Nickel(0)-catalysed diyne–maleimide double-cycloaddition copolymerisation to form poly(bicyclo[2.2.2]oct-7-ene)s

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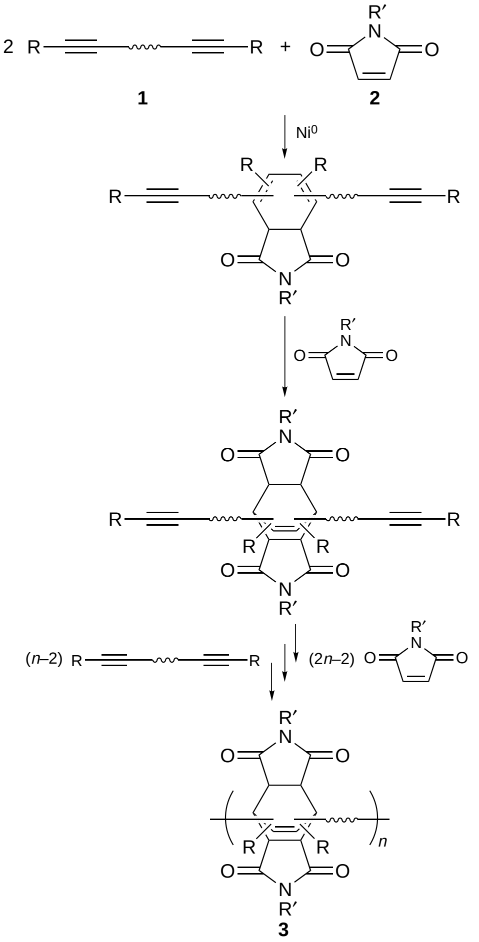
A nickel(0) catalyst effects the double-cycloaddition copolymerisation of diynes with *N*-substituted maleimides to form poly(bicyclo[2.2.2]oct-7-ene)s.

Recently we developed a transition metal-catalysed diyne cycloaddition copolymerisation[1] as a useful method of polymer synthesis, in which one molecule of a cycloaddition component such as carbon dioxide, an isocyanate, a nitrile or elemental sulfur reacts with two diyne molecules to afford a cycloaddition copolymer containing a heterocycle in its repeat unit.[2]

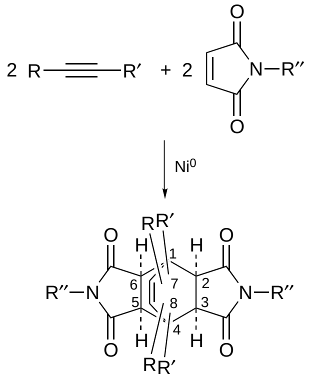
Here we report a new type of transition metal-catalysed diyne cycloaddition copolymerisation with an alkene to afford a cycloaddition copolymer containing a carbocycle in its repeat unit, *i.e.* a nickel(0)-catalysed diyne **1**–*N*-substituted maleimide **2** double-cycloaddition copolymerisation to form a poly(bicyclo[2.2.2]oct-7-ene) **3** having a wholly carbon backbone with an imide functionality (Scheme 1). This diyne–maleimide copolymerisation is characterised by a unique process in which two maleimide molecules connect two diyne molecules by double-cycloaddition to generate a copolymer repeat unit containing a bicyclo[2.2.2]oct-7-ene ring *via* nickel(0)-catalysed formation of a cyclohexadiene intermediate. Cycloaddition of two diyne molecules to one maleimide molecule is followed by Diels–Alder cycloaddition with the second maleimide molecule. This diyne–maleimide copolymerisation is based on our recent study of an efficient and chemoselective nickel(0)-catalysed 2 : 2 monoyne–maleimide double-cycloaddition to afford an *exo,exo*-bicyclo[2.2.2]oct-7-ene derivative stereoselectively (Scheme 2).[3]



〰 = 1,4-C$_6$H$_4$ (**a**), (CH$_2$)$_8$ (**b**), (CH$_2$)$_6$ (**c**)
R = H (**d**), Et (**e**)
R′ = Ph (**f**), C$_8$H$_{17}$ (**g**), Et (**h**)

Scheme 1

The results of the copolymerisation of 1,4-diethynylbenzene **1ad** with *N*-octylmaleimide **2g** are summarised in Table 1. The reaction was carried out in a 50 ml stainless steel autoclave under nitrogen. When a mixture of **1ad** (0.25 mmol) and **2g** (0.5 mmol) in THF (5 ml) was heated at 90 °C for 20 h in the presence of a Ni(CO)$_2$(PPh$_3$)$_2$ catalyst (Ni : **1ad** = 0.1), poly(bicyclo[2.2.2]oct-7-ene) **3adg** with M_n = 27200 and



Scheme 2

Table 1 Nickel(0)-catalysed double-cycloaddition copolymerisation of 1,4-diethynylbenzene **1ad** with *N*-octylmaleimide **2g** to form poly(bicyclo[2.2.2]oct-7-ene)s **3adg**[a]

				3adg		
Catalyst	Ni : **1ad**[b]	**2g** : **1ad**[b]	T/°C	Yield (%)[c]	M_n[d]	M_w/M_n[d]
Ni(CO)$_2$(PPh$_3$)$_2$	0.1	4	90	50	19800	1.9
Ni(CO)$_2$(PPh$_3$)$_2$	0.1	2	90	51	27200	2.1
Ni(CO)$_2$(PPh$_3$)$_2$	0.05	2	90	50	26800	3.5
Ni(CO)$_2$(PPh$_3$)$_2$	0.1	2	110	60	34600	1.9
Ni(CO)$_2$(PPh$_3$)$_2$	0.1	2	130	36	27100	2.6
Ni(cod)$_2$-2PPh$_3$	0.1	2	90	50	16000	2.4
Ni(cod)$_2$	0.1	2	90	91[e]		

[a] Conditions: **1ad** (0.25 mmol), THF (5 ml), 20 h, isolation of **3adg** using CH$_2$Cl$_2$–AcOEt. [b] Molar ratio. [c] Based on 100% conversion of **1ad** to **3adg**. [d] Determined by GPC with polystyrene standards in CHCl$_3$. [e] A CH$_2$Cl$_2$-insoluble copolymer.

M_w/M_n = 2.1 was obtained in 51% yield by concentration of the resulting reaction mixture under vacuum and by precipitation with CH_2Cl_2–AcOEt. Raising the reaction temperature to 110 °C increased the copolymer molecular weight to 34600. A nickel(0) catalyst generated from $Ni(cod)_2$ and 2 equiv. of PPh_3 was also effective, but $Ni(cod)_2$ alone gave an insoluble copolymer, probably due to copolymer branching and/or cross-linking[2c] originating from formation of diyne trimer in the copolymer. Compound **3adg** was formed as a pale yellow powder, which was soluble in THF, CH_2Cl_2 and $CHCl_3$ but insoluble in AcOEt and diethyl ether. The thermal stability of **3adg** was examined by thermogravimetric analysis (TGA) in air, and T_{10} (the temperature causing a 10% weight loss) was 322 °C.

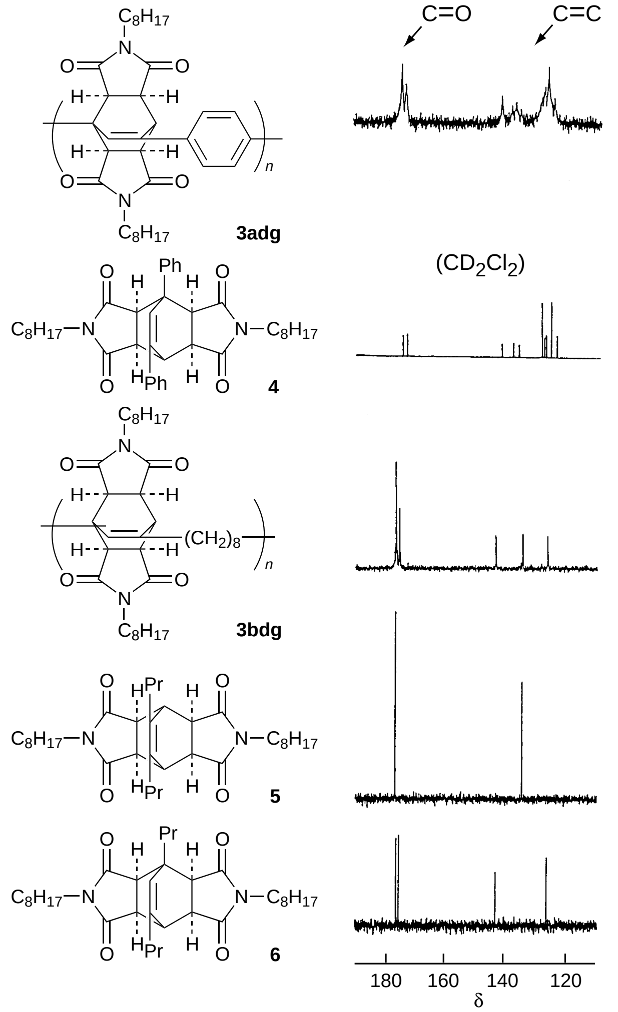


Fig. 1 ^{13}C NMR C=O and C=C signals of poly(bicyclo[2.2.2]oct-7-ene)s **3adg** and **3bdg** together with model compounds **4**–**6** ($CDCl_3$)

Table 2 Nickel(0)-catalysed double-cycloaddition copolymerisation of diynes **1** with maleimides **2** to form poly(bicyclo[2.2.2]oct-7-ene)s **3**[a]

				3			
1	2	2 : 1[b]	T/°C		Yield (%)[c]	M_n[d]	M_w/M_n[d]
bd	**f**	4	110	**bdf**[e]	70	15900	1.3
		2	110		75	12400	2.3
bd	**g**	4	90	**bdg**	96	9300	1.8
		2	90		70	12400	2.4
bd	**h**	4	110	**bdh**[e]	78	5000	1.6
ce	**f**	4	110	**cef**	75	6300	2.8

[a] Conditions: **1** (0.25 mmol), $Ni(CO)_2(PPh_3)_2$: **1** = 0.1, THF (2 ml), 20 h, isolation of **3** using CH_2Cl_2–hexane. [b] Molar ratio. [c] Based on 100% conversion of **1** to **3**. [d] Determined by GPC with polystyrene standards in $CHCl_3$. [e] Isolation from CH_2Cl_2–Et_2O.

Copolymerisations of **1ad** with *N*-phenyl- and *N*-ethyl-maleimides **2f** and **2h** gave insoluble copolymers **3adf** and **3adh**. Thus introduction of a longer *N*-alkyl substituent, such as an octyl group, into the maleimide was necessary for the preparation of a soluble poly(bicyclo[2.2.2]oct-7-ene) from **1ad**.

Poly(bicyclo[2.2.2]oct-7-ene) **3adg** was identified by IR, ^1H and ^{13}C NMR spectroscopy. Comparison of ^{13}C NMR C=O and C=C signals of **3adg** and a model compound of the copolymer repeat unit was most informative. The ^{13}C NMR C=O and C=C signals of **3adg** were similar to those of model compound **4**,[3] obtained regio- and stereo-selectively by the nickel(0)-catalysed cycloaddition reaction of phenylacetylene with **2g** (Fig. 1). This result confirms that the structure of **3adg** contains an *exo,exo*-fused 1,8-phenylene-substituted bicyclo[2.2.2]oct-7-ene ring.

In contrast with the formation of insoluble copolymer **3adf**, dodeca-1,11-diyne **1bd** copolymerised with **2f** to afford soluble copolymer **3bdf**, the difference in solubility being due to the presence of the long alkylene chains (Table 2). Diyne **1bd** copolymerised with **2g** to afford **3bdg** as a colourless resinous solid. The ^{13}C NMR C=O and C=C signals of **3bdg** were a superposition of those of two model compounds **5** and **6**,[3] which were obtained stereo- but nonregio-selectively by nickel(0)-catalysed cycloaddition reaction of pent-1-yne with **2g** (Fig. 1). This fact demonstrates the copolymer structure and indicates that **3bdg** has two kinds of repeat units corresponding to **5** and **6**.

Use of a two-fold excess of the maleimide (maleimide : diyne = 4 : 1) did not influence significantly the copolymer yield and molecular weight when compared with the stoichiometric copolymerisation (maleimide : diyne = 2 : 1) (Tables 1 and 2). An internal diyne, tetradeca-3,11-diyne **1ce**, copolymerised with **2f** at 110 °C to afford **3cef**.

Poly(bicyclo[2.2.2]oct-7-ene)s **3adg** and **3bdg** containing two octyl groups per repeat unit have unique rigid and flexible fence-like structures, respectively, and are potentially interesting, as structurally related comb-like polymers are well known and attract considerable attention on account of their specific properties.[4]

This work was partly supported by a Grant-in-Aid for Scientific Research on Priority Areas (Nos. 06227235 and 07216237) from the Ministry of Education, Science, Sports and Culture, Japan.

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Received, 24th September 1996; Com. 6/06563E