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NETWORK DEFECTS IN POLYACRYLAMIDE GELS

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The weight conversion at the gel point (α_G^w) was determined by the gas bubble method in two sets of polyacrylamide (PAA) gels crosslinked with' N,N'-methylene-bisacrylamide (BA). α_G^w remained practically constant when the crosslinker ratio was $C = 10\%$ (w/w) and the total concentration of comonomers in the feed ranged from $C_T = 5$ to 10 g/100 ml. When C_T was kept constant at 5 g/100 ml and C changed from 0 to 25% (w/w), α_G^w showed a minimum at $C = 7\%$. By comparing the experimental values of α_G^w with those calculated for an ideal network, it was concluded that the crosslinking efficiency of BA is very low. The dependence on C of α_G^w and other properties like the elastic phantom modulus, $|f_{ph}^*|$, and the polymer volume fraction at swelling equilibrium, v_{2s}°, was explained in terms of the formation of network defects: the formation of BA sequences longer than unity and that of intramolecular cycles both have an increasing contribution at $C > 7\%$ but can be neglected at lower values of C.

INTRODUCTION

Polyacrylamide (PAA) networks are usually obtained by crosslinking copolymerization of acrylamide (AA) and N,N'-methylene-bisacrylamide (BA). The resulting hydrophilic gels are known to be heterogeneous [1–11], i.e. there are many defects. The inhomogeneities of these gels are strongly dependent on the crosslinker proportion (C) in the initial feed mixture of comonomers. If C is very low (<4–5% w/w over the total comonomer concentration), the gels obtained are transparent [3]. Nevertheless, they still show a two-phase structure formed by small domains of different polymer concentration and therefore different draining properties [1, 7]. With larger values of C, PAA gels become opaque [3]. A collapsed state for the polymer chains has been found when the BA content in the initial feeding mixture >5% [12].

It has been suggested that microsyneresis [13] and other modes of phase separation [10] may produce heterogeneous networks. The aggregation of BA in water has also been invoked to explain the existence of highly crosslinked regions in PAA gels [1, 4, 5, 7, 11].

In preceding papers [9, 14] we have studied the formation process of PAA networks. AA and BA have different reactivity ratios, and this produces BA sequence which act as the nuclei for compact domains [14]. Changes in reactivity during gelation [14], drifts in the composition of the residual comonomer mixture with conversion [15], and the statistical chemical heterogeneity [16], are other causes of formation of domains with different structure and composition. Some microheterogeneities have also been reported [9].

In this work we study the formation of defects in PAA gels; in particular we analyze the relative amount of elastically inactive cycles and crosslinker sequences in PAA networks obtained with different crosslinker ratios in the feed mixture of comonomers.

EXPERIMENTAL PROCEDURES

Materials

AA and BA were high purity Eastman Kodak products. BA was recrystallized from acetone. As initiator, the redox pair potassium persulphate (PSK)/triethanolamine (TEA) was employed. In all the experiments the initiator concentration was kept constant at $[\text{TEA}] = 8.51 \times 10^{-3}$ M and $[\text{PSK}] = 6.57 \times 10^{-3}$ M. Water used as solvent was purified by a Milli-Q system from Millipore.

Gel point conversion

α_G^w was measured gravimetrically. The gel point was determined by the standard gas bubble method [17–19]. Other viscometric techniques must be discarded since it has been found [20, 21] that they can significantly affect the rate of gelation and the structure of the final network. For each sample, the determination of α_G^w was repeated four times and the mean value was presented.

The total concentration of comonomers, C_T, and the crosslinker ratio, C, of each experiment are given in Table 1. In order to evaluate the degree of polymerization of the primary chains in the gel, linear PAA was synthesized under the same C_T conditions as the gels [22]. The degrees of polymerization obtained by viscometry were: 1.7×10^4, 2.45×10^4 and 3.4×10^4 for AA concentrations 4.96, 7.14 and 9.92 g/100 ml, respectively.

RESULTS

Figure 1(a) shows the dependence of α_G^w on C (w/w), keeping C_T constant at 5 g/100 ml. The vertical bars represent the mean deviation of four experiments. The dispersion of the results is different for
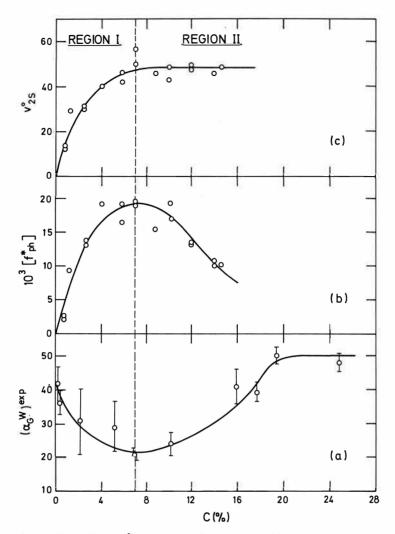
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Fig. 1. (a) α_G^w, (b) $|f_{ph}^*|$ in $N \cdot mm^{-2}$ and (c) polymer volume fraction at swelling equilibrium (v_{2s}°) as a function of the crosslinker ratio $C(\%)$ w/w in the comonomer feed mixture at constant total molar concentration. $|f_{ph}^*|$ and v_{2s}° from Ref. [27].

each independent experiment and very often is quite large. Nevertheless, Fig. 1(a) clearly shows a minimum in the gel conversion when the crosslinker ratio is about 7% (w/w), and suggests a "plateau" above $C \simeq 18\%$. A similar trend has been previously reported for vinyl–divinyl crosslinking copolymerization [19, 23–26]. The plateau is more clearly observed in Ref. [14] because in their experiments C ranges from 0 to 100%. In the present system, the limiting value of C is determined by the solubility of BA in water.

Figures 1(b,c) also summarize the dependence on C of other properties (elastic modulus and swelling equilibrium data, taken from Ref. [27]) of PAA networks obtained at the limiting conversion under similar conditions ($C_T = 6.72$ g/100 ml).

The elastic modulus, $|f_{ph}^*|$, shows a maximum [Fig. 1(b)] at about the same C corresponding to the minimum in α_G^w. The polymer volume fraction at swelling equilibrium v_{2s}° [Fig. 1(c)] increases to reach a plateau at the same C. All these magnitudes are

related to the gel structure and they should be discussed together.

A few experiments have also been made on the dependence of the gel point conversion on C_T, keeping C constant at 10.2% w/w). Results are shown in Table 1. α_G^w does not change appreciably for the dilute solutions considered here and, as expected [22], the trend is for α_G^w to decrease with increasing C_T.

DISCUSSION

Calculation of the conversion at the gel point

According to the theory of branching processes, the critical conversion of vinyls at the gel point, $(\alpha_G^v)^{th}$, is given by the following expression [17]:

$$(\alpha_G^v)^{th} = f_{2o}^v/(\bar{F}_2^v)^2(\bar{x}_w - 1),$$

where f_{2o}^v is the initial mole fraction of vinyl groups of the crosslinker in the feed mixture; $\bar{F}_2^v$ is the accumulated mole fraction of vinyl groups of the crosslinker in the copolymer at the gel point which

Table 1. Experimental and calculated gel point conversion values and crosslinking efficiency

C_T(g/100 ml)	C(% w/w)	$f_{2_0}^v \times 10^2$	$\bar{F}_2^v \times 10^2$	$(\alpha_G^v)^{th} \times 10^2$	$(\alpha_G^w)^{exp} \times 10^2$	$s \times 10^2$	$\bar{F}_2^v s \times 10^4$
4.99	0.140	0.129	0.190	2.11	41.3	5.10	0.97
4.94	0.275	0.254	0.384	1.01	35.1	2.89	1.11
5.03	2.14	1.98	3.03	0.127	29.7	0.43	1.30
5.13	5.32	4.93	7.47	0.052	27.6	0.19	1.43
5.17	6.96	6.45	10.00	0.038	18.7	0.21	2.08
5.27	10.2	9.49	14.23	0.028	22.4	0.13	1.82
5.49	17.6	16.45	22.4	0.019	38.5	0.05	1.17
5.55	19.4	18.19	23.6	0.019	50.1	0.04	0.94
5.74	24.8	23.36	30.0	0.015	47.9	0.03	1.00
7.52	10.2	9.52	13.76	0.021	25.1	0.08	1.16
10.53	10.2	9.49	14.52	0.013	16.4	0.08	1.22

can be calculated by means of the integrated form of the copolymer equation [28] provided that the reactivity ratios are known. For the system AA(1)/BA(2) we have found [14] $r_1 = 0.57$ and $r_2 = 3.4$; $\bar{x}_w$ is the weight-average degree of polymerization of the primary chains which can be estimated from independent experiments on PAA linear chains obtained as described under Experimental Procedures.

In order to compare properly experimental and theoretical values of the gel point conversion, it is necessary to transform experimental weight conversion $(\alpha_G^w)^{exp}$ into molar conversions of vinyl groups $(\alpha_G^v)^{exp}$. This can be done through a mass balance [29], assuming that each BA unit contributes two vinyl groups to the polymer. The values of $f_{2_0}^v$, $\bar{F}_2^v$ and $(\alpha_G^v)^{th}$ are given in Table 1. Theory predicts a monotonous decrease of α_G increasing C at constant C_T (see Table 1). It qualitatively corresponds to the trend of experimental results in region I [Fig. 1(a), $C < 7\%$] but α_G^{th} is always much smaller than α_G^{exp} (Table 1).

The calculation of α_G^{th} involves the implicit assumption [17, 22] that the network is ideal (without defects) and any reacted BA molecule joins two different chains, i.e. forms an intermolecular crosslink [17]. The ratio $s = (\alpha_G^v)^{th}/(\alpha_G^v)^{exp}$ may therefore be used as an estimation of the fraction of intermolecular crosslinks in the real network [22]. Values of s are presented in Table 1, showing the very low crosslinking efficiency of BA over the whole range of crosslinker ratios. Poly(N-ethylacrylamide) and poly(N-butylacrylamide) with BA-like crosslinking agent [17, 18], show the same trend and the same order of magnitude for α_G^{exp} as those presented in this work. However, the predicted α_G^{th} values for those systems [17, 18] are larger than those shown in Table 1. Consequently s values are smaller for PAA gels (Table 1). The reason for that difference must be attributed to the degree of polymerization of primary chains. The propagation rate constant for AA is very large [30] giving rise to very long AA primary chains, decreasing α_G^{th} and s in PAA gels.

From the structural point of view, the low s values found for PAA gels mean that most of the crosslinker incorporated into the network forms part of network defects.

Network defects

Of the many different types of network defects, the non-random distribution of BA and the formation of intramolecular cycles deserve particular attention. The probability that a growing radical, ended in AA, reacts with another AA unit to form an AA–AA dyad is given by [31]:

$$W_1^{AA} = r_1 f_1/(r_1 f_1 + f_2),$$

assuming first-order Markov statistics. The probability that a sequence of n AA units is closed by the addition of a BA unit is given by [31]:

$$W_n^{AA} = (W_1^{AA})^{n-1}(1 - W_1^{AA});$$

and the number-fraction of AA sequences with length n, is

$$X_n^{AA} = nW_n^{AA}/\sum_{n=1}^{\infty} nW_n^{AA}.$$

Table 2 summarizes the probabilities of formation of sequences of AA or BA with length n (W_n^{AA} or W_n^{BA}), and the fraction of sequences with a given length n (X_n^{AA} or X_n^{BA}) at several values of f_{2_0} in the feed mixture.

It can be observed that, at low crosslinker ratios (low f_{2_0}), BA is mostly forming sequences of unit length and therefore knots will be formed by isolated BA units separated by long AA sequences. The distribution of AA sequences is very broad; any sequence has a probability $<1\%$.
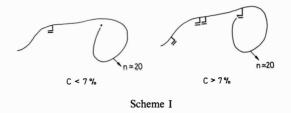
At larger f_{2_0} values, the probability of forming BA sequences longer than unity increases appreciably and the distribution function of AA sequences gets narrower. Multifunctional knots separated by short flexible sequences are formed and therefore the pregel particles in this region will be very compact. Consequently, pendant vinyl groups are immobilized and cannot be observed by ^{1}H-NMR [9].

At the crosslinker ratio corresponding to the minimum of α_G in Fig. 1(a) ($C = 7\%$, $f_{2_0} = 3.35\%$), the average sequence length of AA is 17 and that of the BA is [14] 1.11. Isolated BA units may join two different chains but, when n BA units are in a sequence, each one may join less than two chains for two reasons: (i) steric hindrance will give rise to some pendant unreacted vinyl groups; and (ii) even if all the unsaturations react, the resulting multifunctional knot will join $n + 1$ chains, i.e. $(1 + n^{-1}) < 2$ chains per BA unit.

Elastically inactive cycles can also be formed with different probabilities in both regions. Flexible chains like PAA may show cyclic conformation in which two points separated by about 20 or more monomeric units are in contact [32]. The rate constant for the formation of cycles with n monomeric units depends on $n^{-3/2}$ in theta solvents [33] and is lower in good solvents [34]. The formation of the smallest cycles ($n \simeq 20$) is therefore favoured.

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Table 2. Probability of sequence formation (W_n^{AA} and W_n^{BA}, in %) and number fraction (in %) of AA and BA units in sequences of length n (X_n^{AA} and X_n^{BA}) at different initial BA compositions (f_{BA}°)

Seq n	$f_{BA}^\circ = 0.005$				$f_{BA}^\circ = 0.05$				$f_{BA}^\circ = 0.1$				$f_{BA}^\circ = 0.30$			
	W_n^{BA}	X_n^{BA}	W_n^{AA}	X_n^{AA}	W_n^{BA}	X_n^{BA}	W_n^{AA}	X_n^{AA}	W_n^{BA}	X_n^{BA}	W_n^{AA}	X_n^{AA}	W_n^{BA}	X_n^{BA}	W_n^{AA}	X_n^{AA}
1	98.3	96.4	0.90	0.01	84.8	71.8	8.50	0.72	72.6	52.6	16.3	2.66	40.7	16.5	42.9	18.4
2	1.65	3.24	0.89	0.02	12.9	21.8	7.78	1.32	19.9	28.8	13.6	4.45	24.1	19.6	24.5	21.0
3	0.03	0.08	0.88	0.02	1.96	4.98	7.12	1.81	5.45	11.8	11.4	5.59	14.3	17.5	14.0	18.0
4	—	—	0.88	0.03	0.30	0.01	6.51	2.21	1.49	4.33	9.56	6.24	8.49	13.8	7.99	13.7
5	—	—	0.87	0.04	0.05	0.19	5.91	2.52	0.41	1.48	8.0	6.53	5.03	10.2	4.56	9.79
6	—	—	0.86	0.05	—	—	5.45	2.77	0.11	0.49	6.70	6.55	2.98	7.28	2.60	6.61
7	—	—	0.85	0.05	—	—	4.99	2.96	0.03	0.16	5.60	6.40	1.77	5.04	1.49	4.47
8	—	—	0.84	0.06	—	—	4.56	3.09	—	—	4.69	6.12	1.05	3.41	0.85	2.92
9	—	—	0.84	0.07	—	—	4.18	3.19	—	—	3.93	5.76	0.62	2.28	0.48	1.87
10	—	—	0.83	0.07	—	—	3.82	3.24	—	—	3.29	5.36	0.37	1.50	0.28	1.19
50	—	—	0.58	0.25	—	—	0.11	0.45	—	—	—	—	—	—	—	—
100	—	—	0.37	0.32	—	—	—	—	—	—	—	—	—	—	—	—
200	—	—	0.15	0.26	—	—	—	—	—	—	—	—	—	—	—	—

If a growing radical finds by cyclization an unsaturation in the chain, it may form a permanent intramolecular crosslink or elastically inactive cycle (Scheme I):

Scheme I

In region I, AA sequences are mostly >17 [14] and therefore the growing radical will find by cyclization a pendant vinyl group with very low probability (Scheme I). In this region, the formation of intramolecular cycles will have a minor contribution to the formation of non-effective crosslinks. In region II, the AA sequences will be on average <17 and therefore the probability of forming permanent intramolecular cycles begins to be significant at C 7%, and increases at larger C values (Scheme I). This explains the upturn of α_G in region II in which both intramolecular cycles and BA sequences longer than unity contribute significantly to the total network defects.

Correlation with other properties

The product $\bar{F}_2 s$ represents the fraction of BA units in the copolymer forming part of intermolecular crosslinks. It evaluates the crosslinking density, which is directly related with properties like $|f_{ph}^*|$ and v_{2s}°.

In region I, $\bar{F}_2 s$ increases with increasing C (Table 1) in accordance with the trend [27] of $|f_{ph}^*|$ and v_{2s}° vs C (Fig. 1). It also explains how branching probability reaches the gelation conditions at lower conversions (Fig. 1). Network defects ($\bar{F}_2(1 - s) = \bar{F}_2$ in Table 1) also increases with increasing C making the crosslinking efficiency (s in Table 1) progressively lower. BA, being a flexible molecule, is able to form small cycles by reaction of a BA ended radical with the second unsaturation of the last unit [35, 36] and these are network defects that together with pendant vinyl groups may contribute to decrease the crosslinking efficiency of BA in this region. As previously mentioned, non-random distribution of BA and intramolecular cycles must not be expected in region I.

In region II, $\bar{F}_2 s$ decreases on increasing C, in accordance with the decrease of $|f_{ph}^*|$ and the upturn of α_G. Nevertheless, v_{2s}° levels off in this region instead of decreasing as expected for the decrease in the apparent crosslinking density. It seems therefore that the formation of multifunctional knots and intramolecular cycles, typical of this region, influence in a different way two related properties like $|f_{ph}^*|$ and v_{2s}°. The different solubility of cycles and the formation of biphasic structures should be taken into account.

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