



# BULK POLYMERIZATION OF 1,3,5,7-TETRAVINYL TETRAMETHYLCYCLOTETRASILOXANE INDUCED BY GAMMA RADIATION

LARISSA ALEXANDROVA, FRANCISCO DIAZ, MIGUEL CANSECO,  
DMITRI LIKHATCHEV and RICARDO VERA-GRAZIANO

Instituto de Investigaciones en Materiales, UNAM, Ciudad Universitaria, 04510, Mexico, D.F.,  
Mexico

(Received 26 January 1997; revised 2 May 1997)

**Abstract**—Gamma ray-induced bulk polymerization of 1,3,5,7-tetravinyltetramethylcyclotetrasiloxane at ambient temperature has been investigated. It was found that the polymerization proceeds via a free radical mechanism through the reaction of vinyl groups, and the resulting polymer had a three-dimensional network structure. Kinetic features of the reaction were also studied, strong postpolymerization effects were observed at doses between 8 and 80 kGy. The composition of the sol fractions was determined by high pressure liquid chromatography, and the chemical structure of both the sol and gel fractions was analyzed by FTIR spectroscopy. Thermal stability of the gel fractions, determined by thermogravimetric analysis, and the thermomechanical behavior of unextracted samples were found to depend on the irradiation dose. © 1998 Elsevier Science Ltd. All rights reserved

## 1. INTRODUCTION

Curing of polymer and monomer systems by high energy radiation is known to be very useful for the preparation of highly pure polymeric materials. It can result in the formation of three-dimensional polymer networks or in branched polymers depending on the structure of the exposed monomers. Three-dimensional networks with relatively short distances between crosslinked points are usually produced by irradiation of multiple-unsaturated monomers and oligomers (Woods and Pikaev, 1994).

The high purity of these catalyst-free polymers may be important for various special applications, in particular, for producing medical implants and tissues for plastic surgery (Yuzhelevskii, 1991; Yoshii *et al.*, 1995). Silicones of different structures and molecular weight appear to have been amongst the most suitable materials for these purposes (Halpern and Tong, 1989; Yuzhelevskii, 1991), and so, their synthesis and characterization remain the subject of intensive research.

It has been shown in several papers on radiation chemistry of linear and cyclic siloxanes (Miller, 1959; Wolf and Stewart, 1962; Tabata *et al.*, 1964; Chawla and Pierre, 1972; Lebrun *et al.*, 1984; Naylor and Stannett, 1986) that linear polydimethylsiloxane could be easily crosslinked by irradiation, whereas cyclosiloxanes such as hexamethylcyclotrisiloxane ( $D_3$ ), octamethyltetracyclosiloxane ( $D_4$ ) and decamethylcyclopentasiloxane ( $D_5$ ) are quite stable in the liquid state under irradiation, but could be polymerized by this method via cationic mechanism

if completely dried. Among these,  $D_4$  is the most resistible to irradiation. Radiation-induced polymerization of  $D_4$  at ambient temperature yields less than 10% of a linear or slightly branched polymer, even under super-dry conditions. On the other hand, vinyl monomers can be easily polymerized in bulk under irradiation at this temperature even in the presence of detectable amount of residual water. Free radical mechanism has been shown to predominate in this process (Woods and Pikaev, 1994).

The 1,3,5,7-tetravinyltetramethylcyclotetrasiloxane consists of both cyclic siloxane and vinyl groups. Thus it is expected that this compound can polymerize under relatively low doses of high energy radiation even without drying. This would result in a three dimensional polymer network with a high content of siloxane rings.

In this paper we describe our work on  $\gamma$ -irradiation of this monomer and the characteristics of the resulting polymers.

## 2. EXPERIMENTAL

The 1,3,5,7-tetravinyltetramethylcyclotetrasiloxane ( $D_4V_4$ ), a colorless liquid with b.p. 110°C at 10 mm Hg, was received from Huls America Inc. All samples were triply degassed and dried over calcium hydride in a glass apparatus under  $10^{-5}$  mm Hg at room temperature for 24 h, then condensed in clean ampoules and sealed.

Irradiation was carried out with a  $^{60}\text{Co}$   $\gamma$ -ray source at ambient temperature at a dose rate of 3.3 kGy  $\text{h}^{-1}$ , as determined by Fricke dosimetry. Some ampoules

were opened immediately after an appropriate irradiation time for investigation of the polymerization process, and others were opened after 36 h storage at room temperature to study postpolymerization effects.

The soluble fractions were separated from the gel fraction by soxhlet extraction with hot benzene at 72°C for 24 h. A high pressure liquid chromatography (HPLC) analysis of  $D_4V_4$  before and after thermal treatment at this temperature was performed to ensure that the extraction process did not cause any changes in the sol fraction. The obtained chromatograms were identical. A Differential Scanning Colorimetry (DSC) test showed that thermal polymerization of the monomer can only be initiated at temperatures above 150°C. The hard gels were ground before extraction. The extracted gels were dried to a constant weight under vacuum and the gel content was taken as a weight percent of insoluble polymer in the sample. Infrared spectroscopy (a FTIR spectrophotometer Nicolet 610P) was used to analyze both the sol and gel fractions.

The composition of the soluble parts was determined by high pressure liquid chromatography using a 715 Gilson HPLC system with a spherisorb 5 ODS2 column, using acetonitrile (HPLC grade, Aldrich) as the mobile phase (flow 0.5 ml min<sup>-1</sup>) and a UV-detector (wavelength 210 nm).

The thermal stability of the gel parts was measured in both air and nitrogen with the help of a T.A. Instruments, Thermogravimetric Analyzer TGA 2950 at a heating rate of 5°C min<sup>-1</sup>. The DSC measurements were performed using a T.A. Instruments model 2910, at 10°C min<sup>-1</sup> scanning rate in a nitrogen atmosphere.

The thermomechanical curves of unextracted samples irradiated at different doses were obtained by a penetration technique under a dynamic regime. For this purpose a T.A. Instruments Thermomechanical Analyzer (TMA), model 2940 interfaced with a model 2100 computer/controller was employed. A standard expansion probe and a constant load of 1 N were used. All these measurements were carried out in a nitrogen atmosphere at a heating rate of 10°C min<sup>-1</sup>.

### 3. RESULTS AND DISCUSSION

The vacuum-sealed ampoules of  $D_4V_4$  were irradiated with doses from 5 to 500 kGy. It was found that immediately after irradiation, at doses below 30 kGy, no changes in either the initial phase condition or in the viscosity of the samples were observed. The viscosity increased dramatically at 30 kGy producing a gel. Further irradiation gave soft colorless gels, that became harder as the dose increased, and very hard and transparent glassy-like polymers were obtained at doses above 100 kGy (Fig. 1).

For comparison, samples of  $D_4$  were prepared and irradiated in the same way as  $D_4V_4$ . In contrast to

$D_4V_4$ , these  $D_4$  samples did not exhibit any changes in their physical properties even after irradiation at 500 kGy. Their FTIR-spectra registered before and after irradiation were also identical. This indicates that  $D_4$  can not be polymerized under these conditions, with any appreciable yield. The presence of water traces appears to inhibit the cationic polymerization which is the only possible mechanism for polymerization of this monomer (Naylor *et al.*, 1990). Thus we consider that the polymerization of  $D_4V_4$  which we observed, occurred through the reaction of vinyl groups via basically a free radical reaction and this is consistent with the mechanisms of polymerization of other vinyl monomers (Woods and Pikaev, 1994).

The sol fractions of irradiated samples were obtained by extraction in hot benzene. Because of a very strong UV-absorption of this solvent, acetonitrile was used as the solvent for both UV-spectroscopy and HPLC. Complete solubility of the sol fractions in acetonitrile was reached at 60°C while the monomer was dissolved easily at room temperature.

The UV spectra of the monomer  $D_4V_4$  exhibited a strong absorption maximum at 205 nm. This band could be assigned to the vinyl groups bound with Si-atom, since  $D_4$  that does not contain C=C double bonds has no absorption above 190 nm. The sol fractions of the irradiated samples gave absorption spectra generally similar to  $D_4V_4$ , but the maximum shifted gradually to longer wavelengths with increasing dose and reached the maximum at 214 nm for the sample irradiated at 500 kGy. Irradiation also resulted in the appearance of a shoulder at 235–240 nm that became more pronounced at higher doses.

The shift to longer wavelengths indicates that the sol fraction contained significant amounts of low molecular weight fragments with unsaturated bonds distinct from the vinyl group of  $D_4V_4$ . These fragments could result from both oligomerization of the initial monomer and/or random scission of the crosslinked polymer chains. All these products may have C=C double bonds in various positions and environments, and indeed, some of them may be conjugated. The presence of such bonds is considered to be the main reason for the observed red shift of 205 nm band.

The HPLC analysis indicated that irradiation even at low doses brought about a complete disappearance of the initial monomer in the sol fraction. The chromatogram of the monomer has an intense peak with a retention time of 6.87 min and a very weak peak at 11.21 min. The former practically disappeared at an irradiation dose of only 5 kGy and a new intense peak at 11.17 min appeared. Further irradiation of the samples at higher doses resulted in the reduction of the intensity of this new peak and the appearance of multiple peaks with retention times of 5.5–7.4 min. The yield of the corresponding products, estimated by the area under the peaks, reached about

95% at 500 kGy, while the contents of the fraction with retention time of 11 min fell to 4%.

The HPLC behavior shows that the sol fraction changes its chemical composition upon irradiation. The results suggest that initially, at low doses, dimerization of  $D_4V_4$  takes place and this results in the appearance of the peak at 11.2 min. At higher doses the sol fraction seems to be gradually enriched by low molecular weight products resulting from chain scission.

The FTIR-spectra of the sol fractions of irradiated samples at frequencies between 2000 and  $400\text{ cm}^{-1}$  are very similar to the monomer spectrum, which is presented in Fig. 2(a). A notable difference could be observed at higher wavenumbers where new bands appeared at  $2910$  and  $2860\text{ cm}^{-1}$  upon exposure to radiation. These can be assigned to C-H stretching vibrations in  $sp^3$ -hybridized  $CH_2$ - and CH-groups.

Thus the analysis of the sol fractions by means of HPLC, UV-, and FTIR spectroscopies showed that the sol fraction of the irradiated samples probably consist of very low molecular weight cyclosiloxane oligomers and scission products which are soluble in benzene and hot acetonitrile. The relative amounts of the former and latter depended on the irradiation

dose. Higher doses increased the concentration of the scission's products in the sol fraction.

The kinetics of the  $\gamma$ -radiation induced bulk polymerization of  $D_4V_4$  was followed by gravimetric analysis of the insoluble fractions obtained by extraction of the samples (gel yield, wt%) immediately after irradiation (see Fig. 1). A detectable amount of gel fraction was registered starting from the dose of 30 kGy. The gel yield increased almost linearly up to 200 kGy dose, and then the polymerization rate fell dramatically above 250 kGy.

The obtained kinetic curve can be considered as typical for radiation-induced three-dimensional polymerization of multi-unsaturated monomers (Takacs, 1992; Lopez *et al.*, 1995). After the depletion of the monomer in the first stage of this process a high concentration of pendant double bonds can be found. These can react further increasing the crosslinking density and thus decreasing the mobility of the reactive centers. Their poor accessibility in a highly viscous system appears to be the main reason for the slowdown of the polymerization reaction.

Additional amount of gel was obtained below 80 kGy, if the samples removed from the  $\gamma$ -source were kept sealed at room temperature for several hours. This phenomenon, known as

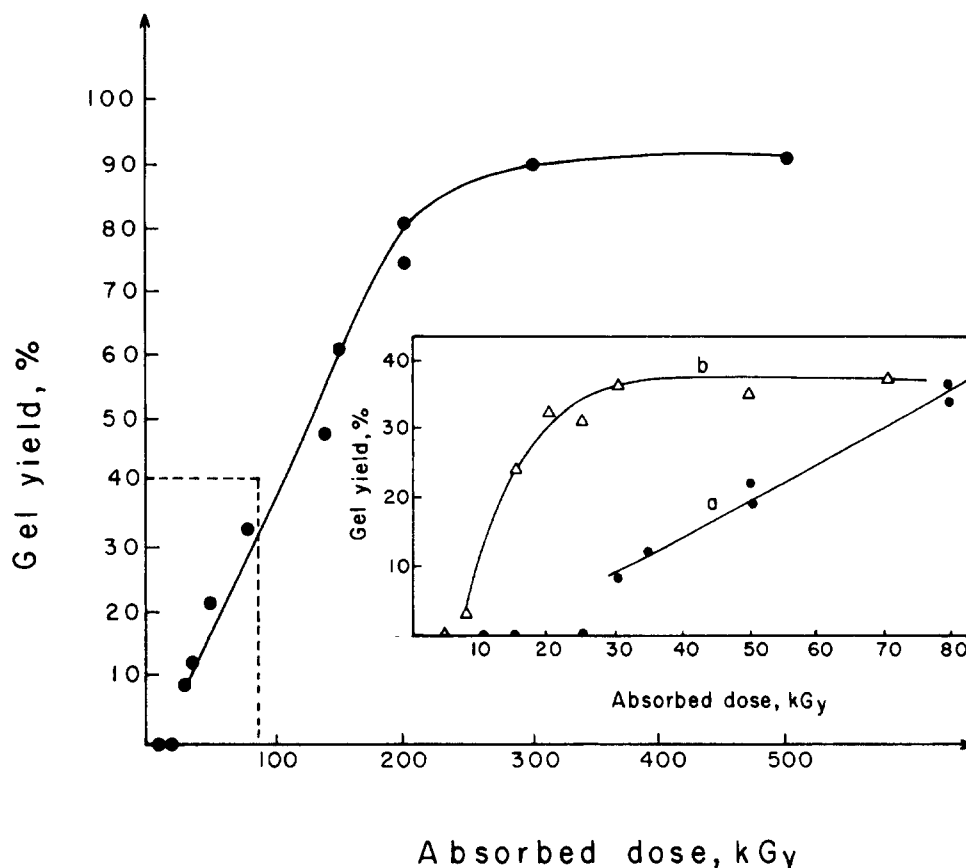


Fig. 1. Dependence of the gel yield on irradiation dose, as obtained immediately after the ampoules were removed from the irradiation source. In the insert the same curve (a) is compared with the total gel yield collected after the sealed ampoules were stored for 36 h at room temperature.

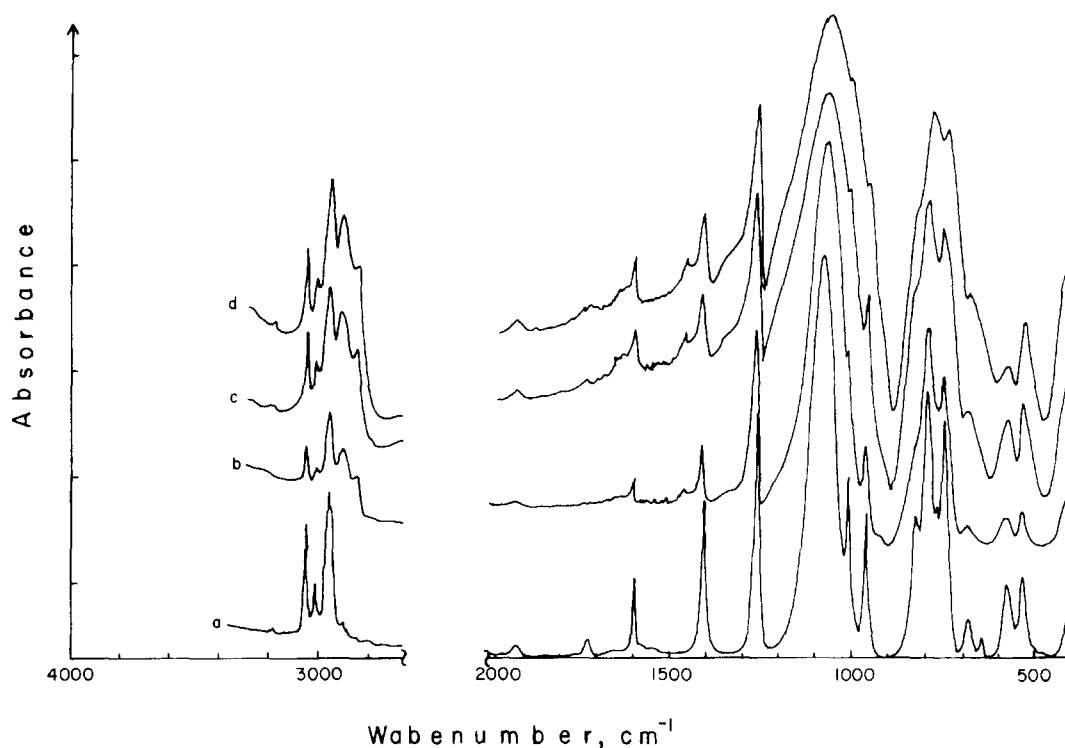


Fig. 2. FTIR spectra of  $D_4V_4$  (a) and the gel fractions formed by irradiation at 35 (b), 140 (c), and 500 kGy (d) doses.

postpolymerization effect (Chapiro, 1962), was observed even for doses of 8–25 kGy when no polymerization was registered during the exposure and the samples were liquid immediately after the irradiation. However after storage for 7–10 h at room temperature the samples showed a jelly-like structure.

The total gel yield obtained by both polymerization under irradiation and postpolymerization after a period of 36 h at room temperature is presented in Fig. 1 (insert, curve b) as a function of the irradiation dose. The primary polymerization curve is also shown in the insert for comparison (curve a). It can be seen that up to approximately 45 kGy the majority of the total gel fraction resulted from the postpolymerization. Then its contribution gradually declines as the yield from the primary reaction increases, and becomes insignificant at about 80 kGy.

The postpolymerization is assumed to depend on both the number of active centers generated on irradiation and their accessibility, controlled by viscosity, in the reaction system. An increase of the viscosity during irradiation above 30 kGy gradually limits the mobility of the polymerization centers and finally results in a kinetic interruption of the postpolymerization at a conversion of about 35%. The effect was not observed at room temperature above 80 kGy, when a hard gel was produced during the irradiation.

The chemical structure of the gel fractions was studied also by FTIR spectroscopy. The spectra are

given in Fig. 2 along with the spectrum of the monomer for comparison. It is important to mention that irradiation of the samples, at all the applied doses did not alter either the relative intensity or the shape of the characteristic cyclic tetrasiloxane absorption band at  $1078\text{ cm}^{-1}$ . This band dominates the spectra of both the monomer and the polymers and was not seen to split into a doublet with maxima at  $1029$  and  $1093\text{ cm}^{-1}$ , typical for linear siloxanes.

In contrast, remarkable transformations were registered in the C=C, C–C, and C–H regions of the spectra. It can be seen that the relative intensities of the vinyl group bands at  $3057$  and  $3017\text{ cm}^{-1}$  (C–H stretching vibrations),  $1599\text{ cm}^{-1}$  (C=C stretching) and  $1408\text{ cm}^{-1}$  (=CH<sub>2</sub> scissors) decreased and the two C–H stretching vibrations of  $sp^3$ -hybridized CH<sub>2</sub>- and CH-groups at  $2910$  and  $2860\text{ cm}^{-1}$  appeared in the polymer spectra. These changes were most apparent below 150 kGy irradiation dose. Further irradiation affected mainly the width of the bands while their relative intensities varied insignificantly.

It can be concluded that radiation induced polymerization of  $D_4V_4$  occurred via free radical mechanism through the vinyl groups without opening of the tetrasiloxane rings. The number of vinyl groups declined due to the polymerization reaction as the dose increased from 8 to 150 kGy, as can be seen from the FTIR spectra in Fig. 2. At higher doses, 150–500 kGy, no significant alteration of the FTIR signature of the gel fractions was noticed. The latter

Table 1. Weight loss temperatures of gel fractions produced by different irradiation doses

Irradiation dose (kGy)	Weight loss temperature by TGA (°C)					
	Initial	Nitrogen			Air	
		5%	10%	5%	10%	
34	472	500	516	356	416	
76	472	503	524	363	425	
200	477	505	528	370	429	
300	483	516	537	381	437	
500	486	516	541	393	441	

might result from the formation of additional unsaturated bonds under high energy irradiation (Charlesby, 1960).

The 5 and 10% weight loss temperatures of the gel fractions in both nitrogen and air are given in Table 1. The thermal decomposition started above 470°C. It can be observed that the temperatures for similar weight loss are higher in nitrogen, than in air. The weight loss also decreases with increasing dose, and this can be attributed to the higher crosslinking density.

No phase transition was found by DSC in the extracted gels obtained after irradiation, independently of the dose. This result confirmed that a

three-dimensional polymer network with high cross-linking density had been formed from the very beginning of the polymerization process.

The hardness of the unextracted samples was measured by TMA using the penetration technique in the temperature range from -150 to 250°C. The thermomechanical curves, presented in Fig. 3 show, as expected, that the harder materials were obtained at higher irradiation doses. The TMA curves of the monomer, and the sample irradiated at 30 kGy, are very similar [Fig. 3 (a) and (b), respectively]. The thermomechanical behavior of the samples produced at 60–70 kGy [Fig. 3(c)] showed very low penetration temperature and could be considered as typical for

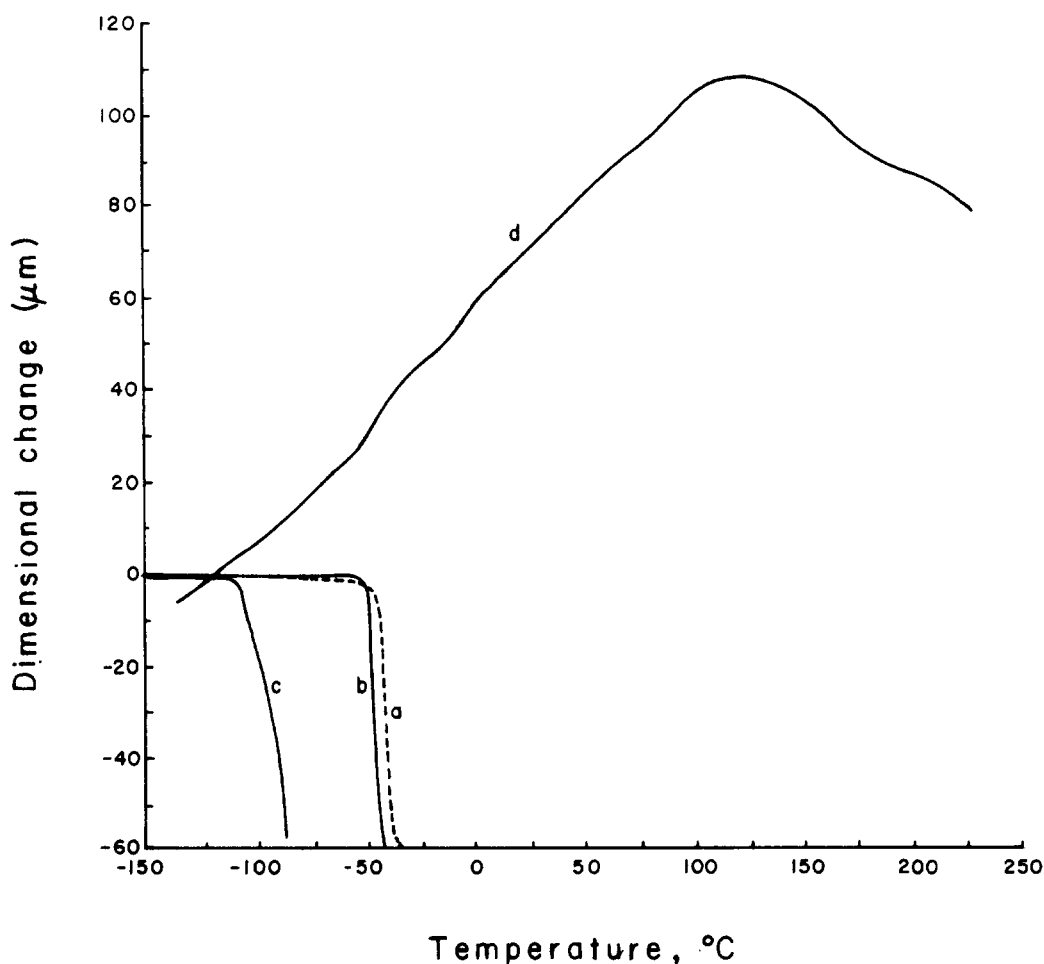


Fig. 3. TMA penetration of  $D_4V_4$  (a) and unextracted samples irradiated at 30 (b), 70 (c), and 140 kGy (d).

the siloxane rubbers with low crosslinking density. The glassy gels resulting from the exposure to 140 kGy exhibited a well-distinguished penetration temperature around 130°C [Fig. 3(d)]. No results were obtained for the hardest samples produced by irradiation above 200 kGy, because they were too brittle to complete the TMA test which might be due to the very high crosslinking density.

#### 4. CONCLUSION

Bulk polymerization of D<sub>4</sub>V<sub>4</sub> induced by  $\gamma$ -irradiation was found to proceed without opening of the tetrasiloxane ring, through the reaction of the vinyl substitutes attributable to a free radical mechanism. The formation of the three-dimensional polymer network started at a dose of about 30 kGy. Further irradiation resulted in the increase of the crosslinking density and hardening of the samples. Strong postpolymerization effects were observed for the doses from 8 to 80 kGy.

The resulting gels demonstrate high thermal stability in inert atmosphere. Their temperatures of the initial weight loss were above 470°C and depended on the crosslinking density of the samples.

*Acknowledgements*—The authors wish to thank Dr Guillermina Burillo and Dr Steven Muhl for useful scientific discussion and Ing. Epifanio Cruz Zaragoza for irradiation of the samples.

#### REFERENCES

- Chapiro, A. (1962) *Radiation Chemistry of Polymeric Systems*. J. Wiley & Sons, New York.
- Charlesby, A. (1960) *Atomic Radiation and Polymers*. Pergamon Press, New York.
- Chawla, A. S. and Pierre, L. E. (1972) Gamma ray-induced liquid state polymerization of hexamethylcyclotrisiloxane and octamethylcyclotetrasiloxane. *Journal of Applied Polymer Science* **16**, 1887.
- Halpern, B. D. and Tong, Y. -C. (1989) Medical applications. In *Encyclopedia of Polymer Science and Engineering*, Vol. 9, 2nd edn. p. 486. Wiley, New York.
- Lebrun, J. J., Deffieux, A. and Sigwalt, P. (1984) The radiation-induced polymerization of hexamethylcyclotrisiloxane and octamethyl cyclotetrasiloxane in the solid and liquid states. *Radiation Physics and Chemistry* **24**, 239.
- Lopez, D., Espaza, R. and Burillo, G. (1995) Crosslinking of polyol(allylcarbonates) by gamma radiation. *Radiation Physics and Chemistry* **45**, 637.
- Miller, A. A. (1959) Radiation chemistry of polydimethylsiloxane. *Journal of Physics and Chemistry* **63**, 3519.
- Naylor, D. M. and Stannett, V. (1986) A study of the ionic polymerization of decamethylcyclopentasiloxane induced by gamma radiation. *Journal of Polymer Science: Part C* **24**, 319.
- Naylor, D. M., Stannett, V., Deffieux, A. and Sigwalt, P. (1990) Radiation-induced polymerization of dimethylcyclotrisiloxanes in the liquid state: I. influence of drying and nature of the propagation mechanism. *Polymer* **31**, 954.
- Tabata, Y., Kimura, H. and Sobue, H. (1964) Radiation-induced polymerization of octamethylcyclotetrasiloxane. *Polymer Letters* **2**, 23.
- Takacs, E. (1992) Interpenetrating-network formation during electron beam crosslinking of an unsaturated polyester-1,6-hexanediol diacrylate monomer system. *Radiation Physics and Chemistry* **40**, 75.
- Wolf, C. J. and Stewart, A. C. (1962) Radiation chemistry of octamethyltetrasiloxane. *Journal of Physics and Chemistry* **66**, 1119.
- Woods, R. J., Pikaev, A. K. (1994) *Applied Radiation Chemistry: Radiation Processing*. Wiley-Interscience, New York.
- Yoshii, F., Makunchi, K., Darwis, D., Iriawan, T. and Razzak, M. T. (1995) Heat resistance poly(vinylalcohol)hydrogel. *Radiation Physics and Chemistry* **46**, 169.
- Yuzhelevskii, Yu. A. (1991) Elastic siloxane materials for endoprosthetic applications. *Artificial Organs* **15**, 392.