A Solid-State ^{13}C Nuclear Magnetic Resonance Study of Cured, Unsaturated Polyester Resins

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ABSTRACT: The styrene sequence distributions and amount of reacted fumarate units in cured, unsaturated polyester resins were studied by solid-state ^{13}C nuclear magnetic resonance. Increasing the styrene content and molar ratio of styrene to the double bonds in the polyester chain increased the amount of diad and n-ad sequences and decreased the amount of monad sequences. At the same time, the amount of reacted fumarate units increased. The glass transition temperature was almost constant for resins with the same composition but different styrene contents. Changing the composition affected the glass transition temperature, which could not be detected for highly crosslinked resins. The mechanical properties were improved with increasing styrene content. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 73: 563–571, 1999

Key words: unsaturated polyester; styrene content; solid-state ^{13}C-NMR; styrene sequence

INTRODUCTION

Unsaturated polyester resins are commonly used in fiber-reinforced composites as matrix resins. The resin is composed of an unsaturated polyester, which is dissolved in styrene. During the processing, the double bonds in the polyester react with the styrene monomer in a free radical copolymerization reaction, which gives a crosslinked network.

The composition of cured unsaturated polyesters has been studied by both liquid and solid-state ^{13}C nuclear magnetic resonance (^{13}C-NMR), and infrared (IR) spectroscopy.[1–9] In liquid ^{13}C-NMR, the cured polyester is hydrolyzed with po-tassium hydroxide (KOH) in an alcohol to a poly-(carboxylic acid) and then esterified with diazo-methane.[1–3] Birley et al.[1] studied the sequence distribution of styrene bridges by making copolymer standards of styrene and diethyl fumarate. They were able to separate monad, diad, and n-ad sequences of styrene from each other. This was possible because the quaternary carbon in styrene gave different resonances, depending on its local environment. ^{13}C-NMR of the hydrolysis products have shown a dependence between the styrene content and the length of the styrene bridges. Increasing the styrene content increases the number of styrene units in a bridge. When the molar ratio of styrene to the double bonds in the polyester chain was about 1 (MR ≈ 1), the number of FSF ≈ SSF ≈ FSS + SSS.[2]

In solid-state ^{13}C-NMR, the cross polarization (CP) and magic angle spinning (MAS) techniques have been used to study the crosslinked resin

directly.[4–9] The advantage in these measurements is that the cured resin is ground to a powder and examined as such. A disadvantage is that there can be some problems with overlapping peaks. Solid-state CP–MAS ^{13}C-NMR measurements have shown that diad distribution is predominant when the MR is below 1, and n-ad distributions dominate when the MR is above 1.[4] Besides the classical techniques of CP–MAS and proton dipolar decoupling (DD), interrupted decoupling has been used.[5] The advantage with this technique is that it suppresses the peaks of CH and CH_2 groups, and only quaternary C and CH_3 groups are detected. The amount of residual unsaturation has been estimated with solid-state ^{13}C-NMR. Peaks of carboxylic carbons (C=O) from fumarate units give different resonances, depending on their local environment. Carboxylic groups in a saturated structure have a resonance at 172 ppm, and those in an unsaturated structure have a resonance at 165 ppm.[4–7] From the measurements, it can be concluded that very high styrene contents were needed to avoid residual unsaturation in the cured resin. Amounts near 50 wt % have been reported.[5] In other measurements, there has been residual unsaturation, even at a styrene content as high as 60 wt %.[7]

Spin–lattice relaxation times in the laboratory and rotating frames for protons (T_1^H and $T_{1\rho}^H$)[7] and in the rotating frame for carbons ($T_{1\rho}^C$)[8] have been measured to study the influence of styrene content and curing temperature on the structure of the crosslinked resin. The measurements in the rotating frame show that $T_{1\rho}$ will go through a maximum when measured as a function of temperature. At the temperature at which $T_{1\rho}$ gets its maximum value, the crosslinking reaction is more complete, and the network is more tightly bonded.

Eisenberg et al.[10] have recently studied the influence of the styrene content on the glass transition temperature (T_g) by thermal mechanical analysis. They showed that T_g of the cured resin increased when the MR increased. In their experiments, they used MR = 2–5. Earlier studies of T_g of the cured product (MR = 1.27–15) have also given different results. A maximum value of T_g of the cured resin has been obtained when the MR was between 2 and 3.[11]

The aim of this work was to study the influence of styrene content on the length of styrene sequences in a cured unsaturated polyester resin and to estimate the amount of unreacted double bonds in a cured polyester. Besides the sequence length, we were interested to see if the styrene content influences the glass transition temperature and the mechanical properties of the cured resins. These relationships are important to understand when developing new polyester resins with enhanced properties. This investigation was done by solid-state ^{13}C-NMR. The analysis is rather straightforward to perform, and only a very small amount of sample is needed, which is an advantage. The thermal properties were studied by thermal analysis, and the mechanical properties were measured with tensile strength testing.

EXPERIMENTAL

Materials

Four unsaturated polyester prepolymers with about the same phthalate/maleate molar ratios were synthesized from maleic anhydride (MA), phthalic anhydride (PA), and propylene glycol (PG) by melt polycondensation, as described earlier.[12] Additionally, one polyester prepolymer was synthesized from MA, PA, and 1,6-hexane diol (HG), and another was made from only propylene glycol and maleic anhydride. All monomers were of standard laboratory grade and were used as received. The prepolymers were dissolved in different amounts of neat styrene to form unsaturated polyester resins (**1–6**). Styrene was used without removal of inhibitors.

Chemical Characterization

The number-average and weight-average molecular masses and molecular mass distributions (MWD) of the polyesters were measured by gel permeation chromatography (GPC) using a Waters 510 HPLC Pump. Three styragel columns with pore size 500, 10^4, and 10^5 Å and a refractive index (RI) detector were used. Tetrahydrofuran (THF) was used as a solvent, and calibration was made with ten polystyrene standards.

The molar ratios (MR) of styrene to the double bonds in the unsaturated polyester and the final compositions of the resins were determined by proton nuclear magnetic resonance (^{1}H-NMR) using a 400-MHz CMX Infinity NMR instrument. ^{1}H-NMR was also used to estimate the extent of maleate (cis) to fumarate (trans) isomerization, which had occurred during the melt polycondensation.

Table I   Chemical Characterization of Studied Unsaturated Polyester Resins

Resin	MA : PA : PG[a]	MR[a]	Styrene[b] (Wt %)	Styrene[c] (Wt %)	$\langle M_n \rangle$[d] (g/mol)	$\langle M_w \rangle$[d] (g/mol)	MWD[d]
1	0.8 : 3 : 4.1	3.4	26	26	1120	2260	2.0
2	0.8 : 3 : 4.2	3.6	30	27	1100	2240	2.0
3	0.8 : 3 : 4.0	4.7	36	33	1190	2490	2.1
4	0.8 : 3 : 4.4	5.7	40	38	1040	2020	1.9
5	0.9 : 3 : 5.1[e]	5.9	40	35	1600	3610	2.2
6	1 : 1.7[f]	1.4	40	43	1580	3530	2.2

[a] Molar ratios determined by ^{1}H-NMR.
[b] Styrene content determined by evaporation.
[c] Styrene content determined by ^{1}H-NMR.
[d] Determined by GPC.
[e] MA : PA : HG.
[f] MA : PG.

The styrene contents of the polyester resins were determined by an evaporation method described previously.[13] These values were also compared with styrene contents calculated from the ^{1}H-NMR measurements.

Thermal Analysis

The glass transition temperature (T_g) and the residual reactivity of the cured resins were determined by a Mettler DSC30 instrument. About 5 to 10 mg of sample was put in an aluminium crucible and sealed with a perforated lid. The samples were heated from -100 to $250°C$, then rapidly cooled to $-100°C$, then reheated from -100 to $250°C$. The heating rate was $10°C/min$, and the analysis were done under a nitrogen atmosphere. The glass transition temperature was detected from the second heating, and the residual reactivity was detected from the first heating.

Solid-State ^{13}C Nuclear Magnetic Resonance

The length of styrene sequences and the amount of unreacted fumarate units were estimated by solid-state ^{13}C-NMR. A 270-MHz CMX Infinity NMR spectrometer was used both for conventional CP–MAS measurements and for interrupted decoupling measurements. In both experiments, a spinning speed of 5 kHz and a radio frequency (rf) field of 62 kHz were used. The recycling time (pulse delay) was 5 s, and the contact time was 2 ms. The number of transients (scans) was between 10,000 and 15,000. In the interrupted decoupling experiments, the dipolar dephasing delay was 50 μs.

Mechanical Properties

For the mechanical testing, 4-mm-thick castings were made from resins **2–4** and **6.** The resin was mixed with 1 wt % MEKP and 1 wt % cobalt octoate solution in styrene and poured into a mold (200 × 300 mm) of metal frames placed on a glass plate. Excess resin was removed by a blade, and a glass plate was placed on top. The castings were allowed to cure for 24 h at room temperature, postcured at 50°C for 24 h, and cut into dumbbell-shaped (100 × 10 × 4 mm) specimens. The specimens were tested in an Instron 1175 tensile strength testing machine equipped with a 5-kN load cell. The draw ratio was 2.0 mm/min. The maximum tensile strength, elasticity constant (Young's modulus), and elongation at break were measured.

RESULTS AND DISCUSSION

Chemical Composition

The chemical composition of the studied polyester resins **1–6** is shown in Table I. Resins **1–4** have almost the same ratio of MA : PA : PG and the same molecular masses and distributions. The only difference is the styrene content and the resins, therefore, have different molar ratios (MR) of styrene to the double bonds in the polyester chain. Resins **5** and **6** have higher molecular masses and broader distributions than the other resins. The cis–trans isomerization of maleate to fumarate was also determined. Resins **1–4** had 96–97% of the maleate isomerized to fumarate,

Table II   Thermal Analysis of Cured Unsaturated Polyester Resins

Cured Resin	Styrene (Wt %)	T_g (°C)	ΔH_{res} (J/g)
1	26	47	22
2	30	46	30
3	36	45	47
4[a]	40	46	33
4a[b]	50	56	50
4b[c]	50	51	28
5	40	−9	29
6	40	—	59

[a] Resin **4** was also diluted to 50 wt % styrene and analyzed before and after postcuring.
[b] **4a** was measured before postcuring.
[c] **4b** was measured after postcuring.

whereas the degree of isomerization was 45% for resin **5** and 94% for resin **6.** The low degree of isomerization of resin **5** depends on the flexible glycol 1,6-hexane diol in the resin. Glycols with long and flexible chains, such as 1,6-hexane diol, have shown to give decreased isomerization. It has also been observed that aromatic acids or anhydrides enhance the degree of cis–trans isomerization.[14] Consequently, the lack of aromatic groups in resin **6** causes a slightly lower degree of isomerization. The styrene content was determined by gravimetric evaporation and by ^{1}H-NMR. The results from ^{1}H-NMR measurements are calculations where the molar fractions of fumarate, phthalic anhydride, propylene glycol, and styrene are converted to masses using their assumed molecular masses in the polymer chain ignoring any end groups. There are several calculation steps, and possible calculation errors from each step are added to the final step. The final error is therefore expected to be larger than in the evaporation method. The styrene contents measured by evaporation are therefore more accurate and used in the rest of the text. However, the two methods give results within 5 wt %. Both methods are therefore suitable to estimate the styrene content.
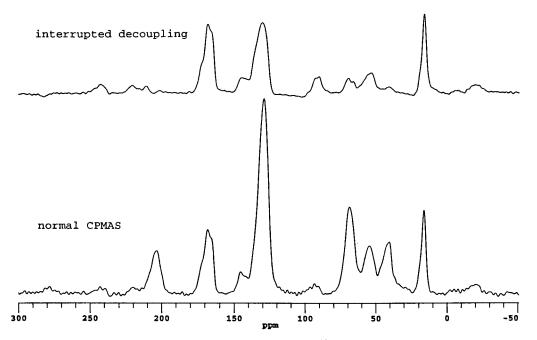
Glass Transition Temperature in the Cured Resin

The results of the thermal analysis are shown in Table II. Resin **4** was also diluted to 50 wt % styrene and analyzed before and after postcuring. The T_g is around 46°C for the polyesters **1–4** when the styrene content is up to 40 wt %. The

styrene content does not have a significant influence on T_g when the polyester composition is the same. The T_g increased slightly when the styrene content increased to 50 wt % (**4b**). When the resin with 50 wt % styrene was compared before and after postcuring, a decrease in T_g could be seen after post curing. Resin **5** had a much lower T_g than the other resins, which is due to the very flexible glycol 1,6-hexane diol. For resin **6,** made from only maleic anhydride and propylene glycol, no T_g could be detected. The obvious reason is that this highly crosslinked polyester has no T_g, as there are no motions of extensive segments of the main chain. The residual reactivities (ΔH_{res}) were also measured, and they were around 20–60 J/g. The residual reactivity decreases after postcuring, as is expected. The residual reactivity was highest for the very reactive resin made from only maleic anhydride and propylene glycol. The styrene content did not influence on the residual reactivity.
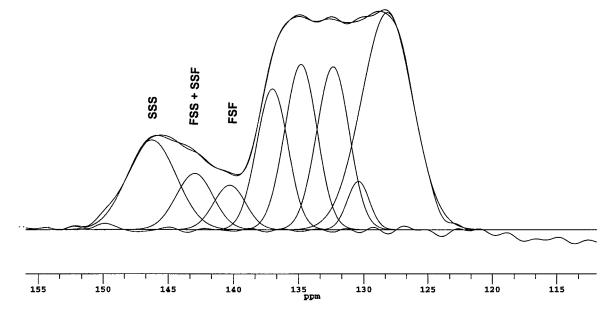
Solid-State ^{13}C-NMR Study of Cured Unsaturated Polyester Resins

Figure 1 shows the difference between a normal CP–MAS ^{13}C-NMR spectrum and an interrupted decoupling NMR spectrum. As can be seen, the intensity of the proton-bearing carbons is much reduced in the interrupted decoupled experiment. The interrupted decoupling method was used for the deconvolution of the peaks around 120–150 ppm to estimate the length of styrene sequences between polyester chains and 160–180 ppm to estimate the amount of unreacted fumarate units present. The deconvolutions are shown in Figures 2 and 3. Three peaks in the 139–150 ppm area have been fitted, presumably corresponding to the four sequences showed by Birley et al.[1] (see Fig. 4 and Table III). The simulation of the peaks was in our experiment done only into three components, combining FSS and SSF to one component, because fitting to four components did not give any improved fit. The chemical shifts in our experiments were somewhat higher than in the liquid state experiments[1] by 0.5–3.9 ppm. The differences between the liquid and solid-state NMR chemical shifts must reflect intermolecular interactions. However, there are also peaks very close to the quaternary styrene carbon which overlap. These peaks come from the other styrene carbons and, more importantly, from the phthalate carbons of the aromatic ring. To try to reduce the effect of these peaks, interrupted decoupling was used. This effectively removes all carbons
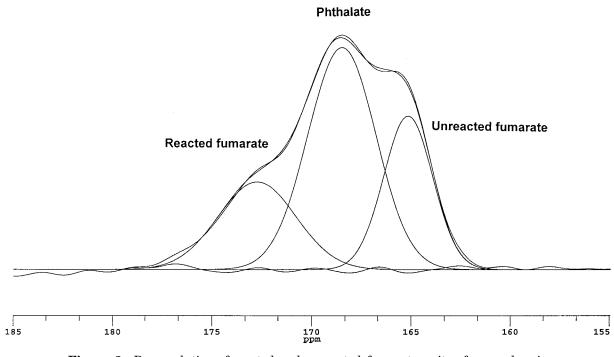
Figure 1 Differences between a normal CP–MAS ^{13}C-NMR spectrum and an interrupted decoupling ^{13}C-NMR spectrum. The reduction of the intensity of the proton-bearing carbons can be observed in the interrupted decoupling ^{13}C-NMR spectrum.

that have a proton attached to them, thus simplifying the spectrum somewhat. It is not totally effective because there are peaks from quaternary carbons of the phthalate unit, which also survive this treatment and can be seen in the spectra.

Figure 3 shows the deconvolution of the carbonyl carbon in the fumarate unit in an unsaturated and a saturated structure. The unreacted fumarate units give a carbonyl chemical shift around 165 ppm, while the reacted fumarate
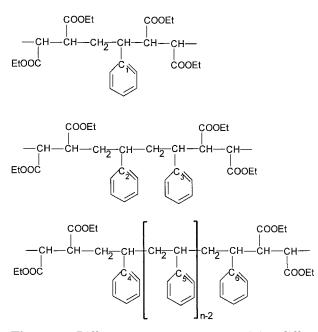

Figure 2 Deconvolution of the FSF, FSS + SSF, and SSS sequence peaks of a cured resin measured by solid-state, interrupted-decoupling ^{13}C-NMR.

Figure 3 Deconvolution of reacted and unreacted fumarate units of a cured resin measured by solid-state, interrupted-decoupling ^{13}C-NMR.

units give a shift around 173 ppm. The same problem with overlapping peaks arises with the carbonyl area since the two peaks due to the

Figure 4 Different styrene sequences, giving different resonances for the quaternary carbon in styrene in ^{13}C-NMR experiments. The chemical shifts are shown in Table III.[1]

reacted and unreacted fumarate units overlap with the carbonyl peaks from the phthalate units. For all cured resins, the fitting has been done with about the same line widths and chemical shifts, so the results are consistent. The results of the deconvolutions are summarized in Table IV.

As can be observed in Table IV, the sequence lengths of styrene increase with increasing styrene content and MR. This is in agreement with results obtained previously.[2–4] The amount of monad distribution (FSF) increased when the styrene content decreased. The diad and n-ad distributions (FSS, SSF, and SSS), on the contrary, increased with increasing styrene content. The amount of unreacted fumarate units was quite high. In the resins with 26 and 30 wt % styrene, less than half of the double bonds in the polyester chain had reacted. One explanation could be that there is not enough free styrene present to react with the fumarate units. However, these resins are very loosely crosslinked when considering that the ratio of MA : PA was about 0.8 : 3 and over the half of the fumarate units are unreacted. Increasing the styrene content to 40 wt % styrene decreases the amount of unreacted fumarate units. As a consequence, the crosslink density should increase when there are more reacted double bonds in the polyester chain and the same

Table III   Resonances of Quaternary Phenyl Carbons in Styrene Sequences

Quaternary Phenyl Carbons	Sequence[a]	Chemical Shift (ppm) Liquid State[1]	Chemical Shift (ppm) Solid State[b]
C_1	monad (FSF)	137.5	140.4
$C_3 + C_6$	diad + n-ad (SSF)	139.1	143.0
$C_2 + C_4$	diad + n-ad (FSS)	142.5	143.0
C_5	n-ad (SSS)	144.0	146.3

[a] F is fumarate and S is styrene
[b] Values are taken from Figure 2.

ratio of MA and PA. On the other hand, T_g should increase with increasing crosslink density, which is not seen in Table II. The resin with 50 wt % styrene was measured before and after postcuring. No significant changes could be seen in the sequence distributions, but the amount of reacted fumarate units increased after postcuring. Resin **5** has comparable sequences with resin **4,** which has the same styrene content. These two resins only differ in the type of glycol used. We can conclude that the glycol used does not influence the length of styrene sequences significantly. For resin **5,** it was not possible to distinguish the peaks from reacted and unreacted fumarate. Resin **6,** which was made from only maleic anhydride and propylene glycol, showed different sequence distributions compared with the other resins. There was approximately equal amounts of FSS, FSS + SSF, and SSS distributions. This implies that resin **6** has much more monad sequences than the other resins. This could be due to the low MR compared with the other resins. The crosslink density is very high for this resin

because no T_g was possible to detect. Taking the amount of reacted double bonds in the polyester as an indicator of the crosslink density, the results are in accordance with the T_g results for resin **6.**

Mechanical Properties of the Cured Resins

The results of the mechanical testing of the cured resins are in Table V. It was not possible to make test species of resins **1** and **5.** Resin **1** cured too fast due to the low styrene content and could not be casted. Resin **5** gave too soft species due to the glycol (1,6-hexane diol) used. Resin **2,** which had the lowest styrene content (30 wt %) of the tested resins, showed much lower mechanical strength than the other resins. The elongation was also much lower. Resins **3** and **4** did not differ much in their mechanical properties, even if the properties were more optimal for resin **3** with 35 wt % styrene. Resin **6** was the most elastic resin due to the lack of any aromatic groups in the polyester composition. The strength properties of resin **6** were

Table IV   Styrene Sequences in Cured Unsaturated Polyester Resins and the Amount of Reacted Fumarate Units

Cured Resin	Styrene (Wt %)	MR	FSF (%)	FSS + SSF (%)	SSS (%)	Reacted Fumarate (%)
1	26	3.4	18	26	56	47
2	30	3.6	17	24	59	49
3	36	4.7	16	19	65	53
4	40	5.7	12	20	68	58
4a	50	ND	9	19	72	52
4b	50	ND	7	22	70	56
5	40	5.9	15	21	64	—
6	40	1.4	30	34	36	69

ND means "not determined."
4a was measured before postcuring.
4b was measured after postcuring.

Table V Mechanical Properties of Cured Unsaturated Polyester Resins

Cured Resin	Tensile Strength (MPa)	Elasticity Constant (MPa)	Elongation at Break (%)
2	13.8	5318	0.28
3	28.9	4262	0.71
4	24.9	4403	0.65
6	24.5	2805	0.97

similar to resin **4,** which had the same styrene content. The elasticity constant or Young's modulus decreased with increasing styrene content from 30 to 36 or 40 wt %. The most elastic resin **6** had much lower Young's modulus than the other studied resins. However, when comparing the mechanical properties with the sequence distributions and the amount of reacted fumarate units, the following observations are possible to make: the mechanical properties are improved when the amount of reacted fumarate units increase; at the same time, shorter lengths of styrene sequences give longer elongation at break.

CONCLUSIONS

Four unsaturated polyesters were synthesized with the same composition differing only in the styrene content. Two other unsaturated polyesters were also synthesized, one in which the glycol was changed to a glycol with longer and more flexible chain and one without any aromatic groups in the structure. All polyesters were diluted in different amounts of styrene. The cis–trans isomerization was very high for resins made from MA, PA, and PG. The degree of isomerization decreased in the resin without any aromatic groups and was very low for the resin made from HG, which is a glycol with a long and flexible chain compared with propylene glycol.

The glass transition temperature was almost equal for the resins with the same composition up to 40 wt % styrene. At a higher styrene content, the glass transition temperature increased. The glass transition temperature before postcuring was higher than after postcuring. The resin made from 1,6-hexane diol had much lower glass transition temperature than the other resins due to the more flexible glycol used. For the resin made from only MA and PG, no glass transition temperature could be measured due to the high crosslink density. The residual reactivity did not depend on the styrene content. After postcuring at 50°C, the residual reactivity decreased compared with the resin cured only at room temperature.

In the solid-state ^{13}C-NMR experiments, it could be observed that the length of styrene sequences increased with increasing styrene content and MR. At the same time, the amount of unreacted double bonds in the polyester chain decreased. This would mean that increasing the styrene content increases the crosslink density. When measuring the resin with 50 wt % before and after postcuring, no significant changes in the lengths of the styrene sequences could be seen. The amount of reacted fumarate units increased after postcuring. The type of glycol used did not influence the sequence lengths. The resin without any aromatic groups, causing low MR, had more monad sequences than resins containing aromatic groups and having higher MR. In very densely crosslinked resins, the amount of reacted fumarate units was much higher than in loosely crosslinked resins.

The mechanical properties improved with increasing styrene content. The strengths of the cured resin and elongation at break increased clearly when increasing the styrene content from 30 to 36 wt %. The resin made from only MA anhydride and PG had about the same tensile strength properties as the resin with aromatic groups at a styrene content of 40 wt %. The elasticity properties were much better for the resin without any aromatic groups.

This work showed that solid-state ^{13}C-NMR measurements are very useful for studying the structure of the cured resin. It gives information about the crosslink density and amount of double bonds that are involved in the free radical copolymerization reaction between styrene monomers and polyester double bonds. This information is very important when developing new polyester resins.

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