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Alternating Copolymerization of 5-Oxazolones with Electrophilic Monomers via Zwitterion Intermediates

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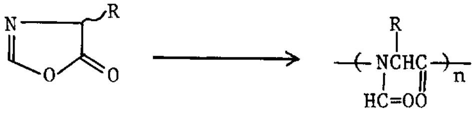
SUMMARY

5-Oxazolone (1a) and 4-methyl-5-oxazolone (1b) were found to serve as a nucleophilic monomer (M_N) toward electrophilic monomers (M_E) like acrylamide (AM) and 2-hydroxyethyl acrylate (HEA). Copolymerizations between these M_N and M_E monomers took place without added initiator at room temperature and at 110 °C to give solid polymers having alternating structures of 3 and 4. The molecular weight of these alternating copolymers is not high. The copolymerization mechanism is explained in terms of zwitterionic intermediates involving a proton-transfer step.

INTRODUCTION

Very recently we have shown that 2-unsubstituted 5-oxazolones 1 are polymerized by a cationic initiator to produce poly(N-formyl-α-peptide)s 2 (1). Monomer 1 can be taken as an analogue of 2-oxazolines which have been found to be reactive nucleophilic monomers (M_N) toward various electrophilic monomers (M_E). Copolymerization between an M_N and an M_E takes place without added initiator, giving rise to an alternating copolymer or a periodic copolymer via zwitterionic intermediates (2). As an extension of these studies, the present paper describes alternating copolymerizations of monomer 1a and 1b as new M_N with acrylamide (AM) and 2-hydroxyethyl acrylate (HEA) as M_E.



1a; R=H   2a; R=H

1b; R=Me   2b; R=Me

RESULTS AND DISCUSSION

The copolymerizations took place without added initiator to produce alternating copolymers 3 and 4 (Table 1). All copolymerizations occurred at room temperature although the polymer yield was very low. At a higher temperature, e.g., 100 or 110 °C, the reaction of 1 with AM gave copolymers in a moderate yield, but reactions using HEA produced copolymers in a reduced amount. 1,4-Hydroquinone was added to the reaction system at a higher reaction temperature to prevent the homopolymerization of AM or HEA.

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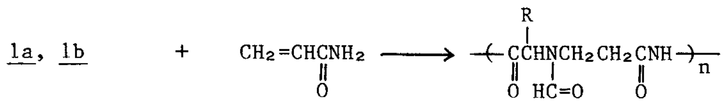
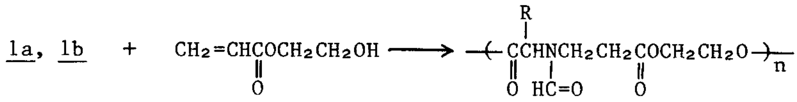


$$\underline{1a},\ \underline{1b} + \underset{\underset{\displaystyle AM}{}}{CH_2{=}CH\overset{}{\underset{\|}{C}}NH_2} \longrightarrow \left(\underset{\underset{O}{\|}}{C}\overset{R}{\underset{}{C}}H\underset{\underset{HC=O}{|}}{N}CH_2CH_2\underset{\underset{O}{\|}}{C}NH\right)_n$$

AM

3a ; R=H

3b ; R=Me



$$\underline{1a},\ \underline{1b} + CH_2{=}CH\underset{\underset{O}{\|}}{C}OCH_2CH_2OH \longrightarrow \left(\underset{\underset{O}{\|}}{C}\overset{R}{C}H\underset{\underset{HC=O}{|}}{N}CH_2CH_2\underset{\underset{O}{\|}}{C}OCH_2CH_2O\right)_n$$

HEA

4a ; R=H

4b ; R=Me

Table 1
Alternating Copolymerization of 5-Oxazolones (1) with Acrylamide (AM) or with 2-Hydroxyethyl Acrylate (HEA)

No	M_N	M_E	Copolymerizations[a]		Copolymers		
			Temp.(°C)	Time(hr)	Yields(%)	Mol.Wt.[b]	Structures
1	1a	AM	r.t.	72	10		3a
2	1a	AM	60	76	28		3a
3[c]	1a	AM	100	72	49	2200	3a
4	1b	AM	r.t.	72	26		3b
5	1b	AM	100	75	54	2800	3b
6[c]	1b	AM	110	73	54	2500	3b
7	1a	HEA	r.t.	72	13		4a
8	1a	HEA	40	48	14		4a
9[c]	1a	HEA	100	72	21	1500	4a
10	1b	HEA	r.t.	72	12		4b
11[c]	1b	HEA	110	72	28	1600	4b

a) An equimolar amount (~3 mmol each) of M_N and M_E monomers in diglyme solvent.
b) Determined by vapor pressure osmometry in DMSO.
c) 1,4-Hydroquinone (0.5 mol % for the monomer) was added.

All isolated copolymers are solids. They are hygroscopic and soluble in dimethyl sulfoxide (DMSO) and in N,N-dimethylformamide (DMF). The molecular weight of these copolymers is not high; less than 3000.

Structures of copolymers were determined mainly by ^{1}H NMR and IR spectroscopy. ^{1}H NMR spectrum of copolymer from 1a and AM (DMSO-d_6 with TMS) showed the following broadened peaks: a singlet peak at δ 8.1 due to HCO, a signal at δ 7.7-6.5 due to NH, three kinds of peaks at δ 4.7-3.5 due to CH_2NCH_2, and a peak at δ 1.8 due to $CCH_2C(=O)$ in an integral ratio 1:1:4.5:2. IR spectrum of the same sample displayed a very strong band at 1660 cm^{-1} due to carbonyl groups. These date are taken to conclude the copolymer structure of imide-formamide type 3a.

The following data of ^{1}H NMR and IR spectroscopy were used in determination of structures of other copolymers. 3b: ^{1}H NMR (DMSO-d_6); δ 7.9 (br. s, 1H, HC(=O), 7.6-6.5 (br., 1H, NH), 5.2-3.8 (br., 3H, $CHNCH_2$), 2.2-1.7 (br., 2H, $CH_2C(=O)$), and 1.6-1.0 (br. s., 3H, CH_3). IR; 1665 cm^{-1} (v.s., $\nu_{c=o}$). 4a: ^{1}H NMR (DMSO-d_6); δ 8.1 (br. s., 1H, HC(=O)), 4.7-3.3 (two singlet-like peaks overlaping with broad signals, 8H, OCH_2CH_2O and CH_2NCH_2), and 1.8 (s., 2H, $CH_2C(=O)$). IR; 1715 cm^{-1} (v.s., $\nu_{c=o}$ due to ester) and 1655 (v.s., $\nu_{c=o}$ due to amide). 4b: ^{1}H NMR (DMSO-d_6); δ 7.8 (br.s., 1H, HC(=O)), 4.6-3.3 (broad two signals, 7H, OCH_2CH_2O and $CHNCH_2$), 1.7 (s., 2H, $CH_2C(=O)$), and 1.5-1.0 (br.s., 3H, CH_3). IR; 1723 cm^{-1} (v.s., $\nu_{c=o}$ due to ester) and 1650 (v.s., $\nu_{c=o}$ due to amide).

Differential scanning calorimetry (DSC) analysis of the copolymers was performed; all samples exhibiting a glass-transition temperature (T_g) lower than 80 °C (Table 2). For comparison, data for homopolymers of 1a and 1b are also included. The DSC scans showed transitions whose two drawn tangents intersected at a single point assigned as the T_g. Polymeric materials involving 1b as either monomer or comonomer showed better thermal properties than the corresponding polymer or copolymer that utilized 1a. It was assumed that there was no large block of polyAM in copolymers 3a and 3b because no thermal transitions could be detected in DSC thermograms around that polymer's T_g of 188 °C (3). Also, because no thermal transitions in the area of 140 °C, the reported T_g value of polyHEA (4), could be detected in DSC thermograms of copolymers 4a and 4b, it was assumed that no sections of this polymer occurred in these two copolymers.

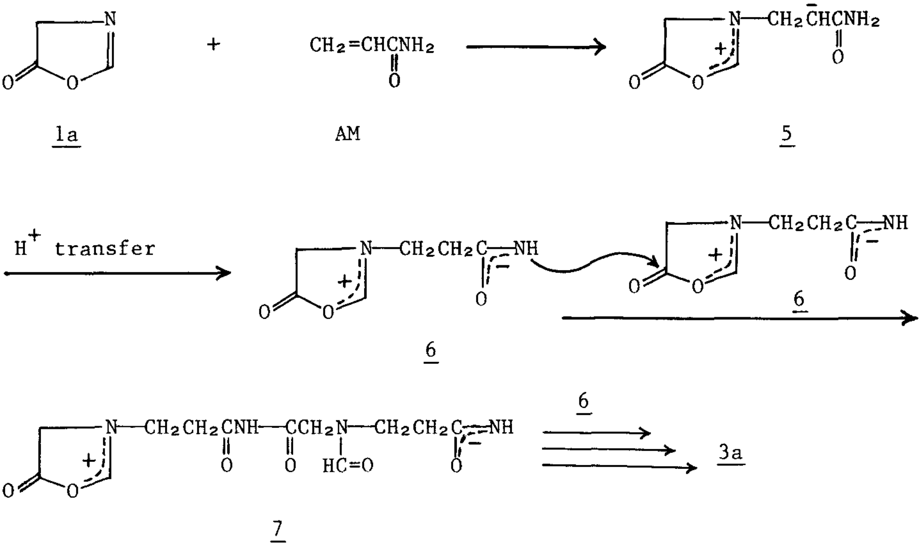
Table 2

DSC Analysis of Homopolymers and Copolymers of 5-Oxazolones

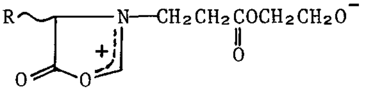
Polymer Samples	Mol. Wt.	T_g(°C)	Decomposition(°C)
2a[a]		66	137
2b[a]		72	147
3a	2200	62	130
3b	2800	77	200
4a	1500	79	132
4b	1600	71	200

a) Obtained as reported (1).

A proposed mechanism for the alternating copolymerization is given below, taking the reaction of 1a with AM as an example. The copolymerization starts with a reaction between a nucelophile 1a and an electrophile AM to produce a genetic zwitterion 6 via a proton-transfer, which involves 5 intra- and/or inter-molecularly. The anionic part of 6 is ambident and in this case the nitrogen atom is the reaction site toward the cationic part of the other zwitterions to form an imide linked dimeric zwitterion 7. Repetition of this reaction mode leads to the formation of alternating copolymer 3a. The reaction mode involving oxygen as the reaction site in the ambident anionic part has been excluded because the imidate linkage (~C(=NH)OC(=O)~) was not detected in an IR spectrum of the copolymer at approximately 1585 cm^{-1} (5).



In the copolymerizations using HEA, a proton-transfer step is also involved and a genetic zwitterion 8 plays an important role both for initiation and propagation leading to alternating copolymers 4.



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EXPERIMENTAL

Materials

All solvents and reagents were used as received or purified by distillation unless otherwise stated. Monomer 1a was prepared by the dehydrating cyclization of N-formylglycine with N,N'-dicyclohexylcarbodiimide (DCC) and obtained as a diglyme solution after co-distillation using diglyme carrier according to our previous study (1). Analogously, monomer 1b was synthesized by the dehydration of N-formyl-D,L-alanine by DCC and isolated by co-distillation with diglyme (concentration = 0.38 mol/l)(1). Acrylamide (AM) (Fisher Co.) was recrystallized from benzene, mp 84-86 °C. 2-Hydroxyethyl acrylate (HEA)(Dow Chem. Co.) was purified by distillation under nitrogen, bp 76 °C (1.6 mmHg).

Copolymerization and Purification of Copolymer

An illustration of the general procedure for the copolymerization of 5-oxazolones with electrophilic monomers is given below using 1b and AM. A 0.213 g (3.0 mmol) of AM was placed in a clean, dry 25 ml round bottomed flask fitted with a magnetic stirring bar. Following this, 1.6 mg (0.015 mmol or 0.5 mol%) of 1,4-hydroquinone was added and the vessel was fitted with a rubber septum which was wired in place. The vessel was flushed with a gentle stream of dry nitrogen for approximately five minutes and then 3.0

mmol of 1b (7.9 ml of a 0.38 mol/1 solution in diglyme) was added via syringe. The reaction was warmed from room temperature to 110 °C and allowed to stir for 73 hr. The reaction was stopped by pouring the contents into a large volume of anhydrous diethyl ether. The precipitated polymeric materials were separated by filtration and then vacuum oven dried for 24 hr. The polymer materials were taken up in a small volume of warm DMSO and passed through a small glass frit by suction filtration to remove any insoluble material. The filtrate was then reprecipitated in approximately 600 ml of anhydrous diethyl ether. After stirring for a period of 24-48 hr, the solid was again collected on the fine glass frit, vacuum dried, and collected for further analysis.

Measurements

The molecular weight was determined by using a Knaur Dampfdruck Osmometer DS-4 in dry DMSO solution in concentrations ranging from 2 mg/ml to 10 mg/ml. IR spectra were obtained by a Perkin-Elmer E1500 spectrometer. ^{1}H NMR spectra were recorded on a Varian T-60 NMR spectrometer. Differential scanning calorimetry (DSC) scans of polymer samples were performed on a Perkin-Elmer DSC-2C equipped with Perkin-Elmer model 3600 Thermal Data Station. Scans were made at 10.0 °C/min with a positive nitrogen flow of 20.0 ml/min.

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