

Mössbauer Studies of Styrene–Acrylonitrile Copolymers Containing Ferric Nitrate

A. S. BRAR* and SUNITA, *Department of Chemistry, Indian Institute of Technology, New Delhi-110016, India*

Synopsis

Styrene (St)–acrylonitrile (AN) copolymers were prepared with and without ferric nitrate by free radical polymerization at 70°C. TGA studies showed that the addition of ferric nitrate has some effect on the thermal behavior of the copolymer. Mössbauer studies of the copolymer, heated at 150, 250, and 480°C for 15 min showed that during the thermal degradation Fe^{3+} species was reduced to Fe^{2+} , and then, finally, it formed $\alpha\text{-Fe}_2\text{O}_3$. The mechanism of thermal degradation has been proposed on the basis of IR, TGA, and Mössbauer studies.

INTRODUCTION

Mössbauer spectroscopy is an efficient tool in investigating the change in oxidation state of iron and its environment during copolymerization and during the thermal degradation of polymers.¹ Metal ions are added as a stabilizer in copolymers as they improve mechanical and thermal properties. Coey et al.² have reported the Mössbauer studies of ferric nitrate containing polyvinyl pyridine and observed the change in Mössbauer parameters with the change in temperature of recording. In our earlier publications, Mössbauer studies of methyl methacrylate–butyl methacrylate,³ ethyl methacrylate–butyl methacrylate,⁴ methyl methacrylate–ethyl methacrylate,⁵ and styrene–acrylonitrile⁶ copolymers containing iron salts have been reported. Brar and Sekhar⁶ have reported the reduction of Fe^{3+} species to Fe^{2+} species in the styrene–acrylonitrile copolymer containing ferric chloride. As a continuation of our earlier works, in this communication we have reported the effect of the addition of ferric nitrate on the thermal behavior of styrene (St)–acrylonitrile (AN) copolymer and also the change in the oxidation state and environment, and various products formed during the thermal degradation of the copolymers have been studied by Mössbauer, TGA, and IR techniques. One of the aims of this study was to study the copolymerization behavior of the St–AN copolymer in the presence of ferric nitrate and to observe the effect of anion during thermal degradation. The difference between the earlier communication⁶ and this paper is that ferric chloride acts as a stabilizer and the Mössbauer spectra of intermediates formed during the thermal degradation is different and intermediates formed are also different in two cases. The mechanism for the thermal degradation of St–AN copolymers is reported.

* To whom all correspondence should be addressed.

EXPERIMENTAL DETAILS

Polymerization

Styrene and acrylonitrile monomers were distilled under vacuum to remove the inhibitor and stored below 5°C. Styrene and acrylonitrile were taken in a round-bottom flask and flushed with purified nitrogen. Benzoyl peroxide 0.5% (by weight) was added, and polymerization was allowed to proceed at 70°C. After about 20 min, the solid ferric nitrate containing 2% (by weight of iron) was added with vigorous stirring and the polymerization was allowed to proceed for 3 h. A similar sample was prepared without the addition of ferric nitrate. The copolymers were precipitated in excess of methanol and washed several times with excess of methanol to remove unreacted monomers and ferric nitrate that are soluble in methanol. The copolymers were dried under vacuum at 30°C for 1 week.

Mössbauer Studies

Mössbauer spectra were recorded on a Mössbauer spectrometer (MS900) (Ranger Scientific Inc., USA), and curve fitting was done as described in our earlier publications.^{3,4,6} The isomer shift values have been reported with respect to centroid of iron foil.

Thermal Gravimetric Analysis (TGA)

TGA of stabilized and unstabilized St-AN copolymers were done on a Perkin-Elmer 7 series thermal analyzer in air atmosphere. The rate of heating was 40°C/min.

IR Studies

Infrared spectra of the copolymers as KBr disks were recorded on a Nicolet FTIR 5D-X Spectrometer in the range of 4000–400 cm⁻¹.

RESULTS AND DISCUSSION

Composition of various copolymers were determined by using ¹H-NMR spectroscopy. ¹H-NMR spectra show peaks at δ 7.7 ppm (due to the phenyl group), δ 1.2–2.3 ppm (due to the CH₂ group), and δ 4.5–4.4 ppm (due to the —CH group). Phenyl and CH₂ group resonance signals were used to determine the copolymer composition. Comonomer mole fractions in feed and in the copolymers are given in Table I.

The Mössbauer spectrum of ferric nitrate gave a single broad band due to the spin-lattice relaxation effect.⁷ The value of the isomer shift was 0.3 mm s⁻¹, which is in agreement with the literature value.⁷ The value of isomer shift shows that the iron is in high-spin +3 oxidation state. The Mössbauer spectrum of the St-AN copolymer containing ferric nitrate is shown in Figure 1. Mössbauer spectrum shows a doublet having the value of the isomer shift (δ) 0.38 mm s⁻¹ and quadrupole splitting (Δ) 0.65 mm s⁻¹. These values are entirely different from pure ferric nitrate. The change in the Mössbauer parameters

TABLE I
Mössbauer Parameters of Styrene-Acrylonitrile Copolymers Containing
Ferric Nitrate as a Stabilizer at Room Temperature

Step no.	Composition of monomers (mole fractions)				δ^a (mm s ⁻¹)	Δ (mm s ⁻¹)
	In feed		Observed in copolymer			
	St	AN	St	AN		
I	0.8	0.2	0.74	0.26	0.37	0.62
II	0.7	0.3	0.69	0.31	0.38	0.67
III	0.6	0.4	0.66	0.33	0.41	0.68
IV	0.5	0.5	0.62	0.38	0.37	0.65
V	0.4	0.6	0.57	0.43	0.38	0.67

^a Isomer shift values are reported with respect to iron foil.

shows strong interaction between ferric moiety and the copolymer lattice. The sharp linewidth of the Mössbauer spectrum of ferric nitrate in the copolymer shows a negligible contribution by spin-lattice relaxation. The reduction of ferric chloride in the St-AN copolymers prepared at 70°C has been reported in our earlier communication,⁶ which may be due to thermal or photoreduction of ferric chloride with monomers; no reduction has been observed during the polymerization of the St-AN copolymer containing ferric nitrate under similar conditions. The Mössbauer spectra of St-AN copolymers of various composition containing ferric nitrate show that the value of isomer shift (δ) and quadrupole

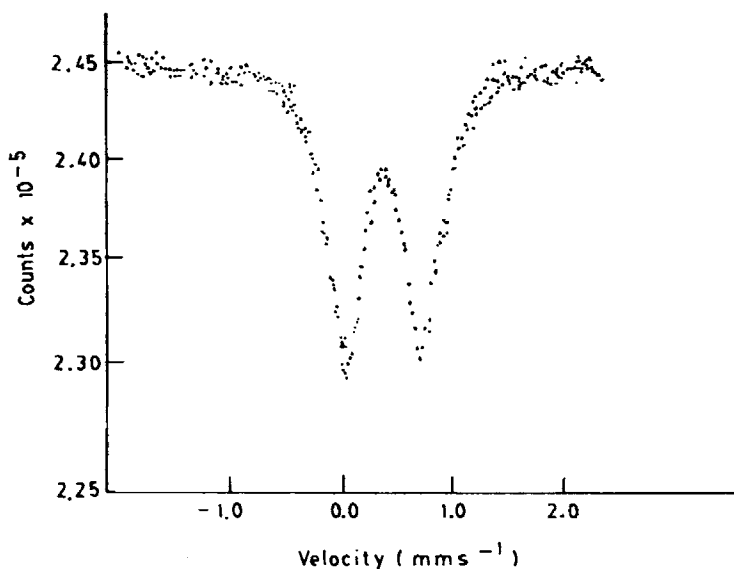


Fig. 1. Mössbauer spectrum of St-AN (St = 0.62 mole fraction) copolymer containing ferric nitrate at room temperature.

splitting (Δ) does not change with the change in the composition of the copolymers (Table I). The Mössbauer parameters show that the nature of interaction of the phenyl and nitrile group with the Fe^{3+} moiety are almost the same. Infrared spectra showed the absorption band at 3050 cm^{-1} to be due to aromatic $-\text{CH}$ stretching, at 2200 cm^{-1} due to the nitrile group, and at 3400 cm^{-1} due to $-\text{OH}$ stretching from water entrapped in the sample containing ferric nitrate. The characteristic peaks due to aromatic $-\text{CH}$ out-of-plane bending ($2000\text{--}1600\text{ cm}^{-1}$), aromatic $-\text{CH}$ asymmetric bending (1462 cm^{-1}), and aromatic $-\text{CH}$ in-plane bending ($1225\text{--}950\text{ cm}^{-1}$) were observed.

The Mössbauer spectrum of St-AN (St = 0.62 mole fraction) copolymer containing ferric nitrate heated at 150°C for 15 min shows the presence of one doublet. The value of δ almost remains the same as for the unheated sample, whereas the values of Δ increases from 0.65 to 0.75 mm s^{-1} , which shows the creation of an asymmetric environment around the iron moiety due to heating. The Mössbauer spectrum of the copolymer heated at 200°C does not show any change in the Mössbauer parameters with respect to the copolymer heated at 150°C (Table II).

Figure 2 shows the Mössbauer spectrum of the St-AN copolymer containing ferric nitrate heated at 250°C for 15 min. The spectrum was fitted into two doublets. One doublet with $\delta = 0.38\text{ mm s}^{-1}$ and $\Delta = 0.75\text{ mm s}^{-1}$ shows the presence of Fe^{3+} moiety, whereas the other doublet with $\delta = 1.06\text{ mm s}^{-1}$ and $\Delta = 1.99\text{ mm s}^{-1}$ indicates the formation of Fe^{2+} species during the thermal degradation of the copolymers. Isomer shift values show that Fe^{3+} reduces to Fe^{2+} during the initial phase of copolymer degradation. The fractional intensities of the doublets show 25.4% formation of Fe^{2+} species. These calculations were done on the basis of assumption that Debye-Waller factors were the same for both Fe^{2+} and Fe^{3+} species. The value of χ^2 for this computer-fitted spectrum was 1.2.

In our earlier publication,⁴ Mössbauer studies of ethyl methacrylate-*n*-butyl methacrylate copolymer containing ferric chloride as a stabilizer showed the reduction to Fe^{2+} species at a temperature of 150°C . The values of $\delta = 1.36\text{ mm s}^{-1}$ and $\Delta = 2.96\text{ mm s}^{-1}$ had been reported for Fe^{2+} species.⁴ The low-

TABLE II
Mössbauer Parameters of Styrene-Acrylonitrile Copolymers Containing Ferric Nitrate as a Stabilizer at Different Temperatures

Step no.	Heating temp. ($^\circ\text{C}$)	δ (mm s^{-1})	Δ (mm s^{-1})	H I (kOe)
1	25	0.37	0.65	—
2	150	0.36	0.75	—
3	200	0.39	0.75	—
4	250	1.06	1.99 due to Fe^{2+}	—
		0.38	0.75 due to Fe^{3+}	
5	300	0.84	1.69 due to Fe^{2+}	—
		0.39	0.67 due to Fe^{3+}	
6	480	0.48	0.42 due to $\alpha\text{-Fe}_2\text{O}_3$	512
		0.42	0.76 due to Fe^{3+}	
7	510	0.47	0.42 due to $\alpha\text{-Fe}_2\text{O}_3$	512

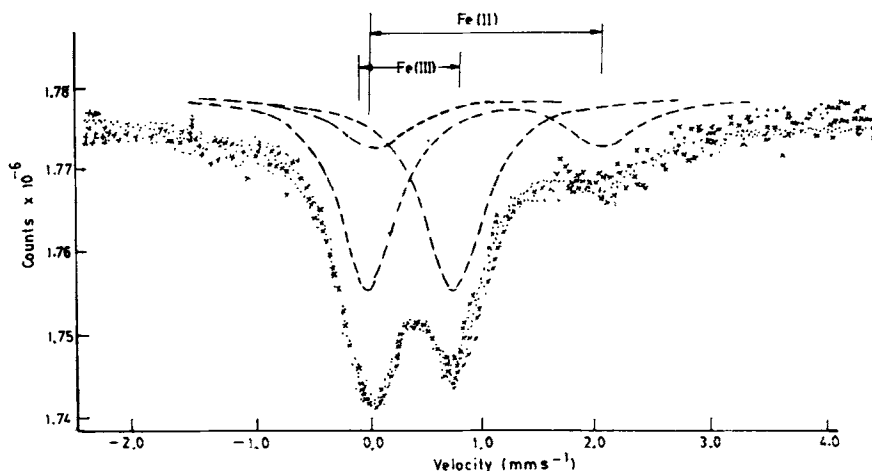


Fig. 2. Mössbauer spectrum of St-AN copolymer containing ferric nitrate heated at 250°C. (*) Computer-fitted points; (O) experimental points; (----) Lorentzian curve fitted from computer fitting.

temperature reduction of Fe^{3+} in EMA-BuMA copolymers may be due to the change in the nature of the stabilizer and the copolymer.⁴ Coey et al.² had reported the reduction of Fe^{3+} to Fe^{2+} species in FeCl_3 -PVP polymers. The values of $\delta = 1.3 \text{ mm s}^{-1}$ and $\Delta = 3.1 \text{ mm s}^{-1}$ are different from the values reported in this paper because of the different nature of iron salt and polymer. The lower value of isomer shift of Fe^{2+} in this copolymer may be due to the presence of nitrate in the polymer system.

The Mössbauer spectrum of the St-AN copolymer containing ferric nitrate heated at 300°C for 15 min is shown in Figure 3. The spectrum shows the

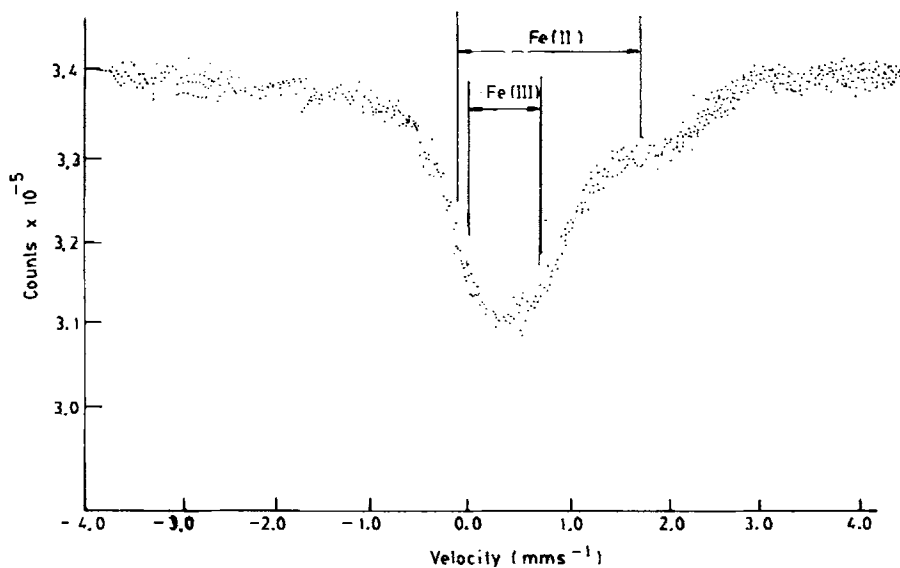


Fig. 3. Mössbauer spectrum of St-AN copolymer containing ferric nitrate heated at 300°C.

presence of the doublet as it was observed at 150°C and a broad line having $\delta = 0.84 \text{ mm s}^{-1}$ and $\Delta = 1.69 \text{ mm s}^{-1}$. The appearance of new broad band having the value of $\delta = 0.39 \text{ mm s}^{-1}$ shows that ferric species in the high-spin state is present. Lorentzian curve shape fitting of the spectrum gave a higher value of χ^2 . The broadening of the spectrum may be due to the decomposition of the copolymer.

The Mössbauer spectrum of the St-AN copolymer containing ferric nitrate heated at 480°C for 15 min is shown in Figure 4. The Mössbauer spectrum shows the presence of one sextet and one doublet around zero velocity. The value of δ , Δ , and the magnetic field at the nucleus are 0.48 mm s^{-1} , 0.42 mm s^{-1} and 512 kOe, respectively. These values show the formation of $\alpha\text{-Fe}_2\text{O}_3$ along with undecomposed copolymer (inner doublet).

The IR spectra of the copolymer heated at 480 and 510°C showed a broad band around 3400 cm^{-1} that may be due to -NH bands formed during thermal degradation of acrylonitrile sequences in the copolymers. Such degradation processes are known to involve the formation of the pyridine type of ring structure.⁸ IR spectroscopy showed the presence of the copolymer system at this temperature. The additional bands were observed at 540 and 457 cm^{-1} , which may be due to $\alpha\text{-Fe}_2\text{O}_3$.⁹ These studies confirm the formation of $\alpha\text{-Fe}_2\text{O}_3$.

TGA of the copolymer samples without and with ferric nitrate are given in Figures 5 and 6. TGA of the copolymer without ferric nitrate shows a 20% weight loss at 118°C, which may be due to the loss of entrapped solvent molecules in the copolymer system. Figure 5 shows that the copolymer system remains stable till 366°C and weight loss at 392°C is 30% and that maximum decomposition occurs at 436°C. TGA of the copolymer containing ferric nitrate shows that the weight loss at 195°C is 5%. Figure 6 shows a 20% weight loss at 340°C and maximum decomposition at 425°C. TGA of the copolymer containing ferric nitrate shows 80% decomposition at 465°C, whereas TGA of the copolymer without ferric nitrate shows 95% weight loss at this temperature. TGA of the copolymer with ferric nitrate shows 93% decomposition at 570°C.

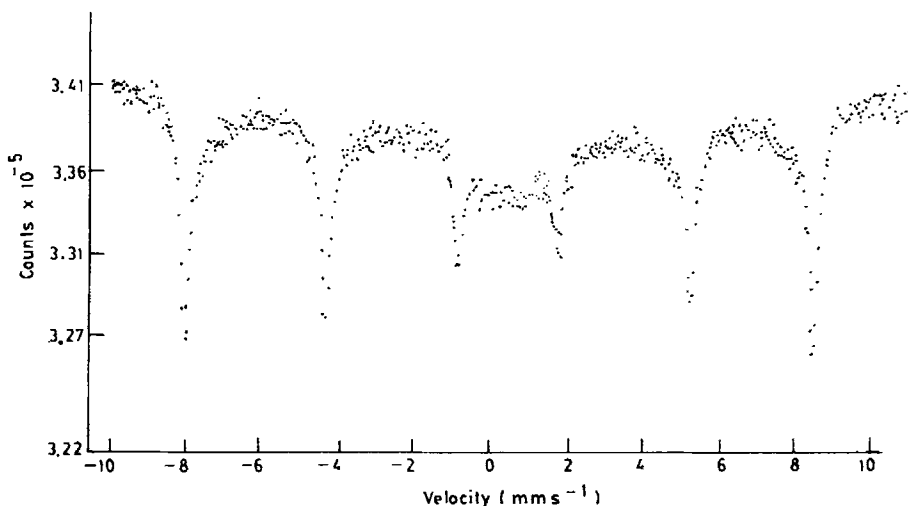


Fig. 4. Mössbauer spectrum of St-AN copolymer containing ferric nitrate heated at 480°C.

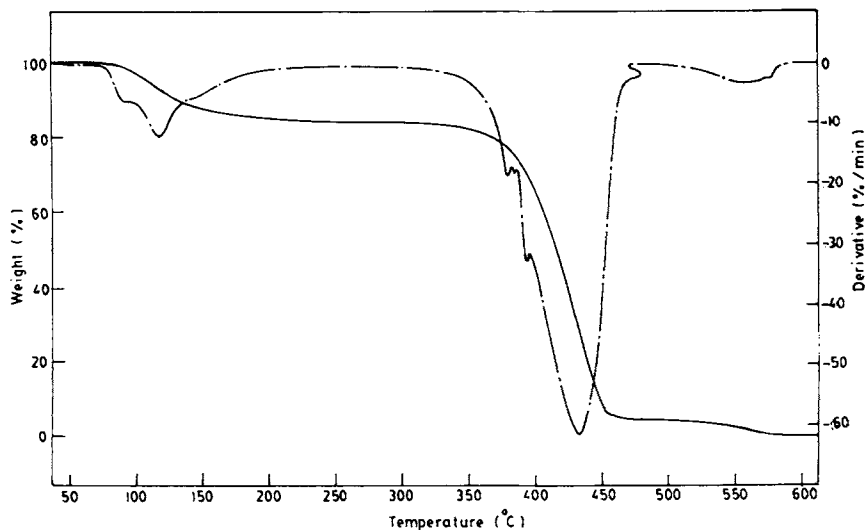


Fig. 5. TGA trace for St-AN (St = 0.62 mole fraction) copolymer without ferric nitrate. (○) Derivative graph; (----) TGA curve.

TGA shows that there is only 2% of the iron oxide content. TGA studies show that the difference in the temperature of maximum degradation in the two systems is not significant, but in the copolymer system containing ferric nitrate, final decomposition temperature (FDT) is higher (570°C) as compared to the copolymer without ferric nitrate (465°C). This thermal decomposition data show that ferric nitrate has some effect on the St-AN copolymer.

From the above TGA, Mössbauer, and IR studies, the most probable mechanism for the thermal degradation of the St-AN copolymer containing ferric nitrate has been suggested and is given below:

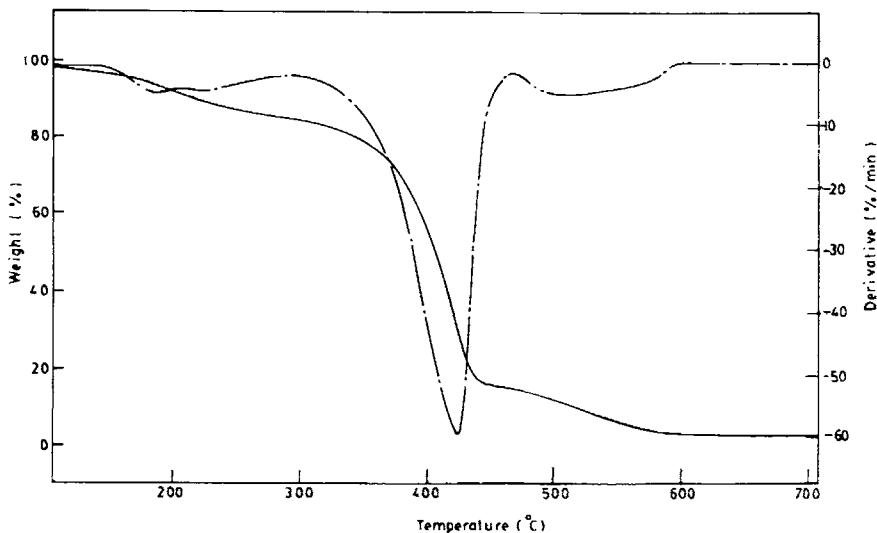
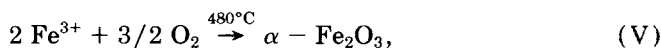
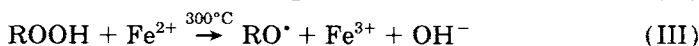
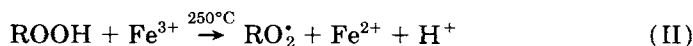
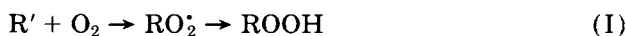


Fig. 6. TGA trace for St-AN (St = 0.62 mole fraction) copolymer containing ferric nitrate. (○) Derivative graph; (----) TGA curve.



where R' represents a polymer chain. The formation of peroxide (R—O—O—H) in step (I) is a common reaction during the thermal degradation process, confirmed by the IR spectra that showed the absorption band at 1050–1100 cm^{-1} due to C—O stretching. The oxidation–reduction reaction in steps (II) and (III) was confirmed by Mössbauer spectroscopy (Figs. 2 and 3, respectively). Finally, at 480°C, the formation of α -Fe₂O₃ was confirmed by both IR and Mössbauer spectroscopy (Fig. 5). The oxidation–reduction reaction is responsible for the stabilization of copolymers. Ferric nitrate can participate in the reaction with hydroperoxide, with the secondary products of oxidation and with oxygen-containing radicals, as shown in the mechanism. The stabilizing effect of ferric nitrate may be due to the incorporation of iron atoms into the copolymer net via oxygen bonds, with additional crosslinks of the Fe(—O—)_n types formed.

References

1. V. I. Goldanski and L. A. Korytko, in *Applications of Mössbauer Spectroscopy*, R. L. Cohen, Ed, Academic, New York, 1976, Vol. 1, p. 287.
2. J. M. D. Coey, A. Meagher, J. M. Kelly, and J. G. Vos., *J. Polym. Sci., Polym. Chem. Ed.*, **22**, 303 (1984).
3. G. S. Kapur and A. S. Brar, *J. Radioanal. Nucl. Chem., Lett.*, **136**, 169 (1989).
4. G. S. Kapur and A. S. Brar, *J. Appl. Polym. Sci.*, in press.
5. A. S. Brar, A. K. Saini, and R. K. Puri, *J. Appl. Polym. Sci.*, **33**, 1447 (1987).
6. A. S. Brar and M. S. Sekhar, *J. Radioanal. Nucl. Chem. Lett.*, **137**, 97 (1989).
7. T. C. Gibbs and N. N. Greenwood, *Mössbauer Spectroscopy*, Chapman and Hall, London, 1971.
8. H. F. Mark, N. G. Gaylord, and N. M. Bikales, *Encyclopedia of Polymer Science and Technology*, Wiley-Interscience, New York, Vol. 1, 1964, p. 374.
9. N. T. McDevitt and W. L. Baun, *Spectrochim. Acta*, **20**, 799 (1964).

Received April 17, 1990

Accepted May 14, 1990