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Cationic Polymerization with Expansion in Volume

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ABSTRACT

It is demonstrated that polymerization of bicyclic monomers in which two rings are opened for every new bond formed in the polymer chain will produce either very small changes in volume or significant expansion.

For a number of industrial applications, such as strain-free composites, potting resins, high gloss coatings, and binders for solid propellants, it appears to be highly desirable to have monomers that will polymerize with near zero shrinkage. For other applications, such as precision castings, high strength adhesives, prestressed plastics, rock-cracking materials, and dental fillings, it appears highly desirable to have monomers that would undergo positive expansion on polymerization. A number of examples from other fields would lead one to predict that such an expansion in volume during polymerization would be highly useful. For example, since water undergoes an expansion in volume of about 4% when it freezes, ice will adhere to almost any surface, including Teflon, which it does not even wet, by what is called micromechanical interaction. Alloys that expand on solidification are used commercially to make precision type, and amalgams that expand are used to fill teeth.

Many composites involving high strength fibers in a polymeric matrix fail because of either poor adhesion between the matrix and the fibers or because of voids and microcracks in the matrix. Both of these problems are at least partially related to the fact that when available materials polymerize or cure, a pronounced shrinkage takes place. In bulk plastics some of these stresses can be relieved with a total shrinkage in the overall dimensions of the article. However, in a composite the reinforcing material, which has a high modulus, will often not permit appreciable shrinkage in the overall dimensions of the molded object, and as a result enormous stresses are built up in the composite. These stresses can be relieved either by an adhesive failure, in which the matrix pulls away from the reinforcing fiber, or by a cohesive failure, in which a void or a microcrack is formed.

For these reasons a research program was initiated to find monomers that undergo either zero shrinkage or expansion on polymerization. Shrinkage that occurs during polymerization arises from a number of factors. One of the most important, however, is the fact that the monomer molecules are located at a van der Waals' distance from one another while in the corresponding polymer the monomeric units move to within a covalent distance of each other. The atoms are thus much closer to one another in the polymer than they were in the original monomer. In some cases the polymer actually packs better than the monomer. This would be true in going from an amorphous or liquid monomer to a semicrystalline polymer to produce a greater than normal shrinkage. On the other hand, in going from a crystalline monomer to an amorphous polymer which may have a great deal of free volume, the shrinkage could be much less than normal.

In a condensation polymerization, one would expect shrinkage, since a small molecule is eliminated during the formation of the new bond. One can get large shrinkages during such condensation polymerization depending on the size of the molecule eliminated. Table 1 lists some typical calculated shrinkages during condensation polymerization. Obviously, the larger the molecule split out during the polymerization, the larger the shrinkage will be. During addition polymerization, even though there is no small molecule eliminated, there is still a fairly large shrinkage in many cases, since the atoms are much closer to one another in the polymer than they were in the monomer. Table 2 lists the shrinkage that occurs in a number of very common monomers. The shrinkage is related, of course, to a

TABLE 1. Calculated Shrinkage During Condensation Polymerization

Monomer A	d_4^{20}	Monomer B	d_4^{20}	Polymer (d_4^{20})	Shrinkage (%)
Adipic acid	1.360	$NH_2(CH_2)_6NH_2$	0.863	1.14	22
Adipic acid	1.360	$O{=}C{=}N(CH_2)_6{-}N{=}C{=}O$	1.0528	1.14	29
Dimethyl adipate	1.0625	$NH_2(CH_2)_6NH_2$	0.863	1.14	31
Dibutyl adipate	0.965	$NH_2(CH_2)_6NH_2$	0.863	1.14	53
Dioctyl adipate	0.913	$NH_2(CH_2)_6NH_2$	0.863	1.14	66

TABLE 2. Calculated Shrinkages for Addition Polymerization [1]

Monomer	Shrinkage (%)
Ethylene	66.0
Vinyl chloride	34.4
Acrylonitrile	31.0
Methyl methacrylate	21.2
Vinyl acetate	20.9
Styrene	14.5
Diallyl phthalate	11.8
N-Vinylcarbazole	7.5
1-Vinylpyrene	6.0

large extent to how many monomer molecules undergo polymerization per unit volume. For example, styrene, which has approximately four times the molecular weight of ethylene, gives a shrinkage during polymerization which is approximately one-quarter of that of ethylene.

In ring-opening polymerization, the shrinkage may be less than in either of the two cases just discussed. Not only is a small molecule not eliminated during the polymerization reaction, but for every bond that undergoes a change from a van der Waals' distance to a covalent distance, another bond goes from a covalent distance to a near van der Waals' distance. Table 3 lists the shrinkage that would occur during the ring-opening polymerization of a number of cyclic monomers. It is obvious from this table that the shrinkage is related to the number of rings being opened per unit volume as well as to the size of the ring. By analogy with the molecular volume of ethylene, one might at first glance expect the shrinkage of ethylene oxide to be approximately 42%. Thus the reduced shrinkage must be at least partly due to the opening of the three-membered ring.

In a program designed to find monomers that would give near zero shrinkage or even expand on polymerization, a fruitful approach appeared to be the study of bicyclic compounds. In such bicyclic monomers, for every bond that undergoes a shift from a van der Waals' distance to a covalent distance, at least two bonds go from a covalent distance to a near van der Waals' distance. In a study of densities

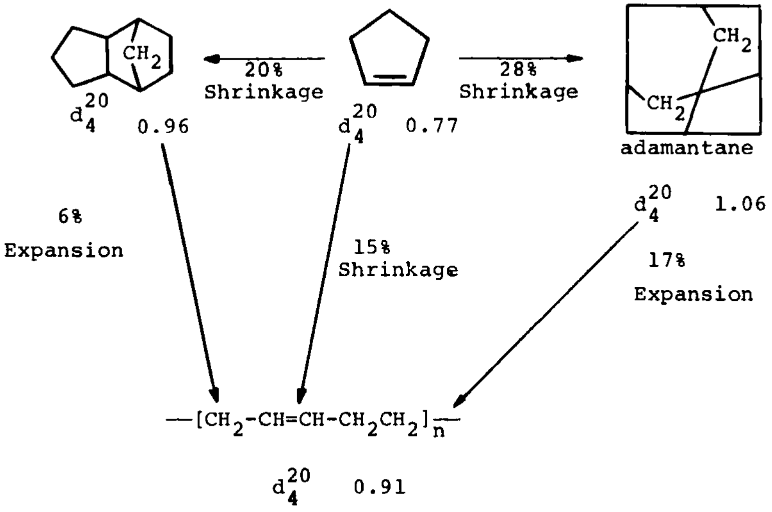
TABLE 3. Calculated Shrinkage during Ring-Opening Polymerization [2, 3]

Monomer	Shrinkage (%)
Ethylene oxide	23
Propylene oxide	17
Cyclopentene	15
Cyclopentane	12
Styrene oxide	9
Cyclooctene	5
Bisphenol-A digylcidyl ether, diethylaminopropylamine	5
Cyclododecatriene	3
5-Oxa-1,2-dithiacycloheptane	3
Dimethylsilane oxide cyclic tetramer	2

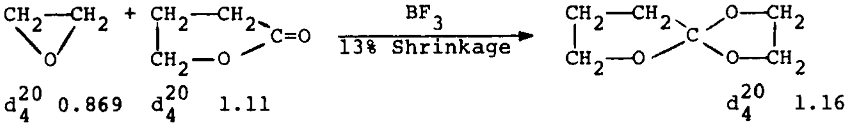
of polycyclic hydrocarbons compared to the densities of the corresponding linear polymers which have the same empirical formula, one can become convinced that this approach would indeed give monomers that expand on polymerization.

In the hypothetical case shown, cyclopentene, which undergoes a 15% shrinkage when it is converted to the polycyclopentenomer, would undergo a 20% shrinkage when converted to its saturated dimer. If a catalyst were available for the polymerization of the saturated dimer to the same polycyclopentomer, a 6% expansion would be predicted. Similarly, if the cyclopentene is converted to adamantane, a 26% shrinkage would result, and if adamantane could somehow be converted to the same cyclopentenomer, a 17% expansion in volume would be calculated. Unfortunately, the catalysts which would make these conversions possible are not known.

For the reasons just discussed, a search was made for oxygen analogs of a number of bicyclic monomers, since catalysts were available for the cationic polymerization of cyclic ethers and cyclic esters. The monomer that appeared particularly attractive was the spiro ortho ester, 1,4,6-trioxaspiro[4,4]nonane, which was first reported by

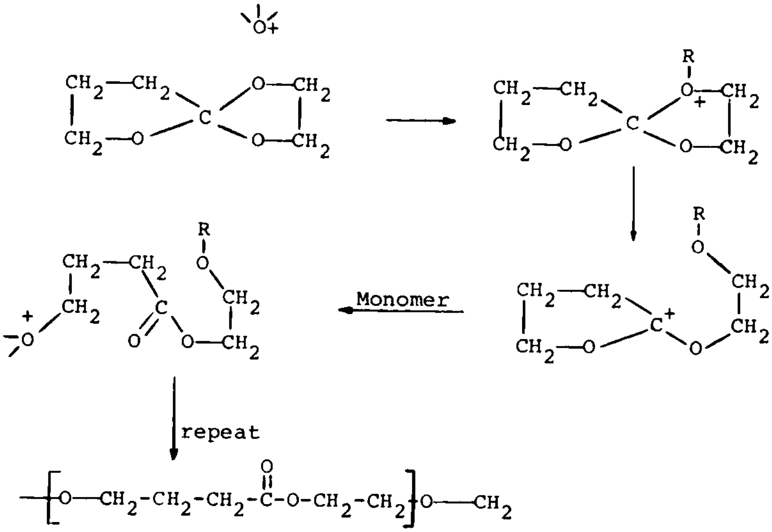


Bodenbenner [4] in 1959. Although there are a number of Japanese patents [5-8] which describe the copolymerization of this monomer with trioxane to produce copolymers with improved thermal stability, no description of the homopolymerization of this monomer appears in the literature. Bodenbenner reported that when the monomer was allowed to stand at room temperature with boron trifluoride, it gave a viscous oil but which was not characterized as to either structure or molecular weight. This spiro ortho ester was synthesized in a 33% yield [9].

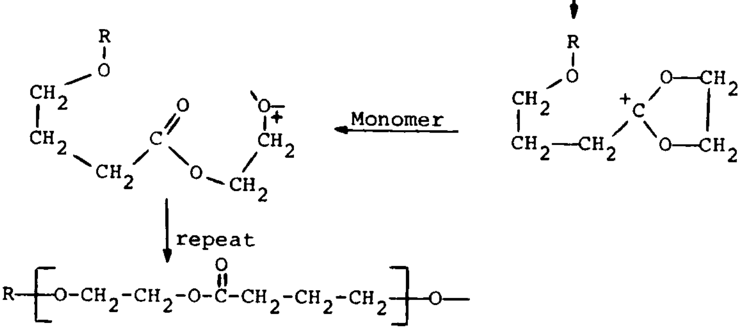


By a comparison of the densities of the materials involved, it is obvious that the spiro compound is a very compact monomer. When this monomer was polymerized in the dilatometer, placed in a constant temperature bath of 25° C in the presence of boron trifluoride, polymerization occurred over a 24-hr period. During the polymerization the meniscus remained essentially at a constant level and indicated a slight increase in volume of 0.1%. Purification of the polymer by reprecipitation gave a 95% yield of a viscous liquid with a molecular weight of about 25,000. Although the polymer was difficult to purify, its density indicated that a slight shrinkage occurred during the polymerization (less than 1%).

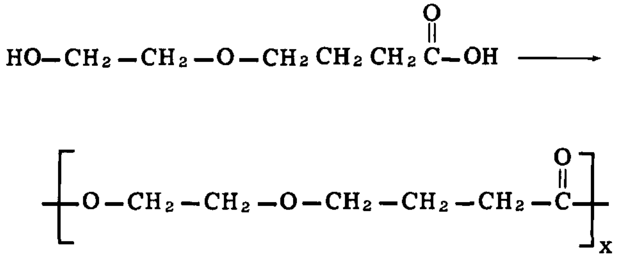
The mechanism of the polymerization undoubtedly involves a oxonium ion:



Since the monomer contains two different types of oxygen atoms, attack can occur at the other oxygen:



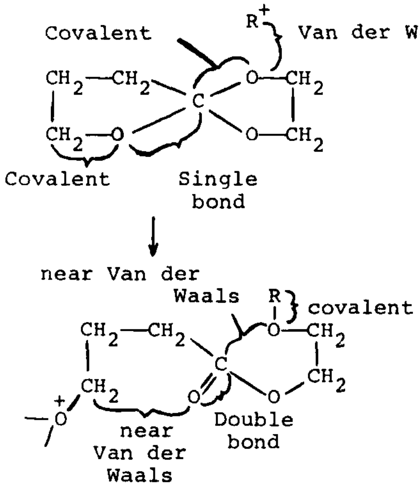
On this basis one would predict the formation of a polyester-ether containing both head-to-tail and head-to-head units. This fact was verified by the synthesis of the head-to-tail polymer by a direct esterification procedure:



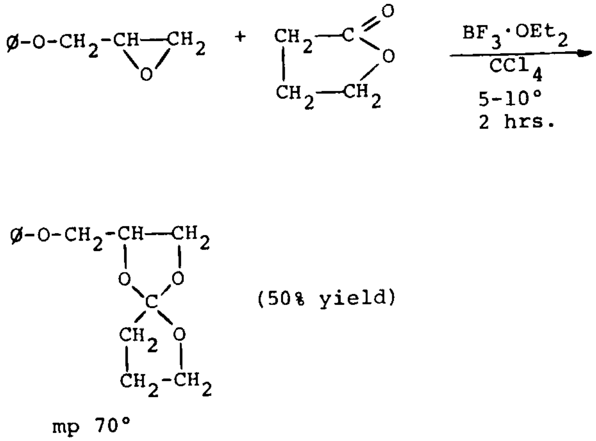
$$HO{-}CH_2{-}CH_2{-}O{-}CH_2CH_2CH_2\overset{\overset{\displaystyle O}{\|}}{C}{-}OH \longrightarrow \left[O{-}CH_2{-}CH_2{-}O{-}CH_2{-}CH_2{-}CH_2{-}\overset{\overset{\displaystyle O}{\|}}{C} \right]_x$$

Comparison of the NMR spectra of the two polymers gave strong evidence for the presence of a head-to-head units (10 to 20%) in the ring-opened polymer.

The reason for this low shrinkage during polymerization can be rationalized by comparing the original monomer with the final ether-containing polyester. There are two processes which would lead to some contraction; one bond goes from a van der Waals' distance to a covalent distance, and one bond goes from a single bond to a double bond. This shrinkage is counterbalanced by the two bonds that go from a covalent distance to a near van der Waals' distance in the final polymer. In this particular case, these processes seem to just about cancel one another.

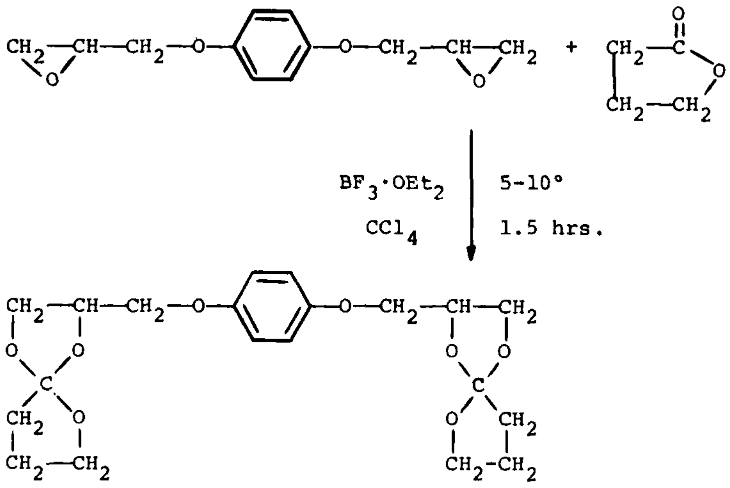


Interesting analogs of this spiro ortho ester can be prepared by the same general technique. For instance, a crystalline monomer from phenyl glycidyl ether can be prepared by the following reaction in a 50% yield [10]:



When this monomer is polymerized at 30° C with boron trifluoride etherate, a polymer results with high molecular weight. From the density of the polymer compared with that of the monomer, one would calculate that a 12% expansion in volume had occurred. When the same process is carried out at 75° C, a 1% shrinkage in volume is calculated. Since the monomer is crystalline, it packs very well, but the polymer is amorphous and does not pack well. Therefore, in addition to the volume change that would occur during polymerization, a large additional change in volume occurs when the crystalline monomer is converted to an amorphous material. Several other cases in which a crystalline monomer is converted to an amorphous polymer with a large increase in volume are discussed later.

Still another variation in this series is the bifunctional monomer that can be prepared from the hydroquinone diglycidyl ether:



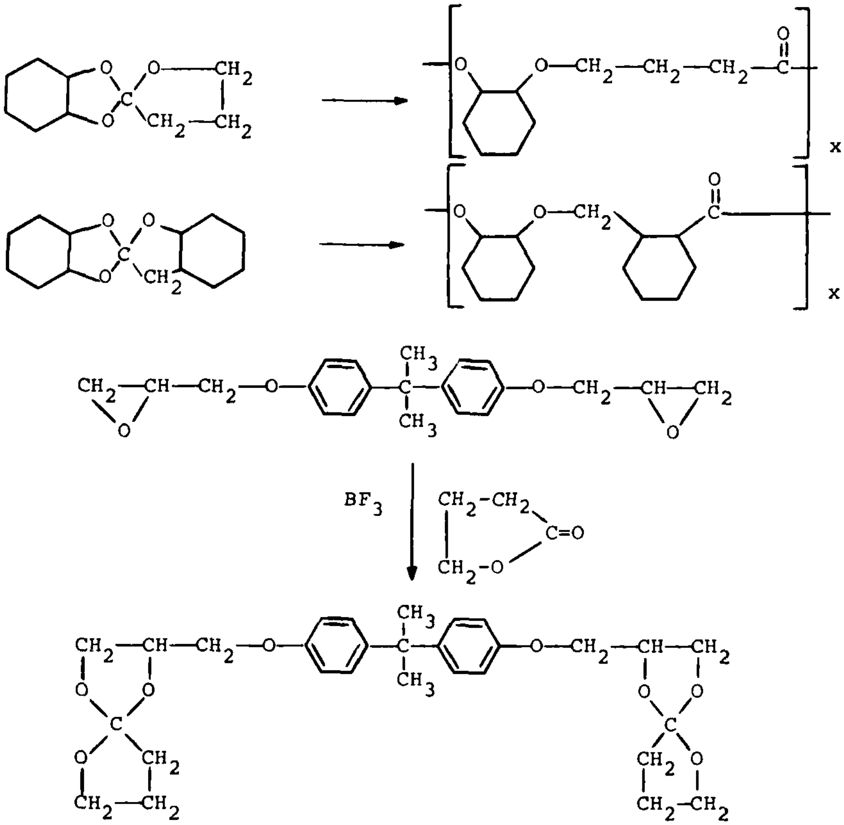
mp 176° (30% yield)

On polymerization this monomer will give a highly cross-linked material, but it can also be used to vulcanize the linear ether-containing polyester obtained from the previously discussed spiro ortho ester.

If one desires a higher melting polymer from an spiro ortho ester, the introduction of cyclohexane rings gives a fairly large increase in the softening point. The introduction of one cyclohexane ring produces a monomer that gives a substantial increase in volume upon polymerization (3%). The introduction of two cyclohexane rings gives a material with a softening point of over 100° C, but there is essentially no change in volume.

Although the adduct between an epoxy resin and the butyrolactone did not give a material that could be isolated in the pure state, it was possible to use this reaction to prepare prepolymers which had a large shrinkage during the initial portion of the reaction when the material was liquid. When this prepolymer was further polymerized with boron trifluoride, a cross-linked material resulted with essentially no change in volume near the last part of the polymerization where the material becomes viscous and gels. This technique should allow the production of strain-free materials at a reasonable cost.

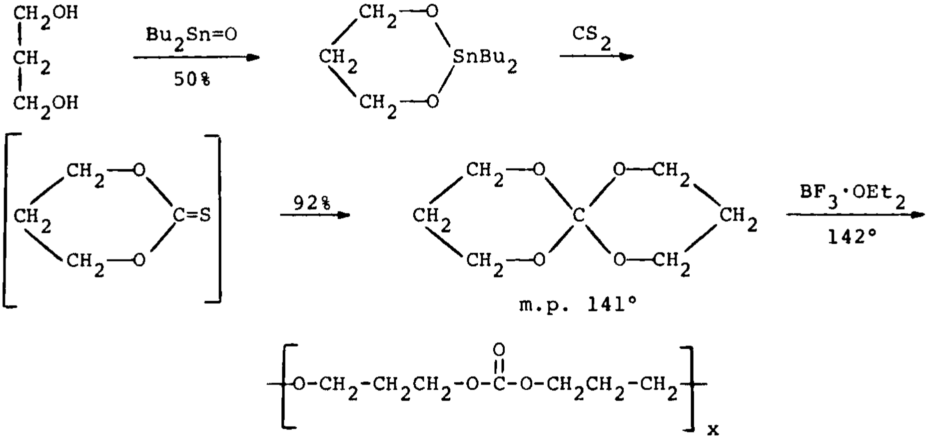
Another very interesting class of compounds appeared to be the spiro ortho carbonates. Sakai, Kobayashi, and Ishii [11] recently described a method for synthesizing ortho carbonates using tin



compounds with carbon disulfide. Using their method, we were able to synthesize a series of spiro ortho carbonates by the following set of reactions. This method worked well for 1,2-, 1,3-, or 1,4-glycols to produce crystalline monomers [12].

Since the spiro ortho carbonate was a highly crystalline material, initial polymerization studies were carried out above its melting point at 142° C. Although the polymerization could be carried out with a variety of cationic catalysts, such as boron trifluoride gas, boron trifluoride etherate, and aluminum chloride, boron trifluoride etherate proved to be the most convenient.

Thus, when the polymerization of molten spiro ortho carbonate was carried out in bulk with boron trifluoride etherate at 142° C, a quantitative yield of polymer was obtained after several hours.



[When polymerization was carried out at higher temperatures, the evolution of a gas (CO_2) was observed.] The polymer was purified by dissolution in chloroform followed by extraction of the solution with water. The structure of the polymeric material was proven not only by elemental analysis, but also by NMR and IR spectra. The polymer had an intrinsic viscosity of 0.26 in chloroform at 25° C. Although the relationship between molecular weight and intrinsic viscosity is unknown for this series of polymers, a reasonable assumption of the constants would indicate a molecular weight in excess of 100,000. These results would indicate that the strain inherent in the ortho carbonate structure provides a strong driving force for the polymerization. A very similar polymerization could be carried out at 100° C by addition of catalyst to the solid monomer.

When the polymerization was carried out in a dilatometer in which the bath was held at a constant temperature (142° C), the meniscus, instead of falling as is the usual case during polymerization, actually rose quite substantially. A calculation of the extent of change in volume indicates an expansion in excess of 2%. This compares very favorably with the very slight increase (0.14%) in volume reported earlier for the polymerization of a spiro ortho ester. This example, then, represents the first reported case in which a substantial amount of expansion in volume occurs during polymerization.

An even more remarkable relationship was discovered when the densities of the monomer and polymer were determined as a function of temperature. Table 4 lists the densities of the two materials at 25, 100, 130, and 142° C.

TABLE 4. Calculation of Expansion During Polymerization

Temperature (° C)	Density of monomer (g/cc)	Density of polymer (g/cc)	Expansion in volume (%)
25	1.31	1.20	9
100	1.30	1.14	14
130	1.30	1.11	17
142	1.12	1.10	2

The density of the amorphous liquid polycarbonate varied quite regularly and smoothly with changes in temperature from 1.20 g/cc at 25° C to 1.10 g/cc at 142° C. The density of the monomer, however, changed quite abruptly when it went from the molten monomer at 142° C to the crystalline monomer at temperatures below its melting point. Obviously, this data shows that the crystalline monomer is considerably more dense than the molten monomer. Similarly, the crystalline monomer was much more dense than the liquid polycarbonate. Thus, when the expansion in volume is calculated from the density of the crystalline monomer, the expansion was 9% at 25° C up to 17% at 130° C. Under ideal conditions the expansion might even be somewhat larger since the density of the crystalline monomer was determined by measuring the volume of a given weight of a solidified molten monomer. Under these conditions it is almost impossible to avoid the presence of some voids or the inclusion of a small amount of amorphous material. By coincidence, however, the 17% expansion is quite close to the expansion already calculated for the conversion of adamantane to polycyclopentenomer [2]. Figure 1 gives the plot of the densities of the monomer and polymer vs temperature.

It is obvious from the data that the conversion of a crystalline monomer to an amorphous polymer represents the ideal case for the large expansion in volume since in most cases the crystalline monomer would be expected to be considerably more dense than the corresponding liquid monomer. This is just the opposite of the case in which a liquid monomer is converted to a crystalline polymer. For example, when liquid ethylene monomer is converted to crystalline polyethylene at 5° C, a 66% shrinkage occurs [3]. It appears that the conversion of a liquid monomer to a crystalline polymer represents the ideal case to get the largest shrinkage during polymerization.

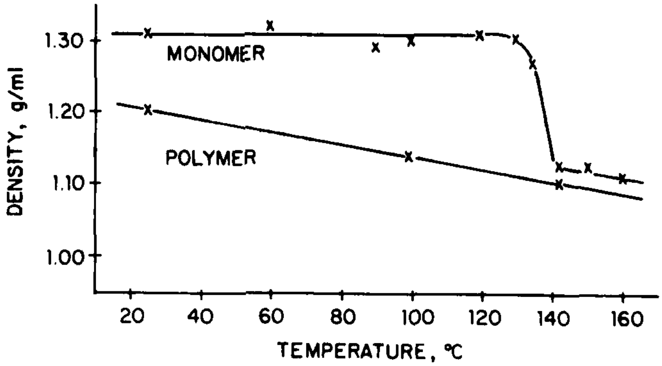
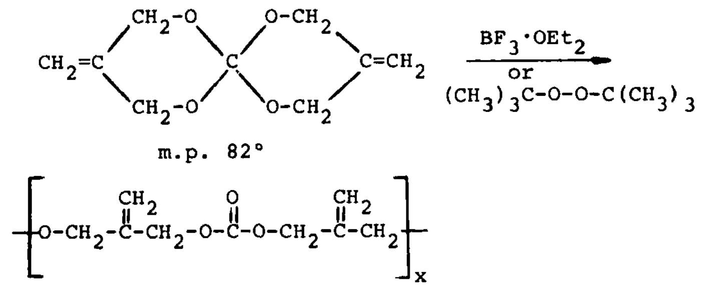


FIG. 1. Densities of the monomeric spiro ortho carbonate and related polyoxycarbonate vs temperature.

An inspection of Fig. 1 indicates that the densities of the monomeric spiro ortho carbonate and the polymer appear to cross above 200°. At that point, one would expect no change in volume during polymerization since the two materials have the same density. Above this critical temperature, one would expect to get shrinkage during the polymerization. Unfortunately, the polymerization cannot be carried out conveniently in this temperature range with the catalysts now available since carbon dioxide is liberated and the polycarbonate is not obtained in a pure form. At the lower end of the temperature scale the two lines appear to intersect again, but one would expect below the glass transition of the polymer that the density line would become more nearly horizontal and become essentially parallel to the line of the density of the monomer.

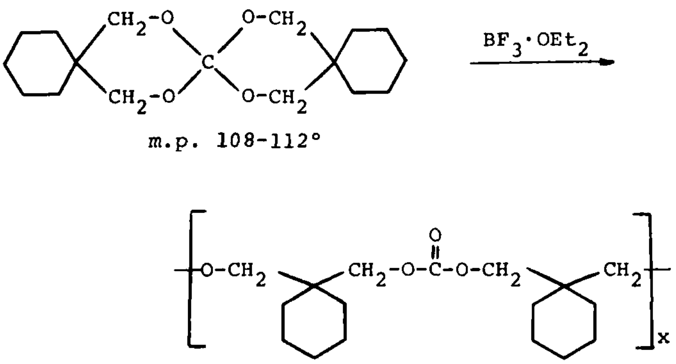
While at first it appeared difficult to find a polymerization procedure that would take full advantage of this large expansion, since the solid monomer is hard to introduce into a mold or a composite, it was found possible to make a slurry of this crystalline material in liquid epoxy monomer and copolymerize the two with controlled shrinkage. Expansion, contraction, or zero change in volume could be obtained depending on the concentration of the crystalline monomer in the slurry. The large volume increase also suggests that the polymerization may be used to replace explosives in cracking rocks in a quarry or for excavations.

A variety of analogs of this spiro ortho carbonate can be prepared and polymerized. One that is of special interest is the 3,9-dimethylene derivative which can be polymerized either cationically or by a free radical technique to produce cross-linked resins at high conversions and linear soluble polymers at low conversions [13]:

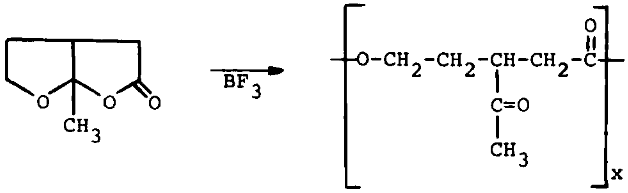


When the polymerization was run at room temperature, a 4.5% expansion in volume occurred, but when the polymerization was carried just below the melting point, an 8% expansion in volume was noted. Polymerization above the melting point of the unsaturated monomer produced a 1.4% expansion at 100° C, while at 115° C the densities of the monomer and the polymer appeared to be equal. Above 115° C, the polymerization produced a shrinkage.

A higher softening polymer in this same series could be prepared from the trispiro analog, which has a melting point of 112° C. Polymerization at room temperature produced a material with an increase in volume of 4%. Just below the melting point it gave a high melting polymer with an expansion of 7%. The spiro ortho carbonates appear to be a very versatile class of compounds for polymerization with expansion in volume.



In order to demonstrate that expansion in volume would take place with bicyclic materials other than spiro derivatives, a ketal lactone was prepared by the method of Lange, Wamhoff, and Korte [14]. Polymerization of this material with either boron trifluoride or a base produced the keto-containing polyester with essentially no change in volume. We have demonstrated, therefore, that polymerization with no change in volume or with expansion in volume is a general phenomena possible with a wide variety of liquid and crystalline cyclic and bicyclic monomers.



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