

Crosslinking of Unsaturated Polyester Resins Studied by Low-Resolution $^1\text{H-NMR}$ Spectroscopy

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ABSTRACT: The curing behavior of five unsaturated polyester resins with different molar ratios of styrene to the double bonds in the polyester chain (MR) was investigated. The gel time was measured according to a standard method by the Society of the Plastic Industry (SPI) and by low-resolution pulse nuclear magnetic resonance (LRP-NMR). The gel and curing times decreased and the maximum temperature of the reaction increased when the MR was decreased. The proton mobilities and populations were measured by LRP-NMR. Three components could be seen in the crosslinking reaction: styrene (very mobile, $T_2 \cong 3$ s), free polyester polymers (less mobile, $T_2 \cong 150$ ms), and cured resin (immobile, $T_2 \cong 0.04$ ms). The third component, cured resin, 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. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **65**: 77–83, 1997

Key words: unsaturated polyester; low-resolution NMR; spin-spin relaxation time; gel time

INTRODUCTION

Unsaturated polyesters are one of the most important matrix resins for glass fiber reinforced composites. Unsaturated polyesters are obtained by the polycondensation of unsaturated and saturated acids or anhydrides with diols. The resulting linear polyester is dissolved in styrene (60 : 40 wt %), and the solution is processed into a rigid crosslinked thermoset in a free radical copolymerization between styrene and the double bonds in the polyester chain.

The crosslinking reaction can be studied by several methods. The gelling of a sample undergoing

curing can be observed by simple tests with a stopwatch.^{1,2} However, many researchers have determined the gel time by rheological measurements.^{3–9} The gel time has been determined either by measuring steady shearing flow properties^{4–9} or by measuring the oscillatory shearing flow properties.^{3,4,8} The steady shearing flow properties only characterize the rheological behavior of materials in the liquid state, whereas the oscillatory shearing flow properties also characterize the rheological properties of a material in both the rubbery and the glassy states.

The restriction of the molecular mobility of unsaturated polyester resins during curing has been investigated by low-resolution nuclear magnetic resonance (NMR) by Bergmann and Demmler¹⁰ and Demmler et al.¹¹ They combined pulse and wide line methods to study the whole curing reaction. They found three kinds of protons: very mo-

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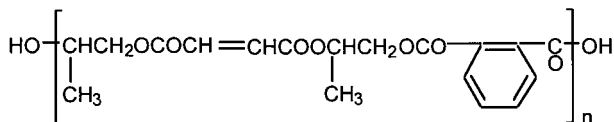


Figure 1 Chemical structure of synthesized unsaturated polyesters.

bile (unpolymerized styrene), less mobile (free polyester polymers), and immobile (cured and glasslike regions).

Low-resolution pulse (LRP)-NMR has mostly been used in medical applications, in oil refineries, in the plastics industry, and especially, in the food industry as a rapid and accurate method. In the food industry, the method was originally developed as a routine method for solid fat content determination of margarines.¹² Today, it is also used to determine solid fat contents in other foods,¹²⁻¹⁴ to monitor the hydrogenation of various oils used in margarines,¹⁵ and to study the states of water during the drying of vegetables.^{16,17}

The aim of this study was to characterize the cure of the resin in more detail by LRP-NMR. In this method, the ¹H-NMR signal, the so-called free induction decay (FID), of the sample is monitored and characterized by the constant T_2 , defined by the exponential decay of the signal $I = I_0 e^{-t/T_2}$ with time. The decay of the FID signal is sensitive to the motion of the molecules, and domains with different mobilities can be distinguished by multicomponent decays having different T_2 values. These T_2 values and the population of each component can be extracted from these decays by fitting the multicomponent decay curves obtained.

EXPERIMENTAL

Materials

Five unsaturated polyester prepolymers with different phthalate/maleate molar ratios were synthesized from maleic anhydride, phthalic anhydride, and 1,2-propylene glycol by melt polycondensation. All monomers were of standard laboratory grade and were used as received. The chemical structure is shown in Figure 1, and the composition is given in Table I. The prepolymers were prepared by a conventional condensation method and carried out under a nitrogen atmosphere. The reaction temperature was 160°C for 5 h, after which the temperature was raised to

220°C for 1 h. The polymerization was ended with a 1-h vacuum (<0.2 bar) to remove residual water and unreacted monomers. The synthesized polyesters were dissolved in neat styrene, right after the completion of the polymerization. Styrene was used without the removal of inhibitors. The crosslinking was initiated by 2 wt % benzoyl peroxide (BPO; Interox BP-50-FT, Germany) at 80°C.

Analysis

The acid numbers of the solid polyesters were determined by a titration method that has been described elsewhere.¹⁸ The molecular mass and molecular mass distribution of polyester molecules were measured by gel permeation chromatography (Waters) with four ultrastayragel columns (10⁴, 10³, 500, and 100 Å pore size) and an refractive index (RI) detector. Tetrahydrofuran (THF) was used as a solvent, and polystyrene standards were used for the calibration.

The molar ratios of the final compositions of the polyesters dissolved in styrene were determined by proton NMR (¹H-NMR), with a Jeol GSX 270. ¹H-NMR was also used to detect the extent of maleate (*cis*) to fumarate (*trans*) isomerization during the melt polycondensation reaction.

The crosslinking was studied by a Society of the Plastic Industry (SPI) standard method.¹⁹ The method is based on changes in electrical conductivity with temperature. A test tube containing polyester dissolved in styrene and initiator (BPO, 2 wt %) is placed in a water bath at 80°C. A thermoelement coupled to a plotter is placed in the middle of the test tube to detect the changes in the temperature of the resin. The gel time is defined as the time for the heat of reaction to rise from 65 to 90°C. The curing time is defined as the time for the heat of reaction to rise from 65°C to the maximum temperature.

In order to analyze the cure of the resin in more detail, we used LRP-NMR. In this type of NMR spectroscopy, relatively weak and inhomogeneous permanent magnets are used and the signal is not transformed from the time domain to the frequency domain, which means that an NMR spectrum is not produced. In this technique, the protons are initially subjected to a constant external magnetic field \mathbf{B}_0 (along the z axis), which causes them to orient either parallel or antiparallel to \mathbf{B}_0 and to precess about that direction at the Larmor frequency. At equilibrium, the spins are according to the Boltzmann distribution spread between the

Table I Composition Determined by $^1\text{H-NMR}$ of Synthesized Polyesters Dissolved in Styrene Before Curing

Resin	MA (mol)	PA (mol)	PG (mol)	<i>cis-trans</i> ^a (%)	Styrene (wt %)	MR
I	0.8	3	4.4	97.5	48	8.5
II	1.6	2	4.4	97.8	44	3.4
III	2.3	1	4.1	97.3	49	2.4
IV (\cong I)	0.9	3	4.2	97.6	43	6.2
V (\cong II)	1.9	2	4.4	97.4	45	3.1

MA, maleic anhydride; PA, phthalic anhydride; PG, 1,2-propylene glycol.

^a *cis-trans* refers to the *cis-trans* isomerization from maleate to fumarate during the melt polycondensation reaction of the polyester.

two corresponding quantum energy levels. The differences in population of these levels give rise to a net magnetization vector \mathbf{M}_0 in the direction of \mathbf{B}_0 , and to get an NMR signal, the system must be perturbed from this equilibrium position, which is done by applying a second magnetic field \mathbf{B}_1 perpendicular to \mathbf{B}_0 . A 90° pulse is the simplest LRP-NMR experiment. The protons are excited by a second magnetic field \mathbf{B}_1 produced by a radio-frequency (rf) pulse along the x axis to rotate \mathbf{M}_0 from the z axis to the y axis. The duration of the rf pulse is only a few microseconds, and the rotation of \mathbf{M}_0 depends on the duration of the pulse. After the rf pulse, the magnetization in the x - y plane can be detected as an FID signal. As the spins return to their equilibrium state, this signal decays in liquids with a characteristic exponential decay constant T_2 . The total number of protons in the sample is proportional to the initial amplitude of the signal, while the magnitude of the decay constant T_2 gives information concerning the mobilities of the protons in the sample. The signal can also consist of protons in different phases, which decay at different rates, in which case, the observed signal is a superposition of many components. The time constant T_2 , at which each component decays, is usually called the spin-spin relaxation time T_2 , and it is short for solid components (microseconds) and long for liquid components (milliseconds to seconds).^{12,20}

The 90° pulse method is only suitable for measuring short T_2 values because the magnet is not homogeneous and the resonance frequency of the protons will vary with their position in the sample. The FID will then decay with an apparent relaxation time T_2^* , which is much shorter than the real one. This incoherence can be avoided by using spin-echo pulse sequences. In this technique, an initial 90° pulse is followed by a 180°

pulse after a delay time τ . After a new delay time τ , a signal echo is formed.

The 180° pulse refocuses the spins that have lost their coherence because of the inhomogeneities in the magnet. The amplitude of the produced echo depends on the proton population and the T_2 .^{20,21} In a Carr-Purcell-Meiboom-Gill (CPMG) pulse sequence, a single 180° pulse is replaced by many equally spaced 180° pulses, and the summit of the spin echoes is measured. This method corrects both inhomogeneities in the magnet and incorrect settings of the 180° pulse.^{20,22}

In our work, short T_2 values were measured directly from the FID after a 90° pulse of $2 \mu\text{s}$ duration with a deadtime of $5 \mu\text{s}$. For long T_2 values, the T_2 was recorded using the CPMG pulse sequence. 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.^{10,11} The populations and T_2 values were plotted with curing time. All experiments were performed on a homebuilt 60-MHz NMR instrument at 80°C .

RESULTS AND DISCUSSION

Characterization of Unsaturated Polyesters

The linear polyesters were characterized by their acid numbers and both their number average ($\langle M_n \rangle$) and weight average ($\langle M_w \rangle$) molecular masses (Table II). All polyesters had acid numbers below 50 mg of KOH/g of sample. The molecular masses ($\langle M_n \rangle$) and ($\langle M_w \rangle$) varied slightly depending on the initially charged monomer composition. Polyesters IV and V were of equivalent

Table II Characterization of Synthesized Unsaturated Polyesters

Polyester	Acid Number ^a	$\langle M_n \rangle^b$ (g/mol)	$\langle M_w \rangle^b$ (g/mol)	$\langle M_w \rangle / \langle M_n \rangle^b$
I	34	1,150	1,750	1.5
II	43	1,300	2,400	1.8
III	23	1,500	4,050	2.7
IV	51	1,200	2,200	1.8
V	38	1,400	2,850	2.0

^a Determined by titration with 0.1N KOH and expressed as mg of KOH/g of sample.

^b Determined by gel permeation chromatography in THF with RI detector.

composition as polyesters I and II but had higher molar masses.

After dissolving in styrene, the compositions of the unsaturated polyesters were determined by ¹H-NMR. The styrene content, the molar ratio of styrene to the double bonds in the polyester chain (MR), and the *cis-trans* isomerization of maleate to fumarate in the polyester chain were determined. These results are summarized in Table I.

As is seen from Table I, the *cis-trans* conversions of maleate to fumarate and the styrene contents are about the same in all five resins. The property that is changing in the resins is the molar ratio of styrene to double bonds in the polyester chain. One may conclude that the polyester molecular chain of resin III has the highest degree of unsaturation per polyester molecular chain. The curing reaction was studied accordingly.

The Curing Reaction

The SPI test is a simple method to determine the gel time (t_{gel}), the curing time (t_{cure}), and the maximum temperature (T_{max}) of the curing reaction. The results are summarized in Table III.

From Tables I and III, we can conclude that the gel time and curing time decrease when the MR decreases. At the same time, the maximum

temperature increases when the MR decreases. These relationships are shown in Figures 2 and 3.

LRP-NMR was used to study the changes in proton mobilities and populations during the curing reaction at 80°C. Three different components were identified: very mobile, less mobile, and immobile ones. The results of the spin-spin relaxation time (T_2) measurements and proton populations are combined in Figures 4 and 5 for polyesters I–III. The results for polyesters IV and V were similar.

The most mobile component ($T_2 \cong 3$ s) corresponds to unpolymerized styrene, the mobility of which decreases during the curing reaction. The less mobile component ($T_2 \cong 150$ ms) corresponds to free polyester polymers, the mobility of which also decreases during the curing reaction. The immobile component ($T_2 \cong 0.04$ ms) corresponds to cured resin and can be identified after the cross-linking has started. These conclusions are based on results by Demmler et al.¹¹ and Bergmann and Demmler.¹⁰

Figures 4 and 5 show that in the beginning of the reaction, there are only two components and the third component can be seen at the gel point. Before the gel point, there is an induction period where it is not possible to see any significant changes in relaxation times. This period is sup-

Table III The Curing Reaction of Unsaturated Polyesters Initiated with 2 wt % BPO at 80°C Studied by an SPI Standard Method and LRP-NMR

Resin	SPI t_{gel} (min)	SPI t_{cure} (min)	SPI T_{max} (°C)	LRP-NMR t_{gel} (min)
I	13	17	94	18
II	4	5	170	6
III	2.5	3.5	235	3
IV	7	9.5	118	8
V	3	4	198	4

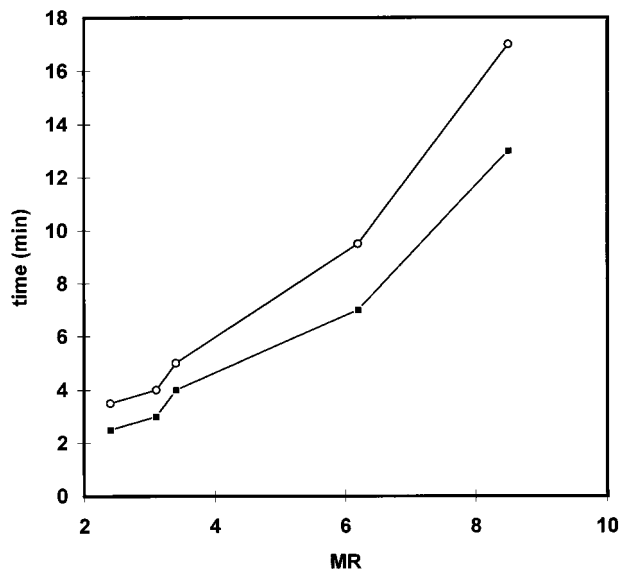


Figure 2 Gel times (closed squares) and curing times (open circles) of unsaturated polyesters with different MR of styrene to double bonds in the polyester chain measured by an SPI standard method. The crosslinking reaction was initiated with 2 wt % BPO at 80°C.

posed to depend on the inhibitors in styrene. At the end of the crosslinking reaction, there are still two components to the FID and the longer T_2 com-

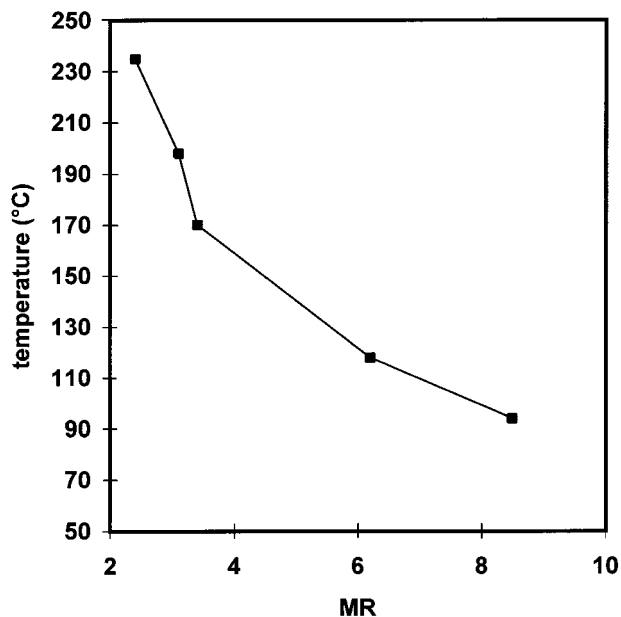


Figure 3 Maximum temperature of curing reactions of unsaturated polyesters with different MR of styrene to double bonds in the polyester chain measured by an SPI standard method. The crosslinking reaction was initiated with 2 wt % BPO at 80°C.

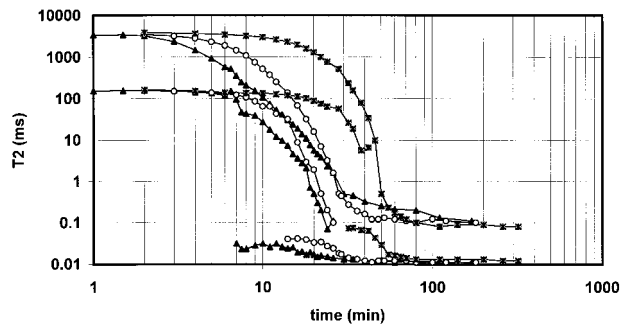


Figure 4 Spin-spin relaxation times of resins (■) I, (○) II, and (▲) III cured with 2 wt % BPO at 80°C. Three components can be detected: $T_2 \cong 3$ s corresponds to unpolymerized styrene, $T_2 \cong 150$ ms corresponds to free polyester polymers, and $T_2 \cong 0.04$ ms corresponds to cured resin.

ponent is assumed to belong to unreacted styrene or regions of uncrosslinked polyester chains.

When the spin-spin relaxation time measurements are compared with the population measurements, one can see that the immobile component is detected earlier in the population measurements. This is because it was difficult to accurately simulate the T_2 decay when this component was very small, at the beginning of the curing reaction. Protons belonging to the cured resin could be detected when their populations reached 6–9%. If the gel time is defined as the time when this component shows, the gel time is a little longer with this method compared with the standard method. The results are compared in Table III. The LRP-NMR measurements were carried out with rather long time intervals during the initial curing of the resin but nonetheless gave

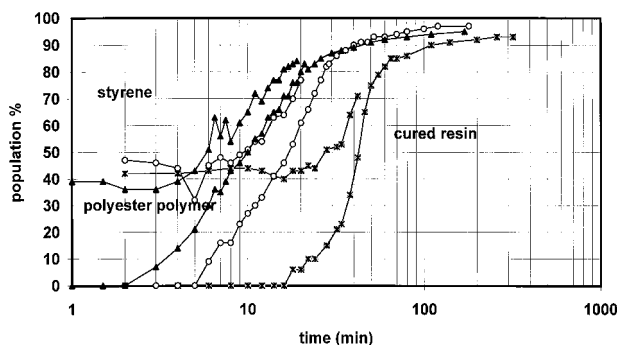


Figure 5 Differences in proton populations of the three components of resins (■) I, (○) II, and (▲) III cured with 2 wt % BPO at 80°C. Unpolymerized styrene and free polyester polymer can be seen in the beginning of the reaction. At the gel point, the formation of cured polyester resin can be seen.

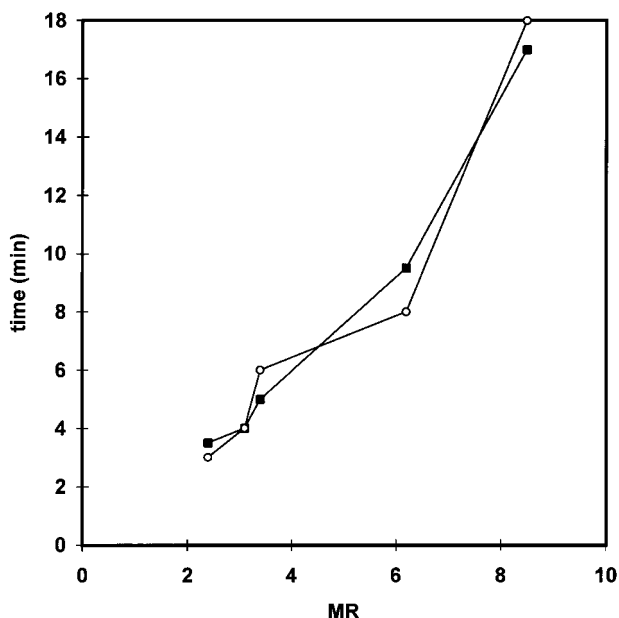


Figure 6 Comparison of (■) curing times measured by the SPI standard method and (○) gel times measured by LRP-NMR.

comparable results. The gel times measured by LRP-NMR were also compared with the curing times measured by the standard method. As one can see in Figure 6, the agreement was even better here.

In the beginning of the reaction, the spin–spin relaxation times are constant for the two mobile components. The crosslinking could not be detected yet. The immobile component is detected shortly after a decrease in the relaxation times for the mobile components. The crosslinking is assumed to begin at the same time, when the mobile components lose their mobilities. The point at which the less mobile component, free polyester polymers, disappears probably occurs later than is indicated on the graphs. This is because this component is difficult to separate out when the population goes below about 10%. We notice that styrene and polyester polymers are losing their mobilities during the crosslinking, and as a result, a very rigid cured resin is formed. At the end of the curing reaction, a more mobile component is left, probably unreacted styrene that has been included in the network pores.

When the molar ratios of styrene to the double bonds in the polyester chain are compared with the results of the spin–spin relaxation time measurements in Figure 4, it is seen that the mobile components start to lose their mobilities earlier when the molar ratio is lower. This correlates well

with the gel time results. Figure 5 shows that in the beginning, there are two components and less than half of the protons belong to the polyester polymers. In the beginning, the populations are quite constant, as are the spin–spin relaxation times. The population of the immobile component is increasing at the same time as the mobile components are losing their mobilities (Fig. 4). The increase in proton populations starts earlier when the molar ratio of styrene to double bonds in the polyester chain is lower. When the resins are compared after 100 min, the proton populations of the cured resins are between 93 and 96%, except for resin I, which has a very high molar ratio. The rest is probably unreacted styrene.

CONCLUSIONS

Five unsaturated polyester resins with about the same molecular masses and isomerization of maleate to fumarate but different amounts of unsaturation were characterized by their curing reactions. It was observed that the curing reaction depends on the molar ratio of styrene to the double bonds in the polyester chain. The *cis*–*trans* conversions were very high, 97.3–97.8%. This isomerization is desirable because fumarate (*trans*) has greater reactivity and results in higher tensile strengths, hardness values, and better chemical resistance than maleate (*cis*) when cured. The high *cis*–*trans* conversions are also in good agreement with the fact that aromatic dibasic acids, such as phthalic anhydride, and sterically hindered or low-reactivity glycols, such as 1,2-propylene glycol, enhance *cis*–*trans* conversion.¹⁸

The gel times were determined by two methods (SPI and LRP-NMR), which gave values of 13, 4, 2.5, 7, and 3 min for resins I, II, III, IV, and V measured by the SPI method and gave values of 18, 6, 3, 8, and 4 min as measured by the LRP-NMR. As one can see, these results are in good agreement with each other. The agreement was even better when the gel time results from LRP-NMR measurements were compared with the curing times (17, 5, 3.5, 9.5, and 4 min) determined by the SPI method. According to this, the gel times are decreasing when the molar ratio of styrene to double bonds in the polyester chain is decreasing, the molar ratio being 8.5, 3.4, 2.4, 6.2, and 3.1 for resins I, II, III, IV, and V. The maximum temperature of the reaction was decreasing when the molar ratio of styrene to the double bonds in the

polyester chain was increased, being 235°C at molar ratio 2.4 and 94°C at molar ratio 8.5.

The characterization of the curing reaction by LRP-NMR shows that the crosslinking reaction consists of at least three components: styrene (very mobile component), free polyester polymers (less mobile), and cured resin (immobile). In the beginning of the reaction, there is an induction period depending on the inhibited styrene, and the spin-spin relaxation times and proton populations of the mobile components are held rather constant. When the copolymerization begins and we can detect the third component, cured resin, the proton mobilities of styrene and polyester molecules rapidly decrease, after which the proton populations of the cured resin start to increase.

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