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^{13}C NMR Analysis of the Polymer Microstructure of a Cured Bis(maleimide)-Styrene Thermoset Resin

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ABSTRACT: In this paper, we describe the analysis of the polymer microstructure of a cured Desbimid-styrene thermosetting resin. Desbimid consists of a number of compounds with the diphenylmethane skeleton and two maleimide, isomaleimide, or acetamide end groups, of which the maleimide group is the most abundant one. This mixture also contains maleic anhydride. The microstructure of the cured material was studied by means of ^{13}C NMR CP-MAS spectroscopy with the help of soluble model polymers. *N-p*-Tolylmaleimide, *N-p*-tolylisomaleimide, and maleic anhydride were copolymerized with styrene up to high conversion. The ^{13}C NMR spectrum of the *N-p*-tolylmaleimide-styrene copolymer (monomer feed ratio 0.4:0.6) provides us with evidence for a strong tendency to form alternating copolymers, inasmuch as all styrene units belong to the alternating MSM (M = maleimide, S = styrene) triad fragments. A copolymerization study with *N*-methylmaleimide and styrene, varying the monomer feed ratio from 0.2 to 0.8, sustains this conclusion. In the case of *N-p*-tolylisomaleimide and maleic anhydride 60-80% of the total amount of all styrene monomer units is incorporated into the MSM (M = isomaleimide or maleic anhydride, S = styrene) triad fragments. The combined results indicate that in the thermosetting system alternating copolymers are also formed.

Introduction

In the field of advanced polymeric composites for structural applications a variety of thermoset resins is being used, among which epoxy resins are the leading systems. Bis(maleimides) (BMI) receive considerable attention due to the combination of dimensional stability at elevated temperatures and intrinsic FST (flame-smoke-toxicity) properties.[1]

We have developed a BMI system, Desbimid, which can be dissolved in styrene and subsequently processed by means of resin transfer molding, filament winding, or prepregging.[2] A ^{1}H NMR analysis revealed that this thermoset consists of a large number of compounds with the diphenylmethane backbone and several groups attached: maleimide, isomaleimide, and acetamide. It also contains 15% of maleic anhydride (Figure 1).[3] The molar ratio of maleimide:isomaleimide:maleic anhydride amounts to 68:20:12, implying that the maleimide moiety is by far the most abundant reactive group.

Polymerization of a homogeneous mixture of 66 wt % Desbimid and 34 wt % styrene in the presence of methyl isobutyl ketone peroxide at room temperature, 70 °C, 130 °C, and 200 °C afforded an insoluble, hard material.[2] Dynamic mechanical analysis in a temperature range between -50 and +300 °C showed only one broad maximum in the tan δ curve at 260 °C due to the glass transition temperature. No maximum could be found in the area around 100 °C, which suggests the absence of poly(styrene). This result triggered our interest in the polymer microstructure.

One of the few techniques to study the molecular structure of insoluble polymers is ^{13}C NMR CP-MAS spectroscopy. However, the moderate resolution of solid-state spectra as compared to solution spectra hinders a detailed analysis. An additional problem is the complex nature of Desbimid. Both limitations prompted us to prepare model copolymers in solution before interpreting the actual solid-state spectrum. *N-p*-tolylmaleimide, *N-p*-tolylisomaleimide, and maleic anhydride were chosen to represent the reactive sites of Desbimid.[4] These monomers and styrene were polymerized to high conversion in order to mimic the cure of the Desbimid-styrene formulation.

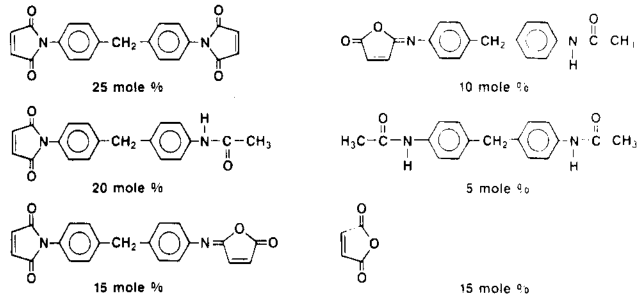

Figure 1. Main components of Desbimid.

Kinetic studies of the copolymerization of N-substituted aromatic maleimides and isomaleimides with styrene to low conversion are known from the literature.[5,6] The experimentally obtained reactivity ratios point to a pronounced tendency to form alternating copolymers. Only in the case of maleic anhydride and styrene have kinetic and structural studies been combined to give a full picture of the polymerization behavior.[7,8]

Experimental Section

Maleic anhydride (MA) (Baker), styrene (St) (Janssen), azoisobutyronitrile (AIBN) (Riedel-de Haen), acetone-d_6 (Merck), *N*-methylmaleimide (NMM) (Aldrich), chloroform-d_1 ($CDCl_3$) (Janssen), dimethyl sulfoxide-d_6 (DMSO-d_6) (Aldrich), toluene (Merck), tetrahydrofuran (THF) (Baker), methanol (Riedel-de Haen), and dioxane (Merck) were used without purification.

Desbimid, *N-p*-tolylmaleimide (NpTMI), *N-p*-tolylisomaleimide (NpTIMI), and *N*-phenylmaleimide (NPMI) were prepared according to published procedures.[2,9,10]

All copolymerizations of NpTMI, NPMI, NpTIMI, MA, and styrene were performed in the same way. The following procedure serves as an example. A mixture of 15.0 g (0.08 mol) of NpTMI, 12.5 g (0.12 mol) of styrene, 0.8 g (4.8 mmol) of AIBN, and 40 mL of toluene was stirred under a nitrogen atmosphere for 3 h at 70 °C. During the polymerization a white solid precipitated.

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Repeated precipitation of the crude product from THF into methanol and subsequent drying in vacuo gave the pure copolymer. Yield: 19.1 g (69 wt %). In the case of NMM and styrene, copolymerizations were carried out up to low conversion using dioxane as the solvent.

^{1}H NMR spectra of the NMM–St copolymers were recorded on a Bruker AC 200 spectrometer at 298 K using $CDCl_3$ as the solvent and locking agent. Generally, the spectra were obtained by using a flip angle of 45°, an acquisition time of 3 s, and a sweep width of 4000 Hz. Spectra were obtained after accumulating 64 scans, using a sample concentration of approximately 1%.

^{13}C NMR spectra of the monomers NpTMI and NpTIMI were recorded in DMSO-d_6 at 298 K with a 400-MHz (Bruker AM 400) spectrometer. All ^{13}C NMR spectra of co-, ter- and quaterpolymers, except NMM–St, were recorded with a 400-MHz Bruker AM 400 spectrometer. The copolymers NpTMI–St, NpTIMI–St, and MA–St and the terpolymer NpTMI–NpTIMI–St were dissolved in acetone-d_6, whereas DMSO-d_6 was used in the case of the remaining terpolymer NpTMI–MA–St and the quaterpolymer NpTMI–NpTIMI–MA–St. Generally, the ^{13}C NMR spectra of the polymers were recorded at 100 MHz and 298 K. The sample concentration was 40% (w/v). Spectra were obtained by using WALTZ-16 ^{1}H decoupling and a pulse delay of 5 s, accumulating 1000 scans with a digital resolution of 0.4 Hz/point, corresponding to a spectral width of 25 000 Hz and a data length of 64K. The flip angle and the acquisition time were 45° and 13 s, respectively.

Monomer sequence placements were determined by comparing relative peak areas of the carbon atoms involved. In performing quantitative NMR measurements, one must take into account differences in nuclear Overhauser effects (NOE) and spin–lattice relaxation times (T_1). No NOE or T_1 values have been determined, but the results of our quantitative approach (vide infra) were compared with the results of an elemental analysis of nitrogen. Good mutual comparison has been obtained (see Discussion). Only mutual comparison of either nonproton-bearing carbons and proton-bearing carbons has been used. Implicitly, we assumed that no differential T_1 effects are present for different stereoisomeric triads (e.g. mm, mr, and rr) or compositional triads, like SSS, SSM, and MSM, or dyads. No differential ^{1}H NOEs were considered to occur. Within these limits peak areas are proportional to the number of carbons involved (cf. discussion of carbonyl and quarternary aromatic carbon signals in the systems St–MA and St–NpTMI). Peak areas were determined via electronic integration methods or planimeter methods.

^{13}C NMR spectra of the NMM–St copolymers were recorded at 75 MHz with a 300-MHz NMR spectrometer (Varian Unity 300), using $CDCl_3$ as the solvent. Typical experimental parameters are flip angle 80°, acquisition time 1.8 s, pulse delay 6 s, spectral width 16 000 Hz, 6000 scans, data length 64 K, WALTZ-16 decoupling, and concentration of approximately 30% w/v.

Solid-state ^{13}C NMR spectra were acquired at room temperature on a Bruker CXP 200 spectrometer operating at 50.3 MHz. Samples were loaded either in an air-driven two-component Beams-Andrew BN-POM rotor with a poly(oxymethylene) (POM) cap or in a double air bearing zirconium oxide rotor. Samples were spun at 3.0–3.5 kHz. The chemical shifts were referenced to the external chemical shift of the crystalline and amorphous POM resonances (both 88.8 ppm) and subsequently used for mutual comparison. Typical cross-polarization pulse sequences used are 4 s, 90° pulse, 1-ms contact time, and a 4-s recycle time collecting 2K points in the time domain for a 20K spectral width. Approximately 8000 free induction decays were collected.

Results and Discussion

First, we prepared the copolymer (I) of styrene and NpTMI from a monomer feed ratio 0.6:0.4 up to 69 wt % conversion. An excess of styrene was added in order to obtain structural information about the possible formation of St–St sequences. Figure 2 shows the ^{13}C NMR spectrum of this copolymer, recorded in acetone-d_6. Three spectral regions are present, viz. the carbonyl pattern between 170 and 180 ppm, the aromatic pattern between 125 and 150 ppm, and a complex pattern due to the aliphatic carbon atoms between 20 and 55 ppm. The chemical shifts of the tolyl moiety can be assigned by using the chemical shifts of toluene adapted with the increment of a maleimide group to benzene[11] (the numbering scheme can be found in Figure 2).

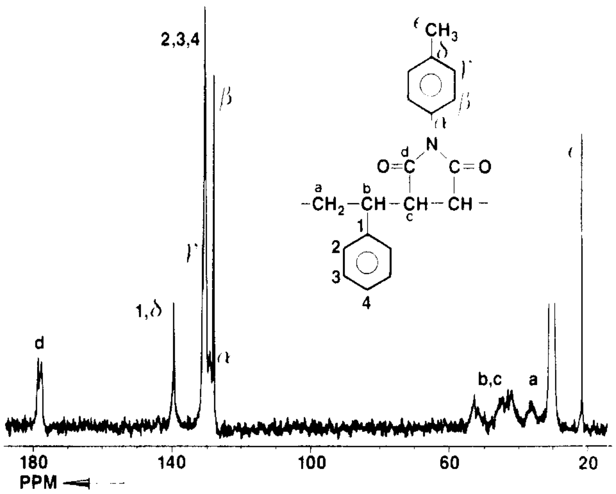

Figure 2. ^{13}C NMR (100-MHz) spectrum of the NpTMI–St copolymer (I), recorded in acetone-d_6.

$$\delta C_x \ (x = \alpha, \beta, \gamma, \delta) = \delta_{exp}(\text{toluene}) + \Delta(\text{maleimide}) \qquad (1)$$

Selected chemical shifts can be found in Table I, including those of NpTMI (Figure 3). According to the results in Table I, the ^{13}C NMR resonances of C-1 and C-δ coincide. This observation is in agreement with the area measurement of the combined resonances at 140 ppm (cf. eq 2b).

The molar fraction of styrene F_{st} can be calculated via two ways (I = peak area):

$$F_{st} = 0.5[I(\text{C-a,b,c}) - 2I(\text{C-}\epsilon)]/\{I(\text{C-}\epsilon) + 0.5[I(\text{C-a,b,c}) - 2I(\text{C-}\epsilon)]\}$$
$$= [I(\text{C-a,b,c}) - 2I(\text{C-}\epsilon)]/I(\text{C-a,b,c}) \qquad (2a)$$

$$F_{st} = [I(\text{C-1} + \text{C-}\delta) - 0.5I(\text{C-d})]/\{0.5I(\text{C-d}) + [I(\text{C-1} + \text{C-}\delta) - 0.5I(\text{C-d})]\} \qquad (2b)$$

Equation 2a is only valid in the case of similar nuclear Overhauser enhancement effects and similar T_1 relaxation times for the aliphatic carbons. However, the overlap of the solvent resonances of acetone-d_6 and C-a,b,c prohibits the use of this equation. Equation 2b holds when differential T_1 effects for the carbonyl and quarternary aromatic carbons are absent. Apparently, this last condition is valid as shown by Roth et al. for MA–St copolymers.[7] The molar fraction of styrene F_{st} incorporated is obtained from eq 2b and amounts to 0.50. This value is in accordance with the value of 0.53 as computed from the N elemental analysis.

^{13}C NMR spectroscopy can also be of use in analyzing the copolymer microstructure. The C-1 of the styrene unit in the case of MA–St copolymers shows a chemical shift dispersion of 8 ppm (139–147 ppm) due to the various arrangements of the styrene-centered triads MSM, SSM, MSS, and SSS (M = MA, S = St).[7,8] The C-1 of the MSM triad can be found at 139 ppm and those of the SSM, MSS, and SSS triads at 141, 145, and 147 ppm, respectively. The C-1 of the NpTMI–St copolymer absorbs at 139 ppm, which points to the presence of almost exclusively MSM triads. No signals occur at lower field up to 147 ppm,

Table I
Selected ^{13}C NMR Chemical Shifts (ppm) of NpTMI and NpTIMI and the NpTMI–St (I) and NpTIMI–St (II) Copolymers[a]

	C-α	C-β	C-γ	C-δ	C-ε	C-d	C-1	C-2	C-3	C-4	C-e	C═C
NpTMI	130.6	128.0	130.5	139.0	21.0	171.3						136.0
NpTIMI	142.0/143.0	124.9/122.1	130.3/130.6	136.4/135.3	21.5/21.4	168.7					151.6/159.0	135.0/144.8, 131.0/129.5
I	128.5 (128.8)	127.4 (126.5)	130.6 (130.3)	139.4 (138.0)	27.0	178.0	139.4	130.0	130.0	130.0		
II	143.9 (142.1)	123.9/121.0 (124.0)/(122.2)	130.0 (130.5)	135.3/134.3 (135.4)/(134.3)	21.6	174.1	139.4/145.0	130.0	130.0	130.0	156.2/164.2	

[a] In the case of NpTIMI and II two values are shown for the anti/syn isomers. Values calculated from eqs 1 and 3 are placed in parentheses.

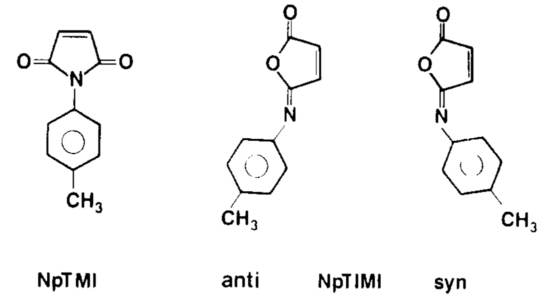

Figure 3. Molecular structures of NpTMI and the anti/syn isomers of NpTIMI.

Table II
Experimental Data from the Copolymerization of NMM and Styrene in Dioxane at 70 °C, Initiated by AIBN

f_{st}	yield (wt %)	F_{st}
0.2	10.5	0.46
0.3	8.5	0.47
0.4	11.0	0.48
0.5	18.6	0.51
0.6	11.0	0.53
0.7	12.6	0.52
0.8	9.0	0.50

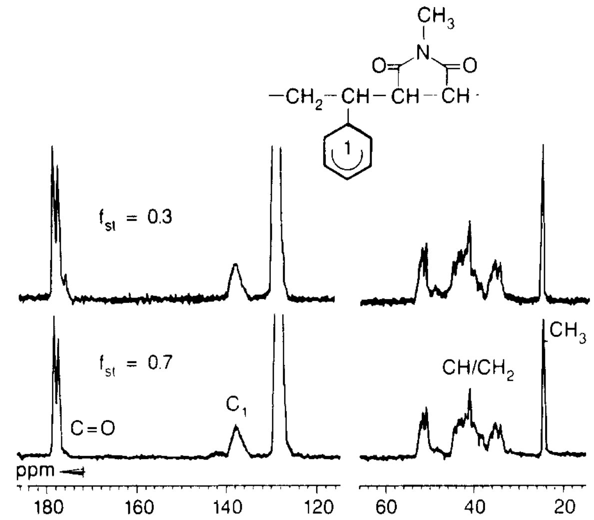

Figure 4. ^{13}C NMR (75-MHz) spectra of the NMM–St copolymers from f_{st} = 0.3 and 0.7, recorded in CDCl$_3$.

although a definite assignment is obscured by the superposition of C-δ on C-1.

In order to circumvent this problem and to study the microstructure of N-substituted maleimide–styrene copolymers in more detail, we carried out the copolymerization of *N*-methylmaleimide (NMM) and styrene at low conversions, varying the monomer feed ratio f_{st} from 0.2 to 0.8 (Table II). The copolymer composition F_{st} was determined by means of ^{1}H NMR spectroscopy. It appears that the copolymers contain almost equal amounts of the two monomer units irrespective of the monomer feed ratio. The ^{13}C NMR spectra of two copolymers from feed ratios f_{st} = 0.3 and 0.7 are depicted in Figure 4.

In both cases a broad signal occurs at 139 ppm, which we assign to the C-1 of the alternating MSM triad. The upper spectrum (f_{st} = 0.3) shows a small peak at the right-hand side of the carbonyl signal. The presence of this peak points to the formation of triads with MM neighbors. In the lower spectrum a small C-1 signal occurs at 142 ppm, which probably belongs to the styrene-rich SSM triad by analogy to the ^{13}C NMR spectra of MA–St copolymers. Both the kinetic and structural data point to a very strong tendency for N-substituted maleimides and styrene to form alternating copolymers.

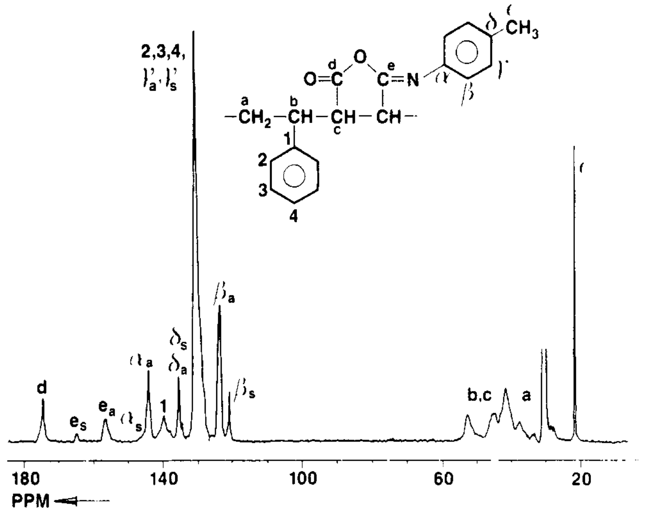

Figure 5. ^{13}C NMR (100-MHz) spectrum of the NpTIMI–St copolymer (II), recorded in acetone-d_6.

The spectrum of the NpTIMI–St (II) copolymer from a monomer feed ratio of 0.4:0.6 appears to be more complex (Figure 5). Typical phenomena are the C═N (C-e) chemical shifts around 160 ppm and the downfield shift of C-α. The isomaleimide exists as two isomers with a syn:anti ratio identical to the value found for the NpTIMI monomer (Figure 3). The chemical shifts .of the tolyl moiety can be assigned via eq 3, using the chemical shifts of toluene adapted with the increment of an isomaleimide group (anti or syn) to benzene[12] (Table I). Part of the C-1 resonance lies at 139 ppm, while another part is masked by C-α. Application of eq 4 leads to a molar fraction of styrene of 0.58 (0.57 from N elemental analysis), of which 0.34 belongs to MSM triads.

$$\delta C_x\ (x = \alpha, \beta, \gamma, \delta) = \delta_{exp}(\text{toluene}) + \Delta(\text{anti/syn isomaleimide}) \quad (3)$$

$$F_{st} = I(\text{C-1})/[I(\text{C-1}) + I(\text{C-d})]$$

$$I(\text{C-1}) = I(1) + [I(\text{C-}\alpha_a + \text{C-}\alpha_s) - I(\text{C-}\delta_a + \text{C-}\delta_s)] \quad (4)$$

The spectral characteristics of the MA–St copolymer (III) from a monomer feed ratio of 0.4:0.6 can be assigned analogously to those described in the literature.[7,8] It appears that F_{st} amounts to 0.50, while an estimation of

Table III
Experimental Data for the Copolymerizations of NpTMI, NpTIMI, and MA with Styrene in Toluene at 70 °C, Initiated by AIBN (Subscripts: 1 = Styrene, 2 = NpTMI, 3 = NpTIMI, and 4 = MA)[a]

	f_1	f_2	f_3	f_4	yield (wt %)	N el an (wt %)
I	0.6	0.4			69	4.5
II	0.6		0.4		66	4.2
III	0.6			0.4	85	
IV	0.6	0.2	0.2		77	4.4
V	0.6	0.2		0.2	68	
VI	0.50	0.17	0.17	0.17	67	2.9

	F_1		F_1(MSM)	F_2		F_3		F_4	
	A	B	B	A	B	A	B	A	B
I	0.53	0.50	0.50	0.47	0.50				
II	0.57	0.58	0.34			0.43	0.42		
III		0.50	0.39						0.50
IV	0.54	0.55			0.26		0.19		
V		0.50			0.24				0.26
VI		0.58			0.18		0.06		0.18

[a] Composition determined by means of N elemental analysis (A) or ^{13}C NMR spectroscopy (B).

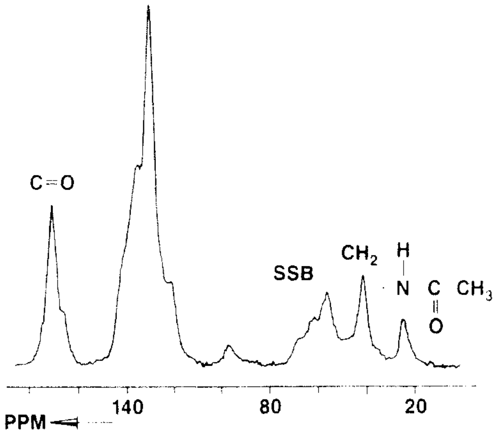

Figure 6. ^{13}C NMR (50-MHz) CP-MAS spectrum of Desbimid (SSB = spinning sideband).

the fraction of C-1 belonging to the MSM (M = MA, S = styrene) triad fraction gives 0.39 (Table III).

The ^{13}C NMR spectra of the NpTMI–NpTIMI–St (IV) and NpTMI–MA–St (V) terpolymers and of the NpTMI–NpTIMI–MA–St (VI) quaterpolymer appear to be superpositions of the individual copolymer spectra. All results are compiled in Table III.

From the results obtained so far it is manifest that all three monomers NpTMI, NpTIMI, and MA prefer to form alternating copolymers with styrene. On the basis of the values of F_1(MSM) we conclude that this tendency decreases in the direction NpTMI > MA > NpTIMI. The composition of the terpolymers IV and V indicates that NpTIMI is less reactive toward styrene than NpTMI and MA. The same conclusion can be drawn from the composition of the quaterpolymer VI. A possible explanation for the anomalous behavior of NpTIMI follows from steric considerations. Addition of the NpTIMI monomer (see also Figure 3) to the styrene radical of the growing chain at the imine side of the former molecule will be less favorable, thus reducing the overall reactivity as compared with NpTMI and MA. Electronic effects, however, cannot be excluded.

The ^{13}C NMR CP-MAS spectrum of Desbimid (Figure 6) consists of broad resonances with hardly any detailed structure. The characteristics of this spectrum are the carbonyl signal at 170 pm, the methylene peak at 40 ppm, the acetamide CH_3 peak at 24 ppm, and the very broad pattern around 135 ppm consisting of the aromatic and vinylic signals.

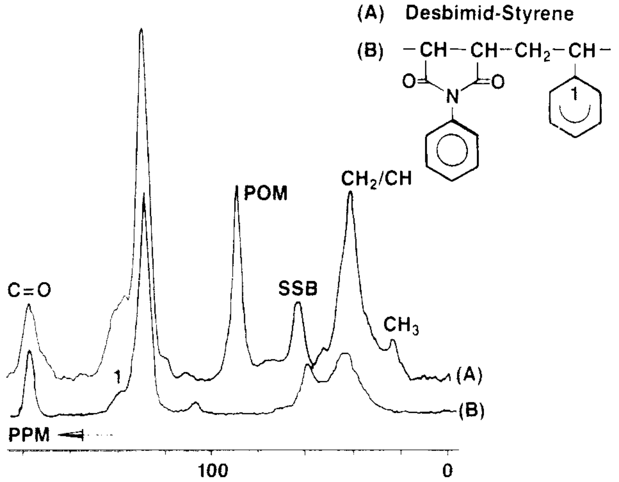

Figure 7. ^{13}C NMR (50-MHz) CP-MAS spectra of cured Desbimid–St (A) and the NPMI–St copolymer (B) (SSB = spinning sideband, POM = poly(oxymethylene)).

The ^{13}C NMR CP-MAS spectrum of a mixture of Desbimid and styrene (66:34 wt ratio, 1 wt % of methyl isobutyl ketone peroxide) cured at room temperature, 70 °C, and 130 °C is depicted in Figure 7. The specific features of this spectrum are the carbonyl signal at 177 ppm, a residual carbonyl signal at 170 ppm, the methylene and methine peaks coinciding at 40 ppm, the acetamide CH_3 peak at 24 ppm, and the aromatic region around 130 ppm. The carbonyl signal shifts to 177 ppm upon curing, while a small amount of the total intensity of the original peak at 170 ppm remains. This residue probably results from incomplete cure and the presence of the acetamide carbonyl. The left-hand shoulder at 140 ppm of the broad pattern around 135 ppm spreads to 145 ppm. So, the distribution of styrene monomer units is somewhat uncertain at this point. Additional information is obtained from the solid-state spectrum of the NPMI–St copolymer, prepared under the same conditions as used for the NpTMI–St copolymer. NPMI was chosen instead of NpTMI in order to avoid the signal due to the CH_3 group. As has been stated before, the chemistry of the Desbimid–St system will be dominated by the maleimide–styrene copolymerization. The shoulder at 140 ppm points to the exclusive formation of alternating MSM triads; no signals are found at lower field down to 147 ppm. By analogy we assign the same microstructure to cured Desbimid–St.

Conclusion

From kinetic and structural studies it appears that *N*-substituted maleimides in particular form alternating copolymers with styrene. This tendency is less strong in the case of *N*-*p*-tolylisomaleimide and maleic anhydride. Comparison of the ^{13}C NMR spectra of model copolymers and the ^{13}C NMR CP-MAS spectrum of cured Desbimid–St leads to the conclusion that in the thermosetting system formation of alternating copolymers between the maleimide moieties and styrene predominates. The fate of the less abundant isomaleimide moieties and maleic anhydride remains uncertain.

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Registry No. I, 88077-72-9; II, 75818-45-0; III, 9011-13-6; IV, 142211-50-5; V, 142188-80-5; VI, 142188-81-6; (NMM)(H_2C=CHPh) (copolymer), 29008-00-2; (desbimid)(styrene) (copolymer), 127052-24-8.