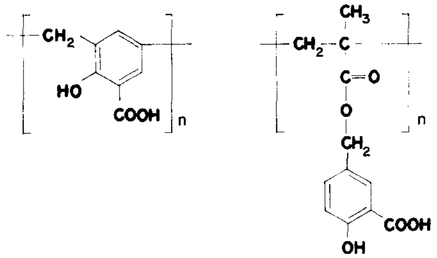
European Polymer Journal. Vol. 12. pp. 525 to 528. Pergamon Press 1976. Printed in Great Britain.

REVERSIBLE CROSS-LINKING BY COMPLEX FORMATION. POLYMERS CONTAINING 2-HYDROXYBENZOIC ACID RESIDUES

DIETRICH BRAUN and HRISANTA BOUDEVSKA*
Deutsches Kunststoff-Institut, Schlossgartenstrasse 6R, D 61 Darmstadt, Germany

(*Received* 3 *September* 1975)

Abstract—Two types of polymers containing 2-hydroxybenzoic acid residues and with the following structures have been prepared:



Complex formation between both polymers and iron(III)-ions leads to cross-linked products. The cross-linking bridges were destroyed by binding the iron in a complex with ethylene diamine tetra-acetic acid.

INTRODUCTION

To study the cross-linking of polymer molecules and to investigate the behaviour of macromolecules in concentrated polymer solutions, we have been searching for fast and simple reactions leading to intra- and intermolecular cross-linking. For this purpose, reactions of polymers and copolymers of *p*-vinyl diphenyl ethylene with sodium have been investigated. These reactions result in the fast formation of radical anions which can easily combine to form cross-linked polymers [1, 2]. The linear polymer is obtained by a polymer analogous reaction of poly-(*p*-vinyl benzophenone). The reaction does not proceed easily and work with radical anions requires special conditions. Furthermore, the cross-links cannot be split again at definite places without affecting the main polymer chains.

Another possibility to perform cross-linking is to use polymers containing complex-forming groups. Most of the reactions of complex formation are very fast and proceed at room temperature. A special requirement for this type of reaction to achieve cross-linking is that the molar ratio of the ligand groups for complex formation in the polymer chain to the complexing agent must be at least two. The stability constant of the complex must be sufficiently high to form cross-linked polymers with strong bridges between the chains. These bridges have the advantage of being destroyed easily when necessary by binding the complex-forming agent in a more stable complex with a suitable low molecular ligand.

As a model for the complex-forming unit in the present investigation, 2-hydroxy benzoic (salicylic) acid was chosen, since its complexes with metals have been well studied. Moreover, chelate complexes of the polycondensation product of salicylic acid with formaldehyde have been obtained with the goal of preparing thermoresistant polymers [3]. The complex-forming reactions in such condensations are not considered to lead to cross-linked products.

Two types of polymers were investigated in the present work: one type containing the 2-hydroxybenzoic residue in the macromolecular chain and the other type having the 2-hydroxybenzoic as a side group on the main chain. Both polymers were transformed into insoluble cross-linked products with iron(III)-ions. The latter form a series of stable complexes with salicylic acid [4]. The cross-linking bridges were destroyed by treating the polymer complexes with a solution of ethylene diamine tetra-acetic acid.

EXPERIMENTAL

Condensation product of salicylic acid with formaldehyde (SAF) [3]

A mixture of salicylic acid (150 g), 35% aqueous formaldehyde (114 g) and oxalic acid (1 g) was heated to 80°; 18% HCl solution (100 ml) was added. The mixture was refluxed with good stirring until a fine white precipitate was formed. The precipitate was filtered, washed with boiling water and dried at 60° under vacuum, to yield 200 g. The polymer was reprecipitated with hot ethanol containing 25% water. Elemental analysis: C = 62.5%, H = 4.3% (calc. C = 63.6%, H = 4.0%); acid number 252 (calc. 265); intrinsic viscosity in acetone at 20° 3.2 cm^3/g.

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* Present address: Central Laboratory for Polymers, Sofia 13, Bulgaria.

Poly (3-carboxy-4-hydroxy benzyl methacrylate) (PCHBM)

1. *5-Chloromethyl salicylic acid (CMSA)* [5]. Salicylic acid (50 g) was dissolved in dioxan (100 ml) and 35% aqueous formaldehyde (100 ml) was added. The solution was saturated with HCl by passage of the gas. During this process the temperature increased to 40–50°. To maintain the temperature at 50°, the reaction vessel was cooled with ice. The reaction mixture was allowed to stand for 12 hr at room temperature before pouring into cold water (500 ml). The precipitate was filtered and dried in vacuum over $CaCl_2$; yield 57.4 g; recrystallized from dry benzene, m.p. 110–120°.

2. *Potassium methacrylate.* K_2CO_3 (55 g) was mixed with ethanol (500 ml). Methacrylic acid (69 g) (99%, stabilized with 200 ppm hydroquinone, Merck) was dropwise added by stirring and refluxing. The reaction mixture was refluxed for 2 hr, then filtered. The filtrate was cooled and the crystals filtered and washed with ether; yield 44 g.

3. *3-Carboxy-4-hydroxy benzyl methacrylate (CHBM).* Potassium methacrylate (3.7 g) was dispersed in dimethylsulphoxide (40 ml). Crude CMSA (5.6 g) was added to the mixture. It was allowed to stand at room temperature for 12 hr. The reaction mixture was then poured into cold water (300 ml). The product was dried in vacuum at room temperature; yield 5.5 g, m.p. 78–80°. Elemental analysis: C = 59.2%, H = 4.7% (calc. C = 61.0%, H = 5.1%). On standing or recrystallizing, the product converted to a resin-like material.

4. *Polymerization of CHBM.* CHBM (3.5 g) was dissolved in acetone (14 g) or ethyl acetate. The white precipitate was filtered off. Azoisobutyronitrile (0.003 g) was added to the solution and the latter refluxed for 28 hr. The solution was poured into ether (140 ml) at 5°. The precipitate formed was filtered, washed with cold ether and dried in vacuum at room temperature; yield 0.5 g. Intrinsic viscosity in acetone at 20° 7.0 cm^3/g.

Complexes with iron(III)-ions

1. *Complex of salicylic acid.* A solution (0.1 M, 5 ml) of salicylic acid in ethanol was mixed with 0.1 N sodium hydroxide (5 ml) (bromothymol blue). A solution of $FeCl_3$ (0.1 M with pH = 1) (2 ml) was added. A blue-violet colour appeared. There was no formation of precipitate; pH = 4.

2. *Complex of SAF.* SAF (3.02 g) was dissolved in ethanol (50 ml). NaOH (1 N, 18 ml) was added to the solution (bromothymol blue). $FeCl_3 \cdot 6H_2O$ (2.7 g) was dissolved in water (50 ml) and 36% HCl (1.5 ml) was added; pH = 2. The solution of SAF was poured into the solution of $FeCl_3$ at 20° with stirring. A brown precipitate was formed immediately; pH = 4. The precipitate was filtered and dried in vacuum at 50°; yield 2.85 g. The product was extracted in a Soxhlet apparatus for 12 hr. Iron content in the complex 0.320 g (11.2%); iron content in the filtrate 0.229 g.

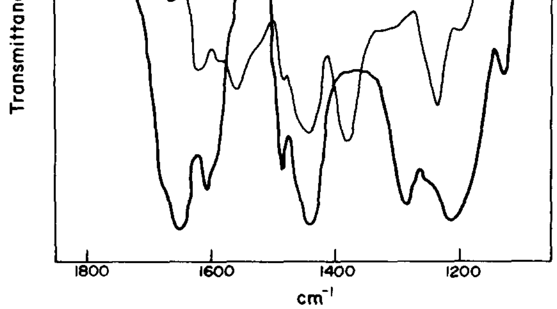


Fig. 1. Infra-red spectra of: —— salicylic acid–formaldehyde polymer (SAF), ——— complex of SAF with iron(III)-ions.

3. *Complex of PCHBM.* PCHBM (0.237 g) was dissolved in a mixture of acetone (15 ml) and ethanol (5 ml). The solution was neutralized with 0.1 N NaOH (9.8 ml). $FeCl_3$ (0.1 M, 5 ml) of pH = 2 was added to the mixture with stirring. A red-brown precipitate was formed immediately; pH = 4. The precipitate was filtered, washed and dried in vacuum at 50°, yield 0.2 g. Iron content in the complex 0.017 g (8.3%); iron content in the filtrate 0.010 g.

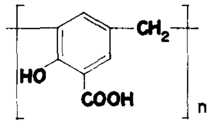
The acid numbers of the polymers were determined by titration of ethanol or acetone solution with 0.1 N NaOH in the presence of bromothymol blue.

The iron contents in the polymer complexes were determined by oxidizing samples to Fe_2O_3. The contents of iron(III) in the filtrates were determined by titration with ethylene diamine tetra-acetic acid (Titriplex III; Merck).

The i.r. spectra were recorded on a Perkin–Elmer 457 spectrophotometer using pressed KBr discs.

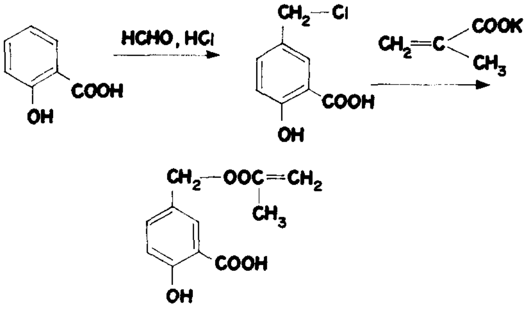
RESULTS AND DISCUSSION

The condensation product of salicylic acid with formaldehyde has the structure



confirmed by the results of the elemental analysis and the acid number. The i.r. spectrum (Fig. 1) shows an absorption at 1660 cm^{-1} characteristic for C=O bond of the carboxylic acid with internal hydrogen binding [6] and absorptions at 1610 and 1490 cm^{-1} characteristic of the benzene ring. The intrinsic viscosity, 3.2 cm^3/g, shows that the polymer has a low molecular mass (the molecular mass of the polymer obtained in the same conditions [3] is 6700). SAF is soluble in ethanol, acetone, dimethylformamide as well as in aqueous solutions of alkali hydroxides and carbonates. This polymer has the complex-forming unit in the backbone chain.

In order to obtain a polymer with complex-forming units as substituents on the backbone, hence making the units more mobile and more accessible for the complex forming reaction, the following synthesis was performed:



The resulting monomer may be copolymerized with various monomers to form products with a definite content of complex-forming units in the polymer chains.

CMSA was prepared by a published method [5]. After one recrystallization, elemental analysis showed that the product is not sufficiently pure (87.4% on the basis of the chlorine content). Repeated recrystallization led to a decrease of the chlorine content from 16.6 to 12.6% Cl. The liberation of HCl, and of additional precipitate containing a small quantity of chlorine (1–1.5%) during recrystallization, indicated that a further condensation occurred, probably similar to the condensation of salicylic acid with formaldehyde. This is in accordance with the observed [7] formation of resin-like products by the chloromethylation of phenols and amines. Moreover, isolation of pure products has also not been possible in the chloromethylation of 1- and 2-naphthol [7].

The i.r. spectrum of CMSA shows the absorption maximum characteristic for internally hydrogen bonded C=O groups and the maxima for the benzene ring.

Because of the impossibility of further purification of CMSA, we prepared CHBM with crude CMSA. The reaction proceeds almost quantitatively as shown by the chlorine content in the filtrate (92% of the calculated value). The i.r. spectrum of CHBM contains a small shoulder at 1700 cm^{-1} indicating the overlapping of the methacrylic C=O group with the C=O group of the salicylic acid, whilst the absorptions at 1325–1330 and 1290 cm^{-1} are characteristic for methacrylates [6]. CHBM is soluble in acetone, chloroform, ether and ethanol. It is not stable; on standing for several hours, it changes into a resin-like hard product insoluble in ether.

CHBM polymerizes in solution in the presence of a radical initiator as usual via the double bonds, as indicated by an easily distinguished i.r. absorption maximum at 1720 cm^{-1} characteristic for the C=O group no longer conjugated with the methacrylic double bond. Elemental analysis and the acid number confirm the structure of the polymer. The yield under the conditions of polymerization was not high. The intrinsic viscosity 7.0 cm^3/g is about twice that of SAF.

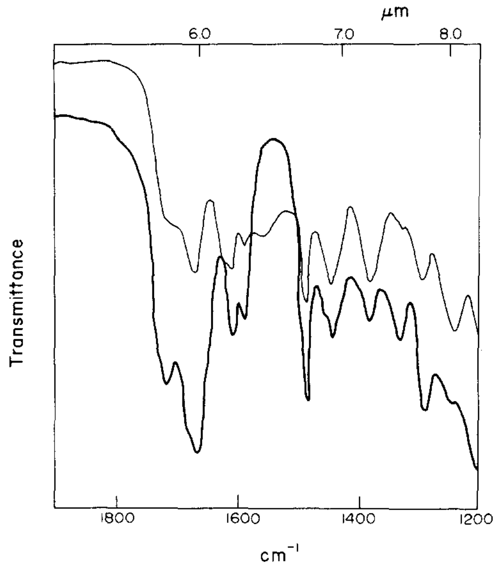
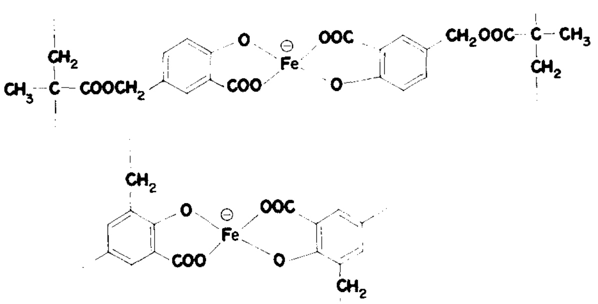


Fig. 2. Infra-red spectra of: —— PCHBM, —— complex of PCHBM with iron(III)-ions.

It is known that salicylic acid forms intensly coloured complexes with iron(III)-ions. The molar ratio 2:1 between salicylic acid units and iron(III)-ions is favourable for the formation of complexes with the same ratio. According to Park [8] we assume the following structures of the complexes:



This complex formation should lead to inter- and intramolecular cross-linking. In fact, adding a solution of iron(III)-ions to a solution of sodium salts of both polymers (SAF and PCHBM) results in red–brown precipitates. The lack of solubility is one of the basic indications of intermolecular cross-linking. The chosen pH-conditions do not allow the formation of insoluble iron(III) hydroxides. After extraction with boiling ethanol, the cross-linked polymer complexes have spectra represented in Fig. 1. The intramolecularly hydrogen bonded C=O groups are destroyed and transformed to a complex bond, which is shown by a decrease of the absorption at 1660–1670 cm^{-1} and its shift to a lower wave number [9].

As one iron(III)-ion is predominantly bound with two salicylic acid units, from the content of iron in the polymer complex it can be calculated that 68.2% of all 2-hydroxybenzoic groups in SAF take part in complex formation. In PCHBM the quantity of groups taking part is slightly higher at 76.3% These results can be explained by the fact that in SAF the salicylic units are included in the chains and their accessibility is restricted by the smaller flexibility of the polymer chain. In PCHBM, the 2-hydroxybenzoic acid units are side-groups on the backbone. The mobility of the substituents here is greater and may cause the percentage of participating units to be slightly higher.

The polymer complexes are not soluble in organic solvents or water.

Both polymers dissolve after brief heating in 0.1 M solution of Titriplex III. In this case the ethylene diamine tetra-acetic acid forms a more stable complex with iron(III)-ions than those with 2-hydroxy benzoic acid units.

CONCLUSION

The reactions of cross-linking and splitting of the cross-linking bridges of the polymer molecules described above are based on complex formation which proceeds quickly at room temperature. These reactions will now be applied for theoretical and practical investigations of cross-linking reactions.

Acknowledgements—This work has been supported by the Deutsche Forschungsgemeinschaft-Sonderforschungsbereich 41. One of us (H.B.) thanks the Deutscher Akademischer Austauschdienst for a grant.

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