

PREPARATION AND CHARACTERIZATION OF N-ACRYLOYL-*p*-AMINOPHENYLACETIC ACID AND ITS POLYMER

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N-acryloyl-*p*-aminophenylacetic acid was obtained by acryloylation of *p*-aminophenylacetic acid. Its polymers were prepared by radical polymerization in an aqueous and inorganic medium. The infrared and NMR spectra of both the monomer and polymer were recorded, and the weight-average molecular weights of polymers were determined by the light scattering method.

So far, neither the preparation of N-acryloyl-*p*-aminophenylacetic acid, $\text{HOOC} \cdot \text{CH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{NH} \cdot \text{CO} \cdot \text{CH}=\text{CH}_2$ (*I*) nor its properties have been described in the literature. The homopolymers of this acid can become important on the grounds of their insignificant solubility in cold water and good solubility of their salts in water. The homopolymers and copolymers of this type of acids can also be used because of the possibility of their modification based on the reaction of the carboxyl groups bonded on polymer chains.

Acid *I* was obtained by acryloylation of *p*-aminophenylacetic acid in an aqueous or organic medium in the presence of sodium carbonate or N,N-dimethylaniline. According to the method of preparation, the resulting compound was either a white flaky product or amorphous powder. It was readily soluble in alcohol and hot water and little soluble in aromatic, aliphatic and chlorinated hydrocarbons and in cold water.

The polymer of acid *I* can be obtained by radical polymerization of the monomeric acid in an aqueous or organic medium. After polymerization of the sodium salt of acid *I* in an aqueous solution of $\text{K}_2\text{S}_2\text{O}_8$ at 60°C lasting two hours, an insoluble polymer (gel) precipitated from the mixture. To obtain a soluble product, the polymerization time had to be considerably reduced. The polymer precipitated from an acidified reaction mixture in the form of a slightly yellowish powder. It was insoluble in water and common organic solvents, dissolved readily in formic acid, trifluoroacetic acid, dimethyl sulfoxide and ethylene glycol monomethyl ether, and with difficulty in dimethylformamide and benzonitrile. Its sodium salt was readily soluble in cold water.

The chemical composition of acid *I* and the structure of its polymer were verified by chemical analysis, NMR and infrared spectra (Figs 1 and 2). The chemical shifts

given in Table I and the band intensities ratio obtained from the NMR spectra are in good accordance with the supposed structure of the monomer. They are similar to those of polyacrylamides¹ prepared radically. The structure is also corroborated by the infrared spectra. The spectra of both the monomer and polymer exhibit a diffusion band of the COOH group in the region from 2400 cm^{-1} and higher, a valency vibration band of the N—H bond at 3300 cm^{-1} and bands corresponding to the vibrations of the C=O band at 1660 and 1690 cm^{-1} and belonging to the —CO—NH— and COOH groups. The presence of the amide group is also evident from the spectrum of the methyl ester of acid *I* prepared during this work. The wide diffusion band of the COOH groups decreased markedly after esterification, while the sharp band in the region of 3300 cm^{-1} , *i.e.* in the region of the valency vibra-

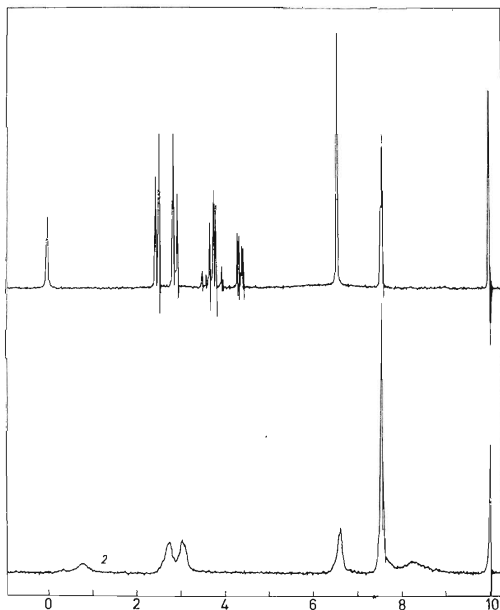


FIG. 1

The NMR Spectra of N-Acryloyl-*p*-aminophenylacetic Acid (1) and Its Polymer (2)

tions of the N—H bond, still remained. In contrast with the monomer, the band of the C=C bond in the frequency region of 1650 cm^{-1} is missing in the spectrum of the polymer.

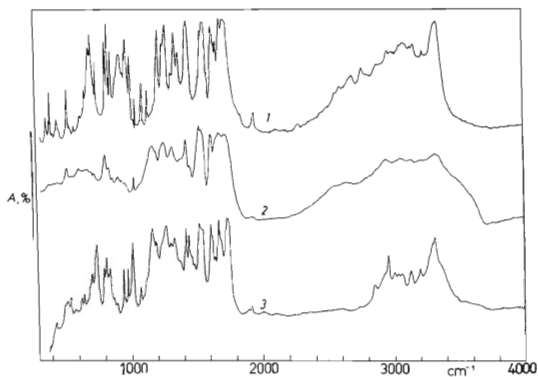


FIG. 2

The IR Spectra of N-Acryloyl-*p*-aminophenylacetic Acid (2), Poly(N-acryloyl-*p*-aminophenylacetic Acid) (1) and Methyl Ester of N-acryloyl-*p*-aminophenylacetic Acid (3)

TABLE I
Parameters of the NMR Spectra of Monomer and Polymer

Compound	Chemical shifts, τ						
	δCH_2	$\delta\text{CH}=\text{CH}_2$	δCH	$\delta\text{CH}_2\text{-ar}$	δar	δCOOH	δNH
Monomer	—	4.4—3.72 multiplet	—	6.5	2.65	—0.03	—
Polymer	8.19	—	7.57 ^a	6.57	2.85	0.73	—

^a In the NMR spectrum is overlapped with the DMSO band (when the spectrum of the polymer was recorded in trifluoroacetic acid, another sharp band — unidentified — was recorded in this region).

EXPERIMENTAL

Chemicals. *p*-Aminophenylacetic acid², m.p. 193°C, acryloyl chloride³, b.p. 74°C, n_D^{20} 1.4330. *N,N*-Dimethylaniline was dried with solid KOH and distilled, b.p. 71°C/12 Torr. Benzene, anal. purity grade, was dried with sodium and distilled. The other chemicals were anal. purity grade.

Preparation of *N*-Acryloyl-*p*-aminophenylacetic Acid (*I*)*

a) *p*-Aminophenylacetic acid, 20 g (0.13 mol) was dissolved in a solution of 16 g (0.15 mol) of calcinated soda in 150 ml water with 0.05 g *p*-benzoquinone added. Then 12 g (0.13 mol) of acryloyl chloride was added to the solution with stirring at 0°C during 2 h. After addition of acryloyl chloride the mixture was stirred at 0°C for another half an hour, and at room temperature for the same time; then the mixture was diluted with water and the brown solution thus obtained was poured into an excess of diluted sulphuric acid. The acid precipitated in the form of a suspension whose pH was adjusted with a solution of sodium acetate to 5–6. After filtration the acid was twice recrystallized from hot water with carboraffin added. Pure acid *I* was obtained in the form of a white light flaky product (4.4 g, *i.e.* 15.9% with respect to the original acid), m.p. 139°C. For $C_{11}H_{11}O_3N$ (205.2) calculated: 64.38% C, 5.4% H, 6.83% N; found: 64.42% C, 5.5% H, 7.07% N; 100 ml of saturated aqueous solution at 20°C contains 0.531 g of acid.

b) A solution of 3.1 g (0.03 mol) of acryloyl chloride in 50 ml of dry benzene was added dropwise to a suspension of 5 g (0.03 mol) *p*-aminophenylacetic acid in a solution of 4 g (0.03 mol) *N,N*-dimethylaniline and 0.05 g of *p*-benzoquinone in 80 ml of benzene at 5°C for 2 h. After the reaction had been completed the mixture was stirred at the same temperature for 15 min and at 60°C for one hour. The reaction mixture divided into two layers was cooled and then shaken with 100 ml of dilute hydrochloric acid (1 : 5), the slightly yellow precipitate thus obtained was filtered off. The raw acid *I* was dissolved in cold methanol with carboraffin added, the solution was filtered and the acid was precipitated with water from pure filtrate. The yield was 2.95 g of pure acid *I* (42.4% with respect to the original acid), m.p. 137°C. For $C_{11}H_{11}O_3N$ found: 64.25% C, 5.52% H, 7.07% N.

Polymerization

a) Into a glass ampoule 1.43 g of acid *I* and 0.04 g of 2,2'-azobis (isobutyronitrile) were weighed and 12 ml of dimethyl sulfoxide was added to the mixture. The ampoule was cooled in solid carbon dioxide several times, evacuated alternately and filled with nitrogen and then sealed *in vacuo*. After heating to 60°C for 6 g its contents were poured into 100 ml of distilled water. The precipitated white polymer was washed with water to neutral reaction and dried *in vacuo* to constant weight. The yield was 1.22 g of the polymer (conversion 85.4%) containing 6.28% of nitrogen; M_w 122,000, d_D^{20} 1.34. The temperature of transition into the plastic state was 150°C; 100 ml of saturated aqueous solution at 20°C contained 0.039 g of the polymer.

b) A solution of 1.02 g of sodium salt of acid *I* and 0.081 g of potassium persulphate in 15 ml of distilled water was heated in an inert atmosphere (*cf.* polymerization *a*) to 60°C for 25 min. The solution was then poured into 30 ml of diluted hydrochloric acid (1 : 10), the white precipitate was washed with water to neutral reaction of the water and dried *in vacuo* to constant weight. The yield of the polymer was 0.86 g (conversion 93.5%); the polymer contained 6.46% of nitrogen, M_w 180 000. The temperature of transition into the plastic state was 210°C. (From the dif-

* Modification of the procedure used for acylation of *p*-aminobenzoic acid⁴.

ferent transition temperature sub *a*) can be inferred that the polymer contained a small amount of dimethyl sulfoxide.)

The infrared spectra were recorded on a Perkin-Elmer 621 spectrometer by using the KBr technique; the NMR spectra were recorded on a PS-100 (Jeol) spectrometer at 100 Mc/s with HMDS as the internal standard ($\tau = 9.95$). The compounds were measured in 0.5 molar solutions of deuterated dimethyl sulfoxide at 22°C, the polymer was measured at 80°C. The density of the polymer was determined pycnometrically, the weight-average molecular weight was determined with a Photo-Gonio-Diffusometer Sofica model 42 000 apparatus.

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