

Carbon-13 Solution and Solid-State NMR Investigation of Alpha-Methylstyrene-co-acrylonitrile

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ABSTRACT: Nuclear magnetic resonance spectroscopy (NMR) gave information on the behavior of alpha-methylstyrene-co-acrylonitrile. The comonomer sequence distribution in the copolymer and the depolymerization process were detected by solution analysis. The solid-state NMR investigation showed that ¹³C routine spectra such as MAS and CPMAS allowed one to obtain information on the molecular domains of chains and also permitted evaluation of the domains' mobility. In this case, the mobile domain was formed by alpha-methylstyrene (AMS). The variable contact time and the proton spin-lattice relaxation time in the rotating-frame parameter were determinant factors to evaluate the dynamic molecular behavior and the homogeneity of the comonomer distribution along the copolymer chains. © 2002 John Wiley & Sons, Inc. *J Appl Polym Sci* 84: 138–143, 2002; DOI 10.1002/app.10275

Key words: NMR; copolymerization; compatibility

INTRODUCTION

The copolymerization reaction of alpha-methylstyrene (AMS) and acrylonitrile (AN) has not been studied much. But some factors, like the stereochemical and reactivity ratio, can cause a difference in the alpha-methylstyrene-co-acrylonitrile (AMSAN) copolymer properties, compared to alpha-methylstyrene-styrene (SAMS) copolymers. In previous thesis work, it was characterized that the conversion curves, as a function of time, showed that AMSAN presents high conversion in a short period of time.¹ This behavior is not observed for SAMS copolymers.² Another important point that needs to be taken into consideration is the formation of a stable radical in AMS

that can hinder the polymerization process. Also, depending on the reaction temperature and the proportion of AN, the depolymerization process can occur.³ In this study, we investigated the formation and the homogeneity of AMSAN by solution and solid-state NMR techniques. Since NMR spectroscopy is a better source to analyze a polymer material, the combination of solution and solid state can give us a good support to evaluate copolymers.^{4–13}

EXPERIMENTAL

Sample Preparation

The copolymers formed by AMSAN were prepared by emulsion at 84°C, in one step, for a 5-h polymerization reaction. The samples were named AMSAN A and B with respect to the acrylonitrile content in the feed.

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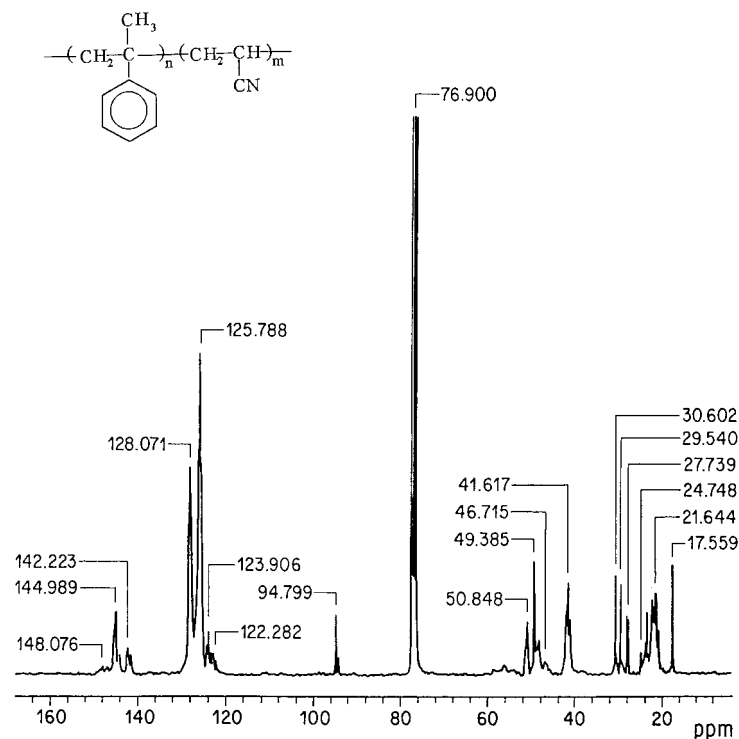


Figure 1 Solution ^{13}C -NMR spectrum of AMSAN A copolymer.

NMR Measurements

The solution NMR spectrum was obtained on a Varian Mercury 300 spectrometer operating at 75.4 MHz for ^{13}C . The ^{13}C -NMR solution spectra were obtained in quantitative conditions: 90° pulse, acquisition time 1.5 s, and delay 10 s at the probe ambient temperature. All solid-state spectra were obtained on a Varian Inova 300 spectrometer operating at 75.4 MHz for ^{13}C . All solid NMR experiments were done at the ambient probe temperature and were performed using gated high decoupling. A zirconium oxide rotor of 7-mm diameter was used to

acquire the NMR spectra at rates of 5.5 kHz. The ^{13}C -NMR spectra were carried out in the cross-polarization mode with magic angle spinning. For the variable contact-time experiment, a range of contact time was established from 200 to 8000 μs . Proton $T_{1\rho}$ values were determined from the intensity decay of ^{13}C peaks with increasing contact times and by delayed contact-time experiments, where the range of spin-locking was 200 to 8000 μs . Both $T_{1\rho}$ measurements were able to give information on the homogeneity and dispersity of the monomers in the copolymers.

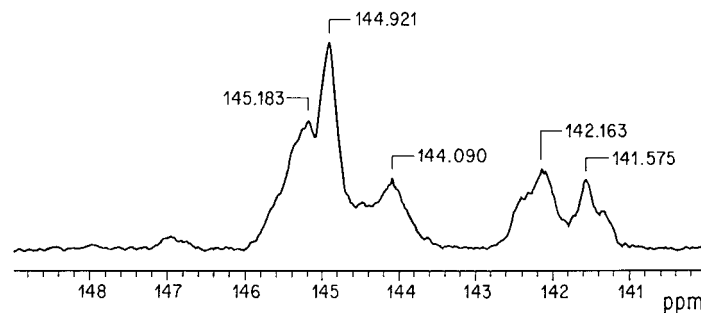


Figure 2 Expansion of the aromatic C_1 carbon (~ 145 ppm) for the AMSAN A copolymer.

Table I Triad Sequences Obtained from the Aromatic C₁ Carbon for the AMSAN A Copolymer

Sample	<i>mm</i>	<i>mr</i>	<i>rr</i>
AMSAN A	31.6	14.8	53.6

RESULTS AND DISCUSSION

Solution Analysis

AMSAN was analyzed by an NMR solution via ¹H and ¹³C. The objective of the ¹H spectra was to determine the ratio between both monomers in the copolymer. The feed of AMS in the reactor was AMSAN A = 25% and AMSAN B = 50%. However, as for the broadening of the ¹H-NMR signals, overlapping signals and the depolymerization process are of concern. It was not possible to measure the ratio between both monomers. It is of importance to point out that in the AMSAN B sample the initial AN monomer proportion caused an instability in the colloidal thermal control during the emulsion copolymerization reaction, due to an acceleration of the propagation step of the AMS monomer insertion. This generated an insoluble product attached to the reactor.

The solution ¹³C spectrum of the AMSAN A copolymer is shown in Figure 1 and some useful information was obtained. First, the proportion between both monomers was determined using the CN line (AN) and aromatic C₁ carbon (AMS) and the proportion of AN was 12%. The sharp

Table II Microstructure and Comonomer Sequence Distributions Obtained from the CN Line for the AMSAN A Copolymer

Comonomer Sequence Distributions	Microstructure				Total
	<i>mm</i>	<i>mm</i> + <i>mr</i>	<i>mr</i>	<i>rr</i>	
AMS-AN-MAS	—	17.8 ^a	—	22.6	40.4
AMS-AMS-AN	—	—	24.7 ^b	—	24.7
AN-AN-AN	12.7	—	11.9	10.3	34.9

^a Just one signal that we suppose to be an *mm* + *mr*.

^b Did not present a good resolution.

NMR signals are due to the depolymerization process. The assignments of triad sequences of the AMS segments were obtained from the aromatic C₁ carbon (~ 145 ppm) (Fig. 2) and are listed in Table I. For AN, its microstructures (*rr*, *mr*, *mm*) and comonomer sequence distributions centered in the AN monomer were measured by the CN lines (Fig. 3) and are listed in Table II. The comonomer sequence distributions centered in the AMS monomer were detected from the methyl line and their values are listed in Table III. Figure 4 shows the expansion of the methyl region for the AMSAN copolymer.

NMR Solid-State Analysis

From the MAS ¹³C-NMR spectra (Fig. 5) using a short delay time between 90° pulses, one can only observe the very mobile region (liquidlike) of the AMSAN copolymers. Also, in this case, only AMS

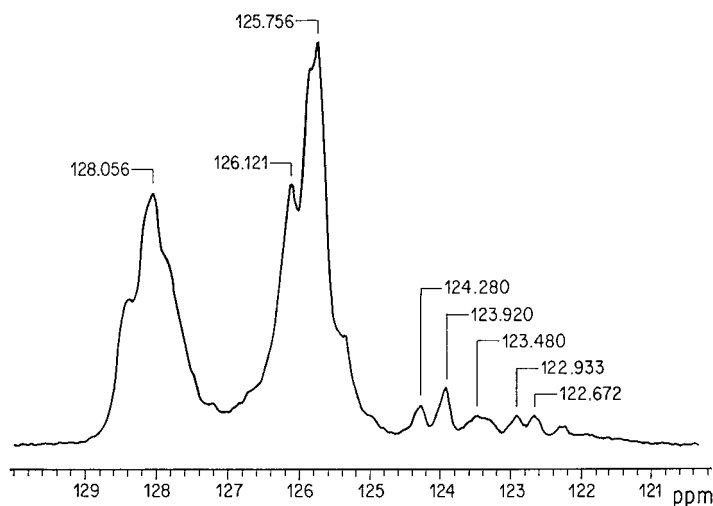
**Figure 3** Expansion of the CN lines for the AMSAN A copolymer.

Table III Comonomer Sequence Distribution Obtained from the Methyl Line of the AMSAN A Copolymer

Sample	AN-AMS-AN	AMS-AMS-AN	AMS-AMS-AMS
AMSAN A	15.0	9.5	35.5

signals were detected. So, as the mobile region is constituted by the AMS monomer, this monomer can promote a plasticization effect on the AN comonomer in the copolymer.

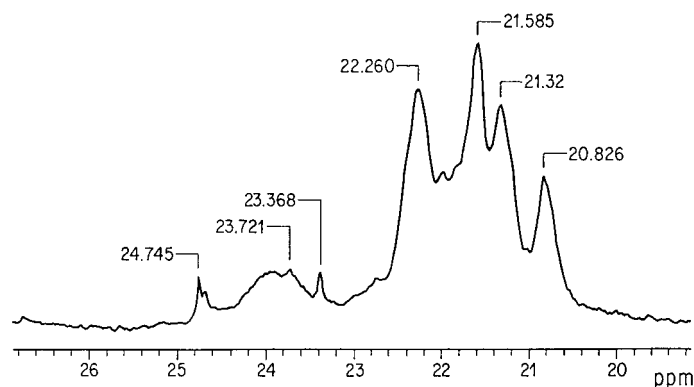
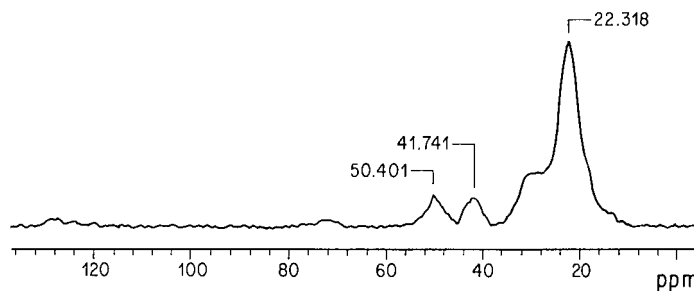
The AMSAN copolymers were also analyzed by ^{13}C solid-state NMR, using the CPMAS technique. The CPMAS ^{13}C for AMSAN B (Fig. 6) showed NMR signals from both monomers and permitted one to make the assignments of each type of carbon.

From the variable contact-time experiment, the distribution form of the ^{13}C decays shows a similar behavior for both copolymers, compared to the homopolymers (Fig. 7). Also, the insertion of AMS causes a change in the distribution form of the copolymers principally in copolymer B, as the AN quantity is higher than in copolymer A.

The values of the proton $T_{1\rho}$ parameter, obtained from the variable contact-time experiment,

for the copolymers and the homopolymers are listed in Tables IV and V. The values for the proton $T_{1\rho}$ parameter are not homogeneous and the chemical-shift values detected for copolymer A are lower than are the values found for copolymer B. These two observations can reflect a random sequencing of the comonomer insertion in the chains. However, AMSAN A presents a better homogeneity of the comonomer distribution in the copolymer chains.

The results shown in Tables IV and V give an indication that, as the copolymers present compositional heterogeneities, the polarization transfer was not very efficient. Also, the copolymer chains are amorphous, reflected by the random sequencing of the comonomer distribution, indicating that AMS can act like a plasticizer. This comonomer, probably, is promoting a plasticization of the copolymer chains, which makes the spatial proxim-

**Figure 4** Expansion of the methyl region for the AMSAN A copolymer.**Figure 5** MAS ^{13}C -NMR spectrum of the AMSAN A copolymer.

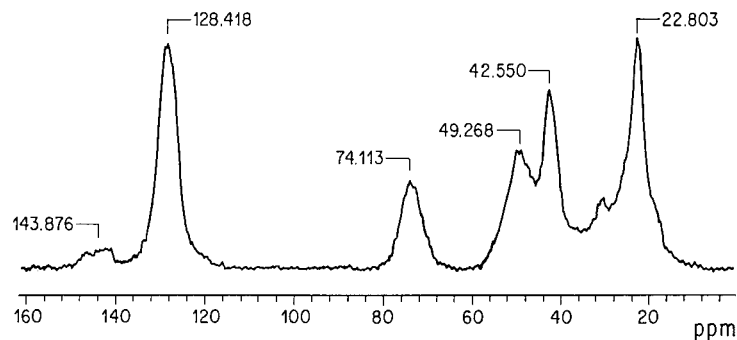


Figure 6 CPMAS ^{13}C spectrum for the AMSAN B copolymer.

ity of the chains not close enough for a good efficiency to transfer the polarization.

To evaluate the distribution of the comonomers along the chains, the $T_1^H\rho$ parameter was measured by a delayed contact-time experiment and the results obtained for both copolymers are listed in Table VI.

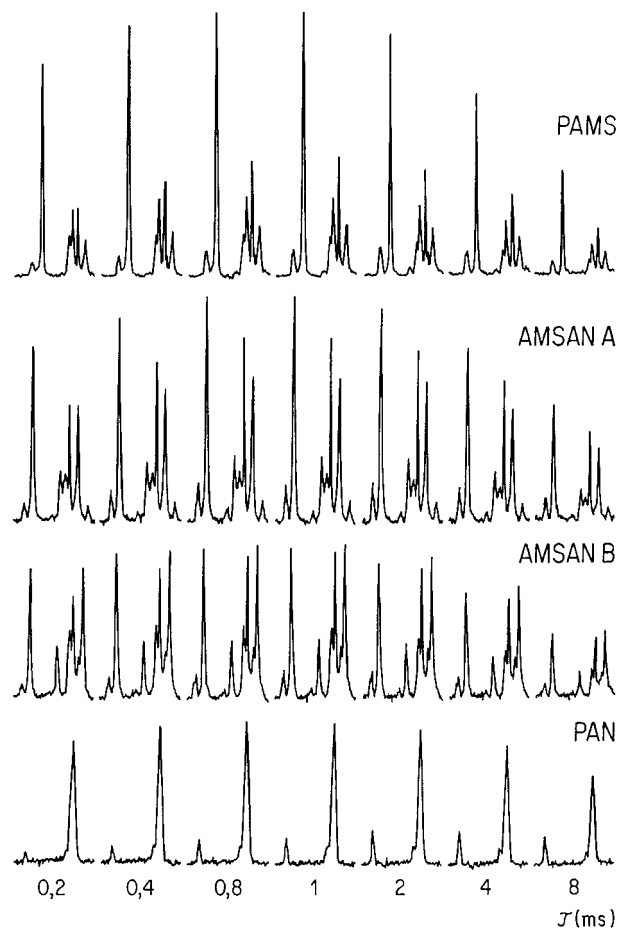


Figure 7 Series of CPMAS ^{13}C spectra for the homopolymers and the AMSAN copolymers.

From the results obtained in Table VI, both copolymers present a reasonable homogeneity dispersion of the comonomers in the chains,

Table IV $T_1^H\rho$ Values for the Resolved Carbons of AMSAN A as a Function of Chemical Shifts Measured by Variable Contact Times

Sample	$T_1^H\rho$ (ms)					
	128.4	125.0	41.1	40.2	25.5	20.0
AMSAN A	—	7.5	—	6.7	—	3.8
PAMS	4.9	—	6.2	—	3.2	—

Table V $T_1^H\rho$ Values for the Resolved Carbons of AMSAN B as a Function of Chemical Shifts Measured by Variable Contact Times

Sample	$T_1^H\rho$ (ms)				
	128.4	42.5	41.1	25.5	22.8
AMSAN B	2.9	5.6	—	—	3.9
PAMS	4.9	—	6.2	3.2	—

Table VI $T_1^H\rho$ Values for the Resolved Carbons of the AMSAN Copolymers as a Function of Chemical Shifts Measured by Delayed Contact Time

Sample	$T_1^H\rho$ (ms)			
	127.8	73.3	41.9	22.3
AMSAN A	8.7	6.2	9.3	—
AMSAN B	9.0	7.6	6.9	7.4
PAMS	4.9	—	6.2	—

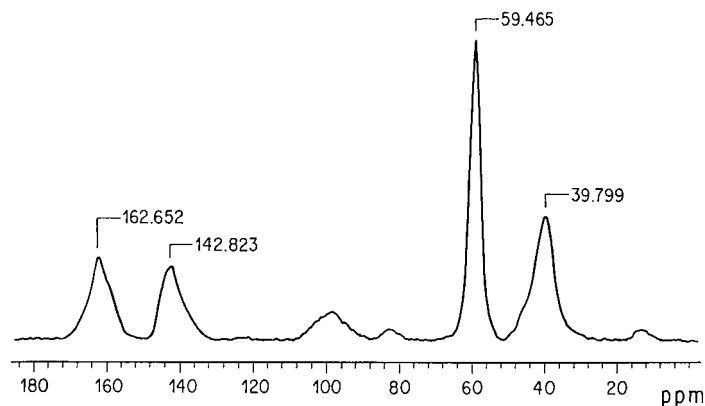


Figure 8 CPMASDD ^{13}C spectrum for the AMSAN B copolymer.

which is, probably, due to the composition of the monomers in the copolymer, considering that the polymerization process is the same. By analyzing the $T_1^H\rho$ parameters, obtained by both NMR experiments, it is seen that the results obtained by those parameters are complementary for this kind of copolymerization process.

The evaluation of the AMSAN copolymers was also carried out by the CPMASDD ^{13}C technique. The CPMASDD ^{13}C spectrum of copolymer B is presented in Figure 8. From this spectrum, only AMS signals were detected, which confirms the fact that this comonomer is acting as a plasticizer in the copolymers. As is known in this type of experiment, only the nonhydrogenated carbons were expected to be detected. But very mobile carbons were also detected, so we can conclude that AMS is a plasticizer.

CONCLUSIONS

Based on the main purpose of this work, the results obtained by solution and solid NMR experiments confirm the fact that the AN content causes an increase in the AMS sequences in the copolymer. Therefore, the high quantity of this comonomer also influences, directly, the depolymerization process of AMS in the AMSAN copolymers.

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