Aqueous polymerization of *N*-acryloyl γ-aminobutyric acid*

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(Received 9 September 1991; revised 22 January 1992)

N-acryloyl γ-aminobutyric acid has been synthesized. It undergoes facile polymerization in aqueous solution under alkaline conditions, in spite of its ampholytic character. This has been attributed to the negligible electrostatic interactions of the pendant charges on the macroradical with that of the incorporated monomer, the charges being far away from the main chain.

(Keywords: *N*-acryloyl γ-aminobutyric acid; polymerization)

Introduction

Polymers with pendant $-CO-NH-(CH_2)_n-COOH$ groups are being increasingly investigated because of their biological activity[1] and their potential use in designing selective flocculants[2]. Barbucci *et al.*[3] have reported the synthesis of *N*-acryloyl glycine and *N*-acryloyl 6-aminocaproic acid and their polymerization in dioxane. Winston and Kirchner[2] synthesized *N*-methacryloyl β-alanine, *N*-methacryloyl glycine and *N*-methacryloyl γ-aminobutyric acid, but did not investigate polymerization of these monomers since their interest was in deriving the corresponding hydroxamate derivatives. They did not isolate *N*-methacryloyl γ-aminobutyric acid. It was reported to readily polymerize during its isolation[2]. All these monomers are hydrophilic and polymerizations in non-aqueous solutions are likely to result in heterogeneous polymerizations. In aqueous solutions, the monomer acquires either positive or negative charge due to its ampholytic character. The aqueous polymerization and copolymerization of monomers containing ionizable groups is complex and depends on pH, nature of the counterion, concentration of the added salt, etc.[4]. In this communication, the synthesis of *N*-acryloyl γ-aminobutyric acid and its polymerization in aqueous solution are reported.

Experimental

N-acryloyl γ-aminobutyric acid was prepared by the method reported by Winston and Kirchner[2]. The acryloyl chloride and γ-aminobutyric acid used were CP grade chemicals (>98%) purchased from E. Merck, Germany. Acryloyl chloride was reacted with γ-aminobutyric acid in aqueous alkali at 5°C. At the end of the reaction, the mixture was acidified and extracted with chloroform. The monomer was recovered by concentrating the chloroform extract using a rotavapour system (maximum temperature 35°C) and adding n-heptane to the concentrate. In the initial experiments, the monomer was observed to undergo polymerization during isolation. However, the spontaneous polymerization during isolation could be avoided by storing the chloroform extract at 5–10°C for ~72 h or more prior to concentration and monomer recovery. The monomer yield was independent of the storage period of the chloroform extract when the period exceeded 72 h. The monomer was purified by recrystallization from chloroform solution (m.p. 98°C).

Elemental analysis. Calculated: C, 53.90%; H, 7.01%; N, 8.92%; O, 30.60%. Found: C, 52.67%; H, 6.84%; N, 9.00%; O, 31.49%.

I.r. (in nujol): 3290 cm^{-1} (–NH), 1560 cm^{-1} (–NH amide), 1620 cm^{-1} (amide C = O), 1720 cm^{-1} (acid C = O), 1660 cm^{-1} (C = C).

^1H n.m.r. ($CDCl_3$: in ppm with respect to TMS) 6.3 q, 6.1 q, 5.65 q (vinyl H), 3.5 q ($CH_2\alpha$ to amide –NH), 1.9 qn ($CH_2\beta$ to amide –NH), 2.5 t (CH_2 next to C = O); after D_2O exchange 3.5 (q → t), 6.1 intensity reduced to half (attributed to acid H).

Polymerizations and copolymerizations were carried out in 0.5 M NaCl solution at 65°C using 0.1% (w/w) potassium peroxydisulphate as initiator. The procedures employed were identical to those reported elsewhere[5]. In the copolymerization experiments, the monomer to comonomer molar ratio used was 1:9 with acrylamide being used as the comonomer.

N.m.r. spectra were recorded using a Bruker MSL-300 n.m.r. spectrometer operating at 300 MHz for ^1H and at 75.48 MHz for ^{13}C. The ^1H n.m.r. for the monomer was recorded in $CDCl_3$ solution. The ^{13}C spectra for the polymer and copolymer were recorded in a gated decoupled mode. The sample was dissolved in a minimum amount of deionized water in a 10 mm o.d. NMR tube and a capillary containing D_2O was used for field frequency locking. Chemical shifts were identified with reference to 67.2 ppm for dioxane.

I.r. spectra were recorded using a Pye Unicam SP3-300 i.r. spectrophotometer in nujol. Viscosity measurements were carried out in 0.12 M NaCl at 30°C using a Ubbelohde viscometer. Potentiometric titrations were carried out using a Mettler DL 25 autotitrator equipped with a Mettler DG 111 combination general purpose glass electrode. The initial pH of the solution

*NCL communication number 5263

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0032-3861/92/112456-03

(concentration ~0.1% w/v) was adjusted to 12.0 using 0.1 N NaOH and the solution was back titrated with 0.1 N HCl. The melting point was recorded with a Thermonix apparatus.

Results and discussion

N-*acryloyl γ-aminobutyric acid.* The monomer was synthesized by reacting acryloyl chloride with γ-aminobutyric acid under alkaline conditions at 0–5°C. At the end of the reaction, the mixture was acidified and repeatedly extracted with chloroform, and dried over anhydrous Na_2SO_4. Attempts to isolate the monomer from the chloroform extract by n-heptane addition were unsuccessful and yielded a sticky mass. When the chloroform extract was stored at low temperature (5–10°C) for ~72 h or more, subsequent concentration and recovery resulted in a white crystalline solid.

As initial attempts to isolate the monomer were unsuccessful, an h.p.l.c. method was used to analyse the monomer content in the chloroform extract. μ-Styragel columns (two columns of 100 Å and one of 500 Å porosity) employed as the stationary phase and tetrahydrofuran as the mobile phase gave satisfactory resolution. The monomer conversion estimated on the basis of acryloyl chloride used and acryloyl chloride present (either as such or as acrylic acid) was ~7% after 30 min and 18% after 2 h. Moreover, the peak due to acryloyl chloride was totally absent in chloroform extract obtained after 2 h showing that the maximum conversion achieved under the reaction conditions employed was <20%. The reasons for the rapid polymerization during isolation (immediately after chloroform extraction) and facile isolation of monomer after ageing the chloroform extract at low temperature for 72 h or more are not understood. It is speculated that the species present in the chloroform extract responsible for polymerization is deactivated during storage at low temperatures.

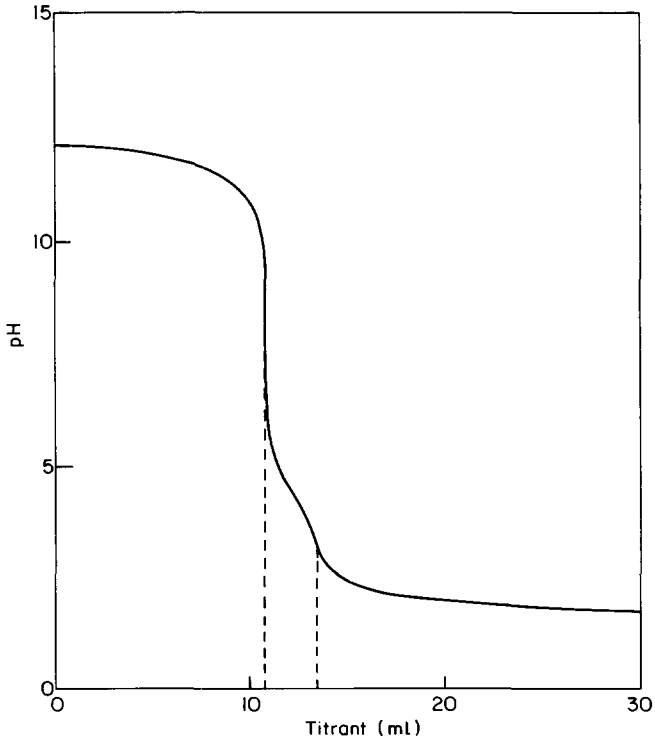

Figure 1 Potentiometric titration curve for *N*-acryloyl γ-aminobutyric acid (50 ml of a 0.1% w/v solution in water; [HCl] = 0.1 N)

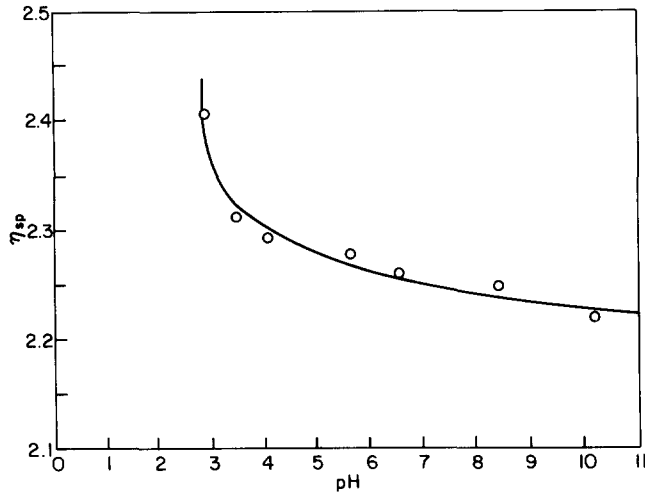

Figure 2 Plot of viscosity *versus* pH for a 1% solution of poly(*N*-acryloyl γ-aminobutyric acid) in 0.12 M NaCl at 30°C

Polymerization and copolymerization. The polymerization and copolymerization of an ionizing monomer are hindered under conditions favouring monomer ionization[6]. The electrostatic interactions between the ionized monomer and the charges on the macroradical retard the propagation reaction. *Figure 1* shows the pH *versus* titration curve obtained by the potentiometric titration of the monomer. It is seen that two equivalence points are obtained at pH values of 6.83 and 3.35. It was confirmed that the titre value at pH 6.83 corresponds to the total protonation of the carboxylate ion. The second equivalence point can only be attributed to the protonation (probably of the amide nitrogen) resulting in the molecule acquiring a positive charge. *N*-acryloyl γ-aminobutyric acid has thus an ampholytic character. In the case of monomers like acrylic acid, the ionization of the monomer can be suppressed either by choosing low pH conditions or by incorporating a sufficient quantity of a neutral salt, conditions which favour facile polymerization. The monomer synthesized is ampholytic. Addition of salts and variation of pH are not likely to achieve the desired objectives. Ionization of the monomer affecting polymerization can also be prevented by carrying out the polymerizations in organic solvents of low dielectric strength. However, the monomer and the resulting polymer are hydrophilic and homogeneous polymerizations are unlikely to be achieved in organic solvents. It may be noted that polymerizations of *N*-acryloyl glycine and *N*-acryloyl 6-aminocaproic acid carried out in dioxane resulted in precipitation polymerization[3].

With a view to determining favourable pH conditions for polymerization, viscosity *versus* pH behaviour of the polymer was examined. For this purpose the polymer formed by the spontaneous polymerization during monomer isolation in the initial experiments was utilized. The polymer was isolated from the concentrated chloroform extract by adding n-heptane and purified by reprecipitation. Specific viscosity *versus* pH of a 1% solution of the polymer in 0.12 M NaCl is shown in *Figure 2*. Initially the solution viscosity decreases sharply, and above pH 6 viscosity decreases gradually. The high viscosity at low pH values can be attributed to the protonation of the amide nitrogen resulting in cationic charges on the polymer. Carboxylic acid groups

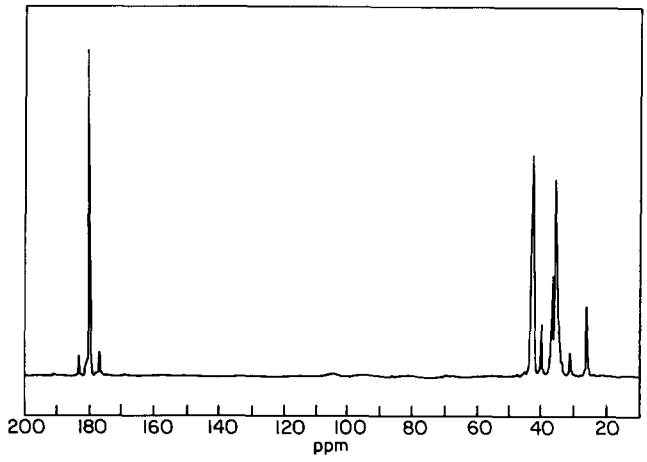

Figure 3 ^{13}C n.m.r. spectrum of poly(acrylamide-*co*-*N*-acryloyl γ-aminobutyric acid): 22 000 accumulations; 45° pulse; 2 s recycle delay

dissociate at high values of pH and the resulting electrostatic repulsions should result in higher viscosities at high values of pH. Contrary to expectations, values of viscosities are lower at higher values of pH. This is attributed to the fact that the electrostatic charges being far removed from the main chain do not greatly contribute to electrostatic interactions. The result would indicate that facile polymerization can occur at high pH values.

Solution polymerizations attempted in 0.5 M NaCl solution at 65°C with 0.1% w/w potassium peroxydisulphate were not successful when carried out in acidic pH conditions. However, reactions carried out at pH 12 resulted in facile polymerization. Monomer conversion was ~80% after ~2 h. The polymer had an intrinsic viscosity of 0.7 dl g^{-1}. The i.r. spectrum of the polymer in nujol showed a broad minimum at 3200–3300 cm^{-1} (–NH), a sharp peak at 1500 cm^{-1} (–NH amide), a broad minimum at 1500–1700 cm^{-1} (amide C = O, acid C = O) and the peak at 1660 cm^{-1} (unsaturation) was absent.

Copolymerization of the monomer with acrylamide was carried out at 65°C in 0.5 M NaCl at pH 12 using 0.1% w/w potassium peroxydisulphate. The molar ratio of the monomer to acrylamide used was 1:9. The polymer was isolated using acetone as the precipitant. Conversion to polymer was 70% after 2 h and the polymer had an intrinsic viscosity of 5.9 dl g^{-1} in 0.12 M NaCl at 30°C.

Figure 3 shows the ^{13}C n.m.r. spectrum for the copolymer. The main chain carbon atoms, both from acrylamide and the monomer moieties, resonate at 34–36 ppm. The signal positions are confirmed from the spectra of the homopolymers (spectra not shown). The amide C = O from polyacrylamide gives a signal at 180 ppm and that due to the monomer moiety is at 176.8 ppm. The signals at 42.7, 26.0 and 35.4 ppm are ascribed to the three methylene groups in the pendant chain. Their presence unequivocally confirms the incorporation of the monomer into the copolymer. The copolymer composition was estimated as the ratio of the peak intensity at 176.8 ppm (amide C = O of the monomer) to the total amide C = O (intensity at 176.8 ppm and 180 ppm). The copolymer has 8 mol% monomer as compared to 10 mol% used in the feed.

The results show that aqueous polymerizations/copolymerizations of *N*-acryloyl γ-aminobutyric acid can be brought about by carrying out the reactions at high pH values. This is ascribed to the negligible electrostatic interactions of the charges far away from the main chain.

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