

Carbon-13 Nuclear Magnetic Resonance Investigation of Styrene- α -Methylstyrene Copolymers

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Received 11 February 2000; accepted 22 August 2000

ABSTRACT: A copolymer based on α -methylstyrene (AMS) was investigated by nuclear magnetic resonance (NMR). The styrene-*co*- α -methylstyrene (SAMS) was analyzed by solution and solid-state NMR techniques. Three copolymers of SAMS with different compositions presented a particular behavior. The solution results showed the copolymer microstructure and the AMS content. The carbon-13 spectra of SAMS C indicated that the AMS CH₃ signal was detected at three distinct chemical shifts, because of the different comonomer-sequences distribution. The proton spin-lattice relaxation time in the rotating frame ($T_{1\rho}^H$) parameter was chosen because it permits the evaluation of changes in the molecular mobility. The values of $T_{1\rho}^H$ found for the copolymers confirmed the random distribution in the samples. The copolymer with a low quantity of AMS (1.7%), when analyzed by this relaxation parameter, showed lower values that were interpreted as an antiplasticization effect. The SAMS copolymer with a higher AMS quantity showed a plasticization effect. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 81: 261–266, 2001

Key words: styrene-*co*- α -methylstyrene copolymer; nuclear magnetic resonance

INTRODUCTION

Copolymerization is widely used to modify polymer properties. For that reason, the monomers chosen have to be adequate to obtain the proper changes in properties.

Copolymers formed by styrene and α -methylstyrene (SAMS) were used as hardeners of polymer chains and to improve the heat resistance to deformation.^{1–4}

Besides the high reactivity of styrene, the low reactivity of AMS, and the stability of the AMS radical,^{4,5} it was already observed that the prod-

ucts obtained by the copolymerization of these monomers presented slow reaction rates and low molecular weights.

The characterization of the chemical structure and the comonomer-sequences distribution along the macromolecular chains, as well as the molecular dynamics, of the copolymers are very important in knowing their mechanical properties. Solution and solid-state nuclear magnetic resonance (NMR) spectroscopies were chosen to investigate these responses. It is known that a NMR solution yields both qualitative and quantitative information and, consequently, the assignment of the comonomer-sequences distribution in the copolymer^{6,7} as well. The resolution of NMR resonances depends on the sample nature, acquisition parameters, analysis temperature, and solvent

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Journal of Applied Polymer Science, Vol. 81, 261–266 (2001)
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Table I AMS Content in SAMS Copolymers

Copolymer	AMS (%)
SAMS A	1.7
SAMS B	17.7
SAMS C	36.8
SAMS D	28.5

used. Magic angle spinning (MAS) and cross-polarization with MAS (CPMAS) are routinely used to obtain high resolution solid-state NMR spectra.^{8,9} CPMAS spectra permit an evaluation of the changes in the chemical shifts, the line shape, and the relaxation parameter due to the solid morphology. From the variable contact-time experiment it is possible to measure the proton spin-lattice relaxation time in the rotating frame ($T_{1\rho}^H$) parameter, which reflects changes in both the microstructure and the molecular mobility of the copolymer. It also permits an assessment of the homogeneity in polymer systems because it is sensitive to the spatial proximity of chains. When

proton $T_{1\rho}$ is measured by the variable contact-time experiment, this parameter is obtained from the intensity decay for all resolved carbons. Thus, one obtains the value of proton $T_{1\rho}$ for hydrogens bonded to all types of carbons, which permits an evaluation of the behavior of the sample. Generally, not all the values of proton $T_{1\rho}$ change with variations in the samples, as in a copolymerization. There are some types of carbon nuclei that do not take part in the interaction between different polymer components. However, a significant change in this parameter and in the chemical shift values can be detected where the interaction occurs.⁹⁻¹⁷ The main purpose of this work was to evaluate the comonomers' sequences distribution and molecular dynamics.

EXPERIMENTAL

Sample Preparation

The copolymers formed by SAMS were prepared by emulsion at 84°C in one step and were named SAMS A, B, C, and D; the A, B, C, and D were

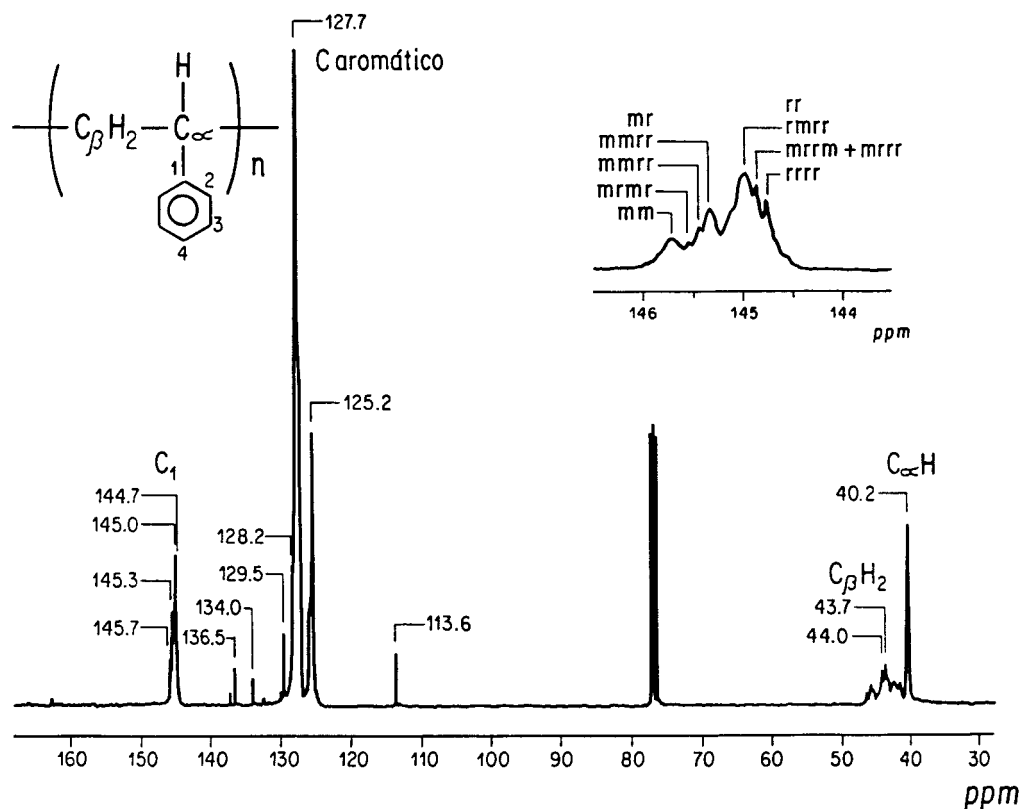


Figure 1 Solution ^{13}C -NMR spectra of polystyrene.

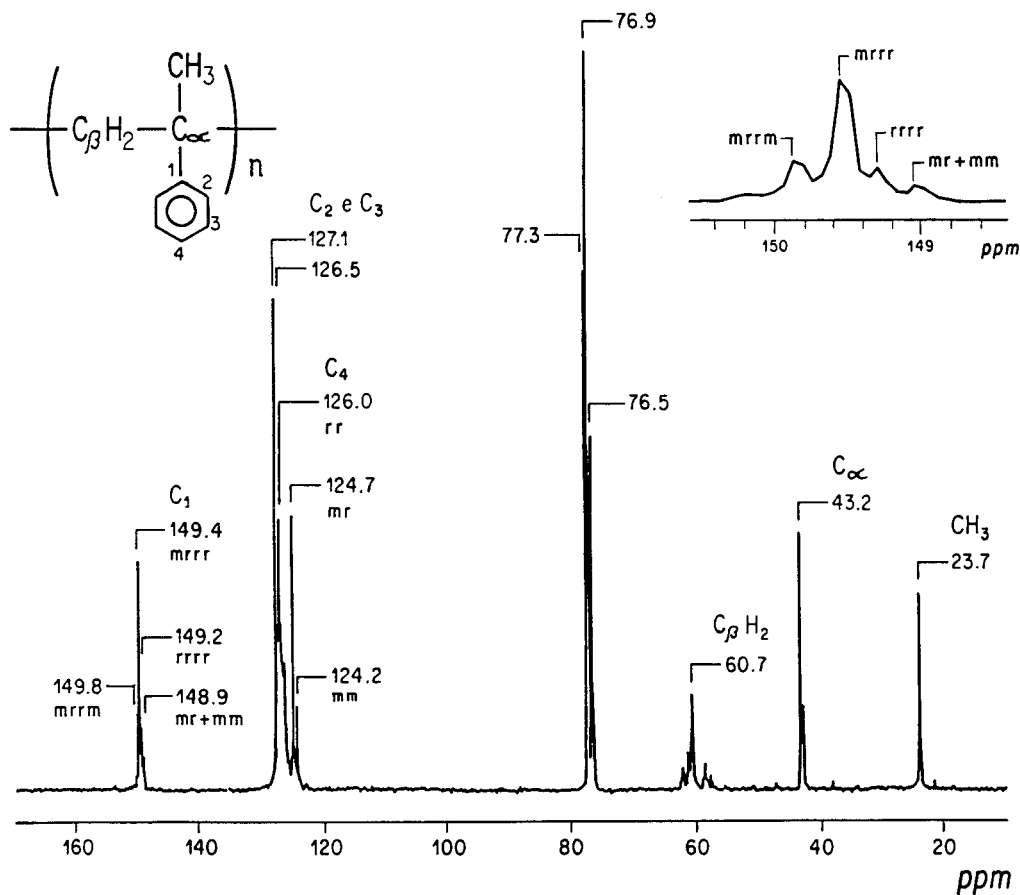


Figure 2 Solution ¹³C-NMR spectra of poly(methylstyrene).

related to the increase of the AMS content. The C and D copolymers were prepared using the same initial proportion of the comonomers, but C had a double quantity of the initiator.

NMR Measurements

All solution NMR spectra were obtained on a Varian Gemini 300 and the solid spectra were obtained on an Inova 300 spectrometer operating at 75.4 MHz for ¹³C. The solution ¹³C spectra were obtained under quantitative conditions using chloroform-*d* as a solvent. All solid NMR experiments were obtained at ambient probe temperature and were performed using gated high power decoupling. A zirconium oxide rotor (7-mm diameter) with Kel-F caps was used to acquire the NMR spectra at rates of 5.5 kHz. The ¹³C-NMR spectra were carried out in the CP mode with MAS. For the variable contact time, a range of contact times was established from 200 to 8000 μs. The CPMAS ¹³C-NMR spectra with dipolar

dephasing were also recorded; the dephasing time was 40 μs. The proton T_{1ρ} values were determined from the intensity decay of the ¹³C peaks with increasing contact times and also from the delayed contact-time experiment.

Differential Scanning Calorimetry (DSC) Measurements

The glass-transition temperature (T_g) measurements were carried out in a Mettler DSC 30 with a heating rate of 20°C/min at temperatures varying between 50 and 250°C.

RESULTS AND DISCUSSION

NMR Solution Analysis

Four copolymer SAMS (SAMS A, B, C, and D) were prepared with different initial ratios of the comonomers. The AMS proportion was 10% for A,

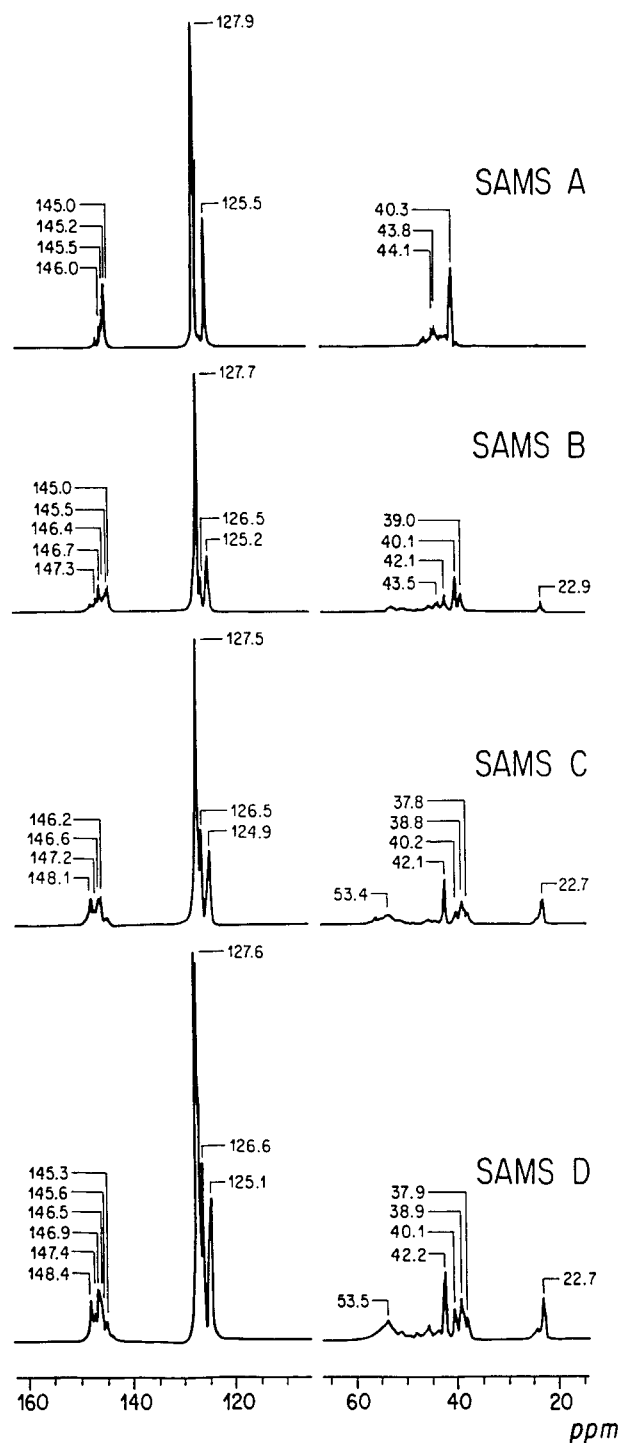


Figure 3 Solution ^{13}C -NMR spectra of SAMS copolymers.

20% for B, and 50% for C and D. The incorporation of the AMS monomer in the distinct SAMS copolymers was evaluated by using ^1H -NMR solution spectra; the values found for the copoly-

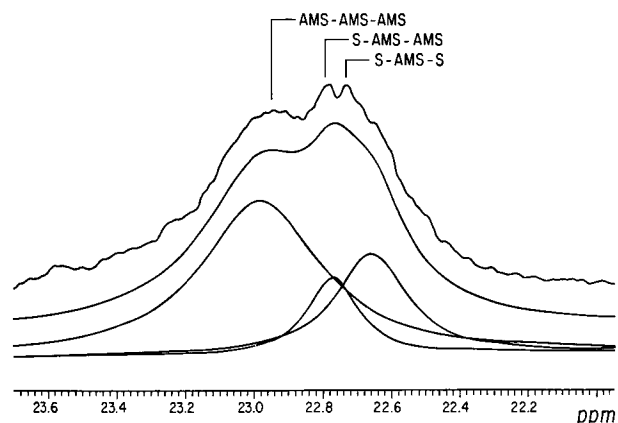


Figure 4 Solution ^{13}C -NMR spectrum of the CH_3 region from the MAS in the SAMS C copolymer.

mers are listed in Table I. The NMR measurements made it clear that the AMS reactivity was slow and the proportion of reaction conversion decreased as the AMS content increased.

It is of importance to point out that the SAMS C and D samples had the same initial comonomer ratio. Therefore, the quantity of the initiator to obtain the SAMS C was doubled. As a consequence, the final proportion acquired by NMR was different from the SAMS D, which was due to the increase of the number of propagation reaction sites.

The solution ^{13}C -NMR spectra of the pure homopolymers are shown in Figures 1 and 2, and solution ^{13}C -NMR spectra of SAMS copolymers are represented in Figure 3. The carbon-13 spectrum of SAMS C showed that the CH_3 signal from the AMS monomer was detected at three distinct chemical shifts (Fig. 4); because of the copolymerization process the comonomers were randomly distributed in

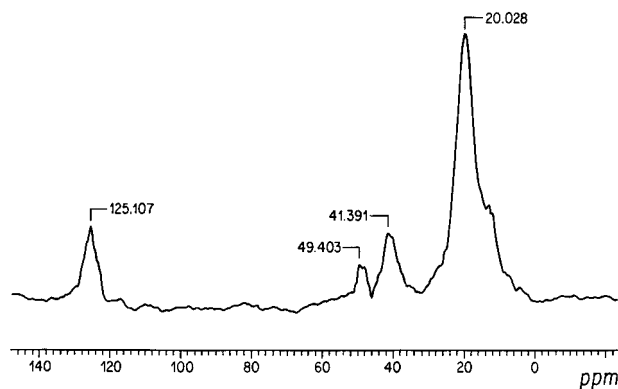


Figure 5 MAS ^{13}C -NMR spectrum of the SAMS C copolymer.

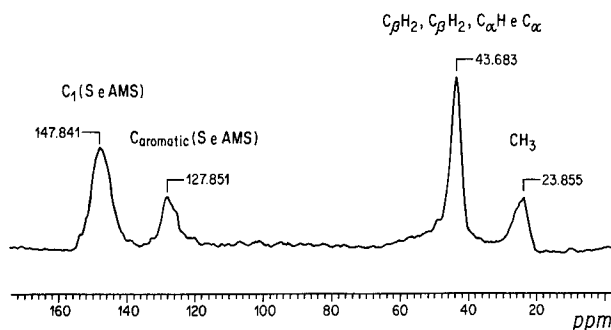


Figure 6 CPMAS ¹³C-NMR spectrum of the SAMS C copolymer.

the copolymer molecule, and different comonomer sequences were detected (AMS-AMS-AMS, AMS-AMS-S = S-AMS-AMS, and S-AMS-S).

NMR Solid-State Analysis

From the MAS ¹³C-NMR (Fig. 5) spectra one can observe that the mobile region of the SAMS copolymers were mainly constituted of the AMS monomer, which promoted a type of plasticization effect on the styrene monomer sequence in the copolymer sequence distribution.

The SAMS copolymers were analyzed by ¹³C solid-state NMR using the CPMAS technique. The CPMAS ¹³C for the SAMS C (Fig. 6) showed that the CH₂ (from AMS) and methyl signals presented low values for the chemical shift, which indicated that this copolymer presented high mobility due to the higher AMS content and principally because the link between both monomers was head to tail.

The proton T_{1ρ} parameter obtained from the variable contact-time experiment for the copolymers and homopolymers was measured. It was

Table III T_{1ρ}^H Values for Resolved Carbons of SAMS Copolymers as Function of Chemical Shifts (δ ¹³C) Measured by Delayed Contact Time

Sample	T _{1ρ} ^H (ms)			
	127.8 δ	73.3 δ	41.9 δ	22.3 δ
SAMS B	8.7	6.2	9.3	—
SAMS D	9.0	7.6	6.9	7.4

also possible to obtain information on the monomer distribution. The ¹³C spectra showed that the CH₃ signal was detected at three distinct chemical shifts. The proton T_{1ρ} parameter (Table II) found for the copolymers confirmed the random distribution in the samples, especially for the SAMS B. The SAMS C presented a better dispersion of the comonomers in the copolymer, but the sequence distribution was completely random. Copolymer D also presented random comonomer sequences in the distribution. The SAMS A did not show any additional information due to the small proportion of AMS.

From the results shown in Table II, one can see that the copolymer with a low quantity of AMS (1.7%), SAMS A, when analyzed by this relaxation parameter, showed lower values that were interpreted as an antiplasticization effect. On the other hand, the SAMS C, which had a higher AMS content, showed a plasticization effect, which corroborated the CPMAS ¹³C spectra signal detections.

The T_{1ρ}^H parameter was also measured with the delayed contact-time experiment. The results

Table II T_{1ρ}^H Values for Resolved Carbons of SAMS Copolymers as Function of Chemical Shifts (δ ¹³C) Measured by Variable Contact Time

Sample	T _{1ρ} ^H (ms)				
	146.6 δ	128.4 δ	41.1 δ	25.5 δ	23.5 δ
PS	5.4	4.0	14.6	—	—
SAMS A	5.0	3.9	6.8	—	—
SAMS B	4.6	3.0	6.7	—	—
SAMS C	7.9	8.5	9.9	—	8.4
SAMS D	—	5.7	5.0	—	—
PAMS	—	4.9	6.2	3.2	—

PS, polystyrene; PAMS, poly(AMS).

Table IV Glass-Transition Temperature (T_g) for Polymers and Copolymers

Sample	T_g (°C)
PS	107.0
SAMS A	108.9
SAMS B	116.2
SAMS C	130.4
SAMS D	128.9
PAMS	160.9

obtained for two of the copolymers are listed in Table III.

In accordance with these results, we can see that as the AMS quantity increased the distribution of the monomers in the copolymers was more homogeneous, because of a better comonomer-sequences dispersion.

In analyzing the $T_{1\rho}^H$ parameter obtained by both NMR experiments we saw that the results obtained by those parameters were complementary for this kind of copolymerization process.

The thermal study involving the measurement of the T_g , obtained by DSC, was carried out to obtain a correlation with the NMR solid-state relaxation parameters. Table IV shows the T_g measurements for the polymers and copolymers that were studied.

The results in Table IV show that the T_g values increased with increasing AMS content in the copolymer. The antiplasticization effect was not evidenced by calorimetry, because NMR is much more sensitive to local segmental motions than the motions scale probed by the T_g .

CONCLUSION

Based on the main purpose of this work, the results obtained by solution and solid NMR experiments confirmed that the AMS content directly influenced the copolymer distribution sequence. This was very

evident in copolymers B and C, which had AMS contents of 17.7 and 36.8%, respectively.

The authors are indebted to PETROBRAS/CENPES/DIQUIM for the use of the NMR spectrometer and for the DSC measurements.

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