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Catalytic curing agents

Decomposition of trihalo and triisothiocyanato borane adducts with tertiary amines in curing epoxy resins: towards an understanding of the mechanism of polymerization

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Summary

Adducts of trichloro and triisothiocyanato borane with alkyldimethylamines are effective latent catalysts for epoxy homopolymerization. The lower stability triisothiocyanato borane adducts initiated the polymerization at lower temperatures than the chloro derivatives. In both cases the borane moiety was converted into $[B(OR)_4]^-$ by reaction with the oxirane ring initiating the reaction by the formation of cations. Free amine was detected in the curing resin but was not directly involved in the polymerization mechanism. The formation of oxazolidone rings was observed when triisothiocyanato borane adducts were used. The behaviour of some of the decomposition products of the adducts was also examined.

Introduction

Adducts formed by trifluoroborane with various Lewis bases, especially primary and secondary aliphatic or aromatic amines, are widely used as catalytic curing agents in the polymerization of oxirane monomers. Similar adducts formed by chloro, bromo and iodo boranes and the same amines are generally unstable and so do not lead to applications in polymerization. More interestingly trichloroborane adducts with the tertiary amines N,N-dimethyloctylamine (DMOA) and N,N-dimethylbenzylamine (DMBA) are latent catalysts of industrial interest for the polymerization of epoxy resins. It has been shown that bromo and iodoborane adducts with the same amines could be used with advantage for the same applications (1). The adduct of triisothiocyanato borane, $B(NCS)_3$, with DMBA was mentioned above as a latent catalyst of medium effectiveness. $B(NCS)_3$ adducts are now easily available for catalytic applications (2,3) because it has been recently shown that BCl_3 and BBr_3 adducts could be converted into their thiocyanato analogues by reaction with KNCS under catalytic phase transfer conditions.

When BF_3 adducts act as catalysts the polymerization proceeds through a cationic mechanism. The first step is the formation of BF_4^- caused by the presence of hydroxyl groups in the reaction medium (4-6). However, the properties of fluororoboranes are often different from those of other haloboranes. In this respect it is worth noting that boron trifluoride forms stable adducts with ethers, whereas various cyclic ethers, including ethylene and propene oxide are cleaved by boron trichloride to give chloro alkoxyboron esters (7). The chloroalkoxy-groups contain either the same number of carbon atoms as the ether or a small integral multiple of it showing that the polymerization of the esters takes place to some

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extent. The behaviour of the adducts of bromo and iodo boranes is probably similar to that of their chloro analogues. Due to the presence of unsaturated NCS groups, the isothiocyanato borane adducts would be expected to act differently if only in the way they decompose in the reaction medium. We have investigated their decomposition in the resin by means of MAS NMR techniques, and the behaviour of the chloroborane adducts has also been examined under the same conditions. In order to obtain more information on the mechanism of polymerization, some reactions have also been performed at the liquid state in phenyl glycidyl ether (PGE) used as a monofunctional model compound. DMOAHCl and $DMOAHBCl_4$ which may form by decomposition of the corresponding adduct were tested as curing agents. Tg and water retention measurements of the materials prepared using $DMOAB(NCS)_3$ as catalyst permitted a rough evaluation of their properties. Besides the Tg measurements, DSC was used to determine the enthalpies of polymerization and the reaction rate was followed by means of IR spectroscopy. Adducts of trichloroborane and triisothiocyanato borane with DMBA and N,N,N',N' tetramethyl 1,4 butane diamine (TMBDA) were prepared and studied. However, most of this work concerns DMOA adducts owing to their excellent solubility in the resin rendering them easy to use as catalytic curing agents.

Experimental

Materials and Methods

DGEBA DER 332, described as an exeptional high purity low molecular weight resin, was obtained from Dow Chemical, the epoxide equivalent weight was 172-176 g mol^{-1}. PGE was purchased from Aldrich. Standard inert atmosphere techniques were used for the syntheses of the adducts. The amines from Aldrich and the solvents were stored over 4 Å molecular sieve from Merck. BCl_3 (Quality N 25) purchased from Alphagaz was used for the synthesis of the adducts.

The IR spectra were obtained on a Nicolet 550 spectrometer. The NMR spectra of solutions were recorded on a Bruker AM 300 spectrometer at 96.28 MHz for ^{11}B with BF_3Et_2O as external reference (positive values downfield), and at 300 MHz for ^1H and 75 MHz for ^{13}C with TMS as reference in both cases. The ^{11}B spectra of the solid materials were also obtained on a MSL 300 spectrometer equipped with a M.A.S. probe head. The sample was placed into a zirconia rotor made spinning at 4 KHz. The DSC analyses were performed on a TA 3000 Mettler apparatus.

Synthesis of BCl_3 adducts

In a typical preparation gaseous BCl_3 (54 mmol) was slowly condensed in a 0.5 dm^3 reaction flask containing 0.2 dm^3 of an hexane solution of the amine (42 mmol) while the reaction mixture was vigorously stirred and maintained at -30 °C. DMBA and TMBDA formed solid adducts which were isolated by filtration, washed with hexane and cold water and dried in a vacuum. The product was then purified by recrystallization from a dichloromethane-hexane mixture yielding 40 mmol of product. The ^{11}B NMR spectra of the adducts dissolved in deuterated chloroform displayed a single peak (δ = 10.4 ppm) common to BCl_3 adducts with tertiary amines (3). The resonance peaks observed for $DMBABCl_3$ by ^1H NMR were δ $C\underline{H}_2$ = 4.53 ppm (singlet), δ $(NC\underline{H}_3)_2$ = 2.79 ppm (quartet) and for the aromatic protons δ $C\underline{H}$ = 7.5 ppm (multiplet).

$DMOABCl_3$ is liquid at room temperature, its purification was carried out on a chromatographic column filled with Florisil (MgO-SiO_2 in a 15/85 ratio) using toluene as solvent. The adduct was rapidly eluted whereas the elution of its ionic impurities required longer times. The ^1H NMR spectra displayed a multiplet at δ = 3.38 ppm due to the $C\underline{H}_2$ group bonded to nitrogen whereas the $NC\underline{H}_3$ groups gave rise to a quartet at δ = 2.90 ppm. The other $C\underline{H}_2$ peaks were located between δ = 0.8 ppm and δ = 1.8 ppm.

Synthesis of $B(NCS)_3$ adducts

Tetraglyme (5.3 cm^3) was added as phase transfer catalyst to a suspension of KNCS (96g) in a chlorobenzene solution (400 cm^3) of $DMBABCl_3$ (24 g), then the mixture was refluxed for 10 hours at 110 °C. The adduct $DMBAB(NCS)_3$ was obtained with a 80% yield and the main boron impurity was the anion $B(NCS)_4^-$. The purification of the adduct was carried out on a Florisil column as described above. The adducts with other amines were prepared according to the same procedure. The ^{11}B NMR spectra of the $B(NCS)_3$ adducts displayed a single peak at δ = -9 ppm. The resonance peaks observed by ^1H NMR for $DMBAB(NCS)_3$ dissolved in $CDCl_3$ were δ $C\underline{H}_2$ = 4.01 ppm (singlet), δ $(NC\underline{H}_3)_2$ = 2.54 ppm (quartet) and for the aromatic protons δ $C\underline{H}$ = 7.51 ppm (multiplet). The following ^1H data were obtained for $DMOAB(NCS)_3$ in $CDCl_3$: δ = 2.93 ppm (triplet) due to the $C\underline{H}_2$ bonded to nitrogen, δ = 2.65 ppm (quartet) assigned to the $NC\underline{H}_3$ groups. The other hydrogen atoms of the chain gave rise to peaks located between δ = 1.2 ppm and δ = 1.7 ppm.

Synthesis of DMOAHCl, DMOAHNCS and $DMOAHBCl_4$

DMOAHCl was obtained by reaction of DMOA (0.063 mol) with HCl (0.063 mol) in aqueous media. Water was distilled off and the product was extracted with a dichloromethane-pentane mixture. After distillation of the solvent, the product was dried in a vacuum at 6 °C for 3 h. The IR spectrum showed an absorption at 2710 cm^{-1} assigned to the NH^+ bond.

DMOAHNCS was prepared by reaction of NH_4SCN (0.039 mol) with DMOA (0.039 mol) at 110 °C, no solvent was used (8). The IR spectrum displayed a strong band at 2060 cm^{-1} due to the C=N bond and two bands of medium intensity at 2500 and 2700 cm^{-1}.

$DMOAHBCl_4$ was prepared by dropwise addition of excess BCl_3 (0.07 mol) to DMOAHCl (0.05 mol) at 0 °C. Excess BCl_3 was pumped off when the reaction was finished. BCl_4^- gave rise to a strong IR absorption at 690 cm^{-1} whereas the NH^+ absorption appeared as a medium intensity band at 2730 cm^{-1}.

Evaluation of the effectiveness of the adducts

In a preliminary step, DSC measurements on various DGEBA-Catalyst mixtures were coupled with Thermogravimetric analysis (TGA) in order to determine the temperature of decomposition of the resin. The decomposition under an argon atmosphere proved to be an exothermic reaction starting at 250 °C and producing a weight loss. The effectiveness of the catalyst was investigated by DSC on 10-15 mg samples between -50 °C and +250 °C with a heating rate of 10 $K.min^{-1}$ (Fig.1). The samples were cooled and heated again (heating rate : 7.5 $K.min^{-1}$) to determine the Tg value.

Kinetics

IR spectroscopy was used as the analytical technique for the study of the DGEBA-$DMOAB(NCS)_3$ system. One drop of reaction mixture was laid between two CsI plates and the whole was placed in a copper vessel maintained at constant temperature (in the 100 °C-140 °C temperature range) under a nitrogen atmosphere. The IR spectra were recorded after cooling the plates to room temperature. The absorbance of the epoxide at 915 cm^{-1} was monitored, taking the peak at 1510 cm^{-1} as internal reference (9). A mechanism whereby a constant number of activated epoxy sites was present during the reaction has been proposed for the polymerization of DGEBA with boron trifluoride-monoethylamine (6). The kinetic data were similarly interpreted in the present work. The polymerization reaction was found to be second order with respect to the epoxy (Fig. 2), $[M]$ and $[M]_o$ being the epoxy concentration at time t and 0 respectively

$$1/[M] - 1/[M]_o = K' t$$

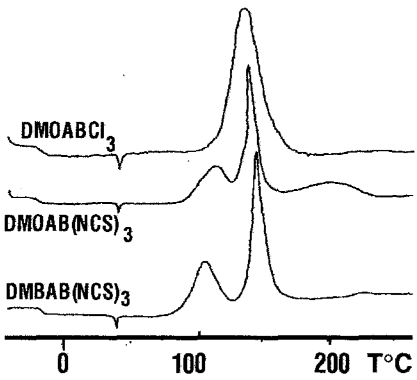


Figure 1 : DSC curves obtained with 5% molar $DMOABCl_3$, $DMOAB(NCS)_3$ and $DMBAB(NCS)_3$. Heating rate: 10 $K.min^{-1}$.

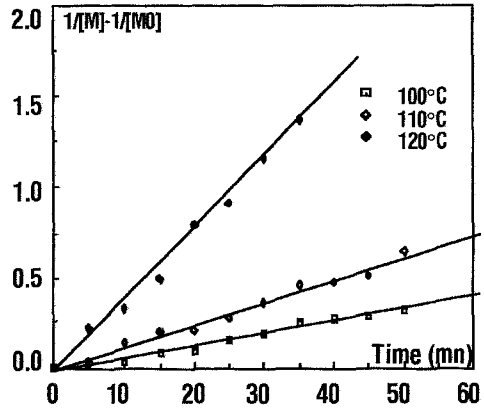


Figure 2 : Epoxide consumption versus time interpreted as a second order reaction. Samples containing 5 % $DMOAB(NCS)_3$.

The apparent constant K' was depending on $[A]_o$ the initial concentration of $DMOAB(NCS)_3$. In the relation $K' = K[A]_o^{\alpha}$, it was found $\alpha > 1$ but not constant because the model used was probably inadequate. An activation energy of 106.6 KJ/mol was calculated from the slope of the curves shown in Fig 2.

Results and discussion

The effectiveness of the adducts has been determined by DSC measurements, the curves shown in Fig.1 for $B(NCS)_3$ adducts display two exothermic peaks at temperatures lower than 160 °C whereas for $DMOABCl_3$ these two peaks are overlapping. IR and NMR analyses showed that a particular step of the reaction could not be assigned to each peak because for instance the adduct was still present in high concentration after the first exothermic transformation. A third exothermic peak of weak intensity was observed at higher temperature and could be attributed to some residual polymerization. It appears from the data reported in Table 1 that the reaction started at lower temperatures when the triisothiocyanato borane adducts were used instead of their trichloro analogues. The material with the highest Tg value has been obtained with samples containing $DMOAB(NCS)_3$ as curing agent. Slightly less favourable values have been observed for TMBDA adducts than for their DMOA analogues. Materials prepared using DMBA adducts exhibited relatively poor properties because the adducts were in the solid state at room temperature and so were difficult to incorporate into the resin. A concentration of 0.05 mol of $DMOAB(NCS)_3$ per epoxy function equivalent led to the highest Tg values and a gel time of only 9 mn at 120 °C. The same catalyst was used for the polymerization of epoxy pellets and when immersed in liquid water the pellets absorbed 4-5 weight percent that is an usual percentage for cured epoxy resins (10).

Curing Agent	Mol/ee	-ΔH(J/g)	Ti	Tm	Tf	Tg
$DMOAB(NCS)_3$	0.015	177	88	121-150	240	50
	0.025	399	90	122-145	245	75
	0.054	492	90	122-153	250	162
	0.07	586	91	123-159	250	120
	0.12	660	92	122-159	250	105
$DMOABCl_3$	0.015	264	100	167	220	37.2
	0.025	433	110	148	200	92.8
	0.054	502	120	156	180	97
	0.07	548	125	149	170	73.8
	0.12	536	128	147	170	60
$DMBAB(NCS)_3$	0.015	98	98	131	210	-8
	0.025	162	100	132	200	-2.4
	0.054	248	102	131	202	26
	0.07	389	101	131	201	26.4
	0.12	419	103	131	198	65
$DMBABCl_3$	0.015	45	80	110-150	160	-6.5
	0.025	90	81	108-149	172	21
	0.054	256	82	109-151	181	35
	0.07	304	83	111-156	182	85.4
	0.12	381	83	111-158	185	116
$TMBDABCl_3$	0.027	498	130	163	220	71
$TMBDAB(NCS)_3$	0.027	472	95	123-148-210	240	125
	0.04	496	94	128-154-185	240	118

Table 1. Behaviour of adducts in the cure of DGEBA.

Mol/ee is the [Catalyst]/[equivalent epoxide] molar ratio. Ti and Tf are the initial and final temperatures of the polymerization reaction. Tm is the temperature measured for the maximum of the exothermic peaks. -ΔH has been calculated from the areas of all the exothermic peaks observed during the polymerization reaction.

Analysis of the ^{11}B MAS NMR spectra of the curing resin in which DMOA adducts had been incorporated showed that the decomposition of trichloro, tribromo and triisocyanato borane adducts led to the formation of the $B(OR)_4^-$ anion giving rise to a single peak at $\delta = 2.80$ ppm. Spectra of DGEBA-$DMOAB(NCS)_3$ mixtures after heating at 100 °C are shown in Fig 3. The position of the $B(OR)_4^-$ peak does not indicate the nature of R which could be either the organic group formed by the borane attack of the monomer, or a hydrogen atom due to some hydrolysis or alcolysis. The former possibility is consistent with the fact that no OH absorption in the 3200-3600 cm^{-1} region could be observed on the IR spectra when a DGEBA-$DMOAB(NCS)_3$ mixture was maintained for 90 mn at 110 °C. Furthermore for a mixture containing $DMOAB(NCS)_3$ and PGE in a 1 to 3 ratio, 32% of the initial thiocyanatoborane was converted into $B(OR)_4^-$ after heating for 15 mn in perfectly dry conditions at 110 °C.

Such a conversion rate can only find its origin in a reaction of the adduct with the epoxy ring. During the polymerization reaction $B(OR)_3$ (or $B(OH)_3$) and $B(NCS)_4^-$ were present in low concentration together with $B(OR)_4^-$.

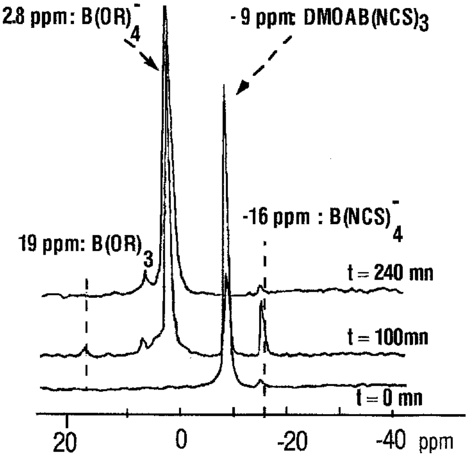


Figure 3 : MAS NMR spectra after different reaction times at 100 °C of solid samples of DGEBA cured in presence of 5.4 mol % $DMOAB(NCS)_3$.

Another important point concerns the behaviour of the amine associated with the halo or isothiocyanatoborane. Its conversion into free amine without any formation of the corresponding trialkylammonium cation was observed in all cases by ^1H NMR. The signals of the two $C\underline{H}_3$ groups bonded to nitrogen yielded significant information owing to the possibility of coupling with atoms coordinated to nitrogen. For instance for $DMOAB(NCS)_3$ dissolved in $CDCl_3$, because of a $^3J(^1H\ ^{11}B)$ coupling of 2.8 Hz a quartet was observed at $\delta = 2.65$ ppm.

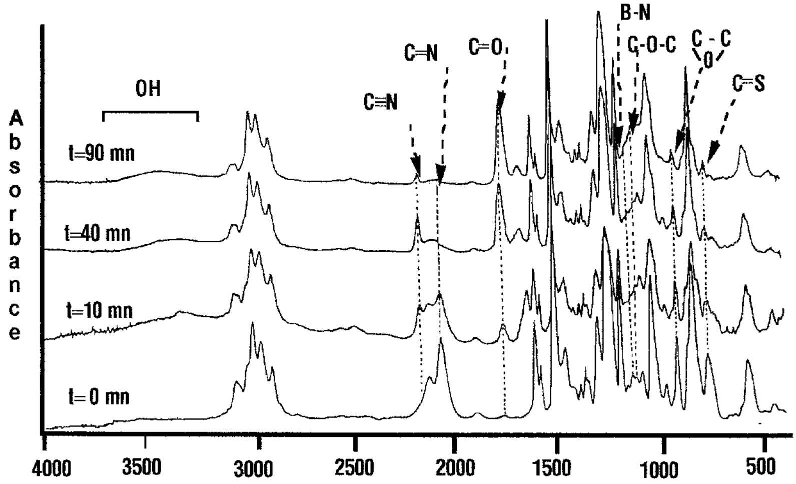


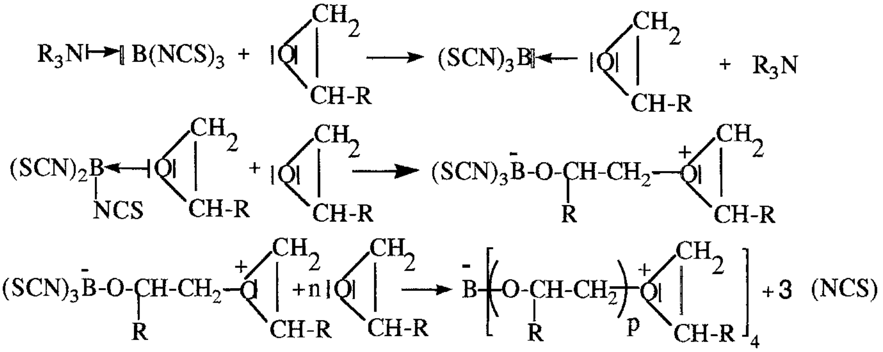
Figure 4 : IR spectra after different reaction times at 110 °C of DGEBA cured in presence of 5.4 mol % $DMOAB(NCS)_3$.

For the cation $DMOAH^+$ the same $C\underline{H}_3$ protons gave rise to a doublet in the same region ($^1H\,^1H$ coupling) whereas only a sharp singlet was observed for the free amine at 2.2 ppm. Turning now to $DMOAH^+$ it is worth noting that the proton coordinated to nitrogen gives rise to a broad resonance peak centred at 6 ppm which could also be easily detected by IR spectroscopy from the $N\text{-}H^+$ absorption band. The frequency of the NH^+ stretching vibration is 2710 cm^{-1} and is located in a region containing few other chemical group frequencies.

From the kinetic data and their interpretation involving a possibly simplistic model in which the concentration of activated species was supposed to be constant, it appears that the reaction proceeds differently when it is initiated by fluoro and thiocayanato adducts. The order of the reaction was one in the former case and two in the latter (Fig.2) but it seems difficult to obtain more information concerning the mechanism. The behaviour of some of the decomposition products of the adducts was also examined : DMOAHCl was inactive as a catalyst whereas DMOAHBCl$_4$ initiated the polymerization. In both cases the intensity of the IR band due to NH$^+$ decreased rapidly because the protons reacted with the monomer. Consequently the initiation of the reaction of polymerization was not due to the release of protons and the activity of DMOAHBCl$_4$ was attributed to the ability common to BCl$_4^-$ and the adducts of generating Lewis acids.

This interpretation takes account of the fact that the free amine which was released in the reaction medium proved to be nearly inactive as a catalyst of polymerization.

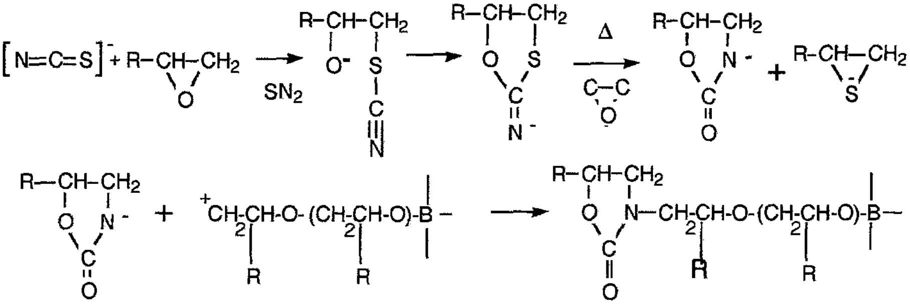
The mechanism in the case of the trichloro or triisothiocyanatoborane adducts could involve the following steps



This mechanism is comparable to those mostly proposed for curing of epoxy resin by means of BF$_3$ complexes in that an oxonium cation forms and the propagation proceeds by the monomer attack of the α-carbon of the cyclic oxonium ion. The main difference observed here is the formation of a B(OR)$_4^-$ anion due to the borane attack of the epoxy ring. The conversion of DMOAB(NCS)$_3$ or DMOABCl$_3$ into B(OR)$_4^-$ must involve the formation of intermediates containing B-N or B-Cl bonds together with B-O bonds. Such intermediates were not observed because they were too reactive towards the epoxy groups.

A particularity of B(NCS)$_3$ adducts is their ability to form SCN$^-$ anions by reaction with the epoxy groups or with hydroxy groups always present in low concentration in the resin. The characteristic IR bands of the NCS groups of DMOAB(NCS)$_3$ are mainly the ν C-N absorptions at 2107 and 2053 cm^{-1} and the ν C-S absorption at 765 cm^{-1}. The intensities of these bands decreased rapidly when the polymeriation reaction took place (Fig.4) showing that the NCS groups were subjected to strong modifications. New bands assigned to intermediates transciently appeared at 2148, 1638 and 1670 cm^{-1} and the spectrum of the final product displayed a strong absorption at 1750 cm^{-1}. The bands in the 1630-1750 cm^{-1} region and particularly the one at 1750 cm^{-1} can be assigned to ν C-O. Similar observations could be made when DMOAHNCS reacted with PGE confirming that the NCS groups disappeared and generated a species containing a C=O bond. A frequency as high as 1750 cm^{-1} has been observed for a C=O bond in the case of oxazolidones (11-13). Several mixtures were obtained by reacting PGE either with DMOAHNCS or with DMOAB(NCS)$_3$. The ^{1}H NMR spectra displayed multiplets between $\delta = 4.09$ and $\delta = 4.20$ ppm ($C\underline{H}_2$) and at $\delta = 4.96$ ppm ($C\underline{H}$) due to oxazolidone rings (11,14,15). The formation of the oxazolidone ring by reaction of alkylisothiocyanates with epoxides has been described (16) as obeying a S_N2 mechanism in its initial step. The reaction scheme also involved the formation of a thiirane, a three membered ring prone to polymerization. Consistently with the presence of thiirane in low concentration (16), the ^{1}H spectra examined above displayed doublets of equal intensities at $\delta = 2.36$ and at $\delta = 2.66$ ppm. These doublets were assigned to the unequivalent protons of the cyclic $C\underline{H}_2$ group.

The behaviour of the NCS$^-$ generated in the resin could be



The improved properties observed for the final materials when the isothiocyanato borane adducts were used instead of their chloro analogues seem to be due to the oxazolidone rings.

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