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Ring opening metathesis polymerization of 2,3-diazanorborn-5-ene derivatives

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Abstract

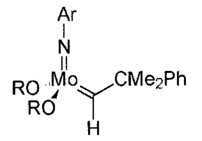
The synthesis and polymerization of 2,3-diazanorborn-5-enes are reported. Reaction of 2,3-diazanorborn-5-ene derivatives **6**–**9** with molybdenum based initiators **1**–**3** leads, in most cases to ring opening metathesis polymerization. By contrast, monomers **6**–**9** are not polymerized by ruthenium based initiator **4**. The polymers were characterized by NMR, GPC and MALDI-TOF mass spectrometry and were found to have narrow molecular weight distributions and to show a resonance attributable to a propagating alkylidene in the ^{1}H NMR spectrum. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Ring opening metathesis polymerization; 2,3-diazanorborn-5-ene; Living polymer

1. Introduction

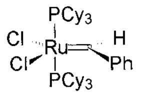
In recent years, there has been much interest in the preparation of polymers with well defined molecular architectures by the ring opening metathesis polymerization (ROMP) of norbornene derivatives [1]. The discovery that metal alkylidene complexes based on molybdenum [2] (e.g. **1**–**3**), ruthenium [3,4] (e.g. **4**) or other metals could initiate such polymerization and allow control over the molecular weight, molecular weight distribution and *cis*/*trans* ratio, as well as permitting the synthesis of block copolymers and tolerating the presence of functional groups, have allowed much progress to be made in this area. In recent publications, we have reported the synthesis and the ROMP of norbornene derivatives of general structure **5** where R is derived from a biologically relevant amino acid [5–7], peptide [8], or nucleic acid derivative [9].

Now we have investigated the ROMP of 2,3-diazanorborn-5-ene derivatives **6**–**9**. These monomers are readily prepared [10–14], and previous work has shown that compounds **6** and **7** exist predominantly as an interconverting mixture of the two *trans*-conformations, whilst imides **8** and **9** exist as an equilibrium mixture of *endo*- and *exo*-isomers [15–18]. Thus it was anticipated that for each monomer, polymerization could occur through a sterically unhindered *exo*- or *trans*-conformation. In addition, the replacement of two CH units by nitrogen atoms was expected to result in the production of polymers with simplified NMR spectra which would aid in tacticity assignments. Finally, there are no previous reports of the ROMP of diazanorbornene derivatives.



Ar= 2,6-diisopropyl phenyl

1 R= Me_3C
2 R= $Me_2(CF_3)C$
3 R= $Me(CF_3)_2C$



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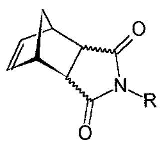

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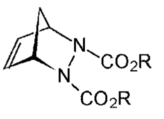
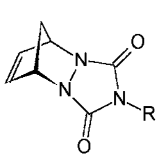


6 R= Et
7 R= Bu^t



8 R= Ph
9 R= Me

2. Results

The polymerization of monomers **6**–**9** was initially

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Table 1
Characterization of polymers derived from monomers **6**–**9**

Monomer	Initiator	δ_H M=CH (ppm)	%-*trans*[a]	M_n[b]	M_w[b]	PDI	T_g (°C)	Yield (%)
6	**1**	Incomplete polymerization						
6	**2**	11.05	31	42 500	53 600	1.26	70	82
6	**3**	11.65	16	26 300	33 100	1.26	72	93
7	**1**	10.55	86	10 300	11 300	1.10	97	100
7	**2**	11.04	34	33 000	39 400	1.19	117	100
7	**3**	11.57	16	18 900	25 900	1.37	87	100
8	**1**	No polymerization						
8	**2**	Incomplete polymerization						
8	**3**	12.38	11	2 717	2 934	1.08	209	91
9	**1**	No polymerization						
9	**2**	Incomplete polymerization						
9	**3**	12.37	13	Abnormal elution from GPC columns19791				

[a] Determined by ^{1}H NMR.

[b] M_n and M_w values for polymers derived from monomers **6** and **7** were determined by GPC analysis of the polymers prepared using a monomer to initiator ratio of between 30 and 100:1 and are referenced to polystyrene standards (374 to 1×10^6 amu). GPC was conducted using a Viscotek T60 dual detector fitted with a Viscotek DG-700 pump and two PSS SDV 10 μm linear columns. Chloroform was used as an eluent at a flow rate of 1 ml/min. M_n and M_w values for the polymer derived from monomer **8** were determined by MALDI-TOF mass spectrometry on the polymer prepared using a 10:1 monomer to initiator ratio as this polymer eluted abnormally during GPC analysis. MALDI-TOF analyses were carried out using a matrix composed of 3-β-indole acrylic acid dissolved in 1:1 water/acetonitrile and a laser power of between 90 and 95. The polymer derived from monomer **9** also eluted abnormally during GPC analysis using $CHCl_3$ or DMSO (at 80°C using a PL GPC210 instrument fitted with two PLgel 10 μm mixed bed—B columns and a flow rate of 1 ml/min) as solvents and did not give molecular ion peaks when analyzed by MALDI-TOF mass spectrometry.

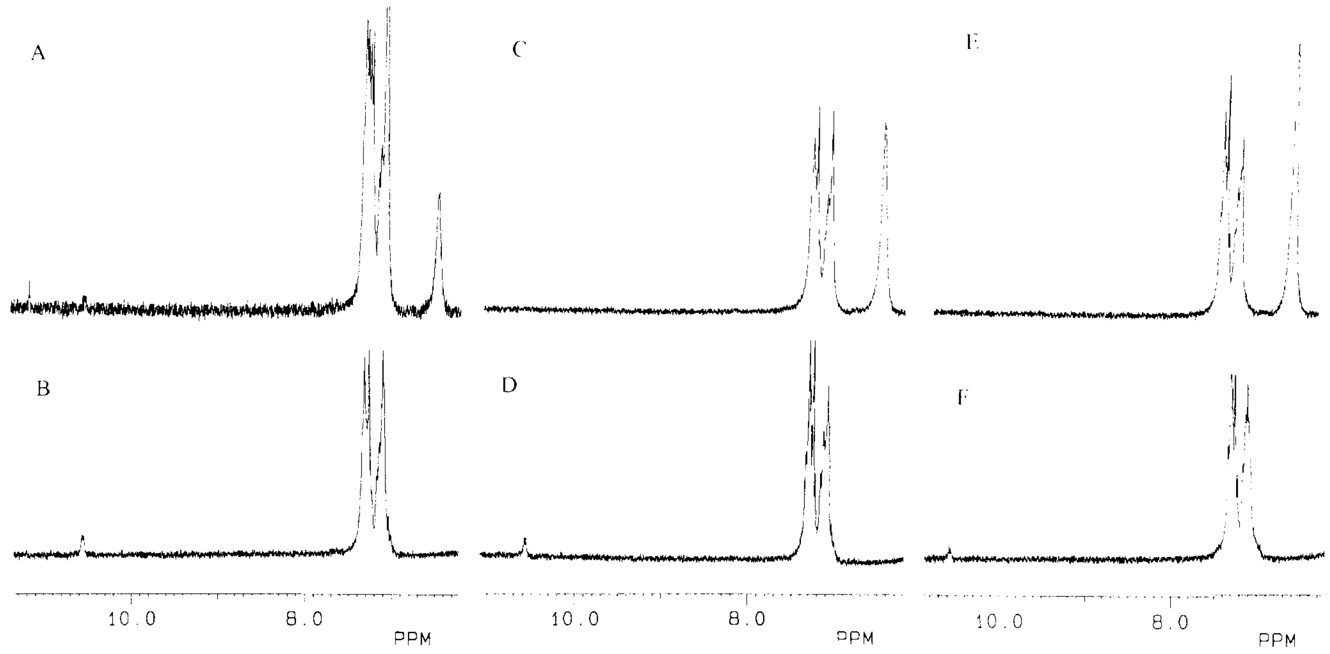

Fig. 1. ^{1}H NMR spectra following the polymerization of monomer **7** by initiator **1** showing the disappearance and reappearance of the propagating alkylidene signal at 10.6 ppm. (The HC=Mo resonance of **1** occurs at 11.2 ppm, the HC=Mo resonance of the propagating alkylidene occurs at 10.6 ppm, the olefinic hydrogens of compound **7** occur at 6.7 ppm. A: 10 min after adding 3 equivalents of **7** to initiator **1**. B: After 165 min. C: 5 min after the addition of a further 3 equivalents of **7** to B. D: After a further 180 min. E: 5 min after the addition of a further 3 equivalents of **7** to D. F: After a further 150 min.)

carried out using ca. 10 mol% of the initiators **1**–**4** in $CDCl_3$. In those cases where a propagating alkylidene signal was observed by ^1H NMR spectroscopy, the polymerizations were repeated using a 100:1 monomer to initiator ratio (using dichloromethane as solvent) and capping the growing polymers with benzaldehyde;[1] the results are collected in Table 1. Only the most reactive initiator, **3**, polymerized all of monomers **6**–**9**. The less reactive initiator **2**, polymerized only monomers **6** and **7**, and the least reactive molybdenum based initiator **1** did not polymerize monomers **8** and **9**, and only partly polymerized monomer **6**. The ruthenium based initiator **4** did not polymerize any of the monomers.

In each case where complete polymerization occurred, a resonance attributable to the hydrogen of the propagating alkylidene was detected between 10.6 and 12.4 ppm in the ^1H NMR spectrum of the polymerization mixture, and the isolated polymers had narrow molecular weight distributions. Curiously, for the combination of monomer **6** with initiator **2** or monomer **7** with initiator **1**, a propagating alkylidene signal was observed only after all of the monomer was consumed. If further monomer was subsequently added to the polymerization reaction, the propagating alkylidene signal again disappeared and reappeared once polymerization was complete as shown in Fig. 1. A possible explanation for this is that the rate of polymerization approximately corresponds to the NMR time scale, causing the alkylidene signal to be broadened until polymerization is complete. For monomers **6** and **7**, no unreacted initiator was detected by NMR provided that more than three equivalents of monomer were used. This indicates that for these monomers K_i is comparable to K_p, whilst for monomers **8** and **9** unreacted initiator was detected by NMR suggesting that K_i is much less than K_p. The proportion of *trans* double bonds in the polymers decreases as the number of fluorine atoms in the initiator is increased, an effect which has previously been observed for other monomers [1,2]. Thermogravimetric analysis revealed T_gs of approximately 70°C for poly-**6** and 200°C for the poly-imides poly-**8**,**9**. For poly-**7**, the T_g does not seem to be related to the *trans*-alkene content of the polymer.[2]

3. Conclusions

2,3-Diazanorborn-5-ene derived compounds **6**–**9** are suitable monomers for ROMP using the molybdenum based initiators **2**–**3**. The monomers are polymerized by a living process to give polymers with a narrow molecular weight distribution. The ruthenium based initiator **4** does not polymerize these monomers.

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[1] Typical experimental procedure: Monomers **6**–**9** (ca. 0.1 g) were first dried by filtration through activated alumina, then dissolved in dichloromethane (2 ml) and a solution of initiators **1**–**3** (typically 5 mg) in dichloromethane (1 ml) was added. The reaction mixture was stirred at room temperature for a specified time before being terminated by the addition of excess benzaldehyde (70 μl). The reaction mixture was stirred for a further 10 min and then poured into hexane (100 ml) to give the polymer as a fibrous solid precipitate. The polymers derived from monomer **7** are soluble in hexane, hence in these cases the terminated polymerization reaction was passed through a column of silica gel, eluting with dichloromethane. Solvents were then removed in vacuo to leave the polymer as a brittle glass-like solid.

[2] Full details of the spectroscopic, analytical, and physical properties of polymers derived from monomers **6**–**9** will be reported in a subsequent paper.