claim 4;

X, R^2 and R^3 are as defined for the compound of formula III in Claim 4; and

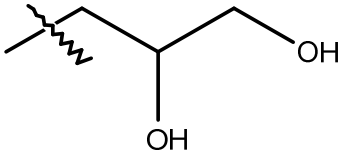
R^1, m and n are as defined for the compound of formula I as defined in Claim 1.

6. The copolymers and processes according to any one of Claims 1 to 5, wherein R^1 represents a straight-chain or branched C_{1-6} alkyl and n represents 0 to 5, optionally wherein R^1 represents a straight-chain C_{2-5} alkyl and n represents 0 to 4 or R^1 represents a straight-chain C_{4-6} alkyl.

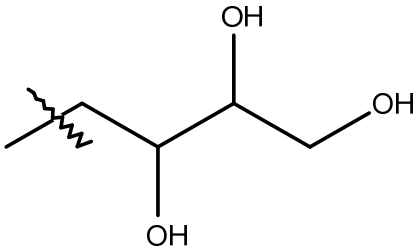
7. The copolymers and processes according to Claim 6, wherein R^1 represents hexyl or a fragment selected from formula Ia-Ic,



Ia



Ib



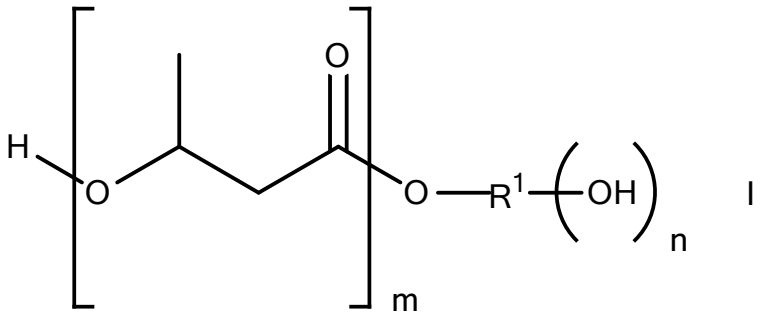
Ic

,

where the wavy line represents the point of attachment of the fragment to the polymer.

8. The copolymers and processes according to any one of Claims 1 to 7, wherein:
   (a) X represents Cl, or, more particularly, Br; and/or
   (b) R^2, R^3 and R^5 are independently selected from C_{1-2} alkyl; and/or
   (c) R^{11} represents straight-chain or branched C_{1-3} alkyl or straight-chain or branched C_{1-3} alkyl substituted by phenyl; and/or
   (d) n represents 0 to 4; and/or
   (e) L represents a straight-chain or branched -O-C_{1-2} alkylene; and/or
   (f) the number average molecular weight of the block copolymer is from 15,000 to 165,000 Daltons (e.g. from 55,000 to 163,000 Daltons, such as from 19,000 to 41,000 Daltons).

9. A polymer having formula I:



wherein:

m represents the repeating unit of the polymer;

R^1 represents a straight-chain or branched C_{1-14} alkyl or a C_{3-10} cycloalkyl that are substituted with n hydroxyl groups;

n represents 0 to 8, and wherein

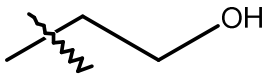
the number average molecular weight of the polymer is from 500 to 80,000 Daltons, optionally wherein:

the polymer has a number average molecular weight of from 1,000 to 10,000 Daltons; and/or

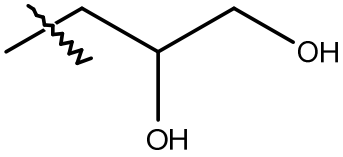
n represents 0 or 2 to 4.

10. The polymer according to Claim 9, wherein R^1 represents a straight-chain or branched C_{1-6} alkyl and n represents 0 to 5, optionally wherein R^1 represents a straight-chain C_{2-5} alkyl and n represents 0 to 4 or R^1 represents a straight-chain C_{4-6} alkyl.

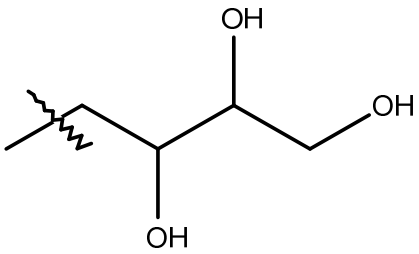
11. The polymer according to Claim 10, wherein $-R^1(OH)_n$ represents hexyl or a fragment selected from formula Ia-Ic,



Ia



Ib



Ic

,

where the wavy line represents the point of attachment of the fragment $-R^1(OH)_n$ to the rest of the polymer.

12. The polymer according to Claim 11, wherein:

(a) when R^1 represents hexyl, the number average molecular weight of the polymer is from 1,000 to 7,000 Daltons;

(b) when R^1 represents the fragment of formula Ia, the number average molecular weight of the polymer is from 750 to 60,000 Daltons;

(c) when R^1 represents the fragment of formula Ib, the number average molecular weight of the polymer is from 750 to 60,000 Daltons (e.g. (e.g. from 1,000 to 7,000 Daltons, such as from 6,000 to 6,500 Daltons); and

(d) when R^1 represents the fragment of formula Ic, the number average molecular weight of the polymer is from 750 to 60,000 Daltons (e.g. from 1,000 to 7,000 Daltons, such as from 4,500 to 4,700 Daltons).

13. The polymer of any one Claims 9 to 12, wherein the polymer of formula I comprises part of a block copolymer, where one of more of the -OH groups in the compound of formula I instead represents -O- and serves to link the compound of formula I to the other components of said block copolymer.

14. A process of preparing a polymer, which process comprises a transesterification reaction to produce a compound of formula I, as defined in any one of Claims 10 to 16,

comprising reaction of a P3HB having a number average molecular weight of from 20,000 to 200,000 Daltons with an alcohol of formula II,

R^1OH II

wherein:

R^1 represents a straight-chain or branched C_{1-14} alkyl, a straight-chain or branched C_{1-14} alkyl substituted with from 0 to 8 hydroxyl groups, a C_{1-10} cycloalkyl or a C_{1-10} cycloalkyl substituted with from 0 to 8 hydroxyl groups, and

the alcohol of formula II is present in a molar excess of from 100 times to 500 times (e.g. 300 times) the molar amount of the P3HB.

15. The process according to Claim 14, wherein:

(a) the transesterification reaction is conducted at a temperature of from 100ºC to 160 ºC for from 1 to 10 days, optionally at a temperature of 140 ºC for from 2 to 5 days; and/or

(b) the transesterification reaction comprises an organic solvent, optionally wherein the solvent is diglyme; and/or

(c) the transesterification reaction further comprises a catalyst, optionally wherein the catalyst is a tin-based catalyst and/or a titanium-based catalyst; and/or

(d) the transesterification reaction is conducted under an inert atmosphere.

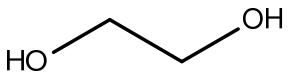
16. The process according to Claim 15(b), wherein the concentration of the alcohol of formula II in the organic solvent is from 0.1 M to 1 M, optionally wherein the concentration is from 0.4 M to 0.5 M.

17. The process according to any one of Claims 14 to 16, wherein R^1 represents a straight-chain or branched C_{1-6} alkyl, or a straight-chain or branched C_{1-6} alkyl substituted with from 0 to 5 hydroxyl groups, optionally wherein:

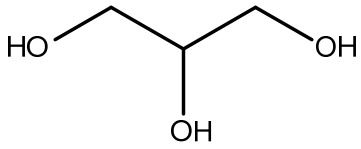
R^1 represents a straight-chain C_{4-6} alkyl or a straight-chain C_{2-5} alkyl substituted with from 0 to 4 hydroxyl groups; and/or

n represents 0 or 2 to 4.

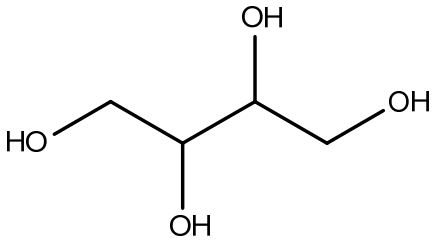
18. The process according to Claim 17, wherein R^1OH represents hexanol or a compound selected from formula Ia'-Ic',



Ia'



Ib'



Ic'

.

19. The process according to Claim 18, wherein:

(a) when R^1 represents hexanol, the number average molecular weight of the compound of formula I is from 1,000 to 7,000 Daltons;

(b) when R^1OH represents the compound of formula Ia, the number average molecular weight of the compound of formula I is from 750 to 60,000 Daltons;

(c) when R^1OH represents the compound of formula Ib, the number average molecular weight of the compound of formula I is from 750 to 60,000 Daltons (e.g. from 1,000 to 7,000 Daltons, such as from 6,000 to 6,500 Daltons); and

(d) when R^1OH represents the compound of formula Ic, the number average molecular weight of the compound of formula I is from 750 to 60,000 Daltons (e.g. from 1,000 to 7,000 Daltons, such as from 4,500 to 4,700 Daltons).

20. A process to provide a block copolymer derived from the compound of formula I as defined in any one of Claims 9 to 13, wherein

(a) the process comprises functionalising the compound of formula I with a suitable reversible addition−fragmentation chain-transfer (RAFT) polymerization agent to form a RAFT precursor compound and reacting the RAFT precursor compound with a monomer suitable for use in RAFT polymerization to form a RAFT-polymerised block copolymer; or

(b) the process comprises reacting the compound of formula I with a suitable di- or polyisocyanate to form a polyurethane, optionally wherein the di- or polyisocyanate is

selected from one or more of the group consisting of diphenylmethane diisocyanate, toluene diisocyanate, hexamethylene diisocyanate, isophorone diisocyanate and polymeric diphenylmethane diisocyanate.