Spontaneous birefringence and photoelasticity of polyacrylamide gels

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During the polymerization of polyacrylamide gels, spontaneous birefringence develops. This effect provides a means of following the kinetics of the polymerization reaction, which is of first-order type. The birefringence appears to be caused by strains that develop in the gel as a result of adherence to the cell walls. Measurements are also described of the stress-optical coefficient in these gels, and the different molecular contributions to this parameter are discussed. Gels in the later stages of polymerization and fully polymerized gels display form birefringence coming from the anisotropic shape of the submolecules (statistical subunits) in the polymer chains.

(Keywords: birefringence; gelation; polyacrylamide; photoelasticity; polymerization kinetics)

INTRODUCTION

Spontaneous birefringence may occur in first order transitions from an isotropic phase to one of lower symmetry. Disordered systems, such as polymers[1] and gels[2] can in certain cases and with suitable thermal treatment develop spherulites, i.e. spherical arrays of crystallites that radiate from a nucleation point but have no overall preferred optic axis. Such systems, when placed between crossed polarizers, transmit a characteristic light pattern that is sometimes, improperly, identified with birefringence.

This paper reports the appearance in a disordered system (a copolymerizing gel) of spontaneous birefringence with well defined optic axes in the macroscopic sample. This birefringence is the result of anisotropic strains that develop during the gelation process. Below we describe the observation in polyacrylamide gels of this effect, which can be used to follow the polymerization kinetics.

In the second part of the paper, we also describe measurements of the photoelastic properties of fully polymerized polyacrylamide gels, with the object of understanding the origin of the spontaneous birefringence, and also of identifying the molecular structures that give rise to the birefringence in these gels.

The original reason for undertaking these experiments was to monitor polymerization kinetics by magnetic birefringence, as has been previously used with success for gels formed with more rigid biological molecules, such as fibrin[3,4]. In the present case, no magnetic alignment was detected during the polymerization of polyacrylamide in magnetic fields up to 12.5 T.

EXPERIMENTAL

The gels were prepared at various acrylamide concentrations (A) between 0.05 and 0.14 g g^{-1}, with bisacrylamide weight fraction (B) varying between 0 and 0.0045 g g^{-1}. The solvent was water, and the precursor fluid, containing 0.70 g l^{-1} ammonium persulphate and 0.28 ml l^{-1} TEMED, was filtered through a 1.2 μm Millipore filter into a quartz cell with a 1 cm optical path and a width of 0.4 cm, held in a copper jacket and stabilized at 20°C. The strain birefringence measurements were made using a larger mould (6.5 ml) from which the gel could be extracted and then placed between two fixed glass plates through which the laser beam passed at normal incidence: when a uniform pressure was applied to the top surface of the gel, the optical path remained constant and the deformation of the sample occurred only in the plane perpendicular to the light beam.

The birefringence experiments, performed on an apparatus described elsewhere[5], made use of a Pöckels cell, a photoelastic modulator and synchronous detection working at 50 kHz.

RESULTS AND DISCUSSION

Spontaneous birefringence

Polyacrylamide gels polymerized in large containers frequently develop moiré patterns of refractive index gradients produced by the exothermic chemical reaction. The establishment of such gradients interferes with observations of the time dependence of birefringence, and for this reason the measurements during polymerization were made in small volume cells. Furthermore, due to static variations in residual strain at different parts of the quartz walls, it is difficult to analyse the spontaneous

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birefringence as a function of position inside the cell. Consequently the observations are only qualitative.

Figure 1 shows the evolution of spontaneous birefringence as a function of time in three different polyacrylamides. Curve A is obtained from a sample with $A=0.08\,\mathrm{g\,g^{-1}}$ and $B=0.0025\,\mathrm{g\,g^{-1}}$, while curve B has $A=0.11$ and $B=0.0015$. Curve C is obtained from a precursor fluid with $A=0.11$ and $B=0$, i.e. giving a non-crosslinked solution at the end of polymerization. In all cases the major onset of polymerization (gel point) occurred about 10 minutes after mixing the solution. In the case of little, or no, crosslinking (curve C), any spontaneous birefringence that appears slowly relaxes to zero.

Figure 1 leads to four points: 1. A change in the sign of the stress-optical coefficient C as a function of polymer concentration (from positive at low concentrations to negative at high concentrations) has previously been reported for polyacrylamide gels[6]. The change in sign of the spontaneous birefringence observed here—in the absence of external constraints—between $A=0.08$ and $0.11\,\mathrm{g\,g^{-1}}$—occurs at the same concentration. It follows that the molecular groupings being aligned are the same in both cases. 2. All the experimental curves of spontaneous birefringence display a small positive bump in the vicinity of the gel point, the latter being visualized in a parallel sample outside the measurement cell. Separate observations show that thermal stresses induced in the quartz cell by the release of heat from the chemical reaction can fully account for this effect, and the appearance of the bump can be taken as an indicator of gelation. 3. The sign of the spontaneous birefringence is consistent with the polymer chains being stretched in the horizontal (x–y) plane. Such alignment can be generated by the weak convection currents driven by the exothermic chemical reaction. An alternative possibility is that the entropic forces governing the polymerizing chains cause them to shrink. The structure of the containing quartz cells, however, allows contact and adhesion of the gel to the lateral walls, but the top surface is free, and therefore contraction can take place only in the vertical direction. Of these two kinds of stress, that due to convection ($g\Delta\rho \simeq 10^2$ dyne cm^{-2}, where g is the acceleration due to gravity and $\Delta\rho \simeq 0.1$ g cm^{-3} is the change in fluid density) is much smaller than the experimentally observed adhesion pressures ($\simeq 10^4$ dyne cm^{-2}). As the final values Δn of the spontaneous birefringence at the end of the reaction can also be produced by a stress $\Delta n/C \simeq 10^4$ dyne cm^{-2} (where C is the stress-optical coefficient, *Figure 2*), it is concluded that the effect is probably the result of adherence to the cell walls.

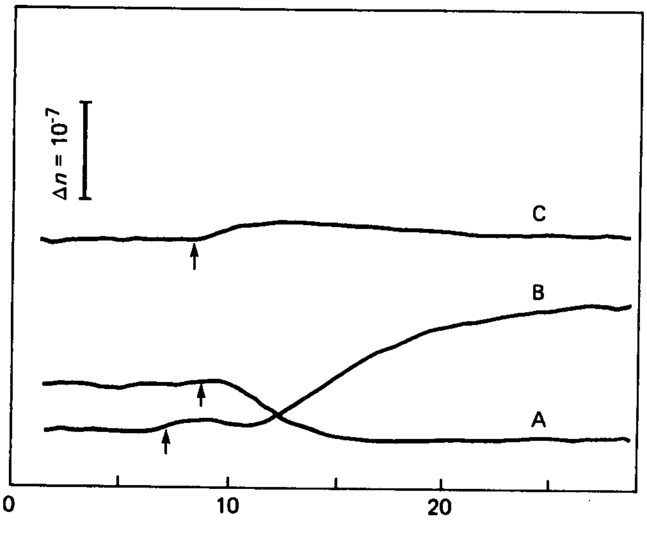

Figure 1 Development of spontaneous birefringence during polymerization in three samples of polyacrylamide–water. (A) $A=0.08$, $B=0.0025$; (B) $A=0.11$, $B=0.0015$; (C) $A=0.11$, $B=0$. The vertical arrows indicate the approximate position of the gel point. The vertical offset levels of these curves are arbitrary and the scale of the change in birefringence is given by the vertical bar in the upper left corner of the figure ($\Delta n=10^{-7}$). The top of the figure is the direction of positive birefringence

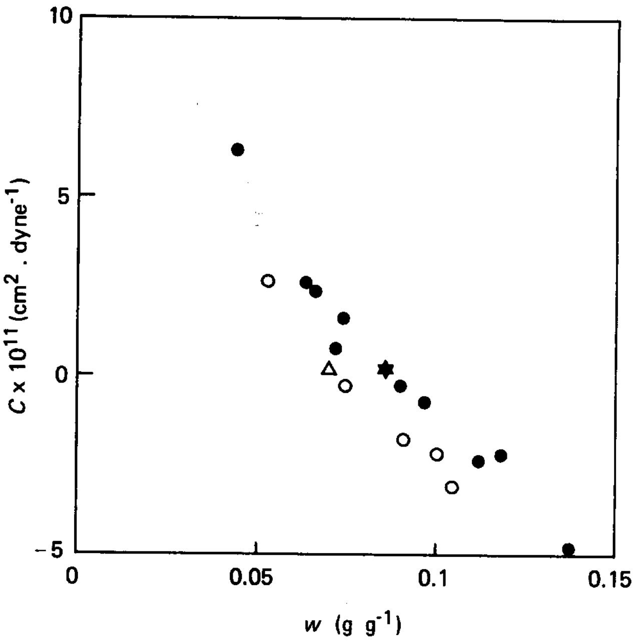

Figure 2 Measured values of the stress birefringence for acrylamide–bisacrylamide copolymer gels in water, as a function of polymer weight fraction, w. (●): acrylamide–bisacrylamide, $A/B=32$; (○): $A/B=100$; (★): gel with $A/B=32$, containing 0.35 M NaCl; (△): gel swollen to equilibrium, $A/B=45$

4. After the initial bump, the shape of the curve is sigmoidal; it yields a straight line on a semilogarithmic plot against time. This behaviour is characteristic of first-order polymerization reactions.

Source of birefringence in polyacrylamide gels

The structure of a typical polyacrylamide gel is as follows. Polymer chains are composed of chemically linked monomers that group into clusters called submolecules[7]. These submolecules form the links of a freely jointed chain or coil that extends between two crosslink points in the gel. The gel contains many such chains connecting a three-dimensional array of crosslinks. Other parts of the gel may be heterogeneous, containing, for instance, only tightly crosslinked bisacrylamide, or, on the contrary, only solvent molecules.

The photoelastic properties of such networks are determined by contributions that can come from three principal sources:

1. Intrinsic optical anisotropy of the monomers.
2. Orientational anisotropy of the solvent molecules surrounding the chains.
3. Form anisotropy due to

(a) Macroscopic heterogeneities (present in most gels);

(b) 'Macroshape' birefringence[1] coming from an overall anisotropic configuration of the polymer coils;

(c) 'Microshape' birefringence that is due to non-spherical submolecules.

When dilute polyacrylamide gels are deswollen in solvents of varying quality, the stress-optical coefficient C undergoes a change in sign, and it is found that C is proportional to $(n_p^2 - n_g^2)^2$, where n_p is the refractive index of the pure polymer and n_g that of the gel[6]. The total observed birefringence is the sum of this positive (concentration dependent) form birefringence and a constant negative intrinsic birefringence[6]. The origin of the form birefringence, however, remains uncertain. The following observations on the same system allow this point to be settled. In what follows, we discuss the contributions to the birefringence from the different sources listed above.

Figure 2 shows the measured values of C *versus* polymer weight fraction, w, of the gels. The sign reversal in C is apparent at approximately $w = 0.09$. All the points on this graph were obtained from gels at their concentration of preparation (w_0), except the point denoted by (△): this datum corresponds to a gel swollen in water to its equilibrium concentration w_e, for which $w_0/w_e = 1.43$. The crosslinking density of this sample was given by $A/B = 45$.

It can be seen from *Figure 2* that increasing the crosslinking density causes a slight shift to the right of the $C(w)$ curve, but the effect is small. Moreover, the value of C does not depend on whether the gel is swollen to a given concentration or prepared initially at the same concentration: it depends only on the polymer weight fraction. This information is sufficient to exclude from consideration one of the possible contributions to form birefringence.

In dilute polymer solutions, macroform birefringence is caused by departures from sphericity induced in the isolated polymer coils. At higher concentrations where coil overlap occurs (semidilute or concentrated region), the mutual penetration of neighbouring coils masks the anisotropic configuration of any given coil. For the anisotropy to become detectable, the coils must be separated, and this involves applying stresses greater than the osmotic restoring force[8]: most gels break under such large applied forces. At low stress, the coils are composed of space-filling correlation spheres of radius, ξ, which can contribute to shape birefringence only if the spheres are deformed. An estimate of the maximum deformation to be expected for a correlation sphere can be found from the ratio of the shear modulus to the osmotic modulus of the gel. This ratio is greatest when the gels are swollen to equilibrium, and, for a given gel, varies approximately[9] as $(w_e/w)^{23/12}$. Thus this contribution, if present, should depend strongly on whether the gel is swollen to equilibrium or not. *Figure 2* shows that this is not the case.

Macroscopic heterogeneities may also contribute to shape birefringence. Measurements of the scattering properties of these gels[10] show that polyacrylamide gels with $A = 0.08$ contain a microsyneretic structure (regions of very high and very low polymer content), the volume fraction of which varies between roughly 0.003 and 0.07 as the value of B is increased from 0.001 to 0.003. Since, however, in this same range, the apparent fractal dimensionality of the heterogeneities varies between 0.5 and 1.5, it is likely that their geometrical shape also varies, so that their contribution to the birefringence is not simply proportional to their volume fraction. Further information can be obtained by making samples of very low bisacrylamide content: two samples of $A = 0.064$ were made, one with $B = 0.00032$ and the other with $B = 0$ (solution). The first gave a (positive) birefringence that coincided within experimental error with the set of points in *Figure 2* with $A/B = 100$. The second, when placed in conditions of continuous flow, also displayed positive strain birefringence. Since these two samples have low or zero inhomogeneity content, it is clear that the observed positive contribution to the birefringence cannot be attributed to the heterogeneities.

It is straightforward to confirm that shape birefringence is indeed present in these gels. Two samples were prepared at the same concentration ($A \simeq 0.09$, $B = 32$), and one of them was placed in contact with 2 g of sucrose, which after a week had diffused through the gel and raised its refractive index from 1.34 to 1.37. On the basis of Hrouz and Ilavský's model[6], this should correspond to an effective gel concentration of about $0.15\,\mathrm{g\,g^{-1}}$. The observed value of the stress-optical coefficient for this sample, namely $C = -6.7 \times 10^{-11}\,\mathrm{cm^2/dyne}$, corresponds, on the least square fit to points (●) of *Figure 2*, to $w = 0.154\,\mathrm{g\,g^{-1}}$. This agreement indicates that shape birefringence is present, and, from the preceding discussion, it can be due only to an aspherical grouping of the monomers in the submolecules ('microshape' birefringence).

It is also important to check that polarization of the water molecules does not play an important role in the birefringence of this material. Polarization effects can be partially screened out by introducing salt into the solvent. For this purpose, a third sample of identical composition to those described in the previous paragraph was prepared, placed in contact with 0.13 g sodium chloride and kept in a dessicator in the presence of water vapour for one week. At the end of this period, the salt had diffused throughout, making the solvent an aqueous NaCl solution of about 0.35 M, for which the Debye–Hückel screening length is approximately 0.5 nm. This sample produced the point represented by (★) in *Figure 2*. Since this concentration of salt is not sufficient to affect significantly the refractive index of the solution, it will not contribute to the shape birefringence. The alignment of this point with the other (●) points in *Figure 2* is therefore an indication that polarization effects of the solvent are negligible.

CONCLUSIONS

The conclusions of this investigation are as follows.

1. During the polymerization of polyacrylamide gels, spontaneous birefringence appears, revealing the presence of long range mechanical constraints. Local constraints (around features much smaller than the laser beam diameter) have no preferred axis in the sample and are therefore not detected by the modulation technique used here.
2. After an initial period of 1–2 min, the polymerization reaction is of first order.
3. Gels in the later stages of polymerization and fully polymerized gels display shape birefringence that originates in the anisotropy of the submolecules composing the polymer chain.

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