

MODEL COMPOUNDS OF HYDROPHILIC GELS. II.*
AN INTERPRETATION OF THE IR SPECTRA OF POLYMERS
BY MEANS OF SUBSTITUTED AMIDES OF PIVALIC ACID

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The following low-molecular-weight model compounds of N-substituted poly(methacrylamides) were prepared: N-(2-hydroxyethyl)pivaloamide, N,N'-ethylenedipivaloamide and N,N-di-(2-pivaloyloxyethyl)pivaloamide. The substances were used to interpret the infrared spectra of the products of aminolysis of poly(2-hydroxyethylmethacrylate) and hydroxyethylation of poly(methacrylamide).

The hydrophilic gels based on poly(hydroxyalkyl methacrylates) have been described by Wichterle¹. Additional studies have been dealing with some derived types — substituted poly(methacrylamides), which were prepared by aminolysis of glycol methacrylate gels², hydroxyethylation of poly(methacrylamides) or polymerization of the corresponding monomers³. In the present work, the infrared spectra of similar hydrophilic polymers are interpreted on the basis of the low-molecular-weight model compounds: N-(2-hydroxyethyl)pivaloamide (*I*) is a model of poly [N-(2-hydroxyethyl)methacrylamide]; N,N'-ethylenedipivaloamide (*II*) is a model of poly(methacrylamide) monosubstituted on the nitrogen atom and of similar polymeric products not containing ester or hydroxyl groups, or of crosslinking sites formed by N,N'-ethylenedimethacrylamide; and N,N-di(2-pivaloyloxyethyl)pivaloamide (*III*) is a model of polymethacrylic esters and disubstituted amides not containing any hydroxyl groups.

The polymeric samples (A—D) were prepared *via* polymeranalogous transformations of poly-[2-hydroxyethyl methacrylate] by its reaction with 2-aminoethanol (sample A), with ethylenediamine (B), bis(2-hydroxyethyl)amine (C), and by the reaction of poly(methacrylamide) with oxiran (sample D). In all cases, less than half the amount of the structural units of the polymers participated in the chemical transformation. The low-molecular-weight reaction components were linked to the polymer by one bond only, since all products were soluble, that is, not cross-linked. On reprecipitation, no important increase in the nitrogen content of sample D could be observed, which may suggest that there was no homopolymer of oxiran present there.

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The infrared spectra of the model compounds (Fig. 1) were compared with those of the polymers prepared (Fig. 2). In the region $1600\text{--}1700\text{ cm}^{-1}$ spectra of all compounds exhibit an intensive band of amide I (valence vibrations $\text{C}=\text{O}$ of the amide group); in the region $2800\text{--}3000\text{ cm}^{-1}$ there are bands characteristic of the valence vibrations of the groups CH_2 and CH_3 . The different contours of the latter bands of models and polymers are in agreement with the assumed ratios of the relevant groups. A broad band in the region $3300\text{--}3400\text{ cm}^{-1}$, consisting of two lines and characterizing the valence vibrations of the $\text{N}\text{--}\text{H}$ and $\text{O}\text{--}\text{H}$ groups, can be found in the spectra of all polymer samples. The shift of the maximum of the latter composite band by 50 cm^{-1} toward a higher wavenumber for sample A compared with

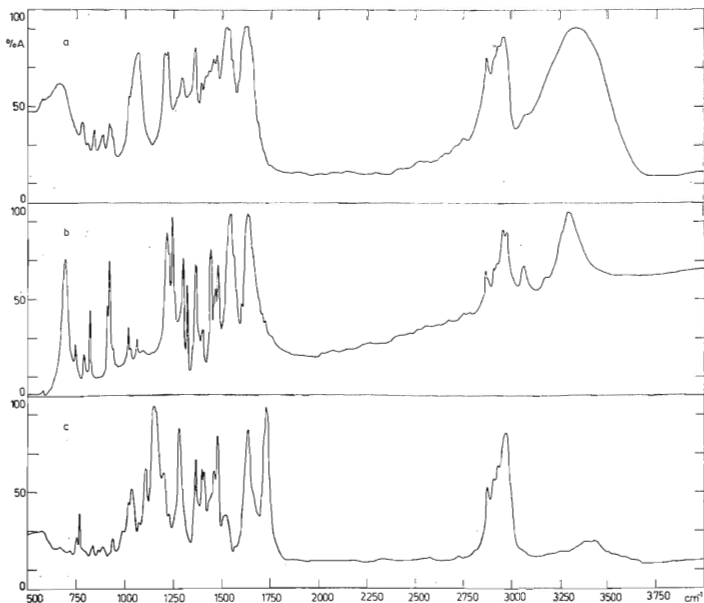


FIG. 1

IR Spectra of Model Compounds

a *N*-(2-Hydroxyethyl)pivaloamide (I), b *N,N'*-ethylenedi(pivaloamide) (II), c *N,N*-di(2-pivaloyloxyethyl)pivaloamide (III).

model *I* corresponds to a lower content of the NH groups after an incomplete aminolysis of the starting polymer; the spectrum also contains the amide II band at 1540 cm^{-1} (deformation vibrations N—H in the interaction with the valence vibration C—N)⁴, as well as the band of the valence vibration C=O of the ester groups at 1730 cm^{-1} , whose presence corresponds to an incomplete conversion during aminolysis. The spectrum of sample A, its complete solubility and the nitrogen content lead to a conclusion that the compound in question is poly-61.8 : 38.2-[2-hydroxyethyl methacrylate-*ir*-N-(2-hydroxyethyl)methacrylamide]. In the spectra of samples *B* and *C*, the absorption band of the valence vibrations of the C=O ester groups lies at 1730 cm^{-1} . In the spectrum of sample B the band at 1640 cm^{-1} could correspond to the deformation vibration of water present in the polymer. The absorption band at 1570 cm^{-1} can correspond – besides the expected vibration of the

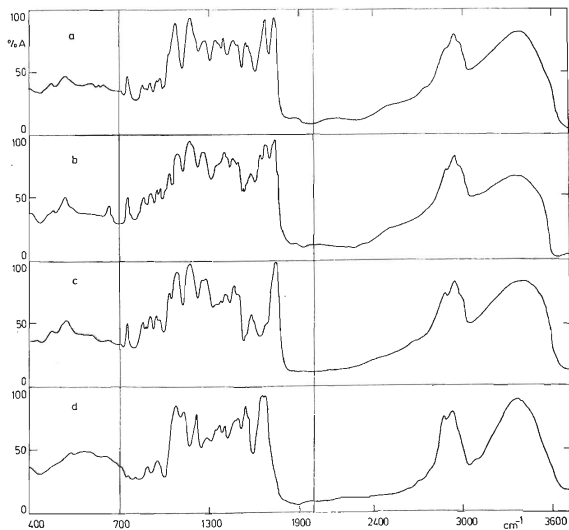


FIG. 2

IR Spectra of Polymer Samples

Reaction products of the aminolysis of poly[2-hydroxyethyl methacrylate] with 2-aminoethanol (a), ethylenediamine (b) and bis(2-hydroxyethyl)amine (c). Product of the reaction between poly(methacrylamide) and oxiran (d).

pendant—NH₂ groups — also to the valence vibrations of the —COO⁻ anion and the deformation vibrations of —NH₃⁺; apparently, these bands overlap the band corresponding to the vibration of amide II. If the fact is neglected that the aminolysis could in part be accompanied by hydrolysis (the course of which cannot be excluded on the basis of the IR spectra), then the nitrogen content, complete solubility of the sample and the majority of the characteristic absorption bands are in accordance with the idea that sample B is poly-74 : 26[2-hydroxyethyl methacrylate-*ir*-N-(2-aminoethyl)methacrylamide]. The spectrum of sample C surprises by the presence of a band at 1570 cm⁻¹, because here, with respect to the composition of the initial reaction mixture, the presence of groups RCONHR, NH₃⁺, and —COO⁻ cannot be expected. It seems that in this case there is a deformation frequency of the secondary amine groups whose origin may be due to the fact that a part of bis-(2-hydroxyethyl)-amine reacted with the polymer by means of a hydroxyl group. In such a case, sample C would be a terpolymer of 2-hydroxyethyl methacrylate (80 mol.%), N,N-di-(2-hydroxyethyl)methacrylamide and 5-hydroxyethyl-3-azapentyl methacrylate. In the spectrum of *sample D*, the band of the C=O valence vibrations of the ROCOR' groups is missing, in accordance with the assumed structure. Moreover, a distinct band at 1120 cm⁻¹ can be seen here, which is absent in all the other spectra of the model substances or polymer compounds and which obviously corresponds to the valence vibration of the C—O ether bond. With respect to the complete solubility of the sample, elemental analysis data and the IR spectrum, oxiran was bonded to the structural units of the starting polymer in a molar ratio of 2 : 1 most probably by mono- or even disubstitution of amino groups and in the form of oligomeric polyoxiran chains. In agreement with this the resulting copolymer also contained some unsubstituted amino groups.

EXPERIMENTAL

The IR spectra were measured with Perkin-Elmer 421 and Zeiss UR-10 spectrometers. Samples I and III were measured as films prepared by melting the compounds between the KBr windows; sample II was measured in the form of a KBr pellet. Films of polymer samples on the AgCl plates were obtained by evaporation of aqueous solutions. The mass spectra were measured using an A.E.I. MS-902 apparatus, the energy of the electrons being 70 eV.

Materials

Pivaloyl chloride was prepared by adding dropwise pivalic acid to thionyl chloride (in an excess of 10 mol.%) while stirring, followed by distilling off the fraction having b.p. 102—103°C (yield 93.7%). In the case of an equimolar ratio of the reaction components the yield was 85.3%, while in the case of a twofold excess of thionyl chloride it was only 5%, since the greatest part of the product was distilled together with thionyl chloride. Besides, 2-aminoethanol, b.p. 170—171°C, ethylenediamine, b.p. 116°C (cont. 20.18% H₂O), bis(2-hydroxyethyl)amine, pure (Lachema), were used. Oxiran was prepared from ethylene chlorohydrin and sodium hydroxide⁵. Poly[2-hydroxyethyl methacrylate] prepared in the Institute, M_w 94 000 (viscometrically, by diluting in dimethylformamide⁶ at 25°C, c 0.24—1.00 g dl⁻¹). Poly(methacrylamide) was obtained by radical polymerization (1% benzoyl peroxide, 10% benzene solution, 80°C, 3 h), M_w 53 000 (viscometrically,^{7,8} by diluting in water at 25°C, c 0.24—1.00 g dl⁻¹).

Model Compounds

N-(2-hydroxyethyl)pivaloamide (I). To 2-aminoethanol (8.61 g, 0.14 mol), a solution of pivaloyl chloride (8.50 g, 0.07 mol) in anhydrous ether (20 cm³) was added dropwise during twenty min while cooling (25°C). 2-Aminoethanol hydrochloride was filtered off, the ether was evaporated *in vacuo*, and the fraction 162—164°C/8 Torr was obtained by following distillation. On cooling, 9.3 g (90.86% calculated per pivaloyl chloride) of crystalline compound, m.p. 40°C, separated from the solution; after crystallization from ether the m.p. was 44°C. The mass spectrum exhibited a molecular peak *m/e* 145. For C₇H₁₅O₂N (145.2) calculated: 57.90% C, 10.41% H, 9.65% N; found: 57.72% C, 10.51% H, 9.86% N.

N,N'-ethylenedipivaloamide (II). Ethylenediamine (5.35 g, 0.089 mol) was added to a solution of pivaloyl chloride (10.70 g, 0.089 mol) in anhydrous ether (50 ml) during thirty min while stirring and cooling (30°C). After distilling off the ether the solid was extracted with warm ethanol (3.25 ml). The joined filtrates were concentrated to a volume of 25 ml; by cooling, 6.2 g of the compound was obtained (61.20% related to pivaloyl chloride; m.p. 167.0—167.5°C). The mass spectrum contained a molecular peak *m/e* 228. For C₁₂H₂₄O₂N₂ (228.3) calculated: 63.12% C, 10.59% H, 12.27% N; found: 62.65% C, 10.49% H and 12.36% N.

N,N-di(2-pivaloyloxyethyl)pivaloamide (III). To a solution of bis(2-hydroxyethyl)amine (10.46 g, 0.097 mol) in 20 ml of anhydrous ether (25°C), a solution of pivaloyl chloride (5 g, 0.050 mol) in anhydrous ether (10 ml) was added dropwise during 30 min while stirring, and the reaction mixture was refluxed for 1 h. After cooling and separation of the layers the lower layer was washed with ether (2 × 10 ml). The joined ether solutions were evaporated, the dry residue was dissolved in 20 ml of warm acetone, and the solution to which sodium bicarbonate (2 g) had been added was filtered. Cooling yielded 5.9 g of crystals (99.50% calculated to pivaloyl chloride), m.p. 54°C. Ions *m/e* 356 and 358 were detected in the mass spectrum. For C₁₉H₃₅O₅N (357.5) calculated: 63.83% C, 9.87% H, 3.92% N; found: 63.72% C, 10.02% H, 4.1% N.

Aminolysis of Poly[2-Hydroxyethyl Methacrylate]

Polymer with an excess of amine added was heated in the ampoules at 140°C for 24 h, precipitated (or again dissolved and precipitated), filtered by suction and dried to constant weight *in vacuo*. Conditions (initial amount of the polymer in g and mol, amine (g, mol), precipitating agent (ml), solvent (ml), precipitating agent (ml), product yield in g, nitrogen content in %, molar conversion in %), for sample A: 3.02, 0.023, 2-aminoethanol (14.04, 0.230), acetone (600), ethanol (100), ether (800), 1.1, 4.13, 38.21; for sample B: 2.01, 0.015, ethylenediamine (9.21, 0.122), acetone (400), dimethylformamide (30), ether (1000), 1.24, 5.64, 26.09; for sample C: 3.05, 0.023, bis-(2-hydroxyethyl)amine (24.47, 0.233), 1-butanol (900), —, —, 1.78, 2.04, 20.16.

Reaction of Poly(Methacrylamide) with Oxiran

Oxiran (1.55 g, 0.035 mol) was added to the polymer (1.43 g, 0.017 mol) in a thick-walled ampoule, rinsed with nitrogen and cooled with dry ice. The sealed ampoule was heated at 85°C for four hours. The product, light-brown in colour, was dissolved in 7 ml of the mixture dimethylformamide-ethanol (5 : 2) and precipitated into ether (150 ml). Sample D thus obtained (1.085 g), composition 53.89% C, 8.47% H, and 8.32% N, was reprecipitated from water (0.17 g in 3 ml) into ethanol (20 ml); the yield was 0.16 g of a compound having the composition 55.5% C, 8.68% H, 8.53% N.

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