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Anionic ring-opening polymerization of 2-phenyl-1,3,4-oxadiazolin-5-one and conversion of the resulting polymer, *N*-benzamido-1-nylon, to *N*-amino-1-nylon

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Summary

The ring-opening polymerization of 2-phenyl-1,3,4-oxadiazolin-5-one (1) was carried out anionically both in bulk and in DMF solution at 140°C for 15 h in the presence of various initiators, such as alkaline metal salts of 1, alkaline metal fluorides and tertiary amines, leading to N-benzamido-1-nylon (2) having $\overline{M}n$s up to 2,000. Hydrolysis of the pendant benzamido groups of the resulting polymer was successfully achieved in aqueous ethanol containing concentrated hydrochloric acid at 100°C to give N-amino-1-nylon (3). The original polymer dissolves easily in aliphatic and aromatic alcohols and polar aprotic solvents, whereas the hydrolyzed polymer is not soluble in these solvents but highly soluble in water. In dilute aqueous solutions, the latter polymer behaves as common polyelectrolytes with flexible backbone. Polymers 2 and 3 began to lose weight in air at around 200 and 170°C, respectively.

Introduction

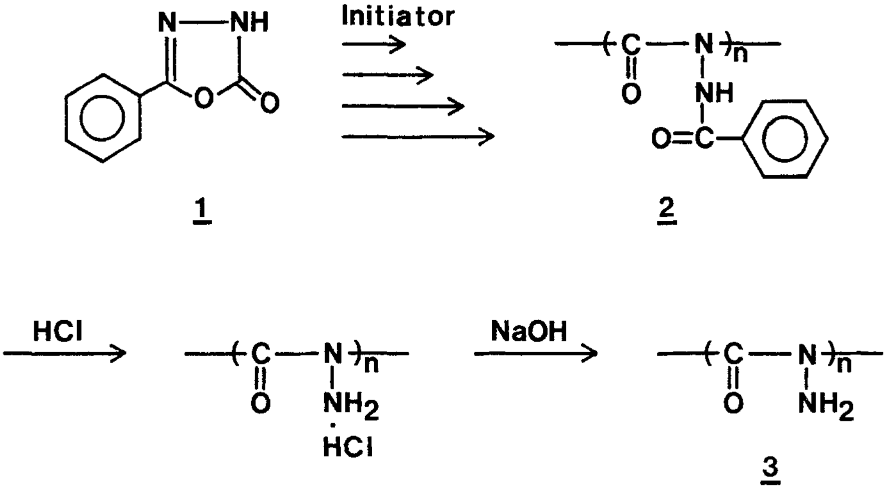
A wide variety of five-membered heterocyclic compounds polymerize by ring-opening. However, cyclic urethanes have poorer ring-opening reactivities (1), because these reactions are essentially reversible and the cyclic urethanes are thermodynamically more stable than the ring-opened polymers.

Previously, Endo and co-workers (2, 3) reported that 2-methyl-1,3,4-oxadiazolin-5-one, a five-membered heterocyclic urethane, undergoes ring-opening polymerization anionically by using an appropriate initiator to give the simplest polyamide, 1-nylon, with pendant benzamido groups on the nitrogen atom. This reaction is noteworthy even though the molecular weight of the polymer obtained was very low, because it is difficult to obtain 1-nylons. The only method previously reported was anionic polymerization of monoisocyanates leading to high-molecular-weight N-substituted-1-nylons (4-8).

We have recently investigated in detail the ring-opening abilities of 2-(substituted)phenyl-1,3,4-oxadiazolin-5-ones toward various nucleophiles and reported that these five-membered heterocyclic urethanes easily react with aliphatic and aromatic amines, (thio)phenols and free L-α-aminoacids giving the corresponding ring-opened adducts in high yields (9-11). These results lead to the suggestion that 2-phenyl-

1,3,4-oxadiazolin-5-one (1) is a very promising monomer for anionic ring-opening polymerization to obtain 1-nylon having higher molecular weights.

The present work is concerned with the detailed study of the anionic ring-opening polymerization of heterocyclic urethane 1 and also the conversion of the resulting polymer, N-benzamido-1-nylon (2), to N-amino-1-nylon (3) by selective hydrolysis of the pendant groups. The properties of the polymers before and after hydrolysis are also discussed.



Experimental

Materials

2-Phenyl-1,3,4-oxadiazolin-5-one 1 (mp 138-139°C) was prepared as previously reported (9). The lithium, sodium and potassium salts of 1 (1-Li, 1-Na and 1-K) were synthesized from the corresponding hydroxides and 1 (2). Other reagent-grade chemicals and solvents were used after purification by the conventional methods.

Ring-opening polymerization

The reactions were carried out both in bulk and in solution at 140°C for 15 h in a 10-mL sealed ampule, in which the atmosphere was replaced with nitrogen. In solution polymerization, N,N-dimethylformamide (DMF) was used as a reaction medium. A typical example of the polymerization is as follows:

A mixture of 1 (0.405 g, 2.5 mmol) and 1-Na (0.046 g, 0.25 mmol) was gradually heated to 140°C to melt homogeneously, which was maintained at that temperature for 15 h with agitation. After cooled to ambient temperature, a small quantity of DMF (1-2 mL) was added to the glassy material obtained. The resultant clear solution was dropped into a large amount of ether. The white powdery precipitate was washed successively with ether and water. Yield: 0.227 g (56%). Reduced viscosity: 0.11 dL/g (in DMF; c=0.5 g/dL; at 30°C).

Infrared (IR) spectrum: 3200 (vs; N-H), 1660 (vs; benzamide C=O) and 1640 cm^{-1} (vs; nylon C=O). ^1H-Nuclear magnetic resonance (^1H-NMR) spectrum: δ 10.1-10.9 (broad s; 1H; N-H) and 7.2-8.4 ppm (m; 5H; C_6H_5).

Hydrolysis of polymer

To a solution of polymer 2 (0.500 g) in 95% aqueous ethanol (50 mL) was added concentrated hydrochloric acid (5 mL) followed by stirring at 100°C for 4 h. After the mixture was neutralized with dilute aqueous sodium hydroxide and then dialyzed overnight against water, the solvent was removed under reduced pressure to give white powdery material. Yield: 0.150 g (84% based on the theoretical structure 3). IR: 3400 (vs; N-H) and 1640 cm^{-1} (vs; C=O). It was difficult to measure ^1H-NMR spectrum because this material was insoluble in any organic solvents.

Measurements

The IR and ^1H-NMR spectra were recorded on a JASCO IR-810 spectrophotometer as potassium bromide disks and on a Hitachi R-24B spectrometer (60 MHz) in dimethyl sulfoxide (DMSO)-d_6 with tetramethylsilane as an internal standard, respectively. Number-average molecular weight ($\overline{Mn}$) and weight-average molecular weight ($\overline{Mw}$) were determined by means of gel permeation chromatography on the basis of a polystyrene calibration on a Tosoh HLC CP-8,000 System using DMF as eluent. Thermogravimetry was performed on powder samples with a Rigaku Denki Thermoflex RC-13 thermal analyzer at a 5K/min heating rate.

Results and discussion

Table 1. Ring-opening polymerization of 1 in bulk[a]

Run	Initiator	Polymer Yield %	Polymer η_{red}[b] dL/g
1	none	0	——
2	1-Li	30	0.09
3	1-Na	56	0.11
4	1-K	30	0.07
5	KF	37	0.08
6	CsF	39	0.07
7	DMBA	17	0.04
8	TEDA	20	0.05
9	TEA	trace	——

[a] Polymerization was carried out with 2.5 mmol of 1 at 140°C for 15 h, 10 mol% of the initiator to 1 being used.

[b] Measured at a polymer concentration of 0.5 g/dL in DMF at 30°C.

Table 2. Ring-opening polymerization of 1 in DMF solution[a]

Run	Initiator	Polymer Yield %	 η_{red}[b] dL/g
1	none	0	——
2	1-Li	54	0.08
3	1-Na	32	0.11
4	1-K	45	0.07
5	KF	30	0.08
6	CsF	27	0.07
7	DMBA	trace	——
8	TEDA	12	——
9	TEA	trace	——

[a] Polymerization was carried out with 2.5 mmol of 1 in 2.5 mL of DMF at 140°C for 15 h, 10 mol% of the initiator to 1 being used.

[b] Measured at a polymer concentration of 0.5 g/dL in DMF at 30°C.

In order to find out the effective initiators for the ring-opening polymerization of 2-phenyl-1,3,4-oxadiazolin-5-one 1, various initiators, such as alkaline metal salts of 1 (1-Li, 1-Na and 1-K), alkaline metal fluorides (potassium fluoride (KF) and cesium fluoride (CsF)) and tertiary amines (N,N-dimethylbenzylamine (DMBA), triethylenediamine (TEDA) and triethylamine (TEA)) were first tested at the concentration of 10 mol% to 1. As can be seen from Tables 1 and 2, in both methods alkaline metal salts of 1 were most effective among the

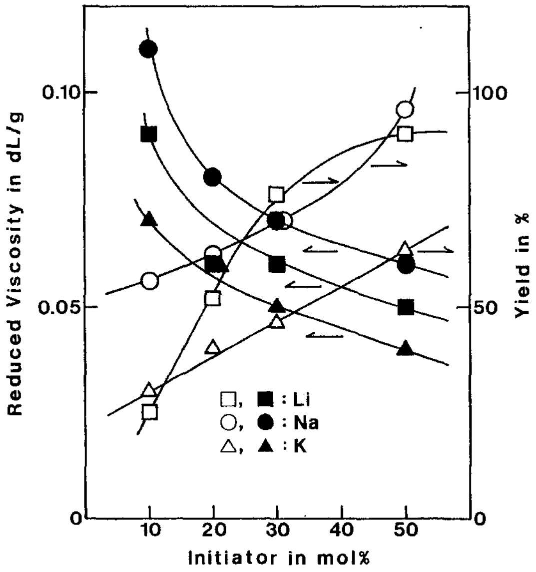


Fig. 1. Effect of initiator concentration on the yield and reduced viscosity of ring-opened polymer 2 in bulk polymerization. Polymerization was carried out with 2.5 mmol of 1 and the initiator at 140°C for 15 h.

initiators used, in terms of the yield and reduced viscosity of the resulting polymer. The effect of concentration of the alkaline metal salts on the polymerization was further studied in detail, and the results are shown in Figures 1 and 2. In all cases, the yield of polymer markedly increased with increasing initiator concentration, whereas the molecular weight decreased. Polymer 2 with the highest reduced viscosity of 0.11 dL/g was obtained by bulk and solution polymerizations both with a 10 mol% of 1-Na to 1. The $\overline{Mn}$ value of this polymer was 2,000. The $\overline{Mw}/\overline{Mn}$ ratio was 1.1, indicating that this ring-opened polymer has extremely narrow molecular weight distribution.

Conversion of ring-opened polymer, N-benzamido-1-nylon 2, to N-amino-1-nylon 3 by selective hydrolysis of the pendant benzamido groups was successfully attained in reasonable yield in 95% aqueous ethanol containing a small amount of concentrated hydrochloric acid at 100°C for 4 h. Amino-free polymer was isolated after neutralization with aqueous sodium hydroxide followed by dialysis against water.

The spectral analyses (IR and/or ^{1}H-NMR) provided supporting evidences for the proposed polymeric structures of both 1-nylons 2 and 3 (Experimental part). The IR spectrum of hydrolyzed polymer 3 exhibited two strong absorptions attributable to amino groups at 3400 cm^{-1} and nylon carbonyl groups at 1640 cm^{-1} with complete disappearance of a strong absorption at 1660 cm^{-1} due to benzamido carbonyl groups of

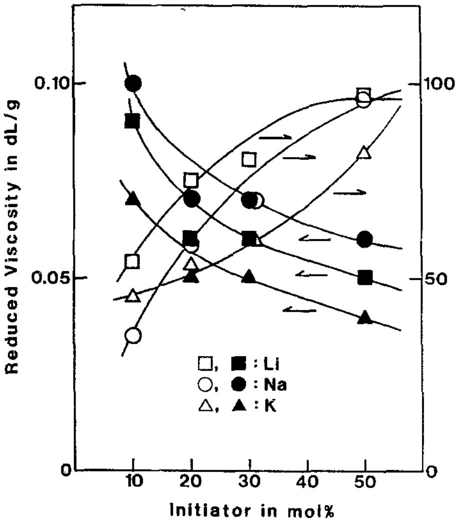


Fig. 2. Effect of initiator concentration on the yield and reduced viscosity of ring-opened polymer 2 in solution polymerization. Polymerization was carried out with 2.5 mmol of 1 and the initiator in 2.5 mL of DMF at 140°C for 15 h.

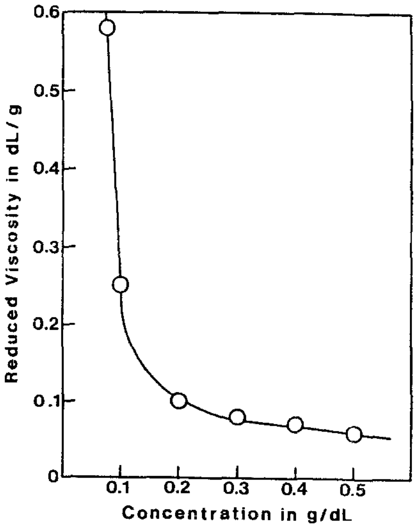


Fig. 3. Viscometric behavior of the dilute solution of N-amino-1-nylon 3 in water at 30°C.

ring-opened polymer 2, suggesting that hydrolysis of the pendant groups progressed selectively.

Ring-opened polymer 2 dissolved easily in aliphatic and aromatic alcohols such as methanol, ethanol and m-cresol and in polar aprotic solvents such as N,N-dimethylacetamide, DMF, DMSO, hexamethylphosphoramide and N-methyl-2-pyrrolidone, whereas hydrolyzed polymer 3 was not soluble in any organic solvents but highly soluble in water. Polymers 2 and 3 began to decompose at around 200 and 170°C in air, respectively.

The solution viscosity of the hydrolyzed polymer was measured using an Ubbelohde viscometer. The aqueous solution was diluted successively with water and the reduced viscosity was determined at each concentration. As shown in Figure 3, the reduced viscosity increased drastically with the decrease in polymer concentration. This viscometric behavior agrees well with that of usual polyelectrolytes with flexible backbone. The conformation of N-amino-1-nylon in solution is, therefore, supposed not to be rigid rod-like one similar to that of α-helical poly-α-aminoacids (12) but to have some flexibility.

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