



Electron beam irradiation of fluoropolymers containing polyethers

E. Bucio^a, G. Burillo^{a,*}, F. Tapia^a, E. Adem^b, G. Cedillo^c, P.E. Cassidy^d

^a Departamento de Química de Radiaciones y Radioquímica, Instituto de Ciencias Nucleares, Universidad Nacional Autónoma de México, Circuito Exterior, Ciudad Universitaria, México DF 04510, Mexico

^b Departamento de Física Experimental, Instituto de Física, Universidad Nacional Autónoma de México, Circuito Exterior, Ciudad Universitaria, México DF 04510, Mexico

^c Instituto de Investigaciones en Materiales, Universidad Nacional Autónoma de México, Circuito Exterior, Ciudad Universitaria, México DF 04510, Mexico

^d Department of Chemistry and Biochemistry, Texas State University, San Marcos, TX 78666, USA

ARTICLE INFO

Article history:

Received 20 May 2008

Accepted 18 August 2008

Keywords:

Electron beam irradiation
Fluoropolymer
Radiochemistry yield (G_s)
Polyether
Films

ABSTRACT

A highly fluorinated monomer, 1,3-bis(1,1,1,3,3,3-hexafluoro-2-pentafluorophenyl methoxy-2-propyl)benzene (12F-FBE) was polymerized with some diphenols by polycondensation and then was electron beam irradiated between 100 and 1000 kGy to determine degradation radiochemistry yield (G_s) by gel permeation chromatography (GPC). The samples were characterized after irradiation by DSC, FTIR, and nuclear magnetic resonance (NMR). The fluoropolymers show apparent degradation in mechanical properties at 300 kGy, except 12F-FBE polymerized with biphenol and bisphenol A, when they did not show any apparent physical change up to 300 kGy; and continue to be flexible and transparent, with a radiochemical yield scission (G_s) of 0.75, 0.53, 0.88, and 0.38 for 12F-FBE/SDL aliphatic, 12F-FBE/biphenol, 12F-FBE/bisphenol A, and 12F-FBE/bisphenol O, respectively. The number average molecular weights for three of the polymers decrease upon 1000 kGy irradiation to 10% of their original values; however, the polymer from bisphenol A is much more stable and its M_n decreases to only 24% of original.

© 2008 Elsevier Ltd. All rights reserved.

1. Introduction

There is an increasing need for the production of light, strong polymeric systems, which can withstand harsh environments such as high temperatures and UV and ionizing radiation. Among these polymeric systems, aromatic polysulfones and polyether ketones are strong candidates for radiation resistant materials; but the production of volatile products upon irradiation can result in the undesirable formation of bubbles. This can lead to the premature failure of stressed components, thus limiting service life (Lewis et al., 1989). The use of graphite fiber-reinforced, polymeric matrix composites for structural applications on weight critical space structures has increased because of high specific strength, stiffness, and low thermal expansion. But experimental studies (Tenney and Slempp, 1989) show that high doses of electron beam irradiation combined with thermal cycling can significantly change the mechanical and physical properties of graphite reinforced polymer matrix composite (Tenney and Slempp, 1989). When polymer matrix composites are used in superconducting magnets for fusion reactors, one of the more serious concerns is their resistance to changes in mechanical and electrical properties upon simultaneous irradiation with neutrons and γ -ray during the fusion reactor operation. From this point of view, several groups of workers have studied the irradiation effects on polymer matrix composites; for

example Egusa et al. (1991) present a review of the progress of several authors in understanding of composites, e.g. epoxy resins such as tetraglycidyl diamino phenyl methane cured with diamino diphenylmethane and polyimides such as polyaminobismaleimide. The most general characteristic of the composite degradation behavior is that the dose dependence of the flexural strength depends not only on the matrix resin in the composite but also on the test temperature. Because of their thermal resistivity and excellent mechanical and electrical properties, fluoropolymers have attracted a great deal of interest from polymer scientists over last 35 years. They have found applications where resistance to harsh chemicals and thermal environments are a fundamental requirement (Forsythe and Hill, 2000; Choi et al., 1997). Much of that work has been directed to making polymers more tractable, soluble, and processable without sacrificing thermal stability (Cassidy et al., 1989). In other papers, fluoropolymers synthesized with high thermal resistivity were studied (Fitch et al., 2003; Bucio et al., 2006). In the work presented in this paper radiation resistance for use at high temperatures and ionizing radiation as materials applicable to aerospace and nuclear reactors was studied.

2. Experimental

2.1. Materials

Bisphenol O and 1,3-bis(1,1,1,3,3,3-hexafluoro-2-hydroxy-2-propyl) benzene (1,3-HFAB) were kindly supplied by Central

* Corresponding author. Tel.: +52 55 56224674; fax: +52 55 56162233.
E-mail address: burillo@nucleares.unam.mx (G. Burillo).

Glass, Japan. Bisphenol A, biphenol, *N,N*-dimethylacetamide (DMAc), and sodium hydride were obtained from Aldrich, and 2,3,4,5,6-pentafluorobenzylbromide was obtained from Oakwood Products, Inc. The diphenols were sublimed before use. Aliphatic spirodilactam-derived diphenol was obtained from Shell Chemical Company, and used as received.

2.2. Polymer synthesis

Synthesis of 1,3-bis(1,1,1,3,3,3-hexafluoro-2-pentafluorophenylmethoxy-2-propyl) benzene (12F-FBE) was reported previously (Fitch et al., 2003). The diphenol and potassium carbonate were added to a mixture of DMAc and toluene in a round-bottom flask fitted with a Dean–Stark trap. The toluene was removed by distillation, and the solution was cooled to room temperature. The monomer, 12F-FBE, was added, and the reaction was stirred at the appropriate temperature for 24 h. The reaction mixture was cooled and poured into 500 ml of rapidly stirred water. The white, fibrous polymer obtained was collected, dried, and dissolved in chloroform and reprecipitated into methanol.

2.3. Irradiation films

Polyethers with molecular weight (M_n) between 24,100 and 53,100 were irradiated in air at doses from 100 to 1000 kGy in a Van de Graaff electron accelerator, 1.3 MeV and a beam current of 5 μ A, at a dose rate of 24.8 kGy/min.

2.4. Measurements

Viscosity average molecular weight, M_v , of the irradiated samples was measured in a solution of chloroform at 25 °C, with

a Ubbelohde viscometer, using Eq. (1):

$$\eta = KM_v^a \quad (1)$$

where $K = 22.9 \times 10^{-3}$ ml/g and $a = 0.73$ (Buttafava et al., 2002).

Number average molecular weight (M_n) was measured at 30 °C in a gel permeation chromatography (GPC) from Waters, Binary Pump 1525 and Waters Detector UV/visible 2489 dual absorbance, using Styragel HR5E and HR4E columns, after calibration with standard polystyrene samples.

Radiochemical yield of scission (G_s) was determined by Eq. (2) (Makhils, 1975):

$$\frac{1}{M_n} = \frac{G_s}{100N_A}D + \frac{1}{M_{n0}} \quad (2)$$

where M_{n0} and M_n are the number average molecular weight initially and after irradiation, respectively, D is the radiation dose expressed in eV/g and N_A is Avogadro's number. A plot of $1/M_w$, $1/M_z$ or $1/M_v$ against radiation dose should give a straight line when degradation is proportional to radiation dose (Charlesby, 1960).

Fourier transforms infrared (in the total attenuated reflection, FTIR-ATR mode) spectra of the started and irradiated samples were analyzed using a Perkin-Elmer Spectrum 100 spectrometer. Differential scanning calorimetry was performed using a DSC 2010 calorimeter (TA Instruments, USA), and nuclear magnetic resonance (NMR) using a Bruker Avance 400 spectrometer.

3. Results and discussion

A highly fluorinated monomer, 1,3-bis(1,1,1,3,3,3-hexafluoro-2-pentafluorophenyl methoxy-2-propyl)benzene (12F-FBE), was polymerized with some diphenols by polycondensation: (a) bisphenol A, (b) biphenyl, (c) SDL aliphatic, and (d) bisphenol O

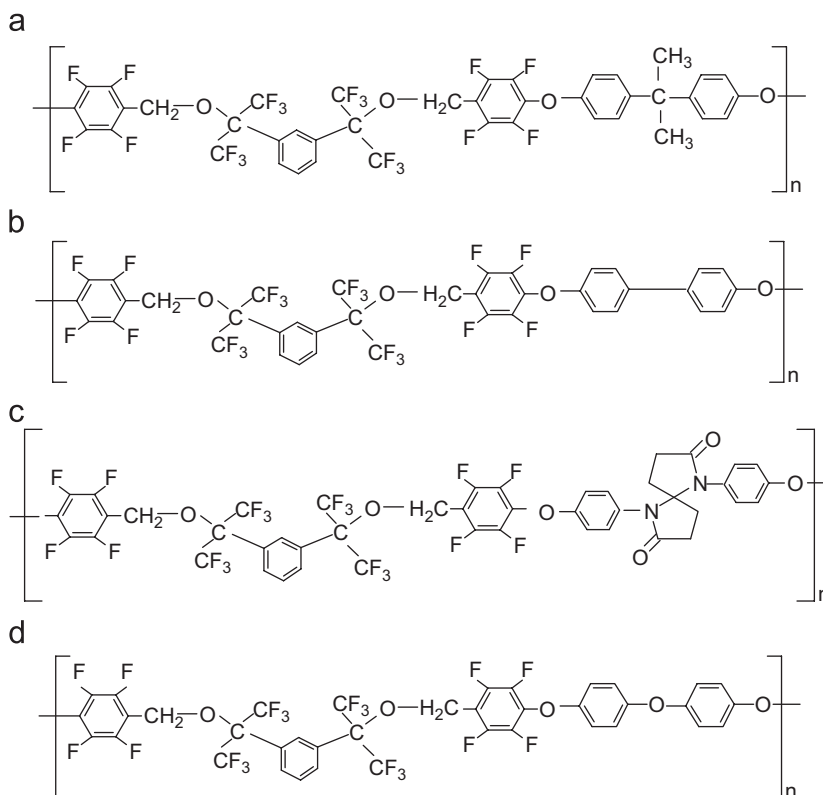


Fig. 1. Structures of polyethers: (a) 12F-FBE/bisphenol A, (b) 12F-FBE/biphenol, (c) 12F-FBE/SDL aliphatic, and (d) 12F-FBE/bisphenol O.

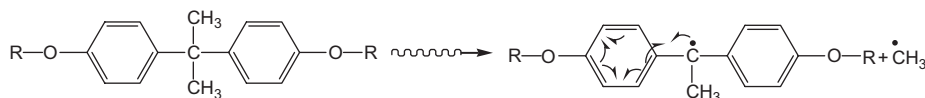


Fig. 2. Resonance effect on irradiation of 12F-FBE/bisphenol A.

Table 1
Degradation radiochemistry yield as a function of dose

| Dose (kGy) | G_s (1×10^{-1}) | | | |
|------------|------------------------------|---------------|-------------------|---------------|
| | 12F-FBE/SDL | 12F-FBE/bis O | 12F-FBE/bisphenol | 12F-FBE/bis A |
| 100 | 6.62 | 4.12 | 6.13 | 8.00 |
| 300 | 7.54 | 3.80 | 5.30 | 8.84 |
| 500 | 4.48 ^a | 7.40 | 7.70 | 13.52 |
| 1000 | 15.23 | 15.40 | 15.52 | 12.52 |

^a Sample with different initial M_n and M_w/M_n .

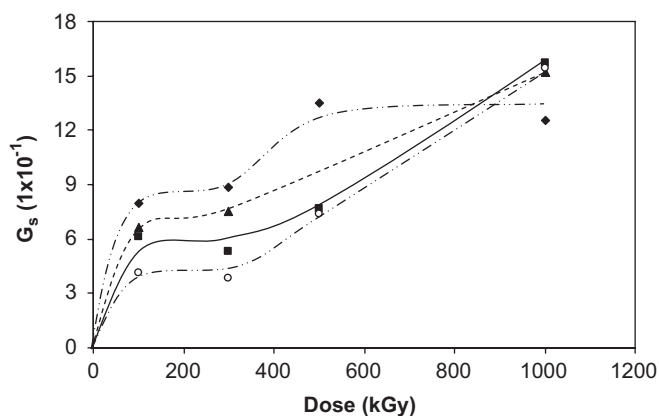


Fig. 3. Degradation radiochemistry yield as a function of dose: (◆) 12F-FBE/bisphenol A, (■) 12F-FBE/bisphenol, (▲) 12F-FBE/SDL aliphatic, and (○) 12F-FBE/bisphenol O.

(Fig. 1). Radiation degradation is mainly due to chain scission when it is irradiated at room temperature in presence of air; but there is also formation of fluorine radicals. These two processes change with the polymer structure, as bisphenol A, the most resistant to degradation at irradiation dose of 1000 kGy; where homolytic scission occurs at the tetra-substituted carbon, of the two benzene groups, the resulting radical being stabilized by resonance (Fig. 2). Radiochemical yield of scission (G_s) of the synthesized polyethers was plotted as a function of radiation dose, at a dose rate of 24.8 kGy/min, and the values are given in Table 1. The radiation resistance (lower G_s) is highly consistent with a more stable configuration, because of the resonance effect of the aromatic groups, in spite of fluorine–carbon bonds which have a low radiation resistance. The G_s of the bisphenol O polymer, the most radiation resistant of the fluoropolymers studied, in spite of less energy of resonance, due to the oxygen atom between two aromatic rings, increased up to a radiation dose of 100 kGy and then leveled off until 300 kGy, with further proportional increase with radiation dose. Same behavior was observed for the other polymers, except for 12F-FBE/SDL aliphatic with a second level off since 500 kGy, in this polymer there are a resonance effect between the adjacent aromatic ring and the $-N-CO-$ of the aliphatic group (Fig. 3).

At a radiation dose of 1000 kGy all the studied compounds had a G_s of about 0.15, except in the case of the compound with bisphenol A with a G_s of 0.12 (Table 1). The number average

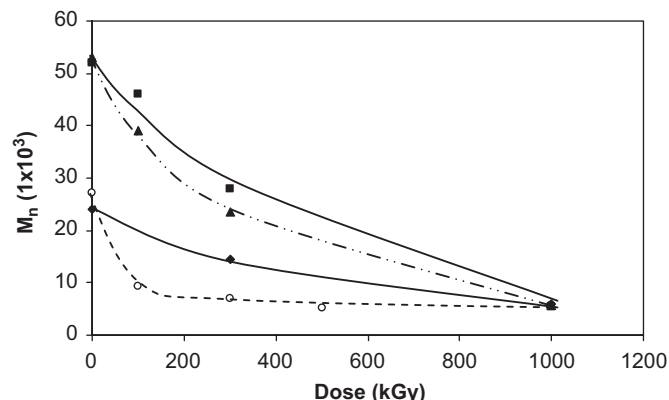


Fig. 4. Degradation M_n as a function of dose: (◆) 12F-FBE/bisphenol A, (■) 12F-FBE/bisphenol, (▲) 12F-FBE/SDL aliphatic, and (○) 12F-FBE/bisphenol O.

Table 2
Degradation of M_n/M_{n0} as a function of dose

| Dose (kGy) | 12F-FBE/SDL | | 12F-FBE/bis O | | 12F-FBE/bisphenol | | 12F-FBE/bis A | |
|------------|--------------|-----------|---------------|-----------|-------------------|-------------------|---------------|-------------------|
| | M_n/M_{n0} | M_w/M_n | M_n/M_{n0} | M_w/M_n | M_n/M_{n0} | M_w/M_n | M_n/M_{n0} | M_w/M_n |
| 0 | | 4.87 | | 2.65 | | 3.59 | | 4.47 |
| 100 | 0.73 | 3.15 | 0.34 | 3.09 | 0.20 | 6.90 ^a | 0.35 | 2.60 ^a |
| 300 | 0.44 | 4.65 | 0.26 | 3.03 | 0.53 | 3.17 | 0.60 | 2.88 |
| 500 | – | – | 0.19 | 2.94 | 0.11 | 3.97 ^a | 0.63 | 1.76 ^a |
| 1000 | 0.10 | 2.64 | 0.09 | 2.81 | 0.10 | 3.06 | 0.24 | 2.92 |

^a Samples with different initial M_n and M_w/M_n .

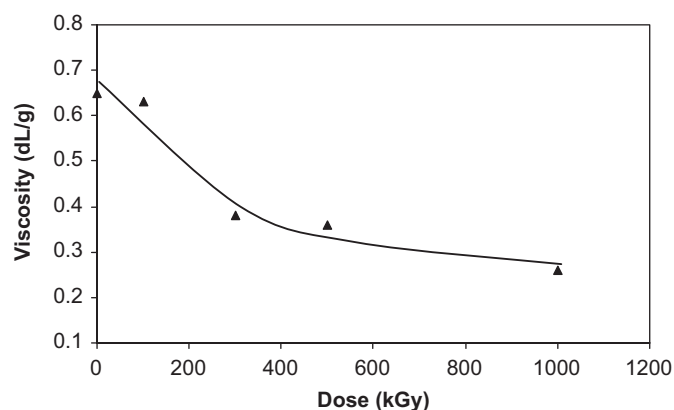


Fig. 5. Viscosity of 12F-FBE/SDL aliphatic as a function of radiation dose.

molecular weight (M_n) decreases exponentially with radiation dose, due mainly to main chain scission on C–O bonds (Fig. 4). Table 2 presents the decreasing M_n/M_{n0} ratio with an increase in radiation dose, where M_{n0} and M_n are the molecular weights before and after irradiation, respectively, and the dispersion of molecular weight (M_w/M_n) at different irradiation doses. Variations of molecular weights correspond with the variation of G_s , where the relationship between initial and post-irradiation molecular weights (M_n/M_{n0}) decrease to a value of about 0.10,

except for the 12F-FBE/bisphenol A, the polymer most resistant to radiation at 1000 kGy. The molecular weight distribution was more uniform after irradiation as anticipated, since longer chains would suffer more cleavage than shorter ones. Fig. 5 showed decrease in viscosity (η) as a function of dose for 12F-FBE/SDL

Table 3
Decrease of viscosity as a function of dose

| Dose (kGy) | Viscosity (η) (dl/g) | | | |
|------------|-----------------------------|---------------|-------------------|---------------|
| | 12F-FBE/SDL | 12F-FBE/bis O | 12F-FBE/ biphenol | 12F-FBE/bis A |
| 0 | 0.65 | 0.38 | 0.47 | 0.29 |
| 300 | 0.38 | 0.16 | 0.10 | 0.04 |

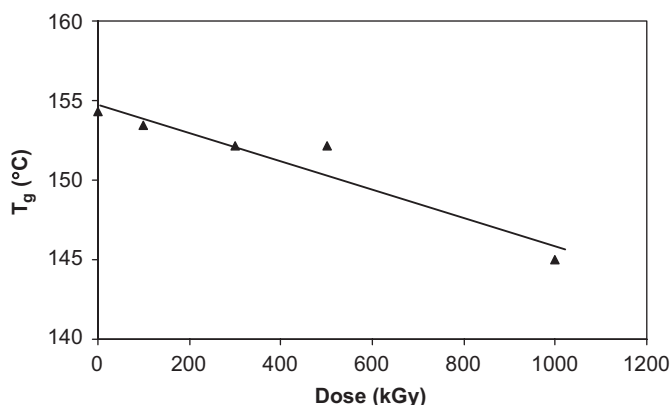


Fig. 6. Glass transition of 12F-FBE/SDL aliphatic as a function of radiation dose.

aliphatic as expected, and in Table 3, decrease on (η) at 300 kGy for all the studied polymers were observed, where bisphenol A, had the lowest percentage of change at 300 kGy; 58% for 12F-FBE/SDL aliphatic, 42% 12F-FBE/bisphenol O, 21% for 12F-FBE/biphenol, and only 13.8% in case of 12F-FBE/bisphenol A. Decrease in T_g with increasing radiation dose was also observed for the 12F-FBE/SDL aliphatic polymer (Fig. 6). Further, a T_g decrease from 154 °C in the initial polymer film to 145 °C in samples irradiated at 100 kGy, indicates radiolysis of several groups in the chain, mainly in the SDL aliphatic group. The structure of polyethers was confirmed by NMR spectra ^{13}C . Infrared determinations of samples before and after irradiation were observed only in 12F-FBE/SDL aliphatic films irradiated at 1000 kGy noting a small shift in the peak if 2960 cm^{-1} , which could indicate the presence of one aldehyde group, and also an intensity decrease of the CF_3^- peak. To confirm these changes, the NMR spectra of ^1H were observed before and after irradiation to 1000 kGy (Fig. 7). In that spectrum, we can observe new signals of aldehydic hydrogen, and a new peak of a hydrogen bonded to a nitrogen, due to radiolysis of the aliphatic group. Also new peaks appear that could be protons of alkanes; thus in the 12F-FBE/SDL aliphatic films there are main chain scissions of C–O bonds and also of the N–C of the aliphatic group.

4. Conclusions

The results of studies by Cassidy et al. (1989) showed that many fluorinated compounds have high thermal stability. Further, reasonably good radiation stability was found in this paper, with apparent conservation of mechanical properties up to a radiation dose of 300 kGy, but with lower G_s of 0.40 for 12F-FBE/biphenol O, and a lower G_s for 12F-FBE/bisphenol A of 0.12 at radiation dose of

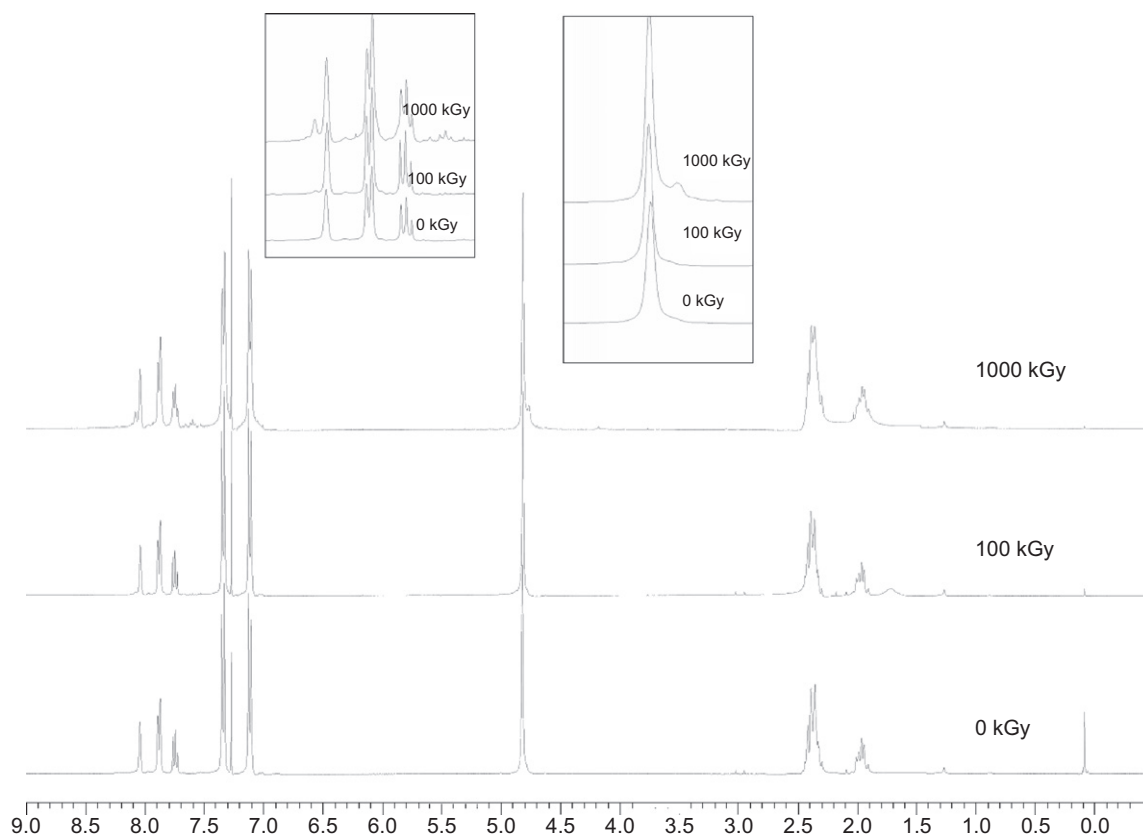


Fig. 7. Spectra of NMR of ^1H for 12F-FBE/SDL aliphatic at 0, 100, and 1000 kGy.

1000 kGy. Molecular weights of the polymers studied decreased to 10–15% of the initial value except for 12F-FBE/bisphenol A; this last polymer conserved 60% of the initial molecular weight at 300 kGy and 24% at 100 kGy of radiation. The main chain scission corresponds to cleavage of the C–O bond and also the C–N bond in the 12F-FBE/SDL aliphatic polymer. Polydispersity values decrease with increase in radiation dose except bisphenol O. More studies are necessary to delineate the mechanism of radiolysis, as well as changes in mechanical properties.

Acknowledgments

The authors wish to express their thanks to Margarito Vásquez from IF-UNAM for technical assistance. This work was supported by DGAPA-UNAM Grant IN200108.

References

- Bucio, E., Fitch, J.W., Venumbaka, S.R., Cassidy, P.E., 2006. Synthesis and characterization of new polyethers containing aliphatic and aromatic spiridilactam. *Des. Monomer. Polym.* 9, 55–62.
- Buttafava, A., Consolati, G., Di Landro, L., Mariano, M., 2002. Gamma-irradiation effects on polyethylene terephthalate studied by positron annihilation lifetime spectroscopy. *Polymer* 43, 7477–7481.
- Cassidy, P.E., Aminabhavi, T.M., Farley, J.M., 1989. Polymers derived from hexafluoroacetone. *JMS-Rev. Macromol. Chem. Phys. C* 29 (2–3), 365–429.
- Charlesby, A., 1960. *Atomic Radiation and Polymers*. Pergamon Press, Oxford, p. 164.
- Choi, E.J., Hill, D.J.T., Kim, K.Y., O'Donnell, J.H., Pomery, J.P., 1997. Synthesis, thermal and radiation sensitivities of fluorine containing methylene-bridged aromatic polyesters. *Polymer* 38, 3669–3676.
- Egusa, S., Seguchi, T., Hagiwara, M., Nakajima, H., Shimamoto, S., Kirk, M.A., Birtcher, R.C., 1991. Radiation degradation studies on the mechanical properties of polymer matrix composites used in fusion magnets. In: Roger, L.C., Shalaby, W.Sh. (Eds.), *Radiation Effects in Polymers*, ACS Symposium Series, vol. 475 (Chapter 38).
- Fitch, J.W., Bucio, E., Martinez, L., Macossay, J., Venumbaka, S.R., Dean, N., Stoakley, D., Cassidy, P.E., 2003. Synthesis and characterization of new fluorine-containing polyethers. *Polymer* 44, 6431–6434.
- Forsythe, J.S., Hill, D.J.T., 2000. The radiation chemistry of fluoropolymers. *Prog. Polym. Sci.* 25, 101–136.
- Lewis, D.A., O'Donnell, J.H., Hedrick, J.L., Ward, T.C., McGrath, J.E., 1989. The effects of radiation on high technology polymers. In: Reichman, E., O'Donnell, J.H. (Eds.), *ACS Symposium Series*, vol. 381 (Chapter 15).
- Makhils, F.A., 1975. *Radiation Physics and Chemistry of Polymers*. Wiley, New York, p. 163.
- Tenney, D.R., Slemple, W.S., 1989. Radiation durability of matrix composites. In: Reichman, E., O'Donnell, J.H. (Eds.), *ACS Symposium Series*, vol. 381 (Chapter 14).