Russian Chemical Bulletin, International Edition, Vol. 59, No. 7, pp. 1349—1352, July, 2010

# Regularities of ring-opening metathesis polymerization of cyclooctene in the presence of molybdenum catalysts

**Yu. E. Begantsova, A. I. Kirillov, L. N. Bochkarev,* and G. A. Abakumov**

G. A. Razuvaev Institute of Organometallic Chemistry, Russian Academy of Sciences,
49 ul. Tropinina, 603950 Nizhny Novgorod, Russian Federation.
Fax: +7 (831) 462 1497. E-mail: lnb@iomc.ras.ru

At the initial stages the polymerization of *cis*-cyclooctene in the bulk with the catalysts $Me_3C—CH=Mo(NAr)(OCMe_2CF_3)_2$, $PhMe_2C—CH=Mo(NAr)(OCMe_2CF_3)_2$, $Me_3Si—CH=Mo(NAr)(OCMe_2CF_3)_2$, and $PhMe_2Si—CH=Mo(NAr)(OCMe_2CF_3)_2$ predominantly affords *cis*-polyoctenamers. The content of the *trans*-units in the polymer increases with an increase in the conversion. The sharpest increase in the *trans*-unit content observed for conversions higher than 80% is related to secondary metathesis reactions. The number-average molecular weights of the polymers increase linearly with the conversion. At conversions above 80% the molecular weights decrease due to the increasing contribution of chain transfer reactions. Polyoctenamers with the increased content of *trans*-units crystallize in two modifications.

**Key words:** ring-opening metathesis polymerization, cyclooctene, molybdenum catalysts, stereoregularity, crystallinity.

Ring-opening metathesis polymerization (ROMP) is an efficient method for the synthesis of diverse macromolecular materials.[1—4]

Among the best known active homogeneous catalysts used in metathesis polymerization of cycloolefins are carbene complexes of molybdenum and tungsten of the type $RCH=M(NAr)(OR')_2$ ($R = Bu^t$, $PhMe_2C$, M = Mo, W, Ar = 2,6-$Pr^i C_6H_3$, R′ = Alkyl, Aryl).[5—7] The catalytic activity of catalysts of this type is determined to a considerable extent by the nature of alcoholate groups and imido ligands.[8] The influence of the nature and structure of carbene fragments on their catalytic properties remains poorly studied. At the same time, the substituent at the carbene carbon can affect both the kinetics of the process and the properties of the product formed during catalysis. We have earlier[9,10] established that the rate of homometathesis of hex-1-ene depends on the nature of the alkylidene substituent of the catalyst. When the catalysts with different structures of the substituent at the carbene carbon atom are used in the ring-opening metathesis polymerization of *cis*-cyclooctene, the polyoctenamers formed differ substantially in the ratio of double *cis*- and *trans*-units.[10,11]

In this work, we studied the metathesis polymerization of *cis*-cyclooctene in the bulk using the molybdenum complexes with different structures of the carbene substituents. We used the complexes with the hydrocarbon carbene fragments $Bu^t—CH=Mo(NAr)(OCMe_2CF_3)_2$ (**1**) and $PhMe_2C—CH=Mo(NAr)(OCMe_2CF_3)_2$ (**2**) and their silicon-containing analogs $Me_3Si—CH=Mo(NAr)(OCMe_2CF_3)_2$ (**3**) and $PhMe_2Si—CH=Mo(NAr)(OCMe_2CF_3)_2$ (**4**).

## Results and Discussion

Ring-opening polymerization of *cis*-cyclooctene was carried out for each catalyst in the whole conversion range. Cyclooctene was polymerized at room temperature in the bulk at the molar ratio monomer : catalyst equal to 300 : 1. The ratio of *cis*- and *trans*-units in the polymers was determined using $^{13}C$ NMR spectroscopy. As indicated by the data obtained, the ratio of *cis*- and *trans*-units for all the catalysts depends, to a considerable extent, on the conversion (Fig. 1). *cis*-Polyoctenamers are predominantly formed at initial conversions: at 10% conversion the content of *trans*-units in the polymer is 7—11%. The content of *trans*-units increases to 19—22% as the conversion increases to 50—65% with compounds **2**—**4** used as catalysis; in the presence of catalyst **1**, the content of *trans*-units reaches 33%. The most considerable content of *trans*-units is achieved at conversions higher than 80%: at the complete conversion of the monomer the fraction of *trans*-units increases to 82—87%.

The ratio of *cis*- and *trans*-units in the polymers formed when the catalysts with different alkylidene fragments are used differs noticeably. According to the mechanism of ROMP of cycloolefins,[1—4] during the polymerization the alkylidene fragment of the initiator is transformed into the terminal group of the growing macromolecule. It can be

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 7, pp. 1319—1323, July, 2010.

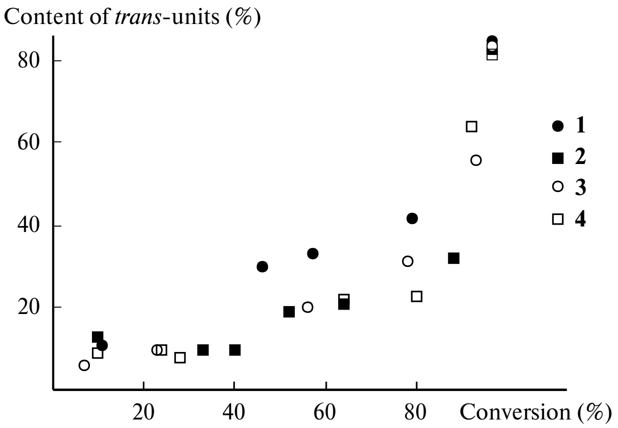

**Fig. 1.** Dependences of the content of *trans*-units on the conversion for polyoctenamers synthesized using molybdenum catalysts **1**—**4**.

assumed that at the propagation stages the terminal group is coordinated with the central metal atom and determines, depending on the structure, the most favorable coordination of the next monomer molecule, which finally results in the predominant formation of the *trans*- or *cis*-unit in the growing macromolecule.

The dependences of the number-average molecular weights ($\bar{M}_n$) of the obtained polyoctenamers on the conversion are shown in Fig. 2. Polyoctenamers synthesized using catalysts **1**—**4** are characterized by a linear increase in the number-average molecular weights with an increase in conversion to 70—80%. The decrease in the $\bar{M}_n$ values with the further increase in conversion indicates the enhancement of the chain transfer reactions at the final polymerization stage.

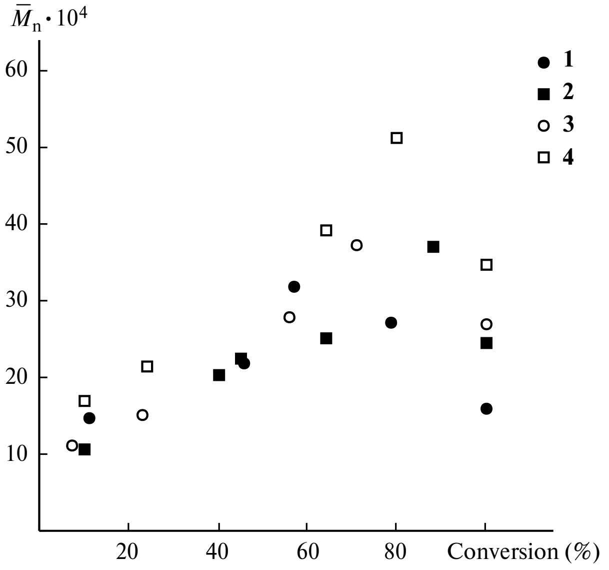

**Fig. 2.** Dependences of the number-average molecular weights on the conversion for polyoctenamers synthesized using catalysts **1**—**4**.

The use of the silicon-containing carbene complex $PhMe_2Si—CH=Mo(NAr)(OCMe_2CF_3)_2$ (**4**) results in the formation of higher-molecular-weight polymers. This is related, most likely, to the lower initiation rate for this catalyst. The absence of the signal of the carbene proton of the catalyst, which is in the composition of the propagating chain, from the $^1$H NMR spectra did not allow us to reliably estimate the $k_p/k_i$ ratio for all catalysts.

The observed increase in the content of *trans*-units in polyoctenamers at conversions higher than 80%, which is accompanied by a decrease in $\bar{M}_n$ of the polyoctenamers formed can be due to the complication of the polymerization process by secondary metathesis reactions. This becomes most noticeable at high conversions when the polymerization is retarded due to an increase in the viscosity of the system and deficient of the monomer.

Processes of intra- and intermolecular chain transfer that occur on the catalysts performing chain propagation are usually attributed to secondary metathesis.[12] It was found by $^1$H NMR spectroscopy for the metathesis polymerization of *cis*-cyclooctene using catalysts **1**—**4** in deuterochloroform that the starting catalyst is retained in the reaction system in a noticeable amount even at a 90% conversion of the monomer. It is most likely that the products of metathesis polymerization are isomerized with the participation of the starting catalyst with different rates, depending on the catalyst nature.

A series of special experiments was carried out to determine the influence of secondary metathesis on the stereoregularity and number-average molecular weight characteristics of the polymers formed. Polyoctenamer containing 17% of *trans*-units was dissolved in deuterochloroform and stored in the presence of the molybdenum catalyst for several hours at room temperature. The characteristics of the polymer determined after the interaction with the catalyst are listed in Table 1. At the catalyst concentration 0.005 mol L$^{-1}$ the content of *trans*-units in poly-

**Table 1.** Characteristics of polyoctenamer after secondary metathesis in deuterochloroform* at different catalyst concentrations (*C*)

| Catalyst | *C* /mol L$^{-1}$ | Ratio *cis* : *trans* | $\bar{M}_n$ ($\bar{M}_w/\bar{M}_n$) |
|---|---|---|---|
| **1** | 0.005 | 74 : 26 | 82100 (1.60) |
| | 0.1 | 17 : 83 | 1700 (2.38) |
| **2** | 0.005 | 76 : 24 | 93500 (1.65) |
| | 0.1 | 21 : 79 | 1900 (2.58) |
| **3** | 0.005 | 78 : 22 | 131700 (1.99) |
| | 0.1 | 22 : 78 | 2400 (3.08) |
| **4** | 0.005 | 79 : 21 | 127700 (1.60) |
| | 0.1 | 20 : 80 | 2100 (4.19) |

* Characteristics of polyoctenamer before secondary metathesis: content of *trans*-units is 17%, $\bar{M}_n$ = 126 200, $\bar{M}_w/\bar{M}_n$ = 1.6.

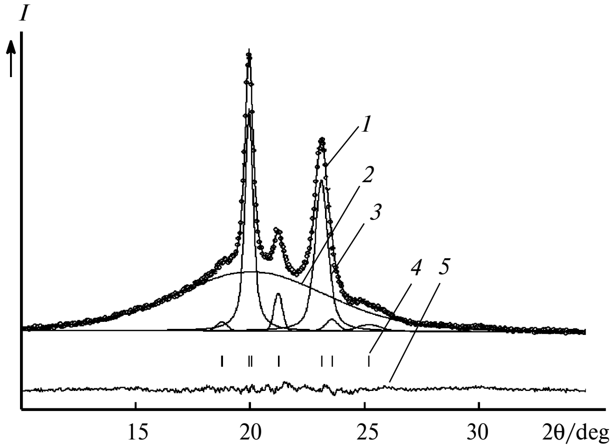

**Fig. 3.** Example for the deconvolution of the X-ray powder diffraction pattern of the sample of polyoctenamer **P4** to the amorphous and crystalline components: points, experimental curve; *1*, theoretical total curve; *2*, amorphous halo; *3*, six calculated peaks of the crystalline phases; *4*, positions of Bragg reflections; *5*, differential curve between the experimental and calculated curves.

octenamer increases insignificantly. With an increase in the catalyst concentration to 0.1 mol $L^{-1}$ the content of *trans*-units in polyoctenamer increases within 1 h to 78—83%. The data on the change in the number-average molecular weights for polyoctenamer after secondary metathesis confirm the influence of chain transfer reactions on the molecular weights and polydispersity of the polymer (see Table 1).

The increase in the content of *trans*-units in polyoctenamers is an energetically favorable process due to the ability of *trans*-segments to crystallization. *trans*-Polyoctenamers are characterized by crystalline polymorphism.[13] It is known that *trans*-polyoctenamers form two modifications differed in spatial packing of polymer chains.[13—16]

Polyoctenamers **P1**—**P6** synthesized using molybdenum catalysts **1**—**4** represent a two-phase system with different crystallinities and different phase ratios. The Profile fitting procedure of the WinPlotr program was used to calculate the crystallinity of the phases and the line broadening to obtain the range of crystallite size. An example for the deconvolution of the X-ray powder diffraction pattern of the sample of polyoctenamer **P4** (Table 2) to the amorphous halo and diffraction peaks is shown in Fig. 3.

The X-ray powder diffraction data presented in Refs 15 (monoclinic, phase IV) and 13 (triclinic, phase III) and the PowderCell 2.3 program were used for the quantitative calculation of the phase composition. The calculations were performed with allowance for the available texture of the samples and correction of the thermal parameters. The result of the quantitative calculation of the phase composition of the sample of polyoctenamer **P5** is shown in Fig. 4.

The results of X-ray powder diffraction studies of samples of polyoctenamers **P1**—**P6** with different contents of *trans*-units obtained using catalysts **1**—**4** are given in Table 2. Crystallinity in the synthesized samples depends on both the content of *trans*-units in polyoctenamer and conditions of synthesis of the sample. Sample **P4** obtained without reprecipitation using catalyst **3** has the highest crystallinity and the largest size of the crystallites. Purification of the sample decreases its crystallinity and changes the ratio of crystalline modifications.

**Table 2.** Synthesis conditions, stereoreguarity, crystallinity ($K$), phase ratios ($C_{\text{IV}}$), and crystallite size ($D_{\text{CSD}}$) in the samples of polyoctenamers **P1**—**P6** synthesized using catalysts **1**—**4**[a]

| Sample | Catalyst | Ratio *cis* : *trans* | $K$ (%) | $C_{\text{IV}}$ (%) | $D_{\text{CSD}}$/nm |
|---|---|---|---|---|---|
| **P1** | **1** | 17 : 83 | 35 | 44 | 20 |
| **P2** | **1**[b] | 9 : 91 | 40 | 75 | 16 |
| **P3** | **2** | 70 : 30 | 0 | 0 | — |
| **P4** | **3**[c] | 15 : 85 | 44 | 10 | 34 |
| **P5** | **3** | 15 : 85 | 34 | 70 | 16 |
| **P6** | **4** | 36 : 64 | 18 | 30 | 20 |

[a] Conditions: [*cis*-cyclooctene]/[catalyst] = 300; in the absence of solvent. The samples after reprecipitation, if otherwise is not indicated.

[b] Conditions: [*cis*-cyclooctene]/[catalyst] = 100; in the absence of solvent.

[c] The sample before reprecipitation.

Thus, it was found that the polymerization of *cis*-cyclooctene in the bulk using the catalysts $Me_3C—CH{=}Mo(NAr)(OCMe_2CF_3)_2$, $PhMe_2C—CH{=}Mo(NAr)(OCMe_2CF_3)_2$, $Me_3Si—CH{=}Mo(NAr)(OCMe_2CF_3)_2$, and $PhMe_2Si—CH{=}Mo(NAr)(OCMe_2CF_3)_2$ at the initial conversions results in the formation of predominantly *cis*-polyoctenamers. The content of double bonds in the *trans*-configuration increases in the polymer with an increase in the conversion and is accompanied by a linear increase in the number-average molecular weights. Crystallization of *trans*-segments of the polymers with high *trans*-unit content is observed. At conversions higher than

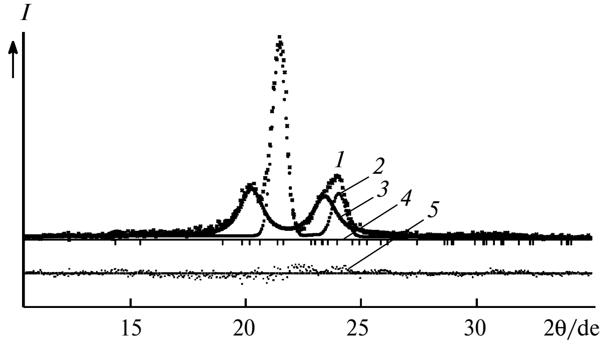

**Fig. 4.** Example for the quantitative calculation of the content of phases in the sample of polyoctenamer **P5**: *1*, experimental curve; *2* and *3*, calculated curves of polyoctenamer in crystalline phases IV and III, respectively; *4*, positions of Bragg reflections; *5*, differential curve between the experimental and calculated curves.

80% the polymerization process is complicated by secondary metathesis reactions leading to a decrease in the molecular weights of the polyoctenamers formed.

## Experimental

Molybdenum catalysts **1**—**4** were synthesized according to known procedures.[10,17,18] Purity of the complexes was monitored by $^1$H NMR spectroscopy.

Prior to use *cis*-cyclooctene (Aldrich) was kept above metallic sodium. Polymerization was carried out in evacuated tubes. The molar ratio [monomer]/[catalyst] = 300 was used for bulk polymerization. Polymerization was carried out in the absence of solvent. The polymerization process was interrupted by the addition of a benzaldehyde solution in THF. Polyoctenamer formed was purified by mutiple reprecipitation with methanol from a THF solution. It was shown in special experiments that the molecular weight characteristics of the samples remain unchanged after reprecipitation of the polymers. The polymer samples were dried *in vacuo* at room temperature to a constant weight.

The molecular weight characteristics of the polymers were determined by gel permeation chromatography on a Knauer liquid chromatograph with a Smartline RID 2300 differential refractometer as a detector using a set of two Phenomenex columns with the Phenogel sorbent with the pore size $10^4$ and $10^5$ Å. The eluent was THF (2 mL min$^{-1}$, 40 °C). The columns were calibrated by 13 polystyrene standards.

The $^1$H and $^{13}$C NMR spectra of the polymer samples were recorded on a Bruker DPX-200 spectrometer (200 MHz) using $CDCl_3$ as a solvent and $Me_4Si$ as an internal standard. The ratio of *cis*- and *trans*-units in the polymers was determined by the $^{13}$C NMR method using a known procedure.[19]

X-ray powder diffraction studies were carried out on a DRON-3M diffractometer (Cu-K$\alpha$ radiation) with the graphite monochromator on a diffracted beam by step scan mode. The transmission recording geometry was used with an increment of 0.05° and an accumulation time of 5 s.

The crystallinity was calculated by the known formula

$$K = S_{cr}/(S_{cr} + S_{am}),$$

where $S_{cr}$ is the total surface area of peaks of the crystalline phases, and $S_{am}$ is the surface area of the amorphous halo. The crystallite sizes were calculated by the Scherer formula

$$D_{CSD} = 0.9\lambda/\beta\cos\theta,$$

where $\lambda$ is the X-ray radiation wavelength (0.1542 nm for the copper anode), $\beta$ is the reduced half-width of the peak in radians, and $\theta$ is the diffraction angle.

**Metathesis bulk polymerization of cyclooctene.** *cis*-Cyclooctene (1.227 g, 11.135 mmol) was added to an evacuated tube containing the catalyst $PhMe_2Si{-}CH{=}Mo(NAr)(OCMe_2CF_3)_2$ (**2**) (25 mg, 0.037 mmol) (molar ratio [monomer]/[catalyst] = = 300). A mixture was magnetically stirred at room temperature, and the process was monitored by the change in the viscosity in the system. Polymerization was interrupted by the addition of a benzaldehyde solution in tetrahydrofuran. After the solid ring-opening product was formed, the reaction mixture was additionally kept at room temperature for 15 h for the complete conversion of the monomer.

Ring-opening polymerizations involving other catalysts were carried out similarly.

**Secondary metathesis in $CDCl_3$.** A solution of the catalyst in $CDCl_3$ was added to a solution of polyoctenamer in $CDCl_3$ (the polymer concentration in the reaction solution based on the monomer unit was 0.5 mol L$^{-1}$). The mixture was stored at room temperature, and the change in the viscosity of the solution was monitored. Two variants of experiments were carried out for each catalyst: at the catalyst concentration 0.005 mol L$^{-1}$ and the reaction time 6 h and at the catalyst concentration 0.1 mol L$^{-1}$ and the reaction time 1 h. No visible change in the viscosity was observed at the catalyst concentration 0.005 mol L$^{-1}$, whereas the viscosity of the polymer solution decreased considerably for 30 min at the catalyst concentration 0.1 mol L$^{-1}$.

## References

1. V. Dragutan, I. Dragutan, H. Fischer, *J. Inorg. Organomet. Polym.*, 2008, **18**, 18.
2. M. R. Buchmeiser, *Chem. Rev.*, 2000, **100**, 1565.
3. J. J. Murphy, K. Nomura, R. M. Paton, *Macromolecules*, 2006, **39**, 3147.
4. K. Nomura, I. Sakai, Y. Imanishi, M. Fujiki, Y. Miyamoto, *Macromol. Rapid Commun.*, 2004, **25**, 571.
5. R. R. Schrock, *Chem. Rev.*, 2002, **102**, 145.
6. R. R. Schrock, A. H. Hoveyda, *Angew. Chem., Int. Ed.*, 2003, **42**, 4592.
7. R. R. Schrock, *J. Mol. Catal. A: Chem.*, 2004, **213**, 21.
8. R. R. Schrock, *Tetrahedron*, 1999, **55**, 8141.
9. L. N. Bochkarev, Yu. E. Begantsova, V. I. Shcherbakov, N. E. Stolyarova, I. K. Grigorieva, I. P. Malysheva, G. V. Basova, A. L. Bochkarev, Yu. P. Barinova, G. K. Fukin, E. V. Baranov, Yu. A. Kurskii, G. A. Abakumov, *J. Organomet. Chem.*, 2005, **690**, 5720.
10. Yu. E. Begantsova, L. N. Bochkarev, Yu. P. Barinova, G. V. Basova, N. E. Stolyarova, I. K. Grigor´eva, I. P. Malysheva, G. K. Fukin, E. V. Baranov, Yu. A. Kurskii, G. A. Abakumov, *Izv. Akad. Nauk*, *Ser. Khim.*, 2007, 247 [*Russ. Chem. Bull., Int. Ed.*, 2007, **56**, 255].
11. A. L. Bochkarev, Yu. E. Begantsova, E. O. Platonova, G. V. Basova, I. K. Grigor´eva, N. E. Stolyarova, I. P. Malysheva, G. K. Fukin, E. V. Baranov, Yu. A. Kurskii, L. N. Bochkarev, G. A. Abakumov, *Izv. Akad. Nauk*, *Ser. Khim.*, 2008, 1840 [*Russ. Chem. Bull.*, *Int. Ed.*, 2008, **57**, 1874].
12. C. W. Bielawski, R. H. Grubbs, *Prog. Polym. Sci.*, 2007, **32**, 1.
13. I. W. Bassi, G. Fagherazzi, *Eur. Polym. J.*, 1968, **4**, 123.
14. G. Natta, G. Dall´Asta, I. W. Bassi, G. Carella, *Makromol. Chem.*, 1966, **91**, 87.
15. G. Natta, *Eur. Polym. J.*, 1967, **3**, 339.
16. G. Natta, I. W. Bassi, G. Fagherazzi, *Eur. Polym. J.*, 1969, **5**, 239.
17. R. R. Schrock, J. S. Murdzek, G. C. Bazan, J. Robbins, M. DiMare, M. B. O´Regan, *J. Am. Chem. Soc.*, 1990, **112**, 3875.
18. J. H. Oskam, H. H. Fox, K. B. Yap, D. H. McConville, R. O´Dell, B. J. Lichtenstein, R. R. Schrock, *J. Organomet. Chem.*, 1993, **459**, 185.
19. P. Dounis, W. J. Feast, A. M. Kenwright, *Polymer*, 1995, **36**, 2787.

*Received July 13, 2009;*
*in revised form December 14, 2009*