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CARBON SUBOXIDE POLYMERS*

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Abstract—On the basis of pyrolysis and hydrolysis measurements, we propose for the polymers of carbon suboxide (prepared with cationic, anionic and radical initiators) a structure consisting of condensed rings of α and γ-pyrone units. On thermolysis the polymer gives CO and CO_2 as the sole gaseous species, with a characteristic thermal spectral pattern. By titration with bases, at least two types of acid sites have been found: they are to be ascribed to α and γ-pyrones with different hydrolysis rates. Measurements of molecular weight by VPO, in water, on the polypyranonic derivative show 6–8 monomeric units per chain.

INTRODUCTION

Carbon suboxide, C_3O_2, is an unsaturated molecule with four cumulated π bonds, which undergoes polymerization yielding an amorphous, powdery solid: its colour ranges from dark-red to black and the solubility in water depends on the method employed for preparing it.

The ability of C_3O_2 to polymerize was first observed by Diels [1], its discoverer; many other experiments have been done on the polymerization. In spite of the large amount of work, the structure of the polymer of C_3O_2 has not yet been unequivocally established. Moreover, conflicting results have been reported on the necessary polymerization conditions, the physical properties and the polymerization mechanism [2–6].

The high reactivity of C_3O_2 and the problems of purification make these studies very difficult. Nevertheless, renewed interest in this polymer has arisen because of its peculiar paramagnetic properties, including its high spin density and photosensitivity [7, 8]. Further, since it has been discovered that it is present on the surface of Mars and Venus [9, 10], and it yields amino acids with hydroxylamine [11] in the presence of metallic ions, a large amount of research has begun all starting from the hypothesis that it is a precursor for the synthesis of biomolecules. Thus, polymers have been described, obtained by thermal initiation after more or less long periods of induction [12], by γ-radiation initiation [4, 13], photoinitiation [12] or many other types of initiators. There is also work on the supposed structure, based both on chemical studies and spectroscopic or X-ray methods. The published data have been obtained for different experimental conditions, so that problems arise in comparison. Nevertheless it is to be noted that the i.r. spectra are the same for all kinds of polymer, suggesting a common basic structure.

Here we report measurements and experimental observations, for a wide range of working conditions, to define the polymerization ability of C_3O_2: we also try to elucidate the structure from data of thermal analyses, acid–base titrations, molecular weight determinations and chemical reactions involving the functional groups.

We reach conclusions somewhat different from those reported so far: the polymer presents a pyrone-like structure with condensed α and γ-pyrone rings, in proportions depending on the preparation method. The molecular weights measured in water on the polymeric derivatives [obtained by reacting $(C_3O_2)_n$ with NH_3] correspond to an average of 6–8 monomeric unit per chain.

EXPERIMENTAL

All reactions and other experiments were carried out under purified N_2. Solvents were purified by standard methods and stored under N_2. Carbon suboxide was prepared from malonic acid and P_4O_{10} [14], and purified by trap-to-trap distillation. The preparations of Pt and Rh complexes were carried out according to published procedures [15].

i.r. Spectra were recorded on a Perkin–Elmer 597 instrument. u.v.-Vis spectra were run on a Perkin Elmer Lambda 5 spectrophotometer. ^{1}H-NMR spectra were recorded on a Varian 360 A instrument. Acid–base titrations were followed by a Amel 335 pH-meter equipped with a glass electrode. Thermogas chromatographic analyses were carried out at the Stazione Sperimentale del Vetro of Murano (Venezia) with a thermoanalytical system assembled locally [16] and with a Perkin–Elmer 900 gas chromatograph equipped with 1 m column of molecular sieves 5A, a thermal conductivity detector, using a programmed temperature between 60 and 250°. Molecular weight measurements were carried out on a VPO Hewlett-Packard 302 B instrument equipped with an H_2O probe, calibrated at 37°C with D(+)monohydrated glucose. Samples were irradiated with γ-rays from a ^{60}Co source [FRAE Institute (CNR) Legnaro (Padova)]. Elemental analyses were performed in the Microanalytical Laboratory of this Department.

Polymerization procedure

In a typical reaction, C_3O_2 was manometrically measured and condensed at −196° in the reaction vessel containing the solvent and equipped with a serum cap. The catalyst was

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added with a syringe and the mixture was kept at the chosen temperature and stirred until the end of reaction. The suspension was filtered off and the solid was washed with the same reaction solvent and dried in high-vacuum.

γ-Radiation polymers

Two different experiments were carried out:

(a) A vial (10 ml) was filled with C_3O_2 at −196°, sealed and irradiated at −196 or −78° with 1 Mrad. The vial was heated to 25° and maintained at that temperature for the post-irradiation period. The resulting brown polymer formed a uniform film all over the surface of the vial, from which it was recovered.

(b) A vessel (500 ml) was filled with C_3O_2 at 0.5 atm and 0° and irradiated at the same temperature with 1 Mrad. The vessel was heated to 25° and kept at this temperature for the post-irradiation period. The resulting polymer was collected as a brown powder from the bottom of the vessel.

Attempts to hydrogenate the polymers

All attempts to hydrogenate the polymers, either solid (with Pt or Pd black, at 50°, 100 atm of H_2 for 20 hr) or dissolved in aq. NaOH solutions (with Ni Raney, at 60°, 100 atm of H_2 for 24 hr) were unsuccessful.

Reaction of polymers with bromine

Polymer (0.4 g) was suspended in CCl_4 and treated with a CCl_4 solution of Br_2. The solid dissolved quickly and the solution became yellow.

Reaction of polymer with HNO_3

Polymer (0.35 g) was treated with conc. HNO_3. The polymer reacted vigorously and the formed gas was collected, recognized as CO_2 and measured; 1 mol of CO_2 was obtained for 1 mol of C_3O_2. The dried residue was soluble in water and contained about 4% of nitrogen.

Reaction of polymers with ammonia

Polymer (0.4 g) was treated with an excess of gaseous NH_3. A exothermic reaction took place at once and the compound became orange-yellow. NH_3 was removed and the residual compound was collected and dried.

Elemental analysis: found (calc) for $(C_3ONH)_n$; C 52.2 (53.7), H 1.7 (1.5), N 21.3 (20.9). i.r. (Nujol); 3105(m), 3165(m), 1645(s) cm^{-1}. ^{1}H-NMR (δ) 7.04 ppm.

The same results were obtained if a suspension of polymer in water was treated with an aqueous solution of ammonia.

RESULTS

Polymerization

Table 1 shows the most relevant data obtained for various experimental conditions. It is seen that C_3O_2 polymerizes in the presence of ionic [both anionic (exp. 1–4) and cationic (exp. 7 and 8)] and organometallic systems (exp. 9 and 10) and under γ-radiation (exp. 12–14), but it does not polymerize in diethylether solutions or in the gaseous phase even at 100° for several days (exp. 16 and 17). Moreover, the polymerization takes place in basic solvent as HMPA and DMF, containing tertiary nitrogen atoms (exp. 18 and 19). Low yields of polymer are obtained with $AlCl_3$ in toluene (exp. 15) and with the heterogeneous systems and Na-methylate in diethylether or metallic Na in THF (exp. 5 and 6).

Although already known that the polymerization of C_3O_2 can be promoted by organic acids and bases, our results indicate that triethylamine and H_2SO_4 are the best catalysts. Organometallic compounds of Pt are also very efficient catalysts. With γ-radiation, polymers can be obtained from liquid or solid C_3O_2 and in the gaseous phase. The result most different from those reported previously is that no thermopolymer forms when gaseous C_3O_2 is heated at 100°. We have no explanation for the non-occurrence of thermopolymerization; we note however that almost all experiments described in the literature are performed either in an i.r. cell with NaCl or KBr windows or in tubes having a high ratio surface/volume. Thus the polymerization may be influenced by the surface as already stated. The polymerization of C_3O_2 in solution of HMPA and DMF is probably due to a mechanism involving an interaction between the monomer and the solvent.

All the polymers, obtained by various procedures, give rise to amorphous powders with colour ranging from dark-red to black: they are only partly soluble in water and insoluble in organic solvents.

Pyrolysis

By heating the polymer in N_2 or He, it undergoes

Table 1. Data of polymerization experiments

Experiment	Initiator	Solvent	Mon./Cat.	Temperature (C)	Time (hr)	Yield	Observations
1	$N(Et)_3$	CH_2Cl_2	25	0	10	High**	
2	$N(Et)_3$	*n*-Heptane	25	0	10	High	
3	$N(Et)_3$	THF§	40	0	10	High	
4	Li-butyl	*n*-Hexane	10	0	10	High	
5	$NaOCH_3$	$(C_2H_5)_2O$	5	0	24	Poor	
6	Na-naphthalene	THF	5	20	24	Poor	
7	H_2SO_4	CH_2Cl_2	25	0	24	High	
8	H_2SO_4	C_6H_6	25	0	24	High	
9	$L_2PtC_2H_4$*	C_6H_6	350	25	24	70%	
10	$LPtCl_2C_2H_4$†	CH_2Cl_2	1000	25	24	High	
11	$(PPh_3)_3$ RhCl	CH_2Cl_2	20	25	24	Nil	
12	$\gamma(^{60}Co)$‡	—	—	0	24	High	Gaseous††
13	$\gamma(^{60}Co)$‡	—	—	−78	24	High	Liquid††
14	$\gamma(^{60}Co)$‡	—	—	−196	24	High	Solid††
15	$AlCl_3$	Toluene	25	0	24	Poor	
16	None	$(C_2H_5)_2O$	—	25	168	Nil	
17	None	—	—	100	168	Nil	
18	None	HMPA¶	—	25	24	High	
19	None	DMFA‖	—	25	24	High	

*$(PPh_3)PtC_2H_4$. †*Trans*-dichloro benzylamine ethylene Pt (II). ‡1 Mrad. §Tetrahydrofuran. ¶Hexamethylphosphoramide. ‖Dimethylformamide. **Over 90%. ††Post-irradiation at 25 .

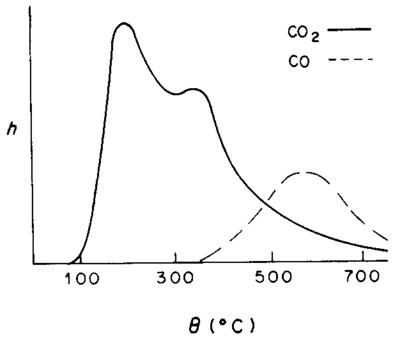


Fig. 1. Pyrolysis of C_3O_2 polymer (exp. 1).

decomposition evolving CO and CO_2 as the only gaseous species; in the presence of O_2, only CO_2 is produced. Previously reported data on the pyrolysis of the polymer have been obtained for different experimental conditions so that no direct comparison is possible. Only Blake and Hyde [3] report "*ad hoc*" pyrolysis data on the thermopolymer obtained at 100° and on γ-initiated polymers. They performed experiments at various fixed temperatures under vacuum by continuous removal and intermittent analyses of the evolved gases. They showed that CO_2 is the only significant product of low temperature pyrolysis, but CO is formed in increasing amounts at higher temperature.

Our experiments have been performed similarly. Loss in weight and composition of the gases evolved during the pyrolysis have been both systematically examined as a function of the temperature, from 20 to 700°. At 700° the residual black solid gives a Debye-photogram typical of graphite.

Figures 1, 2 and 3 show the curves representing, on a arbitrary scale, (h), the relative amounts of CO and CO_2 plotted against the temperature. The graphs present maxima for CO_2 and CO characteristic for each polymer. These diagrams can be roughly divided into three types:

(a) Figure 1. For polymers obtained by initiation with triethylamine, there are two maxima (at 200 and 375°) for CO_2 and one (at 550°) for CO.

(b) Figure 2. For polymers obtained with H_2SO_4 (Fig. 2a) or by γ-radiation of the liquid monomer (Fig. 2b), there are two maxima (at 150 and 375°) for CO_2 and one (at 550°) for CO.

(c) Figure 3. For polymers initiated by Pt complexes (Fig. 3a) or γ-radiation of the monomer in the gaseous phase (Fig. 3b), there are two asymmetric gaussian-shaped curves having a common maximum at 400°.

Incidentally, this last type is almost identical to those reported by Blake and Hodgson [13] for analogous experiments.

It is to be noted that the ratio CO_2/CO, obtained by heating in vacuum samples of polymers at 700° and analysing gas chromatographically the gases evolved, ranges from about 3 for (a), to 1.5 for (b) and to nearly 1.1 for (c). See Table 3, $r(CO_2/CO)$.

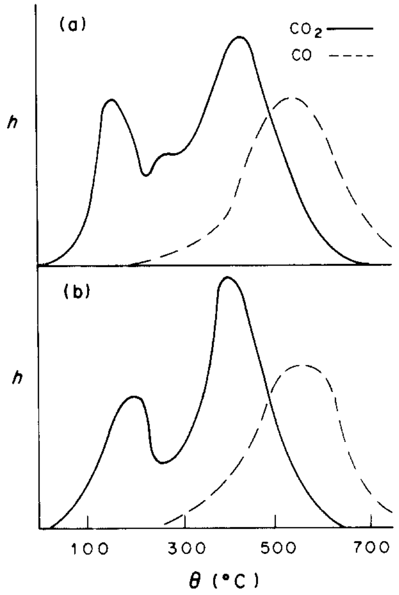


Fig. 2. Pyrolysis of C_3O_2 polymer (exp. 7 and 13).

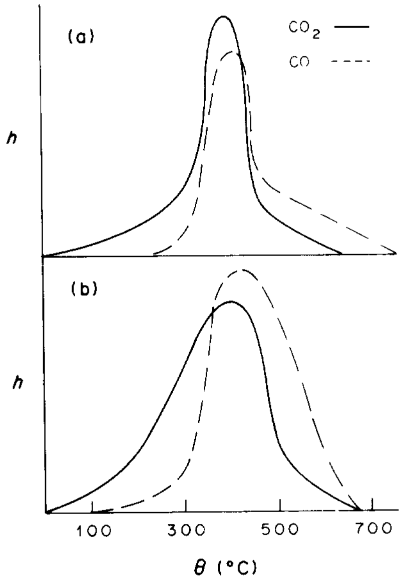


Fig. 3. Pyrolysis of C_3O_2 polymer (exp. 10 and 12).

Table 2. Ratios between α and γ-pyrones in the C_3O_2 polymers, obtained by acid–base titrations

Experiment	Forward titration, eq. p. 1 = A	Back titration, (eq. p. 3 – eq. p. 2) – eq. p. 1 = B	$R = B/A = \alpha/\gamma$
1	2.3	6.1	2.65
7	4.1	5.3	1.29
10	2.3	2.2	0.96
12	1.3	1.5	1.15

ml NaOH N/10.

Hydrolysis

The polymers of C_3O_2 are partly soluble in water and entirely soluble in aq. NaOH, showing their acidic nature: from basic solutions, they can be re-precipitated by adding an excess of mineral acid. This behaviour has been already described and measurements of equivalent weight have been reported: they range, according to the type of polymer, from 68 g/equiv. (per monomeric unit) to 158 g/equiv. and more.

We re-examined these data and showed that in the polymers there are various centres of acidity with different hydrolysis rates.

Samples, weighed in a dry atmosphere, have been suspended in water and then slowly titrated after waiting for the pH value to stabilize. The titration behaviour is typical for a strong acid (Fig. 4a). Equivalent weights obtained this way range from 137 to 252 g/equiv., according to the type of polymer.

When the pH had reached a steady value, a quantity of NaOH was added in excess with respect to the polymer (each C_3O_2 unit was assumed as one equivalent per mole). After 48 hr at room temperature of after 3 hr at 60°, we back-titrated with HCl (Fig. 4b) obtaining two equivalence points (eq. p. 2 and eq. p. 3). Eq. p. 2 corresponds to titration of the excess of NaOH, and eq. p. 3 corresponds to complete hydrolysis of the polymer. Equivalent weights thus obtained are all about 68 g/equiv.

These measurements indicate that there are at least two hydrolyzable groups in the polymer, with different hydrolysis rates, and their relative amounts can be determined.

Molecular weights

So far, only one direct determination of molecular weight for C_3O_2 polymers has been reported. The polymers were prepared at relatively low temperature and the measurements were performed by VPO in DMF and by determining the freezing point depression of DMSO solutions.

Our polymers are practically insoluble in organic solvents including DMF and DMSO, so we prepared a soluble derivative. By reaction of dry gaseous NH_3 with the polymer, a orange-yellow product was obtained. It has the i.r. spectral pattern of an amide and is soluble in water. The aqueous solutions are stable and no hydrolysis occurs. The product is not a polyelectrolyte and its elemental analysis corresponds to (C_3ONH). Molecular weight measurements obtained by VPO in water range from 420 to 560 g/equiv. showing 6–8 monomeric units per chain.

Chemical reactions and water absorption

Although insoluble, the C_3O_2 polymers react with a number of reagents according to their postulated polypyronic structure. Hegar [17] describes the formation of the methylether derivative and the corresponding i.r. spectrum. The polymers react with both gaseous and aqueous NH_3: no hydrogenation occurs heterogeneously with Pd and Pt or with Ni Raney at 100 atm using aqueous solutions of the sodium salt of the polymers. On the contrary, it reacts very well in CCl_4 suspension with Br_2. With concentrated HNO_3, the polymer yields one mole of CO_2 per monomeric unit. The residue is freely soluble in water and contains 4% of nitrogen. All the polymers reported in the literature and those described here contain hydrogen (1–2%). As we have shown, it comes from water and is of two types; viz. structural and adsorbed. In fact, if we use the dry-box, including for weighing, no hydrogen is found in the polymer; when exposed to the air, the polymer undergoes a rapid weight increase up to 3–4% (reaction with terminal active centres) and later, a progressive weight increase up to 10% as maximum (average 6%), depending on the polymer type.

i.r., u.v. and X-ray spectra

The i.r. spectra are all the same, no matter how the polymers have been prepared and are identical to those reported [8] with the exception that in our samples the band at 2175 cm^{-1}, due to the ketenic group, is always absent. The i.r. spectra of the polymer treated with water is simpler than that of the "dry" polymer and shows broadened bands at 1735, 1615, 1460 and 1220 cm^{-1} and a very strong band of non-bonded water at 3500 cm^{-1}. The sodium salt has bands at 1660, 1610, 1530 and 1400 cm^{-1} typical of a carboxylate structure. The ammonia derivative shows a band at 3165 and 1645 cm^{-1} attributed to a polypyranonic structure. u.v. Spectra of the sodium salt in water show a maximum at 412 nm and a shoulder at 312 nm: solutions of ammonia derivatives in water absorb at 358 and 308 nm. All our polymers appear amorphous by the X-ray diffraction.

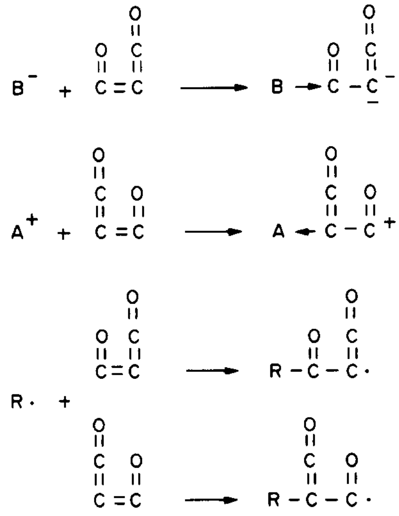
DISCUSSION AND CONCLUSIONS

The above reported data allow us to formulate some hypotheses on the polymerization mechanism and the structure of the polymers.

The molecule of C_3O_2 has alternating sites of negative and positive polarity

$$(\bar{O}=\overset{+}{C}=\bar{C}=\overset{+}{C}=\bar{O})$$

and many centres of reactivity. One among them is the olefinic activated double bond which can give rise to polymerization with ionic and radical initiators as follows:



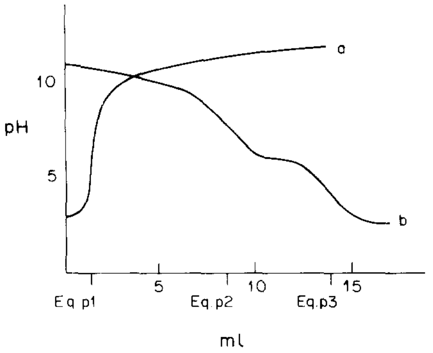


Fig. 4. Forward and back titration of C_3O_2 polymer.

Anionic polymerization (B−) takes place with butyl lithium, NEt_3, pyridine and, in general, with compounds containing tertiary nitrogen atoms (primary and secondary amines react stoichiometrically with C_3O_2 yielding corresponding amides). Sodium alkoxide is probably a poor catalyst, since it is used heterogeneously. In a similar way, acids (H_2SO_4, $HClO_4$) (A^+) lead to polymers of cationic type. With $AlCl_3$ the catalyst particles are quickly coated with polymer, so that no significant yield can be obtained. A third type of polymer ($R^\cdot$) is initiated by the radical C_2O generated through decarbonylation, by metals and γ-radiations. Actually, several compounds of transition metals are able to decarbonylate C_3O_2 giving C_2O: the most efficient are those of Pt, Pd, Ni and Rh [18]. The Wilkinson compound is not a suitable catalyst since it dissociates yielding free phospine, which immediately reacts with nascent C_2O [19]. Radiation-induced polymerization occurs according to two distinct types of mechanism. When the monomer is radiated in the liquid or solid state and then allowed to polymerize at room temperature, a cationic mechanism of chain growth takes place [4]. In this case the polymer adheres to the wall and its thermal decomposition is similar to that of the polymer obtained from H_2SO_4 (Fig. 2a, b). When the monomer is irradiated in the gaseous phase, the polymer forms at the bottom of the vessel, CO is produced and the thermal decomposition follows a course similar to that of the polymer obtained from organometallic compounds (Fig. 3a, b).

A number of polymeric structures have been proposed and have been exhaustively reviewed in recent years. The structure now generally accepted is that proposed by Ziegler [20] and Smith [12] and it consists of condensed α-pyrone rings. Our data are not in agreement with this formulation and support a different hypothesis.

Since the polymerization takes place at the olefinic double bond C1–C2 (Fig. 5 A1, B1, C1), the chain will consist of carbonyl and ketene groups in an orderly or disordered alternate succession; accordingly, these groups can give rise to α (Fig. 5 A2) or γ (Fig. 5 B2) pyronic rings through cyclicization.

As reported above, these polymers produce CO and CO_2 by thermolysis. Data on thermal decomposition of model compounds indicate that the α-pyronic structure gives CO_2 and the γ-pyronic structure gives CO. For instance, thermolysis of α-pyrone a and of homologous compounds give

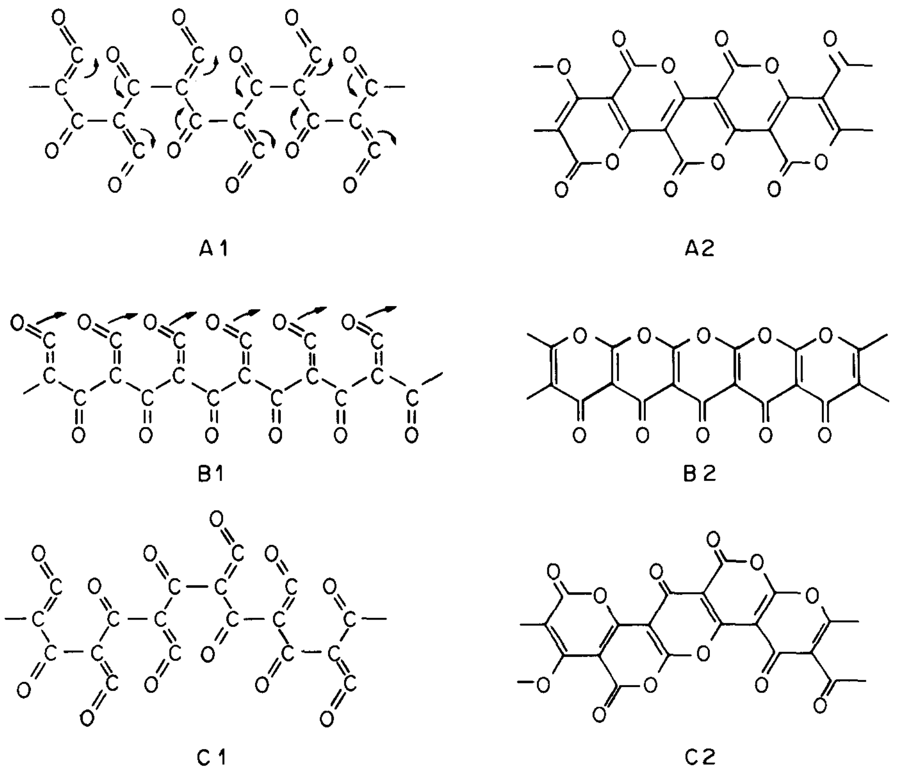
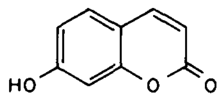
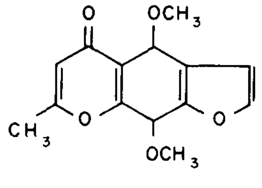


Fig. 5. α, γ and mixed polypyronic structure of C_3O_2 polymer.

quantitatively CO_2; on the other hand, thermolysis of γ-pyrone b and homologous compounds give only CO. Thus the ratio CO_2/CO can be assumed as an index of the polymer composition which in turn depends on the initiation process. We found that the polymers initiated by anionic systems have a ratio between α and γ-pyrones of about 3; CO_2/CO is lower when cationic systems are employed, but is still >1. Radical systems lead to polymers for which CO_2/CO is almost unity.



a



b

It has been shown that the radical C_2O is probably the initiator in this last type of polymerization. It gives rise, in the gas phase, to two different intermediates, one in the triplet and the other in the singlet state. Thus C_2O is likely to work in the former state in which it is quite indiscriminate towards electronic effects. This behaviour has been already described in reactions with olefins [21]. Therefore C_2O is supposed to produce a random copolymer of α and γ-pyrone units.

This hypothesis on the structure is supported by hydrolysis data. Since they are cyclic lactones, α and γ-pyrones readily undergo ring cleavage by hydrolysis, particularly in the presence of alkali. γ-Pyrones hydrolyze more rapidly than α-pyrones. Hydrolysis measurements on model compounds a and b, at pH 9.5, indicated a rate of hydrolysis for b about five times higher than for a. This result can be related to the two equivalence points found in the titration of the polymer itself (eq. p. 1 and eq. p. 3 in Fig. 4): the former is to be ascribed to the γ-pyronic and the latter to α-pyronic moieties in the polymer chain.

By comparing the titration data (in the form of ratio of the amounts of α and γ-pyrones) with the pyrolysis data (ratio of CO_2/CO), surprising agreement is to be noted (Table 3).

Table 3. Comparison between pyrolysis and titration data for C_3O_2 polymers

Experiment	$r(CO_2/CO)$	$R(\alpha/\gamma)$
1	2.9	2.65
7	1.5	1.29
10	1.08	0.96
12	1.06	1.15

Further, these facts prove that the C_3O_2-polymeric structure is in better agreement with the formulation of Fig. 5 C2.

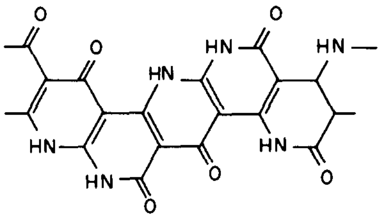
As for the polymerization mechanism, noting the polarity of the carbon atoms in C_3O_2, we can recognize among the many opening and enchainment possibilities the following cases:

(a) Anionic initiation—nucleophilic attack of the lone pair of the tertiary nitrogen atom on the electrophilic C1 of the monomeric unit.

(b) Cationic initiation—electrophilic attack of H^+ on the negatively charged C2.

(c) Radical initiation—attack of C_2O in the singlet state intermediate on the monomeric unit with formation of a random structure of α and γ-pyrone units.

The reaction of the polymer with NH_3 is typical both of α and γ-pyrones, as first discovered by von Pechmann and Walsh [22], in 1884. NH_3 opens the pyrone ring and immediately a ring closure follows to yield 2 and 4 pyridone(s); the reaction is specific and no carbon–carbon bond breaks. The same reaction occurs with the polymer: thus the condensed α and γ-pyrone units turn to α and γ-pyridonic units giving rise to a polymer of the type where each –O– atom of the pyronic ring is substituted with a NH unit.



Elemental analysis, i.r. and ^{1}H-NMR spectra, lack of electrolytic conduction and no hydrolysis at room temperature are all points supporting such a structure. The difference in solubility in water of the two polymeric species is due probably to different rigidities of their structures and to a higher solvatation of –NH– with respect to the –O– sites. Further, the above proposed structure is consistent with the lack of crystallinity of these polymers.

The authors do not put forward speculative hypotheses on the termination mechanism, on the pronounced change of colour with increasing mol. wt and on other physico-chemical properties of the polymer.

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