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Thermostable Trioxane-Dioxolane Copolymers Obtained with Boron Trifluoride: Acrylonitrile Complex as Initiator

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ABSTRACT

Trioxane was copolymerized with small amounts of dioxolane in benzene in the presence of a boron trifluoride:acrylonitrile complex as initiator. The kinetics of reactions was expressed in terms of topoenergetic principles. The copolymerizations had no induction periods and the maximum reaction rate was found proportional to the square of both the initiator and monomers concentrations. A zwitterionic mechanism is suggested for initiation. The activation energy for the system with 5% dioxolane was determined as 18.3 kcal/mol. The melting behavior of the copolymers is briefly discussed as a function of the dioxolane initial content, and is indicative of the amorphous-crystalline coupling phenomenon. The copolymers with ~5% dioxolane are thermostable in air up to 250° and are recommended for practical purposes.

INTRODUCTION

Trioxane has been copolymerized with numerous monomers in order to improve the thermal stability of polyoxymethylene blocks, but only a few of them, such as dioxolane, ethylene oxide, and epichlorohydrin, have proved to be practically reliable owing to their availability, ease of copolymerization, and efficiency in preserving the mechanical properties of polyoxymethylene [1-25]. Commercial materials prepared from these monomers are essentially random copolymers which have been partially depolymerized to remove the thermally and hydrolytically unstable polyformal endgroup segments.

Different reaction systems were thus reported for the synthesis of dioxolane containing trioxane copolymers, e.g., solution [1-4], bulk [5-6], suspension [7], solid state [8, 9], and crystallization copolymerization [19], using cationic initiators [4-6, 10], high energy rays [8, 9], and electrochemical initiation as well [11]. These investigations dealt mainly with kinetic aspects and reactivity ratios of these two monomers [1-8] or with the structure and properties of the products obtained, among which was the thermal stability of copolymers [9, 10]. It was thus established that in order to improve this parameter without any detrimental effect on mechanical characteristics, the amount of the second monomer in the copolymer should not exceed a molar concentration of a few percent. Satisfactory thermal decomposition rates were also reported in the patent literature when boron trifluoride complexes with oxygen- or nitrogen-containing vinyl monomers were used [26-28] for the initiation of trioxane polymerization.

The aim of the present paper is to extend this type of study and to present the kinetics of copolymerization of trioxane with dioxolane using the boron trifluoride-acrylonitrile complex as initiator as well as to discuss briefly the morphology and the thermal stability of the copolymers obtained.

EXPERIMENTAL

Materials

Trioxane (T) was synthesized according to Pratesi's method [29]. It was recrystallized from methylene chloride and finally dried under argon with triethyl aluminum [30]. The purified monomer (mp 61-62°)

was stored as benzene solution of the desired concentration under dry argon.

Dioxolane (D) was prepared from ethylene glycol and paraformaldehyde using H_2SO_4 as catalyst [31]. It was purified over metallic sodium by rectification in a column of high efficiency (bp 74.5° at 760 mmHg).

The complexes of boron trifluoride with acrylonitrile (BF_3.ACN) and methacrylonitrile (BF_3.MACN) were obtained by bubbling gaseous BF_3 in freshly distilled acrylonitrile and methacrylonitrile, respectively [32]. The crude crystals were sublimed in vacuum and dissolved in benzene to the desired concentration. Both the crystals and the solution are highly fumigant in air.

Benzene was dried in the conventional manner. All the other materials were used.

Synthesis of Copolymers

Copolymerizations were carried out in calibrated glass ampules under dry argon. All the reaction mixtures were prepared in argon and handled in vacuum through breakable seals. The ampules were charged with the reaction mixture using the apparatus shown in Fig. 1. The whole apparatus was heated under vacuum several times in order

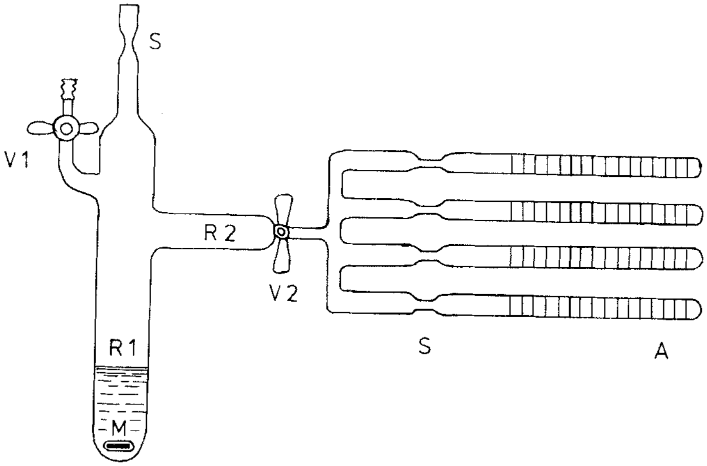


FIG. 1. Glass apparatus for copolymerization. V1, vacuum glass stopcock. V2, vacuum PTFE stopcock. R1 and R2, reservoirs for reaction mixture. A, calibrated ampules. S, sealing neck. M, stirrer.

to remove the water adsorbed on the glass walls (V1 and V2 open) and cooled under a stream of dry argon (V1 and V2 closed in order to keep the ampules under vacuum). The reaction components were then introduced in reservoir R1, mixed, and passed in reservoir R2. The ampules were charged by opening V2, sealed, introduced in a bath thermostated at the desired temperature ± 0.1°, and taken out at different intervals. The copolymers, separated as white powders, were washed with 2% NH_4OH containing methanol, then with pure methanol, dried at 40°, and weighed. All samples were end-capped by acetylation with a mixture of acetic anhydride and dimethylformamide (1:1 volume) in the presence of 3% phenyl β-naphthyl amine (as antioxidant) and 1% sodium acetate (as catalyst).

Characterization of Copolymers

Viscometric measurements were carried out at 60° in p-chlorophenol containing 2% α-pinen as antioxidant (polymer concentration, 0.25 g/dL). Calorimetric determinations were made using a Du Pont 990 DSC apparatus. The thermal stability in air was determined with a Paulik-Paulik Erdey derivatograph (Budapest). Polymer samples were mixed with Al_2O_3 powder used as reference material for DTA measurements.

RESULTS AND DISCUSSION

Synthesis

In order to investigate the influence of the initiator on the reaction system, the total concentration of monomers used was constant, i.e., 3.8 mol/L, but the feed composition had different values. In the first series of experiments the molar ratio in feed was $[T]_0 : [D]_0 = 19$ ($[T]_0$ and $[D]_0$ stand for initial concentration of T and D) and in the second, $[T]_0 : [D]_0 = 9$. The initiator concentration varied between 0.015 and 0.030 mol/L. Unlike other T-D copolymerization reactions using free Lewis acids or their ethereal complex as initiator, where a rather long induction period has been recorded [22, 34], in the present case the maximum rate was recorded in all cases at the initial reaction time (Fig. 2), corresponding to a measuring system of a single type [35], for which the following kinetic equation has been proposed in terms of topoenergetic principles [36]:

$$\ln (1/v_0) \sim \ln \tau = -E/RT + K \qquad (1)$$

where v_0 is the rate at the initial reaction stage, τ represents the global relaxation time of the measuring system, E is the activation

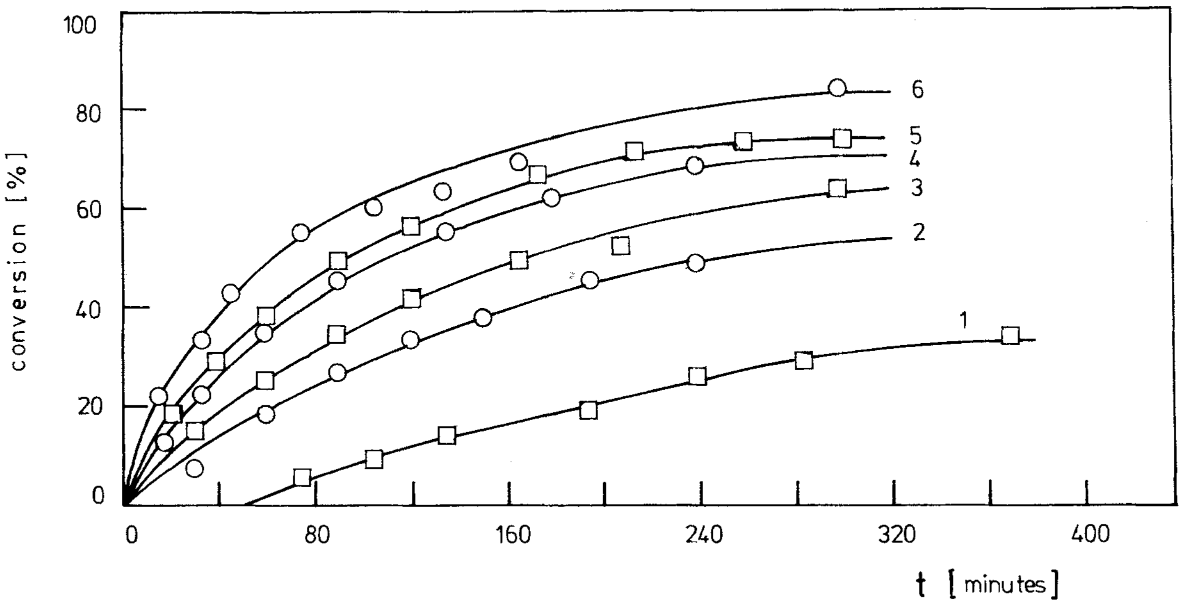


FIG. 2. Conversion curves for T-D copolymerization in benzene at 35°. Initial molar ratio of monomers, $[T]_0 : [D]_0 = 19$ (○) and 9 (□). $[T]_0 + [D]_0 = 3.8$ mol/L. Initiator concentration (BF_3.ACN, mol/L): 0.0150 (1), 0.0153 (2), 0.0210 (3), 0.0202 (4), and 0.0300 (5 and 6).

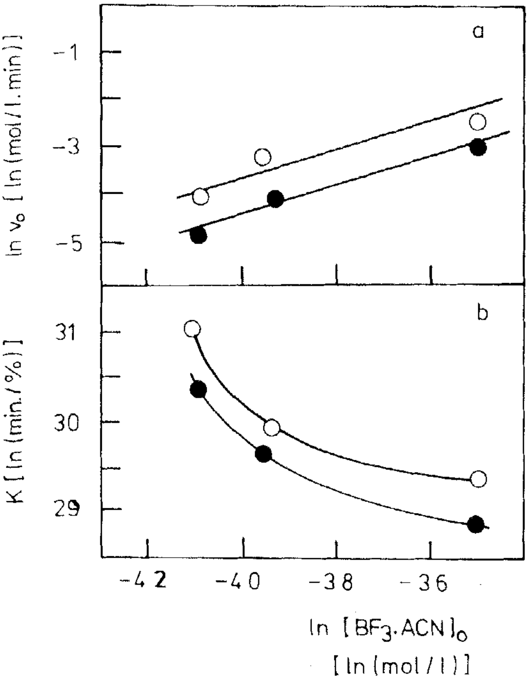


FIG. 3. The dependence of the initial reaction rate (a) and parameter K (b) upon initiator concentration for T-D copolymerization in benzene at 35°. Initial molar ratio of monomers, $[T]_0 : [D]_0 = 19$ (○) and 9 (●). $[T]_0 + [D]_0 = 3.8$ mol/L.

energy of the process, T is the reaction temperature in degrees Kelvin, R is the gas constant, and K is a constant proportional to the inert component of the system which defines its stability (or the amplitude) in the transformation process. In solution polymerizations the inert component should be both the solvent and the "in situ" formed polymer chains with inactive ends. However, in the present case, owing to chain transfer reactions in which the newly formed or forming polymers become active [22], the inert component means all species that do not affect the amplitude of copolymerization and are not transformed during the reactions. Therefore the only true inert component in our case is the solvent (benzene).

The formal notions of topological thermodynamics were introduced by Oster and Auslander [37] in order to give a new expression to nonequilibrium thermodynamics. Though the physical significances of the magnitudes introduced have not been established, the authors tried to modulate certain very intricate processes of transformation by making the assumption that the energetic circuit associated with an evolutive system can be described by the spatial distribution of an elementary circuit [38]. The mathematical instrumentation is rather elaborate and the results obtained do not agree with the real solutions.

New topoenergetic principles have recently been proposed [39] which start from the hypothesis that an equivalent energetic circuit can be associated with an evolutive system and thus eliminate space as a physical variable [39]. Some of these working principles were applied for certain thermally driven transformation processes specific to macromolecular systems, such as crystallization from the melt, ductile-to-brittle transition as a result of amorphous morphology annealing, and oxidation of the amorphous phase in high and low density polyethylenes blended with carbon black [36], as well as thermal oxidation and isomerization of polyacetylenes [40]. At the same time, taking into account the variation of the reaction rate with the temperature, these kinetic models can also be applied to the study of synthesis processes.

Therefore, for the characterization of the T-D copolymerization reaction, one can compare the kinetic data obtained in the classical way with that determined on the basis of Eq. (1). By making a logarithmic plot of the rate versus the initiator concentration (Fig. 3a), a reaction order of 2 was found. The variation of parameter K with the amount of initiator used (Fig. 3b) resulted in an initiator concentration that was higher the lower the inert component of the system. Consequently, the copolymerization process is amplified, i.e., for the same initiator concentration, the system having $[T]_0 : [D]_0 = 19$ is more reactive than that reached in dioxolane. This observation is in good agreement with the large difference between the reactivity ratios of these monomers in cationically initiated copolymerization [3, 8]. As shown by Yamashita et al. [10], the process is a random copolymerization including depolymerization, in which dioxolane is kinetically more reactive but its incorporation is thermodynamically less favorable. The parameter K was estimated after determination of the activation energy of copolymerization (18.3 kcal/mol) from the influence of temperature on the reaction (Fig. 4). The activation energy obtained is close to that found for T-D copolymerization initiated by the $BF_3.ACN$ complex [20], but is almost twice the activation energy of trioxane polymerization in benzene using the same initiator, i.e., 10.3 kcal/mol [41].

In order to investigate the concentration effect of monomers on the reaction course, both the initial ratio of monomers and the initiator concentration were kept constant ($[T]_0 : [D]_0 = 19$ and $[BF_3.ACN] = 0.021$ mol/L), and the total concentration of monomers was varied from 1 to 3.75 mol/L. From the logarithmic plot of the initial copolymerization rate versus the total monomer concentration (Fig. 5, top), it was found that the reaction was again of second order, so that the universal kinetic equation of reactions can be expressed as follows:

$$v_0 \sim ([T]_0 + [D]_0)^2 [BF_3.ACN]^2 \qquad (2)$$

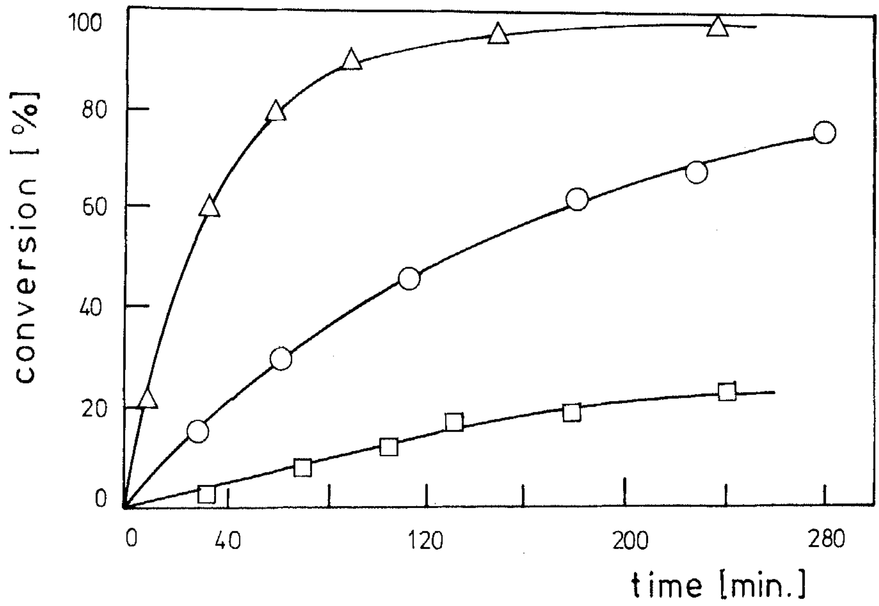


FIG. 4. The influence of temperature on T-D copolymerization in benzene. Reaction conditions: $[T]_0:[D]_0 = 19.7$, $[T]_0 + [D]_0 = 3.8$ mol/L, $[BF_3.ACN] = 0.0202$ mol/L. Temperature; 20° (□), 35° (○), and 55° (△).

The variation of the parameter K with the feed concentration (Fig. 5, bottom) indicates that by increasing the concentration of monomers, the system becomes unstable and the reaction more likely since the inert component decreases.

The initiating capacity of the BF_3.ACN complex in the polymerization of cyclic ethers raises the question of the nature of the mechanism. There is always the equilibrium, especially in solution:

$$BF_3.ACN \rightleftharpoons BF_3 + ACN$$

and one can make the free BF_3 responsible for initiation. However, as mentioned above and shown by Fig. 2, the copolymerization has no induction effect with free Lewis acids [22] and BF_3 in particular [42], so the explanation should be found in the complex itself. The participation of the hydrogen atom from the α position, labilized by the strong electron drawing effect brought about by the complexation

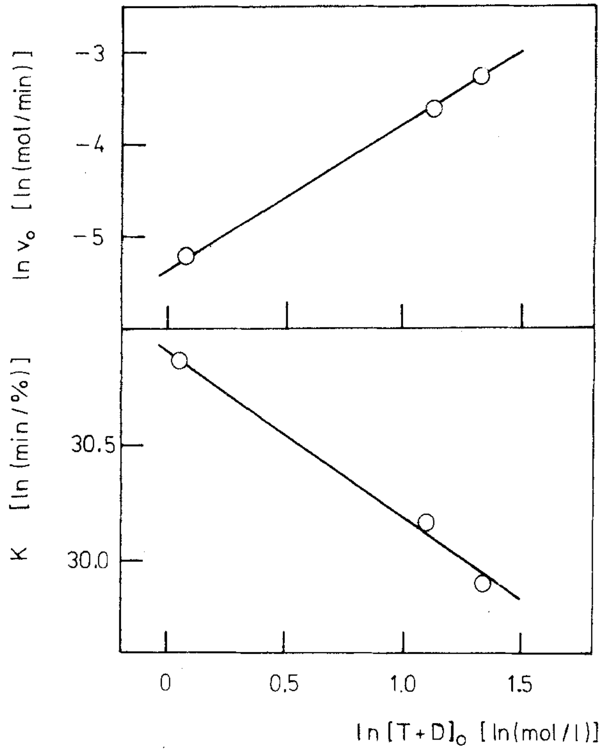
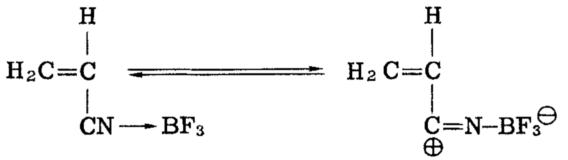
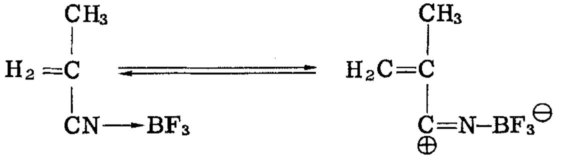


FIG. 5. The dependence of initial reaction rate (top) and of parameter K (bottom) upon the feed concentration for T-D copolymerization in benzene at 35°. $[T]_0:[D]_0 = 19$ and $[BF_3.ACN] = 0.021$ mol/L.



$$H_2C{=}\overset{\displaystyle H}{\underset{\displaystyle CN \rightarrow BF_3}{C}} \rightleftharpoons H_2C{=}\overset{\displaystyle H}{\underset{\displaystyle \overset{\oplus}{C}{=}N{-}BF_3^{\ominus}}{C}}$$

was also ruled out since the BF_3.MACN complex



$$H_2{=}\overset{\displaystyle CH_3}{\underset{\displaystyle CN \rightarrow BF_3}{C}} \rightleftharpoons H_2C{=}\overset{\displaystyle CH_3}{\underset{\displaystyle \overset{\oplus}{C}{=}N{-}BF_3^{\ominus}}{C}}$$

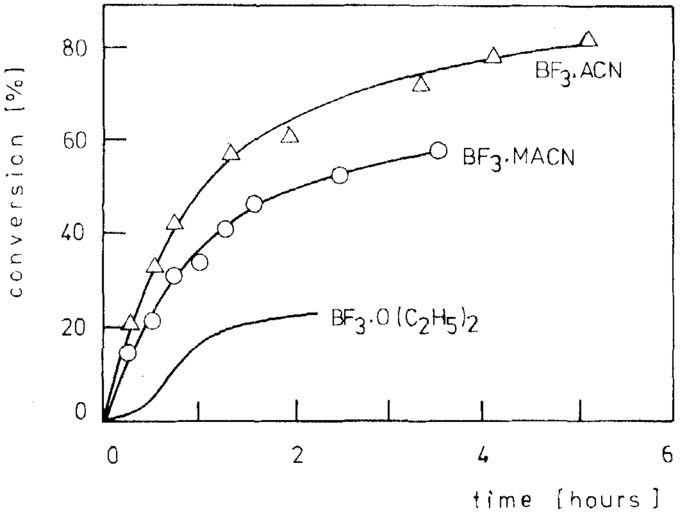
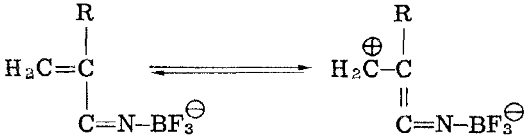


FIG. 6. T-D copolymerization in benzene at 35° using different boron trifluoride complexes for initiation. $[T]_0 + [D]_0 = 19$, $[T]_0 + [D]_0 = 3.8$ mol/L. Initiator concentration, 0.03 mol/L $BF_3.O(C_2H_5)_2$. Data from Ref. 34.

was very active in T-D copolymerization, even more active than the $BF_3.O(C_2H_5)_2$ complex (Fig. 6). Again, the induction period was registered only in the case of the ethereal complex [34]. Therefore, a simple supposition which has not been verified could be related to the zwitterionic activity of complex species:



$$\begin{array}{c} R \\ | \\ H_2C{=}C \\ | \\ C{=}N{-}BF_3^{\ominus} \end{array} \rightleftharpoons \begin{array}{c} R \\ | \\ H_2\overset{\oplus}{C}{-}C \\ \| \\ C{=}N{-}BF_3^{\ominus} \end{array}$$

where R = H, CH_3. However, no matter what the active site and the mechanism of initiation, the rather high activation energy of this copolymerization together with the variation of the K for the initial monomer ratio $[T]_0:[D]_0 = 19$ confirm that dioxolane has a strong retarding effect on reactions despite its rather very low content in the system.

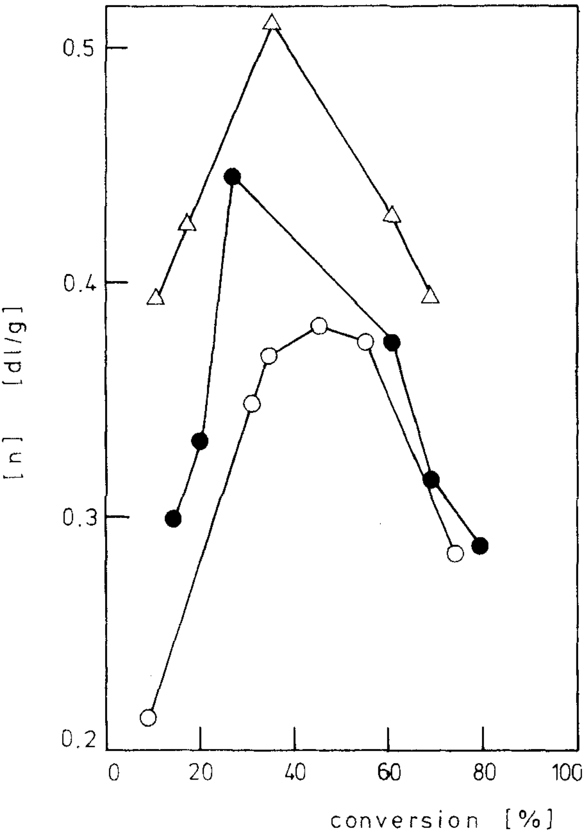


FIG. 7. The variation of intrinsic viscosity with conversion for T-D copolymerization in benzene at 35°. Reaction conditions: $[T]_0 + [D]_0 = 3.8$ mol/L, $[T]_0 : [D]_0 = 19$, $[BF_3.ACN] = 0.021$ mol/L (△); $[T]_0 = 100$, $[D]_0 = 0$, and $[BF_3.ACN] = 0.030$ mol/L (●); and $[T]_0 : [D]_0 = 19$, $[BF_3.ACN] = 0.030$ mol/L (○).

Intrinsic Viscosity

The copolymers were obtained as powdery materials insoluble in most of the usual solvents at room temperature. No benzene or methylene chloride fractions were detected as reported for the initiation of this copolymerization with other systems [22].

As shown earlier by Onyon et al. [16], the intrinsic viscosity of polytrioxane synthesized in cyclohexane with $BF_3.O(C_4H_9)_2$ increases with the monomer concentration but is practically independent of the initiator concentration. As found in the present case, the magnitude

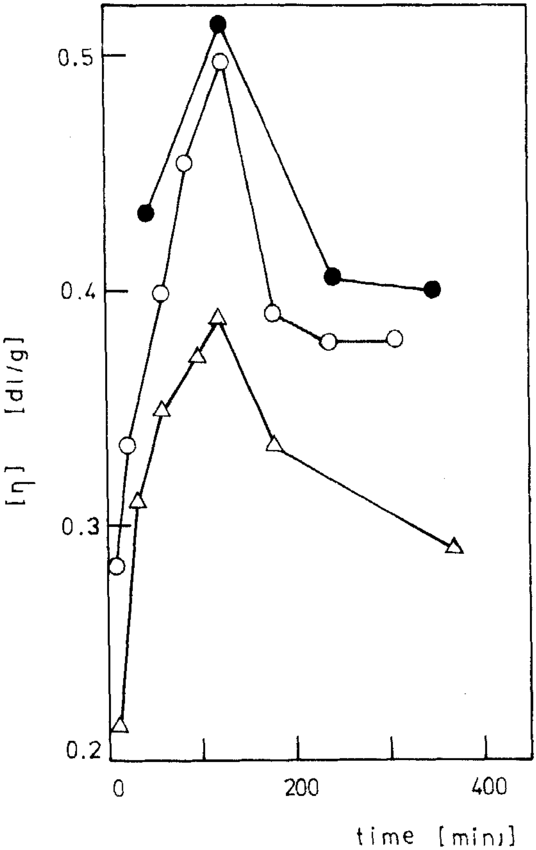


FIG. 8. The variation of intrinsic viscosity of T-D copolymers obtained in benzene at 35° with reaction time. Reaction conditions: $[T]_0:[D]_0 = 19$, $[T]_0 + [D]_0 = 3.8$ mol/L. Initiator concentration: $[BF_3.ACN] = 0.030$ (△), 0.021 (○), and 0.019 (●) mol/L.

of the molecular mass of copolymers, as indicated by their intrinsic viscosity, is a function of both the initiator concentration and the conversion (reaction time). One can observe from Fig. 7 that the intrinsic viscosity of a copolymer obtained at an initial ratio of $[T]_0$: $[D]_0 = 19$ has a continuous variation with a maximum situated in the conversion range of 30-50%. On the other hand, at the end of the reactions the magnitude of the molecular mass, as indicated by the intrinsic viscosity, tends to be stabilized (Fig. 8) due to chain transfer reactions with a scission [18, 20, 22], the maxima of the curves being registered, depending on the initiator concentration, between 120 and 150 min of reaction time.

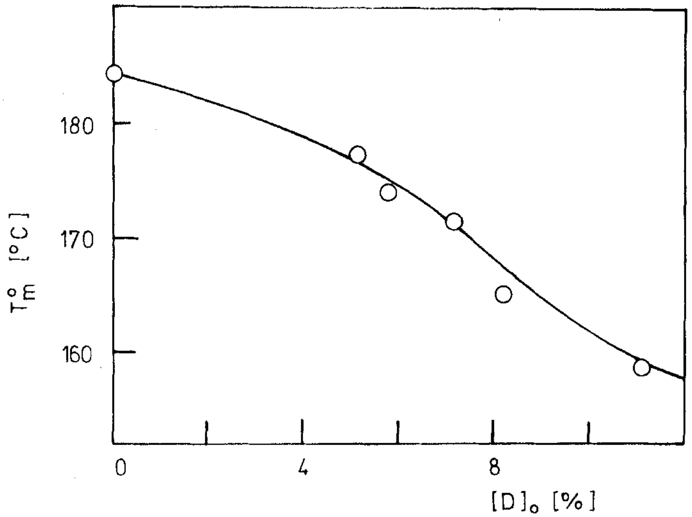


FIG. 9. The dependence of crystalline melting temperature of T-D copolymers, T_m°, upon the initial molar concentration of dioxolane. Reaction conditions: T = 35°, reaction time 300 min, $[T]_0 + [D]_0$ = 3.8 mol/L, $[BF_3.ACN]$ = 0.02 mol/L, and benzene as solvent.

Thermal Behavior

The insertion of thermostable dioxolane sequences, made of alternating ethylene oxide and formal units, in the readily degradable polyoxymethylene chain, i.e., repeating formal units only, induces certain modifications in the crystalline morphology of the polymer as observed in solid-state grafted polyethylenes [43]. Since only the long polyoxymethylene sequences crystallize, the short dioxolane sequences, up to five units [44], are included as defects. The large specific volume of these defects causes a decrease of lamellae as the dioxolane concentration increases, and consequently the melting point of crystalline domains, T_m° [43], should decrease to a limiting value. The variation of T_m° of T-D copolymers as determined by different dioxolane contents, expressed as $[D]_0$, is depicted in Fig. 9. One can notice that T_m° drops by almost 20° as $[D]_0$ increases from 5 to 11% since the crystallizable formal segments are shorter and shorter (the two monomers being distributed randomly in the copolymer) and are in thinner and thinner lamellae [45]. Here T_m° corresponds to the bimodal endotherm peak situated at the highest temperature (Fig. 10).

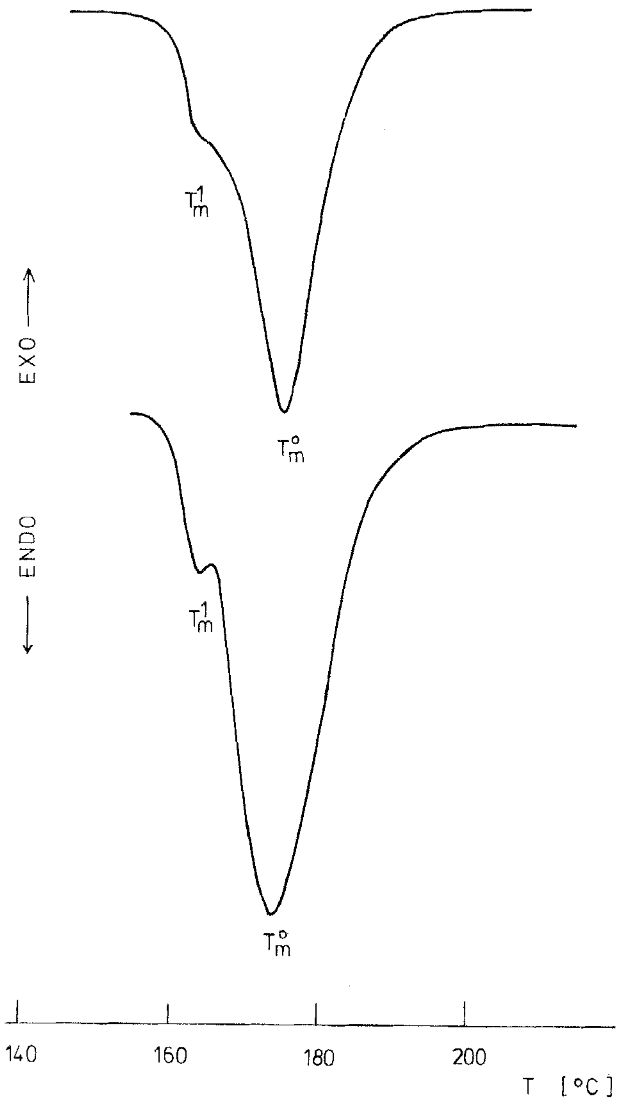


FIG. 10. Typical DSC thermograms for melting of T-D copolymers annealed at 140° for 1 h after two consecutive heatings and quenchings of molten samples at room temperature. The sample with a lower T_m° has a higher content of dioxolane. Recording conditions: 10°/min, 2 mcal/s·in.

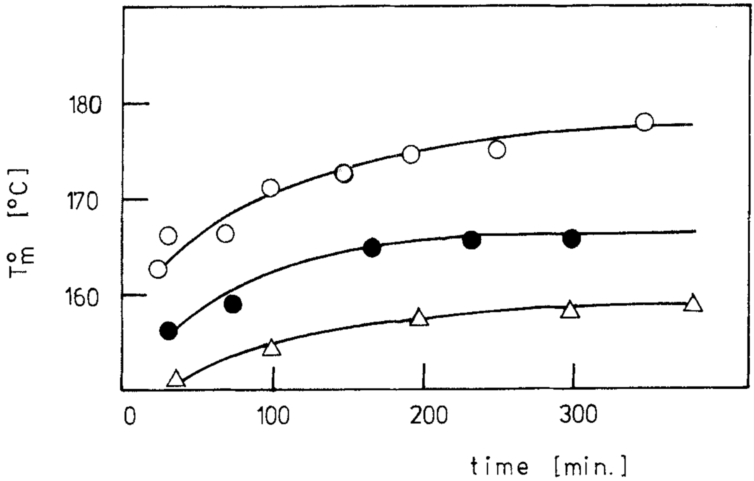


FIG. 11. The change of the crystalline melting temperature of T-D copolymers obtained in benzene at 35° with copolymerization time. Reaction conditions: $[T]_0 + [D]_0 = 3.8$ mol/L, $[BF_3.ACN] = 0.020$ mol/L, $[T]_0:[D]_0 = 19$ (0), 11.5 (●), and 7.9 (△).

It is well known that the magnitude of a transformation temperature estimated through the peak of the endothermal or exothermal process from calorimetric thermograms does not have an absolute character, but as far as a certain geometry is preserved for the entire series of samples, the determination has a correct comparative value.

Initially, the copolymers presented in Fig. 10 were only Soxhlet extracted with acetone at reflux for 5 h after acetylation in order to remove any traces of dioxolane homopolymers or other low molecular species. All samples gave an asymmetric DSC thermogram, the asymmetry increasing with the initial dioxolane content in the feed. In order to elucidate this asymmetry the copolymers were heated twice to 210° prior to analysis and the molten material was cooled down to room temperature and subsequently annealed at 140° for different periods. Supposing that the secondary peak, T_m^1 [43], is the result of certain unstable backbone remnants, it should have vanished as the result of this thermal treatment, but after the annealing it had a tendency to separate from the actual melting endotherm centered at T_m^o, giving rise to the amorphous-crystalline coupling phenomenon [46] proper to most crystalline polymeric materials.

From the plots of Fig. 11 it can also be seen that in each case, depending on the feed composition, T_m^o increases to a limiting value

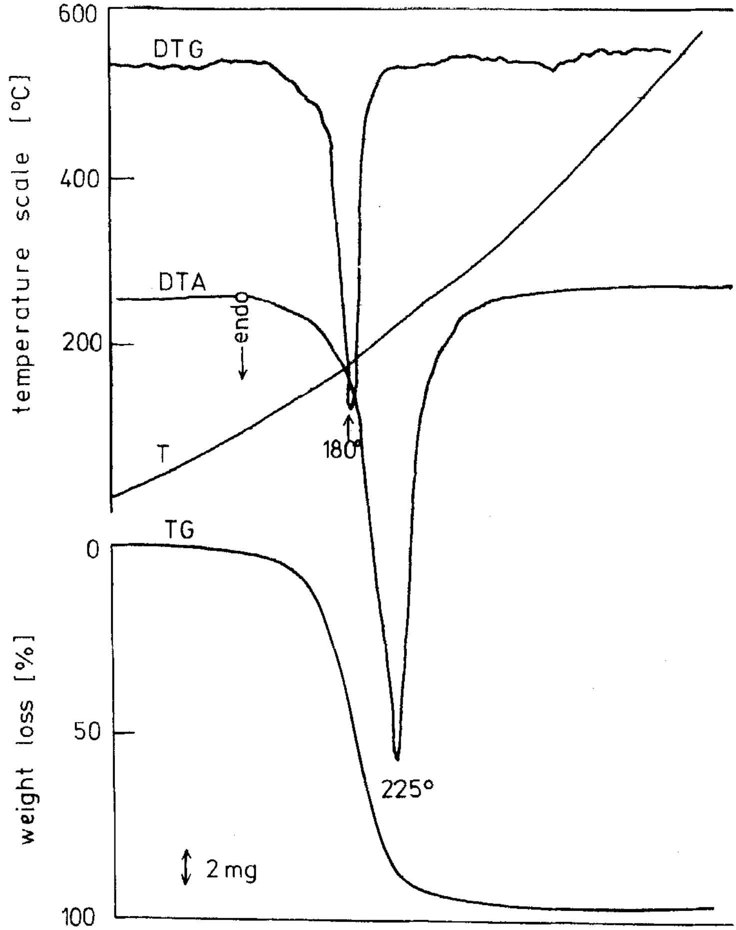


FIG. 12. Derivatogram of polytrioxane obtained in benzene at 35°. Heating rate, 10°/min in air. Synthesis conditions: $[T]_0 = 4$ mol/L and $[BF_3.ACN] = 0.021$ mol/L.

with the reaction time. By making a correlation with the variation of the intrinsic viscosity during copolymerization (Fig. 8), one can conclude that initially, when the reaction rate is high (Fig. 2), the copolymer formed has a low molecular mass (low $[\eta]$) which increases gradually to a maximum value. There is a relatively rapid increase of T_m° (especially when $[D]_0$ is low), and after 120-150 min, when $[\eta]$ starts to decrease, the increase of T_m° is very slow (especially when $[D]_0$ is high).

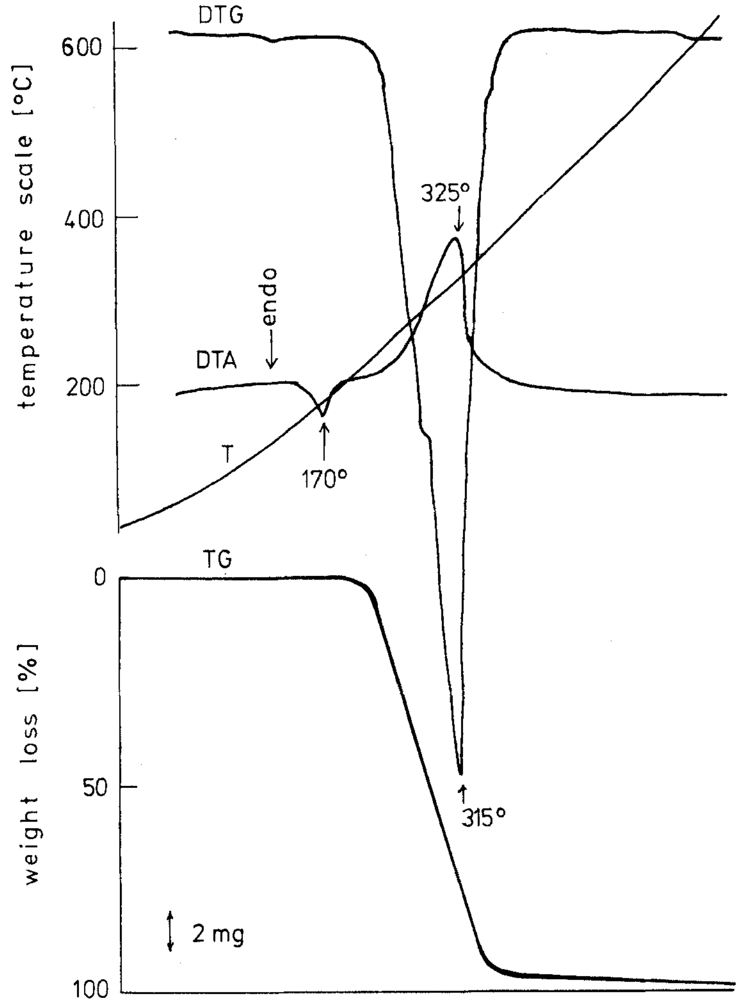


FIG. 13. Derivatogram of Hostaform C. Heating rate, 10°/min in air.

On the other hand, the dioxolane is consumed preferentially in the early stages of the reaction [6] and consequently the copolymer is richer in this monomer (hence a low $T_m°$) than in the later stages of the copolymerization when the microstructure of the copolymer changes to give longer polyoxymethylene sequences (hence an increased $T_m°$) which produce very complicated thermodynamic problems [10] due to side reactions [18, 22].

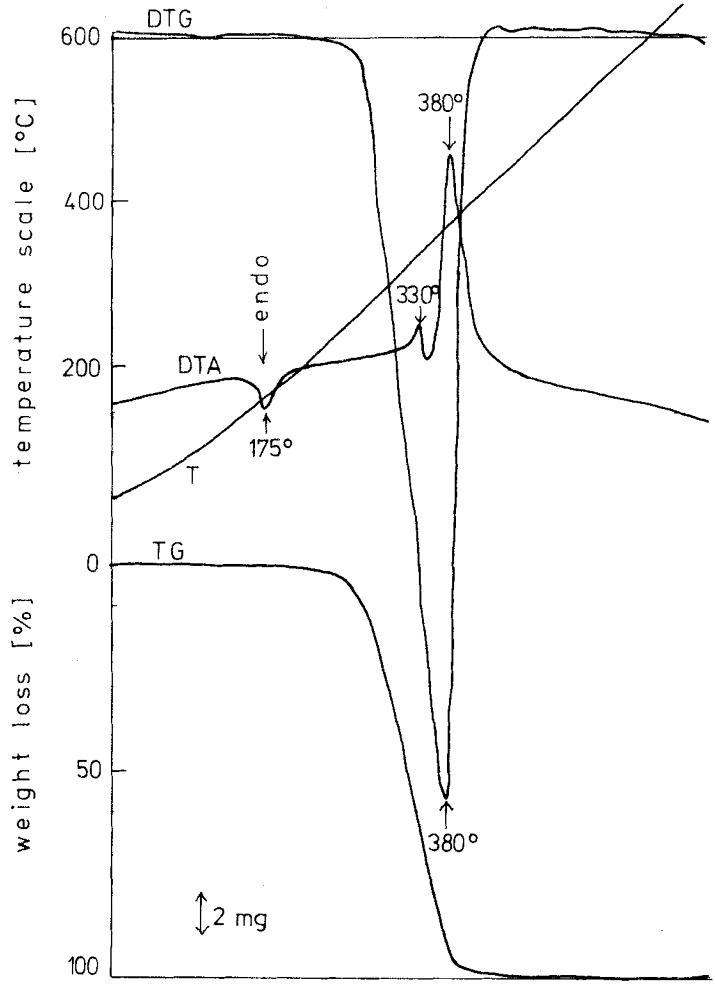


FIG. 14. Derivatogram of T-D copolymer obtained in benzene at 35°. Heating rate, 10°/min in air. Synthesis conditions: $[T]_0 + [D]_0 = 3.8$ mol/L, $[T]_0:[D]_0 = 19$, $[BF_3.ACN] = 0.020$ mol/L.

The thermal stability of the T-D copolymers obtained was compared with that of polytrioxane (PT) obtained in the same conditions and with that of a commercial trioxane-based product Hostaform C (trioxane-ethylene oxide copolymer containing ~95% formal units). Figures 12-14 present the derivatograms of these three materials. One can notice that the least thermostable is the homopolymer (Fig. 12) which, as shown by its DTA curve, starts to degrade during the melting process (no individual melting peak, very distinct depolymerization-vaporization endotherm, and a poor correlation between DTG and DTA curves since the process of degradation is very fast and the thermal sensors cannot follow the weight loss). The degradation of PT is almost complete at 250° (TG curve) and the maximum rate of the destructive process is registered at the melting temperature, i.e., ~ 180°. The commercial copolymer is stable, the endothermic melting transition being quite separate from the thermal effects of degradation on the DTA curve (Fig. 13). Endothermic depolymerization and vaporization of expulsed formaldehyde units are well compensated for by the exothermic oxidation reactions of chain fragments resulting from ethylene-oxide-containing sequences, so that copolymer degradation is registered as an exothermic process. A few percent of weight loss are visible only after the completion of melting (TG curve) and the degradation occurs at a maximum rate after 300° (good correlation between DTA and DTG curves).

In comparison with Hostaform C, the T-D copolymers obtained with BF_3.ACN as initiator seem to be much more thermostable and can be safely processed for practical purposes well above the crystalline melting temperature (Fig. 14). They do not lose weight up to 250° (TG curve) and degrade with a maximum rate after 350° (very good correlation between DTA and DTG curves).

Taking into account that the molar concentration of the initiator, or of complexed acrylonitrile, is very low, it is difficult at this moment to say why this type of initiation leads to improved thermal stability of the resulting copolymers. A simple explanation could be that both in chain growth reactions and in chain scissions the nature of the counterion (or zwitterion) plays an important role and consequently it is the sequential distribution, different from that given by other initiating systems, which can be made responsible for this particular thermal stability of T-D copolymers. A study based on this hypothesis is in progress.

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