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KINETIC ASPECTS OF THE POLYMERIZATION OF 2-SUBSTITUTED 2-OXAZOLINES IN THE PRESENCE OF ELECTRON-ACCEPTORS

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Abstract—The solution polymerization of 2-methyl 2-oxazoline in the presence of microacceptors without or with polymerizable group (viz. 2,4,7-trinitrofluorenone and tetracyanoethylene) was studied. In the first case, the polymerization is first order with respect to both monomer and acceptor. For the second case, the dependence on acceptor concentration exceeds unity. The propagation by reaction of the active species with the zwitterions formed between the two comonomers is believed to be responsible for this behaviour. The experimental results are in excellent agreement with the previously suggested [1] mechanism of polymerization.

INTRODUCTION

Cyclic imino-ethers have been widely studied in order to elucidate the mechanism of the ring opening polymerization. The resulting products also possess excellent properties.

The literature contains examples of cationic homopolymerization or spontaneous copolymerization of 2-oxazolines with some electrophilic comonomers [2]. The kinetic studies have distinguished different mechanisms of the propagation, depending upon the nature of the initiator. Thus, Saegusa and coworkers [3] consider that the izomerization polymerization of 2-oxazolines proceeds via ionic (e.g. oxazolinium tosylate) or covalent-bonded propagating species (in the presence of the alkyl halides).

Recently we have reported [1, 4] the possibility of spontaneous polymerization and copolymerization of 2-substituted 2-oxazolines carrying various side-groups (methyl, *N*-carbazolylethyl, 9-anthrylethyl and 3,5-dinitrophenyl) with micromolecular acceptors (7,7,8,8-tetracyanoquinodimethane, tetracyanoethylene and 2,4,7-trinitrofluorenone) via a charge transfer complex.

This paper covers several aspects of the kinetics of these processes. According to the two situations described in the literature [1] (viz. cationic homopolymerization and zwitterionic copolymerization) two model systems were used, viz. 2-methyl-2-oxazoline-2,4,7-trinitroflourenone and 2-methyl-2-oxazoline-tetracyanoethylene.

EXPERIMENTAL PROCEDURES

Materials

2-methyl-2-oxazoline (MeOx), a commercial product, was refluxed over Na and distilled under argon. 2,4,7-trinitrofluorenone (TNF) (Fluka) was used after recrystallization from methylene chloride. Tetracyanoethylene (TCNE) (Fluka) was recrystallized from benzene and purified twice by sublimation. Acetonitrile (ACN) was refluxed over phosphorus pentoxide and distilled under argon.

Polymerization

The polymerizations were carried out in sealed glass ampoules, in an inert atmosphere, at temperatures between 55 and 75°, with ACN as solvent. The products were precipitated with anhydrous diethyl ether. They were washed with methylene chloride until the filtrate became colourless, in order to remove the excess of micromolecular acceptor. The solid products were dried *in vacuo*, at 60°.

The rates of polymerization (R_p) were obtained using the relation

$$R_p = 1000\, w/vtM,$$

where w = weight of the polymer (g), v = volume of the polymerization system (ml); t = time (sec), M = molecular weight of the monomer. The amount of TCNE used in copolymerization is small enough in the calculation of the molecular weight of the structural unit.

Polymer characterization

Average molecular weights were obtained from gel permeation chromatography (Knauer type apparatus with Styragel columns, permeation range 10^3–10^6 Å), calibration being made with polystyrene standards (Waters Associates). *N*,*N*-dimethylformamide was used as eluent.

RESULTS AND DISCUSSION

According to our previous experimental data [1,4] we have supposed that the initiation of the MeOx polymerization in the presence of organic acceptors takes place by a n-π charge transfer complex (**3**) formed between the oxazoline ring and the acceptor. The complex partially dissociates to an ion-radical (**4**) which, in the case of the acceptors with polymerizable bonds (e.g. TCNE), can couple to zwitterions (**5**).

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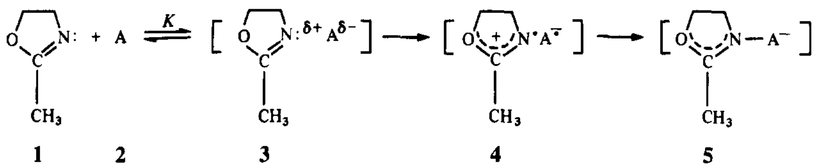
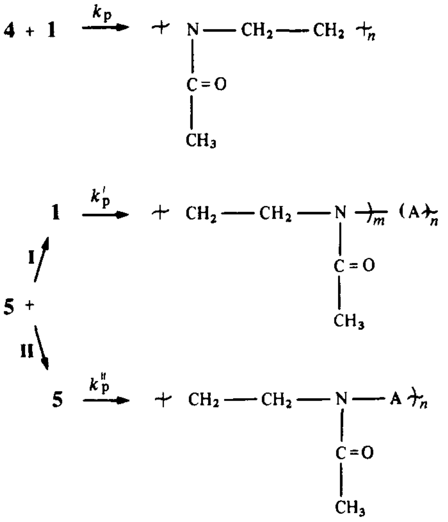
Initiation



The propagation may occur either through the preferential attack at the C_5 atom of the 2-methyl-2-oxazolinium ring by the nucleophilic monomer or by the reaction of the macro-ion with the zwitterion.

Propagation



Since 2-alkyl-substituted 2-oxazolines are susceptible to chain transfer [5], one can consider that termination by chain transfer to monomer prevails in the case of MeOx. Calculations based on the experimental determinations of the molecular weights of the polymerization products for the MeOx–TNF and MeOx–TCNE systems (Table 1) give values of 0.022 and 0.010 respectively for the chain transfer constants. These values are similar to that reported by Litt and coworkers [5] for alkyl oxazolines. The high polydispersity may be due to repolymerization reactions [5].

Assuming that (i) the monomer is predominantly consumed during propagation, (ii) the rate constants are independent of chain length and (iii) the steady state is reached in the system, the following expressions may be derived for the rates of polymerization:

$$R_p = k_p k_i[1][2]/k_t$$

for the MeOx–TNF system and

$$R_p = k_i[1][2](k_p'' K'[2] + k_p')/k_t$$

for the MeOx–TCNE system. K' is the equilibrium constant for the zwitterion (**5**) formation.

The experimental data obtained from the kinetic investigations on the two model systems confirm this conclusion. Thus, for the first system, monomer and acceptor exponents of *ca* 1 (1.00 and 1.06 respectively) were found from the bilogarithmic plots of R_p vs MeOx or TNF (Figs 1 and 2).

The first order dependence of the rate of polymerization on monomer concentration was indicated by the linearity of the plot of ln[1/(1 − conv)] vs time (Fig. 3). The presence of two regions with different slopes was related to the continuous generation of active centres during polymerization. The overall polymerization constant may also be affected by the alteration of the equilibrium constant for the primary charge transfer complex formation in the presence of the N-acylated polyethyleneimine, which has electrodonor character.

By performing the experiments in the 55–75° temperature range, the overall activation energy, E_A, was found to be 76.9 kJ/mol. This high value is due to the

Table 1. Molecular weights of the products of MeOx polymerization in the presence of TNF and TCNE (temperature, 75°; solvent, ACN)

Sample	Acceptor	[A] (mol/l)	[MeOx] (mol/l)	$\bar{M}_w$	$\bar{M}_n$
1	TNF	0.035	8.81	1080	220
2	TNF	0.088	8.81	3520	730
3	TNF	0.176	10.42	2550	450
4	TNF	0.176	7.68	1810	170
5	TNF	0.176	6.43	1530	210
6	TCNE	0.296	7.38	1310	620
7	TCNE	0.221	7.38	1510	1040
8	TCNE	0.148	7.38	1600	880
9	TCNE	0.296	7.87	3790	1670
10	TCNE	0.296	5.51	1990	1225
11	TCNE	0.296	3.94	1690	930
12	TCNE	0.296	2.36	1170	730

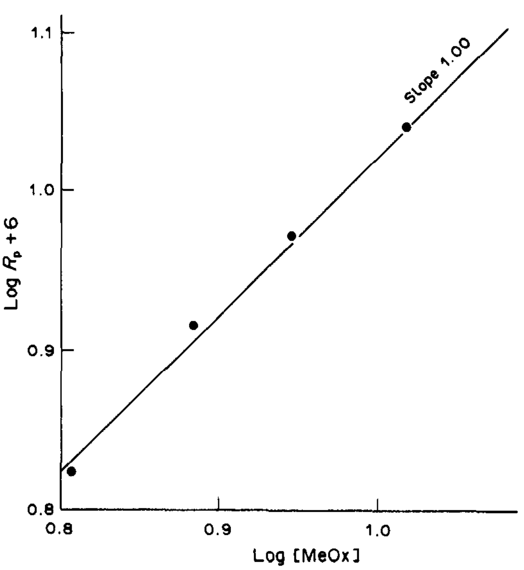


Fig. 1. Plot of propagation rate vs MeOx concentration, [TNF]/[MeOx] = 0.02; temperature 75°; solvent, ACN; time, 24 hr.

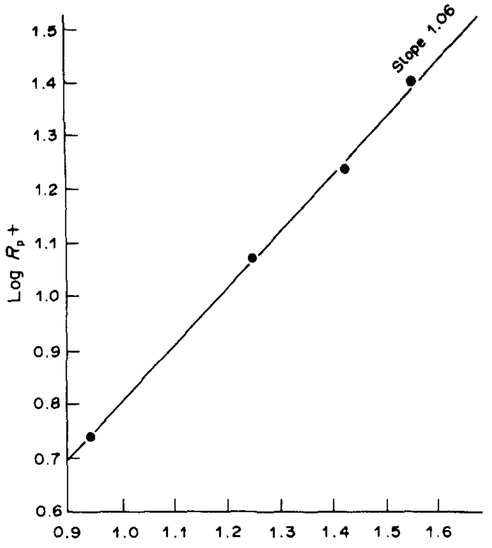


Fig. 2. Plot of propagation rate vs TNF concentration. [MeOx] = 8.81 mol/l; temperature, 75°; solvent, ACN; time, 24 hr.

fact that strong interactions (charge transfer type) exist between the active centre and the acceptor radical-ion.

The kinetic curves, experimetally obtained for the MeOx–TCNE system have pronounced S-shaped character (Fig. 4). The induction period corresponds to the generation of active sites (zwitterions) earlier revealed by the colour change [1]. Its length depends on the electron affinity of the acceptor, temperature, donor/acceptor feed ratio and solvent polarity.

The polymerization occurs very rapidly (E_A = 43.8 kJ/mol). In order to obtain measurable rates, the copolymerizations were performed at low acceptor concentrations (~ 10^{-1} mol/l). Even for this acceptor concentration range, the value of TCNE exponent exceeds unity (1.63) (Fig. 5) suggesting that the propagation also takes place by the second mechanism. Using the slope and the intercept of the R_p/[TCNE] vs [TCNE] plot, $k_p'' \cdot K'/k_p'$ was found to be 68.1 ratio, indicating that propagation by mechanism II is favoured. The maximum yield was attained at an equimolar feed ratio [1], an observation which strongly supports this conclusion.

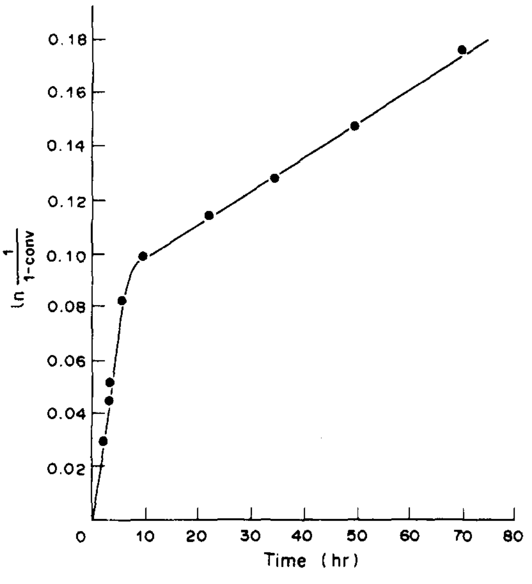


Fig. 3. First order conversion–time plot for the MeOx polymerization in the presence of TNF. [MeOx] = 8.81 mol/l, [TNF] = 0.176 mol/l; temperature, 75°; solvent, ACN.

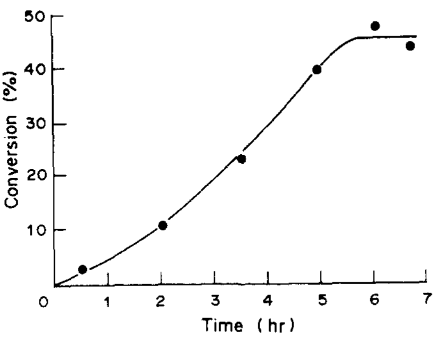


Fig. 4. Time–conversion curve of MeOx–TCNE copolymerization. [MeOx] = 7.38 mol/l; [TCNE] = 0.074 mol/l; temperature, 75°; solvent, ACN.

The value of 1.3 (Fig. 6) for the monomer exponent can be explained by the deactivation of the active sites through reactions other than chain transfer to monomer.

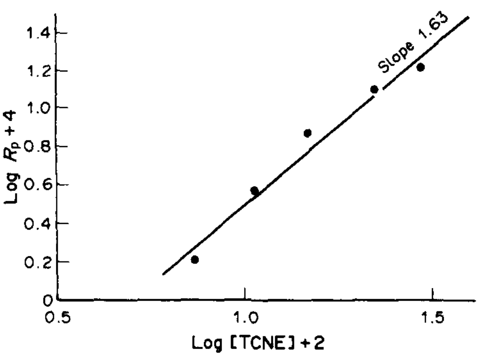


Fig. 5. Plot of propagation rate vs TCNE concentration. [MeOx] = 7.38 mol/l; temperature, 75°; solvent, ACN; time, 40 min.

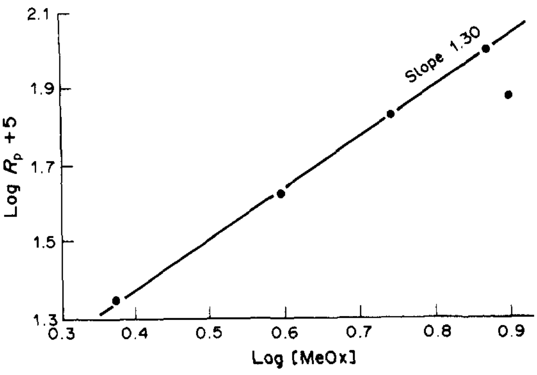


Fig. 6. Rate of propagation as a function of MeOx concentration for the MeOx–TCNE system. [TCNE] = 0.296 mol/l; temperature, 75°; solvent, ACN; time, 2 hr.

In conclusion, the kinetic study confirms the proposed mechanism for polymerization of 2-substituted 2-oxazolines in the presence of micromolecular acceptors with or without polymerizable groups.

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