

Ni-complex-catalysed addition polymerisation of 2-phenyl-1-methylenecyclopropane to afford a polymer with cyclopropylidene groups†

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Received (in Cambridge, UK) 2nd January 2002, Accepted 8th February 2002

First published as an Advance Article on the web 25th February 2002

π -Allyl-nickel complexes initiated addition polymerisation of 2-phenyl-1-methylenecyclopropane to give a polymer with three-membered rings; the formed polymer showed a high T_g and negligible thermal decomposition up to 300 °C.

Cyclic alkenes such as dialkylcyclopropene and cyclobutene undergo metal-complex-promoted addition polymerisation^{1,2} or ring-opening polymerisation,³ in which the release of ring strain caused by the reaction acts as the major driving force. Methylenecyclopropanes, also with a highly strained structure, have been reported to undergo metal-complex-catalysed ring-opening polymerisation rather than simple addition polymerisation.^{4,5} In this paper, we report the Ni-catalysed polymerisation^{6,7} of 2-phenyl-1-methylenecyclopropane to afford a new polymer with phenylcyclopropylidene groups, and having good thermal stability.

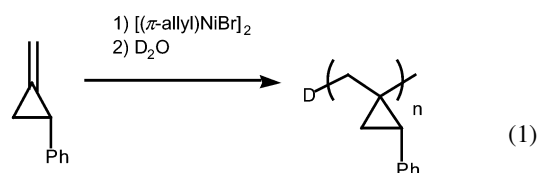
$[(\pi\text{-allyl})\text{NiBr}]_2$ promoted addition polymerisation of 2-phenyl-1-methylenecyclopropane ([monomer]:[Ni] = 70) at room temperature to give polymer **I** that contained a cyclopropylidene group in every repeating unit.⁸ Table 1 summarises the results of polymerisation. The polymerisation proceeded smoothly in toluene, THF, NMP, and CH_2Cl_2 . The reaction with a molar ratio of [monomer]:[Ni] = 200 at -40 °C afforded **I** with $M_n = 29\,000$ and $M_w/M_n = 1.59$ (run 3), while the reaction at room temperature produced the polymer with a lower molecular weight. Since 2-methylbut-1-ene is not polymerised by $[(\pi\text{-allyl})\text{NiBr}]_2$, the strained cyclopropane ring promotes the polymerisation of 2-phenyl-1-methylenecyclopropane. The polymerisation with a bulky diimine ligand, whose Ni complexes catalyse the polymerisation of ethylene and α -olefins,^{6,9} gave **I** in lower yield than the reaction without the addition of the ligand (run 4). Cationic nickel complexes, prepared *in situ* by the reaction of $[(\pi\text{-allyl})\text{NiBr}]_2$ with AgPF_6 ([Ni]:[Ag] = 1:1.2) in the presence of ligands (cod, diimine), also promoted the polymerisation (runs 5–7). The molecular weight of the polymer is almost similar to those obtained by the neutral Ni complex (run 1).

The $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **I** and the spectrum under DEPT conditions (Fig. 1) revealed unambiguously the structure

† Electronic supplementary information (ESI) available: full details of the experimental procedures, DSC and TG profile of **I**. See <http://www.rsc.org/suppdata/cc/b1/b111697e/>

shown below.¹⁰ The absence of $^{13}\text{C}\{^1\text{H}\}$ NMR signals in the region of δ 100–120 indicates that the polymer does not contain any olefinic groups formed *via* C–C bond cleavage of the three-membered ring. The CH_2 carbon signal of the polymer chain and that of the three-membered ring at the respective positions, δ 31–48 and δ 12–23, are inverted under DEPT (135° pulse) conditions (Fig. 1(C)). Assignment of the latter signal was confirmed from the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of the polymer obtained from 2-phenyl-1-methylene-3- ^{13}C -cyclopropane (**I**- ^{13}C).¹¹ The existence of four stereoisomers for each monomer unit of the polymer and the rigidity of the polymer chain (*vide infra*) make these signals broad. The signal of the quaternary carbon of the polymer chain (δ 25) is observed as a single sharp signal in the difference spectrum of $^{13}\text{C}\{^1\text{H}\}$ and DEPT (45° pulse) spectra (Fig. 1(D)), although it severely overlaps with the CH carbon peaks (δ 23–31) in the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum. The sharp and intense signal of the quaternary carbon is attributed to a well-regulated head-to-tail linkage of the monomer units.

The reaction of 2-phenyl-1-methylenecyclopropane with $[(\pi\text{-allyl})\text{NiBr}]_2$ in a molar ratio of [monomer]:[Ni] = 5, followed by the addition of D_2O , produced the polymer whose ^2H NMR spectrum showed a single signal at 1.8 ppm, which was assigned to the $-\text{CH}_2\text{D}$ end group (eqn. 1).



The regulated head-to-tail linkage of the monomer units of **I**, as revealed by $^{13}\text{C}\{^1\text{H}\}$ NMR spectroscopy as well as results of the end group analysis, suggests that the polymerisation proceeds *via* successive 1,2-insertion of 2-phenyl-1-methylenecyclopropane to an alkyl–nickel bond of the growing polymer (Scheme 1). This mechanism is in contrast to the ring-opening polymerisation of 2-phenyl-1-methylenecyclopropane by Pd complexes, where the polymerisation proceeds *via* 2,1-insertion of the monomer to the π -allyl–Pd bond accompanied by C–C bond cleavage of the three-membered ring.⁵

Differential scanning calorimetry (DSC) analysis of **I** (obtained in run 3 of Table 1) revealed a glass transition temperature of 178 °C, which is higher than those of many other

Table 1 Polymerisation of 2-phenyl-1-methylenecyclopropane by nickel complexes^a

Run	Ni complex	Ligand	Solvent	Temp/°C	Time/h	Yield (%)	M_n^b	M_w/M_n^b
1	$[(\pi\text{-allyl})\text{NiBr}]_2$	None	Toluene	rt	3	83	5 700	1.88
2	$[(\pi\text{-allyl})\text{NiBr}]_2$	None	THF	-40	12	Quant.	8 500	1.95
3 ^c	$[(\pi\text{-allyl})\text{NiBr}]_2$	None	THF	-40	24	Quant.	29 000	1.59
4	$[(\pi\text{-allyl})\text{NiBr}]_2$	$\text{ArN}=\text{CH}-\text{CH}=\text{NAr}^d$	Toluene	rt	3	49	4 700	1.75
5	$[(\pi\text{-allyl})\text{NiBr}]_2 + \text{AgPF}_6^e$	cod	THF	rt	3	Quant.	4 000	1.79
6	$[(\pi\text{-allyl})\text{NiBr}]_2 + \text{AgPF}_6^e$	cod	Toluene	rt	3	Quant.	4 600	1.99
7	$[(\pi\text{-allyl})\text{NiBr}]_2 + \text{AgPF}_6^e$	$\text{ArN}=\text{C}(1,8\text{-C}_{10}\text{H}_8)\text{C}=\text{NAr}^d$	THF	rt	3	17	5 200	1.84

^a Reaction conditions: [Ni] = 25 mM, [2-phenyl-1-methylenecyclopropane] = 1.8 M unless otherwise stated. ^b Determined by GPC in THF vs. polystyrene standards. ^c [Ni] = 25 mM, [2-phenyl-1-methylenecyclopropane] = 5.0 M. ^d Ar = $\text{C}_6\text{H}_3(\text{iPr})_2\text{-2,6}$. ^e [Ni]:[Ag] = 1:1.2.

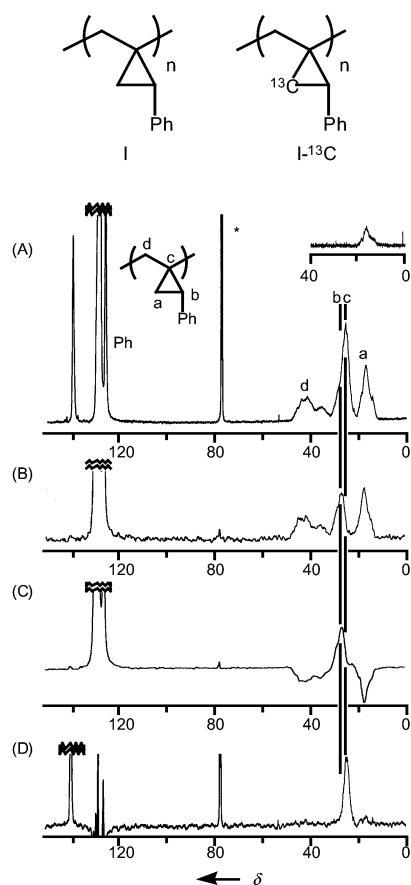
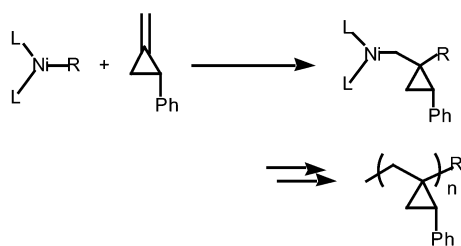


Fig. 1 (A) $^{13}\text{C}\{^1\text{H}\}$ NMR and DEPT NMR spectra ((B) 45° pulse, (C) 135° pulse) of **I** in CDCl_3 at 25°C . The difference spectrum of (B) is shown in (D). The $^{13}\text{C}\{^1\text{H}\}$ NMR signal of **I- ^{13}C** is shown in the inset. The signal marked by an asterisk is due to solvent impurity.



Scheme 1 A plausible mechanism of polymerisation of 2-phenyl-1-methylenecyclopropane by Ni complexes.

known hydrocarbon polymers, such as thermally resistant syndiotactic polystyrene.^{12,13} The results indicate a rigid polymer chain that serves to render the CH_2 and CH carbon signals of the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum broad. The polymer did not decompose up to 300°C in the thermogravimetric (TG) analysis of **I**.¹⁴ Thus, the produced polymer has good thermal stability.

In conclusion, we have demonstrated that Ni-complex-catalysed addition polymerisation of 2-phenyl-1-methylenecy-

clopropane produces a polymer with a new structure and high thermal stability owing to the presence of rigid phenyl-cyclopropylidene groups. The polymerisation without ring opening of the growing polymer is caused by smooth repetition of the 1,2-insertion of the monomer that occurs more rapidly than the possible β -alkyl elimination of the cyclopropylmethylnickel intermediate.^{5,15}

This work was supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Culture, Sports, Science and Technology.

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