

# Cyclopolymerization of dimethyl dipropargylmalonate in supercritical carbon dioxide to give a highly regular polyene containing predominantly five-membered rings†

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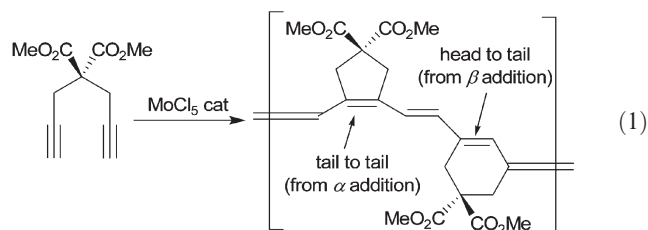
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Poly(dimethyl dipropargylmalonate) synthesized in  $\text{scCO}_2$  contained more than 95% five-membered rings, *i.e.*, highly regular polyene was produced, which shows carbon dioxide as a reaction medium plays a significant role in determining a highly selective polymer structure.

The use of supercritical carbon dioxide ( $\text{scCO}_2$ ) as a solvent for polymerization is attractive because of its low toxicity, cost and nonflammability.<sup>1</sup> The literature has reflected an intensive interest in metal-catalyzed olefin metathesis polymerization in  $\text{scCO}_2$ .<sup>2</sup> However, few examples of substituted acetylene polymerization in  $\text{scCO}_2$  have been reported.<sup>3</sup> 1,6-Heptadiyne is a very interesting example of substituted acetylenes, which can be susceptible to ring-forming polymerization to give a new type of conjugated polymer backbone system.<sup>4–6</sup> The cyclopolymerization of 1,6-heptadiynes containing appropriate substituents at the 4-position has been investigated over the past four decades by both a classical metathesis catalyst and a well-defined alkylidene initiator, producing a mixture of five- and six-membered rings as a consequence of the first terminal triple bond adding to an alkylidene to give either an  $\alpha$ - or a  $\beta$ -substituted metallacyclobutene intermediate ( $\alpha$ - or  $\beta$ -addition, respectively; eqn (1)).<sup>5,6</sup>



Schrock's group has reported that well-defined high oxidation-state molybdenum carbenes cyclopolymerize 1,6-heptadiynes in a living manner to produce polyenes that contain either a mixture of five- and six-membered rings<sup>4</sup> or exclusively six-membered rings.<sup>6</sup> Recently, Nuyken and co-workers<sup>7</sup> have reported cyclopolymerization with both well-defined molybdenum-based initiators such as  $\text{Mo}(\text{N}-2,6\text{-}i\text{-Pr}_2\text{C}_6\text{H}_3)(\text{CHCM}_2\text{Ph})(\text{OC}(\text{CH}_3)_2)_2$ -quinuclidine and with classical metathesis catalysts such as  $\text{MoCl}_5$ - $n\text{-Bu}_4\text{Sn}$ -ethanol-quinuclidine, to produce >95% five-membered rings.

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Cyclopolymerization leading to only five-membered rings has also been accomplished using  $\text{Mo}(\text{CO})_6$ .<sup>8</sup> All these approaches have been focused on the effect of initiator types on the properties of the polymer. Unfortunately, the literature has paid little attention to the effect of solvent on their structure.<sup>4b,5a</sup> Chemical interactions of  $\text{scCO}_2$  with substrates and/or catalysts offer an as yet largely unexplored potential for activity and selectivity control.<sup>9</sup>

We report for the first time the cyclopolymerization of dimethyl dipropargylmalonate (DMDPM) by  $\text{MoCl}_5$ -based metathesis catalysts in  $\text{scCO}_2$ , which encourages the regioselective addition of the first triple bond to an alkylidene. This results in an  $\alpha$ -substituted metallacyclobutene and therefore polyenes that contain predominately five-membered rings in the polymer backbone occur due to the chemical interaction of  $\text{scCO}_2$  with the transition-metal metathesis catalysts.

Full details of general polymerization procedures in supercritical fluid conditions was described in our previous reports.<sup>10</sup> DMDPM is completely soluble in  $\text{scCO}_2$ .<sup>11</sup> However, poly(DMDPM) is essentially insoluble in  $\text{scCO}_2$  even at low molecular weight ( $M_n = 8000$ ), in the range of temperature and pressure investigated in the work. For comparison, the polymerizations of DMDPM were carried out in various solvents, such as 1,4-dioxane,  $\text{CH}_2\text{Cl}_2$  and 1,1,1,2-tetrafluoroethane (R134a) to investigate the solvent effect on the polymerization. The resulting polymer is highly soluble in 1,4-dioxane and  $\text{CH}_2\text{Cl}_2$ , while it exhibits very low solubility in liquid R134a.<sup>12</sup> Based on these measurements the polymerization of DMDPM in  $\text{scCO}_2$  and in R134a began homogeneously, but became heterogeneous as the polymer precipitated. In all of these solvents cyclopolymerization was effectively carried out by  $\text{MoCl}_5$ -based metathesis catalysts and the optimized polymerization results are summarized in Table 1. ( $n\text{-Bu}$ )<sub>4</sub>Sn has been known to be an excellent cocatalyst for the polymerization of mono- and disubstituted acetylenes.<sup>13</sup> In this study, however, ( $n\text{-Bu}$ )<sub>4</sub>Sn had little effect on the polymer yield and the number average molecular weight ( $M_n$ ).  $\text{WCl}_6$  exhibited markedly less effective catalytic activity than  $\text{MoCl}_5$  (results not presented here). As a cocatalyst of  $\text{WCl}_6$ , ( $n\text{-Bu}$ )<sub>4</sub>Sn had no effect on the polymer yield and  $M_n$ , which is consistent with previous reports.<sup>5a</sup> The polymerization initiated by  $\text{MoCl}_5$ / $(n\text{-Bu})_4\text{Sn}$  in 1,4-dioxane (see entry 2 in Table 1) resulted in the highest polymer yield (88%) and  $M_n$  ( $68\,000\text{ g mol}^{-1}$ ), which is similar to the previous report for the cyclopolymerization of diethyl dipropargylmalonate.<sup>7b</sup> The polymerization initiated by  $\text{MoCl}_5$ -based metathesis catalysts in  $\text{scCO}_2$  (see entries 7 and 8 in Table 1) resulted in *ca.* 70% polymer yield and *ca.* 13 000 number average molecular

**Table 1** Cyclopolymerization of dimethyl dipropargylmalonate by transition-metal metathesis catalysts in various solvents<sup>a</sup>

Entry	Solvent	Cat. system	5-Rings <sup>b</sup> (%)	$M_n^c$ /g mol <sup>-1</sup>	MWD <sup>c</sup>	Yield (%)
1 <sup>d</sup>	1,4-Dioxane	MoCl <sub>5</sub>	67(3)	65 000	3.40	86
2 <sup>d</sup>	1,4-Dioxane	MoCl <sub>5</sub> /( <i>n</i> -Bu) <sub>4</sub> Sn	70(2)	68 000	3.31	88
3 <sup>d</sup>	CH <sub>2</sub> Cl <sub>2</sub>	MoCl <sub>5</sub>	73(3)	62 500	3.52	80
4 <sup>d</sup>	CH <sub>2</sub> Cl <sub>2</sub>	MoCl <sub>5</sub> /( <i>n</i> -Bu) <sub>4</sub> Sn	71(1)	65 000	3.56	85
5 <sup>e</sup>	CF <sub>3</sub> CH <sub>2</sub> F	MoCl <sub>5</sub>	65(3)	10 500	2.42	69
6 <sup>e</sup>	CF <sub>3</sub> CH <sub>2</sub> F	MoCl <sub>5</sub> /( <i>n</i> -Bu) <sub>4</sub> Sn	66(2)	11 500	2.36	71
7 <sup>f</sup>	scCO <sub>2</sub>	MoCl <sub>5</sub>	>95(1)	12 500	2.05	70
8 <sup>f</sup>	scCO <sub>2</sub>	MoCl <sub>5</sub> /( <i>n</i> -Bu) <sub>4</sub> Sn	>95(2)	13 500	1.95	73

<sup>a</sup> Conditions of polymerization: [M]<sub>0</sub> = 0.25 mol L<sup>-1</sup>, [Cat.] = [Cocat.] = 5 mM; mol ratio of monomer to catalyst = 50. <sup>b</sup> All spectra were obtained at 25 °C in a 0.05 M solution of Cr(acac)<sub>3</sub> in CDCl<sub>3</sub> at 125 MHz. The percentages of five-membered ring were determined using carbonyl resonances in the region of 170–175 ppm and quaternary carbon resonances in the region of 40–60 ppm. The average is listed here and the difference between the two within parentheses. <sup>c</sup> Determined by GPC vs. polystyrene standard with the RI detector. <sup>d</sup> Polymerization was carried out at 40 °C for 24 h. <sup>e</sup> Polymerization was carried out in R134a at 40 °C and 150 bar for 24 h. <sup>f</sup> Polymerization was carried out at 40 °C and 250 bar for 24 h.

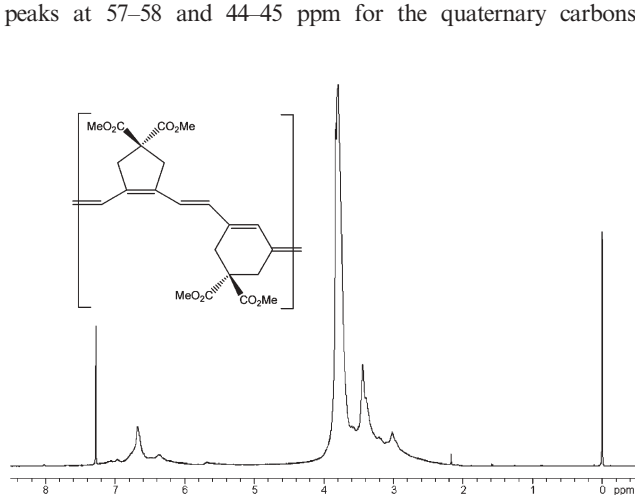
weight, which is lower than those of 1,4-dioxane or CH<sub>2</sub>Cl<sub>2</sub> but similar to those of R134a.

Poly(DMDPM) structure was identified by <sup>1</sup>H and <sup>13</sup>C NMR, IR, and UV-visible spectroscopies. Fig. 1 represents the <sup>1</sup>H NMR spectrum of poly(DMDPM). The new peaks at 6.2–7 ppm are assigned to the resonances of protons on the conjugated double bonds. No acetylenic carbon–hydrogen stretching band of DMDPM (3310 cm<sup>-1</sup>) was found in the IR spectrum of poly(DMDPM) (see ESI†). The UV-visible spectrum of the polymer obtained in THF exhibits a characteristic broad peak at 320–600 nm that is due to a π–π\* transition of conjugated polyene (see ESI†). In the <sup>13</sup>C NMR spectrum, two peaks at 123.3 and 137.1 ppm for vinylene and quaternary pairs of sp<sup>2</sup> carbons and one resonance at 41.7 ppm for a pair of ring CH<sub>2</sub> groups make a complete assignment of resonances possible (see ESI†).

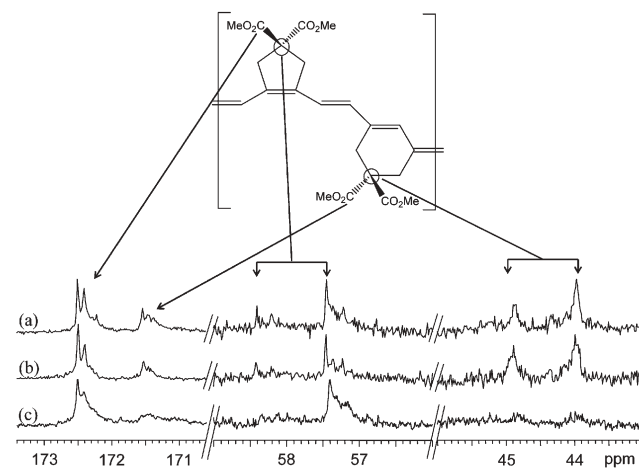
More information can be obtained about the effect of the solvents on the structure of poly(DMDPM) by <sup>13</sup>C NMR spectroscopy. Carbon resonances at 172.5 and 57–58 ppm are characteristic of five-membered rings while resonances at 171.5 and 44–45 ppm are characteristic of six-membered rings. The <sup>13</sup>C NMR spectra of poly(DMDPM) synthesized in 1,4-dioxane, CH<sub>2</sub>Cl<sub>2</sub> or R134a reveal two resonances for the carbonyl carbon atoms at around 171.5 and 172.5 ppm and two major clusters of peaks at 57–58 and 44–45 ppm for the quaternary carbons,

indicating the presence of both five- and six-membered rings in the polymers (see Fig. 2(a) and (b)). The relative amounts of five-membered rings formed in poly(DMDPM) prepared with a variety of solvents are listed in Table 1. Common organic solvents and the type of classical catalysts used appear to play a negligible role in determining the ratio of five- to six-membered rings. This observation is in accordance with other polymerization data for diethyl dipropargylmalonate with MoCl<sub>5</sub>-based initiators, which typically produced *ca.* 70% five-membered rings.<sup>4b</sup> The <sup>13</sup>C NMR spectrum of poly(DMDPM) synthesized in scCO<sub>2</sub>, however, reveals predominantly one carbonyl carbon resonance at 172.5 ppm and one at 57.3 ppm for the quaternary carbon, indicating that it contains >95% five-membered rings (see Fig. 2(c)).

Carbon dioxide is a molecule with several potential reactive coordination sites: the carbon is a Lewis acid center and the oxygens are weak Lewis bases. The carbon can thus be described as the electrophilic center of carbon dioxide and the oxygen atoms as the nucleophilic centers.<sup>14a</sup> Many transition-metal/CO<sub>2</sub> complexes have been described in the literature.<sup>14</sup> According to Carmona *et al.*,<sup>15</sup> molybdenum can form a double coordination with carbon dioxide, in which both carbon dioxide molecules are bonded “side-on” and the coordinated C=O bonds are staggered

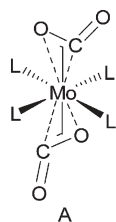


**Fig. 1** <sup>1</sup>H NMR spectrum of poly(dimethyl dipropargylmalonate) (sample: Table 1, entry 7, measured in CDCl<sub>3</sub>).

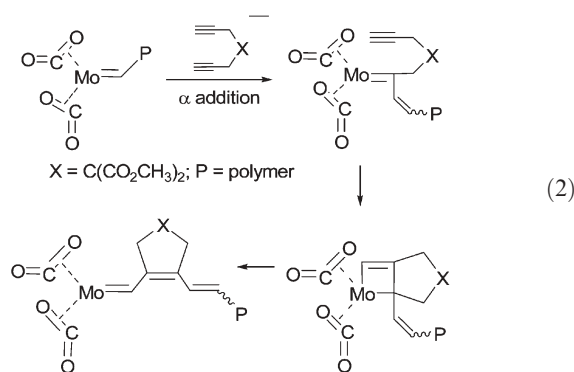


**Fig. 2** <sup>13</sup>C NMR spectra (125 MHz) of the carbonyl carbon resonances and quaternary carbon resonances of poly(DMDPM) synthesized in (a) 1,4-dioxane, (b) CH<sub>2</sub>Cl<sub>2</sub> and (c) supercritical carbon dioxide.

with respect to one another and eclipsed with regard to the *trans*-L–Mo–L (L = ligand) vectors of the equatorial plane (see A).



This type of solvent coordination to metals can strongly affect the selectivity of the reaction by its action as ligands, *i.e.*, coordinating ligands.<sup>16</sup> Furthermore, Trost *et al.*<sup>17</sup> reported that the activity of molybdenum catalysts was strongly ligand dependent. In molecular catalysis, as a general rule, a decrease in activity of a catalyst often results in an increase of selectivity. For example, Nuyken and co-workers<sup>7a</sup> reported that a modification of well-defined molybdenum-based initiators from fluorinated alkoxy ligands to non-fluorinated analogues, *i.e.*, a decrease in activity of the catalyst, led to an increased  $\alpha$ -selectivity. Thus, we assume that the mechanism of cyclopolymerization in *sc*CO<sub>2</sub> consists of addition of the first triple bond to an alkylidene to give more favorably an  $\alpha$ -substituted metallacyclobutene intermediate, in which carbon dioxide acts as coordinating ligands to molybdenum. Intramolecular  $\alpha$ -addition (cyclization) followed by opening of the metallacycle leads to the propagating terminal alkylidene (eqn (2)).



Intramolecular formation of the five-membered ring must be fast relative to intermolecular addition of the second triple bond to a M=C bond, a reaction that would lead to cross-linking. None is observed.

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