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Cationic Polymerization of Exo-2,3-epoxynorbornane

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ABSTRACT

The homopolymerization of exo-2,3-epoxynorbornane and its copolymerization with tetrahydrofuran were carried out at different temperatures in dichloroethane with triphenylmethyl hexafluoroarsenate as the initiator. The reaction products were characterized by infrared and nuclear magnetic resonance (NMR) spectroscopy as well as by gel-permeation chromatography (GPC), viscometry, and differential scanning calorimetry. The products showed low viscosities and exhibited low glass transition temperatures. The GPC molecular weight distributions of the products prepared at different temperatures were multi-nodal, the proportions of the low molecular weight component being higher in reactions carried out at low temperatures. The NMR analyses of the products obtained at various temperatures suggest that the meso content in the polymer decreases as the temperature of reaction is increased.

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INTRODUCTION

The ionic polymerization of cyclic ethers has been the subject of numerous studies [1, 2] during the past two decades, and most of these have been centered on ethylene oxide, propylene oxide (PO), and tetrahydrofuran (THF), with the exception of some homologs of PO and a few five-membered or larger oxygen-carrying rings. The reaction products originating from these polymerizations are widely used in industry for the preparation of various synthetic materials, and their enormous industrial success is generally attributed to the characteristics of their ether linkages which in turn are responsible for their physical properties and chemical stability. The mechanism involved in the polymerization of these oxycyclic monomers and the stereochemistry of their reaction products have also raised continued interest because of their complex nature. This is why the studies on the polymerization of cyclic ethers have drawn so much interest from industrial as well as academic institutions. In this laboratory, the homopolymerization of propylene oxide [3] and butylene oxide [4-7] as well as the copolymerization of propylene oxide with tetrahydrofuran [8-12] have been studied extensively. With a view to discovering new and better materials, an attempt has been made to polymerize epoxides originating from bicyclic olefins, such as, bicyclo[2,2,1]-heptane (norbornane) which has been studied in detail [13] and which shows interesting results. In this work, preliminary studies on the cationic polymerization of *exo*-2,3-epoxynorbornane initiated with triphenylmethyl hexafluoroarsenate and the characterization of their reaction products by various physical methods have been carried out. This article describes the principal results obtained to date.

EXPERIMENTAL

Materials

The monomer, *exo*-2,3-epoxynorbornane (Aldrich Chemical Company, 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 $(C_6H_5)_3C^+AsF_6^-$ (Alfa chemicals), was dissolved in dichloromethane and the solution, filtered. The initiator was 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 the continuous circulation of dry nitrogen and the addition and removal of reactants. The reactors were placed in an alcohol bath maintained at the desired reaction temperature. The required weight of monomer and the desired volume of solvent were added to the reactor and the mixtures were vigorously stirred with a glass covered magnetic stirring bar especially during the period when initiator, in the form of 1,2-dichloroethane solutions, was being added. In this study the polymerizations were carried out at different temperatures with constant initial monomer and initiator concentrations. The reactions were terminated at preset times by the addition of methanolic ammonia, after which all volatile materials in the resulting solution were removed by evaporation under vacuum at 80°C until the residue maintained a constant weight.

Characterization of the Products

GPC Analyses

The distribution of molecular weights of the reaction products was determined with a Waters Associates model 200 gel-permeation chromatograph operated at $25 \pm 0.5^\circ\text{C}$. The separating system consisted of five 4-ft long columns connected in series and packed with cross-linked polystyrene gel having (by the Waters method) pore sizes of 1×10^5 , 2 to 5×10^3 , 1×10^3 , 250, and 60 Å, respectively. The flow of solvent, degassed tetrahydrofuran, was fixed at 1 ml/min while the concentration of the samples to be analyzed was limited to 1% to avoid possible column overloading and peak-shift problems. The instrument was calibrated with polystyrene, poly(oxyethylene glycols) and poly(oxypropylene glycols) of known molecular weights. Molecular weights were calculated as suggested in the Waters Associates manual [14].

Viscometry

An Ubbelohde viscometer was used to measure the flow time of the solvent (o-dichlorobenzene) at 25°C and of the polymer solutions.

From these data the intrinsic viscosity $[\eta]$ of a polymer was calculated by using the one-point method [15].

Infrared Spectroscopy

IR spectra of the polymers on KBr pellets and in carbon tetrachloride solutions were recorded with a Beckman-12 infrared spectrophotometer.

Nuclear Magnetic Resonance Spectroscopy

NMR spectra of the polymer solutions (15% w/v) in *o*-dichlorobenzene at 100°C and in carbon tetrachloride at 75°C were recorded with a Varian Associates 220 MHz spectrometer. TMS was used as the internal reference in all of the runs.

Differential Scanning Calorimetry

A Perkin-Elmer Model DSC-1B differential scanning calorimeter was used to measure glass transition temperatures. Unlike with polystyrene [16] where small quantities (1-3 mg) of polymer and low rates of heating (5-10°C/min) and cooling (1.25°C/min) yielded precise T_g values, larger quantities (15-20 mg) of polymer and higher rates of heating and cooling (40°C/min) were needed to obtain DSC diagrams yielding at best only approximate T_g values for the polymers.

RESULTS AND DISCUSSION

The polyexo-2,3-epoxynorbornanes prepared in the present study showed particular patterns in the IR spectrum which are not encountered in other polyepoxides. For instance, all of the polyexo-2,3-epoxynorbornane samples showed bands at 1735 cm^{-1} (attributed [17] to -CO stretching in esters) with overtones at 3460 cm^{-1} . These bands are not present in the IR spectra of poly(cyclohexene oxides) [18] and were seen only occasionally in the IR spectra of poly(1,2-butylene oxides) [7]. Furthermore, the NMR spectra of polyexo-2,3-epoxynorbornane showed an unusual distribution of its methylene protons. As data on the polymerization of exo-2,3-epoxynorbornane could not be found in the literature, it was impossible to make comparisons and to verify certain ambiguities. It was thought therefore that a qualitative analysis of the monomer itself should first be made to provide background information about its polymer.

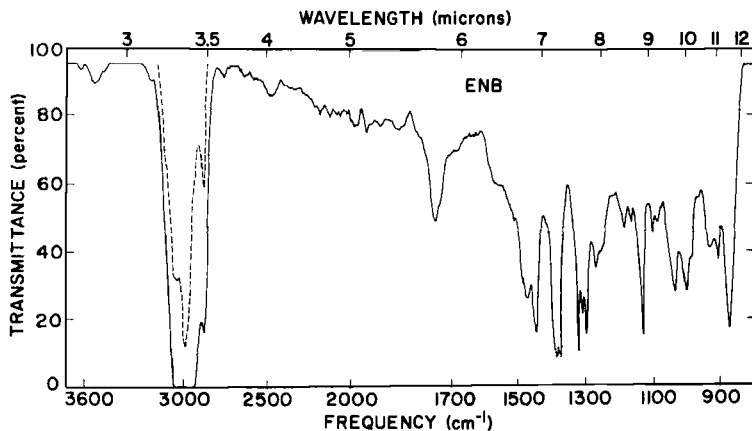
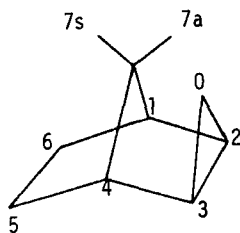


FIG. 1. IR spectrum of exo-2,3-epoxynorbornane in CCl_4 solution.

Some Characteristics of the Exo-2,3-epoxynorbornane Monomer

Exo-2,3-epoxynorbornane is a solid granular compound which gives the impression that it is highly hygroscopic. It is difficult to confirm this visual observation by IR spectroscopy by use of KBr pellet samples, as these are usually opaque or at best only partly transparent; however, its IR spectra when dissolved in CCl_4 (Fig. 1) shows clearly that there are no $-\text{OH}$ groups present in the monomer. The origin of the IR band at 1735 cm^{-1} in the polymer may now be established with more ease, since the monomer itself shows a strong band at 1740 cm^{-1} ; however, the overtones of this band at 3460 cm^{-1} were not seen in the solution spectrum (Fig. 1). The other bands in the IR spectrum of the monomer resemble those found in conventional ethers [17] and thus are not explored here.

An NMR study [19] on the assignment of the various protons in exo-2,3-epoxynorbornane (structure I) showed very interesting results. The spectrum published in the report was obtained with a 60 MHz instrument using 10% solutions in CDCl_3 at room temperature. The τ values listed for the various protons are shown in Table 1, along with new results obtained in this laboratory with a 220-MHz instrument. The same mode of presentation as that used by Tori et al. [19]



I

TABLE 1. NMR Parameters for Exo-2,3-epoxynorbornane

Position of the proton in the monomer (see structure I in text) ^a	τ values	
	Previous data [19]	Present data
H _{2a} , H _{3a}	6.84	7.14
H ₁ , H ₄	7.56	7.70
H _{7a}		8.611
H _{6a}		8.651
H _{5a}	8.65	8.668
H _{6s}		8.886
H _{5s}		8.930
H _{7s}	9.30	9.425

^a a denotes anti and s denotes syn protons.

was retained here: the protons denoted by subscript s are syn and those denoted by a are anti. A comparison of the new results (Fig. 2) with the earlier work [19] clearly shows that the τ values for practically all of the protons are different. This, however, is nothing unusual, since shifts in τ values for the same protons are often noticed on changing the solvent. But what is unusual in the present study is the much improved resolution of the spectrum for the protons

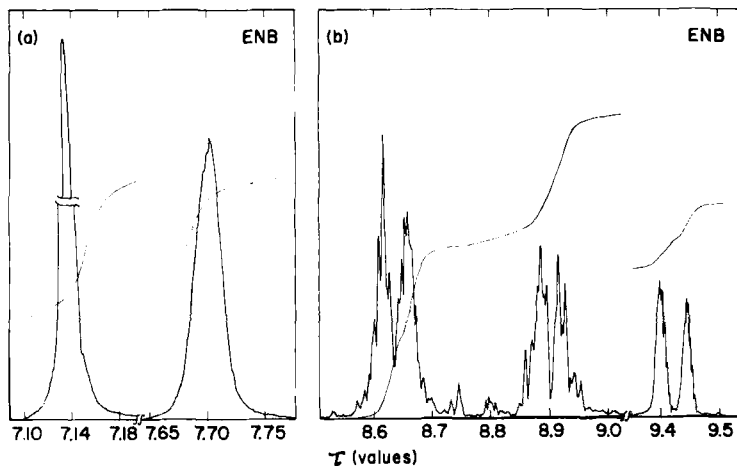


FIG. 2. 220 MHz NMR spectrum of exo-2,3-epoxynorbornane in *o*-dichlorobenzene solution at 100°C with TMS as internal standard. Zones (a) and (b) recorded at 250 MHz sweep width expansion; difference in scale due to different size reductions.

H_{7a} , H_{6a} , H_{5a} , H_{6s} and H_{5s} . One should note that these protons appear together centered around 8.65 τ with the 60 MHz apparatus while in the present study (involving a 220 MHz instrument) it is possible to assign unique values for each of the protons. The assignments given for the various protons listed in Table 1 are based on the assumption that the epoxide ring-current effect is the sole factor responsible for chemically equivalent protons appearing at different τ values. According to some workers [19-23], the epoxide ring generates a ring current which is responsible for shielding certain protons, e.g., the H_{7a} protons in exo-2,3-epoxynorbornane, resulting in a downfield shift of their signal in the NMR spectrum ($\tau = 8.611$) while H_{7s} protons which are not shielded appear as a doublet centered around a value of 9.425 τ . The present assignments could also be valid even if other effects were occurring, e.g., a 1,3-diaxial interaction between the protons and the oxygen atom which deshields the proton. This effect, however, has not been taken into consideration while making proton assignments in this work. The idea of a 1,3-diaxial interaction playing an important role in deshielding the protons

originates from the literature [20-23] and was put forward to explain the deshielding phenomenon in exo-2,3-epoxynorbornane in the work of Tori et al. [19].

Besides furnishing the above additional information, the prime reason for discussing the NMR spectrum of exo-2,3-epoxynorbornane is that the set of H_{7a} , H_{6a} , and H_{5a} protons along with another set (H_{6s} and H_{5s}) are sensitive to configurational changes in the polymer resulting in multiple peaks whereas the H_{7s} protons yield but a singlet which is in a lower magnetic field than that of the H_{7a} protons. It is believed that without this knowledge, the division of the polymer protons (originating from three methylene groups) appearing at τ values of 8.16 (H_{7s}), 8.25-8.8 (H_{7a} , H_{6a} , H_{5a}), and 8.8-9.2 (H_{6s} , H_{5s}) would not have been possible. Configurational analyses of polyexo-2,3-epoxynorbornanes will be discussed later in this text.

Characterization of Polyexo-2,3-epoxynorbornane

In Table 2 are presented some of the results obtained during the triphenylmethyl hexafluoroarsenate-initiated polymerization of exo-2,3-epoxynorbornane in dichloroethane. Polymerizations carried out between -30 and 0°C with initial monomer and initiator concentrations of 0.91 and 9.5×10^{-3} mole/liter, respectively, yield 100% conversion within 10 min. Reactions carried out at -60°C reached 71% conversion in about 15 min, whereas those carried out at higher temperatures (70°C) took still longer, attaining 80% conversion after some 30 min. In each case the final reaction products were characterized by low molecular weights as indicated by their low intrinsic viscosities (0.049 dl/g) determined in *o*-dichlorobenzene at 25°C.

In Fig. 3 are shown the normalized GPC molecular weight distributions of three polymers: PENB-6, PENB-4, and PENB-5 prepared at -60, -30, and 0°C, respectively, the other conditions being those indicated in Table 2. The distributions are very broad; dimers, trimers, and tetramers appear at elution counts situated between 38 and 42 while slightly higher molecular weight polymer shows a maximum elution count at 32.5 corresponding to a \overline{DP} of 20. The higher molecular weight portion of the polymer appears to have a most probable molecular weight distribution with its lower molecular weight region, situated between elution counts 36 and 38, being constantly chipped off by side reactions. The lowest molecular weight region (elution counts 36-42) shows a binodal distribution with peaks at elution counts of 39.5 and 41.0. Furthermore and contrary to

TABLE 2. Triphenylmethyl Hexafluoroarsenate-Initiated Polymerization of Exo-2,3-epoxynorbornane in Dichloroethane at Different Temperatures

	PENB-2	PENB-5	PENB-4	PENB-6	PENB-7
Reaction temp, (°C)	0	0	-30	-60	70
[Monomer] ₀ (mole/liter)	0.931	0.909	0.909	0.854	0.342
[Initiator] ₀ × 10 ³ (mole/liter)	9.51	9.51	9.51	9.51	9.51
Reaction time (min)	10	10	10	15	30
Conversion (%)	100	100	95	71.3	80.3
Intrinsic viscosity [η] (dl/g)	0.049	0.049	0.049	0.049	—
\bar{M}_n (Theoretical) × 10 ⁻²	108	96	91	64	29
\bar{M}_n (GPC) × 10 ⁻²	7.44	6.47	6.36	5.30	4.45
\bar{M}_w (GPC) × 10 ⁻²	15.20	12.90	14.09	14.05	7.16
$\overline{PD} (\bar{M}_w/\bar{M}_n)$	2.04	2.00	2.20	2.65	1.61
T _g (DSC Method) (°C)	≈80	72	72	—	—

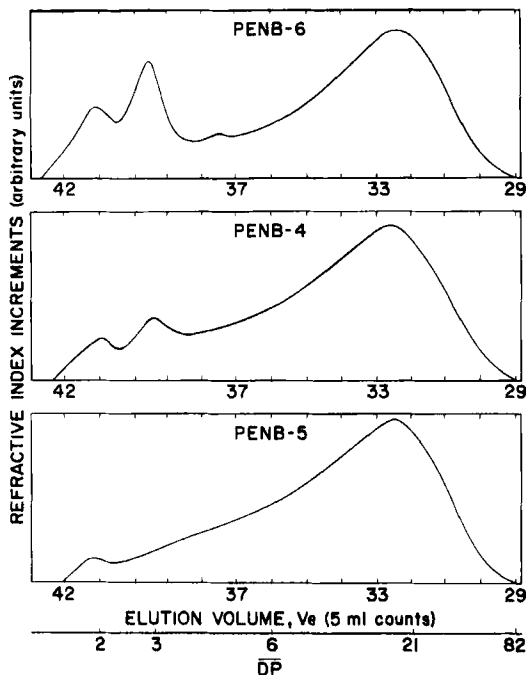


FIG. 3. Normalized GPC molecular weight distributions of PENB-6, PENB-4, PENB-5 (other data in Table 2).

expectations, the quantity of these lowest molecular weight oligomeric materials decreases as the temperature is increased from -60 to -30 and on to 0°C . Overall \bar{M}_n and \bar{M}_w values of the polymers were determined from their GPC curves and are compared with the calculated theoretical values assuming that all of the polymer chains carry but one molecule of initiator at the chain-ends when the reaction is quenched with methanol. The data presented in Table 2 show that there is considerable discrepancy between the \bar{M}_n (GPC) and \bar{M}_n (calculated) values, the latter being 6 to 15 times higher than the former. The situation resembles very much that encountered in the homopolymerization [3, 10-12] and copolymerization [4-9] of epoxides, where considerable differences appear between the calculated and experimental \bar{M}_n values. This has been explained by

invoking the presence of chain-transfer reactions which terminate the propagation at an early stage of the polymerization. These terminations can be expected to regenerate the initiator which in turn would initiate the formation of yet another chain. All of the polymer chains cannot therefore carry an initiator molecule when the reaction is terminated. For instance, in polymer PENB-2 with an initial initiator concentration of 9.5×10^{-3} mole/liter and an \bar{M}_n of 744, the maximum yield of polymer would be 0.064 base-mole/liter if all of the chains carried a molecule of initiator. A value of 9.31 base-mole/liter was obtained for this experiment, which is an excellent indication of the extent to which side reactions are important in these polymerizations. In spite of the side reactions, the polydispersity \bar{M}_w/\bar{M}_n varied regularly with the reaction temperature, decreasing from 2.65 to 2.0 (the most probable distribution) as the temperature was increased from -60 to 0°C .

Table 2 also lists the glass transition temperatures of a few polymer samples. These are rather low (72 - 80°C) due, it is thought, to the presence of the lower molecular weight products in the polymers. The T_g values reported should, however, be taken with some caution because, during a similar study of the glass transition temperature of polystyrene [16], it was found that with a polymer of broad molecular weight distribution the T_g value obtained by differential scanning calorimetry did not correspond to the overall \bar{M}_n of the polymer but rather to the \bar{M}_n of its lowest molecular weight component. In reality, the T_g values of polyexo-2,3-epoxynorbornane with overall \bar{M}_n values ranging between 440 and 744 would certainly be higher than those reported here if the oligomeric material could be excluded.

In Fig. 4 are shown the IR spectra of polymers PENB-6, PENB-4, and PENB-5. These show important peaks at wave numbers (cm^{-1}) of: 3400-3460 (ν as OH and ν as C-O), 2960 (ν as CH_2), 2870 (ν as CH) and 1735 (δ C-O-C also recorded with the monomer), 1650 (δ C=C), 1440-1455 doublet (δ CH_2), 1355 (δ CH_2 and δ CH_3 , the latter being inevitably in the form of end groups), 1000, 1090, 1140, and 1160 (C-O-C antisymmetrical stretching) and finally seven other bands at 880, 860, 840, 800, 760, 710, and 640 (δ CH out-of-plane). The bands at 3460 cm^{-1} and 3400 cm^{-1} are obviously split into a doublet in PENB-6 (-60°C), broad in PENB-4 (-30°C), and sharp, in PENB-5 (0°C) indicating some structural changes related to C-O and C-OH linkages. The other differences in the IR spectra of these polymers lie in the relative intensities of the bands between 640 and 880 cm^{-1} as shown more clearly in Fig. 5.

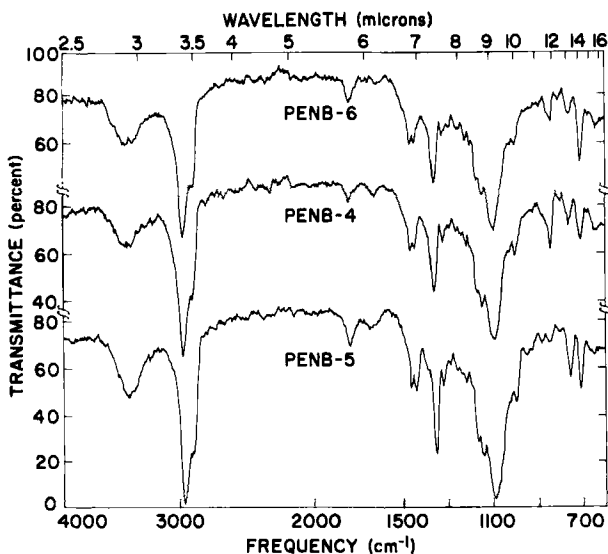


FIG. 4. IR spectra of PENB-6, PENB-4, and PENB-5 run on thin films of the products.

In Table 3 are summarized the normalized peak heights (the sums of the peak heights for the various bands are the same in all cases) in the IR spectra of the monomer and of the three polymers studied, viz., PENB-6, PENB-4, and PENB-5. A preliminary analysis of the data shows that all the IR bands found in the polymers are also found in the monomer, the only difference being in their intensities which in turn depend on the experimental conditions of the polymerizations. Furthermore, of the seven bands listed in Table 3 only four (viz., 710, 760, 840, and 880 cm^{-1}) show sufficient differences in their intensities to warrant a quantitative analyses, the other three (viz. 640, 800, and 860 cm^{-1}) showing but slight differences possibly originating from poor resolution in the IR spectra. The 840 and 860 cm^{-1} bands are nevertheless distinctly separated in the IR spectrum of the monomer, whereas, in the polymer, the latter is far from being well resolved, leaving but the former band for further consideration here.

Of the remaining three bands (viz. 710, 760, and 840 cm^{-1}) the first is very weak in the spectrum of the monomer but quite intense in that of the polymers. Kennedy and Makowski [24], during their studies on the polymerization of norbornane, attributed this band as

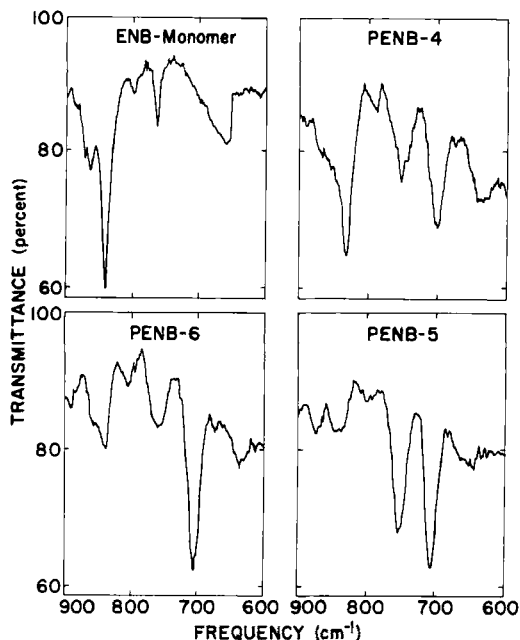


FIG. 5. IR spectra of exo-2,3-epoxynorbornane, PENB-6, PENB-4, and PENB-5 in the range 600-900 cm^{-1} .

well as that at 725 cm^{-1} to the presence of long saturated chains in the polymer. The assignment of the 710 cm^{-1} band directly to long saturated chains seems to be valid for the polymers in the present study as well because this band is intense in all of the polymer samples studied. The band at 760 cm^{-1} observed in the present study may also be attributed to long saturated chains but only indirectly. The presence of oligomers in PENB-6 reduces its intensity which, however, increases as the quantity of low molecular weight products decreases in PENB-5.

The band at 840 cm^{-1} which was attributed [24] to the multiple substitution of the ring may be assigned directly to short saturated chains in the polymer. The assignment is based on the combined results of the GPC molecular weight distributions of polymers PENB-6, PENB-4, and PENB-5 (Fig. 3) and the analyses of the intensity of the 840 cm^{-1} band in their IR spectra. As the oligomeric products decrease, the intensity of the 840 cm^{-1} band decreases,

TABLE 3. Normalized Heights at Different Wave Numbers in the IR Spectrum of Polyexo-2,3-epoxynorbornanes

Sample ^a	Normalized height						
	880 cm ⁻¹	860 cm ⁻¹	840 cm ⁻¹	800-810 cm ⁻¹	760 cm ⁻¹	710 cm ⁻¹	640 cm ⁻¹
ENB Monomer	0.9	3.7	8.7	0.9	2.9	0.8	2.0
PENB-6 (-60°C)	1.2	2.3	3.5	1.3	2.7	7.5	1.5
PENB-4 (-30°C)	1.6	2.8	6.0	1.0	3.1	3.9	1.5
PENB-5 (0°C)	1.5	0.8	1.7	0.8	6.6	7.2	1.2

^a See Table 1 for other data.

while the intensities of the 710 and 760 cm^{-1} bands increase. The 800 cm^{-1} band may be assigned to the presence of bicyclic structures in the linear chain as suggested by Kennedy and Makowski [24]; however, the assignment of the 640 and 880 cm^{-1} bands to vinyl olefins does not seem to be a valid one for the present study because these are also present in the spectrum of the monomer where there are no such structures. These could, however, be attributed to the presence of bicyclic structures in the reactants and the products.

In Fig. 6 are shown NMR spectra obtained with polymer PENB-5 dissolved (a) in carbon tetrachloride at 75°C (PENB-5a) and (b) in *o*-dichlorobenzene at 100°C (PENB-5b). The highlights of these spectra are summarized in Table 4. These are based exclusively on the NMR of the monomer, *exo*-2-3-epoxynorbornane, and on the use of the integrated areas under the various peaks. Mention must be made here that the assignments of chemical shifts to the various methylene protons can be verified by quantitative analyses of their tetrad configurations [25] but this will be discussed later. Qualitatively, one notes in Fig. 6 that the spectra of PENB-5 in carbon tetrachloride as well as in *o*-dichlorobenzene are very well resolved.

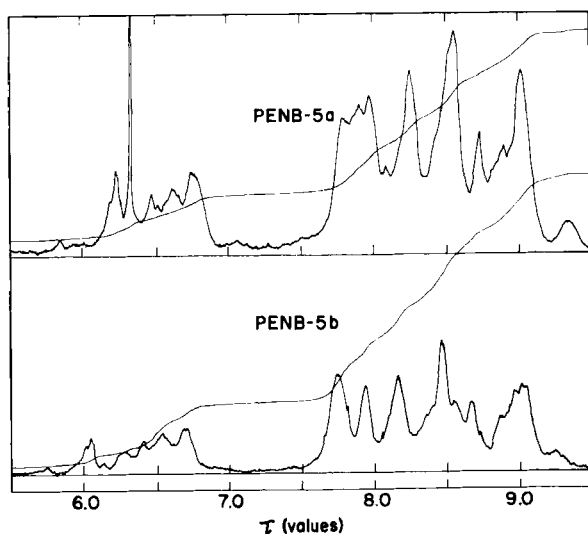


FIG. 6. 220 MHz NMR spectra of PENB-5 recorded at 1000 Hz sweep width expansion for the region $\tau = 5.5-9.5$: in CCl_4 at 75°C (PENB-5a) and in *o*-dichlorobenzene at 100°C (PENB-5b), with TMS as internal standard.

TABLE 4. Chemical Shifts for Polyexo-2,3-epoxynorbornane

Integral proportion of different protons	Nature and environment of proton	Complete zone in which appear the τ values of the protons	τ values of important peaks in different solvents	
			Carbon-tetrachloride	o-Di-chlorobenzene
2	Methine protons flanked by oxygen atoms (H_{2a}, H_{3a}) -CH-O-	5.7-7.1	5.84	5.73
			6.19	6.00
			6.24	6.05
			-	6.13
			6.34	6.27
2	Methine protons flanked by -CH and -CH ₂ (H_1, H_4)	7.3-8.1	7.80	7.74
			7.92	
			7.99	7.94
1	Methylene proton (H_{7s})	8.0-8.3	8.26	8.17
3	Methylene protons (H_{7a}, H_{6a}, H_{5a})	8.3-8.8	8.30, 8.36	8.57
			8.47, 8.57	8.74
			8.67, 8.74	
2	Methylene protons (H_{6s}, H_{5s})	8.8-9.5	8.85	8.87
			8.91	8.93
			9.03	8.98, 9.05
			9.35	9.25

The methine protons H_{2a} and H_{3a} ($\tau = 5.7-7.1$) yield numerous peaks in both solvents which can be assigned to various pentads. The methine protons H_1 and H_4 ($\tau = 7.3-8.1$), however, yield two peaks in o-dichlorobenzene which in carbon tetrachloride are split into three. The methylene protons are better resolved in o-dichlorobenzene, where the H_{7a} , H_{6a} and H_{5a} ($\tau = 8.3-8.8$) and H_{6s} and H_{5s} ($\tau = 8.8-9.5$) protons yield various peaks corresponding to different tetrad configurations.

In Figs. 7 and 8 are shown the expanded NMR spectra ($\tau = 5.6-7.0$ and $\tau = 7.5-9.3$) of polyexo-2,3-epoxynorbornane (PENB-2A, $\bar{M}_w = 1.7 \times 10^3$, $\bar{M}_n = 1.1 \times 10^3$; other data in Table 2) obtained after repeated precipitations of the polymer with methanol which washed away the low molecular weight products from the sample. The spectra were run with a sweep width expansion of 500 Hz instead of 1000 Hz as in PENB-5 to obtain more precise results and with the solutions at 100°C (PENB-2A-a) and at 20°C (PENB-2A-b) to check the effect of temperature on the resolution. Generally, resolution is markedly improved when higher temperatures are used; however, in the present case, the resolution at 20°C was as good as that at 100°C , if not better.

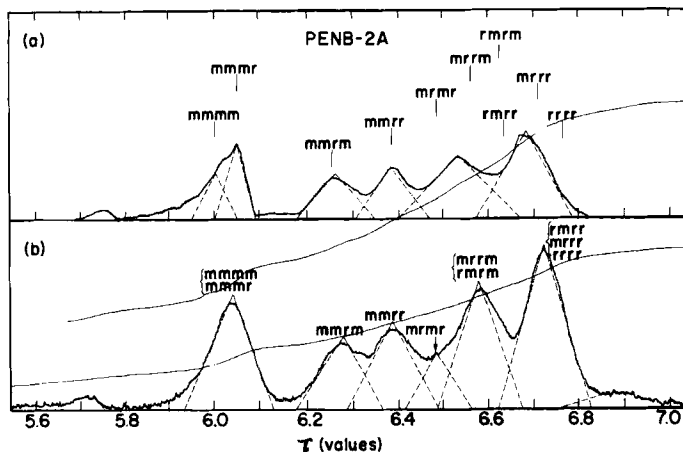


FIG. 7. 220 MHz NMR spectra of PENB-2A recorded at 500 Hz sweep width expansion for the region $\tau = 5.6-7.0$, in o-dichlorobenzene at 100°C (PENB-2A-a) and 20°C (PENB-2A-b) with TMS as internal standard.

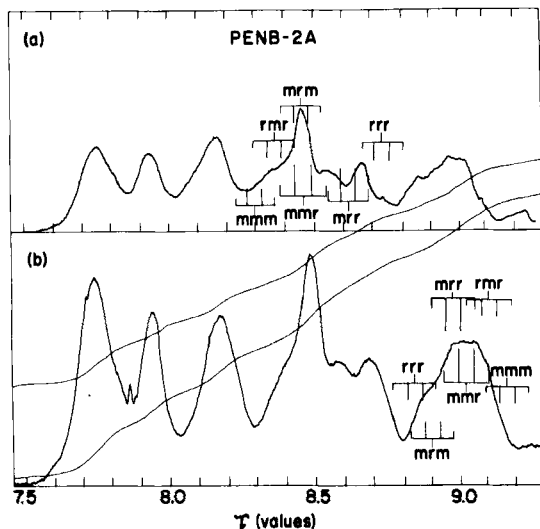


FIG. 8. 220 MHz NMR spectra of PENB-2A recorded at 500 Hz sweep width expansion for the region $\tau = 7.5-9.5$ in *o*-dichlorobenzene at 100°C (PENB-2A-a) and 20°C (PENB-2A-b) with TMS as internal standard.

Before making quantitative analyses on these spectra, the assignment of various chemical shifts to different types of protons must be justified. In the case of the methine protons H_{2a} and H_{3a} ($\tau = 5.6-7.0$), this assignment is not difficult to make; however, such is not the case for the methylene protons. Earlier in the text, the possible assignment of chemical shifts for methylene protons was made exclusively on the basis of the NMR spectrum of the monomer. It was felt that, because the three sets of protons, viz., (H_{7a} , H_{6a} and H_{5a}), (H_{6s} and H_{5s}), and (H_{7s}), appear separately at τ values of 8.65, 8.90, and 9.42 in the spectrum of the monomer with integral proportions of 3:2:1, these might well do so also in the polymer. Indeed, it was observed that the NMR spectrum of the polymer showed the six methylene protons split in the same proportions lending support to the assignments listed in Table 4. It is unlikely, however, that this may be but pure coincidence since other arrangements of the six methylene protons in the polymer may exist which would yield a similar distribution.

The principal reasons for the appearance of a lone hydrogen (H_{7s}) at a τ value of 9.425 in the monomer stem from an epoxide ring-current shielding effect [19] and a 1,3 diaxial interaction [20-22] leading to deshielding of the protons. In the polymer there should be no ring current effects as the epoxide rings no longer exist though there could still be some deshielding and shielding effects due to the presence of the oxygen atoms in the polymer chains. This is evident from the change of the chemical shift for H_{2a} and H_{3a} protons,

where τ goes from a value of 7.14 in the monomer to 6.0-7.10 in the polymer. This is similar to what is known as the neopentyl effect [26, 27] in neopentyl methyl ethers and neopentyl dimethyl amines, where the neopentyl methylene hydrogens in certain preferred conformations are affected by the lone pairs on oxygen and nitrogen, thereby causing downfield or upfield shifting of the protons in the NMR spectra.

Keeping in mind that ring-current effects are nonexistent in the polymer but that certain effects of the neopentyl type may be present, a possible assignment for the other methylene protons could be as follows: H_{7a} and H_{7s} protons would fall between $\tau = 8.8$ and 9.5 and the remaining four, i.e., H_{6s} , H_{6a} , H_{5s} , and H_{5a} , would fall between $\tau = 8.0$ and 8.8, with one of the four protons ($\tau = 8.16$) being insensitive to stereochemical configurations. It is difficult to say which of these assignments in the polymer (the ones based on those of its monomer or the others explained above) is rigorously true. An analysis of the peaks between $\tau = 8.3$ and 9.5 in terms of tetrads was therefore carried out separately for the regions $\tau = 8.3-8.8$ and $\tau = 8.8-9.5$.

In Table 5 are listed the calculated relative pentad intensities for Bernoullian propagations with P_m values of 0.50, 0.55, and 0.60, respectively. Also shown are the experimental relative pentad intensities as calculated from the areas under the peaks observed at different τ values. If the following ten pentads: mmmm, mmmr, mmmr, mmrr, mrrm, mrrm, rrrm, rrrr, mrrr, and rrrr are assigned to different chemical shifts in an increasing order of the magnetic field strength, the best fit between the theoretical and experimental pentad intensities is observed for a P_m value of 0.5.

Using this value, the relative intensities of the following six tetrads: mmm, mmr, rmr, mrm, mrr, and rrr were calculated (see Table 5) and, based on these values and on the fact that the peak intensities of the quartets which are solely responsible for the tetrad structure are in the proportions 1:3:3:1, a theoretical tetrad structure was created to match the experimental one. It was remarked

TABLE 5. Model Testing for Polyexo-2,3-epoxynorbornane (PENB-2a) from Pentad and Tetrad Information

Pentad	Calculated pentad intensity in Bernoullian propagation for different P_m values		Experimental pentad intensity at various chemical shifts		Calculated tetrad intensity for $P_m = 0.5$		Assignment of various chemical shifts to tetrads on the basis of their calculated values			
	$P_m = 0.50$	$P_m = 0.55$	$P_m = 0.60$	$P_m = 0.60$	τ value	Intensity		Tetrad	Intensity	τ value
mmmm	0.062	0.091	0.130	0.069	6.00	0.069	mmm	0.125	8.32	mmm
mmmr	0.125	0.150	0.173	0.113	6.06	0.113	mmr	0.250	8.38	rmr
mmrm	0.125	0.150	0.173	0.125	6.26	0.125	rnr	0.125	8.47	mmr
mmrr	0.125	0.122	0.115	0.142	6.40	0.142	mrr	0.250	8.64	mrn
mrmr	0.062	0.061	0.058	0.066	6.49	0.066				mrr
mrrm	0.062	0.061	0.058	0.184	6.56	0.184	mrn	0.125	8.72	rrr
rrmr	0.125	0.122	0.115		6.62		rrr	0.125		rrr
rrrr	0.125	0.100	0.077		6.64				8.81	rrr
mrrr	0.125	0.100	0.077	0.301	6.71	0.301			8.86	mrn
rrrr	0.062	0.041	0.026		6.76				8.91	mrr
									8.97	mmr
									9.03	rmr
									9.08	mmm

that if the six quartets corresponding to the following tetrads mmm, rmr, mmr + mrm, mrr, and rrr were centered at 8.32, 8.38, 8.47, 8.64, and 8.72 τ , the resulting cumulative tetrad structure would match that of the anti methylene protons between 8.3 and 8.8 τ . Furthermore, for the syn methylene protons appearing between 8.8 and 9.5, the arrangement of the six quartets required to reconstruct the experimental tetrad structure was found to be rrr, mrm, mrr, mmm, rmr, mmm centered at 8.81, 8.86, 8.91, 8.97, 9.03, and 9.08 τ . The assignment of tetrads for the region $\tau = 8.8-9.5$ has been made, keeping in mind the patterns followed by the anti and syn protons of β -methylenes [25]. The geminal coupling constant J for the anti and syn methylene protons as calculated from the spacings of the quartet is 11 Hz.

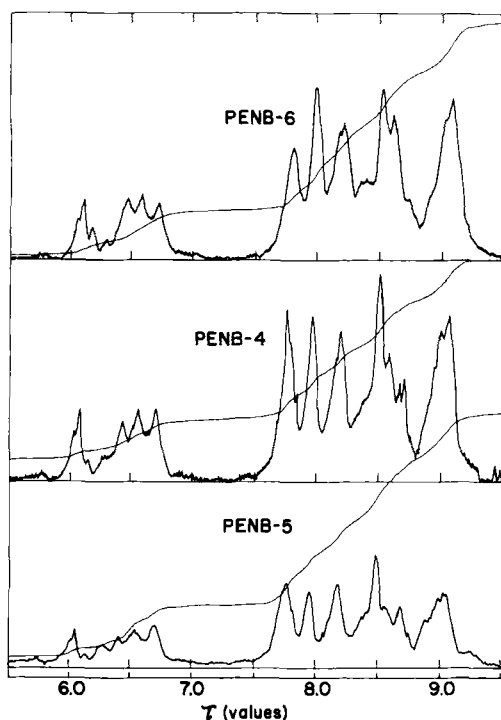


FIG. 9. 220 MHz NMR spectra of PENB-6, PENB-4, and PENB-5 recorded at 1000 Hz sweep width expansion for the region $\tau = 5.5-9.5$ in *o*-dichlorobenzene at 100°C with TMS as internal standard.

TABLE 6. NMR Analyses of Polyexo-2,3-epoxynorbornane Samples Prepared at Different Temperatures

Nature of proton	Chemical shift τ values	Assignment of chemical shift	Relative intensity (%)		
			PENB-6 (-60°C)	PENB-4 (-30°C)	PENB-5 (0°C)
-OH	5.73	-	0.32	0.33	0.25
Methine	6.00	mmmm	1.21	1.57	1.05
protons	6.05	mmmr	1.75	1.73	1.49
H _{2a} , H _{3a}	6.13	mmrm	1.15	0.66	0.37
	6.24		0.89	1.24	1.99
	6.39	mmrr	3.89	3.96	2.79
	6.53	mmr + mrrm + rmmr	4.28	4.68	3.91
	6.67	rmr + mrr + rrr	3.70	4.42	5.52
Methine protons	7.74	racemic	8.07	11.51	13.22
H ₁ , H ₄	7.94	meso	11.33	9.42	7.57
Methylene proton H _{7s}	8.16	-	14.10	11.90	12.29
Methylene protons	8.30	mmmm	2.55	2.55	1.86
H _{7a} , H _{6a}	8.36	mmm + mrr	3.35	4.41	4.65
	8.47	rmr + mmr + mrm	10.05	10.07	11.11

H _{5a}	8.57	mrm + mrr	7.91	6.30	6.14
	8.63	mrr + rrr	2.39	3.73	5.21
	8.74	rrr	1.53	1.63	1.68
Methylene protons H _{6s} , H _{5s}	8.85	rrr + mrm	3.13	2.16	4.22
	8.91	mrm + mrr	3.41	4.22	3.72
	8.97	mrr + mnr	4.98	6.41	4.65
	9.03	mnr + rnr + mmm	9.99	8.11	6.27

In Fig. 9 are shown the NMR spectra of polymers PENB-6, PENB-4, and PENB-5 prepared at different temperatures. From the spectra, the relative intensities for each of the peaks were calculated, and the data are presented in Table 6. The proportions associated with the various peaks are different depending upon the experimental conditions. The changes could originate either from composition changes in the polymer as was observed in the GPC molecular weight distribution curves of the polymers (see Fig. 3) or from changes in the configuration of the polymer due to the different polymerization temperatures used. It is thought that a study of the changes, in terms of configurational differences, should provide a more general picture of the situation. The assignment of chemical shifts in terms of pentads as listed in Table 6 has its origin in the analyses of the PENB-2A polymer which does not contain oligomers. Thus, any additional peaks present in the spectrum of polymers PENB-6, PENB-4, and PENB-5 may be attributed directly to the presence of oligomeric materials. For example, as the proportion of oligomers decreases on increasing the temperature of the reaction (from -60°C for PENB-6 to 0°C for PENB-5), the relative intensity of the peak at $\tau = 6.13$ decreases, while that of the peak at $\tau = 6.24$ increases. In the absence of oligomers (PENB-2A) the $\tau = 6.13$ peak is totally absent, whereas the peak at $\tau = 6.24$ is very intense. This would mean that the pentad mrrm originating from the methine hydrogens of the oligomers appears at $\tau = 6.13$, whereas the same pentad appears at τ value of 6.24 when its origin lies in the higher molecular weight component of the product. Other significant trends in the relative intensities of the various peaks are noticed at $\tau = 6.67, 7.74, 7.94, 8.63,$ and 9.03 , although certain other peaks also show minor changes.

The overall picture describing the significant changes in the proportions of the various peaks with increasing temperature (from -60°C to 0°C) may best be projected as follows: (a) The sum of the pentads rrrr, mrrr and rrrr appearing at $\tau = 6.67$ increases. (b) The proportion of the meso methine protons H_1 and H_4 ($\tau = 7.94$) decreases, while that of the racemic methines ($\tau = 7.74$) increases. (c) The relative intensity of the methylene tetrads mrr and rrr appearing at $\tau = 8.63$ increases. (d) The sum of the methylene tetrads mrr, rrr, and mmm appearing at $\tau = 9.03$ decreases.

All of these observations show that, on changing the polymerization temperature from -60°C (PENB-6) to 0°C (PENB-5), the meso character of the polymer decreases. This consistency in results may be used as indirect support for the assignment (mmmm to rrrr pentads with increasing field strength) of methine protons ($\tau = 6.0\text{--}7.0$) which for a P_m of 0.5 could have been assigned as well in a reverse manner (rrrr to mmmm with increasing field strength).

Copolymerization with Tetrahydrofuran

The homopolymerization of tetrahydrofuran initiated with tri-phenylmethyl salts has been reported in the literature [28-30], and generally the products have been shown to have high molecular weights. With the idea of incorporating the characteristics of poly-THF with those of polyexo-2,3-epoxynorbornane and also with a view to elevating the molecular weights of the products, it was thought of interest to carry out an experiment whereby a 1:1 mixture of tetrahydrofuran and exo-2,3-epoxynorbornane would be copolymerized. Thus, 2.16 g of exo-2,3-epoxynorbornane were mixed with 1.90 g of THF in 20 ml of dichloroethane at 0°C while the initial initiator concentration was set at 9.51×10^{-3} mole/liter. The reaction was quenched with methanol after 10 min. The choice of reaction time was based on the experiments carried out earlier on the homopolymerization of exo-2,3-epoxynorbornane where 100% conversions were obtained within 10 min. In this particular experiment, only 1.02 g (25%) of poly(ENB-THF) was recovered, and the product, a viscous liquid, resembled poly-THF more than granular polyexo-2,3-epoxynorbornane. The products were characterized by GPC, IR, and NMR analyses.

In Fig. 10 is shown the GPC molecular weight distribution of the reaction products. The highlight of this distribution is the intense low molecular weight peak situated between elution counts 39 and 40.

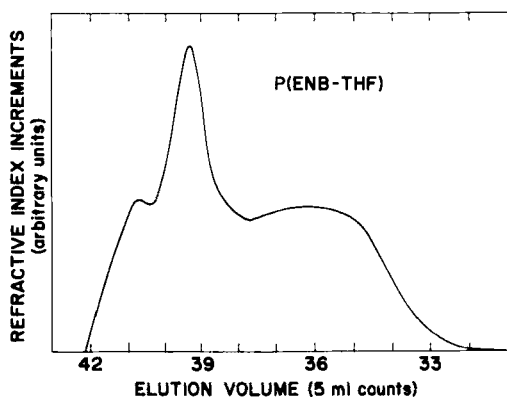


FIG. 10. GPC molecular weight distribution of the products obtained from a 1:1 molar mixture of ENB and THF in dichloroethane at 0°C with 9.51×10^{-3} mole/liter of initiator after 10 min.

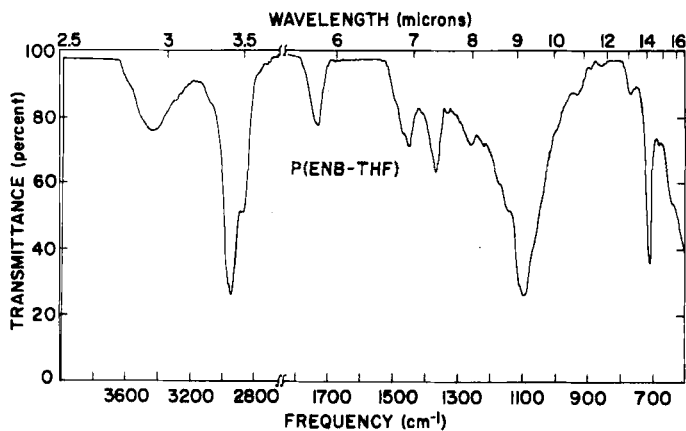


FIG. 11. IR spectrum of the poly(ENB-THF) products recorded directly from a thin film.

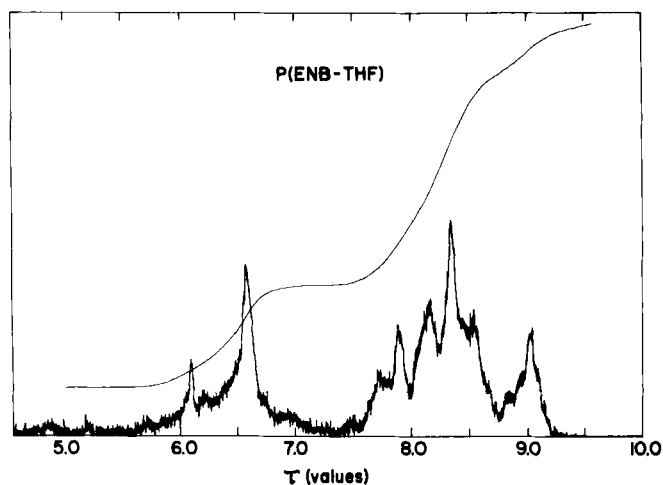


FIG. 12. 220 MHz NMR spectrum of the poly(ENB-THF) products recorded at 2500 Hz sweep width expansion in *o*-dichlorobenzene at 100°C with TMS as internal standard.

The remainder of the distribution resembles that of exo-2,3-epoxynorbornane homopolymer. A comparison of this distribution with those of the PENB-6, PENB-4, and PENB-5 samples suggests that the reaction product poly(ENB-THF) may be made up of two homopolymers instead of a single copolymer, the homopolymer of THF yielding strictly the tetramers appearing at elution count 39 which increases the intensity of this peak considerably. Making use of a GPC calibration curve prepared with samples of polypropylene and polyethylene glycols of known molecular weight, the values of \bar{M}_w and \bar{M}_n were calculated and found to be 4.03×10^2 and 3.10×10^2 , respectively.

In Fig. 11 is shown the infrared spectrum of the poly(ENB-THF) product. This spectrum resembles that of polyexo-2,3-epoxynorbornane, with the only exception that the presence of a THF moiety has enhanced the intensity of the 710 cm^{-1} band, whereas the bands at 760 , 840 , and 880 cm^{-1} which were prominent in the polyexo-2,3-epoxynorbornane spectrum are now of very low intensity. The 760 cm^{-1} band, which was attributed earlier to the presence of low molecular weight products has more or less the same intensity as that of PENB-6 which had a lot of low molecular weight products.

In Fig. 12 is shown the NMR spectrum of the poly(ENB-THF) product. The peaks at 6.6τ and 8.34τ are more prominent than those present in the PENB samples (see Fig. 9). The protons at $\tau = 6.6$ may be attributed to the methylenes flanked by oxygen atoms in poly-THF, whereas those appearing at 8.34τ are methylenes flanked by other methylene protons in poly-THF [30]. From the integral on the NMR spectrum in Fig. 12, the approximate ratio of ENB to THF in the products was found to be 2:1.

CONCLUSIONS

The main conclusions to be drawn from this study may be summarized as follows. Trityl salt-initiated homopolymerization of exo-2,3-epoxynorbornane and its copolymerization with THF yields products with low viscosities and low T_g values. The temperature of reaction in the homopolymerizations plays an important role in determining the distribution of molecular weights. It has been shown that increasing the temperature from -60 to 0°C reduces the proportion of low molecular weight products. An NMR analysis of the polymer suggests that on increasing the temperature the meso character in the polymer decreases.

Detailed studies on the homopolymerization and copolymerization involving exo-2,3-epoxynorbornane are in progress, and the results of these studies will be reported at a later date.

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