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Polymerization and Crystallization of Polytetrahydrofuran and Poly(1,4-epoxycyclohexane)

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ABSTRACT

The polymerization of tetrahydrofuran and 1,4-epoxycyclohexane initiated by triethyloxonium hexachloroantimonate has been studied at temperatures below 0°C. It has been found that during polymerization of tetrahydrofuran in bulk at temperatures of -25°C and below the polymer crystallizes from a solution of its own monomer. The crystallization accelerates the polymerization somewhat. A chain transfer reaction takes place at higher conversion according to molecular weight and molecular weight distribution measurements.

The crystallization of poly(1,4-epoxycyclohexane) during polymerization at -15°C in methylene chloride starts immediately after polymerization has been initiated. At very low conversion the distribution of molecular weight is unimodal and narrow; at higher conversion the distribution of molecular weight is bimodal, the high molecular weight peak becomes more prominent, and the distribution broader with increasing conversion. It is suggested that the low molecular weight peak corresponds to the polymer fraction which has become inaccessible to the monomer during crystallization of the low molecular weight polymer from solution at an early stage of polymerization; the simultaneous polymerization and crystallization taking place on the surface of polymer particles is responsible for the high molecular weight peak and the change of the morphology of the polymer particles.

INTRODUCTION

Concurrent polymerization and crystallization takes place in many important polymer syntheses [1]. The polymerization mechanism is generally a combination of initiation, propagation, termination, and transfer reactions, and the advantage of the simplest possible polymerization process for examination of the mutual influence of polymerization and crystallization is obvious.

In living chain polymerization the termination and transfer reactions are absent and the polymerization is described by initiation and propagation reactions only. If the initiation reaction is faster than propagation, the resulting molecular weight distribution is narrow, and if the crystallization of living chains from solution occurs and the propagation rate is slow in relation to the crystallization rate, the following consecutive processes take place:

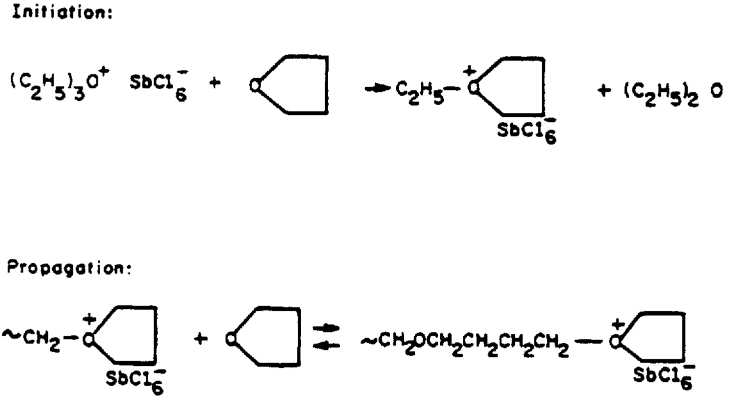
1. Initiation.
2. Propagation in solution until some critical molecular weight and concentration is reached.
3. Crystallization of living polymer molecules from solution.
4. Concurrent polymerization and crystallization of living polymer chains built in the polymer crystals.

Cationic polymerization of tetrahydrofuran seemed to fulfil all these conditions simultaneously. It has been found [2, 3] that under certain conditions the tetrahydrofuran polymerization can be described by living chain mechanism with little or no termination. It has been also reported [3-5] that triethyloxonium cation initiates the polymerization of tetrahydrofuran rapidly, and the rate of initiation is comparable with propagation.

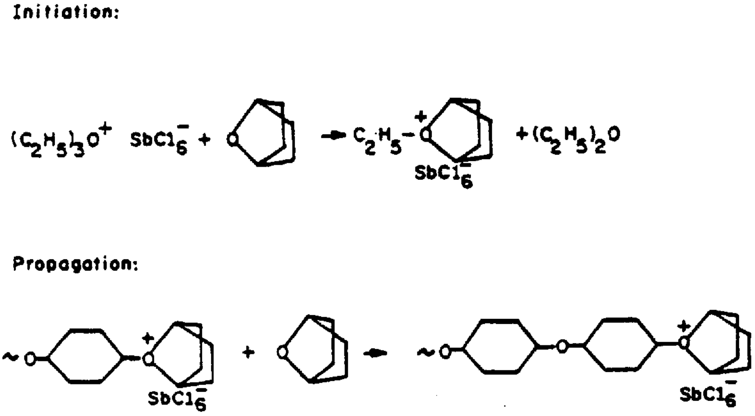
The polymerization mechanism of 1,4-epoxycyclohexane [6, 7] is similar to the polymerization of tetrahydrofuran with the exception that transfer and termination reactions are more enhanced. The polymer is insoluble in common solvents and has a melting point of over 400°C [8] and the polymerization is always accompanied with crystallization, but no work has been reported on polymerization combined with crystallization of polytetrahydrofuran. The initiation and propagation steps of the polymerization of tetrahydrofuran and

1,4-epoxycyclohexane are described by the following chemical reactions.

Polymerization of Tetrahydrofuran



Polymerization of 1,4-Epoxycyclohexane



EXPERIMENTAL

Materials

Tetrahydrofuran and 1,4-epoxycyclohexane were dried by and refluxed over lithium aluminium hydride and distilled under dry nitrogen through a 1-yard column filled with Fenske helices.

Methylene chloride was refluxed over calcium hydride and distilled.

Triethyloxonium hexachloroantimonate was prepared by the Meerwein [9] method. It has been recrystallized from dry methylene chloride under dry nitrogen and kept in evacuated sealed ampoules immersed in liquid air. The melting point determined by differential scanning calorimetry was 133°C followed by decomposition.

Polymerization

A high vacuum technique was used. The reactors containing a sealed glass bulb with a known amount of initiator and a breaker were sealed to the vacuum line and evacuated to about 10^{-4} Torr. Trimethylchlorosilane vapor was used for removing traces of water adsorbed on the glass surface and all vacuum systems were evacuated again to 10^{-4} Torr for 6 hr. The monomer and methylene chloride were left for 24 hr over lithium aluminium hydride and calcium hydride, respectively, in an evacuated vessel sealed to the reactor, and then a known amount was recondensed into the reactor through a breakseal and the reactor was sealed off the vacuum line. The glass bulb was filled with the initiator in a small glove box in a carefully dried atmosphere. The glass bulb was then evacuated and sealed.

The polymerization was carried out in a cryostat at temperatures controlled to 0.1°C. Polymerization was started by breaking the glass bulb and mixing the initiator with the monomer. About 3 min were sufficient for the initiator to be fully dissolved. The onset of crystallization during polymerization was determined visually and was taken as the time when the first trace of turbidity was observed. No sign of liquid phase separation was found (coagulation of particles, formation of a coherent layer). Preliminary experiments with dilute solutions of polytetrahydrofuran in tetrahydrofuran precipitated by cooling at various temperatures down to -78°C have also shown that liquid phase separation is absent. Crystallization of polytetrahydrofuran from solution in toluene at low temperatures has been also reported by other authors [10].

After the time required, the polymerization was stopped by opening the reactor and mixing the content with about a double volume of methanol. Polytetrahydrofuran was recovered and the deactivated initiator was removed as follows: the polymer-methanol-monomer mixture was mixed with water, methanol and monomer were evaporated at room temperature, and polymer was recovered by a multiple extraction with benzene. After evaporation of benzene, the polymer was dried in vacuum.

As poly(1,4-epoxycyclohexane) is insoluble in the reaction medium, it was separated by filtration and dried in vacuum.

Number-Average Molecular Weight

Number-average molecular weights of polytetrahydrofuran were determined with a Hewlett-Packard Vapour Pressure Osmometer. Benzene was used as the solvent at 37° C.

A mixed solvent of phenol with o-dichlorobenzene 1:1 w/w at 130°C was used for number-average molecular weight determination of poly(1,4-epoxycyclohexane) by vapor pressure osmometry.

Molecular Weight Distribution

The Water's Gel Permeation Chromatograph was used for determination of the molecular weight distribution. o-Dichlorobenzene at 40° C was used as a solvent for polytetrahydrofuran, and a mixed solvent of m-cresol with chlorobenzene 1:1 w/w at 25° C has been used for the determination of the molecular weight distribution of poly(1,4-epoxycyclohexane). Benzoic acid 0.25% was added to the solvent to prevent the specific adsorption effect caused by polar groups [11]. Polystyrene standards were used for calibration, and the $\overline{M}_w/\overline{M}_n$ ratio was calculated by the method recommended by the manufacturers of the chromatograph.

RESULTS AND DISCUSSION

The polymerization of tetrahydrofuran was carried out in bulk and initiated by triethyloxonium hexachloroantimonate. Preliminary experiments have shown that at -15° C and above the polymer remains dissolved in its own monomer; at -25° C and below the polymer begins to crystallize from solution after some critical molecular weight and concentration is reached. The results of polymerization at -5° C are shown on Fig. 1. A straight line in coordinates $1/[C] \ln ([M]_0 - [M]_\infty)/([M] - [M]_\infty)$ (where $[C]$ is the initial concentration of the initiator, $[M]_0$ is the initial concentration of the monomer, $[M]_\infty$ is the equilibrium concentration of the monomer calculated from the thermodynamic data [3], and $[M]$ is the concentration of the monomer at the time t) against time was obtained in accordance with the accepted polymerization mechanism [4, 12].

The results of polymerization carried out at -25 and -45° C are shown on Figs. 2 and 3. Two straight lines can be laid through the experimental points of each run. It was observed that their intersection point coincides with the onset of polymer crystallization, suggesting that the crystallization somewhat accelerates the polymerization process.

The number-average molecular weights of polytetrahydrofuran determined by vapor pressure osmometry and calculated from the amount of initiator used and the yield of polymerization are compared in Table 1.

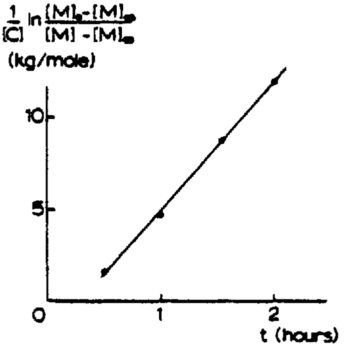


FIG. 1. Polymerization of tetrahydrofuran at -5°C in bulk. [C] = concentration of the initiator (mole/kg), [M] = concentration of the monomer at the time t, $[M]_0$ = initial concentration of the monomer (13.9 mole/kg), and $[M]_\infty$ = equilibrium concentration of the monomer (1.3 mole/kg) calculated from the thermodynamic data of tetrahydrofuran polymerization given by Rosenberg et al. [3].

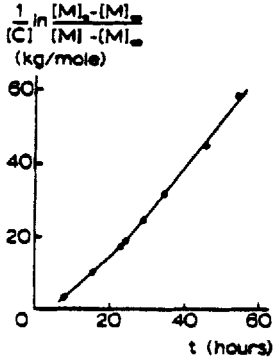


FIG. 2. Polymerization of tetrahydrofuran at -25°C in bulk. [C] = 1×10^{-2} mole/kg. $[M]_\infty$ = 0.57 mole/kg.

It shows that the experimental values of $\overline{M}_n$ do not correspond to the calculated ones at low and high conversions. At low conversions the initiator may not be fully consumed and the calculated $\overline{M}_n$ are lower than the experimental values, at high conversions the experimental $\overline{M}_n$ are lower than the calculated ones, suggesting that a chain transfer

TABLE 1. Polymerization of Tetrahydrofuran in Bulk

Polymerization temp (°C)	Initiator concn × 10^2 (mole/kg)	Conversion (%)	$\overline{M}_n \times 10^{-3}$, calc[a]	$\overline{M}_n \times 10^{-3}$, found	$\overline{M}_w/\overline{M}_n$
-5	1.3	2.0	1.5	2.3	1.07
"	1.0	4.3	4.3	4.6	1.16
"	1.4	10.7	7.5	7.2	1.12
"	1.3	13.5	10.1	9.0	1.42
-25	1.0	3.2	3.2	4.3	
"	"	9.6	9.6	7.8	
"	"	15.3	15.3	9.0	
"	"	16.6	16.6	9.0	
"	"	20.8	20.8	10.4	
"	"	25.8	25.8	12.6	
"	"	34.8	34.8	12.1	
"	"	42.3	42.3	14.7	
-45	1.0	0.6	0.6		1.20
"	"	0.9	0.9	2.3	1.29
"	"	1.2	1.2	3.5	1.19
"	"	2.0	2.0	3.9	1.33
"	"	3.9	3.9	5.8	1.37
"	"	6.3	6.3	6.6	1.41
"	"	8.5	8.5	7.8	1.97

[a] When the concentration of the initiator is 1×10^{-2} mole/kg, $\overline{M}_n \times 10^{-3}$ is numerically equal to the percent conversion.

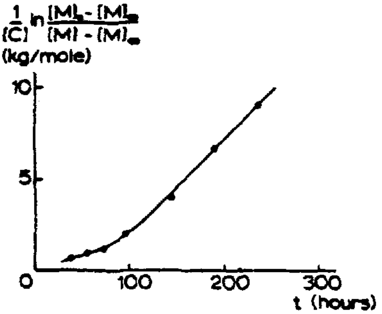


FIG. 3. Polymerization of tetrahydrofuran at -45°C in bulk. $[C] = 1 \times 10^{-2}$ mole/kg, $[M]_\infty = 0.21$ mole/kg.

reaction takes place. The broadening of the molecular weight distribution with increasing conversion, expressed by $\overline{M}_w/\overline{M}_n$ in Table 1, also suggests that a transfer reaction is present. A mechanism of the transfer reaction with polymer and with gegenion was suggested by Dreyfuss and Dreyfuss [13].

It is possible that the acceleration of the polymerization at -45°C is only partly due to the crystallization of the polymer. As the comparison of the experimental and calculated values of $\overline{M}_n$ suggests, the initiator may not be fully consumed at the conversion when the crystallization of polymer begins and therefore the rate of polymerization may be higher at higher conversion when the number of living chains has increased. The crystallization of the polymer does not seem to decelerate the polymerization of tetrahydrofuran even at higher conversion. This could have been anticipated if the propagating ends had been occluded in the crystals and had become inaccessible to the monomer.

It follows from Table 1 and Figs. 2 and 3 that the molecular weight and the concentration of the polymer reached at the point where the polymer begins to crystallize is 9000 and 15% for the polymerization at -25°C and 3900 and 2% for the polymerization at -45°C. As expected, at lower temperature the crystallization of polymer takes place at lower molecular weight and conversion.

It is experimentally difficult to investigate the structure of polytetrahydrofuran crystals formed during polymerization. The melting point of polytetrahydrofuran is rather low (about 30°C), and samples should be kept and examined at low temperature to avoid possible changes due to annealing. However, separate experiments have shown that filtered and pressed crystal mats of solution-crystallized polytetrahydrofuran with number-average extended chain length in the

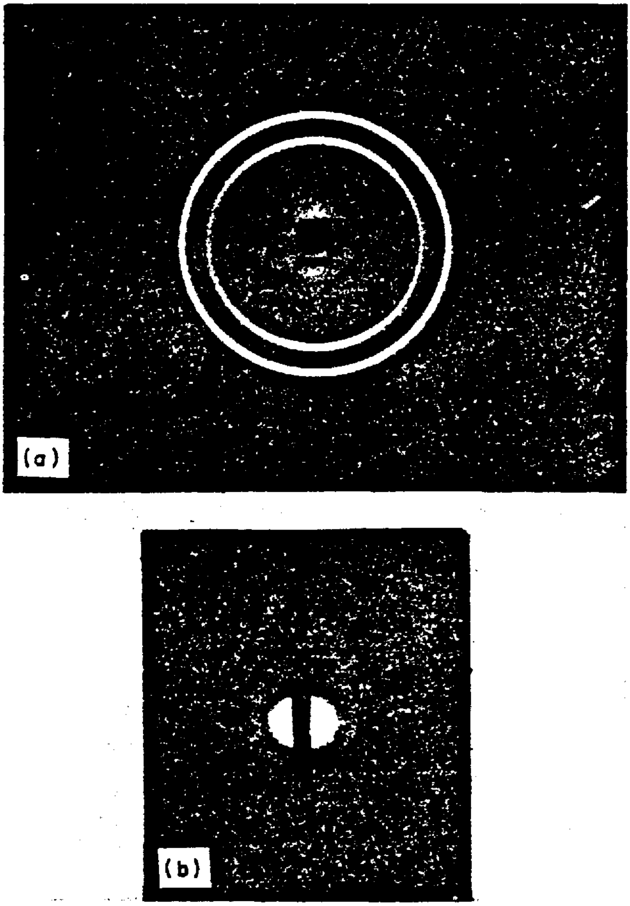


FIG. 4. Wide (a) and low (b) x-ray pattern of the polytetrahydrofuran single crystal mat crystallized at 0°C from mixed solvent of isopropanol with 2-butanol 2:1 v/v. The number-average extended chain length is 1250 Å; the x-ray beam is parallel to the crystal mat surface.

interval from 334 to 1250 Å give low angle x-ray spacing of 110-122 Å (Figs. 4 and 5). Two different solvents and crystallization temperatures were used: tetrahydrofuran and a crystallization temperature of -45°C closely simulating crystallization conditions during polymerization, and thermodynamically poorer mixed solvent of isopropanol with 2-butanol at a crystallization temperature of 0°C. Polytetrahydrofuran crystals

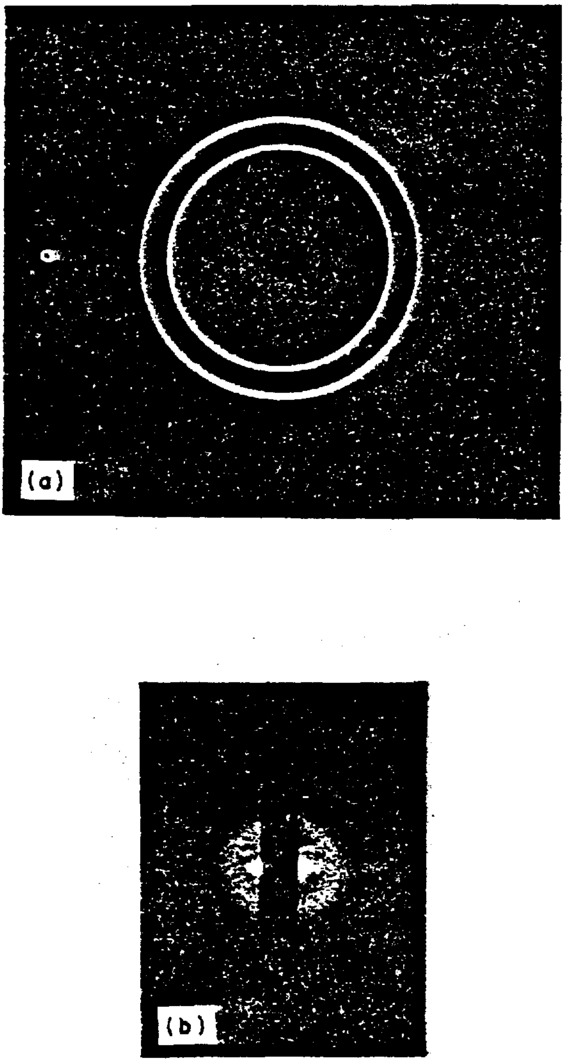


FIG. 5. Wide (a) and low (b) x-ray pattern of the polytetrahydrofuran single crystal mat crystallized at -45°C from tetrahydrofuran. The number-average extended chain length is 490 Å; the x-ray beam is parallel to the crystal mat surface.

were filtered and dried at the crystallization temperature but examined by x-rays at room temperature; thus annealing of crystal mats probably occurred. Nevertheless, annealing, if it occurred, could only increase the lamellar thickness [14] and therefore the thickness of the lamellae as formed at lower temperatures should not exceed the value of 110-122 Å obtained at room temperature and could even be less than this. It follows that the polytetrahydrofuran chains of the chain lengths in question must be folded in such crystals.

As the number-average chain lengths at the onset of crystallization during polymerization of tetrahydrofuran in bulk are 330 and 760 Å at polymerization temperature -45 and -25°C, respectively, folded chain crystals are expected to precipitate during polymerization under these conditions. It has been found [15] that in folded chain crystals of polyethylene the chain ends remain outside the crystals and are accessible to chemical reagents. It is therefore, not surprising that no indication of termination due to the occlusion of living ends has been found in the range of conversions studied in this work. The further polymerization of living ends remaining outside chain folded crystals can give rise to the nucleation of another folded chain layer on the tops of the original lamella. A multilayer structure connected by tie molecules can be eventually expected, but more work is necessary to elucidate this problem.

In order to crystallize living polytetrahydrofuran in the form of extended chain crystals, the polymerization must be carried out at temperatures considerably below -45°C. At these temperatures the polymerization is inconveniently slow and practically stops at -78°C. It was found difficult to decrease the solubility of low molecular weight polytetrahydrofuran by addition of a nonsolvent without decreasing the solubility of the initiator because the initiator solvents are also good solvents for polytetrahydrofuran. Moreover, the dilution of the monomer could decrease the slow polymerization rate even further.

The polymerization of 1,4-epoxycyclohexane initiated by triethyloxonium hexachloroantimonate has been carried out in methylene chloride at the temperature of -15°C. The concentration of the monomer was 2.04 mole/kg and the initiator concentration was 0.7×10^{-2} and 1.4×10^{-2} mole/kg. The results are shown on Figs. 6 and 7 and they give straight lines in coordinates $1/[C] \ln [M]_0/[M]$ against time. The slopes of the lines are identical for both initiator concentrations and give a rate constant value of 2.1 kg/mole hr, close to the rate constant of the polymerization of tetrahydrofuran at the same temperature (2.7 kg/mole hr).

The distribution of molecular weight determined by gel permeation chromatography is shown in Fig. 8, and the corresponding weight-average to number-average molecular weight ratio is given in Table 2. At low conversion the molecular weight distribution is unimodal and narrow, but as polymerization proceeds a high molecular weight peak appears and becomes prominent at high conversion.

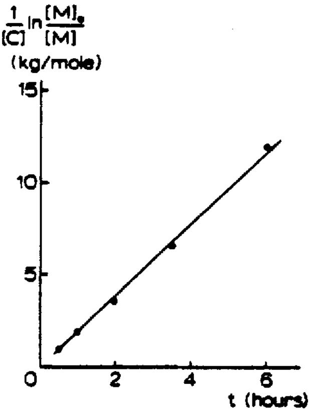


FIG. 6. Polymerization of 1,4-epoxycyclohexane at -15°C in methylene chloride. $[C] = 0.7 \times 10^{-2}$ mole/kg; $[M]_0 = 2.04$ mole/kg.

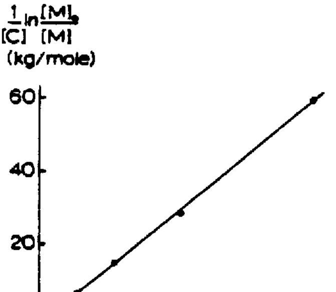


FIG. 7. Polymerization of 1,4-epoxycyclohexane at -15°C in methylene chloride. $[C] = 1.4 \times 10^{-2}$ mole/kg, $[M]_0 = 2.04$ mole/kg.

The number-average molecular weights calculated from the yield of polymerization and the amount of initiator are compared with the molecular weights obtained by vapor pressure osmometry in Table 2. At low conversion the experimental values are much higher than the calculated ones, suggesting that the initiator is not fully consumed; at high conversion the opposite was found, showing that a chain transfer reaction occurs.

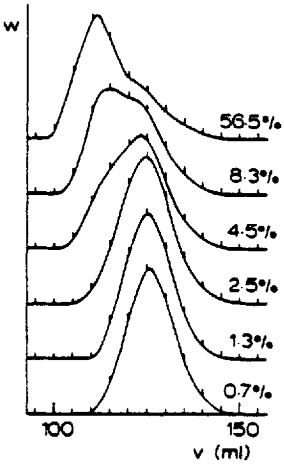


FIG. 8. Gel permeation chromatograph spectra of poly(1,4-epoxycyclohexane) at different conversion: w = weight fraction of the polymer, and v = elution volume (ml).

TABLE 2. Polymerization of 1,4-Epoxycyclohexane in Methylene Chloride[a]

Conversion (%)	$\overline{M}_n \times 10^{-3}$, calc	$\overline{M}_n \times 10^{-3}$, found	$\overline{M}_w/\overline{M}_n$
0.7	0.21	2.03	1.15
1.3	0.39	2.11	1.16
2.5	0.71	2.16	1.30
4.5	1.32	2.50	1.61
8.3	2.41	2.90	1.80
56.5[b]	16.4	3.7	2.90

[a] Concentration of the monomer $[M]_0 = 2.04$ mole/kg; initiator concentration $[C] = 0.7 \times 10^{-2}$ mole/kg; temperature, -15°C.

[b] Temperature, 0°C; polymerization time, 120 hr.

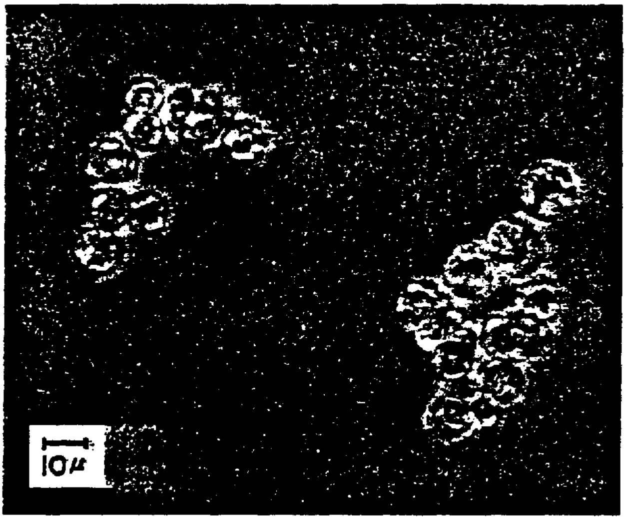


FIG. 9. Optical micrograph of poly(1,4-epoxycyclohexane) particles. Conversion 2.5%, unimodal molecular weight distribution.

The optical micrographs of poly(1,4-epoxycyclohexane) particles are shown in Figs. 9 and 10. It has been observed that at low conversion when polymer has a unimodal molecular weight distribution the particles have a spherical shape, their size is rather uniform, and their volume is proportional to the yield of polymerization. It can be concluded that the particles have been nucleated simultaneously at a very early stage of polymerization and that their number does not change with conversion. At higher conversion, when a bimodal molecular weight distribution is present, large dendritic polymer particles of different size appear and their weight fraction increases with conversion.

Scanning electron micrographs of poly(1,4-epoxycyclohexane) particles at low and high conversion are shown in Figs. 11 and 12-14, respectively. At low conversion the particles are spherical with smooth surfaces, at high conversion the dendrites coexist with the spherical particles. Protruding spikes can be observed on the surface of some spherical particles, suggesting their development into dendrites.

The x-ray pattern of pressed crystal mat of poly(1,4-epoxycyclohexane) consists of unoriented powder rings (Fig. 15). A weak and diffuse ring is observed in the low angle region (Fig. 15), giving the spacing 108 Å and corresponding to the extended chain length of the low molecular weight component.

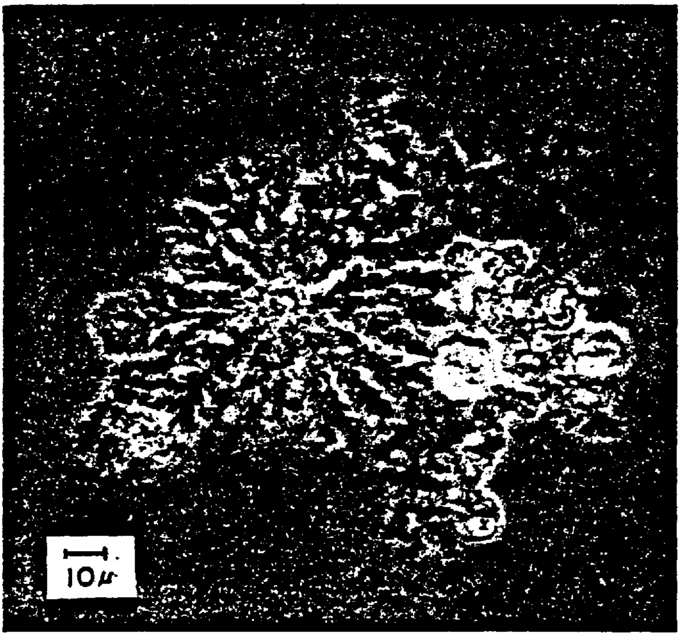


FIG. 10. Optical micrograph of poly(1,4-epoxycyclohexane) particles. Conversion 4.5%, bimodal molecular weight distribution.

The crystallization of poly(1,4-epoxycyclohexane) starts very soon (within several minutes) after polymerization has been initiated. As shown in Table 2, the molecular weight of polymer is higher than the calculated one, suggesting that at low conversion the initiator is not fully consumed and that the initiation and propagation in solution and the crystallization of the low molecular weight polymer occur simultaneously. The living low molecular weight polymer crystallizes from solution in the form of extended chain multilayer spherical particles. In such crystals, most of the living ends are buried in between the layers and their further polymerization is prevented by their inaccessibility to the monomer. Two competitive growth mechanisms can take place on the polymer surface: one caused by the deposition of the next low molecular weight layer and the other caused by the polymerization of the accessible living ends. At low conversion, when the initiator is not yet consumed, new living polymer chains are initiated in solution and, after reaching the

FIG. 11. Scanning electron micrograph of poly(1,4-epoxycyclohexane) particles. Conversion 0.7%, unimodal molecular weight distribution.

solubility threshold, deposit on the particle surface. The molecular weight of the particles therefore remains nearly constant and its distribution corresponds to the unimodal low molecular weight peak on the gel permeation chromatogram. At higher conversion, when the initiator is nearly consumed, the supply of the low molecular weight polymer decreases and the accessible living ends on the particles surface can polymerize and give rise to the high molecular weight peak of the bimodal molecular weight distribution. The low molecular weight polymer crystallized from solution during the early stage of polymerization is conserved inside the polymer particles at high conversion and corresponds to the low molecular weight peak of

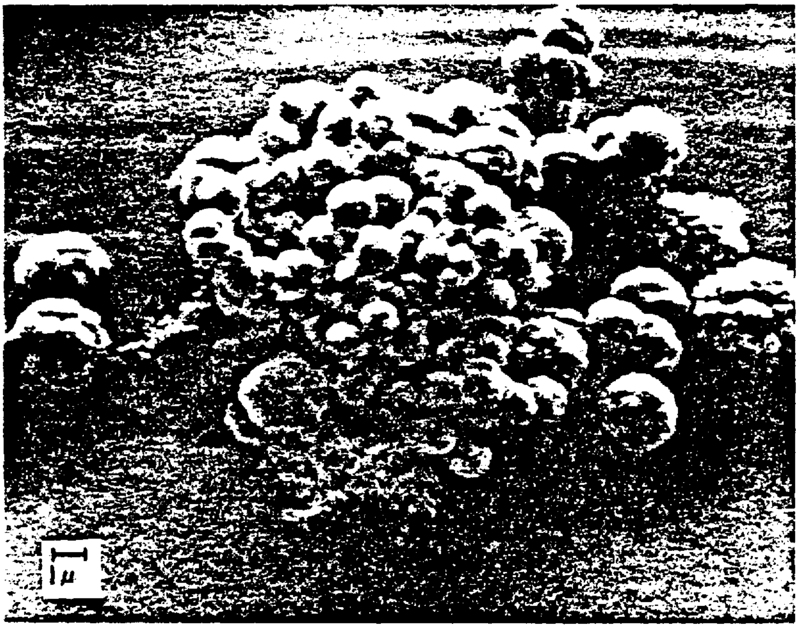


FIG. 12. Scanning electron micrograph of poly(1,4-epoxycyclohexane) particles. Conversion 4.5%, bimodal molecular weight distribution.

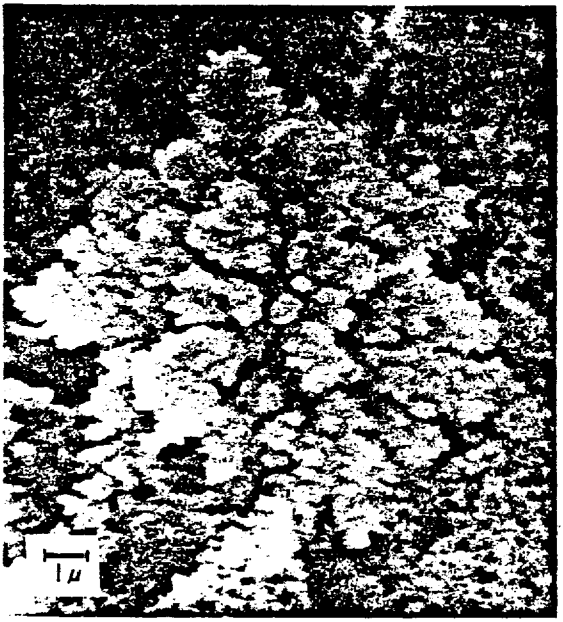


FIG. 13. Scanning electron micrograph of poly(1,4-epoxycyclohexane) particles. Conversion 8.3%, bimodal molecular weight distribution.

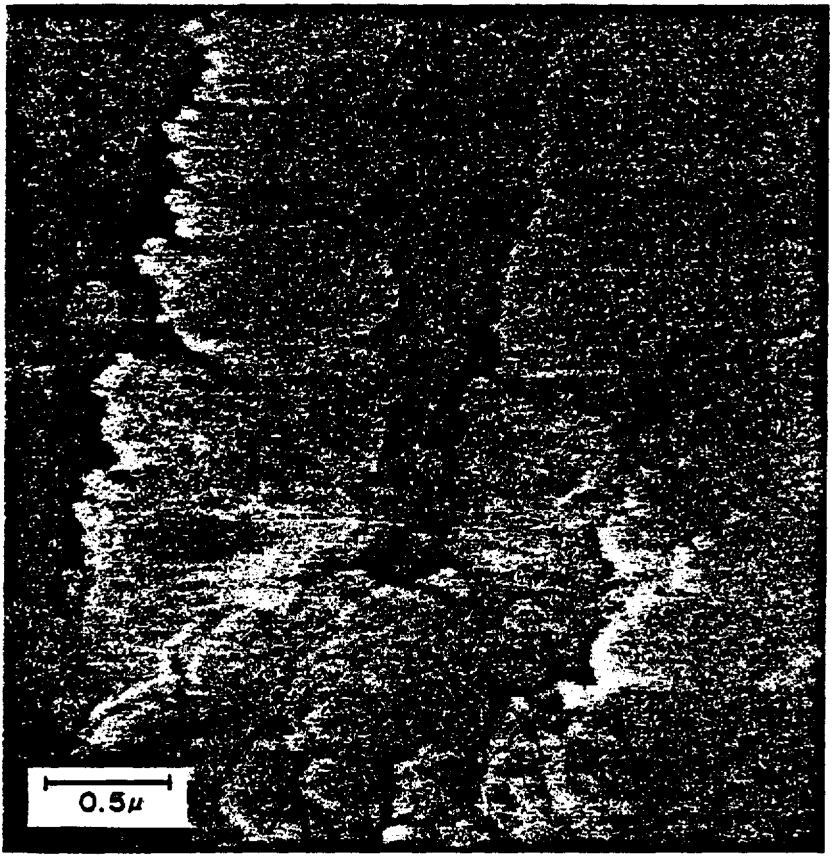


FIG. 14. Scanning electron micrograph of poly(1,4-epoxycyclohexane) particles. Conversion 8.3%, bimodal molecular weight distribution.

the bimodal distribution; its weight fraction decreases with conversion as shown by the gel permeation chromatograph spectra in Fig. 8.

As shown in Table 2, the calculated $\overline{M}_n$ at high conversion are higher than the experimental values, suggesting that a chain transfer reaction is present. Because of the transfer, the growth of the polymer particles at high conversion is never fully determined by the polymerization of the accessible living ends on the surface and, consequently, a simple relation between geometry of the particles and polymerization parameters cannot be expected. A possible chain transfer mechanism has been shown by Baccaredda et al. [16].

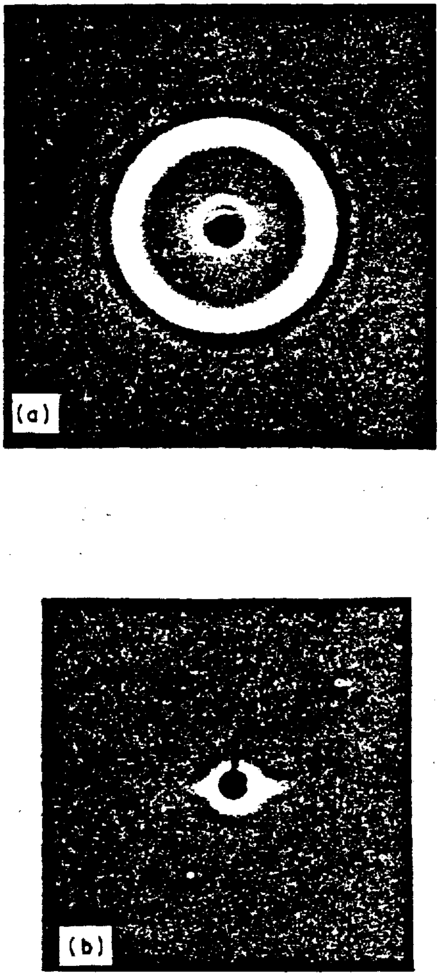


FIG. 15. Wide (a) and low (b) x-ray pattern of pressed crystal mat of poly(1,4-epoxycyclohexane). Conversion 56.5%, bimodal molecular weight distribution.

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