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STRESS-STRAIN BEHAVIOR OF POLYACRYLAMIDE NETWORKS

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ABSTRACT

The mechanical properties of a number of polyacryl-amide gels have been studied by means of elastic measurements in elongation. Different gels were prepared by varying the proportions of both comonomers, acrylamide and N,N-methylene-bisacrylamide which is used as crosslinker, and a very broad range of concentrations was covered. The most important results considered were the elastic phantom modulus, the degree of (equilibrium) swelling and the elongation at rupture. The data were interpreted in terms of the mechanism of the gelation process taking into account a number of parameters that affect the final structure of the gels: comonomer reactivities, sequence length distributions and cycles formation. Consideration of these factors can explain properly all the features of the elastic results as well as some other properties related to the gelation process such as gel point data.

INTRODUCTION

Polyacrylamide (PAA) gels have numerous practical applications and are broadly used in many research techniques (electrophoresis, chromatography, etc.) These gels are usually obtained by radical copolymerization of acrylamide (AA) and a divinyl comonomer, typically N,N-methylenebisacrylamide (BA) as crosslinker. The resulting gel structure is very much dependent

on the polymerization conditions, mainly on the total comonomer concentration (C_T), and on the proportion of crosslinker (C). Results from techniques sensitive to very different properties[1-8] have shown that PAA gels are very heterogeneous, having a structure in which regions of very different degrees of crosslinking coexist. Several qualitative arguments based on the mechanism of the crosslinking reaction have been proposed[2,3,5-7] in order to interpret the properties of the system, but a more elaborated explanation is needed.

In previous studies performed on the kinetics of the gelation process we have found that a number of factors that would affect the final gel structure should be taken into account. In the first place BA, as a monomer, is more reactive than AA since it has two vinyl groups[9,10]. This is a common feature of other systems synthesized by vinyl-divinyl radical copolymerizations. As a result, BA units are not randomly distributed along the primary chains but they can form sequences involving several units[10]. On the other hand, under certain conditions, a large proportion of intramolecular cycles can be formed. This factor has been found to be of paramount importance to interpret the data on the degree of conversion at the gel point[11].

In this work we have studied the mechanical properties of a number of PAA gels covering a wide range of total comonomer concentrations (C_T) and proportion of crosslinker (C). The experiments have been mainly focussed on higly crosslinked gels for which previous studies are scarce. The results have been interpreted in terms of the above mentioned kinetic factors that are responsible for the final gel structure. A comprehensive explanation, which involves mechanical and ultimate properties,swelling equilibrium results and gel point data can be given.

EXPERIMENTAL SECTION

Acrylamide (AA) and N,N'-methylenebisacrylamide (BA) were purchased from Eastman Kodak. BA was used after recrystallization from acetone. The redox pair potassium persulphate (PSK)/ triethanolamine (TEA), both products from Carlo Erba, was used

as the room temperature initiator system. Water was purified from salts and organic matter by a Milli-Q equipment (Millipore) and filtered with a 0.45 μm filter.

Details for the experimental method have been previously reported[12]. Elastic modulus of polyacrylamide (PAA) gels were determined from stress-strain measurements (in extension) on gel samples, inmersed in pure water at swelling equilibrium at 30ºC. The samples, with their final geometry, were prepared in a teflon-glass mould in which two pieces of a woven material were placed at both ends, thus resulting in a sample with firm extremities, suitable for mechanical measurements.

Two series of gels were synthesized, both with initiator concentrations: $[TEA]= 8.51\times10^{-3}M$ and $[PSK]= 6.57\times10^{-3}M$. In the first one, the total comonomers concentration, C_T, was kept constant ($C_T= 6.72$ g/100ml) varying the percentage of cross-linking comonomer, C (0.663 < C < 14.5% w/w). On the other hand, a second set of networks were studied in which C=10% w/w and C_T ranged from 4.99 to 18.0 g/100ml.

The initial dimensions of the samples (L_0 and cross-sectional area) were measured in a relaxed state of the samples, horizontally, to avoid the deformation self induced by the weight of the gels. Cross-sectional areas of the swollen samples were aproximately 70 mm^2.

The relaxation delay between succesive experimental points depends not only on the relaxation of the sample, but on the new swelling equilibrium that must be attained, which is a function of the crosslinking density, and was found to be between 2 and 6 hours.

RESULTS AND DISCUSSION

The elastic results have been interpreted by means of the modulus or "reduced force", which is defined by[13]

$$[f^*] = (f/A^*)v_{2s}^{1/3}/[\alpha - \alpha^{-2}] \tag{1}$$

were f is the elastic force at equilibrium; A^* is the cross-sectional area of the unstretched unswollen sample and v_{2s} is the degree of swelling of the sample (gel volume fraction) at the given deformation α ($\alpha = L/L_0$, L and L_0 being the lengths

of the deformed and undeformed states respectively). As an aproximation, the degree of swelling for each elongation has been expressed by[14]

$$v_{2s} = v°_{2s} \cdot \alpha^{-3/5} \tag{2}$$

where $v°_{2s}$ is the volume fraction at swelling equilibrium in the undeformed state. The cross-sectional area of the dried gel A^*, has been obtained from the one of the swollen sample A_o, assuming isotropic swelling, by means of

$$A^* = A_o (v°_{2s})^{2/3} \tag{3}$$

Data were treated according to the Flory-Erman theory of rubber elasticity[15-17], from which the modulus is given by

$$[f^*] = [f^*_{ph}](1 + f_c/f_{ph}) \tag{4}$$

where $[f^*_{ph}]$ is the modulus for the corresponding phantom network and f_c and f_{ph} are the contributions to the force from the constraints on fluctuations of junctions and from the equivalent phantom network respectively. The ratio f_c/f_{ph} is given by the theory as a function of two parameters, κ, which is a measure of the severity of the constraints, and ζ, which is related to the degree of non-affineness in the relaxation of those constraints with strain[17].

The most important parameter, κ, has been reported to be a function of the degree of crosslinking[18-20] as expressed by the phantom modulus $[f^*_{ph}]$, the dimensions of the polymer chains and the functionality in such a way that for PAA networks the following relationship is found[12]

$$\kappa = 3.32[f^*_{ph}]^{-1/2} \tag{5}$$

Therefore the data were fitted by adjusting simultaneously κ and $[f^*_{ph}]$ along with the value of ζ. The stress-strain isotherms have been reported elsewhere[12]. The most important features that can be drawn from those results are the following:

i) For the lowest values of C (set of gels with

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constant C_T) and the lowest values of C_T (set of gels with
constant C), the modulus is almost invariant when it is repre-
sented as a function of α^{-1}, as expected for very dilute
networks ($C_2 \approx 0$ in the Mooney-Rivlin equation)

ii) When the crosslinker ratio or the total concen-
tration are raised, deviations from the linearity or upturns,
are observed; in both cases this is accompanied with a de-
crease in the rupture elongation. These observations may be
attributed to non-gaussian effects (not accounted for in the
theory of Flory) due to the increasing heterogeneity of the
gels.

A detailed analysis of the type and proportion of network
defects, that are ultimately responsible of the above men-
tioned heterogeneity, is required in order to interpret
properly the elastic measurements.

TABLE I

Characteristics and elastic results on PAA gels obtained at
constant crosslinker proportion C=10%(w/w)

Gel	C_T (g/100ml)	v_{2c}	$[f^*_{ph}]$ (N.mm^{-2})	α_r	$\dfrac{M^{exp}_c}{M^{th}_c}$	v°_{2s}
T-1	18.0	0.145	0.311	1.10	2.13	0.158
			0.336	1.10	2.03	0.156
T-2	15.0	0.119	0.119	1.27	3.97	0.128
			0.150	1.28	5.19	0.126
T-3	11.0	0.0872	0.0685	1.30	6.91	0.0903
			0.0723	1.27	6.36	0.0862
T-4	7.67	0.0600	0.0217	1.35	18.5	0.0587
			0.0265	1.48	14.8	0.0627
T-5	6.72	0.0525	0.0193	1.54	18.6	0.0487
			0.0170	1.64	21.6	0.0484
T-6	4.99	0.0388	0.0074	1.73	41.6	0.0388
			0.0072	1.53	42.3	0.0381

From the point of view of the mechanism of gelation it can
be easily understood that increasing dilution of the initial
monomers mixture (low C_T values), departures from the chemical
crosslinking degree (calculated from the initial proportion of
BA) are going to be large, that is to say, a larger proportion
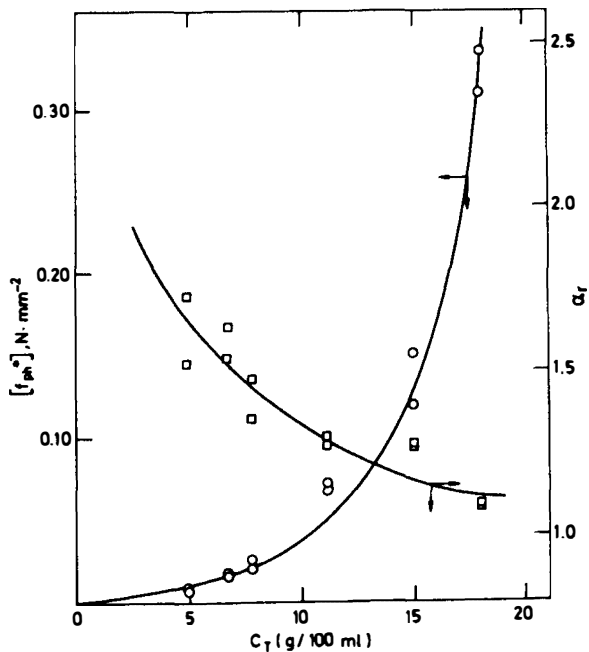of defects and elastically non-effective structures are going

Fig.1.- Phantom modulus$[f^*_{ph}]$,(○), and rupture elongation
α_r,(□), plotted as a function of the total monomer con-
centration C_T (g|100 ml), at fixed crosslinker weight
fraction

to be found[21]. As a consequence the effective crosslinking
degree is going to be reduced, varying also the magnitudes
related with it; this is reflected in the lower values of the
polymer volume fractions,v°_{2s},(Table I) and the lower values
of the elastic modulus (Fig.1). The habit of the variation of
α_r agrees well (Fig.1) with what it has just been mentioned
above; the rupture elongation increases as $[f^*_{ph}]$ decreases,
indicating that larger PAA chains between knots are formed.

Since increasing total concentration (C_T) has the effect
of shortening the chains, a gradual change from gaussian to
non-gaussian behavior results. This is really observed in the
stress-strain isotherms[12].

Another effect, even more important, to explain the up-

turns, that occur simultaneously, is the presence of a large proportion of highly crosslinked regions or clusters that would act as reinforcements[22]. The mechanism from which these clusters are formed will be discussed below.

TABLE II

Characteristics and elastic results on PAA gels obtained at constant total concentration C_T = 6.72 g/100 ml

Gel	C (% w/w)	v_{2c}	$[f^*_{ph}]$ (N.mm^{-2})	α_r	$\dfrac{M^{exp}_c}{M^{th}_c}$	$v°_{2s}$
C-1	0.663	0.0515	0.0026	2.43	7.7	0.0124
			0.0022	2.60	9.9	0.0138
C-2	1.134	0.0515	0.0093	2.21	3.6	0.0293
C-3	2.599	0.0523	0.0130	1.78	6.7	0.0303
			0.0138	1.72	6.7	0.0314
C-4	3.950	0.0522	0.0192	1.72	6.7	0.0403
C-5	5.784	0.0524	0.0165	1.55	12.2	0.0463
			0.0192	1.60	10.3	0.0443
C-6	6.951	0.0521	0.0195	1.43	12.3	0.0501
			0.0190	1.62	12.6	0.0571
C-7	8.756	0.0522	0.0154	1.38	20.1	0.0463
C-8	11.91	0.0523	0.0135	1.44	32.3	0.0475
			0.0135	1.58	32.3	0.0498
C-9	13.98	0.0531	0.0100	1.40	52.2	0.0460
			0.0108	1.44	49.4	--
C-10	14.50	0.0521	0.0103	1.31	53.6	0.0487

With regard to the absolute values of the modulus and its variation with C, keeping constant C_T (Table II), this behavior is more complicated as shown in Fig.2. Increasing BA monomer percentage, first causes an increase in modulus but after C= 5-6%(w/w), the modulus levels off and then decreases. Therefore there is a range of values of C in which the mechanical properties are enhanced, since the modulus has a maximum, without losing ultimate properties (α_r almost remains constant). Increasing further the percentage of crosslinking monomer does not improve the elastic properties of the gels.

At low values of C a linear relationship between shear modulus and BA proportion[23-24] has been reported. However some other studies[7,8] have shown a similar behavior as the one reported here when a broader range of crosslinker concentrations is considered. It should be noticed that the departure from
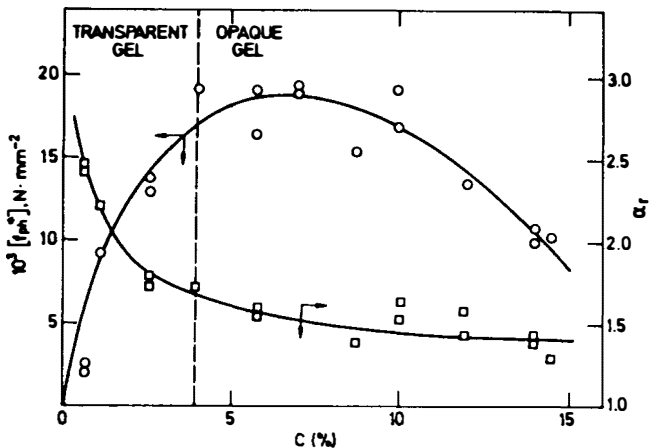
Fig.2.- Phantom modulus $[f^*_{ph}]$,($\circ$) and rupture elongation α ,($\square$), plotted as a function of crosslinker weight fraction C(%), at fixed C_T

linearity coincides with the transparent gel-opaque gel boundary on the phase diagram reported by Bansil and Gupta[25]. On the other hand, the modulus has been reported to increase exponentially with C_T in the transparent gel zone of the phase diagram[7]. The same behavior has been observed here (Fig.1) from samples corresponding to the opaque-gel region.

All these features should be related to the molecular structure of the gels. It is well known that PAA gels are very heterogeneous and a number of different models for their structure have been proposed[1-10]. All these models consider two different regions in the gel: a number of highly cross-linked aggregates or clusters linked together by a more lightly crosslinked gel, thus resulting in a two-phase structure.

In previous studies on the kinetics of the gelation process[9,10], we have reported the different reactivity ratios of both comonomers, AA and BA, being $r_{AA}=0.57$ and $r_{BA}= 3.4$. These values are given as monomer reactivity coefficients and not as vinyl reactivity coefficients, and the higher value for BA is reasonable since BA has two vinyl groups; this is the reason

why the crosslinker seems to enhance the polymerization kine-
tics as observed in other systems[26]. Therefore there are two
important consequences that must be taken into account: the
composition of the feeding mixture changes with conversion and
the primary chains are richer in BA than the feeding mixture.
These effects are dependent on the mole fraction of BA; when
the BA proportion is very small, the differences in the compo-
sition of the primary chains, assuming equal or different va-
lues for r_{AA} and r_{BA}, have presumably little influence on the
macroscopic properties of the final gel. When the amount of
crosslinker is appreciable, there is a conversion dependent
shift on the chemical composition of the gel that may contri-
bute to the total heterogeneity of the system.

At the same time, since BA has larger tendency than AA to
be incorporated into the gel, the crosslinker forms sequences
whose length and probability of appearance may be easily cal-
culated with the assumption of first order Markovian statis-
tics[10,27]. This assumption is justified since any penultimate-
unit (or higher order) effect that may be considered, would
affect essentially the absolute values of the propagation rate
constant and not the composition distribution[28]. Moreover,
since AA has a very high $k_p/k_t^{1/2}$ value, chains with very high
polymerization degrees are formed.

Each sequence of length n may behave as a multifunctional
knot with a functionality given[10] by 2n+2. Obviously, the
existence of BA sequences will reduce the crosslinking ability
of the crosslinker in comparison with the situation in which
the crosslinker is uniformly distributed along the chains. It
can easily be shown[27] that for a network with C=5%(w/w), the
average functionality per knot increases about 9%, but the
number of chains, that may be crosslinked, decreases for about
7.5% with respect to the maximum crosslinking ability (in the
most favourable case in which all the vinyl groups of the BA
sequence are "active").

The elastic modulus is a function of both, the average
functionality and the number of knots. Since increasing func-
tionality is accompanied with a simultaneous decrease of the
number of knots, both effects may compensate each other and
only an upturn at relatively small elongations would be obser-
ved due to the filler effect of the multifunctional knots.

With regard to the form of the stress-strain isotherms, the variation with C of the length of the elastic parts of the chains has even a more decisive influence. As an approximation we can consider a sequence of AA between two BA units (or sequences) as an elastic chain. The number of chain bonds below which the chain may not be described by gaussian statistics[14] can be taken as 100; therefore, sequences of AA with a length shorter than 50 monomer units may be considered as non gaussian chains. For a chain of infinite length it can easily be shown that the percentage of AA sequences with lengths shorter than 50, is given by[27]

$$\sum_{n=1}^{50} W^{AA}_n = (1-W^{AA}_1) \sum_{n=1}^{50} \{ W^{AA}_1 \}^{n-1} = 1-(W^{AA}_1)^{50} \qquad (6)$$

where W^{AA}_n is the probability that a closed sequence of AA has a length n, and W^{AA}_1 is the same probability for a sequence of length 1. For values of C starting from 3-4%(w/w), simple calculations can demonstrate that more than 80% of AA sequences behave as non-gaussian chains. This is in very good accordance with elastic measurements on bimodal poly(dimethylsiloxane) networks[22] which show that a large proportion of shorter chains is necessary to observe upturns of the modulus.

So far we have discussed the direct dependence of the chemical distribution on the elastic behavior of PAA gels. But there is another important group of network imperfections, responsible of the observed maximum in the modulus, that are related also with the composition distribution but via the gelation mechanism. Previous studies on the gelation of PAA networks[11] have reported the existence of a minimum in the dependence of the gel conversion on C, at the same value at which a maximum of the modulus is observed. The minimum of the gel point was explained in terms of a balance between crosslinking and cyclization reactions, both processes involving a pendant vinyl group. When C takes a value around 5-7% (w/w) the sequence length of AA is about 10, that is to say, 20 squeletal bonds. On average, every 10 AA units, the AA sequence is ended by a sequence of BA. On the other hand, the cyclization probability is a function, among other factors, of the cycle length, being maximum for a length of 20 for very flexible polymer chains[21]. Therefore, cyclic formation begins

to be important at this stage. At higher values of C, intra-
molecular reactions rather than crosslinking seem to prevail,
resulting in a large proportion of cycles.

It is particularly interesting to note the coincidence be-
tween the properties of the gels just in the gel point and at
final conversion. This suggests that post-gel reactions do not
differ too much of the pre-gel reactions when very dilute
systems like the one presented here are involved.

The existence of inelastic structures or imperfections on
PAA gels can be evaluated by comparison of the degree of
crosslinking that can be calculated by the phantom moduli,
with the theoretical value obtained if the crosslinking pro-
cess were ideal and the whole gel structure were elastic. From
the phantom modulus, the effective molecular weight between
crosslinks, M_c^{exp}, can be calculated by means of the equation[29]

$$M_c^{exp} = (1 - 2/\phi)(dRT/[f_{ph}^*])(v_{2c})^{2/3} \qquad (7)$$

where ϕ is the functionality; d the density; v_{2c} the volume
fraction of the gel at the moment of the gel formation, and
other symbols have their usual meaning.

The theoretical molecular weight, M_c^{th}, can be calculated
by the equation[12]

$$M_c^{th} = [AA]M_{AA}/(2[BA]) \qquad (8)$$

where [AA] and [BA] are the mole concentrations of AA and BA,
and M_{AA} is the molecular weight of AA.

The comparison has been made as the ratio between experi-
mental and theoretical values of M_c, and is presented in the
fifth column of Tables I and II and in Fig.3.

As can be seen from this figure, departures from ideality
(higher values of the ratio M_c^{exp}/M_c^{th}) are more pronounced
when dilution or crosslinker proportion increase. In both ca-
ses, the crosslinking effectiveness is decreased, but in the
set of gels synthesized at constant C, an asymptotic trend is
suggested; this is consistent with the existence of a critical
value of the total concentration below which only a sol phase
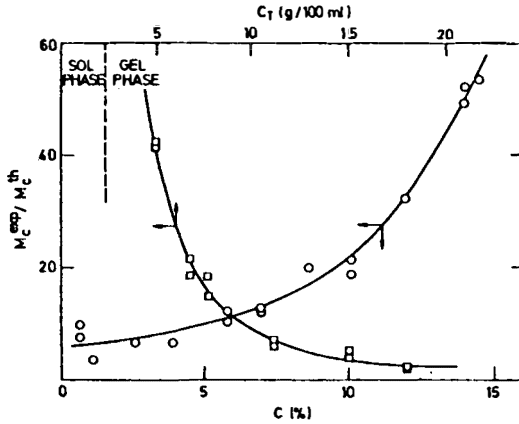would be formed with an infinite value for M_c^{exp}. This critical

Fig.3.- The ratio M^{exp}_c/M^{th}_c plotted as a function of C_T, ($\square$),at constant C, and as a function of C,($\circ$), at constant C_T.

value has been reported by experimental[25] and theoretical studies[30]

When C_T is increased, or C decreased, more perfect gels are formed. In both cases the value of 1 for the ratio M^{exp}_c/M^{th}_c is suggested to be reached because of the greater effectiveness of the crosslinking process. In the former case (high C_T) short chains and high moduli are going to be obtained; whereas in the later case (low C) the crosslinker is going to be more uniformly distributed and low cycles content is going to be obtained.

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