Polymerization of butyl methacrylate by light scattering and the formation of regions of local inhomogeneity

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The polymerization of butyl methacrylate (BMA) at ~60°C above the polymer glass transition temperature has been studied by determining the spectra of the scattered light, and the angular dependence of the total (integrated) scattering intensity. Both phonon velocity and attenuation show a relaxation behaviour during conversion, but the frequency dependent macroscopic shear viscosity does not contribute to the relaxation mechanism. The behaviour of the Rayleigh–Brillouin intensity ratio and the dissymmetry of the total scattered intensity shows that small regions of local inhomogeneities at low concentrations are formed during the polymerization reaction.

INTRODUCTION

The problem of local order and structure in nominally glassy polymers has been the subject of much discussion in the last decade. Bulk scattering investigations including neutron, small angle X-ray and light scattering in a number of polymers indicate an absence of significant non-thermodynamic density fluctuations, whilst electron and optical microscopy of the same polymers support the existence of surface heterogeneities with dimensions ranging from 0.01μ to several microns[1,2].

Light scattering may be used to detect inhomogeneities in the bulk polymer[3–5]. Excess scattering is due to large, static, spherically symmetric randomly distributed strain fields. In some of these experiments[3,5] the polymerization has generally been carried out at temperatures below, or in the region of the glass transition temperature, minimizing any relaxation of internal strains produced by contraction of the material on polymerization. The presence of small amounts of dust, as detected by the high values of the Rayleigh–Brillouin intensity ratio[3,4], may also act as centres for randomly directed local strain fields.

The kinetics of thermal polymerization has been studied by a number of authors[5–8], all of whom have used styrene and polymerized at temperatures below T_g. Loucheux and Benoit[6] studied the angular distribution of the integrated scattered intensity at very low degrees of conversion, showing that very high molecular weight polymer is formed at very low (0.01%) conversion, with the average molecular weight falling as the conversion increased. This behaviour becomes more pronounced as the temperature of the polymerization is reduced from 60–30°C. Jackson and Stevens[7] measured the Brillouin shift and line width as a function of the degree of polymerization and propose a relaxing viscosity model where the characteristic relaxation times are dependent on the degree of polymerization. Coakley *et al.*[5] not only measured the Rayleigh–Brillouin intensities and shift, but also the integrated depolarized intensities as a function of reaction time as the polymerization proceeded to completion at 90°C. More recently Alms *et al.*[8] studied styrene polymerizing thermally at 90°C up to 80% conversion by measuring the spectrum of the depolarized scattered light. This enabled separation of the different contributions from monomer and polymer, allowing the polymerization kinetics and the hydrodynamic behaviour of the constituents to be determined. It was found that the polymerization reaction rate increases with conversion resulting from the large increase in viscosity preventing termination by combination. However, the monomer rotational relaxation time at high conversion is only 50% greater than the initial value, indicating that the monomer motion is not determined by the large macroscopic viscosity, but by some local viscosity.

As the aim of this work is to investigate the possibility of the formation of heterogeneities during the polymerization process, it is necessary to choose a material that (a) may be readily themally polymerized well above the glass transition temperature and (b) have all dust removed, in order that the formation of local strain fields is reduced to a minimum and the final polymer has a well defined thermal history. Therefore, butyl methacrylate (BMA) was chosen as the monomer sample as $T_g \sim 12.5°C$.

EXPERIMENTAL

Sample preparation and polymerization

Clean, dry BMA samples were prepared and passed through $0.2\mu m$ Millipore filters. Thermal free radical polymerization of BMA requires small amounts of initiator if reasonable times (a few hours) are required for completion of the reaction. Hence benzoyl peroxide, (0.1%, w/v), were added to the monomer and the sample refiltered several times through the $0.2\mu m$ Millipore filters and finally into the scattering cell. The contribution to the light scattering from the very small amounts of benzoyl peroxide are discussed later on. The polymerization was

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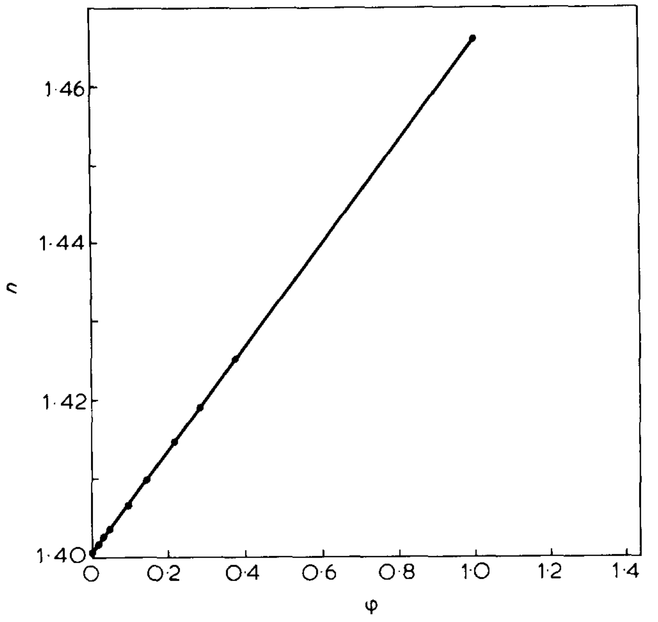

Figure 1 The refractive index n as a function of the volume fraction ϕ of PBMA in BMA

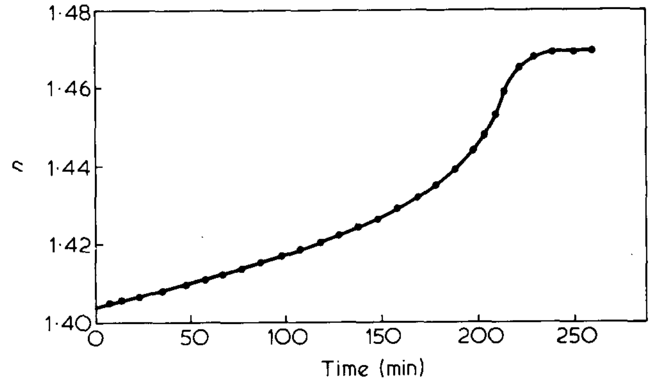

Figure 2 The refractive index n of the polymerizing BMA as a function of time

carried out at 70°C, and at this temperature a conversion of $>99\%$ was achieved after five h.

The degree of conversion of monomer to polymer was monitored by measuring the refractive index of the sample throughout the reaction. By using solutions of fully converted poly(butyl methacrylate) (PBMA) in a monomer (BMA), it was found that the refractive index of the solution was a linear function of volume fraction of PBMA up to 40% PBMA, the maximum fraction that would dissolve in the monomer. As a linear extrapolation of this data also passes accurately through the value of the refractive index of 100% PBMA, it was assumed that a linear variation existed over the whole range of conversion from 0–100%, as shown in *Figure* 1. *Figure* 2 shows the refractive index of the reacting sample as a function of time and *Figure* 3 shows the rate of conversion as a function of volume fraction. It is well known that one of the distinguishing features of free radical polymerization is the acceleration in the rate of conversion after a certain conversion, and is referred to as autoacceleration[9] or the gel effect[10]. As seen from *Figure* 3, until the conversion reaches $\sim 20\%$, the rate of conversion is independent of volume fraction. The rate then increases as the increasing viscosity begins to inhibit chain motion and hence reduces the rate of termination. It then peaks at $\sim 75\%$ conversion and then decreases due to the shortage of monomer.

Light scattering measurements

The laser light scattering spectrometer is shown schematically in *Figure* 4. The maximum power of the argon ion laser output was 400mW in order to ensure the beam did not cause further heating of the sample. The scattering angle was 90° and the acceptance angle of the scattered light detection system was ±0.4°. The finesse of the Fabry–Perot interferometer was in excess of 50 for all measurements, and the free spectral range adjusted so that there was no marked overlap of the peaks during the polymerization. The sample was held in a thermostated container mounted on a high precision Abbe refractometer such that the refractive index of the sample could be determined simultaneously with the scattered spectra.

The total (integrated) angular dependent light scattering measurements were made with a SOFICA light scattering goniometer.

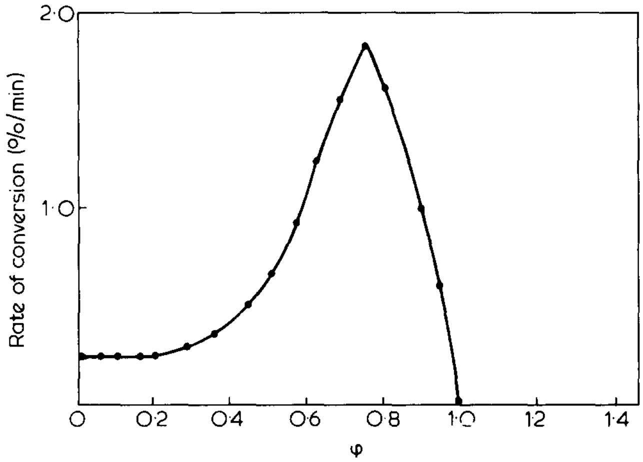

Figure 3 The rate of conversion of BMA to PBMA as a function of the volume fraction ϕ of PBMA in BMA during polymerization

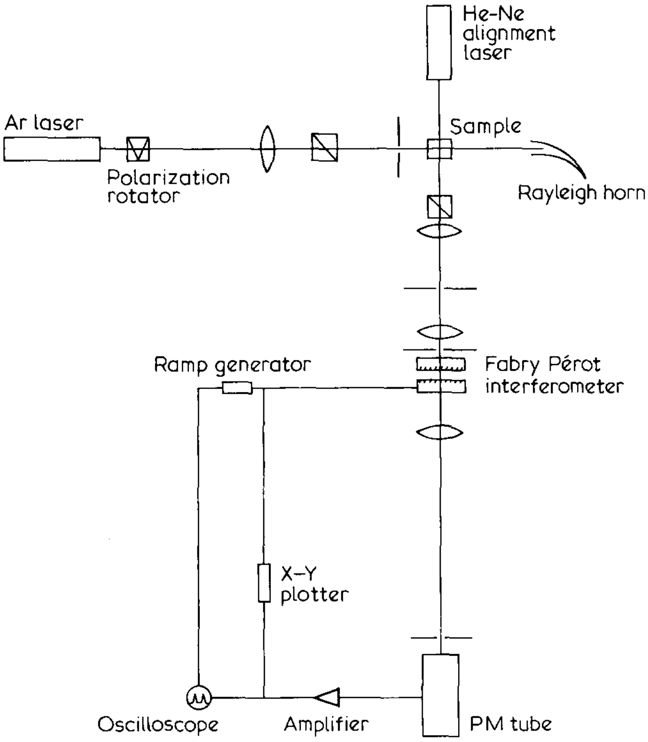

Figure 4 Laser light scattering spectrometer

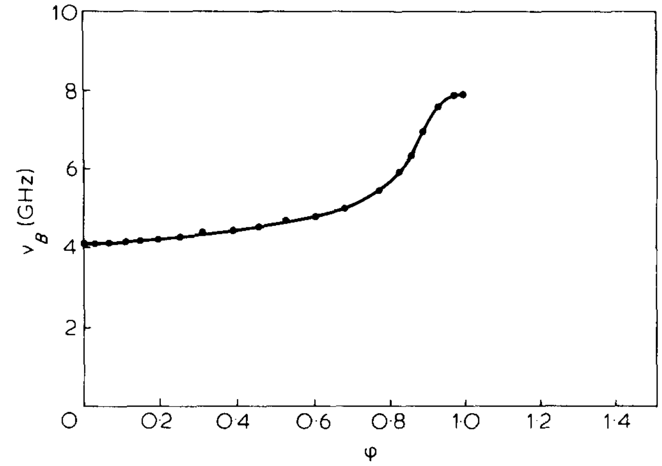

Figure 5 The variation of phonon shift ν_B with volume fraction ϕ of PBMA in BMA during polymerization

RESULTS AND DISCUSSION

Phonon shift and attenuation

The phonon shift ν_B and the attenuation per wavelength $\alpha\lambda$ as a function of the volume fraction of PBMA during the polymerization are shown in *Figures* 5 and 6 respectively, where $\alpha\lambda = \pi\Delta\nu_B/\nu_B$, and $\Delta\nu_B$ is the Brillouin line full width at half peak height. Both *Figures* 5 and 6 show a behaviour characteristic of a relaxation, the monomer and low conversion being in a low frequency region, i.e. the relaxation time associated with the relaxation process $\tau \ll 1/\nu_B$, whilst the final polymer is in or approaching a high frequency region where $\tau \gg 1/\nu_B$. These results are similar to those of Jackson and Stevens[7] for styrene, where a similar relaxation is obtained.

Following the proposal of Jackson and Stevens[7] of the relaxing viscosity model, it may be shown[11] that the phonon velocity V is given by:

$$V = \left(\frac{1}{\rho}\left[K(\omega) + \frac{4}{3}G(\omega)\right]\right)^{1/2}$$

where $K(\omega)$ and $G(\omega)$ are the frequency dependent compression and shear moduli. V may be obtained from the Brillouin shift ν_B, using

$$V = \nu_B\lambda_0/2n\ \sin\theta/2$$

where λ_0 is the vacuum wavelength of the incident beam, n the sample refractive index and θ the scattering angle. The frequency dependent moduli can be written in the form

$$K(\omega) = K_0 + (K_\infty - K_0)\frac{\omega^2\tau_\beta^2}{1+\omega^2\tau_\beta^2}$$

and

$$G(\omega) = \frac{\omega^2\tau_s^2}{1+\omega^2\tau_s^2}$$

where τ_β and τ_s are the compressional and shear viscosity relaxation times respectively, dependent on the degree of polymerization, and the frequency dependent viscosity is described by $\eta(\omega) = \eta_s(\omega) + \eta_\beta(\omega)$, and

$$\eta_s(\omega) = \frac{\eta_s(0)}{1+\omega^2\tau_s}; \qquad \eta_\beta(\omega) = \frac{\eta_\beta(0)}{1+\omega^2\tau_\beta^2}$$

At low frequencies

$$\eta_\beta(0) = (K_\infty - K_0)\tau_\beta,\ \eta_s(0) = G_\infty\tau_s,\ K(\omega) = K(0)$$

K_∞ and G_∞ being the infinite frequency values of the moduli.

The attenuation per wavelength is then given by

$$\alpha\lambda = \frac{4\pi\omega}{3\rho V^2}\cdot\eta(\omega)$$

The near 100% increase of phonon velocity in converting monomer to polymer cannot be accounted for by the increase in density, ρ, of the sample from 0.804 to 1.05 g ml^{-1} and an increase in refractive index from 1.402 to 1.469.

If we now assume, as did Jackson and Stevens[7], that $K_\infty = G_\infty$ and that the infinite frequency velocity V_∞ is attained in the fully polymerized sample, then using the expression

$$V_\infty = \left(\frac{1}{\rho}\left[K_\infty + \frac{4}{3}G_\infty\right]\right)^{1/2}$$

with the measurements giving $V_\infty = 1.97 \times 10^5$cm s^{-1} and the value of ρ polymer $= 1.05$ g ml^{-1}, leads to $G_\infty = K_\infty = 1.75 \times 10^{10}$ dynes cm^{-2}. Thus knowledge of the zero frequency viscosity $\eta_s(0)$ allows estimation of the shear viscosity relaxation time τ_s as a function of degree of polymerization and hence the frequency dependent shear viscosity $\eta_s(\omega)$.

The zero frequency viscosity $\eta_s(0)$ was determined as a function degree of polymerization using a falling sphere viscometer, correcting for finite tube length and diameter using the method of Francis[11]. This data is shown in *Figure* 7, together with the frequency dependent shear viscosity $\eta_s(\omega)$. The peak in $\eta_s(\omega)$ occurs at a volume fraction of PBMA of ~0.05, whilst the experimental data shown in *Figure* 6 peaks at volume fraction of PBMA of 0.75. Hence one is led to the conclusion that in the relaxing viscosity model macroscopic shear viscosity does not contribute significantly to the relaxation in $\alpha\lambda$. It would appear that it is the bulk (compressional) viscosity which

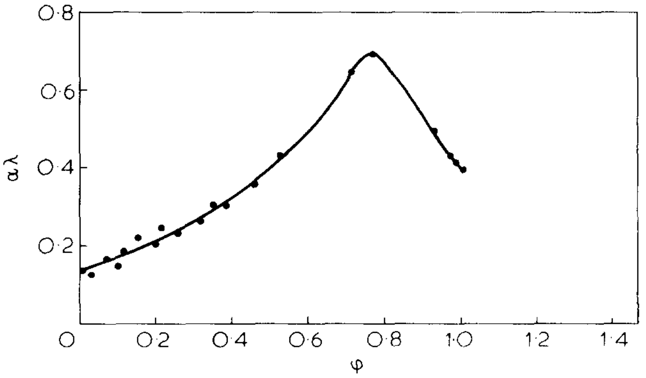

Figure 6 The variation of the phonon attenuation per wavelength αλ as a function of volume fraction ϕ of PBMA in BMA during polymerization

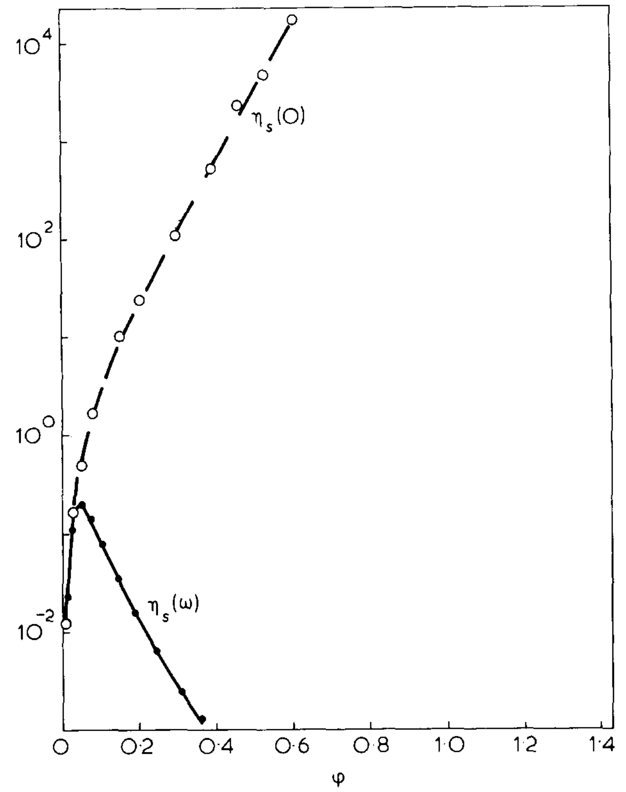

Figure 7 The zero frequency shear viscosity $\eta_S(0)$ shown by ○, and the calculated frequency dependent shear viscosity $\eta_S(\omega)$ shown by ●, as a function of volume fraction ϕ of PBMA in BMA during polymerization

is relaxing, i.e. the phonon lifetimes are governed by the bulk (compressional) molulus alone.

Rayleigh–Brillouin intensity ratio

The I_{VV}spectra contains an anisotropic component, due to intrinsic anisotropy of polarizability of the scatterer and an induced anisotropy due to intermolecular interactions, as well as the isotropic component. Hence it is necessary to subtract from the observed central line intensity I_c, this anisotropic component in order to obtain the correct Rayleigh isotropic scattering component I_R.

For 90° scattering it has been shown[12] that

$$I_{VV}=I_F+4I_r$$

$$I_{VH}=3I_r$$

where the isotropic component $I_F=I_R+I_B$ and I_r is the anisotropic component.

Hence

$$I_{VV}=I_R+2I_B+\frac{4}{3}I_{VH}$$

The I_{VH} spectra contains a number of components due to the relaxation times of the mechanisms contributing to the anisotropy and it is only those contributing to I_c which need to be determined. The ratio $v=I_{VH}^{slow}/I_{VH}^{total}$ may be used to correct for this contribution where I_{VH} is the contribution to I_c due to the narrow Lorentzian occurring in the same spectra range of I_R and which is sitting on a broad background I_{VH}^{fast} where $I_{VH}^{total}=I_{VH}^{slow}+I_{VH}^{fast}$. Hence over the spectra range of the central component

$$I_R=I_c-v.\frac{4}{3}I_{VH}$$

The ratio of the isotropic scattering intensity to the Brillouin intensities as a function of conversion is shown in *Figure* 8. Below a volume fraction of PBMA of 1% the intensity ratio $I_R/2I_B\approx 0.3$.

It has been shown[13] that this ratio may be written, for a relaxing liquid, in the form

$$\frac{I_B}{2I_B}=\frac{V^2(\omega)}{V_0^2}\cdot\gamma-1$$

where $V(\omega)$ is the frequency dependent phonon velocity, V_0 the zero frequency velocity and γ the ratio of the specific heats. In the low frequency region $V(\omega)\rightarrow V_0$ giving the usual expression for the Landau–Placzek ratio for a simple liquid. Comparison of the value of $\gamma-1=0.25$ for BMA with the experimental value of 0.3 shows that the dust level in the initial sample is extremely low and the excess scattering due to the initiator is negligible.

Above a volume fraction of 1% PBMA the intensity ratio rises rapidly to ~10. This is due to the rapid formation of a dilute solution of very high molecular weight polymer chains in monomer increasing I_R, with the subsequent decrease in the intensity due to interactions between the chains occuring at the higher concentrations. The open circles in *Figure* 8 are values of the intensity ratio measured for solutions of the final polymer dissolved in monomer confirming this interpretation[14]. The intensity ratio in this case is not as high as in the polymerizing sample due to the weight average molecular weight of the final polymer being less than that of the polymer produced at these early stages of polymerization.

The intensity ratio decreases to 1.62 when ~70% volume fraction of PBMA is reached, and then rises again. Using the equation immediately above, the intensity ratio may be estimated at 100% as 1.8 assuming $\gamma=1.25$ and $V_0=1.18\times10^5$cm s^{-1} (see ref. 13), as is shown in *Figure* 8. Hence as the reaction proceeds the intensity due to the

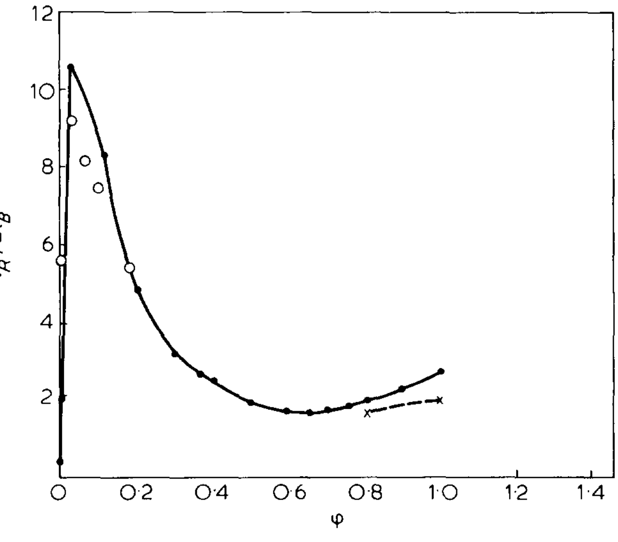

Figure 8 The variation of the ratio of the isotropic scattered intensity to the Brillouin intensities $I_R/2I_B$ with volume fraction ϕ of PBMA in BMA during polymerization. The data for solutions of final PBMA sample in BMA are shown by ○. The values of $I_R/2I_B$ calculated assuming the relaxing liquid model are shown by X

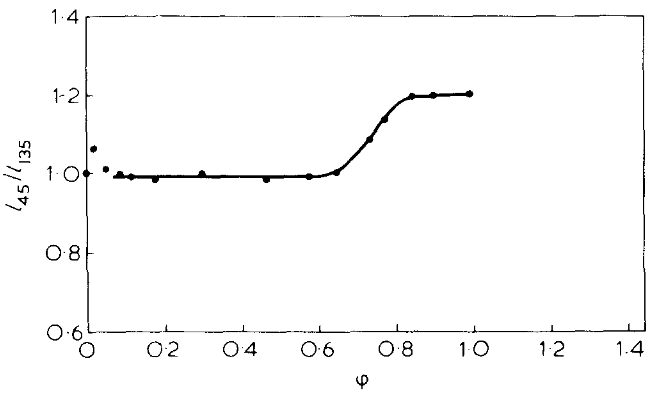

Figure 9 The variation of the dissymmetry I_{45}/I_{135} with volume fraction ϕ of PBMA in BMA during polymerization

solution concentration fluctuations decreases whilst the contribution from the relaxation region becomes significant. However it would also appear that there is another contribution appearing which we suggest is due to the formation of density fluctuations in excess of the thermodynamic fluctuations that normally exist.

Dissymmetry measurements

The dissymmetry $Z = I_{45}/I_{135}$ where I_{45} is the total (integrated) scattered intensity at a scattering angle of 45° and I_{135} the 135° total scattered intensity, is plotted as a function of polymerization and is shown in *Figure* 9.The initial dissymmetry at low conversion is due to the formation of high molecular weight chains in very dilute solution as discussed previously. The important feature is the marked increase in Z at $\sim 70\%$ conversion of the sample showing the formation of regions of excess density fluctuations. In order to determine the size of these Rayleigh Gans scatterers we need to know their shape, concentration and the magnitude of this excess scattering compared to the background scattering due to normal thermodynamic density fluctuations. If we assume that these local inhomogeneities are spherical in shape, and their concentration is sufficiently small ($< 1\%$) such that Z is independent of concentration, and all the observed scattered intensity is excess scattering, then the diameter of the scattering sphere is $\sim 0.04 \mu m$ when $Z = 1.2$ (see ref 15). This is a minimum size, as Z, and hence the sphere diameter increases if all the observed scattering is not solely due to these regions.

Using the simple model of a sphere in a uniform matrix, then the Rayleigh ratio for small, homogeneous, non-absorbing spheres is given by[16]

$$R_{90} = \frac{9\pi^2\eta_0^2}{2\lambda_0^4} \cdot \left[\frac{m^2-1}{m^2+2}\right]^2 V_f v P(90)$$

for 90° scattering and unpolarized incident and scattered light. η_0 is the matrix refractive index, λ_0 the incident light vacuum wavelength, m is n_1/n_0, n_1 the refractive index of the sphere, V_f the volume fraction of spheres, each of volume v, and $P_{(90)}$ the particle structure factor.

R_{90} was determined when the scattering sample had attained 100% conversion. Using benzene as the standardizing material ($R_{90} = 16.3 \times 10^{-6} \mathrm{cm}^{-1}$), then $R_{90} = 5.7 \times 10^{-6} \mathrm{cm}^{-1}$. $P_{(90)}^{-1}$ may be obtained[15] from the value of the dissymmetry Z, i.e. $P_{(90)}^{-1} = 1.136$. Hence we may estimate the volume fraction of spheres in the matrix for various postulated values of the relative density (hence the relative refractive index m) of the spherical region in the matrix. A relative difference in density $\Delta\rho/\rho$ of 1% leads to $m = 1.002$ and $V_f = 1.7 \times 10^{-2}$ whilst for $\Delta\rho/\rho$ of 5% gives $m = 1.008$ and $V_f = 1 \times 10^{-3}$.

CONCLUSIONS

We have shown that the frequency dependent macroscopic shear viscosity does not contribute to the structural relaxation mechanism as postulated by Jackson and Stevens[7], the characteristic (conversion dependent) relaxation time not following that of the macroscopic shear viscosity. This leads us to conclude that the bulk viscosity supplies the relaxation mechanism together with a local, non-macroscopic, shear viscosity as suggested by Alms *et al.*[8]

From the changes in the intensity of light scattered during the polymerization reaction we have shown that small concentrations of local inhomogeneities are formed, superimposed on the normal thermal density fluctuations. As the reaction was performed ~60°C above the glass transition temperature, and the appearance of these inhomogeneities coincides with the autoacceleration of the reaction, it is postulated that the greatly reduced termination rate encourages the formation of local excess density. regions. These regions may act as centres of strain fields, that have been suggested previously[1-4], when the material is cooled to the region of or below T_g. The magnitude of these strain fields are no doubt very dependent on the strain history of the sample and contribute to the macroscopic properties of the polymer, but we must conclude that small regions of inhomogeneity will always be present in the polymer due to their inherent formation during the polymerization reaction.

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