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Radiolytically Induced Polymer Formation in Alkenyl Carboranes: Phase Effects(1,2)†

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Abstract—The primary concern of this investigation has been to determine the effects of the physical state of structurally similar alkenyl substituted carborane monomers on their γ-ray induced polymerization. In the course of the investigation it was shown that 1-vinyl-*o*-carborane apparently exhibits mesomorphic behavior at room temperature. This behavior was isotropic and most probably plastic crystalline in nature, whereas 1-isopropenyl-*o*-carborane exhibited only crystalline behavior below its capillary melting point. In the case of 1-vinyl-*o*-carborane it was shown that polymerization occurs in a " head to tail " manner with a high yield of polymer up to 11–12 units in length. Under the same conditions it was found that 1-isopropenyl-*o*-carborane gave rise to two dimer products which were structurally different. The dimerization of 1-isopropenyl-*o*-carborane appears to be topotatic in nature. The results of this study indicated that the physical state of the monomer has a pronounced effect both qualitatively and quantitatively on the γ-ray induced polymerization of these compounds.

Introduction

It has been shown previously that the alkenyl substituted 1, 2-dicarba-*closo*-dodecaborane (11) compounds provided a relatively high yield of product formation when irradiated with ^{60}Co gamma rays in the condensed state.(4,5) The vinyl- and isopropenyl-substituted compounds, the structures of which are shown in Fig. 1, are of the closed cage type consisting of ten boron atoms and two carbon atoms with the vinyl- or isopropenyl-substituent side chain attached to one of the two equivalent carbons of the cage. These systems are of interest not only because of the high product yields which are obtained but also because of the structural problems involved with the cage being an electron deficient system.(6) This

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results in the cage part of the molecule having a large capacity for the attraction of electrons. As can be seen in Fig. 1 the double bond in the side chain is conjugated to this electron deficient cage.

Structurally these compounds appear to differ only in the substitution of a methyl group for a hydrogen in the side chain. Thus it might be expected on this basis, that these homologous compounds would behave in their radiation induced reactions in a similar manner.

Experimental

The purification of 1-vinyl-*o*-carborane and 1-isopropenyl-*o*-carborane, which were obtained from Alfa Inorganics Inc., was by

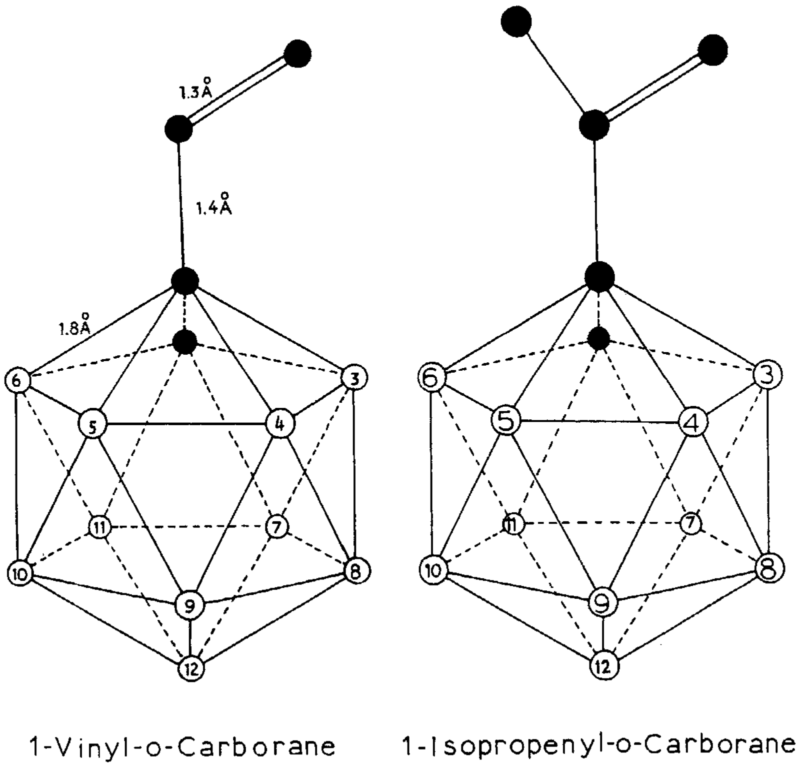

Figure 1. (a) Structure of 1-vinyl-1, 2-dicarba-*closo*-dodecaborane (11); ○ represents boron atoms, ● represents carbon atoms; associated hydrogen atoms are not shown. (b) Structure of 1-isopropenyl-1, 2-dicarba-*closo*-dodecaborane (11); ○ represents boron atoms, ● represents carbon atoms; associated hydrogen atoms are not shown.

vacuum sublimation. It was found in the case of the 1-vinyl-*o*-carborane that the material collecting on the cold finger of the sublimation apparatus was a crystalline material at 0 °C but which on warming to room temperature reverted to a waxy state. A purity check of the material, using thin-layer chromatography, indicated only one component, that of 1-vinyl-*o*-carborane without any non-volatile impurity (for example, a dimer).(4) The material was then examined by gas chromatography for its purity. The results of this test indicated that there was no detectable volatile impurity in the 1-vinyl-*o*-carborane. Table 1 shows the retention times for the various carboranes which could be volatile impurities in the preparation of 1-vinyl-*o*-carborane. None of these have retention times which would not be detectable on the GLC column using standard operating conditions. As a further check the 1-vinyl-*o*-carborane was placed on the column successively in (a) *n*-hexane, (b) chloroform, (c) carbon tetrachloride and (d) acetone as solvents. By varying the conditions of operation of the column, the solvent peak could be brought out at different times. Under these rather rigorous conditions there was no detectable solvent impurity in the 1-vinyl-*o*-carborane. In the case of 1-isopropenyl-*o*-carborane vacuum sublimation of this material resulted in a crystalline product which appeared to remain crystalline at room temperature. Again, this substance gave just one peak or spot without any indication of a

TABLE 1 G. L. C. of the carboranes†‡

Substance	Retention time Minutes
Acetone (solvent)	0.6
o-Carborane	18.6
m-Carborane	3.4
p-Carborane	2.0
1-ethyl-*o*-carborane	11.7
1-vinyl-*o*-carborane	10.2
1-isopropyl-*o*-carborane	14.1
1-isopropenyl-*o*-carborane	13.4

† All samples analyzed under identical conditions.

‡ A 12 foot × ¼ inch column provided base line resolution of all components.

volatile or nonvolatile impurity detectable by GLC and thin-layer chromatography.

Radiolysis of 1-vinyl-*o*-carborane and 1-isopropenyl-*o*-carborane was carried out on ½ g quantities of the sublimed, carefully degassed material. These samples were sealed under vacuum in Pyrex cells and irradiated continuously at various temperatures in the University ^{60}Co Source for times varying from 12 to 60 hours at an average dose rate of 6.5×10^{19} eV/g-hr. The dose rates to the samples were determined from the Fricke dosimeter using appropriate correction factors.(7)

Following irradiation the unreacted monomers were removed by extraction with *n*-hexane. The techniques of separation and analysis of the polymer including determination of their structures have been previously reported.(4,5)

Results

(A) PHYSICAL STATE OF THE CARBORANE MONOMERS

The heating and cooling curves of 1-vinyl-*o*-carborane indicated a halt at the capillary melting point of 79 °C together with a second halt at 11 °C. 1-isopropenyl-*o*-carborane on the other hand showed only one halt, that of the capillary melting point at 47 °C. This led us to suspect the possibility that in the case of 1-vinyl-*o*-carborane, we were dealing with a mesomorphic state between 11 and 79°.

In order to attempt to confirm the possibility that the 1-vinyl-*o*-carborane exists in a mesomorphic state between 11° and 79 °C, the material was examined under a polarizing microscope. The results of this test showed that the material exhibited no birefringence, and if indeed it is a mesophase it is isotropic. However, 1-vinyl-*o*-carborane cooled from the melt under a cover slip showed a distinct ordering pattern as shown in Fig. 2.

In order to further confirm this possibility, differential thermal analysis was carried out on 1-vinyl-*o*-carborane as shown in Fig. 3. As can be seen in this figure, there is a rather large endothermic peak at 11 °C, which is much larger than the peak at 79 °C, the capillary melting point, indicating that there is indeed a large entropy phase transition between the crystalline state at 11 °C and some type of mesomorphic state above 11 °C. Rough estimates by planimetry suggest that the enthalpy change at the wax-liquid transition is only 7 to 8% of the total involved in going from the solid to the liquid, including the large endotherm at 11 °C. The corresponding fractional entropy is in good agreement with a number of well characterized smectic and plastic crystalline substances.(8) Since the transition

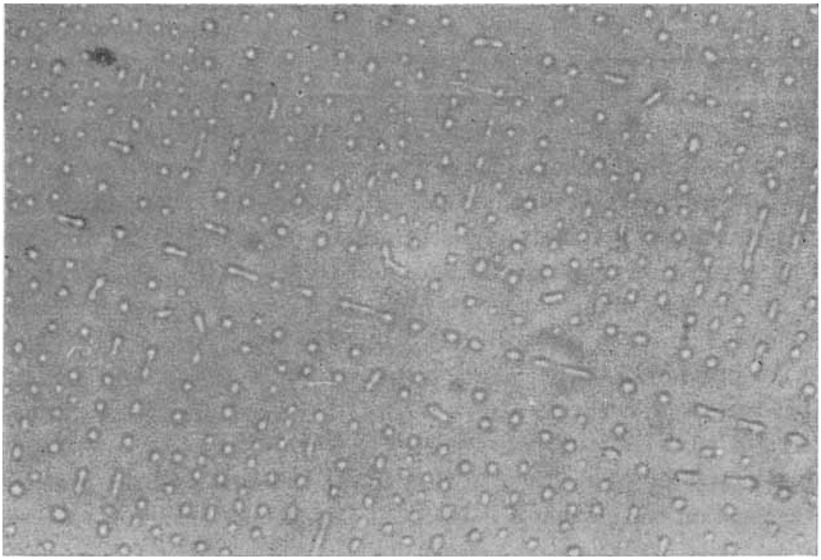

Figure 2. Photomicrograph of the cavitation pattern of 1-vinyl-*o*-carborane cooled from the melt. 100 ×, 25 °C.

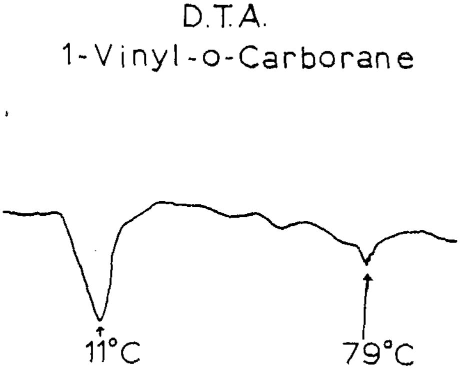

Figure 3. Representative differential thermal analysis of the purified 1-vinyl-*o*-carborane monomer. Irregularities between 11 °C and 79 °C were not reproductible on successive scans.

at 11 °C may be approached reversibly by both heating and cooling, the possibility of a metastable or amorphous state below the capillary melting point appears to be ruled out.

For further confirmation of this property, the X-ray powder diffraction pattern was taken of both the 1-vinyl-*o*-carborane and the 1-isopropenyl-*o*-carborane. The result of this analysis is shown in Table 2. It will be noted here that for 1-vinyl-*o*-carborane there were only two peaks at 14.6° and 16.8° with a relative intensity of 1.00 to 0.61. The d-spacings indicated that the length of the molecule was 6.06 angstroms, in agreement with the calculated length and another interplanar distance was 5.27 angstroms. The 1-isopropenyl-*o*-carborane, on the other hand, is a typical crystalline material showing a relatively large number of diffractions. In determining the X-ray powder diffraction of 1-vinyl-*o*-carborane as shown in this Table a single peak was obtained for each one of the angles, the shape of which is shown in Fig. 4. In a fast scan of these peaks at 1° per minute, the peaks appeared to be sharp and without structure. However on a slow scan at $\frac{1}{4}$° per minute, the peak centered at 16.8° showed some structure. The peak at 14.6° remained a singlet without structure. In view of the fact that a monochromator was used on the system it is believed that this structure of the peak

TABLE 2 X-Ray Powder Diffraction Analysis

Substance	2θ degrees	d(A)	Relative Intensity
1-vinyl-*o*-carborane	14.6	6.06	1.00
	16.8	5.27	0.61
1-isopropenyl-*o*-carborane	13.8	6.41	0.48
	14.0	6.32	0.51
	15.5	5.71	0.48
	15.7	5.64	1.00
	16.3	5.43	0.09
	17.8	4.98	0.15
	20.0	4.44	0.09
	22.3	3.98	weak
	24.4	3.64	weak
	26.5	3.36	weak
	31.8	2.81	weak
	37.9	2.37	weak

at 16.8° may be real. If it is real, it is most probably due to the stacking arrangement of the molecules in the mesomorphic crystal lattice. If this is true then the structure of this peak should be temperature dependent.

These findings have led us to speculate that 1-vinyl-*o*-carborane may belong properly under the classification " Plastic Crystalline ",(8) since its molecular character and resultant bulk thermodynamic properties are comparable with representative plastic crystalline substances. Camphor, for example, is similar to that of a number of the icosahedral carboranes in its macroscopic and microscopic properties (i.e. molecular shape, molecular weight, dipole moment, etc.) Numerous investigations have established the rotational freedom of camphor below its isotropic transition.(9,10,11) It is not clear why there are apparent exceptions among these compounds such as

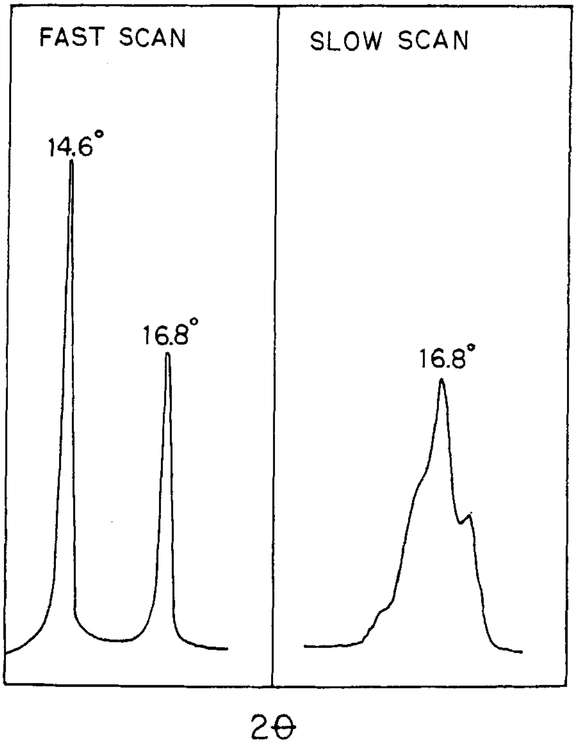

Figure 4. X-ray diffraction scan of 1-vinyl-*o*-carborane; fast scan at 1°/minute; slow scan at 1/4°/minute.

that found for the 1-isopropenyl-*o*-carborane derivative, but the parallelism holds for terpenes as well since a number of them are not plastic crystalline.

(B) RADIOLYSIS OF 1-VINYL- AND 1-ISOPROPENYL-CARBORANES

Under the influence of Cobalt-60 Gamma radiation at 31 °C both 1-vinyl-*o*-carborane and 1-isopropenyl-*o*-carborane polymerized. In the case of 1-vinyl-*o*-carborane there was only one product produced without any other side products and this was a polymer, the structure⁽⁴⁾ of which is shown in Fig. 5. Here the polymerization occurred between the vinyl-side chain and the 9 or 12 boron cage position of another molecule with the retention of a vinyl-type end group for each polymer molecule. This would be a " head to tail " type of polymerization.

In a 60 hour irradiation approximately 50 per cent of the material was converted into polymer. This polymer was shown to have a number average molecular weight of 750, that is between tetramer

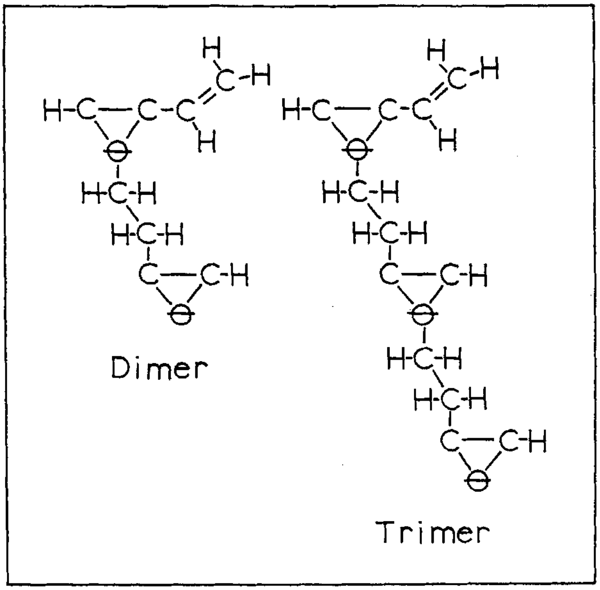

Figure 5. Structure of the polymer formed in the radiolysis of 1-vinyl-*o*-carborane; cage represented by —c——c—.

and pentamer. Separation of a high molecular weight fraction indicated that polymerization had taken place up to 11 to 12 monomer units.

The radiolysis of 1-isopropenyl-*o*-carborane gave rise to not just one product but to two different types of dimers together with some side product gas formation. This gas was in the form of hydrogen and methane, although the amount present was extremely small. Thus the major products were the two types of dimers. The two dimers, the structures⁽⁵⁾ of which are shown in Fig. 6, differ in terms of both structure and yield. In the first case, which has been designated as the side chain polymer and represents about 67 per cent of the total yield, polymerization had taken place through the side chain of the original monomer and a vinyl-type end group was retained. The other dimer, which has been designated as the cage polymer, represents about 33 per cent of the total polymer yield and is similar to that of the 1-vinyl-*o* carborane in that the polymerization had taken place by the attachment of the side chain to a boron of the carborane cage. Again there is retention of a double bond. However, it is not an end group but appears in the chain connecting the two

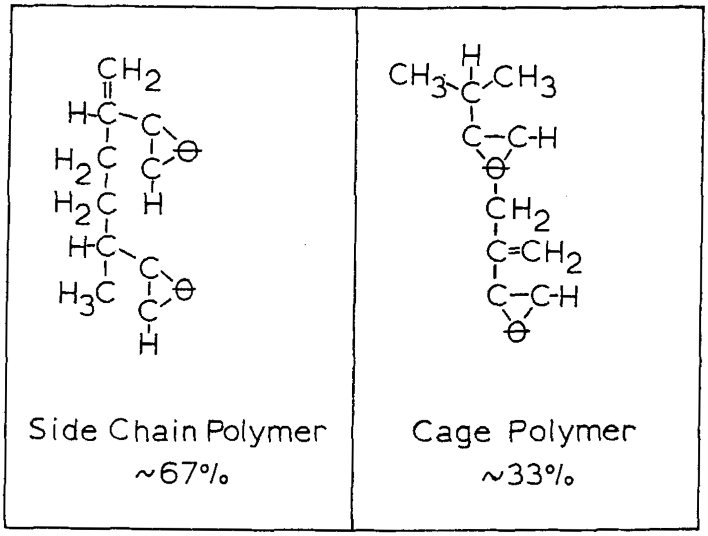

Figure 6. Structures of the two types of polymers formed in the radiolysis of 1-isopropenyl-*o*-carborane; cage represented by —c——c—.

monomer units. In the case of the solid products formed from the 1-isopropenyl-*o*-carborane radiolysis the polymerization was primarily to the dimer with a very small amount of the trimer being present.

A comparison of the per-cent yield of the dimer of the cage type of polymerization is shown in Fig. 7. It will be noted that the 1-vinyl-*o*-carborane polymer shows a deviation at the low doses which drops below the extrapolated value shown by the dotted line. This decrease has been shown to be due primarily to the techniques for extraction of the monomer and the fact that at low doses the chain length has not proceeded much beyond the trimer state even in the case of 1-vinyl-*o*-carborane. Since in extracting the monomer some of the polymer was also lost, in actuality the yield curve is more closely associated in the 1-vinyl-*o*-carborane case with the straight line. However, it will be noted in the case of the dimer formed from 1-isopropenyl-*o*-carborane that the yield increases just as in the case of 1-vinyl-*o*-carborane but begins to level off and reaches an almost constant value above doses of 2 × 10^{21} eV/gm, whereas the 1-vinyl-*o*-carborane polymer continues to rise. This is most likely due to the

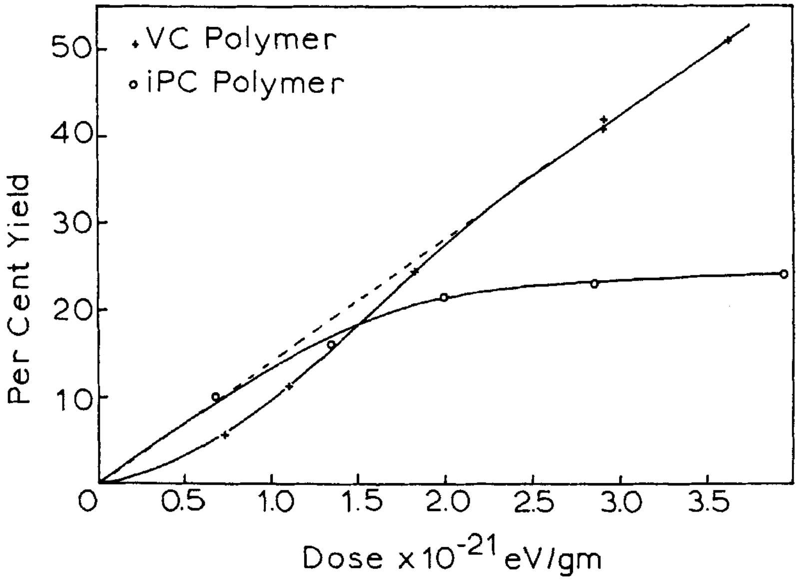

Figure 7. Percent yield of polymer of the cage type as a function of γ-ray dose; VC polymer—polymer formed from radiolysis of 1-vinyl-*o*-carborane; iPC polymer—dimer formed from the radiolysis of 1-isopropenyl-*o*-carborane.

fact that the 1-vinyl-*o*-carborane polymerization was continuing beyond the dimer-trimer stage to the longer chain polymer. In the 50 per cent conversion region it has been shown in the case of 1-vinyl-*o*-carborane that the polymer was of the order of 11 to 12 units in length, whereas at the same total dosage the polymer from 1-isopropenyl-*o*-carborane was still only at the dimer-trimer stage.

(C) TEMPERATURE DEPENDENCE OF POLYMER FORMATION

In order to further investigate the effect of the physical state of the monomer in the radiation induced polymerization of these compounds, they were irradiated for a constant total dose of 1.35×10^{21} eV/gm at a series of temperatures such that the effects in the crystalline, mesomorphic and liquid states could be observed. The results of this study are shown in Table 3. At the higher temperatures, 108 and 172 °C, the monomers were heated for the same length of time, ~24 hours, as they were irradiated to determine if there was any pyrolysis of these compounds. In this pyrolysis study, GLC and capillary melting point data indicated that heating at these temperatures for this period of time left the monomers unchanged.

There are several points to be noted in this Table. First, the percent yield of polymer from 1-vinyl-*o*-carborane increases with temperature from 5 to 172 °C, that is, through the crystalline, mesomorphic and liquid states. Secondly, that in the case of the 1-isopropenyl-*o*-carborane in going from the crystalline to the liquid state, there is in general a drastic decrease in the yield of the dimer of both types. The complete absence of any of the side chain dimer in the liquid state strongly suggests that its formation is completely controlled by the molecular arrangement or periodicity of the crystalline

TABLE 3 Temperature Dependence of Polymer Formation

Temperature °C	State	1-vinyl-*o*-carborane Polymer % Cage Yield	1-isopropenyl-*o*-carborane Polymer % Cage Yield	% Side Chain Yield
5	Crystalline	8.2	—	—
31	Crystalline	—	15.3	30.3
31	Mesomorphic	20.0	—	—
108	Liquid	47.5	1.4	0.0
172	Liquid	86.0	6.7	0.0

lattice. Thus, this may be an example of "topotactic polymerization "(12,13)

Since the 1-vinyl-*o*-carborane cage type of polymer follows the expected trend of increasing yield in going from the crystalline to the mesomorphic to the liquid state, there is at present no reasonable explanation of the decrease in yield of the cage type of dimer in the 1-isopropenyl-*o*-carborane case in going from the crystalline to the liquid state. Nor is it readily understood why polymerization of 1-isopropenyl-*o*-carborance in the liquid state does not proceed beyond the dimer stage. It is, of course, possible that the cage type of polymerization in the crystalline state is also, at least partially, controlled by the lattice arrangement of the molecules.

Conclusions

There are two important conclusions that can be drawn from the work done thus far on these systems:

1. 1-vinyl-*o*-carborane appears to exhibit mesomorphic behavior which is isotropic and most probably plastic crystalline in nature.
2. Although 1-vinyl-*o*-carborane and 1-isopropenyl-*o*-carborane are very similar structurally, the difference in the physical states of the two compounds at ambient temperature has a pronounced effect, both qualitatively and quantitatively, on their Gamma-ray induced polymerization.

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