Spectroscopic Investigation of the High Pressure Ethylene Polymerization *

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Quantitative absorption spectroscopy in the infrared and near-infrared region enables kinetic and thermodynamic investigations to be performed on systems at high temperatures and pressures. The technique is illustrated for the ethylene polymerization. From spectroscopic experiments up to 3 kbar at maximum temperatures of 250 °C, the rate equations of the thermally, of the photochemically, and of the chemically initiated polymerization are determined.

Introduction

Chemical reactions at high pressures and elevated temperatures are of technical and of scientific interest. Among the industrial high-pressure processes, the ammonia synthesis and the ethylene polymerization are of special importance. During recent years an increasing interest in catalytic reactions at moderately high pressures has developed [1]. The scientific investigations have been performed with emphasis on the activation volume which provides some information about the reaction profile [2]. Quite recently, elementary chemical reactions could be measured at high pressure with time resolution in the nanosecond region [3].

In addition to kinetic experiments, detailed information about chemical equilibria and phase equilibria is needed to describe and to understand chemical reactions at high pressures and temperatures. Both the kinetic and thermodynamic investigations suffer from the disadvantage that precise determinations of the nature and especially of the concentration of species under unusual conditions are difficult. The situation has largely improved since infrared and near-infrared spectroscopy at high pressures and temperatures turned out to be well suited for the direct measurement of concentrations [4]. The applicability of the method, which has been tested mostly in unpolar materials depends on the following premises:

(1) Optical high-pressure high-temperature cells with appropriate windows must be available. The optical path length must be precisely known under the experimental conditions.

(2) The species under investigation should have characteristic non-overlapping bands. If mutual overlap occurs, at least one vibrational half-band should be free from overlap.

(3) Measured absorbances must be strictly proportional to concentrations, that is Lambert-Beer's law should be valid.

(4) In order to measure reasonable absorption spectra, the system should be homogeneous. This is especially true at the higher frequencies in the near infrared.

The purpose of the present paper is to illustrate the new technique with results obtained for the high-pressure ethylene polymerization using thermal, photochemical, or chemical initiation. The reaction has already been investigated by several authors [5–12] with pioneering contributions by Ehrlich [6, 7], by v. d. Molen [8], and by Schoenemann, Steiner, Luft, and their groups [9–11]. In the early work, concentrations were determined from experimental overall quantities, such as the pressure drop at constant volume. The papers mentioned above mainly deal with the chemically initiated polymerization. With thermal and with photochemical initiation in homogeneous phase, the first extended investigations have been performed using

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the technique of quantitative infrared and near-infrared spectroscopy at high pressures and temperatures [13, 14].

Experimental

Different types of optical high-pressure high-temperature cells have been developed during recent years [15–22]. In Fig. 1, an optical cell which has been constructed and extensively used for spectroscopic investigations on the ethylene-polyethylene system is shown [19]. The cell for operation to 3 kbar and 300 °C is made from stainless steel (ATS 340, W.-Nr. 2.4969). The radiation penetretes the cell through the cylindrical bore. The optical windows W from synthetic sapphire are sealed with conical steel plugs P pressed against the cell body with flanges Fl by means of eight screws S on each side. For absorption experiments at wavenumbers below 2000 cm^{-1} where sapphire is not transparent, polycrystalline silicon can be used as window material. The distance between the internal surfaces of the windows is the optical path length *l*. The choice of the path length depends on the specific absorption and on the concentration of the species under investigation. The absorption intensity mostly varies by orders of magnitude between fundamental and overtone modes. Some details about the size of l in the system ethylene-polyethylene are presented in the subsequent section. Optical cells of the type shown in Fig. 1 can be constructed with path lengths from slightly below 1 mm up to 100 mm or even more. By means of a steel bellows B fitted into the cross-bore at right angle to the light path, the system under investigation is separated from the pressure generating system filled with water or hydrocarbons. The bellows which has nearly zero pressure difference when maintained in its normal length, enables the pressure to be measured on gauges in the pressurizing system at ambient temperature. An inductive detector I indicates the position of the bellows. Capillary borings which are not shown in Fig. 1 allow the internal volume to be charged and to introduce sheathed thermocouples into the high-pressure fluid. The cell is heated (H) electrically from outside with sheathed resistance wire positioned onto a brass matrix. The optical cell is adjusted into the optical compartment of a spectrometer. The experiments which are presented in this paper were mostly performed on a Fourier transform interferometer (Digilab FTS 14).

Details about the whole set-up and about the experimental procedure in the ethylene polymerizations are presented elsewhere [13, 14, 19, 21]. Pressures are determined to better than ± 4 bar even at 4 kbar. Temperatures are measured to better than ± 0.3 °C. From the spectroscopic experiments which are briefly described in the following section, ethylene concentrations can be determined with an accuracy of ± 3%. Within one kinetic experiment at constant temperature and constant density, relative accuracies of ± 1% are within reach [19]. The oxygen content of the ethylene is of crucial importance for quantitative kinetic experiments, as oxygen can act as initiator and inhibitor. The ethylene which was kindly supplied by the BASF AG contained less than 3 vol.-ppm of oxygen.

Results and Discussion

The ethylene polymerizations have mostly been investigated through near-infrared spectroscopy in the region of the first and second C–H stretching overtones around 5800 cm^{-1} and 8500 cm^{-1}, respectively. The absorption of the C–H-stretching fundamentals and first, second, and third overtones of dense fluid ethylene and of liquid polyethylene is shown in Figure 2. (The notations: first, second, and third overtone characterize the absorption region. They are no correct band assignments. In ethylene, for example, all first and third overtones are symmetry-forbidden and the bands are due to combination modes [23].)

On the ordinate, the molar absorptivity ε is plotted on a logarithmic scale versus the wave-

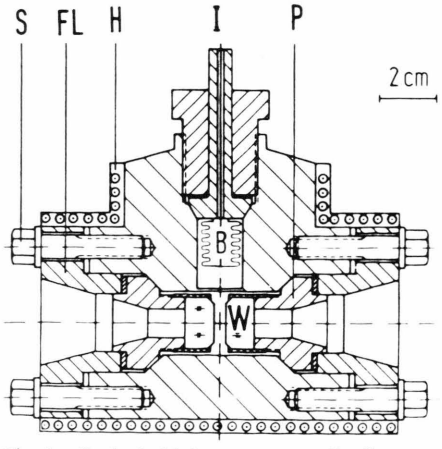

Fig. 1. Optical high-pressure cell. S screw, Fl flange, H heating, I inductive detector, P plug, B bellows, W sapphire window.

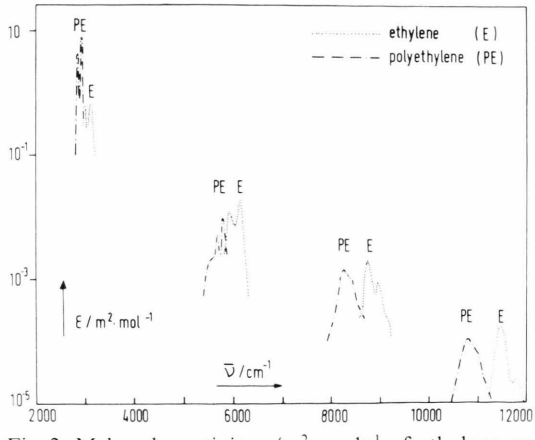

Fig. 2. Molar absorptivity $\varepsilon/m^2 \cdot mol^{-1}$ of ethylene and of polyethylene in the fundamental and in the first, second, and third overtone region of the C–H stretching modes.

number $\bar{\nu}$. $\varepsilon(\bar{\nu})$ is defined as:

$$\varepsilon(\bar{\nu}) = \frac{A(\bar{\nu})}{c\,l} \qquad (1)$$

where $A(\bar{\nu})$ is the absorbance, c the concentration or, in pure materials, the density, and l the optical path length. The molar absorptivity in the band maxima of the C–H stretching fundamentals around 3000 cm^{-1} is by about two orders of magnitude larger than in the first overtone region. In comparison with the fundamental intensity, the absorption of the second C–H stretching overtones around 8500 cm^{-1} is smaller by three and the absorption of the third overtones around 11 000 cm^{-1} is smaller by four orders of magnitude. These large differences in absorption intensity bear important consequences on the choice of the path length. From (1), with ε-values of the ethylene absorption maxima for typical initial polymerization densities of 0.5 g (ethylene) · cm^{-3}, the optical path lengths $l^{(1)}$ for maximum absorbance of $A = 1$ are easily calculated ($A = 1$ ensures that precise absorption measurements are possible).

$l^{(1)}$/mm	Absorption of C–H modes
0.05	fundamentals
1.1	first overtones
12.5	second overtones
140.3	third overtones

Pure dense ethylene thus can be measured with rather different optical path lengths in an extended wavenumber region from 2800 cm^{-1} to 12 000 cm^{-1}. For kinetic experiments on the ethylene-polyethylene system it is highly advantageous to measure in at least two absorption regions, simultaneously. The high molar absorptivity in the fundamental region allows traces of polyethylene in the beginning of the polymerization to be detected. The series of spectra in Fig. 3 shows the polyethylene fundamental band at 2860 cm^{-1} for a total initial conversion to 0.2%. Differences in the polyethylene concentration of about 100 ppm can be determined from the spectra. The (high) ethylene concentrations in the initial period of the reaction are measured in the overtone region. If polymerizations are studied to high conversions, the situation is reversed and polyethylene which then is the major component is measured in the near infrared whereas the remaining small quantities of ethylene are determined in the fundamental region. If an instrument with an extended spectral range is available, within one absorption experiment components which largely differ in concentration (or in molar absorptivity) can be determined, provided the characteristic bands are not severely overlapping. Figure 2 indicates that, to higher wavenumbers, overlap in the ethylene-polyethylene system becomes less serious. The situation in the second overtone region is illustrated in Fig. 4 with spectra measured during a pure ethylene polymerization at 170 °C. The absorption from the band maximum at 8750 cm^{-1} to higher wavenumbers is exclusively due to ethylene whereas in the region from the maximum at 8260 cm^{-1} to lower wavenumbers only polyethylene is absorbing. The polymerization is observed to a maximum conversion of 70%.

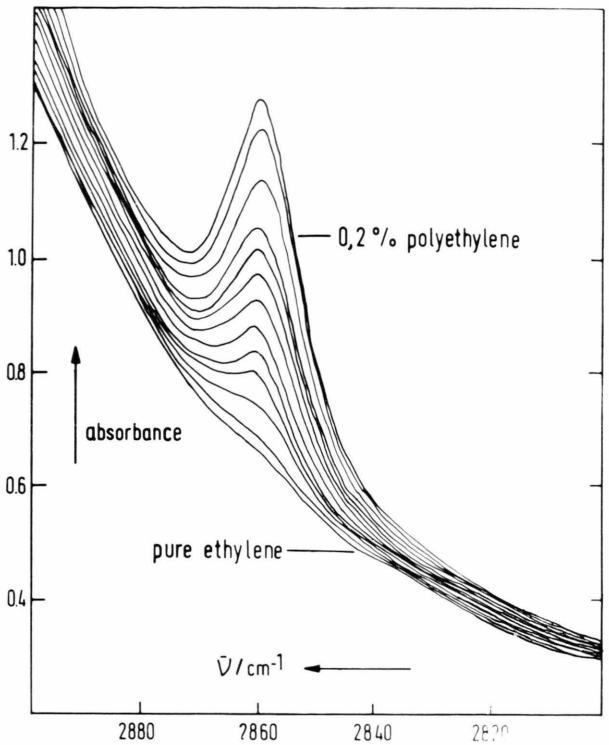

Fig. 3. Infrared absorption of the polyethylene C–H stretching mode around 2860 cm^{-1} measured during a high-pressure ethylene polymerization to 0.2% conversion.

Spectra recorded during a polymerization at 235 °C in the first overtone region of the C–H stretching fundamentals are shown in Figure 5. The ethylene bands decrease and the polyethylene absorption increases. The overlap of ethylene and

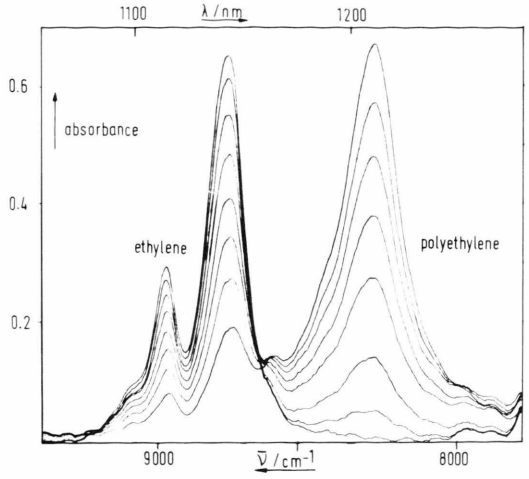

Fig. 4. Near-infrared absorption in the second overtone region of the C–H stretching modes in ethylene and polyethylene measured during a polymerization at 170 °C. The initial pure ethylene density is 0.52 g · cm^{-3}. The optical path length is 8.9 mm.

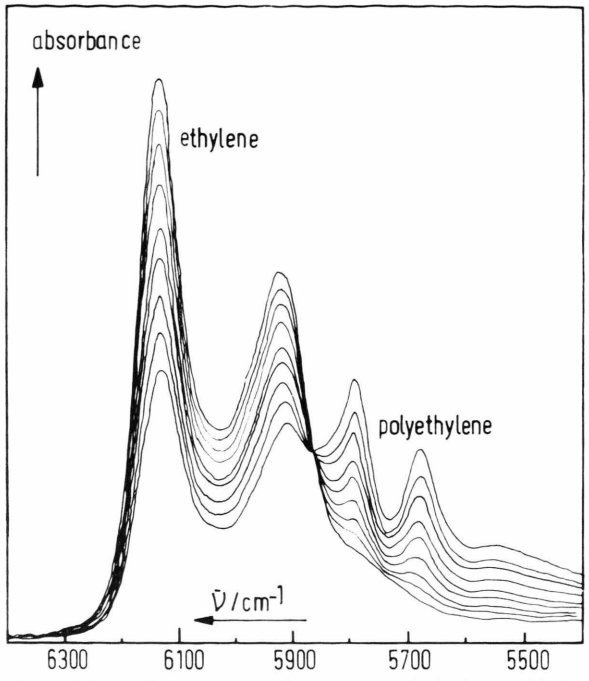

Fig. 5. Near-infrared absorption measured during a high-pressure ethylene polymerization at 235 °C.

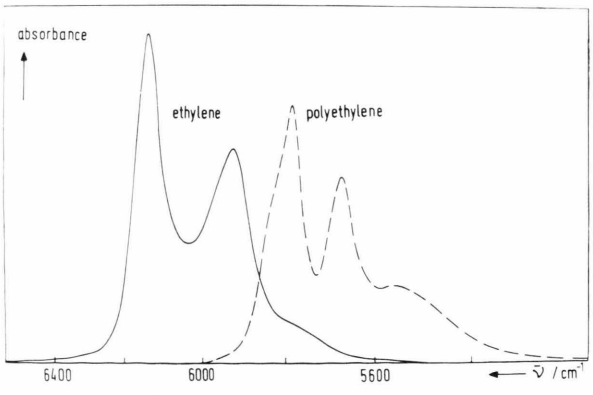

Fig. 6. Near-infrared absorption of pure ethylene and of pure polyethylene in the wavenumber region of the C–H stretching first overtones.

polyethylene bands is demonstrated in Fig. 6 with spectra measured on the individual pure components [21]. The absorption from the band maximum at 6140 cm^{-1} toward higher wavenumbers is exclusively due to ethylene. The non-overlapping half-bands are essential for quantitative spectroscopy in an extended pressure and temperature region because experiments at constant wavenumber, e.g. in the band maximum, are insufficient for quantitative analysis due to the strong dependence of band-shape on the dynamics in the fluid state. Total band absorbances can only rarely be used because of overlap (Figs. 4–6). In order to be perfectly suited for quantitative work, the integrated molar absorptivity B of a band (or half-band) must be constant within the experimental pressure and temperature region. B is defined as:

$$B = \int \varepsilon(\bar{\nu}) \cdot \mathrm{d}\bar{\nu}. \qquad (2)$$

For pure ethylene, $B^{1/2}(\nu_5 + \nu_9)$, the high-wavenumber half-band of the combination mode $\nu_5 + \nu_9$ with maximum absorption at about 6140 cm^{-1} is plotted versus density for various temperatures in Figure 7. The integration is performed from the band maximum to 6500 cm^{-1}. Within the experimental accuracy of ± 2%, the half-band intensity is independent of temperature and of density. (In pure ethylene at 200 °C a density of 0.5 g · cm^{-3} corresponds to a pressure of 2012 bar). The $\nu_5 + \nu_9$ high-wavenumber half-band is thus well suited for quantitative high-pressure work. Various other bands and half-bands in ethylene and in saturated hydrocarbons have been investigated [23–26]. Most of them show the same type of behaviour as is illustrated in Figure 7. In same cases, however, a decrease in molar integrated intensity is found toward the highest densities. It may be concluded that several characteristic non-overlapping half-

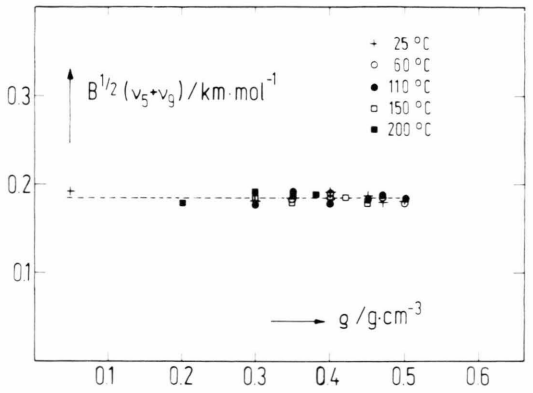

Fig. 7. Density dependence of the integrated molar absorptivity $B^{1/2}(\nu_5 + \nu_9)$ of the high wavenumber half-band of the $\nu_5 + \nu_9$ combination mode in pure ethylene at various temperatures between 25 °C and 200 °C.

bands exist for ethylene and for polyethylene that enable quantitative work at high pressures and temperatures to be made via infrared and near-infrared spectroscopy. As optical layers in the region from 0.5 mm to 20 mm are easily installed, the first and second overtones of C–H stretching modes are especially important for studies on compressed ethylene-polyethylene. For special applications, such as the determination of small initial conversions (Fig. 3), the fundamental region and for spectroscopic work in larger vessels the third overtones offer special advantages.

For the appearance of the spectra as in Figs. 4 and 5 it is immaterial whether the polymerization is initiated thermally, photochemically, or chemically (with trace amounts of initiator). It seems, however, reasonable to discuss the results of polymerizations with these different kinds of initiation, separately.

A) Thermal Polymerization of Pure Ethylene

The investigation of the thermally initiated (or spontaneous) polymerization of ethylene is interesting on several grounds: (i) The initial system of pure ethylene is well-defined. (ii) A problem, already discussed in the literature, relates to the question whether a thermal reaction which should proceed via diradicals can yield high molecular mass polyethylenes. Diradicals should be highly vulnerable to cyclization in early stages of the propagation. (iii) If a thermal reaction occurs, the kinetics must be precisely known in order to determine its contribution in chemically and photochemically initiated experiments where it cannot be eliminated as parallel reaction.

Details about the experiments are given elsewhere [13, 14]. For the present purpose it is important to note that the oxygen content was very low (1 vol.-ppm, BASF AG). The experimental spectra when measured in the first and second overtone look as in Figs. 4 and 5, respectively. The half-band intensities directly yield the time dependence of concentrations. From subsequent spectra, reaction rates are determined. As high purity ethylene was used and as the reactions were measured only to moderately high conversions (25%), a simple rate law was supposed to be adequate:

$$r_0/\mathrm{mol\,(CH_2)\,l^{-1}\,s^{-1}} = k_0 c_E^m \qquad (3)$$

r_0 is the overall reaction rate, k_0 the overall reaction rate coefficient, c_E the ethylene concentration in mole CH_2-groups per liter, and m the overall reaction order. The applicability of (3) is easily tested by plotting r_0-data as deduced from the spectra versus the spectroscopically determined ethylene density on a double logarithmic scale. The results of two polymerizations at 235 °C are shown in Figure 8.

The data nicely fit onto a straight line, which yields (cf. (3)) the overall reaction order m and the overall rate coefficient k_0. From a series of experiments between 180 °C and 250 °C at pressures around 2 kbar [13, 14], $m = 2.5 \pm 0.2$ is found.The

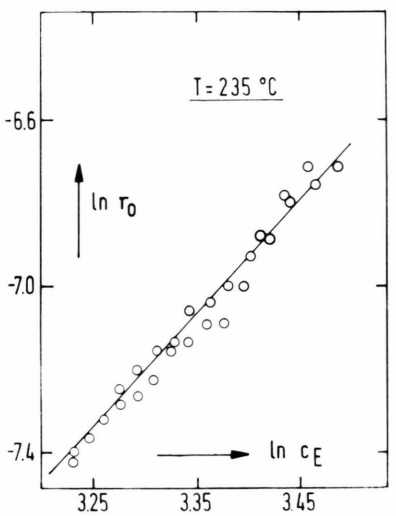

Fig. 8. Logarithm of the overall reaction rate r_0/mol$(CH_2)\,l^{-1}\,s^{-1}$ plotted versus the logarithm of the ethylene concentration c_E/mol$(CH_2)\,l^{-1}$ for the high-pressure pure ethylene polymerization at 235 °C.

experimental k_0's are plotted versus T^{-1} in Figure 9. The slope of the straight line fitted to the data yields the overall activation energy:

$$E_0 = 136.3 \pm 8 \text{ kJ} \cdot \text{mol}^{-1} .$$

The kinetic data for the thermal pure ethylene polymerization between 180 °C and 250 °C at a mean pressure of 2 kbar are well represented by a kinetic equation of the type (3):

$$r_0/\text{mol}\,(CH_2)\,l^{-1}\,s^{-1} = 2.03 \cdot 10^7 \exp\{-16\,465\,T^{-1}\}\,c_E^{2.5} . \quad (4)$$

With the well-known formalism for the description of ideal radical homo-polymerizations, the overall quantities are easily related to kinetic parameters of individual steps of the chain reaction [13]. The equation for the rate coefficients is:

$$k_0 = k_p k_t^{-0.5} k_i^{0.5} , \quad (5)$$

where k_p, k_t, and k_i are the rate coefficients of the propagation, termination, and initiation steps, respectively. From (5), the relation between the activation energies follows:

$$E_0 = E_p - 0.5\,E_t + 0.5\,E_i . \quad (6)$$

A mean value of $E_p - 0.5\,E_t = 31.4 \pm 6 \text{ kJ} \cdot \text{mol}^{-1}$ is deduced [13] from several published data [6, 27, 28]. From spectroscopic experiments on the chemically initiated ethylene polymerization [19], as will be described in the final part of this paper, almost the same value ($31 \pm 8 \text{ kJ} \cdot \text{mol}^{-1}$) is derived. With $E_p - 0.5\,E_t = 31.4 \text{ kJ} \cdot \text{mol}^{-1}$ and with the experimental value of $E_0 = 136.3 \text{ kJ} \cdot \text{mol}^{-1}$, the activation energy of the initiation step is calculated from (6) to be:

$$E_i = 209.8 \pm 16 \text{ kJ} \cdot \text{mol}^{-1} .$$

This high value provides strong evidence that the reaction is thermally initiated. The barrier to internal rotation in gaseous ethylene which must be considered as an upper limiting value for E_i is only slightly higher ($263 \text{ kJ} \cdot \text{mol}^{-1}$).

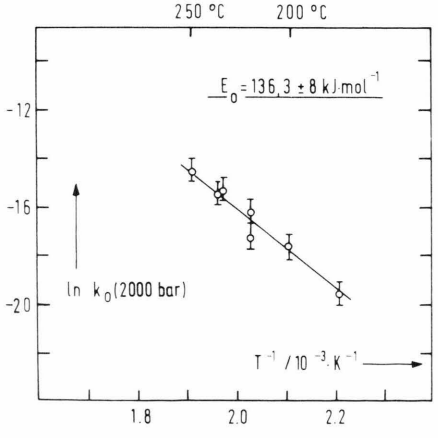

Fig. 9. Temperature dependence of the overall rate coefficient $k_0/l^{1.5} \cdot \text{mol}(CH_2)^{-1.5} \cdot s^{-1}$ for thermal pure ethylene polymerizations at pressures around 2000 bar.

The mean molecular masses and the mass distributions have been analyzed [29]. For polymerizations at 225 °C and 2 kbar to low conversion (2%), the number and mass averages are found to be $\bar{M}_n = 79\,700 \text{ g} \cdot \text{mol}^{-1}$ and $\bar{M}_w = 198\,200 \text{ g} \cdot \text{mol}^{-1}$, respectively. A detailed analysis of the molecular masses [29] supports the above conclusion that a thermally initiated polymerization to high molecular mass polyethylene takes place. The arguments that high molecular mass products occur although the primary intermediate is presumably a diradical are presented elsewhere [13]. Additional support for high molecular polymers from diradicals is provided by the recent work of Lingnau and Meyerhoff [30] on the thermal polymerization of methyl methacrylate.

Equation (4) represents pure ethylene polymerizations between 180 °C and 250 °C. The kinetic equation can also be used to estimate polymerization rates at lower or higher temperatures. In Table 1, reaction times, t (3%), for an initial conversion starting from $0.5 \text{ g} \cdot \text{cm}^{-3}$ pure ethylene (35.65 mole $CH_2 \cdot l^{-1}$) to 3% polyethylene (at 2 kbar) are presented. At least up to 250 °C, the thermal polymerization is too slow as to contribute to the chemically initiated reaction in technical processes. The situation may change toward very high temperatures: At 350 °C, three percent polyethylene occur after 0.52 s. The value of t (3%) = 6.43 days extrapolated for 150 °C is interesting as a critical polymerization boundary is reported for ethylene polymerizations in the presence of oxygen at about that temperature [6, 7, 31]. At temperatures below this boundary, presumably due to inhibition by oxygen, an extremely slow polymerization occurs. The t (3%)-value in Table 1 (or (4)) may provide a useful reference in order to conclude from kinetic data measured in the presence of oxygen whether the

Table 1. High-pressure polymerization of pure ethylene. Reaction time $t(3\%)$ for an initial conversion of 3% ($P = 2000$ bar, $\varrho_0 = 0.5$ g · cm^{-3} ethylene).

Temperature/ °C	$t(3\%)$
150	$5.56 \cdot 10^5$ s = 6.43 days
200	$1.13 \cdot 10^4$ s = 3.14 hours
250	$3.24 \cdot 10^2$ s = 5.4 minutes
300	$2.07 \cdot 10^1$ s = 20.7 seconds

The values for 150 °C and 300 °C are extrapolated from the experiments between 180 °C and 250 °C.

reaction is inhibited in the sense that it is slower than the thermal polymerization.

B) Photopolymerization of Pure Ethylene

With uv-radiation, ethylene may be polymerized at fairly low temperatures. Rabel and Ueberreiter [32] studied the reaction even at −20 °C. Below about 120 °C, however, depending on the applied pressure and on the molecular mass of the polyethylenes, the reaction proceeds in heterogeneous phase which poses problems for a quantitative description of the kinetic data. A few photochemical high-pressure ethylene polymerizations using photoinitiators have also been performed in homogeneous phase with emphasis on the determination of individual rate coefficients k_p and k_t [33, 34]. Through quantitative near-infrared spectroscopy the kinetics of pure ethylene polymerized with the 250 nm to 350 nm radiation from a high intensity mercury lamp were measured by Heym [14]. As is described in her thesis, the photo-conversion was determined from spectra recorded just before and immediately after the illumination interval which was typically in the order of some seconds up to a few minutes.

The overall reaction rate r_0 at conversions between 25% and 55% as determined from the change in the ethylene concentration c_E during a precisely measured period of steady illumination is plotted versus c_E for experiments at 200 °C and 220 °C on a double logarithmic scale in Figure 10. For each temperature the data closely fit onto a straight line which suggests that (3) is adequate also for the photochemical pure ethylene polymerization. In the initial period of the reaction which is not shown in Fig. 10, the observed polymerization rates are smaller than those extrapolated from the straight line fit. From the slopes in Fig. 10, the overall

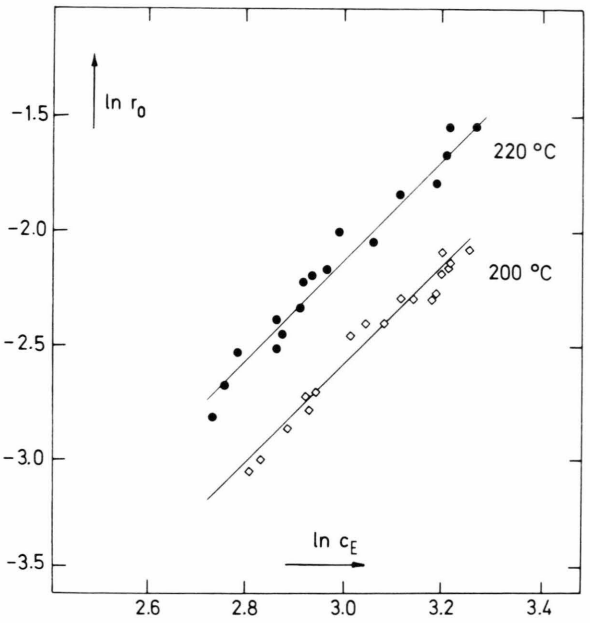

Fig. 10. Logarithm of the overall reaction rate r_0/ mol$(CH_2) \cdot l^{-1} \cdot s^{-1}$ plotted versus the logarithm of the ethylene concentration c_E/mol$(CH_2) \cdot l^{-1}$ for photochemically initiated high-pressure ethylene polymerizations at 200 °C and 220 °C.

reaction order of the photochemical reaction is found to be $m = 2 \pm 0.2$. The overall rate coefficients k_0 (2000 bar) which refer to a mean pressure of 2 kbar are plotted on a log k_0 versus T^{-1} diagram in Figure 11.

The slope yields the overall activation energy:

$$E_0 = 37 \pm 8 \text{ kJ} \cdot \text{mol}^{-1}.$$

The photochemical initiation, to a first approximation, should be independent of temperature. With $E_i = 0$, (6) for the photopolymerization of pure ethylene reduces to

$$E_0 = E_p - 0.5\, E_t; \tag{7}$$

E_0 from Fig. 11 agrees with the previously cited value of $E_p - 0.5\, E_t = 31.4 \pm 6$ kJ · mol^{-1} within the limits of experimental accuracy. The kinetic parameters are summarized within the rate law:

$$r_0/\text{mol}(CH_2)\, l^{-1}\, s^{-1} = 2.92 \exp\{-4450\, T^{-1}\}\, c_E^2. \tag{8}$$

It must be noted that the pre-exponential term in (8) contains the characteristics of the illumination

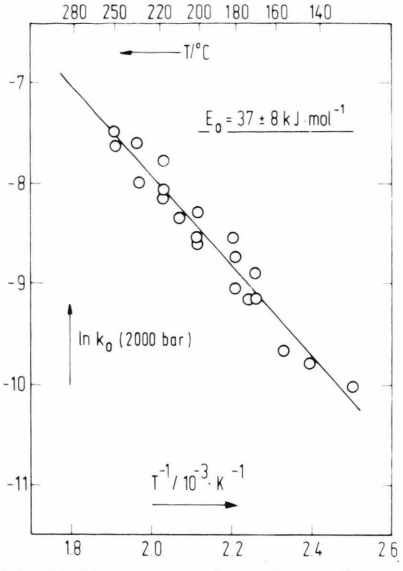

Fig. 11. Temperature dependence of the overall rate coefficient $k_0/l \cdot \text{mol}(CH_2)^{-1} \cdot s^{-1}$ for photochemically initiated ethylene polymerizations at pressures around 2000 bar.

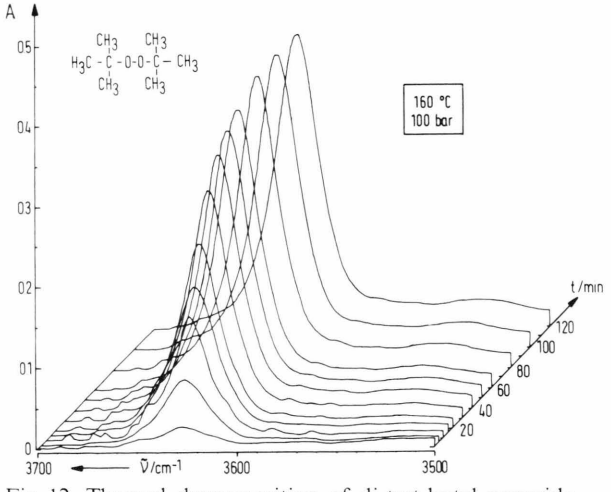

Fig. 12. Thermal decomposition of di-tert-butyl peroxide in n-heptane solution at 160 °C and 100 bar studied via quantitative spectroscopy on the O–H stretch of tertiary butanole which is the main product.

equipment, such as the output and the spectrum of the light source, the quality of the optical components (quartz condensors, optical high-pressure windows) and the irradiation geometry.

The quantum yield Φ has not yet been precisely measured. This quantity should markedly depend on the temperature, the ethylene density and because of the solution viscosity, on the polyethylene concentration. A very crude determination for 200 °C suggests that Φ is between 100 and 1000 which indicates that, on an average, one absorbed quantum induces a kinetic chain where between 100 and 1000 monomer molecules are added. The actual degree of polymerization as determined by viscosity experiments [29], is by about a factor of twenty larger which probably means that the polymerization efficiency of the primary activated species is fairly low. The information contained in the above Φ-values is relatively poor as polychromatic light has been used. It seems promising to continue the photopolymerization work with exciplex lasers as light source. With monochromatic light, precise determinations of the quantum yield as a function of temperature, pressure, and laser frequency are within reach. These experiments are in preparation [35]. Actually, the spectra in Fig. 4 have been measured during a laser induced polymerization.

C) Chemically Initiated Ethylene Polymerization

The high-pressure ethylene polymerization with chemical initiation by peroxides or by oxygen is an important industrial process. The reaction has been investigated by several groups [5–12] using overall quantities, e.g. the pressure drop at constant volume, to measure the polymerization rate. With the quantitative spectroscopic technique the ethylene and polyethylene concentrations can be directly measured. As compared to the thermal reaction, however, two problems arise: (i) At identical pressures and temperatures the polymerization is much faster and (ii) in addition to ethylene (and polyethylene) the initiator concentrations must be accurately known.

Lendle [19] succeeded to measure ethylene concentrations during polymerizations initiated by di-tert-butyl peroxide (DTBP). The time to scan one spectrum was typical in the order of a few seconds. The peroxide concentration, however, is too low as to be determined directly from spectra on the reaction mixture. The actual concentration thus is calculated from the known initial concentration and from the rate law which was determined, also via high-pressure high-temperature spectroscopy, for the thermal decomposition of peroxides in n-heptane solution [18]. In Fig. 12, spectra measured during a DTBP decomposition at 160 °C and 100 bar are

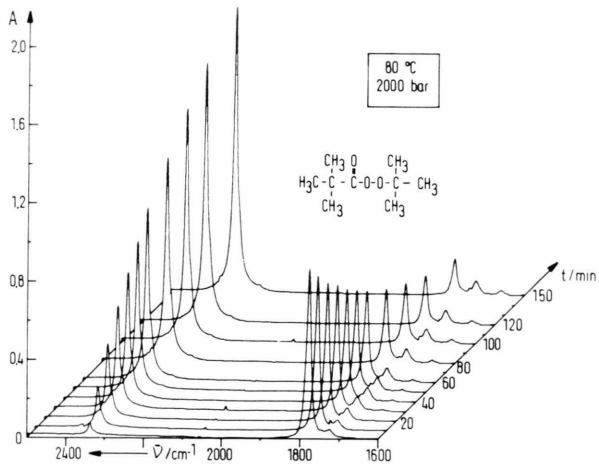

Fig. 13. Thermal decomposition of tert-butyl peroxypivalate in n-heptane solution at 80 °C and 2000 bar studied via quantitative infrared spectroscopy in the C–O stretching region of the peroxide and of CO_2 which is one of the products.

shown. The reaction is probed via the infrared absorption of the O–H stretch of tertiary butanole (TB) at 3624 cm^{-1} which is the main product in dilute (0.1 molar) n-heptane solution. The validity of Lambert-Beer's law for the 3624 cm^{-1} band at the experimental temperatures, pressures and at the low TB-concentrations was established in independent experiments. Thus concentrations are directly obtained from the spectra. The technique is described in more detail, elsewhere [18, 36]. The experiments performed up to 2.3 kbar and 200 °C demonstrate that, at least to three half-lives, the decomposition follows a first order rate law:

$$r(P, T) = -\,\mathrm{d}c_{\mathrm{DTBP}}/\mathrm{d}t = k_{\mathrm{d}}(P, T) \cdot c_{\mathrm{DTBP}} \qquad (9)$$

with

$$k_{\mathrm{d}}(P, T)/\mathrm{s}^{-1} = 1.41 \cdot 10^{15} \cdot \exp\{-T^{-1}(18226 + 0.121\,P)\}\,, \qquad (10)$$

where P is in bar and T in Kelvin. The activation energy in (10) is $E_a = 151.4 \pm 1.6$ kJ · mol^{-1} and the activation volume is $\Delta V^{\neq} = 10.1 \pm 1.1$ $cm^3 \cdot mol^{-1}$.

The decomposition of tert-butyl peroxypivalate (TBPP) has also been studied. In addition to the O–H stretch as in Fig. 12, several other characteristic vibrations enable the reaction to be followed. In Fig. 13, spectra measured during an experiment at 80 °C and 2000 bar with an 0.01 molar initial peroxide concentration are shown. The band at 1775 cm^{-1} which is the carbonyl stretch of the peroxide decreases while the CO_2 absorption at 2340 cm^{-1} increases during the reaction. The weak band at 1725 cm^{-1} is due to acetone which, together with TB, is formed out of the tert-butoxy radical. The kinetic analysis of the TBPP decomposition at pressures up to 2 kbar and temperatures between 65 °C and 105 °C yields a first order rate law as in (9) (with concentrations c_{TBPP}). The temperature and pressure dependent rate coefficient k is found to be

$$k(P, T)/\mathrm{s}^{-1} = 2.20 \cdot 10^{14} \cdot \exp\{-T^{-1}(14691 + 0.0192\,P)\}\,, \qquad (11)$$

where pressures and temperatures are again in bar and Kelvin, respectively. The activation energy in (11) is $E_a = 122.3 \pm 3$ kJ · mol^{-1} and the activation volume is $\Delta V^{\neq} = 1.6 \pm 1$ $cm^3 \cdot mol^{-1}$. A detailed discussion of the data is given in the original literature [18, 36, 37].

The kinetics of the high-pressure ethylene polymerization initiated by DTBP have been measured spectroscopically between 130 °C and 165 °C [19]. The reaction mixture with initial peroxide contents between 12 mol-ppm and 45 mol-ppm was prepared from the pure components. Figure 14 shows near-infrared spectra recorded during a polymerization at 155 °C with an initial ethylene density of 0.55 g · cm^{-3} and a DTBP-concentration of 12 ppm. The pressure decreases from 2300 bar in the be-

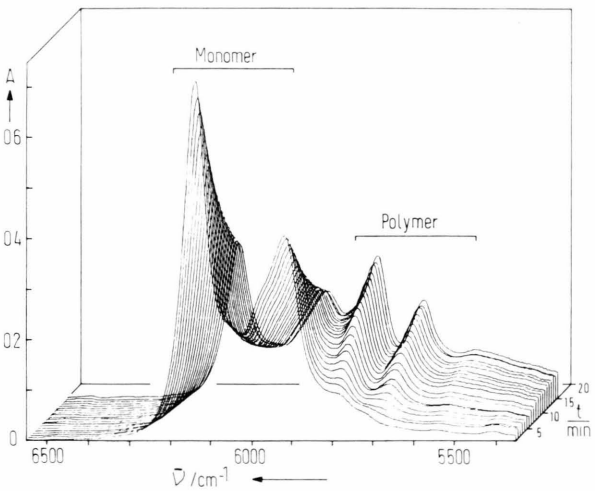

Fig. 14. Near-infrared spectra measured in time intervals of 45 s during a chemically initiated high-pressure ethylene polymerization at 155 °C. The initial di-tert-butyl peroxide concentration is 12 mol-ppm. The pressure drop during the reaction is from 2500 bar to about 900 bar.

ginning of the reaction to 860 bar after 15 min when, as is indicated in the spectra, a conversion of about 50 percent has been reached.

The well-known formalism of the ideal radical polymerization (12) may be used to represent the data:

$$r_0 = k_0 c_M c_I^{0.5}, \tag{12}$$

where c_M and c_I are the monomer and initiator concentrations, respectively. For the special situation of ethylene polymerized by DTBP, the logarithm of the overall rate (12) becomes:

$$\ln r_0 = \ln k_0 + \ln (c_E \cdot c_{DTBP}^{0.5}). \tag{13}$$

r_0 and c_E are obtained from the spectra and c_{DTBP} is calculated from (9) and (10) for known initial peroxide concentration. The overall rate coefficient k_0 is not directly obtained from a double logarithmic plot according to (13) as the pressure changes during the isothermal reaction at constant volume. The variation of k_0 with pressure is given by the activation volume $\Delta V_0^{\neq}$:

$$(\delta \ln k_0/\delta P)_T = -\Delta V_0^{\neq}/RT. \tag{14}$$

With (14) the r_0-data of each polymerization experiment may be shifted to a common reference pressure which was arbitrarily chosen to $P_r = 1000$ bar. The correction term $\Delta \ln r_0$ is calculated from

$$\left(\frac{\Delta \ln r_0}{P - 1000}\right)_T = \left(\frac{\Delta \ln k_0}{P - 1000}\right) = \frac{-\Delta V_0^{\neq}}{RT}. \tag{15}$$

$\Delta V_0^{\neq}$ is derived from the experiments in the following way: From different assumed values of $\Delta V_0^{\neq}$, different sets of $\ln r_0(1000\text{ bar})$-values are calculated for each isothermal experiment. $\Delta V_0^{\neq}$ is found from that data set which yields a straight line plot with the slope 1 for $\ln r_0(1000\text{ bar})$ versus $\ln(c_E \cdot c_{DTBP}^{0.5})$ according to (13). From fifteen experiments between 130 °C and 165 °C, the overall activation volume of the high-pressure ethylene polymerization is derived to be

$$\Delta V_0^{\neq} = -17.5 \pm 5\ \text{cm}^3 \cdot \text{mol}^{-1}.$$

From the ordinate of a straight line plot of $\ln r_0(1000\text{ bar})$ versus $\ln(c_E \cdot c_{DTBP}^{0.5})$, the overall polymerization rate coefficient $k_0(1000\text{ bar})$ is obtained. In Fig. 15, $\ln k_0(1000\text{ bar})$ is plotted versus T^{-1}. The data nicely fit onto a straight line. From the slope, the overall activation energy of the

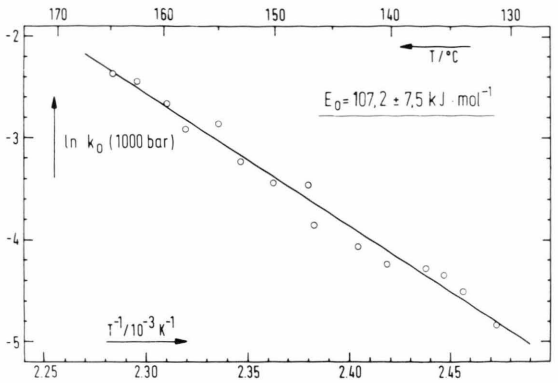

Fig. 15. Temperature dependence of the overall rate coefficient $k_0/l^{0.5} \cdot \text{mol}^{-0.5} \cdot \text{s}^{-1}$ for the chemically, with di-tert-butyl peroxide, initiated ethylene polymerization at the reference pressure of $P_r = 1000$ bar.

ethylene polymerization with DTBP is found:

$$E_0 = 107.2 \pm 7.5\ \text{kJ} \cdot \text{mol}^{-1}.$$

The results indicate that under well-defined conditions, the chemically initiated high-pressure ethylene polymerization follows the ideal rate law (12). From the overall rate coefficients at the reference pressure of 1 kbar and with E_0 and $\Delta V_0^{\neq}$, the pressure and temperature dependent overall rate coefficient turns out to be

$$k_0(P, T)/l^{0.5}\,\text{mol}^{-0.5}\,\text{s}^{-1} = 5.85 \cdot 10^{11} \exp\{-T^{-1}(12898 - 0.210(P - 1000))\}, \tag{16}$$

where P and T are in bar and Kelvin, respectively. The concentrations of both components, ethylene and DTBP, in (12) must be in moles · l^{-1} if k_0 is determined from (16).

From (9), (10), (12), and (16) the overall polymerization rate for given pressures and temperatures may be calculated. As kinetic equations have been used for the representation of the data, the results should be reliable even slightly beyond the $P - T$ limits of the experiments [19]. It is important to note that the calculation of $r_0(P, T)$ from (9), (10), (12), and (16) in the region of the experiments is exclusively based on experimental material without any assumptions. For example, the question whether the efficiency factor f of the peroxide decomposition is equal to unity, is immaterial. This is no longer true if (5) is used to derive values for $k_p k_t^{-0.5}$ from the experimental k_0-data, (16), and from the independently measured decomposition

rate constant k_d of the peroxide, (10). Assuming the initiation rate constant k_i in the high-pressure ethylene polymerization with DTBP as initiator to be related to k_d by $k_i = 2fk_d$ with a radical efficiency factor $f = 1$, yields

$$k_p k_t^{-0.5}/l^{0.5}\,\mathrm{mol}^{-0.5}\,\mathrm{s}^{-0.5} \qquad (17)$$
$$= 11.02 \cdot 10^3 \exp\{-T^{-1}(3724 - 0.272\,(P - 1000))\}$$

with P in bar and T in K.

Data for $k_p k_t^{-0.5}$ are fundamental kinetic quantities of the high-pressure ethylene polymerization. Moreover, they are of special importance in applied polymer kinetics as they enable, by inversion of the procedure which has been used for their determination, overall polymerization rates r_0 to be calculated or estimated for high-pressure ethylene polymerizations with a different kind of initiation, provided the initiator decomposition rate law is known as a function of pressure and temperature. Such decompositions in inert solvents are much easier to be measured than polymerizations and for various initiators kinetic parameters are already available [36, 38].

The reliability of an overall reaction rate r_0 derived from $k_p k_t^{-0.5}$ and from experimental decomposition rates, such as (9) and (10), mainly depends on the actual size of the efficiency factor f. If the same value of f holds for the DTBP-experiments and for those with an arbitrary initiator I' from which only the decomposition rate in an inert solvent is known, the calculated r_0-values of the ethylene polymerization with this initiator should be quite reasonable. It is, however, advisable to perform at least one or two polymerization experiments in order to learn from a comparison of measured and calculated rates whether the efficiencies are indeed of the same size. The r_0-data determined according to (12), of course, cannot describe kinetic peculiarities in the initial period of the reaction and at high conversions, such as inhibition by trace amounts of oxygen and the occurrence of a Norrish-Trommsdorff effect, respectively.

Only relatively few data on $k_p k_t^{-0.5}$ for the homogeneous high-pressure ethylene polymerization are reported in the literature [7, 8, 12]. They are smaller than the values from (17) by about a factor of three. This discrepancy is not due to the assumption of $f = 1$ contained in (17) as lower radical efficiencies for the polymerization with DTBP yield still higher $k_p k_t^{-0.5}$-values. The difficulties of experiments at high pressures and temperatures impose certain limitations on the accuracy of the kinetic data. Moreover, the procedures to deduce $k_p k_t^{-0.5}$ from measured rates and to extrapolate them to a common reference pressure have been made by different groups in different ways. Thus the discrepancy in the absolute value of $k_p k_t^{-0.5}$ should not be overestimated. The activation parameters of $k_p k_t^{-0.5}$, (17), are in excellent agreement with literature data:

	This work	Ehrlich et al. [7]	v. d. Molen [8]
$E_p - 0.5\,E_t$/kJ · mol^{-1}	31	32	30
$\Delta V_p^{\neq} - 0.5\,\Delta V_t^{\neq}$/cm^3 · mol^{-1}	−22.6	−23	−22

The calculation of overall polymerization rates from the sole knowledge of the decomposition rate of a peroxide is easily performed for the high-pressure ethylene polymerization initiated by TBPP using the kinetic data (11). The data for the overall rate coefficient at 2000 bar, k_0(2000 bar), are plotted together with the corresponding data for the polymerization initiated by DTBP and for the thermally and photochemically initiated pure ethylene polymerizations in Figure 16.

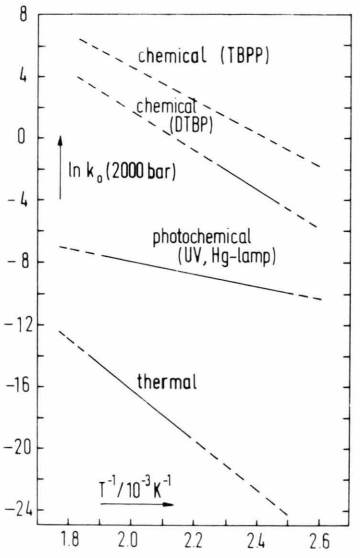

Fig. 16. Comparison of overall rate coefficients k_0(2000 bar) for ethylene polymerizations at 2000 bar initiated in different ways. The solid lines indicate the temperature regions where experiments have been performed.

It should be noted that only the solid part of the straight lines is measured. The k_0's differ by orders of magnitude. At 160 °C, the k_0-values with chemical initiation are by about ten orders of magnitude above the thermal and by about four orders of magnitude above the photochemical rate coefficients. A direct comparison on the basis of polymerization rates is provided by (4), (8), and (12). For an initial ethylene density of 0.53 g · cm^{-3} at 150 °C and 2000 bar (and initiator concentrations of $I_0 = 1 \cdot 10^{-3}$ mol · l^{-1} in the chemically initiated reactions) the reaction times t (3%) to reach an initial conversion of 3 percent are calculated:

t (3%):	0.5	s	chemical (TBPP) [19],
	10	s	photochemical [14],
	17	s	chemical (DTBP) [19],
	142	h	thermal [13, 14].

The photochemical polymerization of pure ethylene can be further increased if exciplex lasers are used as light sources. A preliminary experiment with a standard EMG 100 laser (Lambda Physik) on the KrF line at 248 nm at 150 °C and 0.52 g · cm^{-3} ethylene density indicated that three percent conversion are attainable by about 100 laser pulses each of 10 ns duration [35]. At a laser repetition rate of 100 Hz this very short irradiation time corresponds to an overall reaction time of 1 s.

The quantitative spectroscopic technique which has been illustrated by studies on the homopolymerization of ethylene is also applicable to copolymerizations, among them, the ethylene-carbon monoxide high-pressure polymerization is presently investigated [39]. The near-infrared spectrum of carbon monoxide has partly been measured to high pressures and temperatures [40]. The data indicate that spectroscopic studies of homogeneous as well as heterogeneous catalytic reactions at moderate and high pressures with CO as one of the components are within reach. Moreover, a wide variety of chemical, especially organic reactions may be studied via quantitative spectroscopy in an extended pressure and temperature regime. It needs not to be emphasized in detail that the spectroscopic technique which yields concentrations at high pressures and temperatures is also well suited for thermodynamic investigations under extreme conditions.

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