Nieto, J. L., Baselga, J., Hernández-Fuentes, I., Llorente, M. A., Piérola, I. F. (1987). Polyacrylamide networks. Kinetic and structural studies by high field H-NMR with polymerization in situ. *European Polymer Journal*, 23 (7), pp. 551-555.

DOI: 10.1016/0014-3057(87)90111-X

POLYACRYLAMIDE NETWORKS. KINETIC AND STRUCTURAL STUDIES BY HIGH FIELD ^{1}H-NMR WITH POLYMERIZATION *IN SITU*

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The crosslinking polymerization of acrylamide (AA) and *N,N*-methylene-bis-acrylamide (BA) in aqueous solution at 22°C has been studied by H.R. ^{1}H-NMR spectroscopy. The initial comonomer mixture was placed inside the NMR spectrometer probe head and the polymerization was followed for 10 hr. This procedure allows measurement of the instant composition of the residual comonomer mixture even during and after gelation and therefore to calculate the composition of the formed copolymer or network. When the reaction was finished, the structure of the most mobile part of the network was also analyzed.

INTRODUCTION

The numerous applications of polyacrylamide (PAA) networks depend on its structure. It has been noted by several authors [1–7] that the network structure is highly dependent on the concentration of acrylamide (AA) and the tetrafunctional comonomer, typically *N,N′*-methylene-bis-acrylamide (BA). Structural studies have usually been made on the final reaction product. Results from techniques sensitive to very different properties (electron microscopy [2], Raman spectroscopy [3], swelling equilibrium [4], DSC [3], neutron and light scattering [5], permeation [6] and mechanical measurements [7]) show that PAA gels are heterogeneous.

In order to justify the formation of microdomains of different characteristics, several arguments based on the mechanism or kinetics of the crosslinking reaction have been proposed. Richards and Temple [4] assume the existence of clusters of BA which is water soluble but more hydrophobic than AA. This fact would cause the formation of large BA sequences in the first reaction steps, but BA solubility increases during the polymerization and so BA sequence length would decrease [4]. This non-random distribution of BA in the network would explain, according to this hypothesis, the PAA gel heterogeneity. Gupta and Bansil [3] resort to kinetic arguments; they assume the existence of polymer domains rich in BA with plenty of branches and side chains which are quite polydisperse in size. Weiss *et al.* [6] propose a two phase structure with different segmental densities and so different draining properties; the most concentrated domains would be produced in the first reaction stages in such a way that the monomer mixture composition of each shell around the growth centre would be reproduced in the copolymer. In the last stages of reaction, some linking chains between the microgel particles would be formed and that would constitute the dilute phase [6]. Hsu and Cohen [2] examined the structure of PAA gels by means of scanning electron microscopy, confirming the existence of highly crosslinked regions and estimating their size from micrographs. The explanation for such regions is, as before [3, 4], the formation of aggregates by BA; some support for that suggestion is found by comparing the heterogeneity of gels prepared in pure water and those prepared in water–glycerol mixtures.

All these hypotheses about the building up of the macromolecular structure need experimental support. The aim of this work is to follow the process of network formation by means of high field ^{1}H-NMR spectroscopy with polymerization *in situ*.

Dušek and Spěváček [8] made an interesting study of vinyl–divinyl copolymerization by NMR on low conversion soluble copolymers. In that work, NMR spectroscopy was revealed as a powerful technique to characterize the microstructure of polymer sols. This is not the case for polymer gels, since the line-width of the ^{1}H-NMR spectra increases with microviscosity and therefore, the signal coming from protons close to some network knot or regions of high segmental density becomes broad and at room temperatures it is usually lost in the noise. Nevertheless we have made use of the technique because at higher temperatures the fringes and most flexible parts of the network can be directly observed. The whole macromolecular composition can also be measured, at room temperature, at each stage of the polymerization through the difference between the initial and the actual comonomer concentration, provided by the NMR spectra. The method we have employed has moreover the advantage that it does not perturb the system and leads to the sample composition even during and after gelation.

MATERIALS AND METHODS

Reagents

AA and BA were high purity Eastman Kodak products, and D_2O (99.98%) was from Scharlau. As initiator, the redox system potassium persulphate (PS)/triethanolamine

(TEA) was employed. Both PS and TEA were Carlo Erba RPE products.

^{1}H-NMR spectra

Proton NMR spectra were obtained at 360 MHz on a Bruker WM-360 spectrometer in the Fourier mode. Recording conditions were 8 μsec pulse width (90° flip angle), 3000 Hz sweep width, 16K points and 13 scans. A relaxation delay of 20 sec between pulses was used to ensure that quantitative signals from the differently relaxing protons of both molecules were obtained.

The kinetics were followed by running several spectra in a 10 hr period, followed by the plotting of the integral curve corresponding to monomer signals on a suitable scale. Although the $-CH_2-$ bridge signal from the network overlaps with that of the methylenic protons of the BA monomer, there is no problem in the integration because of the very different line-widths of the two signals, the former being lost in the noise except at high temperature. Figure 1 illustrates how the intensities of the signals from the monomers were reduced during the polymerization. The temperature was maintained at 22°C with the help of the standard Brucker accessory. At the end of the polymerization, the temperature was raised to 90°C and a new spectrum was recorded (Fig. 3).

Samples preparation

Samples were prepared as follows: TEA, AA and BA were dissolved in D_2O in the NMR 5 mm tube. PS, also dissolved in D_2O, was added and the mixture was deaerated by bubbling N_2 for 1 min. The sample tube was introduced in the probe and, from then on, the spectra were recorded.

The use of D_2O of the highest degree of deuteration available plus the previous exchange of the amide protons of AA and BA with D_2O (followed by freeze-drying) was shown to be necessary to maintain the solvent residual signal at a minimum. This procedure permitted accurate integration of the $-CH_2-$ signals of BA, that lie very close to the HDO signal. 1% of hydroquinone (HQ) was added to the AA monomer to prevent polymerization during the freeze drying.

Concentrations used were 6.57×10^{-3}M for PS, 1.12×10^{-3}M for TEA, 0.512M for AA and 0.0915M for BA. The overall comonomer concentration was 5.05(g/100ml) and there was 27.9% by weight of crosslinking agent ($f^0_{BA} = 0.148$, $f^0_{AA} = 0.250$).

RESULTS AND DISCUSSION

Time course of the polymer composition

During polymerization the NMR spectra show four signals (Fig. 1). One of the CH_2 = vinylic protons resonates at 5.85 ppm; the second of the CH_2 = protons and the CH = vinylic proton give overlapping signals centered at 6.28 ppm. Two clearly resolved singlets corresponding to residual HDO and the methylenic protons of BA appear at 4.84 and 4.79 ppm respectively. Protons of the polymer skeleton or crosslinks produce very broad signals which are incorporated in the base line and therefore they do not appear in the spectra at 22°C. The network spectrum obtained at the end of the polymerization and at 90°C will be analyzed below.

The integrals of multiplets at 6.28 and 5.85 ppm. ($I2v$ and $I1v$) are proportional to $2C_{AA} + 4C_{BA}$ and $C_{AA} + 2C_{BA}$ respectively, where C_{AA} and C_{BA} are the instant molar concentrations of the comonomers. The integral of the signal at 4.79 ppm ($I2b$) is proportional to $2C_{BA}$ and therefore, the conversion degrees of AA (α_{AA}) and BA (α_{BA}) and the total conversion degree (α_T) can be calculated by comparing the

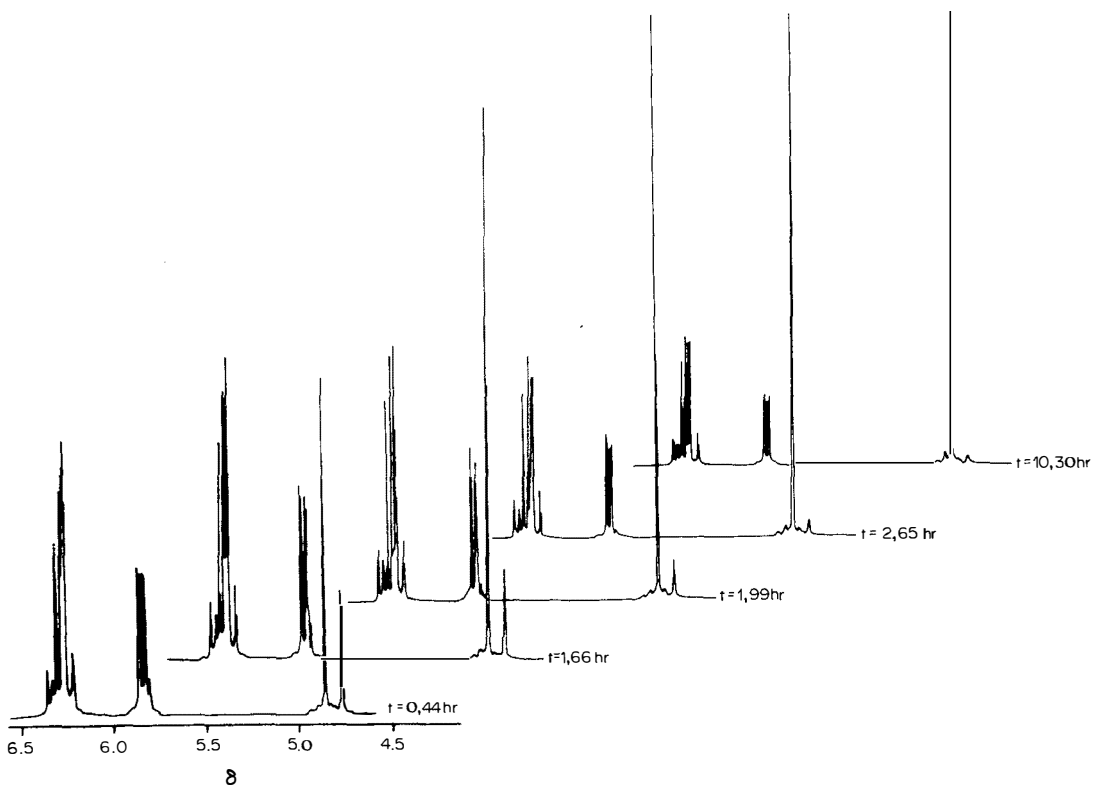

Fig. 1. ^{1}H-NMR spectra of the comonomer mixture during the polymerization process.

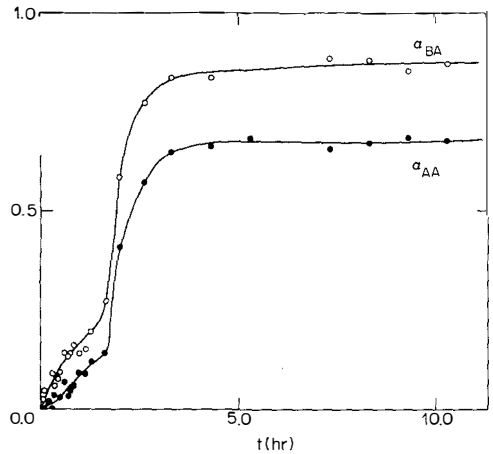

Fig. 2. Conversion of acrylamide and *N,N'*-methylene-bis-acrylamide (α_{AA} and α_{BA}) as a function of polymerization time (t).

integrals $I2v$, $I1v$ and $I2b$ with the corresponding values at time zero, indicated with subscript "0".

The average values obtained from the equivalent equations (1) and (2), (3) and (4) and (5) to (7) have been used as α_T, α_{BA} and α_{AA} respectively

$$\alpha_T(1) = 1 - [(I2v - I2b)/(I2v - I2b)_0] \quad (1)$$

$$\alpha_t(2) = 1 - [(I1v - 0.5\,I2b)/(I1v - 0.5\,I2b)_0] \quad (2)$$

$$\alpha_{BA}(1) = 1 - (I2b/I2b_0) \quad (3)$$

$$\alpha_{BA}(2) = (\alpha_T - \alpha_{AA} f^0_{AA})/f^0_{BA} \quad (4)$$

$$\alpha_{AA}(1) = 1 - [(I2v - 2\,I2b)/(I2v - 2\,I2b)_0] \quad (5)$$

$$\alpha_{AA}(2) = 1 - [(I1v - I2b)/(I1v - I2b)_0] \quad (6)$$

$$\alpha_{AA}(3) = 1 - [(I2v + I1v - 3\,I2b)/(I2v + I1v - 3\,I2b)_0] \quad (7)$$

where f_{BA} and f_{AA} are the molar fractions of the comonomers AA and BA in the reaction mixture.

To calculate α_{AA} and α_T, it must be assumed that each BA reacts either through one of its two unsaturations or through both simultaneously. It is well-known for similar networks of hydrophobic character that pendant vinyl groups can be formed in the first reaction steps [9, 10]. Nevertheless, we have assumed that the concentration of pendant vinyl groups can be neglected throughout the reaction because, given the low BA content, the opposite hypothesis gives the same α_{AA} dependence on time and only slightly different values.

The AA and BA conversion degrees are shown in Fig. 2 as a function of the polymerization time. In less than two hours, when α_{AA} and α_{BA} are about 15% and 25% respectively, a large discontinuity corresponding to the gel point is observed. It has also been found for other comonomer concentrations [11] when HQ is present in the reaction mixture (as explained in the experimental part, the hydroquinone concentration is 1% of that of AA). The effect of HQ is to delay gelation toward larger conversions [11].

During gelation, the polymerization rate becomes 8 times larger and about 50% of the initial AA and 60% of the initial BA, react suddenly. After gelation the reaction is almost stopped without reaching 100%. At any time α_{BA} is larger than α_{AA}, which is evidence of the larger reactivity of BA.

Table 1. Comonomer mixture composition (f_{BA}) and copolymer composition (F_{BA}) as a function of the total conversion degree (α_T)

α_T	f_{BA}	F_{BA}
0	0.148	0.250
0.165*	0.131	0.253
0.710†	0.075	0.183

*Gel point.
†Total limit conversion.

The molar fraction of AA and BA in the copolymer (F_{AA} and F_{BA}) as well as in the residual comonomer mixture (f_{AA} and f_{BA}) have been calculated from C_{AA} and C_{BA} by means of standard expressions. f_{AA} increases slowly during polymerization (Table 1) changing by about 10% over the whole conversion range. As a consequence, F_{AA} also increases in about the same proportion. F_{AA} values at low conversions in Table 1 ($\alpha_T < 10\%$) are extrapolated values since the error in calculated values is 10 times larger than the error in f_{AA}.

Characteristics of the final network

Figure 3 shows the ^1H spectrum of the network at the end of the polymerization and at 90°C. Three new bands corresponding to polymeric protons appear. Only 30% of the whole crosslinked polymer, fringes and the most flexible part of the network, is observed even at the high temperatures. In Fig. 4 the ^1H spectrum of a linear PAA sample, synthesized in a similar way to the network, is also shown.

Similar splitting of the CH_2 and CH skeletal bands can be seen in both spectra, although better resolved in the linear polymer. The skeletal CH_2 band at 2.2 ppm appears to be split into three peaks, two sides corresponding to meso (m) dyads and a central (which overlaps with the right part of the previous doublet) corresponding to racemic (r) dyads. The percentage of each kind of dyad can therefore be estimated as [12]:

$$m(\%) = 200\, I_m / I\mathrm{CH}_{2_p}$$

where I_m represents the integral of the first peak of the CH_2 band and $I\mathrm{CH}_{2_p}$ represents the integral of the whole band.

The linear polymer has 52% meso dyads whereas the observable part of the network, although its determination is much more uncertain, seems to be more isotactic ($70 \pm 10\%$ meso). It has been suggested by other authors [13] that radical PAA has some tendency to isotacticity but no quantitative determination has previously been made.

The skeletal CH band appears at about 2.8 ppm. A shoulder in the low field side can be seen for both the linear polymer and the network (Figs 3 and 4). This shoulder, with relative intensity temperature independent, can be assigned to head-to-head addition and corresponds to 15% of the monomeric unions. Swant and Morawetz [14] have found by another technique the same order of magnitude for head-to-head unions in linear PAA synthesized under conditions similar to our samples.

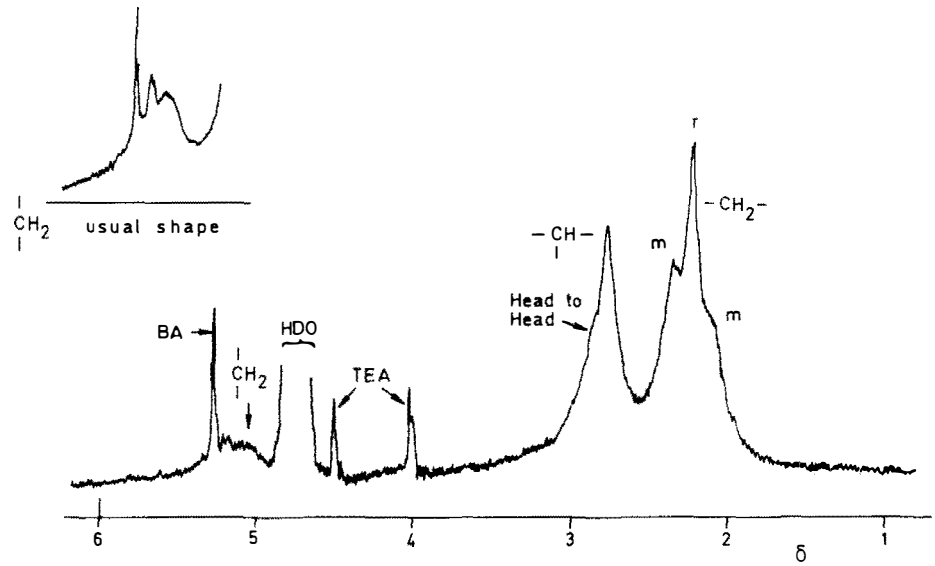

Fig. 3. High temperature (90°C) ^{1}H-NMR spectrum of the final network. The usual shape of the methylenic bridge protons band is inserted.

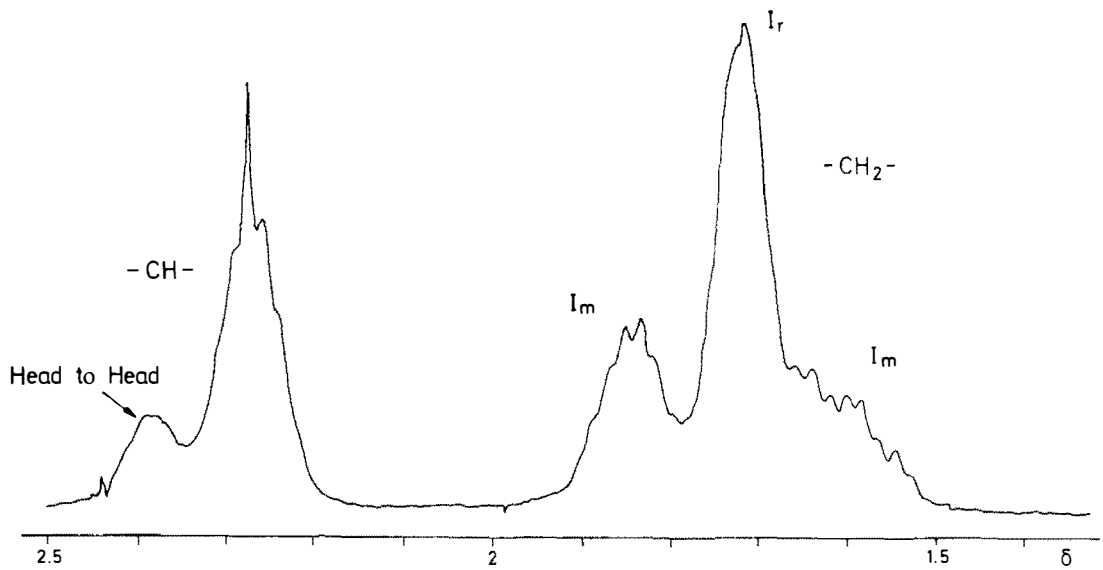

Fig. 4. ^{1}H-NMR spectrum of linear polyacrylamide obtained under the same conditions as the network.

In the high temperature spectrum, the HDO signal appears at 4.7 ppm and the CH_2 bridge protons give usually at 5.2 ppm a broad band in which three different signals can be seen (Fig. 3). The sharp line at lower field corresponds to unreacted BA monomer. The broad and intense line at higher field can be assigned to methylenic protons bridged by their two vinylic sides to the polymer. The intermediate character of the third line, in both chemical shift and line width, certainly suggests its assignments to BA monomer linked to the chain by only one of its vinylic groups. (No measurable concentration of pendant vinylic groups can be observed in the high temperature spectrum of the network studied in this work.)

CONCLUSIONS

Polyacrylamide networks are heterogeneous because of the mechanism of crosslinking polymerization, in which, three stages can be distinguished.

(i) The pre-network formation that involves 15% of the initial AA and 25% of the initial BA. (ii) The gelation process in which 50% AA and 60% BA react suddenly and (iii) the slow crosslinking after gelation that does not contribute significantly to α_T.

The composition of the polymer formed in each stage is different and therefore microdomains of different structure will be formed. Head-to-head additions may also cause microheterogeneities.

Acknowledgements—We are indebted to Dr A. Horta and Dr P. de Porcellinis for many helpful discussions.

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