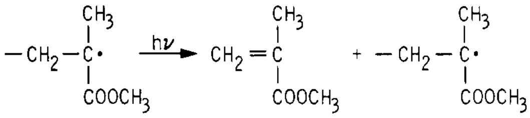
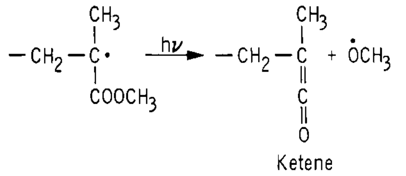
photochemical processes may be postulated as in eq 5 and 6. Intriguing support for process represented by eq 5



$$-CH_2-\overset{CH_3}{\underset{COOCH_3}{C}}\cdot \xrightarrow{h\nu} CH_2=\overset{CH_3}{\underset{COOCH_3}{C}} + -CH_2-\overset{CH_3}{\underset{COOCH_3}{C}}\cdot \qquad (5)$$



$$-CH_2-\overset{CH_3}{\underset{COOCH_3}{C}}\cdot \xrightarrow{h\nu} -CH_2-\overset{CH_3}{C}=C=O + \dot{O}CH_3 \qquad (6)$$

comes from a comparison of Fox's[2] data with ours. This is given in Table III. The quantum yields of chain scission are comparable, but the quantum yield of monomer formation is only about 0.01 in our study, while Fox et al. found this quantity to be 0.20. In other words, while we find approximately 0.2 unzipping steps per chain radical (i.e., approximately 80% of the chain radicals decay without forming any monomer), Fox found that there were approximately five unzipping processes per chain radical created by chain scission. It is noteworthy that a relatively broad-band source was used by Fox et al. which could induce considerable long-wavelength (250–250 nm) absorption by the propagating radical and induce unzipping via eq 5. Rates of some of these proposed abstraction processes (eq 2) may be significantly affected by the tacticity of the polymer chain. There is evidence that rates of degradation induced by exposure to an electron beam[19] and ultraviolet radiation[20] is significantly affected by the isomeric form in poly(methyl methacrylate). Henry and Gardener[20] observed that the rates of photodegradation of the isotactic and syndiotactic forms are significantly different. Their results also indicated that the number of bond breaks per gram of mixture of isomers was considerably less than what would be expected if each isomeric form was degrading independently. Our current work on this system involves an attempt to establish an unequivocal assignment of the lowest excited state of poly(methyl methacrylate) and study of the wavelength dependence of the quantum yields of various primary processes.

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Polymerization of Trioxane Initiated by Isomeric 2,4,5-Trisubstituted 1,3-Dioxolan-2-ylium Salts

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ABSTRACT: Polymerization of trioxane initiated by isomeric 2,4,5-trisubstituted 1,3-dioxolan-2-ylium hexafluoroarsenates was studied. The initiation was found to proceed by cationation. The influence of initiator nature on the rate of polymerization is discussed.

The polymerization rate of some unsaturated derivatives of 2,4,5-trisubstituted 1,3-dioxolane (1) was found to depend on the type and configuration of the substituents.[1] However, saturated analogues of 1 do not polymerize at all, although they react with triphenylmethylium salts, e.g., Ph_3CSbCl_6, to yield stable products.[2] We stated previously[3] that these products, i.e., the isomeric 2,4,5-trisubstituted 1,3-dioxolan-2-ylium hexachloroantimonates, exhibited a catalytic activity toward the trioxane monomer, whereby the course of polymerization depended distinctly on the structure of the trisubstituted 1,3-dioxolan-2-ylium cation.

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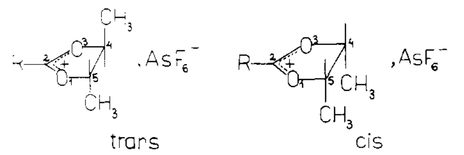
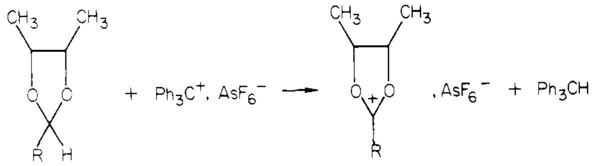


Figure 1. 2,4,5-Trisubstituted 1,3-dioxolan-2-ylium salt stereoisomers.

Elucidation of the nature of this effect was the main aim of the present work. The proper solution of this problem was possible only by the elimination of the influence of the anion, since $SbCl_5$ resulting from $SbCl_6^-$ decomposition is known to be a very active initiator for trioxane.[4] The use of the analogous hexafluoroarsenates was thus considered to be promising in view of the higher stability of that anion.[5]

Experimental Section

(A) Preparation of Initiators. The following salts were synthesized by the method described previously:[2]



1

2a, R = $(CH_3)_2CH$
b, R = C_6H_5
c, R = $C_6H_5CH{=}CH$

In each case the cis and trans isomers were synthesized separately (Figure 1).

The analogous hexachloroantimonate salts (3) were obtained[2] by starting from Ph_3CSbCl_6.

The tritylium salts used [Ph_3CSbCl_6 (Fluka AG, Buchs SG) and Ph_3CAsF_6 (Merck)] were purified by recrystallization; $SbCl_5$ (POCh) was distilled.

(B) Polymerization. After being purified with KOH and Na, the trioxane was polymerized in ampules at room temperature in CH_2Cl_2 solution; the monomer and initiator concentrations were kept at $M_0 = 4$ and $I_0 = 10^{-2}$ mol/L, respectively.

The reaction was quenched by the addition of Et_3N, and polymer was filtered off, washed with CH_2Cl_2, and dried under vacuum. The degree of conversion was determined gravimetrically.

(C) Spectroscopic Measurements. ^1H NMR spectra were run on a JNM-C-60H (JEOL) apparatus (CH_2Cl_2, Me_4Si). IR spectra were recorded on a UR-20 (Zeiss Jena) spectrophotometer, using samples in KBr.

(D) Controlled Thermodegradation. Degradation of samples was performed at 140° C in the presence of catalytic amounts of triethylamine.

Results

(1) Conversion-Time Curves. Unfortunately, no literature data concerning the trioxane polymerization by dioxolenium salts were available. The conversion-time curves were obtained for our experimental conditions by using well-known tritylium initiators besides *cis*-**2a** and *cis*-**3a** (Figure 2). According to reported data,[4] a triphenylmethylium salt with a stable hexafluoroarsenate anion (initiating by slow hydride transfer only) shows a long induction period and is thus less active than the analogous hexachloroantimonate. The latter generates $SbCl_5$ which is extremely active with respect to trioxane. However, such behavior was not observed in the case of 1,3-dioxolan-2-ylium salts. The dioxolenium initiator, e.g., *cis*-**2a**, becomes less active when the counterion is changed from AsF_6^- to $SbCl_6^-$. The same is true for other 1,3-dioxolan-2-ylium cations. Considering the quite different anion effect found for dioxolenium initiators when compared with tritylium initiators, the former may be supposed to act via a different initiation mechanism.

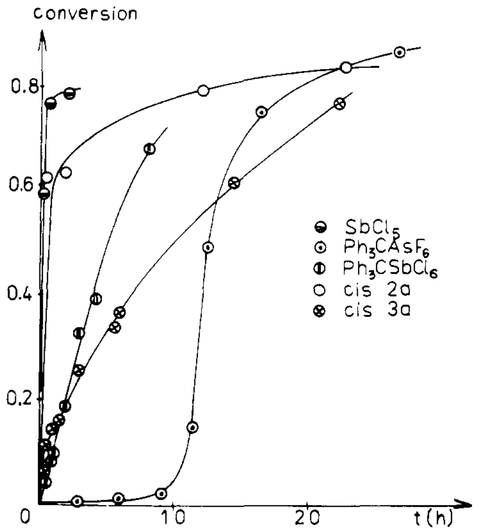


Figure 2. Conversion-time curves for trioxane polymerization initiated by *cis*-**2a**, *cis*-**3a**, tritylium hexafluoroarsenate and hexachloroantimonate, and additionally by $SbCl_5$.

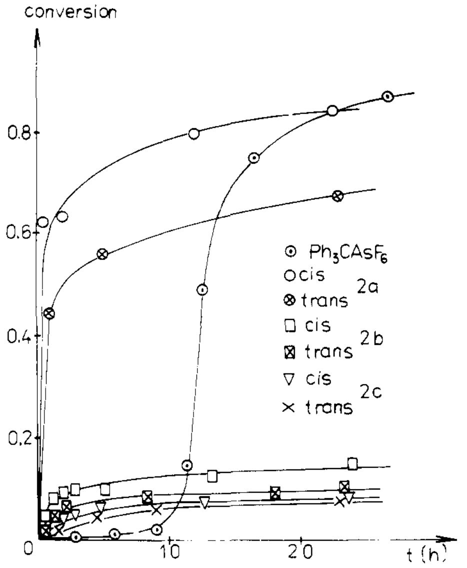


Figure 3. Conversion-time curves for trioxane polymerization initiated by tritylium and 2,4,5-trisbustituted 1,3-dioxolan-2-ylium hexafluoroarsenates.

Figure 3 shows the course of the polymerization of trioxane initiated by the cis and trans isomers of **2a-c**. Since the same experimental conditions were kept and the salts with the same anions were used, the observed differences in conversion-time curves resulted obviously from differences in the initiator cation nature only. Thus, the initiators investigated may be arranged in the following order according to their catalytic activity, i.e., to the respective rates of polymer formation. The most active are those with an isopropyl substituent attached to the C-2 carbon atom, while the initiators with aromatic substituents, and particularly those with a styryl substituent, are less active. In the case of each substituent at C-2, independently of its nature, the salt with cis configuration is more active than its trans form. This relationship coincides with that previously found[3] for hexachloroantimonate analogues.

(2) Initiation Mechanism. The initiation mechanism was followed by ^1H NMR spectroscopy. Figure 4 presents the spectrum of a model system consisting of trioxane and

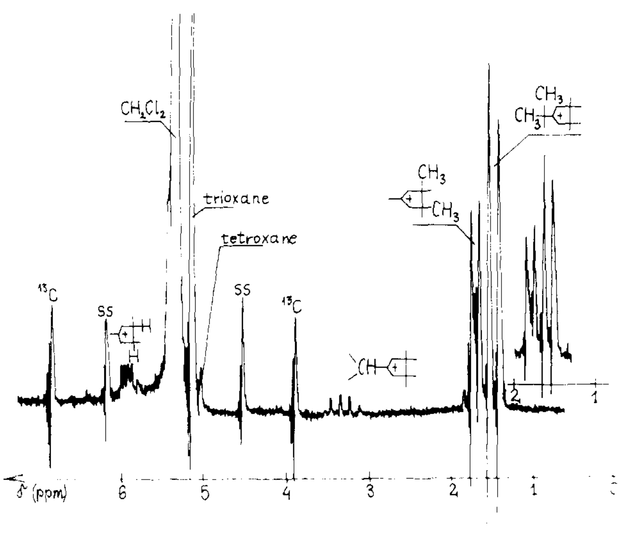
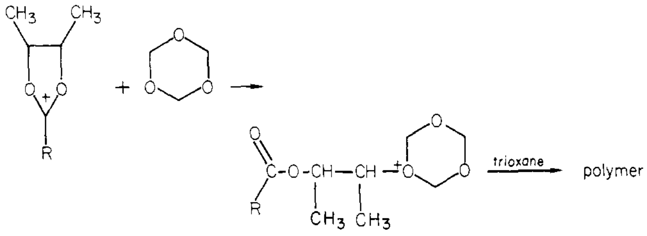


Figure 4. NMR spectrum of the trioxane-2-isopropyl-4,5-dimethyl-1,3-dioxolan-2-ylium hexafluoroarsenate model system (upper run recorded after further monomer addition).

2a (approximate concentrations 1 and 10^{-1} mol/L, respectively). Only monomer, initiator, and solvent signals are seen in that spectrum, although solid polymer was observed close to the probe walls, which indicated that the polymerization had been proceeding.

Further addition of trioxane results in a reduction of the intensity of initiator methyl signals (upper run), which would suggest that the initiator was incorporated into the precipitating polymer. On the basis of this fact, it may be concluded that the initiation involves a cationation process:



If that were true, the presence of ester end groups should have been found in the resulting polymer. Unfortunately, owing to the insolubility of the polymer, only the IR spectra of its samples in KBr could be examined. Since this technique is not sufficiently sensitive, the content of the end groups was increased by the controlled thermal degradation of polymer samples, the ester group being assumed to remain unaltered. Figure 5 presents the IR spectra of the degraded and undegraded trioxane polymer obtained with a *cis*-**2b** initiator. The strong band at 1740 cm^{-1} was assigned to the carbonyl group of degraded trioxane polymer. One could attribute its origin to the degradation process itself. To exclude such a possibility we performed the degradation of polymers obtained by tritylium and SbCl$_5$ initiators, known to possess no ester end groups. No carbonyl bands were detected in that case in the respective IR spectra, which confirmed the above-proposed scheme of initiation.

Discussion

Let us consider now the following fundamental facts to be derived from the above-presented experimental results.

(i) Trioxane polymerization initiated by the series of trisubstituted 1,3-dioxolan-2-ylium salts (**2**) proceeds at different rates, and different conversions are attained, depending on the structure of the cation, although the same counterion and experimental conditions were employed.

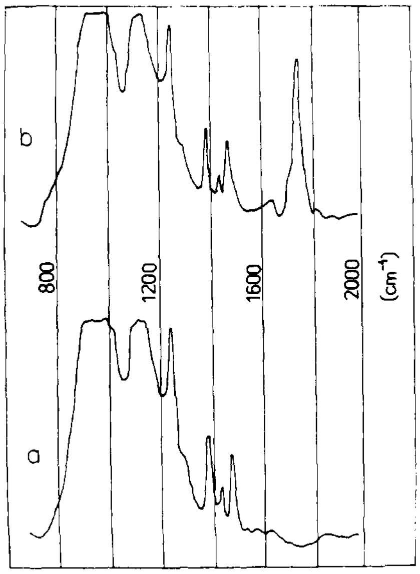


Figure 5. IR spectra of undegraded (a) and degraded (b) trioxane polymer obtained when initiating by dioxolenium salt.

(ii) Initiation involves the formation of a "thermodynamic product", i.e., monomer cationation, a process known to be generally slow.[5,6]

From i and ii we can conclude that slow and/or inefficient initiation determines the overall rate of the process. Consequently, we can attribute the differences in the conversion-time curves observed to different initiation rates and/or efficiencies, depending on the properties of the individual initiators. Since the salts investigated differ in both the chemical and geometrical structure of the 1,3-dioxolan-2-ylium cation, these two factors may be considered to influence the initiation step involving the attack of a nucleophile, i.e., trioxane at the C-4,5 position of cation, followed by the formation of an ester end group in the ring-opening step. The nucleophilic attack may be assumed to depend on the positive charge at C-4,5 and steric hindrance effects in the dioxolenium cation. It was suggested recently[7] that the former factor did not explain the differences in the reactivities of stereoisomeric salts. The smaller steric hindrance effects in the cis salt isomers are therefore presumably responsible for their greater reactivity when compared with the respective trans forms. Furthermore, the torsional tension at C-4,5 position should be stronger in the cis than in the trans isomers, since the methyl-methyl cis-vicinal interaction is stronger than the methyl-proton one. This may influence the ring stability, so that ring opening for the cis isomers is much easier than that for the trans isomers, since the ability to form a thermodynamic product decreases with increasing ring stability.[6] Both these stereochemical factors, namely, steric hindrance and torsional tension, coincide, which results in higher observed polymerization rates when salts having a cis configuration are used as initiators.

On the other hand, the enhancement of ring stability resulting from a greater delocalization of the positive charge may be responsible for the observed low catalytic activities of salts with aryl substituents at C-2. This factor influences the ring-opening step and has been recently confirmed by the estimated positive charge distribution.[7] The lowest catalytic activity observed for **2c** may be also due to the high stability of the ring resulting from the allylic resonance.[8]

It is not certain, however, which factor is more important in the initiation step, i.e., the rate or efficiency of initiation. A quantitative treatment of this problem should therefore be performed.

Conclusions

The 2,4,5-trisubstituted isomers of 1,3-dioxolan-2-ylium salts presented above were found to be new and interesting initiators for the polymerization of trioxane. They were shown to initiate the polymerization via simple monomer cationation, a considerable effect of the structure of the cation being found.

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Effect of Stiffness on the First Cumulant and Polymer Dimensions in Solution

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ABSTRACT: The first cumulant of the intermediate scattering function, the hydrodynamic radius, and the radius of gyration are calculated in the case of linear stiff chains. Two different models are used to characterize chain stiffness: broken-chain and sliding-rod models. The crossover from flexible to rodlike behavior in the intermediate-q region is investigated. It is found that, in the Rouse limit, $\Omega \sim q^{2+1/\nu}$ for $qbn < 1$ and q^3 for $qbn > 1$, where $\nu = {}^1/_2$ or ${}^3/_5$, depending on whether the solvent conditions correspond to Θ or good solvent. In the Zimm limit, $\Omega \sim q^3$ for $qbn < 1$ but $\Omega \sim q^3 \ln(1/qb)$ for $qbn > 1$. Hence, the intermediate asymptotic region is now divided into two subasymptotic regions due to the presence of a rodlike behavior for $qbn > 1$. The diffusion coefficient in the small-q region is also investigated. These results are useful in the interpretation of light and neutron scattering experiments.

I. Introduction

In this paper we investigate the effect of chain stiffness on various properties of polymer solutions. Specifically, we calculate the static structure factor, the radius of gyration, the first cumulant, and the hydrodynamic radius for stiff chains. The chain stiffness is included through the equilibrium distribution function in monomer configuration space because dynamic properties such as the first cumulant are expressed, in the present formalism, in terms of static correlation functions. The calculations are carried out for two chain models: The first is the broken-chain model in which the actual polymer is represented by a sequence of rods connected together by universal joints. Each rod contains an equal number of monomers distributed along the rod at equal distances. This model may be realistic for molecules such as DNA. The second is the sliding-rod model, in which the polymer is treated around each monomer locally as a rod of chemical length n but as a flexible Gaussian chain for chemical lengths larger than n. The length of the rod at each monomer represents the local stiffness of the actual chain. As opposed to the broken-chain model, the locations of the rods relative to the chain are not fixed in this model but rather allowed to slide along the chain from monomer to monomer. The sliding-rod model, which is inspired by the "blob" concept introduced recently in chain statistics,[1,2] may be interpreted as a discrete version of the conventional wormlike-chain representation[3] of polymer molecules. It may be a realistic description of polyelectrolytes in solutions.[4]

The main motivation of this paper is to calculate the first cumulant, including stiffness, for all values of q, with particular attention to the transition from a single rod to a completely flexible-chain behavior. Our purpose is not to reexamine, with a slightly modified model, the equilibrium properties of stiff chains which have already been studied extensively in the literature[3-8] but rather to study the effect of stiffness on some dynamical properties (e.g., first cumulant in the intermediate-q range) which have been accessible experimentally only recently by dynamic light[9] and neutron[10] scattering techniques. In this sense, the present work is an extension of our previous work based on linear response theory to stiff chains. The first cumulant of the intermediate scattering function is given by[11]

$$\Omega(q) = \langle \rho^* \mathcal{L} \rho \rangle / \langle \rho^* \rho \rangle \tag{1}$$

where ρ is the monomer density in Fourier space. $\mathcal{L}$ is the dynamical operator that governs the time dependence of ρ, and $\langle\ \rangle$ denotes thermal average with respect to the equilibrium distribution in polymer configuration space.

This expression of Ω can accommodate any choice of the equilibrium distribution and the dynamical operator $\mathcal{L}$. We have used it extensively to investigate the effect of temperature and concentration on the dynamical properties of linear flexible polymers in solution, in the framework of Kirkwood–Riseman theory.[9,11-14] Others[15] have extended these calculations to branched polymers. In the present calculation we use the same dynamical model[16,17] with two different equilibrium distributions appropriate for the broken-chain and sliding-rod chain models that take into account the chain stiffness. The bond-length and bond-angle constraints involved in these

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