Radiation-Induced Graft Copolymerization of 2-Hydroxyethyl Methacrylate onto Chloroprene Rubber Membrane. II. Characterization of Grafting Copolymer

YUE-E FANG,[1] CHAO-XIONG MA,[1] QING CHEN,[1] XIAO-BING LU[2]

[1] Department of Applied Chemistry, University of Science and Technology of China, Hefei, Anhui, 230026, People's Republic of China

[2] Department of Chemistry, University of Science and Engineering of Dalian, 116011, People's Republic of China

Received July 1997; accepted 9 September 1997

ABSTRACT: The cobalt-60 radiation-induced graft copolymerization of 2-hydroxyethyl methacrylate (HEMA) onto a chloroprene rubber (CR) membrane has been studied in ethanol. The structure, morphology, crystallinity, thermal stability, and hydrophility of graft copolymer were characterized by means of Fourier transform infrared photoacoustic spectroscopy, scanning electron microscopy, wide-angle X-ray diffraction, differential thermal gravimetric analysis, and contact angle test methods, respectively. The permeabilities of urea, creatinine, and creatine through the CR and CR-*g*-HEMA membranes are investigated in a dialysis cell, and the permeation mechanism is also discussed. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 68: 1745–1750, 1998

Key words: radiation-induced; HEMA; CR membrane; permeation rate; permeation coefficient

INTRODUCTION

Radiation-induced graft copolymerization is a well-known important method for modification of the chemical and physical properties of polymeric materials. So far, it has been used to prepare hundreds of interesting materials, some of them on a large scale. In recent years, much effort has been spent on application of this method for medical purposes to increase biocompatibility of various polymeric materials because of its merits in simplifying the whole treating process, minimizing the processing time, and leaving no detrimental residue. Extensive investigations have been performed on modification of polyethylene (PE), poly(tetrafluoroethylene), silastics, and polyurethanes by radiation-induced graft polymerization of different monomers: 2-hydroxyethyl methacrylate (HEMA), acrylimide, and its derivatives.[1–6] The graft of acrylamide, HEMA, 2,3-epoxypropyl methacrylate, and 2,3-dihydroxypropyl methacrylate onto polyurethane films was studied by Jansen and colleagues.[7,8] The distribution of grafted layer along the film thickness was examined using infrared (IR) spectroscopy. Ohtsuka and associates[9] reported on hemodialysis membranes prepared from latexes of acrylonitrile–methyl acrylate–acrylamide graft copolymerization onto poly(vinyl alcohol). The radiation-induced graft copolymerization of acrylamide onto a PE prosthesis was carried out by Pekala and coworkers.[10,11] Hydrophility of the prosthesis was increased.

The present work studied the grafting of HEMA onto chloroprene rubber (CR-*g*-HEMA) membrane (which has excellent chemical and physical properties) by the simultaneous radiation grafting technique to obtain new materials with de-

Correspondence to: Y.-E. Fang.

Journal of Applied Polymer Science, Vol. 68, 1745–1750 (1998)
 CCC 0021-8995/98/111745-06

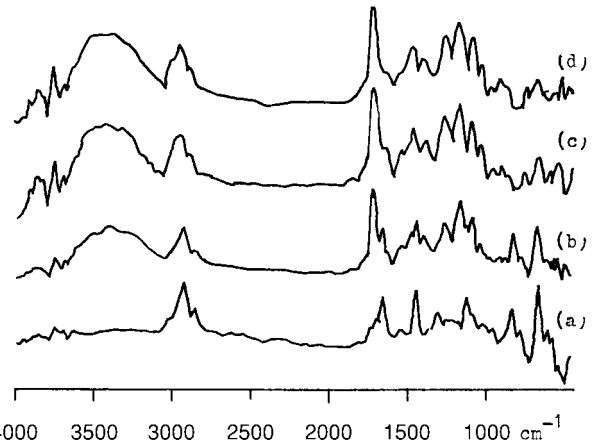

Figure 1 FTIR-PAS spectra of CR and CR-*g*-HEMA membranes with different degrees of grafting (%): (a) 0; (b) 48.5; (c) 103.4; (d) 155.1.

sired properties. The structure, morphology, crystallinity, thermal stability, hydrophilicity, and permeability were characterized by means of Fourier transform infrared (FTIR) spectroscopy, scanning electron microscopy (SEM), wide-angle X-ray diffraction (WAXD), TG, contact angle tester, and dialysis methods, respectively.

EXPERIMENTAL

Materials

A-90 type chloroprene rubber (CR) was made by Denka Kagaku Kogyo Kabushiki Kaisha Niigataken, Japan: $\bar{M}_n = 1.45 \times 10^5$; $\bar{M}_w/\bar{M}_n = 3.59$; Mooney viscosity (Male + 4 at 100°C), is 80–90; chlorine content is 40 wt %; degree of branching is about 2.1 wt %. HEMA was purchased from Aldrich Chemical Company (Steinheim, Germany). Toluene, ethanol, and other reagents (all analytical grade) were used without further purification.

Grafting Procedure

A total of 5 g of CR was dissolved in toluene (100 mL) with constant stirring. The solution was filtered and poured into a glass dish. The dish was maintained at room temperature until the solvent was completely removed. After about 2 days, membranes with 50-μm thickness were obtained.

Samples of the obtained membranes (50 × 50 mm) were washed with nonaqueous ethanol and dried at 40°C under vacuum (10 mmHg) for 12 h. The initial membrane weight, W_0 was measured. The samples were immersed in grafting solution (a mixture of HEMA and ethanol, 1 : 4) in grafting vessels, bubbled with N_2 gas (99.5%) for 5 min to remove oxygen, and then irradiated in a 60,000-Ci Co-60 source at different grafting conditions.

The grafted membranes were extracted in ethanol for 24 h. The extracted membranes were dried at 40°C under vacuum for 12 h, and the grafted membrane weights (W_g) were determined. The degree of grafting was calculated using the following equation:

$$\text{degree of grafting (\%)} = (W_g - W_0)/W_0 \times 100$$

Characterization of Membranes

The structures of membranes were studied by a Nicolet 170 SX FTIR Photoacoustic Spectroscope (FTIR-PAS). Their surface morphologies were observed by a Hitachi X-650 scanning electron microscope. A Rigaku D/Max-rA WAXD instrument was used to investigate the crystallinity of these membranes. The thermal stabilities of both the CR and the grafted membranes were determined in a WR-3 type thermal analyzer (TG). The water–membrane contact angles were measured by a JY-82 type contact angle tester. The mechanical properties of membranes under dry and wet states were measured using a DCS-5000 universal tensile tester at room temperature with crosshead speed of 100 mm/min and load of 5 Kg.

Determination of Water Content

Samples of the membranes (50 × 50 mm) were dried at 40°C under vacuum (10 mmHg) for 12 h. The initial sample weight (W_d) was measured. The samples were immersed in a beaker filled with distilled water at room temperature for 48 h, and then removed from the beaker, quickly blotted with filter paper to remove excess surface water, and weighed immediately in a microbalance (W_w). The water content was calculated from the following expression:

$$\text{water content (\%)} = (W_w - W_d)/W_d \times 100$$

Dialysis Experiment

The CR membrane (or its grafted membrane) was fixed in a quartz cell as a partition membrane. The 7.9×10^{-3} mol/L urea (or 2.1×10^{-3} mol/L creatinine or 3.1×10^{-3} mol/L creatine) aqueous

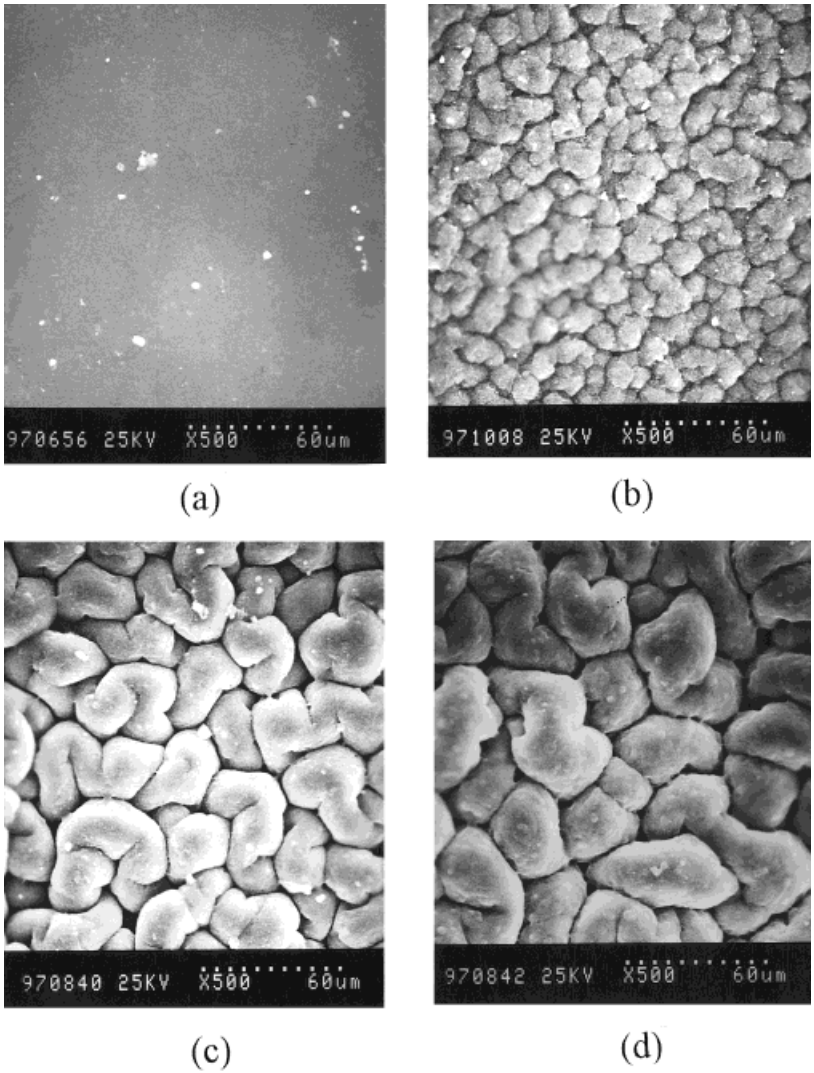

Figure 2 Scanning electron micrographs of CR and CR-*g*-HEMA membranes with different degree of grafting (%): (a) 0; (b) 48.5; (c) 103.4; (d) 208.8.

solution was poured into the left compartment of the cell, and an equal volume of distilled water into the right. The cell was placed into a constant temperature bath of 37 ± 0.5°C. The dialysis procedure was carried out with continuous stirring.

The concentration of solute in both chambers was determined by means of an ultraviolet-spectrophotometric method. The permeation coefficients were calculated by an equation found in the literature.[12]

RESULTS AND DISCUSSION

Structure and Morphology

For a medical polymer, it is very important that the material has not only certain strength and stability but also good bicompatibity. The surface structure and morphology of materials have a great influence on anticoagulation. The main purpose of radiation-induced grafting of HEMA onto a CR membrane is the improvement of blood compatibility and the prevention of coagulation.

The structures of CR and CR-*g*-HEMA membranes were measured by means of an FTIR-PAS method, as shown in Figure 1. When the FTIR-PAS spectra of Figure 1(a) are compared with Figure 1(b–d), it is seen that in the spectra of the CR-*g*-HEMA membranes two new absorption peaks appear, one at about 3450 cm^{-1} (hydroxyl group) and the other at 1720 cm^{-1} (ester carboxyl group). The two new peaks of CR-*g*-HEMA membranes all increase with the degree of grafting.

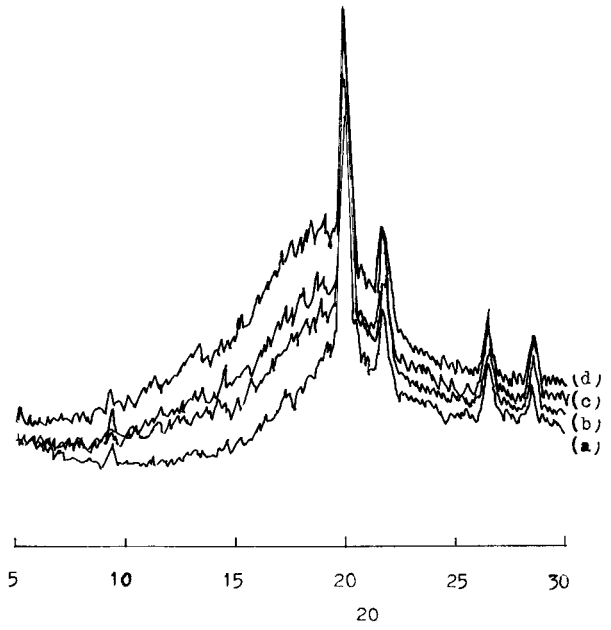

Figure 3 X-ray diffraction diagrams of CR and CR-*g*-HEMA membranes with different degree of grafting (%): (a) 0; (b) 48.5; (c) 103.4; (d) 208.8.

The results prove that HEMA was grafted onto the CR membrane.

The CR membrane is transparent, whereas CR-*g*-HEMA membranes are opaque. The scanning electron micrographs of the CR membranes with various degrees of grafting are shown in Figure 2. There are distinct spheres of poly(2-hydroxyethyl methacrylate) (PHEMA) embedded in the matrix of the membrane of low degree of grafting, whose size is rather well-distributed. With a higher degree of grafting, the surface of CR-*g*-HEMA membranes appears to be a regular gathering structure similar to the "large intestines" type, as shown in Figure 2(c,d). This indicates that the grafted chains of PHEMA increased with degree of grafting.

Crystallinity

In Figure 3, the WAXD patterns of CR and CR-*g*-HEMA membranes are shown. The X-ray diffraction pattern of the crystalline form of polychloroprene is shown in Figure 3(a). When the WAXD patterns of Figure 3(a) are compared with Figure 3(b–d), it is seen that an amorphous region, in 2θ = 7 to 30 degrees, increases with increasing degree of grafting. This is due to the grafted PHEMA chains on the CR membrane.

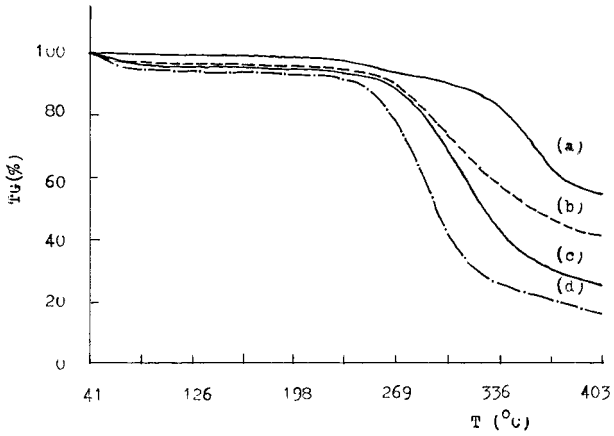

Figure 4 TG curves of CR and CR-*g*-HEMA membranes with different degrees of grafting (%): (a) 0; (b) 48.5; (c) 103.4; (d) 208.8.

Thermal Stability

Figure 4 illustrates the TG curves of the membranes. The initial decomposition temperatures are 328.2, 284.8, 278.1, and 255.2°C for CR, 48.5% grafting, 103.4% grafting, and 208.8% grafting membranes, respectively. Accordingly, we see that thermal stability of the membranes decreases with increasing degree of grafting. The reason may be that the grafted chains of PHEMA decompose easily in comparison with CR macromolecules.

Hydrophilicity

Due to the existence of hydroxyl and carboxyl groups in HEMA molecules, the contact angles of water–membrane decrease with increasing degree of grafting, as shown in Figure 5. The water

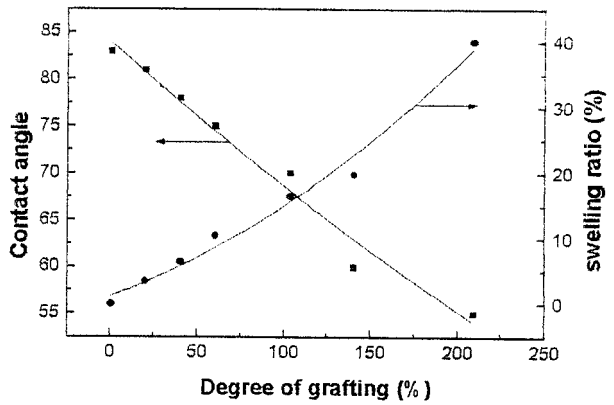

Figure 5 Plots of contact angle of water–membrane and swelling ratio versus degree of grafting.

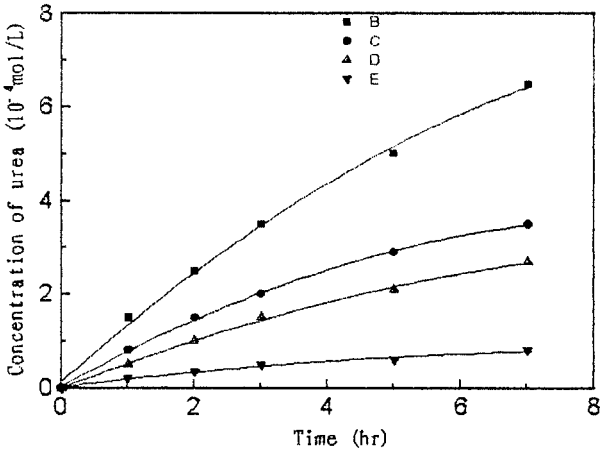

Figure 6 Change in the concentration of urea through CR and CR-*g*-HEMA membranes in a dialysis cell at 37 ± 0.5°C. Degree of grafting (%): (a) 0; (b) 60.5; (c) 103.4; (d) 208.8. $[\text{urea}]_0 = 7.9 \times 10^{-3}$ mol/L.

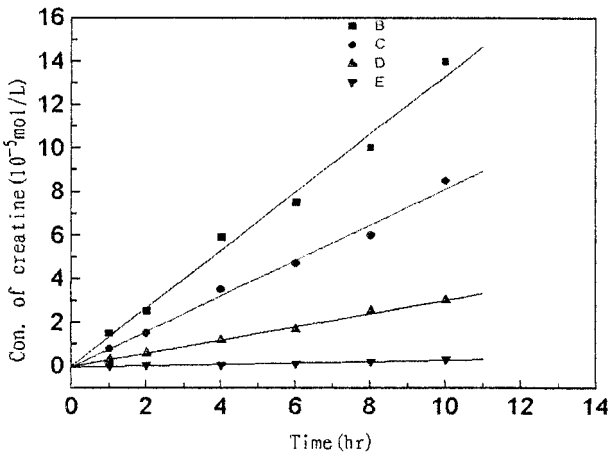

Figure 8 Change in the concentration of creatine through CR and CR-*g*-HEMA membranes in a dialysis cell at 37 ± 0.5°C. Degree of grafting (%): (a) 0; (b) 60.5; (c) 103.4; (d) 208.8. $[\text{creatine}]_0 = 3.1 \times 10^{-3}$ mol/L.

content of membranes increases with degree of grafting.

Permeability

It is seen in Figures 6–8, that the permeation rate of urea, creatinine, and creatine through the grafted membranes increases with degree of grafting. The average permeation rates of urea, creatinine, and creatine through the CR-*g*-HEMA membrane of 208.8% graft are about 8.6, 33.8, and 28.7 times that through the CR membrane, respectively. The permeation process is a function of the diffusion and solubility of the permeated solute in the membrane. Thus the enhanced permeability which the CR-*g*-HEMA membranes exhibit in this study must be interpreted on the basis of solubility and diffusion effects. To permeate hydrous solutes, the hydrophilicity and crystallinity of membrane are important factors controlling permeation rate. It is obvious that, with higher degree of grafting, the hydrophilicity and amorphous region of membrane increase, thus benefiting the mobility of macromolecule chain segments and improving the diffusion of permeated solute in the membrane. Compared with the CR-*g*-HEMA membranes, the permeation rate of urea, creatinine, or creatine through CR membrane is very low, due to its hydrophobic macromolecule chain retarding the diffusion of these hydrous solutes.

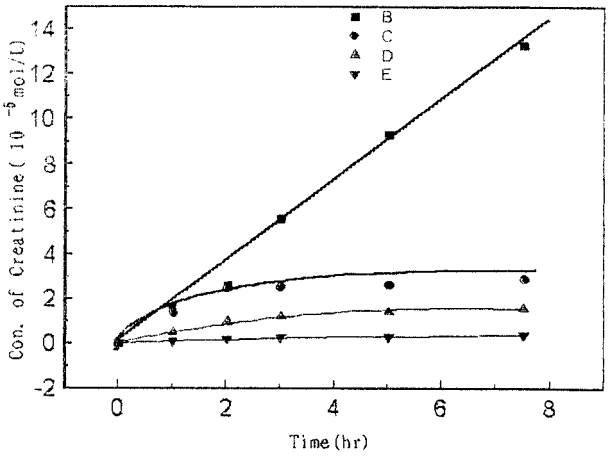

Figure 7 Change in the concentration of creatinine through CR and CR-*g*-HEMA membranes in a dialysis cell at 37 ± 0.5°C. Degree of grafting (%): (a) 0; (b) 60.5; (c) 103.4; (d) 208.8. $[\text{creatinine}]_0 = 2.1 \times 10^{-3}$ mol/L.

The permeation coefficients of various solutes through CR and CR-*g*-HEMA membranes with different degrees of grafting are listed in Table I. The permeation coefficients of urea, creatinine, and creatine through the CR-*g*-HEMA membrane of 208.8% grafting are 78.2, 14.2, and 11.2 ($\times 10^{-8}$ cm^2/s), respectively.

CONCLUSIONS

1. As compared with CR membranes, the crystallinity and thermal stability of CR-*g*-HEMA

Table I Permeability of the CR and CR-*g*-HEMA Membranes with Different Degrees of Grafting

Sample	Degree of Grafting (%)	Thickness (μm)	Mechanical Properties (wet)		Permeation Coefficient ($\times 10^{-8}$ cm^2/s)		
			Tensile Strength (MPa)	Elongation at Break (%)	Urea	Creatinine	Creatine
1	0	30	11.46	807	9.1	0.42	0.39
2	60.5	35	11.32	80	31.2	1.68	2.37
3	103.4	41	7.98	100	40.8	3.05	6.75
4	208.8	52	6.71	120	78.2	14.20	11.20

membrane decreased and the hydrophility increased, due to the existence of a large number of hydroxyl and carboxylic groups in the PHEMA macromolecular chains.

2. The transparency of the CR-*g*-HEMA membranes decreases with increasing degree of grafting. The SEM data on the CR-*g*-HEMA membrane, of low degree of grafting, clearly show many spheres of PHEMA embedded in the CR matrix, whose size is rather well-distributed. With a higher degree of grafting, the surfaces of CR-*g*-HEMA membranes appear to be a regular gathering structure similar to "large intestines."
3. The CR-*g*-HEMA membranes show higher permeabilities to various hydrous solutes, in comparison with CR membranes. The average permeation rates of urea, creatinine, and creatine through the CR-*g*-HEMA membrane of 208.8% graft are about 8.6, 33.8, and 28.7 times that through the CR membrane, respectively. The enhanced permeability, which the CR-*g*-HEMA membrane exhibits in this study, can be interpreted as a consequence of the plasticizing effect of water in the swollen membrane, thus benefiting the mobility of macromolecular chain segments and improving the diffusion of permeated solutes in the membrane.
4. The permeability of the CR membrane can be improved by using radiation-induced graft copolymerization of hydrophilic monomers, such as HEMA, etc., onto a CR matrix and also controlled by changing the degree of grafting.
5. These investigations of the permeabilities of CR-*g*-HEMA membranes prepared by means of the direct radiation method indicate the possibility of practical use as a dialysis membrane.

REFERENCES

1. A. S. Hoffman, *Radiat. Phys. Chem.,* **18,** 323 (1981).
2. A. S. Hoffman, D. Cohn, S. R. Hanson, L. A. Harker, T. A. Horbett, B. D. Ratner, and L. O. Reynolds, *Radiat. Phys. Chem.,* **22,** 267 (1983).
3. A. S. Hoffman, W. R. Gombotz, S. Uenoyama, L. C. Dong, and G. Schmer, *Radiat. Phys. Chem.,* **27,** 265 (1986).
4. B. D. Ratner, in *Surface and Interfacial Aspects of Biomedical Polymer,* Vol. 1, J. D. Andrade, Ed., Plenum Press, New York, 1985, p. 373.
5. D. Cohn, A. S. Hoffman, and B. D. Ratner, *J. Appl. Polym. Sci.,* **33,** 1 (1987).
6. W. Gombotz, A. S. Hoffman, G. Schmer, and S. Uenoyama, *Radiat. Phys. Chem.,* **25,** 549 (1985).
7. B. Jansen and G. Ellinghorst, *J. Polym. Sci., Polym. Symp.,* **66,** 465 (1979).
8. B. Jansen, A. Ludwicka, and L. W. Storz, *Radiat. Phys. Chem.,* **25,** 529 (1985).
9. Y. Ohtsuka, Y. Hirabayashi, J. Masubuchi, and N. Kaneko, *Kobunshi Ronbunshu,* **36,** 257 (1979).
10. W. Pekala, J. Rosiak, A. Ruoinska Rybus, K. Burozak, S. Galant, and T. Goiozynska, *Radiat. Phys. Chem.,* **27,** 275 (1986).
11. W. Pekala, T. Achmatowicz, and J. Kroh, *Radiat. Phys. Chem.,* **28,** 173 (1986).
12. S. C. Yoon and M. S. Jhon, *J. Appl. Polym. Sci.,* **27,** 3133 (1982).