

was filtered under reduced pressure, then washed several times with methanol and after drying weight recovered was (0.1 gm).

2-3-2 Preparation of polymeric S-o-chlorobenzyl xanthate

Prepared by dropwise addition of o-chlorobenzyl chloride (0.36gm, 2.27 mmole) to the aqueous xanthate solution (12 ml, 2.27 mmole).

The mixture was heated under reflux for 1hr and after evaporation of the solvent the precipitate formed was filtered under reduced pressure and washed with methanol several times and weight after drying was (0.12 gm).

2-4 preparation of polyene

(0.18gm) polymeric S-o-chlorobenzyl xanthate was heated in an opened round bottomed flask (25 ml) in oil bath and the temperature was raised to 280°C for 1hr then the heating was continued for 7hrs after lowering the temperature to 250°C, weight recovered was (0.155 gm).

2-5 preparation of polymeric ammonium xanthate

A solution of ammonium chloride (0.121 gm, 2.27 mmole) in water (10 ml) was added to (12 ml, 2.27 mmole) of aqueous xanthate solution with stirring then the solution was heated under reflux for 1hr then the colour of the solution changed to yellowish green then the solution was heated further for 3hrs and the mixture was transferred into a beaker (50 ml) then some of the solvent was evaporated then a colourless rubbery material was formed then filtered and after washing several times with diethyl ether with stirring a white precipitate was formed then after drying weight recovered was (0.21gm).

2-6 Preparation of crosslinked polymeric dixanthate

Iodine (0.86 gm, 3.4 mmole) was dissolved in potassium iodide (10 %, 15 ml), the mixture was heated under reflux for 15min then a red solution was formed then the aqueous xanthate solution (34 ml, 6.8 mmole) was added step by step to the iodine solution, then the mixture was heated on a water bath for 2hrs then a white precipitate was formed and after filtration under reduced pressure washed several times with hot water then after drying weight recovered was (0.025 gm).

3 – Results and discussion :

3-1 Esterification of polymeric xanthates

Polymers (1) and (2) in scheme 1 were prepared by the condensation reaction of polymeric sodium xanthate salt with 1,3-dibromopropane and o-chlorobenzyl chloride respectively.

The structure of polymer (1) was supported by the infrared spectrum which showed a strong band at (1074 cm^{-1}) due to $\nu_{\text{str.}}$ of (C = S) bond and a band at (1251 cm^{-1}) due to $\nu_{\text{str.}}$ of (C – O) bond of ester.

The product was analysed for (C, H, S) elemental analysis giving the following results (C = 35.67 %, H = 5.56 % and S = 2.63 %) with a degree of substitution (Ds) of 5 % depending on sulfur analysis.

Also the infrared spectrum of polymer (2) showed a strong band at (1093 cm^{-1}) due to $\nu_{\text{str.}}$ of (C = S) bond and a band at (1236 cm^{-1}) due to $\nu_{\text{str.}}$ of (C – O) bond of ester. Also the spectrum showed a band at (1575 cm^{-1}) due to (C = C) aromatic and a band at (744 cm^{-1}) due to

(C – H) aromatic out of plane bending for 1,2-disubstitution benzene.

The uv spectrum showed three bands at (195, 260, 308 nm) due to $n - \sigma^*$, B – band, $n - \pi^*$ transitions respectively.

3-2 Polymeric ammonium xanthate

It was prepared by the reaction of polymeric sodium xanthate with ammonium chloride as shown in scheme 1.

The IR spectrum showed a characteristic absorption of (–NH) bending at (1404 cm^{-1}) and (–NH) stretching at (3141 and 3041 cm^{-1}) and a medium stretching band at (1095 cm^{-1}) due to (C = S) bond and at (1139 cm^{-1}) due to (C – O) of ester respectively.

The uv spectrum showed bands at (195, 210, 276 nm) due to $n - \sigma^*$, $\pi - \pi^*$, $n - \pi^*$ respectively.

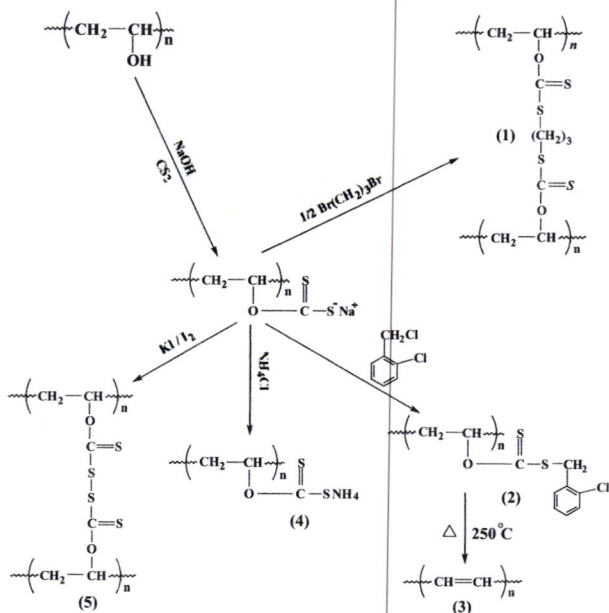
3-3 Polymeric crosslinked dixanthate

This polymeric material has been prepared by the reaction of aqueous polymeric sodium xanthate with iodine in potassium iodide with heating as shown in the experimental part and structure was supported by observing two characteristic stretching absorptions at (1085, 1095 cm^{-1}) due to (C = S) and (C – O) respectively, also the spectrum showed a strong band at (462 cm^{-1}) due to (S – S) str. v.b..

3-4 Elimination reaction of polymeric xanthates ester

The polymeric S-O-Chlorobenzyl xanthate was heated to above 280 °C in an opened vessel for about 8hrs.

The reaction shown in scheme 1 and the structure of the product was supported by the IR spectrum which showed a strong band at (1652 cm^{-1}) due to str. of (C = C) and at (680 cm^{-1}) due to the bending vib. of olefinic (C–H) and also showed the disappearance of absorptions at (1236, 1093 cm^{-1}) due to (C – O), (C = S) str. respectively and also the disappearance of the (C = C) str. and (C–H) bend. at (1575, 744 cm^{-1}) of benzene ring respectively.



Scheme 1: preparation and reactions of polymeric xanthate sodium salt .

4 – Reference :

- 1- P. Hodge and D. C. Sherrington , polymer – supported reactions in organic synthesis , wiley , (1980).
- 2- T. Morikawa, Sci. Ind. (japan), 27, 291, (1953); [Chem. Abstr. 49, 1585, (1952)].
- 3- I. M. Fingauz , M. P. Dokuchaev , A. F.V. Eva and G. A. Shirikova , J. poly. Sci, 56, 245, (1962) .
- 4- C. S. Lee and W. W. Daley , Adv. Polym. Sci., 15, 61, (1974) .
- 5- M. Chanda , K. F. O. Drisscoll and G. M. Rempel, Reactive polym. 5, 157 and 225, (1987) .
- 6- N. Zain al-Abdeen, M. Sc. Thesis, univ. of Tikrit, (1996).