

Mössbauer Studies of Methylmethacrylate and Ethyl Methacrylate Copolymers Containing Ferric Chloride

A. S. BRAR,* A. K. SAINI, and R. K. PURI,† *Department of Chemistry, Indian Institute of Technology, Delhi, New Delhi-110016, India*

Synopsis

The copolymers of methyl methacrylate and ethyl methacrylate containing ferric chloride were prepared with varying compositions and subjected to Mössbauer studies. Mössbauer spectra show no reduction of ferric species to ferrous during the polymerization process. The Mössbauer parameters show the irregular environment around the ferric ion. The TGA studies show the thermal stabilizing behavior of ferric chloride in copolymers.

INTRODUCTION

Mössbauer spectroscopy is a very effective tool for the studies of polymers containing Mössbauer active metal ions (iron and tin).¹⁻³ The change in oxidation state of metal ion and the nature of environments can be investigated very accurately by this technique. Polymers containing metal ions are an important class of materials, due to improved mechanical and thermal properties. It is well known that metal ions incorporated into polymers often crosslink the macromolecular chain and produce a marked modification of their mechanical properties. Atactic polyvinylpyridine containing ferric chloride has been investigated with Mössbauer spectroscopy. Different types of iron centers were characterized from ⁵⁷Fe Mössbauer spectra.⁴ It has been used to study the stabilization of polyethylene with iron chloride. The addition of ferric chloride improves properties of irradiated polyethylene.¹ Perusal of literature shows that no Mössbauer investigation of copolymers of methyl methacrylate (MMA) and ethyl methacrylate (EMA) containing ferric chloride has been reported. In this communication the nature and environments of ferric chloride in MMA-EMA copolymers and its effect on the thermal degradations of copolymers shall be reported using Mössbauer spectroscopy.

EXPERIMENTAL

Preparation of Samples. The polymers and copolymers of MMA and EMA were prepared, with different compositions of copolymers given in Table I, using 1% benzoyl peroxide as an initiator at 50°C. The same samples were prepared containing 2% ferric chloride as a stabilizer. The stabilizer was added

*Author to whom correspondence should be addressed.

†Department of Physics, Indian Institute of Technology, Delhi, New Delhi-110016.

TABLE I
Percentage of Monomers in Copolymer (mol %)^a

Monomers	A	B	C	D	E	F
MMA	0	20.5(26.0)	50.8(49.0)	60.7(64.0)	80.5(82.0)	1.00
EMA	1.00	79.5(74.0)	49.2(51.0)	39.3(36.0)	19.5(18.0)	0.00

^aMole percentage of monomers in copolymers are given in brackets and in feed without brackets.

after 1 h of the start of polymerization. The sample were precipitated with methanol. Ferric chloride retarded the rate of polymerization by taking part in termination reactions. The length of polymerization was from 3 to 3.5 h, approximately. The percentage conversion was 10% (approximately). The percentage of MMA and EMA in different copolymers in unstabilized and stabilized with ferric chloride were within the experimental error.

Mössbauer Measurements. Mössbauer spectra were recorded on a Mössbauer spectrometer "Canbera 31 series" coupled with a multichannel analyzer with constant acceleration drive. The source ⁵⁷Co (Pd) was kept at room temperature. The spectrum of sodium nitroprusside dihydrate has been taken as the standard to calculate Mössbauer parameters. The uncertainty in the values of parameters is $\pm 0.02 \text{ mm s}^{-1}$.

Molecular Weight Determination. Molecular weight was determined by the viscosity measurement method. Chloroform was used as solvent. All the measurements were done at $25 \pm 0.1^\circ\text{C}$. The capillary size of viscometer was 0.5 mm, and the time of flow of pure solvent was 120 s. Since the Mark-Houwink constants for MMA-EMA copolymers are not reported. We have taken the constants equal to that of PMMA from literature.⁵

Thermal Gravimetric Analysis (TGA). TGA of stabilized and unstabilized samples were carried out on TGA (Dupont 1090) in a static air atmosphere. The heating rate was kept at $10^\circ\text{C}/\text{min}$.

RESULTS AND DISCUSSIONS

Isomer shift is useful to determine the oxidation state of iron in the various polymers. The *s*-electron density at iron nucleus is also influenced by the nature of bonding with polymers. Quadrapole splitting values give information about the nature of environments about the iron nucleus (symmetrical or assymmetrical), magnetic hyperfine interaction gives the value of magnetic field at the iron nucleus. All these parameters are useful to determine the nature of bonding of iron with the polymers chain.

Mössbauer spectra of PMMA, PEMA, and MMA-EMA copolymers containing ferric chloride as a stabilizer show iron is in oxidation state $3+$. A doublet was observed in all the cases. Mössbauer spectra was shown in Figure 1. Mössbauer study shows that there is no effect of polymerization process on the oxidation state of iron. Mössbauer parameters of all the samples are shown in Table II. The isomers shift and quadrapole splitting of PEMA are higher than those of PMMA which shows that the substitution of methyl group by ethyl group changes the *s*-electron density of iron and the ethyl group being a bulkier group than methyl, creates more assymmetric environ-

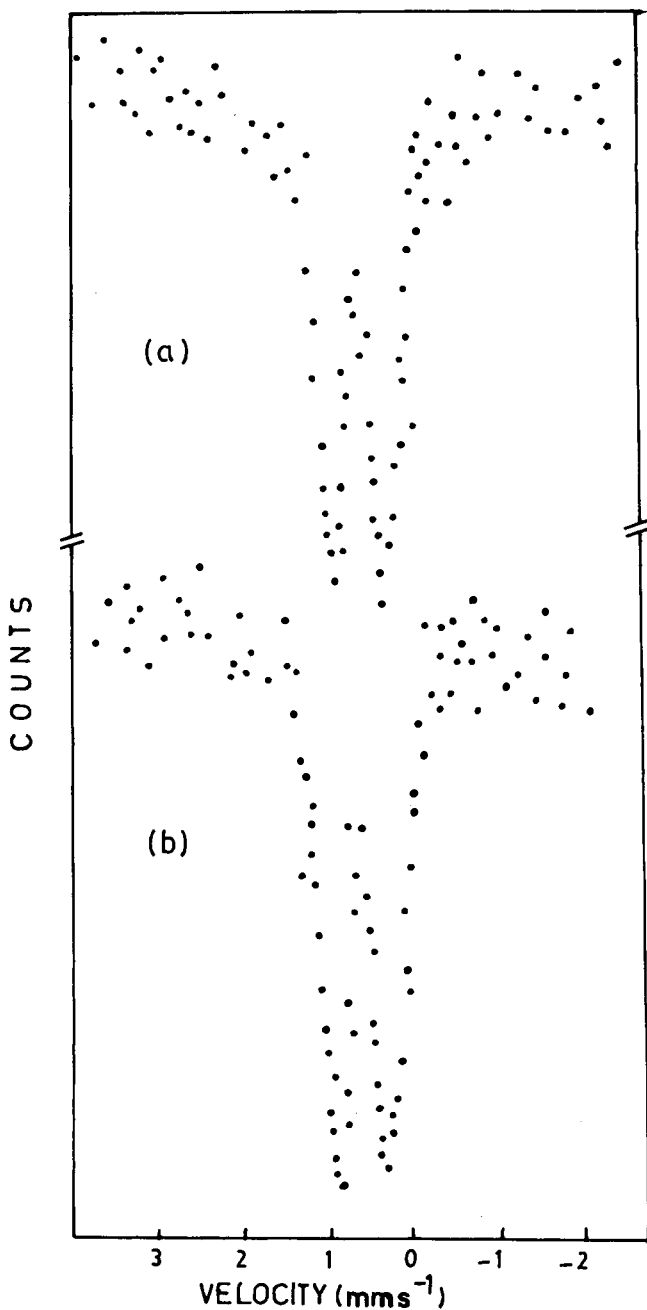


Fig. 1(A). Mössbauer spectra of polymers containing ferric chloride: (a) poly(methyl methacrylate); (b) poly(ethyl methacrylate)

ment and around the iron nuclei. The isomer shifts of all the copolymers are ranging from 0.56 to 0.64 mm s^{-1} , i.e., in between the isomer shifts of PMMA and PEMA. Since there is no regular trend in the isomer shifts of the copolymers, this leads to the conclusion that there is no regularity in the environment of iron nuclei. The irregularity in the environment of iron nuclei

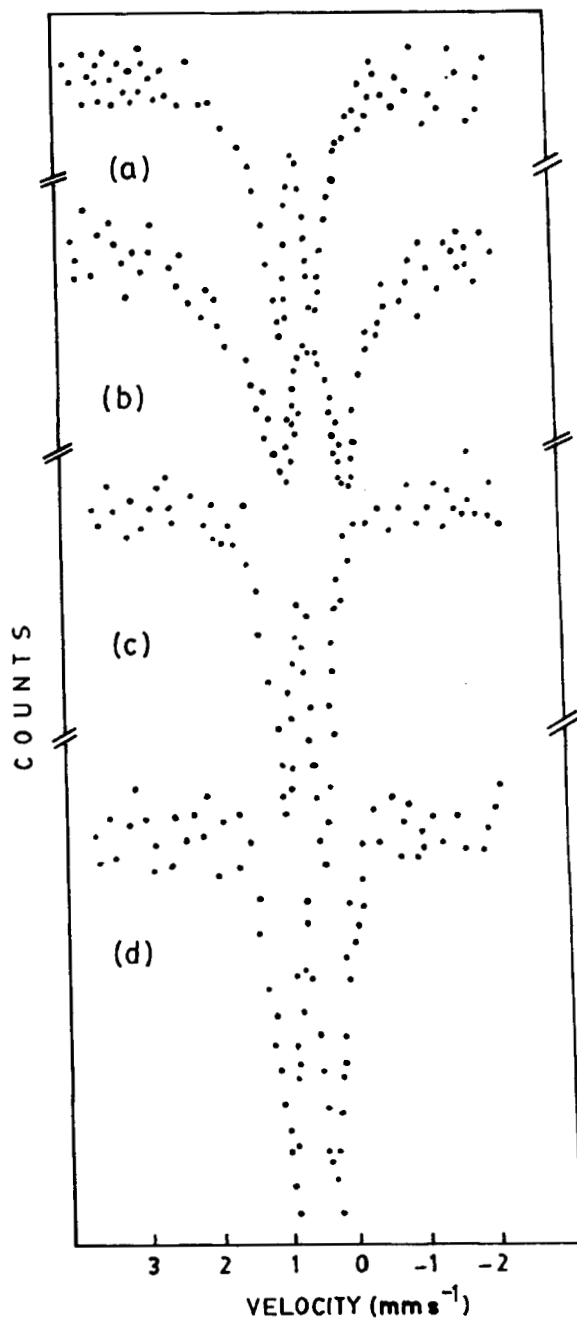


Fig. 1(B). Mössbauer spectra of the copolymers containing ferric chloride: (a) B; (b) C; (c) D; (d) E.

TABLE II
Mössbauer Parameters of the Samples

Samples	Isomer shifts (mm s^{-1})	Quadrupole splitting (mm s^{-1})	Width at half height (mm s^{-1})	
			τ_1	τ_2
A	0.64	0.64	0.22	0.24
B	0.59	0.57	0.19	0.22
C	0.50	0.57	0.24	0.22
D	0.59	0.57	0.22	0.19
E	0.61	0.66	0.19	0.22
F	0.56	0.53	0.22	0.22

is due to the different comonomer composition in the copolymers and the atactic nature of copolymer chains. Had there been regular sequences in the copolymers chains, the isomer shifts would have shown a regular variation with comonomer compositions.

The quadrupole splitting also shows a similar trend in the ferric ion environment. Quadrupole splitting for PEMA is higher than that of PMMA. The range of quadrupole splitting for copolymers is $0.53\text{--}0.64 \text{ mm s}^{-1}$, i.e., in between the quadrupole splitting of PEMA and PMMA showing the irregular variations in the environment of ferric ion.

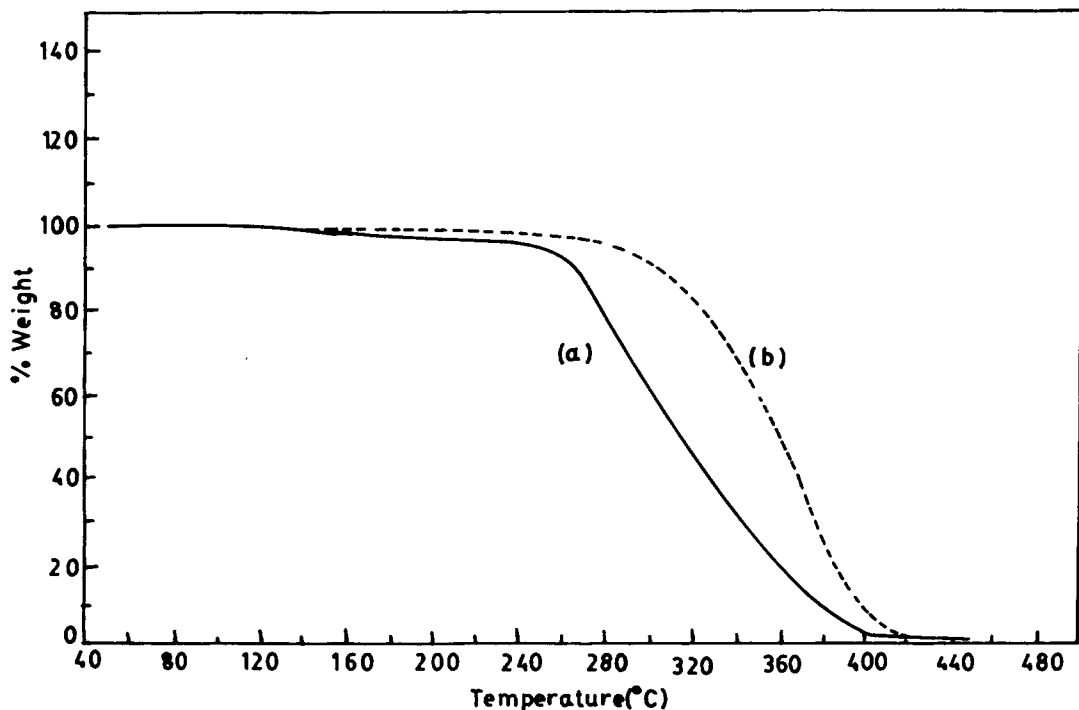


Fig. 2. TGA curves of a copolymer E: (a) without ferric chloride; (b) with ferric chloride

TABLE III
Degradation Temperature of Stabilized and Unstabilized Samples

Samples	Unstabilized			Stabilized		
	Initial temp of degradation (°C)	Temp of maximum degradation (°C)	Final temp of degradation (°C)	Initial temp of degradation (°C)	Temp of degradation (°C)	Final temp of degradation (°C)
A	260	288	360	321	377	420
B	260	286	380	322	380	410
C	252	277	400	312	372	412
D	270	294	385	332	385	416
E	263	285	370	327	381	401
F	280	310	400	342	390	424

TABLE IV
Molecular Weights of Samples^a

Samples	Unstabilized		Stabilized	
	Intrinsic viscosity	Mol wt $\times 10^{-3}$	Intrinsic viscosity	Mol wt $\times 10^{-3}$
A	1.6	26	1.8	28
B	1.6	26	1.6	26
C	1.7	29	1.5	25
D	1.6	26	1.7	27
E	1.6	26	1.6	26
F	1.7	27	1.7	27

^a Mark-Houwink constants $K = 4.8 \times 10^{-3}$ mL/g, $a = 0.8$.

The TGA studies of the samples show that thermal stability of samples has improved tremendously in the presence of ferric chloride. It has been increased by 50–80°C in all samples. TGA curve of stabilized and unstabilized samples are shown in Figure 2. The temperature of thermal decompositions are given in Table III. The stabilizing effect of ferric chloride is due to its participation in the reaction with the oxygen of air, the secondary products of copolymer oxidation and oxygen containing radicals, but during the thermal decomposition no reduction to Fe^{2+} species has been observed.

The viscosity measurements show that there is not much difference in the molecular weight of stabilized and unstabilized copolymers. The values of intrinsic viscosity and molecular weights are given in Table IV. Since the molecular weight of stabilized and unstabilized copolymers are approximately the same this shows that the ferric chloride acts as a stabilizer.

The copolymer sample (C) was exposed to γ -radiations of 100 Mrad. Mössbauer spectrum shows line broadening only. There was no reduction of Fe^{3+} to Fe^{2+} , which shows that ferric species in the copolymers is stable and resistant to degradation.

CONCLUSION

Mössbauer studies show that ferric chloride does not undergo oxidation-reduction reaction during the polymerization processes. The stabilizer increases the stability of copolymers, PMMA and PEMA by approximately 50–80°C. Molecular weights of stabilized and unstabilized samples are of the same order. There was no effect of γ -irradiation on the oxidation state of metal ion contained in samples except line broadening in the Mössbauer spectrum.

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