the conjugates and the controls were subjected, in parallel, to exhaustive washing with buffered salt solution until both the enzyme activity of the conjugates became constant and the enzyme activity of the controls was zero. This dual check ensured that the possibility of non-specific adsorption of enzyme was eliminated. Spherosil Type XOB 015- and Type XOC 005-based carbonic anhydrase conjugates were found to have respective protein contents of 7.2 and 4.2 mg g^{-1}. Carbonic anhydrase activity was determined by spectrophotometric estimation at 348 nm of 4-nitrophenol produced on enzyme hydrolysis of 4-nitrophenylacetate[10]. The activities of the bound carbonic anhydrase relative to equivalent amounts of the free enzyme in solution were 10.6 and 6.4%, respectively. Spherosil Type XOB 015- and Type XOC 005-based horseradish peroxidase conjugates had respective protein contents of 2.9 and 0.8 mg g^{-1}. Horseradish peroxidase activity was determined by spectrophotometric estimation at 420 nm of purpurogallin produced on enzyme oxidation of pyrogallol in the presence of hydrogen peroxide[11]. The activities of the bound horseradish peroxidase relative to equivalent amounts of the free enzyme in solution were 0.5 and 1.24%, respectively.

Currently we are investigating copolymers incorporating

Monomer I, Monomer II and other functionally active acrylate monomers. Our aim is to use these to prepare other porous silica-based composites suitable for application as heterogeneous catalysts and as solid phase reagents.

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Photoelasticity of glassy polymers

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The birefringence of plastically deformed glassy polymers is known to be related to molecular orientation induced by the deformation process[1,2,3]. However, the birefringence (often comparable in amount) that arises while a glassy polymer is elastically deformed is much less understood, despite the use of such materials in photoelastic stress analysis.

In this Communication we discuss the effect of elastic deformation on the local electric field, showing that this can produce a negative component of birefringence of approximately the correct magnitude for poly(methyl methacrylate) (PMMA).

Figure 1 shows the birefringence of PMMA (ICI Perspex) for tensile specimens held at constant length at approximately 20°C, birefringence being measured with a six-order Berek compensator. By using a wide-angle X-ray diffraction method of orientation measurement[4], we have shown that the chain orientation in the elastically deformed specimens is negligible in comparison with that in plastically deformed specimens having the same birefringence. However, diffraction measurements did show that, as might be expected, the average interchain spacing parallel to the extension direction increased during elastic straining whereas that perpendicular to the extension direction decreased. These changes, shown in *Figure 2*, are discussed elsewhere[5]. They imply that the material surrounding any particular chain segment can no longer be considered to be isotropic and the usual Lorentz treatment of the local field[6] cannot be applied.

In anisotropic crystals, the local field has been evaluated

by summing over all the lattice points using special methods to achieve convergence[7]. Such methods cannot be applied to anisotropic non-crystalline solids and so we have used a modification of the Lorentz approach originally proposed by Havelock[8] in 1908 for inorganic glasses. This models the local anisotropy of the strained solid by allowing the imaginary spherical cavity of the Lorentz model to deform into an ellipsoid. This effectively compensates for the local anisotropy and allows the continued use of the assumption that the molecules inside the cavity make no net contribution to the field. We have used the measured changes in interchain spacings to give the axial ratio of the ellipsoid, whereas Havelock assumed that the cavity deformed by the same amount as the solid.

For an ellipsoidal cavity with semi-axes (a, b, c), the local field, E', due to an applied field, E, is given (in SI units) by[8]:

$$E'_x = E_x + \frac{1}{\epsilon_0} A_x P_x \text{ etc.} \tag{1}$$

where P is the polarization of the solid and the correction factors are

$$A_x = \frac{abc}{2} \int_0^\infty \frac{du}{(a^2 + u)^{3/2}(b^2 + u)^{1/2}(c^2 + u)^{1/2}} \tag{2}$$

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Table 1

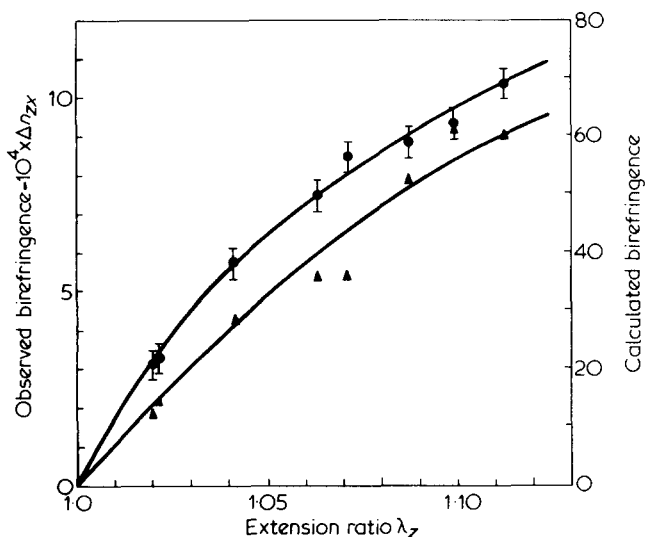| Extension ratio λ_z	Ellipsoid axes			Birefringence $10^4 \times \Delta n_{zx}$	
	a = b	c	$10^3(A_z-A_x)$	Calculated	Observed
1.000	1.000	1.000	0	0	0
1.020	0.998	1.004	−2.40	−12.1	−3.1
1.021	0.999	1.006	−2.79	−14.1	−3.25
1.041	0.996	1.010	−5.57	−28.1	−5.70
1.063	0.993	1.011	−7.17	−36.1	−7.45
1.071	0.993	1.011	−7.17	−36.1	−8.45
1.087	0.989	1.015	−10.3	−52.1	−8.8
1.099	0.987	1.017	−11.9	−60.1	−9.3
1.112	0.989	1.019	−11.9	−60.0	−10.3

Figure 1 Elastic birefringence of PMMA in uniaxial tension at room temperature ● — observed; ▲ — calculated

which are equivalent to the depolarizing factors for an ellipsoid[9]. For a spherical cavity, $A_x = A_y = A_z = 1/3$ giving the usual Lorentz field.

Now using,

$$P_x = N\alpha_x E'_x = \epsilon_0(n_x^2 - 1)E_x$$

where N is the number of molecules per unit volume, α is the molecular polarizibility and n_x is the refractive index in the x-direction, we obtain from equation (1):

$$\frac{N\alpha_x}{\epsilon_0} = \frac{n_x^2 - 1}{1 + A_x(n_x^2 - 1)}$$

and by partial differentiation, the birefringence (assumed small) is given by:

$$n_z - n_x = \Delta n_{zx} = \frac{N(\bar{n}^2 + 2)^2}{18\epsilon_0\bar{n}}(\alpha_z - \alpha_x) + \frac{(\bar{n}^2 - 1)^2}{2\bar{n}}(A_z - A_x) \qquad (3)$$

where the first term on the right hand side is the usual contribution from orientation of units with anisotropic polarizibility and the second term is from the modified local field.

But, from equation (2):

$$(A_z - A_x) = \frac{abc(a^2 - c^2)}{2} \int_0^\infty \frac{du}{(a^2 + u)^{3/2}(b^2 + u)^{1/2}(c^2 + u)^{3/2}} \qquad (4)$$

and, since the integral is always positive, $(A_z - A_x)$ always has the same sign as $(a^2 - c^2)$. Hence for extension along the z-direction, the second component of birefringence is always negative.

Table 1 shows the ellipsoid axes derived from the changes in interchain spacing (*Figure 2*), the factor $(A_z - A_x)$ calculated by numerical integration of equation (4) and the resultant birefringence from equation (3) using $\bar{n} = 1.492$ and assuming $(\alpha_z - \alpha_x)$ is zero, i.e. no molecular orientation. The observed and calculated birefringences are compared in *Figure 1*. As can be seen, the observed is approximately one sixth of the calculated but both have a similar dependence on extension ratio.

The discrepancy between the results may be due to an over-simplified model. Firstly, we have assumed that the undeformed solid is isotropic on a local scale. This is reasonable in an inorganic glass but in a polymer such as PMMA, with a fairly rigid backbone, the orientations of neighbouring chain segments are likely to be correlated, i.e. there will be some local anisotropy in the undeformed solid. It is possible that deformation will have less of an effect if anisotropy is already present.

Secondly, we have taken $(\alpha_z - \alpha_x)$ as zero in equation (3). Although X-ray diffraction shows very little chain orientation, local conformational changes during deformation may give some anisotropy of molecular polarizibility. A small *positive* value for $(\alpha_z - \alpha_x)$ would give a less negative bire-
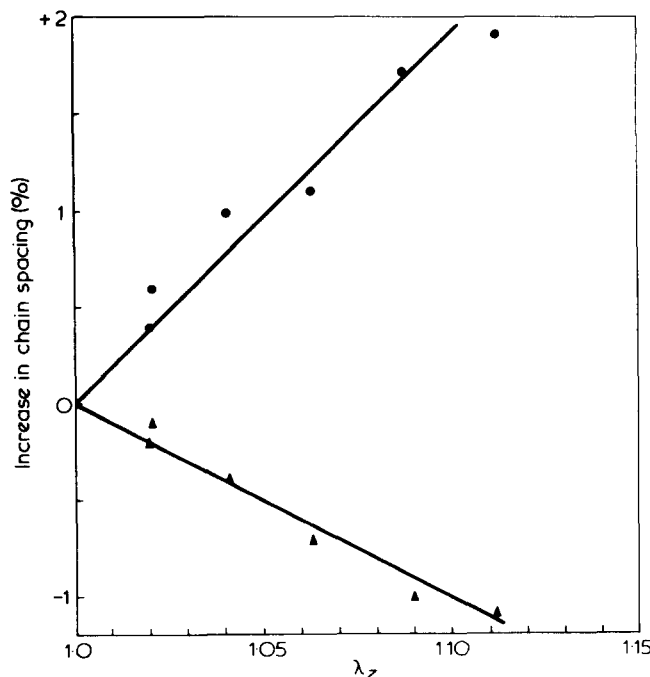

Figure 2 Change in interchain spacing calculated from change in cosec θ, where 2θ is the position of the first diffraction halo. $(2\theta = 13.2°$ for CuK$_\alpha$ radiation when $\lambda_z = 1.00$; this corresponds to a spacing of abour 7 Å.) ●, z - direction (meridian); ▲, x - direction (equator)

fringence as observed. This anisotropy could be due to the orientation of ester groups similar to the alignment of phenyl groups suggested to account for the positive photoelastic effect in polystyrene[10].

However, since the ester groups contribute much of the X-ray scattering from PMMA, changes in their orientation should have a quite visible effect on the scattering pattern[11]. In fact, undeformed and elastically deformed specimens give very similar patterns in the higher-angle region that comes from scattering within the chains.

Hence we conclude that the negative photoelasticity in PMMA is due to the 'local-field effect' but the theory needs to include the influence of correlation of segmental orientation before it can predict the observed values precisely.

Stein and Hong[12] have incorporated a similar modification into the theory of the stress optical coefficient of rubbers.

Further support for the local-field theory comes from LeGrand's findings[13] (which we have confirmed) that the strain optical coefficient of PMMA is almost independent of temperature over the range 20–70°C. The theory predicts that the birefringence at constant elastic strain should decrease slowly with increasing temperature, due to the lowering of refractive index caused by thermal expansion.

In the elastic strain region, the local-field effect does, of course, give a negative component of birefringence for all materials. For polymers, this term will only dominate for materials such as glassy PMMA where orientation of units

with highly anisotropic polarizibility does not occur during elastic deformation.

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Graph-like state of matter: 13. A caution on critical exponents

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There are two main different approaches to the modelling of the free energy ΔG of mixing a polymer solution: (a) the classical mean field approximation theories (for a review see Koningsveld[1]) and (b) the modern theories[2] based on continuum approximations to the singularities featured in the lattice-graph models of the Ising-type.

The latter (especially renormalisation group and *SCF*) theories seek to relate the subtleties of critical phenomena to analytic singularities of asymptotic continuum models, through critical exponents. According to scaling arguments, these exponents are interrelated by a hypothesis of universality[3] which should embrace phase equilibria in polymer solutions. The 'phenomenological' mean-field theories are content to operate within the framework of Gibbs, Maxwell and van der Waals now recognised as the essential lowest level of description. At this level the ΔG function extends through the metastable domain to spinodal loci. No analytical singularity is postulated at spinodal or even specifically at critical points, and accordingly suitable Taylor series are available if necessary.

Thus consider the following generalisation of the (mean-field) Flory-Huggins theory for a monodisperse solution in the usual notation (with $\Phi_o = 1 - \Phi$ = volume fraction of solvent):

$$\frac{\Delta G}{RT} = \Phi_o \ln \Phi_o + \Phi m^{-1} \ln \Phi + \Phi_o \Phi \frac{(\beta_o + \beta_1/T)}{(1 - \gamma\Phi)}; \quad m = M/c$$

(1)

It has the advantage that all parameters ($\beta_o, \beta_1, \gamma, c = 117.76$) have a molecular interpretation[4]. The derived analytical spinodal curves ($T = T(\Phi)$ for $J \equiv \partial(\Delta G/RT)/\partial\Phi = 0$), fit extensive data on polystyrene/cyclohexane (PS/CH) only moderately. The data include 70 spinodal points for 11 PS samples in the range of molecular weight $5.1 \times 10^4 \leqslant M \leqslant 2.6 \times 10^6$, with the standard deviation $\sigma = 4.7 \times 10^{-3}$ of J from zero. For the historic theory ($\gamma = 0$) the misfit is severe ($\sigma = 2.2 \times 10^{-2}$), and attributed to the location of the critical and measurable spinodal points in the region of concentration $\Phi^* \simeq \lambda^{-1}$. In this region, the coils of volume $\lambda_0 m^{3/2} \equiv \lambda m$ ($\lambda_0 \approx 0.57$ for[5] PS/CH and m is the chain length taking solvent = 1), if prevented from overlapping, would just fill the solution volume. Flory[6] warned that the Flory-Huggins theory would break down there because the segment density becomes non-uniform (statistically heterogeneous). Accordingly, Koningsveld *et al.*[5] in their 'bridging theory' tried to span this concentration range by modelling the solution roughly as a pseudo two-phase