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POLYACRYLAMIDE GELS. PROCESS OF NETWORK FORMATION

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This paper refers to the crosslinking copolymerization of acrylamide (AA or monomer-1) and N,N'-methylene-bisacrylamide (BA or monomer-2) in aqueous solution at 22°, covering a broad range of comonomer concentrations. The extent of reaction, p_T, the composition of the remaining comonomer mixture, f_2, and the copolymer composition, F_2, have been determined by high resolution ^{1}H-NMR with polymerization *in situ*. The non-linear regression fit of f_2 as a function of p_T yields almost the same values for the reactivity ratios for any of the studied comonomers feeds. The instant copolymer composition changes with the copolymerization time due to a shift in the residual comonomer composition and, to a smaller extent, to changes in the comonomer relative reactivities. This effect contributes to the heterogeneity of the final network.

INTRODUCTION

Crosslinking copolymerizations of a monovinylic monomer and a crosslinker with more than one unsaturation per molecule have been the subject of many theoretical and experimental studies. The systems styrene/divinylbenzene [1–6] (S/DVB) and acrylamide/N,N'-methylene-bis-acrylamide [7–14] (AA/BA) are the most studied cases because of their relative simplicity and their important technical applications.

The mechanism of polyacrylamide (PAA) gelation has been investigated under various conditions. Severe external constraints [12] like an intense X-ray beam or the acceleration field of an ultracentrifuge cause the appearance of interpenetrated three-dimensional structures which determine the morphology of the resulting gel. Less drastic conditions, like a flow field, also modify the morphology of the networks [15, 16]; even under uniform and static conditions (as in our case), many heterogeneities can develop during network formation [10]. Network characteristics have usually been studied on the final product of the reaction (see Refs [2, 11 and 13]). In this paper we present results on the changes of PAA gel composition during the crosslinking reaction. A similar attempt has been made [1] on the system S/DVB by means of i.r. spectrometry. Here we employ HR ^{1}H-NMR with polymerization *in situ*, following a method recently developed [7]. It is thus possible to determine the consumption of each comonomer as a function of the overall conversion and therefore to follow the process of network formation [7, 8, 17].

EXPERIMENTAL PROCEDURES

Six experiments (C1 to C6, Table 1) were run with different feeds. In all cases the initiator concentration

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(6.57 10^{-3} M potassium persulphate/1.12 10^{-3} M triethanolamine) and polymerization temperature (22°) were fixed. Solutions of AA and BA (Eastman Kodak) in D_2O (Scharlau) had concentrations as shown in Table 1. Sample preparation and recording of ^{1}H-NMR spectra (Bruker WM-360) have been reported [7, 8].

RESULTS AND DISCUSSION

^{1}H-NMR spectra of AA/BA solutions were run during the polymerization by means of the experimental method already described [7]. Protons joined to vinyl groups of both comonomers and to the methylene bridge of BA give different signals with integrals (ICH_{2v}, ICH_v and ICH_{2b} respectively) proportional to the instant molar concentrations of the comonomers. Comonomer consumption causes decrease of ICH_{2v}, ICH_v and ICH_{2b} as shown in Fig. 1 for a typical experiment (C1). The total molar conversion (p_T), the molar conversion of BA (p_{BA}) and other quantities such as the molar fractions of the residual comonomers (f_1, f_2) can thus be calculated [7] as a function of the polymerization time (t). Six experiments (C1 to C6) were performed with different initial concentrations of AA and BA (Table 1).

p_T Includes AA molecules and BA molecules incorporated through one or both unsaturations. Pre-networks obtained under conditions in which gelation does not take place [18] show no signal corresponding to vinyl groups in ^{1}H-NMR spectra run at 22°. In such pre-networks, the existence of pendant vinyl groups is highly probable [19] but they are immobilized in compact structures and their protons produce very broad signals that disappear in the base line [7]. Therefore to determine p_T, we have considered that, when a BA molecule reacts with the first vinyl group, ICH_{2v} and ICH_v decrease as if two vinyl groups were consumed.

In Fig. 1 three different reaction steps can clearly be observed [7, 8]. In the first 4 hr, the 3 integrals

Table 1. Initial polymerization conditions and adjusting parameters

Run	AA (mol/l)	BA (mol/l)	C_T (g/100 ml)	$(f_2^0)^{ex}$	$(f_2^0)^{ad}$	r_1	r_2
C1	0.2634	0.1233	3.77	0.3190	0.3189	0.570	3.40
C2	0.5121	0.0915	5.05	0.1520	0.1516	0.569	3.89
C3	0.5909	0.0461	4.91	0.0723	0.0723	0.570	3.40
C4	0.0736	0.0934	1.96	0.5590	0.560	0.570	3.40
C5	0.1791	0.0445	1.96	0.1990	0.1880	0.570	3.40
C6	1.2840	0.0740	10.30	0.0545	0.0491	0.570	3.05

C_T—Total concentration of comonomers in g/100 ml.
$(f_2^0)^{ex}$—Experimental f_2^0 values.
$(f_2^0)^{ad}$—Adjusted f_2^0 values.

decrease slowly. The gelation process then begins and the rate of polymerization increases appreciably. After 7 hr, the postgel reaction proceeds slowly. This is the general behaviour observed in each experiment. Our concern is how the copolymer composition is or is not modified in those steps of the crosslinking copolymerization.

Figure 2 shows how the dependence of p_2 on p_T shows a change of slope simultaneous with the gel point. The points of interception in Fig. 2 allow calculation of the total conversion at the gel point, p_T^G, marked by arrows. p_T^G values calculated from Fig. 2 are very similar to those found by the gas bubble method [10] and show the same dependence on the crosslinker proportion and the total comonomer concentration.

At conversions below p_T^G, p_2 is higher than p_T at any moment because the rate of BA reaction is higher than that for AA [8]. At the gel point, the rate of reaction increases for both AA and BA [7] but more so for AA. At conversions above p_T^G, the slopes in Fig. 2 decrease and approach unity, indicating a similar reactivity for both comonomers during gelation. Nevertheless, this change in the relative rates of reaction is small and it does not produce abrupt changes in the composition of the copolymer or in the remaining comonomer mixture (Figs 3 and 4).

Figure 3 shows the experimental results for the variation of f_2 with total conversion p_T, for the six experiments summarized in Table 1. The solid line represents f_2 values calculated by the expression of Meyer and Lowry [20].

$$(1 - p_T)(f_2^0)^{\alpha}(1 - f_2^0)^{\beta}(f_2^0 - \epsilon)^{-\gamma}$$
$$= (f_2)^{\alpha}(1 - f_2)^{\beta}(f_2 - \epsilon)^{-\gamma} \quad (1)$$

where α, β, ϵ and γ are functions of the reactivity ratios r_1 and r_2. The superscript 0 refers to the composition of the initial feeding mixture.

A non-linear regression fit of f_2 vs p_T in each experiment yields the set of f_2^0, r_1 and r_2 values that best reproduce the experimental results for the whole range of conversions (Table 1). We have employed a non-linear regression fit program based on the Newton–Gauss method. A steepest descent correction has been employed to avoid slow convergence when the starting guesses for the parameters are too far from the final solution. The parameters we have considered are f_2^0, α, β, ϵ and γ from equation (1), and from them it is possible [20] to obtain r_1 and r_2. f_2^0 was known in each experiment (Table 1) but the fit is very sensitive to variations of f_2^0 smaller than the experimental error; consequently we have left f_2^0 as an adjusting parameter. The starting guess for f_2^0 has been the experimental value (Table 1) and the adjusted value has not been very different in any case (Table 1). The initial values of the parameters α, β, ϵ and γ have been calculated with the r_1 and r_2 values previously determined [8] by the Kelen–Tüdős method with extrapolated values at $p_T = 0$ ($r_1 = 0.57$, $r_2 = 3.4$).

It can be observed in Figs 3 and 5 how the f_2 values calculated with equation (1) and the parameters of Table 1 reproduce fairly well the experimental results, in particular at conversions below the gel point. Concordance between the reactivity ratios obtained by this fitting procedure and those previously calculated [8] with extrapolated values at $p_T = 0$ is excellent. This suggests that only one set of r_1, r_2 values can reproduce satisfactorily the course of the polymerization under any condition.
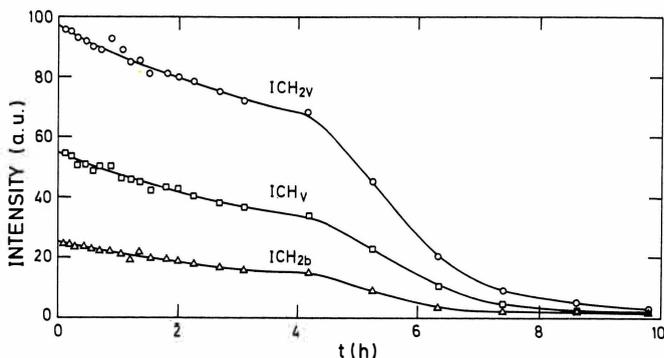

Fig. 1. Dependence on the polymerization time, t, of the integrated signals from protons in vinyl groups (ICH_{2v}, ICH_v) and in the methylene bridge of BA (ICH_{2b}) in experiment C1 (see Table 1).
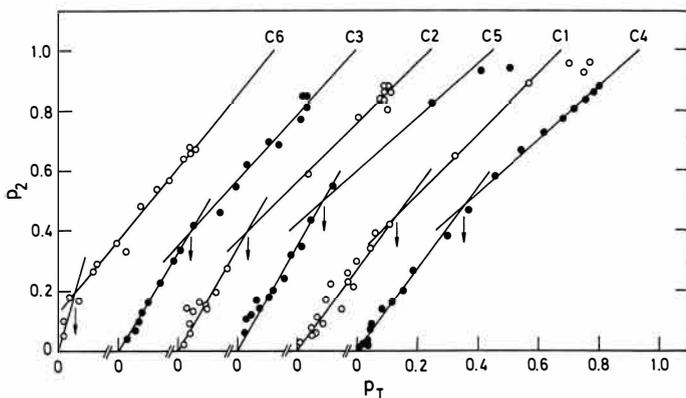
Fig. 2. Molar conversion of BA, p_2, as a function of the total molar conversion, p_T, for the six experiments of Table 1.

The question now is whether or not the reactivity of BA changes significantly in the various steps of the polymerization. During gelation, the viscosity increases but it has been reported that the Tromssdorf effect does not modify [21] r_1 and r_2. On the other hand, the local concentration of pendant vinyl groups around the growing radicals may be larger than the overall concentration and they may compete with comonomers, in particular duing gelation [1]. Scheme I shows all the possible reactions of growing radicals ending in either AA or BA groups [22]. The reactions
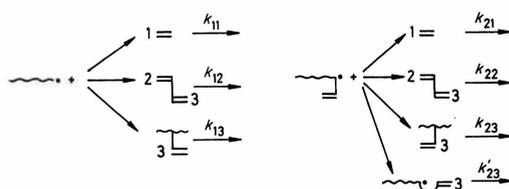
Scheme I

with pendant vinyl groups (k_{13}, k_{23} and k'_{23}) do not lead to changes in ICH_{2v}, ICH_v or ICH_{2b} and, therefore, they are not included in the calculated r_1, r_2 values. Only k_{11}, k_{12}, k_{21} and k_{22} are taken into account in r_1, r_2 values of Table 1. k_{12} and k_{22} correspond to the reaction of only one vinyl group in
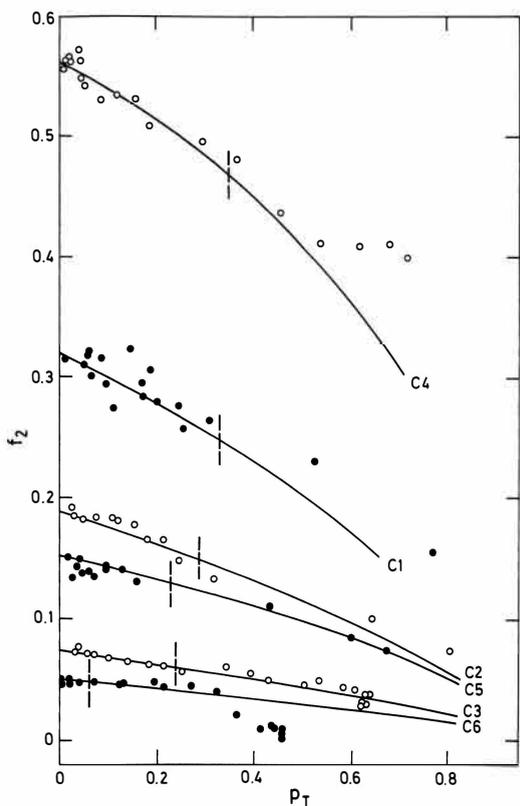

Fig. 3. Experimental f_2 values plotted as a function of conversion (p_T) for the six experiments of Table 1. (——) Values calculated by means of equation (1), as described in the text. Vertical bars correspond to the gel point.
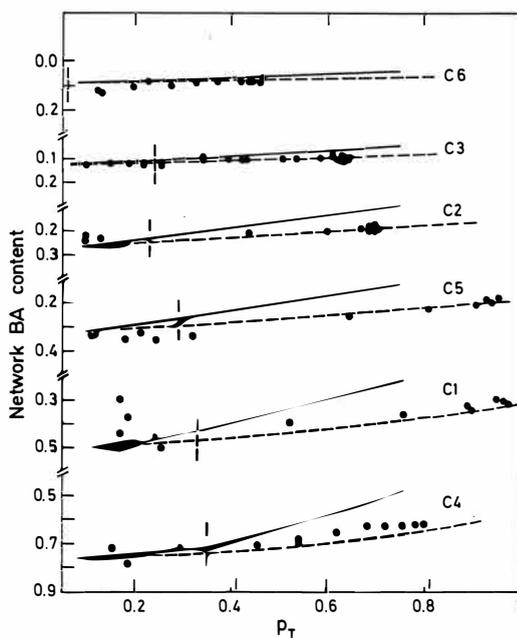

Fig. 4. Accumulated, F_2^{ac}, and instantaneous, F_2, copolymer composition at different p_T. (----) F_2^{ac} values calculated by means of equation (2), and (——) calculated F_2 values as described in the text. Vertical bars correspond to the gel point.
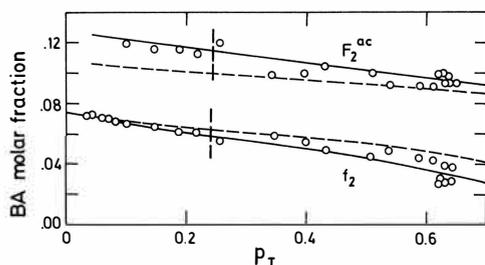
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Fig. 5. Comparison of experimental f_2 and F_2^{ac} values with those calculated with $r_1 = 0.57$, $r_2 = 3.4$, (——) and $r_1 = 0.66$ $r_2 = 1.77$ (----), for experiment C3. The vertical bars represent the gel point.

BA but the probability of having an effective collision is double. To discount this statistical effect, we should calculate new reactivity ratios: $r_1' = 0.57 \times 2 = 1.14$ and $r_2' = 3.4/2 = 1.7$. These new values represent only the reactivity of the growing radicals with vinyl groups 1 or 2, and it is evident that, even discounting the statistical effect, BA is more reactive than AA.

By applying the Kelen–Tüdős method to compositions of copolymers formed at $p_T = 0.35$, when the gelation takes place for any of the studied initial condition (see Fig. 2), we have found [8] $r_1 = 0.66$ and $r_2 = 1.77$. Figure 5 shows how these reactivity ratios fit, with equation (1), the experimental results of f_2 above the gel point. The calculated curve fits slightly better than the curve constructed with r_1, r_2 of Table 1. We must therefore conclude that a constant set of r_1, r_2 values is sufficient to explain the experimental results, but it is not essential since two sets of r_1, r_2 values could also explain the experimental results of f_2. On other hand, r_1, r_2 values of Table 1 reproduce not only the variation of f_2 with p_T, but also the results for the accumulated copolymer composition, F_2^{ac}, as shown in Fig. 5 for C3 and in Fig. 4 for all the experiments. F_2^{ac} was calculated by the expression:

$$F_2^{ac} = (1/p_T)[f_2^0 - f_2(1 - p_T)] \qquad (2)$$

and using f_2 values from equation (1); r_1, r_2 are taken from Table 1 for Fig. 4 and those indicated for Fig. 5.

The shift of f_2 with p_T (Fig. 3) makes different the chemical composition of the gel formed at any moment of the polymerization, F_2, even without taking into account changes in r_1, r_2. Figure 4 shows how F_2, calculated by the Skeist equation [23], changes with p_T. This fact introduces another element of heterogeneity that is particularly important when f_2^0 is about 0.5. When f_2^0 is about 0.05 or less, F_2 and F_2^{ac} at $p_T = 0.5$ differ by less than 2% and therefore changes in composition during the copolymerization can be considered negligible.

CONCLUSIONS

Three different steps have clearly been observed in the crosslinking copolymerization of AA/BA, viz. pre-gel reactions, gelation and postgel reactions. In the pregel step, the soluble particles formed are richer in BA than the comonomer feed because of the higher reactivity of BA for both statistical and chemical

reasons. At the gel point, the rate of reaction increases for both comonomers but the increment is larger for AA. During gelation, the pre-gel particles are joined by chains which are slightly richer in AA than expected according to the initial reactivities of AA and BA. Nevertheless this enrichment of the copolymer in AA due to changes in the relative reactivities of the comonomers is less important than the enrichment due to shifts in the residual comonomer composition on conversion. Nothing can be said about postgel reactions, since they probably involve pendant vinyl groups which are not observed by our method.

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