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Relaxation times and *in situ* kinetic analysis during network evolution of epoxy via a nickel catalyst of imidazole

Abdollah Omrani[a,b,*], Ayret Mollova[a], Carlos Mattea[a], Siegfried Stapf[a]

[a] *FG Technische Physik II/Polymerphysik, Fakultät für Mathematik und Naturwissenschaften, Technische Universität Ilmenau, Postfach 100565, D-98684 Ilmenau, Germany*
[b] *Faculty of Chemistry, University of Mazandaran, PO Box 453, Babolsar, Iran*

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ABSTRACT

A research work has been conducted to investigate relaxation time changes with curing schedule, time, and concentration of DGEBA cured with Im_6NiBr_2. Our results demonstrate that low field NMR relaxometry is a facile and easy protocol to evaluate storage stability of one-pot epoxy based compositions. The DGEBA–Im_6NiBr_2 mixtures consistently display a greater degree of latency and a slower rate of the relaxation time decrease over the parent DGEBA–imidazole mixture. The results obtained on storage stability using NMR method are in reliable agreement to those reported previously using DSC and FT-IR approaches [1]. High field NMR techniques at elevated temperatures were utilized to determine the rate constants of both polymerization stages. The results exhibit that the rate constant of the first step is more sensitive, in comparison to the second stage, to the isothermal temperature used. By reference to the reaction between DGEBA and Im_6NiBr_2, ^1H NMR at elevated temperature was shown to be a simple technique, available for on-line process monitoring, for obtaining the degree of cure enabling kinetic parameters. This study highlights the usefulness of the high temperature bulk ^1H NMR technique in kinetic studies of epoxy-metal organic curing agent systems.

1. Introduction

Epoxy resins have been widely used in electronic packaging industries due to their ease of processing and low cost [2–4]. They are commonly used as polymeric matrix in various emerging technologies owing to their excellent heat and chemical resistance [5,6]. There are a number of candidate techniques that could be utilized to monitor epoxy resin curing. The list includes: dielectric spectroscopy (DEA) [7–9], dynamic mechanical analysis (DMA) [10,11], FT-IR [12,13], DSC [14], pulsed ultra sound [15–17], and nuclear magnetic resonance [18–20]. An accurate inspection of the above list shows that DEA and DMA methods are unsuitable for industrial applications since they need a special sample configuration, an electrode for DEA, and are as such not truly non-invasive. Additionally, FT-IR and DSC methods were extensively used previously. The NMR technique is truly non-invasive and provides complementary information on the cure process. NMR measures the mobility of magnetically active nuclei and can supply data on the microscopic changes in the resin as it cures. However, NMR is most sensitive to the mobility of H nuclei and this is a particular advantage in the study of epoxy resin adhesives because hydrogen plays a key role in the curing reaction. Accordingly, non-invasive and non-destructive techniques are highly appreciated for process monitoring in an industrial set-up. Epoxy resins can be cured by a large variety of chemicals such as amines, acid anhydrides, phenol-formaldehyde, sulfur and phosphorous compounds, and metal-organic curing agents. The curing reaction of the system based on DGEBA exhibits a kinetic scheme characterized by an initial acceleration due to autocatalyze. As curing proceeds and the resin becomes rigid, the glass transition temperature (T_g) increases. For curing temperatures below the ultimate T_g, the reaction rate follows chemically controlled kinetics. When T_g reaches the curing temperature, the resin state changes from a rubbery form to a glassy state and the reaction rate will experience diffusion controlled kinetics. It is well known that imidazole and its derivatives can produce cured epoxy having good thermal, physical, and mechanical properties [21,22]. The main disadvantage of imidazoles one-pot compositions is poor storage stability. Hence, considerable research has been conducted to meet the problem. The preparation of transition metal–imidazole complexes is a facile way to improve storage stability and to control the curing reaction as well [23–26].

The spin–lattice relaxation time, T_1, and the spin–spin relaxation time, T_2, which are a function of the distribution of correlation times characteristic for reorientations within molecules, are readily available and useful parameters for investigating the polymers'

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[*] Corresponding author at: Faculty of Chemistry, University of Mazandaran, PO Box 453, Babolsar, Iran. Tel.: +98 11252 42025; fax: +98 11252 42002.
E-mail address: omrani@umz.ac.ir (A. Omrani).

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structural order, chain entanglement, and the presence of permanent cross-links. The entanglement of the polymer chain, especially in the case of epoxy curing, restricts the chain mobility as the resin reacts with the curing agent. The transverse relaxation time T_2, directly reflects the degree of residual dipolar interactions which, for instance, are averaged out due to fast motion in a liquid; for a given material, T_2 will thus always decrease with decreasing mobility and will assume a minimum value in a crystalline or glass-like structure. The longitudinal relaxation time T_1, on the other hand, will be minimal when energy between the spin system and the lattice can be exchanged most efficiently, i.e. when the Larmor frequency $\omega = \gamma B$ is of the order of the reciprocal average reorientation time τ (where γ is the gyromagnetic ration of the nucleus, here ^{1}H; and B is the magnetic flux density). For $\omega\tau \ll 1$, T_1 increases with shorter values of τ; for $\omega\tau \gg 1$, which is the most common case for highly viscous or solid materials, T_1 is expected to increase with growing τ, with the exact relation depending on the nature of the reorientation processes. Since in polymers, the contribution of the relatively short-range chain motion are dominating for the computation of the NMR relaxation times, evaluation of T_1 and T_2 can offer a sensitive and on-line probe to investigate storage stability via information about the local chain mobility. Exploring the effect of intermolecular coupling on the mobility during bulk polymerization or curing reaction is also possible. This paper is a continuation of our previous publications [1,27,28] on the same epoxy composition where we studied curing mechanism, cure kinetics, and final properties of this system using various techniques. However, the goals of the present work are: (1) to present low-field NMR relaxometry as a powerful, reliable, and easy approach to evaluate storage stability of epoxy based one-pot compositions in industrial applications, (2) to carry out a kinetic analysis using high field NMR measurements at elevated temperatures on DGEBA–Im_6NiBr_2 system which have not been presented in the literature, (3) to correlate the data obtained in low field to those collected by high field NMR measurements.

2. Experimental

2.1. Materials

The commercial epoxy prepolymer D. E. R 332 possessing epoxy equivalent weight (EEW) of 175 g/equiv. was donated by Aldrich chemical company. The curing agent was a nickel catalyst of imidazole, Im_6NiBr_2, which synthesized using the method reported in the literature [29] and characterized in our lab. Imidazole was obtained from Merck. The EEW of the used resin was found to be 174.9 g/equiv. using NMR technique.

2.2. Sample preparation

Compositions of 5, 15, and 30 wt% of Im_6NiBr_2 in D.E. R 332 were made by dispersing the nickel salt directly in the resin for 15 min. For comparative study, a mixture involving 5 wt% imidazole (Im) was used. Since the epoxy resin viscosity is high and the curing agent was a solid material, it would be so difficult to prepare one-pot epoxy composition into NMR sample tube. All the samples for NMR measurements were prepared by inserting one-pot epoxy compositions into the NMR sample tubes at room temperature using a 5 ml syringe under pressure. This procedure, indeed, allows minimizing the effects of unwanted phenomena (reactions and phase separation) during preparation of the samples for NMR tests at both high and low fields measurements. For the relaxation time measurements, the NMR tubes were stored in a vacuum oven at 25 °C and after specific time intervals they subjected by relaxometry traces. To clarify the effect of thermal curing on the relaxation times, two epoxy compositions having 15 wt% Im_6NiBr_2 and 5 wt% imidazole were examined. The DGEBA–Im_6NiBr_2 (15 wt%) composition was cured into a NMR tube at 115 °C at various times and then post-cured at 180 °C for 90 min to evaluate the relaxation times of the fully cured material. The DGEBA–Im (5 wt%) composition was cured at 70 °C for different times and finally post-cured at 120 °C for 60 min. For high field NMR tests, the epoxy composition including 15 wt% of the nickel salt was cured *in situ* at four isothermal temperatures of 70, 80, 90, and 100 °C. The NMR data were analyzed to calculate the rate constants of the both steps in the polymerization mechanism of epoxy–Im_6NiBr_2 system.

2.3. NMR measurements

A low field NMR minispec mq 40 NMR analyzer, Bruker, operating at 40 MHz for hydrogen nuclei was employed for the relaxometry tests. Proton spin–lattice relaxation times were measured by the inversion-recovery pulse sequence using 20 data points with 64 scans for liquid samples, 256 scans for semi solid materials, and 2048 scans for completely solid thermosets. Proton spin–spin relaxation time was determined using CPMG pulse sequence having 10 s of recycle delay. The T_1 and T_2 numerical values and relative intensities were obtained by fitting the exponential data using the instrument software. ^{1}H NMR spectra were obtained using a Bruker Spectrospin high field NMR operating at 300 MHz. Measurements were conducted at high temperatures to obtain enhanced peak resolution and the spectra subsequently analyzed using Bruker Topspin 1.3 software. A minimum of 32 scans were collected. The NMR sample tube was loaded into the probe after reaching temperature to a desired amount. At defined time intervals, the NMR spectra have been recorded and the free-induction decay (FID) signals stored. The ratio of the integrals of the epoxide methylene protons (the doublet at 2.52 ppm) and an internal standard (the methyl protons in isopropylidene bridge as a singlet at 1.55 ppm) was obtained and used to calculate the epoxide concentration and conversion according to the following equations:

$$[\mathrm{Epoxide}] = \frac{I}{I_0} \qquad (1)$$

$$\alpha = 1 - [\mathrm{epoxide}] \qquad (2)$$

where I is the ratio of the integral of epoxide and methyl group signals and I_0 is the same ratio at the beginning of the curing reaction, actually at time = 0.

3. Results and discussion

3.1. Storage stability at room temperature

Our previous study on the storage stability of DGEBA–Im_6NiBr_2 system showed that the one-pot composition is stable for about 1 month at room temperature. Clearly, at room temperature the most important factor that has major effect on storage stability is direct interaction between the epoxide groups in DGEBA and Im_6NiBr_2. Imidazoles are cool curing agents of epoxy resins because they are capable of polymerizing epoxy resin at room temperature. Any type of interaction between the components which results in solidification of the epoxy will reduce storage stability. By exploring changes in epoxide bond vibration at 914 cm^{-1} (peak area) using FT-IR measurements and/or evaluation of reaction enthalpy by means of DSC experiments at various times, it is possible to investigate the storage stability [1]. On the other hand, both NMR relaxation times permit us to estimate sample behavior at molecular level. They are sensitive to fast motions and particularly, to rigidity of materials [30,31]. Since changes in molecular mobility can be detected by T_1 and T_2 measurements at constant temperature for various times,

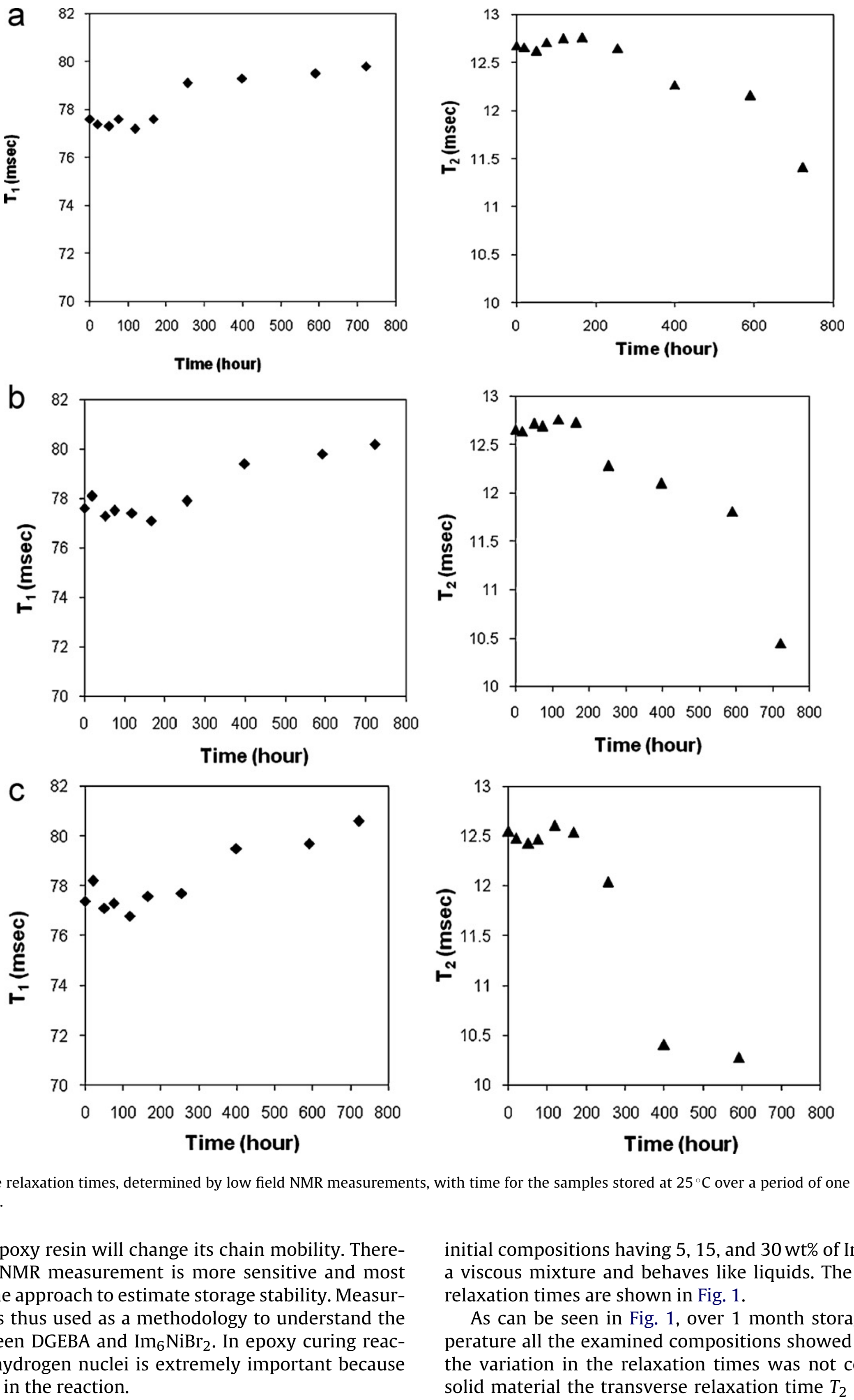

Fig. 1. Changes in the relaxation times, determined by low field NMR measurements, with time for the samples stored at 25 °C over a period of one month: (a) 5 wt%. (b) 15 wt% and (c) 30 wt%.

solidification of epoxy resin will change its chain mobility. Therefore, a low field NMR measurement is more sensitive and most convenient on-line approach to estimate storage stability. Measuring T_1 and T_2 was thus used as a methodology to understand the interaction between DGEBA and Im_6NiBr_2. In epoxy curing reaction tracking of hydrogen nuclei is extremely important because they are involved in the reaction.

Although our previous studies revealed that the optimum level of the nickel salt that should be loaded into epoxy resin is 15 wt%, we have examined various epoxy compositions to clarify the effect of Im_6NiBr_2 concentration on the relaxation times and to check the capability of the method in estimating storage stability. The initial compositions having 5, 15, and 30 wt% of Im_6NiBr_2 involves a viscous mixture and behaves like liquids. The changes in both relaxation times are shown in Fig. 1.

As can be seen in Fig. 1, over 1 month storage at room temperature all the examined compositions showed good stability as the variation in the relaxation times was not considerable. In a solid material the transverse relaxation time T_2 is short typically well below 50 μs. Apparently, after about 1 month considerable solidification between the components did not occur since T_2 variations were only minor. However, as the curing agent concentration increased the stability of the reacting components was somewhat decreased at room temperature. This could be described accord-

Table 1
Results from low field NMR relaxometry on imidazole (5 wt%) mixed epoxy that was stored at 25 °C.

Time (h)	T_1 (ms)	T_2 (ms)	Time (h)	T_1 (ms)	T_2 (ms)
0	77.6	13.17	165	136	0.115
19	89.3	4.92	255	138	0.109
30	98.7	1.17	399	146	0.102
50	110.3	0.47	591	150	0.101
74	120.4	0.203	722	160	0.094
117	133	0.118	–	–	–

ing to the fact that at high Im_6NiBr_2 concentrations freer imidazole will be available in the system resulting in some solidification at low temperatures. For the optimum composition, the value of T_2 was reduced about 16% from its initial amount after 1 month. Considerable decrease in T_2 value for high concentration of 30 wt% was observed after 396 h. A comparative study was done by measuring the relaxation times for the epoxy–imidazole system. As pointed out before, imidazoles can promote epoxide ring opening polymerization at low temperatures very fast and this should be reflected by considerable changes in the relaxation times with time as well. Table 1 shows the values of T_1 and T_2 in terms of storage time. Low storage stability of DGEBA–Im composition was clearly seen as expected. Fast reaction between the components results in solidification at very short times as evidenced by appearance of the sample tube.

After 117 h, the value of T_2 was reduced from 13.17 to 0.118 ms. It is worthy to note that the values of T_1 and T_2 for pure DGEBA and Im_6NiBr_2 were found to be (77.4, 11.66) and (290, 0.158) ms, respectively. The final value of T_2 still remains well above that would be expected for a completely rigid lattice, i.e. a fully grafted material. Consequently, the resulting polymer has a low concentration of grafted points and are mostly produced linear fragments with grafts having low functionality. This is due to the fact that the etherification reaction, which results in cross-linking, is considerable at elevated temperatures for the epoxy polymerization.

3.2. *Effect of curing schedule on the relaxation times*

Two experiments were designed at high temperatures to explore variation of the relaxation times with curing time. These experiments allow gaining some insights into build-up of the epoxy network by low field NMR measurements. DGEBA was cured using imidazole (5 wt%) and Im_6NiBr_2 (15 wt%) at 70 and 120 °C, respectively. The changes in T_1 and T_2 were illustrated as a function of curing time. Temperatures of 120 and 180 °C for 120 min were imposed on the samples as post-curing treatment. Fig. 2 exhibits variation of the relaxation times versus time for the both mixtures. Obviously, the imidazole cured sample showed higher values of T_1 and smaller values of T_2 than those obtained for the Im_6NiBr_2 cured sample demonstrating that more solidified structure was achieved in the case of free imidazole. For the cured mixture using the nickel complex, it was also seen that the level of solidification is even lower after the post-curing protocol as a result of topological restrictions. It is noteworthy that, after postcuring, the value of T_1 for the Im and Im_6NiBr_2 cured epoxy were found to be 215 and 160 ms, respectively. The corresponding values of T_2 were determined as 0.107 and 0.113 ms. The importance of the topological restrictions can be verified by inspection of the decay curves which were not exponential. Such a deviation from exponential behav-

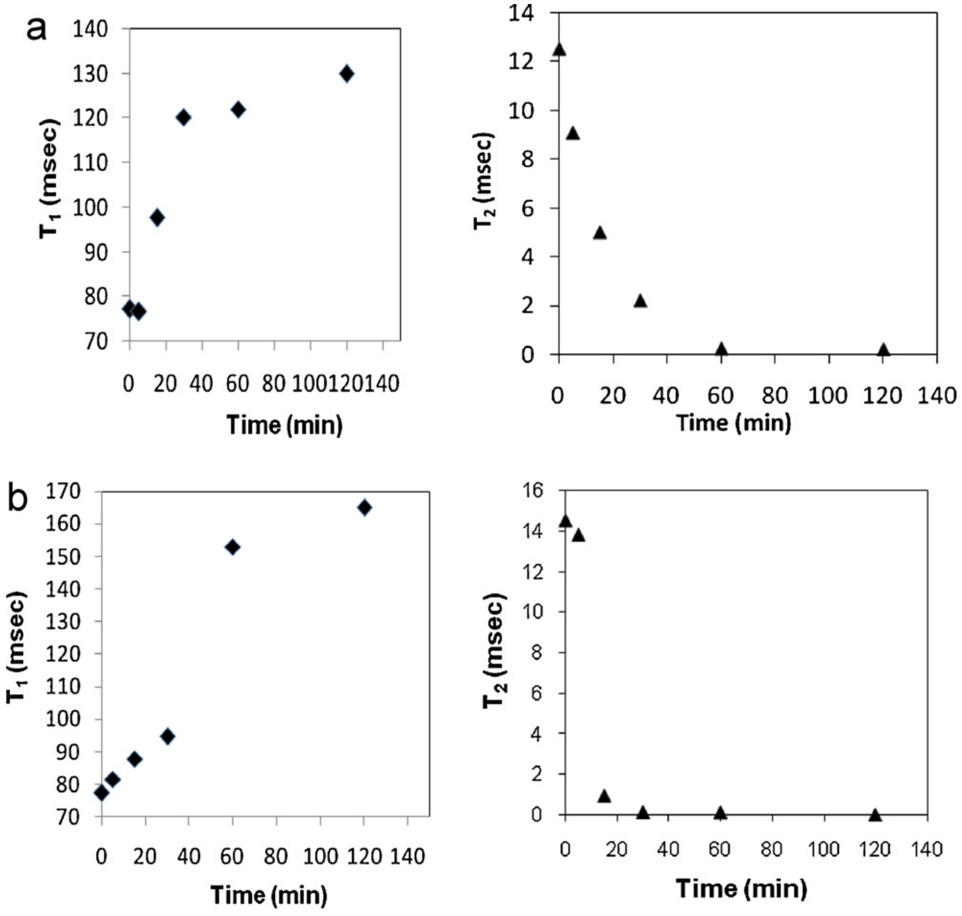

Fig. 2. Variation of the relaxation times, determined by low field NMR measurements with isothermal curing time for (a) Im_6NiBr_2 and (b) imidazole cured samples.

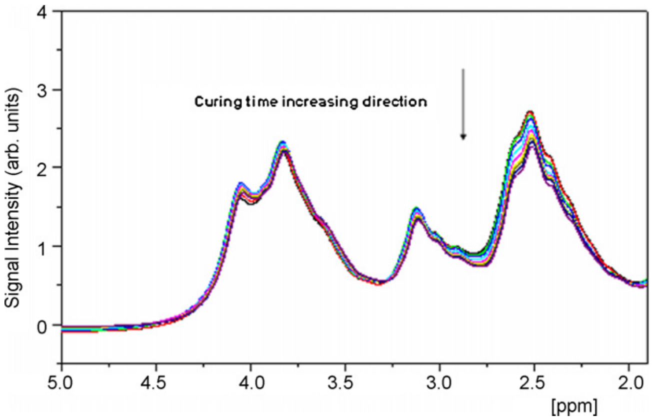

Fig. 3. ^{1}H NMR spectra (in a selected region) of progressively cured DGEBA/Im_6NiBr_2 (15 wt%) sample at 90 °C.

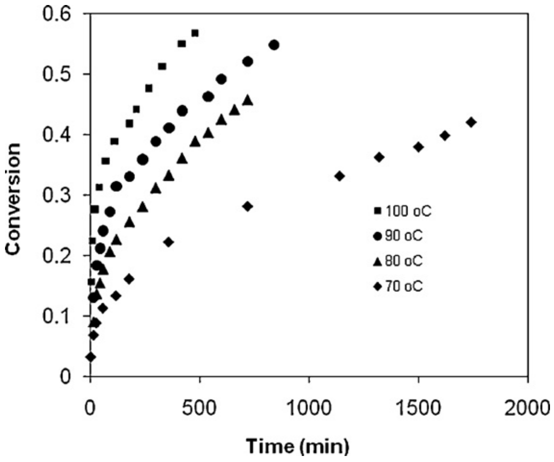

Fig. 4. Degree of epoxide group conversion versus time at various isothermal temperatures for the cured samples containing Im_6NiBr_2 (15 wt%).

ior will occur in the case of largely hindered mobility as the result of topological restrictions. The kinetic dependency of T_2 was evidently caused by an increased concentration of higher functionality grafts/cross-links and by increased viscosity of the reacting system due to the formation of both linear and branched reaction products [32]. By increasing curing time, the value of T_2 decays rapidly and then slowly reaches a value that is a characteristic of glassy polymers (see Fig. 2).

The curves for the time dependence of T_2 exhibited a tendency toward a limiting value as the time increased. The nodes evidently exert an effect on the anisotropy of the movement of the inter-node chains at high frequencies of motion in these systems.

3.3. Kinetic study using in situ high field ^{1}H NMR measurements

Isothermal curing of DGEBA–Im_6NiBr_2 (15 wt%) mixture was carried out at 70, 80, 90, and 100 °C using a Bruker 300 MHz NMR equipped with a high temperature probe. Curing of epoxy resins using metal-organic curing agent is a complex process since, as we discussed in our last publications, there are at least three various polymerization paths in the process. The first is due to a direct interaction between epoxide ring and the nickel catalyst. If the curing temperature is higher than the value at which the imidazole–Ni linkage can be broken, free imidazole will be released into the reaction medium. Therefore, the second polymerization route would be polymerization of DGEBA using the available free imidazole which is well known in the literature in terms of its mechanism and final properties [1,28]. Ring opening polymerization of DGEBA via $NiBr_2$ is the third possible polymerization path. Obviously, this mechanism becomes significant when the curing temperature reaches a point at which all of the six imidazole ligands could be broken. Therefore, to obtain reliable kinetic parameters and to correlate the data between high and low fields NMR measurements, we set our experiments at 70, 80, 90, and 100 °C, respectively. As was discussed before, low field NMR measurements were carried out at room temperature where the second and the third polymerization paths are negligible. We have selected these isothermal temperatures since we believed that at such low temperatures the nickel salt is still stable toward heating. This means that the most available form of the curing agent is Im_6NiBr_2 and, then, we can ignore the contribution of the other polymerization routes. In other words, we have purposely chosen these isothermal temperatures because we wanted the curing reaction to be limited by direct interaction between DGEBA and Im_6NiBr_2. This procedure does allow estimating the rate constants of the reaction between the components which would be more interesting. Fig. 3 shows stacked plots of NMR spectra for the sample cured at 90 °C for 27 h. Even under the prevailing conditions of rather poor resolution due to the high sample viscosity, the epoxide methylene proton peaks near 2.52 ppm are sufficiently isolated from the remaining spectral features to allow the calculation of the epoxide group concentration and conversion. The fractional conversion of the resin at each stage of the reac-

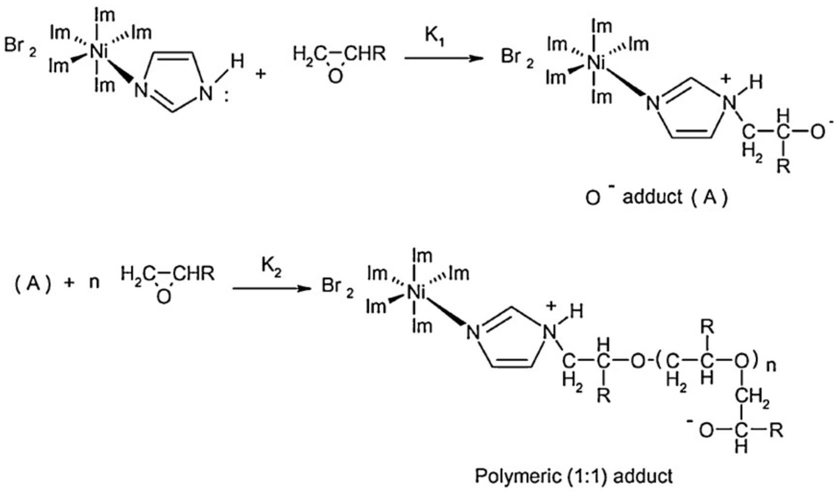

Fig. 5. Proposed model for a two-step mechanism in the DGEBA/Im_6NiBr_2 polymerization.

Table 2
Kinetic parameters at various isothermal temperatures obtained from ^{1}H NMR data of DGEBA/Im_6NiBr_2 (15 wt%) cure.

T (°C)	K_1 (min^{-1})	K_2 (min^{-1})	E_a (kJ/mol)	Ln A
70	0.0007	0.0002		
80	0.0015	0.0006	$E_{a,1}$ = 46.97	9.33
90	0.0021	0.0008	$E_{a,2}$ = 54.95	10.98
100	0.0027	0.001		

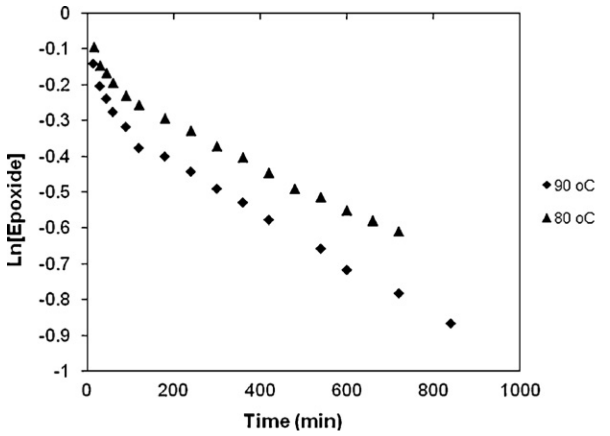

Fig. 6. Consecutive first-order plots for DGEBA/Im_6NiBr_2 system at 80 and 90 °C showing derivation of the rate constants.

tion can be calculated from the relative integration of the epoxide methylene using the internal standard.

Fig. 4 exhibits the fractional conversion of the resin as a function of curing time at various temperatures. High conversion level has been launched as a result of high curing temperature. The rate of epoxide group conversion is very low at the lowest curing temperature, i.e. 70 °C. After 29 h, the reaction has progressed to a degree of 42%.

Two step polymerization of DGEBA using Im_6NiBr_2 was shown in Fig. 5 [27].

By plotting the logarithm of the epoxide concentration against time, as shown in Fig. 6, two consecutive first-order processes can clearly be identified.

The rate constants of K_1 and K_2 were calculated by means of these plots and the results are shown in Table 2.

The first order kinetic analysis algorithm is suitable for the system under study because the nickel salt acts as a real catalyst; note that it has previously been used for the similar systems [33]. We proved in our last observation that Im_6NiBr_2 can be regenerated during the curing reaction [27]. By assuming Arrhenius type dependence for both rate constants, the pre-exponential factor and activation energies were also calculated and listed in Table 2. The value of E_a for the second step is higher due to the importance of the steric factor for this stage. Estimation of both rate constants is the most important advantage of *in situ* NMR measurement in bulk state.

4. Conclusions

High temperature ^{1}H NMR measurements for the blends of DGEBA and a nickel catalyst of imidazole in the absence of solvent have been shown to yield spectra providing the derivation of kinetic parameters. Our results on storage stability by analyzing the relaxation times from low field NMR data were in good concordance with those reported using DSC and FT-IR techniques obtained previously. The results of this work demonstrate ^{1}H NMR spectroscopy is valuable for monitoring kinetics of polymerization between epoxy resin and a metal-organic curing agent. There is an advantage in monitoring the curing reaction in bulk since there is no precipitation of materials due to non-compatibility of the polymer with the solvent. The complexation of imidazole with nickel efficiently arrests the polyetherification reaction at ambient temperature until the temperature is elevated to the value needed to break Ni–imidazole linkage. The latent nature and improved storage stability of compositions having Im_6NiBr_2 were clearly demonstrated and confirmed by the relaxation time measurements. The relaxation time of DGEBA–Im_6NiBr_2 mixtures decreases at a slower rate in the early stages of storage relative to the parent epoxy–imidazole system. After a period of 98 h, the composition containing 15 wt% Im_6NiBr_2 display a considerable reduction in the relaxation times, indicating the latent nature and improved storage stability of the nickel complex over the parent system. The most interesting finding in the present study was the change of the NMR relaxation times at low magnetic fields which was found to be dependent on the employed cure schedule, time, and concentration. The relaxation data indicated that the direct measurements of proton T_1 and T_2 using low field NMR could be a powerful tool to evaluate DGEBA–Im_6NiBr_2 system. Both relaxation times are able to provide further insight into domain formation and homogeneity in the polymer matrix.

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