

Electroinitiated Polymerization of Trioxane Dispersed in *n*-Hexane and *n*-Heptane

GIULIANO MENGOLI and GRAZIANO VIDOTTO, *Laboratorio di Polarografia ed Elettrochimica Preparativa del Consiglio Nazionale delle Ricerche, Padova, Italy*

Synopsis

The possibility of electroinitiating the polymerization of melted trioxane dispersed in *n*-hexane and *n*-heptane has been investigated. It was found that the addition under stirring of an electrolyte to these dispersions added a satisfactory electrolytic conductivity: this fact allows, by a fast current pulse, the anode transfer of a charge suitable to initiate the polymerization process. The kinetics of the polymerization do not exhibit substantial induction periods and depend both on the charge initially transferred to the system and on the diluent-to-monomer ratio. The molecular weights of the products, which are generally high, are controlled by the same parameters and by the extent of the monomer-to-polymer conversion. The effect on the process of the background electrolytes perchlorate and tetrafluoroborate of tetrabutylammonium has been investigated, and the possible initiation mechanism has been discussed. The conditions also for obtaining thermally stabilized products by trioxane-1,3-dioxolane copolymerization in the same systems have been shortly investigated.

INTRODUCTION

We have already investigated in previous papers the electroinitiated polymerization of trioxane in both highly polar solvents^{1,2} and in bulk.³ It has been found that the trioxane polymerization carried out in acetonitrile, for instance, gives only oligomeric poly(oxy methylenes) at low current yield, while in benzonitrile and in nitrobenzene, one obtains products with higher molecular weights and yields. The solvent affects the polymerization process either with regard to reaction rate or molecular weight and therefore affects the physical properties of the resulting products.

The bulk electroinitiated polymerization presents, on the contrary, a substantially "living" character, and the reaction rates and the molecular weights of the corresponding products can be varied by acting on the electrode charge transfer, that is, on the active species initially supplied to the system. Several limits are, however, imposed on such a control by the highly exothermic character of the reaction and by its rapid kinetic course that can be of the flash type in the case of well-anhydrous monomer. Moreover, the formation of one insoluble block of high mechanical resistance at high conversion makes it considerably difficult to recover and handle the obtained polymer.

In the polymerization systems constituted by trioxane and initiated by chemical catalysts, it is preferred to operate in the presence of an inert diluting liquid.⁴ A saturated hydrocarbon is normally selected having a boiling point slightly above the trioxane melting point where the monomer is only partially dissolved and mostly dispersed. Under these conditions, the heat of polymerization reaction as well as the physical particle size of the products are controlled.⁴

This paper investigates the feasibility of electrocatalysis for the polymerization of trioxane dispersed in *n*-hexane and *n*-heptane hydrocarbons. The best operating conditions of the system and the role played by diluent dispersing agents of nonpolar paraffin type have been examined.

EXPERIMENTAL

Materials

Trioxane (TRO), a pure Merck product, was dried using CaH₂ powder and distilled under ambient nitrogen. The fraction boiling at 114°C was selected. 1,3-Dioxolane (DOX), a pure Merck-Schuchardt product, was purified using the same method as TRO. *n*-Hexane and *n*-heptane, R. P. C. Erba products, were dried using Na/K alloy and distilled before use. Tetrabutylammonium perchlorate (TBAP) and tetrabutylammonium tetrafluoroborate (TBBF₄) were prepared from tetrabutylammonium hydroxide and perchloric and fluoboric acids, respectively.

Apparatus and Procedure

The electrolyses were conducted using an amperostat at high-outlet potential (800 volts), capable of supplying currents in the range of 0.5–50 mA. A U-shaped cell was used having a 2-cm² platinum net as anode and a mercury cathode; the latter, filling completely a cell compartment, was separated from the anode compartment by sintered glass. Only one compartment of the cell was thus charged with the reaction mixture: with respect to a regular cell with separated compartments, this type involved a decrease in the electric resistance and a minimum of reagents. This device could be adopted because the current intensity was always extremely low and the cathodic product (tetraalkylammonium amalgam dispersed in the cathode) has practically no possibility of contacting the polymeric active centers insoluble in the reaction medium. The cell was supplied with a double jacket for the circulation of the thermostatic liquid, and the reaction compartment could be submitted to regular mixing by a stirrer adjustable up to 900 rpm, coaxial to the anode platinum net. Once initiated, the polymerization was stopped at the desired conversion before its spontaneous exhaustion by adding methanol-NH₃ to the system. Monomer-to-polymer conversion was gravimetrically determined from the resulting polymer or gas-chromatographically metering the residual monomer.

The molecular weights of the purified and dried samples were viscometrically determined at 25° in hexafluoroacetonesesquihydrate containing 2% of the triethylamine according to the relation⁵

$$[\eta] = 4.6 \cdot 10^{-2} \bar{M}_v^{0.74}$$

where $[\eta]$ is expressed in ml/g and \bar{M}_v is the viscometric average molecular weight.

RESULTS AND DISCUSSION

Polymer Yield and Molecular Weights in the *n*-Hexane/TRO Systems

Figure 1 reports the solubility of solid TRO in *n*-hexane and *n*-heptane. At the operating temperature selected (65.5°C), slightly higher than the melting temperature of TRO (62–64°), there is a further increase in solubility; thus, about 13% of TRO in *n*-hexane (g/ml) is in solution. Higher TRO concentrations in *n*-hexane lead to the formation of two distinct phases: liquid TRO and a saturated solution of TRO in *n*-hexane. By submitting these systems to suitable and regular stirring (a standard rate of 500 rpm was selected), one obtains homogeneous dispersions. The dispersions after the addition of an electrolyte at diluent-monomer molar ratios ranging from 2 to 0.2 present a satisfactory electrolytic conductivity; in fact, currents of 5–15 mA/cm² are obtained by applying a voltage from 100 to 200 volts to the previously described cell type.

When a charge beyond a given threshold limit, likely due to the presence of impurities, is transferred with a rapid current impulse to one of these *n*-

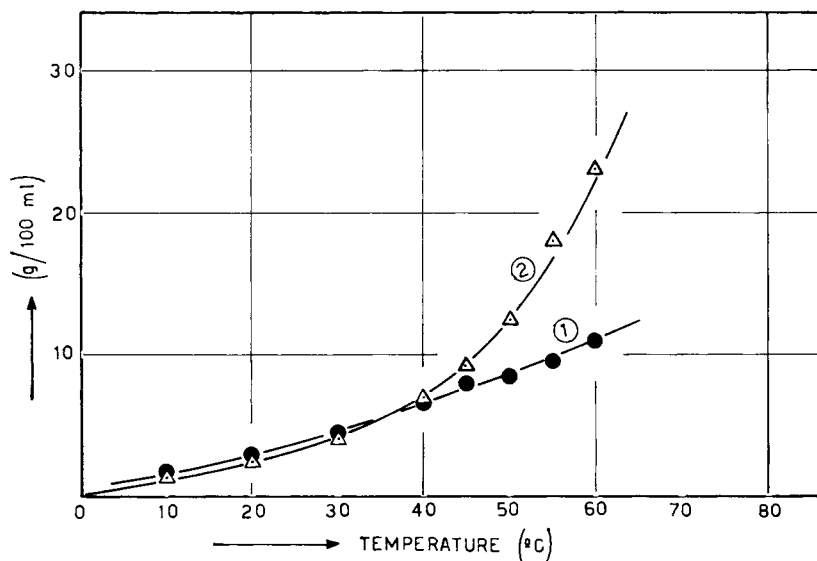


Fig. 1. Solubility of TRO in *n*-hexane (curve 1) and *n*-heptane (curve 2) as a function of temperature.

TABLE I
 Polymerization of TRO in *n*-Hexane for Various Polymerization Times^a

Run no.	Reaction time, min	Polymer yield, %	$\bar{M}_v \times 10^{-3}$	Polymer moles/Faraday
1	1	1.5	5.5	35
2	2	5.5	21.0	34
3	3	6.0	28.0	28
4	5	9.0	50.0	23
5	9	18.0	54.0	43
6	12	28.0	60.0	60
7	15	23.0	53.0	56
8	40	43.0	80.0	69
9	120	47.5	74	83

^a Initial conditions: TRO = 0.22 mole; *n*-hexane = 0.153 mole; TBAP = 1.17×10^{-3} mole; furnished charge = 1.55×10^{-6} Faraday; *t* = 65.5°C.

hexane/TRO systems, TRO polymerization is initiated as evidenced by the separation and gradual grow of a polymeric solid phase.

Table I reports the data relative to a set of polymerization runs performed at 65.5°C by supplying a 1.55×10^{-6} Faraday charge with a total current of 10 mA within 15 sec to the system consisting of 0.222 moles TRO, 0.153 moles *n*-hexane, and 1.17×10^{-3} moles TBAP and stopping the reaction at different reaction times by the addition of CH₃OH/NH₃.

Each experimental operation was carried out under similar conditions, and the reagents used were drawn from the same purified and anhydrous stocks. As can be observed, monomer-to-polymer conversion and the polymerization degree of the products increase with time up to a maximum value of about 45%. As appears from Table I, the number of polymer moles formed by each Faraday (such a number is largely approximate since it is computed from \bar{M}_v) is always, from the very beginning, much larger than unity and presents slightly increasing values on increasing conversion for monomer consumption above $\simeq 6\%$. In other words, the polymerization in the first stages presents a large multiplication of the molecules produced for each active center anodically formed in the system; the propagation reaction subsequently shows a living character (polymerization degree increases with conversion) even if the system is still affected by some weak transfer and termination reaction.

The process does not seem to differ qualitatively from the electroinitiated bulk polymerization³ where the large number of polymer moles found from the first stages has been attributed to the transfer with residual water traces that limit the polymer chain without affecting the kinetics and, once consumed, allow the addition of the monomer to the living active centers of the polymer. In the present system, the subsequent weak transfer and termination reactions are likely to be attributed to the *n*-hexane diluent or to impurities there included, since in the corresponding bulk polymerization initiated by a comparable charge transfer at the same temperature, conversion and molecular weight continuously increase up to complete monomer-to-polymer conversion.

TABLE II
 TRO polymerization for various $[n\text{-hexane}]/[\text{TRO}]$ initial ratios

Run no.	$n\text{-Hexane}$, ml	TRO, g	$[n\text{-hexane}]/[\text{TRO}]$	Furnished charge, Faraday $\times 10^6$	Reaction time, min	$\bar{M}_v \times 10^{-3}$	Polymer yield, %	Polymer moles/Faraday
10	30	10	2.09	3.36	8	15	25.0	50
11	21	15	0.97	3.36	8	30	30.0	44
12	20	20	0.69	3.36	8	46	33.0	42
13	16	25	0.45	3.36	8	80	35.0	32
14 ^a	20	11	1.25	0.83	40	27	33.5	165
15 ^a	20	15	0.93	1.15	40	38	40.5	139
8 ^a	20	20	0.69	1.55	40	80	43.0	69
16 ^a	10	30	0.205	2.33	40	100	49.0	63

^a Experiments with the same Faraday/TRO ratio; $t = 65.5^\circ\text{C}$; TBAP = 1.17×10^{-3} mole.

 TABLE III
 TRO Polymerization in $n\text{-Hexane}$ Initiated by Different Charge Transfers^a

Run no.	Charge, Faraday $\times 10^6$	$\bar{M}_v \times 10^{-3}$	Polymer yield, %	Polymer moles/Faraday
17	0.77	—	—	—
4	1.55	50	9	23
18	2.33	40	20	43
19	3.11	35	22	41
20	4.66	25	29	50
21	6.22	18	32	57
22	7.76	18	37	53
8 ^b	1.55	80	43	69
23 ^b	3.11	48	50	67
24 ^b	4.66	35	55	67
25 ^b	0.93	31	10.0	69

^a Initial conditions: TRO = 0.222 mole; $n\text{-hexane}$ = 0.153 mole; TBAP = 1.17×10^{-3} mole; $t = 65.5^\circ\text{C}$; reaction time = 5 min.

^b Reaction time = 40 min.

On the other hand, the extent of transfer and termination reactions occurring with the diluent $n\text{-hexane}$ (or with related impurities) are better evidenced by polymerization experiments performed at various initial $[n\text{-hexane}]/[\text{TRO}]$ ratios and stopped at a fixed time; the experimental conditions and the results obtained from these runs are reported in Table II. Experiments 14–16 of Table II performed at the same $[\text{Faraday}]/[\text{TRO}]$ ratio clearly indicate that a chain-limiting process is bound to the diluent $n\text{-hexane}$, whereas experiments 10–13 are affected by some additional effects due to the fact they have not been carried out at constant $[\text{Faraday}]/[\text{TRO}]$ ratio. With regard to this, the data reported in Table III allow to determine the effect of the charge transferred to initiate polymerization on the conversions and molecular weight of the products; all the experimental conditions are specified in the table. As can be observed,

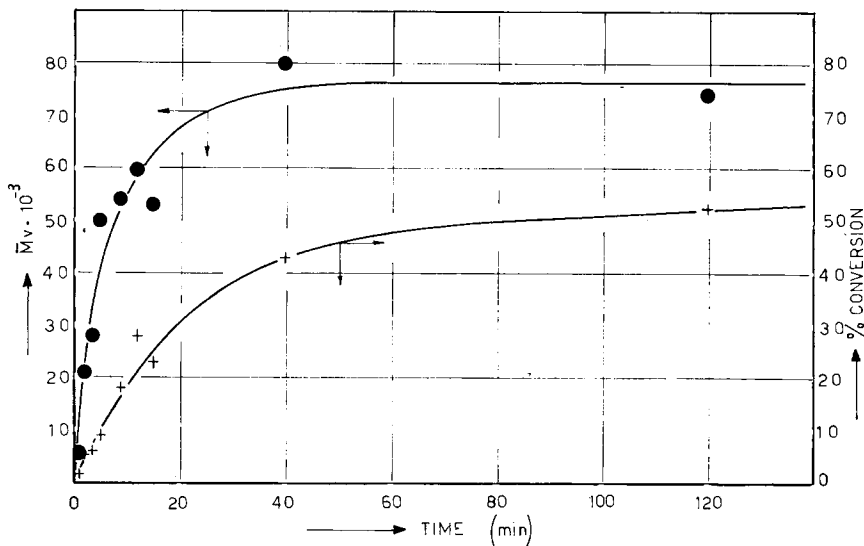


Fig. 2. Conversion and molecular weight of poly(oxymethylene) as a function of time for TRO polymerization in *n*-hexane.

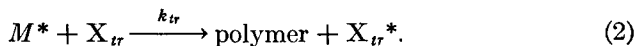
there is a threshold charge below which TRO polymerization is not initiated²; for a charge larger than the threshold, the conversion at a given time increases while the degree of polymerization generally decreases with the furnished charge.

Summarizing from Tables I-III, the reaction variables which affect the molecular weight of the polymers are (a) the extent of the monomer-to-polymer conversion, (b) the initiator concentration (i.e., the furnished charge), and (c) the concentration of the diluent *n*-hexane.

An increase in the molecular weight of the polymers formed in the course of polymerization is found only when the rate of the propagation and possible transfer reactions are smaller than that of initiation.^{6,7} Under these conditions, the number-average degree of polymerization \bar{P} expressed as ratio of monomer consumed $[M]_0 - [M]$ to the number of polymer moles formed, that is, to the number of initiation and transfer acts, is described by eq. (1)^{6,7}:

$$\bar{P} = \frac{[M]_0 - [M]}{\alpha[C]_0 + k_{tr} \int [M^*][X_{tr}] dt} \quad (1)$$

where α is a constant which denotes the mole concentration of growing ends produced per mole of catalyst $[C]$, $[M^*]$ is the active center concentration, and $[X_{tr}]$ is the concentration of the transfer agent affecting the polymerization according to reaction:



Now, the present system is not easily suitable for rigorous analysis owing to its high heterogeneity and the experimental difficulty of determining

\bar{M}_n in so wide a range of molecular weights for products insoluble in all the usual solvents. However, the data of Tables I-III suggest a qualitative agreement with eq. (1) when substituting $[F]$ the Faraday/l initially transferred for $[C]_0$. The dependence of \bar{P} on the fractional conversion derived from eq. (1) is related to the chemical nature of X_{tr} : it has been shown⁷ that if the transfer agent is water, its consumption during the polymerization leads to a continuous strong increase in \bar{P} .

On the other hand, if the transfer agent X_{tr} does not substantially decrease during the polymerization, the \bar{P} of the product initially increases reaching a maximum, then decreases on increasing the conversion.

Here, according to the plot of Figure 2, the strong increase of the molecular weights in a limited range of the conversion followed by a substantial constancy or decrease in the same suggest that, after the water consumption, some slight transfer might be ascribed to *n*-hexane itself.

Kinetics and Initiation Mechanism

From the data of Table III, the relation between the transferred charge and the polymerization reaction clearly appears even if the kinetic process (conversion at a given time) may be linearly bound to the promoting charge only at the lowest conversions (see Fig. 3, curves 1 and 2); the deviation found at the highest initiator concentrations is likely to be caused by the critical variation of the physical properties of the system occurring at the highest conversions either owing to the volume of the polymeric solid phase or the variation in the dispersed monomer phase/dissolved phase ratio.

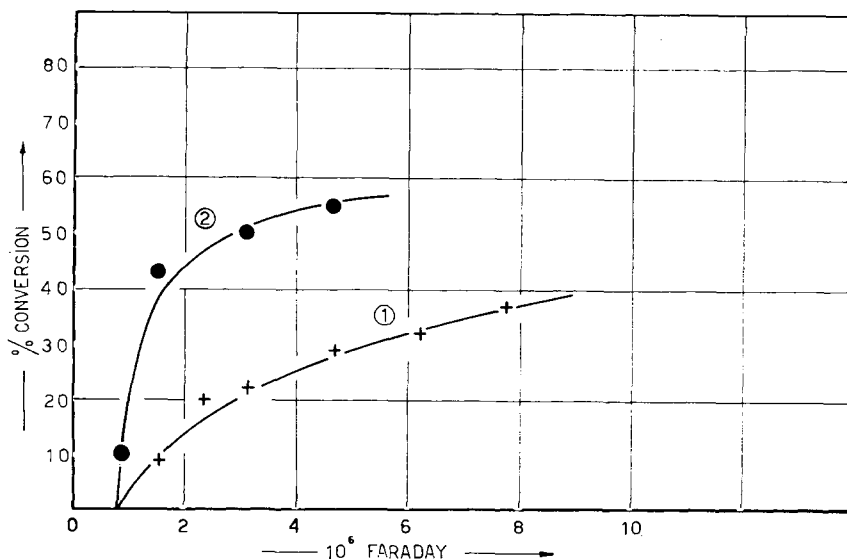


Fig. 3. Conversion at fixed time as a function of charge furnished to polymerization system TRO/*n*-hexane.

Moreover, the basis of the data of Table I showing evidence of a living character of the process and of Table II showing a decrease of conversion at a given time with increase in $[n\text{-hexane}]/[\text{TRO}]$ ratio, the system under study can be probably described by a kinetic law.

The process presents a rapid initiation, and at least in its initial stage the monomer decay might follow a law of the type:

$$-\frac{d[M]}{dt} = k_p[M^*][M]. \quad (3)$$

Using this equation and giving $[M]$ the initial TRO value referred to the total volume of the system and $[M^*]$ the value of the transferred Faradays/l after subtracting the threshold value, an indicative value of k_p , a specific propagation constant might be deduced from the initial slope of kinetic curves of the type reported in Figure 2 and built up by points from the conversion data of Table I.

The replacement of Faraday/l for $[M^*]$ presumes an unit efficiency for the anode initiation reaction whose nature has not so far been considered in this paper. We have previously found³ in the analysis of current potential curves for the $\text{CH}_3\text{CN}/\text{TRO}/\text{TBAP}$ system, that the only anode process taking place is the oxidation of ClO_4^- ion. Since $n\text{-hexane}$ is not suitable for direct anode oxidation, the initiation reaction in the present system seems still attributable to the oxidation of perchlorate ion. Since this process produces perchloric acid,⁸ the polymerization is electrocatalyzed via H^+ ions: furthermore, as each charge transfer involves the formation of an H^+ ion, once a threshold value with possible basic impurities is consumed, it appears reasonable to attribute a unit efficiency to the transferred Faradays.

However, in order to support these findings and to verify the effect of the support electrolyte on the product and best operation conditions for its synthesis, a series of experiments was carried out using different electrolytes and different electrolyte concentrations; the results obtained are reported in Table IV. Runs 26–29 refer to polymerizations electroinitiated under the same experimental conditions but with different TBAP concentration. The results show that TBAP electrolyte, at least for the concentration range examined, does not substantially affect the molecular weights of the polymers and therefore probably does not take part in any chain-limiting process. On the other hand, a certain difference in the conversion at a given time could concern the variation in the chemical-physical characteristics of the dispersion caused by variation in the ionic force.

Runs 30–35 were performed using TBBF_4 electrolyte. Considerable increase of molecular weights and conversions can be observed which are not reached with TBAB for the same $n\text{-hexane}/\text{TRO}$ ratio. What is still more remarkable is the increase in both the threshold value and the charge required to initiate the process; the differences, in fact, exceed a magnitude order. From such comparison, particularly as regards the charge for initiating the process, it clearly appears that the anode process is only

TABLE IV
TRO Polymerization in *n*-Hexane for Various Amounts
of TBAP and TBBF₄ Background Electrolytes*

Run no.	TBAP, moles	TBBF ₄ , moles	Furnished charge, Faraday	Reaction time, min	Polymer yield, %	$\bar{M}_v \times 10^{-3}$	Polymer moles/Faraday
26	$1.46 \cdot 10^{-4}$	—	$3.36 \cdot 10^{-6}$	8	25.0	42	35
27	$4.40 \cdot 10^{-4}$	—	$3.36 \cdot 10^{-6}$	8	28.0	50	33
12	$1.17 \cdot 10^{-3}$	—	$3.36 \cdot 10^{-6}$	8	33.0	46	42
28	$2.93 \cdot 10^{-3}$	—	$3.36 \cdot 10^{-6}$	8	45.0	40	67
29	$5.86 \cdot 10^{-3}$	—	$3.36 \cdot 10^{-6}$	8	38.0	55	41
30	—	$3.3 \cdot 10^{-3}$	$3.73 \cdot 10^{-5}$	15	52.5	84	3.3
31	—	$6.6 \cdot 10^{-4}$	$8.28 \cdot 10^{-5}$	15	65.0	70	2.2
32	—	$13.2 \cdot 10^{-4}$	$3.73 \cdot 10^{-5}$	30	—	—	—
33	—	$13.2 \cdot 10^{-4}$	$6.60 \cdot 10^{-5}$	15	60.0	68	2.8
34	—	$13.2 \cdot 10^{-4}$	$15.55 \cdot 10^{-5}$	15	78.0	48	2.1
35	—	$26.4 \cdot 10^{-4}$	$13.05 \cdot 10^{-5}$	15	76.5	54	2.2

* Initial conditions: TRO = 0.222 mole; *n*-hexane = 0.153 mole; *t* = 65.5°C.

bound to the oxidation of the support electrolyte, which likely does not involve the formation of the same initiator ion H⁺ in the electroinitiation with TBBF₄ electrolyte as indicated by the sharp decrease in the kinetic chain length. Even if the electrolytic initiation with TBBF₄ can presently only be speculated upon, it could be reasonably supposed that the anodic reaction involves the formation of BF₃ or other "acid" species of boron. On the other hand, conversions and molecular weights higher than those with the TBAP electrolyte might imply that there is a difference in the structure of the growing chain ends due to the different counterion between the two polymerization systems.⁷

Electroinitiated Polymerization of TRO in *n*-Heptane

As appears from curve 2 of figure 1, the TRO solubility in the proximity of its melting point increases in *n*-heptane much more rapidly than in *n*-hexane and is higher by 30% w/v at the operating temperature selected (65.5°C). For the same diluent-to-monomer ratio, the amount of dispersed TRO phase in *n*-heptane is considerably reduced with respect to the previous *n*-hexane/TRO system.

Table V reports the data of a set of polymerization experiments carried out by supplying a charge of 1.55×10^{-6} Faradays to the system 0.222 moles TRO, 0.137 mole *n*-heptane, and 1.17×10^{-3} moles TBAP (i.e., with a *n*-heptane/TRO ratio of 0.62) using a total current of 10 mA for 15 sec. The reactions were stopped at different times by addition of NH₃/CH₃OH. Figure 4 thus obtained illustrates the kinetic trend of conversions and molecular weights built up by points. A higher process rate leading to higher limit conversions and therefore to lower molecular weights of the products of the products appears with respect to polymerization in *n*-hexane. The

TABLE V
 Polymerization of TRO in *n*-Heptane for Various Polymerization Times*

Run no.	Reaction time, min	Polymer yield, %	$M_v \times 10^{-3}$	Polymer moles/Faraday
36	1	1.2	2.2	70
37	2	5.0	5.6	115
38	3	15.5	28.0	71
39	7	27.0	33.0	106
40	16	48.0	33.0	188
41	36	58.5	30.0	251
42	120	60	26.0	297

* Initial conditions: TRO = 0.222 mole; *n*-heptane = 0.137 mole; TBAP = 1.17×10^{-3} mole; furnished charge = 1.55×10^{-6} Faraday; $t = 65.5^\circ\text{C}$.

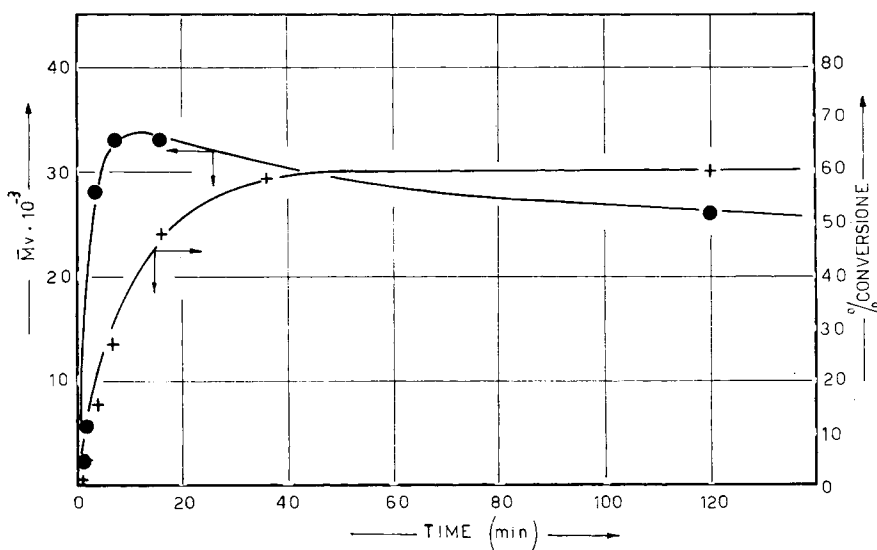


Fig. 4. Conversion and molecular weight of poly(oxymethylene) as a function of time for TRO polymerization in *n*-heptane.

number of polymer molecules formed for each Faraday supplied to the system is on the average always higher than in the correspond polymerization conducted in *n*-hexane and increases more appreciably with monomer-to-polymer conversion; these data would explain the lower molecular weights obtained with a more active role played by *n*-heptane as a transfer agent with respect to *n*-hexane.

Since the two diluents obtained from the same dehydration present the the same H_2O content and the chemical reactivity should, moreover, be very close owing to their similar structure, the higher activity of *n*-heptane as a transfer agent with respect to *n*-hexane could be attributed to its higher dissolving power toward the monomer. In this regard, there is a strict connection between the polymer increase in Figure 4 and the data reported by

TABLE VI
Polymerization of TRO for Various [*n*-heptane]/[TRO] Initial Ratios^a

Run no.	<i>n</i> -Heptane, ml	TRO, g	[<i>n</i> -Heptane]/[TRO] ratio	Furnished charge, Faraday $\times 10^6$	Reaction time, min	$\bar{M}_v \times 10^{-3}$	Polymer yield, %	Polymer moles/Faraday
43	30	10	1.870	3.36	8	15.0	27.0	54
44	25	15	1.040	3.36	8	28.0	42.0	67
45	20	20	0.620	3.36	8	24.0	58.0	144
46	15	25	0.370	3.36	8	58.0	60.0	77
47 ^b	20	10	1.240	0.78	36	17.5	47.0	345
48 ^b	20	15	0.830	1.18	36	27.0	57.5	270
41 ^b	20	20	0.620	1.55	36	30.0	58.5	251
49 ^b	10	20	0.305	1.55	36	52.0	65.0	161

^a $t = 65.5^\circ\text{C}$; TBAP = 1.17×10^{-3} mole.

^b Experiments with the same [Faraday]/[TRO] ratio.

TABLE VII
Polymerization of TRO in *n*-Heptane Performed at Different Temperatures^a

Run no.	$t, ^\circ\text{C}$	Polymer yield, %	$\bar{M}_v \times 10^{-3}$
45	65.5	58.0	24.0
50	76.5	55.0	18.5
51	86.5	50.0	21.0

^a Initial conditions: TRO = 0.222 mole; *n*-heptane = 0.137 mole; TBAP = 1.17×10^{-3} mole; furnished charge = 3.36×10^{-6} Faraday.

Onyon⁹ for the polymerization of TRO dissolved in cyclohexane; after the initial formation of a high number of oligomers, the polymerizations show a living character in the increase in molecular weight with conversion up to a limiting value which afterward decreases on increasing conversion (that is, on increasing the *n*-heptane/TRO ratio).

A further evidence of the specific action of *n*-heptane diluent is given by the experiments of Table VI, conducted at various *n*-heptane/TRO ratios. Even if the data reported cannot be quantitatively utilized due to the reasons discussed for Tables II and III, it clearly appears that rates (conversion at a given time) and molecular weights decrease on increasing the *n*-heptane/TRO ratio. The rate decrease indicates a real termination or degradative chain transfer of the active centers to *n*-heptane if the polymerization rate depends on monomer concentration at the first power, while the decrease of the molecular weight at almost constant conversion is evidence of the chain transfer action of *n*-heptane.

The relation between the dissolving power and the activity of *n*-heptane as chain transfer agent could also be supported by the data of Table VII, where the products obtained at different temperatures are compared. While in previous investigations on TRO polymerization in different solvents, a considerable increase of the molecular weight with temperature has gen-

erally been experienced, that is, the activation energy of propagation was superior to any other activation energy concerning the chain-limiting reactions, an opposite tendency is now verified while TRO passes from a partially dispersed phase at 65.5°C to a completely dissolved one at 85.5°C.

Physical Properties of the Resulting Polymers

As in the discussion of the previous results, the polymer samples obtained from the various experiments consisted of two fractions.¹⁰ The first is formed by oligomers, produced mainly in the initial stages of the reaction by the H₂O present in the system. The second fraction is formed by high polymer and represents the prevailing part of the product.

While the weight loss at 222°C is approximately 4–5%/min for high molecular weights ($\sim 100,000$), the nonfractionated polymers undergo thermal decomposition also well below their melting temperature; a sample produced in the previous systems and heated, for instance, to 120°C could therefore exhibit an initial rapid loss of per cent weight owing the main decomposition of oligomers, and tend later to a more constant weight. Among the thermal stabilization methods applied to the polymer, the copolymerization with 1,3-dioxolane has been tried; Table VIII reports the results obtained from the polymerization of TRO in *n*-hexane dispersions of various contents of 1,3-dioxolane. The operating conditions are specified in the table. The effect of DOX inserted into the polymer molecules on the thermal stability of the product is shown in Figure 5, giving

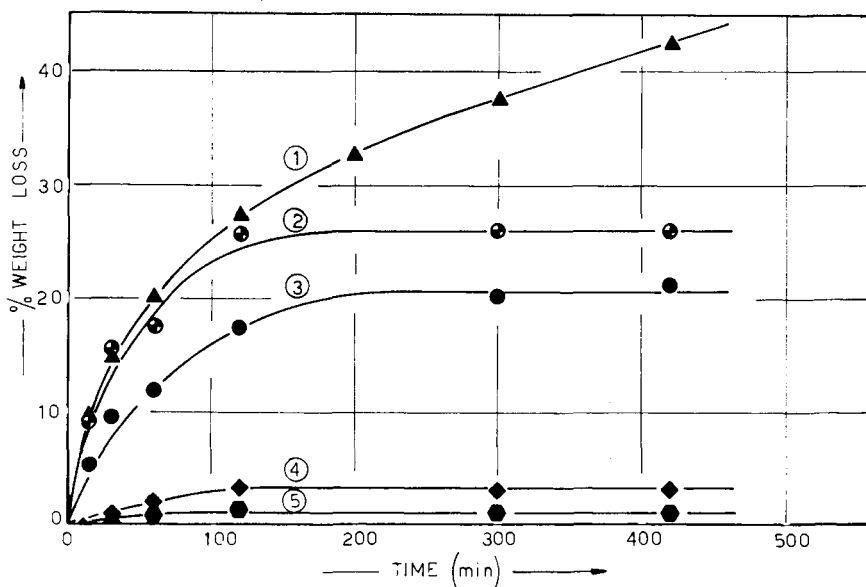


Fig. 5. Weight loss for poly(oxymethylene) $\bar{M}_n \approx 50,000$ (curve 1) and for polymers prepared with initial ratio [TRO]/[DOX] equal to 37.70 (curve 2), 18.90 (curve 3), 7.55 (curve 4), and 3.76 (curve 5).

TABLE VIII
Copolymerization of TRO with DOX in *n*-Hexane with Different
[TRO]/[DOX] Initial Ratios^a

Run no.	DOX, ml	[TRO]/[DOX]	Polymer yield, %	[η]
52	0.5	37.70	55.0	245
53	1.0	18.90	68.0	260
54	2.5	7.55	63.5	220
55	5.0	3.76	67.0	320

^a Conditions: TRO = 0.278 mole; *n*-hexane = 0.191 mole; TBAP = 1.17×10^{-3} mole; reaction time = 30 min; $t = 65.5^\circ\text{C}$; furnished charge = 1.55×10^{-6} Faraday.

weight per cent losses of TRO copolymers samples of different composition versus time at 120°C . As can be observed, on increasing DOX content, before the high polymer and also after, the resulting oligomers are strongly stabilized. In addition, the overall weight losses of the samples appears considerably reduced also at standard temperature of 222°C .

The authors acknowledge the technical assistance of F. Furlanetto of the C.N.R.

References

1. G. Mengoli and G. Vidotto, *Makromol. Chem.*, **165**, 137 (1973).
2. G. Mengoli and G. Vidotto, *Makromol. Chem.*, **165**, 145 (1973).
3. G. Mengoli and G. Vidotto, *Makromol. Chem.*, **175**, 898 (1974).
4. W. Wilson, R. F. Hill, and H. May (to British Industrial Plastics Limited), Brit. Pat. 878,163 (1961).
5. L. Höhr, V. Jaacks, H. Cherdron, S. Iwabuchi, and W. Kern, *Makromol. Chem.*, **103**, 279 (1967).
6. T. Kagiya, M. Hatta, and K. Fukui, *Kobunshi Kagaku*, **20**, 730 (1963).
7. S. Okamura, T. Higashimura and T. Miki, *Progr. Polym. Sci. Japan*, **3**, 97 (1972).
8. A. M. Maki and D. H. Geske, *J. Chem. Phys.*, **30**, 1356 (1959).
9. P. F. Onyon and K. J. Taylor, *Eur. Polym. J.*, **1**, 133 (1965).
10. S. Penczek, J. Fejgin, P. Kubisa, K. Matyjaszewski, and M. Tomaszewicz, *Makromol. Chem.*, **172**, 243 (1973).

Received February 21, 1974

Revised April 16, 1974