Polymer Bulletin 26, 665–672 (1991)

Polymer Bulletin

Sorption and thermal polymerization of vinyl monomers in low density polyethylene-iron (III) oxide composite

Mössbauer studies

Maria José Araujo Sales[1], **Vicente Walmick Vieira**[2], **and Glaucione Gomes de Barros**[3]

[1]Departamento de Química FESPI, Ilhéus, Brasil
[2]Departamento de Física, Universidade do Ceará, Fortaleza, Brasil
[3]Departamento de Química, Universidade de Brasília, Brasília, Brasil

ABSTRACT

The nature of the species produced after sorption and thermal polymerization of acrylic acid, methyl methacrylate and 4-vinylpyridine in low density polyethylene-iron (III) oxide composite was investigated by Mössbauer and IR spectroscopies. The values of the Mössbauer parameters indicate no change in the oxidation state of iron (III) in the LDPE-Fe_2O_3 composite before and after sorption and thermal polymerization of the monomers. Acrylic acid interacts with iron (III) oxide particles yielding acrylates, hydroacrylates, polyacrylates and polyhydroacrylates. The iron (III) oxide particles remained unchanged after sorption and thermal polymerization of methyl methacrylate although some thermal polymerization is observed in the presence of Fe_2O_3 -doped LDPE. Iron (III) oxide acts as catalyst for the radical polymerization of methyl methacrylate on LDPE-Fe_2O_3. The interaction of iron (III) oxide and 4-vinylpyridine after its sorption and thermal polymerization in LDPE-Fe_2O_3 is mainly by coordination bonding of the pyridine ring of the polymer to the iron of Fe_2O_3.

INTRODUCTION

Mössbauer spectroscopy has been widely used in polymer research (1,2,3). It was shown to be a powerful method for analysis of the chemical environment of polymers containing a suitable Mössbauer nucleus (4,5). From the Mössbauer parameters (isomer shift and quadrupole splitting) significant information concerning the geometrical arrangement of the coordination sphere and the symmetry of the charge distribution can be extracted (6,7).

Iron (III) oxide doped polytetrafluoroethylene (PTFE) obtained by sorption and *in situ* oxidation of iron pentacarbonyl $Fe(CO)_5$ has been investigated by Mössbauer spectroscopy (8). The iron (III) oxide in PTFE matrix showed to be ultrafine, spherical superparamagnetic particles of α Fe_2O_3. Also the effect of X-rays on preirradiated PTFE-Fe_2O_3 followed by acrylic acid (AA) sorption was investigated by Mössbauer spectroscopy (9).

Low density polyethylene (LDPE) can be modified by acrylic acid (AA) sorption and *in situ* thermal polymerization (10). The extent of AA polymerization is larger in iron (III) oxide doped LDPE. It has also been observed that iron (III) oxide has a strong effect on the thermal polymerizations of methyl methacrylate (MMA) and 4-vinylpyridine (4VP) in LDPE-Fe_2O_3 composite matrix (11).

In this paper, we use Mössbauer spectroscopy to obtain information on the effect of iron (III) oxide on the thermal polymerization of vinyl monomers in LDPE-Fe_2O_3 composite matrix.

EXPERIMENTAL

Acrylic acid (AA) was supplied by Cia. Química Brasileira and destilled under vacuum. Methyl methacrylate (MMA) and 4-vinylpyridine (4VP) were purchased from Aldrich Chem. Co. Hydroquinone monomethyl ether (HMME) was supplied by Cia. Rhodia Brasileira. It was purified by sucessive crystallization in acetone. Iron pentacarbonyl $Fe(CO)_5$ was supplied by BASF (Germany). Low density polyethylene (LDPE) sheets (d=918g/10cm , MI=1.15g/10 min.) were donated by Poliolefinas (São Paulo).

The sorption and in situ oxidation of $Fe(CO)_5$ in LDPE films (3x4cm) followed the procedure previously described (10). The thermal polymerization of vinyl monomers on LDPE-Fe_2O_3 composite followed the procedure described by Barros and Galembeck (10). The reaction was carried out at 90 °C, under N_2 atmosphere.

Infrared spectra were recorded on a Perkin Elmer spectrophotometer mod. 283. The differential spectra were measured using a bare LDPE film in the reference beam. Mössbauer spectra were run before and after the monomer sorption on LDPE-Fe_2O_3 composite. They were obtained at room temperature, using a CO(Rh) source in a conventional constant acceleration spectrometer operating in a transmission geometry mode. Mössbauer parameters were determined by computer fitting using a least-square routine. The required iron content in the sample was 5 mg/cm^2 which was achieved by folding up each film in several layers. The isomer shifts (IS) showed are relative to metallic iron.

RESULTS

Films of LDPE-Fe_2O_3 were immersed in AA (98%), MMA (99%) and 4VP (98%) for specified periods of time at 90 °C. After reaction the films were washed and dried. The mass increase for each sample were calculated by gravimetry. The characteristics of the samples are specified in Table 1.

TABLE 1. Characteristics of sample after sorption and thermal polymerization of vinyl monomers.

Sample	Specification	Fe_2O_3 (%)	Mass Increment After Reaction (%)
S1	LDPE-Fe_2O_3	0.3	-----
S2	LDPE-Fe_2O_3 After AA Sorption	0.5	1.7
S3	LDPE-Fe_2O_3 After MMA Sorption	0.4	49.8
S4	LDPE-Fe_2O_3 After 4VP Sorption	0.6	1.5

The IR spectra of the samples are shown in Fig. 1. Fig. 1a shows the IR spectrum of LDPE-Fe_2O_3 after AA sorption at 90 ^oC (sample S2). The spectrum showed strong absorption at 1770 cm $^{-1}$ (ν , C=O) and peaks at 1630 cm^{-1} (ν, C=C) characteristic of AA monomer and at 1520-1570 cm $^{-1}$ (ν_a , COO $^-$) as discussed in previous work (10). LDPE-Fe_2O_3 after sorption and thermal polymerization of MMA (sample S3) showed an IR spectrum with a peak at 1730 cm^{-1} (ν, C = O) and absence of the peak at 1630 cm $^{-1}$ (ν , C = C) Fig. 1b. The spectrum of LDPE-Fe_2O_3 after sorption and thermal polymerization of 4VP (sample S4) showed peaks at 1610 cm $^{-1}$ (ν , C = C of pyridine ring) and at 840 cm $^{-1}$ (δ , CH of pyridine ring) and absence of the peak at 940 cm $^{-1}$ (δ , CH vinyl) (Fig. 1c).

The Mössbauer spectra of samples S2, S3, S4 and LDPE-Fe_2O_3 composite (S1), are shown in Fig. 2. The spectra showed similar patterns of a doublet typical of superparamagnetic particles (12). However the Mössbauer parameters showed different values (Table 2).

TABLE 2. Mössbauer parameters of LDPE-Fe_2O_3 after sorption and thermal polymerization of vinyl monomers.

Sample	IS (mm/s)	QS (mm/s)	Γ (mm/s)
S1	0.36	0.79	0.31
S2	0.36	0.82	0.26
S3	0.43	0.61	0.45
S4	0.22	0.36	0.32

The sample S1 (LDPE-Fe_2O_3) exhibited IS=0.36 mm/s characteristic of Fe(III) with coordination or ionic bond (13). This value was similar to that found to iron (III) oxide doped PTFE matrix (IS-0.31-0.38 mm/s) (14). The quadrupole splitting (QS) of 0.79 mm/s is characteristic of Fe(III) with a highly asymmetric charge environment and it is in the range of the value found to PTFE-Fe_2O_3 (QS= 0.66-0.86 mm/s) (14). According Kündig et al. (15) the QS value found suggest an average of diameter particle size of 180-100A^o to the superparamagnetic Fe_2O_3 particles in LDPE matrix, previously suggested to Fe_2O_3 doped PTFE (8).

LDPE-Fe_2O_3 after AA sorption and thermal polymerization (S2) showed Mössbauer parameters values of IS 0.43mm/s and QS = 0.62 mm/s. They were quite different of those found to LDPE-Fe_2O_3 and PTFE after AA sorption (9) but quite similar to the values found to PTFE-Fe_2O_3 preirradiated or after acetic acid sorption (Table 2). Theses values are similar to the values found in the literature to iron (III) acrylate (17). The IR spectrum of the sample S2 also exhibited peak at 1520-1570 cm $^{-1}$ (ν a, COO$^-$) (10). In this way iron (III) acrylate, hydroacrylate, poly (acrylate) and poly (hydroacrylate) are found in LDPE-Fe_2O_3 after sorption

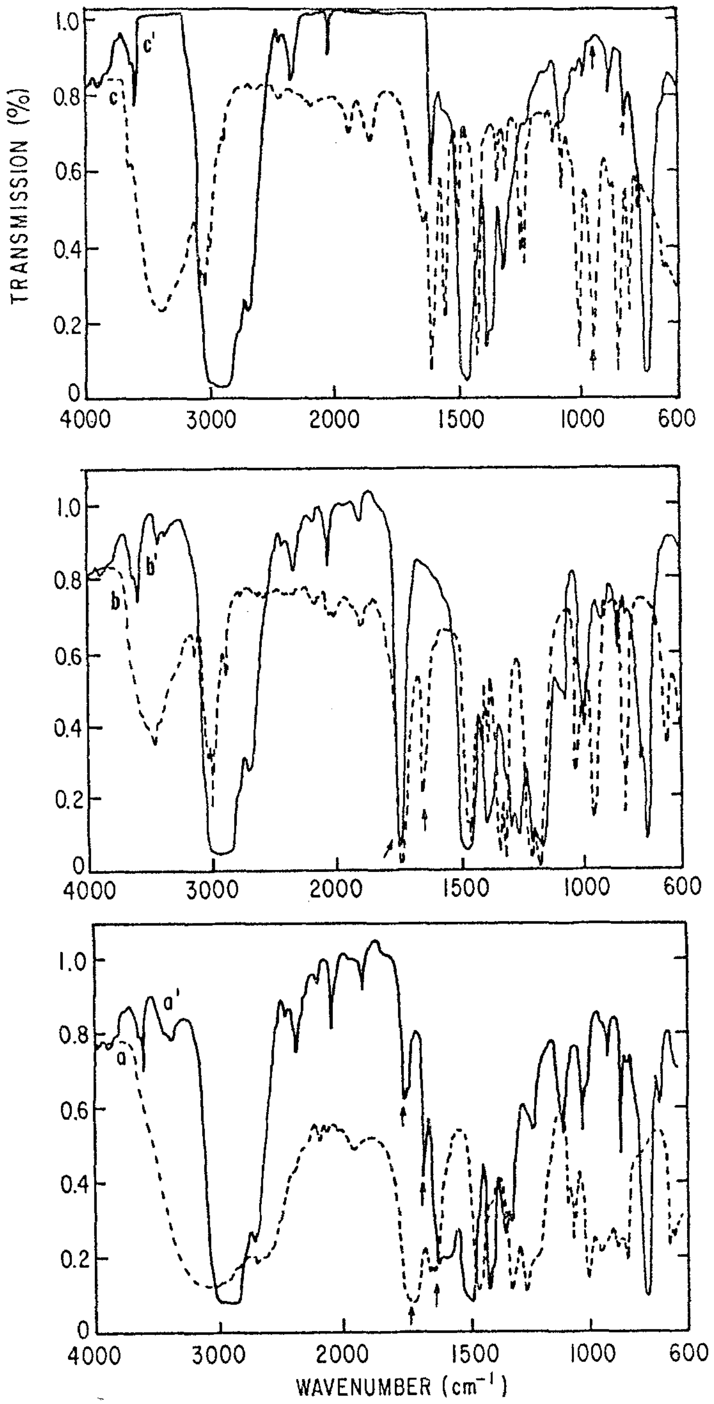


Fig. 1 IR spectra of LDPE-Fe_2O_3 after sorption and thermal polymerization of vinyl monomers. (a) AA; (b) MMA; (c) 4VP; (a', b', c') after sorption and thermal polymerization of the monomers. Reaction temperature: 90 °C.

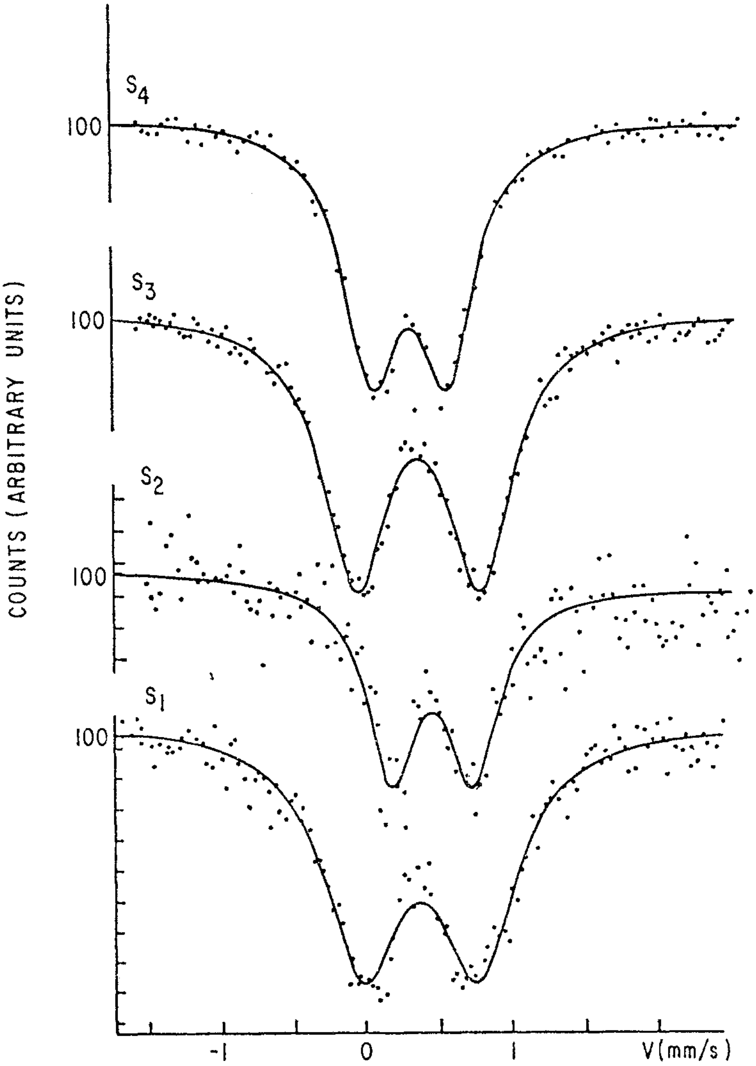


Fig. 2 Mössbauer spectra.

(S1) LDPE-Fe_2O_3; (S2) AA; (S3) MMA and (S4) 4VP after their sorptions and thermal polymerizations on LDPE-Fe_2O_3.

and thermal polymerization of AA confirming our previous work (10).

LDPE-Fe_2O_3 composite after sorption and thermal polymerization of MMA (S3) showed no significant changes of their Mössbauer parameter values (IS = 0.36 mm/s and QS = 0.82 mm/s) as compared to that obtained to LDPE-Fe_2O_3 (Table 2). This suggests the same environment for iron (III) oxide particles before and after MMA sorption and thermal polymerization. The Fe_2O_3 particles in LDPE matrix do not interact with MMA during the thermal polymerization into the matrix.

The Mössbauer spectrum of LDPE-Fe_2O_3 after sorption and thermal polymerization of 4VP exhibited different parameters compared to those observed for LDPE-Fe_2O_3 (Table 2). The IS value of 0.22 mm/s and QS = 0.36 mm/s are lower than those observed to LDPE-Fe_2O_3. The low values of IS and QS indicate that Fe (III) is in a quite symmetric and in a high electronic density environment. Also, the IR spectrum of LDPE-Fe_2O_3 after sorption and thermal polymerization of 4VP showed a shift of 5cm^{-1} of the peak at 1605 cm^{-1} (ν , C-C pyridine ring). The low IS value and the shift observed in the IR spectrum suggest a coordination of iron (III) to poly (4VP) (1).

DISCUSSION

The Mössbauer spectra recorded for several samples revealed the nature of the species produced after the sorption and thermal polymerization of the monomers AA, MMA and 4VP on the composite matrix LDPE-Fe_2O_3. Several proposals for the effect of iron(III) oxide on the radical polymerization of vinyl monomers are discussed in the literature (17, 18).

Iron (III) oxide can act as (18, 19):

i) catalyst, in the polymerization of MMA in aqueous solution by lowering the activation energy of the reaction: ii) reaction activator by electron transfer mechanism,

$$M + Fe(III) \longrightarrow M^{\cdot} + Fe(II) + H^+$$

iii) inhibitor,

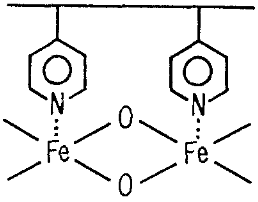
$$R^{\cdot} + Fe(III) \longrightarrow R^+ + Fe(II) \quad \text{or,}$$

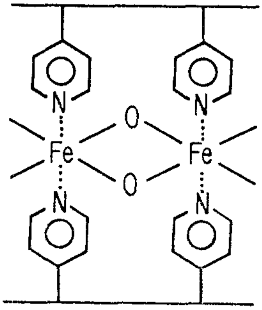
$$R^{\cdot} + Fe(III) \longrightarrow R + Fe(II) \quad H^+$$

However, Mössbauer spectroscopy studies showed no changes in the oxidation state of iron (III) on LDPE-Fe_2O_3 composite before and after sorption and thermal polymerization of AA, MMA and 4VP.

The iron (III) oxide remained unaltered after sorption and thermal polymerization of MMA in LDPE-Fe_2O_3 although, the thermal polymerization of MMA can be increased by Fe_2O_3 doped in LDPE (11). Such behavior was previously observed using AA (10). It is probable that iron(III) is acting as catalyst on the radical polymerization reaction lowering the activation energy reaction of MMA (17). These results also confirmed that the AA interaction with iron (III) oxide after it sorption and thermal polymerization on LDPE-Fe_2O_3 matrix is on surface of oxide particles which can absorb the AA monomer (producing acrylates, hydroacrylates, etc) increasing its local concentration and therefore the polymer formation as suggested previously (10). In this case, no change of the oxidation state of iron (III) oxide was detected by Mössbauer spectroscopy possibly due to the low concentration of the oxidized species.

Finally, the results obtained using LDPE-Fe_2O_3 after sorption and thermal polymerization of 4VP suggest a coordination bonding between the iron (III) oxide and poly 4VP produced into the matrix. The following squemes are proposed for the interaction:





ADKNOWLEDGMENT

We thanks Prof. H. Frisch for the review of this text. This work was supported by CNPq (Brasilian Research Foundation) grants.

REFERENCES

1. Coey J. M.D., Meagher A., Kelly J.M. and Vos J.G., (1984) J. Polymer Sci. Polym. Chem. Ed: 22: 303

2. Kucharski Z., Pron A., Suwalski J., Kulszewicz I., Billand D. and Bernier P., (1984) Solid State Comm. 50 (15): 397

3. Rachlewicz K., Pretrzyk J. and Drabent K., (1985) Thermochimica Acta 93: 81

4. Bauminger E.R., May L., Nowik I. and Heitner-Wirquin C., (1986) Hyperfine Interactions 29: 1335

5. Kucharski Z. Josefowicz M., Suwalski J., Pron A. and Lefraut Z., (1985) Mol. Cryst. Liq. Cryst. 117: 133

6. Brooks J.S., Care C.M. and Plimley S. (1984) Hyperfine Interactions 20: 151

7. Huang T.C. and Wei H.H. (1986) Hyperfine Interactions 28: 887

8. Galembeck F., Leite N.F., Miranda L.C.M. Rechenberg H.R. and Vargas H. (1980) Phys. Stat. Solid (a) 60: 63

9. Barros G.G. de and Galembeck F. (1987) J. Polym. Sci. Part. A: 25: 2369

10. Barros G.G. de and Galembeck F. (1986) Polym. Bull. 16: 499

11. Sales M.J.A. and Barros G.G. de, to be published

12. Greenwood N.M. and Gibbs T.C. (1971) Mössbauer Spectroscopy, Chapman and Hall London

13. Janot L. and Decroix P. (1976) Centre de Researches Arqueologiques Notes et Monographies Techniques No. 4, CNRS

14. Barros G.G. de, Vieira V.W. and Galembeck F. (1988) Polym. Bull. 19: 275

15. Kündig, W., Bömmel H., Constabaris G., Lindquist R.H. (1966) Phys. Rev. 142: 327

16. Sharma P.R., Grupta H.M. and Tripathi K.C. (1982) Proc. International Conference of Application of Mössbauer Effect. Indian National Academy p. 409

17. Amoustafa A.B., Abd-el-Hakim AA. (1976) J. Polym. Sci Polym. Chem. Ed. 14: 433

18. Yamaguchi T., Tanaka H., Moustafa A.B., Ono T., Ito H., Itabashi O., Endo M., Ohuchi M. and Saito L. (1974) Chem. & Ind. 619

19. Narita H., Sakamoto Y. and Machida S. (1972) Makromol.Chem. 152: 143

Accepted May 29, 1991 K