

PREPARATION AND CHARACTERISTICS OF *o*-ACRYLOYLOXY- AND *o*-METHACRYLOYLOXYBENZOIC ACIDS AND THEIR POLYMERS

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Acryloylation and methacryloylation of sodium salicylate in an anhydrous medium yielded *o*-acryloyloxybenzoic and *o*-methacryloyloxybenzoic acids. Their radical polymerization or the polymerization of aqueous solutions of their sodium salts gave the respective polymers. The infrared and NMR spectra of monomers and polymers were recorded, and the antiinflammatory activity of the polymer of *o*-methacryloyloxybenzoic acids was verified.

Polymers containing carboxyphenyloxylic groups have attracted attention only in the recent times^{1,2}. The Schotten-Baumann reaction was used to prepare *p*-methacryloyloxybenzoic acid from *p*-hydroxybenzoic acid¹, and *o*- and *p*-carboalkoxyphenyl acrylates from alkyl esters of salicylic or *p*-hydroxybenzoic acids². We first prepared poly(vinyl alcohol) with the end groups of *p*-aminosalicylic acid and verified its antituberculosis activity *in vitro*³; later on we prepared *o*-acryloyloxy- and *o*-methacryloyloxybenzoic acids⁴ and their polymers⁵.

The best results in the preparation of *o*-acryloyloxybenzoic (*I*) and *o*-methacryloyloxybenzoic (*II*) acids respectively were obtained by acryloylation and methacryloylation of sodium salicylate suspended in benzene, toluene, or heptane. Both compounds are white, crystalline and can be stored unchanged at room temperature for several years. They are soluble in benzene, chloroform, tetrachloromethane, ether, acetone, ethanol, acetic acid and in an aqueous solution of sodium bicarbonate, and insoluble in aliphatic hydrocarbons and water.

The homogeneous radical polymerization of acids can be carried out in a solution of 1,4-dioxane and in an aqueous solution of their salts. During the polymerization of both monomers in benzene the homopolymers precipitate from the solutions. Copolymers with styrene and isoprene were also prepared from *o*-acryloyloxybenzoic acid. The polymer of *o*-methacryloyloxybenzoic acid having a comparatively low molecular weight, was prepared with *n*-dodecyl mercaptan as the regulator of the degree of polymerization. The polymer with \bar{M}_n 1800 was found to possess

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antiinflammatory activity⁶, which was somewhat lower compared to 3-acetoxybenzoic acid. The polymerization of *o*-methacryloyloxybenzoic acid without regulator yielded a high-molecular weight polymer, soluble in an aqueous solution of sodium bicarbonate, but unlike the low-molecular weight polymer insoluble in organic polar solvents.

The assumed structure of monomers *I*, *II* prepared by us and of the respective polymers (*I'*, *II'*) is confirmed by the infrared spectra. The strong absorption of all compounds within the wave frequency range from 753 to 760 cm⁻¹ corresponds to the characteristic out-of-plane vibrations of the C—H bonds of the *ortho*-substituted benzene ring. Three absorption maxima in the region from 1487 to 1612 cm⁻¹ also can be assigned to the benzene ring. The absorption bands at 907 and 998 cm⁻¹ in the spectrum of acid *I* and at 902 cm⁻¹ in the spectrum of acid *II* are due to the out-of-plane deformational vibration; absorptions at 1640 cm⁻¹ and at 1646 cm⁻¹ found with *I* and *II* are due to the valency vibration of the aliphatic C=C bond, and are lacking in the spectra of polymers *I'* and *II'*. All compounds under investigation exhibit strong absorption in the wave frequency region from 1694 to 1762 cm⁻¹ characteristic of the carbonyl group. In the case of monomers the absorption maxima of the C=O groups from the free carboxylic group markedly differ by their lower wave frequency from those from the ester group; in the spectra of polymers the bands of both C=O groups coincide. The presence of the CH₃ group in monomer *II* is indicated by the absorption at 1383 cm⁻¹. In the spectrum of polymer *II'* the maximum at this wave frequency coincides with another band.

The chemical shifts of protons in the NMR spectra of acids *I* and *II* and of polymers *I'* and *II'* also confirm that all four compounds possess the chemical composition and structure outlined above.

EXPERIMENTAL

Chemicals. Sodium salicylate was prepared by the gradual addition of a calculated amount of sodium bicarbonate into a suspension of salicylic acid in a double weight quantity of water, followed by removal of the water by distillation at reduced pressure and drying of the sodium salt in the air. Acryloyl chloride⁷, b.p. 76–78°C, n_D^{20} 1.4346, methacryloyl chloride⁸, b.p. 96 to 97°C, n_D^{20} 1.4433. The other chemicals were reagent grade.

Analytical procedures. The density of acids and their polymers was determined pycnometrically in light petroleum. The viscosity of polymer solutions was measured in an Ubbelohde viscometer. The number average molecular weight of polymers was determined osmometrically in the vapour phase with a Hitachi-Perkin-Elmer, model 115 apparatus. The infrared spectra were recorded with a Perkin-Elmer 621 spectrometer by the KBr technique, the NMR spectra were recorded with a PS-100 (Jeol) spectrometer at 100 Mc/s with HMDS as the internal standard ($\tau = 9.95$). The latter measurements were carried out with 10% solutions (w/v) of monomers in CDCl₃ and 10% polymer solutions in DMSO-d₆.

o-Acryloyloxybenzoic Acid (*I*)

To a mixture of 80 g (0.45 mol) of sodium salicylate, 100 ml benzene and 0.2 g hydroquinone, a solution of 46 g (0.51 mol) of acryloyl chloride in 100 ml benzene was added with stirring during 1 h; the mixture was heated with constant stirring at 50°C for 5 h. On cooling to room temperature, filtration, distilling off benzene at reduced pressure, twofold crystallization of the solid residue (86 g) from benzene (with carboraffin added) and reprecipitation from an aqueous solution of sodium bicarbonate with hydrochloric acid, the yield was 34 g (39.6%) of *I*, m.p. 114°C, d_4^{20} 1.335. IR spectrum: 760 (Ar—H), 907, 998 (—CH=CH₂), 1487, 1579, 1608 (Ar), 1640 (—CH=CH₂), 1694 (—COOH), 1751 cm⁻¹ (—COOAr). NMR spectrum (CDCl₃): δ 7.05–8.10 (m, 4 H, aromatic protons), 5.85–6.67 (m, 3 H, —CH=CH₂). For C₁₀H₈O₄ (192.2) calculated: 62.45% C, 4.19% H; found: 62.35% C, 4.24% H.

o-Methacryloyloxybenzoic Acid (*II*)

By the same procedure as used for the preparation of *I*, 89 g of raw *II* was obtained from a mixture of 80 g (0.45 mol) sodium salicylate, 200 ml toluene, 0.2 g hydroquinone and 54 g (0.52 mol) methacryloyl chloride. After threefold precipitation of *II* from an aqueous solution of the sodium salt (bleached with carboraffin) with hydrochloric acid the final product (39 g; 42.4%) had m.p. 94°C, d_4^{20} 1.327. IR spectrum: 753 (Ar—H), 902 (—C=CH₂), 1383 (—CH₃), 1493, 1580, 1611 (Ar), 1646 (—C=CH₂), 1714 (—COOH), 1750 cm⁻¹ (—COOAr). NMR spectrum (CDCl₃): δ 7.20–8.20 (m, 4 H, aromatic protons), 5.77–6.40 (m, 2 H, =C=CH₂), 2.07 (s, 3 H, —CH₃). For C₁₁H₁₀O₄ (206.2) calculated: 64.07% C, 4.89% H; found: 64.08% C, 4.93% H.

Polymerization of *I*

A) The solution of 7 g of *I* and 0.014 g of 2,2'-azobis(isobutyronitrile) in 7.9 ml of benzene was heated in a sealed glass ampoule freed from air oxygen to 60°C for 24 h. The white porous block thus obtained was crushed and digested twice in 50 ml of boiling benzene; on drying in the air the yield was 6.3 g of the polymer (*I'*), density d_4^{20} 1.37, $[\eta]$ 0.64 dl/g (1,4-dioxan, 20°C). The powderlike polymer was sintered within the temperature range of 145 to 150°C. It was soluble in 1,4-dioxane, dimethylformamide, dimethyl sulphoxide, and in an aqueous solution of sodium bicarbonate, was strongly swollen in ethyl alcohol, acetone, and chloroform, and was insoluble in benzene, toluene, tetrachloromethane and light petroleum. IR spectrum: 753 (Ar—H), 1494, 1588, 1612 (Ar), 1762 cm⁻¹ (—COOH, —COOAr). NMR spectrum (dimethylsulphoxide-d₆): δ 6.80–7.87 (m, 4 H, aromatic protons), 3.10 (bs, 1 H, CH), 2.00 (bs, 2 H, CH₂). *B*) 2.4 g *I*, 1.32 g of anhydrous sodium carbonate, 0.68 g of potassium persulphate and 12.5 g of distilled water were weighed and placed in a glass ampoule. The latter was freed from air oxygen, sealed and heated to 60°C for 17 h. 1.2 g of *I'* was precipitated from an aqueous solution of the polymer of the sodium salt of *I* by adding dilute hydrochloric acid (1 : 1). The analysis of the polymer gave 62.84% C and 4.14% H.

Polymerization of *II*

A) Similarly to the polymerization of *I* by procedure *A*, 11.2 g of white powder was obtained from a mixture of 14.4 g *II*, 0.15 g of 2,2'-azobis(isobutyronitrile), 0.1 g of dodecyl mercaptan and 30 ml of benzene. After that the product was purified by precipitation with heptane from a solution in 70 ml of chloroform, and dried in the air; the yield was 10 g of polymer (*II'*), d_4^{20} = 1.38, M_n 1800, $[\eta]$ 0.053 dl/g (chloroform, 20°C). The powder was sintered within the tem-

perature range of 185 to 190°C. It was soluble in ethyl alcohol, acetone, chloroform, 1,4-dioxane, dimethyl sulphoxide and in an aqueous solution of sodium bicarbonate, and insoluble in benzene, toluene, tetrachloromethane, and light petroleum. IR spectrum: 754 (Ar—H), 1491, 1589, 1612 (Ar), 1754 cm^{-1} (—COOH, —COOAr). NMR spectrum (dimethyl sulphoxide- d_6): δ 7.20—7.90 (m, 4 H, aromatic protons), 2.50 (bs, 2 H, CH_2), 1.40 (s, 3 H, CH_3). *B*) The heating of a mixture of 7 g of *II*, 0.014 g of 2,2'-azobis(isobutyronitrile) and 7.9 ml of benzene to 60°C for 60 h, isolation of the polymer and its boiling in benzene yielded 6.6 g of powderlike polymer. Unlike the low-molecular weight polymer described in the preceding chapter the polymer was insoluble in organic solvents, but could be dissolved in an aqueous solution of sodium bicarbonate (1%), $[\eta]$ 1.64 dl/g (20°C).

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