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Diallylacylhydrazines as monomers for polyfunctional water-soluble polymers

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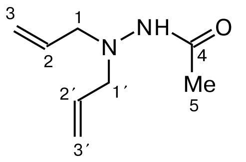
Allylation of acetohydrazide afforded the corresponding diallylacylhydrazine, which can be used for syntheses of water-soluble polyfunctional polymers.

Key words: allylation, diallylacylhydrazines, copolymerization, water-soluble polymer.

Water-soluble polyfunctional polymers are of permanent interest because of their use as efficient metal-extracting agents, flocculants, structure-forming agents for soils, viricides, bactericides, and membrane-active agents.**1** Among monomers used for syntheses of such polymers, quaternary dualkyldiallylammonium salts**2—4** play an important role along with *N*-vinyllactams and *N*-vinylamides of aliphatic acids. These classes of compounds are characterized by high reactivity in radical homo- and copolymerization. Meanwhile, it has been established that many allylic monomers, including diallylamine and diallylalkylamine, are not polymerized in the presence of radical initiators.**5** Their reactivity can be enhanced by the introduction of an electron-withdrawing group into the molecule. In this work, we evaluated the possibility of preparation of polymers based on *N*,*N*-diallyl-*N*´-acetylhydrazine (DAAH, **1**), which was synthesized by the reaction of the starting acetohydrazide with allyl halide.



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In the presence of the radical initiator (AIBN), DAAH was shown to undergo no homopolymerization and no copolymerization with the typical vinyl monomer (methyl methacrylate) but it is easily copolymerized with SO_2 acting as the monomer-acceptor to form a ~1 : 1 copolymer.

Already mixing of the comonomers at 20—80 °C produces the instant formation of a viscous amber-colored product. A comparison of the NMR spectra of the monomer and the product of its reaction with SO_2 shows noticeable differences in the chemical shifts of signals of the double bond atoms. In the ^{13}C NMR spectrum of the product, the doublet signal of the C(2) and C(2´) atoms exhibits an 1.6 ppm upfiled shift, whereas the triplet signal of the C(3) and C(3´) atoms is characterized by a 7 ppm downfield shift. The signals of protons at the C(3) and C(3´) atoms in the ^{1}H NMR spectra are shifted downfield by 0.2 ppm. These shifts of signals of the carbon atoms and protons in the spectrum of the product indicate the redistribution of the π-electron density and suggest the formation of the [DAAH...SO_2] donor-acceptor complex of SO_2 with the double bond. The UV spectroscopic studies in a chloroform medium showed that a new charge-transfer band with λ_{max} = 263 nm appeared in a mixture of DAAH with SO_2 (for SO_2 λ_{max} = 275.9 nm). This fact also favors the above assumption.**6**

In the presence of the radical initiator, the [DAAH...SO_2] complex is readily polymerized in the bulk at 80 °C. The copolymer yield rapidly achieved 30% and then remained at this level. The polymer formed is water-soluble but is partially soluble in DMSO and insoluble in the most of common organic solvents (Me_2CO, alcohols, chlorinated hydrocarbons, AcOEt, PhH). A solution of the copolymer in water has the polyelectrolyte effect, *i.e*, the viscosity increases with dilution. The intrinsic viscosity in a 1 *M* aqueous solution of NaCl is 1 dL g^{-1}.

The study of the NMR spectra of the copolymer suggests the following structure: the formation of the symmetric stereoisomeric *cis*/*trans*-copolymer is indicated by only four pairs of signals in the high-field region of the ^{13}C NMR spectrum of the copolymer. The approximate ratio of *cis*/*trans*-stereoisomers estimated from the ^{13}C NMR spectra is 4 : 1 with predomination of the *cis*-structure. Two pairs of triplet signals in the low-field region correspond to the carbon atoms of the CH_2 groups bound with the NNHC(O)Me and SO_2 functional groups, and the pair of doublet signals at 35.2 and 37.6 ppm are assigned to the tertiary carbon atoms of the stereoisomeric copolymer. Based on these data and analysis of the 2D C—H COSY spectra containing cross-peaks that indi-

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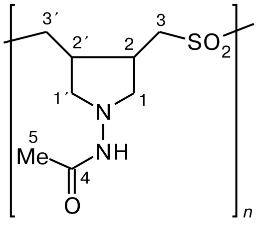
cate the strong difference between the chemical shifts of the pseudo-axial and pseudo-equatorial geminal protons of the NCH_2 fragments inherent in five-membered heterocycles, we can conclude the formation of *cis/trans*-isomeric cyclic copolymer **2** with alternating disubstituted pyrrolidinium units. The copolymer structure contains no units of the diallylacylhydrazine homopolymer, because the ^{13}C NMR spectrum of compound **2** does not exhibit upfield triplet signals of two *cis/trans*-methylene $C(3)H_2$ and $C(3')H_2$ groups at 27.3 ppm analogous to those presented previously for the homopolymer of *N*,*N*-dialkyl-*N*,*N*-diallylammonium halides.[7] An attempt to obtain high-resolution ^1H NMR spectra was unsuccessful.



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Thus, diallyl derivatives of acylhydrazines are promising monomers for syntheses of water-soluble polyfunctional polymers.

Experimental

NMR spectra were obtained on a Bruker AM-300 spectrometer with an operating frequency of 75.46 MHz (^{13}C) and 300 MHz (^1H) using D_2O as the solvent and DSS (3-(trimethylsilyl)propane-1-sulfonic acid, sodium salt) as the internal standard. IR spectra were recorded in thin layers on a UR-20 spectrometer (Carl Zeiss). UV spectra were recorded in chloroform solutions on a Shimadzu UV-3100 spectrophotometer.

N*,*N*-Diallyl-*N*´-acetylhydrazine.** ***A. Finely pulverized anhydrous Na_2SO_4 (45 g, 0.32 mol) and solid KOH (88.5 g, 1.58 mol) were added to a solution of acetohydrazide[8] (58.3 g, 0.79 mol) in BuOH (150 mL). Then distilled $CH_2=CHCH_2Cl$ (129 mL, 1.58 mol) was added dropwise with stirring. The reaction mixture was heated in a water bath for 1 h until a neutral reaction was achieved, filtered, and concentrated. The residue was distilled *in vacuo*. The yield was 59.4 g (49%), R_f 0.62 (isoamyl alcohol—AcOH—H_2O, 10 : 1.5 : 10), b.p. 117—125 °C (5 Torr), n_D^{23} 1.4770.

B. Sodium (2.6 g, 0.13 mol) was dissolved in Pr^iOH (70 mL). The mixture was heated until the formed alcoholate dissolved completely. Acetohydrazide (4.8 g, 0.065 mol) was added to the resulting solution, which was stirred until complete dissolution. Then distilled $CH_2=CHCH_2Br$ (11 mL, 0.13 mol) was added dropwise with stirring. The mixture was heated in a water bath for 4 h until the neutral reaction was achieved. The reaction mixture was filtered and concentrated. The residue was distilled *in vacuo*. The yield was 3.5 g (36%), b.p. 117—125 °C (5 Torr). UV ($CHCl_3$), λ_{max}/nm (ε): 243 (166). IR, ν/cm^{-1}: 930, 995 (C—CH=CH_2); 1550 (amide II); 1625—1670 (amide I, C=C); 3020, 3085 (=C—H); 3200—3230 (N—H). ^{13}C NMR, δ: 20.1 (q, C(5)); 60.9 (t, C(1)); 119.7 (t, C(3)); 132.4 (d, C(2)); 175.1 (s, C(4)). ^1H NMR, δ: 1.97 (s, 3 H, Me); 3.68 (d, 4 H, $C(1)H_2$, $C(1')H_2$, *J* = 6.8 Hz); 4.80 (br.s, NH, HDO, H_2O); 5.22 (d, 2 H, *trans*-$C(3)H_2$, *trans*-$C(3')H_2$, *J* = 16.3 Hz); 5.24 (d, 2 H, *cis*-$C(3)H_2$, *cis*-$C(3')H_2$, *J* = 10.0 Hz); 5.75—5.95 (m, 2 H, C(2)H, C(2´)H).

The product of DAAH with SO_2 is formed by mixing of equimolar amounts of DAAH with SO_2. UV ($CHCl_3$), λ_{max}/nm (ε): 263 (320). ^{13}C NMR, δ: 22.1 (q, C(5)); 62.7 (t, C(1), C(1´)); 126.7 (t, C(3), C(3´)); 130.8 (d, C(2), C(2´)); 174.0 (s, C(4)). ^1H NMR, δ: 1.95 (s, 3 H, Me); 3.72 (d, 4 H, $C(1)H_2$, $C(1')H_2$, *J* = 6.9 Hz); 4.83 (br.s, NH, HDO, H_2O); 5.42 (d, 2 H, *cis*-$C(3)H_2$, *cis*-$C(3')H_2$, *J* = 9.5 Hz); 5.47 (d, 2 H, *trans*-$C(3)H_2$, *trans*-$C(3')H_2$, *J* = 18.3 Hz); 5.80—5.95 (m, 2 H, C(2)H, C(2´)H).

Copolymer of DAAH with SO_2. A cooled (−195 °C) glass 10-mL ampule containing condensed SO_2 (0.94 g, $1.4 \cdot 10^{-2}$ mol) was filled with DAAH (2.01 g, $1.3 \cdot 10^{-2}$ mol) and AIBN (0.06 g). The ampule was closed, placed in a thermostat, and kept at 80 °C for 12 h. The ampule was cooled to ~20 °C, its contents was diluted with distilled water (2 mL), and the copolymer was precipitated in acetone (20 mL). The precipitate formed was filtered off and dried *in vacuo*. The yield was 0.74 g (25%). Found (%): C, 44.02; H, 6.60; N, 12.80; S, 14.64. $(C_8H_{14}N_2O_3S)_n$. Calculated (%): C, 44.04; H, 6.42; N, 12.84; S, 14.68. IR, ν/cm^{-1}: 1126, 1302 (SO_2); 1564 (amide II); 1658 (amide I); 3200 (N—H). ^{13}C NMR of *cis*-copolymer, δ: 22.5 (q, C(5)); 35.2 (d, C(2), C(2´)); 54.1 (t, C(3), C(3´)); 61.3 (t, C(1), C(1´)); 174.2 (s, C(4)). ^{13}C NMR of *trans*-copolymer, δ: 21.9 (q, C(5)); 37.6 (d, C(2), C(2´)); 55.2 (t, C(3), C(3´)); 63.8 (t, C(1), C(1´)); 179.1 (s, C(4)).

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