Stereoselectivity of the ring-opening polymerization of cyclo-octadiene-1,5

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Stereoselectivity of the ring-opening polymerization of cyclo-octadiene-1,5 (COD) in the presence of WCl_6-$[(i\text{-}C_4H_9)_2Al]_2O$ has been studied. It has been shown that with COD just as in the case of cyclo-octene (CO) and bicyclo [6.1.0] nonene-4 (BCN) studied previously, the polymer microstructure is determined by two factors: 'the stereoselectivity of an elementary act of cyclo-olefin ring-opening' and secondary isomerization reactions of a polymer chain. The ^{13}C n.m.r. study shows that variation in the microstructure with conversion is accounted for by isomerization of a polymer chain. Arguments supporting the hypothesis of the formation of two types of units at the same active site are discussed, based on results of investigation of sequences of *cis*-and *trans* units in the polymer chain and the temperature dependence of stereoselectivity of an elementary act of ring-opening with COD, CO and BCN.

INTRODUCTION

Previously we studied the stereoselectivity of the ring-opening polymerization of cyclooctene (CO)[1] and bicyclo[6.1.0]nonene-4 (BCN)[2] using WCl_6-$[(i\text{-}C_4H_9)_2Al]_2O$ (TBAO) catalyst system. Here we report on our studies of the stereoselectivity of the ring-opening polymerization of cyclooctadiene-1,5 (COD). Such an investigation enables a comparison to be made between the stereoselectivity of the insertion of several eight-membered cyclo-olefins under similar conditions. Also, in studying the stereoselectivity of COD polymerization it is possible to obtain more detailed information on the polymer microstructure by determining the *cis–trans* units sequences in the polymer chain using the ^{13}C and ^1H n.m.r. spectroscopy.

EXPERIMENTAL

The COD polymerization was carried out using WCl_6-$[(i\text{-}C_4H_9)_2Al]_2O$ catalyst system. The experimental procedure was identical with that utilized previously[1]. In all the experiments the initial monomer concentration was 1,5 M.

The polymerization conditions were chosen so as to minimize the isomerization of the polymer chains[1].

The microstructure of polymers was determined from their ^{13}C n.m.r. spectra (5% solutions in $CDCl_3$, TMS—internal stantard). The spectra were recorded on a Bruker HX-270 spectrometer operating at 67.88 MHz for carbon resonance. The number of scans for 8 KHz spectrum was about 500 with a pulse repetition time of 7 s.

The proton spectra of the samples (0.02% solutions in hexachlorobutadiene) were recorded on the same spectrometer operating at 270 MHz. To provide a higher resolution in the olefinic part of the spectrum homonuclear spin–spin decoupling of the methylene protons was used.

It should be noted that separation of signals due to different triads of *cis*- and *trans*-units in the ^1H spectrum was possible using hexachlorobutadiene as a solvent. All attempts to achieve a similar effect using solvents such as CCl_4, C_2Cl_4 and C_6D_6 were unsuccessful. The disadvantage of hexachlorobutadiene as solvent is a *cis–trans-* isomerization of polymer during sample preparation. Special experiments demonstrated that the amount of *trans*-units increased slowly when the polyoctadienamers-1,5 dissolved in hexachlorobutadiene on storage.

RESULTS AND DISCUSSION

The data on stereoselectivity of COD and BCN polymerization initiated by the TBAO/WCl_6 catalyst system suggest that the main conclusions made in our research of the CO ring-opening polymerization are also true for some other cyclo-olefins, at least in the temperature range studied. *Figure 1* shows the

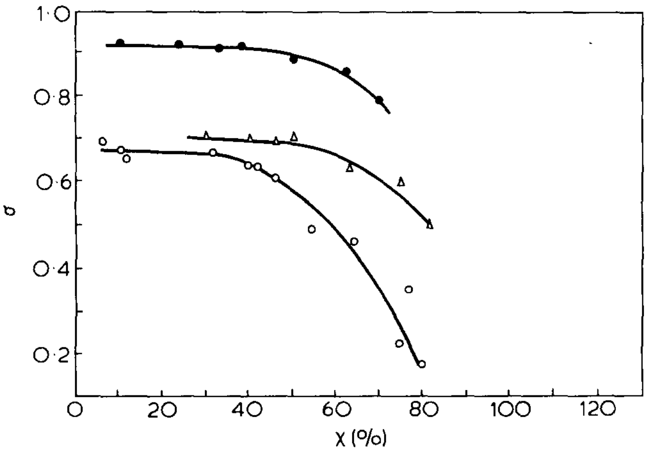

Figure 1 Microstructure-conversion relationship for the ring-opening polymerization of cyclo-octene, (△); bicyclo[6,1,0]nonene-4, (○); and cyclo-octadiene 1.5, (●). Polymerization temperature: +14°C for CO and COD and +18°C for BCN

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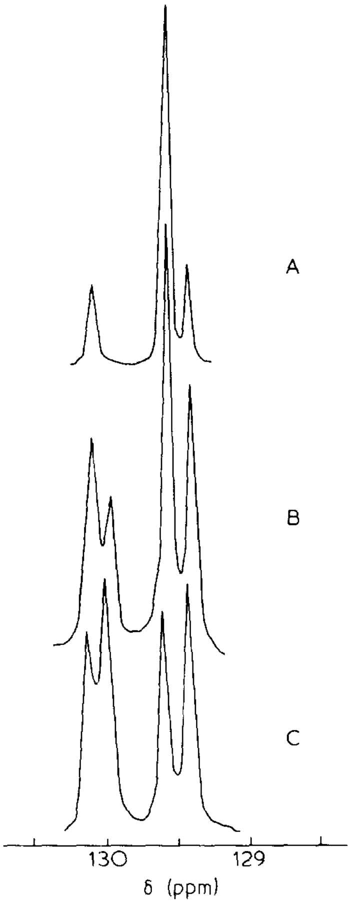


Figure 2 Olefinic part of ^{13}C n.m.r. spectra of polyoctadienamers 1.5 prepared at different conversions: 24% (A); 56% (B); 78% (C)

experimental data on the polymerization of three monomers CO, BCN and COD, represented as *cis*-units content (σ-conversion (x) relationships. The extrapolation of the relationship $\sigma=\sigma(x)$ for a zero conversion gives the value $\sigma_0=\lim_{x\to 0}\sigma(x)$ which we have interpreted as the stereoselectivity of an elementary act of cyclo-olefin insertion. It has been shown that σ_0 is independent of the monomer concentration and on the catalyst component concentration and ratio but does depend on the polymerization temperature[1].

In the course of polymerization of all the three monomers studied (CO, BCN and COD) the *cis*-units content decreases with conversion, which is believed to be due to the isomerization of polymer chains formed[1]. A characteristic feature of polymerization of the three cyclo-olefins is an increase in the contribution of secondary isomerization reactions with increasing TBAO/WCl$_6$ ratio.

Secondary isomerization reactions of polymer chains during COD polymerization can be detected by examining the evolution of ^{13}C n.m.r. spectra of polyoctadienamers-1,5 with conversion (*Figure 2*).

Using assignment of signals in the spectra of 1,4-polybutadiene[3] given in *Table 1* the comparison can be made between the observed signals and those calculated under the assumption that the *cis*- and *trans*- units are randomly distributed along the polymer chain (*Table 1*).

An essential feature of the ^{13}C n.m.r. spectra of polyoctadienamers-1,5 produced at low conversions is the absence of a signal at 130.08 ppm (*Figure 2*, spectrum A) which is due to *TTC* and *TTT* type sequences. The explanation is that in the COD ring-opening polymerization of the two double bonds available, only one is cleaved, the other entering the polymer chain in its *cis*-configuration. If a decrease in *cis*-units content is due to isomerization of polymer chains, the *cis–trans* distribution in polyoctadienamer-1,5 will approach the random distribution of *cis–trans* units in 1,4-polybutadiene, which has been confirmed experimentally (*Table 1*).

Thus, in case of COD polymerization, in contrast to CO and BCN, the extrapolation of the microstructure-conversion relationship for $x=0$ gives the value σ_0, which still cannot be regarded as 'the stereoselectivity of an elementary act of insertion of COD molecule', because the contribution of the inert COD double bond to the polymer microstructure should be taken into account. Let us pass from the obtained σ_0 value to the real stereoselectivity of an elementary act S_0, using equation 1:

$$S_0=2\sigma_0-1 \qquad (1)$$

The $\sigma=\sigma(x)$ relationships for COD polymerization at different temperatures are presented in *Figure 3*.

Figure 4 shows relationships $\log\frac{S_0}{1-S_0}$ vs. $1/T$ for COD, BCN and CO (for BCN and CO $S_0=\sigma_0$). From *Figure 4*, S_0 decreases in all cases, the relationship $\log\frac{S_0}{1-S_0}$ vs. $1/T$ being linear in the temperature range studied and the slope of curves being -3.7, -1.0, and -7.4 kcal mol^{-1} for CO, BCN and COD, respectively.

With polyoctadienamer-1,5 it is possible to determine the proportion of *cis*- and *trans*-units and the mode of their distribution along a polymer chain using ^{13}C and ^{1}H

Table 1 Assignment and intensity distribution of olefinic signals in the ^{13}C n.m.r. spectrum of polyoctadienamers-1.5. (*Figure 2*) Calculated values are enclosed in brackets. Polymerization temperature +40°C, (WCl$_6$) = 4.8×10^{-4} mol l^{-1}, (TBAO) = 3.8×10^{-4} mol l^{-1}

δ	ppm	130.19	130.08	129.67	129.49
Type of triad		*CTC* + 1/2 *TTC*	*TTT* + 1/2 *TTC*	*CCC* + 1/2 *CCT*	*TCT* + 1/2 *CCT*
X (%)	σ		Intensities (±0.02)		
24	0.82	0.18 (0.15)	0 (0.04)	0.63 (0.66)	0.19 (0.15)
56	0.61	0.24 (0.24)	0.15 (0.15)	0.36 (0.37)	0.25 (0.24)
78	0.48	0.24 (0.25)	0.28 (0.27)	0.23 (0.23)	0.25 (0.25)

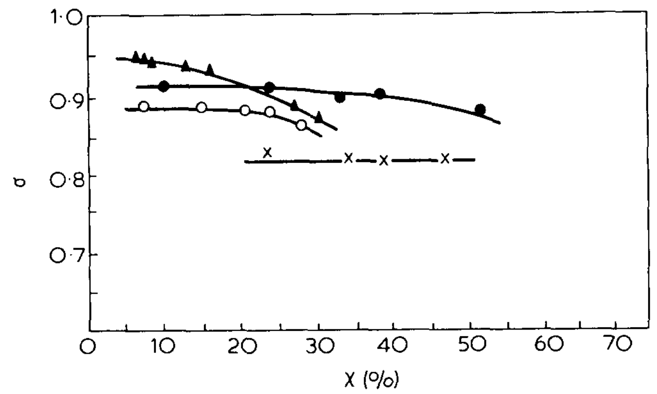


Figure 3 Microstructure — conversion relationship for the polymerization of COD. Polymerization temperature: +40°, (X); +28° (○); +14°, (●); 0°, (▲); $(WCl_6) = 4.2 \times 10^{-4}$ mol l^{-1}, $(TBAO) = 1.6 \times 10^{-4}$ mol l^{-1}, (X); (○); $(WCl_6) = 7.3 \times 10^{-4}$ mol l^{-1}, $(TBAO) = 5.5 \times 10^{-4}$ mol l^{-1}, (●), (▲)

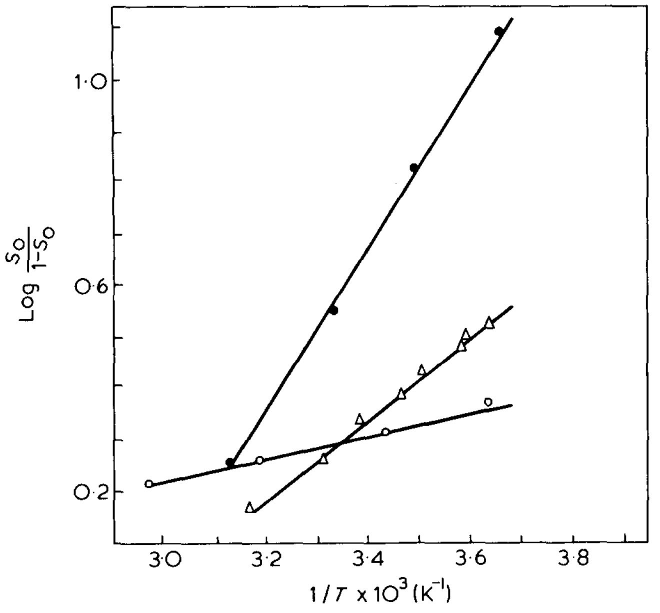
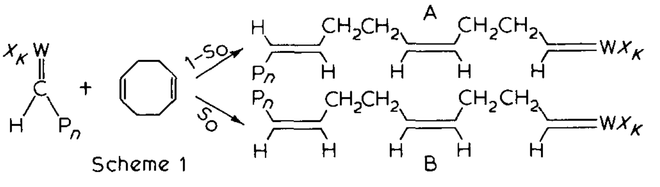


Figure 4 Relationship log $S_0/1 - S_0$ vs. $1/T$ for the ring-opening polymerization of CO, (△); BCN, (○); COD, (●)

n.m.r. spectra[3,4]. Naturally, the mode of distribution of *cis–trans* units is of interest only for the samples prepared in the absence of secondary isomerization reactions. When interpreting the ratio of intensities observed in the spectrum one should take into account a specific feature of COD polymerization: of the two double bonds available only one is cleaved, the other entering the polymer chain in the *cis*-configuration.

The polymerization of COD by a carbene mechanism[5] can be represented by scheme 1:



Scheme 1

It can be seen from scheme 1 that the polymer chain is formed from the two types of structural units A and B, the chain propagation occurring in such a way that the double bond adjacent to the carbene active site is always of *cis*-configuration. In this case the polymerization process can be characterized by conditional probabilities of addition: $P_{A/B}$ and $P_{B/A}$, where $P_{A/B}$, is the conditional probability of addition of B unit when the terminal unit is A; $P_{B/A}$, is the conditional probability of addition of A unit when the terminal unit is B. The value of the sum $P_{A/B} + P_{B/A}$ enables a conclusion to be made about the mechanism of stereoregulation during the polymer chain propagation. The $P_{A/B}$ and $P_{B/A}$ values can be calculated if proportion of (AA), (AB) and (BB) diads is known[6].

Hence, to solve the problem it is necessary to pass from the observed triad combinations of *CCC*, *CCT*, *TCT*, *CTC*, *TTC* and *TTT* units of polybutadiene-1,4 to (AA), (AB) and (BB) diads of polyoctadienamer-1,5. It should be emphasized once again that *TTT* and *TTC* triads were disregarded because they could be formed only as a result of secondary isomerization (see *Table 1*).

Examination shows (Appendix 1) that the mode of distribution of A and B type units in polyoctadienamer-1,5 is provided only by ^{1}H n.m.r. spectra. The olefinic part of the ^{1}H spectrum of the polyoctadienamer-1,5 is presented in *Figure 5* (^{13}C spectrum of the sample was treated in *Figure 2*, spectrum a). Five signals are observed in the ^{1}H spectrum, their integral intensities and assignments are given in *Table 2*.

The appearance of the small signal, 5.456 ppm, we associate with the isomerization reaction of the polymer during sample preparation (see Experimental section). For this reason the contribution of this signal to the total

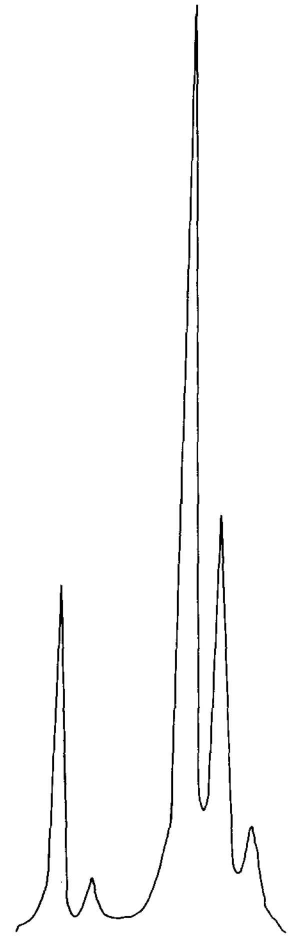


Figure 5 Olefinic part of ^{1}H spectrum of polyoctadienamer-1,5 obtained in the absence of isomerization reaction

Table 2 Assignments[4] and intensity distribution of olefinic signals in the ^{1}H spectrum of polyoctadienamer-1,5

δ, ppm	5.465	5.456	5.431	5.422	5.413
Assignment	*CTC*	*TTC*	*CCC*	*CCT*	*TCT*
Intensity	0.17	0.02	0.53	0.22	0.06

intensity distribution was not taken into account. Quantitative calculations using equations A8–A11 presented in Appendix 1 gave the following values of conditional probabilities $P_{A/B}$ and $P_{B/A}$:

$$P_{A/B}=0.63 \qquad P_{B/A}=0.34$$

The sum $P_{A/B}+P_{B/A}$ is close to unity, hence, A and B type units are randomly distributed along a polymer chain. This conclusion is in agreement with the previously advanced idea that *cis*- and *trans*-units are formed at the same active site. It is worth noting that for polyoctenamers obtained with WCl_6–TBAO in the absence of secondary isomerization *cis*- and *trans*-units are also randomly distributed along a polymer chain, as evidenced by ^{13}C n.m.r.[7].

The temperature dependence of S_0 established in this study for the polymerization of three different cyclo-olefins supports the idea that the stereoselectivity of an elementary act of insertion of a cyclo-olefin molecule is determined by kinetic factors. This is supported by the following two facts:

(i) the amount of units having a thermodynamically unfavourable configuration increases with decreasing temperature;

(ii) $\log\frac{S_0}{1-S_0}$ value shows linear dependence on the reverse temperature.

The obtained stereoselectivity value of an elementary act of cyclo-olefin ring-opening, S_0, is most likely to be accounted for by the properties of an active site such as the ligand environment and the oxidation state of transition metal (catalyst systems of the highest stereoselectivity with $S_0=1$ have been reported[8]. If it is true, a function $S_0=S_0\ (T)$ for a given cyclo-olefin can be selected as a criterion of structural identity of active sites promoting polymerization. Attempts to make use of such an approach have been reported in studies in the metathesis of acyclic olefins[9,10].

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APPENDIX 1

The proportion of observed triads (*CCC*), (*TCT*), (*CCT*) and (*CTC*) in the ^{1}H and ^{13}C n.m.r. spectra may be expressed by formulas A1–A4 in terms of proportions of diads (AA), (AB), (BA) and (BB) type:

$$(CTC)=1/2(AA)+1/2(BA) \tag{A1}$$

$$(CCC)=(BB)+1/2(BA) \tag{A2}$$

$$(CCT)=1/2(AB)+1/2(BA) \tag{A3}$$

$$(TCT)=1/2(AA) \tag{A4}$$

The proportion of diads of (AA), (AB), (BA) and (BB) can be expressed in terms of $P_{A/B}$ and $P_{B/A}$[6]:

$$(AA)=P_{B/A}(1-P_{A/B})/(P_{B/A}+P_{A/B}) \tag{A5}$$

$$(AB)=(BA)=\frac{P_{A/B}P_{B/A}}{(P_{B/A}+P_{A/B})} \tag{A6}$$

$$(BB)=P_{A/B}(1-P_{B/A})/(P_{B/A}+P_{A/B}) \tag{A7}$$

Substituting equation (A5)–(A7) in equation (A1)–(A4) we obtain:

$$(CTC)=P_{B/A}/2(P_{B/A}+P_{A/B}) \tag{A8}$$

$$(CCC)=2P_{A/B}-P_{A/B}P_{B/A}/2(P_{B/A}+P_{A/B}) \tag{A9}$$

$$(CCT)=P_{A/B}P_{B/A}/(P_{A/B}+P_{B/A}) \tag{A10}$$

$$(TCT)=P_{B/A}-P_{A/B}P_{B/A}/2(P_{A/B}+P_{B/A}) \tag{A11}$$

The triad sequences of *cis*- and *trans*-units of 1,4-polybutadiene appear in the ^{1}H spectra as separate signals[4], hence equations A8–A11 can be regarded as a set of three independent equations with two unknown members $P_{A/B}$ and $P_{B/A}$. Thus the mode of distribution of A and B type units in polyoctadienamer-1,5 can be determined from its ^{1}H n.m.r. spectra.

In the olefinic part of the carbon spectra of polyoctadienamer-1,5 there appear three signals that are linear combinations of resonances from different triads of *cis*- and *trans*-units (see *Table 1*). Taking into account that $(TTC)=(TTT)=0$ we obtain:

$$(CTC)=\frac{P_{B/A}}{2(P_{A/B}+P_{B/A})} \tag{A12}$$

$$(CCC)+1/2(CCT)=\frac{P_{A/B}}{(P_{A/B}+P_{B/A})} \tag{A13}$$

$$(TCT)+1/2(CCT)=\frac{P_{B/A}}{2(P_{A/B}+P_{B/A})} \tag{A14}$$

Calculation predicts that from the ^{13}C n.m.r. spectra of polyoctadienamer-1,5 it is impossible to estimate the value of probabilities $P_{A/B}$ and $P_{B/A}$.