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(18) The relative intensity of the peak assigned to the CH_2Br group (δ 3.2 ppm, doublet (7 Hz)) to that assigned to the CH group (δ 1.8 ppm) in the recurring unit is about 1:7.8. This ratio corresponds to a formulation of $H-(CH_2C_6H_{10}CH_2)_{7.8}-Br$ ($\bar{M}_n$ = 930) if one assumes that the polymer contains, on the average, one CH_2Br as the terminal groups. The formulation roughly agrees with analytical data of the polymer (Found: C, 77.9; H, 12.2; Br, 9.0. Calcd: C, 79.7; H, 11.7; Br, 8.5).

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Synthesis and Properties of Poly[*N*-(1,1-dimethyl-3-oxobutyl)acrylamide oxime][†]

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ABSTRACT: The synthesis and properties of poly[*N*-(1,1-dimethyl-3-oxobutyl)acrylamide oxime] are described for the first time. The polymer is readily prepared by direct oximation of the polymeric ketone. The polymeric oxime is a stable, glassy polymer that is soluble in alkali at pH values above 12.5. Both the amide and oximate ion functional groups are stable in aqueous alkali for periods of over 1 year. These conclusions are based upon detailed studies of polymer solutions with ^{13}C NMR.

Introduction

In our laboratory we were seeking a polymer that would be soluble and stable in highly alkaline, aqueous solutions but that would be insoluble, optically clear, and water insensitive at pH values below 10–12. Poly[*N*-(1,1-dimethyl-3-oxobutyl)acrylamide], which is commonly referred to as polydiacetoneacrylamide (PDAA), is a very interesting glassy polymer that is readily available from monomeric DAA, which has been described.[1–3] We decided to investigate the synthesis and resulting properties of PDAA oxime in the hope that the oxime functional group would confer the desired chemical and physical properties.

A literature search revealed that DAA oxime monomer, although mentioned, was said not to copolymerize with DAA.[4] A patent on DAA oxime does not mention vinyl polymerization but is directed to its use as a reagent for epoxy resin curing.[5] The isocyanate derivatives of PDAA oxime have been reported.[6] In that work, the PDAA oxime was prepared by oximation of PDAA as an intermediate,

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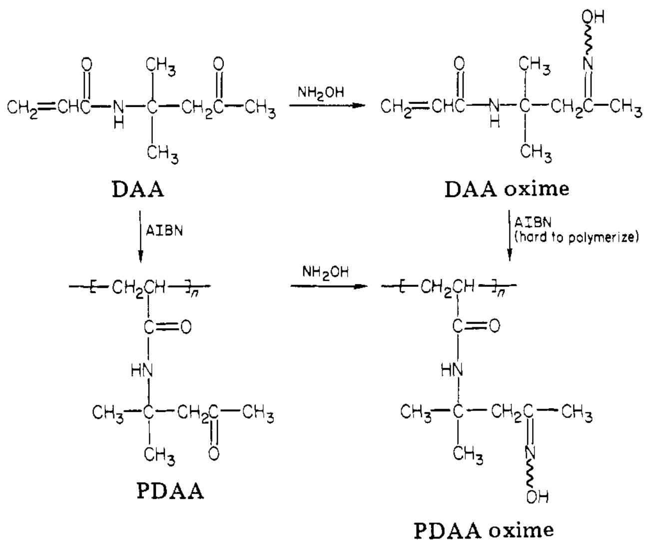
Scheme I



but no polymer properties or degrees of substitution were given.

In our work we first prepared DAA oxime monomer by reaction of DAA with hydroxylamine (Scheme I). We found the oxime monomer very difficult to polymerize and were able to obtain only low yields of polymer of low molecular weight under forcing conditions with large amounts of catalysts. We used the polymer, prepared in this way, however, to ascertain the properties we sought. Very clear films were obtained from solvents and these films were water resistant. The polymer readily dissolved in aqueous alkali and reversibly precipitated when the pH was lowered to below 12.5. Both the amide and oxime groups of PDAA oxime are stable in strong alkali (5–10%) for periods of over 1 year. In the case of the oxime group, the higher alkali protects the group from hydrolysis since the oxime group is now a negatively charged ion. The group is actually less stable at pH values of 10–12 wherein many of the oxime groups are un-ionized and attacked by dilute alkali more readily.

After these encouraging initial results, we decided to see if we could first prepare PDAA of any molecular weight range and then quantitatively oximate the polymer. The procedure we selected was the one used for oximating hindered ketones such as camphor.[7] In this type of oximation, the reaction is run in alkali, so that the reaction is driven by anion formation. We found we can readily prepare polyoximes in this manner. Depending on the original conditions used for preparing PDAA, our oximes ranged in properties from lacquers that readily dissolved in alkali to very high polymers that produced stable alkaline gels.

Experimental Section

Diacetoneacrylamide Oxime (DAAOX). Diacetoneacrylamide (402 g) was dissolved in 1.5 L of distilled water, and hydroxylamine hydrochloride (175 g) was added with good stirring. Stirring was maintained and a solution of potassium carbonate (175 g) in 250 mL of distilled water was added at room temperature over a period of 20 min. After addition was complete the major portion of oxime had already settled out. The somewhat pasty product was agitated an additional hour, filtered, and then washed with 200 mL of ice water. This was dried at 40 °C in a vacuum oven. The crude product was recrystallized from ethyl acetate and washed with first an ethyl acetate–hexane mixture and then hexane. The product was dried at 40 °C in a vacuum oven to give 291 g (65%) of oxime, mp 112–114 °C. Anal. Calcd for $C_9H_{16}N_2O_2$: C, 58.67; H, 8.75; N, 15.21. Found: C, 58.57; H, 8.74; N, 15.38. ^{13}C NMR shows the product to be a mixture of syn and anti isomers, with the syn-methyl isomer predominating (86%).

Poly(diacetoneacrylamide oxime) (PDAAOX). To 660 mL of ethanol were added with stirring 660 mL of *tert*-butyl alcohol and 480 g of diacetoneacrylamide (2.84 mol). A gentle stream of nitrogen was passed through the solution for 1 h. The solution was heated to 35 °C with an oil bath, and 0.4 g of azobisisobutyronitrile was added. The temperature of the solution was raised to 60–65 °C. At this temperature the polymerization begins and the heat of polymerization brings the reaction to reflux. The bath was brought to 80 °C and the reflux was continued gently for 4 h. The nitrogen stream was stopped and 1900 mL of ethanol was added. Then, *after the solution had become homogeneous*, 216.1 g (2.98 mol) of hydroxylamine hydrochloride (96%) was added. Over 45 min 210 mL of 45% potassium hydroxide was added dropwise. If the reaction did not return to reflux, the reaction was brought to reflux and held for 2 h. The reaction mixture was then cooled, and another 210 mL of 45% potassium hydroxide was added. The salts were removed by filtration and washed with two 200-mL portions of ethanol. The resulting clear solution of polymer was added to 15 L of water to give a clear aqueous solution. The polymer was precipitated by adding 10% HCl until the pH of the slurry was 8. The slurry of granular polymer was filtered and dried at 45 °C to constant weight to give 457 g (95%) of poly(diacetoneacrylamide oxime). The resulting polymer shows no ketone band at 1710 cm^{-1} and has an inherent viscosity in 0.5 N KOH of 0.6 dL/g. ^{13}C NMR shows the polymer to be a mixture of syn and anti isomers, with the syn-methyl isomer predominating (93%). The intrinsic viscosity was determined in absolute ethanol to be 0.16 dL/g at 25 °C.

The polymer is soluble in methanol, ethanol, chloroform, dimethylformamide, tetrahydrofuran, acetic acid, and acetone. The polymer swells in ethyl acetate and is insoluble in hexane, toluene, and ether. Besides the above polymer, which is essentially a homopolymer, quantitative oximation having occurred, copolymers of DAA and DAAOX are easily prepared by partially oximating PDAA.

Molecular Weight Studies. A number of molecular weight studies were done on PDAAOX as well as the original PDAA. This latter material was isolated from the original polymerization of DAA prior to oximation and dried. The intrinsic viscosity in absolute ethanol was 0.34 dL/g at 25 °C.

The number-average molecular weight was determined by osmometry. Stock solutions of PDAA and PDAAOX were prepared in ethanol. After the polymers were allowed to stand for 24 h, complete dissolution was observed with no evidence of turbidity. The osmometric data for both polymer solutions were recorded at 40 °C with a Wescan Model 231 recording osmometer that was calibrated with hydrostatic pressure at 45 °C. No detectable transfer of polymer through the membrane was noted.

A plot of the data for each polymer in the usual fashion (Π/C vs. C) shows a similar intercept at $C = 0$ for both polymers, which calculates M_n to be 70 000 daltons. The slope of the PDAA data and therefore the virial coefficients, A_2, are positive, indicating a good solvent–polymer interaction. The A_2 value for PDAAOX is negative, however, meaning that the polymer has more self-interactions (oxime hydrogen bonds) and that the solvent is much poorer. A single measurement on an 80% oximated polymer shows an almost ideal behavior, with A_2 virtually equal to zero.

A combination of size exclusion chromatography and light scattering was employed to gain additional data, especially as to the weight-average molecular weight and polydispersity of PDAA and PDAAOX. A Waters liquid chromatograph that had as detectors a Chromatrix KMX-6 light scattering photometer in series with a Waters R401 differential refractometer was used. In addition, static light scattering measurements were made with the KMX-6 photometer alone. Refractive index and incremental refractive index (du/dc) measurements were made at 632.8 nm with a Chromatrix RMX-16 differential refractometer. Several columns were used from Bio-Rad with acetic acid (0.3 M) and potassium acetate (0.05 M) in methanol at 2 mL/min. These columns were designated Biogel TSK50, TSK40, TSK30, and TSK20. A different set of columns was used with tetrahydrofuran as the solvent. These columns were Waters Styragel 10^5, 10^4, and 10^3-Å columns, again with flow rates of 2 mL/min. The data obtained show the weight-average molecular weights in ethanol

Table I

^{13}C NMR Spectroscopic Data for DAAOX and PDAAOX[a]

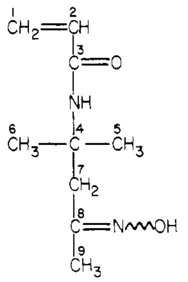
		carbon atom							
compd	*E*,*Z*,[h] %	C1	C2	C3	C4	C5,6	C7	C8	C9
diacetoneacrylamide oxime[b]	*E*,[f] 86	124.6	132.8	166.8	52.6	36.4	43.7	153.5	15.1
	Z,[f] 14	124.6	132.8	166.8	53.1	36.4	40.9[g]	153.5	21.4
poly(diacetoneacrylamide oxime)[c]	*E*,[f] 93	36.6[d]	45.0[d]	176.6	55.1	27.6	45.9[e]	157.2	17.1
	Z,[f] 7	36.6[d]	45.0[d]	176.6	56.2	27.6	45.9[e]	157.2	23.3

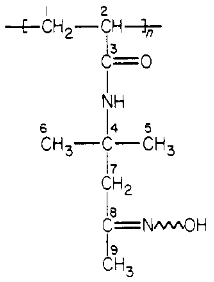
[a] Chemical shifts are reported in ppm downfield (+) from tetramethylsilane. [b] Spectra were run at 5% (w/v) in dimethyl sulfoxide-d_6 solution. [c] Spectra were run at 5% (w/v) in 1.5 M KOH, H_2O. [d] ^{13}C NMR line was very broad. [e] This ^{13}C NMR line was broad and partially masked by polymer repeat unit lines. [f] See Experimental Section for conditions that permitted quantitative assignments of the *Z* and *E* forms. [g] Masked by solvent lines in Me_2SO-d_6; chemical shift assignment was made in methylene chloride-d_2 at 20% (w/v). [h] *Z* is anti-methyl and *E* is syn-methyl designation.

by light scattering to be 175 000 daltons for PDAA and 184 000 daltons for PDAAOX. The gel permeation values with methanol were 182 000 and 187 000 daltons. The gel permeation values in tetrahydrofuran were anomalously high in the case of PDAAOX, indicating strong hydrogen bonding in this poor solvent. The value was 170 000 daltons for PDAA and 321 000 daltons for PDAAOX.

If we choose the molecular weight values for these measurements resulting from the common solvent, ethanol, then the polydispersity (M_w/M_n) is 2.5.

^{13}C NMR Studies. The ^{13}C NMR spectroscopic studies were carried out on a Bruker 270-MHz NMR spectrometer. Samples were referenced by external dioxane/D_2O in a capillary at 67.4 ppm relative to tetramethylsilane. The quantitative measurements were carried out by integrating spectra obtained with suppressed NOE gated decoupling and a pulse delay and acquisition time that combined are greater than $5T_1$(max). The peaks used for the *E*/*Z* ratios were those of the C9 methyl carbon for one value and those of the C4 quaternary carbon for another. The values reported are the average of these two measurements, with an experimental error of ±3%. The DAA OX monomer was run in Me_2SO-d_6 at 5% (w/v) in a 10-mm tube with a concentric capillary for referencing. The PDAAOX sample was run in 1.5 M KOH, H_2O at 5% (w/v) in a 10-mm tube with a concentric capillary for referencing. The results are reported in Table I.





Results and Discussion

PDAA is water insoluble but hygroscopic and shows a high water vapor transmission rate. The polymer is glassy, $n_D = 1.5005$, with a T_g of 85–88 °C. The unperturbed chain dimensions and the effect of having a bulky but solubilizing side chain have recently been reported.[8] PDAAOX is also glassy and optically clear, $n_D = 1.5227$. However, it is much more water resistant, and the T_g is raised to 118 °C. This means that it is likely that the oxime groups are participating in hydrogen-bonding interactions that are very likely occurring between chains through interaction of the oxime-bearing side chains. The polymer is still a mixture of isomers, with about 93% of the syn-methyl isomer. We have observed that derivatization can change the syn–anti isomer ratio.

We decided to see if the reason that DAA oxime would not polymerize was due to the fact that the oxime group was an inhibitor. To test this theory, we prepared acetone oxime and added it to a solution of DAA. A very strong inhibitory effect on polymerization was noted. If a derivative of the DAA oxime monomer is prepared such as an ester, ether, or carbamate, polymerization proceeds readily.

In summary, we have found PDAAOX to be a very interesting and useful polymer that possesses all of the properties we were seeking.[9]

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Registry No. Diacetoneacrylamide, 2873-97-4; (*E*)-diacetoneacrylamide oxime, 86689-82-9; (*Z*)-diacetoneacrylamide oxime, 86689-83-0.

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