On the Cationic Polymerization of 2,2-Dimethyl-1,3-dioxole and 2,2-Diphenyl-1,3-dioxole

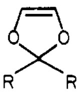
M. K. Akkapeddi and H. K. Reimschuessel*

Corporate Research Center, Allied Chemical Corporation, Morristown, New Jersey 07960.

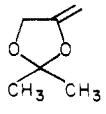
Received April 18, 1979

ABSTRACT: Cationic polymerization of 2,2-dimethyl-1,3-dioxole (I) yields a polymer which contains both trans and cis monomer units as evidenced by ^{1}H NMR of the CH_3 region ($P_{\text{trans}} \simeq 0.7$). The ^{13}C NMR spectrum also seems to support this configurational structure although cis (anti) and trans CH_3 carbons could not be resolved, even at 67.8 MHz. The 2,2-diphenyl-1,3-dioxole (II), a new monomer, has been shown to be polymerized by $BF_3\cdot Et_2O$ at 25 °C, yielding a low molecular weight polymer. The ^{13}C NMR data for the ipso carbon in poly-II suggests the presence of both cis and trans monomer units in the chain. Isomerization of the propagating cyclic carbenium ion appears to be a competing reaction in the polymerization of II.

The synthesis and cationic polymerization of 1,3-dioxole (Ia) and 2,2-dimethyl-1,3-dioxole (I) were first reported by Field,[1] who found that with BF_3 as the initiator at −78 °C, Ia yielded a cross-linked polymer and I a predominantly soluble one with small fractions of insoluble material. The polymerization of Ia and I was presumed to proceed through the double bond, analogous to the cationic polymerization of vinyl ethers, but the formation of cross-linked polymer in the case of Ia was attributed to a competing ring-opening polymerization of 1,3-dioxolane units in the chain. The greater ring stability imparted by the substituents at the 2-position in the 1,3-dioxolane unit accounted for the formation of soluble polymer from I. No further evidence was presented for the structure of the poly-I, especially regarding the stereochemistry. We have recently reported[2] the ^{13}C NMR evidence for the configurational structure of poly(vinylene carbonate) and its hydrolysis product, viz., poly(hydroxymethylene). Since poly-I must also, in principle, yield poly(hydroxymethylene) upon hydrolysis, we were interested in studying the configurational structure of poly-I and its hydrolysis product and in determining if the stereochemistry is different from that of poly(vinylene carbonate). Since 2,2-diphenyl-1,3-dioxole (II), a hitherto unknown compound, contains bulkier phenyl groups, it was of interest to determine if II is polymerizable and if so whether its polymerization is influenced by steric control in the propagation step. Steric factors would be expected to favor the syndiotactic placement of monomer units, thus possibly leading to stereoregular poly(hydroxymethylene) after hydrolysis. It was also of interest to determine the extent, if any, of isomerization polymerization occurring in a fashion similar to that reported[3] for 2,2-dimethyl-4-methylene-1,3-dioxolane (III).



Ia, R = H
I, R = CH_3
II, R = Ph



III

Experimental Section

2,2-Dimethyl-1,3-dioxole (I) was prepared according to the method of Field:[1] ^{1}H NMR ($CDCl_3$) δ 1.5 (s, CH_3, 6 H), 6.17 (s, –CH=CH–, 2 H); ^{13}C NMR ($CDCl_3$) (from Me_4Si) δ 24.92 (CH_3), 114.16 (>C<), 126.69 (=CH–).

2,2-Diphenyl-1,3-dioxolane (IV). A mixture of benzophenone (182 g, 1 mol), cyclohexane (500 mL), ethylene glycol (70 g, 1.13 mol), and *p*-toluenesulfonic acid (3 g) was refluxed with stirring in an azeotropic water-removal assembly for 18 h. After the theoretical amount of water was collected from the reaction mixture, the contents were neutralized with powdered sodium acetate (10 g), and the solvent was removed under reduced pressure. The residue was carefully distilled on a fractionating column (12 in. glass-helices packed) to collect the major fraction at 121 °C (0.7 mm) in 90% yield: mp 56 °C [lit.[4] bp 125 °C (0.9 mm) or 168 °C (10 mm)]; ^{1}H NMR ($CDCl_3$) δ 4.07 (s, –CH_2O–, 4 H), 7.45 (m, arom, 10 H); ^{13}C NMR ($CDCl_3$) δ 64.88 (CH_2O), 109.16 (>C<), 126.15 (phenyl, para), 128.06 ± 0.05 (phenyl, ortho, and meta), 142.2 (phenyl, ipso).

4,5-Dichloro-2,2-diphenyl-1,3-dioxolane (V). A solution of IV (90.4 g, 0.4 mol) in CCl_4 (250 mL) was heated to 70 °C, and then a slow stream of chlorine gas was bubbled into the solution while irradiating it with a GE spot lamp (500 W) such that a gentle reflux was maintained. After about 60 g of chlorine was added (1.5 h), the reaction was stopped, and the solvent was removed under reduced pressure. The residue, which solidified upon cooling, was recrystallized from hexane to obtain V as a white, crystalline solid, which is quite sensitive to moisture: yield 85%; mp 72 °C; ^{1}H NMR ($CDCl_3$) δ 6.56 (s, CH, 2 H) and 7.36 (m, arom, 10 H); ^{13}C NMR ($CDCl_3$) δ 95.39 (–CHO–), 130.03 (>C<), 125.63 (phenyl, para), 128.05 (phenyl, ortho), 128.6 (phenyl, meta), and 140.81 (phenyl, ipso).

2,2-Diphenyl-1,3-dioxole (II). A mixture of V (73.8 g, 0.25 mole), anhydrous diethyl ether (500 mL), powdered magnesium metal (30 g), and a trace of iodine was refluxed with stirring under nitrogen for 72 h. The contents were then filtered, and the filtrate was concentrated under reduced pressure. The residue so obtained consisted of >90% of the product II with benzophenone as a minor side product (~8%). It was recrystallized three times from hexane to obtain II in >99.8% purity (by GC) in 46% yield: mp 58 °C; ^{1}H NMR ($CDCl_3$) δ 6.28 (s, –HC=CH–, 2 H), 7.37 (m, arom, 10 H); ^{13}C NMR ($CDCl_3$) δ 113.63 (–C–), 126.12 (phenyl, meta), 127.12 (phenyl, para), 128.01 (phenyl, ortho), 128.62 (–CH=CH–), 141.2 (phenyl, ipso).

2,2-Dimethyl-4-methylene-1,3-dioxolane (III).[3,5] A mixture of 3-chloro-1,2-propanediol (221 g, 2 mol), acetone (600 mL), petroleum ether (35–60 °C) (600 mL), and *p*-toluenesulfonic acid (5 g) was refluxed in an azeotropic water removal assembly for 48 h. After neutralization with powdered sodium acetate (10 g), the contents were concentrated, and the residue was distilled at 150 °C (760 mm) [lit.[3] bp 55 °C (15 mm)] to obtain 2,2-dimethyl-4-chloromethyl-1,3-dioxolane (VI) in 84% yield. VI was dehydrochlorinated with KOH as described in the literature[5] to obtain III in 65% yield: ^{1}H NMR ($CDCl_3$) δ 1.46 (s, CH_3, 6 H), 3.89 (m, vinyl, 1 H), 4.3 (m, vinyl, 1 H), 4.5 (t, –CH_2O–, 2 H); ^{13}C NMR ($CDCl_3$) δ 24.07 (CH_3), 66.45 (CH_2O), 77.64 (=CH_2), 111.9 (>C<), 156.39 (=C(O$^-$)–).

***cis*- and *trans*-2,2,4,5-tetramethyl-1,3-dioxolanes (VIIa and VIIb)** were prepared as described in the literature[6] (^{1}H and ^{13}C NMR: see Table II).

Poly(2,2-dimethyl-1,3-dioxole) (Poly-I). A solution of I (2.5 g) in dry toluene (12.5 mL) was cooled to −78 °C under nitrogen,

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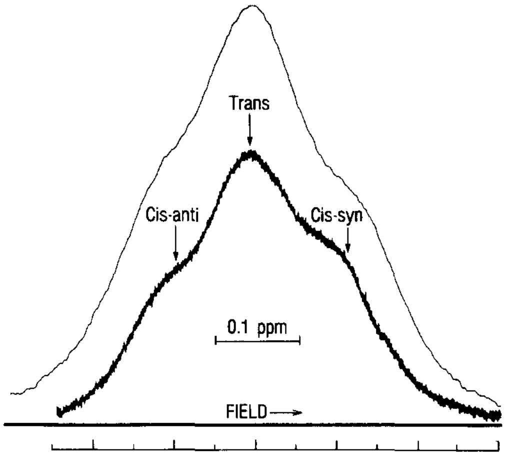


Figure 1. ^1H NMR spectrum of the poly(2,2-dimethyl-1,3-dioxole)-methyl region (top, 270 MHz; bottom, 100 MHz) in pyridine-d_5 at 100 °C.

and freshly distilled $BF_3{\cdot}Et_2O$ (0.05 g in 1 mL of toluene) was added to the monomer solution. The contents were kept at −78 °C for 18 h. The viscous transparent polymerization mixture was treated with triethylamine (1 mL) added dropwise with stirring at −78 °C. The solution was then poured into excess petroleum ether, and the precipitated polymer was filtered, rinsed with an ether–petroleum ether (1:1) mixture, and then dried, yield 63%.

Poly(2,2-diphenyl-1,3-dioxole) (Poly-II). A solution of II (5 g) in dry toluene (25 mL) was purged with nitrogen followed by the addition of the $BF_3{\cdot}Et_2O$ (0.1 g in 1 mL of toluene) at room temperature. The polymerization mixture was stirred at room temperature under nitrogen for 18 h, and the polymer was precipitated from the dark solution to an excess of a diethyl ether–petroleum ether mixture (1:1), yield 72%.

Poly(2,2-dimethyl-4-methylene-1,3-dioxolane) (Poly-III). IIII was polymerized at −78 °C in toluene, using $BF_3{\cdot}Et_2O$ as initiator as described for poly-I, yield ≃100%.

Hydrolysis of poly-I. A solution of poly-I (2 g) in aqueous ethanol (50 mL, 80%) was treated with 3 drops of concentrated HCl and refluxed with stirring for 18 h. No precipitation of poly(hydroxymethylene) occurred. The brownish solution was added to excess cold water to precipitate the polymer. ^1H NMR (Me_2SO-d_6) indicated peaks at δ 1.4 (CH_3), 4.1 (CHOD), and 4.46 (HOD), respectively. The polymer was suspended in 1% aqueous HCl solution and heated with stirring at 80 °C for 12 h. Slow precipitation of a gel-like polymer occurred accompanied by considerable darkening. The contents were poured into excess methanol, and the solid was filtered and dried, yield 30%. IR examination of solid indicated it to be identical with the poly(hydroxymethylene) derived from base hydrolysis of poly(vinylene carbonate). The filtrate was neutralized and concentrated to obtain a dark brown residue which was soluble in water and ethanol. The residue consisted of a complex mixture of oligomeric degradation products and was not further characterized.

Carbonyl Analysis of Polymers. Typically, a 5% solution of polymer in aqueous EtOH (80%) was reacted with hydrazine at 60 °C for 24 h. The solution was poured into excess cold water, and the precipitated polymer was filtered, washed with water, and dried under vacuum over P_2O_5. The nitrogen content in the polymer was determined by elemental analysis, and the mole percent of the carbonyl group in the polymer was calculated from this value.

Protonation Experiment. Into an 8-mm NMR tube was charged 0.1 mL of FSO_3H and 0.1 mL of SbF_5 followed by condensation of 0.8 mL of liquid SO_2 at −50 °C. This solution was further cooled to −78 °C, and a solution of II or III (0.2 g in 0.3 mL of CD_2Cl_2) was added with agitation. The tube was sealed, and the ^{13}C NMR spectrum of the mixture was recorded at −50 °C.

Methods. ^1H NMR spectra were recorded on a Varian T-60 (60 MHz), a Varian HA-100 (100 MHz), or a Bruker HX-270 (270 MHz) instrument. ^{13}C NMR spectra were recorded on a Varian CFT-20 (20 MHz) or a Bruker HX-270 (67.8 MHz) instrument. High resolution NMR spectra of polymers were obtained in pyridine-d_5 solution (15% w/v) at 100 °C. Relative peak areas for the methyl region in poly-I (Figures 1 and 2) were measured by using a duPont 301 curve analyzer.

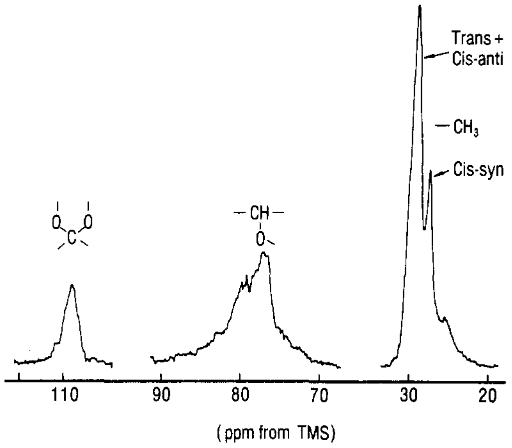


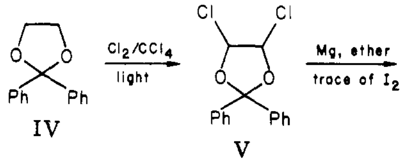
Figure 2. ^1H decoupled ^{13}C NMR spectrum of poly(2,2-dimethyl-1,3-dioxole) in pyridine-d_5 at 100 °C (67.8 MHz).

Infrared spectra were recorded on a Perkin-Elmer Model 283 spectrophotometer.

Inherent viscosities were measured in toluene at 25 °C in an Ubbelohde type viscometer. Molecular weights ($\bar{M}_n$) were measured, using a corona wescan vapor pressure osmometer (VPO).

Results and Discussion

2,2-Dimethyl-1,3-dioxole (I) was synthesized according to Field[1] by a reaction scheme involving Diels-Alder reaction of anthracene and vinylene carbonate followed by hydrolysis and acetonization of the adduct. The final step consisted of thermal cracking of the anthracene–I adduct to I which was found to be accompanied by small amounts of acetone and 2-methylfuran as byproducts. The monomer was purified by careful fractional distillation from 1% $NaBH_4$. 2,2-Diphenyl-1,3-dioxolane (II) was chlorinated to 4,5-dichloro-2,2-diphenyl-1,3-dioxolane (V) followed by dechlorination with magnesium in anhydrous ether. 2,2-Dimethyl-4-methylene-1,3-dioxolane (III) was prepared by acetonization of 3-chloro-1,2-propanediol followed by dehydrochlorination of the 4-chloromethyl-2,2-dimethyl-1,3-dioxolane. The monomers I, II, and III were polymerized with $BF_3{\cdot}Et_2O$ as the initiator (Table I). It may be noted that in spite of the bulky phenyl substituents, 2,2-diphenyl-1,3-dioxole is capable of cationic polymerization, the driving force for which seems to be the electron-rich nature of the olefin and stabilization of the propagating carbenium ion by the adjacent oxygen. However, compared to I and III, the rate of polymerization of II is extremely slow at −78 °C, with good yields of the polymer being obtained only at room temperature, a fact undoubtedly attributable to steric reasons. The polymerizability of the monomers may be placed in the order III > I > II.



High resolution ^1H NMR (100 MHz and 270 MHz) of poly-I in pyridine-d_5 at 100 °C showed a broad unresolved peak for the backbone methine protons at δ 4.2, but the methyl region showed resolution into three observable peaks that were analyzed using the duPont curve resolver

Table I
Polymerization of Unsaturated 1,3-Dioxolane Monomers

monomer[d]	polymerization conditions	yield, %	η_{inh}[a]	C=O content, mol %
I (2.5 g)	$BF_3 \cdot Et_2O$ (0.05 g), toluene (13.5 mL), −78 °C, 18 h	63	$\bar{M}_n = 5350$[b]	0.7
I (2 g)	$BF_3 \cdot Et_2O$ (0.1 g), CH_2Cl_2 (10 mL), −78 °C, 18 h	85	0.28	
I (5 g)	$BF_3 \cdot Et_2O$ (0.15 g), CH_2Cl_2 (10 mL), −10 °C, 3 h	100	cross-linked	
II (5 g)	$BF_3 \cdot Et_2O$ (0.1 g), toluene (25 mL), −78 °C, 48 h	0		
II (2 g)	$BF_3 \cdot Et_2O$ (0.05 g), CH_2Cl_2 (10 mL), −15 °C, 18 h	8		
II (5 g)	$BF_3 \cdot Et_2O$ (0.1 g), toluene (25 mL), 25 °C, 18 h	72	$\bar{M}_n = 3983$[c]	9.3
III (5 g)	$BF_3 \cdot Et_2O$ (0.05 g), toluene (25 mL), −78 °C, 18 h	100	0.3	34.8
III (5 g)	$BF_3 \cdot Et_2O$ (0.15 g), CH_2Cl_2 (10 mL), −78 °C, 2 h	92	0.1	

[a] Measured in toluene at 25 °C. [b] In DMF (VPO). [c] In toluene (VPO). [d] I, 2,2-dimethyl-1,3-dioxole; II, 2,2-diphenyl-1,3-dioxole; III, 4-methylene-2,2-dimethyl-1,3-dioxolane.

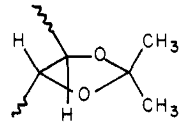
Table II
Chemical Shifts of
cis- and *trans*-2,2,4,5-Tetramethyl-1,3-dioxolanes (VIIa,b)

		δ[a]			
		CH_3	CH_3 (gem)	CH	>C<
cis	^{1}H NMR	1.15	1.34 (syn) 1.46 (anti)	4.26	
	^{13}C NMR	15.59	25.83 (syn) 28.69 (anti)	74	107.32
trans	^{1}H NMR	1.27	1.42	3.64	
	^{13}C NMR	16.91	27.36	78.37	107.53

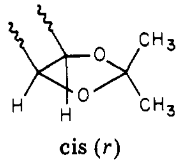
[a] ppm from Me_4Si, in $CDCl_3$.

and found to be in the ratio of 0.15:0.7:0.15 with the upfield and the downfield peaks separated from the central peak by 0.11 and 0.083 ppm, respectively (Figure 1).

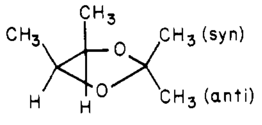
In analogy to the polymerization of vinylene carbonate,[2] the polymerization of 2,2-dimethyl-1,3-dioxole can give rise to trans (*m*) or cis (*r*) monomer units in the chain. The trans monomer unit must give rise to a single CH_3 peak due to symmetry, while the cis monomer unit must show two magnetically nonequivalent CH_3 peaks. On the basis of shielding effects, the chemical shifts of the CH_3 peaks are assignable in the order cis-anti > trans > cis-syn. Thus the central peak in the observed spectrum is assigned to the trans monomer unit, and the equal upfield and downfield peaks are assigned to the cis monomer unit. This assignment was confirmed by the observed chemical shifts for the *gem*-dimethyl groups in *cis*- and *trans*-2,2,4,5-tetramethyl-1,3-dioxolanes (VIIa and VIIb) (Table II). In ^{1}H NMR, *cis-syn-*, *cis-anti-*, and *trans*-methyl groups of the ketal group were observed at δ 1.34, 1.46, and 1.42, respectively. In ^{13}C NMR, the corresponding resonances were observed at δ 25.83, 28.69, and 27.36, respectively. Poly-I obtained under the conditions described in Table I must then be considered atactic with some preference for trans propagation ($P_{trans} \simeq 0.7$). Both the 20- and 67.8-MHz ^{13}C NMR spectra of poly-I showed two peaks for the methyl carbons about 2 ppm apart with the larger downfield peak showing a possible shoulder (Figure 2). On the basis of ^{1}H NMR results, the upfield peak is assigned to the *cis-syn*-CH_3 resonance, and the larger downfield peak is assigned to the *trans*-CH_3 resonance with an overlapping *cis-anti*-CH_3 resonance. The relative intensity of the peaks was not significantly affected when toluene was replaced by CH_2Cl_2 in the polymerization. Thus both ^{1}H and ^{13}C NMR indicate that although trans propagation is favored, significant cis propagation, nonetheless, takes place in the cationic polymerization of I ($P_{cis} \simeq 0.3$). *cis*-1,2-Dimethoxyethylene, on the other hand, is reported[7] to yield a predominantly threo-diisotactic polymer with $BF_3 \cdot Et_2O$ at −78 °C, indicating a very high degree of trans propagation ($P_{rr} \sim 0.77$ to 0.93). The high degree of stereoregularity was attributed to the chelation of the growing carbenium ion pair with the penultimate chain unit. Apparently ion pair chelation is not as efficient in the polymerization of I.



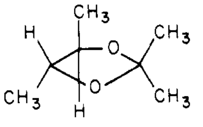
trans (*m*)



cis (*r*)



VIIa
cis (meso)



VIIb
trans (racemic)

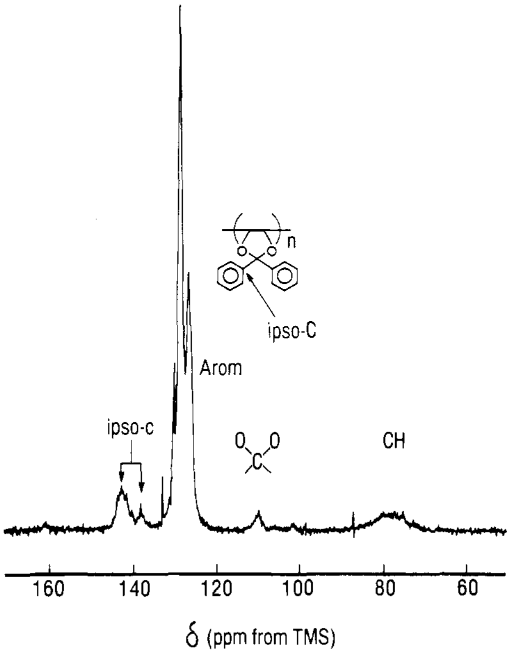


Figure 3. ^{1}H decoupled ^{13}C NMR spectrum of poly(2,2-diphenyl-1,3-dioxole) (20 MHz, 40% w/v in Me_2SO-d_6 at 100 °C).

^{1}H NMR (100 MHz) of poly(2,2-diphenyl-1,3-dioxole) (poly-II) gave very broad signals for the backbone methine protons at δ 4.4 and for the aromatic protons at δ 7.2, thus providing little stereochemical information. The ^{13}C NMR spectrum of poly-II also showed little stereochemical information for the methine and quaternary carbons (Figure 3). However, since the ipso carbon of a phenyl group normally appears downfield and well separated from the remaining ortho, meta, and para phenyl carbons, it could

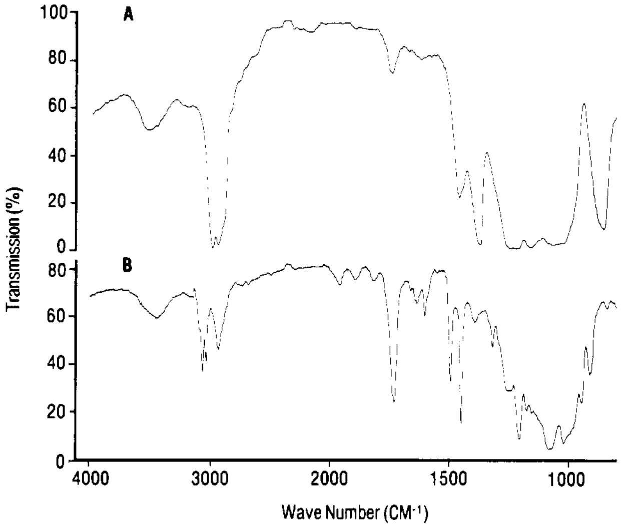


Figure 4. Infrared spectrum of (KBR disk) (A) poly(2,2-dimethyl-1,3-dioxole and (B) poly(2,2-diphenyl-1,3-dioxole).

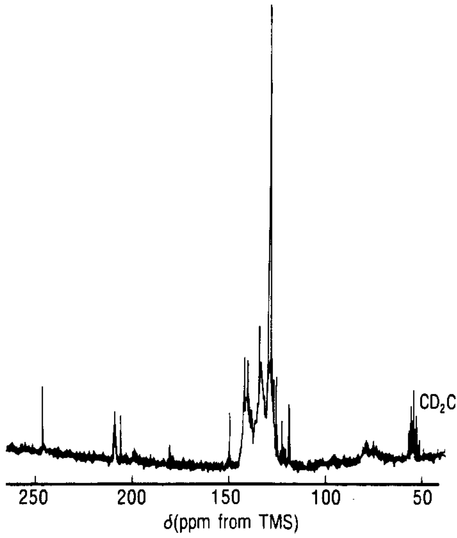
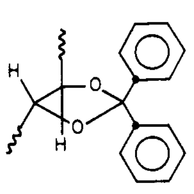
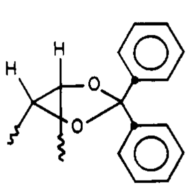


Figure 5. ^1H decoupled ^{13}C NMR spectrum of the 2,2-diphenyl-1,3-dioxolan-4-yl cation at −50 °C (20 MHz) (FSO_3H + SbF_5 in liquid SO_2).

be considered as a useful stereochemical probe. In the observed spectrum (Figure 3), two signals were found at δ 138 and 142.5 in the ratio of 1:6 for the ipso carbon.



trans



cis-anti; cis-syn

The upfield peak may be assigned to the cis-syn carbon and the large downfield peak may be a combination of trans and an overlapping cis-anti carbon resonance, analogous to the case of the CH_3 groups in poly-I, by assuming poly-II to be homogeneous in structure. On the basis of this assumption, poly-II must also be considered to be atactic with some preference for the trans propagation (P_{trans} = 0.714). IR of poly-II (Figure 4B) showed a significant band at 1732 cm^{-1} for the carbonyl group. This might result from a possible rearrangement of the propagating cyclic carbenium ion to an acyclic carbenium ion leading to pendant aldehyde groups in the chain or end groups resulting from possible hydrolysis of chain ends.

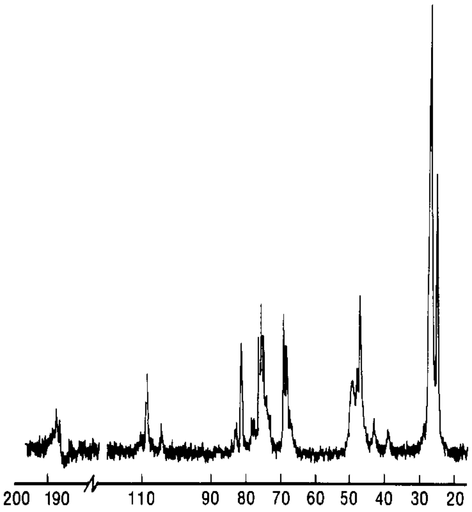
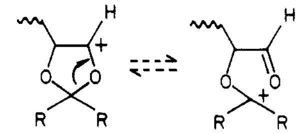
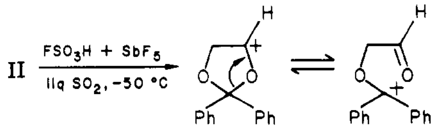


Figure 6. ^1H decoupled ^{13}C NMR spectrum of poly(2,2-dimethyl-4-methylene-1,3-dioxolane) (20 MHz, 20% in C_6D_6 at 100 °C).



A quantitative estimation of the carbonyl groups in the polymer by hydrazone formation and nitrogen analysis gave a value of 9.3 mol % for the carbonyl content. Although the molecular weight of the polymer is low (DP ≃ 18), the extent of the carbonyl groups observed indicates that they might be originated from the rearrangement reaction. As a model for the propagation reaction, protonation of 2,2-diphenyl-1,3-dioxole was studied in the superacid medium, FSO_3H–SbF_5 in liquid SO_2 at −50 °C. The stable carbocationic species so generated were examined by the ^1H decoupled ^{13}C NMR spectrum (Figure 5). The major carbenium ion species observed at 246.98 ppm is assignable to the unrearranged 2,2-diphenyl-1,3-dioxolan-4-yl cation (VIII), but the three other resonances at 210.76, 210.13, and 206.98 ppm may result from the rearrangement of the cyclic carbenium ion VIII to the acyclic carbenium ion IX. Resonance stabilization in IX



VIII IX

is expected to increase the shielding effect on the carbenium carbon, and hence its chemical shift must be upfield relative to VIII. Poly-I showed only a weak band in the IR at 1732 cm^{-1} for the carbonyl group (Figure 4A), which analyzed to be ~0.7 mol % as determined by the nitrogen analysis of the corresponding hydrazone. Since the polymer had a DP_n ≃ 54, the observed low carbonyl content may only be attributed to possible end groups, within experimental error. Thus the isomerization of the propagating cyclic carbenium ion does not seem to occur to any significant extent and may at best be only a chain-terminating process in the polymerization of I. However, in the case of 4-methylene-2,2-dimethyl-1,3-dioxolane (III), substantial isomerization occurred during the cationic polymerization at −78 °C, since the polymer obtained showed a strong carbonyl band at 1725 cm^{-1} and

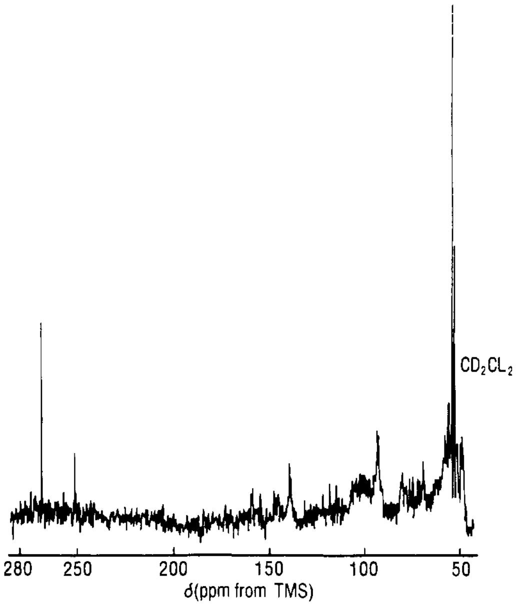
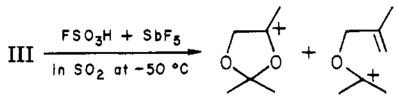


Figure 7. ${}^1H$ decoupled ${}^{13}C$ NMR spectrum of the 2,2,4-trimethyl-1,3-dioxolan-4-yl cation ($FSO_3H + SbF_5$ in liquid SO_2 at −50 °C).

nitrogen analysis of the corresponding hydrazone indicated it to be ~34.8 mol %. ${}^{13}C$ NMR of poly-II (Figure 6) provided further evidence for the presence of a significant amount of isomerized monomer units in the chain since the peaks observed at δ 187.5 and 27.3 may be attributed to the carbonyl and acyclic methyl groups (i.e., $-OC(CH_3)_2-$), respectively. These results are in agreement with those reported by Goodman and Abe[3] for the polymerization of III. Although the authors did not elaborate further on the mechanism, they suggested the intermediacy of the carbenium ion, while Kennedy[8] suggested a concerted bimolecular mechanism involving the nucleophilic attack of the olefin on the 2-position of the 1,3-dioxolane ring with simultaneous ring opening. Our own results favor the mechanism involving the rearrangement of the propagating cyclic carbenium ion to an acyclic carbenium ion. Protonation of III in the superacid medium showed in the ${}^{13}C$ NMR both the cyclic X and the rearranged XI carbenium ions at δ 269.56 and 252.03, respectively (Figure 7).



X XI

Acidic hydrolysis of poly-I and poly-II was found to cause considerable degradation, probably involving the chain end or the main-chain carbonyl functionality. The poly(hydroxymethylene) obtained from poly-I in low yield showed an IR spectrum essentially identical with that obtained from poly(vinylene carbonate), consistent with the atactic structure of the polymers.

Acknowledgment. The authors are indebted to Mr. G. E. Babbitt for obtaining the 20-MHz ${}^{13}C$ NMR spectra and Mr. R. A. Kirk for experimental assistance. The ${}^1H$ and ${}^{13}C$ NMR spectra on the Bruker HX 270 instrument (270 MHz) were kindly provided by Mr. P. Demou of the Department of Chemistry, Yale University, New Haven, CT 06520.

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Polycation–Polyanion Complexes in the Linear Diblock Copolymer of Poly(styrene sulfonate)/Poly(2-vinylpyridinium) Salt

R. Varoqui,* Q. Tran, and E. Pefferkorn
Centre de Recherche sur les Macromolécules, 67083 Strasbourg Cedex, France.
Received January 4, 1979

ABSTRACT: From spectrophotometric analysis in aqueous medium, the degree of ionization of poly(2-vinylpyridine) in a linear diblock copolymer of a poly(styrene sulfonate)/poly(2-vinylpyridine) salt was obtained as a function of pH. The spectrophotometric titration curve was compared with the titration curves of a diblock copolymer of poly(ethylene oxide)/poly(2-vinylpyridine) and of homopoly(2-vinylpyridine). The strong increase of basicity of pyridine groups in the polyampholyte copolymer is explained by invoking a stoichiometric interaction between oppositely charged groups. The formation of an internal polysalt is discussed in relation to conformational changes obtained from viscosity data.

Polyelectrolyte complexes are the result of mixing two highly, but oppositely, charged homopolymers in aqueous media. Studies on the electrochemical behavior and the application of these complexes in various fields have been reported.[1-3] Less attention seems to have been paid thus far to the properties of charged block copolymers in dilute aqueous solutions. Stille have reported on the properties of block copolymers containing cationic sequences based on 2-vinylpyridine and anionic sequences based on methacrylic acid.[4] The copolymers were polyampholytes and their use in the formation of desalination membranes was stressed.[5]

Since charged block copolymers are models for a special kind of polyelectrolyte, it seemed desirable to undertake a more systematic investigation of their polyelectrolyte properties. In this preliminary paper we report on the

0024-9297/79/2212-0831$01.00/0