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Epoxide Oligomer Modified by N-Di(Tert-Butylperoxymethyl)Monoethanolamine

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EPOXIDE OLIGOMER MODIFIED BY N-DI(TERT-BUTYLPEROXYMETHYL)MONOETHANOLAMINE

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ABSTRACT

A new oligoperoxide (OPN), has been obtained by the condensation of an epoxide oligomer based on 4,4'-dihydroxy-2,2-diphenylpropane catalyzed by $[BF_3 \cdot (C_2H_5O]$ at 318 K in dry benzene. The structure of the OPN product was confirmed by IR spectroscopy and chemical analysis. Thermogravimetric analysis showed that the presence of nitrogen decreases the stability of the O-O-bond for the OPN relative to that in ordinary peroxide oligomers (OP). OPN may be used as a curing agent for polymeric compositions having unsaturated polymers (UP). The

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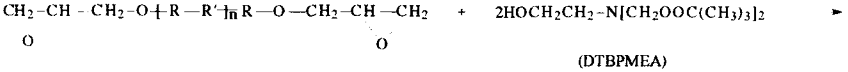
formation of a space polymer from 363 to 383 K occurs due to a polymerization process which is initiated by the decomposition of peroxy groups. In curing at higher temperatures (383 - 423 K) other functional groups of OPN also participate in polymerization reactions.

INTRODUCTION

Peroxide oligomers (OP) are the products of epoxide modification by organic hydroperoxides and peroxides. OP can be used as curing agents for unsaturated and saturated oligomers and as elastomers [1-3]. Space polymer formation may proceed from OP between 403 and 423 K through a radical mechanism due to the decomposition of O-O-groups.

In this report we describe results concerning peroxide oligomers which contain nitrogen (OPN). The interest in the exploration of OPN hinges on the observation that peroxy groups in these products possess a lesser thermostability than OP, i.e. OPN decomposition proceeds at lower temperatures relative to OP.

The OPN studied below are the products of the chemical modification of an epoxide, based on the reaction of 4,4′-dihydroxy-2,2-diphenylpropane with N-di(tert-butylperoxymethyl)monoethanol- amine (DTBPMEA). The primary hydroxy groups of DTBPMEA react with epoxy groups of the epoxide oligomer, catalyzed by $[BF_3 \cdot (C_2H_5)_2O]$, resulting in the OPN, and may be depicted as follows [4]:



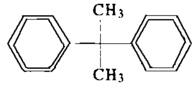
$$\underset{\;\;O}{CH_2-CH}-CH_2-O\!+\!R-R'\!+_{n}R-O-CH_2-\underset{O}{CH-CH_2} \;+\; 2HOCH_2CH_2-N[CH_2OOC(CH_3)_3]_2 \rightarrow$$

(DTBPMEA)

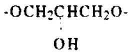
$$\longrightarrow [(CH_3)_3COOCH_2]_2N(CH_2)_2R'[-R-R']_n-R-R'-(CH_2)_2N[CH_2OOC(CH_3)_3]_2$$

(OPN)

where: R =



; R' =



$-OCH_2\underset{OH}{C}HCH_2O-$

In order to prevent the $[BF_3\cdot(C_2H_5)_2O]$ catalyzed homopolymerization of the epoxide the reagents have to be sequentially loaded in the reaction vessel. This provides a surplus of hydroxy groups in the reaction mass balance. The reaction occurs in dry benzene while heating.

MATERIALS

The epoxide oligomer was prepared by the condensation of 4,4'-dihydroxy-2,2-diphenylpropane with epichlorohydryn in the presence of non-aqueous sodium hydroxide [5]. The molecular weight M_η (determined by cryoscopy in dioxane) was 350 daltons. The percentage composition of epoxy groups (determined by addition of HCl) was 22.3%.

DTBPMEA was prepared from monoethanolamine and tert-butylperoximethanol; its characteristics are as follows: M_η (cryoscopy in dioxane) was 250 daltons: percentage composition of active oxygen (determined by iodometric analysis) was $O_{act.}$, 12.5%; N, 5.38%; Calcd for $C_{12}H_{27}NO_5$: M, 265.35; $O_{act.}$, 12.06%; N, 5.27%.

The complex $BF_3\cdot(C_2H_5)_2O)$ was purified by distillation under argon at 428 K. Benzene was dried by distillation from phosphorus pentoxide.

ANALYSIS

Proton NMR spectra were recorded on a TESLA BS-487-C 80 spectrometer in $CDCl_3$. IR spectra were recorded on a

SHIMADZU spectrophotometer. Polymer samples were dissolved in methylene chloride as films cast directly on NaCl plates. Thermal decomposition studies of OPN and its composition were carried out by the Differential Thermal Analysis method on a Q-1500-D derivatograph. The rate of heating was 0.083 deg/sec. A stirrer and dropping funnel reactor was employed for modification of the epoxide by DTBPMEA. A solution of 90.2 g (0.34 molar) DTBPMEA in 300 ml of anhydrous benzene was cooled to between 278 and 283 K. $[BF_3(C_2H_5)_2O]$ was then added in an amount sufficient for obtaining pH 4. The temperature was raised to 318 K and a solution of 50 g of epoxide in 200 ml of anhydrous benzene was then added dropwise. The reaction mixture was stirred at this temperature for 1 to 2 hrs and then neutralized with 5% aqueous NaOH. After washing with water to attain pH 7, the benzene was evaporated and the resultant residue was dried at 200 Pa and 318-333 K to constant mass. The OPN was obtained as a 122 g of a yellowish resin, for an 87% reaction yield. OP characteristics follow: M (cryoscopy in benzene), 650; $O_{act.}$, 3.6; N, 2.7. Calcd. for formula OPN: M, 870; $O_{act.}$, 3.6, N, 3.2. The structure of the OPN was confirmed by the methods of chemical and IR spectra analysis.

For the investigation of OPN structural properties an unsaturated polyester was used as a component of the composition. The unsaturated polyester was produced by polycondensation of ethylenglycol, propylenglycol, phthalic and maleic anhydride (M_η 1400, 40% content of carboxylic groups, as well as oligoesteracrilate (OEA) - α-methacriloyloxy-ω-methacriloyl-oligooxyethylene, having M_η 1290. For preparation of compositions the components were dissolved in acetone to give a solution with a concentration of approximately 60%. The amount of OPN in these compositions were: 10, 25, 50 and 75% by mass. The percentage composition of the gel-fraction was determinated by Soxhlet extraction with acetone for 18 hrs.

IR spectra were recorded after heating the compositions at 363, 383, 403 and 423 K for 1 hr, from 4000 to 700 cm^{-1}. The structural features of the OPN were assigned by the observed absorption bands as follows: 1385, 1365, 870 cm^{-1} due to a $(CH_3)_3C$- group, 870 cm^{-1} due to a $(CH_3)_3CO$- group, 1635 and 980 cm^{-1} due to a carbon-carbon double bond, 1740 and 1280 cm^{-1} due to the oscillation of the C(O)O- group in esters, 1720 cm^{-1} due to absorption by a C=O- group, and 3330 and 3445 cm^{-1} due to absorption by an HO- group.

RESULTS AND DISCUSSION

As seen by the IR spectra of OPN an absorption at 910 cm^{-1} was absent. Proton NMR of OPN lacked responses at 2.7 and 2.1 ppm. These observations suggest complete substitution of epoxy groups in the starting materials.

The presence of peroxy groups in the reaction product was confirmed by the presence of a faint IR absorbtion band at 870 cm^{-1} corresponding to a $(CH_3)_3C$- group, and two absorbtion bands at 1380 and 1360 cm^{-1} which are indicative of $(CH_3)_3C$- groups. From proton NMR spectra the $(CH_3)_3C$- groups were attributed to a peak at 1.2 ppm. The presence of OH- groups in OPN has yet to be proven by an absorbtion in IR spectra at 3400 cm^{-1} and by the peak at 4.7 ppm in H-NMR spectra.

The results of a thermal stability investigation on OPN are given in Table 1 showing that the decomposition of -O-O- groups of OPN starts at 348 K. The extent of decomposition increases as the temperature is increased to 403 K.

The investigation of curing properties of OPN for results (Table 2 and Table 3), showed that the gel-

Table 1. Thermostability of OPN

The temperature of the beginning of mass loss, K	The mass loss, (%) at temperature, K			
	363	383	403	423
348	0.5	1.3	3.8	6.4

Table 2. Percentage composition of gel-fraction in polymeric compositions,having UP and OPN.

The temperature of curing, K	Curing time, hrs.	Correlation of OPN and UP, mas.		
		10:90	25:75	50:50
383	0.5	2.5	3.4	30.0
	1.0	3.4	4.0	50.4
	1.5	7.2	8.2	59.8
	2.0	8.3	12.0	62.5
	2.5	13.8	25.1	67.1
393	0.5	15.0	16.2	37.6
	1.0	21.3	23.4	58.0
	1.5	26.2	28.7	67.5
	2.0	41.4	44.3	72.0
	2.5	45.0	50.6	75.2
403	0.5	21.4	23.0	45.4
	1.0	39.0	42.2	63.5
	1.5	57.3	60.0	74.1
	2.0	60.2	65.1	78.7
	2.5	64.3	70.8	82.3

Table 3. Percentage composition of gel-fraction in polymeric compositions, having OEA and OPN.

The temperature of curing, K	Curing time, hrs.	Correlation of OPN and UP, mas.		
		10:90	25:75	50:50
383	0.5	35.2	37.3	70.5
	1.0	60.5	64.6	82.6
	1.5	76.4	78.1	89.3
	2.0	84.2	87.9	95.7
	2.5	90.0	94.5	97.3
393	0.5	60.2	70.3	84.4
	1.0	87.0	90.5	93.7
	1.5	94.3	96.8	99.8
	2.0	96.6	98.8	99.8
	2.5	99.0	99.8	99.9
403	0.5	83.1	85.5	91.4
	1.0	91.3	94.6	97.7
	1.5	96.5	99.7	99.9
	2.0	99.0	99.8	99.9
	2.5	99.2	99.8	99.9

fraction formation depends on the temperature proportion of components in the composition, and the structure of OPN. If the composition contains 10-25% of OPN the gel-fraction portion does not exceed 50% from 383 to 393 K. The increasing temperature and percentage composition of OPN promotes the fraction of space-polymer. These results agree with data given in Table 1 which confirm that from

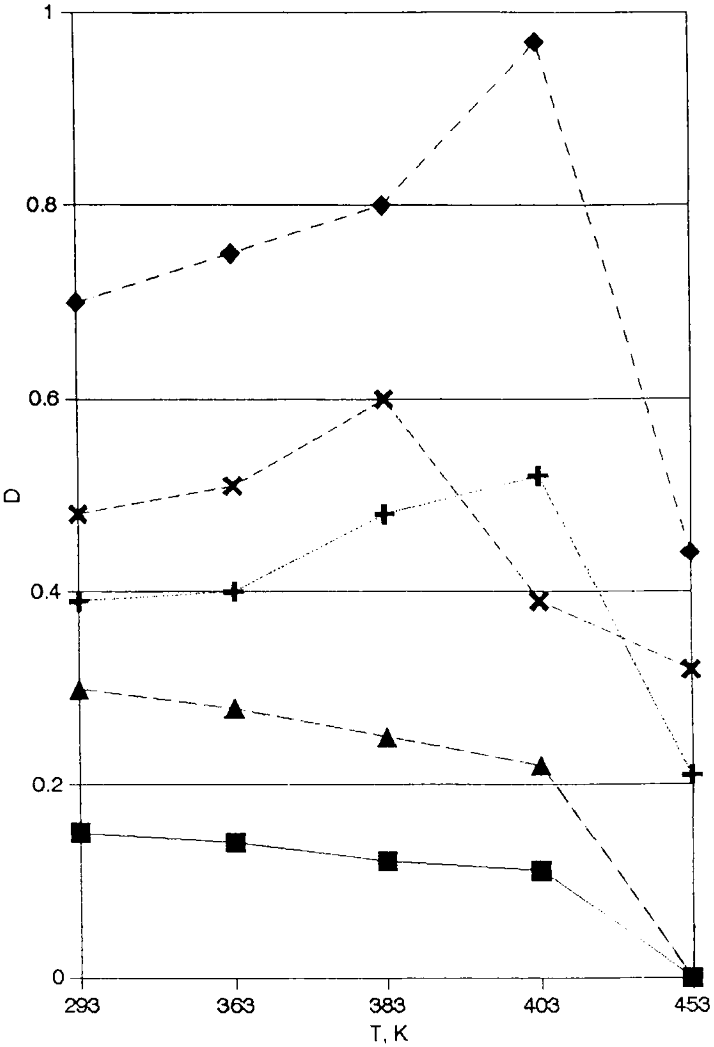


Fig. 1. Change of IR spectral bond density (D) with curing temperature of compositions: 1 - 1635 cm^{-1}; 2 - 980 cm^{-1} (C-C-double bonds); 3 - 1280 cm^{-1}; 4 - 1740 cm^{-1} (C(O)O- group) and 5 - the percentage composition of carboxylic groups. Compositions, having OPN and UP (1, 2, 3, 4), OPN and OEA (5), with correlation of components 50:50 % by mass.

383 to 393 K the decomposition of O-O- bonds as well as the polymerization process of UP occurs slowly. Comparisons of the data, given in Tables 2 and 3 shows that the reactivity of double bonds in OEA exceeds that for UP.

Further examination of the IR spectra reveals that the formation of space polymers is a result of reaction of O-O- bonds of OPN with C=C- bonds of UP. Thus, the occurrence of structuring from 363 to 403 K leads to decreasing IR absorbtion bonds at 1635 and 980 cm^{-1} which were assigned to C=C- carbon-carbon double bonds. Simultaneously, the intensity of absorbtion bonds due to -COOH (1720, 3300 cm^{-1}) and HO- (3445 cm^{-1}) increase. These observation indicate reactions between carboxylic and hydroxyl groups forming ester functionalities. But, increasing the temperature to 433 K leads to sharp decrease in the intensity of these bands (see Fig. 1), as a result of chemical reaction between these functionalities.

The data, shown in Fig. 1 suggest that curing of compositions at 403 and 423 K occurs not only because of a polymerization process but also as a result of reactions between the functional groups of components in the composition.

OEA differs from the UP in that it has double bonds only, so the curing process in this compositions occurs due to decomposition of -O-O- bounds and space polymerization of OEA molecules.

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