

Synthesis of Polyenamines with Pendant Hydroxyl Groups by Ring-Opening Polyaddition of 5,5'-Oxalylbis(3,4-dihydro-2H-pyran) with Diamines

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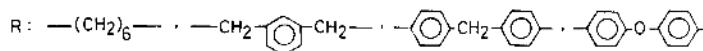
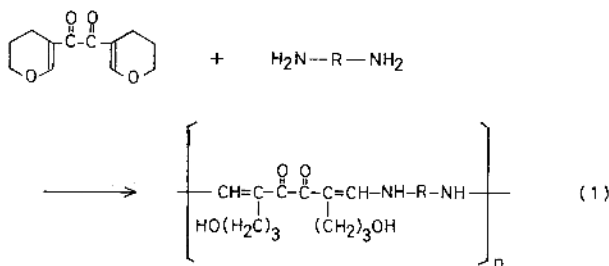
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ABSTRACT: A new class of polyenamines with pendant hydroxyl groups was synthesized by the ring-opening polyaddition of 5,5'-oxalylbis(3,4-dihydro-2H-pyran) with diamines through vinyl-ogous nucleophilic substitution. Solution polymerization carried out in alcoholic solvents such as *m*-cresol at room temperature afforded polymers having inherent viscosities of 0.1–0.27 in quantitative yields. The hydroxyl-containing polyenamines were soluble in a limited number of solvents and had low softening temperatures, below 200°C.

KEY WORDS Ring-Opening Polyaddition / 5,5'-Oxalylbis(3,4-dihydro-2H-pyran) / Diamines / Hydroxyl-Containing Polyamides / Solubility / Softening Temperature /

Recently, it was reported from our laboratory that polyenamines were readily synthesized by the polycondensation of reactive bis(ethoxyvinyl ketone) and analogs with diamines under mild polymerization conditions.^{1,2} We proposed the term “vinyl-ogous nucleophilic substitution polymerization” to account for this type of the polycondensation. The vinyl-ogous nucleophilic substitution can be extended to aminolysis of cyclic vinyl ethers having an electron-withdrawing carbonyl group at the β -

position, leading to ring-opened adducts. We have found that 5,5'-oxalylbis(3,4-dihydro-2H-pyran) (OBDP) met the important requirement of high reactivity for a reactive cyclic monomer which undergoes ring-opening polyaddition with diamines to yield polyenamines with pendant hydroxyl groups. This may provide the first example of a successful ring-opening polyaddition through vinyl-ogous nucleophilic substitution polymerization.



EXPERIMENTAL

Materials

5,5'-Oxalylbis(3,4-dihydro-2H-pyran) (OBDP). This compound was prepared according to the procedure of Effenberger³ in 50% yield by the addition of oxalyl chloride to 3,4-dihydro-2H-pyran, followed by dehydrochlorination with triethylamine. Recrystallization from a mixture of petroleum ether and ethanol (4:1 by vol) afforded white needles, mp 115–116°C [lit.³ mp 113°C]. IR (KBr) 1600 cm⁻¹ (C=O).

Diamines. Hexamethylenediamine (HMDA) and *m*-xylylenediamine (MXDA) were distilled *in vacuo* before use. Bis(4-aminophenyl)methane (MDA) and bis(4-aminophenyl) ether (ODA), both of which were supplied by Sumitomo Chemical Co., were purified by recrystallization from benzene and tetrahydrofuran, respectively.

Solvents and Reagents. *m*-Cresol was purified by vacuum distillation and stored over 4 Å molecular sieves. Benzyl alcohol, *p*-chloroaniline, and other reagents were obtained commercially and used as received.

Model Reaction

4,4'-Oxalylbis[5-(p-chlorophenylimino)1-pentanol] (*Ib*). To a solution of 0.444 g (2 mmol) of OBDP in 5 ml of ethanol 0.510 g (4 mmol) of *p*-chloroaniline was added, and the solution was refluxed with stirring for 2 days. After the solution had been cooled in a refrigerator, the yellow precipitate which formed was collected by filtration and dried. The yield was 0.91 g (95%). Recrystallization from ethanol afforded small yellow crystals, mp 204°C (by DTA). IR (KBr) 3310 (O–H) and 1680 cm⁻¹ (C=O).

Anal. Calcd for C₂₄H₂₆Cl₂N₂O₄: C, 60.38%; H, 5.49%; N, 5.87%. Found: C, 60.4%; H, 5.7%; N, 5.6%.

Polymerization

Synthesis of Polyamine III. To a solution of 0.582 g (5 mmol) of HMDA in 3.8 ml of *m*-cresol 1.111 g (5 mmol) of OBDP was added, and the polymerization was continued with stirring at room temperature for 7 days. The resulting solution was poured into 300 ml of ether. The product was filtered off, washed thoroughly with ether, and dried. The yield was 1.68 g (99%). The inherent viscosity of the polymer in *m*-cresol was 0.25 dl/g, measured at a

concentration of 0.5 g/dl at 30°C. IR (KBr) 3260 (O–H and N–H), 1630 (C=O), and 1540 cm⁻¹ (N–H).

Anal. Calcd for (C₁₈H₃₀N₂O₄)_n: C, 63.88%; H, 8.93%; N, 8.28%. Found: C, 63.6%; H, 8.6%; N, 8.3%.

Synthesis of Polyamine VI. A mixture of 0.501 g (2.5 mmol) of ODA and 0.556 g (2.5 mmol) of OBDP in 2.7 ml of *m*-cresol was reacted at 80°C with stirring. After 4 days of polymerization, the polymer was isolated by precipitation with 300 ml of ether. It weighed 0.97 g (97%), and its inherent viscosity was 0.13 dl/g. IR (KBr) 3340 (O–H) and 1960 cm⁻¹ (C=O).

Anal. Calcd for (C₂₄H₂₆N₂O₅)_n: C, 68.23%; H, 6.20%; N, 6.63%. Found: C, 68.5%; H, 5.7%; N, 6.6%.

RESULTS AND DISCUSSION

Model Reaction

The reactivity of 5-acyl-3,4-dihydro-2H-pyrans toward nucleophiles has been practically unknown to date. Therefore, the analysis of the monomer OBDP was first investigated in detail to demonstrate the feasibility of this reaction for polymer formation and to obtain a model compound for use in polymer identification.

The reaction of OBDP with various amines was carried out in ethanol both at room temperature and at an elevated temperature. The reaction with *p*-chloroaniline yielded a readily crystallizable product having a carbonyl absorption at 1680 cm⁻¹, believed to be due to the ring-opened adduct I (through path A), and not to the condensation product II (through path B) [eq 2].

Similarly, other amines such as aniline, benzylamine, and butylamine were found to react with OBDP to afford the corresponding oily ring-opened adducts.

This type of ring-opening reaction proceeds through a vinylogous nucleophilic addition-elimination mechanism, as shown in eq 3, analogous to that proposed for the polycondensation of bis-(ethoxyvinyl ketones) with diamines.^{1,2}

The infrared spectrum of the reaction product I, given in Figure 1, exhibited strong bands at 3310 and 1680 cm⁻¹ probably assignable to an O–H stretching and a carbonyl absorption, respectively, and no clearly detectable band at around 1540 cm⁻¹ due to

Synthesis of Hydroxyl-Containing Polyenamines

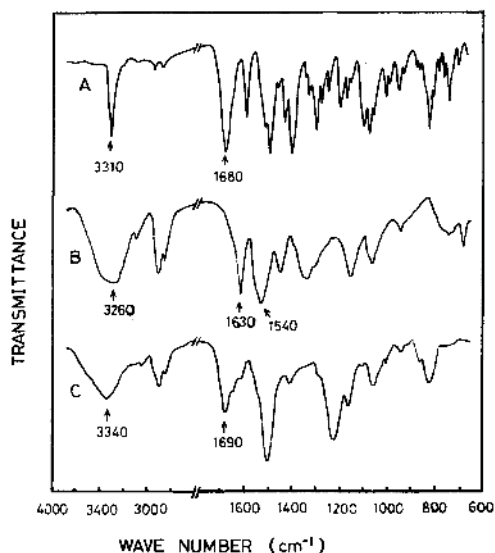
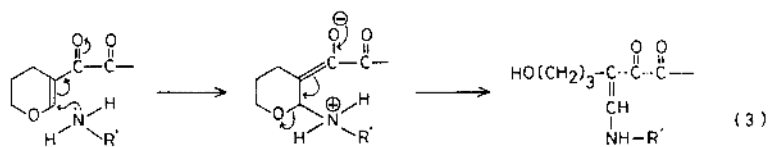
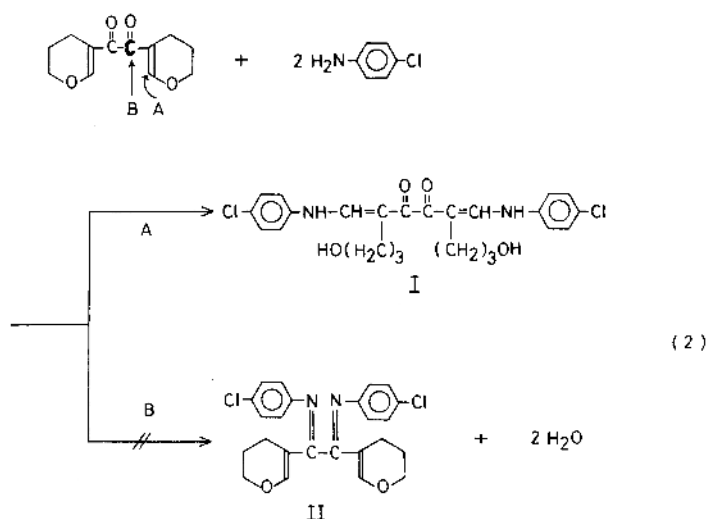
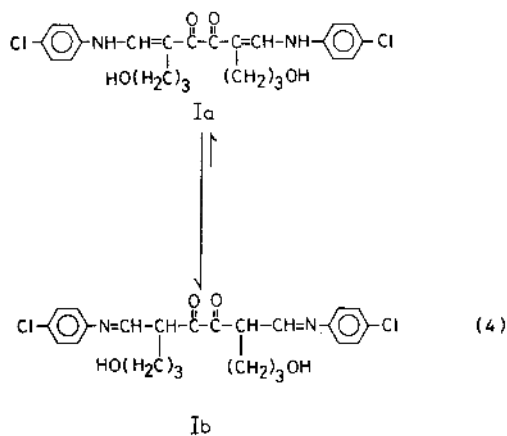


Figure 1. IR spectra of model compound and polyenamines: (A) the compound Ib; (B) the polymer III; (C) the polymer VI.

an N-H deformation. Therefore, this compound is presumed to exist mainly in the imine form (Ib), rather than the enamine form (Ia) [eq 4].



Polymerization

The high-yield model reaction of OBDP was extended to the ring-opening polyaddition with diamines, which proceeds according to eq 1. The results of the polymerization are summarized in Table I.

It has been shown that alcoholic solvents were the best reaction media for the production of hydroxyl-containing polyamides from bis-4-butanolide and

Table I. Conditions and results of the ring-opening polyaddition of the cyclic monomer OBDP with diamines

Polymer	Diamine	Polymerization conditions ^a				Polymer	
		Solvent ^b	Concn, wt%	Temp, °C	Time, day	Yield, %	η_{inh}^c dl/g
III	HMDA	CR	17	20	1	84	0.15
III	HMDA	CR	17	80	1	91	0.14
III	HMDA	CR	30	20	7	99	0.25
III	HMDA	CR	30	80	2	99	0.25
III	HMDA	CR	40	20	7	99	0.24
III	HMDA	BA	25	20	2	99	0.21
III	HMDA	CR-MA ^d	17	20	2	99	0.27
III	HMDA	CR-MA ^e	17	20	1	99	0.21
IV	MXDA	CR	17	20	2	93	0.10
IV	MXDA	CR	30	20	7	99	0.12
IV	MXDA	BA	27	20	1	99	0.10 ^f
V	MDA	CR	30	50	4	92	0.12
VI	ODA	CR	30	80	4	97	0.13

^a Polymerization was carried out with 2.5–5.0 mmol of OBDP and of diamine.

^b CR, *m*-cresol; BA, benzyl alcohol; MA, methanol.

^c Measured at a concentration of 0.5 g/dl in *m*-cresol at 30°C.

^d Mixture of methanol and *m*-cresol (8:2 by wt).

^e Mixture of methanol and *m*-cresol (9:1 by wt).

^f Measured in benzyl alcohol.

diamines.⁴ In the present case, alcoholic solvents such as benzyl alcohol, *m*-cresol, and a mixture of *m*-cresol and methanol, were also used successfully for the preparation of hydroxyl-containing polyenamines, in which the polymerization proceeded in homogeneous solution. The polymerization temperature was found to have no effect, over a temperature range of 20–80°C, on the inherent viscosity of the resulting polymers. The molecular weight tended to increase to some extent with increasing monomer concentration. Under these polymerization conditions, the ring-opened polymers having inherent viscosities in the range of 0.1–0.27 dl/g were obtained in almost quantitative yields. The formation of the polymers with relatively low molecular weight may be attributable to the lower reactivity of OBDP as compared to the reactivity of 1,6-diethoxy-1,5-hexadiene-3,4-dione having an open-chain structure.²

The formation of the polymers was confirmed by means of IR spectroscopy and elemental analyses. Figure 1 shows the IR spectra of the polymers III and VI. These spectra suggest that the polyenamines derived from aliphatic diamines (HMDA and

MXDA) differ in structure from the polymers obtained from aromatic diamines (MDA and ODA). The spectra of the aromatic polymers (V and VI) exhibited an O–H stretching band at 3340 cm⁻¹ and a strong carbonyl stretching at 1690 cm⁻¹, which compares favorably with that of the model compound I. Therefore, these polymers appear to exist predominantly in the imine form similar to the structure Ib. On the other hand, the spectra of the aliphatic polymers (III and IV) showed an overlapped O–H and N–H stretching band near 3260 cm⁻¹, a sharp carbonyl stretching at 1630 cm⁻¹, and a strong N–H deformation at 1540 cm⁻¹. This probably indicates that the aliphatic polymers exist mainly in the enamine form.

Properties of Polymers

These hydroxyl-containing polyenamines were soluble in *m*-cresol, benzyl alcohol, and 1-methyl-2-pyrrolidone, and practically insoluble in other common organic solvents. They dissolved in acidic media such as concd. sulfuric, dichloroacetic, and formic acids, with degradation of the polymer main chain, analogous to other polyenamines.^{1,2}

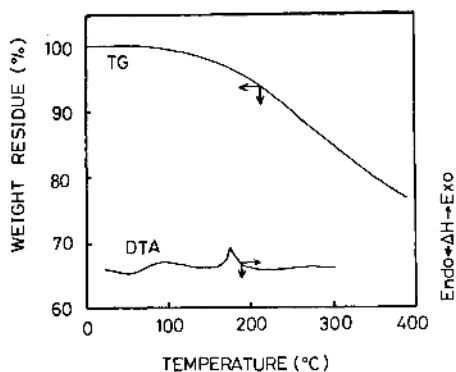


Figure 2. DTA and TG thermograms for the polyenamine V: DTA in air at a heating rate of 10°C/min, and TG in nitrogen at a heating rate of 5°C/min.

All of the polymers softened at temperatures below 200°C, and began to decompose above the softening temperature, as observed by DTA and TG (Figure 2). The thermal behavior data are summarized in Table II.

Acknowledgment. The authors are indebted to

Table II. Thermal behavior data of the polyenamines

Polymer	Softening temp, °C ^a	Main exothermic peak temp, °C ^b	Decomposition temp, °C ^c
III	67–104	147	210
IV	133–141	160	240
V	152–159	174	245
VI	180–197	—	245

^a Observed visually on a hot-stage microscope.

^b Determined by DTA in air at a heating rate of 10°C/min.

^c A 10% weight-loss temperature observed by TG in nitrogen at a heating rate of 5°C/min.

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