polymer reports

Acrylate monomers based on 2,6-piperazinedione

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Iminodiacetic acid has been used as the starting material for the preparation of 2,6-piperazinedione, 1-hydroxy- and 1-methyl-2,6-piperazinedione. These piperazinediones have been used to prepare the corresponding 4-acryloyl-2,6-piperazinediones.

Keywords Synthesis; acrylate monomers; 2,6-piperazinedione; iminodiacetic acid

INTRODUCTION

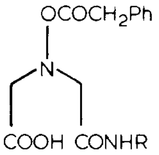
During the course of a systematic investigation into the synthesis of new polyamides with hydrocarbon backbones, we required a number of acrylate monomers based on 2,6-piperazinedione. This dione has been prepared previously from iminodiacetonitrile *via* cyclization with hydroxylamine[1,2]. However, in our hands, the literature methods gave only low yields of the desired product. Starting from iminodiacetic acid, we have devised a more practical general route to the synthesis of acrylate monomers based on 2,6-piperazinediones. This is the subject of the present report.

RESULTS AND DISCUSSION

Iminodiacetic acid was treated with benzyloxycarbonyl chloride to give the corresponding *N*-benzyloxycarbonyl-iminodiacetic acid[3]. Cyclization of this protected diacid was effected with acetic anhydride to produce *N*-benzyloxycarbonyliminodiacetic anhydride. Reaction of this anhydride with concentrated aqueous ammonia produced the monoamide (1; R = H)[4]. Cyclization of the monoamide to form 4-benzyloxycarbonyl-2,6-piperazinedione (2; R = H) was achieved by heating *in vacuo* at 180°C. The benzyloxycarbonyl group was conveniently removed by treatment with hydrogen bromide in acetic acid followed by neutralization with triethylamine to give 2,6-piperazinedione in good yield (73%).

During the course of the synthesis described above it was realised that *N*-benzyloxycarbonyl-iminodiacetic anhydride was a key intermediate for the synthesis of *N*-substituted piperazinediones. Reaction of the anhydride with hydroxylamine and methylamine, followed by dicyclohexylcarbodiimide mediated cyclization (heating under vacuum resulted in charring and low yields of product) gave the protected piperazinediones (2; R = OH and Me) respectively. Similar reactions of the anhydride were carried out with other amine nucleophiles, for example O-methylhydroxylamine and *N*-aminomorpholine when the corresponding *N*-benzyloxycarbonyl substituted piperazinediones (2; R = OMe, *N*-morpholino were obtained. The benzyloxycarbonyl group was removed from the piperazinediones (3; R = OH, Me) by treatment with hydrogen bromide to give 1-hydroxy- and 1-methyl-2,6-piperazinedione respectively.

The suitability of 2,6-piperazinedione, 1-hydroxy- and 1-methyl-2,6-piperazinedione, for the preparation of acrylate monomers was investigated. Treatment of aqueous solutions of the piperazinediones with acryloyl chloride in the presence of sodium hydrogen carbonate produced the acrylates (3; R = H, OH, Me) respectively[5,6].



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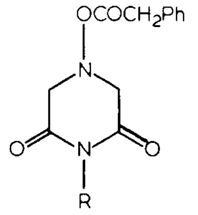

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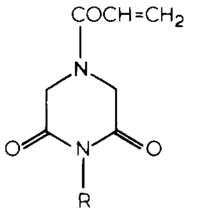

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EXPERIMENTAL

N-*Benzyloxycarbonyliminodiacetic acid*

Iminodiacetic acid (250 g, 1.88 mol) was dissolved in water (1000 cm^3) containing sodium hydroxide (150 g, 3.75 mol). Sodium carbonate (298 g, 2.82 mol) was added to the stirred solution which was cooled to 0°C. Benzyloxycarbonyl chloride (529 g, 3.10 mol) was added slowly to the stirred solution over 1 h. The solution was stirred for 1 h and excess sodium carbonate removed by filtration. The aqueous solution was extracted with diethyl ether (3×100 cm^3) and acidified to pH 2. This solution was extracted with chloroform (4×200 cm^3) and the chloroform extracts were dried (magnesium sulphate) and evaporated to give *N*-benzyloxycarbonyl-iminodiacetic acid (377 g, 75%) as a colourless oil which crystallized from chloroform–light petroleum (b.p. 40°–60°C), m.p. 98°–100°C. $C_{12}H_{13}NO_6$ Calculated: C 53.93 H 4.90 N 5.24 O 35.92; *M*, 267, found: C 53.93 H 4.87 N 5.23 O 36.06 M^+ 267. ^{1}H n.m.r. ($CDCl_3$); $\delta = 4.2$ (s, 4H, H_2C–N–CH_2), 5.1 (s, 2H, H_2C–O–), 7.3 (s, 5H, phenyl protons), 10.9 ppm [s, 2H, $(COOH)_2$].

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N-Benzyloxycarbonyliminodiacetic anhydride

N-Benzyloxycarbonyliminodiacetic acid (134 g, 0.50 mol) was dissolved in acetic anhydride (500 cm^3) and stirred for 2 h. The acetic anhydride was evaporated at 60°C to give *N*-benzyloxycarbonyliminodiacetic anhydride (112 g, 90%) as an oil which crystallized from chloroform-diethyl ether as a white solid m.p. 102°–104°C. $C_{12}H_{11}NO_5$ Calculated: C 57.88 H 4.45 N 5.63 O 32.13; *M*, 249, found: C 57.92 H 4.48 N 5.75 O 32.22; M^+, 249. ^{1}H n.m.r. [$(CDCl_3)$]: $\delta = 4.4$ (s, 4H, H_2C–N–CH_2), 5.1 (s, 2H, H_2C–O), 7.3 ppm (s, 5H phenyl protons).

3-Benzyloxycarbonyliminodiacetic Acid Monoamide (1; R = H)

N-Benzyloxycarbonyliminodiacetic anhydride (20 g, 0.080 mol) was dissolved in dry 1,4-dioxan (60 cm^3) and aqueous 14 M ammonia (3 cm^3) was added. Heat was evolved and after 1 h 3-benzyloxycarbonyliminodiacetic acid monoamide (1; R = H) (11.3 g, 53%) was deposited m.p. 167°–169°C (from water). $C_{12}H_{14}N_2O_5$ Calculated: C 54.13 H 5.30 N 10.52 O 30.04; *M*, 266, found: C 54.10 H 5.23 N 10.60 O 30.47; M^+, 266. ^{1}H n.m.r. [$(CD_3)_2CO$]: $\delta = 4.1$ (s, 4H, H_2C–N–CH_2) 5.1 (s, 2H, H_2C–O), 6.4 (s, 2H, NH_2, exchangeable with D_2O), 7.2 ppm (s, 5H, phenyl protons).

The amides (1; R = OMe, Me) were prepared similarly.

4-Benzyloxycarbonyl-2,6-piperazinedione (2; R = H)

3-Benzyloxycarbonyliminodiacetic acid monoamide (1; R = H) (0.72 g, 0.0027 mol) was heated at 180° under vacuum (1 mm Hg) for 3 h. The brown residue was dissolved in the minimum of hot methanol and charcoal was added. After filtration, the methanol was evaporated to give 4-benzyloxycarbonyl-2,6-piperazinedione (2; R = H) (0.44 g, 66%) as a pale yellow solid m.p. 168°C (from methanol). $C_{12}H_{12}N_2O_4$ Calculated: C 58.06 H 4.87 N 11.29 O 25.78; *M*, 248, found: C 58.17 H 4.83 N 11.44 O 25.72; M^+, 248. ^{1}H n.m.r. [$(CD_3)_2CO$]: $\delta = 2.75$ (s, 1H, NH, exchangeable with D_2O), 4.3 (s, 4H, H_2C–N–CH_2), 5.1 (s, 2H, H_2C–O), 7.3 ppm (s, 5H, phenyl protons).

2,6-Piperazinedione

Finely powdered 4-benzyloxycarbonyl-2,6-piperazinedione (2; R = H) (2.44 g, 0.0098 mol) was added to a solution of 45% w/v hydrogen bromide in glacial acetic acid (10 cm^3) and the reaction mixture was left with occasional shaking until gas evolution ceased. Dry diethyl ether (100 cm^3) was added and the mixture was left at 0°C for 16 h to give a white solid which was washed exhaustively with dry diethyl ether. The solid was 2,6-piperazinedione hydrobromide (1.79 g, 94%). The hydrobromide salt (0.71 g, 0.0036 mol) was added to triethylamine (3 cm^3) and the mixture was stirred for 20 min at room temperature before being washed with chloroform (4 x 5 cm^3) and dry diethyl ether (2 x 5 cm^3) to give 2,6-piperazinedione (0.30 g, 73%) as a brown solid m.p. 190°–212°C decomp. (from methanol) $C_4H_6N_2O_2$ Calculated: C 42.14 H 5.31 N 24.58; *M*, 114. found: C 42.11 H 5.35 N 24.62 M^+, 114. ^{1}H n.m.r. (D_2O): $\delta = 3.5$ ppm (s, H_2C–N–CH_2).

1-Methyl-2,6-piperazinedione

N-Benzyloxycarbonyliminodiacetic anhydride (5.0 g, 0.02 mol) was dissolved in 1,4-dioxan (25 cm^3) and aqueous 25% w/v methylamine (10 cm^3) was added. After 2 h the solvent was removed on a rotary evaporator at 60°C to give a viscous oil. The oil was heated at 160°C for 2 h under vacuum (1 mm Hg) and then dissolved in hot methanol. On evaporation of the methanol 4-benzyloxycarbonyl-1-methyl-2,6-piperazinedione (2; R = Me) (2.46 g, 47%) was obtained as white crystals m.p. 75°–78°C (from methanol). $C_{13}H_{14}N_2O_4$ Calculated: C 59.59 H 5.39 N 10.69; *M*, 262. Found: C 59.48 H 5.35 N 10.71; M^+, 262.

4-Benzyloxycarbonyl-1-methyl-2,6-piperazinedione (11.47 g, 0.044 mol) was added to 45% w/v hydrogen bromide in glacial acetic acid (25 cm^3). Reaction conditions and the work-up procedure were as described previously. 1-Methyl-2,6-piperazinedione hydrobromide (7.63 g, 83%) was isolated. The hydrobromide salt (1.14 g, 0.0055 mol) was dissolved in water (2 cm^3) containing sodium hydrogen carbonate (1.20 g, 0.014 mol). The solution was extracted with chloroform (4 x 10 cm^3), the chloroform extracts were dried (magnesium sulphate) and evaporated to give 1-methyl-2,6-piperazinedione (0.36 g, 52%) as white crystals m.p. 70°–72°C (from acetone–light petroleum b.p. 40°–60°C) $C_5H_8N_2O_2$ Calculated: C 46.91 H 6.30 N 21.89; *M*, 128. Found: C 47.18 H 6.30 N 21.66; M^+, 128. ^{1}H n.m.r. [$(CD_3)_2CO$]: $\delta = 3.6$ (s, 4H, H_2C–N–CH_2), 3.0 (s, 3H, N–CH_3), 2.7 ppm (s, 1H, NH, exchangeable with D_2O).

1-Hydroxy-2,6-piperazinedione

In similar series of reactions *N*-benzyloxycarbonyliminodiacetic anydride (5.0 g, 0.02 mol) was treated with hydroxylamine to give 4-benzyloxycarbonyl-1-hydroxy-2-6-piperazinedione (2; R = OH) (2.73 g, 52%) as white crystals m.p. 169°C (from acetone). $C_{12}H_{12}N_2O_5$ Calculated: C 54.55 H 4.58 N 10.60 O 30.28; *M*, 264. Found: C 54.38 H 4.42 N 10.71 O 30.50; M^+, 264.

The reaction of 4-benzyloxycarbonyl-1-hydroxy-2,6-piperazinedione (2; R = OH) (26.4 g, 0.10 mol) with hydrogen bromide gave 1-hydroxy-2,6-piperazinedione (9.8 g, 79%) as a white solid m.p. 178°C (from water). $C_4H_6N_2O_3$ Calculated: C 36.95 H 4.65 N 21.55 O 36.92; *M*, 130. Found: C 37.06 H 4.97 N 22.00 O 36.62 M^+ 130. ^{1}H n.m.r. [D_2O] $\delta = 3.7$ ppm (s, H_2C–N–CH_2).

Acrylate monomers

4-Acryloyl-2,6-piperazinedione (3; R = H). 2,6-Piperazinedione (0.50 g, 0.0044 mol) and sodium hydrogen carbonate (0.70, 0.0083 mol) were added to water (3 cm^3) and the mixture was cooled to 0°C. Acryloyl chloride (0.61 g, 0.0068 mol) was added dropwise and 4-acryloyl-2,6-piperazinedione (3; R = H) (0.36 g, 49%) was deposited as a brown solid m.p. 143°C (from acetone–light petroleum b.p. 40°–60°C). $C_7H_8N_2O_3$ Calculated: C 50.04 H 4.80 N 16.68; *M*, 168. Found C 49.9 H 4.8 N 16.6; M^+, 168. ^{1}H n.m.r. [$(CD_3)_2CO$] $\delta = 4.5$ (s, 4H, H_2C–N–CH_2), 5.6–6.1 (m, 2H, $H_2C=$), 6.6–7.1 (m, 1H, $HC=$), 10.0 ppm (s, 1H, NH).

4-Acryloyl-1-methyl-2,6-piperazinedione (3; R = Me). 1-Methyl-2,6-piperazinedione hydrobromide (4.02 g, 0.019 mol) was dissolved in water (12 cm^3) containing sodium hydrogen carbonate (4.85 g, 0.058 mol). The reaction mixture was cooled to 0°C and acryloyl chloride (2.10 g, 0.023 mol) was added dropwise. The solution was stirred for 20 min and extracted with chloroform (3 x 25 cm^3). The chloroform extracts were dried (magnesium sulphate) and evaporated to give an oil. The oil was crystallized from chloroform–light petroleum (b.p. 40°–60°C) to give 4-acryloyl-1-methyl-2,6-piperazinedione (3; R = Me) (3.34 g, 89%) as a white crystalline solid m.p. 75°–77°C. $C_8H_1{}^0N_2O_3$ Calculated: C 52.79 H 5.54 N 15.39; *M*, 182. Found: C 52.63 H 5.53 N 15.30 M^+ 182, ^{1}H n.m.r. $[(CD_3)_2CO]$: $\delta = 6.6$–7.1 (m, 1H, HC =), 5.6–6.35 (m, 2H, CH_2 =), 4.55 (s, 4H, H_2C–N–CH_2), 3.05 ppm (s, 3H, N–CH_3).

4-Acryloyl-1-hydroxy-2,6-piperazinedione (*3; R = OH*). 1-Hydroxy-2,6-piperazinedione was added to water (3 cm^3), the suspension was heated to 65°C and cooled to 0°C. Acryloyl chloride (0.35 g, 0.0039 mol) was added dropwise and the solution was stirred for 1 h. 4-Acryloyl-1-hydroxy-2,-6-piperazinedione (3; R = OH) (1.13 g, 81%) was deposited as a white solid m.p. 142° (from acetone-diethyl ether). Calculated: *M*, 184; Found: M^+, 184.

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Annealing of polyethylene crystals in the hexagonal phase

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The kinetics of thickening of polyethylene crystals in the hexagonal phase is studied. Distributions of thickness, *L*, of bands and/or lamellae are obtained by electron microscopy for a specimen annealed at $p = 6.1$ kbar, $T = 242$°C for 30, 300, 3600 and 86 400 seconds. The dependence of the average band thickness $\bar{L}(t)$ on the annealing time *t* can be expressed as $\bar{L}(t) = 46\cdot\log(t/t_0) + \bar{L}(t_0)$ [nm]. Moreover, these distributions can be superposed on each other if we scale *L* by $\bar{L}(t)$. A model for the thickening process of a lamellae is proposed; coalescence of two bands occurs by disappearance of the boundary with the rate proportional to $\exp(-\alpha L)$. The value of α depends on the mobility of defects in the boundary and is discussed in detail.

Keywords Polyethylene; high pressure; annealing; hexagonal phase; morphology; lamella

INTRODUCTION

Standard methods of crystallizing polyethylene, including melt- and solution-crystallization, give lamellar structures several tens of nm thick.

Wunderlich[1] first observed the band structure, several hundred nm thick (extended chain crystals, *ECC*), on crystallization under high pressure. Bassett[2] postulated that *ECC* are formed on crystallization under high pressure through the hexagonal phase. Several laboratories have attempted to verify this hypothesis and failed; the hexagonal phase was not always necessary for the formation of *ECC*[3].

Effects of annealing on lamellar and/or band thickness have been reported[4–6], and for a constant annealing time, lamellar thickness increases in the hexagonal phase much more rapidly than in the orthorhombic phase.

Here, the kinetics of lamellar thickening in the hexagonal phase are reported. A model of the thickening process involving coalescence of lamellae is proposed. The results of the simulation on this model are compared with the experimental results.

EXPERIMENTAL

The material used was unfractionated high density polyethylene, Sholex 6009 ($M_n = 1.4 \times 10^4$, $M_w = 1.14 \times 10^5$). The material was melt-crystallized at atmospheric pressure, annealed at 120°C for 1 day, and then used. The long period obtained by small-angle X-ray scattering (SAXS) was 29 nm.

The high pressure differential thermal analysis (d.t.a.) cell used for annealing is shown in *Figure 1*. Pressure was measured by a calibrated manganine gauge using silicone oil as pressure transmitting fluid. Temperature was measured by a copper–constantan thermocouple.

A 7 mg sample for d.t.a. was pushed onto the thermocouple by a screw, and another sample for observation of fracture surface about 12 × 7 × 1 mm^3, was placed into the slit shown in *Figure 1*. After elevating the pressure to ~6 kbar, the cell was heated at 5 K min^{-1}. Samples were annealed for selected times at $P = 6.1$ kbar and $T = 242$°C, just above the temperature at which the orthorhombic→hexagonal phase occurs, as confirmed by d.t.a. Cooling to room temperature was then carried out at an initial rate of 60 K min^{-1}. Annealing times were 30, 300, 3600 and 86 400 s.

Annealed samples were fractured in liquid nitrogen, and the fracture surfaces observed in an electron microscope using a two-stage replica technique. Crystal thickness distributions were obtained as follows. Two sets of parallel lines, mutually orthogonal, were drawn on the photographs at intervals of 440 nm. Crystal thickness was measured along the striation direction at the intersection

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