

SEQUENCE DISTRIBUTION IN ACRYLONITRILE-METHYLMETHACRYLATE RANDOM COPOLYMERS
 BY N.M.R. SPECTROSCOPY

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ABSTRACT

The sequence distribution studies on the acrylonitrile-methylmethacrylate copolymer of high methylmethacrylate (M) content ($30\% < M < 75\%$) by NMR studies is reported in this paper. A tentative assignment has been made for the isolated M centered unit AMA, 2M centered units MMA (or AMM) based on the shape of the peaks observed for methoxy and α -methyl protons. The presence of MMM type of triad sequences is indicated by the pattern of α -methyl protons.

INTRODUCTION

NMR is one of the most important techniques for the determination of sequence distribution in polymer and copolymer systems. Using this method, the syndiotactic, isotactic and heterotactic triad distribution in polymethylmethacrylate (PM) and polyacrylonitrile (PA) have been studied in detail by a number of workers¹⁻⁹. However, not much work has been done in the case of acrylonitrile-methylmethacrylate (A-M), copolymers. The work of Pham¹⁰ in this system is mainly confined to copolymer samples of low methylmethacrylate (M) content ($1\% \leq M \leq 20\%$). Hence, an attempt has been made to determine the sequence distribution of A-M copolymers of high M content and also to determine the % composition of these samples and to compare with the values obtained by the chemical analysis.

MATERIALS AND METHODS

A-M copolymers of four different compositions (MA₁, MA₂, MA₃ and MA₄) were prepared by free radical polymerisation using benzoyl peroxide (0.05 mole %) as initiator¹¹ and the percentage of conversion was about 20. Table I gives the monomer feed, the percentage of conversion and the mole% of A. A content was analysed by N₂ analysis.

The NMR spectra were recorded by a varian HA-100 Spectrometer at 120°C. Deuterated dimethylsulfoxide (*d*₆-DMSO) was used as solvent. The concentration of the solutions used is 10%. Tetramethylsilane (TMS) is used as internal reference. Figure 1 shows the spectra of copolymers, as well as of the parent homopolymers.

RESULTS AND DISCUSSION

The spectrum of pure PM (Fig. 1) has the following peaks. The methoxy protons of PM homopolymers^{2,10,3} in *d*₆-DMSO resonate at 6.27 τ . The methylene protons appear at 8.05 τ and 8.11 τ respectively; α -methyl protons appear between 8.6-9.4 τ , which consists of three peaks at 8.78 τ , 8.95 τ and 9.11 τ corresponding to isotactic, heterotactic and syndiotactic triad sequences respectively.

The spectrum of PA homopolymer shows a quintuplet from methine (CH) protons centered at 6.72 τ . Methylene protons appear as a complex pattern in the range 7.4-8.0 τ . This has been attributed to the combination of two isotactic and syndiotactic diads^{1,4,10} centered at 7.76 τ and 7.79 τ respectively.

In the A-M copolymer systems (Fig. 1) four groups of peaks are observed, as noticed by Pham¹⁰. The peaks in the range 5.8-6.4 τ corresponding to

TABLE I

Initiator: Benzoyl peroxide

Solvent: DMF.
 Temperature: 60 \pm 0.05°C

Copolymers	Mole % of A in Monomer feed	% of Conversion	Composition ^a		Composition ^b	
			A%	M%	A%	M%
MA ₁	37.6	20.2	28.9	71.1	28.9	71.1
MA ₂	57.2	10.4	41.5	58.5	42.2	57.8
MA ₃	74.6	21.9	56.6	43.4	54.1	45.9
MA ₄	84.2	17.6	65.7	34.3	65.1	34.9

^a by N₂ analysis, ^b from NMR.

AMA, whereas a pronounced shoulder in all the methoxy peaks represents the configurational triad distribution of 2M centered MMA (or AMM) type of units. This shoulder becomes less pronounced as M content is decreased. Triad sequences of the type MMM are not observed clearly in these peaks, which should appear at a slightly higher field (*i.e.*, at 6.27 τ). These observations are in conformity with those made by Pham¹⁰. But, from the α -methyl proton peaks, it was assumed that triad sequences of MMM type are present. This can be clarified by obtaining spectra with better resolution or by simulating these peaks. This work is in progress.

The composition of the copolymers by NMR analysis has been determined by the method of Pham¹⁰ using the following relation

$$\text{Mma}\% = \frac{(1/3) \text{ Integral of Methoxy (or } \alpha\text{-n.ethyl) protons}}{(1/2) \text{ Integral of methine protons.}}$$

These values are given in Table I. They agree well with the values obtained by N₂ analysis.

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THE DEFORMATION BEHAVIOUR OF S.G. IRONS

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ABSTRACT

The deformation behaviour under compression at room temperature of cast and ferritised S.G. (Spheroidal Graphite) irons has been studied to understand their high ductility. It has been established that on deformation the spheroidal graphite particles distort considerably and take to ellipsoidal shapes. The deformability index values suggest that graphite, although brittle by itself, deforms to a greater extent than either ferrite or pearlite in the matrix. It has also been found that an increase in strain decreases the deformability index of graphite.

S. G. IRONS also known as nodular irons or ductile irons, are extensively used in industry^{1,2}. They are stronger than gray cast irons and their superior strength is understood in terms of the smaller graphite (crack) length. Their good ductility is, however, not well understood.

It is now known that the ductility of two-phase materials is mostly dependent on the volume fraction and shape and is independent of the nature, strength or size (in the range of 1 to 200 μ) of the second phase particles^{3,4}. The mechanism of fracture is, however, different for two-phase materials containing hard and soft particles. The former gives rise to stress concentrations resulting in the formation of holes in their vicinity. If the second phase, particles are soft, they undergo equal or more deformations than the specimen as a whole.

The amount of deformation undergone by the dispersed phase in comparison with that of the specimen is expressed in terms of the deformability index, ν , given by

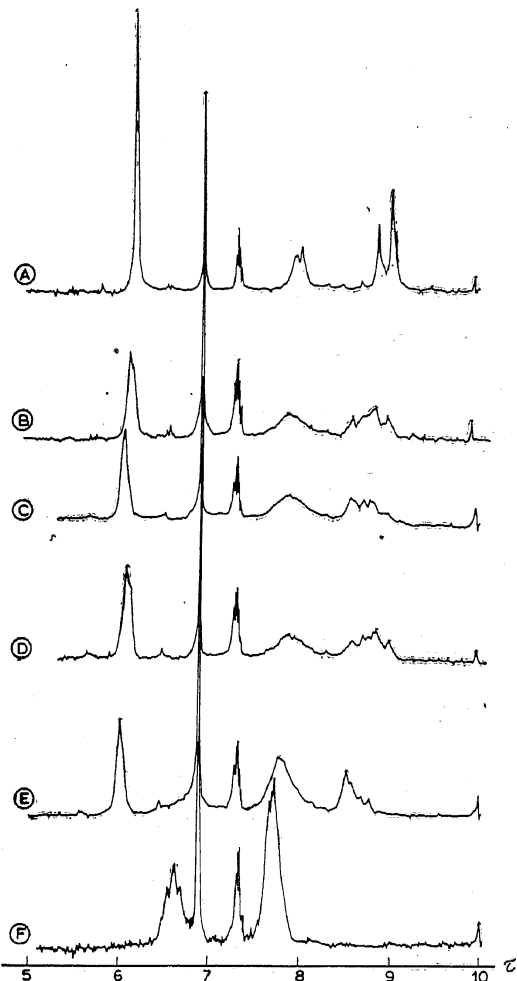
$$\nu = \frac{\text{amount of deformation undergone by the second phase}}{\text{amount of the deformation undergone by the specimen as a whole}}$$

Malkiewioz and Rudnik⁵ showed that the deformability index for tensile stress conditions is given by

$$\nu = \frac{2 \log (b/a)}{3 \log (l_f/l_0)}$$

where l_0 and l_f are the initial and final lengths of the specimen and b and a are the major and minor axes of the ellipsoidal shape of the inclusion obtained after deformation.

methoxy protons of the copolymers appear at a slightly lower field as compared to that of PM. It is also noticed that as the composition of M is increased, the peaks move to slightly higher field.



NMR SPECTRA AT 100 MHz. (A)-PMMA, (B)-MA1, (C)-MA2
(D)-MA3, (E)-MA4 AND (F)-PAN

FIG. 1

The quintuplet observed in the case of PA homopolymer for methine (CH) protons is not present in all the polymer samples studied ($M \leq 20\%$). In fact, these peaks diminished when the mole% of M was increased from 4.4 to 20.0 in the systems studied by Pham¹⁰.

The peaks between 7.6 and 8.5 τ are due to methylene protons of the copolymers. All these peaks appear as a broad band. The peaks move from lower to higher field as M content is increased.

The α -methyl protons resonate in the range 8.4 to 9.2 τ . These peaks appear at a slightly lower field as compared to peaks of α -methyl protons of PM.

The shift noticed corresponding to methoxy and α -methyl protons for the spectra recorded in *d*7-DMF is different from what is observed for the copolymers in *d*6-DMSO. This may be due to the solvent effect.

Absorptions near 7.46 τ , and those in the range of 7.34-7.08 τ are due to hydrogen atoms remaining in *d*6-DMSO and to water absorbed in the solvent respectively¹.

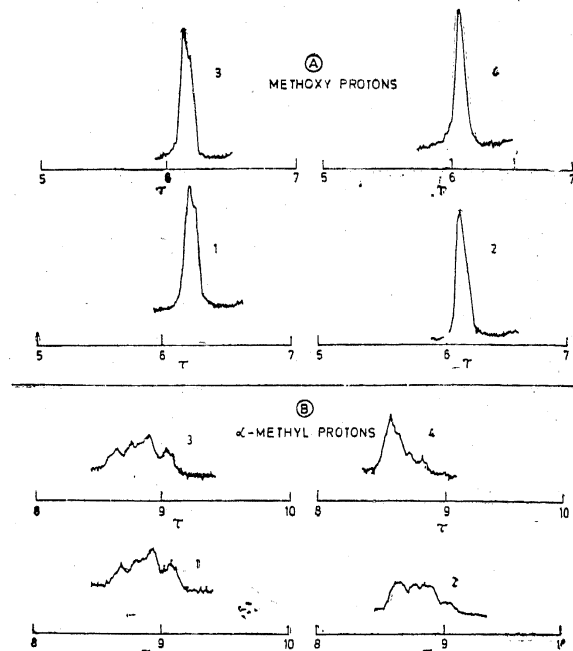


FIG. 2 NMR SPECTRA AT 100 MHz (1) MA1, (2) MA2, (3) MA3 & (4) MA4

The α -methyl proton peaks of the copolymers (Figs. 1 and 2) are a complex combination of different types of triad sequences, as observed by Pham¹⁰. The peak in all the copolymer systems (in *d*6-DMSO) appears as a broad one and this broadening increases as the M content is increased in the copolymer as pointed out by Pham. These α -methyl peaks comprise of triad sequences of isolated M centered units (*i.e.* AMA type). Pham¹⁰ observed a shoulder at 8.83 τ (*i.e.*, 1.17 δ value) which he related to 2M centered MMA (or AMM) triad sequences. He expected that the intensity of this peak might increase as the composition of M increases in this system. If this is the case, shoulder appearing at 8.71 τ value in MA₄ might be the same type of 2M centered sequences, but for the other copolymers, it is difficult to say anything about these sequences from the spectrum. Since the composition of M in all the copolymers are high, it is possible to assume that the 2M centered MMA (or AMM) type sequences appear in abundance in addition to the triad sequences of MMM type. The reason for this assumption is that the broad spectrum of α -methyl peaks is slowly shifted to higher field as M content is increased, where the α -methyl protons of PM appear. In addition to that a gradual increase of the peaks connected to syndiotactic and heterotactic type of peaks observed in PM is also noticed.

The methoxy protons peaks of the copolymer (Figs. 1 and 2) correspond to triad distribution of the type