Radiation Grafting of MMA onto PVC Films

EL-SAYED A. HEGAZY, A. R. EBAID,* S. A. EL-SHARABASY,[†] A. M. MOUSA,[‡] and A. Y. HASSAN,[†] *National Centre for Radiation Research and Technology, P. O. Box 29, Nasr City, Cairo, Egypt*

Synopsis

An approach to the problem of producing poly(vinyl chloride) (PVC) graft copolymer exhibiting good mechanical properties and electrical resistance that suits its uses as an electrical insulator has been investigated. Graft copolymerization of methyl methacrylate (MMA) onto PVC using γ-radiation as initiator has been studied. PVC was chemically modified, and the effect of the change in its chemical and physical structure on its properties was investigated. In this grafting system, different solvents were tried and it was found that the most suitable diluent for the grafting of MMA onto PVC films is methanol. An appreciable improvement in tensile properties of the graft copolymer was achieved. The most suitable degree of grafting, concerning electrical insulation efficiency, was found to be near 80%. Gel determination in the graft copolymer was carried out, and a crosslinked network structure was formed. Increasing the crosslinking content in the graft copolymer leads to a decrease in the extent of swelling due to the less diffusivity of the solutions through such network structure.

INTRODUCTION

Polymer chemists have been successful in applying copolymerization techniques to develop graft copolymers of synthetic macromolecules. Copolymerization is attractive to the chemist as a means of modification of macromolecules, since, in general, better properties can be achieved. In recent years, chemical modification of poly(vinyl chloride) (PVC) has been of considerable interest. The radiation-induced graft polymerization of 4-vinyl pyridine onto rigid and plasticized PVC films has shown that a crosslinked network structure was formed and the gelled part increased as the degree of grafting increased.[1,2] Such films also showed good mechanical strength. The postradiation grafting of acrylamide onto polyethylene films results in a graft copolymer having good mechanical properties.[3] The graft copolymer that had a degree of grafting less than 100% possessed high electrical resistance, which suits its use as an electric insulator.[3,4] Various methods are available for graft copolymerization of vinyl monomers onto poly(ethylene terephthalate) (PET) fibers.[5] These include activation of the fiber either through radiation or by chemical initiation. Ionizing radiations such as γ-rays from a Co-60 source and high-energy electrons from accelerators interact with the PET fibers and produce radicals, two of which were identified[6] to be $-O-CH-CH_2-O-$, and $-CO-C_6H_3-CO-$. These radical sites initiate grafting by interaction with monomer molecules.

* Faculty of Science, Helwan University, Cairo, Egypt.
[†] Faculty of Science (Girls), Al-Azhar University, Cairo, Egypt.
[‡] Faculty of Science, Ain Shams University, Cairo, Egypt.

Journal of Applied Polymer Science, Vol. 41, 2941–2950 (1990)
 CCC 0021-8995/90/11-122941-10$04.00

In the chemical initiation method, the active sites can be created by forming hydroperoxide units at several points along the chain in a random manner and allowing it to decompose into the active form thermally in the presence of the monomer. Stannett and co-workers[7-10] studied various aspects of radiation grafting on polymers. Sakurada et al.[11] studied the PET–styrene copolymerization and from the chemical structure found a low degree of grafting of styrene that was attributed to low sensitivity of PET to radiation.

The preparation and some properties of graft copolymers obtained by radiation-induced graft copolymerization of different vinyl and acrylic monomers onto polymeric substrates were investigated.[12-16] These graft copolymers showed great promise in practical applications as ion-exchange membranes and/or as reverse osmosis ones for the desalination of saline and brackish water.

The postradiation grafting of 4-vinyl pyridine,[17] acrylamide,[3,18] and acrylic acid[14] onto polyethylene and fluorinated polymers has shown that the grafted films possessed good properties and homogeneous distribution of the graft chains in trunk polymers.

In this study, the graft copolymerization of methyl methacrylate (MMA) onto PVC using γ-radiation as initiator has been investigated. Electrical properties, gel determination, swelling, and mechanical properties of the graft copolymer were also studied.

EXPERIMENTAL

Materials

PVC was supplied by the Egyptian Electrical Cables Co., and it contains the following additives: plasticizer (dioctyl phthalate 20%), stabilizer (tribasic lead sulfate), and filler (calcium carbonate). Chlorine content = 56%, and its density = 1.4 g/cm^3. MMA was of 99.5% purity, stabilized with 0.01% hydroquinone (BDH Chemicals Ltd., Poole, England). The other solvents and reagents were of reagent grade and were used as received.

Graft Copolymerization

Strips (5 × 9 cm) of 100 μm-thick PVC film were washed with methanol, dried at room temperature (30°C) in a vacuum oven, weighed, and then immersed in an MMA solvent mixture in sealed ampoules. The direct radiation grafting method was used in different atmospheres (air, nitrogen, and vacuum).

In the case of irradiation in nitrogen gas, the glass ampoules containing the monomer solution and the films were deaerated by bubbling nitrogen gas for 5–7 min and then subjected to γ-radiation from a Co-60 source. The dose rate was determined during irradiation processes using a Fricke dosimeter[19,20] and was found to be 0.15 Gy/s. The films were then removed and extracted with toluene at 60°C to remove the residual monomer and any homopolymer that may have formed. These films were then dried in a vacuum oven (10^{-2} Torr) at 40–50°C to constant weight. The degree of grafting was determined by the percentage increase in weight as follows:

$$\text{Degree of grafting } \% = \frac{W_g - W_0}{W_0} \times 100$$

where W_g and W_0 represent the weights of grafted and initial PVC films, respectively.

Swelling Measurements

The clean, dried, graft-copolymer films of known weight were immersed in distilled water, methanol, and benzene until equilibrium was reached (24 h in most cases). The films were removed, blotted with absorbent paper, and quickly weighed. The percent liquid uptake was calculated as follows:

$$\text{liquid uptake}\ (\%) = (W_s - W_g)/W_g \times 100$$

where W_s and W_g represent the weights of wet and dry films, respectively.

Mechanical Property Measurements

Dumbell-shaped specimens 80 mm long, with a neck of 25 mm width, were measured, using an Instron (Zwick & GO Kg. Mod Z 125 No. 23781/1964) at a crosshead speed of 50 mm/min.

Electrical Conductivity Measurements

The electrical conductivity of the films was measured with a Multimega ohm meter-MOM 11 from WTW Instruments (West Germany).

Gel Determination

The insoluble parts in the grafted films were determined by Soxhlet extraction with refluxing cyclohexanone for 6 h. The gel percent was calculated as follows:

$$\text{gel}\ (\%) = \frac{W_E}{W_g} \times 100$$

where W_g and W_E represent the weight of dry grafted films and the insoluble parts, respectively. The contents of polymethyl methacrylate (W_{PMMA}) and polyvinyl chloride (W_{PVC}) in the insoluble part were determined from the following equations:

$$W_{PMMA}\ (\%) = \frac{W_g - W_0}{W_E} \times 100$$

$$W_{PVC}\ (\%) = 100 - W_{PMMA}$$

or

$$W_{PVC}\ (\%) = \frac{W_E - (W_g - W_0)}{W_E} \times 100$$

where W_0 represents the initial weight of PVC film.

RESULTS AND DISCUSSION

It is demonstrated in this study that the reaction medium plays an important role in grafting of MMA onto PVC. In this grafting system, different solvents were investigated and it was found that the most suitable diluent for the grafting of MMA onto PVC films is methanol. Figure 1 shows the degree of grafting as a function of irradiation time for various MMA concentrations at 30°C. It can be seen that the degree of grafting increases gradually with irradiation time and tends to level off at higher doses, especially for the higher MMA concentrations.

Figure 2 shows the relationship between the degree of grafting and MMA concentration at low and high irradiation doses. It is obvious that, at low irradiation dose, the degree of grafting increases with MMA concentration and the increasing rate of grafting yield tends to decrease above 40 wt % of MMA concentration. However, at higher irradiation dose, the relationship between the degree of grafting and MMA concentration gives an S-shaped curve with a maximum value at 60 wt %.

This result may be explained by the decreased effect of diluent and the increased viscosity of the system containing high MMA concentration, i.e., near to bulk polymerization conditions (Trommsdorf effect).

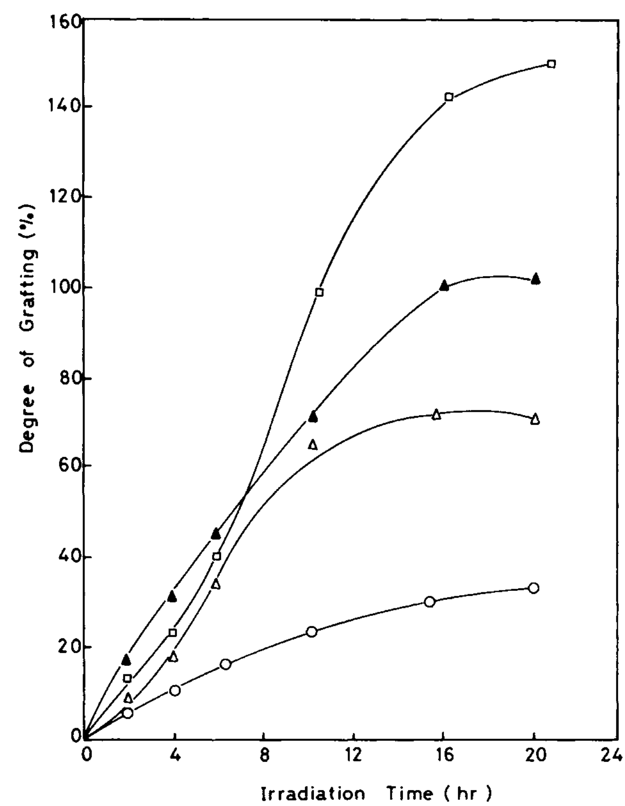

Fig. 1. Degree of grafting vs. irradiation time for different MMA concentrations (wt %): (○) 20; (△) 40; (□) 60; (▲) 90.

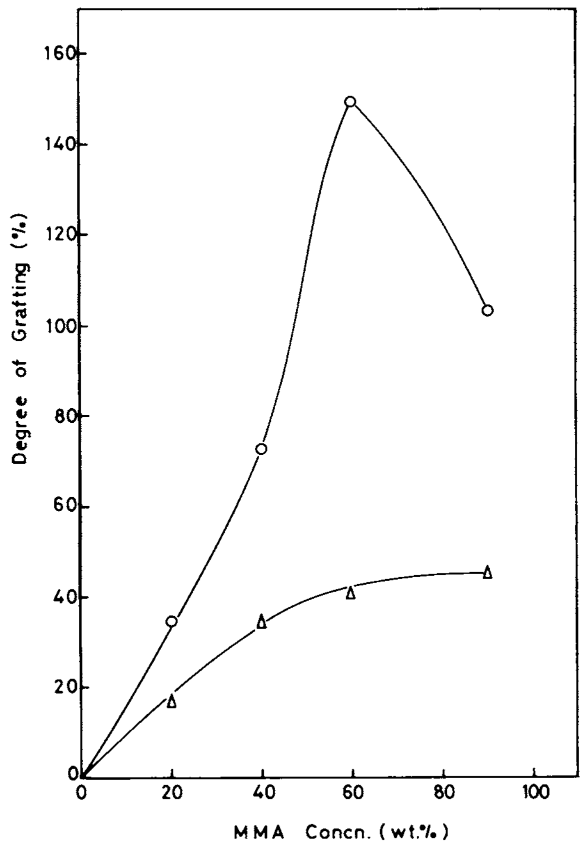

Fig. 2. Degree of grafting vs. MMA concentration at two different irradiation doses (kGy): (△) 3.2; (○) 10.8.

Figure 3 shows the logarithmic relationship between the initial rate of grafting and MMA concentration. The dependence of the grafting rate on monomer concentration was found to be 0.84.

Mechanical Properties of the Graft Copolymers

The changes in tensile strength and elongation percent at break with the degree of grafting were investigated, and the results are shown in Figure 4. It can be seen that the tensile strength increases with the degree of grafting to a maximum value at a degree of grafting around 40%. Thereafter, the tensile strength tends to decrease at higher degrees of grafting to give almost the same values as that of the ungrafted irradiated PVC films. The elongation percent decreases with increasing degree of grafting. The grafting of MMA onto PVC films results in appreciable improvement in the tensile strength, but the elongation generally decreases as the degree of grafting increases.

The improvement in tensile strength and the decrease in elongation percent, caused by grafting, can be reasonably explained by the formation of a crosslinked network structure in PVC via the grafted chains. The rigidity of PVC increased

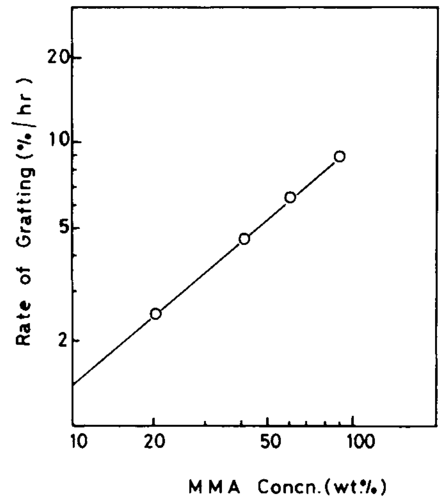

Fig. 3. Logarithmic relationship between the initial rate of grafting and MMA concentration.

with increasing PMMA grafted chains of high T_g; therefore, the tensile strength increased and the elongation percent decreased.

Swelling Behavior of the PVC–PMMA Copolymer

The goal of this study is to improve the mechanical and electrical properties of PVC insulators by graft copolymerization of MMA onto PVC with γ-radiation. Because electric insulators may come in contact with water during practical conditions, the study of the swelling behavior of a PMMA–PVC graft copolymer is very important. To obtain information on their swelling behavior in different media, two other liquids were also considered, namely, benzene and methanol. Swelling behavior of the grafted PVC films was measured in water, benzene, and methanol at room temperature (30°C). The effect of degree of grafting on the swelling percent for such grafted films is seen in Figure 5. As shown, no significant swelling is observed for the grafted films in water. The grafted films show higher swelling values in methanol than those in water. The swelling percent of the grafted films in benzene increases sharply with the degree of grafting until a degree of grafting of about 25%, then it increases at a lower rate.

The diffusivity of water and organic solvents into the polymer matrix appears to depend mainly on the polymer morphology and also on its hydrophilic–hydrophobic characteristics. The swelling extent tends to decrease at high degrees of grafting because of the higher content of crosslinked network structure formed in the graft copolymer.

Gel Determination in the PVC–PMMA Graft Copolymer

The insoluble part of the graft copolymer after extraction with cyclohexanone, i.e., the gelled part, was determined for films having various degrees of grafting (Fig. 6). It can be seen that the gel percent increases with degree of grafting, and it tends to level off at higher degrees of grafting.

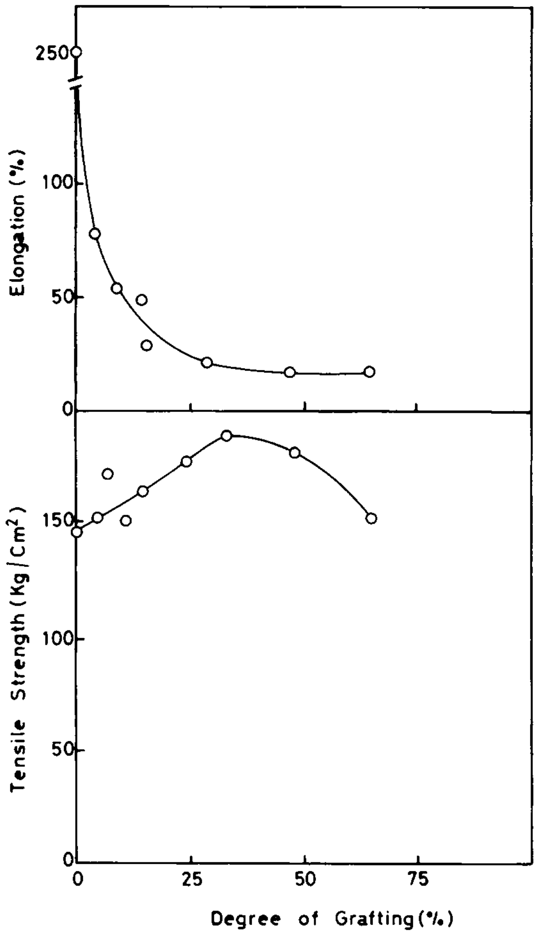

Fig. 4. Change in tensile strength and elongation percent for PVC-*g*-PMMA copolymer with degree of grafting.

The content of PMMA and PVC in the insoluble part (gelled part) was determined for the graft copolymers having various degrees of grafting (Fig. 7). The PVC content in the insoluble part decreases with increasing the degree of grafting, whereas the PMMA content increases with the degree of grafting. Such a synchronized process can be useful for the determination of the ratio of PVC/PMMA in the graft copolymer by adjusting the degree of grafting. To obtain a graft copolymer having an insoluble part of PVC/PMMA with a, e.g., 30/70 ratio, the graft copolymer should have a degree of grafting around 150%.

Gel formation in the graft copolymer may indicate that some of the grafted chains are included in a crosslinked network structure. It is also considered that some of the gelled part is caused in PVC by interaction between the active sites formed on irradiation during the direct radiation-induced grafting process.

Electrical Conductivity of the PVC-PMMA Graft Copolymer Films

Figure 8 shows the effect of the degree of grafting on the electrical conductivity of the PVC-PMMA graft copolymer films at room temperature (30°C).

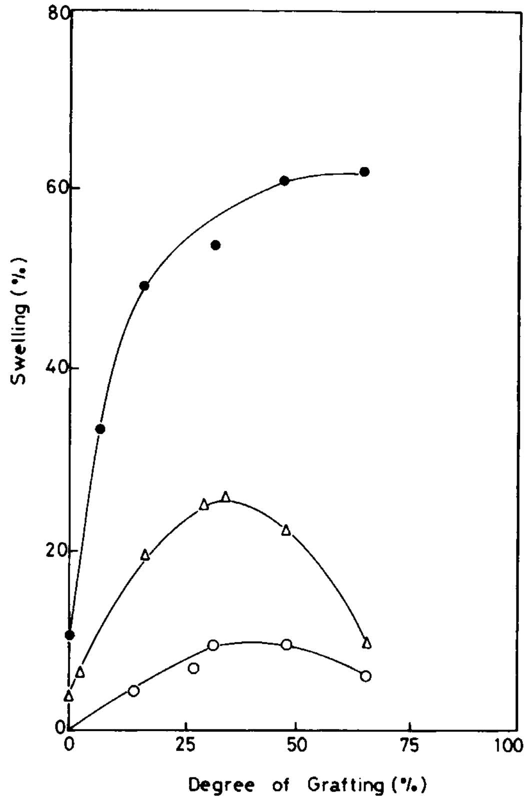

Fig. 5. Swelling percent for PVC-g-PMMA copolymer as a function of degree of grafting in different solutions: (○) water; (△) methanol; (●) benzene.

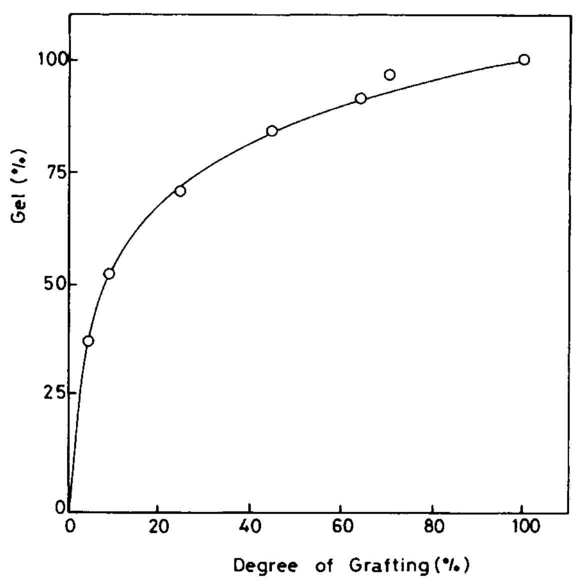

Fig. 6. Gel percent as a function of degree of grafting in the PVC-g-PMMA copolymer.

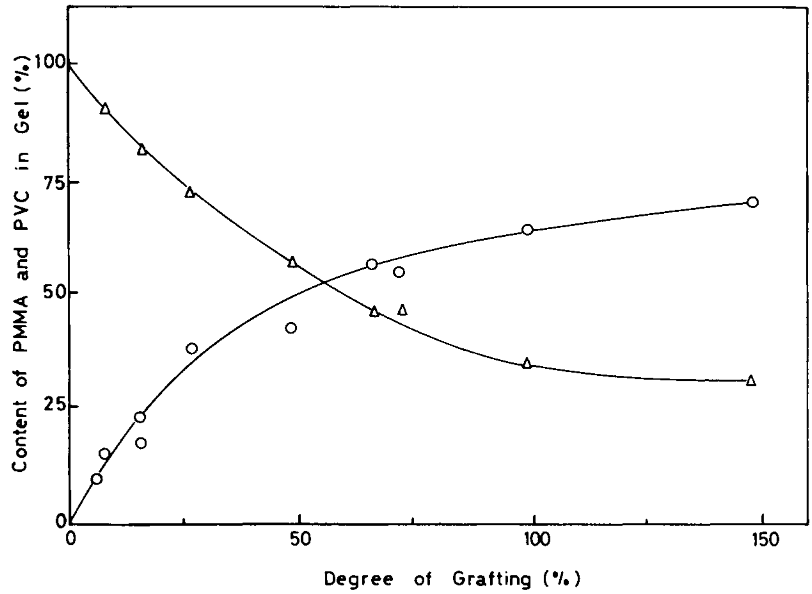

Fig. 7. Gel composition at various degrees of grafting for extracted grafted PVC films: (○) PMMA; (△) PVC.

It is obvious that the electrical conductivity decreases with the degree of grafting. It was reported[4] that the electrical conductivity of PMMA is lower than that of PVC because of the difference in their polarity. PMMA is nonionic in nature;

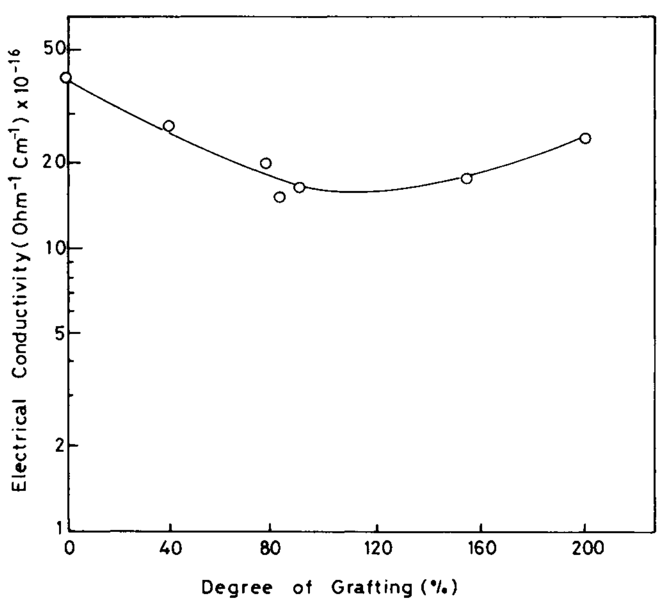

Fig. 8. Semilogarithmic relationship between the electrical conductivity of the PVC-*g*-PMMA copolymer and degree of grafting.

consequently, a decrease in the electrical conductivity of its graft copolymer with PVC is expected.

It can be also concluded that the most suitable degree of grafting, concerning the electrical insulation efficiency, is around 80%. At higher than this value, many factors may interfere such as the accumulation of radiation products at high doses and the complexity of the system.

References

1. E. A. Hegazy, A. M. Dessouki, M. El-Dessouky, and N. El-Sawy, *Radiat. Phys. Chem.*, **26**(2), 143 (1985).
2. A. M. Dessouki, E. A. Hegazy, M. El-Dessouky, and N. El-Sawy, *Radiat. Phys. Chem.*, **26**(2), 157 (1985).
3. E. A. Hegazy, M. El-Dessouky, and S. A. El-Sharabasy, *Radiat. Phys. Chem.*, **27**(5), 323 (1986).
4. A. A. El-Sayed, A. M. Mousa, S. A. El-Konsol Basha, and W. M. Khalil, *Polym. Bull.*, **5**, 209 (1981).
5. S. Misra, P. L. Nayak, and G. Sahu, *J. Appl. Polym. Sci.*, **27**, 3875 (1982).
6. D. Campbell, K. Arai, and D. T. Turner, *J. Polym. Sci.*, **A4**, 2597 (1966).
7. V. T. Stannett, J. L. Williams, and G. S. P. Verma, *Polym. Prepr. Am. Chem. Soc. Div. Polym. Chem.*, **12**(2), 504 (1971).
8. K. Ishigure, K. Yoshida, and V. T. Stannett, *J. Macromol. Sci., Chem.*, **7**(4), 813 (1973).
9. V. Stannett, D. K. Woods, L. G. Roldon, S. B. Sello, and C. V. Stevens, *Text. Res. J.*, **43**(4), 205 (1973).
10. I. Valagiu and V. Stannett, *Rev. Roum. Chim.*, **17**(1–2), 379 (1972).
11. I. Sakurada, Y. Ikada, and T. Kawahara, *J. Polym. Sci., Part A-1,* **11**, 2329 (1973).
12. E. A. Hegazy, *J. Polym. Sci., Polym. Chem. Ed.*, **22**, 493 (1984).
13. E. A. Hegazy, A. M. Dessouki, and H. El-Boohy, *J. Polym. Sci., Polym. Chem. Ed.*, **24**, 1933 (1986).
14. E. A. Hegazy, N. B. El-Assy, A. Rabie, I. Ishigaki, and J. Okamoto, *J. Polym. Sci., Polym. Chem. Ed.*, **22**, 597 (1984).
15. E. A. Hegazy, N. H. Taher, and H. Kamal, *J. Appl. Polym. Sci.*, **38**, 1229 (1989).
16. N. H. Taher, E. A. Hagezy, A. M. Dessouki, and M. B. El-Arnaouty, *Radiat. Phys. Chem.*, **33**(2), 129 (1989).
17. E. A. Hegazy and A. M. Dessouki, *Radiat. Phys. Chem.*, **28**(3), 273 (1986).
18. E. A. Hegazy, N. B. El-Assy, N. H. Taher, and A. M. Dessouki, *Radiat. Phys. Chem.*, **33**(6), 539 (1989).
19. H. Fricke and E. J. Hart, in *Radiation Dosimetery,* F. H. Attix and W. C. Roesch, Eds., Academic Press, New York, 1968, Vol. 2, p. 167.
20. *Manual of Food Irradiation Dosimetry,* Technical Report, Series No. 178, IAEA, 1977.

Received March 31, 1989
Accepted February 26, 1990