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Trityl Salt-Initiated Cationic Polymerization of 1,2-Cyclohexene Oxide: Structural Analyses of the Products

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ABSTRACT

The polymerization of 1,2-cyclohexene oxide was carried out at 0°C in dichloroethane with triphenylmethyl hexafluoroarsenate as the initiator. A typical reaction product (PCHO-1) was analyzed by infrared and nuclear magnetic resonance spectroscopy as well as by gel-permeation chromatography, x-ray diffraction, and differential scanning calorimetry (DSC). The x-ray and DSC data show that PCHO-1 is an amorphous substance. The results of the NMR analyses show that the propagation step in the trityl salt-initiated polymerization obeys Bernoullian statistics with a P_m value of 0.38.

INTRODUCTION

The polymerization of 1,2-cyclohexene oxide by use of conventional cationic [1-6], anionic [7], and free-radical [8, 9] initiators has been

reported in the literature. Results are also available on irradiation-induced ionic polymerizations [10-13] of this monomer. The characterization of poly(1,2-cyclohexene oxide) by viscosity and osmometry determinations [14], by x-ray diffraction [13], by infrared (IR) [9], and nuclear magnetic resonance (NMR) [1] spectroscopy has also been carried out. The data available on NMR, however, are limited to deducing the steric structure of the polymer by comparing its NMR spectra with those obtained with trans-1,2-cyclohexanediol and cis-1,2-cyclohexanediol. With a view to extending these studies, the polymerization of 1,2-cyclohexene oxide was carried out in dichloroethane (as solvent) by use of triphenylmethyl hexafluoroarsenate as the initiator. The principal results on the characterization of a typical product (PCHO-1) of the reaction, form the subject of this publication.

EXPERIMENTAL

Materials

The monomer, 1,2-cyclohexene oxide (Aldrich Chemical Co. 98%) was used as such. The solvent 1,2-dichloroethane (Fisher certified) was refluxed over calcium hydride for 24 hr, then distilled on a column from which the middle cut was collected and stored under nitrogen.

The initiator, triphenylmethyl hexafluoroarsenate (C_6H_5)₃C⁺AsF₆⁻ (Alfa Chemicals) was dissolved in dichloromethane and the solution, filtered. The initiator was then precipitated from the solution by the addition of anhydrous carbon tetrachloride and recovered by filtration. It was washed further with carbon tetrachloride before being dried and preserved under vacuum.

Experimental Procedure

The polymerizations were carried out in Pyrex glass reactors provided with appropriate openings for continuous circulation of dry nitrogen and the addition and removal of reactants. The reactors were placed in an alcohol bath maintained at a temperature of 0°C. The reactants, monomer (~ 1 M) and solvent, were added to the reactor. These were then vigorously stirred with a glass-covered magnetic stirring bar while the initiator ($\sim 10^{-2}$ M) was slowly added to the solution. The reactions required about 4 hr to reach 100% conversion. The initiator was then destroyed by the addition of methanolic ammonia, after which all volatile materials in the resulting solution were removed by evaporation under vacuum at 60°C until the residue maintained a constant weight.

Characterization of the Products

Infrared Spectroscopy. IR spectra of the monomer and the polymers as thin films or on KBr pellets were recorded with a Beckman-12 infrared spectrophotometer.

Nuclear Magnetic Resonance Spectroscopy. Spectra of the polymer solutions (15% W/V) in o-dichlorobenzene at 115°C and in carbon tetrachloride at 75°C were recorded with a Varian Associates 220 MHz NMR spectrophotometer. TMS was used as the internal reference for all the runs.

X-Ray Diffraction. The x-ray diffraction spectra on poly(1,2-cyclohexene oxide) powders were obtained with a Philips Generator equipped with a vertical goniometer and a special sample holder for transmission studies. A copper target was used in conjunction with a nickel filter which eliminated β radiation and allowed only $K\alpha$ radiation. The powder samples were supported by pieces of Scotch tape.

Glass Transition Temperature (T_g) Measurements.

T_g values were measured with a Perkin-Elmer DSC-2 instrument equipped with an autoscanning zero device which enabled excellent baselines to be obtained. Polymer samples (10 mg) were placed in standard DSC aluminum pans, while similar empty pans were used on the reference side for each T_g measurement. Both the sample and reference pans were closed with aluminum covers which were sealed in place with a special sample pan press. The pans were then deposited in the appropriate places of the cell compartment of the instrument, where a continuous stream of pure dry helium was made to flow at a rate of 20 cm³/min. In order to have a homogeneous polymer sample, it was heated for few seconds to a temperature 30°K above the estimated T_g values after which it was quenched through the glass transition region at a rate of 320°K/min. After quenching, the samples were heated successively at different heating rates and in each case the T_g values were measured at the half ΔC_p height [15].

RESULTS AND DISCUSSION

Poly(1,2-cyclohexene oxide) samples prepared in the present study showed slightly different patterns in their IR spectra as compared to those observed for poly(exo-2,3-epoxynorbornanes) (PENB)

[16]. The 1735 cm^{-1} peak present in PENB and attributed [17] to $-\text{CO}$ stretching, was missing from the poly(1,2-cyclohexene oxide) spectrum. In the case of PENB, the qualitative information, e. g., IR and NMR spectra, on its monomer, *exo*-2,3-epoxynorbornane, yielded data which proved of great help in the interpretation of the complex results obtained with the polymer. Keeping this in mind, the monomer, 1,2-cyclohexene oxide, was analyzed with both the NMR and IR techniques to provide background information about its polymer.

Some Characteristics of the 1,2-Cyclohexene Oxide Monomer

In Fig. 1 is shown the NMR spectrum of 1,2-cyclohexene oxide observed in *o*-dichlorobenzene at 115°C . The assignments of various syn(s) and anti(a) protons in 1,2-cyclohexene oxide (structure I in Fig. 1) are as follows: H_1, H_2 : 7.0-7.2 τ , center at 7.09; $\text{H}_{3a}, \text{H}_{6a}$: 8.0-8.2 τ , peaks at (8.10, 8.13, 8.16, 8.19, and 8.22 τ); $\text{H}_{3s}, \text{H}_{6s}$: 8.2-8.4 τ , peaks at (8.28, 8.31, 8.34, 8.37, and 8.40 τ); $\text{H}_{4a}, \text{H}_{5a}$: 8.5-8.75 τ , peaks at (8.56, 8.59, 8.62, 8.65, 8.68, and 8.71 τ); $\text{H}_{4s}, \text{H}_{5s}$: 8.75-9.0 τ , peaks at (8.82, 8.85, 8.88, 8.91, 8.94, and 8.97 τ).

These assignments are made by use of the concept that the epoxide ring generates a ring current [18-22] which is responsible for shielding certain protons, resulting in a downfield shift of their signal in the NMR spectrum. Other arguments, e. g., diaxial interactions between the protons and the oxygen atom which deshields the protons [19-22], have also been retained.

In Fig. 2 is shown the IR spectrum of 1,2-cyclohexene oxide (CHO) which shows important peaks at the following wave numbers (cm^{-1}): 3000 (ν CH of methine), 2940 ($\nu_{\text{as}} \text{CH}_2$), 2860 ($\nu_{\text{s}} \text{CH}_2$), 1460, 1440 (δCH_2), 1360, 1350 (δCH_2), 1270 (so-called 8 μ band; symmetric stretching of ring) 975, 890, 875 (so-called 11 μ band; asymmetric stretching of ring), 835, 780, and 750 (so-called 12 μ band).

Characterization of Poly(1,2-cyclohexene Oxide)

In Fig. 2 is also shown the IR spectrum of PCHO-1 which carries most but not all of the bands present in CHO, the following being the more prominent ones: 2930 ($\nu_{\text{as}} \text{CH}_2$), 2850 ($\nu_{\text{s}} \text{CH}_2, \nu \text{CH}$), 1450 (δCH_2), 1365 (δCH_2 and δCH_3 , the latter being in the form of end groups), 1150, 1080 (C-O-C antisymmetric stretching), 890, 850, 780, and 755 (δCH out-of-plane).

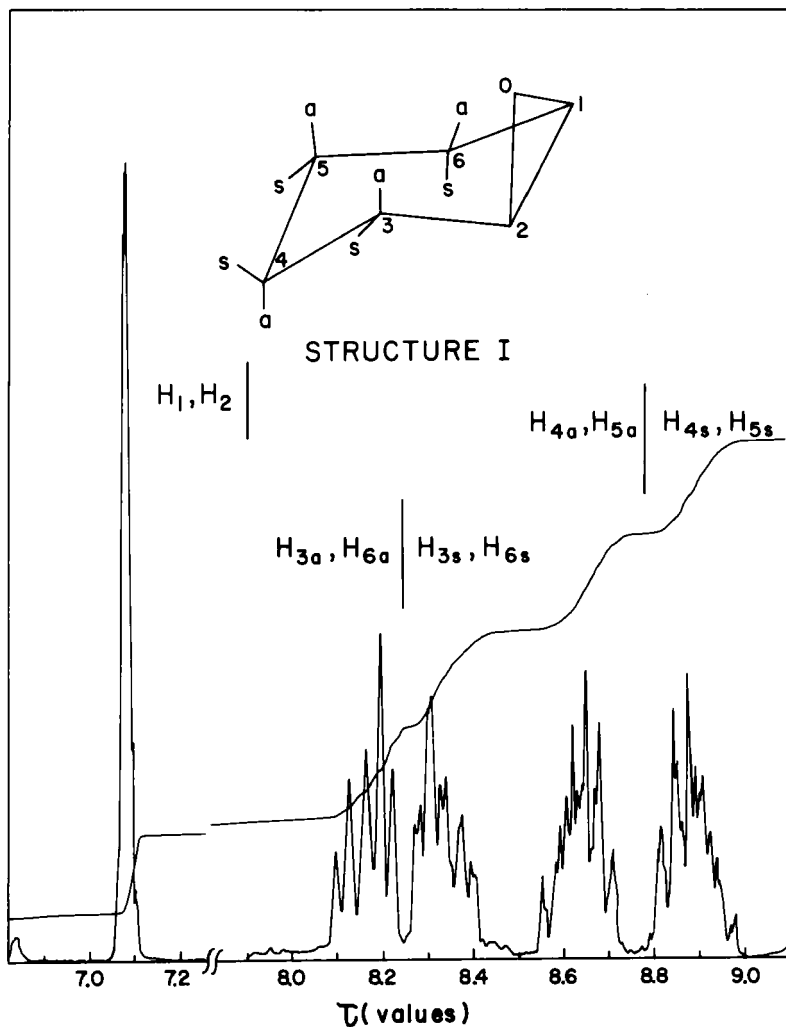


FIG. 1. 220 MHz NMR spectrum of 1,2-cyclohexene oxide (CHO) in *o*-dichlorobenzene solution at 115°C with TMS as the internal standard.

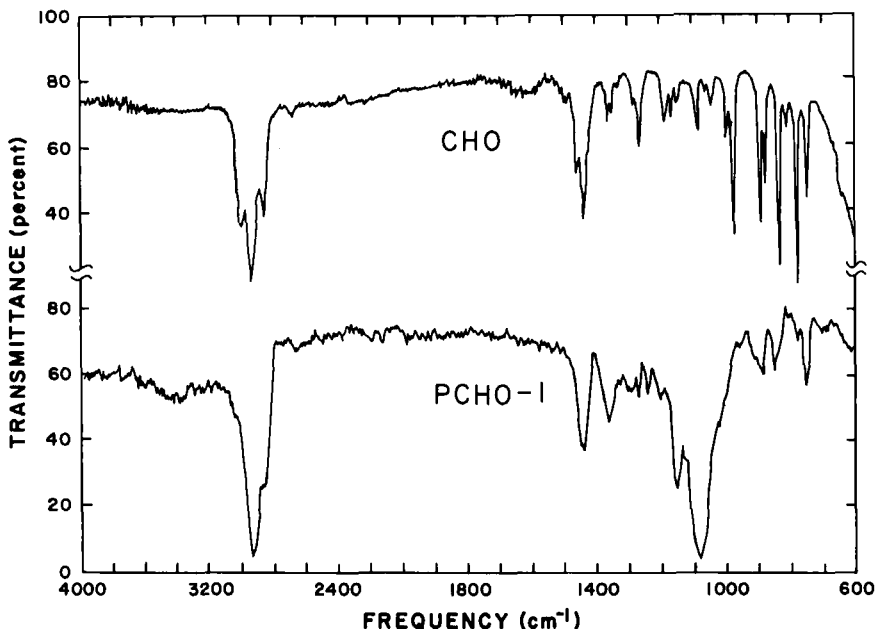


FIG. 2. IR spectra of 1,2-cyclohexene oxide (CHO) and poly(1,2-cyclohexene oxide) (PCHO-1) recorded from thin films and KBr pellets, respectively.

These assignments for PCHO-1 agree well with those of Bacskai [1] for his poly(cyclohexene oxides) prepared with aluminum alkyl catalysts. They agree also with those of Suga and Aoyama [9], who polymerized 1,2-cyclohexene oxide using α, α' -azobisisobutyronitrile. A comparison of the IR spectra of CHO and PCHO-1 shows that the typical epoxide bands characteristic of the monomer (CHO) are missing from that of the polymer (PCHO-1) while a new intense band associated with the ether linkage appears on polymerization. This would suggest that the polymerization of CHO proceeds through the opening of the epoxide ring. The initiation step in the polymerization reaction is thought to be that involving direct addition of the carbocation $(C_6H_5)_3C^+$ to the epoxide, as was suggested in the case of 1,2-butylene oxide [23]. This is in agreement with the initiation step proposed by Bacskai [1] during the aluminum alkyl-initiated polymerization of CHO, where the coordination of the aluminum alkyl with epoxide is followed by the rapid addition of monomer molecules to the complex.

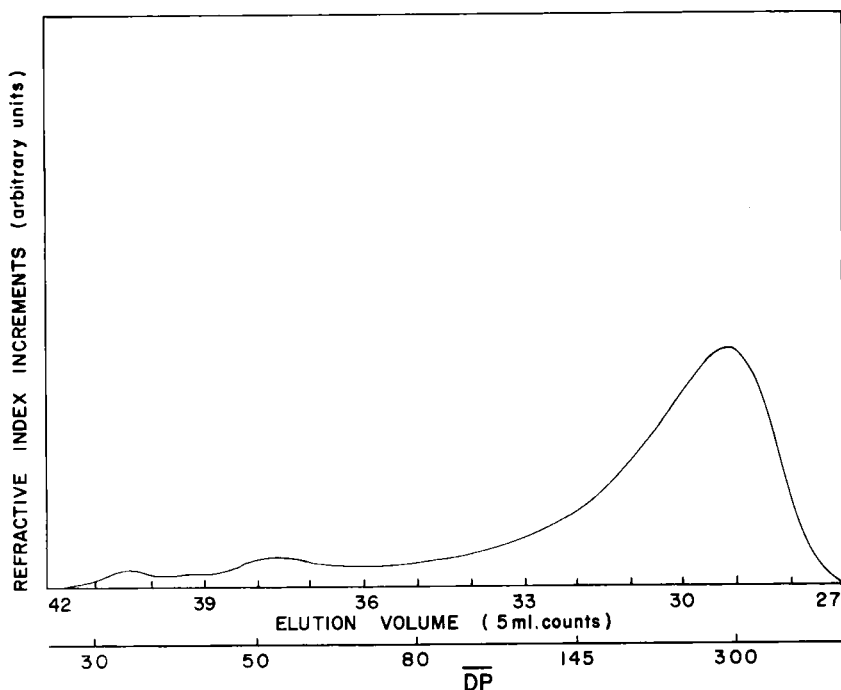


FIG. 3. GPC molecular weight distribution of poly(1,2-cyclohexene oxide) (PCHO-1).

In Fig. 3 is shown the GPC molecular weight distribution of PCHO-1. The plot of $\log \bar{M}_w$ (\bar{M}_w computed from the viscosity data of PCHO samples and the $[\eta]$ versus \bar{M} relation of Mele et al. [14]), versus elution volume V_e for poly(cyclohexene oxide) gave \bar{M}_w and \bar{M}_n values of 2.2×10^4 and 1.7×10^4 , respectively, for PCHO-1 ($[\eta] = 0.14$ dl/g). One notes that the GPC molecular weight distribution of PCHO-1 is very different from those of poly-exo-2,3-epoxy-norbornane [16], which contained high proportions of low molecular weight, presumably cyclic oligomers. This shows that the polymerization products in the present case are linear polyethers similar to those of Bacskai [1].

In Fig. 4 is shown an x-ray diffraction curve for PCHO-1. The absence of sharp peaks characteristic of a crystalline material suggest that PCHO-1 prepared with $(C_6H_5)_3C^+ AsF_6^-$ as initiator is amorphous. Alkylaluminum [1] as well as alkylaluminum-water

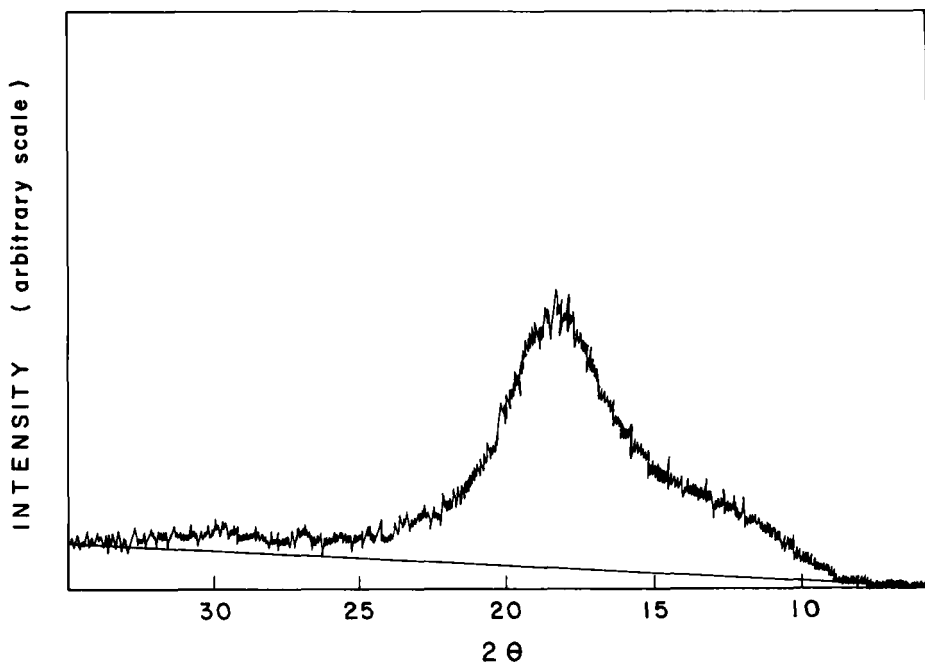


FIG. 4. X-ray diffraction pattern of poly(1,2-cyclohexene oxide) (PCHO-1).

[24] initiated polymerizations of 1,2-cyclohexene oxide also yield amorphous polymers.

In Fig. 5 are shown typical DSC-2 thermograms of unannealed PCHO-1 in the glass transition region at different heating rates. The thermograms are characterized by only one zone of glass transition where the base line changes in the endothermic direction. An exothermic peak due to crystallization was not observed which, once again, shows that PCHO-1 is amorphous. In the glass transition zone, T_g was evaluated at the half height of the observed ΔC_p , i. e., the change in the heat capacity at the glass transition [15], as shown in Fig. 5. The values of T_g at heating rates (q) of 40, 20, 10, 5, and $2.5^\circ\text{K}/\text{min}$ were 340, 339, 337, 335.5, and 334.5°K , respectively. The extrapolated value (T_{g_e}) at $q = 1^\circ\text{K}/\text{min}$ by using the relation: $\log q = a - b/T_g$ [15] was found to be 332°K . This value is 10 to 15°K lower than those found for polyexo-2,3-epoxynorbornanes [16].

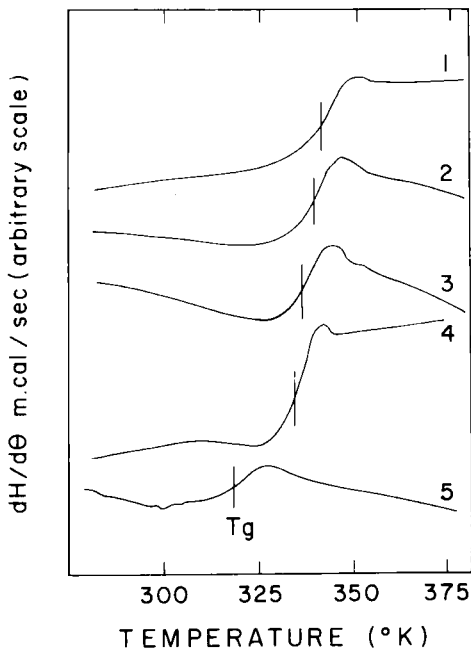


FIG. 5. Typical DSC-2 thermograms of unannealed poly(1,2-cyclohexene oxide) (PCHO-1) obtained in the glass transition region at various heating rates: (1) 40, (2) 20, (3) 10, (4) 5, and (5) 2.5°K/min.

In Fig. 6 is shown the NMR spectrum of PCHO-1 observed in CCl_4 at 75°C and in Fig. 7 is shown the NMR spectrum of PCHO-1 observed in *o*-dichlorobenzene at 115°C. These spectra are different from those of Bacskai [1] (recorded in CHCl_3) who observed a singlet at 6.54 τ for the methine protons and a broad peak at 8.48 τ for the methylene protons. The highlights of the spectra of PCHO-1 (skeletal structure II in Fig. 7) in the two solvents are listed in Table 1.

These assignments are based on the NMR spectrum of the monomer CHO as well as the proton assignments made in the case of poly(*exo*-2,3-epoxynorbornane)[16] whose meso pentads corresponding to methine protons were placed at a lower magnetic field (6.0 τ) as compared to the racemic pentads (6.76 τ). The three peaks (at 6.51, 6.59, and 6.67 τ in CCl_4) and (at 6.35, 6.43, and 6.49 τ in *o*-dichlorobenzene) attributed to mm, mr, and rr triads have intensity values of 0.15, 0.47, and 0.38, respectively. By making use of these intensity values, in combination with the equations [25],

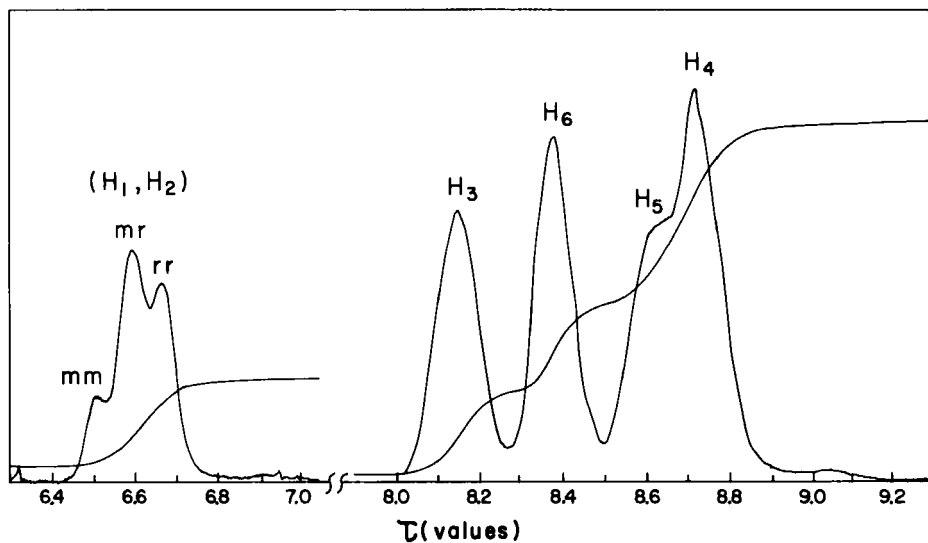


FIG. 6. 220 MHz NMR spectrum of poly(1,2-cyclohexene oxide) (PCHO-1) observed at 250 Hz sweep width expansion for the region 6.4 to 9.2 τ in CCl_4 at 75°C .

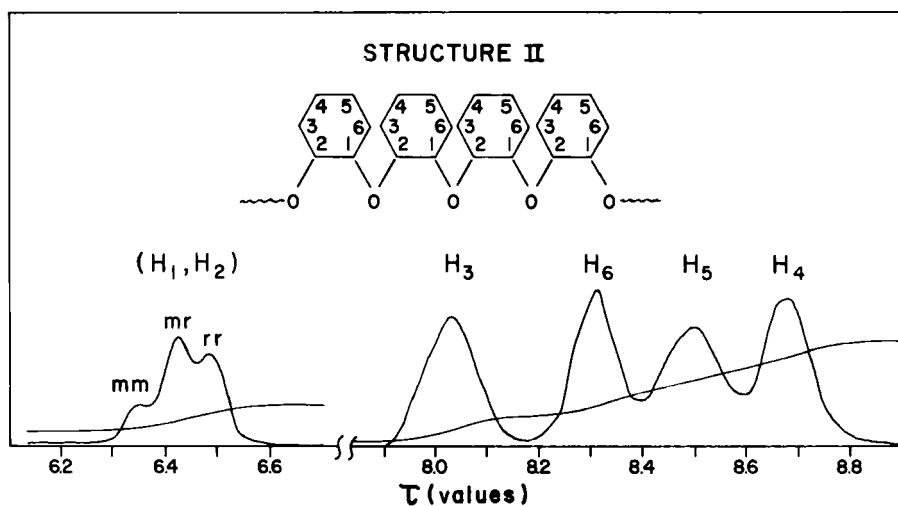


FIG. 7. 220 MHz NMR spectrum of poly(1,2-cyclohexene oxide) (PCHO-1) observed at 250 Hz sweep width expansion for the region 6.2 to 8.8 τ in *o*-dichlorobenzene at 115°C .

TABLE 1. Features of NMR Spectra of PCHO-1

Solvent	Protons	Peak position, τ
CCl ₄	Methine protons H ₁ , H ₂	6.4-6.8 (peaks at 6.51, 6.59 and 6.67 τ attributed to mm, mr and rr triads, respectively)
	Methylene protons H ₃	8.0-8.2; center at 8.15
	Methylene protons H ₆	8.2-8.5; center at 8.38
	Methylene protons H ₅	8.5-8.7; center at 8.60
	Methylene protons H ₄	8.7-8.9; center at 8.72
o-Dichlorobenzene	Methine protons H ₁ , H ₂	6.3-6.6 (peaks at 6.35, 6.43 and 6.49 τ attributed to mm, mr and rr triads, respectively)
	Methylene protons H ₃	7.9-8.15; center at 8.03
	Methylene protons H ₆	8.15-8.4; center at 8.31
	Methylene protons H ₅	8.4-8.6; center at 8.50
	Methylene protons H ₄	8.6-8.8; center at 8.68

$$mm = P_m^2$$

$$mr = 2P_m(1 - P_m)$$

$$rr = (1 - P_m)^2$$

a P_m value of 0.38 was calculated for the propagation statistics (Bernoullian) in the present study.

These studies show that the structure of poly(1,2-cyclohexene oxide) prepared with trityl salts is not stereoregular poly-trans as was found by Bacskai [1] in his alkylaluminum-initiated polymerization of CHO, but a mixture of cis and trans structures. Vandenberg [3] had indeed indicated that head-to-head and head-to-tail polymerization of CHO is possible, and the resulting polymers are amorphous.

CONCLUSIONS

The principal conclusions to be drawn from this study may be summed up as follows: (1) trityl salt-initiated polymerizations of CHO yield powdery, linear, amorphous polymers with T_g values of about 332°K; (2) the NMR spectra of these polymers show that the propagation reaction follows Bernoullian statistics with $P_m = 0.38$. The methylene protons H_3 , H_4 , H_5 and H_6 which appear at different τ values, depending upon their neighboring environment, are not equivalent.

Studies on other aspects of 1,2-cyclohexene oxide polymerizations are in progress and will be reported on at a later date.

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