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ABSTRACT

Since free radical ring-opening polymerization made it possible to introduce functional groups, such as esters, carbonates, thioesters, and amides, into the backbone of an addition polymer, it was reasoned that simple hydrolysis of these copolymers would produce the desired oligomers that could be terminated with various combinations of hydroxyl, amino, thiol, and carboxyl groups. Thus the copolymerization of 2-methylene-1,3-dioxepane and styrene (r_1=0.021 and r_2=22.6) gave a copolymer containing 10 mole-percent of an ester-containing unit with 100% ring opening at 120°C. Hydrolysis of this copolymer gave an oligomer terminated with a hydroxyl group and a carboxylic acid group. Similarly the copolymerization of 2-methylene-1,3-dioxepane and ethylene gave a series of biodegradable polyethylene copolymers containing 2.1 to 10.4% ester-containing units. Hydrolysis of these copolymers gave a series of ethylene oligomers with nine to forty-seven ethylene units and terminated with a hydroxyl group and a carboxylic acid group. By the same general method oligomers of various monomers that are terminated with a methylamino

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group and a carboxylic acid group from N-methyl-2-methylene-1,3-oxazolidine and with a thiol group and a carboxyl group from 2-methylene-1,3-oxathiolane.

When 3,9-dimethylene-1,5,7,11-tetraoxaspiro[5.5]undecane was copolymerized with a wide variety of monomers, copolymers containing the carbonate group in the backbone of the polymers by double ring opening were obtained. When styrene was used as the comonomer, styrene copolymers containing 4 to 10% carbonate-containing units were obtained. Hydrolysis with base gave a series of styrene oligomers that were terminated with hydroxyl groups.

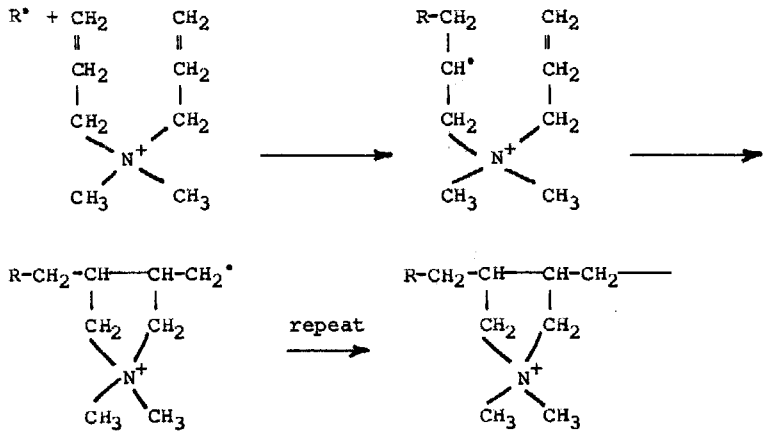
A restudy of the copolymerization of diethyl ketene acetal with styrene gave a styrene co-oligomer containing some ketene acetal units but terminated with an ethyl group and a carboethoxy group. Thus part of the ketene acetal was acting as a chain-transfer agent, functioning by an addition-elimination mechanism. When this process was extended to benzyl methyl ketene acetal and styrene, a styrene oligomer that is terminated by a benzyl group and a carbomethoxy group resulted. Apparently the high stability of the benzyl free radical promotes complete elimination and 100% chain transfer. At 120°, styrene and benzyl methyl ketene acetal (1:1) in the presence of di-tert-butyl peroxide gave a 25% conversion of a styrene oligomer containing an average of four styrene units terminated with a benzyl group and a carbomethoxy group. Hydrolysis gave an oligomer capped with a carboxylic acid group. The use of di(hydroxymethylbenzyl)-containing ketene acetals will produce an oligomer capped by hydroxyl groups by direct polymerization.

INTRODUCTION

Although functionally terminated oligomers are commercially important for the production of polyurethanes and block polyesters, very few oligomers are synthesized by a convenient

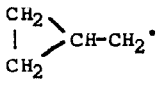
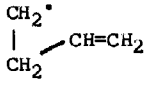
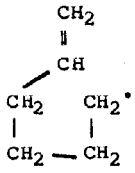
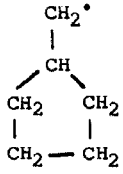
and inexpensive free radical process. Most functionally terminated oligomers are produced either by ionic addition polymerization or condensation reactions. The hydroxy-terminated polybutadiene produced by a free radical process by Arco Chemical Company is one of the few exceptions. Polymerization of butadiene and sulfur by a free radical mechanism that involves a ring-opening of the S_8 ring followed by reduction of the resulting polysulfide groups to give a mercapto-terminated polymer has found limited use [1]. Since it was shown that free radical ring-opening polymerization [2] made it possible to introduce functional groups, such as esters [3], carbonates [4], thioesters [5], and amides [6], into the backbone of an addition polymer, it was reasoned that simple hydrolysis would produce the desired oligomers that could be terminated with various combinations of hydroxyl, amino, thiol, and carboxylic acid groups.

Even though the ionic ring-opening polymerization of heterocyclic compounds, such as ethylene oxide, tetrahydrofuran, ethylenimine, β-propiolactone and caprolactam, as well as the Ziegler-Natta metathesis ring-opening polymerization of cyclic olefins, such as cyclopentene and norbornene, are well known, free radical ring-opening polymerizations are quite rare. The few examples of free-radical ring-opening polymerization that are reported in the literature include derivatives of vinylcyclopropane [7,8], o-xylylene dimer [9], derivatives of bicyclo[1.1.0]-butane [10], and elemental sulfur [11]. Simple unstrained five- or six-membered carbocyclic rings have not been shown to undergo radical ring opening readily, and in fact the open-chain radicals have been shown to be less stable than the corresponding unstrained cyclic radical. For example, Butler and Angelo [12] found that diallyldimethylammonium bromide would undergo inter-intramolecular polymerization to produce a soluble polymer. Apparently the reaction is kinetically controlled to form the five-membered ring rather than the thermodynamically favored six-membered ring.



The course of some of these ring-opening and ring-closing polymerizations can be explained by the recent data of Maillard, Forrest, and Ingold [13] that is listed in Table I.
They studied the transformations in the cyclopropylmethyl and the cyclopentylmethyl series by electron spin resonance. In the case of the three-membered radical the reaction involves ring opening since the energy is favorable and the rate of reaction is very high. In the case of the five membered ring system the reaction proceeds in the direction of ring-closure since the energetics of that reaction is favorable and the rate of the ring closure is

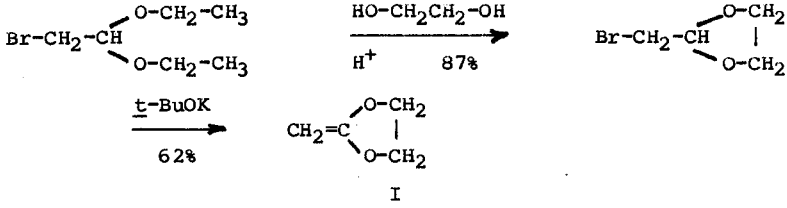
Table I

		k_{250}, s^{-1}	E, kcal/mol	log A/s^{-1}
		1.3×10^8	5.94	12.48
		1.0×10^5	7.8	10.7

also moderately high. However, thermodynamic calculation in these laboratories indicated that the introduction of an oxygen atom into the ring would favor ring opening by producing the more stable carbonyl double bond.

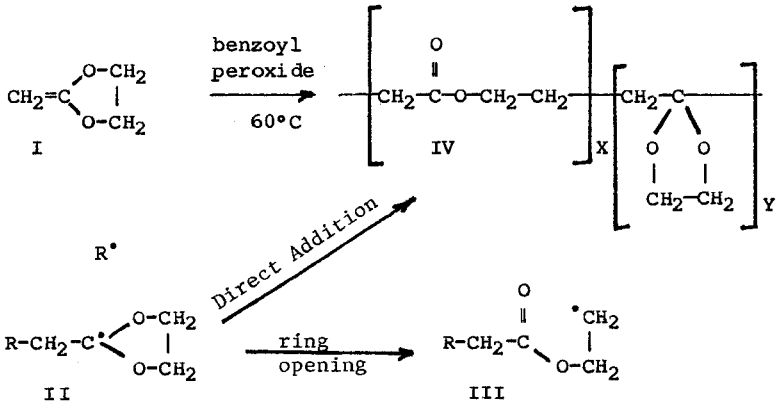
OLIGOMERS BY FREE RADICAL COPOLYMERIZATION FOLLOWED BY HYDROLYSIS

We, therefore, undertook a reinvestigation of the cyclic ketene acetal, 2-methylene-1,3-dioxolane (I), that had been prepared by McElvain and Curry [14]. Although McElvain and Beyerstedt [15] reported that benzoyl peroxide had no appreciable effect on diethyl ketene acetal, no such study was reported [14] for the 2-methylene-1,3-dioxolane (I). The synthesis was carried out as follows [6]:



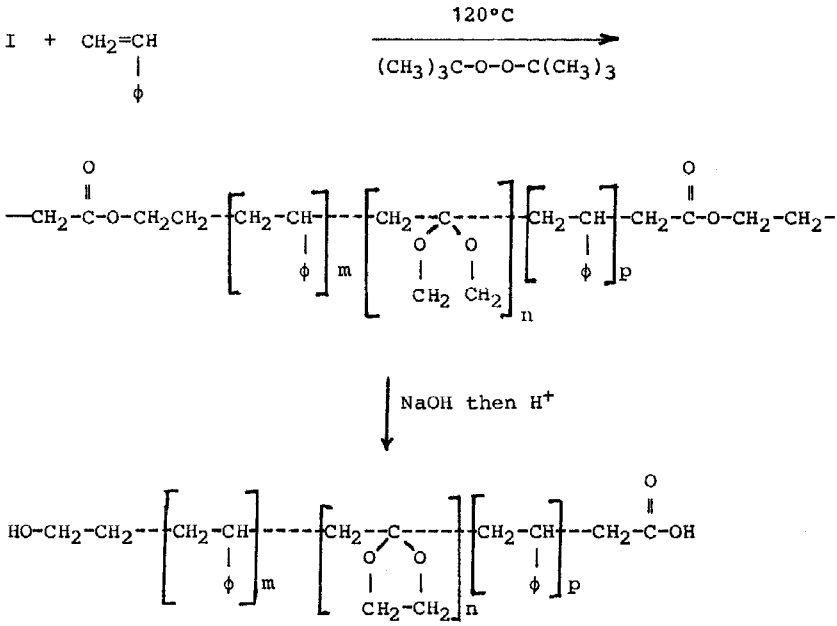
I

Treatment of this monomer with benzoyl peroxide gave a high molecular weight polyester by a free radical ring-opening polymerization which can be rationalized by the accompanying scheme. The structure of the polyester IV was established by analysis and hydrolysis as well as infrared and NMR spectroscopy.

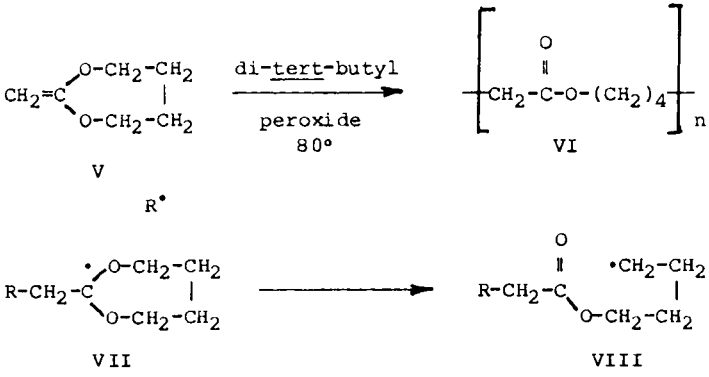


At 60°C only 50% of the rings were opened and at 120°C, 87% of the rings were opened [6]; high dilution also favored the extent of ring opening. There was a competition between the direct addition of the intermediate radical II and its ring opening to the radical III. An alternative method of analysis of the extent of ring opening was the basic hydrolysis of the copolymer IV, which cleaved the ester groups but left the cyclic ketals intact.

Copolymerization of styrene and I gave a copolymer containing both ring-opened and nonring-opened units.

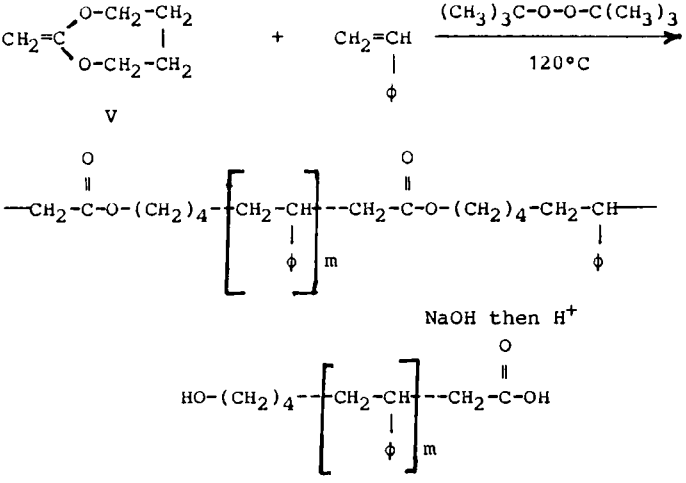


In a program to find other cyclic acetals that would undergo quantitative ring opening even at room temperature we prepared the seven-membered ketene acetal, 2-methylene1,3-dioxepane (V), which underwent essentially complete ring opening at room temperature. This process makes possible the quantitative introduction of an ester group in the backbone of an addition polymer.



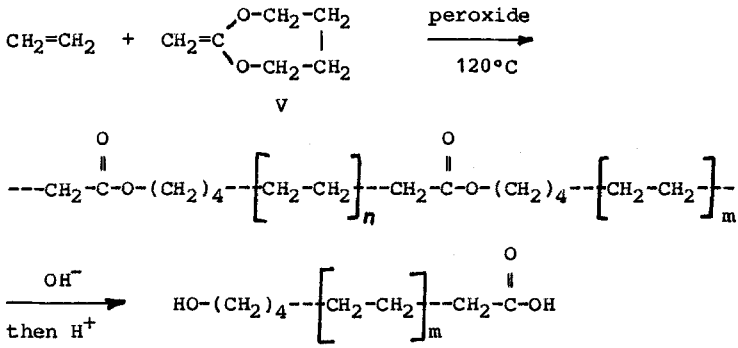
Apparently the seven-membered ring increases the steric hindrance in the intermediate free radical VII to eliminate practically all of the direct addition and also introduces a small amount of strain so that the ring opening to the radical VIII is accelerated.

When the seven-membered ketene acetal V was copolymerized with styrene, 4-vinylanisole, vinyl acetate, ethylene, and vinyl chloride, copolymers with ester groups in the main chain were obtained, all with quantitative ring opening. For example, by the use of a large amount of styrene and a small amount of the ketene acetal V, followed by hydrolysis, an oligomer of styrene was produced that was capped with a hydroxyl group and a carboxylic acid group.



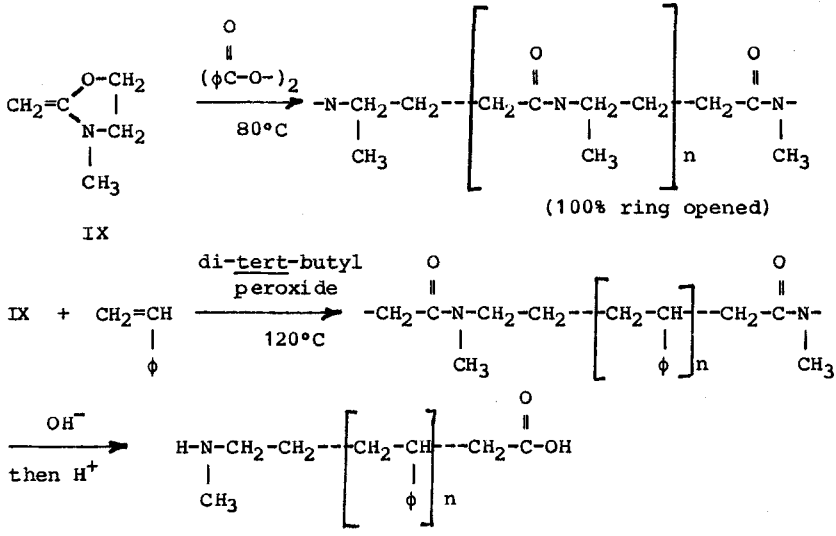
In the copolymerization of the ketene acetal V with styrene, r_1 is 0.021 and r_2 is 22.6 at 120°C. With a mixture containing about 80% V and 20% styrene, a copolymer containing 90 mole-% styrene and 10 mole-% ester-containing units was obtained. The hydrolysis of this copolymer gave an oligomer of styrene containing an average of about nine styrene units end capped with the hydroxyl and carboxylic acid groups. Thus a very general method has been developed for the synthesis of a wide variety of oligomers with any desired molecular weight range. Of course, since the copolymers are random, the molecular weight distribution of the oligomers is quite broad. However, these oligomers should prove quite useful for the synthesis of polyurethanes and block polyesters.

Although most synthetic polymers are nonbiodegradable since they have not been on the earth long enough for microorganisms or enzyme systems to have evolved to utilize them as food, polyesters that are relatively low molecular weight and rather low melting are biodegradable [16]. This observation is related to the fact that poly(β-hydroxybutyric acid) occurs widely in nature and many micro-organisms use this polyester to store energy in the same way that animals use fat. On the other hand, no synthetic addition polymer was known that was readily biodegradable. In an effort to produce a biodegradable addition polymer the 2-methylene-1,3-dioxepane (V) and ethylene were copolymerized at 120°C for 30 minutes at a pressure of 1800 psi to give a low conversion of copolymers with ester-containing units varying from 2.1 to 10.4 mole-%. The copolymers were in fact biodegradable with the copolymers containing the high amount of ester groups being rapidly degraded and the copolymers containing only 2.1% comonomer only slowly degraded [17]. Apparently there are enzymes in the micro-organisms that are capable of hydrolyzing the ester linkages in the ethylene copolymer to produce the oligomers with terminal carboxylic acid groups; these oligomers are then degraded as analogs of fatty acids by the normal metabolic processes.



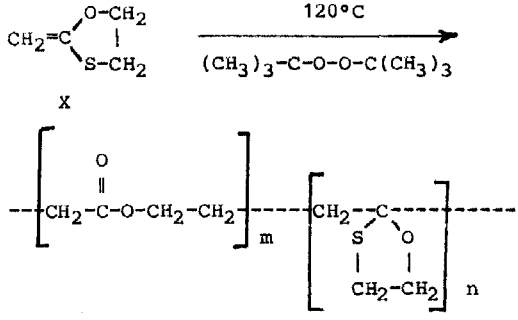
In a separate step the ethylene-2-methylene-1,3-dioxepane copolymer was hydrolyzed to give oligomers that were capped with a hydroxyl group at one end and a carboxylic acid group at the other. When the ester-containing unit was 2.1 mole-%, the value of n was approximately 47 and when it was 10.4 mole-%, the value of n was approximately 9. The copolymers with 6 or less mole-% of the ester-containing units had melting points in excess of 90°C.

Since the nitrogen analogs of the cyclic ketene acetals were readily synthesized and would polymerize with essentially 100% ring opening, their copolymerization with a variety of monomers was undertaken [6].

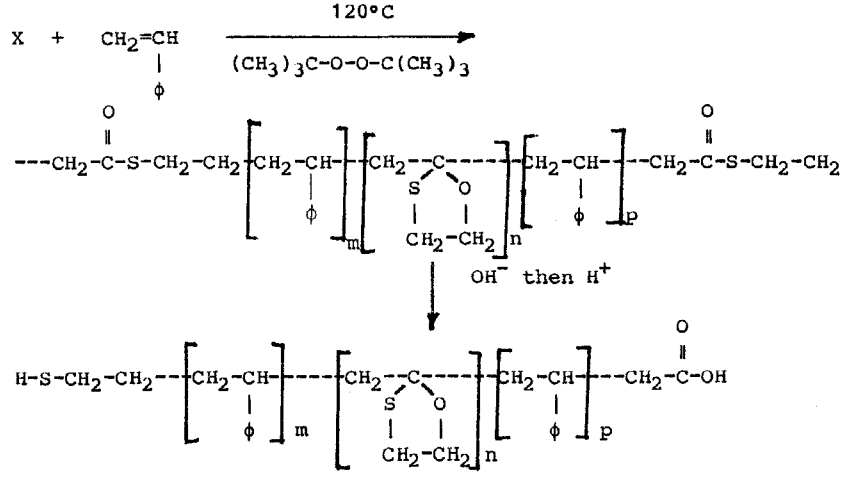


Thus the amide linkage is sufficiently more stable than the ester group to greatly favor the ring opening. Copolymerization of IX with styrene proceeded with essentially quantitative ring opening [6]. In the case of the copolymer with styrene and IX, the copolymer was readily hydrolyzed to give an oligomer of styrene capped with an aminomethyl group and a carboxylic acid group.

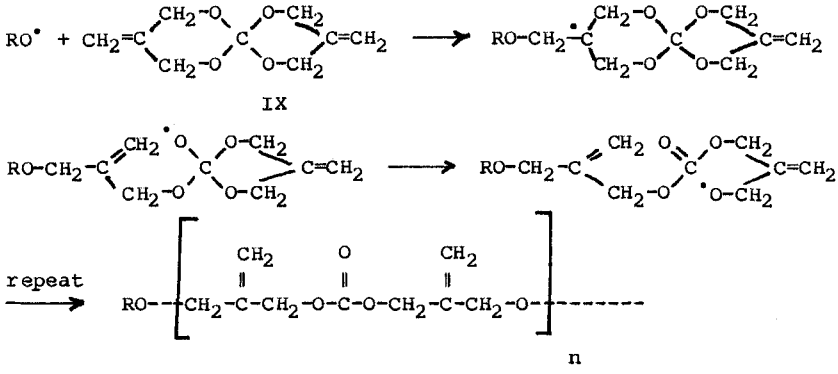
Although the sulfur analog of the cyclic ketene acetal X was prepared and polymerized, apparently the resulting thioester is higher energy than the ordinary ester and therefore retards the extent of ring opening. Even at 120°C only 45% of the rings were opened.



Nevertheless, copolymerization of X with styrene gave a copolymer containing some thioester groups and hydrolysis of this copolymer gave an oligomer capped with a mercaptan and a carboxylic acid group.

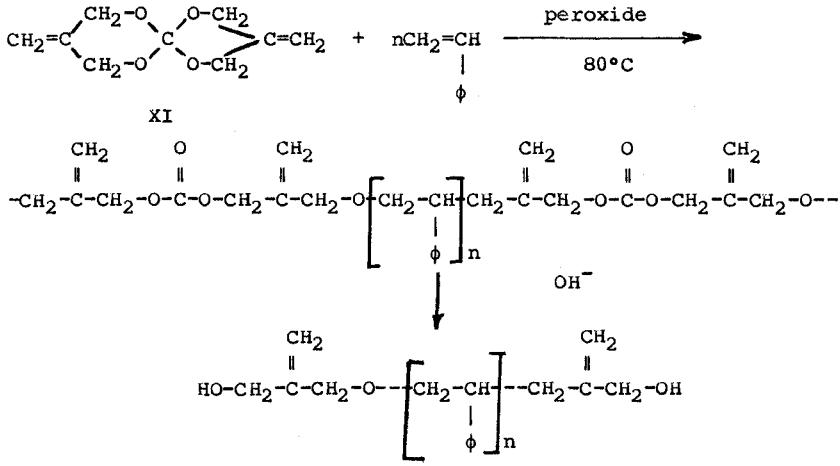


The unsaturated spiro ortho carbonates have been shown to undergo double ring opening in a free radical polymerization to introduce a carbonate group in the backbone of an addition polymer [19].



IX

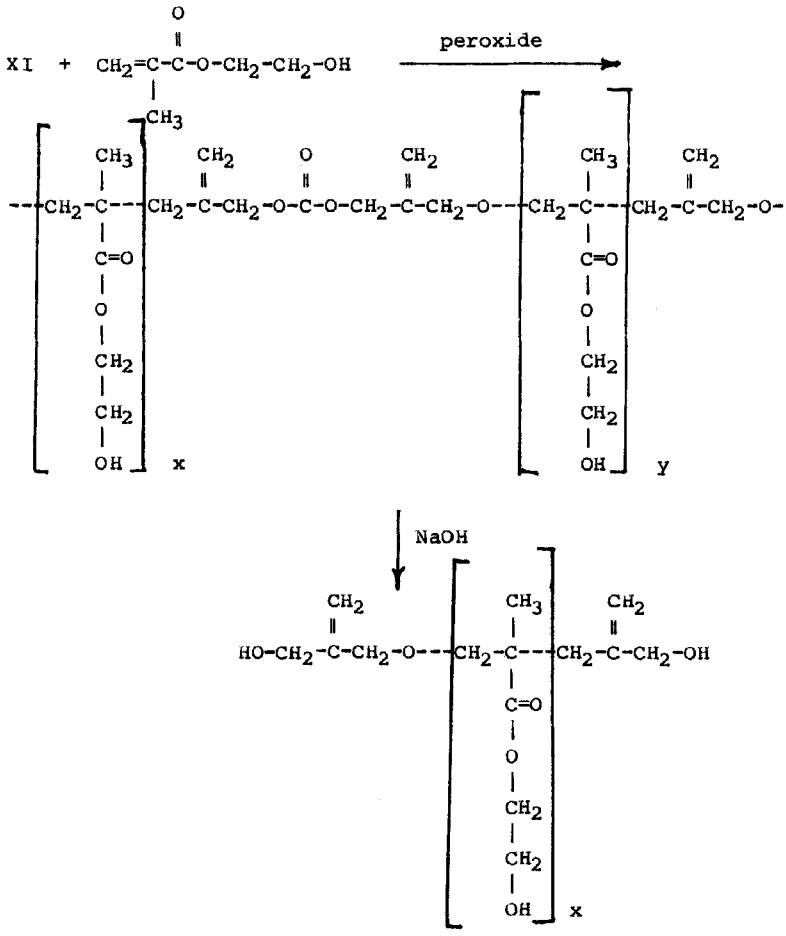
The driving force for the ring opening is the relief of the strain in the spiro system and the formation of the stable carbonate double bond. The double ring opening is probably a concerted process from the initial radical addition product to the open-chain radical. Even though the spiro compound XI is an allyl monomer, it does copolymerize with a wide variety of comonomers. For example, XI will copolymerize with styrene to give a copolymer containing carbonate groups in the main polymer chain [20]. Hydrolysis gives the oligomeric polystyrene capped



XI

with reactive hydroxyl groups [2].

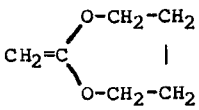
Another example of this same procedure is the copolymerization of the 3,9-dimethylene-1,5,7,11-tetraoxaspiro[5.5]undecane (XI) with hydroxyethyl methacrylate (HEMA) to produce a water soluble copolymer with carbonate groups in the backbone which was shown to be biodegradable. When a copolymer containing 14 mol-% of the ring-opened units was hydrolyzed in an alcoholic solution containing 1% sodium hydroxide for 3 hours at room temperature, an oligomer, that was endcapped with hydroxyl groups and had a viscosity average molecular weight that was one fifth that of the original copolymer, were obtained



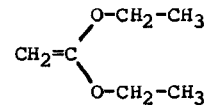
Thus, it is possible by simple free radical copolymerization with monomers that undergo ring opening followed by hydrolysis of the resulting copolymer to produce a variety of oligomers of any desired average molecular weight capped with a choice of reactive end groups.

KETENE ACETALS AS CHAIN TRANSER AGENTS

Since the cyclic ketene acetal V will undergo free radical

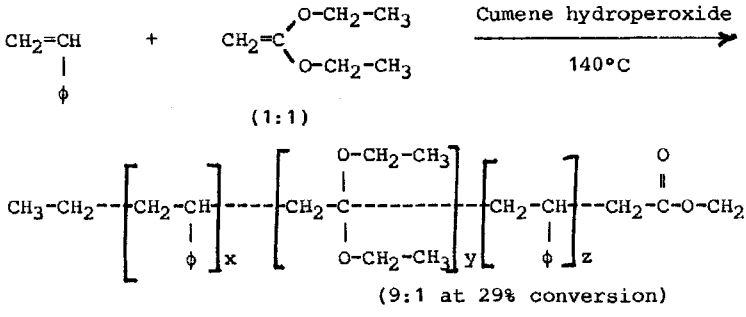


V

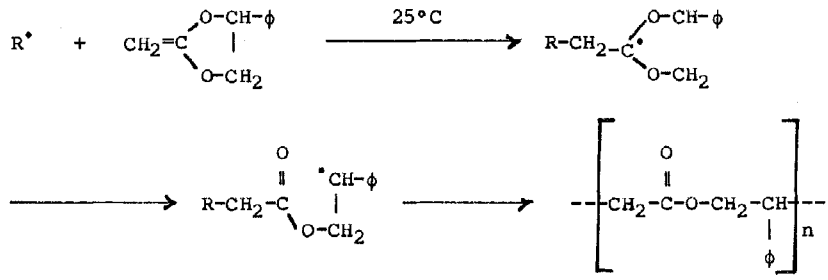


XII

polymerization to produce an ester group, it was reasoned that the open chain ketene acetal XII should also form an ester by chain transfer. Johnson, Barnes, and McElvain [21] reported that benzoyl peroxide treatment had no appreciable effect on XII, but the criteria that they used for that determination is not clear. We have verified that treatment of XII with a peroxide does not result in a high molecular weight polymer but because the monomer undergoes a chain transfer reaction. When an equimolar mixture of styrene and diethyl ketene acetal (XII) was heated at 140°C in the presence of cumene hydroperoxide, a co-oligomer of styrene and the acetal XII was obtained at a 29% conversion. An elemental analysis indicated the oligomer consisted of 90 mole-% styrene and spectral studies indicated that the oligomer was capped with a carboethoxy group at one end. The ketene acetal units appear to be about equally divided between the copolymerized units and the endcapped chain transfer units. Thus it appears that XII is less reactive in the elimination process than is the 2-methylene-1,3-dioxolane (I) which undergoes cleavage to an extent of over 90% at 140°C.

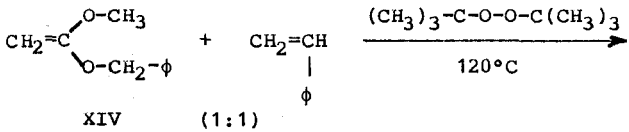


Since the diethyl ketene acetal (XII) appears to be an effective chain transfer agent as well as a comonomer, a search was made to find a ketene acetal that would be a more efficient chain transfer agent. It was reported earlier that the introduction of a phenyl group into the 2-methylene-1,3-dioxolane ring system would so stabilize the ring-opened free radical that the 4-phenyl -2-methylene-1,3-dioxolane (XIII) would undergo 100% ring opening even at room temperature [22].

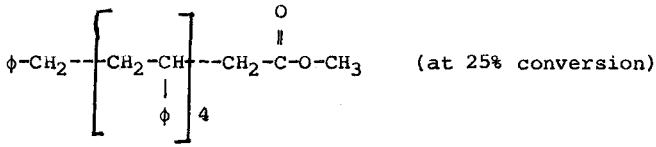


On this basis it was reasoned that a benzyl group in a ketene acetal should greatly increase the extent of cleavage during polymerization and, therefore, should increase the efficiency of chain transfer.

When an equimolar mixture benzyl methyl ketene acetal (XIV) and styrene was heated at 120°C in the presence of di-tert-butyl peroxide, an oligomer with 80% styrene units and capped with a carbomethoxy group was obtained.

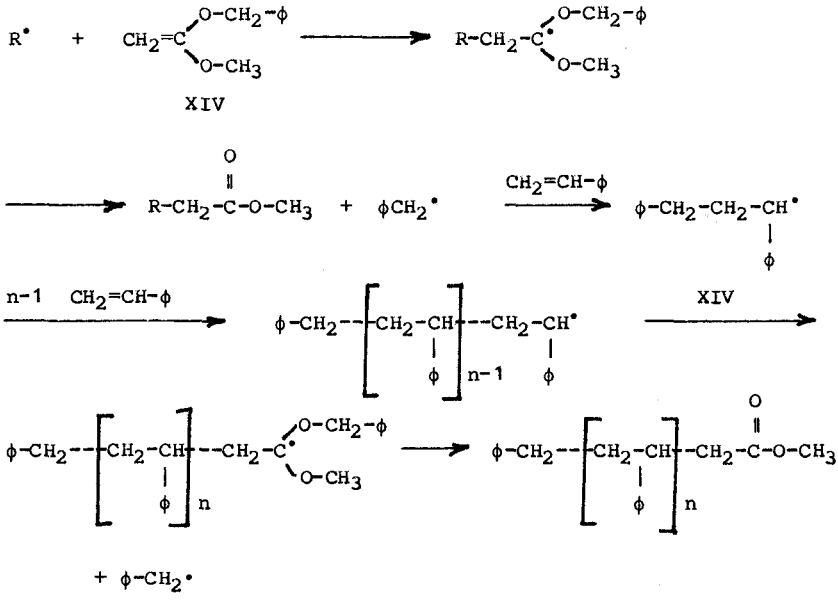


XIV (1:1)



(at 25% conversion)

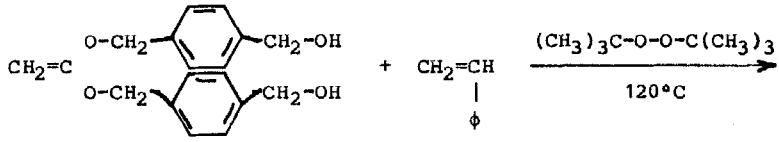
Apparently the additional stabilization of the eliminated free radical by the phenyl group promotes essentially quantitative cleavage. The mechanism of the production of the end-capped oligomer is probably as follows:

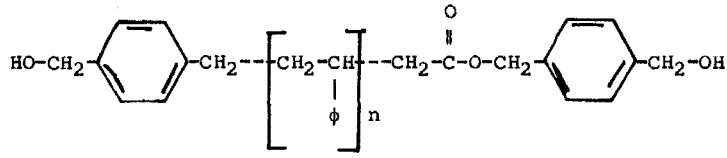


Although there are other unsaturated compounds that will undergo addition-elimination with free radicals, the benzyl ketene acetal XIV appears to be the most active double bond as far as rate of addition is concerned and the most efficient as

far as regards to the extent of elimination is concerned. A comparison with the list of chain transfer agents listed in the Polymer Handbook [23] indicated that only the sulfur compounds appear to be more effective than XIV. Hydrolysis of the end-capped oligomer gives a macromer that is terminated with a carboxylic acid group.

In an effort to find a way to utilize the chain transfer properties of the ketene acetals to give oligomers that are end-capped at both ends with funtional groups without hydrolysis, di(p-hydroxymethylbenzyl) ketene acetal (XV) was prepared. Preliminary studies show that copolymerization of XV with styrene gives an oligomer of styrene with hydroxyl-containing groups at both ends.





Thus it appears that ketene acetals can be used effectively to produce oligomers with a variety of end groups by free radical processes.

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