Investigations of 2-Ethyl-2-oxazoline Polymerizations in Chlorobenzene

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ABSTRACT: Polymerizations of 2-ethyl-2-oxazoline initiated by alkyl iodides in chlorobenzene have been investigated with regard to their living character, mechanisms, and kinetics. The rate-determining step was found to be an "initial propagation reaction" for the case of benzyl iodide as the initiator and initiation in the case of the less reactive 1-iodobutane as initiator. Conversion of active covalent species to ionic species during the course of polymerization was observed in both cases. Absolute number-average molecular weights and molecular weight distributions were analyzed using gel permeation chromatography with universal calibration in a solvent mixture (THF/MeOH). Consistent with the living nature of the systems, the number-average molecular weights of the polymers increased proportionally to monomer conversion. However, the molecular weight distributions of these polymers were found to be broader than a Poisson distribution.

Introduction

Earlier work on the polymerization of 2-aryl- and 2-alkyl-2-oxazolines dates back to the mid-1960s.[1–14] Polymers derived from the methyl- and ethyl-substituted derivatives are of particular interest because of their water solubility, especially in this era of environmental consciousness. Thus, an understanding of the polymerization mechanisms of these polymers has become important from a fundamental as well as an applications point of view. Preparation of well-defined polymeric materials (control of molecular masses, polydispersities, and end-group functionalities) depends on this fundamental knowledge.

Previous mechanistic investigations have primarily been focused on polymerization of 2-phenyl-, 2-methyl-, unsubstituted, and, more recently, 2-(perfluoroalkyl)-2-oxazolines,[6–14] and much of this work has been done using a polar solvent such as acetonitrile. Two types of propagation routes have been identified based on ionic or covalent active species, depending upon reaction conditions and counterion structure.[6,8–12] These polymerizations have generally been considered "living" even though detailed evaluations in some cases have not been reported. In terms of mechanistic studies, 2-ethyl-2-oxazoline has received relatively little attention. In contrast to its methyl counterpart, poly(2-ethyl-2-oxazoline) is soluble in less polar solvents such as chlorobenzene and THF. One of our primary goals in studying the polyoxazolines is to investigate the preparation of block copolymers comprised of polar polyoxazolines as one block and less polar materials such as poly(dimethylsiloxane) and poly(alkyl vinyl ether)s as the other blocks.[15,16] Successful preparation of these materials in solvents such as chlorobenzene is important since chlorobenzene is a solvent for both blocks of the various copolymers. However, since ionic polymerizations are sensitive to solvents, we recognized that the polymerization mechanism of 2-ethyl-2-oxazoline in chlorobenzene could differ substantially from that of the methyl derivative in a relatively polar solvent such as acetonitrile.

In this paper, the polymerization mechanism and kinetics of 2-ethyl-2-oxazoline in chlorobenzene, investigated using ^{1}H NMR, are discussed. The living nature of this polymerization system has been evaluated with the aid of gel permeation chromatography for the determination of absolute molecular weights.

Experimental Section

Materials. Chlorobenzene-d_5 (Aldrich, 98.5$^+$% D) was stirred over calcium hydride and distilled under nitrogen. 1-Iodobutane (Aldrich, 99%) was fractionally distilled from phosphorus pentoxide under nitrogen. Benzyl iodide was synthesized from benzyl chloride (Aldrich, 97%) and sodium iodide (Aldrich, 98%). To a solution of 15.1 mL (0.13 mol) of benzyl chloride in 130 mL of acetone was added 30.2 g (0.20 mol) of sodium iodide, and the mixture was refluxed for 1 h. The solids were removed by filtration, and the filtrate was concentrated by a rotavap. The residue was diluted with 100 mL of deionized water plus 100 mL of diethyl ether. The ether layer was retained and washed with 5% aqueous sodium thiosulfate and then water; then it was dried over magnesium sulfate. The solvent was evaporated and the resulting thick syrup was dissolved in 50 mL of hexanes and allowed to crystallize in a freezer. Immediately prior to each reaction, benzyl iodide diluted with a small amount of hexane was dried under vacuum in the dark to a constant weight. Then a stock solution of benzyl iodide in the polymerization solvent was prepared. Special caution should be exercised when handling this compound since it is a strong lachrymator. The purification of chlorobenzene and 2-ethyl-2-oxazoline was done as reported previously.[17] Methanolic KOH (Fisher, 0.1 N) was used as received.

Experiments. Polymerization mechanisms and kinetics of 2-ethyl-2-oxazoline were investigated using variable-temperature ^{1}H NMR (Varian Unity 400 operated at 399.952 MHz) inside the NMR probe as the polymerizations proceeded. A 5-mm screw cap NMR tube fitted with a PTFE/silicone septum was flame dried under vacuum, filled with nitrogen, and preweighed. Then desired amounts of initiator, monomer, and chlorobenzene-d_5 solvent were added via syringes. The tube was weighed between each addition in order that exact weights of each component were obtained. The resultant molar ratio of monomer to initiator was ca. 5 and the concentration of monomer was 25% w/v, resulting in a molar concentration of initiator of ca. 0.4 mol/L and monomer of ca. 2.0 mol/L. The NMR tube was then heated inside the NMR spectrometer probe at 80 or 110 °C, and NMR spectra were taken every 5 min to every 2 h depending on the polymerization rates of the particular system. To obtain rate constants, the intensity changes of the peaks of interest from the NMR spectra were collected and analyzed according to kinetic equations.

The molecular weight–conversion experiment was carried out in the following manner. To a flame-dried round-bottom flask were charged 30 mL of chlorobenzene, 10.2 mL of 2-ethyl-2-oxazoline, and benzyl iodide/chlorobenzene stock solution to make

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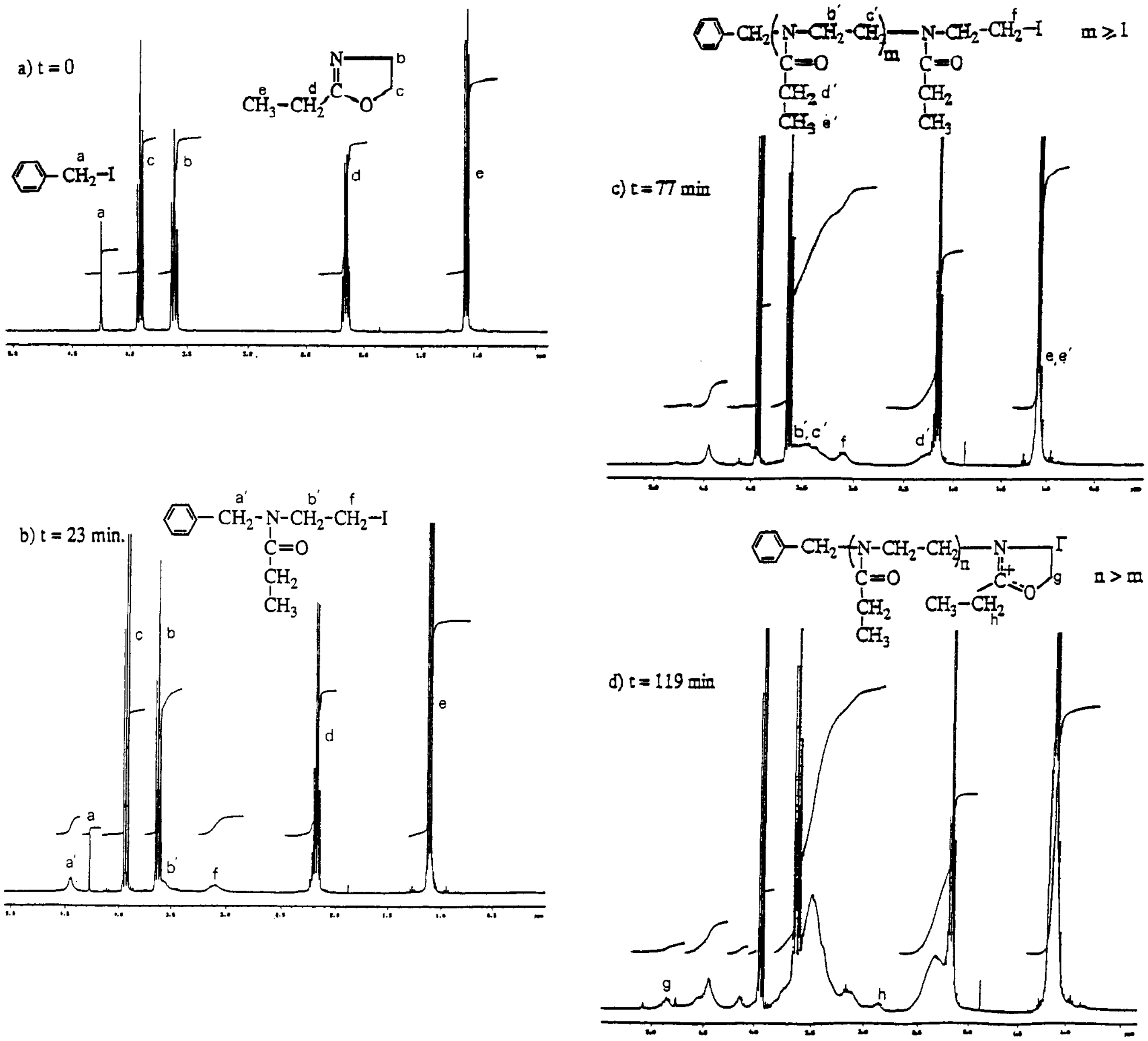


Figure 1. ^{1}H NMR of polymerization kinetics of 2-ethyl-2-oxazoline initiated by benzyl iodide at 80 °C: (a) t = 0; (b) t = 23 min; (c) t = 77 min; t = 119 min.

a final targeted number-average molecular weight of 40 000. The reaction mixture was stirred at room temperature for 30 min and then heated in a 110 °C oil bath. Samples were removed at specified time intervals and their conversion was determined by ^{1}H NMR. Aliquots of these samples were terminated with KOH/MeOH and dried at room temperature under vacuum as thin films. Their absolute number-average molecular weights were determined using a Waters 150C GPC using differential viscosity and refractive index dual detectors and universal calibration on 4 × (300 × 7.8 mm i.d.) steel columns packed with 10-mm Permagel.

Results and Discussion

Professor Saegusa and his colleagues have previously used ^{1}H NMR to study the kinetics of 2-methyl-2-oxazoline and unsubstituted 2-oxazoline[8–12] polymerizations. As NMR instrumentation has improved, high resolution and accuracy as well as on-line detection have correspondingly improved, rendering such techniques even more valuable. In this study, a 400-MHz ^{1}H NMR spectrometer with a variable-temperature probe was used. Reactions were run in the spectrometer and fid's were collected at programed intervals as the polymerizations proceeded.

Kinetic studies of 2-ethyl-2-oxazoline polymerizations using benzyl iodide as the initiator were carried out at 80 and 110 °C in deuterated chlorobenzene. To obtain accurate data on initiator conversion, the lower temperature, slower, reaction was used in conjunction with a low monomer to initiator ratio (ca. 5). Figure 1 illustrates a series of ^{1}H NMR spectra used to obtain initiator and monomer conversion data. The monomer protons (Figure 1a) resonating at δ 1.1, 2.2, 3.6, and 3.95 shift and/or broaden in the polymer once the monomer polymerizes. The peak corresponding to the initiator in this region appears at δ 4.29 ($C_6H_5CH_2I$). The methylene monomer peak at δ 3.95 and the initiator peak at δ 4.29 were free from overlap with any other peaks during the polymerization; thus their intensities were used to calculate the unreacted monomer and initiator concentrations as a function of reaction time. The methyl peak at δ 1.1 only broadened during polymerization and thus was used as an internal reference.

The plot of $\ln([M]/[M_0])$ and $\ln([I]/[I_0])$ vs time (Figure 2) summarizes the results of this experiment. The overall shape of the $\ln([M]/[M_0])$–time plot is convex, indicating acceleration of monomer consumption as time and conversion increase. Clearly, the rate(s) of early polymerization step(s) are slower than those of later ones. The slight concavity at the beginning of the curve is probably

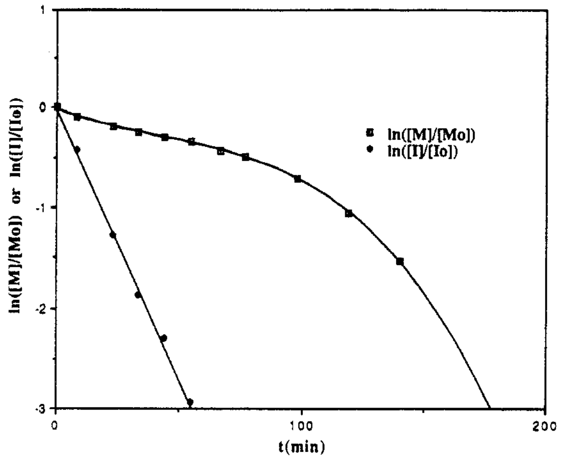


Figure 2. Initiator and monomer concentrations as a function of time for the polymerization of 2-ethyl-2-oxazoline initiated by benzyl iodide at 80 °C.

due to a faster reaction between the benzyl iodide initiator and the monomer than between the initiation product and the monomer. It is noteworthy that, in an earlier study of 2-methyl-2-oxazoline polymerization kinetics in acetonitrile using methyl tosylate and methyl iodide as initiators,[9,11] Saegusa also identified a slower early propagation step than subsequent steps. Following Saegusa's[9] data treatment method, we subdivided our monomer conversion curve into two portions: the early slope of the curve was used for calculating k_{p1}, and the later slope was used for determining k_{pn}. In this manner, the following set of rate constants were derived: $k_i = 3.26 \times 10^{-4}$ L/mol·s, $k_{p1} = 1.8 \times 10^{-4}$ L/mol·s, and $k_{pn} = 7.88 \times 10^{-4}$ L/mol·s.

Generic equations describing each step of a chain polymerization process exhibiting this type of kinetics can be written as

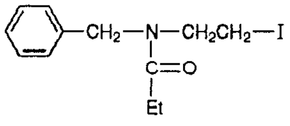
$$\mathrm{I} + \mathrm{M} \xrightarrow{k_i} \mathrm{IM} \tag{1}$$

$$\mathrm{IM} + \mathrm{M} \xrightarrow{k_{p1}} \mathrm{IM}_2 \tag{2}$$

$$\mathrm{IM}_j + \mathrm{M} \xrightarrow{k_{pj}} \mathrm{IM}_{j+1} \qquad j \geq 2 \tag{3}$$

Two propagation reactions have been written separately since rates of at least two different reactions are involved. Termination and chain transfer have not been included since neither of these types of reactions has been detected in this polymerization system (based on molecular weight vs conversion data to be discussed later in this paper). Ring-opening polymerizations of 2-alkyl-2-oxazolines are considered S_N2 in nature, and it appears reasonable to attribute the two propagation rates to two S_N2 reactions with the monomer as the nucleophile and two different active species as the substrates.

The high-resolution NMR spectra collected for the kinetic measurements were used to probe and correlate the chemical structures of active species with propagation rates (refer to Figure 1). Early in the polymerization, at t = 23 min (Figure 1b), the benzyl iodide initiator peak at δ 4.29 has substantially decreased while new peaks at δ 4.45, 3.55, and 3.1, identified as being due to structure 1,[18] appeared. Importantly, peaks in the chemical shift range where a cationic oxazolinium ion should resonate, around δ 4.2 and 4.8 (according to ref 9), remained absent at this time. As the reaction proceeded (t = 77 min, Figure 1c), almost all of the benzyl iodide had reacted as evidenced by the disappearance of the initiator peak at δ 4.29, and only very small peaks between δ 4.0 and 5.0, characteristic of the oxazolinium ion, had appeared. At this point, there were ca. 2.3 polymerized monomer repeat units per initiator. Thus, some propagation had taken place prior to the appearance of appreciable amounts of oxazolinium ion. At higher conversions (t = 119 min, Figure 1d; there were ca. 3.7 monomer units per initiator polymerized at this point), peaks at δ 2.87 (assigned to the pendant methylene of the oxazolinium ion) and at 4.15 and 4.87, due to the cationic active species, had grown appreciably. It is worth pointing out that, unfortunately, it was not possible to obtain from the spectroscopic data, quantitative information regarding the total number of active species present or the progression of change of active species. These peaks were broadened in the nonpolar solvent and partially overlapped, and the multiple types of active end groups meant that each peak was even smaller than in the normal case for polymer end groups.



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Saegusa[9,11] previously suggested that the rate enhancement in 2-methyloxazoline polymerizations in acetonitrile occurred after the first monomer addition and attributed this to a stabilizing interaction between the amide carbonyl group of the penultimate unit with the active oxazolinium ring (this effect, of course, cannot be present in the first propagation step). The NMR spectra collected in the present case imply a transformation of the major propagation species from covalent to ionic during the early stages of polymerization. It is not clear exactly when this conversion occurs. It seems reasonable to expect dipole interactions between amide carbonyl groups and the cationic oxazolinium ion to provide added stability for the cation, but this effect could be intra- as well as intermolecular. On the basis of these observations, a mechanism is proposed for the polymerization of 2-ethyl-2-oxazoline in chlorobenzene (Scheme I). In this mechanism, the initiation product is a covalent species and there is a transition from the covalent propagating species to ionic species during the first few propagation steps. This proposed mechanism can completely account for the observed differences among the rate constants. For example, k_{pn} is greater than both k_{p1} and k_i. It is reasonable that the reaction rate of a monomer with an ionic species should be faster than that of the same monomer with a covalent species. In addition, note that k_i is greater than k_{p1}. This is also reasonable since benzyl iodide should be more reactive than the covalent propagating species, which is, by comparison, an unactivated alkyl iodide. It should be noted that, when similar experiments were conducted at 110 °C (the normal polymerization temperature), similar changes in NMR spectra and similar trends in k_i, k_{p1}, and k_{pn} values as compared to the 80 °C case (Table I) were observed.

To probe the effects of different initiator structures, the kinetics of 2-ethyl-2-oxazoline polymerizations in chlorobenzene using 1-iodobutane as initiator were also studied at 80 °C. In comparison with benzyl iodide as the initiator, several differences in this polymerization were observed. Unlike the benzyl iodide initiated system, 1-iodobutane initiated polymerizations displayed rather long incubation periods (ca. 5 h). This is logical in view of the difference in reactivity between the two substrates toward nucleophilic substitution. As this polymerization

Scheme I. Polymerization Mechanism of 2-Ethyl-2-oxazoline

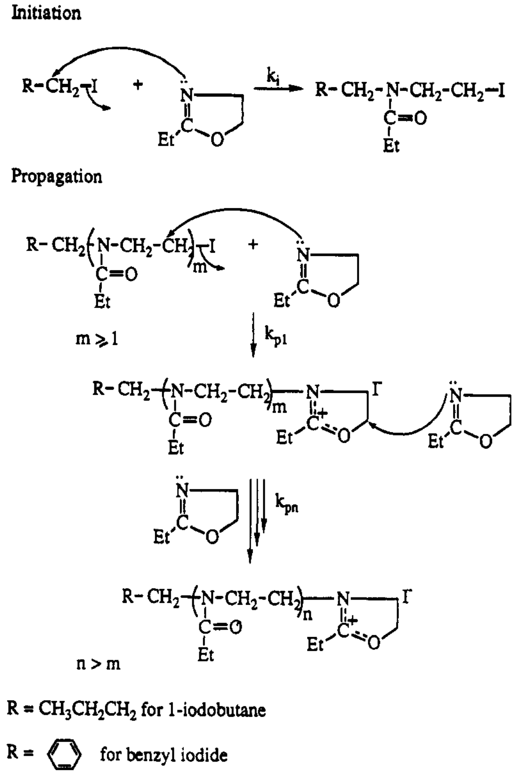

Table I. Polymerization Rate Constants of 2-Ethyl-2-oxazoline[a]

initiator	temp (°C)	$[M_0]/[I_0]$	$k_i \times 10^4$ (L/mol·s)	$k_{p1} \times 10^4$ (L/mol·s)	$k_{pn} \times 10^4$ (L/mol·s)
benzyl iodide	80	5.65	3.26	1.8	7.88
	110	4.28	37.4	14.3	63.3
1-iodobutane	80	5.36	0.095		2.616

[a] Solvent: chlorobenzene-d_5.

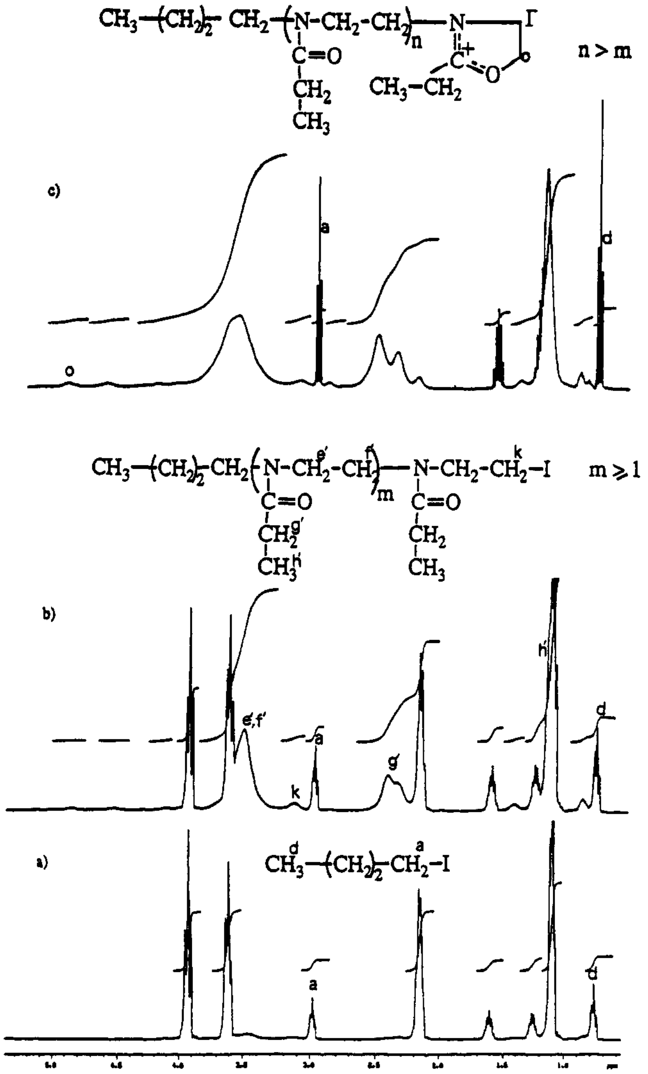

Figure 3. ^{1}H NMR of polymerization kinetics of 2-ethyl-2-oxazoline initiated by 1-iodobutane at 80 °C: (a) $t = 5.75$ h; (b) $t = 12$ h; (c) $t > 22$ h.

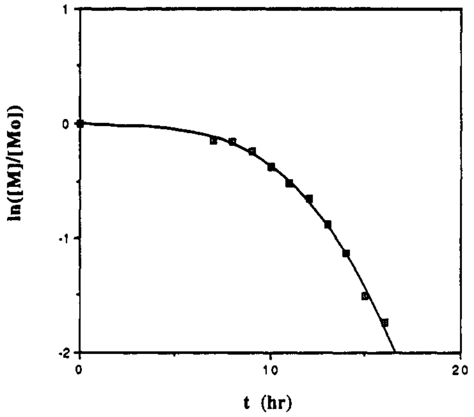

Figure 4. Monomer concentration as a function of time for the polymerization of 2-ethyl-2-oxazoline initiated by 1-iodobutane at 80 °C.

proceeded, the intensity of methylene protons adjacent to iodide from the initiator decreased very slowly. A substantial amount of the initiator remained unreacted at the end of polymerization (Figure 3c, $t > 22$ h; at least 50% of the initiator does not become incorporated using an initial monomer to initiator ratio of ca. 5). Similar to observations made in benzyl iodide initiated polymerizations, at an early stage of polymerization (Figure 3a, $t = 5.75$ h), new peaks around δ 3.2 and 3.5, corresponding to the open-chain form of the initiation product, appeared as the intensity of initiator decreased. The expected oxazolinium propagating species did not appear until a later stage in the polymerization (Figure 3b, $t = 12$ h) and their intensities were low compared to the peak intensity at δ 3.2. These observations again suggested the existence of covalent propagating species at the early stages of polymerization in a rather nonpolar solvent. Since no inflection point at the beginning of polymerization was observed on the $\ln([M]/[M_0])$ vs time plot (Figure 4), the initiation rate in this case is probably not faster than the initial propagation step. The convex shape of the plot indicates slow initiation and/or slow initial propagation step(s). The derivation of rate constants is more complicated than that in the case of benzyl iodide. The methylene peak due to the initiator and the initiation product are partially overlapped (deconvolution was not feasible due to differences in peak shape of the two peaks). Thus, the change of initiator concentration as a function of time could not be accurately determined from NMR spectra, and only monomer concentration as a function of time was calculated. Rate constants were estimated according to the following equation:[19]

$$\frac{1}{[I]_0}\frac{d\ln[M]}{dt} + k_p = (k_p - k_i)\exp\left(-k_i\int_0^t [M]\,dt\right) \quad (4)$$

where $[I_0]$ is the initial initiator concentration and [M] is the instantaneous monomer concentration. The value of k_i was estimated by calculating $d\ln[M]/dt$ at $t = 0$. Then the value of k_i was substituted into eq 4 and the equation was fitted by iteration to determine k_p. These values are

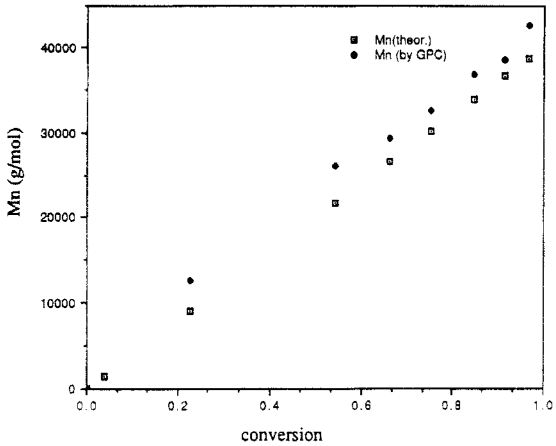

Figure 5. M_n vs monomer conversion plot for the polymerization of 2-ethyl-2-oxazoline initiated by benzyl iodide at 110 °C.

listed in Table I. It is evident that the initiation rate constant in the case of 1-iodobutane as initiator is much smaller than that in the case of benzyl iodide as initiator. This is consistent with the relative reactivity of these two reagents toward nucleophilic substitution. The smaller propagation rate constant for the case of 1-iodobutane as compared to that of k_{pn} in the case of benzyl iodide is probably caused by the change in method of calculation where the initial propagation steps are not distinguished from the subsequent propagation steps. After the initiation step, the reactive species in the propagation steps should not be significantly different between the two initiator cases.

The living characteristics of polymerization of 2-ethyl-2-oxazoline initiated by benzyl iodide in chlorobenzene were evaluated using a molecular weight–conversion experiment. It should be noted, however, that the molecular weight measurements were not as straightforward as expected. GPC traces in THF as the GPC solvent all exhibited an unusual sharp cutoff on the high molecular weight side, behavior which is often indicative of polymer adsorption onto some component of the GPC apparatus. Moreover, the number-average molecular weights calculated from those chromatograms were consistently much lower than the expected values based on NMR conversion data. To eliminate these abnormal effects, a series of chromatography experiments using different solvent compositions of THF/MeOH as well as different sample concentrations were conducted. A 75/15 (v/v) THF/MeOH solvent combination yielded symmetrical peaks with the expected molecular weights. Similar results were also obtained using a THF/2-propanol mixture. The measured number-average molecular weight was plotted against conversion (Figure 5). A straight line can be drawn through these data points, implying the molecular weight increases linearly with conversion and that chain transfer reactions are absent from the polymerization system. However, the molecular weight distributions of these oligomers, with polydispersities of ca. 1.3, were not as narrow as might be expected from a perfect living system. A number of factors may contribute to the broadening of molecular weight distribution, for example, equilibrium between different active species. Further investigations would be required to determine the actual cause of this broadening. Nevertheless, the polydispersities of these oligomers remained essentially the same throughout the course of the polymerizations. Thus, at least a majority of the polymer chains are long-lived (within detectable limits using GPC).

Conclusions

The polymerization of 2-ethyl-2-oxazoline in chlorobenzene initiated by activated halides such as benzyl iodide was found to be chain transfer free as evidenced by a linear relationship between number-average molecular weight and monomer conversion. Both covalent and ionic active species were present in these systems, and NMR spectra suggest conversion of the covalent active species to ionic species during the early course of polymerization. Smaller initiation and initial propagation rate constants than subsequent propagation rate constants were derived. Use of a less reactive alkyl halide, 1-iodobutane, slows the initiation step, yielding much smaller initiation rate constants than when using benzyl iodide as initiator.

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(18) NMR peak assignments for structure 1 were made based on the following rationale: The new peak at δ 4.45 can be assigned to the benzyl methylene of the initiation product. The peak at δ 3.1 is likely due to a methylene connected to an iodine. For example, the methylene protons next to iodine in 1-iodobutane resonate at δ 3.2 in $CDCl_3$. As expected, the area under the peak at δ 3.1 matched that of the peak at δ 4.45. The peak at δ 3.55 was not well resolved from the monomer peak at δ 3.6. Thus, the intensity of this peak (δ 3.55) was determined by subtracting the area under the peak at δ 3.95 from the total area of the peaks at δ 3.55 and 3.6 and was also found to match that of the peaks at δ 4.45 and 3.1. Thus the peak at δ 3.55 can be assigned to a methylene that is connected to a heteroatom, nitrogen.
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