Polymer Bulletin 1, 723–725 (1979)

Polymer Bulletin

Synthesis of Some New Divalent Metal Salts of Mono(hydroxyethyl)phthalate

B. Durairaj and K. Venkatarao

Department of Physical Chemistry, University of Madras,
A. C. College Campus, Madras-600 025, India

Summary

Divalent metal salts of mono(hydroxyethyl)phthalate (HEP) were considered to be of interest as difunctional ionic monomers and are useful for the preparation of condensation polymers. Recently, Matsuda[1] reported the preparation of Ca, Mg and Zn salts of mono(hydroxyethyl)phthalate and their polymers[2-7]. He prepared these salts by the reaction of HEP with the respective divalent metal oxides. But so far there was no report on the preparation of Pb^{2+} and Mn^{2+} salts of HEP. Since metal dicarboxylates can be obtained by the reaction of organic dibasic acids and metal acetates[8], Pb^{2+} and Mn^{2+} acetates can similarly react with HEP to give their respective salts at the optimum temperature. We report here the synthesis and characterisation of Pb^{2+} and Mn^{2+} salts of mono(hydroxyethyl)phthalate (HEP).

Preparation of Divalent Metal Salts of mono(hydroxyethyl)phthalate

A three-necked flask was fitted with a stirrer, a condenser and a thermometer. In this 124 g (2 mole) of ethylene glycol was placed. Then 74 g (0.5 mole) of phthalic anhydride was added slowly with stirring at 85 - 90°C over 30 min. After this, the reaction mixture was stirred continuously for 2 hr at the same temperature and 82 g (0.25 mole) of $Pb(CH_3COO)_2.3H_2O$ (experiment (1)) or 61.24 g (0.25 mole) of $Mn(CH_3COO)_2.4H_2O$ (experiment (2)) was added to the hot reaction mixture. The product began to separate as a precipitate within 10 min but the stirring was continued for additional 30 min at the same temperature. The precipitate separated was treated as follows:

In the case of experiment (1) the precipitate was filtered, washed several times first with acetone, then with dilute acetic acid (0.5% v/v) (to remove unreacted lead acetate) followed by water and finally with acetone.

0170-0839/79/0001/0723/$01.00

In the case of experiment (2) the precipitate was filtered, washed several times first with acetone, then with absolute ethanol (to remove unreacted manganese acetate) and finally with acetone. The precipitate was dried in vacuo at 70°C.

The details of preparation and analytical data for Pb^{2+} and Mn^{2+} salts are shown in Table I and Table II. For both the salts the experimentally determined values of percentage of hydroxyl group, elemental analysis and percentage of metal content are found to agre with the calculated values.

Table I

Synthesis of Divalent Metal salts of HEP

Metal	Experiment	Mole ratio of EG/PA	Reaction temperature	Time hr	Yield %	Colour
Pb	1	4	85 - 90°C	3	84	White
Mn	2	4	85 - 90°C	2.5	87	Pale pink

EG : Ethylene glycol; PA : Phthalic anhydride

Table II

Analytical Data for Divalent Metal salts of HEP

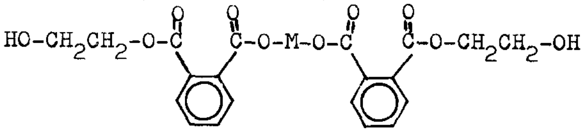
Expt.	Metal salt	Hydroxyl group %	Elemental Analysis C%	H%	M%
1	Pb(2+) salt				
	Found:	2.36	38.04	2.53	33.5
	Calcd:	(2.72)	(38.41)	(2.88)	(33.1)
2	Mn(2+) salt				
	Found:	2.50	50.66	3.66	11.8
	Calcd:	(3.59)	(50.77)	(3.80)	(11.6)

Infrared spectra of the metal salts were taken in Perkin Elmei 577 spectrophotometer using KBr disc method. The spectra were identical, showing the absorptions at 3500 cm^{-1} (Pb salt), 3470 cm^{-1} (Mn salt) (OH-stretching); 1730 cm^{-1} (Pb salt), 1705 cm^{-1} (Mn salt) (C=O stretching) and 1410 cm^{-1} and 1585 cm^{-1} (Pb and Mn salt) characteristic of carboxylate groups.

TGH curves of the above two salts were taken in a Perkin Elmer TGS-2 instrument in nitrogen atmosphere. The TGA curves show that the Pb salt starts to decompose at 147°C whereas for the Mn salt the initial decomposition starts only at 251°C.

The Mn salt is soluble in water whereas the Pb salt is insoluble. Further both the salts are insoluble in all other organic solvents.

The structure of the above two salts is



M = Mn or Pb

Condensation polymers of these monomers with different isocyanates have been sythesised and their characterisation is unde
progress.

Acknowledgment

One of the authors (B.D.) is thankful to University Grants Commission for the award of a Junior Research Fellowship. We are also thankful to Prof. H. Kothandaraman for his encouragement to do this work.

References

1) H.MATSUDA, J. Polym. Sci. Polym. Chem. Ed., **12**, 455 (1974)
2) H.MATSUDA, J. Polym. Sci. Polym. Chem. Ed., **12**, 469 (1974)
3) H.MATSUDA, J. Polym. Sci. Polym. Chem. Ed., **12**, 2419 (1974)
4) H.MATSUDA, J. Macromol. Sci.-chem., **A9**, 397 (1975)
5) H.MATSUDA, J. Polym. Sci. Polym. Chem. Ed., **14**, 1783 (1976)
6) H.MATSUDA, J. Appl. Polym. Sci., **20**, 995 (1976)
7) H.MATSUDA, J. Macromol. Sci,-chem., **A10**, 1143 (1976)
8) J.ECONOMY, J.H.MASON and L.C.WOHRER, J. Polym. Sci. Polym. Chem. Ed., **8**, 2231 (1970)

Received July 19, 1979