COMMUNICATION

ChemComm
www.rsc.org/chemcomm

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

Daisuke Takeuchi and Kohtaro Osakada*

Chemical Resources Laboratory, Tokyo Institute of Technology, 4259, Nagatsuta-cho, Midori-ku, Yokohama, Japan. E-mail: kosakada@res.titech.ac.jp; Fax: +81-45-924-5224; Tel: +81-45-924-5224

Received (in Cambridge, UK) 2nd January 2002, Accepted 8th February 2002
First published as an Advance Article on the web 25th February 2002

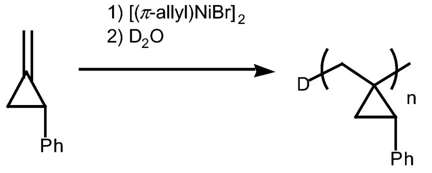
π-Allyl-nickel complexes initiated addition polymerisation of 2-phenyl-1-methylenecyclopropane to give a polymer with three-membered rings; the formed polymer showed a high T_g and negligible thermal decomposition up to 300 °C.

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.

[(π-Allyl)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 [(π-allyl)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 [(π-allyl)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 $^{13}C\{^1H\}$ NMR spectrum of **I** and the spectrum under DEPT conditions (Fig. 1) revealed unambiguously the structure shown below.[10] The absence of $^{13}C\{^1H\}$ 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 $^{13}C\{^1H\}$ 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 $^{13}C\{^1H\}$ and DEPT (45° pulse) spectra (Fig. 1(D)), although it severely overlaps with the CH carbon peaks (δ 23–31) in the $^{13}C\{^1H\}$ 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 [(π-allyl)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 $-CH_2D$ end group (eqn. 1).



(1)

The regulated head-to-tail linkage of the monomer units of **I**, as revealed by $^{13}C\{^1H\}$ 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]

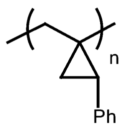
Run	Ni complex	Ligand	Solvent	Temp/°C	Time/h	Yield (%)	M_n[b]	M_w/M_n[b]
1	[(π-allyl)NiBr]$_2$	None	Toluene	rt	3	83	5 700	1.88
2	[(π-allyl)NiBr]$_2$	None	THF	−40	12	Quant.	8 500	1.95
3[c]	[(π-allyl)NiBr]$_2$	None	THF	−40	24	Quant.	29 000	1.59
4	[(π-allyl)NiBr]$_2$	ArN = CH-CH = NAr[d]	Toluene	rt	3	49	4 700	1.75
5	[(π-allyl)NiBr]$_2$ + $AgPF_6$[e]	cod	THF	rt	3	Quant.	4 000	1.79
6	[(π-allyl)NiBr]$_2$ + $AgPF_6$[e]	cod	Toluene	rt	3	Quant.	4 600	1.99
7	[(π-allyl)NiBr]$_2$ + $AgPF_6$[e]	ArN = C(1,8-$C_{10}H_8$)C = 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 = $C_6H_3(^iPr)_2$-2,6. [e] [Ni] : [Ag] = 1 : 1.2.

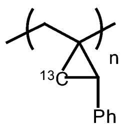
---

† 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/

DOI: 10.1039/b111697e



I



I-^{13}C

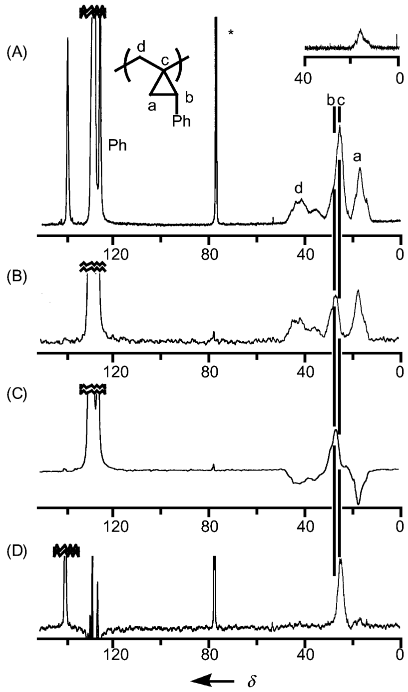
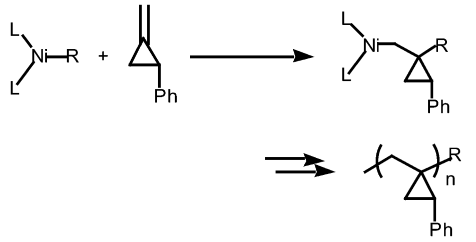


Fig. 1 (A) $^{13}C\{^1H\}$ NMR and DEPT NMR spectra ((B) 45° pulse, (C) 135° pulse) of **I** in $CDCl_3$ at 25 °C. The difference spectrum of (B) from (A) is shown in (D). The $^{13}C\{^1H\}$ NMR signal of **I**-^{13}C is shown in the inset. The signal marked by an asterisk is due to solvent impurity.



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 $^{13}C\{^1H\}$ 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-methylenecyclopropane produces a polymer with a new structure and high thermal stability owing to the presence of rigid phenylcyclopropylidene 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.

Notes and references

1 Addition polymerisation of cyclobutene by Ziegler–Natta catalyst: G. Natta, G. Dall′Asta, G. Mazzanti and G. Motroni, *Makromol. Chem.*, 1963, **69**, 163; G. Dall′Asta, *J. Polym. Sci., Part A1*, 1968, **6**, 2397; V. A. Kormer, I. A. Poletayeva and T. L. Yufa, *J. Polym. Sci., Part A1*, 1972, **10**, 251.

2 Addition polymerisation of cyclopropenes: K. B. Wiberg and W. J. Bartley, *J. Am. Chem. Soc.*, 1960, **82**, 6375; S. Rush, A. Reinmuth, W. Risse, J. O′Brien, D. R. Ferro and I. Tritto, *J. Am. Chem. Soc.*, 1996, **118**, 12230; ; Polymerisation of cyclopentene by Pd and Ni complexes has also been reported: S. J. McLain, J. Feldman, E. F. McCord, K. H. Gardner, M. F. Teasley, E. B. Coughlin, K. J. Sweetman, L. K. Johnson and M. Brookhart, *Macromolecules*, 1998, **31**, 6705.

3 Ring-opening polymerisation of dialkylcyclobutene by transition metal catalysts: G. Dall′Asta, G. Mazzanti, G. Natta and L. Porri, *Makromol. Chem.*, 1962, **56**, 224; B. R. Maughon and R. H. Grubbs, *Macromolecules*, 1997, **30**, 3459.

4 L. Jia, X. Yang, A. M. Seyam, I. D. L. Albert, P-F. Fu, S. Yang and T. J. Marks, *J. Am. Chem. Soc.*, 1996, **118**, 7900.

5 D. Takeuchi, S. Kim and K. Osakada, *Angew. Chem., Int. Ed.*, 2001, **40**, 2685.

6 Ni complex catalysed polymerisation of olefins: S. D. Ittel, L. K. Johnson and M. Brookhart, *Chem. Rev.*, 2000, **100**, 1169; G. J. P. Britovsek, V. C. Gibson and D. F. Wass, *Angew. Chem., Int. Ed.*, 1999, **38**, 428; S. Mecking, *Coord. Chem. Rev.*, 2000, **203**, 325.

7 Reaction of Ni complexes with methylenecyclopropane: P. Binger, A. Brinkmann and J. McMeeking, *Liebigs Ann. Chem.*, 1977, 1065. Recently, nickel complexes with diimine ligands were found to bring about addition polymerisation of cyclopentene; see ref. 2.

8 The ring strain relieved upon hydrogenation of the double bond in methylenecyclopropane has been reported to be 53.6 kcal mol^{-1}: P. Binger and H. M. Büch, *Top. Curr. Chem.*, 1987, **135**, 77.

9 R. F. de Souza, R. S. Mauler, L. C. Simon, F. F. Nunes, D. V. S. Vescia and A. Cavagnolli, *Macromol. Rapid Commun.*, 1997, **18**, 795.

10 Selected NMR data of the structurally related compound: 1,1-dimethyl-2-phenylcyclopropane: ^1H NMR ($CDCl_3$): δ 0.81, 0.84 (2H, m, CH_2), 0.85 (3H, s, CH_3), 1.28 (3H, s, CH_3), 1.93 (1H, m, CH), and 7.18–7.34 (5H, m, Ph). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 18.3 (CH_2), 19.0 (C), 20.3 (CH_3), 27.4 (CH_3), 29.7 (CH), 125.4 (*p*-Ph), 127.8, 128.9 (*o*, *m*-Ph), and 140.3 (*ipso*-Ph).

11 The purity of ^{13}C of the monomer is *ca.* 99%.

12 N. Ishihara, M. Kuramoto and M. Uoi, *Macromolecules*, 1988, **21**, 3356.

13 A hydrocarbon polymer with a cycloalkanediyl moiety in the main chain has been reported to show the highest glass-transition temperature among hydrocarbon polymers (231 °C). See: I. Natori, K. Imaizumi, H. Yamagishi and M. Kazunori, *J. Polym. Sci., Part B: Polym. Phys.*, 1998, **36**, 1657.

14 Thermal weight loss of **I** (obtained in run 3 of Table 1) in 5% is observed at 353 °C.

15 S. Hajela and J. E. Bercaw, *Organometallics.*, 1994, **13**, 1147.