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Priority communication

Organosulfur compounds as promoters in the $Mo(CO)_6$-catalyzed ring opening metathesis polymerization of norbornenes

Chung-Wai Shiau, Jitendra A. Sattigeri, Clifton K.-F. Shen, Tien-Yau Luh *

Department of Chemistry, National Taiwan University, Taipei 106, Taiwan, ROC

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Abstract

Thioethers, dithioacetals and thioketones, but not mercaptans, are active promoters for the Group 6 metal carbonyl-catalyzed ring opening metathesis polymerization (ROMP) of norbornenes. © 1999 Elsevier Science S.A. All rights reserved.

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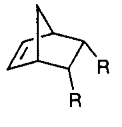
Group 6 metal carbonyls are thiophilic reagents to promote homolytic cleavage of the carbon–sulfur bond [1,2]. A sulfur-containing metallic product is suggested [2]. Some of these metallic intermediates are highly reactive [2,3], and it is envisaged that such species may serve as an active catalyst for further reactions. Recently, haloalkanes are found to be promoters for the $Mo(CO)_6$-mediated metathesis reactions under photolytic conditions [4]. Phenols [5] and various Lewis acids [6] are also known to facilitate Group 6 metal carbonyl-catalyzed metathesis reactions. The authors felt that the sulfur-containing species generated in situ from the Group 6 metal carbonyl-mediated desulfurization reaction may also serve as an efficient olefin metathesis catalyst.

At the beginning of this investigation, a chlorobenzene solution of **1a** with 0.3 mol% each of $Mo(CO)_6$ and 2,2-diphenyldithiolane was heated under reflux for 10 min (entry 1). Rubber-like solid **2a** was formed immediately and the M_n is 45 K (PDI = 3.1). The NMR spectrum of this polymer is consistent with the corresponding ring opening metathesis polymerization (ROMP) of **1a** prepared by Grubbs's ruthenium carbene catalyst [7]. Table 1 summarizes representative results of the ROMP of **1** under different conditions. It is noteworthy that the reaction does not proceed in the absence of the organosulfur compound. The reaction can proceed in the dark, no irradiation being required under these conditions.



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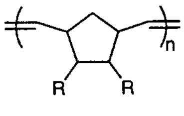

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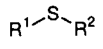
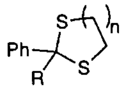
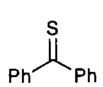


3 a $R^1 = R^2 = Pr$
b $R^1 = Bn$, $R^2 = Et$



4 a R = Ph, n = 1
b R = Ph, n = 2
c R = H, n = 1



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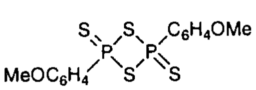

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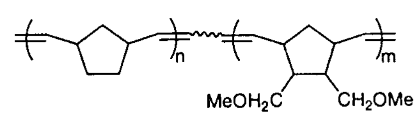

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* Corresponding author. Fax: + 886-2-2364-4971.

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Table 1
Organosulphur compound-promoted M(CO)$_6$-catalyzed ROMP of **1**

Entry	**1**	Promoter	M(C0)$_6$	Solvent	Reaction time	**2** (%yield)	$M_n/10^4$ (PDI)	E/Z
1	**a**	**4a**	Mo	PhCl	10 min	**a** (95)	4.5 (3.1)	1/1
2	**a**	**4a**	W	PhCl	30 min	**a** (72)	4.8 (2.4)	1/1
3	**a**	**4a**	Mo	THF	15 h	**a** (30)	5.0 (2.7)	1/2
4	**a**	**4b**	Mo	THF	5 h	**a** (45)	9.7 (2.1)	1/3
5	**a**	**3a**	Mo	THF	5 h	**a** (25)	1.2 (5.6)	1/1.5
6	**a**	**3b**	Mo	PhCl	20 min	**a** (78)	11.9 (1.9)	1/1
7	**a**	**3b**	Mo	THF	5 h	**a** (23)	6.2 (3.3)	1/2
8	**a**	**5**	Mo	PhCl	20 min	**a** (85)	8.9 (2.7)	1/1
9	**a**	**5**	Mo	THF	10 h	**a** (32)	3.3 (6.4)	1/2
10	**a**	**6**	Mo	PhCl	30 min	**a** (74)	5.3 (3.1)	1/1
11	**a**	**6**	Mo	THF	10 h	**a** (59)	15.2 (1.7)	1/2.5
12	**b**	**4c**	Mo	PhCCl$_3$	4 h	**b** (43)	14.5 (2.2)	1/1

As can be seen from Table 1, thioethers **3**, dithioacetals **4** as well as thioketones **5** were active promoters for the Mo(CO)$_6$-catalyzed ROMP of **1**. Lawesson reagent **6**, which contains phosphorus–sulfur double bond, was also an active promoter. W(CO)$_6$ appeared to be less reactive, with a longer reaction time being required (entry 2). The reaction can also be carried out in ethereal solvents. Although a higher temperature will shorten the reaction time and increase the yield of **2**, better Z-selectivity was slightly favored when the reaction was carried out in refluxing THF (entries 3–5, 7, 9 and 11).

Substituted norbornene such as **1b** was less reactive. Elevated temperature (refluxing chlorobenzene or trichlorotoluene) was required for a smooth transformation (entry 12). When a solution of **1b** was heated with 1 mol% of Mo(CO)$_6$ and **4a** in chlorobenzene under reflux for 1 h followed by addition of one equivalent of **1a** and refluxed for an additional 5 h, a block copolymer **7** ($M_n = 1.1 \times 10^5$ and PDI = 2.3) was obtained and the ratio of the constituent monomeric moieties rising from **1b** and **1a** was 1.3: 1.

Mercaptans were inactive for these reactions. It is known that the carbon–sulfur bond in mercaptans can be reduced via a radical mechanism under these conditions and the S–H moiety provides the hydrogen source for the radical abstraction [1]. It was felt that other hydrogen source that can be abstracted by a radical may also prohibit the reaction. Indeed, when the reaction was carried out in diglyme under reflux, no ROMP of **1a** was observed. Presumably, the C–H bonds in diglyme can undergo radical abstraction under these conditions [1]. Elemental sulfur was ineffective for this catalytic process.

Although the actual mode of the reaction remains unclear, a sulfur containing species is speculated. Treatment of **4a** with Mo(CO)$_6$ in refluxing chlorobenzene yielded, in addition to tetraphenylethylene, an insoluble and very air-sensitive black species **8** that exhibited broad absorptions for the carbonyl moieties (1945–2000 cm^{-1}) in the IR region. When **8** was treated with NaOH followed by acidification, hydrogen sulfide was liberated. It is noteworthy that **8** can also serve as a catalyst for the ROMP of norbornene. For example, **2** was obtained in excellent yield with a similar M_n (ca. 45 000) when **1a** was treated with **8** in refluxing chlorobenzene for 10 min.

In summary, the authors have depicted for the first time that an organosulfur compound can serve as a promoter for the Group 6 metal carbonyl-catalyzed ROMP of norbornenes. Investigations on the nature of this catalytic system and extension to other cyclic olefinic substances are in progress.

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