Poly(carbon suboxide). Characterization, Polymerization, and Radical Structure

A. W. Snow,[1] H. Haubenstock,* and N.-L. Yang

The City University of New York, The College of Staten Island, Staten Island, New York 10301.

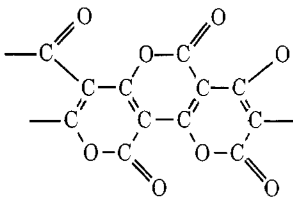
Received June 30, 1977

ABSTRACT: Poly(carbon suboxide) has been characterized as a paramagnetic oligomer having a degree of polymerization between 5 and 6 and two ketenyl functional groups per molecule. The ESR absorption was used to derive a polymerization rate law of first order with respect to both monomer and polymer. The polymerization was shown not to involve a propagating free radical, and a mechanism involving a zwitterionic ketocarbene intermediate and a Wolff rearrangement termination is proposed. Exposure of the polymer to water vapor resulted in proportionate decreases in the intensities of the ketenyl IR and ESR absorptions. The paramagnetism is proposed to originate from an electron transfer between polymer molecules stabilized by a ketenyl and carbonyl terminated polyene chain contained within the polymer's ladder structure.

Carbon suboxide, a linear molecule with four cumulated double bonds (**1**), was discovered by Diels[2] who also observed its polymerization to a highly colored solid. The polymer forms as a yellow to dark brown film on container surfaces from a gaseous monomer phase, with its color depending on film thickness. It precipitates as a dark brown powder from a liquid monomer phase or from organic solvents. The polymerization has been observed to be preceded by an induction period which increases with decreasing temperature and decreasing monomer pressure.

$O{=}C{=}C{=}C{=}O$

1



2

The structure of the thermopolymer is considered to be a poly(α-pyrone) (**2**) by several groups of investigators.[3,4] Evidence in support of this structure includes infrared and visible–ultraviolet spectroscopic studies,[3-5] thermal decomposition studies,[3,4] and x-ray diffraction studies.[4]

The thermopolymer of carbon suboxide, C_3O_2, has been reported to possess the interesting properties of paramagnetism and photosensitivity as manifested by a remarkably intense photosensitive ESR singlet absorption.[6,7] The ESR method has now been used in a kinetic study of the thermal polymerization of carbon suboxide. One of the important reasons for carrying out this kinetic study was to establish the paramagnetism as an intrinsic property of the solid polymer. Another objective was to carry out quantitative measurements of the effect of various additives, which included oxygen, nitric oxide, olefins, and carbonyl compounds on the polymerization rate. The insolubility of the polymer in most organic solvents has in the past precluded molecular weight measurements. Our finding that polymer prepared at relatively low temperatures is soluble in dimethylformamide (DMF) and in dimethyl sulfoxide (DMSO) has made possible the accurate determination of molecular weights and other characterization studies. The results of the studies are reported in this paper and possible mechanisms for the polymerization are discussed. This paper also presents an attempt to relate the paramagnetic center with the polymer structure. The paramagnetic center has been reported to have a g value of 2.0050 and a spin density of 2.5×10^{18} spin/g and to obey the Curie–Weiss law.[6] The ESR spectrum of a polymer obtained from C_3O_2 with a 16% ^{13}C enrichment at the central atom displayed hyperfine structure with a 9 G ^{13}C coupling constant.[6] These results are interpreted as a π type spin center confined to a single polymer molecule in a doublet ground state. A more complete molecular description of this polymer radical requires characterization experiments which can further relate the radical structure to the polymer. Such a connecting experiment is found by exploiting the hygroscopic property of the polymer. The paramagnetism is found to be irreversibly quenched on exposure to moisture, and, by investigating simultaneous structural changes in the polymer, structural requirements of the radical are elucidated.

Results

Kinetic ESR Measurements of the Thermal Bulk Polymerization. The kinetics of the thermal bulk polymerization of carbon suboxide were followed by ESR measurements. The polymerization rate was followed by monitoring the peak-to-peak intensity, D, of the ESR signal. The line width of 2.3 G and the line shape[6] remained constant throughout the conversion. The reaction order with respect to polymer was first order (Figure 1). It was found that signal intensity is proportional to polymer concentration (vide infra). An Arrhenius plot was linear over the 0 to 50 °C temperature range yielding an activation energy of 9.9 kcal/mol and a frequency factor of $2.4 \times 10^3\ s^{-1}$ (Figure 2). The initial monomer concentration was varied by the addition of toluene as an inert diluent, and a plot of the natural logarithm of the slopes of each of the $\ln D$ vs. time plots was made against the natural logarithm of the initial monomer concentration.

Considering the order n in monomer is to be determined, $d[P]/dt = k[P][M]^n$ and $\ln[P] = k[M]^n t + C$, where the slope of an $\ln [P]$ vs. t plot is equal to $k[M]^n$ when [M] is in excess.

$$\ln [\text{slope}] = n \ln [M] + \log k$$

The slope of this plot, which corresponds to the reaction order with respect to monomer, was 0.98 indicating first order (Figure 3). The overall rate law is then $d[P]/dt = k[M][P]$ where M refers to the C_3O_2 monomer and P to the C_3O_2 thermopolymer.

This is the same rate law obtained by Smith[8] based on optical measurements at 370 nm and by Blake[9] based on monomer pressure measurements for the gas-phase polymerization. This supports the conclusion that the paramagnetism is a property of the carbon suboxide polymer in the solid state and is not due to formation of a side product. It was further confirmed by parallel measurements of the ESR signal in-

0024-9297/78/2211-0077$01.00/0

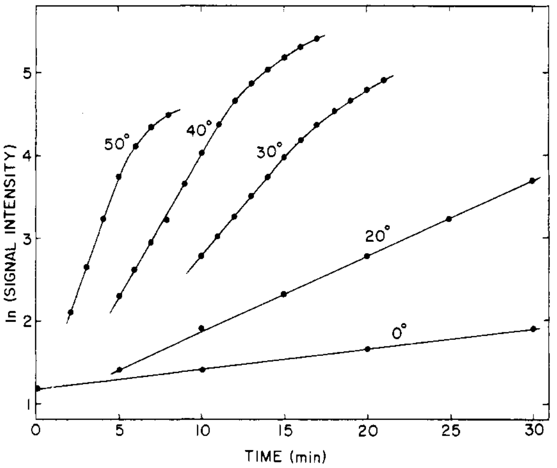


Figure 1. Plot of the logarithm of the relative ESR peak-to-peak signal intensity against postinduction period time at 0, 20, 30, 40, and 50 °C.

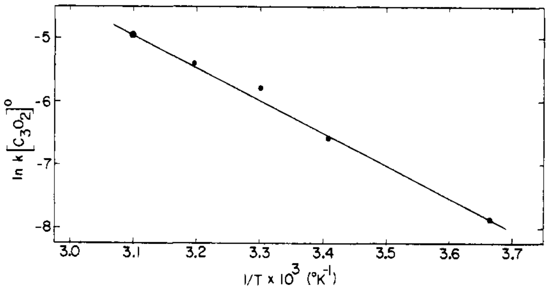


Figure 2. Arrhenius plot for carbon suboxide polymerizations over a 50 °C temperature range.

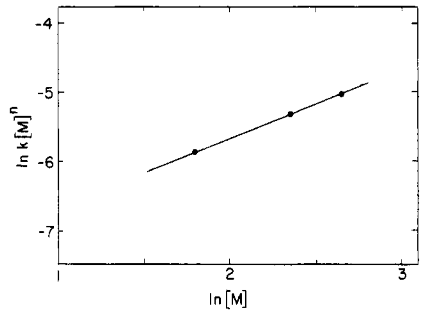


Figure 3. Plot of ln $k[M]^n$ against ln [M] to obtain monomer reaction order.

tensity and optical absorbance of the polymer at 370 nm at various extents of conversion during polymerization at 100 °C. The spin density was related linearly to the optical density.[7] The possibility that the paramagnetism is due to a buried radical intermediate is precluded by evidence that propagation does not involve a radical intermediate (vide infra).

Effect of Additives on the Polymerization Rate of Carbon Suboxide. In order to obtain additional information on the polymerization process, various potential inhibitors or retarding agents were added to carbon suboxide, and the rate of polymer deposition from the gas phase was quantitatively studied at 100 °C. To the monomer at a pressure of 330 mm Hg was added either an equimolar quantity of inhibitor based on pressure measurements, or room temperature vapor pressure of additive if less than 330 mmHg. The additives used were oxygen, nitric oxide, 3-methyl-1-butene, 1,3-butadiene, acetone, and acetaldehyde. Polymerization rates were followed by ESR measurements and the results are shown in Figure 4 together with a control run containing no additive.

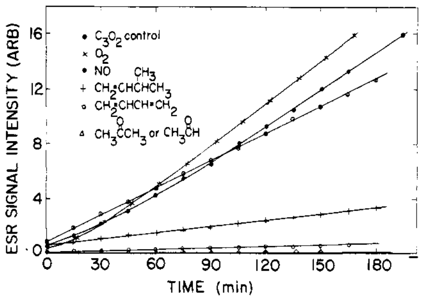
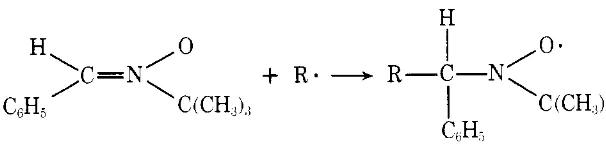


Figure 4. Effect of additives on carbon suboxide postinduction period polymerization rate.

The presence of oxygen and nitric oxide, when compared with the control, had no appreciable effect on the polymerization rate. Nitric oxide had a dramatic effect on the ESR signal's line shape (see Experimental Section) while oxygen did not change the ESR signal line shape. The lack of an effect on the rate in the presence of oxygen and nitric oxide had also been observed by Blake[9] who concluded that the reaction does not take place by a gas-phase free-radical mechanism. Oxygen is well known to be an efficient radical scavenger and commonly is observed to inhibit radical polymerization.[10] Nitric oxide is also known as an efficient radical scavenger.[11]

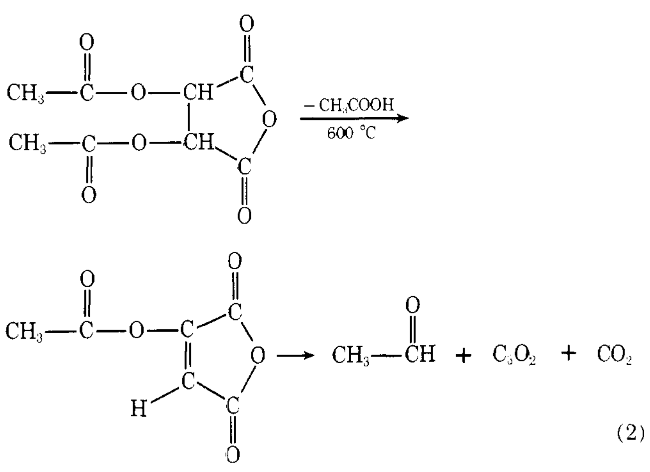
Carbon suboxide's susceptibility to radical polymerization was also tested by an attempted copolymerization of equimolar quantities of carbon suboxide and styrene initiated by AIBN at 60 °C in toluene solution. The infrared spectrum of the polymeric product was identical with that of a styrene homopolymer control, and no carbonyl absorption was detected. In another experiment carbon suboxide was polymerized in bulk and in toluene solution in the presence of a phenyl-*tert*-butylnitrone spin trap. This compound adds reactive radicals with the formation of a stable nitroxy radical[12] (eq 1).



(1)

The nitroxy radical has a characteristic ESR spectrum consisting of a triplet of doublets due to the nitrogen ($a_N = 15$ G) and hydrogen ($a_H = 2$–3 G) splittings. No nitroxy radical spectrum was observed from either the bulk or the toluene solution polymerizations. The observed 2.3-G signal of the polymer[7] remained unchanged. The nitrone was verified to be active by obtaining a typical nitroxy radical spectrum on heating to 60 °C in a toluene solution of azobis(isobutyronitrile). On the basis of these various observations it is concluded that the polymerization does not involve a propagating reactive radical species. It is not considered probable that carbon suboxide monomer would be attacked by the paramagnetic polymer species[7] since C_3O_2 is inert to radicals as reactive as the styryl radical while the paramagnetic polymer is not reactive enough to attack the nitrone spin trap.

Significant retardation was observed with the alkene additives and particularly with acetone or acetaldehyde, as is seen from Figure 4. It has been experimentally observed that carbon suboxide prepared by the pyrolysis of diacetyltartaric anhydride (eq 2) is more stable toward polymerization than that prepared by the dehydration of malonic acid. We have observed infrared impurity bands at 3.65, 5.75, 7.2, and 9.0 μm in carbon suboxide prepared by the pyrolysis of diacetyltartaric anhydride. These impurity bands are attributed to the presence of acetaldehyde, formed as one of the products of the pyrolysis reaction. The relative stability of carbon suboxide prepared by the pyrolysis method is probably due in part to the presence of acetaldehyde, which retards polymerization of the monomer.



(2)

Reaction of Poly(carbon suboxide) with Water and Various Nucleophiles. On exposure to moisture, the C_3O_2 thermopolymer irreversibly absorbs water and assumes a reddish hue which has earned it the designation "red carbon" or "red coal" in the older literature. When this red color development was quantitatively followed by obtaining visible–ultraviolet spectra of a thin polymer film prepared at 100 °C after successive exposures to trace quantities of water vapor, a decay of an absorption at 370 nm and growth of a more intense absorption at 480 nm was observed (Figure 5). This change would indicate that in addition to composition, the polymer's electronic structure is being altered.

In the infrared spectrum of a polymer film prepared at room temperature, water vapor exposure resulted in a broadening of the more intense bands and a slight decline in the band at 8.2 μm (Figure 6). However, a weak ketenyl band at 4.6 μm disappeared completely with a corresponding growth of a broad carboxyl O–H stretching band at 3.3 μm. An alternate assignment of the band at 4.6 μm to absorbed monomer by Smith[3] has been disputed by Blake[4] on the basis of an 80-cm^{-1} difference between it and the monomer's most intense band. While preparing the film it was observed that monomer was absorbed by the polymer but appeared as a band at 4.46 μm, well separated from the ketenyl absorption at 4.6 μm, and could be removed by pumping with a mechanical pump for 0.5 h in contrast to Smith's 15 h of hard pumping at high vacuum. A mass spectrum of the polymer showed fragments corresponding to CO^+ and CO_2^+ but no fragment corresponding to $C_3O_2^+$. There was some difficulty experienced in maintaining a high vacuum (10^{-7} mmHg) with the polymer present. It was observed that C_3O_2 reacts very slowly with water, while this ketenyl absorption is very sensitive to moisture. This ketenyl band assignment is consistent with the observation that the polymer becomes acidic on exposure to water.

The polymer's ESR absorption was found to parallel the decay of the ketenyl absorption on exposure to water vapor. This suggested a connection between the ketenyl group and the unpaired electron. To determine whether the relationship is quantitatively proportional, simultaneous ESR and ketenyl IR absorption intensity measurements were made after successive exposures to water vapor. The quartz cell was transparent in the infrared between 2.5 and 4.8 μm which permitted monitoring the decay of the 4.6 μm ketenyl band as well as the growth of a 3.3 μm carboxylic acid band. The cell was evacuated between exposures and the ESR and IR spectral changes after nine successive exposures are shown in Figure 7. Since the ESR line shape and width did not change, the ESR absorption was measured as the peak-to-peak signal intensity. In the IR spectra, the carboxylic acid peak was found to tail into the ketenyl absorption, so the base of the ketenyl band was taken to correspond to the extrapolated level of the carboxylic acid band. The ketenyl band intensity was taken as the absorbance difference between the maxima and extrapolated base of the peak. A plot of the ESR signal intensity against the ketenyl band absorbance was linear (Figure 8) indicating the existence of the unpaired electron to be dependent on the presence of the ketenyl functional group.

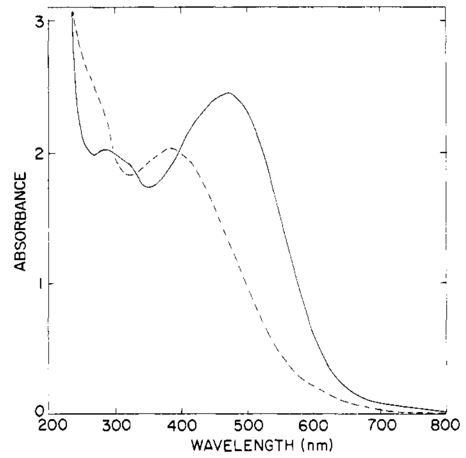


Figure 5. Effect of water vapor exposure on the visible–ultraviolet spectrum of a poly(carbon suboxide) film. Broken line, before exposure. Solid line, after exposure.

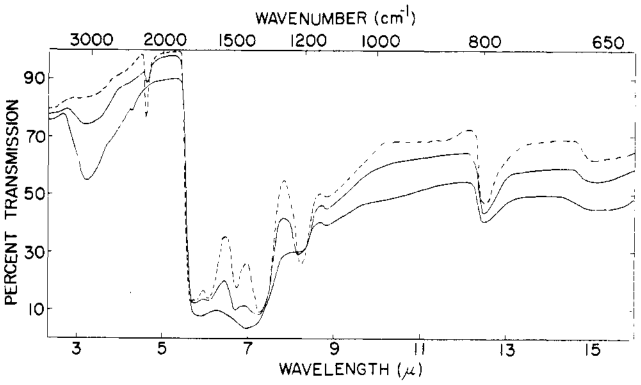


Figure 6. Effect of water vapor exposure on the infrared spectrum of a poly(carbon suboxide) film. Broken line, before exposure. Solid line, after successive exposures.

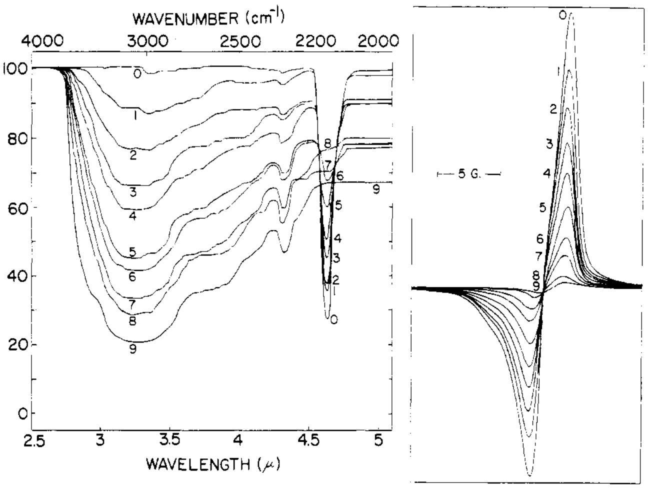


Figure 7. Simultaneous decay of poly(carbon suboxide) infrared ketenyl and ESR absorptions on successive exposures to trace quantities of water vapor.

It was of interest to compare the effectiveness of water with

Table I
ESR and Ketenyl IR Absorption Decay by Exposure to Various Reagents

Exposure conditions	Trace, 5 min exposure		Vapor pressure, 12 h exposure		1 atm pressure, 100 °C heating, 12 h exposure				Less than 20% decay	
Reagent	H_2O	≫	CH_3OH	≫	NH_3,	CH_3NH_2,	HCl	>	CH_3SH,	H_2S
Dipole moment	1.85		1.70		1.47	1.31	1.08		1.52	0.97

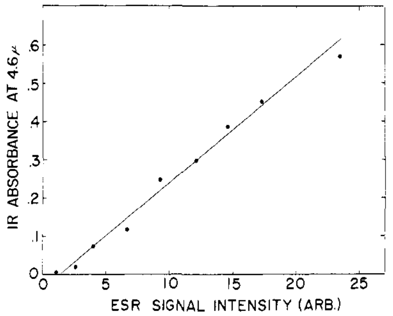


Figure 8. Relation between ketenyl IR and ESR absorptions of poly(carbon suboxide) after successive exposures to trace quantities of water vapor.

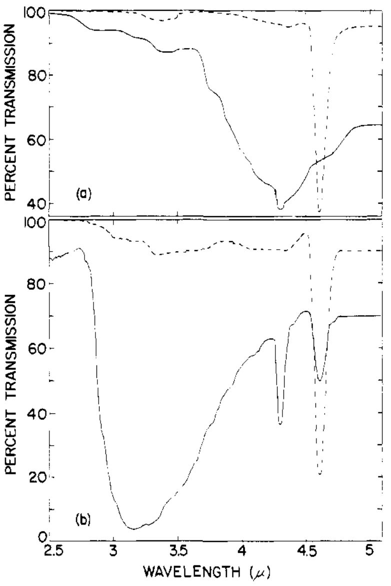


Figure 9. Infrared spectra of poly(carbon suboxide) exposed to D_2O (a) and NH_3 (b). Broken line, before exposure. Solid line, after exposure.

other nucleophiles on quenching the ESR and ketenyl IR absorptions. Interaction of the polymer with methanol as well as with nitrogen and sulfur analogues of water and methanol provided additional information about the spin center and ketenyl group. All of the reagents were either gases or had substantial vapor pressures at room temperature so the nucleophilic effectiveness could be semiquantitatively measured by increasing the severity of the exposure conditions. This was done by first increasing the exposure time for a few millimeters pressure of nucleophile, then by increasing the reagent pressure up to 1 atm and finally by increasing the exposure temperature up to 100 °C. The results are summarized in Table I. In each case a linear relationship was observed between the ESR signal and ketenyl band intensities. It was initially expected that nucleophilic strength would be the most important factor in reagent reactivity, and it was a surprise to find that water was by far the most effective reagent. A more important factor appears to be the nucleophile polarity as indicated by the dipole moments, which, with the exception of methylmercaptan, parallels the reagent reactivity. This result suggests that the poly(carbon suboxide) film has a significant ionic character which may protect the buried ketenyl groups from the less polar but more powerful nucleophiles. In fact, the attack of ammonia and methylamine is very slow but results in a bleaching of the film to a light yellow color. An elemental analysis of an ammonia exposed C_3O_2 polymer corresponded very closely to a stoichiometry of $C_3O_2 \cdot NH_3$ (see Table III). A shift from a lactone carbonyl (5.85 µm) to an amide (6.2 µm) carbonyl absorption in the IR indicates that ammonia penetrates the film by slowly attacking the lactone bands. A possible explanation for methylmercaptan's lack of effectiveness may be poor penetration into the polymer film. Considering the film to have an ionic character and to be of high density (1.65 g/cm^3), the mercaptan with its weak hydrogen bonding capacity and large size would be expected to be less effective than the smaller and more strongly hydrogen bonding ammonia molecule.

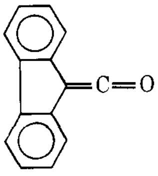
In solution the normal reactivity of ketenes with three of the nucleophiles is in the order:[13]

amine ≫ water > methanol

Hydrogen chloride is also reported to react rapidly with substituted as well as unsubstituted ketenes.[13] The reactivity toward water or alcohol of various substituted ketenes has been found to increase with increasing substitution and conjugation with the substituent. For H_2O:

$$(C_6H_5)_2C{=}C{=}O > (C_2H_5)_2C{=}C{=}O > (CH_3)_2C{=}C{=}O > H_2C{=}C{=}O$$

For CH_3OH:



> $(C_6H_5)_2C{=}C{=}O$

$$> C_6H_5(CH_3)C{=}C{=}O > CH_3CH{=}C{=}O$$

Since the poly(carbon suboxide) structure is highly conjugated, a pendent ketenyl group should readily react with any nucleophile capable of penetrating the polymer film. These observations would support the contention that penetration of the polymer film by the nucleophile is responsible for the observed reactivity order.

In the IR spectrum of the exposed polymers the weak absorption that develops at 4.3 µm (Figure 6) is of unknown origin but must be connected with the hydrolysis of the polymer. When D_2O was substituted for water, its frequency remained constant while the carboxylic acid O–H band shifted to a lower frequency (Figure 9a). The band was also present when other nucleophiles are substituted for water and is particularly strong in the case of ammonia (Figure 9b). These observations indicate that this weak band does not arise from a bond formed with the nucleophile or a hydrogen transfer.

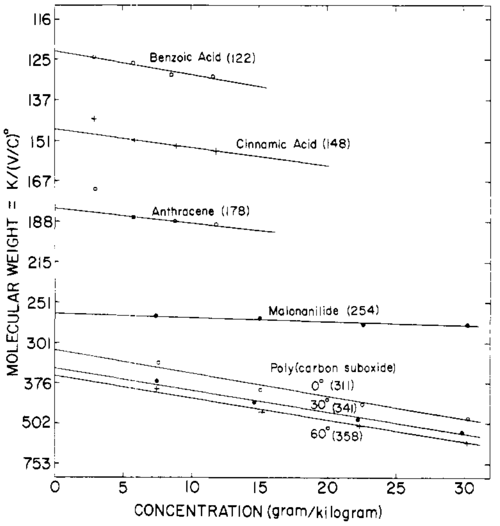


Figure 10. Vapor pressure osmometer molecular weights of carbon suboxide polymers prepared at 0, 30, and 60 °C and of assorted compounds in *N*,*N*-dimethylformamide at 75 °C.

Table II
Solubility and Molecular and Equivalent Weights of Carbon Suboxide Polymers

Sample	DMF solubility, %	M_n, g/mol	Equiv wt, g/equiv	M_n/ equiv wt
0 °C polymer	100	311	141	2.2
30 °C polymer	100	341	154	2.2
60 °C polymer	66	358[a]	164[a]/199[b]	2.2[a]
30 °C polymer, H_2O soluble	100	281	130	2.2
30 °C polymer, H_2O insoluble	100	288	133	2.2

[a] DMF soluble fraction. [b] DMF insoluble fraction.

Molecular Weight, Equivalent Weight, and Elemental Analysis. Since the ketenyl functional groups can readily be converted into acid groups, it should be possible to titrate them and, by comparing the molecular weight with the equivalent weight, determine the number of ketenyl groups per polymer molecule.

While no direct molecular weight measurement has been reported for this polymer, a calculated x-ray diffraction pattern, based on six C_3O_2 units in the fused ring poly(α-pyrone) structure, was found to be in very good agreement with the observed pattern.[4] The x-ray diffraction data also predicted an increase in molecular weight with increasing polymerization temperature. Molecular weight measurements, obtained by vapor pressure osmometry in DMF solution at 75 °C for the 0 °C, 30 °C and soluble fraction of the 60 °C polymers were 311, 341, and 358 g/mol, respectively (Figure 10).

Since the polymer displays acid–base behavior in solution, there was some question as to whether it is monomeric and un-ionized under the molecular weight measurement conditions. Molecular weight measurements were made on benzoic acid and cinnamic acid to observe whether dimerization or dissociation was general behavior of unsaturated organic acids in DMF at 75 °C. Experimental molecular weights were in excellent agreement with monomeric acid molecular weights (Figure 10). This result would support the experimental molecular weights as being representative of the polymer size. To further check the validity of the polymer molecular weight, a measurement on the 0 °C polymer was made by measuring the freezing point depression of DMSO solutions. A molecular weight of 312 g/mol was obtained in excellent agreement with the VPO result of 311 g/mol. Since the polymer is sensitive to moisture, it was of interest to observe whether an exhaustive exposure to water would result in a large change in polymer properties. The effect of extraction with water was about a 50 to 60 g/mol drop in the molecular weight (Table II) with no significant difference between the H_2O soluble and H_2O insoluble fractions.

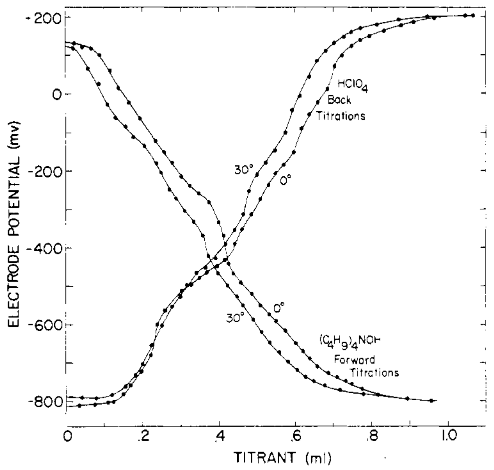


Figure 11. Forward and back titrations of DMF solutions of carbon suboxide polymers prepared at 0 and 30 °C with 0.42 N tetrabutylammonium hydroxide in 2-propanol and 0.42 N perchloric acid in 2-propanol.

Previous equivalent weight measurements on the polymer were made in aqueous solutions and were based on titration curves with poorly defined equivalence points. Smith[3] has reported a value of 68 g/equiv without presenting data while Hegar[14] reported a value of 158 g/equiv. In the nonaqueous system employed in this work, titration curves for the polymer were sharper than in an aqueous system covering an electrode potential range of 900 to 1000 mV as opposed to 300 mV for an aqueous system, but sharp equivalence points were not observed (Figure 11). Since compounds as weakly acidic as β-naphthol (pK = 9.51) could be titrated to a sharp equivalence point with this system, the polymer is probably a complex mixture of carboxylic acids with different pK's. The results of the forward titrations are presented in Table II. It is immediately seen that, like the molecular weight, the equivalent weight increases with increasing polymerization temperature and that the number of acidic protons per polymer molecule remains constant at slightly over two. It was observed that the DMF insoluble fraction of the 60 °C polymer could be titrated and went into solution as the titration proceeded. Its equivalent weight would indicate that its molecular weight is also higher than that for the DMF soluble fraction.

With the water-extracted polymers, the equivalent weight dropped with the molecular weight while the ratio between them remained constant (Table II). It was initially expected that water would enter the polymer by first hydrolyzing the ketenyl groups followed by hydrolyzing the lactone bonds. This would result in a small increase in the molecular weight and a large decrease in the equivalent weight at high degrees of hydrolysis. The most probable explanation for the contrary experimental result is a decarboxylation. Carboxylic acids with an olefin bond in the α-β or β-γ position are known to decarboxylate to nonacidic products.[15] This would keep the equivalent weight from dropping, and the greater mass of the departing CO_2 molecules could outweigh the addition of the H_2O molecules to account for the molecular weight decrease.

When the polymer is prepared from highly purified C_3O_2 and rigorously protected from moisture, it would be expected

Table III
Poly(carbon suboxide) Elemental Analysis

Sample	% C	% H	% N	m	n	M_n	DP
$(C_3O_2)_n$ calcd	52.94	0					
0 °C polymer unextracted	46.50	1.76		0.65	0.12		
DMF extracted	50.90	2.33		0.69	0.48	311	5.2
60 °C polymer unextracted	49.55	1.48		0.50	0.21		
DMF soluble	50.50	2.55		0.75	0.51	358	6.0
DMF insoluble	50.51	1.92		0.60	0.37		
30 °C polymer H_2O soluble	53.20	3.12		0.81	0.70	281	5.4
H_2O insoluble	52.38	3.09		0.82	0.67	287	5.4
30 °C polymer NH_3 exposed	44.54	3.92	16.56				
$C_3O_2 \cdot NH_3$ calcd	42.35	3.63	16.47				

to have no hydrogen content and the same stoichiometry as the monomer. This was experimentally confirmed by Schmidt, Boehm, and Hofmann[16] and Blake and Hyde.[17] When the polymer is exposed to air, hydrogen contents up to 3% have been reported.[16] Elemental analyses were performed on the DMF extracted and unextracted 0 and 60 °C samples as well as on the water extracted and ammonia exposed samples. The results are presented in Table III. The analyses show that a limited air exposure resulted in an uptake of moisture sufficient to produce a hydrogen content of between 1 and 2%. The carbon content also shows a significant drop due to the added weight of the water molecule. After the polymer was extracted with DMF and worked up, the hydrogen content increased further, but the carbon content rose indicating more is occurring than just hydrolysis. A decarboxylation can account for the carbon content increase since two oxygen atoms are lost for every one carbon atom. When the polymer was extracted with water, in addition to further increases in the hydrogen and carbon contents the molecular weight dropped. This may be explained by decarboxylation occurring to an extent comparable to hydrolysis. If the polymer composition is assumed to be determined by the number of C_3O_2 and H_2O molecules that enter the polymer and the number of CO_2 molecules that depart, these quantities may be calculated from the carbon and hydrogen contents and the molecular weight. Considering the polymer to be initially composed of p C_3O_2 units, its C_3O_2 composition will be altered by the addition of m H_2O molecules per C_3O_2 unit and the loss of n CO_2 molecules per C_3O_2 unit.

$$\text{composition} = C_3O_2 + m(H_2O) - n(CO_2)$$

The percentages of carbon and hydrogen, expressed as decimal fractions, are given by:

$$\%\,C = \frac{12(\text{mol C})}{12(\text{mol C}) + 16(\text{mol O}) + 1(\text{mol H})}$$

$$\%\,H = \frac{1(\text{mol H})}{12(\text{mol C}) + 16(\text{mol O}) + 1(\text{mol H})}$$

From the stoichiometry of C_3O_2, H_2O, and CO_2:

$$\text{mol C} = 3 - n; \quad \text{mol O} = 2 - 2n + m; \quad \text{mol H} = 2m$$

$$\%\,C = \frac{36 - 12n}{68 - 44n + 18m}; \quad \%\,H = \frac{2m}{68 - 44n + 18m}$$

or

$$n = \frac{17(\%\,C)H - 9}{11(\%\,C)H - 3}; \quad H = \frac{1}{1 - 9(\%\,H)}$$

$$m = \frac{34 - 22n}{(1/\%\,H) - 9}$$

The degree of polymerization, p, is obtained from n, m, and the molecular weight.

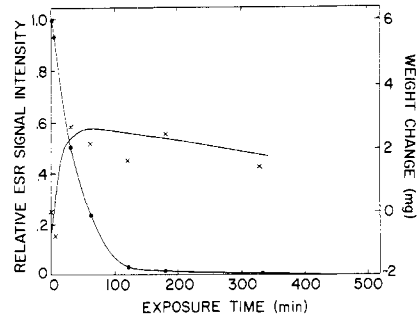


Figure 12. ESR signal decay (●) and polymer weight gain (×) as a function of water vapor exposure time for 25 mg of polymer sample.

$$M_n = p(\text{mol wt } C_3O_2) + pm(\text{mol wt } H_2O) - pn(\text{mol wt } CO_2)$$

$$p = \frac{M_n}{68 + 18m - 44n}$$

Values for n, m, and p (DP) based on experimental data are presented in Table III. These results show that appreciable hydrolysis occurs only on exposure to air and that decarboxylation becomes more significant during extraction and workup. The degrees of polymerization range between 5 and 6 and show a definite increase with increasing polymerization temperature. This DP size and temperature dependence are in very good agreement with the results of Blake's x-ray diffraction experiment.[4] The analysis of the ammoniated sample is in good agreement with that calculated for one NH_3 unit reacted per C_3O_2 unit. This would correspond to an opening of the lactone bond, of which there is one per C_3O_2 unit, to form an amide functional group and is supported by the shift of a lactone carbonyl absorption to an amide absorption in the IR. These results would indicate that the lactone bonds of the polymer are not stable enough under workup conditions toward water or ammonia to permit determination of the number of hydrolyzed or ammoniated ketenyl groups per polymer molecule by titration or nitrogen analysis.

Another approach to the analysis of the polymer molecule–ketenyl group functionality was to assume that the ketenyl groups are much more reactive than the lactone bonds toward water. Under mild exposure conditions, the quantity of water required to react with a known quantity of polymer up to the point where the ketenyl groups are no longer present was determined. This was done by simultaneously following the quantity of water uptake by weighing and the relative quantity of ketenyl groups present by ESR. These measurements using a 25-mg polymer film are plotted against exposure time in Figure 12. The ESR signal intensity, which was normalized to 1 before exposure, lost 95% of its intensity after 100 min exposure while the H_2O weight gain passed through a maxima at about 2.4 mg. Taking the 2.4 mg of water as the effective hydrolyzing mass, the following degree of polymerization may be calculated assuming two ketenyl groups per polymer molecule.

$$\mathrm{DP} = \frac{0.025\ \text{g of P}}{0.0024\ \text{g of } H_2O \times (\text{mol}/18\ \text{g}) \times (\text{mol of P}/2\ \text{mol of } H_2O)} \bigg/ \frac{68\ \text{g of } C_3O_2\ \text{unit}}{\text{mol of } C_3O_2\ \text{unit}} = 5.5$$

This result agrees well with the DP range of 5 to 6 result from the elemental analysis although it is a minimum since lactone hydrolysis is not taken into account. This indicates that there are two ketenyl groups per polymer molecule.

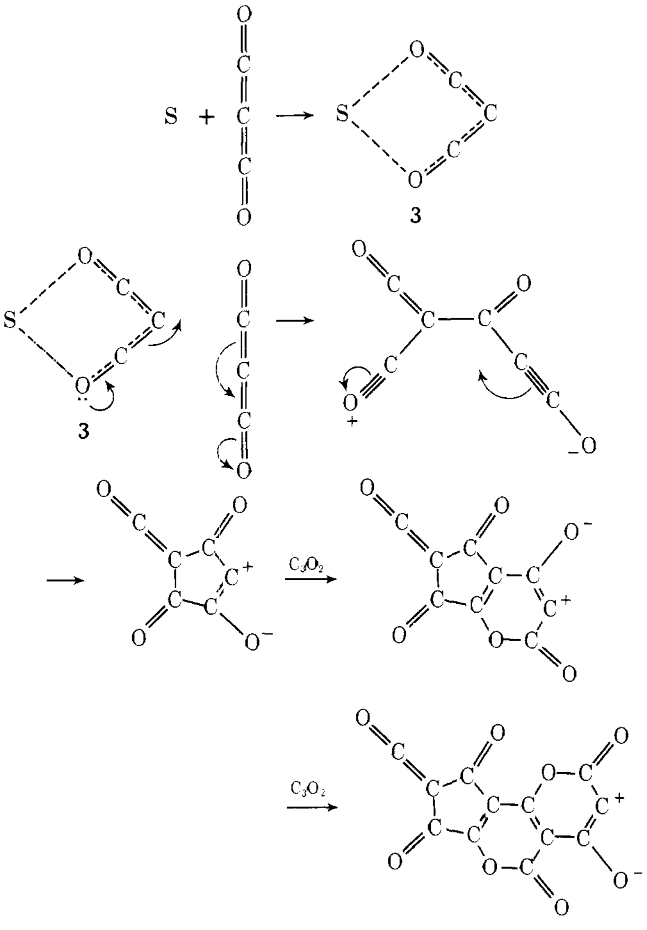
Polymerization Mechanism

A mechanism for polymerization of carbon suboxide was suggested by Ziegler[5a] involving initiation by water or acetic acid with the formation of an acetone dicarboxylic anhydride intermediate. This mechanism would predict the formation of ladder polymers of inordinately high molecular weight or would require appreciable quantities of water or acetic acid to be present. It was recognized by Ziegler that "high-temperature" polymerizations may be excepions to this mechamism.[18]

It was suggested by Ulrich[19] that the polymer could arise from an initial noncatalyzed formation of a dimer which would further react with carbon suboxide to give polymer. A conjugated carbon backbone may be formed by [4 + 2] cycloaddition of a growing polymeric α-acylketene with monomer.

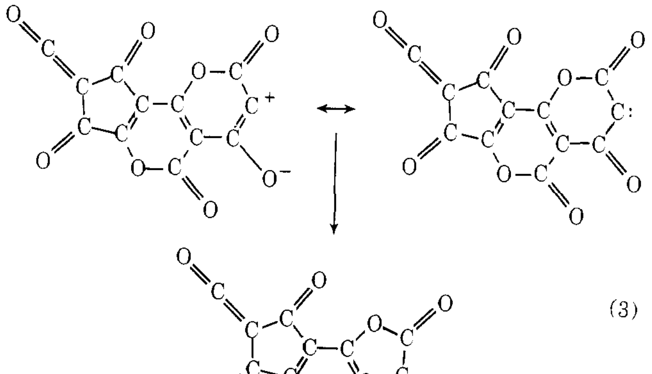
A difficulty with the cycloaddition mechanism of Ulrich is that a reactive acylketene is generated at each step, there is no obvious termination step, and it is hard to see why high molecular weight polymer is not produced.

An alternative mechanism which can be considered involves an intermediate zwitterionic ketocarbene:



In the initial step in this mechanism a complex **3** is formed between the monomer in a bent configuration and a site S provided by polymer, or perhaps less effectively, the container surface. Bending at the central carbon atom has been found to be remarkably facile as indicated by an observed bending frequency of 63 cm^{-1}.[20] The central carbon atom has been shown to have a high electron density by ^{13}C NMR.[21] The molecule has also been calculated to have high electron densities at the oxygen atoms and central carbon atom[22] which would facilitate complexing in a bent configuration by S. Poorer complexing ability of a surface site compared with polymer can account for the observed induction periods. There is some evidence for an attraction between monomer and polymer. The infrared spectrum of a polymer film was obtained by polymerizing C_3O_2 onto the NaCl windows of a 100-mm gas cell at room temperature followed by pumping the monomer from the cell once sufficient polymer had formed. The most intense band of the monomer at 4.46 μm which is well resolved from the polymer's 4.6 μm ketenyl band required 30 min of pumping with a mechanical pump to remove. This mechanism can accommodate the observed first order rate dependencies on monomer and polymer if it is assumed that either the complexation step of polymer with monomer is rate limiting, or alternatively, in the presence of excess monomer where essentially all of the polymer molecules are complexed, the slow step may be reaction of the complex **3** with monomer (the second step in the reaction sequence). In the zwitterionic mechanism, termination can arise by a competitive Wolff rearrangement as shown in eq 3 for a tetramer. Other possible termination pathways leading to a ketenyl end group may also be envisioned.

While ketocarbenes are known to readily undergo Wolff rearrangement, they have also been postulated to react via 1,3-dipolar addition as zwitterions. For example the uncatalyzed reaction of ketene with diazoacetophenone[23] has been interpreted as a 1,3-dipolar addition of a zwitterionic ketocarbene.[24]



(3)

The inability of oxygen to retard the polymerization of C_3O_2 does not rule out ketocarbenes as intermediates. While carbenes are known to react with oxygen,[25] in a study of the fate of ketocarbenes in the presence of oxygen, it was found that the substituents present on the ketocarbene determined whether reaction with oxygen occurred or whether the ketocarbene followed other pathways, including zwitterionic cycloaddition.[26] The ketocarbene intermediate may be expected to react with additives containing multiple C,C or C,O bonds, including those compounds which have been observed to retard the polymerization of carbon suboxide.

It is clear that further work will be required to elucidate the details of the mechanistic pathway for the polymerization of carbon suboxide. Both the mechanism proposed by Ulrich[19] and the above zwitterionic mechanism lead to a functionality of two ketenyl groups per molecule.

Polymer Radical Structure

The following criteria must be satisfied in proposing a specific structure for the poly(carbon suboxide) radical.

First it is necessary to consider that the polymer is composed of only oxygen and carbon both of which are even electron atoms. To have an unpaired electron localized to a polymer molecule, it is necessary to be in a triplet state or to undergo electron transfer between polymer molecules. An electron transfer is favored since the ESR spectra at room temperature or at temperatures as low as 5 °K showed no evidence of a triplet state in the form of zero-field splitting or a half-field ($\Delta M = 2$) transition.[6,7] The resolution of ^{13}C hyperfine structure would preclude the possibility of an exchange-narrowed triplet. Photomagnetic behavior, observed for this polymer where only signal intensity and not line shape are affected,[7] has been characterized as a property of charge-transfer donor–acceptor pairs in the solid state.[27] The greater susceptibility of the polymer to the more polar spin quenching nucleophiles suggests the polymer possesses some ionic character. Attributing the paramagnetism to electron transfer requires that the polymer molecule be provided with donor and acceptor sites to stabilize either a positive or negative charge.

The second criterion is that there must be two ketenyl groups per polymer molecule and the unpaired electron's existance is dependent on their presence.

Third is that the ESR signal's ^{13}C coupling constant of 9 G stipulates that the unpaired electron must be in a π-delocalized system with an appreciable spin density at an atomic site corresponding to the monomer's central carbon atom.[6,7]

Fourth, the g value of 2.0050 indicates that oxygen must be an important constituent of the π-delocalized system.[6,7]

Finally, the ketenyl group should be conjugated with the π system to account for the visible–ultraviolet spectrum change on exposure to water.

Considering the polymer's repeat unit structure, it is necessary to supply two end groups. Since each polymer molecule must have two ketenyl groups, the end positions are the logical places for them. These can be formed with C_3O_2 additions by opening just one double bond resulting in a five-membered terminal ring[3] as in Figure 13. Since each molecule must have a donor and acceptor site to stabilize a positive or negative charge, it is important how the ketenyl groups are placed. A close examination of this structure shows a polyene chain running through the ladder structure, and the end groups have been placed in such a way that one end is terminated by a ketenyl group and the other by a carbonyl group. For an acceptor site a carbonyl group is proposed and for a donor site a ketenyl group. Dipole moments for the analogous small molecules of formaldehyde (2.3 D) and ketene (1.4 D) indicate that the charged resonance structure in Figure 13 makes a reasonable contribution.[28] Since oxygen carries a charge better than carbon, a carbonyl group will more readily accept an electron and a ketenyl group will more readily release one. Connecting these two groups with a polyene chain creates a pathway for extinguishing the charge on the carbon resulting in a stable charged resonance structure (center of Figure 13). Electron transfer can be pictured as occurring from this charged structure and the resultant radical ions may be stabilized by resonance with the polyene chain (bottom of Figure 13).

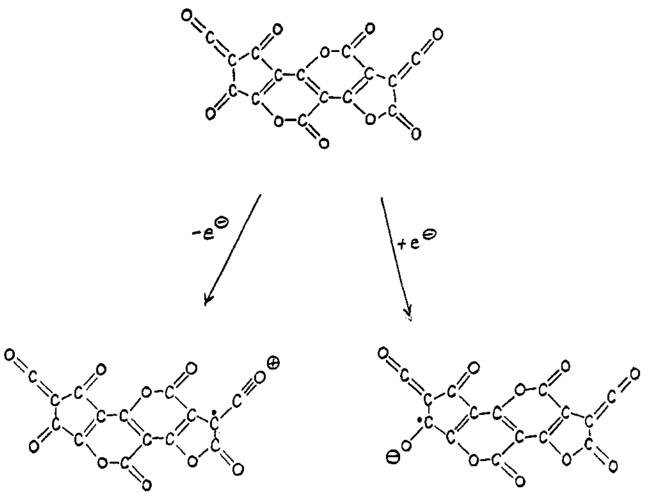


Figure 13. Proposed structures for poly(carbon suboxide) resonance forms and radical ions.

The ESR signal intensity of 2.5×10^{18} spin/g[6,7] associated with this poly(carbon suboxide) system corresponds to one spin for every 600 polymer molecules based on a degree of polymerization of six. Nonstoichiometry between the spin density and molecular density is commonly observed with organic donor–acceptor charge-transfer systems.[27,29] The explanation for this appears to be that there is a limit to the amount of charge an organic matrix can support. Kearns and Calvin[27] have proposed a mechanism for donor–acceptor charge-transfer composites which appears to be applicable to homogeneous systems as well. Charge transfer is proposed to occur by the following equilibrium:

$$D_i + A_i \rightleftarrows \underset{\text{singlet or triplet}}{[D_i^{\delta+}\text{–}A_i^{\delta-}]} \rightleftarrows \underset{\text{doublet}}{D^+} + \underset{\text{doublet}}{A^-}$$

where D_i and A_i represent neutral donor and acceptor molecules, $[D_i^{\delta+}\text{–}A_i^{\delta-}]$ represents a charge-transfer complex, and D^+ and A^- are singly charged donor and acceptor molecules. As the extent of electron transfer increases, the distance between neighboring charge centers decreases and the amount of energy required to maintain charges against attracting and repelling coulombic forces increases. A point is reached where the energy gained by charge transfer is balanced by the energy required to overcome the coulombic forces in the matrix and electron transfer ceases. This applies to the poly(carbon suboxide) system as follows. The complex has a singlet multiplicity consistant with the absence of an ESR triplet spectrum. The energy required for further complex ionization is greater than can be supplied thermally without disrupting the polymer structure as observed by the Curie law behavior. The energy can be supplied by irradiating with light. The photogenerated unpaired electrons may recouple immediately or be transferred to adjacent un-ionized polymer molecules to couple later with an unpaired electron on an opposite charged molecule. This would be consistent with the indistinguishability of the photogenerated and residual unpaired electrons in the ESR spectrum and the square root dependence of the photoenhancement of the ESR signal on the intensity of the irradiating light.[7]

Summary

Paramagnetism has been found to be an intrinsic property of poly(carbon suboxide) in the solid state. The ESR absorption has been used to derive a polymerization rate law of first order with respect to both monomer and polymer. Carbonyl compounds effectively inhibit polymerization while oxygen and nitric oxide showed no inhibiting effect. Poly(carbon suboxide) was found to be oligomeric with a DP between 5 and 6 and to have a ketenyl group functionality of two. A proportionate relationship was observed between the intensities of the ketenyl IR and ESR absorptions. A polymerization mechanism involving a zwitterionic ketocarbene intermediate and a Wolff rearrangement termination was pro-

posed. The paramagnetism was proposed to originate from an electron transfer between polymer molecules stabilized by a polyene chain within the ladder structure.

Experimental Section

Preparation of Carbon Suboxide and Polymers. Carbon suboxide was prepared by the malonic acid dehydration method[30] and distilled to infrared purity as described elsewhere.[6,7] Polymer films were prepared by admitting C_3O_2 vapor to an evacuated 100-mL cell and heating a selected surface of the cell. The color of the films depended on the thickness required for spectroscopic measurement ranging from light yellow for visible–ultraviolet spectra to dark brown for infrared spectra. Infrared spectra over a 2.5 to 16 μm range were obtained using a Perkin-Elmer 100-mm NaCl gas cell. For nucleophile exposure experiments where simultaneous ESR and IR measurements were made, a cell with a flat quartz tip[7] was used. The quartz tip was transparent in the IR between 2.5 and 4.8 μm. Reagents examined included water, methanol, ammonia, methylamine, hydrochloric acid, hydrogen sulfide, and methyl mercaptan. With the exception of water, all were distilled to infrared purity.

Polymer samples for characterization by molecular and equivalent weight measurements and elemental analysis were prepared under bulk conditions by sealing 1-mL quantities of liquid C_3O_2 in 10 × 75 mm Pyrex tubes and immersing the tubes in thermostated baths at 0, 30, and 60 °C. For unknown reasons, it was found necessary to place the sealed tubes in a horizontal position so that the monomer does not fill the space between opposite walls. When stood up in the vertical position, the tubes frequently failed with increasing explosive force as the temperature was raised. This occurred at a latter stage of the polymerization when most of the monomer appeared to be polymerized. It was thought that the polymer may be less dense than the monomer and cause excessive pressure on opposite walls of the tube at high conversion but the polymer was found experimentally to be more dense (1.65 g/cm^3) than the monomer (1.11 g/cm^3).[31] An attempt to obtain a 90 °C sample resulted in a very powerful explosion in spite of placing the tube on its side. Samples were polymerized for 2 days and no C_3O_2 odor was detected on opening indicating complete conversion. One sample prepared for nitrogen elemental analysis was opened, submerged in an ammonia-saturated P_2O_5-dried DMF solution covered by a nitrogen atmosphere, and allowed to stand for 2 weeks. Samples were not protected from air during transfers but were stored in desiccators and extracted in closed systems.

Solubility in DMF was examined by extracting 0.3- to 0.4-g quantities of polymer in a Soxhlet extractor with P_2O_5-dried DMF at a reduced pressure of 20 mmHg until the extract was colorless. At this pressure DMF refluxed at 50 to 60 °C which minimized decomposition of the soluble polymer. The soluble fraction of the polymer was recovered by concentrating to a 5-mL volume under reduced pressure followed by precipitation by adding dropwise to a 500-mL stirred volume of diethyl ether. The flocculent brown polymer precipitate was filtered from the DMF–ether mixture through a sintered glass extractor cup, washed with ether, extracted for 1 day with anhydrous ether, and vacuum dried overnight. The 0 and 30 °C samples were found to be totally extractable in DMF while only 66% of the 60 °C sample was extractable.

Water solubility was examined by substituting distilled water for DMF in the extractor and the pressure was adjusted (ca. 10 cmHg) so that the water had a 50 °C reflux temperature. After 2 days the extract of a 30 °C polymer had only a tinge of color and the extraction was stopped. The soluble fraction was concentrated to a 5-mL volume, diluted with 100 mL of DMF and reconcentrated to a 5-mL volume. The water-insoluble fraction was extracted with DMF and concentrated to a 5-mL volume. The two polymer fractions were worked up by precipitation and extraction with ether and vacuum dried as described above. Fifty-five percent of the 30 °C polymer was extracted with water. In appearance, it was lighter brown in color than samples not extracted with water.

Molecular Weight and Equivalent Weight Measurements. Molecular weight measurements were made using a Hewlett Packard Model 302B vapor pressure osmometer at 75 °C with standard and polymer DMF solution concentrations ranging from 2 to 30 g/kg. DMF was dried and purified by stirring over P_2O_5 overnight then over KOH pellets followed by distillation at 100 °C (14 cmHg pressure). Standards used were cinnamic acid, benzoic acid, anthracene, and malonanilide and an instrument constant of 9.03×10^3 μV kg/mol was determined. The molecular weight measurement of the 0 °C polymer was crosschecked by freezing point depression of a dimethyl sulfoxide (DMSO) solution with a cryoscopic cell constructed similar to that described by Ross and Glasgow.[32] Temperature was measured with a linear thermistor and an instrument constant of 5.95 deg kg/mol was determined using benzil as a standard.

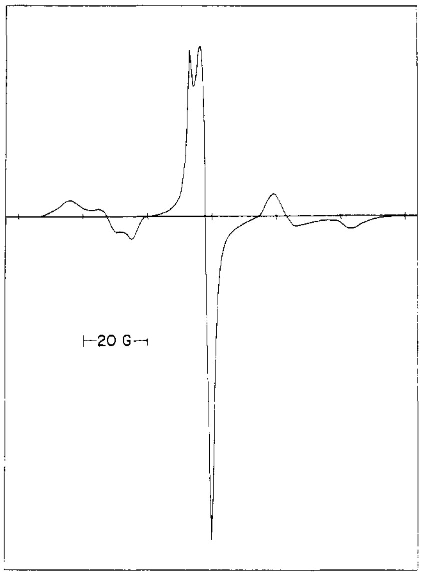


Figure 14. ESR spectrum of poly(carbon suboxide) polymerized in the presence of nitric oxide.

Equivalent weight measurements were made by potentiometrically titrating 40-mg quantities of polymer in DMF solution with a 0.4 N tetrabutylammonium hydroxide titrant in 2-propanol prepared from a 25% solution of tetrabutylammonium hydroxide in methanol (Matheson Coleman and Bell, Norwood, Ohio). The solutions were back titrated with a 0.4 N perchloric acid titrant in 2-propanol to ensure that the acid–base behavior was reversible. The equivalence point for the forward titration was taken at the point where the titration curve levels off (Figure 11). The volume of titrant required for the polymer in the back titration was taken between the upward curvature where excess hydroxide titrant had been neutralized and the point where the curve levels off. The equivalent weights obtained from the back titrations averaged approximately 5 g/equiv greater than those from the forward titrations.

The elemental analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, N.Y.

Spectroscopic Measurements. ESR measurements were made using JEOL-ME-3X, X-band ESR spectrometer with TE_{105} cylindrical dual cavity. Signal intensities were measured as peak-to-peak intensities against a manganese marker, consisting of Mn^{2+} in MgO, in the reference position of the cavity. Visible ultraviolet measurements were made using a Cary Model 118C spectrophotometer, and infrared measurements were made using a Beckman IR 8 spectrophotometer.

Kinetic Measurements of the Thermal Bulk Polymerization. Samples of monomer were prepared by transfer in vacuo to a glass tube sealed at one end (i.d. 2 mm, o.d. 3 mm) until the liquid height was about 1 cm which corresponds to approximately 35 mg. The tube was cooled with liquid nitrogen and sealed at a total length of 2.0 to 2.5 cm. These samples were placed in ESR cells and were short enough for total exposure in the cavity. The ESR spectrometer was equipped for temperature control in one position of the dual cavity with a JEOL Model JES-VCT-2AX variable temperature controller. Temperature was measured by inserting an iron–constantan thermocouple into the sample position of the cavity. Due to an induction period, samples for the 0 and 20 °C polymerization were initially placed in a 30 °C water bath until the first trace of color was observed and then immediately transferred to the cavity which was preset at the desired temperature. The signal growth rate was monitored by scanning the magnetic field repetitively.

For polymerizations carried out in the presence of potential inhibitors, a cell[7] was employed which had a cylindrical quartz tip which was heated to 100 °C by immersion in an oil bath. Polymer was formed by gas deposition and the rate of polymer formation was followed by ESR measurements. A carbon suboxide pressure of 330 mmHg (vapor pressure at −13 °C) was used. Either equimolar quantities of inhibitor based on pressure measurements or room-temperature vapor pressures of inhibitor if less than 330 mmHg were used. Normally 30 to 60 min of heating were required before a faint yellow film appeared at the tip of the cell. At this point ESR signal intensity measurements were made against a Mn^{2+} marker every 15 min. Measurements involved bringing the cell tip rapidly to room temperature with a 5-s immersion in water and scanning the signal and marker. The measurement time was 4 min and is not included in the polymerization time.

In the case of the additive nitric oxide, a second signal in the ESR spectrum, having a central line at a lower magnetic field and wing structure between 20 and 30 G on either side, overlapped the normally observed 2.3 G signal (Figure 14). The spectrum did not change as polymerization proceeded. Evacuation of the cell for 1 h did not change the spectrum indicating it is not a weak association of polymer with the nitric oxide molecule. When preformed polymer was exposed to nitric oxide, a shoulder maximum on the ESR signal slowly developed at a point corresponding to the new line's central maximum. The nature of the interaction between polymer and nitric oxide is not known.

Acknowledgment. The authors are indebted to the Faculty Research Award Program, the City University of New York, Grant No. 1620, 11084, and 11420 and to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for a grant to N.L.Y.

References and Notes

(1) Based in part on a doctoral dissertation submitted by A. W. Snow in partial fulfillment of the requirements for the degree of Doctor of Philosophy at the Graduate School of the City University of New York.

(2) O. Diels and B. Wolf, *Ber.*, **39**, 689 (1906).

(3) R. N. Smith, D. A. Young, E. N. Smith, and C. C. Carter, *Inorg. Chem.*, **2**, 829 (1963).

(4) A. R. Blake, W. T. Eeles, and P. P. Jennings, *Trans. Faraday Soc.*, **60**, 691 (1964).

(5) (a) E. Ziegler, H. Junek, and H. Bieman, *Monatsh. Chem.*, **92**, 927 (1961); (b) H. Sterk, P. Tritthart, and E. Ziegler, *ibid.*, **101**, 1851 (1970).

(6) A. Snow, N.-L. Yang, and H. Haubenstock, *Carbon*, **14**, 177 (1976).

(7) N.-L. Yang, A. Snow, H. Haubenstock, and F. Bramwell, *J. Polym. Sci.*, in press.

(8) R. N. Smith, *Trans. Faraday Soc.*, **62**, 1881 (1966).

(9) A. R. Blake, *J. Chem. Soc.*, 3866 (1965).

(10) C. Walling, "Free Radicals in Solution", Wiley, New York, N.Y., 1957, p 169; I. M. Kolthoff and F. A. Bovey, *Chem. Rev.*, **42**, 491 (1948).

(11) B. Vollmert, "Polymer Chemistry", Springer-Verlag, New York, N.Y., 1973, p 61.

(12) T. Kunitake and S. Murakami, *J. Polym. Sci.*, **12**, 67 (1974); E. G. Janzen, *Acc. Chem. Res.*, **4**, 31 (1971).

(13) R. N. Lacey, "The Chemistry of Alkenes", S. Patai, Ed., Chapter 14, Interscience, New York, N.Y., 1964, Chapter 14.

(14) G. Hegar, "Beitrag zur Chemie des Kohlensuboxides", Ph.D. Thesis, Zurich, 1961.

(15) J. March, "Advanced Organic Chemistry: Reactions, Mechanisms and Structure", McGraw-Hill, New York, N.Y., 1968, pp 477 and 478.

(16) V. L. Schmidt, H. P. Boehm, and U. Hofmann, *Z. Anorg. Allg. Chem.*, **282**, 16 (1955).

(17) A. R. Blake and A. F. Hyde, *Trans. Faraday Soc.*, **60**, 1775 (1964).

(18) T. Kappe and E. Ziegler, *Angew. Chem., Int. Ed. Engl.*, **13**, 491 (1974).

(19) H. Ulrich, "Cycloaddition Reactions of Heterocumulenes", Academic Press, New York, N.Y., 1967, Chapter 3.

(20) W. H. Smith and G. E. Leroi, *J. Chem. Phys.*, **45**, 1767 (1966).

(21) E. A. Williams, J. D. Cargiola, and A. Ewo, *Chem. Commun.*, 366 (1975).

(22) J. F. Olsen and L. Burnelle, *J. Phys. Chem.*, **73**, 2298 (1967); J. R. Sabin and H. Kim, *J. Chem. Phys.*, **56**, 2195 (1972).

(23) W. Ried and H. Mengler, *Justus Liebigs Ann. Chem.*, **678**, 113 (1964).

(24) W. J. Baron, M. R. DeCamp, M. E. Hendrick, M. Jones, Jr., R. H. Levin, and M. B. Sohn in "Carbenes", Vol. 1, M. Jones, Jr., and R. A. Moss, Ed., Wiley, New York, N.Y., 1973, p 107.

(25) P. P. Gaspar and G. S. Hammond, ref 24, Vol. II, 1975, p 319 ff.

(26) M. Tanaka, T. Nagai, and N. Tokura, *J. Org. Chem.*, **38**, 1602 (1973).

(27) D. R. Kearns and M. Calvin, *J. Am. Chem. Soc.*, **83**, 2110 (1961).

(28) C. L. Angyal, G. A. Barclay, A. A. Hurkins, and R. J. W. LeFevre, *J. Chem. Soc.*, 2583 (1951); K. Ingold, *Chem. Rev.*, **15**, 552 (1947).

(29) D. Bijl, H. Kainer, and A. C. Rose-Innes, *J. Chem. Phys.*, **35**, 765 (1959); J. W. Eastman, G. M. Androes, and M. Calvin, *ibid.*, **36**, 1197 (1962); L. S. Singer and J. Kommandeur, *J. Phys. Chem.*, **34**, 133 (1961).

(30) G. Brauer, "Handbook of Preparative Inorganic Chemistry", 2nd ed, Academic Press, New York, N.Y., p 648.

(31) L. B. Dashkevich and V. G. Berlin, *Russ. Chem. Rev.*, **36**, 391 (1967).

(32) G. S. Ross and A. R. Glassgow, *Anal. Chem.*, **36**, 700 (1964).

Three-Dimensional Crystalline Structure of Cellulose Triacetate II[1a]

E. Roche,*[1b] H. Chanzy,*[1b] M. Boudeulle,[1c] R. H. Marchessault,[1d] and P. Sundararajan[1d]

Centre de Recherches sur les Macromolécules Végétales (CNRS),
53 X, 38041 Grenoble Cédex, France; Laboratoire de Minéralogie-Cristallographie
(ERA 600), Université Claude Bernard, Lyon, France; and Départment de Chimie,
Université de Montréal, Montréal, Canada. Received August 5, 1977

ABSTRACT: The three-dimensional structure of cellulose triacetate II (CTA II) was derived from an x-ray and electron diffraction analysis using intensity data from fiber and single-crystal patterns. The unit cell is orthorombic with space group $P_{2_12_12_1}$ and dimensions a = 24.68 Å, b = 11.52 Å, and c (fiber axis) = 10.54 Å. A CTA II Model was built from the known structure of the central residue of cellotriose undecaacetate. This model was first refined through a conformational and packing analysis and then tested against the diffraction information. The resulting structure consists of antiparallel pairs of parallel CTA II chains. In projection, it has the same gross feature as the projection proposed earlier by Dulmage but it differs extensively in its details such as the glucose ring geometry and the conformation of the acetyl groups. Acetyl groups linked to C(6) are in the gg conformation. Those linked to C(2) and C(3) adopt the planar geometry identical to the one always found in the crystalline structure of acetyl sugars.

The well-known polymorphism in cellulose science and technology[2a] is found also in cellulose derivatives. Perhaps the most familiar case is the cellulose triacetate (CTA) system where the terminology CTA I and CTA II reflects the following reversible and nonreversible crystalline transformations (scheme A). Scheme A of transformation was clearly established by Sprague et al. in 1958[2b] and despite a few controversial reports[3,4] this scheme is now widely accepted.

$$\begin{tikzcd}
\text{cellulose I} \arrow[r, shift left] \arrow[d] \arrow[dr] & \text{CTA I} \arrow[l, shift left] \arrow[d] \arrow[dl] \\
\text{cellulose II} \arrow[r, shift left] & \text{CTA II} \arrow[l, shift left]
\end{tikzcd} \qquad (A)$$

Our recent morphological and structural study[5-7] of the polymorphic transformation of *valonia* cellulose followed

0024-9297/78/2211-0086$01.00/0