High-Resolution Carbon Nuclear Magnetic Resonance Study of Styrene/α-Methylstyrene/Acrylonitrile Terpolymers

Regina F. Nogueira,[1,2] Maria Inês B. Tavares[2]

[1]*COPPE/UFRJ, Ilha do Fundão, Rio de Janeiro, Brazil, CP 68502*
[2]*IMA/UFRJ, C. T., Bloco J, Cidade Universitária, Ilha do Fundão, Rio de Janeiro, RJ, Brazil, CP 68525*

ABSTRACT: Terpolymers formed from styrene, α-methylstyrene (AMS), and acrylonitrile (AN) were prepared in different proportions. According to the reaction conditions, the terpolymers presented random sequence distributions. AMS, because of steric hindrance, presented a high degree of instability, which promoted depolymerization. AN promoted a long insertion of AMS monomers, which caused an acceleration of the propagation reaction. This also caused a depolymerization process. With ^{13}C-NMR solution analysis, it was possible to detect the depolymerization process. With solid-state NMR results, it was demonstrated that AMS constituted the highest mobility domain. Finally, the values determined for the proton spin–lattice relaxation time in the rotating frame confirmed that the prepared terpolymers were random, but a homogeneous monomer distribution sequence was also observed from this parameter. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 88: 1004–1009, 2003

Key words: NMR; copolymerization; terpolymers

INTRODUCTION

Styrene/α-methystyrene (SAMS)[1] and α-methylstyrene/acrylonitrile (AMSAN)[2] copolymers were previously studied to determine the behavior of the styrene/α-methylstyrene/acrylonitrile (SAMSAN) terpolymer. The terpolymerization reaction was a method employed to substitute part of the styrene (S) in the styrene/acrylonitrile (SAN) resin to obtain a new product with higher thermal resistance. The main purpose of this work was to apply the same NMR methodology[1–11] to characterize both copolymers and evaluate the terpolymer behavior. For this purpose, we used solution and solid-state NMR, employing several techniques that allowed us to obtain the responses of the chemical and molecular dynamics of the samples.[3–11]

EXPERIMENTAL

Sample preparation

The SAMSAN terpolymers were prepared by an emulsion at 84°C in one step with a 5-h polymerization reaction. They were named SAMSAN A, B, and C according to the increase in the α-methylstyrene (AMS) content in the feed.

NMR measurements

The solution NMR spectrum was obtained on a Varian Mercury 300 spectrometer (Palo Alto, CA) operating at 75.4 MHz for ^{13}C-NMR; the ^{13}C-NMR solution spectra were obtained under quantitative conditions. All solid-state spectra were obtained on a Varian Inova 300 spectrometer operating at 75.4 MHz for ^{13}C-NMR. All solid experiments were performed at the ambient probe temperature and were performed with gated high decoupling. A zirconium oxide rotor 7 mm in diameter was used to acquire the NMR spectra at rates of 5.5 kHz. The ^{13}C-NMR spectra were created in the cross-polarization mode with magic-angle spinning (MAS). For the variable-contact-time experiments, a range of contact times was established, from 200 to 8000 μs. Proton spin lattice relaxation time in the rotating frame ($T_1\rho$) values were determined from the intensity decay of ^{13}C peaks with increasing contact times and also by delayed-contact-time experiments with a spin-locking window varying from 200 to 8000 μs. The dipolar dephasing experiments were performed with a dephasing time of $\tau = 40$ μs.

RESULTS AND DISCUSSION

Solution analysis

The proton spectra were recorded under three different conditions so that good spectra would be obtained
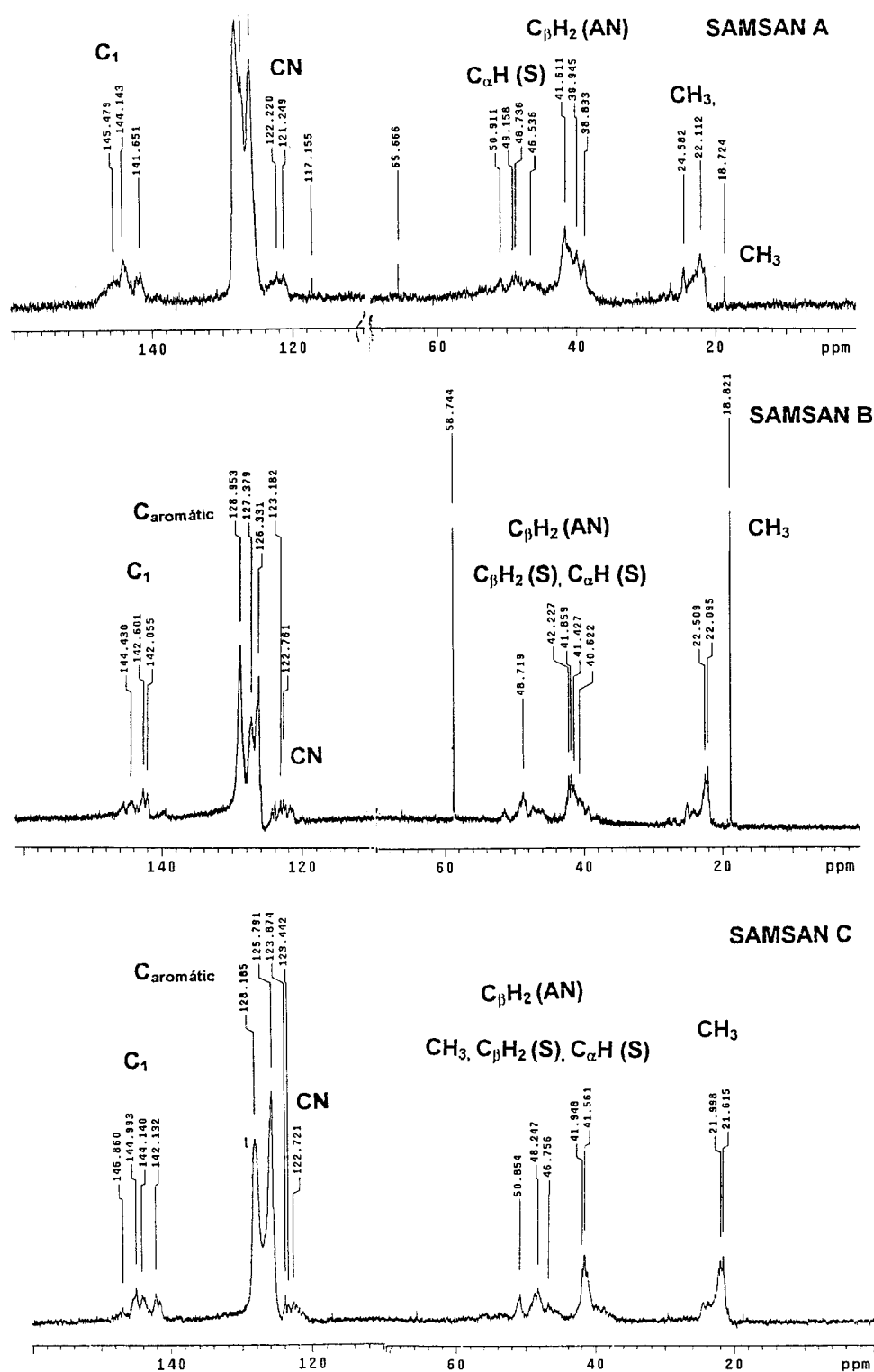
Figure 1 Solution ^{13}C-NMR spectra for all the terpolymers.

for measuring the proportions among the monomers. The first spectrum was acquired at 300 MHz at the probe ambient temperature. The spectrum showed very broad signals and, consequently, overlapped signals. For increased resolution, the second analysis was recorded at 600 MHz at the probe ambient tempera-ture. Unfortunately, the obtained spectrum was not as good as the first one. The third condition chosen was 300 MHz but at 50°C. The spectrum obtained showed a better resolution than the two others did. However, the signals were still wide enough to permit area integration and to calculate the proportion of the
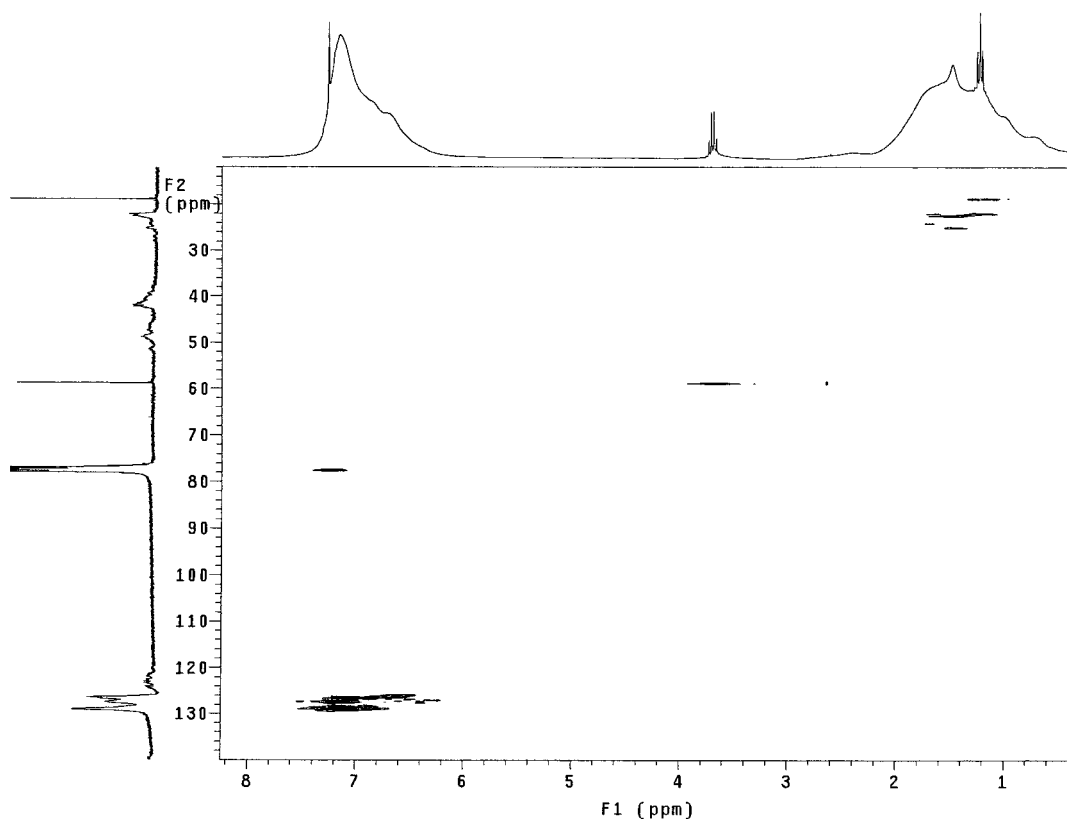
Figure 2 2D HETCOR spectrum of SAMSAN B.

monomers in the terpolymer chains. In all the spectra, very sharp signals were detected. These signals derived from the depolymerization process. So, these two facts mentioned before make us measure the proportion of monomers with ^{13}C-NMR solution. The analyses of ^{13}C spectra were performed at quantitative conditions (Fig. 1). The spectrum presented sharp signals. Therefore, overlapped signals were also detected. The aromatic carbons from S and AMS (125–128 ppm), CH_2 and CH from S and CH_2 from AMS (40–42 ppm), and CH derived from acrylonitrile (AN) and CH_3 from AMS (25–21 ppm) were overlapped. The two-dimensional heteronuclear chemical-shift correlation (2D HETCOR) spectrum (Fig. 2) helps us to assign the methyl and methyne regions. Very sharp signals, which were attributed to the depolymerization process, were also detected. Therefore, the microstructure configuration sequence distribution (triad) of the AN monomer insertion was determined from

the CN group in the terpolymer chains (Table I). The terpolymer triad sequence distribution centered in AMS was extracted from the methyl resonances because the methyl group in the homopolymer did not present a spread related to the microstructures on account of the monomer insertion. Table II shows the percentage of triads centered in the AMS monomer due to the monomer insertion distribution in the terpolymer chains. Figure 3 exhibits the triad centered in the AMS monomer sequence distribution of the methyl region for the terpolymers SAMSAN B and SAMSAN C.

From Table II, it is clear that the terpolymer presented a random monomer sequence distribution along the macromolecular chains, as already expected for the type of polymerization process and the monomer structure and reactivity ratio.

TABLE I
Microstructure Configuration Sequence Distribution of AN Monomer Insertion in the Terpolymer Chains

Terpolymer	Microstructure (%)		
	mm	mr	rr
SAMSAN B	27.5	44.5	28.0
SAMSAN C	40.0	39.7	20.3

TABLE II
Triad Percentage of Sequence Distribution Centered in the MAS in the Terpolymer Chains

Terpolymer	AMSAMSAMS	Triads (%) ANAMSAMS + SAMSAMS	SAMSAN + SAMSS ANAMSAN
SAMSAN B	25.0	71.0	4.0
SAMSAN C	6.0	65.0	29.0

SAMSAN B

Figure 5 CP-MAS ^{13}C-NMR spectrum of SAMSAN B.
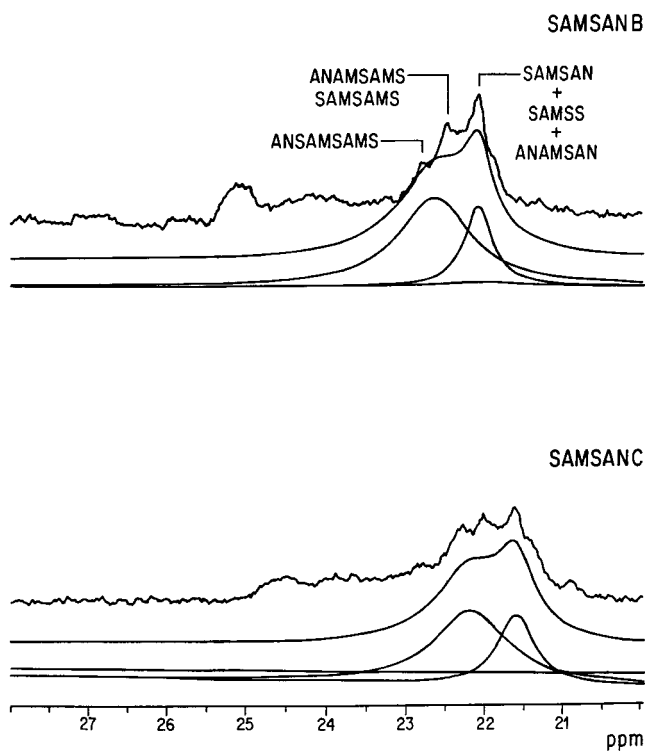

Figure 3 Triads centered in the AMS monomer sequence distribution of the methyl region for the terpolymers SAMSAN B and SAMSAN C.

Solid-state NMR analysis

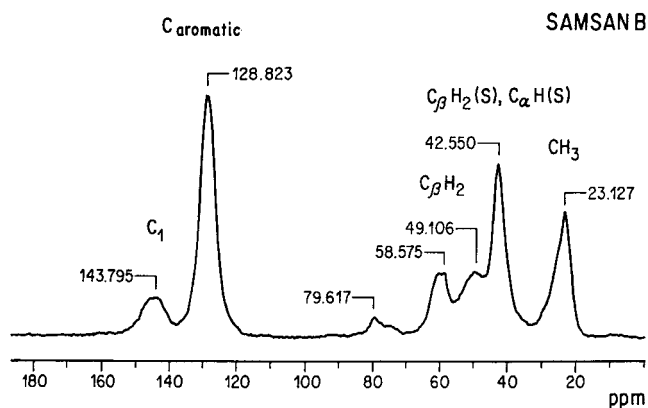From the MAS ^{13}C-NMR spectra, one can observe that the mobile region of the SAMSAN terpolymers was constituted by the AMS monomer, which promoted an increase in the molecular mobility of the terpolymer chains; this can be considered a type of plasticization effect. The same behavior was observed for the copolymers SAMS[1] and AMSAN,[2] which were studied previously as patterns for the terpolymers. This kind of plasticization effect detected in the terpolymers could be responsible for better mechanical properties in comparison with those of the SAN resin. Figure 4 exhibits the MAS ^{13}C-NMR spectrum of SAMSAN C.

The cross-polarity/magic-angle-spinning (CP-MAS) ^{13}C-NMR spectra showed large signals because the terpolymers prepared were atactic and amorphous, and they also exhibited overlapped signals, which were also detected in the ^{13}C-NMR solution spectra. However, the assignments of the terpolymer chemical structure could be made. Figure 5 shows the CP-MAS ^{13}C-NMR spectrum of SAMSAN B.
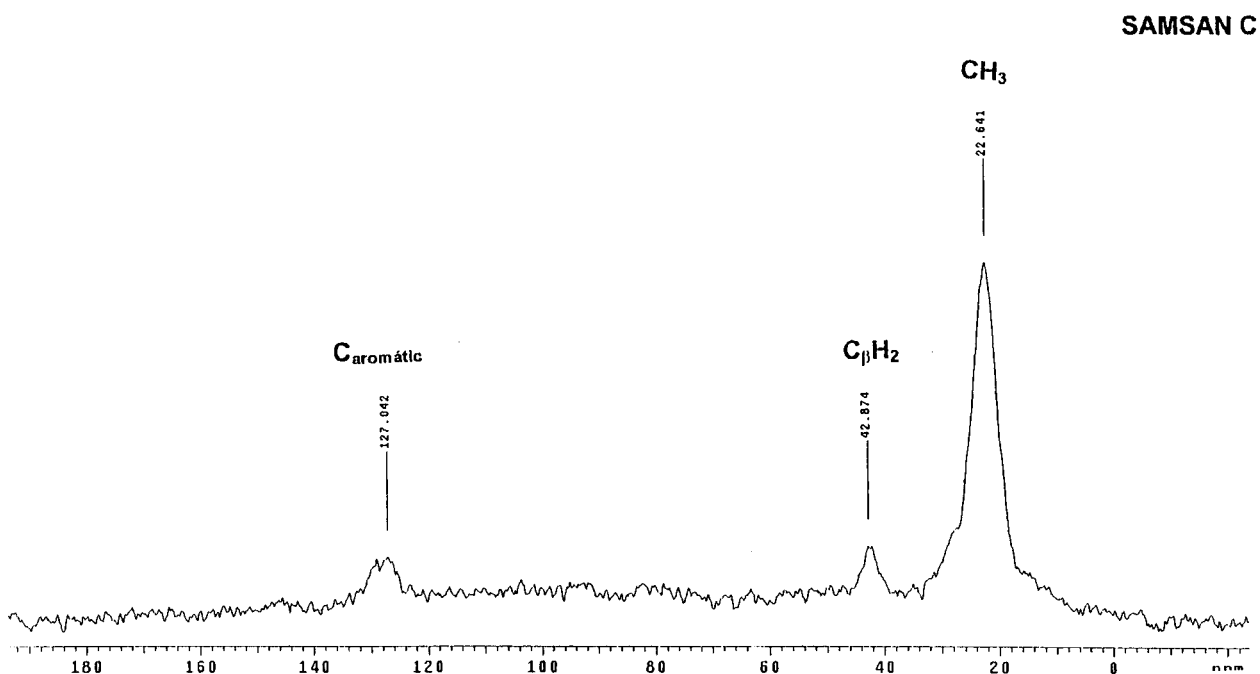

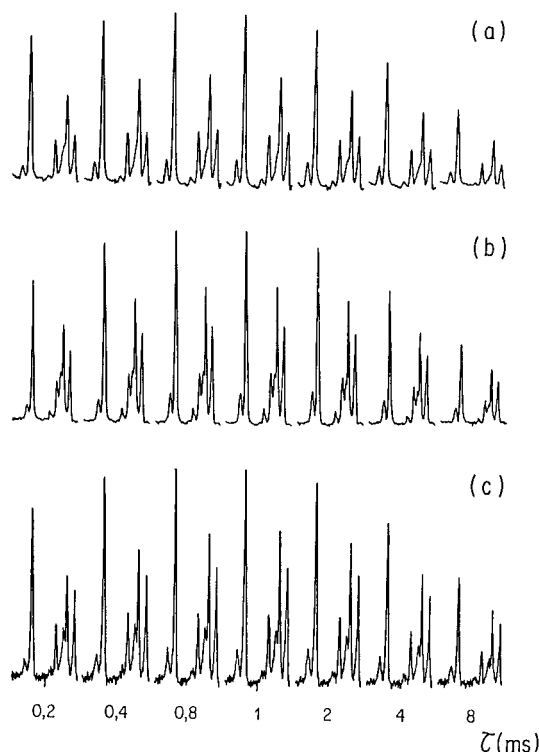**Figure 4** MAS ^{13}C-NMR spectrum of SAMSAN C.

Figure 6 Distribution forms of the ^{13}C decay for all the terpolymers.

The distribution forms of the ^{13}C decay, observed from the variable-contact-time experiments, showed similar behaviors for all the terpolymers (Fig. 6). Comparing the decays for the different terpolymers, one can observe that they did not present a significant difference. Despite the polymerization process, these decays were also a function of the monomer distribution.

The terpolymer proton $T_1\rho$ parameter, obtained from the variable-contact-time experiments, is listed in Tables III and IV. Analyzing the proton $T_1\rho$ values, one can see that the efficiency of polarization transfer was good enough for the SAMSAN B terpolymers, as a result of better spatial proximity, because of the packing and arrangements of the molecular chains.

The proton spin lattice relaxation time in the rotating frame ($T_1^H\rho$) parameter was also measured by delayed-contact-time experiments. The results obtained for the terpolymers are listed in Tables V and VI.

TABLE III
T_1^H-p (ms) Values for the Resolved Carbons of
SAMSAN A and C as a Function of Chemical Shifts
Measured by Variable Contact Time

Sample	$\delta^{13}C$				
	46.2	125.0	69.3	42.7	23.0
SAMSAN A	18.1	3.9	9.7	6.2	4.3
SAMSAN C	10.1	5.3	3.5	6.5	6.3

TABLE IV
$T_1^H\rho$ (ms) Values for the Resolved Carbons of SAMSAN
B as a Function of Chemical Shifts Measured by
Variable Contact Time

Sample	$\delta^{13}C$				
	143.3	128.8	49.7	42.6	23.1
SAMSAN B	6.4	5.9	5.7	5.3	5.2

From the $T_1^H\rho$ data, it can be seen that terpolymer C presented a better distribution of monomers along the chains; this terpolymer seemed to have the monomers distributed more homogeneously along the chains. Terpolymer B also presented good homogeneity. Both $T_1^H\rho$ and chemical-shift values of aromatic C_1 were shorter than those of the two others, indicating that some change in the molecular mobility was happening, probably because of the AMS content. The same behavior was found with the variable contact time (VTC) data.

From the relaxation data, both $T_1\rho$ measurements were able to inform on the homogeneity and monomer distribution in the terpolymer chains.

Figure 7 shows the cross-polarization magic angle spinning with dipolar dephase (CP-MASDD) ^{13}C-NMR spectrum of terpolymer B. The detected signals referred to AMS and S, but the signals related to AN were not observed because of the signal width. The line width also confirmed that the linkage of the chains was random, and this is evidence of the presence of different microstructures and monomer distributions along the chains, as they were amorphous.

CONCLUSIONS

The results obtained by solution and solid-state NMR experiments confirmed that AMS acted as a plasticizer in the terpolymers, as already observed for AMSAN

TABLE V
$T_1^H\rho$ (ms) Values for the Resolved Carbons of SAMSAN
A and C as a Function of Chemical Shifts Measured by
Delayed Contact Time

Sample	$\delta^{13}C$			
	146.2	128.8	42.7	23.5
SAMSAN A	4.9	8.6	8.4	7.3
SAMSAN C	7.3	6.7	7.0	7.0

TABLE VI
$T_1^H\rho$ (ms) Values for the Resolved Carbons of the
SAMSAN B Terpolymer as a Function of Chemical
Shifts Measured by Delayed Contact Time

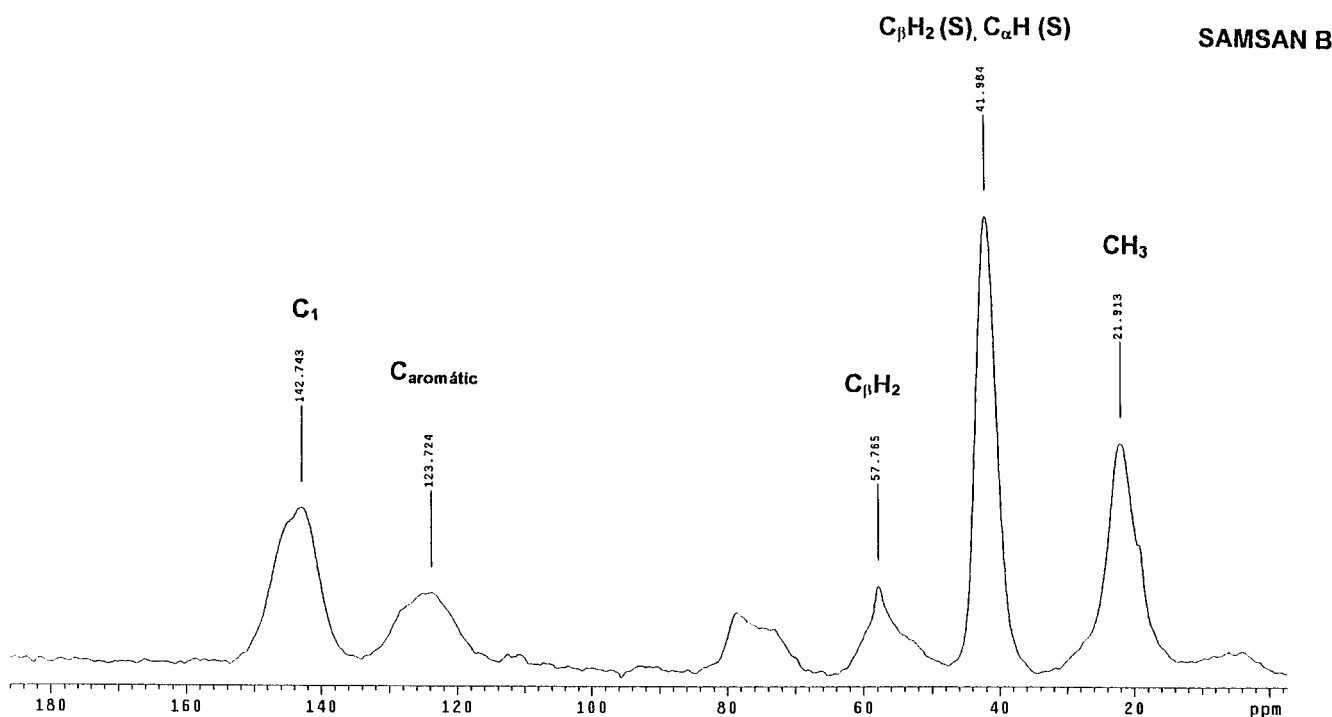| Sample	$\delta^{13}C$			
	128.1	58.1	48.6	22.4
SAMSAN B	9.0	7.6	6.9	7.4

Figure 7 CP-MASDD ^{13}C-NMR spectrum of SAMSAN B.

copolymers.[2] The amount of AN influenced AMS insertion in the SAMSAN terpolymers and also caused a depolymerization process of AMS long chains. A larger amount of AN promoted instability in the emulsion reaction, which caused a loss of control over the reaction temperature.

References

1. Nogueira, R. F.; Tavares, M. I. B. J Appl Polym Sci 2001, 81, 261.
2. Nogueira, R. F.; Tavares, M. I. B. J Appl Polym Sci, to appear.
3. Bovey, F. A.; Mirau, P. A. NMR of Polymers; Academic: New York, 1996.
4. Silva, N. M.; Tavares, M. I. B. J Appl Polym Sci 1996, 60, 663.
5. Tavares, M. I. B.; Monteiro, E. E. C.; Harris, R. K.; Kenwright, A. Eur Polym J 1994, 30, 1089.
6. Souza, C. M. G.; Tavares, M. I. B. Polym Test 1998, 17, 533.
7. Stael, G. C.; D'Almeida, J. R. M.; Menezes, S. M. C.; Tavares, M. I. B. Polym Test 1998, 17, 147.
8. Costa, D. A.; Oliveira, C. M. F.; Tavares, M. I. B. J Appl Polym Sci 1998, 69, 129.
9. Souza, C. M. G.; Tavares, M. I. B. J Appl Polym Sci 1998, 70, 2457.
10. Silva, E. P.; Tavares, M. I. B. Polym Bull 1998, 41, 307.
11. Silva, N. M.; Tavares, M. I. B.; Stejskal, E. O. Macromolecules 2000, 33, 115.