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POLYMERIZATION BY BIS(ETHYLXANTHATO)-NICKEL(II) AS AN INITIATOR. I. POLYMERIZATION OF STYRENE OXIDE

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Key Words: Styrene Oxide, Bis(ethylxanthato)nickel(II),
Cationic, Coordination

ABSTRACT

Bis(ethylxanthato)nickel(II) was identified by FTIR, DSC, MS and X-ray powder diffraction methods. It has a monoclinic structure with cell parameters of $a=14.800(3)\text{Å}$, $b=14.088(1)\text{Å}$, $c=13.274(8)\text{Å}$; $\beta=101.13^\circ(8)^\circ$. It decomposes at above 170°C . Styrene oxide was polymerized with bis(ethylxanthato)nickel(II) under air, nitrogen and vacuum conditions. The structure of the resulting polymers was determined by means of FTIR, ^{13}C NMR, X-ray diffraction, vapor pressure osmometer and DSC. Low molecular weight and partially crystalline polymers have regular head to tail and irregular head to head structure indicating that the oxirane ring opened both at α ($-\text{CH}-\text{O}$) and β ($-\text{CH}_2-\text{O}$) positions. Ring opening reaction proceeds via cationic or/and coordination cationic mechanism with formation of oxonium ion.

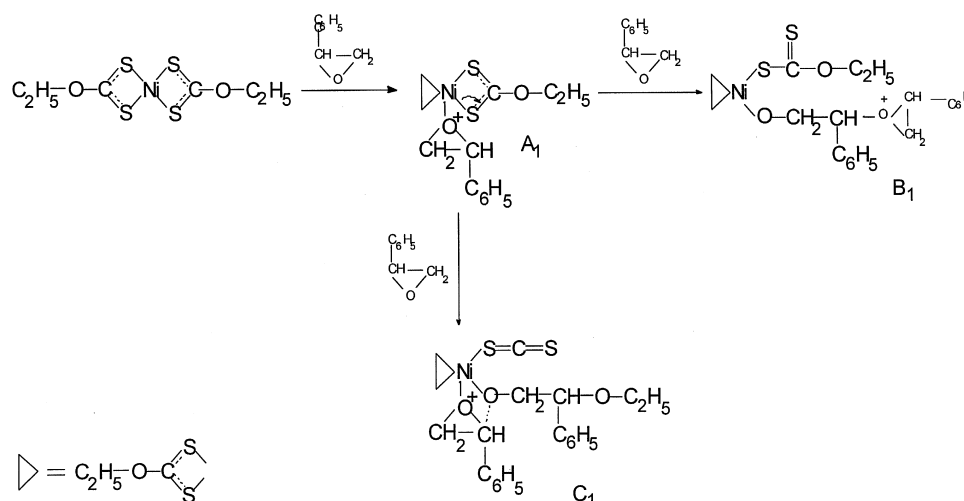
INTRODUCTION

Xanthates, $-\text{S}_2\text{COR}$, are salts of xanthic acid, which is essentially alkyl dithiocarbonic acid with two oxygen atoms in carbonic acid replaced by sulfur and one hydrogen atom replaced by an alkyl group [1]. Metal xanthates are most well known as reagent in mineral flotation and have also been used in analytical

chemistry. They can be synthesized easily and are safe to handle. Alkali and alkaline earth metallic xanthates are fairly soluble in water and are strong electrolytes [2-4].

Xanthates and dithiocarbamates of metals have been reported to be effective catalysts in the polymerization of olefin oxide and vinyl monomers to high molecular weight polymers [5-8]. It was found that the initiation ability of xanthates increased with increasing acidity of alcohol of the alkoxide group, such as, *tert*-butyl > *sec*-butyl > *n*-butyl > isopropyl = ethyl > benzyl. The effect of the counterion of xanthate on the polymerization was increased in the following order: potassium > sodium > lithium. This behavior shows the relation with decreasing electronegativity of the metal ion [7].

Nickel xanthates have been the most thoroughly studied with more than twenty structural investigations [3, 9, 10]. Nickel atom is comprised of two chelating xanthate ligands in the expected square planar array. Weak inter-molecular Ni-S interactions, above and below the NiS₄ plane, have been noted in several structures leading to a tetragonally distorted Ni atom environments. Structure of nickel ethylxanthate, bis(ethylxanthato)nickel(II), Ni(S₂COEt)₂ molecule is given below:



Two different crystal structures have been reported for bis(ethylxanthato)nickel(II), a triclinic form [11], as circular crystals and an orthorhombic form [3, 11, 12] as plate-like crystals.

In the present work, the X-ray powder structure of bis(ethylxanthato)nickel(II), and the decomposition product will be investigated. This will serve two purposes: (1) the mechanism of polymer initiation will be esti-

mated, that will give information, as to whether the initiation starts with a decomposition fragment of the catalyst molecule or whole molecule; (2) the metal salt that may form after fragmentation of a catalyst molecule may give a blend with polymer that may be conductive. For this purpose, a monomer which gives low molecular weight polymer that can give a blend with NiS is selected. Styrene oxide used for polymerization has been reported to polymerize with various initiators [13-24]. The polymer has low molecular weight and a low degree of stereoregularity.

EXPERIMENTAL

Materials

Reagent quality styrene oxide (Aldrich Chem. Co.) was dried over CaH_2 , and distilled under reduced pressure. Other solvents were purified by drying on CaH_2 and then distilled.

Procedures

Preparation of Bis(ethylxanthato)nickel(II)

A sample of 1.85 g (6.77 mmoles) of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ was dissolved in about 30 ml H_2O , and to this solution 2.17g (13.54 mmoles) potassium ethyl xanthate which was also dissolved in about 20 ml H_2O added dropwise as the solution was stirred with magnetic stirrer. Immediate precipitate formation occurred. The brown orange precipitate of bis(ethylxanthato)nickel(II) was filtered and washed with water, then with cold ethanol and dried under reduced pressure.

Preparation of Polymer

Styrene oxide was polymerized with bis(ethylxanthato)nickel(II) by mixing monomer and initiator in different mole ratios (e.g. 154, 304, etc.) and allowed for polymerization under nitrogen, air atmosphere or vacuum at different temperatures. After the desired time of polymerization, dichloromethane was added to the mixture to precipitate black nickel sulfide, keeping poly(styreneoxide) in solution. The mixture was separated by filtration and polymer in dichloromethane precipitated with an excess addition of methanol. It was then separated by filtration and dried to constant weight. This was called

methanol insoluble fraction. The methanol in liquid part was removed by evaporation and the solid obtained was called methanol soluble fraction. The percent conversion for both methanol insoluble and soluble fractions were calculated gravimetrically.

Characterization and Instrumentations

FTIR spectra of samples were taken with a Nicolet DX 510 FTIR spectrometer using KBr pellets.

^{13}C NMR spectra of polymers were taken in d-dimethylsulfoxide by using a Bruker GmbH DPX, 400 Mhz high performance digital FT-NMR spectrometer.

X-ray diffractogram of powdered samples were obtained by using a computer controlled automatic Huber-Guinier G600 powder diffractometer on a Enraf Nonius Delft Generator type FR 582 equipped with Cu X-ray tube (30 kV and 20 mA).

Direct pyrolysis were carried out on a Balzers QMG 311 quadropole mass spectrometer equipped with a PC for data analysis. Evolved gas analysis were done by Fisons Instrument VG platform II mass spectrometry by using 70 eV electron energy 180°C and 300°C as a source and probe temperature, respectively. The source vacuum was 1.2×10^{-5} mbar and analyzer 3×10^{-6} mbar.

Molecular weight determinations were done with a Knauer vapor pressure osmometer in toluene at 45°C and a Ubbelohde type glass viscometer in benzene at 30°C. Glass transition temperatures and melting points of polymer samples were determined by using a Perkin Elmer Thermal Analyzer System DC4. Samples of 5.0-10.0 mg were scanned in the temperature range of 0°C- 350°C at a heating rate of 10°C/min. Thermal gravimetric analysis of polymer samples were done by using a Dupont Instruments 951 Thermogravimetric Analyzer.

RESULTS AND DISCUSSION

Characterization of Bis(ethylxanthato)nickel(II)

The characterization of bis(ethylxanthato)nickel(II), $\text{Ni}(\text{Etxan})_2$, was done by FTIR, DSC, MS and X-ray.

The FTIR spectrum of $\text{Ni}(\text{Etxan})_2$ is given in Figure 1. Peaks at 1115 cm^{-1} and 1025 cm^{-1} are assigned to C-O-C and S-S bands, respectively. The peak

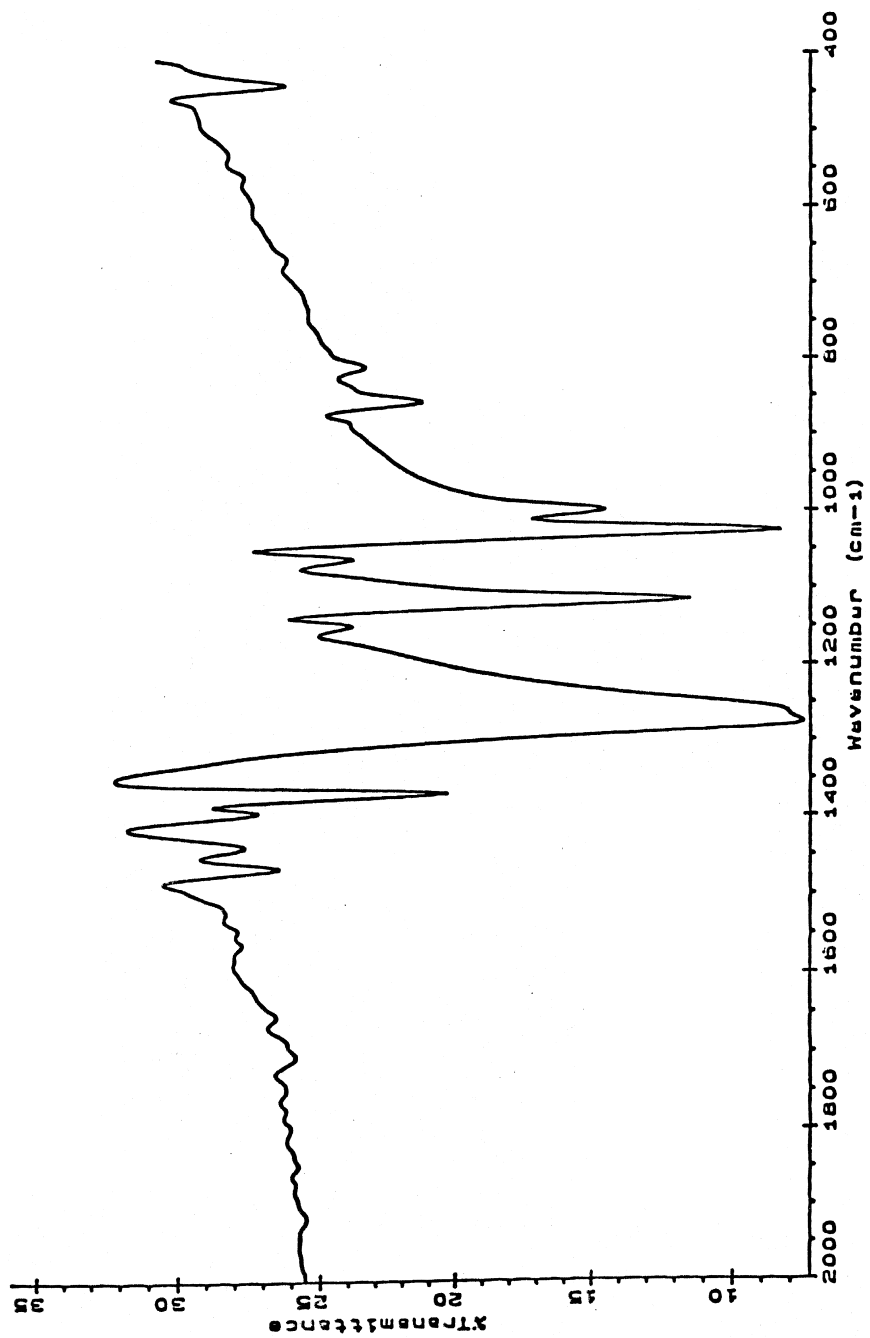


Figure 1. FTIR spectrum of bis(ethylxanthato)nickel(II).

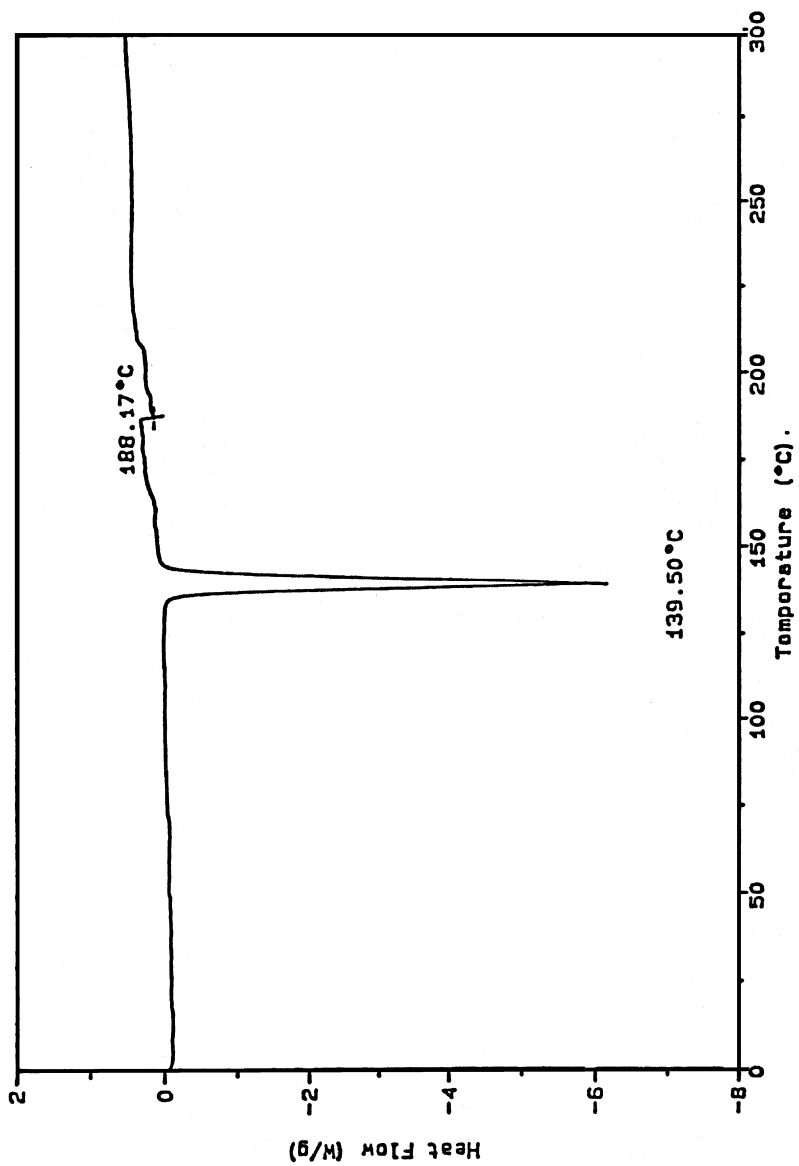


Figure 2. DSC thermogram of bis(ethylxanthato)nickel(II).

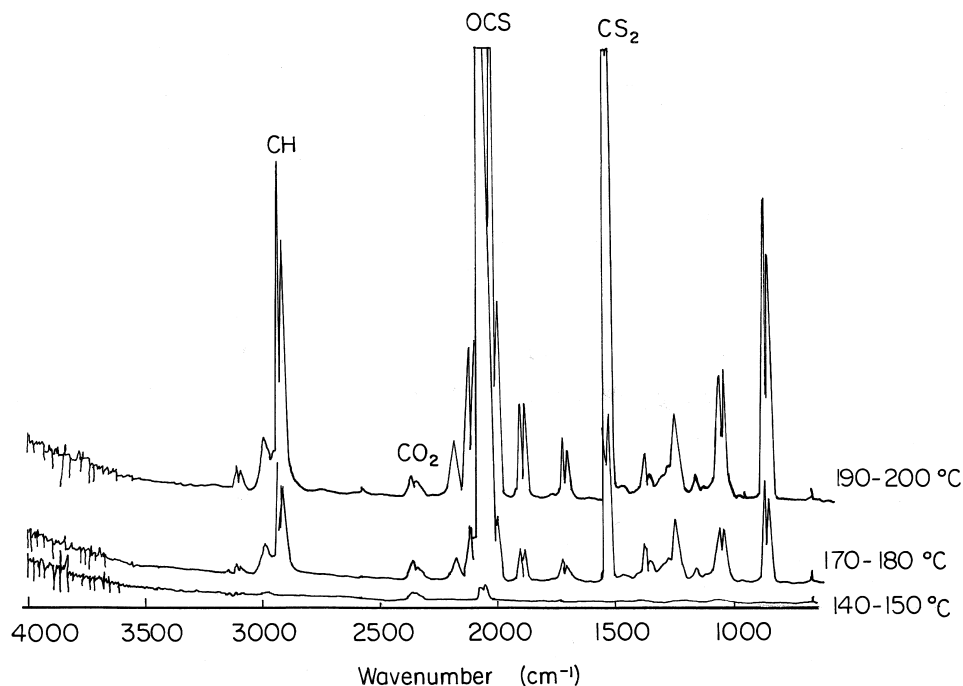


Figure 3. FTIR spectrum of pyrolysis products of bis(ethylxanthato)nickel(II).

at 1275 cm^{-1} shows Ni-S groups, and that at 1375 cm^{-1} and 1450 cm^{-1} correspond to $-\text{CH}_3$ and $-\text{CH}_2-$ groups, respectively. Since all the peaks are relatively sharp, the structure is quite regular.

The DSC thermogram of $\text{Ni}(\text{EtXan})_2$ is given in Figure 2. There is a sharp melting point at 139.5°C and decomposition starts at 188°C . In order to get a complete idea about decomposition temperature and products, the pyrolysis products were analyzed by FTIR and direct pyrolysis mass spectroscopy investigation were carried out.

The FTIR spectra of pyrolysis products of $\text{Ni}(\text{EtXan})_2$ are given in Figure 3. The decomposition started to be effective above 170°C . However, maximum decomposition was reached at $190\text{--}200^\circ\text{C}$. The main products were OCS, CS_2 and CH. Therefore, for the polymerization reaction at 135 to 165°C up to decomposition temperature, the initiator is the whole molecule instead of decomposition fragment.

The direct pyrolysis mass spectroscopy, Figure 4, showed that thermal decomposition of $\text{Ni}(\text{EtXan})_2$ started at around 40°C and maximum ion yield observed at 249°C . The MS products and relative intensities are given in Table

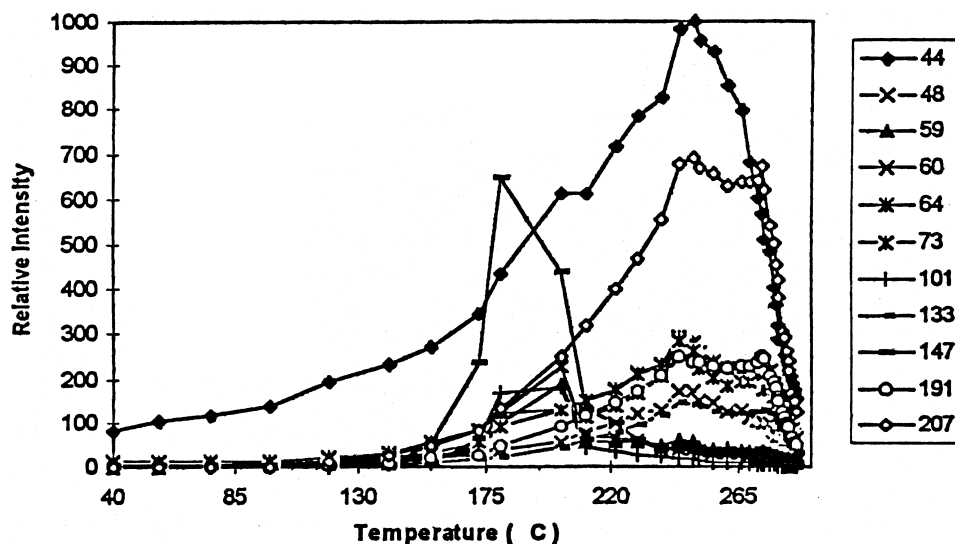


Figure 4. Ion temperature profiles of some characteristic peaks of bis(ethylxanthato)nickel(II).

1. The base peak observed at 44 amu is assigned to $\text{CH}_3\text{CH}_2\text{O}^+$. The other ions with their relative intensities are given in the table.

Crystal structure of $\text{Ni}(\text{EtXan})_2$ was studied by the powder pattern of the sample. The cell parameters reported [13] were tried for indexing the spectrum data. However, it was not possible to index the reflected peaks with these parameters. Further trials were repeated with new cell parameters, and satisfactory results were obtained for a monoclinic cell with cell parameters of $a = 14.800(3)$ Å, $b = 14.085(1)$ Å, $c = 13.274(8)$ Å, $\beta = 101.13(8)$. The results showed that $\text{Ni}(\text{EtXan})_2$ can crystallize in at least three different modifications; triclinic [11], orthorhombic [3, 12] and monoclinic. The role of different crystal structures of $\text{Ni}(\text{EtXan})_2$ on the initiation of polymerization will be investigated in the future.

Polymerization of Styrene Oxide

Bulk polymerization of styrene oxide initiated with bis(ethylxanthato)nickel(II) was carried out under nitrogen, air atmosphere and vacuum. In order to optimize the reaction condition, the effect of monomer to initiator ratio, temperature and polymerization time were studied.

Results of polymerization of styrene oxide in air atmosphere at various temperatures are given in Table 2. As seen in the table, methanol insoluble poly(styrene oxide) was obtained above 110°C , and percent conversion

TABLE 1. Relative Intensities and Assigned Chemical Formulas of the Most Intense and/or Characteristic Ions Observed During the Direct Pyrolysis Mass Spectrometric Analysis of Bis(Ethylxanthato)Nickel(II)

m/z	Relative Intensity	Chemical Assignments
44	1000	$\text{CH}_3\text{-CH}_2\text{-O}^+$
48	171	$\text{CH}_3\text{-SH}^+$
59	189	$\text{CH}_3\text{-CH}_2\text{-O-CH}_2^+$
60	229	COS^+
64	291	S_2 or SO_2
73	286	$\text{CH}_3\text{-CH}_2\text{-O-CH}_2\text{-CH}_2^+$
101	168	$\begin{array}{c} \text{O} \\ \\ \text{C}_2\text{H}_5\text{-O-C-CH}_2\text{-CH}_2^+ \end{array}$
133	136	$\begin{array}{c} \text{S} \\ \\ \text{CH}_2\text{=CH-O-C-S-CH}_2^+ \end{array}$
147	648	$\begin{array}{cc} \text{S} & \text{O} \\ & \\ \text{CH}_2\text{=CH-O-C-S-C}^+ \end{array}$
175	241	$\begin{array}{cc} \text{S} & \text{O} \\ & \\ \text{CH}_3\text{-CH}_2\text{-O-C-S-C-CH=CH}^+ \end{array}$
191	149	$\begin{array}{cc} \text{S} & \text{S} \\ & \\ \text{CH}_3\text{-CH}_2\text{-O-C-S-C-CH=CH}^+ \end{array}$
207	688	$\begin{array}{cc} \text{S} & \text{O} \\ & \\ \text{CH}_3\text{-CH}_2\text{-O-C-S-C-O-CH=CH}^+ \end{array}$

increased with the increasing temperature. However, since we already observed the degradation of initiator above 170°C , the polymerization temperature of $150 \pm 5^\circ\text{C}$ was selected for further studies.

The change of percent conversion for methanol soluble and methanol insoluble fraction with mole ratio of monomer (M) to initiator (I) are given in Table 3. The total conversion (e.g. methanol soluble and methanol insoluble) is highest (93%) for M: I ratio of 154. The intrinsic viscosities for methanol insoluble fractions are also included in the table. The intrinsic viscosities do not

TABLE 2. Effect of Temperature on Percent Conversion to Poly(Styrene Oxide) Under Air at 3 Hours at Constant M/ I Ratio (154)

T (°C)	% Conversion (methanol insoluble)
110 <	—
115 ± 5	10.0
135 ± 5	27.0
155 ± 5	29.0
175 ± 5	37.0

change much up to the mole ratio of 1845. However, in this case, the percent conversion to methanol insoluble fraction is quite low. Thus, in polymerization reaction the mole ratio of M: I used were taken as 154.

The effect of reflux time on percent conversion under nitrogen and air atmosphere were studied at $155 \pm 5^\circ\text{C}$, and the results for methanol insoluble fractions are given in Figure 5. Percent conversion to poly(styrene oxide) prepared under nitrogen increased rapidly after 2 hours of induction period and then reached to a limiting value of about 45% after 10 hours. When the reaction was carried out under air atmosphere, percent conversion increased almost linearly with increasing reflux time and limiting value of about 60% was reached after 12 hours.

The higher limiting conversion and presence of no induction period in the air atmosphere may be due to increasing activity of initiator in the presence of oxygen.

Polymerization rate was slower under vacuum. The limiting conversion after 120 hours, polymerization time was 29% for methanol insoluble fraction, detailed work under vacuum conditions is in progress.

The DSC thermograms showed T_g of $20^\circ\text{C} \pm 2^\circ\text{C}$ and melting points for different samples varied from 146°C to 254°C . The M_n measured by osmometric method for polymer obtained under nitrogen atmosphere and 12 hours polymerization time was 2200.

FTIR Characterizations

FTIR spectra of monomer and poly(styrene oxide) samples obtained

TABLE 3. Effect of Varies M/I Ratio (Mol) on Percent Conversion to Poly(Styrene Oxide) Under Air Atmosphere at 6 Hours in the $150\pm 5^\circ\text{C}$ Temperature Range

M/ I Ratio (mol)	% Conversion		Intrinsic Viscosity* (dl.g ⁻¹)
	Methanol Insoluble	Methanol Soluble	
154	33	60	0.017
304	31	39	0.018
615	30	42	0.018
1845	10	76	0.022
3691	—	85	—

* Intrinsic viscosity of methanol insoluble poly(styrene oxide)

under nitrogen and air atmosphere are given in Figure 6. The characteristic absorption peaks of epoxide in monomer spectrum are observed at about 1250, 875 and 800 cm^{-1} . They change to broad peak at 1150 -1050 cm^{-1} indicating ether, -C-O-C-, group in polymer spectrum due to opening of the epoxide ring. The broad and weak peak around 3450 cm^{-1} shows the OH end group in the polymer chains. The aromatic CH stretching bands at 3060-3027 cm^{-1} in monomer spectrum retain their position in the spectrum of polymer. Similarly, the peaks at 1650-2000 cm^{-1} and 650-1000 cm^{-1} assigned to CH out of plane mode of

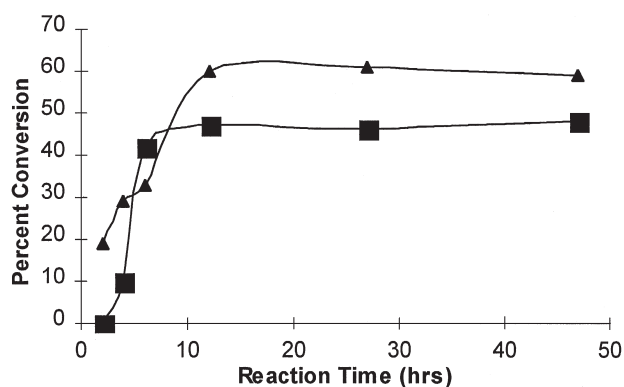


Figure 5. Percent conversion versus reaction time curve of poly(styrene oxide) obtained ▲ under air atmosphere, ■ under nitrogen at constant M/I ratio (154) at $150\pm 5^\circ\text{C}$.

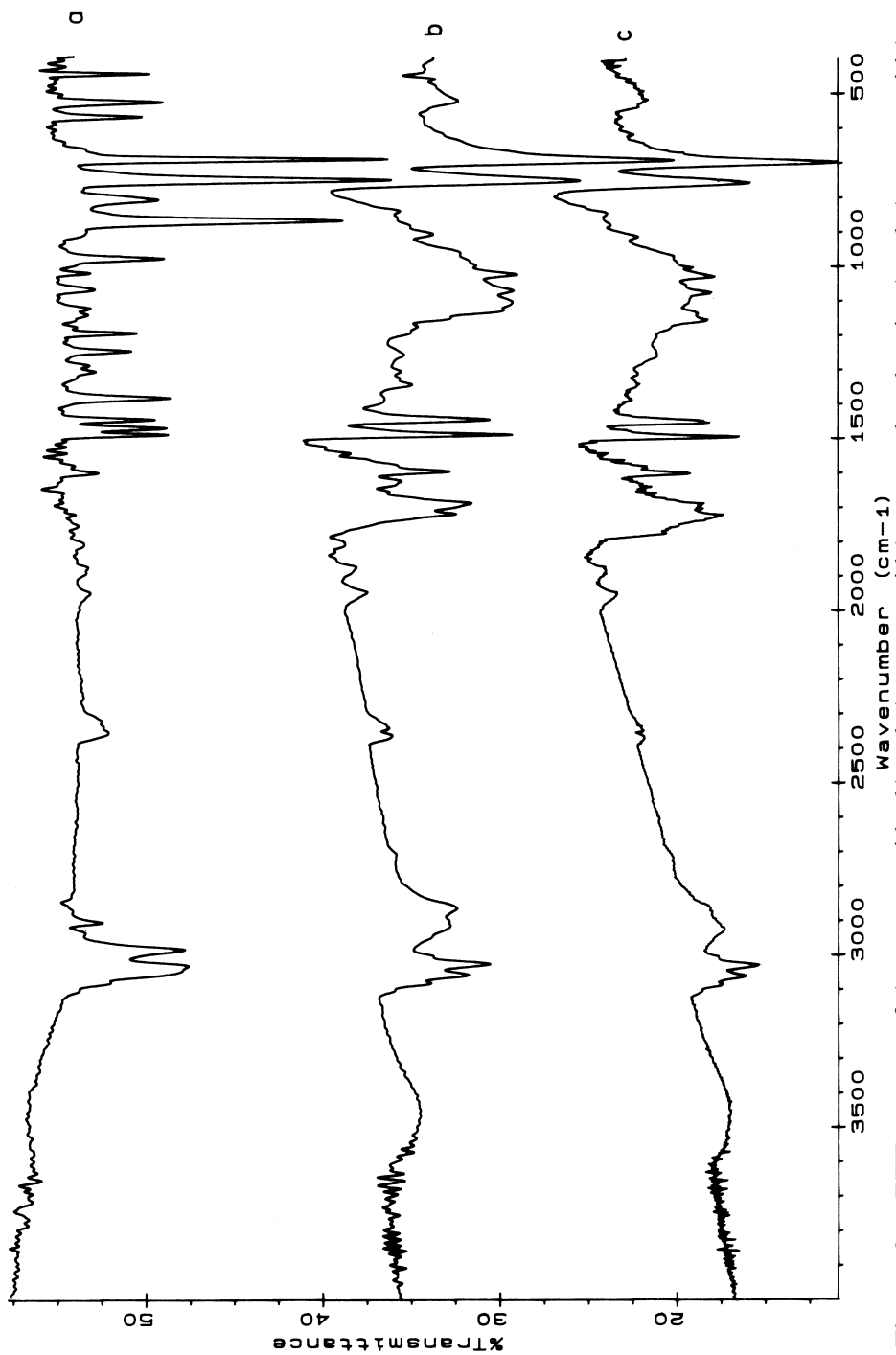


Figure 6. FTIR spectra of a) styrene oxide, b) poly(styrene oxide) prepared under air, c) poly(styrene oxide) prepared under nitrogen.

mono-substituted benzene and peaks at 1600, 1493, 1450 cm^{-1} corresponding to C=C bond in benzene ring exist in both monomer and polymer spectra.

There are small variations in peak shapes in the FTIR spectra of polymer samples obtained under nitrogen or air atmosphere and also at different polymerization times. In addition to broad a hydroxyl peak at around 3450 cm^{-1} , the carbonyl absorption peak appears in the polymer spectrum at about 1720 cm^{-1} , which may be an indication of degradation of the polymer chain [14].

^{13}C NMR Characterizations

The polymer obtained under nitrogen and air atmosphere might have both or either of α (-CH-O) and β (-CH₂-O) opening with irregular head to head and regular head to tail sequences.

Tacticity of the polymer chain relating to type of ring opening and the presence of degradation products can best be studied by NMR spectra. There are a few publications [5, 11, 14, 22] reporting the NMR investigations of poly(styrene oxide) obtained by anionic and $\text{Zn}(\text{C}_2\text{H}_5)_2$ catalysts. The ^{13}C NMR spectrum of poly(styrene oxide) obtained by $\text{Ni}(\text{Etan})_2$ catalyst under nitrogen (PSTO1), in air atmosphere (PSTO 2) and under vacuum (PSTO 3) for polymerization times of 30 hours, 47 hours, and 120 hours, respectively, are given in Figure 7. In the ^{13}C NMR spectra, the aromatic carbons (126-130 ppm) gave a complex pattern from which no useful information could be derived. Peaks in the range of 50-75 ppm are assigned to CH₂ end groups or degradative CH₂ groups.

In the spectrum of PSTO1, the CH₂ (H-T) peak at 75.0 ppm gives no splitting. Besides, the intensity of CH₂ resonance is higher than that of both CH₂ (T-T, 77.3 ppm) and CH (H-H, 77.7 ppm and 78.2 ppm) resonance. Therefore, the isotactic fraction is higher. In the spectrum of PSTO2, the intensities of CH₂ (H-T, 74.9 ppm), CH₂ (T-T, 77.3 ppm) and CH (H-H, 77.7 ppm) are almost equal. Splitting observed in 77.3 ppm CH₂ (T-T) indicate atactic character. Thus, stereoregular fraction in PSTO 2 is less compared to that in PSTO 1. The intensity of CH₂ (H-T) in spectrum of PSTO 3 is much more than that of CH (H-H) and CH₂ (T-T) signals (ratio of about 6.07: 0.79). The polymer obtained under vacuum is most stereoregular (isotactic). On the other hand, the number of CH₂ peaks assigned as end group or degradative carbons are also more in PSTO 3.

Thermal and Mass Spectral Investigations

Since polymers obtained under different conditions show slight varia-

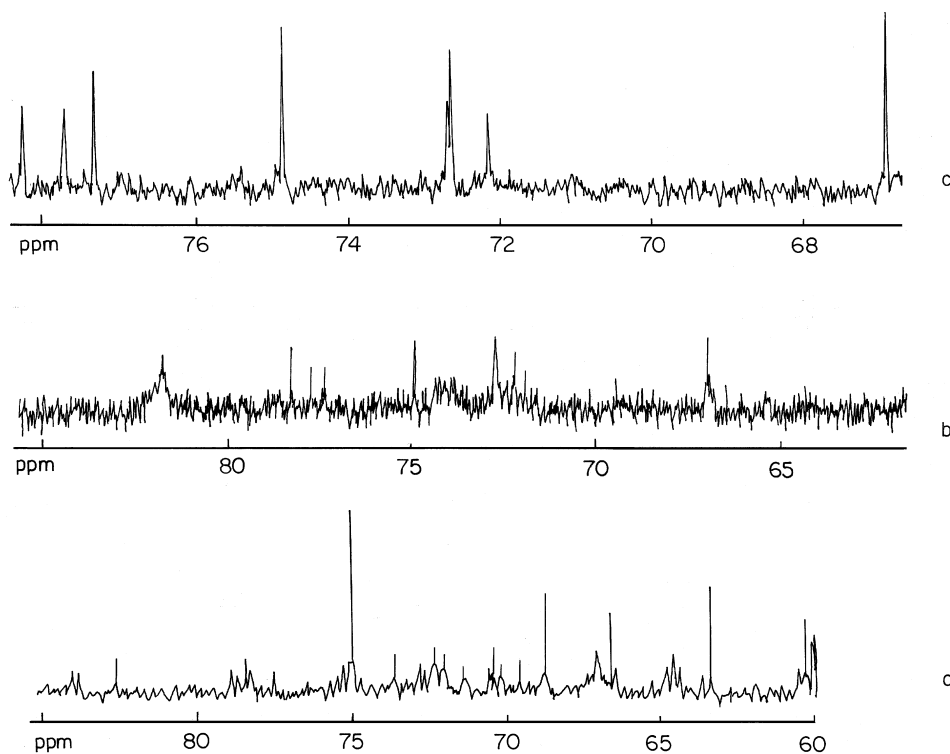


Figure 7. ^{13}C NMR spectra of poly(styrene oxide) prepared under a) vacuum, b) air, c) nitrogen.

tions in tacticity, they were subjected to thermal analysis and evolved gas analysis by mass spectrometry to clarify the structural differences in the polymers.

A typical evolved gas analysis result is given in Figure 8 and relative intensities and assigned chemical formulas of the most intense and/or characteristic ions, observed during evolved gas analysis, are given in Tables 4-6 for PSTO1, PSTO2, and PSTO3, respectively.

For all three samples, the base peaks were observed at 91 amu, and it was assigned as $\text{C}_6\text{H}_5\text{CH}_2^+$. The other evolved gases shows high percentages of $\text{C}_6\text{H}_5\text{CH}_2\text{CH}_2^+$ and C_6H_5^+ . These results show clearly that polymerization takes place by ring opening process. However, variations in the percentage of different fragments in each sample can be attributed to configurational differences in different samples.

Thermal gravimetric analysis of PSTO1 and PSTO2 showed that decomposition of polymers starts at about 100°C and almost 90% weight loss is observed between 100°C and 360°C .

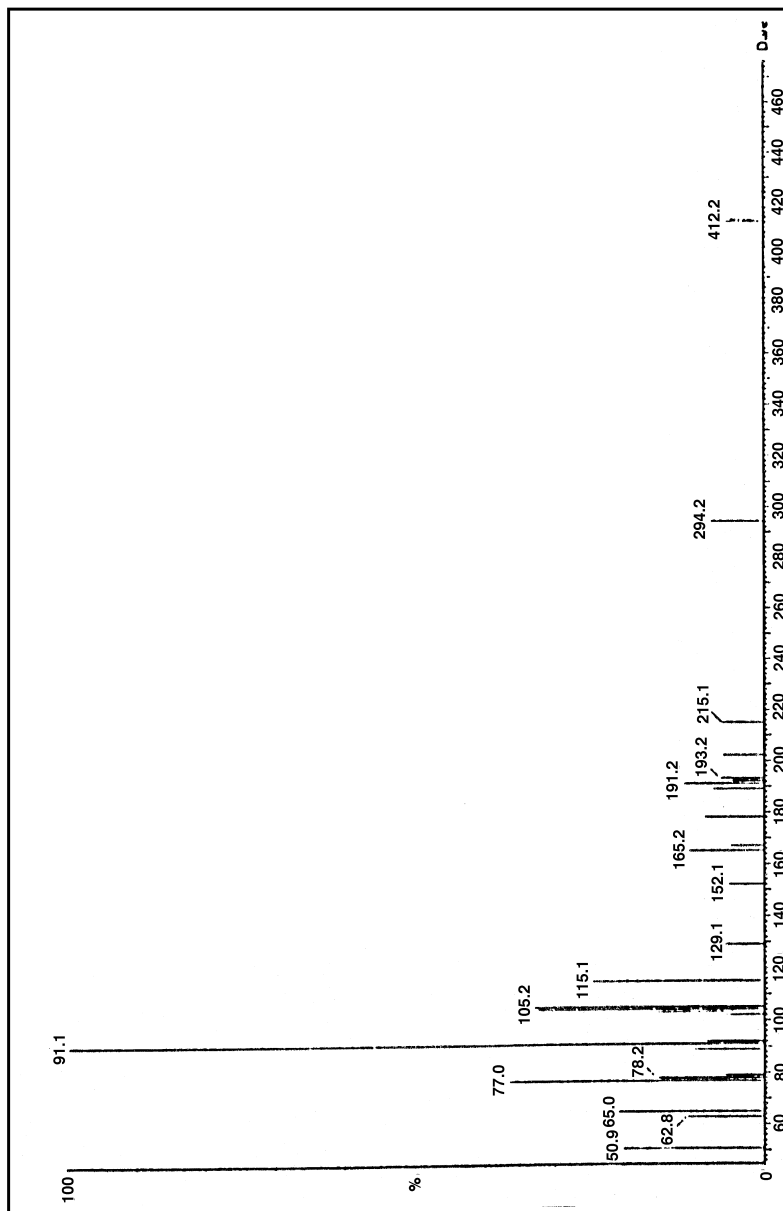


Figure 8. Evolved gas analysis of PSTO1 by MS.

TABLE 4. Relative Intensities and Assigned Chemical Formulas of the Most Intense and/or Characteristic Ions Observed During Evolved Gas Analysis of PSTO1 by MS

m/z	Relative Intensity	Chemical Assignments
51	206	$C_4H_3^+$
62	112	$\begin{array}{c} \text{OH} \\ \\ \text{CH}_3\text{-O-CH}_2^+ \end{array}$
65	219	$C_5H_5^+$
77	375	$C_6H_5^+$
78	150	$C_6H_6^+$
79	62	$C_6H_7^+$
89	100	$\begin{array}{c} \text{O} \\ \\ \text{CH}_3\text{-CH}_2\text{-C-O-CH}_3^+ \end{array}$
91	1000	$C_6H_5\text{-CH}_2^+$
92	88	$C_6H_5\text{-CH}_3^+$
105	337	$C_6H_6\text{-CH=CH}_2^+$
115	256	$\begin{array}{c} \text{O} \quad \text{O} \\ \quad \\ \text{CH}_3\text{-C-O-CH}_2\text{-C-CH}_2^+ \end{array}$
152	62	$\begin{array}{c} \text{O} \\ \\ \text{C}_6\text{H}_5\text{-CH}_2\text{-C-O-CH}_3^+ \end{array}$
165	118	$\begin{array}{c} \text{OH} \quad \text{O} \\ \quad \\ \text{C}_6\text{H}_5\text{-CH-CH}_2\text{-O-CH}^+ \end{array}$
178	193	$\begin{array}{c} \text{O} \quad \text{O} \\ \quad \\ \text{C}_6\text{H}_5\text{-C-CH}_2\text{-O-CH}^+ \end{array}$
189	88	$\begin{array}{c} \text{O} \quad \text{O} \\ \quad \\ \text{C}_6\text{H}_5\text{-C-CH}_2\text{-O-C-CH=CH}^+ \end{array}$
191	122	$\begin{array}{c} \text{O} \quad \text{O} \\ \quad \\ \text{C}_6\text{H}_6\text{-C-CH}_2\text{-O-C-CH=CH}_2^+ \end{array}$

X-ray Diffractogram Investigations

Crystallinity of poly(styrene oxide) samples, which were prepared under nitrogen and air atmosphere, were determined by X-ray powder diffraction method. The indexing of observed peaks showed the crystal structure to be monoclinic with cell parameter $a = 18.875(7) \text{ \AA}$, $b = 9.460(2) \text{ \AA}$, $c = 14.406(1) \text{ \AA}$, $\beta = 105.87^\circ$, $Z = 8$. Samples are partially crystalline with both amorphous and crystalline parts.

TABLE 5. Relative Intensities and Assigned Chemical Formulas of the Most Intense and/or characteristic Ions Observed During Evolved Gas Analysis of PSTO2 by MS

m/z	Relative Intensity	Chemical Assignments
51	500	$C_4H_3^+$
62	150	$\begin{array}{c} \text{OH} \\ \\ \text{CH}_3\text{-O-CH}_2^+ \end{array}$
65	230	$C_5H_5^+$
77	640	$C_6H_5^+$
78	210	$C_6H_6^+$
84	180	$\begin{array}{c} \text{O} \\ \\ \text{CH}_2=\text{CH-C-O-CH}_2^+ \end{array}$
86	130	$\begin{array}{c} \text{O} \\ \\ \text{CH}_3\text{-CH}_2\text{-C-O-CH}_2^+ \end{array}$
91	1000	$C_6H_5\text{-CH}_2^+$
92	75	$C_6H_5\text{-CH}_3^+$
103	440	$C_6H_5\text{-CH=CH}^+$
105	700	$C_6H_6\text{-CH=CH}_2^+$
107	120	$\begin{array}{c} \text{OH} \\ \\ \text{C}_6\text{H}_5\text{-CH}^+ \end{array}$
115	270	$\begin{array}{c} \text{O} \quad \quad \text{O} \\ \quad \quad \\ \text{CH}_3\text{-C-O-CH}_2\text{-C-CH}_2^+ \end{array}$
120	330	$\begin{array}{c} \text{O} \\ / \quad \backslash \\ \text{C}_6\text{H}_5\text{-CH} \quad \text{-CH}_2 \end{array}$
131	100	$\begin{array}{c} \text{O} \\ \\ \text{C}_6\text{H}_5\text{-CH=CH-CH}^+ \end{array}$
149	140	$\begin{array}{c} \text{O} \\ \\ \text{C}_6\text{H}_5\text{-CH}_2\text{-CH}_2\text{-C}^+ \end{array}$
165	118	$\begin{array}{c} \text{OH} \quad \quad \text{O} \\ \quad \quad \quad \\ \text{C}_6\text{H}_5\text{-CH-CH}_2\text{-O-CH}^+ \end{array}$

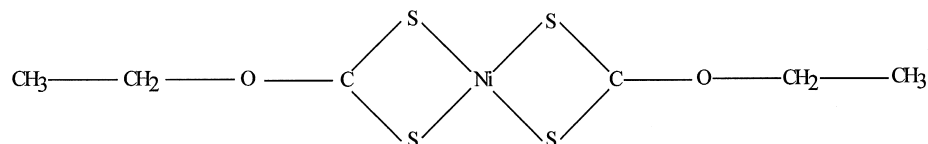
Polymerization Mechanism of Styrene Oxide

In order to elucidate the reaction mechanism of polymerization of styrene oxide with bis(ethylxanthato)nickel(II), polymerization was carried out in the presence of free radicalic (quinone), cationic (pyridine) inhibitors and chlorinated solvent. Reaction of styrene oxide was also carried out with free lig-

TABLE 6. Relative Intensities and Assigned Chemical Formulas of the Most Intense and/or Characteristic Ions Observed During Evolved Gas Analysis of PSTO3 by MS

m/z	Relative Intensity	Chemical Assignments
51	160	$C_4H_3^+$
62	200	$\begin{array}{c} \text{OH} \\ \\ \text{CH}_3\text{-O-CH}_2^+ \end{array}$
65	230	$C_5H_5^+$
77	360	$C_6H_5^+$
78	210	$C_6H_6^+$
79	210	$C_6H_7^+$
91	1000	$C_6H_5\text{-CH}_2^+$
92	120	$C_6H_5\text{-CH}_3^+$
103	260	$C_6H_5\text{-CH=CH}^+$
104	280	$C_6H_5\text{-CH=CH}_2^+$
105	510	$C_6H_6\text{-CH=CH}_2^+$
107	120	$\begin{array}{c} \text{OH} \\ \\ \text{C}_6\text{H}_5\text{-CH}^+ \end{array}$
115	290	$\begin{array}{c} \text{O} \quad \text{O} \\ \quad \\ \text{CH}_3\text{-C-O-CH}_2\text{-C-CH}_2^+ \end{array}$
120	120	$\begin{array}{c} \text{O} \\ / \quad \backslash \\ \text{C}_6\text{H}_5\text{-CH} \quad \text{-CH}_2 \end{array}$
165	73	$\begin{array}{c} \text{OH} \quad \text{O} \\ \quad \\ \text{C}_6\text{H}_5\text{-CH-CH}_2\text{-O-CH}^+ \end{array}$
178	93	$\begin{array}{c} \text{O} \quad \text{O} \\ \quad \\ \text{C}_6\text{H}_5\text{-C-CH}_2\text{-O-CH}^+ \end{array}$
191	93	$\begin{array}{c} \text{O} \quad \text{O} \\ \quad \\ \text{C}_6\text{H}_6\text{-C-CH}_2\text{-O-C-CH=CH}_2^+ \end{array}$

and $\text{-S}_2\text{COR}$ to check if the free ligand, which might arise due to thermal decomposition of bis(ethylxanthato)nickel(II) could be responsible for the polymerization. However, no polymer was obtained when styrene oxide was refluxed with free ligand ($\text{-S}_2\text{COR}$) with the same monomer to initiator ratio. The polymerization reaction was conducted in a chlorinated solvent to scavenge possible anions, and also in the presence of a radical scavenger (quinone) where no detectable inhibition effect was observed in both cases. However, polymerization did not



Scheme 1. Mechanism of initiation and propagation for the polymerization of styrene oxide by using nickel ethyl xanthate.

occur in the presence of stoichiometric amount of pyridine, which has been reported to polymerize styrene oxide [25]. It is also known as a cationic inhibitor. Since Ni(II) is a soft acid ion, it prefers soft base ligands such as S, rather than N or O. Therefore, replacement of ethylxanthate ligand by pyridine is not possible. On the other hand, coordination of pyridine to the central atom via axial position cannot be ruled out. When pyridine coordinates with nickel more firmly and blocks it, no monomer could coordinate with Ni to start polymerization. Therefore, in the light of the above findings, it was thought that polymerization proceeded in cationic or coordinate cationic mechanism. Predicted manners of initiation and propagation steps of polymerization of styrene oxide by using bis(ethylxanthato)nickel(II) are illustrated in Scheme 1.

The route going through A1→B1 represents cationic mechanism and A1→C1 represents coordinate cationic mechanism. Polymerization proceeds through formation of oxonium ion in both mechanisms.

CONCLUSION

Styrene oxide can be polymerized to partially isotactic crystalline polymers by using bis(ethylxanthato)nickel(II) as an initiator. Polymerization was found to proceed faster in the presence of air. Under all polymerization conditions, a black precipitate product was obtained. This was shown by X-ray method to be a blend of NiS and polymer. The conductivity measurements showed the product to be nonconductive. However, further work will be carried out to find if conductivity can be induced to the product by some type of doping or electrochemical treatment. Polymers obtained under air, nitrogen and vacuum have both α and β opening with head to head and regular head to tail sequences showing slight variation in tacticity. However, evolved gas analysis of the polymers showed that their degradation products are almost the same, indicating chemical similarities of the polymer chains independent of the polymerization conditions.

Polymerization of styrene oxide by using bis(ethylxanthato)nickel(II) was found to proceed via cationic and / or coordination cationic mechanism.

It can be concluded that bis(ethylxanthato)nickel(II) is a promising catalyst for polymerization reaction. The preparation of the catalyst is quite easy, it can be handled safely and worked under normal conditions without requiring complex instrumentation. Furthermore, it has the advantage of giving higher conversions to polymer in relatively shorter times in comparison to xanthates and carbamates of zinc [5, 6].

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