Nickel(0)-catalysed alkyne–dimaleimide double-cycloaddition copolymerisation to form poly(imide)s

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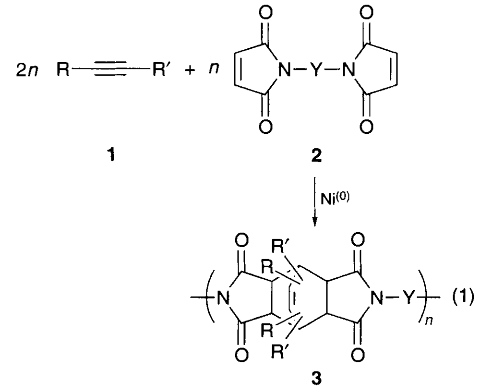
A nickel(0) catalyst effects the double-cycloaddition copolymerisation of alkynes with dimaleimides to form poly(imide)s.

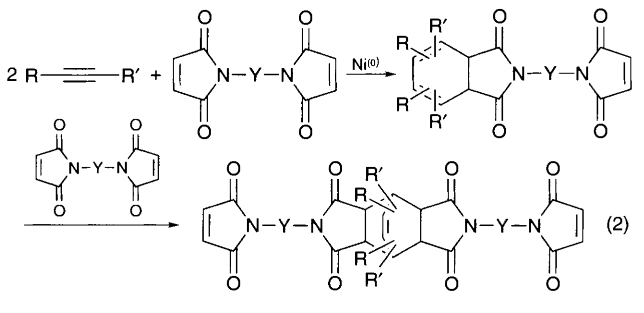
The development of a new method of polymer synthesis utilising a transition metal catalyst's characteristic organic reaction has attracted recent attention.[1] Here we report a new type of transition metal-catalysed polymer synthesis, *i.e.* a nickel(0)-catalysed alkyne–dimaleimide double-cycloaddition copolymerisation to form a poly(imide) [eqn. (1)]. This alkyne–dimaleimide copolymerisation is characterised by a unique and complex process in which two alkyne molecules connect two dimaleimide molecules by double-cycloaddition to generate a copolymer repeat unit containing a bicyclo[2.2.2]oct-7-ene ring *via* a nickel(0)-catalysed formation of a cyclohexadiene intermediate and its subsequent Diels–Alder cycloaddition with the dimaleimide [eqn. (2)]. This alkyne–dimaleimide copolymerisation is based on our recent study of an efficient and chemoselective nickel(0)-catalysed 2 : 2 alkyne–maleimide cycloaddition to afford an *exo,exo*-bicyclo[2.2.2]oct-7-ene derivative [eqn. (3)],[2a] which is a noteworthy reaction because efficient transition metal-catalysed [2 + 2 + 2] alkyne–alkene cycloaddition reactions are few.[3] The present nickel(0)-catalysed alkyne–dimaleimide double-cycloaddition copolymerisation is a new method of poly(imide) synthesis and accordingly affords a variety of new poly(imide)s by various combinations of alkynes and dimaleimides.

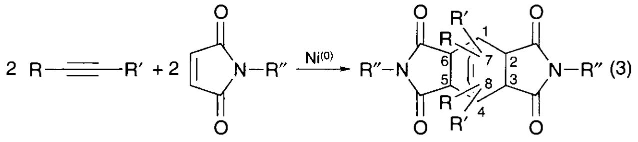


1 **2** **3**

1a R = C_8H_{17}; R′ = H
b R = R′ = C_6H_{13}
c R = Ph; R′ = H
d R = HC≡C(CH$_2$)$_4$; R′ = H
e R = OEt; R′ = H

2a Y = 1,1′,4,4′-$C_6H_4CH_2C_6H_4$
b Y = $(CH_2)_6$
c Y = 1,1′,4,4′-$C_6H_4OC_6H_4$
d Y = 1,4-C_6H_4
e Y = 1,3-C_6H_4





The results of the copolymerisation are summarised in Table 1. The reaction was carried out in a 50 ml stainless steel autoclave under nitrogen. When a mixture of dec-1-yne **1a** (1 mmol) and *N,N′*-1,1′-(4,4′-methylenediphenylene)dimaleimide **2a** (0.5 mmol) was heated at 90 °C for 20 h in dioxane (10 ml) in the presence of a nickel(0) catalyst generated from Ni(cod)$_2$ (Ni : alkyne = 0.05) and 2 equiv. of PPh$_3$, poly(imide) **3aa** with M_n = 8500 and M_w/M_n = 1.9† was obtained in 68% yield by concentration of the resulting reaction mixture under vacuum and precipitation with methylene chloride–diethyl ether. Compound **3aa** consisted of a white powder which was soluble in methylene chloride, chloroform and THF, partly soluble in benzene, but insoluble in diethyl ether and methanol.

Dimaleimide **2a** also copolymerised with tetradec-7-yne **1b**, but its copolymerisation with phenylacetylene **1c** and pent-1-yne or hex-3-yne produced totally and partly insoluble copolymers, respectively. These results indicate that the introduction of a relatively long alkyl group such as an octyl group or two hexyl groups into the alkyne is necessary for the preparation of a soluble poly(imide) from **2a**.[4] Thus the nickel(0)-catalysed copolymerisations of **1a** and **1b** with various dimaleimides such as *N,N′*-1,1′-(4,4′-oxydiphenylene)-

Table 1 Nickel(0)-catalysed alkyne **1**–dimaleimide **2** double-cycloaddition copolymerisation to form poly(imide)s **3** [eqn. (1)][a]

		3			
1	**2**		Yield (%)[b]	M_n[c]	M_w/M_n[c]
a	**a**	**aa**	68	8500	1.9
b	**a**	**ba**	49[d]	12 100	2.2
c	**b**	**cb**	33	4500	1.9
a	**b**	**ab**	53	15 000	1.4
d	**b**	**db**	69[e]	5400	2.7
e	**b**	**eb**	41	5000	1.7
a	**c**	**ac**	92	7400	2.3
a	**d**	**ad**	71	8800	1.7
b	**d**	**bd**	23[d]	7700	1.8
a	**e**	**ae**	91	8300	1.9

[a] **1** = 1 mmol; **1** : **2** = 2; Ni(cod)$_2$-2PPh$_3$: **1** = 0.05; 1,4-dioxane (10 ml); 90 °C; 20 h. [b] Based on the quantitative formation of **3**. [c] Determined by GPC with polystyrene standards in CHCl$_3$. [d] 150 °C. [e] **1d** = 0.5 mmol; **1d** : **2b** = 1.

dimaleimide **2c**, *N,N'*-1,4-phenylenedimaleimide **2d** and *N,N'*-1,3-phenylenedimaleimide **2e** afforded soluble poly(imide)s **3ac**, **3ad**, **3ae** and **3bd** with M_n = 7000–9000.

The introduction of a relatively long alkylene group connecting two maleimide moieties into the dimaleimide was also effective in the preparation of a soluble poly(imide). *N,N'*-1,6-Hexylenedimaleimide **2b** was found to be a versatile dimaleimide component and copolymerised with **1c** to form soluble poly(imide) **3cb** while the **1c–2a** and **1c–2d** copolymerisations produced insoluble copolymers. The **1a–2b** copolymerisation afforded poly(imide) **3ab** with M_n = 15000 and M_w/M_n = 1.4.

The structures of poly(imide)s **3** were determined by IR, ^{1}H and ^{13}C NMR spectroscopy. Comparison of the ^{13}C NMR C=O and C=C (a vinylene-type bridge of a bicyclic ring) signals between a poly(imide) and a model compound of a poly(imide) repeat unit was most decisive. Two regioisomeric model compounds **A** and **B** (**A** : **B** = 1.1) were obtained quantitatively with an *exo,exo*-stereoselectivity by the nickel(0)-catalysed reaction of pent-1-yne with *N*-octylmaleimide [eqn. (3), Fig. 1].[2a] The ^{13}C NMR C=O and C=C signals of **3ab** and **3ad** were similar to those of **A** and **B** except the phenylene C=C signals of **3ad** (Fig. 1). This fact demonstrates that the efficient nickel(0)-catalysed **1a–2b** and **1a–2d** double-cycloaddition copolymerisations occurred to afford poly(imide)s **3ab** and **3ad** with an *exo,exo*-stereochemistry. Poly(imide)s **3aa**, **3ac**, **3ae**, **3ba**, **3bd** and **3cb** were similarly identified spectroscopically using model compounds prepared by the nickel(0)-catalysed 2 : 2 cycloaddition of *N*-phenyl-, *N*-octyl- or *N*-ethyl-maleimide with **1c**, pent-1-yne or hex-3-yne,[2a] in which **1c** yielded a 1,8-diphenyl-substituted bicyclo[2.2.2]oct-7-ene ring regioselectively [eqn. (3)]. The relative composition of the two types of repeat units corresponding to **A** and **B** in **3aa** was determined to be **A** : **B** = 1.1 by using a ^{1}H NMR relative peak area of the signal at δ 5.70 (a vinylene-type proton) to the signal at δ 4.19 (two protons of a methylene group connecting two phenylenes). This value was the same as that obtained from the model reaction.

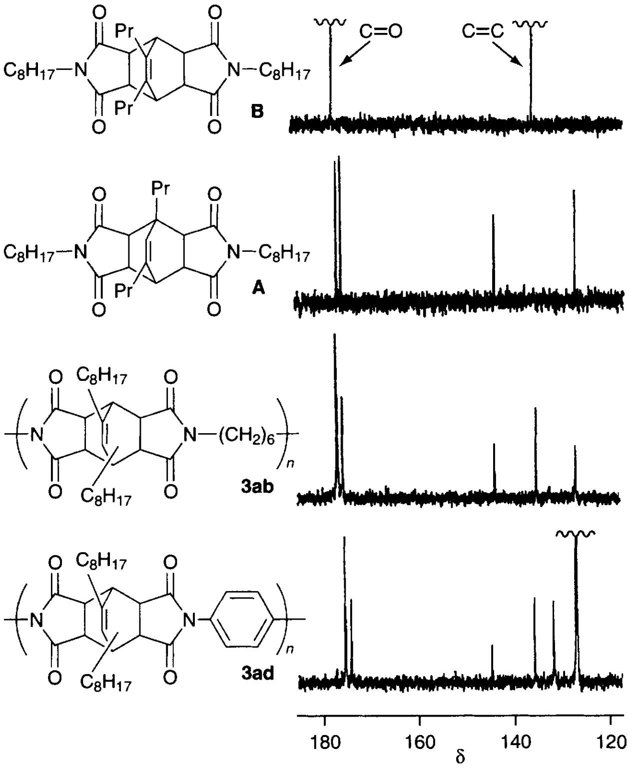
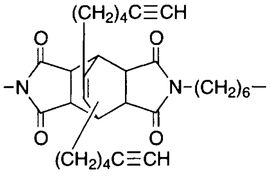
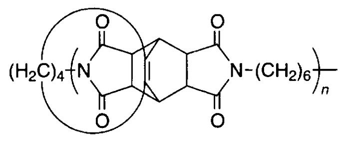


Fig. 1 ^{13}C NMR (CDCl$_3$) C=O and C=C signals of poly(imide)s **3ab** and **3ad** together with model compounds **A** and **B**



C



3db

Unique poly(imide)s were also formed. Octa-1,7-diyne **1d** acted as two monoyne molecules to produce the soluble poly(imide) **3db** containing pendant cyclohexene rings formed by a regioselective intramolecular cyclisation of **1d** without the formation of an alkynyl-substituted bicyclo[2.2.2]oct-7-ene structure **C**, which may generate a cross-link to produce an insoluble copolymer. An alkyne with an electron-releasing functional group could be used: ethoxyacetylene **1e** copolymerised with **2b** to produce **3eb** with a vinyl ether moiety. Poly(imide) **3eb** had a repeat unit containing a regioselectively formed 1,8-diethoxy-substituted bicyclo[2.2.2]oct-7-ene ring. In contrast, but-3-yn-2-one, *i.e.* an alkyne with an electron-withdrawing group, did not undergo copolymerisation.

The thermal stability of **3** was examined by thermogravimetric analysis (TGA) in air. T_{10}, the temperature causing a 10% mass loss, was 341, 362 and 343 °C for **3aa**, **3ad** and **3ae**, respectively.

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Footnote

† All reported M_n and M_w values were relative to polystyrene standards as determined by GPC in chloroform.

References

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