Poly(oxymethylene) crystals grown in the polymerization of trioxane initiated with perchloric acid in nitrobenzene

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SUMMARY

Nascent crystalline poly(oxymethylene) (POM) was synthesized by cationic polymerization of trioxane with anhydrous perchloric acid in nitrobenzene solution. The high polarity of the solvent enabled to obtain high molecular weight polymer. Also the yield obtained indicates that the polymerization reached the expected thermodynamic ceiling-equilibrium. The participation of free oxy carbenium ions from growing POM-chains are relevant on the mechanism of polymerization and crystallization. After an induction period, hexagonal single crystals of POM are formed whose macro conformation correspond to extended chain crystals. Thermal data is in agreement with this morphology, typical of a simultaneous polymerization and crystallization. The spiral growth of the crystals proceeds by a catalyzed crystal growth process.

INTRODUCTION

It is well known that the solution polymerization of trioxane (TOX), under appropriate experimental conditions, is an example of a simultaneous polymerization and crystallization. This heterogeneous reaction is characterized by a reversible polymerization-depolymerization equilibrium between the dissolved monomer and the solid polymer.

Several articles have been published (1-6) on the kinetics of trioxane polymerization in solution using various solvents and different initiators. In addition, the kinetics of the crystal growth of POM have been extensively studied (7,8). This was carried out by electron and light microscopy of POM-crystals obtained with different concentrations of perchloric acid or acetyl perchlorate initiators in dichloromethane solution. In both cases, the fact that the initiators are adsorbed on the crystal surface (assuming a Langmuir type adsorption), enabled a discussion of polymerization mechanisms and their correlation with crystal growth. This could be explained with a catalyzed crystal growth process. Also the spiral growth of the crystals, could be quantitatively interpreted on the basis of the BCF-theory of crystal growth (9).

However, the polymerization of trioxane initiated with anhydrous perchloric acid in nitrobenzene solution has not been studied extensively. Besides, it seemed to be of interest to find reaction conditions for the trioxane/$HClO_4$/nitrobenzene system, that would allow optimum morphological observations of crystal growth by electron microscopy. Thus, experimental conditions of polymerization were found to obtain a similar and low rates of polymerization and crystallization. By Wunderlich's principle (10) two different types of macroconformations could be obtained. If the rate of polymerization is very high in comparison to the rate of crystallization, then polymerization and crystallization set up separate steps, and a folded-chain crystal can be expected. The other possibility is when the rate of polymerization is equal or similar to the rate of crystallization. This would mean that polymerization and crystallization would occur simultaneously or in successive steps. The polymer crystals obtained would have an extended chain structure.

Under the experimental conditions of the present work, i.e., with a trioxane concentration of 1.58 mol/l and initiator of 5.10^{-6} mol/l, low and similar rates of polymerization and crystallization were obtained. Thus, single extended chain POM-crystals were obtained. The concentration of trioxane was then chosen to solve the solubility problem limits of monomer in the solvent at 35°C. It was possible to obtain a low rate of polymerization necessary to get well-defined hexagonal POM single crystals because the trioxane concentration matched the equilibrium concentration of this monomer in nitrobenzene of 1.5 mol/l at 35°C (11), i.e., the equilibrium between trioxane and dissolved POM-chains or oligomers.

Due to the polarity of nitrobenzene high molecular weight products were obtained, because the polymer formed more readily under this conditions, favoring dissociation of propagating species. Due to the solvation of the active oxycarbenium ions of growing POM-chains, the following equilibrium is possible:

$$H\text{\textasciitilde\textasciitilde}OCH_2OCH_2\ OClO_3 \rightleftarrows H\text{\textasciitilde\textasciitilde}OCH_2O\overset{+}{C}H_2\overset{-}{O}ClO_3 \rightleftarrows H\text{-}OCH_2O\overset{+}{C}H_2\ +\ \overset{-}{O}ClO_3$$

Covalent   Ion pair   Free ion

The equilibrium would be expected to be favorable to the right and a faster polymerization to a higher molecular weight polymer must result. For this reason, free oxycarbenium ions are probably involved in the polymerization and crystallization. Thus, the initiator concentration must be very low for low polymerization and crystallization rates.

EXPERIMENTAL

Trioxane was purified as described previously (8). Nitrobenzene was dried by refluxing over phosphoric anhydride for 48 h and then distilled under vacuum before polymerization. Anhydrous perchloric acid was prepared and purified according to

Smith (12), was added as a nitrobenzene solution and used du-
ring the first 24 h. The reactions were carried out as repor-
ted previously (7,8) in nitrobenzene solvent at 35°C. The to-
tal concentration of the monomer in each polymerization was
1.58 mol/l and the initiator concentration was 5.10^{-6} mol/l.
The polymerizations were stopped by adding a solution of trie-
thylamine in methanol at different reaction times. Yields we-
re determined gravimetrically on the basis of the initial amount
of trioxane. The polymer crystals were carefully filtered and
washed with CH_3OH, CH_2Cl_2 and acetone and then dried under va-
cuum at room temperature.

The molecular weights of the specimens were determined vis-
cosimetrically. Hexafluoroacetone sesquihydrate solvent was
used at 25°C in the presence of 1 vol. % triethylamine. The me
thod has been described previously by Höhr et al. (13).

The morphology of the single crystals was studied by elec-
tron microscopy (TEM, Philips EM-200). Replicas were prepared
in the standard way from methanol suspension (shadowed with 20°
using Pt-C) (4). Thermal data was measured with a Perkin-Elmer
DSC-2, differential scanning calorimeter at 20°C/min. The tem-
perature scale was calibrated with indium.

RESULTS AND DISCUSSION

The time-conversion curve (Figure 1) shows at the beginning
of the polymerization an induction period typical of the poly-
merization of trioxane (1,2). The time required for the appea-
rance of the first crystals was 10 min visualized by turbidity
in the heterogeneous system. The maximun yield of 85% indica-
tes, that the reaction reached its expected thermodynamic cei-
ling-equilibrium. Such conversion is possible due to the pola
rity of nitrobenzene. Analogous results were obtained when
trioxane was polymerized by boron trifluoride etherate initia-
tor in the same solvent (4). Polymerization and crystalliza-
tion most likely involve the participation of free oxycarbenium
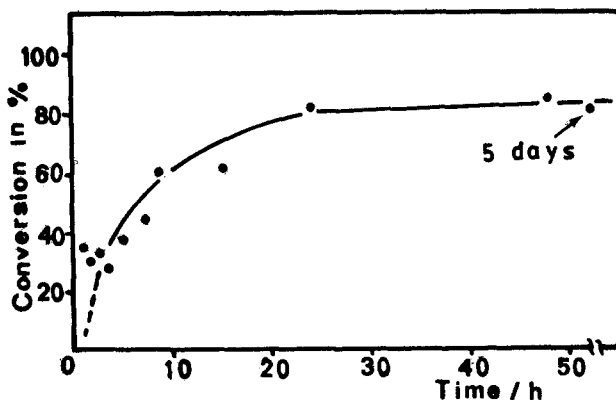
Figure 1.
Relationship between
conversion and poly-
merization time.
[TOX] = 1.58 mol/l,
Nitrobenzene as sol-
vent. Temperature:
35°C.
$[HClO_4] = 5.10^{-6}$ mol/l

ions. The active terminal oxycarbenium ions may react at the
same time with trioxane (by addition) or with folded POM chains
(by intermolecular transacetylation). Figure 2 shows, the trans
fer of one terminal growing polymer chain along the front of a
growing crystal by attack of the oxycarbenium ion to a POM fol-
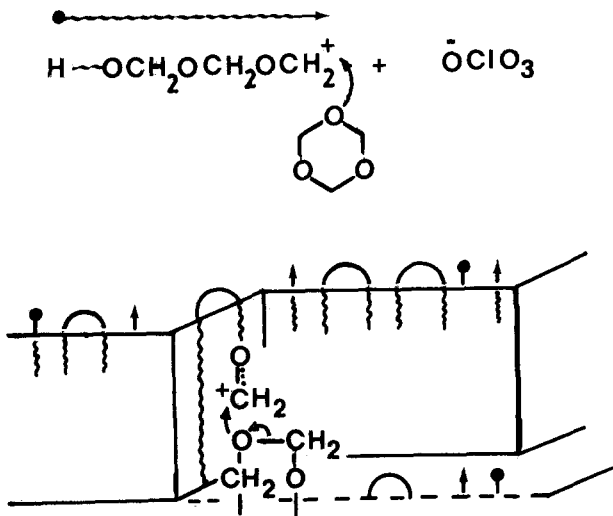ded chain located in the crystal lattice.

Figure 2.
Free oxycarbenium
ion of a terminal
growing polymer
chain.
Crystal growth by
transfer of the ca-
tionic active termi
nal polymer chain
along with the front
growing crystal, by
an intermolecular
transacetylation
reaction.

In the polymerization of trioxane initiated with different
$HClO_4$ concentrations (from 1.10^{-5} to 5.10^{-4} mol/l) by using di
chloromethane solvent, the maximun yield ranged only from 1.3
to 20% depending on the initiator concentration (7). This result
demonstrates the influence of the solvent and the fact that sol
vation of the active chain ends gives high yields. Transfer
with the solvent does not exist. The existence of oxycarbenium
ions in the polymerization of 1,3-dioxolane was demonstrated by
^{1}H-NMR(14).

Other chemical reactions are also involved on the mechanisms
of polymerization and crystallization of POM, as we reported be
fore (7,8).

The viscosity molecular weights of the polymers ranged from
30,000 to 92,000 depending upon the polymerization time. The
values are plotted in Figure 3. At the beginning, the molecu-
lar weights increased slowly, due to the low initiator concen-
tration. Unfortunately, the conversion below 1 h was very low,
so there was not enough product for a molecular weight determi
nation. When thermodynamically stable crystallization nuclei
were formed, the overall polymerization process started and con
sequently the molecular weight increased rapidly, and then was
constant after 15 h, reaching a maximun molecular weight of

92,000. The molecular weights were obtained when tioxane was polymerized on CH_2Cl_2 are ranging between 5,000 and 15,000 by using the same initiator, $HClO_4$ (7).
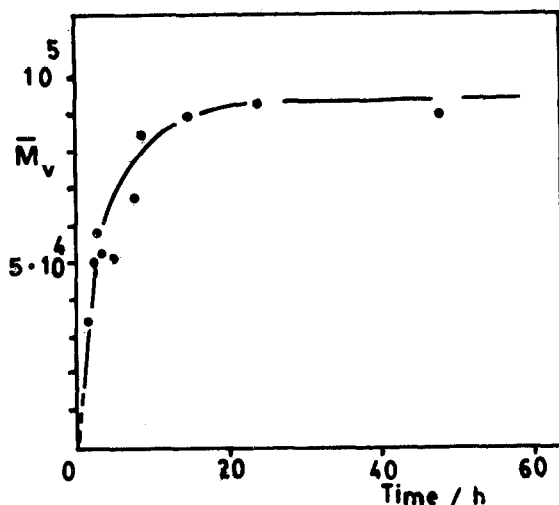

Figure 3.
Molecular weight ($\overline{M}v$) as a function of polymerization time.

The morphology of the crystal structure was studied by electron microscopy before the polymerization equilibrium. Hexagonal single POM crystals were obtained and they are representative for all the electron micrographs studied. During the induction period, soluble oligomers were obtained in the reaction medium. It was assumed that chain folded crystals are primarily formed as soon as the oligomers become to a length which make them insoluble in the polymerization system (3,4). Further reaction can take place on the surface of these crystals. Immediately, after the nucleation period and during the first 55 min, only a turbidity it is formed due to the presence of hexagonal single crystals with a diameter of ca. 2.5 μm. After a period of time, these crystals also started to grow in thickness by growing spirals due to screw dislocations on the formerly smooth lamellar surfaces (Figure 4 a, b). The electron micrographs show that growth proceeds initially in a [001] direction. The Burgers vector is found parallel to this plane, that means normal to the surface of the lamellar primary nucleus. They look like a polymer single crystals which are obtained from solution crystallization of high preformed molecular weight poly(oxymethylene) (10a). It was also observed spirals growth with regular rotation. The crystals show also a lateral growing at the [100] planes. The lateral growth of the hexagonal base lamella is due to the addition of monomer or oligomers to the active chains ends (15). Higher polymerization times only produced an agglomeration of several crystals, not suitable for electron microscopy analysis.

It is remarkable that the thickness growth of the crystals is developed on the basis of only one spiral growth. The sa-

me phenomenon was found when the polymerization was carried out by using $HClO_4$ or acetyl perchlorate in CH_2Cl_2 solution, as initiators (7,8). A different growth process occurs, when BF_3-etherate was used as initiator on the trioxane polymerization (4).
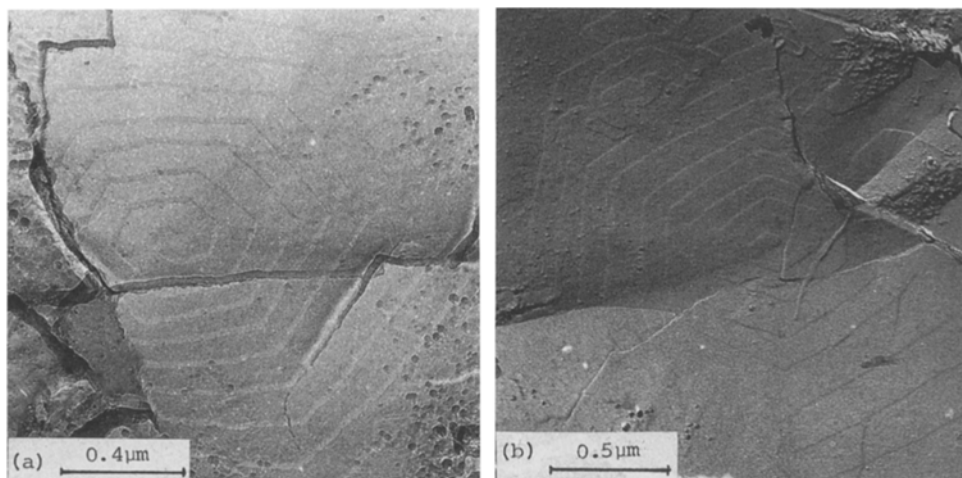

Figure 4. Electron micrographs of as-polymerized POM-single crystals. Note the regular spiral growth and the regular spirals step width. (a) Obtained after 1 h reaction time; 36% conversion. (b) 5 h polymerization time; 40% conversion.

The step width of the spiral growth, d, can be measured with precision from the electron micrographs (See Figure 4 a,b). d, was determined in crystals obtained at different polymerization times, and a common value of ca. 150 nm was found. That means that d is not depending on the reaction times. We believed that the step width of the spirals should depend on the concentration of the initiator for each specific polymerization systems. It was found a similar result, when the polymerization was carried out in dichloromethane solution by using $HClO_4$ or acetyl perchlorate as initiators (7,8). In dichloromethane solution the expected value of the step width d, is of ca. 400 nm with a concentration of $HClO_4$ of 5.10^{-6} mol/l, which was used in the present work. However, in nitrobenzene solution a value of only 150 nm was found for the same initiator concentration and this verify the influence of solvent nature on the mechanism of polymerization and crystallization. As was discussed before, the solvent polarity allows the existence of free oxycarbenium ions, and therefore the addition of monomer to this cationic chain ends it is carried out more rapidly, and therefore the evolution of the spiral growth is also faster.

The regular spiral growth of the crystals presents other interesting example of the theory of the crystal growth of Burton, Cabrera and Frank (9).

The electron micrographs of fracture surfaces showed the most common feature of extended chain crystals, that is, the striated appearance (Figure 5). The sample consists of lamellae with a rather large distribution in crystal thickness. The average crystal thickness is about 0.6 μm. This type of macroconformation had been previously observed, e.g., using high pressures during the crystallization of the polymer from the melt (10). In a lower yield, these extended chain crystals have also been obtained from the polymerization in solution of trioxane (4,6,7, 8). This extended-chain macroconformation is typical of a simultaneous polymerization and crystallization process.

It is necessary to consider that there are many inactive polymer chain ends included as defects in the polymer crystal lattice. This possibility was discussed previously, as other mechanism of POM crystal growth (7).
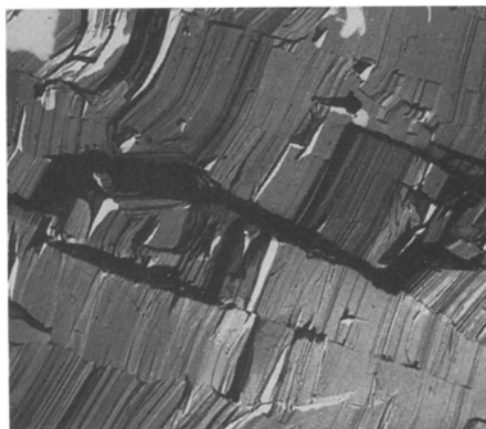
Figure 5.
Fracture surface of extended chain crystals of POM.

5 h polymerization time; 40% conversion.

0.5 μm

In order to study the correlation between the crystal morphology of the samples with their thermal behaviour, the melting temperatures of the as-polymerized POM were determined by differential scanning calorimetry. The maximum of the melt peaks were defined as the melting temperatures. It was observed that peak temperatures, increases gradually as the polymerization proceeds, reflecting the increase in molecular weight during polymerization. The polymer crystals shown always a single melting endotherm with a half width of 3-5 °C, which implies the crystal size distribution in the samples. The polymers formed in the early stages of polymerization decomposed considerably during the measurements. Therefore, quantitative determination of the heat of melting has not been made. It can be seen that the specimens of the longest polymerization time (24 h) shows a very narrow melting peak at a temperature of 184°C. The melting points of the polymers shifted between 178° C and 184°C. This values are typical for thermodynamically stable extended-chain POM crystals (16). These results are in agreement with the macroconformation observed by electron microscopy.

The overall results obtained during this investigation allow us to conclude that polymerization takes place on active centers located on the solid surface of single poly(oxymethylene) crystals. The reaction can be characterized by the term simultaneous polymerization and crystallization, whenever the reaction proceeds from a dissolved monomer directly to the crystalline polymer without forming intermediates (10). Thus the crystal growth phenomenon must be understood as a catalyzed crystal growth process.

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