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Crosslinking behaviour of diolmodified epoxies

3. C-13 NMR measurements in the liquid state

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Summary

Diglycidyl ether of bisphenol A (BADGE) reacts with aliphatic alcohols to form different products, depending on the type of accelerator and the alcohol mole fraction. Using liquid state C-13 NMR different reactive groups as oxirane rings, primary and secondary hydroxyl groups were detected in dependence of the epoxide consumption. Crosslink and junction point resonances were identified by varying the cure state.

Indroduction

The physical, chemical and ultimate mechanical properties of thermosetting polymers rely on their crosslinked structure. In particular, epoxy resin systems have been extensively studied using DSC (1, 2, 11), FTIR (3, 4), HPLC (5, 11) and dynamic mechanical analysis (6). However, none of these techniques provides to identify direct chemical structures of the epoxy network, whereas high resolution C-13 NMR detects carbon resonances that directly reflect the chemical structures of the system (4).

This paper considers the usefulness of liquid state C-13 NMR for investigating the chemical structures and the reaction course of the reaction of diglycidyl ether of bisphenol A (BADGE) with butane-1,4-diol (BD) in the presence of the different accelerators, $Mg(ClO_4)_2 \cdot 2\ H_2O$ as an acidic (Lewis-type) and N,N-dimethyl-benzylamine (DMBA) as a basic accelerator. The effect of these accelerators on the reaction course of BADGE reacting with aliphatic alcohols has not been completely elucidated. Nevertheless, some facts are known to be true (5):

1. Acceleration with magnesium perchlorate in a temperature range between 70 and 110 ^{0}C leads to the formation of uniform oligohydroxy ethers. The ratio of the reaction rates k_1 (primary hydroxyl group + epoxide group) and k_2 (secondary hydroxyl group + epoxide group) is decisive for the real consumption of the alcohol and for the extend of the network formation. It was found to be independent of the reaction temperature (5).

2. Using DMBA as the accelerator, the number of starting step increases as the reaction temperature rises. The ratio k_1/k_2 changes and leads to superimposed reaction

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This different reaction behaviour in both systems was investigated by NMR methods. In this paper we report the results of high resolution liquid-state C-13 NMR measurements. Further work concerns the application of high resolution solid-state C-13 CP-MAS-NMR on the same polymeric systems (7).

Experimental

Chemicals: Diglycidyl ether of bisphenol A (BADGE), butane-1,4-diol (BD), magnesium perchlorate and N,N-dimethylbenzylamine (DMBA) are commercially available products. BADGE was recrystallized from acetone-methanol (m.p. = 42 °C).

Preparation of prepolymers: BADGE, BD and the accelerator were mixed in a given molar ratio, 1:0.25, 0.5, 0.75, 1:0,03 $Mg(ClO_4)_2 \cdot 2H_2O$ for series 3.1 to 3.4; 1:0.25, 0.5, 0.75, 1:0.05 DMBA for series 4.1 to 4.4, in a thermoregulated glass reactor. The reaction proceeded at 100 °C if magnesium perchlorate was used as the accelerator and at 60 °C if DMBA was used. The reaction was interrupted at different epoxide consumption steps and the reaction products were stored at - 20 °C. Determination of the epoxide consumption was carried out by a direct titration method with tetraethylammoniumbromide and perchloric acid at room temperature (8) and by NMR (this work).

Analysis: ^{13}C-NMR spectra are collected on a Bruker HK 90 R spectrometer operating at a frequency of 22.635 MHz using $CDCl_3$ as solvent and reference signal (77.0 ppm). About 10^4 FIDs were accumulated at room temperature with the parameters sweep width 4500 Hz, aquisition time 0.9 s, pulse width 3.5 us (corresponding 30 dec. pulses). Computer integrals were used for the intensities. The conditions for quantitative analyse are fulfiled because the pulse repetition rate (aquisition time) is larger than $3T_1$ for the interesting carbons except the quaternary carbons (for the T_1 values in BADGE at the frequency range used see (9)).

Results and Discussion

The curing of the epoxy resin with butane-1,4-diol causes several changes in the C-13 NMR spectra, shown in Figure 1 for sample 4.4 with 70.0 % epoxide consumption. The most obvious change is the decrease in the epoxy resonance (oxirane methine at 49.8 and methylene carbon resonance at 44.1 ppm) with increasing epoxide consumption relative to the interior methine peaks of the BADGE aromatics (127.5 and 114.0 ppm). Similar decays can be found for the adjacent glycidyl ether carbons at 68.5 ppm. As well as the glycidyl ether carbon (68.7 and 68.5 ppm), the quaternary carbon resonances of the BADGE aromatics (156.0 and 155.8 ppm, 143.1 and 142.9 ppm) split into dubletts with increasing epoxide consumption (Fig. 1). One of the dublett signals corresponds to the decreasing monomer mole fraction with increasing epoxide consumption (68.5, 155.8 and 143.1

ppm). The other one increases with the epoxide consumption corresponding to curing reactions (68.7, 156.0 and 142.9 ppm).

Epoxide consumptions were determined from the intensity ratios of corresponding signals. Significant differences between epoxide consumptions measured by titration methods and NMR only occur for samples 3.1 and 4.1 (higher titration values).

For the line assignments of BADGE signals compare ref. (4) and (9). The signals of monomeric BD were found at 61.9 ppm (methylene carbon adjacent to the primary hydroxyl group) and 29.2 ppm (methylene carbon).

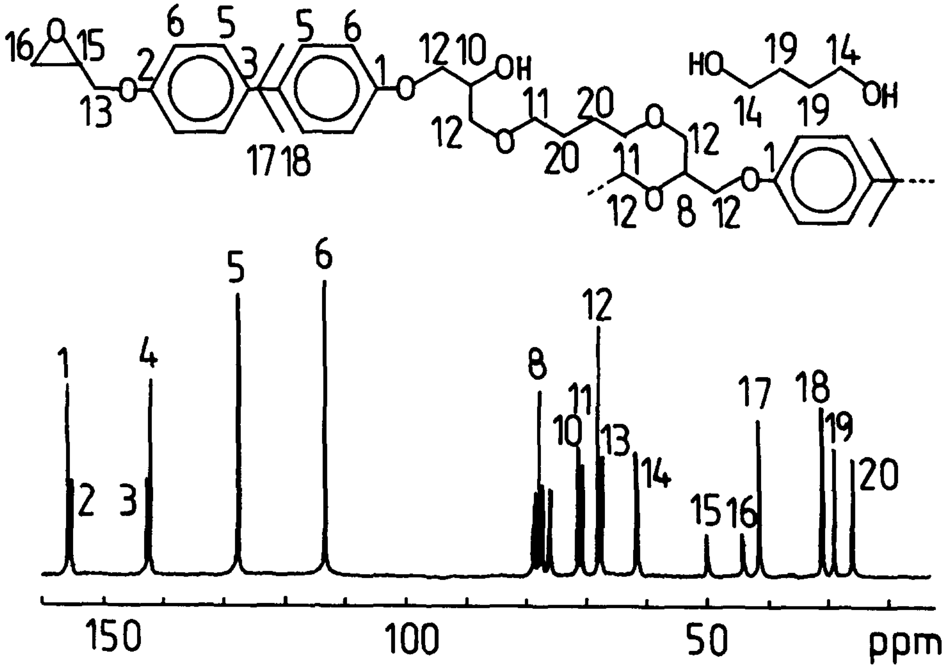

Figure 1. C-13 NMR spectrum of the system BADGE : BD : DMBA = 1 : 1 : 0,05 (sample 4.4). Conversion of epoxide : 70 %, Solvent : $CDCl_3$ (triplet at 77.0 ppm)

The reaction of BD with BADGE changes the chemical shifts of these signals to 70.9 ppm (downfield shift) corresponding to ether linkages and to 25.9 ppm (upfield shift). The mole fraction of monomeric BD corresponding to the content of primary hydroxyl groups is shown in Figure 2 for the methylene carbons of BD in dependence on the epoxide consumption determined by NMR.

In the magnesium perchlorate accelerated samples (3.1 to 3.4), the mole fraction of primary hydroxyl groups exponentially vanishes with increasing epoxide consumption.

Otherwise, that of the DMBA-accelerated samples seems to approximate to a constant value between 30 and 40 % residual primary hydroxyl groups after a faster reduction at the beginning of the epoxide conversion. That means, BD in the DMBA-accelerated samples acts as an initiator of BADGE etherification and is not necessary for further processes.

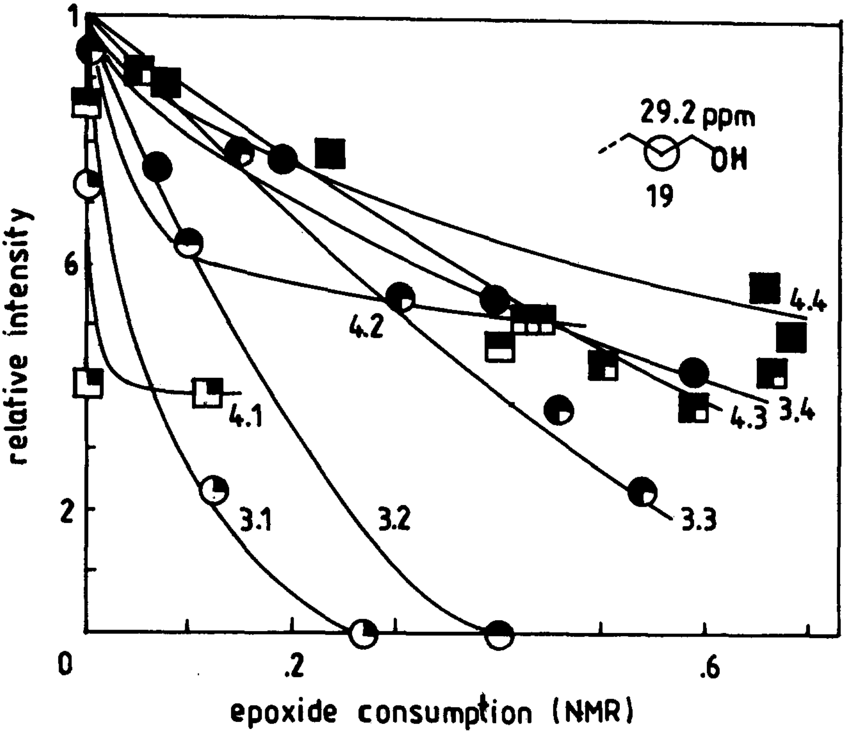

Figure 2. Relative intensity of BD methylene carbons at 25.9 ppm corresponding to the mole fraction of primary hydroxyl groups vs. epoxide consumption (decrease of relative intensity of oxirane methylene carbons)

We obtained similar curves for the other methylene carbon adjacent to the primary hydroxyl group. The line assignments are supported by the constancy of the sum of intensities of the corresponding signals at 61.9 and 70.9 ppm (signals 14 and 11, see Fig. 1), at 29.2 and 25.9 ppm (signals 19 and 20).

NMR signals of the accelerators are not visible because their mole fraction in the mixture is very low.

Secondary alcohol groups are represented by the signal at 71.4 ppm. Their intensities depend only on the epoxide consumption as shown in Figure 3. No influence of the accelerator and the BO mole fraction is to be seen.

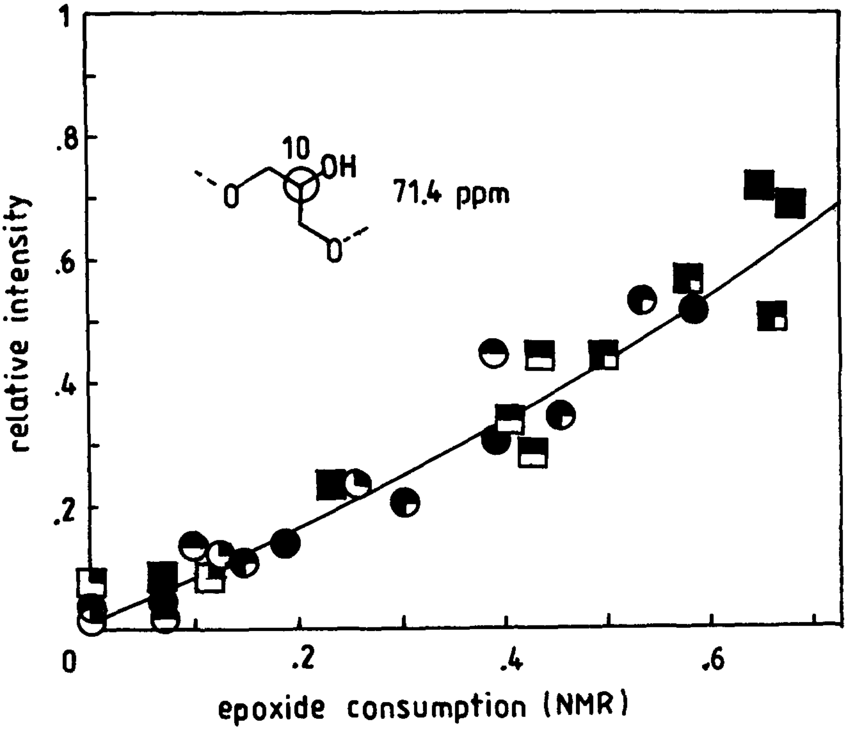

Figure 3. Relative intensity of the secondary alcohol internal methine carbon at 71.4 ppm corresponding to the mole fraction of secondary hydroxyl groups vs. epoxide oonsumption (decrease of relative intensity of oxirane methylene carbons).

Only the DMBA-accelerated samples 4.1 to 4.4 show a signal at 77.2 ppm (signal 8 overlapped to the $CDCl_3$ solvent triplet at 77.0 ppm) even at low epoxy consumption which we assign to ether crosslink methine carbons. The assignment is supported by off-resonance experiments and using DMSO as the solvent (signal 8 without overlap of other signals split into a dublett as the other methine carbon signals in the spectrum). The difference of the chemical shift of these signals to the glycidyl ether carbon at 68.7 ppm is almost the same as calculated by Weisenberger and Koenig (10) for a diester and ether substituted propane (8.5 ppm) as the model system. Another support is the fact that in the solid state NMR spectra of the cured sample two signals are visible (overlapped, 77.5 and 68.5 ppm) corresponding to crosslink and junction point ether carbons (7).

Conclusions

High resolution liquid-state C-13 NMR proved to be a suitable method for the investigation of the reaction courses and the selectivity of the ring-opening and etherification reaction of BADGE and BD with different accelerators. $Mg(ClO_4)_2 \cdot 2\,H_2O$ accelerated systems react with a large selectivity ratio between primary and secondary hydroxyl groups. The concentration of the primary hydroxyl group decreases, leading to a complete reaction of BADGE with BD. DMBA accelerated systems are characterized by a remaining fraction of primary alcohols even at high epoxide conversions and furthermore by the presence of ether crosslink carbons.

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