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Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597274>

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Ioan I. Negulescu^a; Gheorghe Dragan^b; Mihai Dimonie^c; Nguyen Viet Bac^c

^a "Petru Poni" Institute of Macromolecular Chemistry, Jassy, Romania ^b Center of Physical Chemistry, Bucharest, Romania ^c National Institute of Chemistry, Bucharest, Romania

To cite this Article Negulescu, Ioan I. , Dragan, Gheorghe , Dimonie, Mihai and Bac, Nguyen Viet(1987) 'Thermal Degradation of Trioxane-Dioxqlane Copolymers Obtained with Boron Trifluoride-Acrylonitrile Complex as Initiator', *Journal of Macromolecular Science, Part A*, 24: 7, 787 – 796

To link to this Article: DOI: 10.1080/00222338708082094

URL: <http://dx.doi.org/10.1080/00222338708082094>

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THERMAL DEGRADATION OF TRIOXANE-DIOXOLANE COPOLYMERS OBTAINED WITH BORON TRIFLUORIDE-ACRYLONITRILE COMPLEX AS INITIATOR

IOAN I. NEGULESCU

“Petru Poni” Institute of Macromolecular Chemistry
Jassy 6600, Romania

GHEORGHE DRAGAN

Center of Physical Chemistry
Bucharest 77208, Romania

MIHAI DIMONIE and NGUYEN VIET BAC

National Institute of Chemistry
Bucharest 77208, Romania

ABSTRACT

The thermal degradation of certain trioxane-dioxolane copolymers obtained with boron trifluoride-acrylonitrile complex as initiator has been investigated. The thermal stability of samples, discussed in terms of topoenergetic values, was related both to copolymer composition and conversion. The most thermostable copolymers (~5% weight loss at 300°C in air), having 5-8% dioxolane units, had the highest intrinsic viscosity in the series and were isolated at 35-50% conversion. The results obtained were compared with similar data for a commercial trioxane-ethylene oxide copolymer containing 95% formal units.

INTRODUCTION

Polyoxymethylene materials of practical interest are conventionally prepared by cationic copolymerization of trioxane or formaldehyde with cyclic ethers, such as dioxolane and ethylene oxide, in order to improve the thermal stability of polyformal sequences [1-4]. The thermal stability of copolymers is further enhanced by limited depolymerization to remove the chain fragments with thermally and hydrolytically unstable end groups. Since only the polyoxymethylene sequences crystallize, the dioxolane or ethylene oxide blocks are incorporated as morphological defects and, consequently, the melting temperature of the copolymer is lowered to a limiting value [5]. On the other hand, the crystalline morphology determines both the nature and the extent of thermal degradation of these materials. Satisfactory thermal decomposition rates were reported in the patent literature when boron trifluoride complexes with oxygen- or nitrogen-containing vinyl monomers were used for the initiation of trioxane polymerization [6, 7].

The aim of the present paper is to extend this type of study and to present the thermal stability of certain trioxane-dioxolane (T-D) copolymers synthesized with boron trifluoride-acrylonitrile complex as initiator.

EXPERIMENTAL

Monomeric trioxane and dioxolane were synthesized in the usual manner from paraformaldehyde, and paraformaldehyde and ethylene glycol, respectively, using H_2SO_4 as catalyst. The boron trifluoride-acrylonitrile complex was obtained by direct contact of these derivatives. The copolymerization was carried out in benzene at 35°C in glass ampules. All the reaction mixtures were prepared in vacuum through breakable seals [5]. The copolymers were end-capped by acetylation with an acetic anhydride-dimethylformamide mixture at 150°C and subsequent Soxhlet extraction with acetone at reflux in order to remove any traces of dioxolane. The commercial trioxane-ethylene oxide copolymer (Hostaform C), containing 95% formal units, was used as received.

Thermogravimetric curves were recorded with a Paulik-Paulik-Erdey (Budapest) derivatograph. Topoenergetic parameters were obtained with a Du Pont 990 DSC apparatus under isothermal conditions.

Viscometric measurements were carried out at 60°C in *p*-chlorophenol containing 2% α -pinene as antioxidant (polymer concentration, 0.25 g/dL).

RESULTS AND DISCUSSION

Recently some general aspects of the morphology of composite systems have been reviewed in topoenergetic terms relative to the associated energetic circuits, and it was concluded that typical polymer behavior is characteristic for all composite systems, no matter what the nature of the transformation process involved [9]. In short, topoenergetic formalism has as its objective the replacement of the real nonequilibrium system by components with elementary behavior, such as dissipative, capacitive, and inductive, defined by constitutive equations. The basic concepts were initially introduced by Oster and Auslander [10, 11]. The adaptation of these concepts to real cases led to the basic working principle that all nonequilibrium systems are of a composite nature [12].

Most transformation processes are thermally driven, and their evolution can be studied in calorimetric systems such as *in vivo* measuring systems [12-14]. The transfer of the whole system from a starting temperature T , at which the process can be sensed in the measuring sensitivity range, and the consideration of constitutive equations for energetic elements in the respective circuit allow the formulation of the following kinetic equation [9, 15]:

$$\ln(t_m T) = -E/(RT) + k \quad (1)$$

where t_m is the time required for the maximum intensity of the conversion process (i.e., thermal degradation in the present case) to be reached, T is the absolute transformation temperature (in kelvins), E represents the activation energy of the process, R is the gas constant, and k is a parameter proportional to E and to the amount of inert component (i.e., in this case to the most thermostable) in the sample. This equation was verified for certain thermally driven transformation processes specific to macromolecular systems, including 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 [13-15]; as well as synthesis [9, 16] or reactions of polymeric materials [17, 18].

In the domains of validity, parameters E and k univocally define the behavior of the system in the energetic circuit under consideration. From the physical point of view, in the present case the two quantities can establish the behavior of a system during thermal degradation relative to another one considered as standard. In the absolute units of the measuring system, the

TABLE 1. Thermal Stability of Certain Trioxane Polymers Expressed in Topoenergetic Terms According to Eqs. (1) and (2)

Material	Comonomer content, ^a %	Intrinsic viscosity, ^b dL/g	E_r , kJ/mol	k_r , [ln (s·K)]	k_s , $\left(\ln \frac{s \cdot K}{\text{kJ/mol}}\right)$
Homopolymer	0.0	0.502	123	-22.7	-27.5
Hostaform C	5.0 ^c	0.815	85	-7.9	-12.4
T-D copolymer, 57% conversion	5.0	0.445	35	-0.3	-3.9
T-D copolymer, 35% conversion	8.1	0.479	28	4.6	1.3
T-D copolymer, 49% conversion	8.1	0.510	22	6.0	2.9

^aInitial molar concentration in feed.

^bDetermined in *p*-chlorophenol.

^cApproximate molar concentration of ethylene oxide.

amplitude (i.e., the extent) of the process with respect to the standard system is expressed by parameter k . However, the definition of amplitude in terms of parameter k may be considered as rather approximate since k depends on E [9] and, therefore, the following magnitude has been defined [15]:

$$\kappa = k - \ln E. \quad (2)$$

Table 1 presents these parameters for a series of trioxane polymers. The samples are listed in increasing order of thermal stability according to the magnitudes of k and κ . It is obvious that the content of dioxolane in a copolymer affects the thermal stability. It was, however, established that in order to improve this property without any detrimental effect on mechanical characteristics, the amount of the second monomer in the trioxane copolymer should not exceed a few mole percent.

The inert component (measured by κ) increases both with the comonomer content and the molecular weight (indicated by the intrinsic viscosity). Furthermore, from the variation of intrinsic viscosity with conversion for a T-D copolymer containing 5% dioxolane units (Fig. 1), one can see that κ varies continuously with a maximum at 30-50% conversion. Due to transfer reactions with scission which characterize the cationic polymerizations of cyclic ethers [19-21], the intrinsic viscosity thereafter drops rather quickly. Therefore, a sample taken at 70% conversion has an intrinsic viscosity similar to one isolated in the early stages of copolymerization. On the other hand, the dioxolane is consumed preferentially in the early stages of the polymerization and, consequently, the early copolymer is rich in this monomer than in the later stages when the copolymer has longer polyoxymethylene sequences which resemble the homopolymer, and hence a lower thermal stability [5]. Indeed, as shown by the corresponding values of k and κ for T-D Copolymers 4 and 5 (Fig. 2), the molecular weight, dictated by conversion [16, 22], determines the thermal stability (i.e., positive k and κ).

The above observations are in good agreement with the nonisothermal treatment of these materials (Fig. 3): the homopolymer (characterized by large negative k and κ , Table 1) is less thermally stable than the commercial standard. But the most thermostable sample, with ~5% weight loss at 300°C, is the T-D copolymer which, according to Fig. 1, corresponds to the maximum intrinsic viscosity. The last conclusion is also supported by the data of Fig. 4, which presents the weight loss at three temperatures for T-D copolymers synthesized under the same conditions but at different conversions.

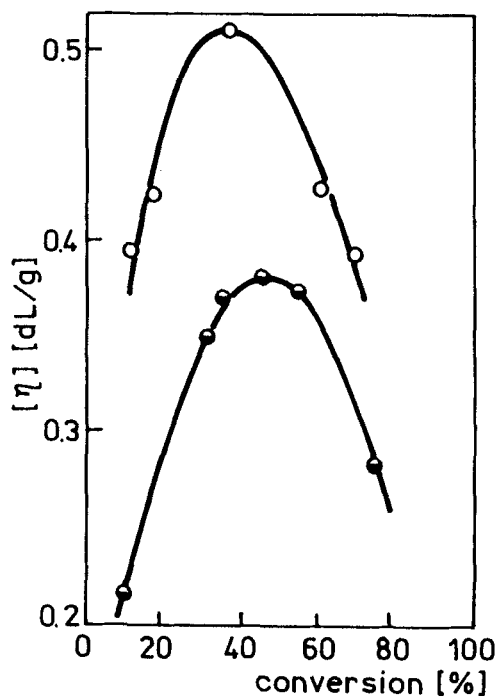


FIG. 1. Variation of intrinsic viscosity of two trioxane-dioxolane copolymers with conversion. Reaction conditions: concentration of monomers, 3.8 mol/L; initial molar concentration of dioxolane, 0.05; initiator concentration, 0.02 (○) and 0.03 mol/L (●).

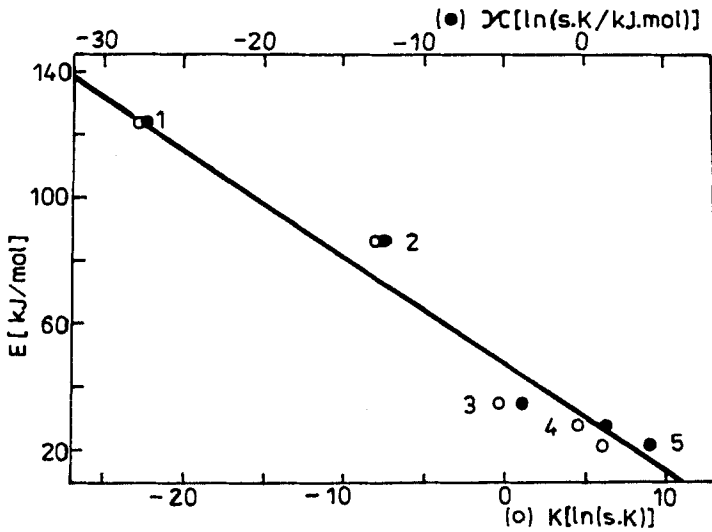


FIG. 2. Topoenergetic parameters for thermal decomposition of some trioxane copolymers: (1) Hostaform C, standard; (2) T-D copolymer with 0.05 molar concentration of dioxolane taken at 57% conversion; (3) *idem.*, with 0.08 dioxolane and 26% conversion; (4) *idem.*, with 0.08 dioxolane and 43% conversion; (5) *idem.*, with 0.05 dioxolane and 45% conversion.

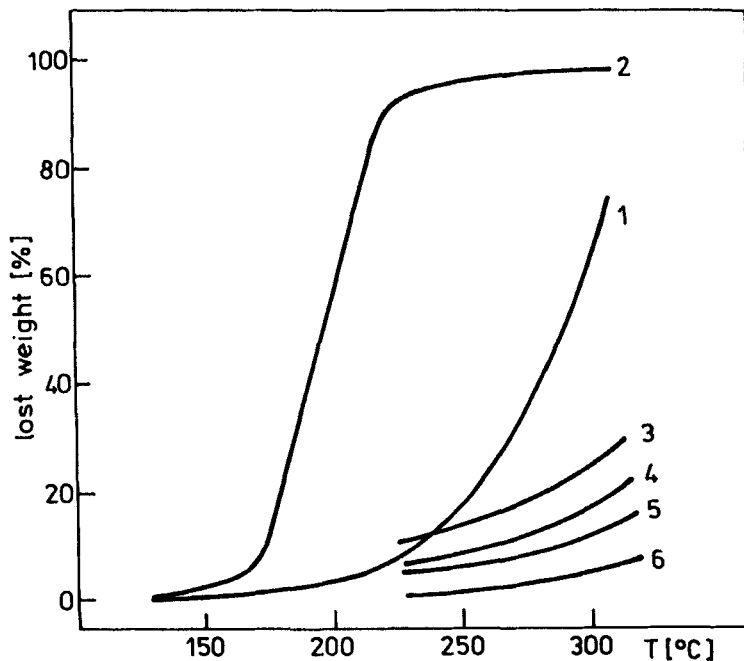


FIG. 3. Thermal stability in air of some trioxane copolymers expressed by weight loss under nonisothermal conditions. Heating rate, $10^{\circ}\text{C}/\text{min}$. (1) Hostaform C; (2) homopolymer; (3) T-D copolymer with 0.05 molar concentration of dioxolane taken at 57% conversion; (4) *idem.*, conversion 6%; (5) *idem.*, conversion 14%; (6) *idem.*, conversion 45%.

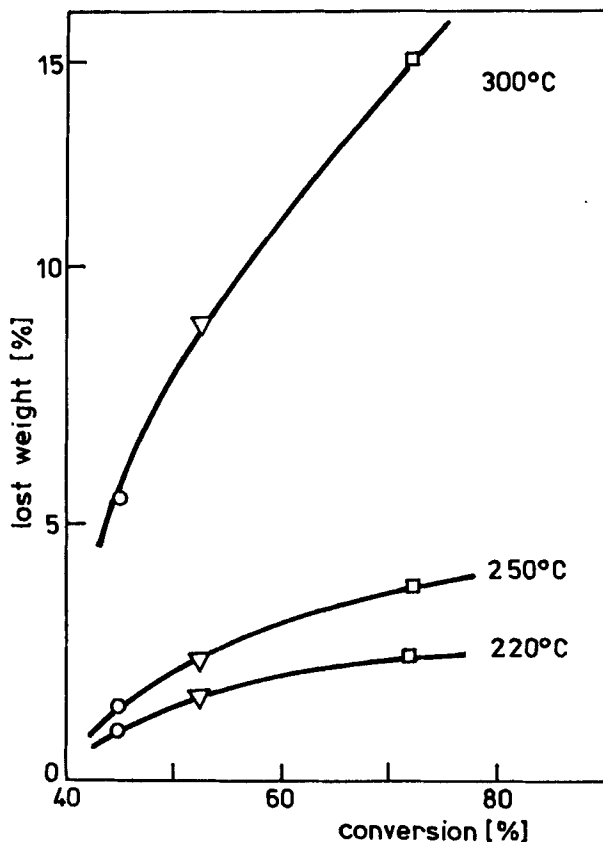


FIG. 4. Thermal decomposition in air of T-D copolymers with 0.05 molar concentration of dioxolane taken at different conversions: 45% (○), 54% (▽), and 73% (□). Heating rate, 10°C/min.

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Received January 9, 1986

Revision received September 22, 1986