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Kinetics and Thermodynamics of the Metathesis Reaction of Cycloolefins. 2. Molecular Weight Distribution[†,‡]

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ABSTRACT: The metathesis reaction of cycloolefins results in cyclic oligomers and a linear polymer as demonstrated directly by means of GPC in conjunction with a laser small-angle light scattering detector. The polymer shows a most probable molecular weight distribution. The oligomer concentration in the kinetically controlled regime is proportional to $x^{-3/2}$ (x being the degree of polymerization), in accord with a carbene back-biting mechanism. When the thermodynamic equilibrium is established, the oligomer distribution is determined by a ring-chain equilibrium. From a Jacobson-Stockmayer plot of the cyclooctene oligomer concentration a characteristic ratio of 5.8 is derived for polyoctenylene and 13.9 for polynorbornene. In the former case the non-Θ character of the solvent of the reaction, chlorobenzene, becomes evident, yielding a Mark-Houwink exponent $a = 0.68$.

Introduction

The metathesis reaction of olefins is a trans-alkylidenation reaction.[2] The mechanism of the reaction was shown to follow a nonpairwise pathway,[3] and the active species is assumed to comprise a transition-metal-carbene complex,[4] the carbene ligand being exchanged against an alkylidene group of the olefins. The metathesis reaction of cycloolefins[5] results in polymers. According to the carbene mechanism, the polymerization occurs by insertion of the monomer into the transition-metal-carbene bond. The molecular weight of the polymers can be controlled by the addition of acyclic olefins.[6] The polymer is assumed to consist of linear open-chain molecules.[7] In general, besides the polymer, residual monomer[8] and/or a homologous series of cyclic oligomers[9] are formed by a "back-biting" reaction. The relation between acyclic polymer and cyclic oligomers was discussed in terms of a ring-chain equilibrium.[10] The equilibrium, however, is not established instantaneously; in some instances cyclic oligomers are not observed at all. This can be attributed to kinetic hindrance, i.e., to a partially deactivated catalyst.[11] Hence one clearly can distinguish between a kinetically and a thermodynamically controlled regime of the reaction.

The product distribution to be observed under kinetic and thermodynamic control is the subject of the present paper.

Experimental Part

Argon (Linde) was passed over columns filled with molecular sieves, metallic K on Al_2O_3, and Cr(II) on SiO_2 (reduced Phillips catalyst).

Chlorobenzene (Fluka) was purified by chromatography over molecular sieves (4 Å) and aluminum oxide (Woelm, activity super 1) and subsequent refluxing over CaH_2 under an Ar atmosphere; it was distilled off before use.

WCl_6 (Alfa Ventron, "resublimed") was stored under an Ar atmosphere and dissolved in chlorobenzene (0.05 M) before use.

$(CH_3)_4Sn$ (Aldrich) was stored over molecular sieves under an Ar atmosphere. Before use it was dissolved in chlorobenzene (0.1 M).

Cyclooctene (Hüls) was refluxed over K and distilled before use. The absence of cycloocta-1,3-diene was examined by GC. Residual cyclooctane (2-3%) was used as internal standard for the determination of conversion by GC.

Norbornene (Aldrich) was treated in a similar way.

Polymerizations were performed in a glass apparatus under an Ar atmosphere at room temperature. Monomer and solvent (chlorobenzene) were introduced first; the solutions of the catalyst

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[†] Dedicated to Professor Walter H. Stockmayer on the occasion of his 70th birthday.

[‡] Part 1 is ref 1.

components were added simultaneously, the Sn:W molar ratio being 2:1 in all cases and the monomer:WCl_6 molar ratio being between 100 and 500. The mixtures were magnetically stirred. The reactions were quenched by the addition of methanol. Before the products were examined by GPC, the solutions were passed over a 1-cm-long column filled with Al_2O_3 to remove residual catalyst. Then the solvent was distilled off and the samples were redissolved in THF.

In general, the samples can be safely stored at −20 °C after addition of ionol (di-*tert*-butyl-*p*-cresol).

The analysis of oligomers and polymers was performed by means of different GPC setups:

GPC I: Servagel 3000; particle diameter, 42–50 μm; length, 2 m; flow rate, 15 mL/h (THF); detector, differential refractometer Waters R 403.

GPC II: PL (Polymer Laboratories) gel; particle size, 5 μm; pore width, 10 and 50 nm; length, 50 cm of each; pump, Waters 600 A; flow rate, 0.5 mL/min (THF); detector, differential refractometer Waters R 401 or Melz LCD 201 and UV Waters 440 (254 nm).

GPC III: μ-Styragel (Waters); particle diameter, 15 μm; pore width, 10, 50, 10^2, 10^3, and 10^4 nm; two columns (length, 30 cm) of each; pump, Waters 600 A; flow rate, 1 mL/min; detector, R 401, LCD 201, Waters 440, small-angle laser light scattering (SALLS) detector Chromatix KMX 6 (633 nm) in conjunction with a μl computer (Computer Center, University of Bayreuth).

The refractive index increment was determined by means of a Chromatix KMX 16 laser differential refractometer (633 nm).

Distribution of Oligomers

(a) Kinetically Controlled Regime. The basis for developing a distribution function of the cyclic oligomers is the carbene mechanism and, in particular, the back-biting reaction mentioned above.

The probability density for the two ends of a chain segment with x monomer units to be situated in the same unit volume according to Kuhn[13] is given by

$$W_x(0) = (3/2\pi\langle r_x^2\rangle)^{3/2} \qquad (1)$$

$\langle r_x^2\rangle$ is the mean square end-to-end distance of the chain segment, being proportional[21] to the number of monomer units x in the segment:

$$\langle r_x^2\rangle = C_x n_0 l^2 x \qquad (2)$$

where C_x is the characteristic ratio, n_0 is the number of bonds per monomer unit, and l is the averaged bond length.

The rate of formation of a ring with x monomer units, M_x, is given by

$$d[M_x]/dt = k_x[C^*] \qquad (3)$$

where [C*] is the concentration of active chain ends, e.g., transition-metal–carbene bonds, and k_x is the respective rate constant.

Assuming equal reactivity of all double bonds along the chain and assuming further a strain- or enthalpy-free back-biting reaction, k_x should be proportional to $W_x(0)$:

$$k_x \sim W_x(0) \sim x^{-3/2} \qquad (4)$$

Integration of eq 3 yields in conjunction with eq 4

$$[M_x]_t = A_t x^{-3/2} \qquad (5)$$

A_t being a time-dependent proportionality constant. This equation suffers from the fact that the distribution of the back-biting species is not taken into account.

In particular, in the early stage of the reaction (kinetically controlled regime) the average chain length is still small. To form a cyclic oligomer with x monomer units the back-biting chain has to have at least a degree of polymerization of x. Therefore a factor q_x has to be added to the right-hand side of eq 5, taking into account the limited fraction of chains with a minimum degree of polymerization to form the cycle M_x:

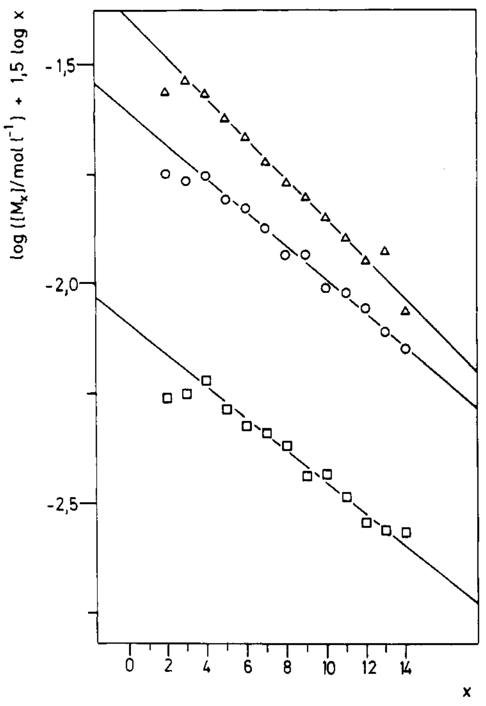


Figure 1. Concentration of cyclooctene oligomers as a function of degree of polymerization plotted according to eq 9: (□) 6.5% conversion; (○) 21.0% conversion; (△) 35.0% conversion. $[COE]_0$ = 0.5 mol L^{-1}, [COE]/[W] = 100, $WCl_6/(CH_3)_4Sn$ = 1:2, solvent chlorobenzene, room temperature.

$$[M_x]_t = A_t x^{-3/2} q_x \qquad (6)$$

The molar mass distribution of the living species cannot be determined experimentally. It is reasonable, however, to assume a most probable distribution as observed for the polymer (cf. below). Then the number fraction $n(x)$ of polymers with a degree of polymerization of x is

$$n(x) = \text{constant} \times \alpha^x \qquad (7)$$

$$q_x = \alpha^x$$

with α being the characteristic parameter of the distribution ($\alpha = 1 - 1/P_n$). Substitution into eq 6 yields

$$[M_x]_t = A_t x^{-3/2} \alpha^x \qquad (8)$$

Equation 8 can be linearized to yield

$$\log [M_x]_t + 1.5 \log x = \log A_t + x \log \alpha \qquad (9)$$

A plot of the left-hand side of eq 9 against x should yield a straight line with a slope of log α. As Figure 1 shows, linearity is fulfilled quite satisfactorily, although some scatter is observed.[22]

The analogous analysis of oligomer concentrations obtained with catalytic systems other than the one used for the experiments given in Figure 1 leads to straight lines as well. This may indicate that the results are compatible with the assumption made with respect to the mechanism of the reaction, i.e., chain growth with consecutive ring formation by back-biting. A stepwise (pairwise) oligomer formation should result in a most probable distribution of oligomers.

(b) Thermodynamically Controlled Regime. The thermodynamically controlled regime is characterized by a ring–chain equilibrium[10] as observed with many other polyreactions.[13]

According to Jacobson and Stockmayer,[14] the equilibrium constant K_x for a cyclic oligomer in a ring–chain equilibrium is given by

$$K_x = \frac{W_x(0)}{N_A\sigma_{Rx}} = \frac{1}{N_A\sigma_{Rx}}\left(\frac{3}{2\pi\langle {r_x}^2\rangle}\right)^{3/2} \tag{10a}$$

$$K_x = \left(\frac{3}{2\pi}\right)^{3/2}\frac{1}{N_A\sigma_R}(n_0 l^2 c_x)^{-3/2}x^{-5/2} \tag{10b}$$

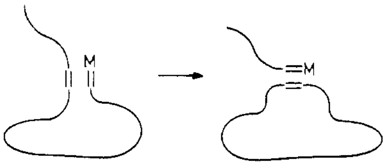
where K_x is defined by the equilibrium between an acyclic polymer with degree of polymerization of y on the one side and the cyclic oligomer with a degree of polymerization of x and the residual acyclic polymer with a degree of polymerization of $y - x$ on the other.

$$-M_y- \rightleftharpoons -M_{y-x}- + M_x \tag{11}$$

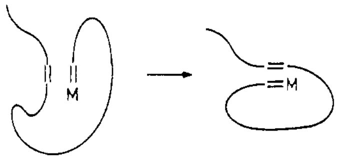
$$K_x = \frac{[-M_{y-x}-][M_x]}{[-M_y-]} = \frac{[M_x]}{\alpha^x} \tag{12}$$

N_A is Avogadro's number and $\sigma_{Rx} = x\sigma_R$ is the symmetry number of the cyclic oligomer, σ_R being the symmetry number of the cyclic monomer. At sufficiently high P_n ($\geq$100), α can be approximated by 1 and $K_x = [M_x]$. Hence a plot of log $[M_x]$ vs. log x is expected to result in a straight line with a slope of -2.5 (according to eq 10).

Equation 10 can also be deduced from kinetic arguments. First, it is to be taken into a account that only half of the possible back-biting situations lead to the formation of cyclic oligomers, namely, eq 13a.



(13a)



(13b)

Following eq 3, 4, and 7 the rate of formation of cyclics M_x is given by

$$\frac{d[M_x]}{dt} = \frac{W_x(0)}{2N_A}\alpha^x k_M[C^*] \tag{14}$$

The rate of reaction of a cyclic oligomer is proportional to its concentration and the number of double bonds, i.e., x:

$$-\frac{d[M_x]}{dt} = k_M[M_x]x[C^*] \tag{15}$$

For equilibrium it follows from eq 14 and 15 that

$$[M_x] = \frac{W_x(0)}{2N_A x}\alpha^x \tag{16}$$

which corresponds to eq 10a (considering also eq 12b). This is an independent proof for the symmetry number to be 2.

Figure 2 shows a corresponding plot. For the lower members of the homologous series of cyclic oligomers the prerequisites of eg 10 evidently are not fulfilled, e.g., the Gaussian statistics of the distribution of the segment end-to-end distances and the enthalpy-free character of the reaction.

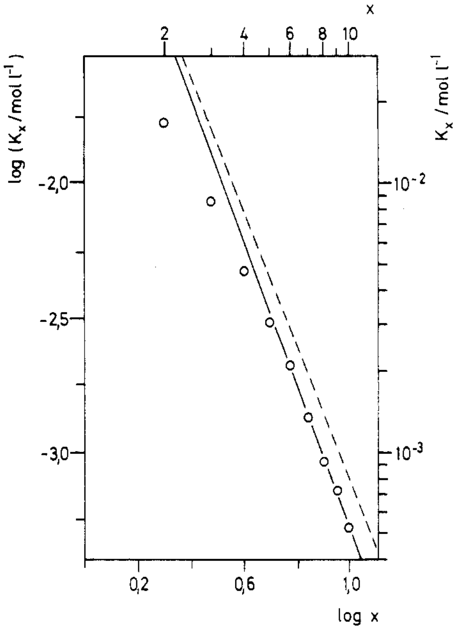


Figure 2. Jacobson–Stockmayer plot of cyclooctene oligomers. Conversion 100%, reaction time 4 h, to guarantee the establishment of the thermodynamic equilibrium. $[COE]_0 = 0.28$ mol L^{-1}; other conditions as given in Figure 1. The broken line has a slope of -2.5.

For the higher members of the series, however, the relationship seems to be steeper than predicted. This discrepancy probably is due to the fact that the equilibrium was achieved in a thermodynamically good solvent instead of a Θ-solvent. Equation 10, however, was developed for the unperturbed dimensions.

Using[15]

$$\langle {r_x}^2\rangle = x^{(2a-1)/3}\langle {r_x}^2\rangle_\Theta \tag{17}$$

where a is the exponent of the Mark–Houwink relation between intrinsic viscosity and molecular weight, eq 10 may be transformed into

$$K_x = \left(\frac{3}{2\pi}\right)^{3/2}\frac{1}{N_A\sigma_R}(C_x n_0 l^2)^{-3/2}x^{-(2+a)} \tag{18}$$

From the slope of the straight line in Figure 2 a value of $a = 0.68$ may be calculated. This is a reasonable exponent as compared with the systems polyoctenylene/toluene (0.67),[16] polypentenylene/toluene (0.69),[17] and polybutadiene/toluene (0.72).[18]

The characteristic ratio as calculated from Figure 2 is for polyoctenylene (70% trans)

$$C_\infty = 5.8$$

with $l = 1.515$ Å and $\sigma_R = 2$ for cyclooctene. This value is identical with that for 1,4-polybutadiene (trans) and is between the value for polyethylene (6.7) and *cis*-1,4-polybutadiene (4.9).

Cutoff Point

The cutoff point is by definition the monomer concentration below which only cyclics are formed. This limiting monomer concentration is identical with the limiting oligomer concentration c_{oligmer} (in base mol L^{-1}). At the cutoff point, the equilibrium cyclic concentration is achieved and remains constant. The excess monomer is consumed to form the polymer.

$$c_{\text{oligomer}} = \sum_x x[M_x]$$

Values from Figure 2 yield $c_{\text{oligmer}} = 0.21$ base mol L^{-1}. This concentration agrees well with that to be read off

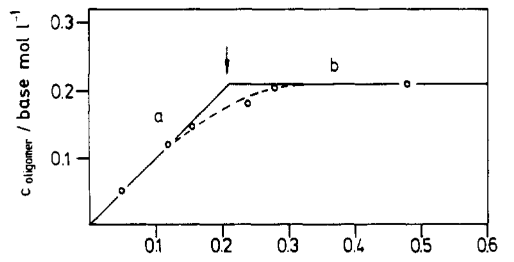


Figure 3. Oligomer fraction as a function of initial monomer concentration for cyclooctene. Conditions as given in Figure 1. (a): $\sum_x x[M_x] = [COE]_0$; (b): $\sum_x x[M_x]$ = constant = 0.21 base mol L^{-1}.

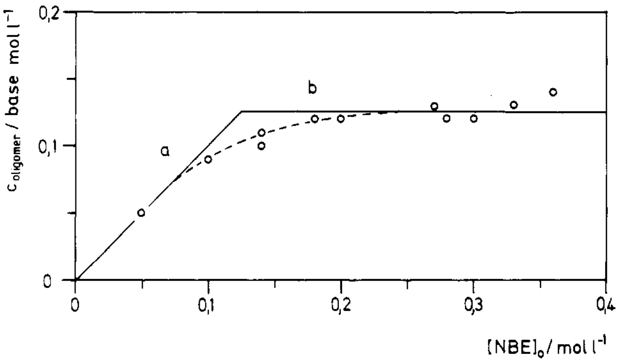


Figure 4. Oligomer fraction as a function of initial monomer concentration for norbornene. [NBE]/[W] = 100; $WCl_6/(CH_3)_4Sn$ = 1:2; solvent chlorobenzene, room temperature. (a): $\sum_x x[M_x] = [NBE]_0$; (b): $\sum_x x[M_x]$ = constant = 0.125 base mol L^{-1}.

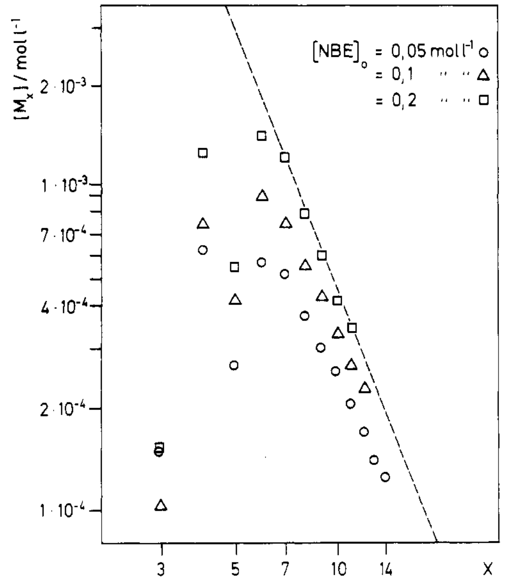


Figure 5. Plot of molar norbornene oligomer concentration as a function of degree of oligomerization according to Jacobson and Stockmayer for different initial monomer concentrations, $[NBE]_0$: (○) 0.05; (△) 0.1; (□) 0.2 mol L^{-1}. The slope of the broken line is −2.5.

Figure 3, which shows the yield of oligomers for cyclooctene.

Norbornene

In the case of the metathetical polymerization of norbornene, a ring-chain equilibrium was observed only recently.[19]

Figure 4 shows the dependence of the concentration of cyclics on the initial monomer concentration, and Figure 5 a Jacobson–Stockmayer plot. The cutoff point observed is c = 0.125 base mol L^{-1}, and the slope of the Jacobson–Stockmayer plot is close to −2.5. Hence, for polynorbornene, chlorobenzene may be regarded as a Θ-solvent.

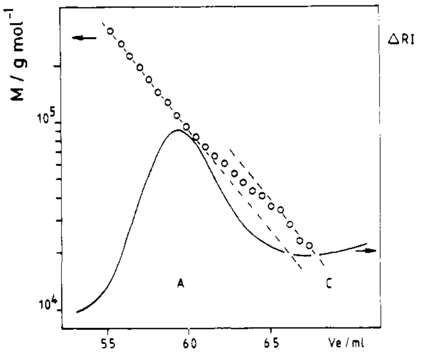


Figure 6. GPC elution curve (full line) and calibration curve (open circles and broken lines) for a metathetical polymer of norbornene as obtained by using both differential refractometer and small-angle laser light scattering apparatus as detectors. (Setup GPC III, low molecular weight fraction omitted). $[NBE]_0$ = 0.14 mol L^{-1}; other conditions as given in Figure 4.

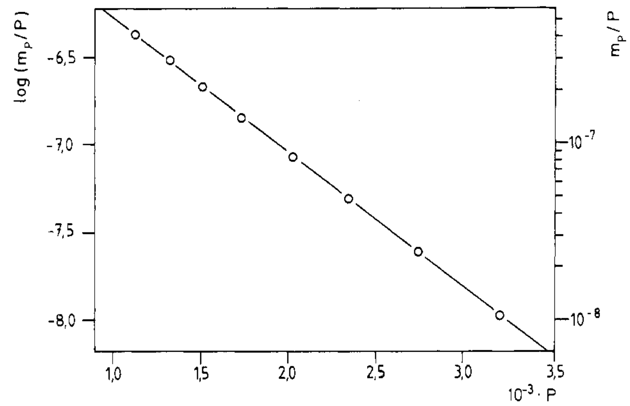


Figure 7. Most probable molecular weight distribution plot for polynorbornene according to eq 17. Experimental conditions as given in Figure 6.

The characteristic ratio C_∞ (resulting from Figure 5) turns out to be 13.9 and thus rather high.

In the case of polynorbornene, the molecular weight distribution of the total methathesis products was investigated by GPC using a SALLS detector. In Figure 6 the elution curve is shown together with the calibration curve as derived from the absolute molecular weight values of the individual fractions as continuously determined by means of the light scattering detector.

Although in the oligomeric region the scattering intensity is low because of both small concentration and small size of the molecules, it is clearly seen that two calibration curves result, one for the open-chain high molecular weight polymers and one for the cyclic oligomers, the latter being shifted to larger elution volumes as compared with the former, expected.[20]

Moreover, Figure 7 shows that the molecular weight distribution of the polymer very closely corresponds to a Schulz–Flory distribution.

$$m_P = P\,(\ln^2 \alpha)\alpha^P \qquad (19a)$$

$$\log (m_P/P) = \log (\ln^2 \alpha) + P \log \alpha \qquad (19b)$$

This is a general observation, which surprisingly also can be made when—probably because of partial deactivation of the catalyst—no oligomers are found as in the case of the polymerization of norbornene in the presence of small amounts (0.2 mol %) of isoprene[11] (Figure 8).

The full analysis of the molecular weight distribution of the linear polymers by means of GPC allows the de-

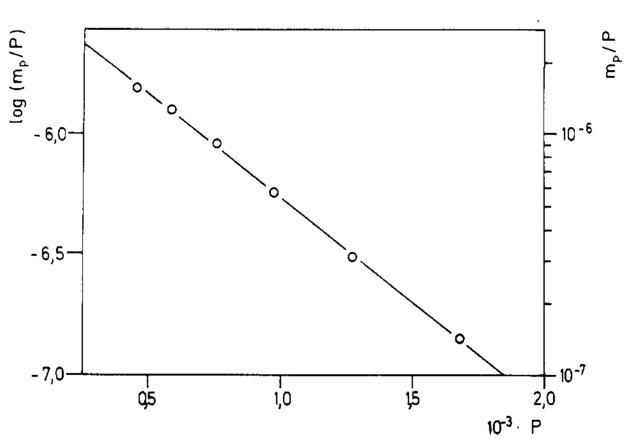


Figure 8. Most probable molecular weight distribution plot for polynorbornene as obtained in the presence of 0.2 mol % (with respect to [NBE]) isoprene. $[NBE]_0 = 0.3$ mol L^{-1}; other experimental conditions as given in Figure 4.

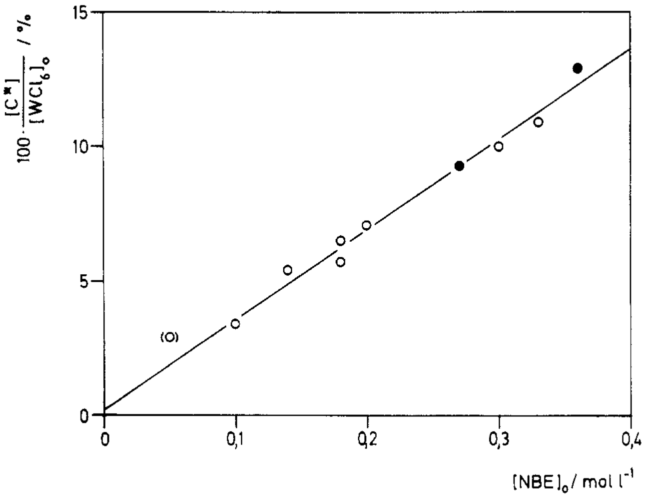


Figure 9. Molar fraction of active sites $[C^*]/[WCl_6]_0$ as a function of initial monomer (NBE) concentration. Experimental conditions as given in Figure 6. (○) $[NBE]_0/[WCl_6]_0 \approx 100$; (●) $[NBE]_0/(WCl_6)_0 \approx 180$.

termination of P_w and P_n. For a most probable distribution as obtained in the present case it can be shown that $P_w = P_{GPC,max}$, where $P_{GPC,max}$ is the degree of polymerization corresponding to the maximum of the GPC elution curve. This equality in the limits of experimental error is well reproduced; i.e., from Figure 8 it results that $P_w = 1000$ and $P_{GPC,max} = 980$.

The knowledge of P_n, on the other hand, allows the determination of the molar concentration of active sites $[C^*]$ according to

$$P_n = c_{polymer}/[C^*]$$

$c_{polymer}$ being the total concentration of the polymer in base mol L^{-1}.

In Figure 9 the molar fraction of active sites with respect to the initial WCl_6 concentration is plotted vs. the initial monomer (NBE) concentration. The linear relationship suggests that the monomer is taking part in the formation of the active species.

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Registry No. Poly(1,3-cyclopentanediyl-1,2-ethenediyl), 42813-64-9; cyclooctene homopolymer, 25267-51-0; poly(1-octene-1,8-diyl) (SRU), 28702-45-6; poly(2-norbornene) (homopolymer), 25038-76-0.

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(22) It should be noted that a cis–trans isomerization reaction in the course of the polymerization will influence the absolute position or the intercept of the straight line in Figure 1 but not the slope. Therefore, in general, the microstructure deliberately is not taken into account in this paper.