Evidence for Two Gel Effects During the Bulk Polymerization of Ethyl Acrylate from DSC, Rayleigh and Brillouin Scattering

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SUMMARY

DSC studies of the bulk polymerization of ethyl acrylate have revealed the occurrence of irregular kinetic behaviour during the initial stage of the reaction at less than 5 per cent monomer conversion. Simultaneously, a maximum in the 90° Rayleigh scattering was observed. The transient inhomogeneity and the shoulders on the rate-time curves are attributed to a localized gel effect which precedes the general gel effect.

INTRODUCTION

Due to a high heat of polymerization, a relatively small heat capacity and a strong tendency for auto-acceleration, the bulk polymerization of acrylates may easily run out of control. This may result in the formation of popcorn polymers or eventually in explosion of the reacting system (RAUCH-PUNTIGAM and VÖLKER, 1967). Even during the slow, light-induced bulk polymerization at room temperature of small quantities of monomer which were in good thermal contact with a large heat sink, an irregular kinetic behaviour has been observed. The rate vs. time curve, as measured with isothermal DSC, exhibited a clearly visible shoulder which points to two distinct periods of acceleration (BRESSERS and KLOOSTERBOER, 1980).

It will be shown below that this shoulder is connected with a transient inhomogeneity as observed from light scattering. The observed kinetic and optical behaviour may be described with a simple model, based on a locally enhanced rate of reaction.

EXPERIMENTAL

Chemicals. Poly (ethyl acrylate), secondary molecular weight standard (Aldrich), $M_w = 125.000$ and $M_n = 38.600$ was freed from its solvent (toluene) by evaporation at 70°C under vacuum. Ethyl acrylate and benzoin methyl ether (BME) were used as previously described (BRESSERS and KLOOSTERBOER, 1980).

Sample preparation. 5.10^{-3} solutions of photoinitiator (BME) in inhibitor-free monomer were prepared in a dry nitrogen glove box, installed in a room with yellow light ($\lambda > 500$ nm). 1 ml portions were filtered through a 0.2 μm filter (Millipore) and transferred to 1 cm quartz suprasil fluorescence cells. The sample solutions were further degassed by bubbling purified nitrogen through the solutions before tightly closing the cuvettes.

Polymerization was carried out as described (BRESSERS and KLOOSTERBOER, 1980).

Light intensities used were between 10^{-4} and 10^{-3} W cm^{-2} as measured with a spectroradiometer (EG & G, type 580/585).

90° Rayleigh scattering was measured during polymerization on a relative scale using a Ramanor HG 2S Raman spectrometer by setting the instrument at the laser wavelength. The light source used was a Coherent Radiation 4W argon ion laser, wavelength 514 nm. The use of the Raman spectrometer enables the degree of conversion to be calculated from measurement of the C = C and C = O bands before and after UV irradiation (KLOOSTERBOER and BRESSERS, to be published). UV light from the laser excitation source was removed by using a cut-off filter.

Brillouin spectra were measured at 90° before and during polymerization using a five-pass Fabry-Perot interferometer connected to a Burleigh DASI stabilization and data acquisition system. The instrument has a finesse of 100 and a contrast of 10^{12}. Spectra were recorded using a free spectral range of 0.83 cm^{-1} (25 GHz). Excitation source: 0.5 W argon ion laser, 514 nm (Spectraphysics 170) with UV cut-off filter.

RESULTS AND DISCUSSION

Fig. 1 shows the 90° Rayleigh scattering, recorded during the light-induced bulk polymerization of ethyl acrylate. Initially, a high level of dust spikes is noticed.
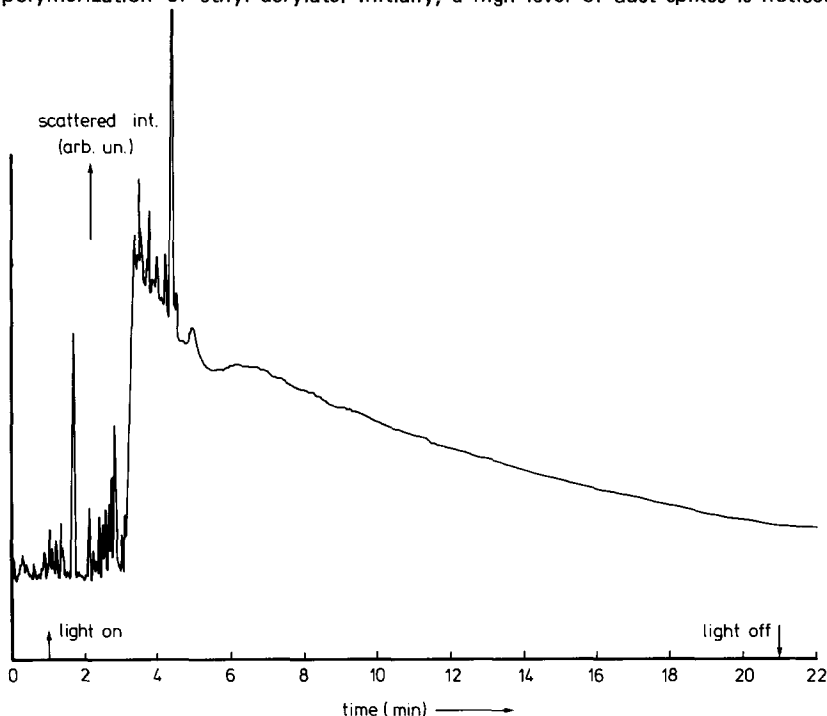

Fig. 1. 90° Rayleigh scattering, recorded during the light-induced bulk polymerization of ethyl acrylate. Initiator: 5.10^{-2}M BME.

After 1 minute the UV light was turned on and after a short induction period the signal increased and passed through a maximum. Here, the dust spikes disappeared, indicating a strongly reduced mobility of the dust particles, caused by the increased viscosity of the sample. The scattering maximum clearly points to a transient in-homogeneity and the simultaneous disappearance of the dust spikes shows that gelation occurs. After turning off the light a conversion of 10 per cent was measured, showing that the maximum scattering occurs at a degree of conversion of only a few per cent. However, it might be argued that either the intense laser radiation alone or its combined action with the UV radiation might influence the rate of the reaction at the laser focus and therefore locally enhance the Rayleigh scattering.

The "burning out" of e.g. fluorescent impurities is well known in the laser-Raman spectroscopy of polymers (HENDRA, 1974) and such a process might involve the production of radicals. Indeed, sometimes the laser beam produced a trace of poly-merized material in the sample. However, the formation of such traces was pre-vented by appropriate filtering of the UV light from the excitation source of the laser.

In order to be sure that no specific rate enhancement occurs at the laser focus we also measured Brillouin spectra. A Brillouin spectrum yields information at two levels: the intensity of the central Rayleigh peak is influenced by aggregation at the molecular level as well as by bulk phenomena such as strain fields, whereas the shift and bandwidth of the Brillouin peaks are related only to bulk properties of the sample (PATTERSON, 1978). The observed shift is proportional to the velocity of propagation of longitudinal hypersound waves which in turn is related to the com-pression modulus of the sample. The bandwidth is proportional to the damping of the hypersound waves. Rayleigh and Brillouin measurements both refer to the same volume, namely that part of the incident laser beam which is "seen" by the spectro-meter, i.e. a cylinder with a length and a diameter of $\sim 50~\mu m$.

Fig. 2a shows a plot of Brillouin shift and bandwidth as a function of time for the slow, light-induced bulk polymerization of ethyl acrylate. During polymerization the shift gradually increases and with it the compression modulus. The bandwidth passes through a maximum when the frequency of the hypersound waves equals the relaxation frequency of the viscosity at that particular degree of conversion (JACK-SON and STEVENS, 1973). It can be seen that during the initial period of approxi-mately 5 minutes both curves are relatively flat, indicating that only minor changes occur in the bulk properties of the sample.

Fig. 2b shows a plot of the Landau-Placzek ratio $I_R/2I_B$ (I_R is the intensity of the central Rayleigh peak and $2~I_B$ is the total Brillouin intensity) as a function of time. This ratio passes through a sharp maximum during the initial period. The maximum obviously occurs at a very low degree of conversion.

Measurement of separate traces, obtained by locking the spectrometer at either the Rayleigh peak or one of the Brillouin peaks showed that only the Rayleigh signal went through a sharp maximum whereas the Brillouin signal remained flat. Later on, at higher degrees of conversion, the Brillouin intensity diminished, causing the $I_R/2I_B$ ratio to increase again. The spectra did not change upon interruption of the UV irradiation.

Static measurements for a series of solutions of different concentrations of commer-cial poly (ethyl acrylate) in ethyl acrylate as solvent show that a maximum value of $I_R/2I_B$ occurs at a concentration of 2.5 per cent (Fig. 3). This maximum was reached from both sides, by increasing the polymer concentration as well as by

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Fig. 2a.
Brillouin shift (•) and bandwidth
(x) recorded during the light-
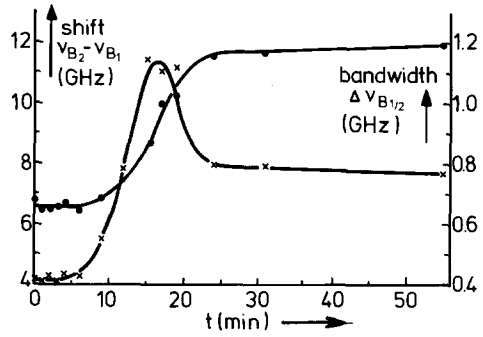induced bulk polymerization of
ethyl acrylate.

Fig. 2b.
Landau-Placzek ratio $I_R/2I_B$ re-
corded during the light-induced
polymerization of ethyl acrylate.
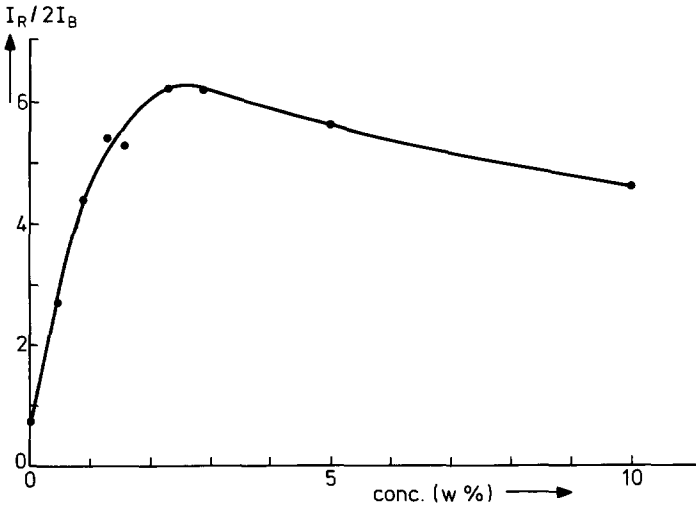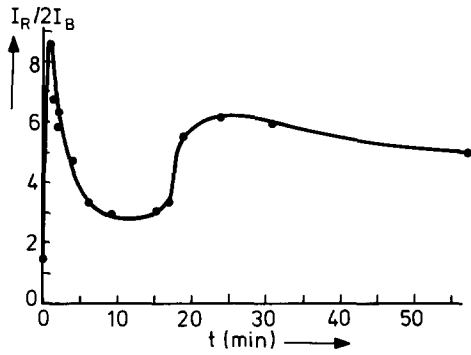Initiator: $5.10^{-2}M$ BME.

Fig. 3. Landau-Placzek ratio $I_R/2I_B$ as a function of the concentration of poly(ethyl acrylate) in ethyl-acrylate.

dilution of a concentrated solution. This points to a reversible aggregation of the polymer coils. Similar maxima have been reported by TAGER and ANDREEVA (1967) for the 90° Rayleigh scattering of polystyrene in benzene. The position of the maxima was found to depend on the molecular weight of the polymer.

Two main phenomena have been observed, both occurring at a few per cent conversion: transient inhomogeneity from light scattering and a shoulder on the rate-time curve from DSC. Their relation, that is the influence of the transient inhomogeneity on the kinetics of the polymerization reaction will now be discussed.

Consider initiation occurring somewhere in the bulk monomer. The polymer molecule produced will assume a random coil conformation, a coil which is filled or swollen with the monomeric solvent. The solvent also contains the initiator. The next initiation may either occur in the bulk of the solution with the formation of a new coil or within a swollen coil already formed. It is assumed that the mobility of a growing macroradical will be restricted as compared with regions outside the coils already formed. This means that some type of auto-acceleration, a gel or Trommsdorff effect will occur within the coil. Therefore, the reaction will proceed faster inside the coil than outside it. Since the coils are supposed to be rather rare and loosely "wound-up", the reacting monomer in the coil may be easily replenished by diffusion from the bulk of the solution, such that a concentration equilibrium is maintained. This will cause further swelling of the coil so that the viscosity within it remains more or less constant. The light scattering will increase with the number and the size of the coils. During this period no strong acceleration is expected: if the viscosity does not change rapidly, rate enhancement will be mainly caused by the increasing volume fraction of the coils. With a further increase of the volume fraction of the coils, the homogeneity of the sample will increase again and hence the light scattering will diminish. At the moment that the whole sample volume is occupied with the swollen coils the homogeneity is restored but the monomer equilibrium can no longer be maintained and the viscosity will rapidly increase and with it the overall rate of polymerization. The increase of the rate of reaction will continue until the monomer has completely reacted. Then it drops to zero. This is exactly what has been observed with DSC. What might be called the occurrence of two gel or Trommsdorff effects gives at least a qualitatively plausible explanation for the observed kinetic and optical phenomena during the slow, light-induced bulk polymerization of ethyl acrylate.

Similar phenomena are not necessarily expected for all bulk polymerizing monomers. The kinetics, observed with acrylates, are probably strongly influenced by the occurrence of cross-linking via tertiary hydrogen abstraction, right in the beginning of the reaction. This is generally considered as being the cause of the almost immediate onset of auto-acceleration in the bulk polymerization of acrylates (RAUCH-PUNTIGAM and VÖLKER, 1967, p. 169). Cross-linking will cause a further reduction of the mobility of macroradicals within the coils already formed.
In addition, local rates of reaction might also be enhanced by complexation phenomena such as observed in the template polymerization of methyl methacrylate (GONS et al., 1975).

ACKNOWLEDGEMENT

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