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Aqueous Ring-Opening Metathesis Polymerization of *exo,exo*-2,3-Bis(methoxymethyl)-7-oxanorbornene Catalyzed by Ruthenium Trichloride

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ABSTRACT: *exo,exo*-2,3-Bis(methoxymethyl)-7-oxanorbornene was polymerized by ring-opening metathesis polymerization (ROMP) catalyzed by commercial ruthenium trichloride with aqueous ethanol as solvent. The rate of polymerization (R_p) was followed by ^{13}C NMR as a function of monomer, catalyst, and water concentration. Molecular weights and polydispersities (gel permeation chromatography) were determined as a function of conversion. The results were broadly consistent with a chain reaction but with unusual features: e.g., R_p increased as the catalyst concentration decreased, and the molecular weight was independent of the catalyst concentration. A reaction scheme involving self-deactivation by the catalyst satisfactorily explained the results.

Introduction

Recent publications (Novak and Grubbs[1,2] and Feast and Harrison[3,4]) have described the ring-opening metathesis polymerization (ROMP) of oxanorbornene derivatives {7-oxabicyclo[2.2.1]hept-5-ene derivatives} catalyzed by ruthenium trichloride in alcoholic and aqueous solvents. The emphasis in the experimental work was on the molecular weight and microstructure of the product. No detailed measurements of the rate of reaction have been published, though an "initiation period" (time to the first detection of the polymer) was used by Novak and Grubbs[2] as a measure of reactivity.

Here we describe a study of the polymerization of *exo,exo*-2,3-bis(methoxymethyl)-7-oxanorbornene (BMM-7-ON), i.e., *exo,exo*-2,3-bis(methoxymethyl)-7-oxabicyclo[2.2.1]hept-5-ene, catalyzed by commercial ruthenium trichloride in aqueous ethanol. Attention was paid to the determination of the polymerization rate as a function of monomer, catalyst, and water concentration and of the molecular weight as a function of conversion.

Experimental Section

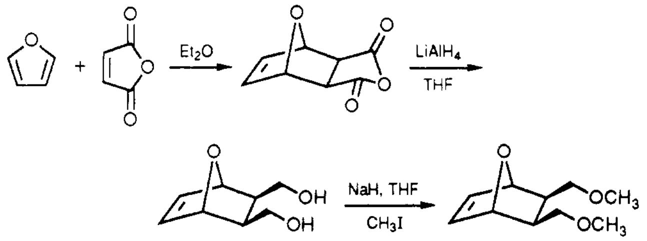
Materials. Laboratory-grade reagents and solvents from a variety of suppliers were used as received. These included ruthenium trichloride (Aldrich Chemical Co., Ltd.), ethanol-d_6 (Aldrich; anhydrous, 99+ atom % D), and deuterium oxide (Aldrich; 100.0 atom % D). For purposes of calculating concentrations, the catalyst was assumed to be $RuCl_3·3H_2O$.

exo,exo-2,3-Bis(methoxymethyl)-7-oxanorbornene was prepared by the Diels–Alder reaction of furan with maleic anhydride followed by reduction and methylation:[5,7] see Scheme I. The product was purified by chromatography through silica gel with 1:2 ethyl acetate and petroleum ether. The overall yield, based on maleic anhydride, was 47 mol %. [^{1}H NMR ($CDCl_3$, 300 MHz) δ 6.34 (s, 2 H), 4.82 (s, 2 H), 3.50–3.25 (m, 4 H), 3.34 (s, 6 H), 1.90 (m, 2 H)].

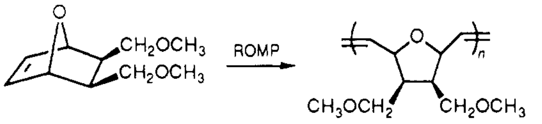
Polymerization. Ring-opening metathesis polymerization (see Scheme II) was carried out at 60–70 °C under a range of conditions, as described later. Provided that the solvent contained at least 50 vol % ethanol, the polymerizing systems were homogeneous.

For many purposes polymerization was carried out in conventional laboratory glassware. For example, the monomer (1.3 g, 7.1 mmol) and $RuCl_3·3H_2O$ (62.5 mg, 0.23 mmol) were dissolved in 10 vol % H_2O in ethanol (3.4 cm^3). The closed 5-cm^3 reaction flask was held in an oil bath at 60 °C and stirred for a time (up to 20 h for high conversion) before diluting with THF and precipitating the polymer from solution by adding pentane. The precipitated polymer was separated and dried under vacuum. The yield of the polymer recovered was comparable to that estimated from the conversion/time curve established by NMR (see below): in the present case it was >80 wt % based on the monomer.

Scheme I



Scheme II



For determination of the molecular weight and the molecular weight distribution as a function of conversion, polymerization was carried out as described above and samples, each 0.02 cm^3 of the reaction mixture, were taken at selected times. Polymers were recovered by evacuating the solvent at room temperature under vacuum and examined by GPC. In a parallel experiment, under the same reaction conditions, conversion was determined as a function of time as described below.

For determination of the conversion as a function of time, reactions were followed by ^{13}C NMR. The required amounts of monomer, catalyst, and solvent (D_2O/CD_3CD_2OD) were mixed in a standard 5-mm NMR sample tube, which was then inserted into the probe which had been preequilibrated at the desired temperature. The consumption of the monomer during polymerization was monitored by recording ^{13}C NMR spectra at different time intervals. The polymer was precipitated and recovered as described above.

The rate of polymerization on adding additional monomer to a completed polymerization was determined as follows. Polym-

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erization was carried out under customary conditions, e.g., 70 °C, 10 vol % D_2O in C_2D_5OD, initial monomer concentration $[M]_0 = 1.45$ mol dm^{-3}, initial catalyst concentration $[C]_0 = 0.049$ mol dm^{-3}. ^{13}C spectra were recorded at selected time intervals, as described above. When the conversion exceeded 90%, monomer and solvent were added so that the monomer concentration was brought back to its initial value. Adjustments were made for dilution by the polymer already formed and for any residual monomer from step 1. No more catalyst was added. The reaction was then continued at the same temperature, and ^{13}C spectra were recorded as before. The polymer was precipitated and recovered as described above.

Infrequently it was noted that prolonged contact with the catalyst led to a product which was insoluble in THF. The results presented below pertain almost entirely to soluble polymers.

NMR Spectroscopy. ^1H and ^{13}C NMR spectra were obtained using a Bruker Spectrospin AC300E spectrometer operating at 300 MHz for ^1H and 75.5 MHz for ^{13}C. The solvents were either $CDCl_3$ or, in the kinetic runs (as described below), ethanol-d_6 plus D_2O.

To determine the rate of polymerization, ^{13}C spectra were acquired from time to time using a pulse interval of 1.34 s and a flip angle of 45°. The time taken to record each spectrum (4 min) was considerably shorter than the time scale of a polymerization (up to 24 h), as was the time of thermal equilibration after insertion of the tube (~5 min). The acquisition conditions did not allow complete relaxation of the monomer and polymer peaks between pulses, so the relative intensities of these peaks in the same spectrum were not directly comparable. However, the relative intensities of the monomer and polymer peaks in successive spectra did accurately reflect the course of the polymerization.

Gel Permeation Chromatography. The GPC system consisted of four μ-Styragel columns (length 30 cm, internal diameter 7.5 mm, nominal pore sizes 500, 10^3, 10^4, and 10^6 Å). The eluent was tetrahydrofuran (THF) at 25 °C and a flow rate of 1 cm^3 min^{-1}. Samples were injected at a concentration of 3 g dm^{-3}. The system was calibrated with polystyrene standards of known molecular weights. Molecular weights were determined either directly from the elution volume at the peak of the GPC curve (M_{pk}) or by numerical integration of the GPC data via a microcomputer (M_w, M_n).

Results

Polymer Microstructure. ^1H and ^{13}C NMR spectra of the polymer produced with $CDCl_3$ as solvent are shown in Figure 1. The assignments given on the spectra are taken from the work of Feast and Harrison,[3] who reported and assigned ^1H and ^{13}C NMR spectra of the present monomer and its polymers prepared using osmium, iridium, and ruthenium trichlorides in water. The resonances of the olefinic and allylic ^1H and ^{13}C nuclei were split by cis/trans isomerism of the double bond, with smaller unassigned splittings from meso/racemic stereoisomerism of adjacent rings. The proportion of the cis isomer, derived from the intensity of the olefinic ^1H resonances, was about 20%: this value is approximately half of the proportion of the cis isomer found in polymers prepared using $RuCl_3$ catalyst in water:[3] presumably the difference is attributable to the use of the ethanol + water as solvent in the preparation.

Rate of Polymerization. A selection of olefinic ^{13}C spectra recorded for the determination of the polymerization rate is shown in Figure 2. The decrease in the intensity of the resonance at $\delta_c = 138.5$, assigned to the olefinic carbons of the monomer, served to monitor the conversion to the polymer. The resonance at $\delta_c \sim 135.4$, split by cis/trans isomerism (see above), was less suited to our purpose.

Plots of fractional conversion against time are shown in Figure 3. The rate accelerated over the first few hours of the reaction. The initial slow period of the reaction appears much more prominent when the data are presented as a plot of reciprocal monomer concentration against time: see Figure 4. In this plot, after the initial period, a straight-line region extends over a wide range of conversion, from 10 to 90% conversion in Figure 4.

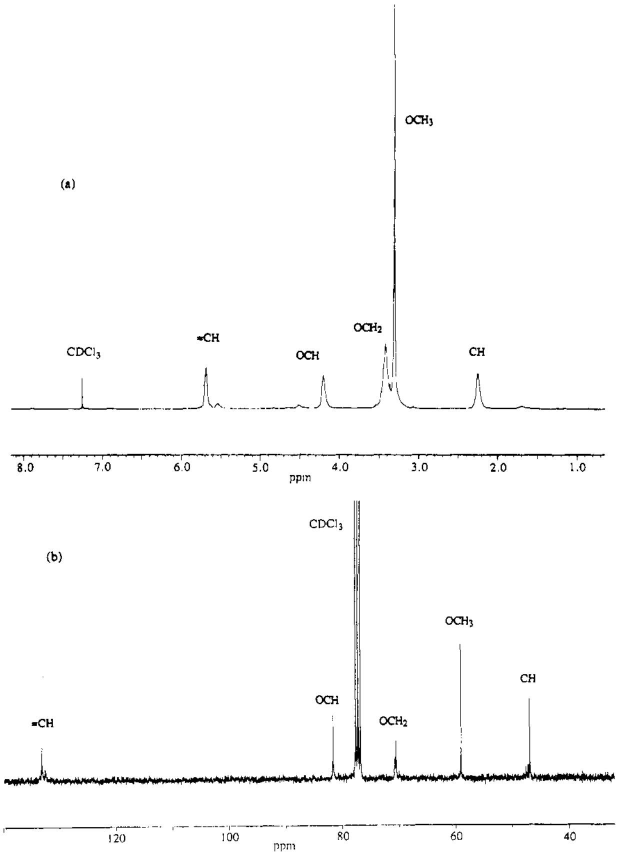

Figure 1. (a) ^1H and (b) ^{13}C NMR spectra of poly[*exo,exo*-2,3-bis(methoxymethyl)-7-oxanorbornene] polymerized (aqueous ROMP) at 70 °C with commercial $RuCl_3$ catalyst and 10 vol % D_2O in CD_3CD_2OD as solvent.

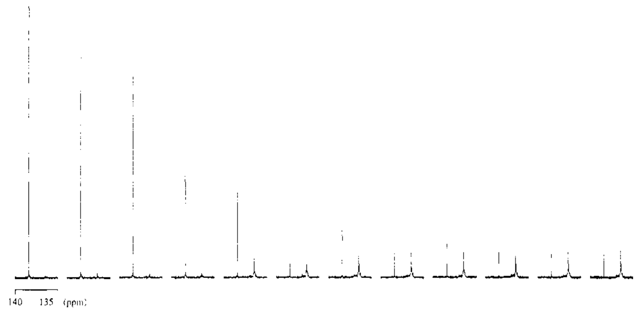

Figure 2. ^{13}C NMR spectra of the olefinic carbon region taken during the aqueous ROMP of *exo,exo*-2,3-bis(methoxymethyl)-7-oxanorbornene (catalyst, commercial $RuCl_3$; solvent, 10 vol % D_2O in CD_3CD_2OD, $T = 70$ °C). The peak at $\delta_c = 138.5$, assigned to the olefinic carbons of the monomer, was used to monitor the conversion to the polymer. From left to right the spectra were recorded at 0, 1, 2, 3, 5, 7, 9, 11, 13, 15, 17, 19, and 21 h.

The effect of varying the catalyst concentration at constant water and monomer concentrations is shown in Figures 3 and 4. After the initial slow period, which was more protracted at high catalyst concentration, each reaction gave a good straight-line plot of reciprocal monomer concentration against time (see Figure 4). Surprisingly, the rate of polymerization increased as the catalyst concentration was decreased. The results of the rate measurements are given in Table I, i.e., time and conversion at the end of the initial slow period and the

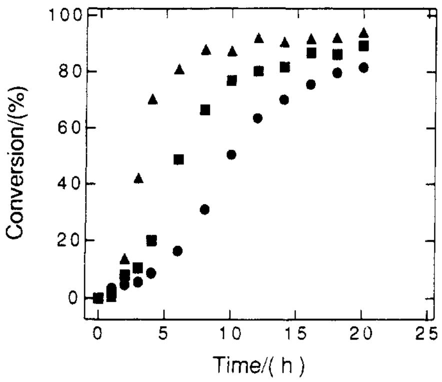

Figure 3. Conversion versus time in the aqueous ROMP of *exo,exo*-2,3-bis(methoxymethyl)-7-oxanorbornene (catalyst, commercial $RuCl_3$; solvent, 10 vol % D_2O in CD_3CD_2OD; $T = 70$ °C). The catalyst concentrations were (▲) 5.07, (■) 17.3, and (●) 53 mmol dm^{-3}. The initial monomer concentration was 1.57 mol dm^{-3} in each case.

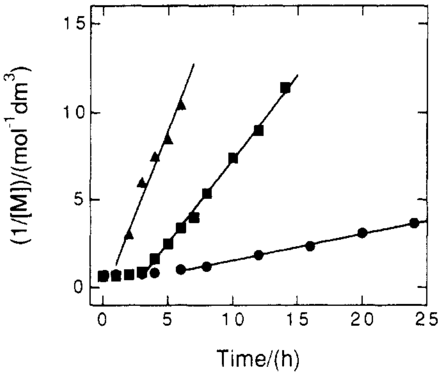

Figure 4. Second-order plots of inverse monomer concentration against time in the aqueous ROMP of *exo,exo*-2,3-bis(methoxymethyl)-7-oxanorbornene (catalyst, commercial $RuCl_3$; solvent, 10 vol % D_2O in CD_3CD_2OD; $T = 70$ °C). The catalyst concentrations were (▲) 5.07, (■) 17.3, and (●) 53 mmol dm^{-3}. The initial monomer concentration was 1.57 mol dm^{-3} in each case.

slope of the straight-line portion of the 1/[M] versus time plot, i.e., the pseudo-second-order rate constant k.

Values of k are plotted against catalyst concentration in Figure 5. The effect of reducing the catalyst concentration to low levels was explored. Rapid polymerization rates were measured at concentrations as low as 2.0 mmol dm^{-3} (mole ratio of monomer to catalyst of 800 or so). No polymerization was detected at or below 1.0 mmol dm^{-3}, possibly as a result of the reaction of the catalyst with impurities in the monomer and solvent. The presence of nitrogen- or sulfur-containing compounds at the 1.0 mmol dm^{-3} level would suffice to deactivate the reactive center.[8]

The external order in the monomer was investigated by determining k at two catalyst concentrations for monomer concentrations in the range 2.5–0.4 mol dm^{-3}. These experiments confirmed the second-order dependence of the rate on monomer concentration and also indicated that k could be reproduced to about ±40%. Values of k and an indication of the extent of the induction period are given in Table I. The effect of water on the polymerization rate is illustrated by the results plotted in Figure 6.

Molecular Weight and Molecular Weight Distribution. GPC curves of all samples were unimodal and fairly broad. Molecular weights at the peak (M_{pk}) are listed in Tables I and II, together with the widths of the number distributions of molecular weight (measured by M_w/M_n). The values are all "as if polystyrene".

For solvents comprising 10–50 vol % water in ethanol, values of $M_{pk} = (1\text{–}3) \times 10^5$ and $M_w/M_n \sim 2$ were consistently found, irrespective of the catalyst concentration (and, over the limited range studied, the monomer concentration). As indicated by the data listed in Table II, the molecular weight and molecular weight distribution of the polymer did not change appreciably with conversion over the range examined (10–90%). From the molecular weights recorded, the ratio of the number of polymer chains produced to the number of catalyst molecules added was small. Rough calculations, comparing initial catalyst concentrations with polymer concentrations at the end of the reaction, place the ratio in the range 0.5–0.02.

At higher water contents (90 and 100 vol %), the values of M_{pk} were about 7×10^5 but the polydispersity was unchanged.

Effect of Adding Fresh Monomer. The polymerization profile of fresh monomer added at the end of the polymerization was checked by means of ^{13}C NMR. As described earlier (see the Experimental Section) the initial monomer concentration in each step was the same. The results of the experiment are shown in Figure 7: the reaction profiles in the two stages are essentially the same. The molecular weight ($M_{pk} \sim 200\,000$) and the molecular weight distribution ($M_w/M_n \sim 2$) were also essentially unchanged by further polymerization. In this experiment, the ratio of the number of polymer chains produced to the number of catalyst molecules added initially was $R \sim 0.03$ after stage 1 and $R \sim 0.06$ after stage 2. Presumably the polymerization of the second portion of the monomer was initiated by excess catalyst.

Discussion

Comparison with Previous Results. No systematic rate measurements have been published for aqueous ROMP systems prior to this work. Use of the initiation period to assess the reaction rate[1,2,9] can be complicated by the initial slow period, whereby the first stages of polymerization are not necessarily representative of the overall reaction. For example, changing from 10 to 0 vol % water in ethanol (other conditions being constant) increases the steady-state rate of polymerization but at the same time increases the initial slow period: see Table I.

Molecular weights and polydispersities can be compared with previous work. Our molecular weights are in substantial agreement with those reported by Novak and Grubbs:[1,2,9] i.e., about 10^5 for polymerization in solvents of low water content and about 10^6 in water itself. Our molecular weight distributions invariably conform to the "most probable", for which $M_w/M_n \sim 2$, whereas Novak and Grubbs report narrower distributions from ROMP in water. The reason for this discrepancy is not known. We note that Feast and Harrison[3] report a high polydispersity ($M_w/M_n \sim 2.5$) for a polymer produced by ROMP catalyzed by $RuCl_3$ in water but that their polymer had a relatively low molecular weight, near 10^5.

Reaction Scheme. The majority of our results are for ROMP of *exo,exo*-2,3-bis(methoxymethyl)-7-oxanorbornene with 10 vol % water in ethanol (or its deuterated analogue) as solvent. Consequently, discussion centers on results for that system. Indications are that similar considerations will apply to ROMP in solvents of low to moderate water content (10–50 vol %) but that additional considerations might apply to polymerization in solvents of high water content or in dry ethanol. Unfortunately time was not available for an investigation of the rates of ROMP in more than one solvent system.

The reaction rates and molecular weights at a given catalyst concentration can be rationalized within a con-

Table I
ROMP of *exo,exo*-2,3-Bis(methoxymethyl)-7-oxanorbornene Catalyzed by Commercial $RuCl_3$: Polymerization in NMR Tubes[a]

$[C]_0$, mol dm^{-3}	water, vol %	monomer, mol dm^{-3}	$k \times 10^4$, dm^3 mol^{-1} s^{-1}	slow period time, h	slow period convn, %	final convn, %	$10^{-5}M_{pk}$ (GPC)	M_w/M_n (GPC)
0.0006	10	1.57	no reaction					
0.0010	10	1.57	no reaction					
0.0020	10	1.57	8.08	1.0	15	93.1	2.8	1.8
0.0051	10	1.57	5.31	1.5	14	95.2	1.6	1.9
0.010	10	1.57	3.33	2.5	16	89.6	1.5	1.8
0.017	10	2.5–0.4	1.81[c]	4.0	20	94.4	2.5	1.8
0.029	10	1.57	0.80	5.5	26	88.5	1.8	1.9
0.053	10	1.6–0.7	0.60[c]	6.0	16	81.7	2.0	2.0
0.053	0	1.57	1.28	10.0	36	90.7	*b*	*b*
0.053	30	1.57	2.81	2.0	26	96.3	2.0	1.9
0.053	50	1.57	6.11	1.5	20	91.2	1.5	2.1

[a] Polymerization conditions: 70 °C; ethanol/water solvent. [b] Polymer incompletely soluble in THF. [c] Averages of several runs with different monomer concentrations; the other results in the table are for $[M]_0 = 1.57$ mol dm^{-3}.

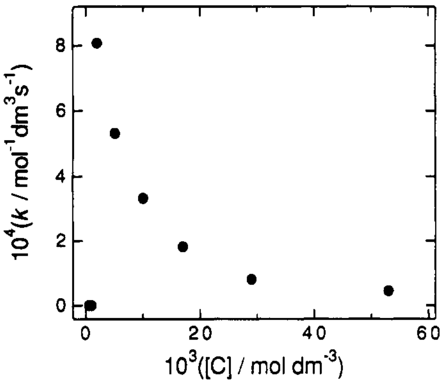

Figure 5. Pseudo-second-order rate constant versus catalyst concentration in the aqueous ROMP of *exo,exo*-2,3-bis(methoxymethyl)-7-oxanorbornene (catalyst, commercial $RuCl_3$; solvent, 10 vol % D_2O in CD_3CD_2OD; $T = 70$ °C).

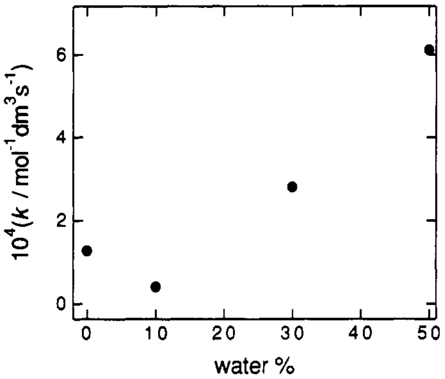

Figure 6. Effect of the water concentration on the pseudo-second-order rate constant (k) in the aqueous ROMP of *exo,exo*-2,3-bis(methoxymethyl)-7-oxanorbornene (catalyst, commercial $RuCl_3$; solvent, D_2O in CD_3CD_2OD; $T = 70$ °C). The initial monomer concentration was 1.53 mol dm^{-3}. The catalyst concentration was 0.053 mol dm^{-3}.

ventional framework: i.e., a chain reaction involving slow formation of an active species (initiation) and slow termination of the chain, giving rise to a steady-state concentration of active species, and a rapid propagation reaction, with a kinetic chain length of about 1000 steps limited mainly by chain transfer. The unusual features of the polymerization are the inverted dependence of the rate on the catalyst concentration and the independence of the molecular weight on the catalyst and monomer concentrations. In any explanation, the composition of commercial ruthenium trichloride[8] must be borne in mind. However, it was noted that rates of reaction and molecular weights were reasonably well-reproduced (about ±40%) when using ruthenium trichloride from different batches (but the same supplier), even when catalyst levels were very low. Accordingly, we seek an explanation of the effects in terms of the concentrations of the major reactants rather than minor impurities.

Table II
ROMP of *exo,exo*-2,3-Bis(methoxymethyl)-7-oxanorbornene Catalyzed by Commercial $RuCl_3$: Polymerization in Laboratory Glassware[a]

$[C]_0$, mol dm^{-3}	water, vol %	T, °C	time, h	convn, %	$10^{-5}M_{pk}$ (GPC)	M_w/M_n (GPC)
0.017	10	70	2.0	11	1.7	1.7
0.017	10	70	4.0	20	1.6	1.9
0.017	10	70	6.0	49	1.9	1.8
0.017	10	70	8.0	66	1.6	1.7
0.017	10	70	18	86	1.3	1.8
0.017	10	70	20	89	1.3	1.8
0.017	90	60	4.0	86	7.0	2.0
0.017	100	60	5.0	98	6.5	2.0

[a] Polymerization conditions: $[M]_0 = 1.57$ mol dm^{-3}; ethanol/water solvent. The polymers were insoluble in 90% and 100% water.

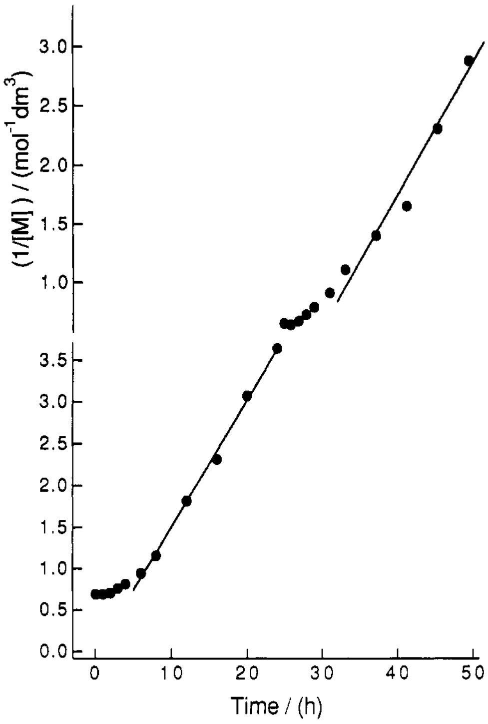

Figure 7. Effect of adding fresh monomer on completion of the aqueous ROMP of an initial charge of *exo,exo*-2,3-bis(methoxymethyl)-7-oxanorbornene (catalyst, commercial $RuCl_3$; solvent, 10 vol % D_2O in CD_3CD_2OD; $T = 70$ °C). In each stage the initial monomer concentration was 1.45 mol dm^{-3}. The catalyst concentration was 0.049 mol dm^{-3}.

The following formal scheme fits the results. It is assumed that catalyst is added in the form Ru^{III}. Reactions i, ii, and vii are not necessary to our immediate purpose: the form of the rate and molecular weight equations is unchanged by their inclusion. Equilibria i and ii are included in view of recent evidence which favors an Ru^{II} π-complex with monomer as the active species.[9,10] Reaction vii is included to accommodate related work on copolymerization, which will be published shortly.[11]

(i) $2C^{III} \rightleftarrows C^{II} + C^{IV}$ disproportionation K_0

(ii) $C^{II} + M \rightleftarrows \Pi$ π-complex formation K_1

(iii) $\Pi \rightarrow P^*$ initiation (slow) k_i

(iv) $P^* + nC \rightleftarrows PC_n$ deactivation/reactivation k_d, k_{-d}

(v) $P^* + M \rightarrow P^*$ propagation k_p

(vi) $P^* + M \rightarrow P + P^*$ transfer to monomer $k_{tr,m}$

(vii) $P^* + P \rightarrow P + P^*$ transfer to polymer $k_{tr,p}$

(viii) $P^* \rightarrow P$ termination k_t

It is assumed that K_0 and K_1 are small, so that C, which formally represents the Ru^{III} concentration in whatever form (possibly $[RuCl_2(H_2O)_4]^+Cl^-$),[8] is practically equivalent to the total Ru concentration. Equilibria i and ii lead to

$$[C^{II}] = K_0^{1/2}[C]$$

$$[\Pi] = K_1K_0^{1/2}[C][M]$$

i.e.

$$[\Pi] \propto [C][M]$$

It is assumed that equilibrium iv is multistage: e.g.

$$P^* + C \rightleftarrows PC_1, \quad PC_1 + C \rightleftarrows PC_2, \quad \text{etc.}$$

Accordingly, the parameter n will have a value which depends on the position of equilibrium.

Rate of Polymerization. Application of the steady state to the active species, P*, gives

$$d[P^*]/dt = 0 = k_i'[C][M] - k_d[P^*][C]^n + k_{-d}[PC_n] - k_t[P^*]$$

where $k_i' = k_iK_1K_0^{1/2}$. If it is assumed that equilibrium iv lies well to the right (i.e., that $k_d \gg k_{-d}$), then $[PC_n] \sim [P^*]$ and

$$[P^*] \sim k_i'[C][M]/\{k_d[C]^n - k_{-d} + k_t\}$$

or with $k_d \gg k_{-d}$

$$[P^*] \sim k_i'[M]/k_d[C]^{n-1}$$

Hence, the rate of polymerization is

$$R_p \sim k_p[P^*][M] \sim k'[M]^2[C]^{1-n}$$

where $k' = k_i'k_p/k_d$, or

$$R_p \sim k[M]^2 \tag{1}$$

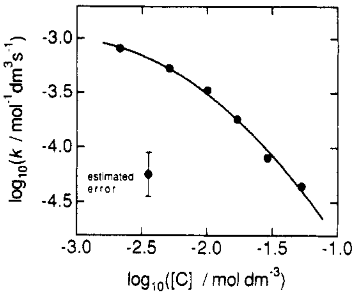

Figure 8. Double-logarithmic plot of pseudo-second-order rate constant (k) against catalyst concentration for the aqueous ROMP of *exo,exo*-2,3-bis(methoxymethyl)-7-oxanorbornene (catalyst, commercial $RuCl_3$; solvent, 10 vol % D_2O in CD_3CD_2OD; T = 70 °C). The reproducibility of the determination of log k is indicated. The curve is the best (least-squares) quadratic fit to the data.

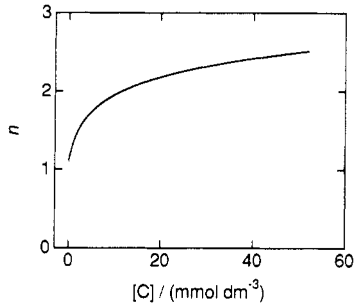

Figure 9. Advancement (n) of equilibrium iii versus catalyst concentration. The curve is derived from the quadratic fit to the data illustrated in Figure 8.

where

$$k = k'[C]^{1-n} \tag{2}$$

This last relationship suggests a plot of log k against log [C], as shown in Figure 8. The results are well-fitted (least squares) by a quadratic function

$$\log 10^4k = -6.99 - 2.56 \log [C] - 0.41 (\log [C])^2$$

where k is in dm^3 mol^{-1} s^{-1} and [C] is in mol dm^{-3}. The slope is $(1 - n)$; hence, n is given by

$$n = 3.56 + 0.82 \log [C] \tag{3}$$

The values of n obtained in this way are plotted against [C] in Figure 9. As can be seen, n falls sharply as the catalyst concentration approaches the lowest values for which rates were measured ([C] = 0.002 mol dm^{-3}) and reaches a value of about 2.5 at the highest catalyst concentrations used. The least-squares analysis indicates an error in the quadratic fit of a point of at least ±30%. Consequently the upper limit of n cannot be defined more precisely than either 2 or 3.

If it is assumed that the reaction stopped at very low catalyst concentration because of impurities in the solvent or monomer, then the catalyst concentrations at all levels should be reduced by a small amount. Accounting for this effect, e.g., by deducting 1.5 mmol dm^{-3} from each catalyst concentration, did not change the overall result significantly.

Chain Length. The kinetic chain length, ν, is equivalent to the number-average chain length of the polymer, x_n, since termination involves only one active chain. In the usual way for high polymer, ignoring the initiation step and noting that transfer to polymer does not affect the number-average chain length, we use

$$\nu = x_n = \text{rate of propagation}/(\text{rate of termination} + \text{rate of transfer to monomer})$$

to obtain

$$x_n = k_p[M]/\{k_t + k_{tr,m}[M]\}$$

Hence the chain length (molecular weight) is independent of the catalyst concentration. The effect of conversion, i.e., of lowering the concentration of the monomer, depends on the relative values of the two terms in the denominator of the expression for x_n, i.e., k_t and $k_{tr,m}[M]$. If transfer to monomer is favored over termination, then $k_{tr,m} \gg k_t$, and x_n will be independent of the monomer concentration unless [M] is very small; i.e., x_n will be independent of conversion until very high conversion is reached. The molecular weight distribution will be most probable (i.e., $M_w/M_n \sim 2$), since this is the result of both chain-limiting reactions: (vi) transfer to monomer and (viii) termination. Transfer to polymer, by secondary metathesis at random points along the chain, would not change either the molecular weight or the polydispersity.

Effect of Water. The reported[1,2,9] increase in polymerization rate with water concentration was confirmed at water concentrations higher than 10 vol %, including the high rate for ROMP in water itself. Within the proposed mechanism, this must be attributed to an increase in the concentration of the active centers, [P*], presumably through equilibrium iv. The high molecular weights found for polymers prepared in solvents of high water content (but not moderate water content) are consistent with an increase in the reactivity of the active center toward propagation relative to transfer to monomer (i.e., a decrease in the chain-transfer constant $C_{tr} = k_{tr,m}/k_p$). However, it must be remembered that we have no substantial evidence to confirm that the reaction scheme which successfully explains the results for solvents with low water content applies equally to systems with high water contents.

Concluding Remarks. It can be seen that the scheme provides a basis for understanding the second-order dependence of R_p on the monomer concentration (via eq 1) and, in particular, the unusual dependence of R_p on the catalyst concentration (via eq 2 and equilibrium iv). It also provides an explanation of the observed molecular weights: i.e., the independence of the molecular weight on the catalyst and monomer concentrations, as well as the polydispersity of the product, $M_w/M_n \sim 2$.

The curious effect of the catalyst concentration upon the rate of reaction, i.e., that an increase in the catalyst concentration has a deleterious effect upon the rate of reaction, begs further investigation. The use of a preformed ruthenium carbene complex in further kinetic and mechanistic studies is indicated.

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