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RECENT ADVANCES IN FREE-RADICAL RING-OPENING POLYMERIZATION

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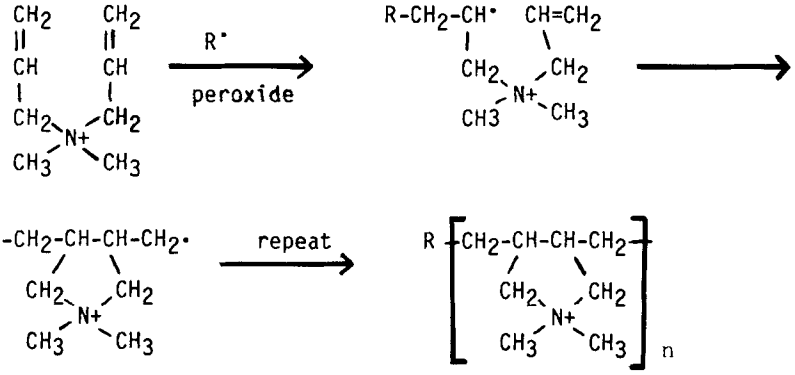
ABSTRACT

Although cyclic ketene acetals, such as 2-methylene-1,3-dioxepane, undergo quantitative free-radical ring-opening polymerization, their reactivity in copolymerization is rather low. In order to find a series of monomers that have high reactivities in copolymerization and still undergo free radical ring-opening polymerization, a series of cyclic acrylates was synthesized and polymerized. For example, β-bromolactic acid condensed with benzaldehyde to give a cyclic acetal lactone which on treatment with base gave the cyclic acrylate. Free-radical solution polymerization at 140°C of the cyclic acrylate, which produced a benzyl radical upon ring opening, gave quantitative ring opening. However, in bulk at 120°C, only 20% of the rings were opened during polymerization. The resulting polymers containing the pyruvate ester units were shown to be highly biodegradable with microorganisms. Vesicles containing these cyclic acrylates on the end of one of the hydrophobic chains of the lipidlike molecules were shown to undergo free-radical ring-opening polymerization to give polymerized vesicles which were biodegradable. In order to discover groups other than carbonyl groups and strained rings that would promote free-radical ring-opening polymerization, a series of spiromethylenecyclohexadienes were prepared and polymerized. Thus, 3-methylenespiro[5,5]undeca-1,4-diene in bulk at 130°C gave a polymer in which 79% of the rings had opened and in solu-

tion at 130°C gave a polymer in which nearly all of the rings had opened. A benzo derivative, 3-methylene-8,9-benzo [5,5] undeca-1,4,8-triene, gave a polymer that is essentially an alternating copolymer of *p*-xylylene and *o*-xylylene and has a very high thermal decomposition temperature. A tricyclic dispirocyclohexadiene derivative was shown to undergo double free-radical ring-opening polymerization to give a polymer with expansion in volume containing a *p*-phenylene group in the backbone.

INTRODUCTION

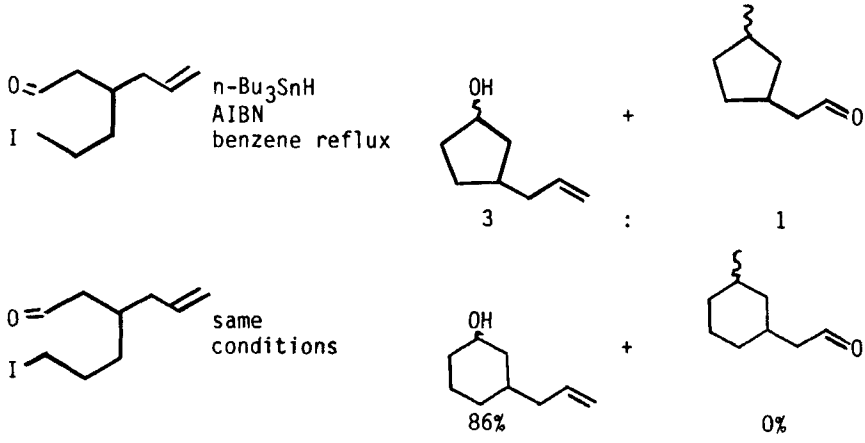
Although ionic ring-opening polymerization, such as that of ethylene oxide, ϵ-caprolactam, and Ziegler-Natta ring-opening of cyclic olefins, is quite common, free-radical ring-opening polymerization is comparatively rare. The few examples of the latter reported in the literature involve either relief of the strain in a vinylcyclopropane [1] or the aromatization of a spiromethylenecyclohexadiene [2]. This rarity of examples of free-radical ring-opening polymerization undoubtedly results from the fact that, in compounds containing a carbon-carbon double bond, free radical ring-closing reactions are quite common. For example, Butler and Angelo [3] in 1957 reported that, when diallyldimethylammonium bromide was polymerized by a free radical process, a soluble polymer containing five-membered rings was obtained by an interintramolecular polymerization.



The data of Maillard, Forrest, and Ingold [4] offer a basis for an explanation of these differences in the two types of radical polymerization. When they studied the transformation of the cyclopropylmethyl and cyclopentylmethyl radical series with electron spin resonance, they found that in the case of the cyclopropylmethyl radical the reaction involved opening of the three-

membered ring since the energy was favorable, with an activation energy of about 6 kcal/mol and the rate of the transformation was very fast. However, in the case of the five-membered ring system, the reaction proceeded in the direction of ring closure since the energetics favor that reaction with an activation energy of about 8 kcal/mol, and the rate of the ring closure is also moderately high. Since a carbon-oxygen double bond is at least 40 kcal/mol more stable than a carbon-carbon double bond, it was reasoned that the replacement of the carbon-carbon double bond in the cyclopentylmethyl-5-hexenyl radical system with a carbon-oxygen double bond would reverse the direction of the reaction and thus favor the ring-opening process. In other words, the ring-opening process would then be favored by at least 30 kcal/mol through the formation of the more stable carbon-oxygen double bond. In a series of papers we reported the application of this principle to a series of free-radical ring-opening polymerizations involving cyclic ketene acetals [5], cyclic ketene aminals [6], cyclic thioketene acetals [7], cyclic vinyl ethers [8], unsaturated spiro-orthoesters [9], and unsaturated spiroorthocarbonates [10].

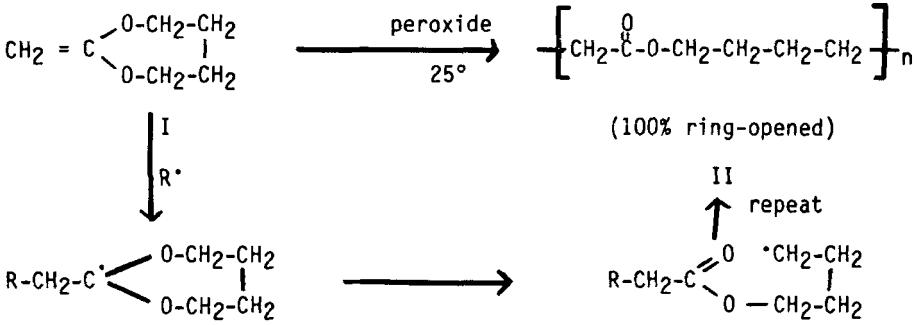
A recent publication by Tsang et al. [11] appears to be at odds with these results although the conditions of the two studies are somewhat different. They found that, in competition of a free-radical ring-closing process of a five-membered ring between addition to an aldehyde and a carbon-to-carbon double bond, the ring closure to the olefinic double bond was favored 3 to 1 at 80°C. On the other hand, in a six-membered ring competition, the addition product involving the aldehyde was obtained in 86% yield.



However, all of our free-radical ring-opening reactions involve an elimination reaction with the formation of an ester, a carbonate, an amide, a thioester, or

a ketone group, and none involves an aldehyde group. Presumably, steric effects will be much greater with an ester group than with an aldehyde.

For example, it was shown in our laboratories that the cyclic ketene acetal, 2-methylene-1,3-dioxepane (I), would undergo quantitative ring opening to produce the high molecular weight polyester II by a radical process. This process represented the first example of the synthesis of a polyester by a radical

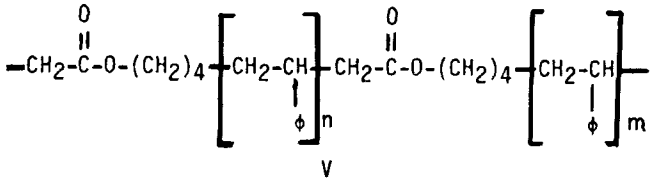


III IV

process and the first general method for the introduction of a functional group into the backbone of an addition polymer. In a series of studies, it was shown that the extent of ring opening in these series of compounds was favored by any group, such as a phenyl group, in the intermediate IV that would stabilize the resulting radical or by any structural feature in intermediate III that would increase ring strain or hinder the addition of the nonring-opened radical to the monomer I.

It was also shown that the cyclic monomers discussed above would copolymerize with a variety of common monomers to produce copolymers with esters, amides, thioesters, and carbonates in the backbone of the copolymer. For example, the 2-methylenedioxepane (I) will copolymerize with styrene to produce the copolymer V.

I

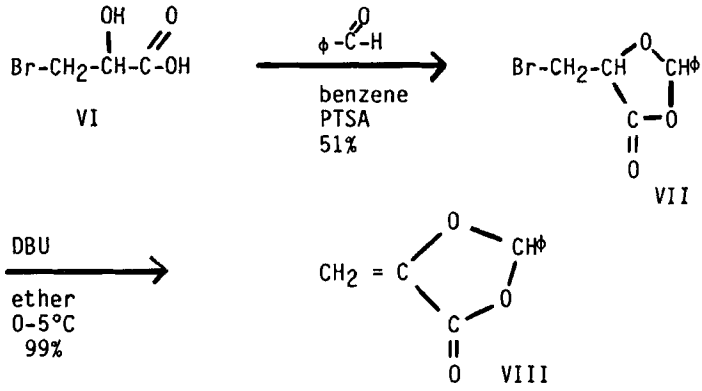


V

It was found that the presence of the ester group in the backbone of the copolymer gave a polymer that was more heat resistant than polystyrene and biodegradable. In addition, hydrolysis of V gave oligomers of styrene that were capped on one end with a carboxyl group and on the other end with a hydroxyl group.

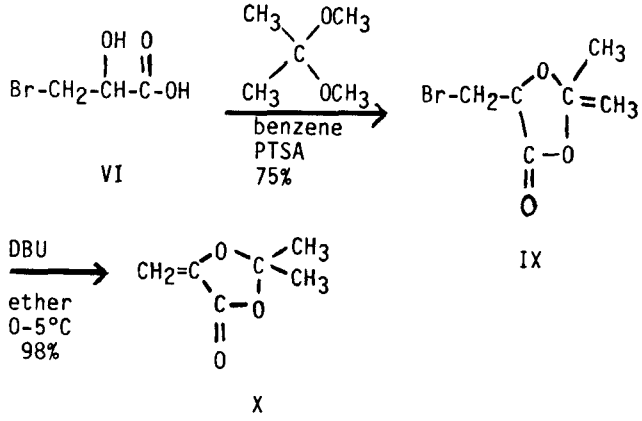
RESULTS AND DISCUSSION

One of the deficiencies of the cyclic ketene acetals is their rather low reactivity relative to monomers, such as styrene. Thus, in the copolymerization of 2-methylene-1,3-dioxepane with styrene, $r_1 = 0.021$ and $r_2 = 22.6$ at 120°C [6]. In a research project designed to produce more reactive cyclic monomers, a series of cyclic acrylates were prepared and polymerized. Various cyclic acrylates were prepared in good yields by the following scheme [12].



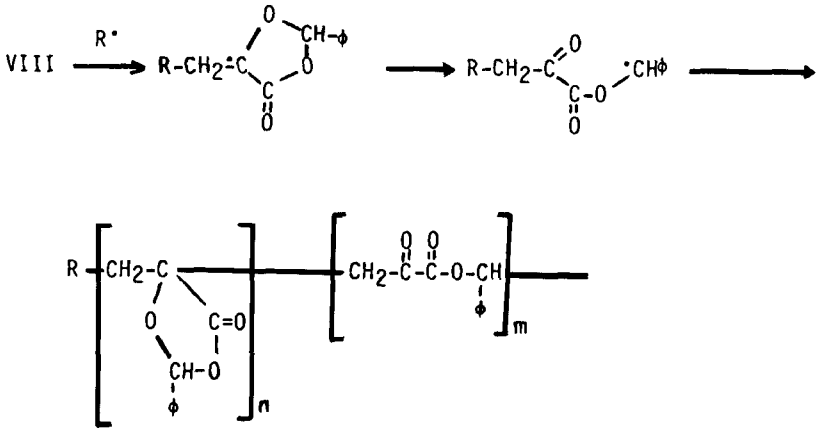
The acetal formation to give VII proceeds easily and, since the hydrogen atom in VII is activated by the carbonyl group, a strong base is not needed for the dehydrobromination. DBU is strong enough to promote the elimination in good yields but apparently not strong enough to promote polymerization.

When a ketone was used in this sequence of reactions to produce a disubstituted intermediate, a different approach was necessary. Thus, the direct ketal formation in this series does not proceed in as good a yield as in the acetal formation. However, the use of a ketal interchange reaction gives good yields.



Likhterov et al. [13] recently reported the synthesis of compounds VIII and X in 60-80% yields from the chloro derivatives with triethylamine without any experimental details or reported attempts at polymerization.

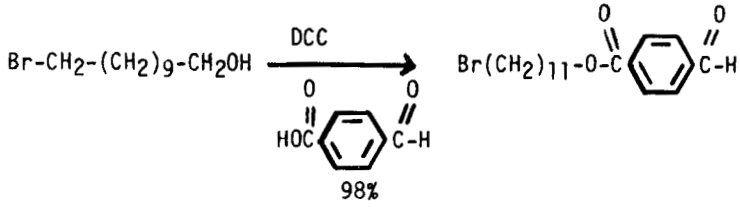
When the polymerization of VIII was carried out at 120°C in bulk, a copolymer consisting of 20% ring-opened units and 80% nonring-opened units was obtained.

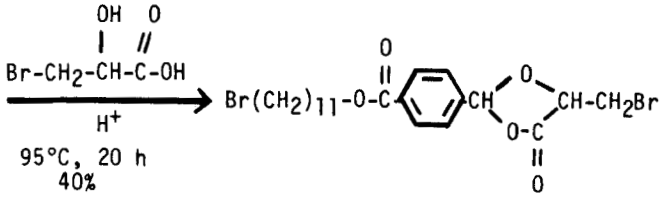


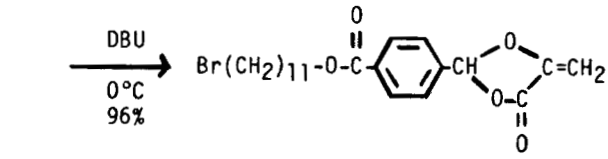
When the temperature was raised to 140°C and the polymerization was carried out in a solution of *t*-butylbenzene, essentially quantitative ring opening occurred. With monomer X at 120°C in bulk, the polymerization gave a mixture containing about 50% ring-opened units and 50% nonring-opened units. Again at 140°C and in *t*-butylbenzene solvent, polymerization of X gave nearly 100% ring opening. These cyclic acrylates copolymerized readily with styrene and methyl methacrylate to give copolymers that should be both photodegradable and biodegradable. The homopolymers of VIII and X prepared at high temperatures and in solution were shown to be highly biodegradable. Previous work [14] had shown that the introduction of an ester group into the backbone of an addition polymer [15] would render the polymer biodegradable. It was not surprising that the introduction of a pyruvate ester group into the backbone of an addition polymer was even more effective than a simple ester unit since pyruvates are common intermediates in many biological systems.

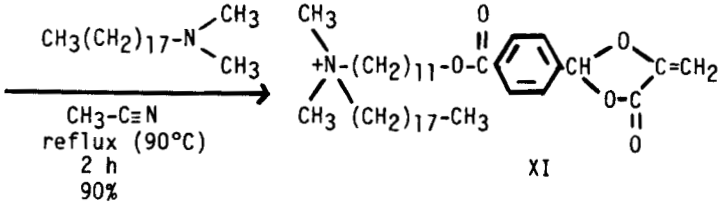
An interesting extension of this work is the preparation of biodegradable polymerized vesicles. Vesicles have attracted much attention lately because they mimic body membranes and liposomes. As a result, they appear very useful for the delivery of drugs and for encapsulating sensitive biologically active materials. However, since many of the simple vesicles are not very stable under many biological conditions, attempts have been made to stabilize the vesicles by incorporating a polymerizable entity into the lipidlike molecules, formation of the vesicle, followed by polymerization of the monomers in the vesicle. Although this approach works, it usually renders the polymerized vesicle nonbiodegradable and thus limits its use in the body [16]. Only the polymerized vesicles of Samuel et al. [16d], who crosslinked through a disulfide group, appear to be at all biodegradable. Since we had demonstrated that the introduction of pyruvate ester groups into the backbone of several addition polymers renders them highly biodegradable, it appeared attractive to introduce a cyclic acrylate into the lipidlike molecules of the vesicles which, upon polymerization, would produce polymerized vesicles with pyruvate ester groups in the polymer backbone. Thus the vesicles should be stable enough to deliver a drug or to protect a sensitive material but yet biodegradable in the body. The cyclic acrylates appeared especially attractive since the conditions for the synthesis are quite mild.

The required lipidlike molecule containing the cyclic acrylate XI was prepared by the series of reactions shown on page 788. The cyclic acrylate XI will form vesicles that can be polymerized to form the polymerized vesicles containing polymer XII. Furthermore, polymer XII was shown to be biodegradable. Research is in progress to determine the physical char-

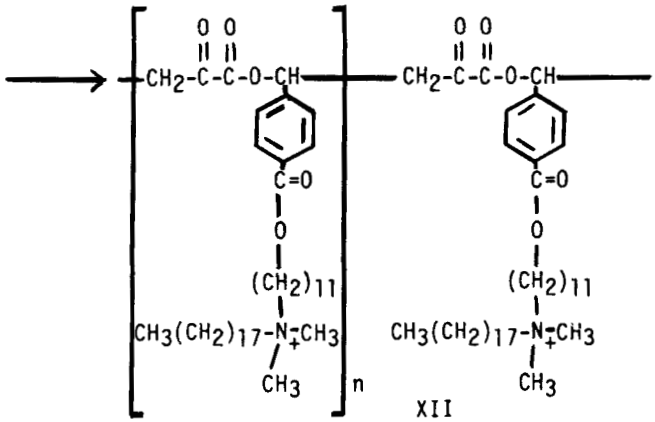








XI

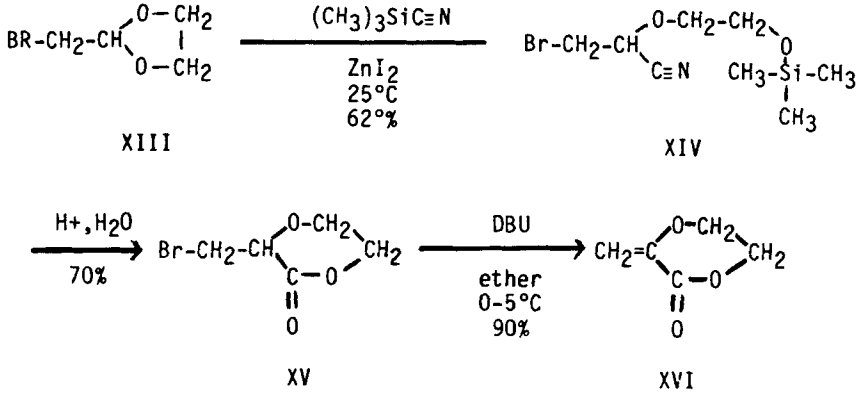


XII

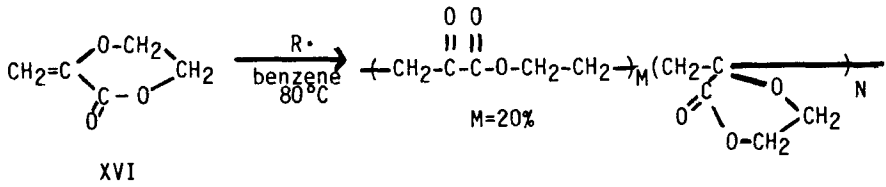
acteristics of these polymerized vesicles and to determine the effectiveness of these systems to deliver drugs in the body.

In an effort to find a synthetic process to prepare cyclic acrylates containing six- and seven-membered rings, we adapted the procedure of Kirchmeyer et al. [17] for the insertion of a carbonyl group into a cyclic acetal. The required 2-halomethyl-1,3-dioxolanes were available from our earlier work on the synthesis of 2-methylene-1,3-dioxolanes [18].

For example, when 2-bromomethyl-1,3-dioxolane (XIII) was treated with trimethylcyanosilane and zinc iodide at room temperature, a 62% yield of the ring-opened intermediate XIV was obtained. Hydrolysis of XIV followed by ring-closure gave a 70% yield of the cyclic intermediate XV. Since XV is a β-bromoacrylate, the elimination can be carried out with a base that is not strong enough to polymerize the resulting cyclic acrylate XVI. Thus, the treatment of XV with DBU at 0-5°C produced the cyclic acrylate XVI in 90% yield.

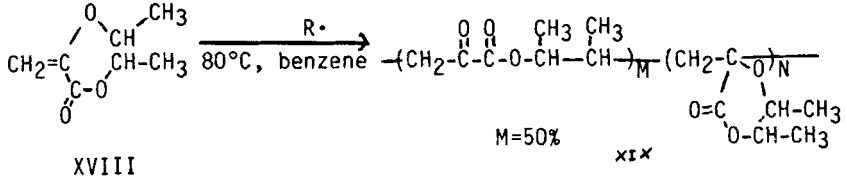


When XVI was treated with benzoyl peroxide in a benzene solution, polymer XVII was obtained in which only 20% of the rings had been opened.



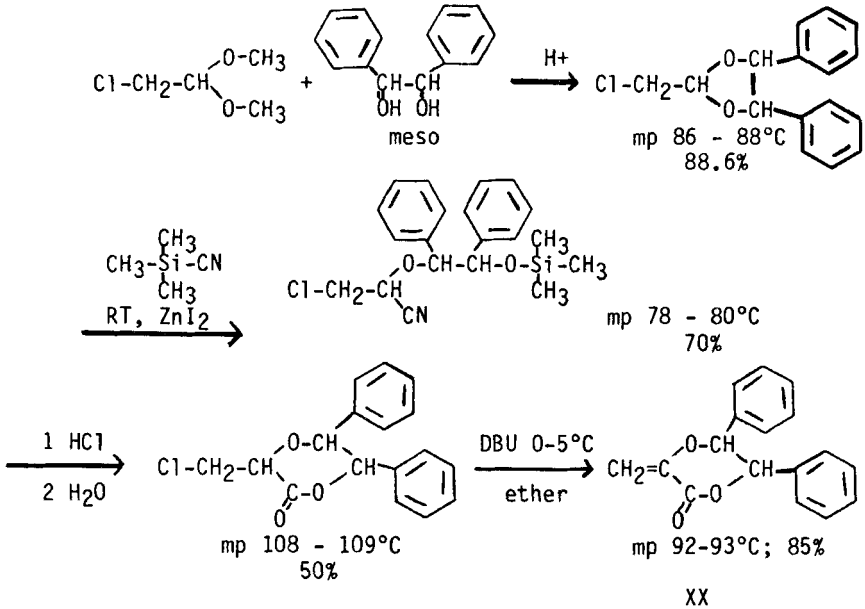
When the analogous dimethyl derivative XVIII was polymerized under very similar conditions, polymer XIX was obtained in which 50% of the rings had been opened. Apparently the secondary radical that results during ring open-

ing of XVIII is sufficiently more stable than the primary radical formed during ring opening of XVI to give a higher extent of ring opening.



XVIII XIX

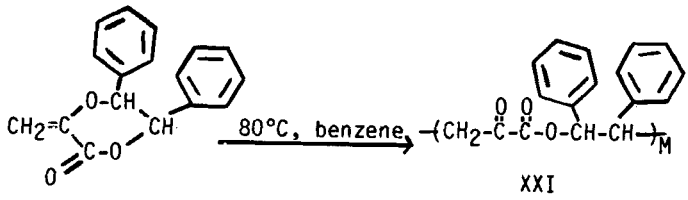
Since the introduction of a phenyl group greatly increased the extent of ring opening in the 2-methylene-1,3-dioxolane series, a phenyl derivative XX was prepared by the following series of reactions:



XX

When XX was treated with benzoyl peroxide in benzene at 80°C, polymer XXI was obtained in which all of the rings had been opened. Thus, the benzyl free radical formed during ring opening of XX is sufficiently more stable than the primary radical formed from XVI that complete ring opening occurred.

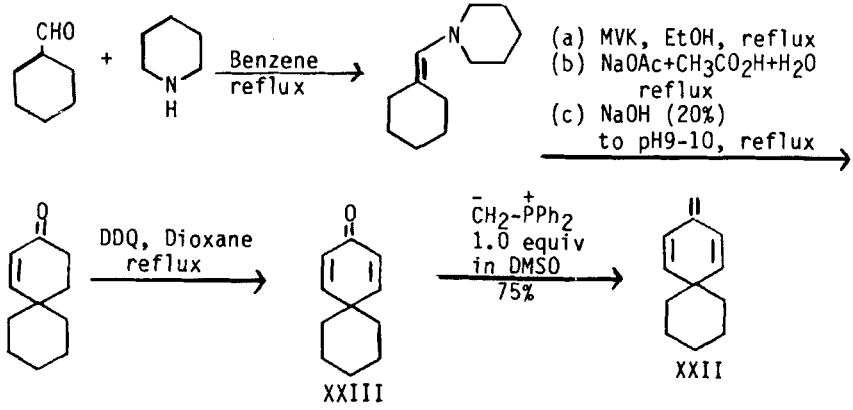
One of the earliest examples of free-radical ring-opening polymerization was reported by Errede [2] in 1961, who found that spirodi-*o*-xylylene would homopolymerize to give the corresponding poly-*o*-xylyene. We



XX XXI

reasoned that the homolytic opening of a five- or six-membered ring would cost less than 8 kcal/mol of energy [4] while the formation of the aromatic ring would gain about 36 kcal/mol. Thus, the process should be quite favorable thermodynamically. We therefore undertook a research program to study the polymerization of a series of methylenespirohexadienes to determine their tendency to undergo ring opening and their reactivity toward polymerization and copolymerization.

The desired monomer, 3-methylenespiro[5,5]undeca-1,4-diene (XXII), was prepared in an overall yield of 24% by the following series of reactions:



XXIII XXII

The intermediate cyclohexadienone, spiro[5,5]undeca-1,4-diene-3-one (XXIII), was prepared in large scale by the procedure of Kane [19] in 36% overall yield. A Wittig reaction [20] gave the corresponding methylene derivative XXII in 75% yield. In agreement with the results of Murray [21], it was found that when 1.5 equivalents of methyltriphenylphosphonium bromide and 2 equivalents of sodium hydride were used, the major product was 3-ethylidenespiro-[5,5]undeca-1,4-diene. The methylene monomer XXII was a colorless liquid that was stable under nitrogen in a freezer, but at room temperature in air the

TABLE 1. Homopolymerizations of XXII at Various Temperatures

Initiator	Temperature, °C	Time, h	Polymer yield, %	Solubility	Extent of ring opening,[a] mol%
Benzoyl peroxide	85	72	42	Soluble in $CHCl_3$, C_6H_6	43
Benzoyl peroxide	100	48	80	33% Soluble in $CHCl_3$	61
				67% Insoluble in common solvents[b]	70
t-Butyl peroxide	130	12		Insoluble in common solvents[b]	79
t-Butyl peroxide[c]	130	12		Insoluble in common solvents[b]	98

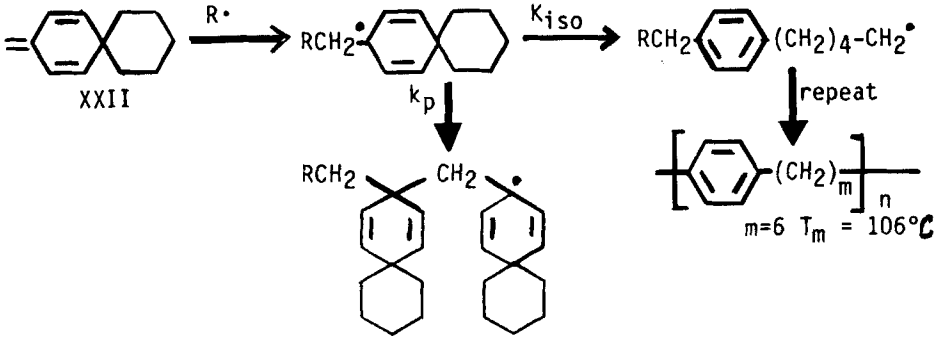
[a]From 200 MHz ^{1}H-NMR study.
[b]Below 80°C.
[c]Solution polymerization (3:1 benzene/monomer wt/wt).

material gradually became brown and underwent spontaneous polymerization to a low molecular weight polymer.

Homopolymerizations of monomer XXII were carried out at different temperatures to determine the effect of temperature on the extent of ring opening. For example, when XXII was polymerized at 85°C over a period of 72 h with 2 mol% benzoyl peroxide as the initiator, a white powder was isolated after purification. The 200 MHz ^{1}H-NMR spectrum showed signals at δ6.75-7.20, corresponding to the aromatic protons, at δ2.55 corresponding to benzylic methylene protons (both indicative of ring opening), and at δ5.25 and 5.61, corresponding to the vinyl protons (indicative of nonring opening). Thus the integration of the areas of the peaks at either δ6.25-7.20 or at 2.55 versus those at δ5.25 and 5.61 could be used to determine the extent of ring opening. The results of this study are listed in Table 1.

It can be seen from Table 1 that at 85°C only 43% of the rings had opened, but as the temperature of polymerization was increased to 130°C, the extent of ring opening increased to 79%. Furthermore, when the polymerization

was carried out in a solvent at 130°C, the extent of ring opening was nearly quantitative. These results are consistent with the following scheme:



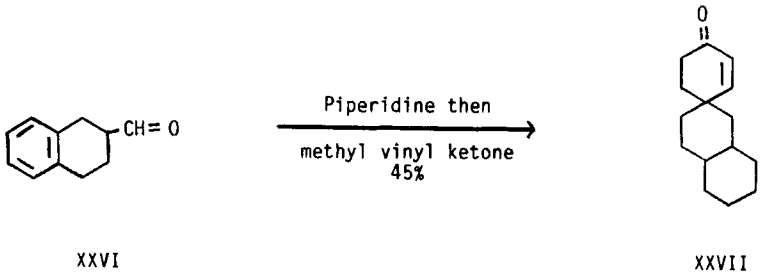
Even though the ring-opening step is thermodynamically favorable, the rate of the competitive direct addition of the intermediate radical to the monomer XXII at 85°C is faster. Carrying out the polymerization in solution favors the ring-opening process since it is a unimolecular reaction while the direct addition to monomer is a bimolecular reaction.

Polymer XXIV with nearly quantitative ring opening was shown to be insoluble in all common solvents below 80°C. The NMR spectrum was obtained by dissolving the polymer in phenyl ether at 180°C (about 1 g/100 mL), cooling to obtain a supersaturated solution at room temperature, and adding to $DCCl_3$. X-ray diffraction on an unoriented film showed a sharp ring pattern indicative of crystallinity. A further indication of the regular structure of polymer XXIV was shown by a DSC scan which showed a T_m at 106°C and a T_g at 6°C. Thus, decreasing the concentration of monomer XXII favors free-radical ring opening.

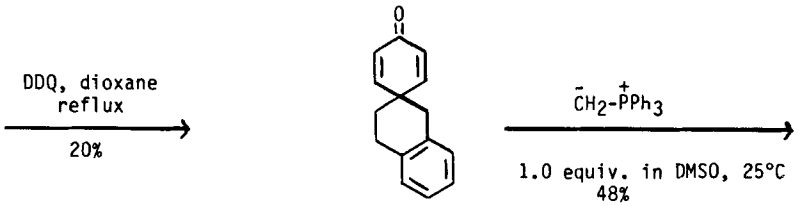
Monomer XXII was also shown to have a relatively high reactivity in copolymerization. Thus, when equimolar amounts of XXII and styrene were copolymerized at 130°C in the presence of 2 mol% *t*-butyl peroxide as the initiator for 4 h, a solid copolymer was obtained which contained 42% units from monomer XXII, of which 92% were ring opened.

A research program to determine some of the factors that influence the extent of ring opening in this new unsaturated spiro system was undertaken. Since the introduction of an aromatic group into the 2-methylene-1,3-dioxolane system increased the extent of ring opening to nearly 100% even at room temperature during free radical polymerization, it was of interest to synthesize 3′,4′-dihydro-4-methylenespiro[2,5-cyclohexadiene-1,2′(1′*H*)naphthalene] (XXV), which would be expected to produce a benzyl radical upon ring open-

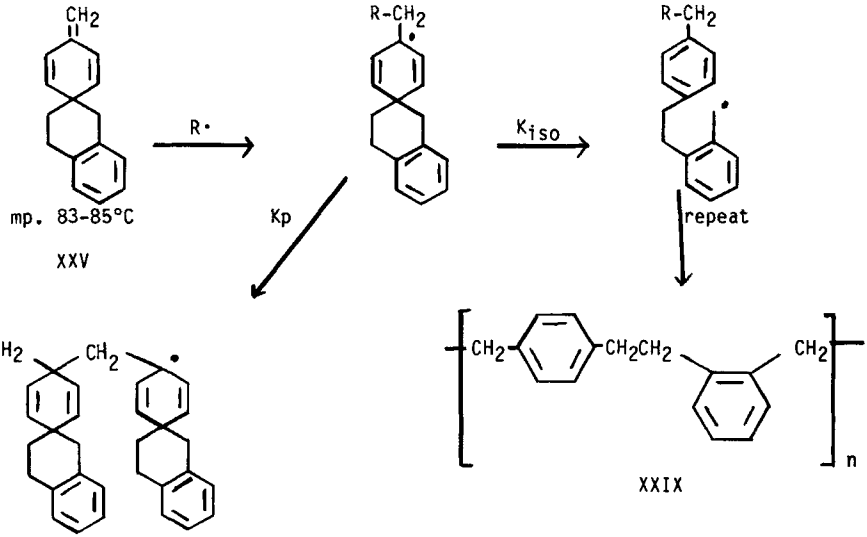
ing. The starting material for the synthesis of XXV was 1,2,3,4-tetrahydro-2-naphthaldehyde (XXVI), which was prepared by the method of Alder and Fremery [22] in 44% yield from *o*-xylylene dibromide and acrolein. By the general method of Kane [19] described previously, XXVI was converted to



XXVI XXVII



XXVIII



XXV XXIX

the ketone XXVII in 45% yield by the treatment of the enamine derived from XXVI with methyl vinyl ketone. Oxidation of XXVII with DDQ gave the dienone XXVIII in 20% yield. Finally, the conversion of XXVIII to XXV was accomplished in 48% yield in a Wittig reaction.

When XXV was treated in the bulk at 100°C with 2 mol% benzoyl peroxide, a white solid polymer XXIX, $[\eta]$ 0.253, was obtained in nearly quantitative yield. The extent of ring opening was determined by a 200-MHz NMR study to be in excess of 95% since only a trace of absorption in the δ5.0-6.0 region corresponding to vinyl protons was detected. Under comparable conditions, monomer XXII would be expected to undergo only 67% ring opening. Thermodynamic data indicate that the benzyl radical is about 13 kcal/mol more stable than the corresponding primary radical, thus giving an additional driving force for ring opening of XXV. The extent of ring opening is, however, determined by the relative rates of the direct addition, K_p, and the ring opening, K_{iso}.

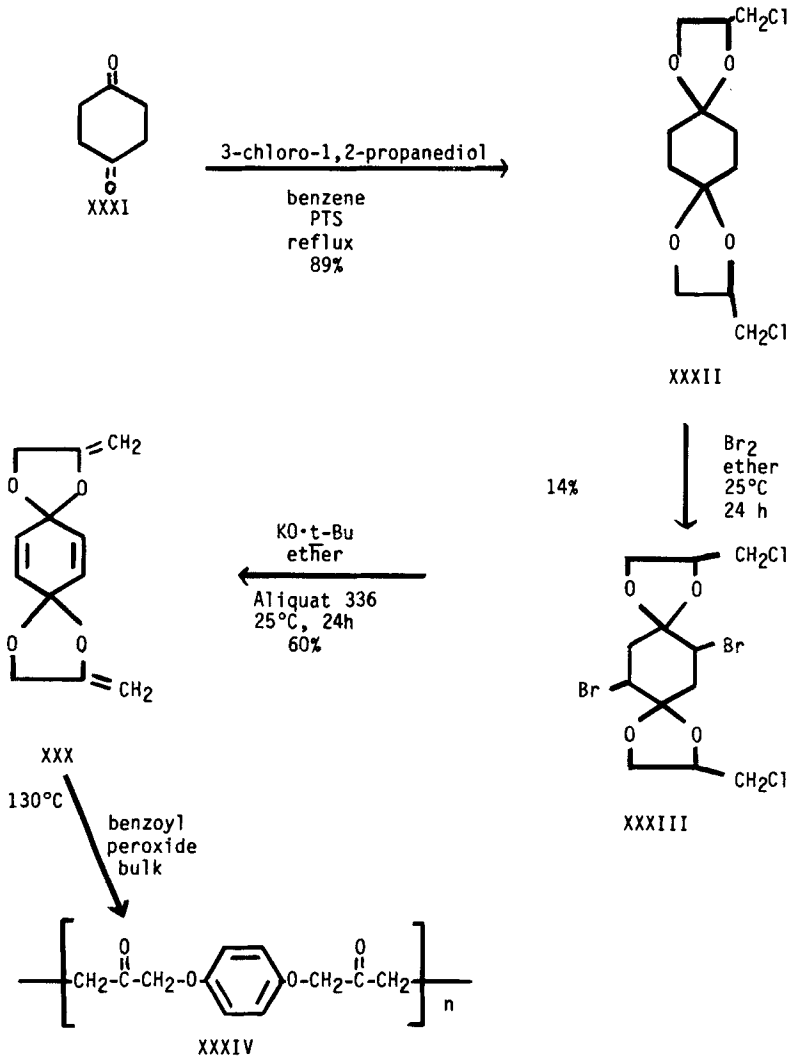
DSC analysis showed that XXIX had a T_m of 107°C and a T_g of 61°C. For comparison, poly(*p*-xylylene) has a T_m above 400°C [23] while poly(*o*-xylylene) was reported to melt at 110°C [2]. Apparently the *o*-xylylene unit prevents the polymer from fitting into a compact crystal lattice. The *ortho* unit also increases solubility since XXIX is fairly soluble in benzene and chloroform at room temperature. TGA analysis of XXIX under nitrogen at a heating rate of 10°C/min showed that more than 90% of the polymer remained at 425°C and 50% remained at 460°C.

In order to evaluate the relative reactivity of monomer XXV, copolymerization of XXV and styrene in a 1:3 molar mixture was carried out at 85°C in the presence of 2 mol% benzoyl peroxide. A solid copolymer, $[\eta]$ 0.366, was obtained in 93% conversion that was shown by an NMR study to contain 26 mol% of the triene monomer units, all of which were ring opened. Thus monomer XXV appears to be quite reactive.

Since the formation of an aromatic ring appears to be a strong driving force for ring opening during free-radical polymerization, a research effort was initiated in order to determine whether this concept could be used in multiple ring opening so that free-radical polymerization would take place with expansion in volume. It was shown earlier that, whenever two or more rings are opened for every new bond formed in the backbone of the polymer, expansion in volume occurs. With this in mind, the synthesis of an unsaturated diketal of *p*-quinone, 2,10-dimethylene-1,4,9,12-tetraoxadispiro-[4.2.4.2] tetradeca-6,13-diene (XXX) was undertaken.

Since Heller et al. [24] were able to prepare the saturated diketal of *p*-benzoquinone, we adapted their general procedure for the preparation of the diunsaturated analog XXX. Thus, 1,4-cyclohexanedione XXXI was con-

verted into the dichloromethyldiketal XXXII in 89% yield by removing the water by azeotropic distillation with 3-chloro-1,2-propanediol. Bromination in ether at room temperature gave a mixture of bromides from which one isomer, XXXIII, mp 37-38°C, was isolated in 14% yield. Treatment of XXXIII with potassium *t*-butoxide in the presence of Aliquat 336 gave the desired monomer XXX in 60% yield. The crude mixture of the dibromides gave a higher amount of XXX.



Polymerization of XXX in the bulk at 130°C in a sealed glass tube under nitrogen with 2 mol% *t*-butyl peroxide gave polymer XXIV that was totally soluble in DMF. The polymerization took place with essentially no change in volume or possibly a very slight increase. A similar polymerization carried out in refluxing xylene under nitrogen for 3 h gave a very similar polymer. An NMR spectral study indicated that 100% double ring opening had occurred with the formation of the aromatic ring.

Thus it has been demonstrated that the driving force generated by aromatization during polymerization is sufficient to promote both free radical ring-opening polymerization and double ring-opening polymerization. This method appears to be an excellent method for the introduction of a *p*-phenylene unit into the backbone of an addition polymer. This additional driving force for ring opening should make possible the synthesis of a whole new class of monomers that will undergo polymerization with expansion in volume.

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