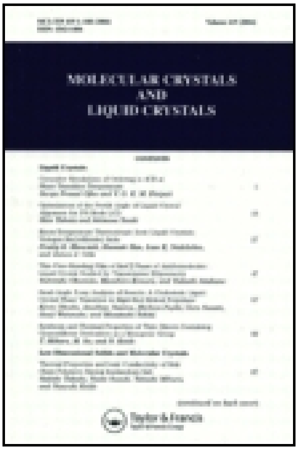

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KINETICS OF THE RADIATION INDUCED POLYMERIZATION OF A DIACETYLENE STUDIED BY ANALYSIS OF THE MOLECULAR WEIGHT DISTRIBUTION

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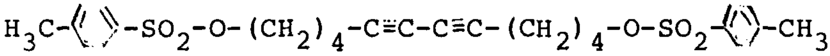
Abstract The molecular weight distribution as dependent on conversion, has been investigated for the radiation induced topochemical polymerization of the diacetylene monomer Dodeca-5,7-diyne-1, 12-ylene-bis(p-toluene sulfonate) ("TS-12"). The kinetic chain length increases with conversion from about 60 in the early stages to 2000 at 10 percent conversion and then stays constant to high (70 percent) conversion. The rate of chain initiation is constant up to high conversions. A G-value of 1.2 was determined. The chain ends produced in the course of the reaction are inactive for further polymerization reactions.

INTRODUCTION

The solid state polymerization of diacetylenes has grown into an interesting research subject because it provides the means to produce macroscopic and nearly defect free single crystals of polymers with a polyconjugated backbone.[1-4] Information on the chain length of these polymers was lacking, however, for a long time due to the insolubility of most of the poly(diacetylenes).[5] It was only through the analysis of the elastic behaviour that limited information on the chain length in partially polymerized crystals could be obtained, e. g.

through Brillouin-spectroscopy.[6,7] In the recent years poly(diacetylenes) became available which dissolve readily in the usual organic solvents; thus molecular weight determinations were possible by the usual methods such as light scattering (LS), osmometry, gelpermeation chromatography (GPC) etc.[8-10]

Dodeca-5,7-diyne-1,12-ylene-bis(p-toluene sulfonate) (1) ("TS-12") is an example of a diacetylene which shows a similar polymerization behaviour as the much investigated hexadyne-1,6-diol bis(p-toluene sulfonate) (PTS) but unlike this compound gives rise to a polymer soluble in many different solvents.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In a previous publication we have demonstrated that the polymers derived from 1 exist in the form of a random coil when dissolved.[11] In the following we want to report on the molecular weight distribution as dependent on the parameters of the reaction, such as the extent of conversion, radiation dose and temperature.

EXPERIMENTAL

The preparation, purification and crystallization of the monomer 1 was performed as described previously.[11] The polymerization was carried out exposing single crystals of the typical size of 1x1x0.2 mm to the radiation of a ^{60}Co-γ-source (0.3 Mrad h^{-1}). In two sets of experiments the samples were thermostated at 0 and 30°C ± 1 deg.

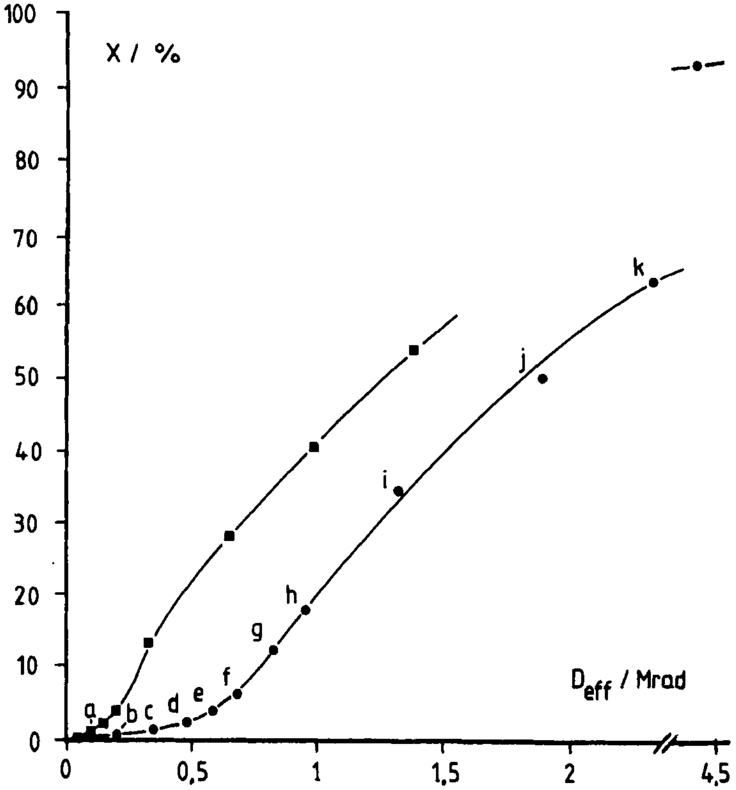

FIGURE 1. Conversion X vs. effective dose D_{eff} at (■) $0^{\circ}C$ and (●) $30^{\circ}C$.

resp. during the irradiation. Once the crystals had been irradiated, they were usually dissolved in 1,2-dichlorethane immediately, but not longer than 3 hours after the irradiation had been finished. The polymer dissolved in less than one hour without leaving any insoluble residue. The concentration was adjusted to a value between

5 and 50 mg ml^{-1} and the appropriate amount of the solution was injected as soon as possible into a gpc-apparatus. The gpc set-up was the one described previously.[11] The conversion was determined spectroscopically measuring the optical density of a solution in 1,2-dichlorethane with a known total concentration of monomer plus polymer. From the extinction in the absorption peak of the polymer at 470 nm (ε_{max} = 16700 $l(mol\ cm)^{-1}$) the concentration of the polymer and thus the extent of conversion could be determined.

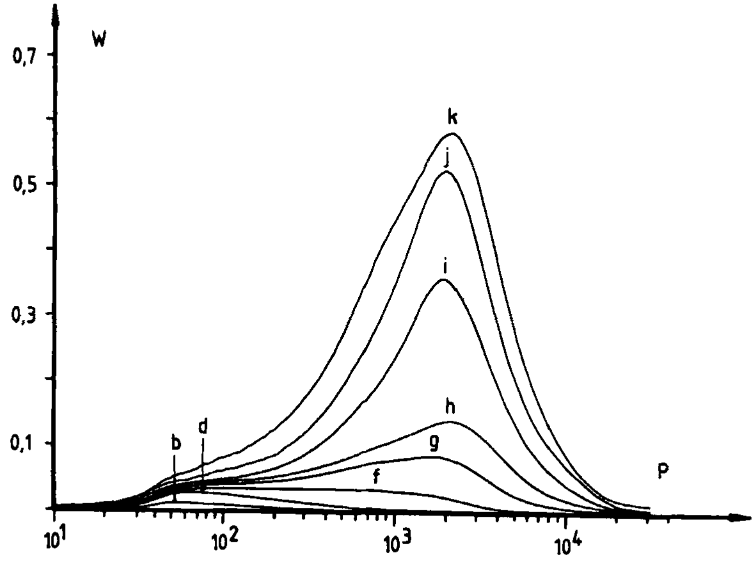

FIGURE 2. Molecular weight distribution of the polymer of TS-12 at various conversions. The letters correspond to the conversion vs. dose curve in Fig. 1.

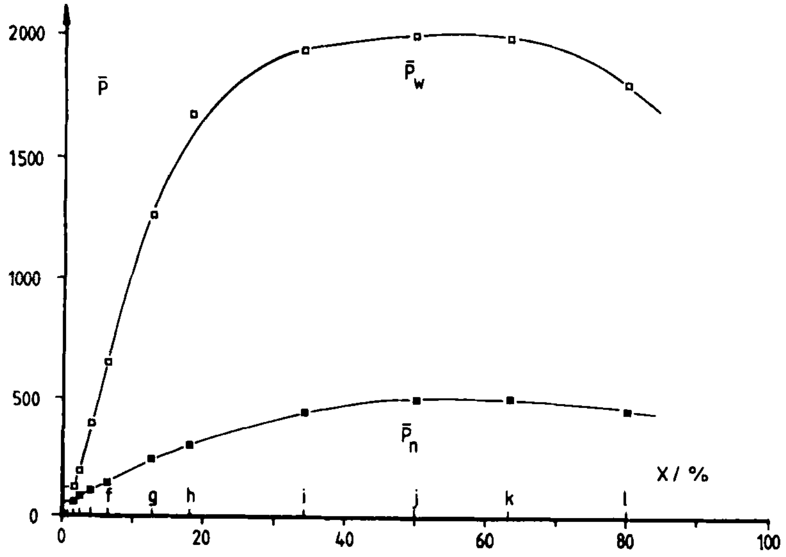

FIGURE 3. Number average degree of polymerization $\bar{P}_n$ and weight average $\bar{P}_w$ vs. conversion for polymerization at 30°C; the small letters correspond to data on Fig. 1.

RESULTS

Fig. 1 shows the conversion X (in percent) as depending on the effective radiation dose, D_{eff}. D_{eff} is defined by equat. 1; it is the fraction of the total does D absorbed by the monomer in a polymerizing crystal.

$$D_{eff} = \int_0^D (1-X)\, dD$$

The radiation-dose (time)-conversion curve shows features well known from the polymerization behaviour of PTS.[3-5] A rapid conversion only takes place when the well defined, slow induction period is over. The length of the induction period increases with temperature but, independently of temperature, quantitative conversion is always reached.

Fig. 2 shows the molecular weight distribution of samples obtained at various conversions as indicated by the small letters a-k in Fig. 1. These distribution curves have been obtained directly from the gpc-diagrams making use of the calibration described in our previous publication.[11] The results are reported in a semilogarithmic scale such that $W \cdot d(\log P)$ is the weight fraction of the polymer the degree of polymerization of which is found between $\log P$ and $\log P + d(\log P)$. The areas under the curves have been normalized so that the total area is proportional to the conversion in each case.

The maximum of the distribution function is found at $P=60$ if the conversion is not larger than 2 percent; in other words the most probable chain is build up from 60 monomer units. As the conversion increases the maximum of the distribution function shifts rapidly to larger values. The polymer formed initally remains intact however. Consequently, the distribution becomes broader. The peak position of the distribution curve reaches a fixed value, if a conversion of approximately 10 percent has been reached corresponding to a chain length of ca. 2000 units. It is very interesting to note that up to ca. 70 percent conversion the shape of the distribution curves

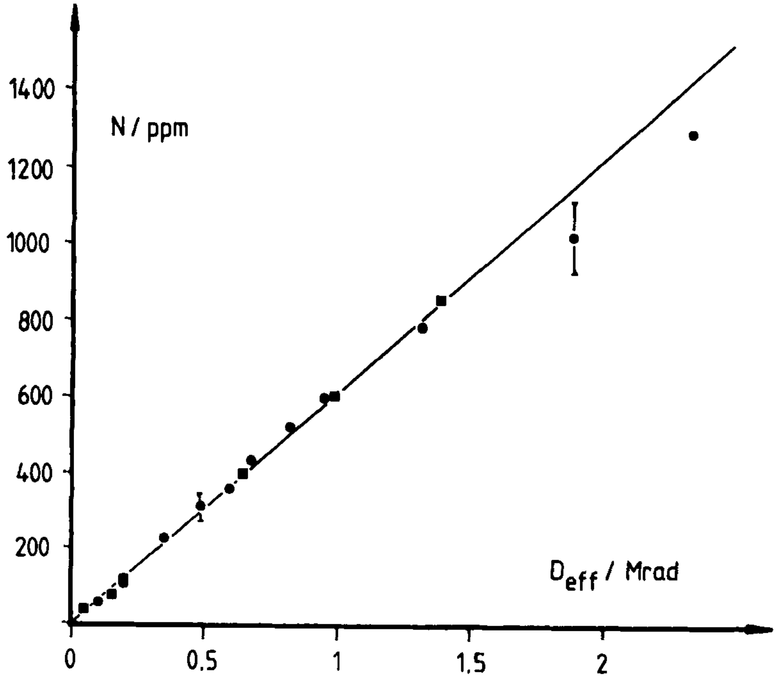

FIGURE 4. Number of chains, N, formed vs. radiation dose, D_{eff} at (■) 0°C and (●) 30°C.

does not change but only the total amount of polymer increases. Even at a conversion of 70 percent, the short chains formed in the beginning of the reaction during the induction period may be readily identified in the gpc-chromatograms. The number average $\overline{P}_n$ and the weight average $\overline{P}_w$ evaluated from the distribution curves are plotted vs. the conversion X in Fig. 3. Qualitatively the dependence of $\overline{P}_w$ on conversion agrees very well with the data reported by Leyrer et al. for the case of PTS where the chain length dependent

Youngs-modulus of a partially converted single crystal had been considered.[6,7]

DISCUSSION

The following important features are deduced from the shape and a quantitative evaluation of the distribution curves:

1) The short chains formed in the initial stages of the polymerization remain intact up to the highest conversion investigated. Consequently, chains cannot grow any further once they have been formed or, in other words, the chain ends are "dead" for further polymerization.

2) At high conversion ($X > 70$ percent) a sudden increase in chain length, as expected for cases where recombination between reactive chain ends is possible, does not take place. This is also in agreement with the first statement.

3) The autocatalytic behaviour of the reaction rate is due to a conversion dependent kinetic chain length and not to an increase of initiation events as the conversion increases.

The latter statement can be proven quantitatively from the available data. The number of independent chains, N, are calculated from the ratio of the conversion X to the number average degree of polymerization: $N = X/\overline{P}_n$.

The number of chains found in the sample at conversion X are thus plotted vs. D_{eff} in Fig. 4 giving a straight line over most of the range investigated. This is the proof that the chains are initiated at constant rate and, since the data at the two temperatures investigated fit the same line, that the initiation rate is practically independent of the temperature within the limited range studied here. From the slope of the curve the initiation rate k_I is calculated to be $6.25 \cdot 10^{-4}$ chains/Mrad (ppm). The latter value may be used to determine the G-value [12,13] of the initiation, which is equivalent to the quantum yield in photochemical reactions, according to [13]:

$$G = \frac{9.65 \cdot 10^5}{M_{mon}} \cdot k_I = 1.2 \text{ (events per 100 eV)}.$$

M_{mon} is the molecular weight of a monomer unit.

This G-value compares well with information available from other radiation induced solid-state reactions; [12,13] a value between 1 and 7 is usually found.

With the experiments described so far it has been possible to separate for the first time effects of the kinetic chain length from effects related to the chain initiation event. Although a detailed information on the chemical nature of the initiation reaction and of the structure of the chain ends is still lacking, the kinetics of the solid-state polymerization can now be developed on much safer grounds than just based on the knowledge of the time conversion curve and the change in lattice parameters. It is probably reasonable to explain the conversion dependence of the kinetic chain length by a side reaction leading to "dead" chain ends which itself may depend on the small geometrical changes of the lattice in the course of the reaction. Further work to elucidate this reaction is in progress.

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