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Cationic Copolymerization of 1,3,5-Trioxane with 1,3-Dioxepane: A Comprehensive Approach to the Polyacetal Process

Karthikeyan Sharavanan,[§] Esteban Ortega,[†] Michel Moreau,[†] Cédric Lorthioir,[‡] Françoise Lauprêtre,[‡] Philippe Desbois,[§] Martin Klatt,[§] and Jean-Pierre Vairon*,[†]

[†]*Laboratoire de Chimie des Polymères (CNRS − UMR 7610), Université Pierre et Marie Curie- Paris 6, Case 185 4, Place Jussieu, 75252 Paris Cedex 05, France,* [‡]*Institut de Chimie et des Matériaux Paris-Est (CNRS − UMR 7182), 2-8 rue Henri Dunant, 94320 Thiais, France, and* [§]*BASF Research, GKT/U B1, D-67056 Ludwigshafen, Germany*

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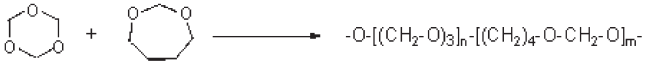
ABSTRACT: The bulk copolymerization of 1,3,5-trioxane (TOX) with 1,3-dioxepane (DXP) initiated by perchloric acid hydrate(s) is studied at 80 °C with DXP/TOX initial ratios from 20/80 to 3/97 w/w. As usually observed for the polyacetal synthesis, the polymerization takes place within seconds to tenths of seconds and proceeds in two steps, a homogeneous ("induction") period, followed by a very rapid heterogeneous propagation−crystallization step. The influence of the reaction conditions was systematically examined (diluent of initiator, comonomer concentration, transfer to residual water), and the products formed during the short induction period were identified using NMR. The difference between the respective basicities of the comonomers is such that during the induction period the initiation takes place on the DXP, and for DXP initial concentrations above its equilibrium value $[DXP]_{eq,ss}$ the early formed soluble polymer is either the homopolymer or a DXP highly enriched copolymer. The precipitation step starts only after the concentration of DXP is lowered enough to allow the copolymerization with TOX to proceed significantly and the poly(oxymethylene) $-[CH_2-O]_n-$ sequences to reach their critical crystallization length. This critical concentration was found constant whatever the initial DXP/TOX ratio. For initial concentrations lower than $[DXP]_{eq,ss}$ (i.e., DXP/TOX ≤ 5/95 w/w), the DXP cannot homopolymerize and should be consumed by single unit insertion during a copolymerization effective since the early beginning. Therefore, during the further heterogeneous propagation−crystallization step, the insertion of two successive DXP units in the copolymer chain becomes highly improbable. The copolymer formed by both propagation and transacetalization processes is either inserted into the crystal (or its immediate interface) if only isolated DXP units are present along the poly(oxymethylene) chain or rejected in the amorphous phase if preformed DXP sequences are present. The latter situation occurs for DXP/TOX initial ratios ≥ 10/90 w/w. This is in agreement with our previous measurements of the crystal partitioning coefficient, which confirmed that the tetramethyleneoxy $-[(CH_2)_4-O]-$ units from DXP are progressively rejected into the increasing amorphous fraction for initial DXP richer compositions. Coherent chemical pathways are proposed for the overall process, which are in accordance with the experimental behaviors during both homogeneous and heterogeneous steps.

1. Introduction

Except for the poly(oxymethylene) (POM) obtained by anionic homopolymerization of methanal, the usual process for the production of industrial polyacetals is essentially the cationic copolymerization of 1,3,5-trioxane (TOX) with a few percent of ethylene oxide or cyclic acetals (dioxolane, dioxepane, etc.) (Scheme 1).

Scheme 1. Copolymerization of 1,3,5-Trioxane with 1,3-Dioxepane



The random introduction of $-[(CH_2)_{n\geq 2}-O]-$ units limits the unzipping of the chain and improves thus the thermal stability of the $-(CH_2-O)_n-$ POM. The copolymerization of TOX as well its homopolymerization, conducted in the bulk molten monomer−comonomer mixture, present very specific features because propagation is essentially heterophasic at the interface between the liquid medium and the precipitated crystalline (co)polymer. The reaction starts by a so-called "induction" period during which the medium remains clear and the conversion very limited, followed by a rapid heterogeneous propagation−crystallization process going to complete conversion as soon as the $-(CH_2-O)_n-$ sequences are long enough to nucleate the crystallization. Since the pioneering work of Kern and Jaacks (induction period),[1] Wegner et al. (heterophasic propagation),[2] and Yenikolopyan et al. (thermodynamics),[3] a huge number of papers and patents have been devoted to the (co)polymerization of TOX considered either in the presence of a polar or nonpolar diluent or in bulk.

Several sound reviews[4a,4b,5] summarize all of these approaches, pointing out the numerous unclear aspects of this very complex (co)polymerization, especially the key role of the induction period in the understanding of the overall process and in the control of the stability of the final product.

The duration of the induction stage can be modulated depending on the conditions of the (co)polymerization (use of a solvent, nature of initiating system, nature of comonomer, monomer-to-comonomer ratio, residual water, reactant concentrations and purities, temperature, etc.). It is very short (a few seconds) in the

*To whom correspondence should be addressed. E-mail: jean-pierre.vairon@upmc.fr. Fax: +33144277089.

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case of the homopolymerization of TOX in bulk at the usual temperature (above T_m of monomer) and is much longer in the case of the copolymerization. Therefore, most of the previous basic studies on mechanisms or kinetics were conducted in solution at lower temperatures than in the melt and involved an initiation by BF_3 or its etherates leading to induction periods from minutes to hours, long enough to be experimentally followed by isolation of intermediates or in situ NMR. After an early controversy,[1,6−10] there is now a general agreement to consider that the reaction is initiated by the Brönsted acid resulting, in very low concentration, from the equilibrated reaction of BF_3/OR_2 with residual water (co-initiation) (Scheme 2).

In the case of homopolymerization initiated by BF_3 or its etherates, the protonated TOX unzips to methanal, which further reacts with it to give higher cyclooxanes until the building up of equilibrium (or steady state) concentrations of the intermediates and the formation of linear POM sequences. This might contribute to delay the precipitation step and lead to longer induction periods.[1a,5,8a] Propagation can proceed via oxonium and/or oxocarbenium ions, and these species are reasonably assumed to remain stable and active. The reported formation of methanal during the induction period, resulting from thermodynamic depolymerization of open chain active ends, indicates that oxocarbenium ions are in equilibrium with oxonium ions. This is also supported by the observation of methoxy and formate end groups resulting from hydride shift processes in transfer reactions to monomer or polymer, because oxonium ions do not abstract hydride anions.[1c,4a,4b,5,11−14]

Chain transfer to residual water can also take place and justifies the experimentally observed hydroxyl end groups, whereas transfer to polymer (transacetalization) can generate macrocycles when it occurs intrachain[12b] or lead to random redistribution of sequences (scrambling) when it occurs interchain,[15,16] the latter process becoming particularly critical for the thermal stability of the final product in the case of copolymerization.

When TOX is copolymerized, the much higher basicity (three to four orders of magnitude)[8a,8b] of the usual comonomers (ethylene oxide, 1,3-dioxolane, 1,3-dioxepane) should lead essentially to protonation of the comonomer and to subsequent initiation of a copolymerization consuming much more rapidly the comonomer until its concentration becomes low enough, allowing then a progressive incorporation of the TOX units and sequences.[16] Methanal, and then higher cyclics including those resulting from the comonomer, are still formed during an induction period, which is much longer for copolymerization owing to the favored initial formation of soluble copolymers. Most of the basic research work was performed in solution at rather low temperatures and with high comonomer concentration to extend the induction period or even to avoid the precipitation stage, which does not necessarily reflect the situation for industrial processes.

The copolymerization was extensively studied with ethylene oxide and dioxolane[4b,5] but paradoxically not much with dioxepane (DXP); furthermore, very few studies were devoted to initiation by strong protic acids. It was reported that even with acid concentrations 100−300 times lower than those when using BF_3-OR_2, the rates of polymerization were noticeably higher.[18] The observed induction periods are much shorter (a few tenths of seconds), indicating a higher initiation efficiency but making the experimental approach of the induction step much more difficult.

Unfortunately, the abundant literature on the (co)polymerization of TOX did not yet provide any coherent correlation between the reactions and observed phenomena in the homogeneous and heterogeneous stages, and a comprehensive vision of the overall process is still missing.

We report here on the bulk copolymerization of TOX with 1,3-dioxepane (DXP) in the melt at 80 °C, initiated by $HClO_4$ under conditions as close as possible to those of the industrial process, considering both the chemistry during the induction period and the relevant crystallization behavior in the second step. A general and consistent pathway is proposed for the overall polyacetal synthesis.

2. Experimental Section

2.1. Reactants. *2.1.1. Monomers. 2.1.1.1. 1,3,5-Trioxane.* Crystallized TOX was provided by BASF. It was obtained directly from the plant by crystallization from the melt under nitrogen. It was dehydrated by refluxing at 120 °C over sodium and under nitrogen for at least 24 h. It was then distilled through a condenser thermoregulated at 70 °C, and the main fraction was collected in the molten state in a double-jacketed graduated tube equipped with a Teflon stopcock, also maintained at 70 °C.

2.1.1.2. 1,3-Dioxepane. DXP was obtained from BASF. DXP was refluxed at 125 °C over sodium for 24 h under nitrogen. After refluxing, DXP was distilled under atmospheric pressure at 145 °C in a calibrated tube equipped with a stopcock and was stored under nitrogen in the dark.

2.1.2. Diluents

2.1.2.1. 2,5,8,11-Tetraoxadodecane (*Triglyme*). Triglyme (TRIG) (Clariant) was refluxed over sodium for 2 h under reduced pressure and distilled (85 °C/ 6 Torr).

2.1.2.2. 1,4-Dioxane. Dioxane (DOX, Aldrich) was refluxed over sodium for 2 h at 105 °C and then distilled under vacuum.

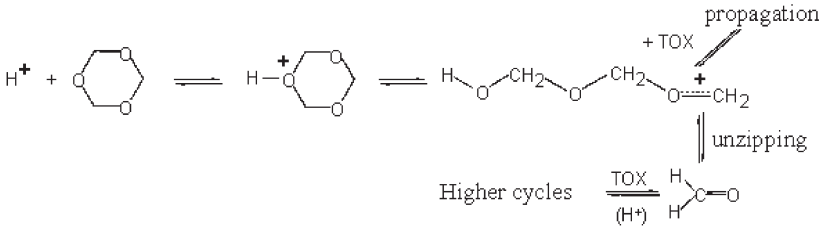
2.1.2.3. Toluene. Toluene (TOL, Aldrich) was refluxed over sodium for a few hours at 125 °C and then distilled.

For all diluents, the main fraction was collected under nitrogen in a calibrated tube equipped with two Teflon stopcocks, to be used when required.

2.2. Polymerization Techniques. *2.2.1. Preparation of Initiator Solution.* Initiator solutions were prepared by the addition of 95.69 mg of the perchloric acid hydrate (Aldrich; $HClO_4$ 70% w in water) in 1 L of dry diluent (TRIG, DOX, or TOL) in a glovebox under a dry nitrogen atmosphere.

2.2.2. Homopolymerization of Trioxane. Freshly distilled TOX (5 g) was introduced in a glass tube equipped with a small magnetic stirrer and previously heated in an oven at 80 °C for 2 h; it was then placed in an oil bath maintained at 80 °C. The initiator solution ($HClO_4$ hydrate in diluent) was added with a micropipet with tip (i.e., 100 μL; 2.0 ppm). The time between the introduction of the monomer in the dry glass tube and the introduction of the initiator solution was lower than 30 s. The end of the induction period was defined by the precipitation of the solid polymer.

Scheme 2. Polymerization of 1,3,5-Trioxane with a Protonic Initiator



2.2.3. Copolymerization with Dioxepane. Copolymerizations of TOX with DXP were performed at 80 °C as for the bulk TOX homopolymerization. Typically, for an 80/20 (w/w) copolymerization, dry DXP (1 g) was added to the molten TOX (4 g) in a glass tube. Then, 100 μL (2 ppm) of the initiator solution was introduced in the thermoregulated mixture. Depending on the TOX/DXP ratio, the induction period is defined either by the precipitation of the solid polymer ($[TOX]_o$ > 90% w) or by the appearance of turbidity in the very viscous medium ($[TOX]_o$ < 90% w).

2.2.4. Kinetic Experiments. Copolymerizations were deactivated at different time intervals during the induction period by the addition of 20 μL of pyridine in the clear medium. First, sample was collected after 3 s. An aliquot of this mixture was introduced in a NMR tube; then, deuterated acetone was added. Then, the DXP comonomer consumption was determined from the ^{1}H NMR spectrum. For SEC analysis, deactivated samples were directly dissolved in THF.

2.3. Polymer Characterization. *2.3.1. Nuclear Magnetic Resonance Measurements.* ^{1}H NMR spectra were acquired in deuterated acetone on a Bruker AC 200 or 300 MHz.

2.3.2. Size Exclusion Chromatography. Size exclusion chromatography (SEC) in tetrahydrofuran was used for TOX/DXP copolymers with DXP content >5%. A Waters instrument thermoregulated at 40 °C was equipped with two linear columns (3 PPS SDV 8 × 300 mm, 5 μm) and with two detectors [RI (LDC Analytical, refractor Monitor IV); UV operating at 254 nm (Waters 484)]. The sample concentrations were 5 mg/mL, and a 1 mL/min flow rate was used. For high percentages of TOX (97/3), SEC analysis was realized at 40 °C in hexafluoroisopropanol (HFIP) with 0.05% of CF_3COOK using two PL gel columns. The sample concentrations were 1.5 mg/mL, and the flow rate was 0.5 mL/min. Molar masses were calculated from a calibration curve based on PS standards in THF and on PMMA standards in HFIP.

3. Results and Discussion

3.1. Influence of the Reaction Conditions on the ≪Induction≫ Period in the Bulk TOX and TOX-DXP (Co)polymerizations initiated by $HClO_4$. *3.1.1. Influence of the Diluent of the Initiator in the Homopolymerization of TOX.* As described in the Experimental Section, we prepared the initiator solutions by dissolving the required amount of the hydrate(s) of perchloric acid [$H^+(H_2O)_{2.4}$, ClO_4^-] in diluents of variable polarity and basicity (or proton-binding capability):[8a,8b,19] TRIG ($\varepsilon_{25} \approx 7.5$; assumed to be more basic than glyme, $pK_b \leq 6$), DOX ($\varepsilon_{25} \approx 2.2$; $pK_b \approx 5.7$), TOL ($\varepsilon_{25} \approx 2.4$). Therefore, the type and concentration of species present in the initiator solution should strongly depend on the diluent used.

A series of bulk homopolymerizations of TOX, using the three different diluents for the initiator solution, were performed at 80 °C. The observed induction periods appear considerably shorter when DOX or TOL is used (Figure 1).

This can be explained by a concentration of the available initiating hydronium ions, which is lower when TRIG is used as the diluent of $HClO_4$ than when DOX or TOL are used, and thus by a slower initiation (Scheme 3). This agrees with the much higher proton-binding ability of TRIG with respect to DOX, even if their reported pK_b values are close.

The respective solvating powers of TRIG and DOX toward cations are illustrated by the early results M. Szwarc's group obtained with the lithium cation, which were recently rediscussed by J. Smid et al.[20] For the fluorenyl lithium in DOX at 25 °C, the observed fraction of solvent-separated ion pairs does not exceed 2%, but the addition of a small amount of TRIG ($\sim 10^{-2}$ mol L^{-1}) in DOX increases this fraction up to 50%. Similar solvation ability is expected

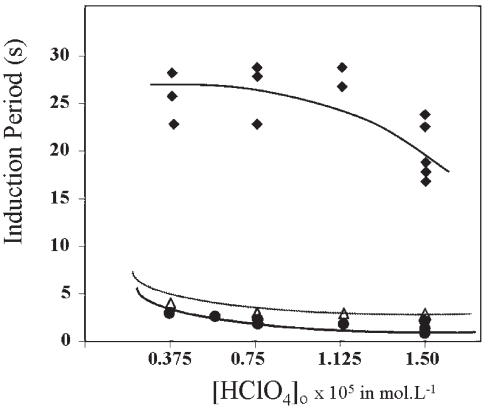


Figure 1. Bulk homopolymerization of 1,3,5-trioxane at 80 °C. Dependence of the induction period on diluent and concentration of the initiator: ◆, triglyme; △, toluene; ●, dioxane.

with respect to the proton, the TRIG replacing the water of the hydroxonium and shifting the equilibrium toward the solvated species.

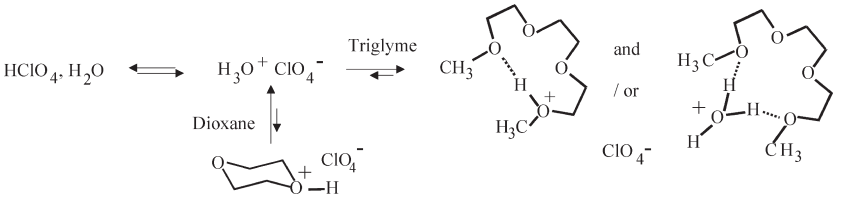
It was recently proposed that the protonation of diglyme and TRIG in water occurs at only one basic site, preferentially the terminal ether group, and that the equilibrium constant is much higher than for simple ethers.[21] Furthermore, it was also proposed that, at least in the gas phase, both the proton and the hydroxonium ion can be engaged in polydentate structures with the glymes.[22] This supports a much stronger complexation of the proton by the TRIG than by DOX. Similarly, the oxocarbenium ends should be much more strongly solvated by TRIG than by DOX, even in the presence of a very large excess of the less basic TOX monomer ($pK_b \approx 10$),[8a] leading to a significant difference in reactivities (Scheme 4), and this should affect the overall initiation and propagation rates.

When TRIG is used, the slowing down of the reactions involved during the induction period (protonation, formation of methanal and cycles, propagation, etc.) and the resulting significant increase in this clear period agree with a higher proportion of much less reactive (or inactive) solvated species. Nevertheless, even if the overall rate of propagation is decreased by the solvation, the rapid exchange between solvated and unsolvated species makes that the rate of growing of each individual chain should be the same, and the time for the POM sequences to reach their critical crystallization length should also be the same for all chains whatever their number. In other words, the duration of the induction period should be independent of the total concentration of propagating species but dependent on their average reactivity. Results in Figure 1 show that the induction period is not much dependent on the initiator concentration but highly sensitive to the nature of the solvating agent.

3.1.2. Effect of Comonomer Concentration in the TOX-DXP Copolymerization. Increasing the concentration of DXP comonomer in the molten TOX increases the induction period dramatically (Figure 2). The induction periods considered in Figure 2 correspond to the appearance of crystallization. Crystallization appears sharply for the lowest DXP concentrations (TOX/DXP ratios from 97/3 to 90/10 w/w). For the 80/20 ratio, the reaction medium becomes turbid and very viscous ("gel") after 20−30 s, much before the precipitation starts. For lower ratios, the medium remains clear and homogeneous until full conversion.

The DXP ($pK_b \approx 6.13$)[8b] is four orders of magnitude more basic than the TOX and therefore should be protonated first. As far as its concentration is high enough, it starts to

Scheme 3. Perchloric Acid Complexation using Dioxane or Triglyme as Diluent for the Initiator Solution



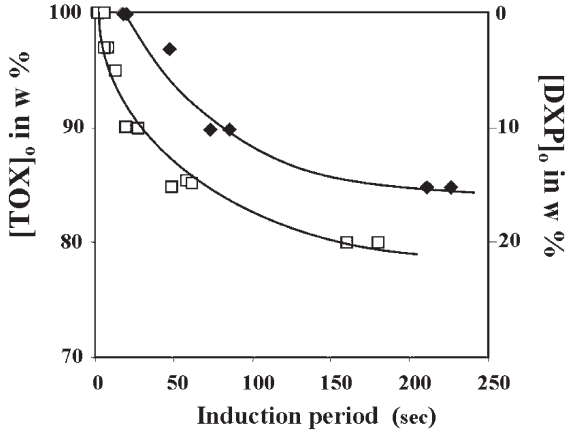
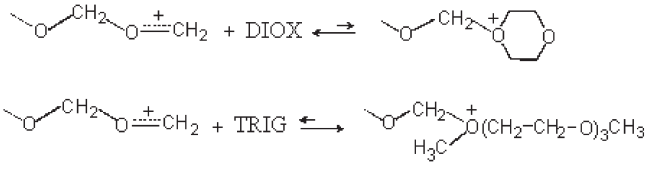


Figure 2. Copolymerization of 1,3,5-trioxane with 1,3-dioxepane in bulk at 80 °C. Variation of the induction period depending on the initial DXP content, using triglyme (◆) and dioxane (□) as diluents for the initiator solution.

Scheme 4. Complexation of the Oxocarbenium Ends by Dioxane and Triglyme



homopolymerize essentially, and the significant insertion of trioxymethylene units from TOX is delayed. Therefore, the time to reach the crystallization of the oxymethylene sequences is longer. This agrees with previous observations reported in the literature, but it must be noticed that the corresponding studies involved rather high comonomer concentrations and were generally performed in solution with added solvents.[1c,17] As expected, the induction period for the copolymerization is longer when TRIG is used as diluent of the initiator, indicating a similar complexation behavior for TOX-DXP copolymerization and TOX homopolymerization.

3.1.3. Effect of Residual Water on Both Induction and Precipitation Periods. Transfer to water retards the polymerization, decreases the average molecular weights, and delays the crystallization step.[23,24] The overall water content in the polymerization medium is the sum of the water inherent to the initiator (hydrate(s) of perchloric acid) and of the adventitious water from the other reactants (TRIG, DOX, monomers), but, owing to their thorough dehydration, the latter concentration can be neglected with respect to the former one. Series of bulk homopolymerizations of TOX were performed in the presence of a controlled amount of added water using TRIG and DOX solutions of the initiator (Table 1).

Table 1. Homopolymerization of Trioxane at 80 °C in Bulk[a]

initiator diluent	$[H_2O]/[H^+]^b$	induction period (s)
triglyme	2.34[c]	26
	3.01	128
	5.30	180
	5.58	277
dioxane	2.34[c]	1
	63.6	2
	186.4	4

[a] Dependence of the induction period on the amount of water present in the medium, using triglyme and dioxane initiator solution. [b] $[H^+]_o = 1.5 \times 10^{-5}$ mol L^{-1} [c] H_2O from ($HClO_4$, 2.4H_2O).

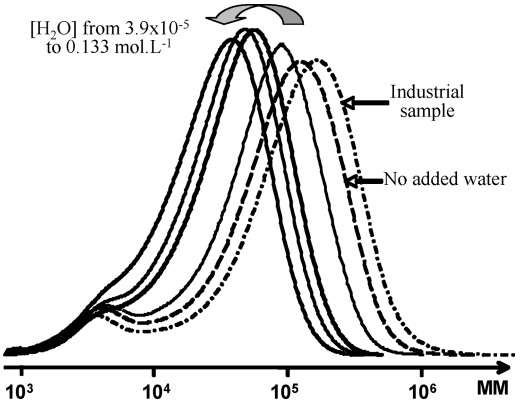


Figure 3. SEC Chromatograms of TOX/DXP copolymers (97/3, w/w) obtained in bulk at 80 °C. Variation of molar masses depending on the initial water concentration (PMMA standards).

A dramatic effect of water on the induction period is observed when TRIG is used. This can be explained by the transfer to water of unsolvated active centers in very low concentration. This reversible transfer not only decreases the MWs but significantly contributes to lower the instantaneous active center concentration by shifting the equilibrium toward hydroxyl end groups, slowing down the propagation and delaying the crystallization. When the poorly solvating DOX is used for the initiator solution, the effect is much less sensitive, even for high amounts of added water. Again, these observations agree with a predominant participation of oxocarbenium ends rather than of unsolvated oxonium ends in the propagation process.

Bulk copolymerizations with a low concentration of DXP ($[DXP]_o = 0.33$ mol L^{-1}, TOX-DXP 97/3 w/w) were also performed in the presence of added water using both DOX and TRIG initiator solutions. The effect of water is similar to that observed for the homopolymerization of TOX, again much more pronounced when TRIG is used. The reversible transfer to water occurs during both the homogeneous and the heterogeneous steps, and the molecular weights of the final copolymers decrease rapidly with the amount of water initially present in the medium (Figure 3).

We took the MW of the copolymer obtained without added water as a reference. A small low side peak

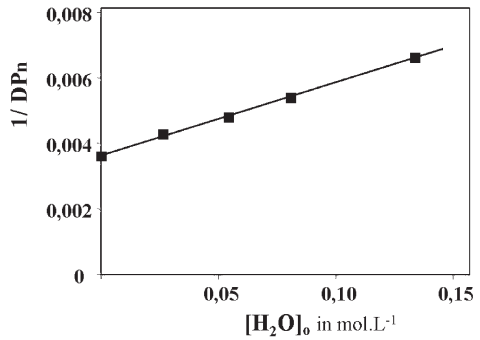


Figure 4. Copolymerization of trioxane with dioxepane (97/3, w/w) at 80 °C in bulk. Variation of the degree of polymerization (DP_n) depending on the initial concentration of water.

(MW ≈ 2000−3000) appears invariable in all samples, including the industrial one. It could result from soluble DXP-enriched oligomers or from macrocycles formed from TOX during both steps. An SEC analysis performed on a homopolymer of TOX prepared under the same conditions does not exhibit this low-MW peak, leading to the conclusion that it should correspond to a remaining soluble DXP-enriched copolymer, linear or macrocyclic, which was not significantly engaged in the transacetalization processes in both stages of the polymerization. This might indicate that the transacetalization predominantly takes place on the POM sequences issued from TOX units rather than on tetramethyleneoxy sequences issued from DXP, even if it can also occur on these latter sequences. (See Figure 6.)

Because the MWs were measured on the final copolymer containing 97% TOX, we used the simple Mayo equation to reach the transfer constant to H_2O

$$\frac{1}{DP_n} = \frac{C_{trH_2O}}{[TOX]_o} \cdot [H_2O] + C_{trM} + C_{trP} + \frac{1}{DP_{th}}$$

considering a rapid and complete initiation leading to stable active ends, a complete conversion of TOX, and assuming a complete consumption of water. A linear plot of $1/DP_n$ versus $[H_2O]$ is obtained (Figure 4). Considering that the term $1/DP_{th}$ is negligible, this leads to $C_{trH_2O} \approx 0.27$ and $\Sigma C_{trM,P} \approx 3.6 \times 10^{-3}$.

These values are obviously rough approximations because (i) the DXP content (3%) was neglected in the calculation of DP_n and (ii) the M_n of the final copolymer includes the small low MW side peak. Nevertheless it must be noticed that the transfer constant to water appears to be about 70 times more important than the sum of transfer constants to monomer and polymer. This transfer constant to water at 80 °C is one order of magnitude lower than the surprisingly high value ($k_{trH_2O} > k_p$) reported by Baader et al. in the case of the homopolymerization of TOX in CH_2Cl_2 solution at 25 °C,[23] but a direct comparison is not valid because our experiments were performed in bulk and essentially involved transfer processes at the liquid−solid interface during the precipitation step.

As previously reported in the literature, an utmost dehydration of the reagents is a necessary condition to obtain high molecular weights, even if in the case of initiation by $HClO_4$ the water from the acid hydrate(s) cannot be avoided.

3.1.4. Soluble (Co)polymers Formed during the Induction Period: A Kinetic Approach. A series of bulk copolymerizations were performed at 80 °C using initial TOX/DXP ratios increasing from 80/20 to 97/3 w/w (Table 2). For these experiments, DOX was used as the diluent of initiator, and

Table 2. DXP Concentration at the End of the Induction Period Depending on the Initial TOX/DXP Ratio using Dioxane Initiator Solution[a]

TOX/DXP w/w	$[DXP]_o$ mol L^{-1}	DXP conversion during the induction period (%)	[DXP] at the end of the induction period (mol L^{-1})
80/20	2.20	80	0.44 ± 0.05[b]
90/10	1.12	35	0.72 ± 0.1[c]
95/5	0.57	18	0.48 ± 0.05[c]
97/3	0.33	10[d]	

[a] $[H^+]_o = 1.5 \times 10^{-5}$ mol L^{-1}. [b] Just before turbid gel. [c] Just before crystallization. [d] Extrapolated from Figure 8.

under these conditions, the homogeneous period is short (from ~3 to 30 s). The formation of soluble copolymers was followed all along the homogeneous period, that is, until the occurrence of crystallization. In the case of the 80/20 ratio, the end of the clear period was considered at the occurrence of the turbid gel.

For each experiment, the reaction was stopped at different times, and the corresponding media were directly analyzed by ^1H NMR spectroscopy (Figure 5). We confirmed the pentad assignments reported by Cui et al. from in situ ^1H and ^{13}C NMR studies devoted to a TOX-DXP copolymer prepared under concentration conditions for which the medium remains homogeneous (TOX/DXP ≈ 73/27 w/w).[25a,25b]

The different (co)polymers were identified via their pentad sequences, defined using Cui's notation, where M is the $-[CH_2-O]-$ unit and B is the $-[(CH_2)_4-O]-$ unit. Therefore, a TOX molecule generates a $-[(CH_2-O)_3]-$ sequence noted MMM, and a DXP molecule generates a $-[CH_2-O-(CH_2)_4-O]-$ sequence noted MB. The homopolymer of DXP (or DXP highly enriched copolymer) is quantified through its MB<u>M</u>BM pentad, whereas the TOX-DXP copolymer is quantified via the other <u>M</u>-centered pentads (Figure 5).

The time evolutions of the soluble (co)polymers formed are shown in Figure 6 for the 80/20 and 90/10 w/w TOX/DXP ratios. It clearly appears that for the 80/20 ratio, the DXP comonomer is rapidly consumed, producing essentially its homopolymer (or highly enriched copolymer) during the first half of the induction period. Then, when the concentration of DXP is significantly lowered, the soluble copolymer appears, and the concentration of the DXP homopolymer starts to decrease. This decrease can result both from the transacetalization processes with the copolymer and from the re-equilibration of the homopropagation of DXP (shift from a possible initial kinetic control to a thermodynamic one). This initial formation of the DXP homopolymer and its further decrease have also been observed and reported by Cui et al. for the 73/27 w/w TOX/DXP ratio. This is confirmed by the evolution with time of the MW of the soluble macromolecules formed in the case of the TOX/DXP 80/20 experiment (Figure 7).

In the SEC chromatograms, the M_{peak} increases during the first half of the induction period; then, it levels off. This is in agreement with an initial rapid formation of homopoly(dioxepane) (or DXP highly enriched copolymer), followed by simultaneous depolymerization and transacetalization, whereas TOX units are more and more incorporated. A few oligomers are observed in the 300−3000 MW range, and they could also contribute to the side peak observed in the final copolymer (Figure 3), but it should be noticed that no characteristic ^1H NMR resonance of methanal was observed, leading to discard the formation of higher cyclooxanes from TOX all along the induction period. This agrees

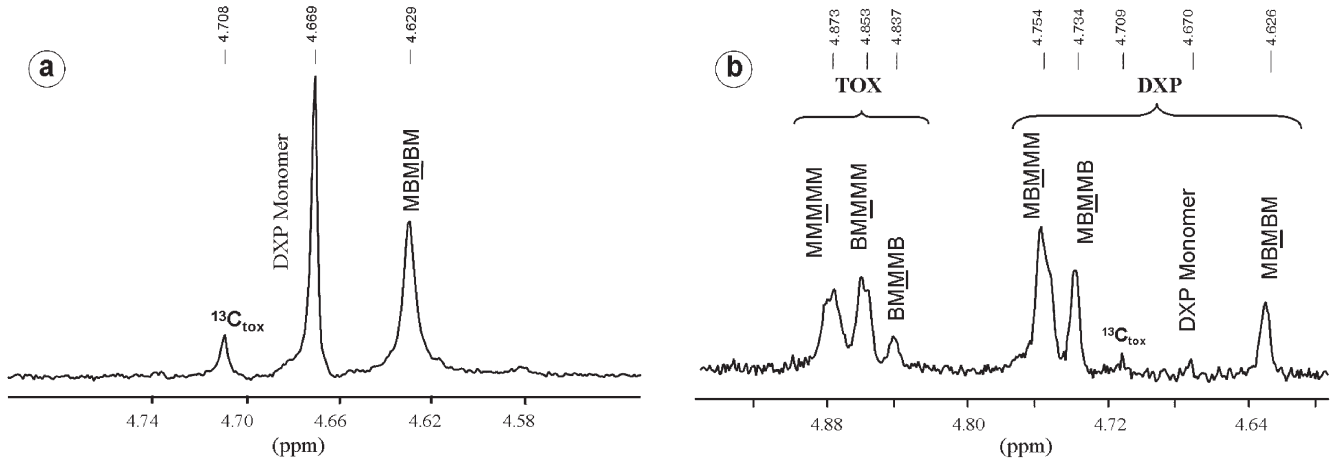


Figure 5. ^{1}H NMR spectra of TOX/DXP copolymers (80/20 w/w, bulk, 80 °C) in acetone-d_6 (a) after 3 s and (b) after 25 s just before the end of the induction period.

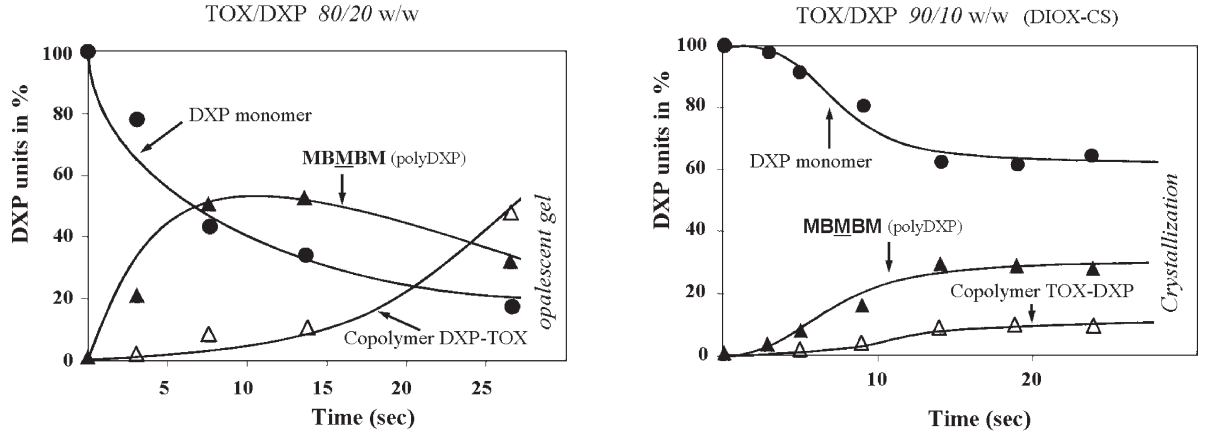


Figure 6. Copolymerization of trioxane with dioxepane at 80 °C in bulk. Consumption of the DXP monomer (●) and variation of the DXP unit content in the poly(DXP) (▲) and in the DXP/TOX copolymer (△) during the induction period for different TOX/DXP ratios. (a) DXP/TOX 20/80 w/w; (b) DXP/TOX 10/90 w/w.

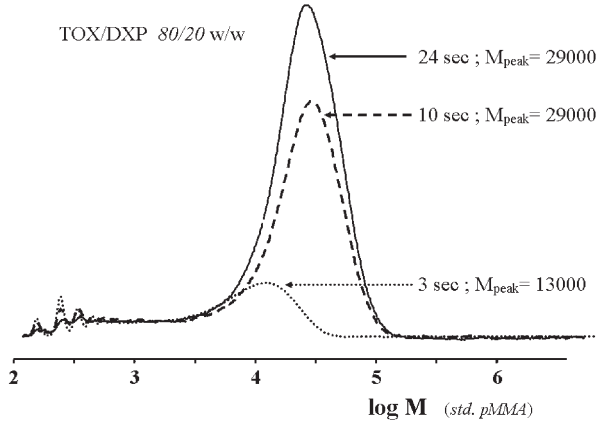


Figure 7. TOX/DXP copolymerization (80/20 w/w). SEC chromatograms of polymers obtained in bulk at 80 °C. Variation of (co)polymer molar masses with time during the induction period.

with a largely predominant protonation of DXP with respect to TOX in the initiation process.

For the lower initial concentrations of DXP, the conversion during the induction period is drastically slowed down and leveled off, as shown for the 90/10 comonomer ratio in Figure 6 and Table 2.

For the 95/5 and 97/3 ratios, the induction periods were too short, and the (co)polymers formed in too low concentration to be accurately identified and followed with time. Nevertheless, the concentration of remaining DXP at the end of the induction period could be estimated by NMR from the last samples removed for each experiment (Table 2 and Figure 8).

The values are only approximate because of the difficulty of sampling immediately before precipitation, but, interestingly, the remaining DXP concentration at the end of the induction period appears to be roughly constant (~0.5 to 0.7 mol L^{-1}). This [DXP] concentration is the critical one below which the TOX sequences of the copolymer are long enough to crystallize spontaneously in bulk at 80 °C.

Because long sequences of DXP units can be formed depending on the initial DXP/TOX ratio, the thermodynamic aspects of the DXP polymerization must also be considered. Its homopolymerization is an equilibrium reaction and the $[DXP]_{eq,ss}$ calculated from the two sets of thermodynamic parameters (ΔH_{ss}, ΔS_{ss}) available in the literature varies at 80 °C from 1.12 mol L^{-1} in benzene solution to 1.92 mol L^{-1} in methylene dichloride solution.[26,27] In the present case of the TOX-DXP copolymerization, the TOX plays the role of the solvent for the homopolymerization of DXP in the early stage of the induction period. A direct comparison with the literature values would not be

reliable because the DXP equilibrium concentration should be dependent on DXP-TOX, poly(DXP-TOX), and poly(DXP-DXP) interactions, presently not quantified. Nevertheless, the NMR analysis shows that some homopolymer of DXP (or highly enriched copolymer) is still formed during the induction period for the 90/10 ratio ($[DXP]_o = 1.12$ mol L^{-1}), whereas it is hardly detectable for the 95/5 ratio ($[DXP]_o = 0.57$ mol L^{-1}). Therefore, under our conditions, the equilibrium value $[DXP]_{eq,ss}$ could be reasonably assumed to be in the range of 0.6 to 1 mol L^{-1}. Obviously, in the second part of the induction period, when the TOX units start to be significantly incorporated, the concept of equilibrium concentration valid for the homopolymerization of DXP does not apply anymore.[28] Anyway, for TOX/DXP $\approx$ 97/3 w/w, $[DXP]_o \approx 0.3$ mol L^{-1}, in which the initial comonomer concentration is noticeably lower than $[DXP]_{eq,ss}$, it can be considered that the long sequences of DXP units cannot form and the soluble macromolecules observed during the induction period should essentially be the copolymer with isolated butylene oxide $-[CH_2-O-(CH_2)_4-O]-$ units distributed statistically along the $-(CH_2-O)_n-$ POM chain. This fits well with the experimental observations for the 95/5 and 97/3 initial ratios, that is, first a very short induction period as the TOX is consumed since the early beginning and its sequences reach rapidly their critical length, and second a very low DXP consumption during this induction period.

The fact that the equilibrium concentration $[DXP]_{eq,ss}$ lies in the same range as the critical DXP concentration allowing spontaneous crystallization of TOX sequences is purely fortuitous.

3.2. Chemical Processes during the Precipitation-Crystallization Period. We have shown above that the composition of the polymerization medium at the transition between the homogeneous and heterogeneous stages differs noticeably depending on the initial conditions.

When its initial concentration is higher than its equilibrium concentration, $[DXP]_{eq,ss}$, the DXP homopolymerizes first and then copolymerizes with TOX. Because the active species resulting from DXP and TOX are stable, the growing chain ends of the soluble DXP homopolymer (or highly DXP-enriched copolymer) add more and more TOX units, which, together with simultaneous transacetalization processes, should lead to the progressive formation of copolymer chains comprising both sequences of TOX units and sequences of DXP units (case a, Figure 9). Therefore, a large part of the DXP comonomer can be consumed during the induction period (> 80% in the case of TOX/DXP 80/20).

When the DXP initial concentration is lower than its equilibrium concentration, the comonomer should be inserted as isolated units (case b, Figure 9), at least predominantly, because it has been shown that even for some thermodynamically nonpolymerizable monomers very short oligomers can be formed.[31] In this situation, the comonomer consumption is drastically slowed down, and most of the initial DXP remains in the medium when precipitation starts. Nevertheless, the remaining DXP concentration at the beginning of the precipitation stage is low, roughly constant (0.5 to 0.7 mol L^{-1}) whatever the initial TOX/DXP ratio, and close to or lower than the equilibrium value, $[DXP]_{eq,ss}$. Therefore, when the second step starts, the only differences in the medium for the various initial DXP/TOX ratios are the composition of the soluble copolymer present and the

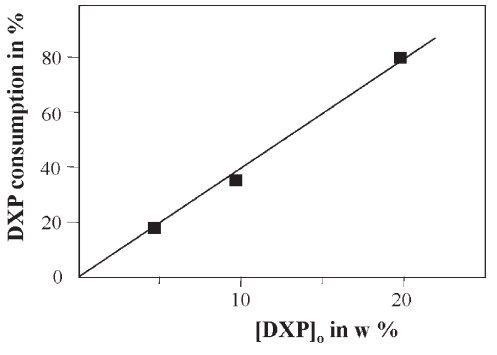


Figure 8. TOX/DXP copolymerization in bulk at 80 °C. Conversion of DXP monomer during the induction period depending on initial DXP concentration (weight %) in the feed.

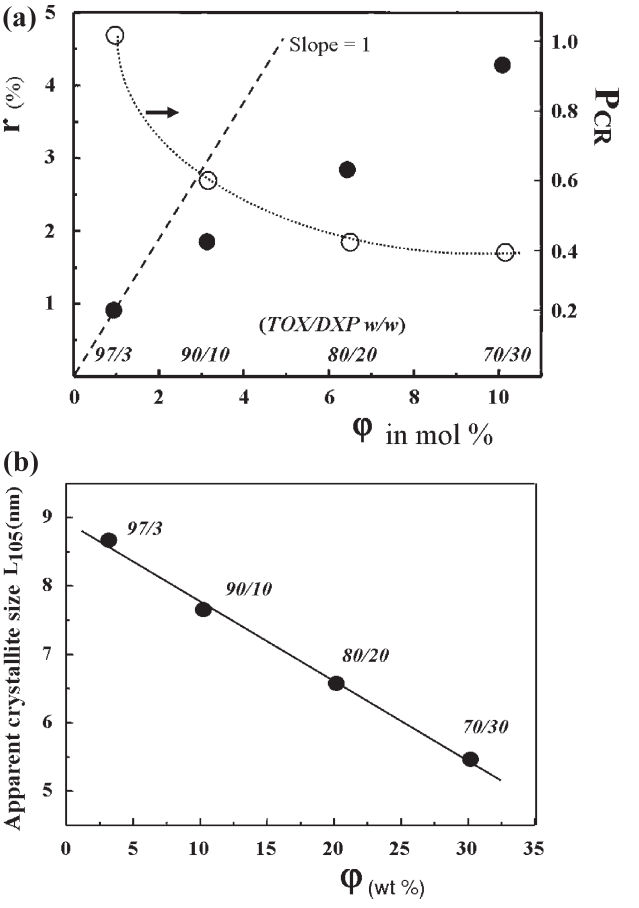
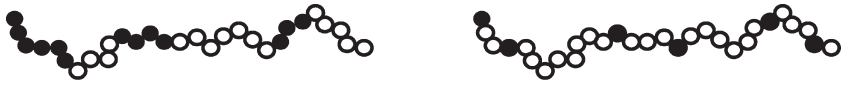


Figure 10. (a) Variation of the concentration, r, of tetramethylene oxide units (B) in the interfacial and crystalline regions and the partitioning coefficient, P_{CR}, of the B units with the global molar fraction φ of B units in the TOX/DXP copolymers (from ref 29). (b) Influence of DXP content on the apparent crystallite size, L_{105}, estimated from WAXS measurements (from ref 29).



a) b)

Figure 9. Distribution of DXP units (●) in the TOX/DXP copolymer: (a) copolymer with sequences of DXP units; (b) copolymer with isolated DXP units.

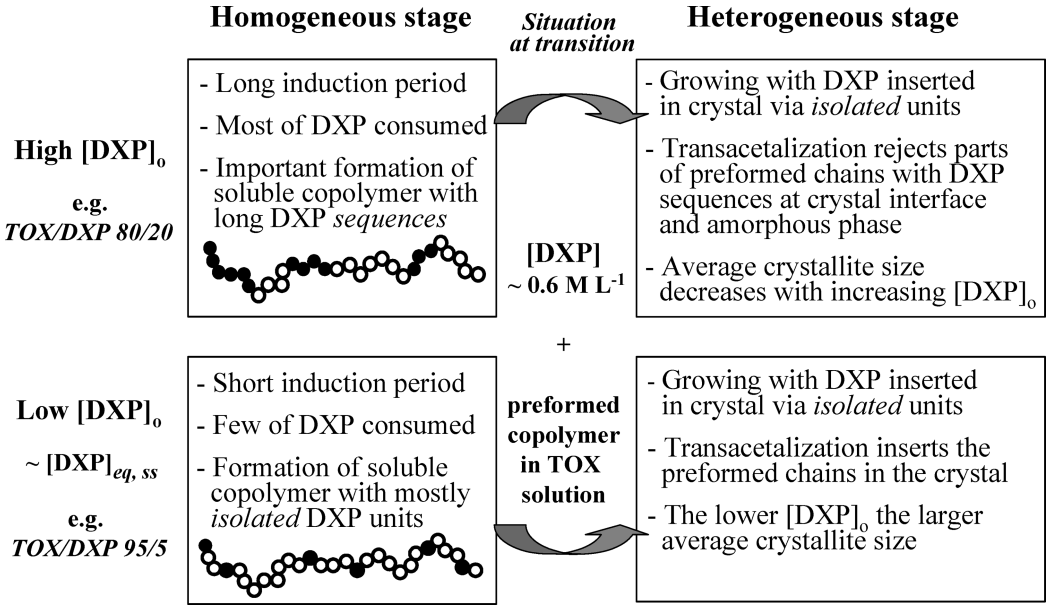


Figure 11. Simplified overview of the TOX-DXP copolymerization process in bulk.

amount of this copolymer, which can already include the largest part of the DXP if the initial concentration of the comonomer in the feed is high enough. Therefore, whatever the initial DXP content, the very rapid heterogeneous formation of the polyacetal in the second step should simultaneously involve: (i) the growth of copolymer chains initiated by the active centers located at the interface (faces, sides, defects) of the crystal, followed either by insertion of the copolymer sequences in the crystal or by rejection into the amorphous phase; (ii) the formation of short TOX-DXP copolymers, soluble in the molten TOX, essentially with isolated DXP unit insertion; (iii) the transfer processes of the active centers immobilized at the crystalline interface to all types of still soluble copolymers, which contain isolated units or sequences of DXP, again followed by either insertion in the crystal or rejection into the amorphous phase; and (iv) the transfer processes of the active ends of growing soluble copolymer chains to the POM units accessible at the surface of the crystal.

These considerations are valid only if the DXP units can be accommodated in the POM crystal. This raises the question of the location of the DXP units in the final solid copolymer.

To figure out the chemical processes during the crystallization−polymerization stage, we carried out and recently published[29] a morphological study (solid-state NMR, WAXS, DSC) of the final solid copolymer obtained under our copolymerization conditions for the different TOX/DXP initial ratios considered above. It has been shown that in these semicrystalline TOX-DXP copolymers, a part of the DXP units, involved in isolated MMMBM and MBMMM pentads, is located in the crystalline phase and in the crystalline/amorphous interfacial regions. The sequences composed of more than one DXP unit should be rejected into the amorphous phase. The fraction, r, of B units over the total number of B and M units in the crystalline phase, including the noncrystalline/crystalline interfaces, was estimated as well as the corresponding partitioning coefficient, $P_{CI/CR}$. This latter corresponds to the ratio of r over the fraction φ of B units in the copolymer and thus indicates the propensity for the DXP comonomer to be inserted in the crystallites and in the interfacial zones. The variations of r and $P_{CR/CI}$ with the global molar fraction φ of B units in the copolymers are recalled in Figure 10a. For the lowest TOX/DXP ratio (97/3) and within the limits of experimental error, $P_{CR/CI}=1$. This means that the concentration of B units is the same in both amorphous and crystalline phases, that is, 3% w/w, but the distribution of these B units along the POM chain should be quite different for the macromolecules of the two phases. As the initial concentration of DXP is increased in the feed, the partitioning coefficient $P_{CR/CI}$ decreases down to a plateau value, indicating that the relative amount of B units inserted in the crystalline (and interfacial) regions gets lower and lower. A decrease in the average crystallite size (Figure 10b) occurs simultaneously with this progressive rejection of DXP into the amorphous phase. If an active center located on the crystal adds several successive units of DXP, then the sequence cannot enter the crystal, and the active chain grows outside until either the formation of a TOX sequence is long enough to allow a further crystalline accommodation or the occurrence of a transfer event.

Therefore, these results are in general agreement with the conclusions of the chemical approach of the induction period we developed in the previous section.

Nevertheless, it still remains to explain the occurrence of the low-MW small side peak observed on the SEC chromatograms of the final copolymers TOX/DXP 97/3 w/w. (See Figure 3.) This peak seems to be independent, both in intensity and MW, from the transfer to water, and, as discussed above, should correspond to oligomers and/or macrocycles rich in DXP. They are most probably formed during the precipitation step and, owing to their composition, should remain in the amorphous phase. An SEC separation of the macromolecules corresponding to the small side peak is necessary for a further identification.

4. Conclusions

This work reports the bulk copolymerization at 80 °C of TOX with DXP initiated by hydrate(s) of perchloric acid. The chemical processes involved in both homogeneous ("induction") and heterogeneous propagation−crystallization stages were considered, and a consistent description of the global polyacetal process is proposed (Figure 11).

The duration of the clear (or induction) period as well as the products formed during that step vary sharply with the reaction conditions (initiator solution, residual water, comonomer ratio), and their dependences were analyzed. It is shown that depending on its proton solvation ability, the diluent of the perchloric acid plays a key role in the active center concentration, the rate of propagation, and the duration of the clear period. The molar masses of the copolymer are very sensitive to trace amount of water, and the corresponding chain transfer constant was evaluated ($C_{tr,H_2O} \approx 0.27$), showing that transfer processes to water are even more important than transfer processes to monomer and polymer.

For initial concentrations of DXP higher than its estimated equilibrium concentration, $[DXP]_{eq,ss}$, in homopolymerization, that is, >0.6 to 1 mol L^{-1} (roughly $>5\%$ w), the DXP essentially homopolymerizes first, then progressively inserts TOX units until a low enough DXP concentration is reached to allow the formation of crystallizable POM sequences. Therefore, the DXP consumption during the induction period varies considerably depending on its initial concentration (from ~80% for $[DXP]_o = 2.20$ mol L^{-1} w to 15% for $[DXP]_o = 0.57$ mol L^{-1} w). Whatever the initial concentration of DXP, its consumption lasts until an invariable critical concentration $[DXP]_{crit}$ is reached and the precipitation stage starts. Fortuitously, this value also lies around 0.6 mol L^{-1}, but it is not a thermodynamic parameter and is not related to the equilibrium concentration.

For initial concentrations of DXP ($<5\%$ w) lower than its equilibrium concentration, the DXP cannot homopolymerize and is essentially inserted as isolated units. A copolymer with TOX sequences is formed since the early beginning of the reaction. The duration of the induction period is shortened accordingly, and the consumption of DXP in that clear stage remains limited.

The composition of the reacting medium when the crystallization step starts varies with the initial conditions. Whatever the initial concentration of DXP above 0.57 mol L^{-1} w, the comonomer concentration present in the reacting medium at the beginning of the crystallization stage is low (~0.6 mol L^{-1}) and the more or less abundant DXP enriched copolymer formed during the induction period remains soluble in the molten TOX. The propagation proceeds at the POM crystal interface (essentially) and in solution, but in both cases, the DXP is inserted along the chain as isolated units for thermodynamic and morphological reasons because the POM crystal accommodates exclusively the TOX sequences with isolated DXP units. The previously formed DXP-rich copolymer chains can participate in the transacetalization processes, but most of them should be rejected in the final amorphous phase, lowering the crystallinity and the thermal stability of the resulting solid polyacetal. When the initial concentration of DXP lies below 0.6 mol L^{-1}, that is, for DXP/TOX ratios lower than 5/95 w/w, most of this comonomer is still present in the reacting medium when the precipitation starts, together with some previously formed copolymer bearing isolated DXP units. In that case, during the second step, most of polyacetal chains contain isolated DXP units and thus can be accommodated in the crystalline phase. This corresponds to the most random distribution of the DXP along the POM chain, to the lowest amount of amorphous copolymer, and thus to the highest crystallinity and stability of the final polyacetal, as compared with samples with higher DXP content.

In principle, such a scheme should apply to the other usual polyacetal processes, that is, involving dioxolane and even ethylene oxide, because this latter comonomer with high thermodynamic polymerizability due to ring strain is known to be in situ transformed in dioxolane and higher cyclic acetals.[5,12b,17,30]

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