Correlation of Viscoelastic Properties with Low-Resolution ¹H-NMR Measurements of Crosslinking Unsaturated Polyesters

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ABSTRACT: The curing reaction of four synthezized and five commercial unsaturated polyester resins were characterized by low-resolution pulse ¹H-NMR and rheological measurements. The rheological measurements were done both by steady shearing flow and oscillatory shearing flow measurements. For the synthesized resins, which did not contain any inhibiting, these methods were quite comparable when measuring the gel time. Differences in measured gel times could be seen in the commercial resins. We concluded that the time taken from low-resolution pulse ¹H-NMR measurements was not actually the gel time, but the time at which the resins go from the microgel formation stage to the transition stage. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 68: 671–680, 1998

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INTRODUCTION

Unsaturated polyester resins are commonly used in fiber-reinforced composites as matrix resins. The resin is composed of an unsaturated polyester that is dissolved in styrene. During the processing, the double bond in the polyester reacts with the styrene monomer in a free radical reaction that gives a rigid thermoset. This crosslinking or curing reaction is very complex. The resin solution can be pictured as coiled polyester chains swollen in styrene in which reactions may occur inside, outside, and at the surface of the coil. Reactions can take place between two styrene monomers (homopolymerization), between styrene and a double bond in the polyester chain (intermolecular crosslinking or branching), and between two double bonds in the polyester chains (intramolecular crosslinking).[1]

Yang and Suspene[2] have proposed a gelation model that describes the crosslinking mechanism in four stages. They followed the reaction until the gel point by measuring the viscosity. In the first stage, the "induction stage," the viscosity remains nearly constant and no polymerization occurs. In the following "microgel formation stage," the viscosity increases slightly. The viscosity starts to rise faster in the next "transition stage." The last stage before the gel point is the "macrogelation stage," where a macrogel is formed and the viscosity rises very rapidly. A similar model was proposed by Hsu and Lee[3]; besides these stages, they took into consideration a fifth stage called postgelation. They also divided the transition

stage into two parts, with or without phase separation.

The crosslinking can be studied by several methods. The simplest is to observe the macroscopic geling and determine the gel time using a stopwatch.[4,5] This is commonly used in industry. More accurate results can be obtained by rheological measurements.[6–11] The gel time can be determined either by measuring steady shearing flow properties,[6–9] or by measuring oscillatory shearing flow properties.[9–11] The steady shearing flow measurement characterizes only the rheological behavior of a curing material in the liquid state, whereas the oscillatory shearing flow measurement also characterizes the rheological properties of a curing material in both the rubbery and glassy states.

Because it is not possible in steady shearing flow measurements to approach infinite viscosity (η_∞), the gel time is determined in this case by plotting the ratio of the initial viscosity at time 0 (η_0) to the viscosity at time t (η_t) against curing time, and by extrapolating this to 0.[6–9] There are, however, several disadvantages with this method.[12] The gel point is found by extrapolating; the liquid behaves shear thinning near the gel point, and the network can be broken by the shear flow that leads to longer gel times. This is avoided in oscillatory shearing flow experiments.[13] The gel point is detected herein as the crossover point of the storage modulus G' and the loss modulus G'' $(G' = G''$ or $\tan \delta = 1)$.

The crosslinking of unsaturated polyesters has also been studied by NMR measurements.[14–16] In a recent article, we presented low-resolution pulse ^{1}H-NMR (LRP-NMR) measurements of the crosslinking reaction.[14] Proton mobilities and populations were measured, and we could identify three components in the crosslinking reaction. There are very mobile protons from free styrene, less mobile protons from free polyester molecules, and immobile protons that come from the cured resin. This component could be detected at the gel point. At this point, the proton mobilities of styrene and free polyester polymers were rapidly decreasing and the proton populations of the cured resin started to increase. The same NMR technique has also been used to measure the geling of wood adhesives.[17] The gel time was taken as the time when there was a rapid change in the mobilities of the protons in the system.

Demmler and coworkers[15] and Bergmann and Demmler[16] described the curing reaction in three stages using pulse and wide-line NMR methods.

The first stage was an "inhibition stage," where the spin–spin relaxation times (T_2) are quite constant for the two mobile components. This stage ends when the spin–spin relaxation times start to decrease for the mobile components just before the third immobile component can be seen. The second stage is the "copolymerization stage," where the mobile components continue to lose their mobility and population. This stage begins at the gel point. The third stage is called the "diffusion-controlled stage" and herein the mobility and population of the most mobile component still decrease. Differences in the mobility and population in the less mobile component (unsaturated polyester) are insignificant.

Many researchers have studied the curing reaction by thermal analysis.[6–11,18,19] Measurements have been done both isothermally and in the scanning mode. The main heat of reaction comes from the propagation reaction during curing and a small part comes from the decomposition of the initiator, which can be neglected. Isothermally measured crosslinking usually gives a lower reaction exotherm than measurements done in the scanning mode.

The aim of this study was to characterize the cure of different unsaturated polyester resins in more detail by LRP-NMR and by comparing these results with steady shearing flow, oscillatory shearing flow, and thermal analysis. We investigated how the molar ratio (MR) of styrene to the double bonds in the polyester chain (MR), molecular mass, and mobility changes during the reaction influence gel time.

EXPERIMENTAL

Materials

Both synthesized and commercial unsaturated polyester resins were studied. Four unsaturated polyester prepolymers with different phthalate/maleate MR were synthesized from maleic anhydride, phthalic anhydride, and 1,2-propylene glycol by melt polycondensation, as described previously.[14] All monomers were of standard laboratory grade and were used as received. The prepolymers were dissolved in neat styrene to form unsaturated polyester resins (**1–4**). Styrene was used without removal of inhibitors. In addition, five commercial unsaturated polyester resins (**5–9**) provided by the Neste Group were investigated. Crosslinking was initiated by

2 wt % methyl ethyl ketone peroxide (MEKP) with 2 wt % of 1% cobalt salt in styrene as a promoter at 25°C, and by 2 wt % benzoyl peroxide (BPO; Interox BP-50-FT, Peroxid-Chemie GmbH, München, Germany) at 80°C.

Chemical Characterization

The molecular mass and molecular mass distribution were measured by gel permeation chromatography (GPC; Waters Associates, Milford, MA) equipped with four ultrastyragel columns (10^4, 10^3, 500, and 100 Å pore size) and a refractive index detector. Tetrahydrofuran was used as a solvent, and polystyrene standards were used for the calibration. The MR of styrene to the double bonds in the unsaturated polyester was determined by ^{1}H-NMR using a Varian Gemini 2000 200 MHz instrument. ^{1}H-NMR was also used to estimate the extent of maleate (*cis*) to fumarate (*trans*) isomerization that had occurred during the melt polycondensation. The styrene content of the polyester resins was determined by using an evaporation method. A known amount of resin was weighed on an aluminium foil of known weight. The foil containing the resin was placed in an oven (120°C) for 10 min, whereafter the foil was weighed again. The styrene content was calculated from the weight loss.

Viscoelastic Properties

A Bohlin VOR rheometer with a controlled shear/strain or strain rate was used to study the change in viscoelastic properties of the resins during crosslinking at 25 and 80°C. The measurements were done using a cone and plate geometry where the diameter of the cone was 30 mm and the cone angle was 5°. The gap between the cone and plate was 150 μm in each experiment. The gel time was determined by both measuring steady shearing flow properties and by measuring oscillatory shearing flow properties. In the steady shearing flow measurements, shear rates of 1.17 and 4.65 s^{-1} were used, and the gel time was determined by plotting the ratio of the initial viscosity to the viscosity during the cure against time and extrapolating the ratio to 0. Oscillatory shearing flow measurements were done with a frequency of 1 Hz and a strain amplitude of 10%. Comparisons were also made with measurements at frequencies of 0.5 and 5 Hz. The gel time was determined as the crossover point of G' and G''.

LRP-NMR

The whole curing reaction of the resin was analyzed by using LRP-NMR, according to the method described previously.[14] All experiments were performed on a homebuilt 60 MHz NMR instrument. For long T_2 values, the T_2 was recorded using the Carr-Purcell Meiboom-Gill[20] method. For short T_2 values, the T_2 was measured directly from the free induction decay after a 90° pulse of 2 μs duration with a deadtime of 5 μs. These two sets of data were combined to give the T_2 relaxation behavior over the entire signal decay. From this, the different T_2 decays together with their populations could be measured as described previously.[14–16] The populations and T_2 values were plotted with curing time.

Thermal Analysis

The reaction exotherms of the curing reaction of resins **5–9** were measured isothermally at 80°C by a Mettler 27 HP in 4 MPa nitrogen atmosphere. The isothermal runs were ended when no further exotherm was left. The samples were then reheated in the scanning mode, from 80 to 250°C (10°C min^{-1}) to get the residual reactivity from the isothermal reaction. From these values, the degree of cure was calculated using the formulas

$$\Delta H_{tot} = \Delta H_{iso} + \Delta H_{res} \qquad (1)$$

and

$$\alpha_t = \Delta H_t / \Delta H_{tot} \qquad (2)$$

where ΔH_{tot} is the total heat of the reaction taken from the heat of the isothermal reaction ΔH_{iso}, and the residual heat ΔH_{res} from the scanning measurement. α_t is the degree of cure at time t.

The resins were initiated with 2 wt % BPO, and a sample size of about 20 mg was used.

RESULTS AND DISCUSSION

Chemical Characterization

The chemical composition of the studied unsaturated polyesters are given in Table I. The resins **1–6** contained phthalic anhydride, whereas the resins **7–9** contained isophthalic acid. All resins had typical molecular mass distributions for unsaturated polyesters, ranging from 2200 to 7200 g mol^{-1} in weight average molecular masses. The

Table I Properties of Studied Unsaturated Polyester Resins (1–9)

Resin	Type of Diacid[a]	$\langle M_n \rangle$[b] (g mol^{-1})	$\langle M_w \rangle$[b] (g mol^{-1})	D[b]	η[c] (Pa s)	MR[d]	Styrene[e] (wt %)
1	Phthal	1500	2300	1.5	0.18	6	41
2	Phthal	2900	7200	2.5	1.17	5.1	40
3	Phthal	1900	3600	1.9	0.45	2.7	40
4	Phthal	1600	2800	1.7	0.63	1.8	39
5	Phthal	980	2200	2.2	0.56	3	39
6	Phthal	970	2200	2.2	0.32	2.5	41
7	Iso	1600	4500	2.9	0.36	2.1	42
8	Iso	1900	4400	2.3	0.72	1.5	35
9	Iso	1200	3400	2.8	3.4	1	33

[a] phthal, phthalic anhydride; iso, isophthalic acid.
[b] Determined by gel permeation chromatography in tetrahydrofuran with refractive index.
[c] Viscosity determined at 25°C by steady shearing flow with shear rate 1.17 s^{-1}.
[d] MR, molar ratio styrene/polyester double bonds, determined by ^{1}H-NMR.
[e] Determined by evaporation.

styrene content was between 39 and 42 wt % for all resins, except resins **8** and **9,** which were of lower styrene content. The degree of *cis-trans* isomerization of maleate to fumarate in the polyester was, according to the ^{1}H-NMR measurements, complete in all resins except resin **8,** which had an 80% *cis-trans* conversion. The reason for this is obviously due to the type of glycol used in the polyester formulation.[21]

The MR of styrene to the double bonds in the polyester chain varied a lot. Resins **1** and **2** had the highest ratios of 6 and 5.1, respectively, whereas resins **8** and **9** had the lowest ratios: 1.5 and 1, respectively. All other resins had ratios between 1.8 and 3. The ratio is directly related to the reactivity of the polyester resin at a certain styrene content and can therefore be used to estimate the curing behavior of a certain resin composition.

The viscosity of the resin solutions at 25°C depended on the styrene content and the molecular mass of the prepolymers. A lower styrene content gives of course a higher viscosity, if the molecular mass of the polyester is in the same range. If the molecular mass is higher, will this additionally increase the viscosity as in resin **2.** The viscosity was also compared with the MR, and it could be seen that a lower MR gives a higher viscosity.

Curing Reaction Studied by Rheological Methods

Crosslinking of the synthesized unsaturated polyester resins **1–4** was studied by using two different curing systems. At 25°C, a redox system consisting of 2 wt % MEKP and 2 wt % cobalt salt

was used as an initiator. This oxidoreduction of metal salts by peroxides produces free radicals, and it is a very efficient and commonly used method to initiate the crosslinking of unsaturated polyesters. At 80°C, crosslinking was initiated by the thermal decomposition of BPO, which is commonly used for the curing of molding compounds. The commercial resins **5–9** were crosslinked at 80°C using BPO. The curing was followed until the gel point with both steady shearing flow and oscillatory shearing flow measurements. The results are summarized in Tables II and III. From Table II, it can be seen that the gel times at 25°C are about the same independent of the method and frequency used. The gel times were very short, so the small differences in gel times are probably due to differences in mixing times of the initiator and the times it took to place the mixed samples between the cone and plate and start the experiments. From Table III, it can be seen that comparable results are achieved also at 80°C independent of the frequency or shear rate, even if there was a tendency to get longer gel times in the steady shearing flow experiments. This has been reported earlier.[6,9] The gel time for resin **4** was not possible to measure at 0.5 Hz, because the range was not large enough. From Table III, it can also be seen that the commercial resins **5–9** had much longer gel times than the synthesized resins **1–4** at 80°C. The reason for this is that resins **5–9** were inhibited to longer gel times, whereas resins **1–4** were not inhibited.

The measured gel times for resins **1–4** were also compared with the MR of styrene to the double bonds in the polyester chain (Fig. 1). The gel

Table II Gel Times (in s) of Polyester Resins 1–4 Cured at 25°C with 2 wt % MEKP as Initiator and 2 wt % Cobalt Salt as Promotor, Measured by Steady Shearing Flow (1.17 s⁻¹), and by Extrapolating η_0/η_t to 0, and Oscillatory Shearing Flow at 0.5, 1, and 5 Hz

Resin	Frequency 0.5 Hz	Frequency 1 Hz	Frequency 5 Hz	Shear Rate 1.17 s⁻¹	Average Gel Time (s)
1	580	560	610	610	590
2	250	270	280	210	253
3	170	180	190	150	173
4	110	90	110	80	98

time at 25°C increased as the amount of unsaturation in the polyester chain decreased and the MR increased. This is in agreement with our previous results.[14] The same effect could be seen at 80°C, except that resin **2** (MR = 5.1) had a shorter gel time than resin **3** (MR = 2.7). This could be due to the fact that a higher molecular mass decreases the gel time, and this effect will dominate herein. The same effect can be seen for resin **1** (MR = 6) and resin **2;** they both have about the same polyester composition, but different molecular masses.

It was more difficult to conclude anything about the relation between MR and the gel times for the resins **5–9.** Some conclusions could be drawn from results in Tables I and III. The gel times for the isophthalic type resins **7–9** were increased if the MR was increased, even if resin **8** (MR = 1.5) and resin **9** (MR = 1) had about the same gel times (within the average deviation). This can be explained by the fact that a higher molecular mass gives shorter gel times or by the assumption that the glycol used in resin **8** causes faster curing. Resin **5** (MR = 3) and resin **6** (MR = 2.5), which were of the phthalic type and had similar molecular masses, showed different behavior, compared with all of the other resins. The MR dependence was inverted, compared with the other resins. Herein, lower MRs gave longer gel time, which can be explained by the different amount of inhibitors used in these resins.

From the rheological measurements, a gelation mechanism similar to the one described by Yang and Suspene[2] could be observed (Fig. 2). In the beginning, the viscosity was quite constant, but near the gel point the viscosity started to increase rapidly. Commercial resins **5–9** showed a different rheological behavior during curing than resins **1–4.** These resins had an almost constant or very small uniform increase in viscosity until near the gel point when the viscosity started to increase rapidly. Resins **5–9** showed an increase in viscosity that could be divided into three stages (Fig. 3). In the first stage, the viscosity increased quickly, which is probably due to the microgel formation. In the next stage, the viscosity was almost constant or increased only slightly, as in the transition stage. In the last stage before the gel point, the viscosity started to rise very rapidly; this is

Table III Gel Times (in s) of Polyester Resins 1–9 Cured at 80°C with 2 wt % BPO as Initiator, Measured by Steady Shearing Flow (1.17 and 4.65 s⁻¹) and by Extrapolating η_0/η_t to 0, and Oscillatory Shearing Flow at 0.5, 1, and 5 Hz

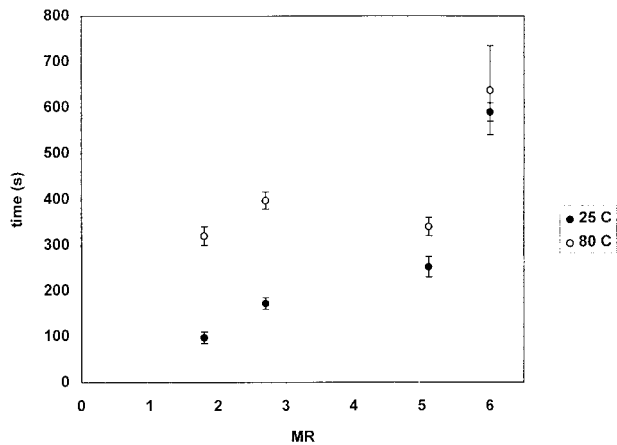| Resin	Frequency 0.5 Hz	Frequency 1 Hz	Frequency 5 Hz	Shear Rate 1.17 s⁻¹	Shear Rate 4.65 s⁻¹	Average Gel Time (s)
1	680	550	790	530	ND	638
2	300	350	340	360	ND	340
3	360	410	410	410	ND	398
4	ND	300	310	350	ND	320
5	1590	1700	1710	1570	1700	1654
6	2560	2380	2490	2290	2200	2384
7	1940	1950	1990	1850	1970	1940
8	950	1070	1190	1530	1470	1236
9	1220	1060	1180	1620	1570	1330

ND, not determined.

Figure 1 Average gel time of unsaturated polyester resins **1–4** measured by rheological measurements at 25°C with 2 wt % MEKP and 2 wt % cobalt salt, and at 80°C with 2 wt % BPO.

the macrogelation stage. A clear dependence between the MR and viscosity in the beginning was observed; the viscosity increased when the MR decreased. This observation has also been made previously and is due to the styrene diffusion effect.[7]

In steady shearing flow experiments, shear-dependent behavior could be observed, giving much lower viscosities at higher shear rates. From the oscillatory shearing flow experiments, the following observation was made. The storage modulus G' and loss modulus G'' had the highest values in the experiments done at 5 Hz and the lowest at 0.5 Hz at the crossover point (gel point).

Curing Reaction Studied by LRP-NMR

LRP-NMR was used to study the changes in proton mobilities and populations during curing reaction at 80°C. The measurements were not possible to do at 25°C with the NMR spectrometer used. Three different components could be identified: very mobile, less mobile and immobile ones. As an example, the results of the spin–spin relaxation time (T_2) measurements and proton populations for resin **1** are showed in Figures 4 and 5, and the estimated gel times in Table IV.

The results of resins **1–4** are in accordance with our previous ones,[14] and the same conclusions can be drawn (Fig. 4). The most mobile component belongs to free styrene and has T_2 values between 1000 and 3000 ms in the beginning and around 0.1 ms at the end of the curing reaction. The less mobile component corresponds to polyester polymers that have T_2 values around 100 ms in the beginning of the reaction. The T_2 will decrease as the curing reaction continues. The immobile component is assumed to be cured resin that can be identified when the crosslinking has started. The T_2 values for this component are between 0.06 and 0.01 ms. The curing reaction can be divided into three stages, as has been described previously.[15,16] In the beginning, only two components could be seen: a very mobile and a less mobile, which correspond to free styrene and polyester polymers. The values of T_2 are quite constant at this stage, which has been called the "inhibition stage." It ends when the two components start to lose their mobilities and the third immobile
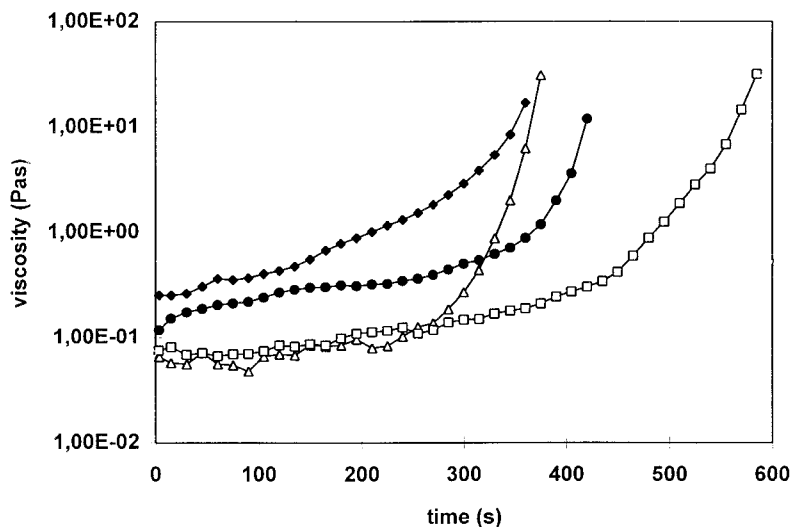

Figure 2 Crosslinking reaction (80°C, 2 wt % BPO) of resins **1–4** studied by steady shearing flow measurements with shear rate 1.17 s^{-1}.
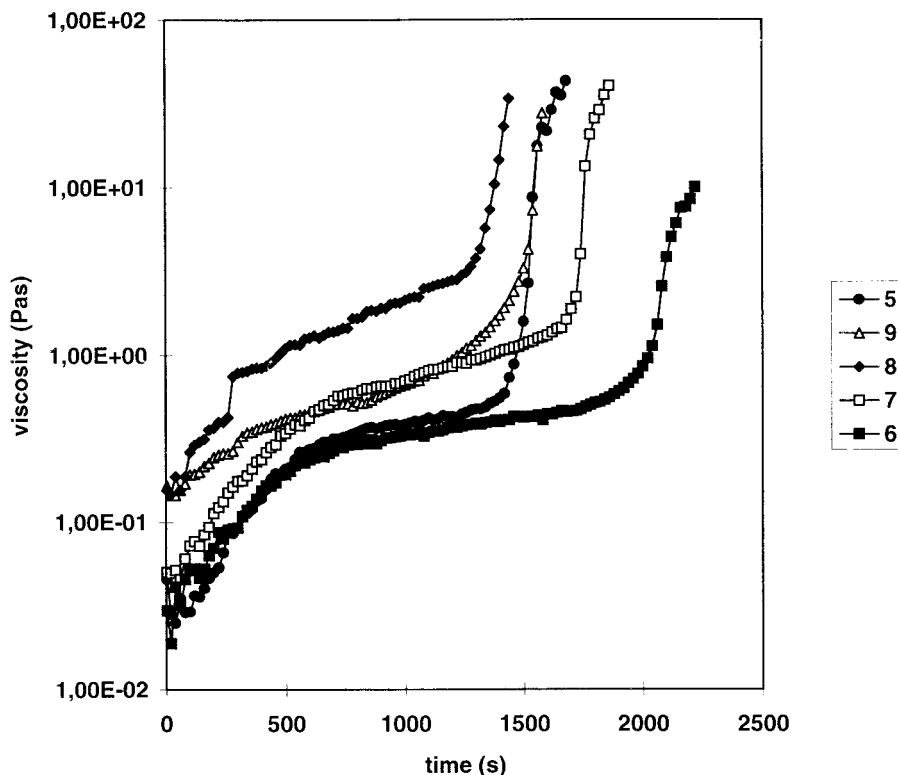
Figure 3 Crosslinking reaction (80°C, 2 wt % BPO) of resins **5–9** studied by steady shearing flow measurements with shear rate 1.17 s^{-1}.

component (cured resin) shows up. The second stage has been called the "copolymerization stage," and it begins at the gel point. At this stage, the mobilities continue to decrease. At the third stage, called the "diffusion-controlled stage," the mobility of the most mobile component is still decreasing, but there are no significant changes in mobility for polyester polymers.

The gel times were determined as described previously[14] as the time when the third component could be seen in a 90° pulse experiment. The results are summarized in Table IV. These results were compared with the gel times obtained by rheological measurements. As can be seen from Tables III and IV, resins **1–4** give quite comparable results. Resin **4,** which is the fastest geling resin, showed a shorter gel time when measured by LRP-NMR. Also, resin **2** shows a longer gel time than resin **3** in LRP-NMR, which is expected if we neglect the effect of molecular mass. For resins **5–9,** the situation is more complicated (Tables III and IV). From these differences, we conclude that the gel point taken from the LRP-NMR is not actually the gel point for resins **5–9.** This point, when the third component could be seen, appeared at the time as the transition from the

microgel formation stage to the transition stage in viscosity measurements (Fig. 3). This kind of viscosity increase could not be seen for resins **1–4.**

From the T_2 values at the gel point measured by LRP-NMR, we can conclude that the styrene component is still quite mobile. The less mobile component, polyester polymer, has also most of its mobility left. The proton population of the cured resin was around 10% at the gel point.

Heat of the Curing Reaction Studied by Thermal Analysis

Calorimetric measurements were done for resins **5–9,** because different gel times had been obtained depending on if rheological measurements or LRP-NMR were used. Results of the isothermal reaction exotherms (ΔH_{iso}), total reaction exotherm ($\Delta H_{tot} = \Delta H_{iso} + \Delta H_{res}$), time to the maximum reaction exotherm (t_{max}), degree of cure at the gel point (α_{gel}), and degree of cure of the isothermal reaction (α_{iso}) are summarized in Table V. α_{gel} was taken from the average gel time in the rheological measurements.

The time to the maximum reaction exotherm (t_{max}) came around the average gel time from
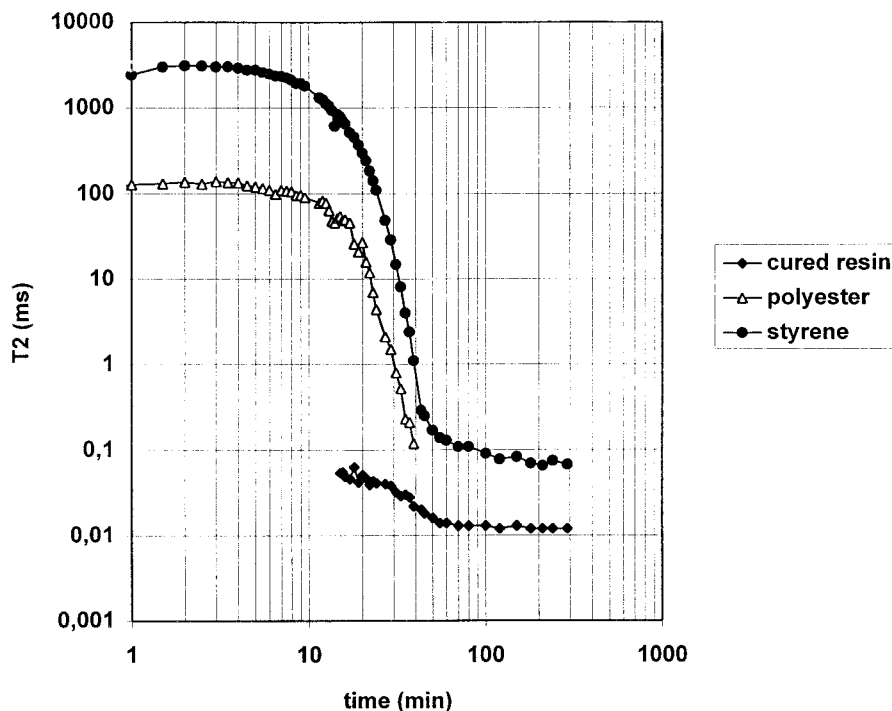
Figure 4 Spin–spin relaxation times (T_2) of resin **1** in a LRP-NMR measurement at 80°C with 2 wt % BPO.

rheological measurements, except for resin **6.** For resin **5,** the gel times measured at low frequency (0.5 Hz) and at low shear rate (1.17 s^{-1}) showed
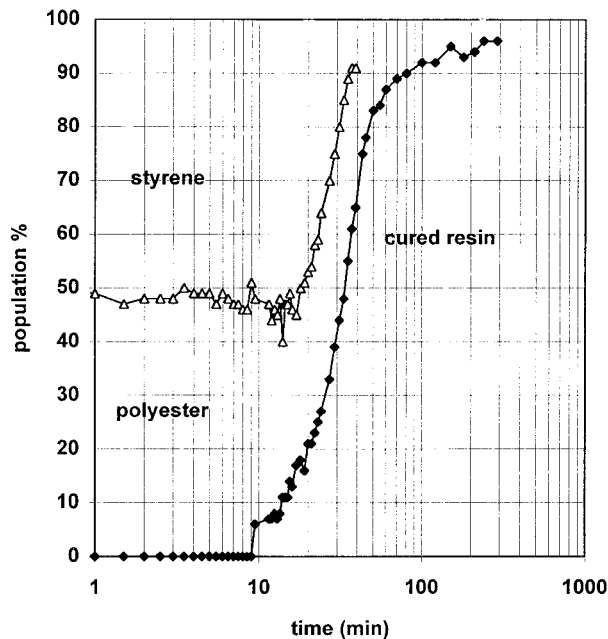
the best comparability with t_{max}. For resins **8** and **9,** the gel times in steady shearing flow measurements showed the best comparability with t_{max}. Resin **7** had constantly longer gel times than the time to the maximum reaction exotherm. The gel times measured by LRP-NMR came around the midpoint in the increase of the reaction exotherm,

Figure 5 Proton population of different components in resin **1** from a LRP-NMR measurement at 80°C with 2 wt % BPO.

Table IV   Gel Times of Unsaturated Polyester Resins Initiated with 2 wt % BPO at 80°C and Determined by LRP-NMR

Resin	t_{gel} (s)	T_2 Styrene[a] (ms)	T_2 Polyester[a] (ms)	Population % (Cured Resin)[b]
1	570	1796	91	6
2	420	1278	66	10
3	270	1597	94	13
4	180	1660	103	10
5	720	924	68	9
6	780	609	56	10
7	720	904	89	13
8	600	1017	88	14
9	480	702	60	16

[a] T_2 times at the gel point.
[b] Population of the cured component at the gel point.

Table V   Isothermal Reaction Exotherms (ΔH_{iso}), Residual Reaction Exotherm (ΔH_{res}), Total Reaction Exotherm (ΔH_{tot}), Times to the Maximum Reaction Exotherm (t_{max}), Degree of Cure at the Gel Point (α_{gel}), and Degree of Cure of the Reaction (α_{cure}) for Resins 5–9 Cured with 2 wt % BPO at 80°C

Resin	δH_{iso} (J g^{-1})	ΔH_{res} (J g^{-1})	ΔH_{tot} (J g^{-1})	t_{max} (s)	α_{gel} (%)	α_{cure} (%)
5	222.8	29.2	252.0	1551	32.3	88.4
6	251.7	33.8	285.5	1530	74.8	88.2
7	273.8	50.6	324.4	1420	55.9	84.4
8	216.2	54.7	270.9	1596	26.3	79.8
9	231.7	56.5	288.2	1640	17.0	80.4

except for resin **9,** where it came in the beginning of the main reaction exotherm.

The degree of cure after the isothermal reaction (α_{iso}) was higher for the phthalic-type resins (**5** and **6**) than for the isophthalic type resins (**7–9**). This is a consequence of the higher residual reactivity in the isophthalic resins. It has been reported earlier that a lower degree of cure could be seen when the amount of fumarate increases.[22,23] The amount of fumarate is highest when the MR is lowest, and the same effect could be seen in our resins. The degree of cure at the gel point (α_{gel}) was higher than expected, but correlate with the time to the maximum reaction exotherm. Resin **6** with the highest degree of cure at the gel point (0.75) had the highest deviation between the average gel time measured by rheological measurements and the time to the maximum reaction exotherm. The same could be observed for resin **7,** that had constantly higher rheologically measured gel times than t_{max}, and the degree of cure was also very high at the gel point (0.56). This could be because intramolecular reactions are more dominating in resins **6** and **7,** which have the highest styrene content than in the other resins. The lower reaction exotherm and degree of cure for resin **8,** compared with resin **9,** could be due to the lower degree of *cis-trans* isomerization of maleate to fumarate in the polyester. This isomerization is desirable because fumarate (*trans*) has greater reactivity.[21]

CONCLUSIONS

Two different methods were compared to measure the gel time of the unsaturated polyester resins at 80°C with 2 wt % BPO as initiator, rheological measurements, and LRP-NMR. For the simple synthesized resins **1–4,** without any additives,

these two methods gave quite comparable results. Resins **5–9,** which were inhibited to delay the gel time, showed different behavior. The gel time measured by LRP-NMR came much earlier than the gel times measured by rheological measurements. From this, we concluded that the time we got from the LRP-NMR measurements was not actually the gel time. The time was more likely to be compared with the time when resins go from the microgel formation stage to the transition stage during the pregel formation. The curing of resins **5–9** was also characterized by thermal analysis, because of this deviation. The measurements showed that the rheological gel point came around the maximum reaction exotherm and the time taken from LRP-NMR measurements around the midpoint in the increase of the reaction exotherm.

The influence of the molecular masses, the molar ratio of styrene to the double bonds in the polyester chain (MR), and the type of aromatic acid used in the resin, on the crosslinking reaction were studied. Resins **1–4** were studied both at 25 and 80°C and resins **5–9** only at 80°C. The following conclusion could be made: the gel time increases when the MR increases if everything else is equal. Higher molecular masses decreased the gel time. The resins consisting of phthalic anhydride had higher final degree of cure than the resins of isophthalic type. The degree of cure was also depending on the MR, giving higher final degrees of cure at higher MR.

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