ciably the intrinsic viscosity values at high molecular weight and zero frequency. But the situation becomes more critical at very high frequency where $[\eta]_Z$ completely vanishes. A positive value of the observed second Newtonian viscosity in this region can be at least partially explained by the constant additive term if the term is positive. If it is negative it even increases the demand for some other explanation, for instance by the nonvanishing term resulting from partial coil rigidity as described by internal coil viscosity. Hence this analysis seems to corroborate the need fcr the introduction of internal viscosity in order to explain the finite limiting value of intrinsic viscosity at high frequency shear flow field.

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Effect of pressure upon the dissociation of the benzoyloxy radical

The rate of dissociation of benzoyl peroxide into radicals is decreased by application of high pressures[1,2]. The benzoyloxy radicals first formed in the dissociation can dissociate further:

$$C_6H_5.CO.O. \rightarrow C_6H_5. + CO_2 \quad (1)$$

but there appears to have been no study of the effect of pressure upon this reaction.

The initiation processes in a radical polymerization initiated by benzoyl peroxide are:

$$C_6H_5.CO.O. + M \rightarrow$$

$$\rightarrow C_6H_5.CO.O.M. \quad (2)$$

$$C_6H_5. + M \rightarrow C_6H_5.M. \quad (3)$$

where M represents a molecule of the monomer. Ordinarily, the phenyl radicals produced in reaction (1) are subsequently consumed in reaction (3)[3]. The rate at which phenyl radicals enter polymer to form end-groups is therefore the rate of reaction (1); reaction (2) can be followed directly by measurement of the rate at which benzoyloxy end-groups are formed. The necessary end-group analyses can be performed by using suitably labelled benzoyl peroxide. Comparisons of the numbers of benzoyloxy and phenyl end-groups in polymers produced from solutions of a monomer in a diluent allow evaluation of k_1/k_2, the magnitude of which depends markedly upon the nature of the monomer[4].

If $\Delta V_1^{\ddagger}$ and $\Delta V_2^{\ddagger}$ are the volumes of activation for reactions (1) and (2), $(\Delta V_1^{\ddagger} - \Delta V_2^{\ddagger})$ could be evaluated from end-group analyses on polymers produced at various pressures. It is expected that $\Delta V_1^{\ddagger}$ would be positive and $\Delta V_2^{\ddagger}$ negative since reaction (1) is a dissociation and reaction (2) an association. $\Delta V_1^{\ddagger}$ might be comparable with $\Delta V^{\ddagger}$ for the dissociation of a molecule into radicals, and $\Delta V_2^{\ddagger}$ with $\Delta V^{\ddagger}$ for the growth reaction in a radical polymerization. These views have been tested for the polymerizations of styrene and methyl methacrylate at 60°C with toluene as diluent.

Benzoyl peroxide was labelled in its rings with tritium and in its carboxyl groups with ^{14}C; materials were assayed by scintillation counting in solution[5]. Low conversion polymerizations were performed in tubes of stainless steel[6,7] at pressures up to 4×10^8 N/m^2 (4000 bar) for styrene and up to 2×10^8 N/m^2 for methyl methacrylate; corrections were made for the compressibilities of monomers and diluents.[8] There were no systematic differences between results for polymerizations at atmospheric pressure in steel and glass vessels, or between those with toluene and those with benzene (the diluent used in most of the previous studies).

Pressure had a pronounced effect upon the balance between benzoyloxy and phenyl end-groups, as indicated by the typical results displayed in *Figure 1*; from the slopes of such plots, values of k_1/k_2 were found. Plots of $\ln(k_1/k_2)$ vs. pressure (see *Figures 2* and *3*) show that $(\Delta V_1^{\ddagger} - \Delta V_2^{\ddagger})$ varies with pressure for both monomers but, from the initial slopes of these curves, the values are 21 ± 3 and 15 ± 2 cm^3/mol for styrene and methyl methacrylate respectively as the monomers.

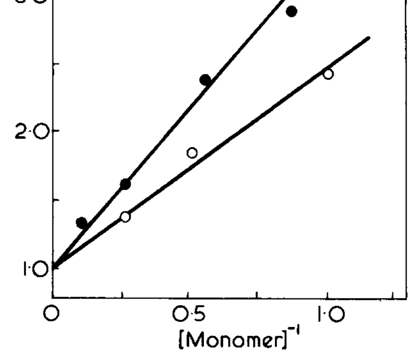

Figure 1 Variation of x, (number of benzoyloxy end-groups)/sum of numbers of benzoyloxy and phenyl end-groups), with molar concentration of monomeric methyl methacrylate for polymerizations at 60°C with toluene as diluent. ●, pressure = 0.3×10^8 N/m^2; ○, pressure = 1.5×10^8 N/m^2

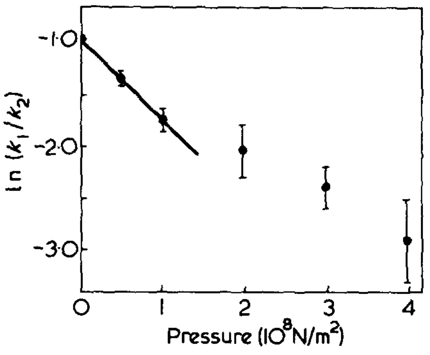

Figure 2 Plot of $\ln(k_1/k_2)$ vs. pressure for polymerization of styrene in toluene at 60°C; k_1/k_2 in dm^3/mol

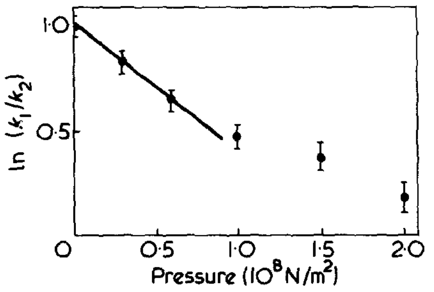

Figure 3 As for *Figure 2*, but with methyl methacrylate as monomer

Neuman[9] has pointed out that, although observed values of $\Delta V^\ddagger$ for homolytic scission reactions range from about +1 to +13 cm^3/mol, the true value for the actual scission process is +4 to +5 cm^3/mol; the lower values can be attributed to solvation effects where the transition state is polar and the larger values arise in systems where the observed rates are complicated by cage effects and there are contributions to $\Delta V^\ddagger$ from recombination and separative diffusion terms. If $\Delta V_1^\ddagger$ (for dissociation of $C_6H_5.CO.O.$) is taken as 4 cm^3/mol then the present results lead to values of -17 ± 3 and -11 ± 2 cm^3/mol for $\Delta V_2^\ddagger$ for additions of the radical to styrene and methyl methacrylate respectively. $\Delta V^\ddagger$ for the growth reaction in the radical polymerization of a vinyl monomer is thought not to be very sensitive to the nature of the monomer; values of about -18 and about -19 cm^3/mol have been given for styrene[10] and methyl methacrylate[11] respectively. The values of $\Delta V_2^\ddagger$ suggested now for addition of the benzoyloxy radical to monomers are generally similar to those found for the growth reactions in the polymerizations. It is known[4] that polar effects are important in the reactions of the benzoyloxy radical and this fact may be significant in connections with values of $\Delta V^\ddagger$ for reactions involving the radical; this possibility is being tested by examination of effects of the nature of the diluent upon values of $(\Delta V_1^\ddagger - \Delta V_2^\ddagger)$.

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Correlations in the molecular weight distribution of polymers

It is a well-known fact that the molecular weight distribution (*MWD*) has a preponderant influence on the mechanical and rheological properties of polymers.

Widely used parameters to characterize the *MWD* are $\bar{M}_w$ and $Q = \bar{M}_w/\bar{M}_n$, i.e. the ratio between the weight-average and the number-average molecular weights. It has been shown that the influence of the shear rate on the apparent viscosity of a polymer melt or concentrated solution at a given $\bar{M}_w$ is very much dependent on the value of Q[1].

An important question is whether the parameter Q gives a sufficient description of the *MWD*, in other words, whether there exists a sufficiently universal relationship between the ratios $\bar{M}_w/\bar{M}_n, \bar{M}_z/\bar{M}_w, \bar{M}_{z+1}/\bar{M}_z$ etc. If this question can be answered in the affirmative, dimensionless η–$\dot{\gamma}$ relationships (master curves) may be reliable; if not, one can hardly expect a universal set of η–$\dot{\gamma}$ master curves even for one single polymer.

Theoretical *MWDs* of the Schulz–Flory type give a partial answer only, viz. for those polymers whose mechanism of formation is rather clear-cut and leads to Q values between 1 and 2. In practice, however, most polymers (unblended!) show Q values between 1.05 and 20 or even higher[1].

Calculations by Graessley[2] on the influence of molecular weight distributions on the η–$\dot{\gamma}$ relationship start from an arbitrary *MWD*. Using his formulae, Cote and Shida[3] demonstrated that parameter Q is insufficient to describe the effect, since blends with identical Q values but different *MWDs* were calculated to show a very

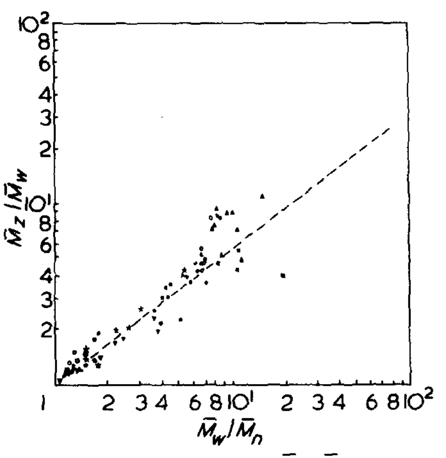

Figure 1 Relation between $\bar{M}_w/\bar{M}_n$ and $\bar{M}_z/\bar{M}_w$, literature data. PE: ●, Mendelson *et al.* (ref 4); □, Mills (ref 5); ■, Saeda *et al.* (ref 6); △, Shah and Darby (ref 7); ▲, Wales (ref 8). PS: ▽, Cotton *et al.* (ref 9); ▼, Chee and Rudin (ref 10); ◇, Mills (ref 5). *PP*: ◆, Thomas (ref 11). PMMA: ⊕, Mills (ref 5). PDMS: ○, Mills (ref 5). BR: ☆, Dunlop and Williams (ref 13)