

Mössbauer Studies of Ferric Chloride Containing Ethyl Methacrylate-*n*-Butyl Methacrylate Copolymer

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Synopsis

Ethyl methacrylate (EMA)-*n*-butyl methacrylate (*n*BuMA) copolymer containing anhydrous ferric chloride was prepared by free radical polymerization at 70°C. TGA studies show that the addition of ferric chloride increases the thermal stability of the copolymer. Mössbauer studies of the copolymers showed the presence of Fe³⁺ species only. Mössbauer studies of the copolymer heated at 150°C, 250°C, and 500°C for 1 h showed that during the thermal degradation, Fe³⁺ species are reduced to Fe²⁺ and then finally α -Fe₂O₃ is formed. The mechanism of thermal degradation has been proposed on the basis of IR, TGA, and Mössbauer studies.

INTRODUCTION

⁵⁷Fe—Mössbauer spectroscopy has extensively been applied to study polymers like atactic poly(vinyl pyridine)¹ and irradiated poly(ethylene)² containing ferric chloride. The metal ions like tin and iron act as thermal stabilizers and improve the physico-mechanical properties of the polymers.¹⁻⁴ In our earlier publications, we have reported the Mössbauer studies of ferric chloride containing methyl methacrylate—ethyl methacrylate copolymers⁵ and polymethacrylates.^{6,7} In the continuation of our earlier works, in the title investigation, we report the effect of addition of ferric chloride on the thermal stability of ethyl methacrylate-*n*-butyl methacrylate copolymer and the change in oxidation state, environments, and various products formed during the thermal degradation of EMA-*n*BuMA copolymer using Mössbauer spectroscopy. A mechanism for the thermal degradation of EMA-*n*BuMA copolymer shall be proposed.

EXPERIMENTAL

Polymerization: Ethyl methacrylate and *n*-butyl methacrylate monomers (Fluka AG) were distilled under vacuum to remove inhibitor and stored below 5°C. Ethyl methacrylate and *n*-butyl methacrylate were taken in a round bottom flask and flushed with purified nitrogen. Benzoylperoxide (0.5%) was added and polymerization was allowed to proceed at 70°C. After about 20 min, the ferric chloride corresponding to 2% weight of iron was added with vigorous stirring and the polymerization was allowed to proceed. A similar sample was

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prepared without the addition of ferric chloride. The polymers were precipitated in excess of methanol and dried under vacuum at 60°C.

Mössbauer Measurements: Mössbauer spectra were recorded on a Mössbauer spectrometer MS 900 from Ranger Scientific Inc., USA, combined with a multichannel analyzer with data transfer to the Apple IIe computer. The 25 mCi ^{57}Co (Cu) source was kept at room temperature (25°C). All the spectra were recorded at room temperature. The spectrum of iron foil has been taken as the reference standard to calculate Mössbauer parameters. The uncertainty in the values of parameters is ± 0.01 mm/s. The Mössbauer parameters were calculated by fitting the spectra to Lorentzian curve distribution for different component subspectra. The curve fitting was carried out on a ICL 2960 computer using an iterative, nonlinear least square standard program LOGFIT2 IBM/155, at IIT Delhi.

Thermal Gravimetric Analysis (TGA): TGA of stabilized and unstabilized EMA-*n*BuMA copolymers were done on Dupont 1090 Thermal Analyzer in air atmosphere.

IR Studies: Infrared spectra of the samples as KBr disks, were recorded on a Nicolet FTIR 5 D-X Spectrometer in the range of 4000 to 400 cm^{-1} .

RESULTS AND DISCUSSION

Figure 1 shows the Mössbauer spectrum of ethyl methacrylate-*n*-butyl methacrylate (EMA-*n*BuMA) copolymer containing ferric chloride. From the spectrum isomer shift (δ), 0.41 mm/s and quadrupole splitting (Δ) 0.60 mm/s were calculated which indicate the presence of iron in +3 high spin oxidation state and in an unsymmetric environment in the copolymer. However, the data are slightly different from those reported for ferric chloride; i.e., δ 0.57 mm/s and Δ 0.63 mm/s as a result of ferric chloride-copolymer chains interactions.⁸ Mössbauer parameters show that no reduction of Fe^{3+} is taking place during

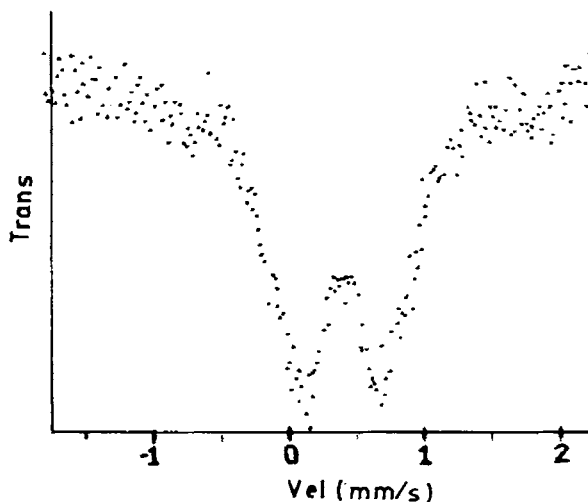


Fig. 1. Mössbauer spectrum of ferric chloride containing EMA-*n*BuMA copolymer.

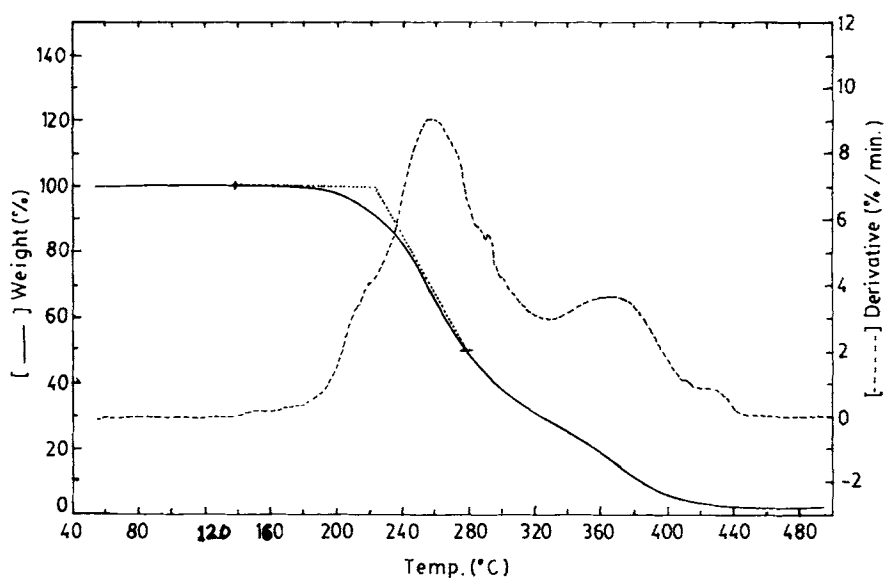


Fig. 2. Thermogravimetric trace for the EMA-*n*BuMA copolymer without ferric chloride.

polymerization process. Ferric chloride-polymer interaction results in the increased s-electron density at the iron nucleus as evident from the isomer shift value.

Figure 2 shows the TGA trace for EMA-*n*BuMA copolymer without ferric chloride. The copolymer has an initial decomposition temperature (IDT) of

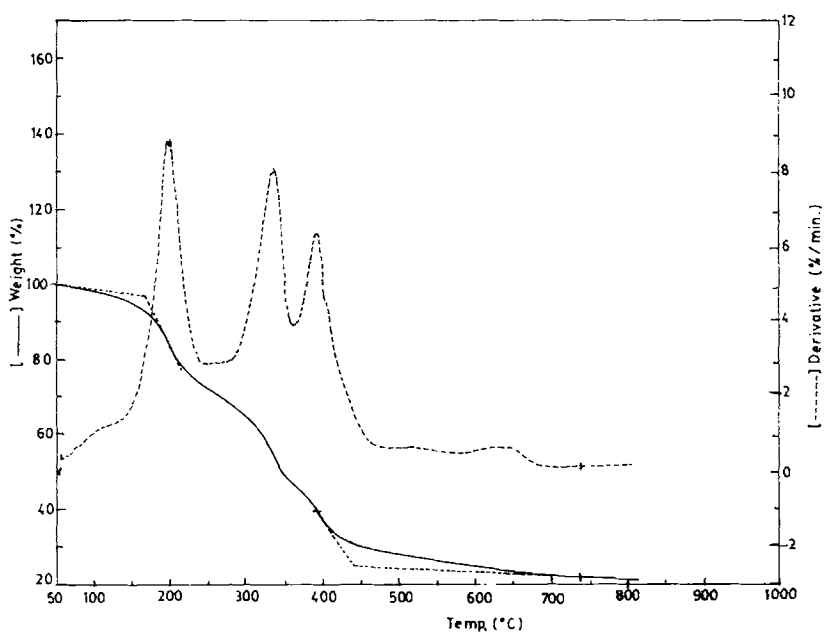


Fig. 3. Thermogravimetric trace for the ferric chloride containing EMA-*n*BuMA copolymer.

220°C and final decomposition temperature (FDT) of 404°C. The temperature at which 50% weight loss takes place is 275°C. The corresponding TGA trace for EMA-*n*BuMA copolymer with ferric chloride is shown in Figure 3. The ferric chloride-containing copolymer shows the weight loss in different steps which is due to the formation of some stabilized products during the thermal degradation. Weight loss starts around 170°C in this case which may be due to the loss of entrapped water molecules absorbed by ferric chloride during its addition to the monomer solution or in the later stages, when present in the polymer. Presence of water is also confirmed by IR studies and it was found difficult to remove unless rigorous precautions are taken. Ferric chloride in the copolymer acts as a thermal stabilizer. The temperature at which 50% weight loss takes place has increased to 345°C for the ferric chloride containing copolymer. Similarly the FDT has increased to 441°C. The TGA trace for the ferric chloride containing copolymer shows three DTA endothermic peaks at 197°C, 336°C, and 390°C. The peak at 197°C is due to the loss of entrapped water. To look into the functionalities present during the thermal degradation of the copolymer, IR spectra of the copolymer heated at 197°C, 336°C, and 390°C for 10 min were recorded. Typical IR spectrum for the sample heated at 390°C is shown in Figure 4. The characteristic peaks due to -CH stretching (2937 cm^{-1}), $>\text{C-O}$ stretching (1737 cm^{-1}), -CH asymmetric bending (1462 cm^{-1}), C-O-C asymmetric stretching (1150 cm^{-1}) and C-O-C symmetric stretching (1025 cm^{-1}) were observed. The IR spectra of copolymer heated at 336°C and 390°C showed a broad band around 3400 cm^{-1} due to -OH stretching. The origin of -OH band will be explained later while giving the mechanism for thermal degradation of the copolymer.

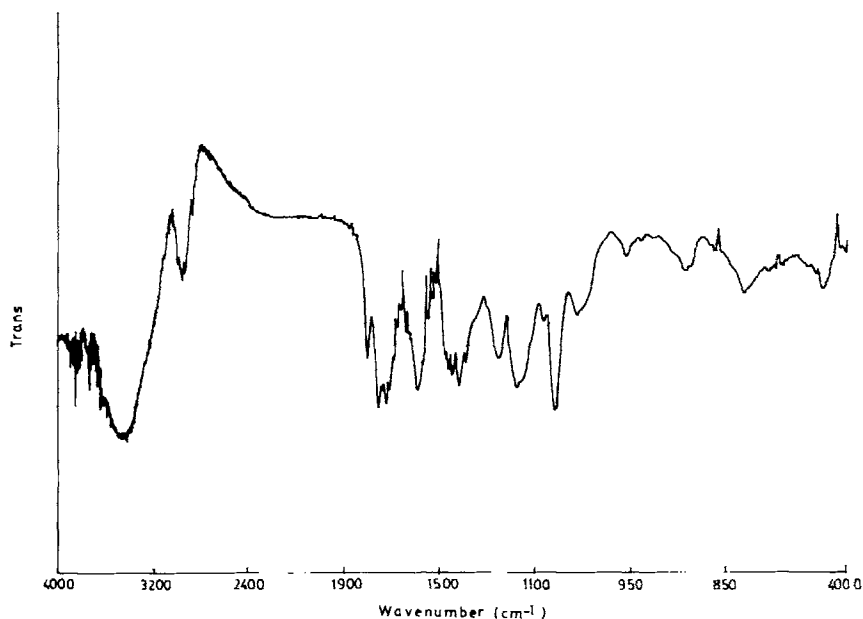


Fig. 4. Infrared spectrum of ferric chloride containing EMA-*n*BuMA copolymer heated at 390°C.

Figure 5 showing the Mössbauer spectrum of EMA-*n*BuMA copolymers containing ferric chloride, heated at 150°C for 1 h reveals the presence of two doublets. One doublet has δ 0.42 mm/s and Δ 0.56 mm/s shows the presence of Fe^{3+} species. While the other doublet with δ 1.26 mm/s and Δ 2.96 mm/s indicates the formation of Fe^{2+} species during the thermal degradation of the ferric chloride-containing copolymer. This type of reduction has previously been observed in the case of ferric chloride containing ethyl methacrylate,⁷ but no Fe^{2+} species was detected in the case of ferric chloride containing PMMA, PBuMA,⁶ and MMA-EMA copolymers.⁵ The formation of Fe^{2+} species during the heating process seems to be a feature of EMA polymers. Comparing with the Mössbauer parameters for unheated EMA-*n*BuMA copolymers, not much change in the environment around Fe^{3+} is observed. Spectral fractional intensity data show that 22% of Fe^{3+} is reduced to Fe^{2+} during the initial phase of copolymer decomposition. Any quantitative discussion of IR spectra in connection with the modification of Mössbauer spectra is not possible because Mössbauer spectra reflect the nature and environments of iron in the copolymer and IR spectra were recorded to support the presence of copolymer at various stages of degradation.

Figure 6 shows the Mössbauer spectrum of EMA-*n*BuMA copolymer containing ferric chloride heated at 250°C for 1 h. The spectrum reveals the presence of three doublets. One doublet with δ 0.44 mm/s and Δ 0.53 mm/s is due to the presence of Fe^{3+} species. Not much change in the *s*-electron density around Fe^{3+} is observed, whereas a decreased quadrupole splitting value indicates more symmetric environment around Fe^{3+} species after heating. Two other doublets with δ 1.08, 1.39 mm/s and Δ 2.52, 2.68 mm/s indicate the presence of Fe^{2+} species in high spin state. The different quadrupole splitting values for Fe^{2+} result from their different environments. Spectral fractional intensities from the computer fitted spectrum

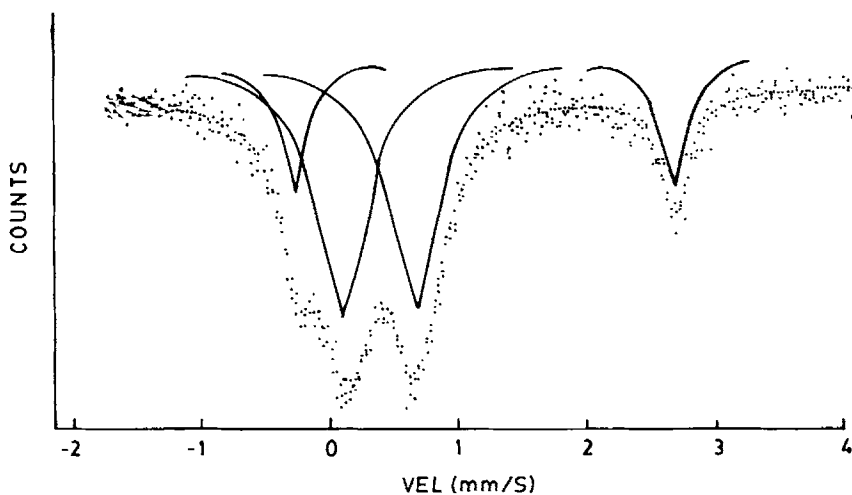


Fig. 5. Mössbauer spectrum of ferric chloride containing EMA-*n*BuMA copolymer heated at 150°C for 1 h.

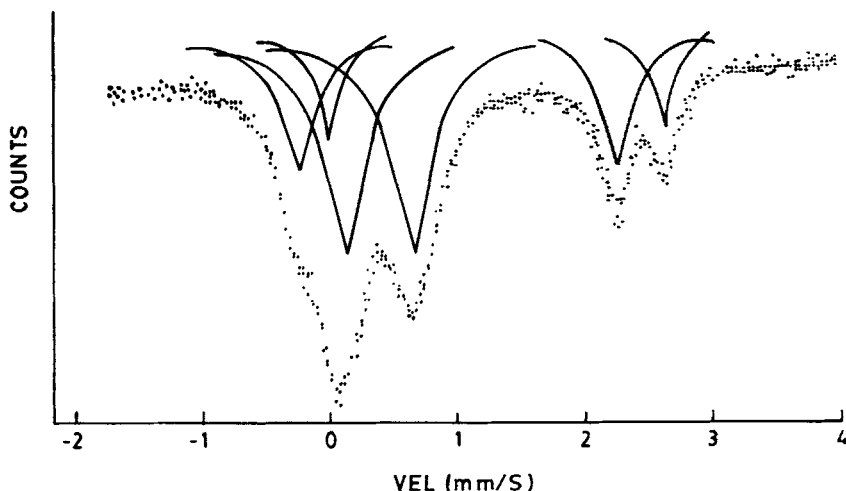
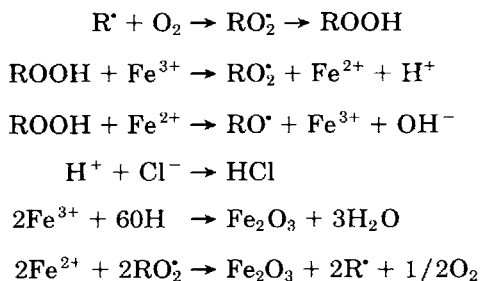


Fig. 6. Mössbauer spectrum of ferric chloride containing EMA-*n*BuMA copolymer heated at 250°C for 1 h.

show that 58% of the iron is present in +3 oxidation state and rest in +2 state.

On heating the copolymer sample at still higher temperature; i.e., at 500°C for 1 h, a sextet is observed in Mössbauer spectrum (Fig. 7). The value of isomer shift, quadrupole splitting, and magnetic field at the nucleus are 0.33 mm/s, 0.42 mm/s, and 512 KOe respectively. These values are indicating the formation of α -Fe₂O₃ and are in good agreement with the literature values.⁹ The infrared spectrum also showed the complete absence of bands due to functional groups of copolymer. TGA, IR, and Mössbauer studies show the complete decomposition of copolymer. The bands observed at 539.4 cm⁻¹ and 457.4 cm⁻¹ are due to α -Fe₂O₃. The ferric chloride-containing copolymer sample heated at 150°C was kept in air for about one month and its Mössbauer spectrum was recorded (Fig. 8). The spectrum shows a doublet with δ 0.39 mm/s and Δ 0.53 mm/s indicating the oxidation of Fe²⁺ species to Fe³⁺ on exposure to air for such a long period.

From the above TGA, Mössbauer, and IR studies, the most probable mechanism for the thermal degradation of EMA-*n*BuMA copolymer containing ferric chloride can be given as follows:



where R represents a polymer chain. The oxidation reduction reaction is re-

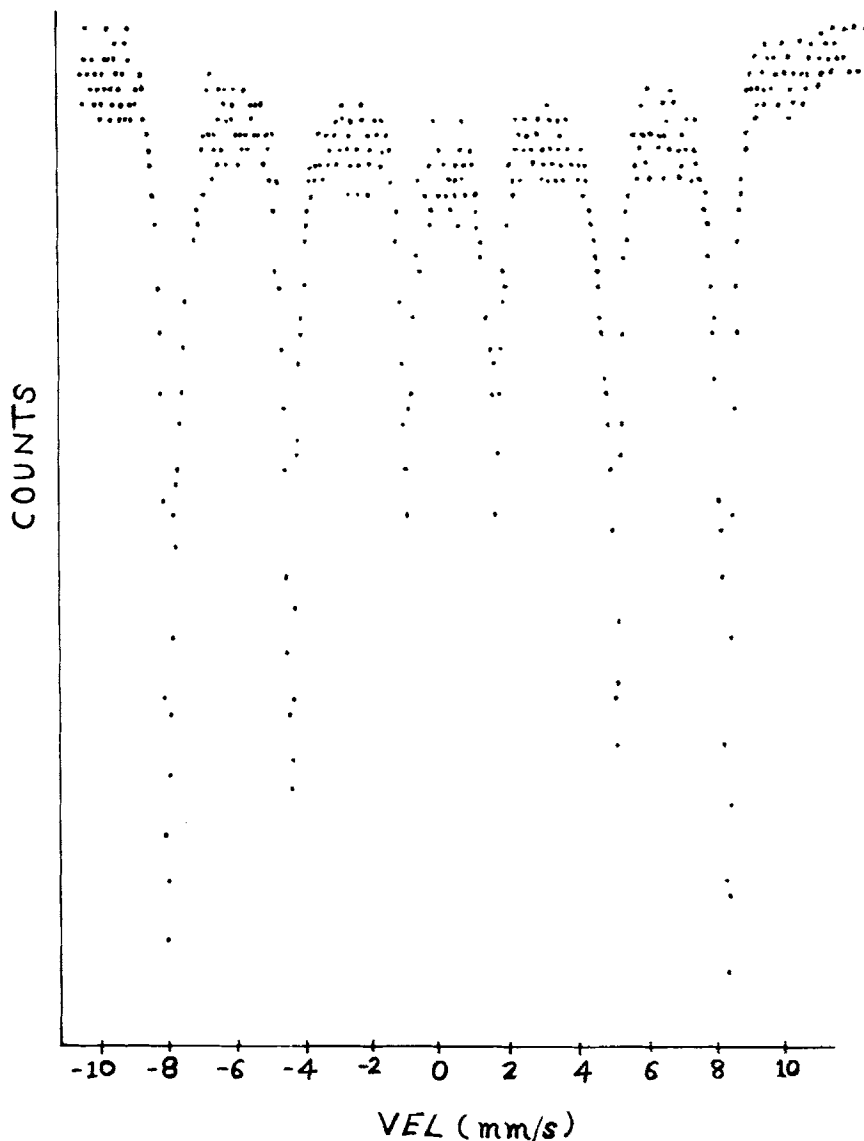


Fig. 7. Mössbauer spectrum of ferric chloride containing EMA-*n*BuMA copolymer heated at 500°C for 1 h.

responsible for the stabilization of copolymer. Iron chloride can participate in reaction with hydroperoxide, with the secondary products of oxidation and with oxygen-containing radicals, as shown in the mechanism. The stabilizing effect of ferric chloride may be due to the incorporation of iron atoms into the copolymer net via oxygen bonds, with additional crosslinks of the $\text{Fe}(-\text{O}-)_n$ type being formed resulting in the improved physico-mechanical properties of the copolymer. The formation of water during thermal degradation was corroborated by the IR spectra of the heated copolymer samples.

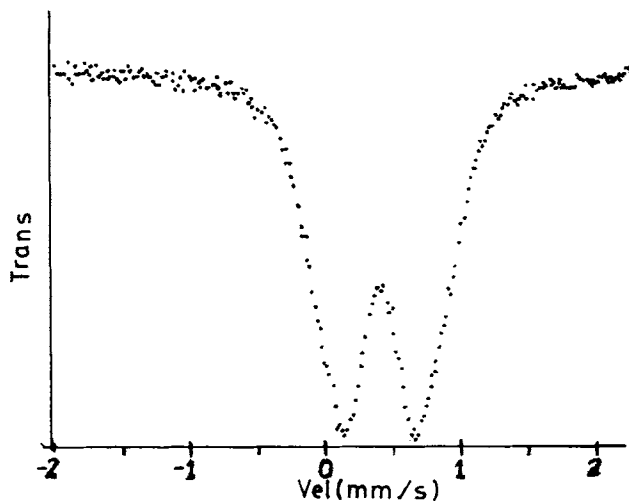


Fig. 8. Mössbauer spectrum of ferric chloride containing EMA-*n*BuMA copolymer heated at 150°C, exposed to air at room temperature for one month.

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