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### Melting Behavior of Thermostable Trioxane-Dioxolane Copolymers Obtained with Boron Trifluoride: Acrylonitrile Complex as Initiator

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## Melting Behavior of Thermostable Trioxane-Dioxolane Copolymers Obtained with Boron Trifluoride:Acrylonitrile Complex as Initiator

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### ABSTRACT

The splitting of DSC melting endotherms of thermostable trioxane-dioxolane copolymers obtained with boron trifluoride:acrylonitrile complex as initiator, which were recorded before and after the annealing of samples at 140°C, was believed to result from an amorphous-crystalline coupling phenomenon brought about by noncrystallizable dioxolane fragments. Quantitative interpretations were made based on the total melting enthalpy and splitting factors after precipitation of dioxolane

sequences as crystalline defects by annealing. The results obtained were compared with similar data registered for a commercial trioxane containing copolymer, namely Hostaform C.

## INTRODUCTION

Commercially interesting polyoxymethylene copolymers are conventionally prepared by cationic polymerization of trioxane or formaldehyde and cyclic ethers such as dioxolane and ethylene oxide [1-4]. The participation of the second monomer usually amounts to a few percent in order to maximize melting point, hardness, tensile strength, modulus, and other physical properties of the copolymers. In order to keep the weight loss of polymers at a low level during stabilization, i.e., the operation made by depolymerization to remove the thermally and hydrolytically unstable polyformal endgroup segments, a random distribution of comonomers is desired. In the case of dioxolane, the copolymerization proceeds randomly and includes depolymerization [5], but even if its incorporation in the copolymer is thermodynamically less favorable [6], the comonomer is not randomly distributed [7]. The dioxolane block length of approximately five monomer units was calculated by Penchev et al. from the solvolytic stability of dioxolane containing polyoxymethylene copolymers [8]. Since only formal segments can crystallize to give rise to crystalline lamellae, the dioxolane blocks are incorporated as morphological defects. The large specific volume of these defects brings about a dimensional decrease of lamellae as the dioxolane concentration increases and consequently the melting temperature of the copolymer,  $T_m^0$ , is lowered to a limiting value [9]. On the other hand, the annealing process will determine a local precipitation of defects in interlamellar amorphous domains which will result in a lamellar disaggregation followed by a recrystallization by thickening of the lamellae.

The aim of the present paper is to show the universal phenomenon of precipitation of morphological defects by modification of melting endotherms of certain thermostable trioxane-dioxolane copolymers synthesized in the presence of boron trifluoride:acrylonitrile complex as initiator.

## EXPERIMENTAL

Trioxane (T) and dioxolane (D) were synthesized in the usual manner and the boron trifluoride:acrylonitrile complex was obtained by direct contact of these derivatives. The copolymerization was carried out in glass ampules. All the reaction mixtures were

prepared in vacuum through breakable seals [9]. The copolymers were end-capped by acetylation with an acetic anhydride-dimethylformamide mixture at 150° and subsequent Soxhlet extracted with acetone at reflux in order to remove any traces of dioxolane.

Melting endotherms were registered using a Du Pont 990 DSC apparatus. The annealing of copolymer samples (~ 5 mg) was made in the DSC apparatus (unsealed aluminum pans were used) at 140° in air after two consecutive heatings to 210° and quenchings at room temperature. Recording conditions: heating rate 10°/min and sensitivity 1 mcal/s·in.

## RESULTS AND DISCUSSION

The melting behavior of trioxane-dioxolane copolymers (TDC) was analyzed in comparison with that of a commercial polyoxymethylene containing sequences of ethylene oxide, namely Hostaform C. Both the investigated copolymers and Hostaform C are stable well above the melting range (150-180°) and no overlapping with any degradative processes were observed in their DTA curves [9].

Typical DSC melting thermograms of TDC which were not thermally treated are shown in Fig. 1. If the peak (or shoulder) which

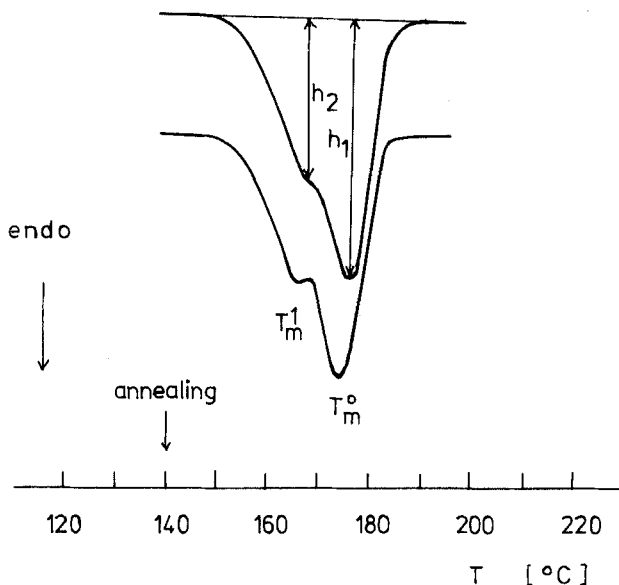


FIG. 1. Typical melting thermograms of trioxane-dioxolane copolymers. A higher  $T_m^0$  corresponds to a lower content of dioxolane in a copolymer.

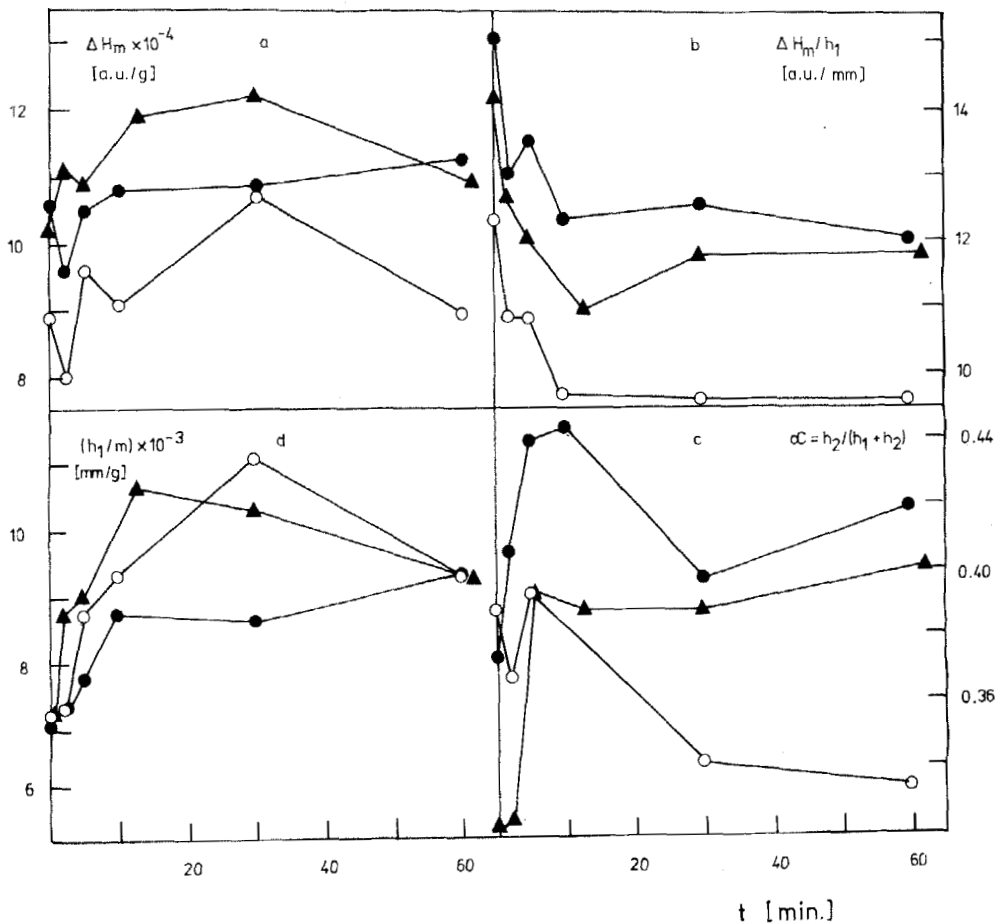


FIG. 2. The change of the crystalline morphology of trioxanedioxolane copolymers after annealing at 140°. Reaction conditions for synthesis according to Table 1: A ( $\circ$ ), B ( $\bullet$ ), and C ( $\blacktriangle$ ). a: Variation of the melting enthalpy. b: Variation of the amorphous-crystalline coupling coefficient. c: Variation of the splitting coefficient. d: Variation of the melting intensity at  $T_m^0$ .

appears at a lower temperature, denoted as  $T_m^1$  [10], is given by certain unstable polymeric species, it should vanish as a result of the thermal treatment, but after the annealing at 140° it has the tendency to separate from the actual melting endotherm of  $T_m^0$  [10], showing an amorphous-crystalline coupling phenomenon. This

TABLE 1. Reaction Conditions for the Synthesis of Trioxane-Dioxolane Copolymers Using Boron Trifluoride:Acrylonitrile Complex as Initiator in Benzene at 35°

Copolymer sample	Feed composition [T] <sub>0</sub> / [D] <sub>0</sub>	Concentration of monomers [T] <sub>0</sub> + [D] <sub>0</sub> (mol/L)	Initiator concentration (mol/L)	Reaction conversion time	
				min	%
A	12.4	3.82	0.0197	65	23
B	12.4	3.82	0.0197	225	66
C	20.0	2.13	0.0225	75	39

phenomenon is similar to that previously observed and reported on other crystalline polymers [ 10] or copolymers [ 11] annealed below the  $T_m^0$  melting point. By a rigorous study of this phenomenon [ 10]

it was revealed that in crystalline morphology the lamellar areas separate from the amorphous domains as a result of the applied treatments and that the kinetics of this process strongly depends on molecular configuration and conformation. The molecular defects in lamellar areas are responsible for morphological modifications by their migration toward a local amorphous domain. The resulting amorphous-crystalline coupling was quantitatively determined on the basis of the primary magnitudes associated to splitted endotherms corresponding to  $T_m^0$  and  $T_m^1$  peaks, namely  $h_1$  and  $h_2$ , which represent the heights from the base-line of the two peaks (in millimeters), respectively, and the total melting enthalpy,  $\Delta H_m$ , expressed in unit of endotherm peak area, i.e., related to the mass of the specimen. The following derived parameters related to amorphous-crystalline coupling were previously defined: the splitting coefficient,  $\alpha = h_2 / (h_1 + h_2)$ , the melting enthalpy of the crystalline phase,  $(1 - \alpha)\Delta H_m$ , and the ratio  $\Delta H_m / h_1$ .

The amorphous-crystalline transformation processes imply transport phenomena which are basically thermally activated and allow the determination of a universal activation energy [ 10] such as that reported for linear species of polyethylene by using the x-ray diffraction technique [ 12, 13]. A structural model of the amorphous-crystalline coupling that resulted after the precipitation of defects has recently been proposed by Dragan [ 10].

The change of the crystalline morphology of TDC of different compositions after the annealing at 140° for different periods of time, showing the variation of these parameters, is presented in Fig. 2. One can see that the annealing process is composed of two distinct

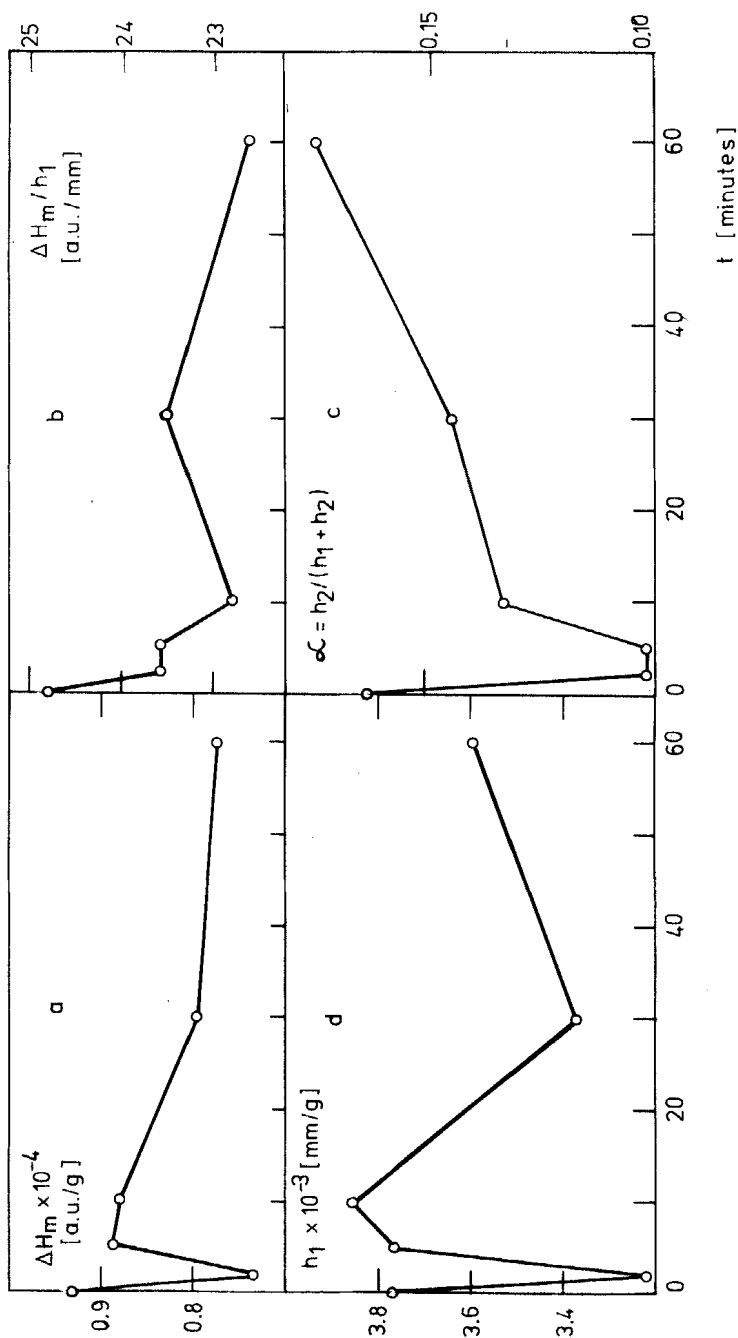


FIG. 3. The change of the crystalline morphology of Hostaform C after annealing at 140°. a: Variation of the melting enthalpy. b: Variation of the amorphous-crystalline coupling coefficient. c: Variation of the splitting coefficient. d: Variation of the melting intensity at  $T_m^0$ .

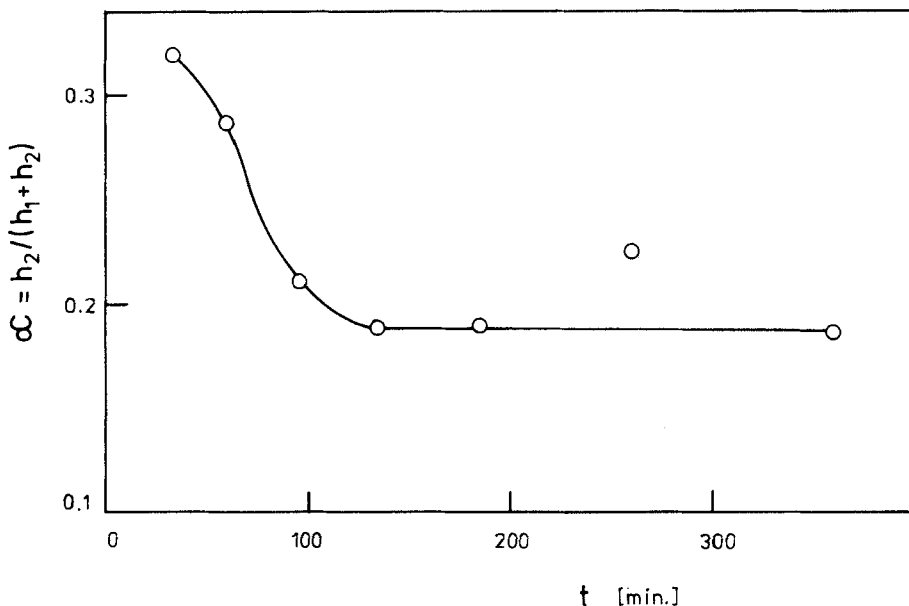


FIG. 4. The dependence of the splitting coefficient upon the synthesis time of TDC. Reaction conditions: temperature, 35°;  $[T]_0 : [D]_0 = 19.1$ ;  $[T]_0 - [D]_0 = 3.06$  mol/L;  $[BF_3 \cdot ACN] = 0.0221$  mol/L. Samples were annealed at 140° for 60 min.

stages as follows. The precipitation of dioxolane blocks toward local amorphous domains occurs in the first minutes of thermal treatment so that the crystalline lamellae are partially destroyed and consequently the splitting coefficient increases and the coupling coefficient  $\Delta H_m / h_1$  decreases. The content of dioxolane and its distribution in the copolymer play an important role in the behavior of TDC in this first stage. Thus, for a low D content ( $< 5\%$ ), the decrease of  $\Delta H_m / h_1$  is brought about by the sharp increase of  $h_1$  since  $\Delta H_m$  registers a certain increase too, while in the case of copolymers with  $[T]_0 : [D]_0 = 12.4$  the coupling coefficient decreases mainly due to the decrease of  $\Delta H_m$ . It has been shown by Ito et al. [6] that in the later stages of T-D copolymerization the microstructure of the copolymer changes to give longer polyformal sequences. This fact is also reflected by the magnitudes of  $\Delta H_m / h_1$  and  $\alpha$  associated with TDC samples synthesized at different reaction times, namely that the amorphous-crystalline coupling process is stronger for the copolymer obtained at higher conversion. In the second stage, since the



annealing temperature is rather close to the lower limit of the melting range (Fig. 1), additional crystallization takes place through the thickening of lamellar fragments, so that both  $\Delta H_m$  and  $h_1$  increase in all cases. The decrease of  $\alpha$  after the precipitation of defects, while  $\Delta H_m/h_1$  continues to decrease, indicates that the dioxolane blocks are large enough to cause a complete separation of local amorphous domains from the crystalline lamellar fragments. A marked decrease of the splitting coefficient is observed for the copolymer obtained at 23% conversion (Fig. 2c). It can be explained by the low density of interlamellar tie-molecules determined by the low molecular mass of copolymers separated at low conversions [9]. After 60 min of thermal treatment the amorphous-crystalline coupling approaches a limiting value (Fig. 2b). One can observe that the highest values for  $\Delta H_m/h_1$  are obtained for high conversions (Sample B) or low contents of dioxolane in TDC (Sample C, see Table 1).

Figure 3 presents the change of the same parameters after the annealing of Hostaform C. The decrease of  $\Delta H_m/h_1$  is brought about in this case by a simultaneous decrease of  $\Delta H_m$  and  $h_1$ . The crystalline domains diminished as morphological defects separated since both  $\Delta H_m$  and  $h_1$  continued to decrease in the second stage and after 60 min of treatment their magnitudes were lower than the initial values.

The variation of  $\alpha$  with copolymerization time for a sample annealed for 60 min is shown in Fig. 4. The splitting coefficient drops to a limiting value determined by dioxolane consumption and the increase of polyoxymethylene sequences in the later stages of the reaction [6, 9]. For the TDC obtained at a low conversion (Sample A, Table 1) and Hostaform C sample, the short stepwise decrease of  $\Delta H_m/h_1$  registered in the first stage is associated with a decrease of  $\alpha$  and  $\Delta H_m$  to minimum values, indicating that the precipitation process of morphological defects is also activated in volume, as observed from density measurements for other polymers [14].

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