Evaluation of the Diethylene Glycol Bis(allyl carbonate)/Acrylic Acid Copolymer Behavior by Solid-State ^{13}C-NMR

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ABSTRACT: The dynamic behavior of diethylene glycol bis(allyl carbonate) (CR-39)/acrylic acid (AA) copolymers was evaluated by ^{13}C high-resolution solid-state nuclear magnetic resonance (NMR). The NMR data showed that the copolymerization of CR-39 and AA generated copolymers with different molecular behaviors as a function of AA content, which promoted changes in the crosslinking of CR-39 chains and in the intramolecular forces. The copolymerization process influenced the sequence distribution and domain formation of the monomers, which is a consequence of the dispersion of comonomers along the macromolecular chains. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 96: 740–745, 2005

Key words: CR-39; acrylic acid; NMR; copolymerization; crosslinking

INTRODUCTION

The polymer poly[diethylene glycol bis(allyl carbonate)] (CR-39) is frequently used for optical lenses. Because of its two double bonds, one of which is available to be polymerized and/or copolymerized and the other of which is available for crosslinking, the CR-39/acrylic acid (AA) copolymer has advantages over other materials, thus allowing its widespread use in the optical industry. The copolymerization of CR-39 and AA yields a copolymer with good chemical characteristics such as good impact resistance and low density. In its application to focusing lenses, it does not require further treatment after formation of lenses because the copolymerization reaction is completed in the lenses mold. All these properties are derived from the structure and macromolecular ordination of the monomers along the copolymer chains. The sequence distribution of monomers in the copolymer is responsible for the properties of the material. The dynamic and intermolecular interactions of the chains are two dominating factors whose influence leads directly to understanding the copolymer properties.

Solid-state ^{13}C-NMR spectroscopy is one of the most powerful tools for the chemical characterization and molecular dynamic studies of copolymers. The main advantage of NMR over other characterization methods for such polymer materials is the potential of NMR to provide information on the molecular behavior of new copolymers with respect to particular applications.[1-4] With the expansion and the development of new techniques, NMR has been used in a wide variety of different and specific pulse sequences.[5] Based on this, use of NMR yields an abundance of information on the behavior of sample materials in different timescales, and permits development of a methodology to characterize the molecular dynamic of samples.[5-10] Evaluation of the dynamic behavior of the copolymers can be accomplished by applying ^{13}C magic-angle spinning (MAS)/^{13}C cross-polarization magic-angle spinning (CPMAS), particularly for proton spin–lattice relaxation time in the rotating frame ($T_1^H\rho$), which can be measured indirectly both by variable contact time (VCT) experiment and by delayed contact time (DCT) experiment.[11]

Very few studies on the chemical behavior of CR-39/AA copolymers have been published in the literature. The focus of this work was to use solid-state NMR techniques to understand the chemical structure ordination and the dynamic behavior of the copolymer formed by CR-39 and AA.

EXPERIMENTAL

All solid-state spectra were obtained on an Inova 300 spectrometer (Varian Associates, Palo Alto, CA) operating at 75.4 MHz for [13]C. All solid-state NMR experiments were done at ambient probe temperature and were performed using gated high decoupling. A zirconium oxide rotor (7 mm diameter) was used to acquire the NMR spectra at rates of 5.8 kHz. The ^{13}C-NMR spectra were carried out using MAS, with

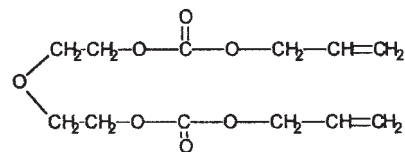short recycle delay (0.3 s) between 90° pulses, in the cross-polarization mode with magic angle spinning (CPMAS), with a recycle delay of 2 s; the VCT experiment covered a range of contact times from 200 to 8000 μs. Proton $T_{1\rho}$ values were determined from the intensity decay of ^{13}C peaks with increasing contact times and also by DCT experiment, with a range of spin-locking from 200 to 8000 μs.

Structure 1

RESULTS AND DISCUSSION

The molecular dynamics of four copolymers formed by CR-39 (Structure 1), with 5, 10, 25, and 50% of AA, were investigated by the NMR techniques described in the previous section.

By use of the MAS ^{13}C-NMR technique (applied to examine only the mobile region), it was observed that the mobility group in the copolymers was mainly composed of CH_2—O groups from both comonomers. Moreover, with increasing AA content in the copolymer the signal becomes narrow, which suggests an increase in the molecular mobility caused by AA con-

tent, which probably hampers the formation of crosslinking in CR-39 chains (Fig. 1).

Figure 2 shows the CPMAS ^{13}C spectra of CR-39 and its copolymers with AA. From these spectra some useful information was detected. The CR-39 homopolymer signals were located at 155.5 ppm (C=O), 132.3 ppm (=CH), 119.4 ppm (=CH_2), 68.7 ppm (CH_2—O), and 32.6 ppm (CH_2). The poly-(acrylic acid) showed signals at 178.7 ppm (C=O), 42.3 ppm ($C_\alpha H$), and 35 ppm ($C_\beta H_2$). For the copolymers, the peak at 178.7 ppm, derived from the C=O of AA, was detected only when 10% of AA was incorporated, and it is split into at least two peaks as a result of the forms of intermolecular
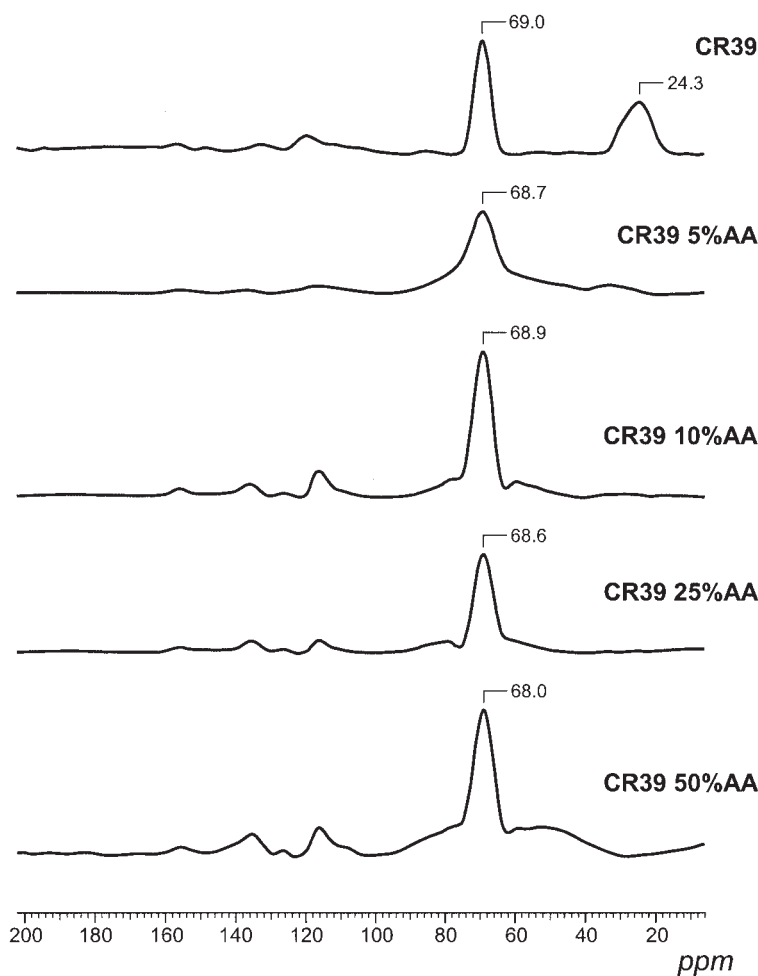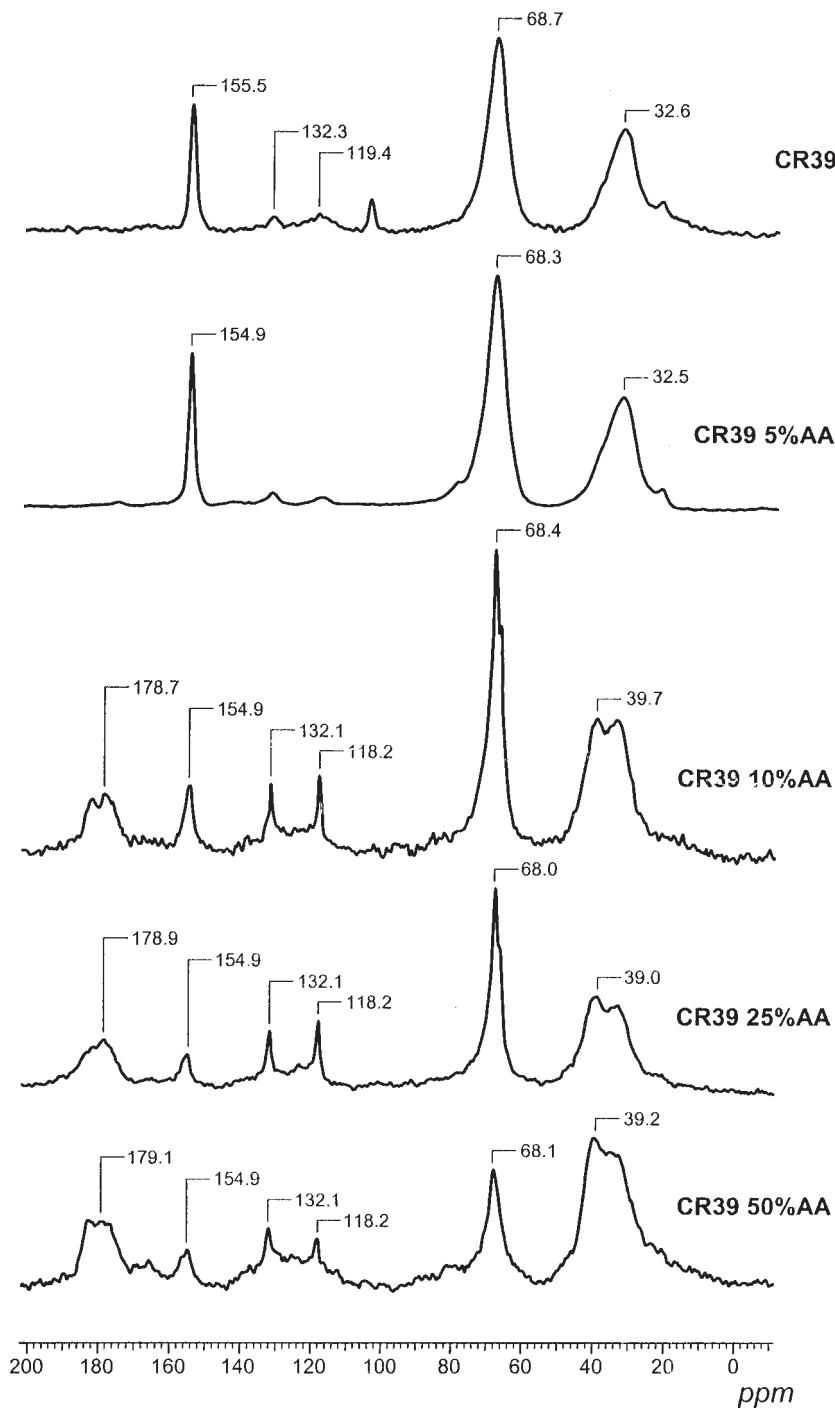

Figure 1 A series of MAS spectrum of CR-39 and their copolymers with acrylic acid.

Figure 2 A series of CPMAS spectrum of CR-39 and their copolymers with acrylic acid.

hydrogen bonds and/or as a result of the distribution sequence of monomers along the chains. The peak detected at 68.7 ppm becomes narrow when 10% of AA is incorporated into the copolymer compared to the pure CR-39 and a shoulder was also observed. The comonomer distribution caused a change in the molecular motion. An overlapping NMR signal at 39.7 and 32.5 ppm, after incorporation of 10% of AA in the copolymer, comes from the

CH_2 derived from both monomers; it is also clear that as the AA content increases the signal at around 39 ppm also increases. The random AA monomer distribution in the copolymer chains can promote an increase in the molecular mobility in these chains, which affects the linewidth of the NMR signals.

Tables I and II show the values of $T_1^H\rho$ measured by variation contact time and delayed contact time, respectively. The $T_1^H\rho$ is an informative parameter for

TABLE I
Proton Spin–Lattice Relation Time in the Rotating Frame, Obtained by Variable Contact Time for CR-39 and Its Copolymers with AA

Sample	δ (ppm)		
	154.9	68.3	32.5
		$T_1^H\rho$ (ms)	
CR-39	3.4	3.4	3.3
CR-39 5% AA	4.1	4.3	4.0
CR-39 10% AA	9.0	2.9	1.7
CR-39 25% AA	13.9	14.9	—
CR-39 50% AA	1.6	4.3	2.1

TABLE II
Proton Spin–Lattice Relation Time in the Rotating Frame, Obtained by Delayed Contact Time for CR-39 and Its Copolymers with AA

Sample	δ (ppm)		
	154.9	68.3	32.5
		$T_1^H\rho$ (ms)	
CR-39	2.5	2.6	2.7
CR-39 5% AA	3.3	2.9	3.0
CR-39 10% AA	1.0	1.6	1.4
CR-39 25% AA	1.4	1.8	1.4
CR-39 50% AA	1.3	1.4	2.0

chemical and structural characterization because it is sensitive to molecular mobility. When this parameter is measured by VCT, it has a contribution of contact time during the polarization transfer, which depends on the spatial proximity of the chains. In this experiment the intensity of signals was dependent on the rate of cross-polarization (CP) ($1/T_{CH}$) for each ^{13}C nucleus.

From the values of $T_1^H\rho$ listed in Table I, it can be seen that both CR-39 and the copolymer CR-39/AA 95/5 were characterized by a homogeneous dynamic behavior with respect to monomer distribution along the macromolecular chains: as a consequence there was good spin contact. No significant change in the relaxation parameter was characterized. Therefore, when 10% or more of AA is incorporated into the
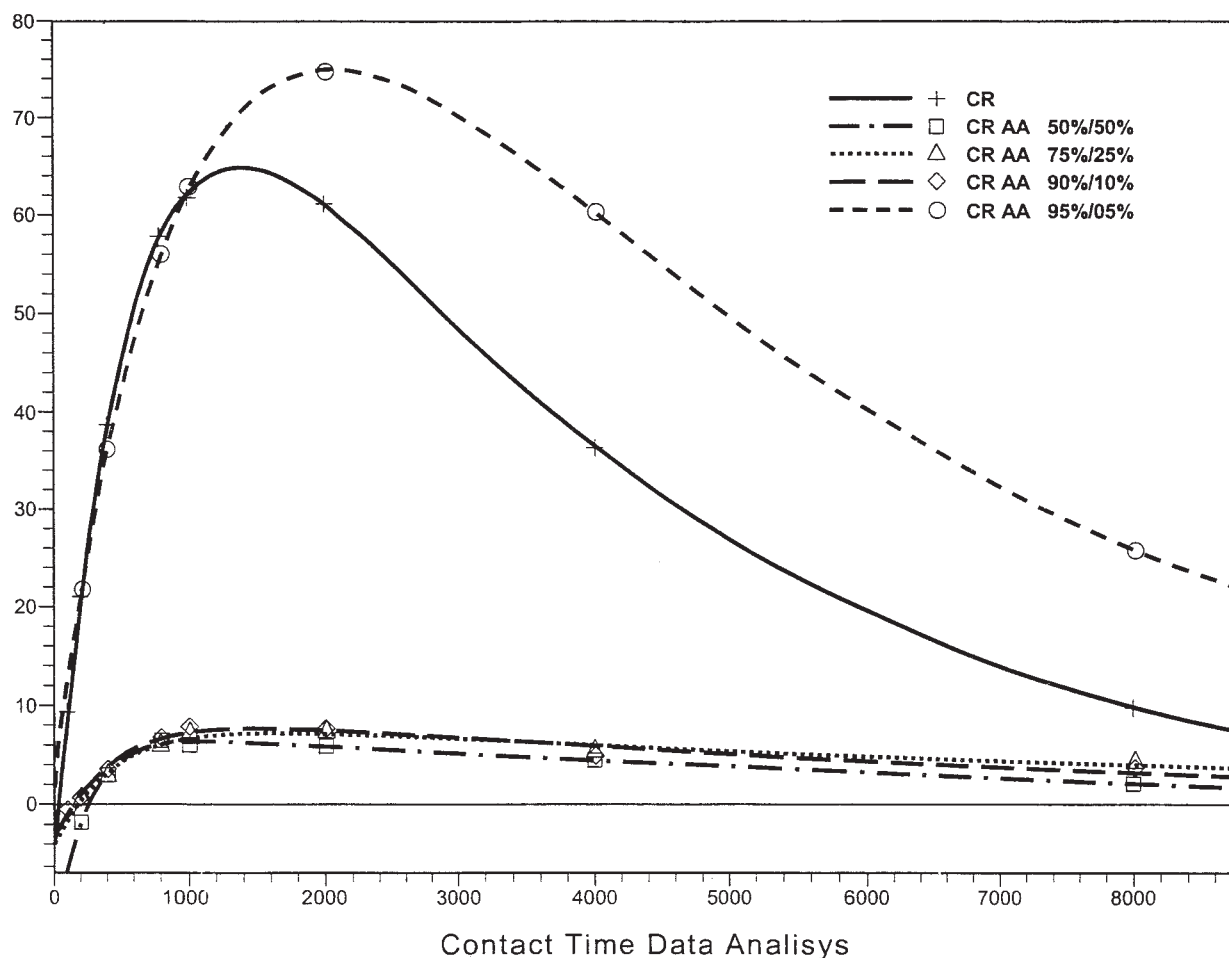
Figure 3 Contact time data analysis.
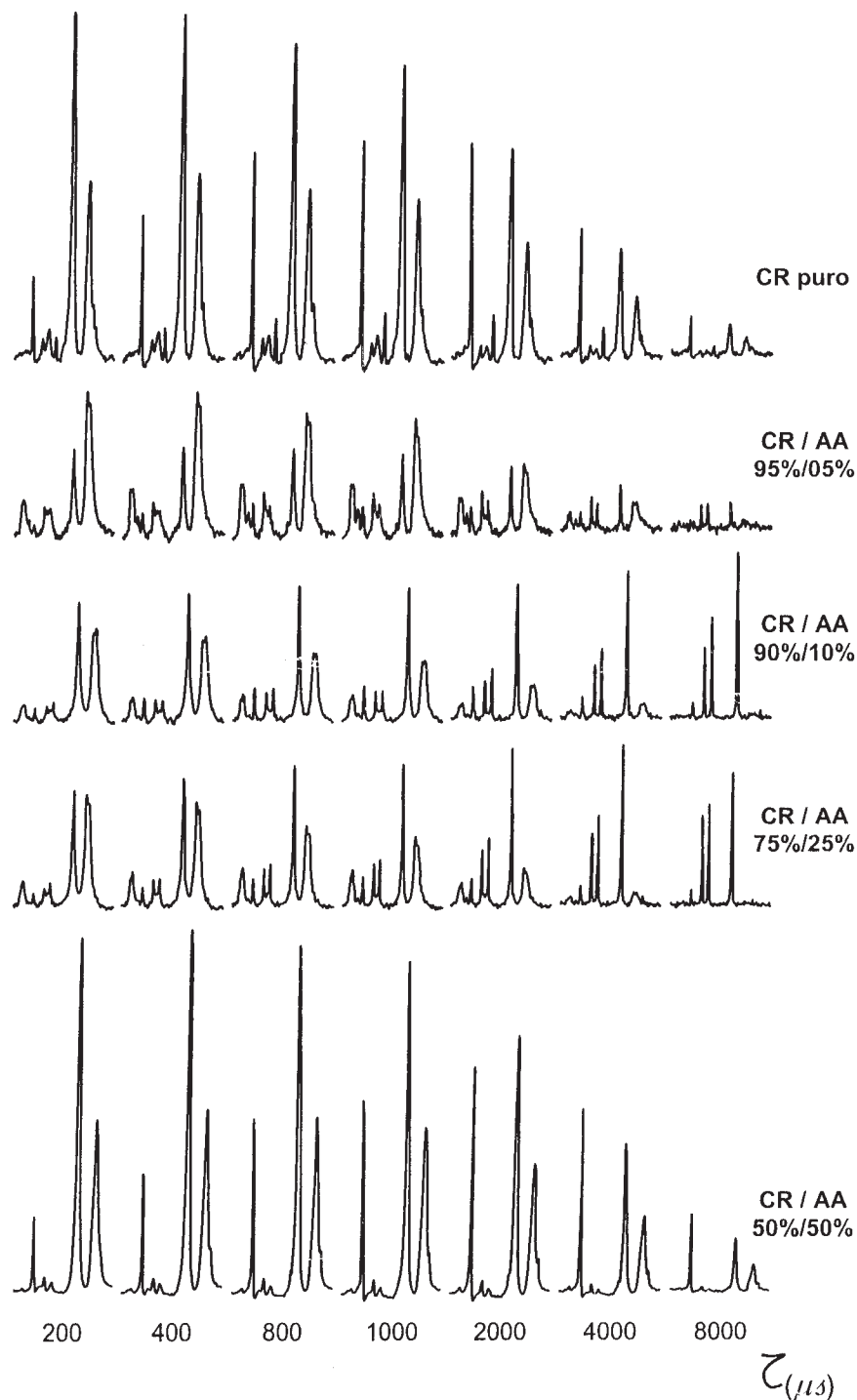
Figure 4 A series of variation contact time experiment of CR-39 and their copolymers with acrylic acid.

copolymer, a drastic change in the molecular mobility occurs, probably attributable to the distribution of comonomers, formation of domains, and, consequently, packing of chains.

Figure 3 shows the logarithmic intensity versus the proton spin-locking time (τ) of the carbonyl carbon located at 154.9 ppm, for CR-39, CR-39 5% AA, CR-39 25% AA, and CR-39 50% AA. A single $T_1{}^H\rho$ decay for

CR-39 and for the copolymers with AA means that a strong dipolar coupling exists between protons, which promotes efficient spin diffusion along the chains. The CR-39 and CR-39 5% AA showed a similar shape, although there was a small difference between both copolymer and homopolymer. By observing CR-39 10% AA and other copolymers, a significant change in the curves' shape may be noted, indicating a change in

the molecular mobility of the copolymer, which is responsible for the changes in both the properties and the dynamic behavior, because the comonomer's sequences along the chains can interfere in the crosslinking of CR-39 chains, thus promoting an increase in the mobility.

Table II shows the $T_1{}^H\rho$ values, measured by DCT, compared with the values measured by VCT, given that the DCT experiment provides the $T_1{}^H\rho$ values without cross-polarization interference.

Table II shows that the addition of 5% of AA formed a copolymer that did not substantially change the molecular dynamic behavior of the CR-39, which indicates that this proportion did not affect the formation of crosslinks in the CR-39/AA copolymer. Therefore, the molecular mobility changed with incorporation of ≥10% of AA monomer, whereupon a sharp decrease in the relaxation parameter was characterized because of the changes in the distribution of monomers in the macromolecular chains; in this case the AA promoted a reduction in the crosslinking of CR-39.

From the relaxation parameter, measured by both experiments, one can see that these copolymers are formed by segments that are composed of one rich in CR-39, one formed by AA, and a third one formed by the random distribution of both comonomers.

Analysis of the distribution form of VCT ^{13}C decays (Fig. 4) shows that for the copolymers with 5 and 10% of AA there was only a negligible change compared to that of the CR-39 homopolymer. Therefore, the addition of 25 and 50% of AA caused some variation in the distribution form, attributed primarily to molecular mobility, thus confirming the results extracted from the other techniques described earlier.

CONCLUSIONS

CR-39 and CR-39/AA copolymers were analyzed by the same techniques to compare their molecular behaviors. The NMR data showed that CR-39 homopolymer is amorphous and rigid because the signals are very broad, which can be related to the presence of crosslinking, and values of the relaxation parameter were compatible with these characteristics. From the NMR results it is clear that the copolymerization of CR-39 and AA formed copolymers with different molecular behaviors as a function of AA, which promotes changes in the crosslinking of CR-39 chains. The differences arise from a change in the molecular mobility caused by insertion of the AA comonomer along the macromolecular chains. The copolymerization process influences both the form of distribution and the formation of domains.

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