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Thermally and Light-Induced Polymerization of Ethyl Acrylate and Methyl Methacrylate, Studied by DSC

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SUMMARY

Differential scanning calorimetry (DSC) is a useful method for studying polymerization reactions. Due to the heat of polymerization, high temperatures may develop. In order to prevent the reaction from running out of control, polymerizations should be carried out very slowly. Even then, an irregular kinetic behaviour has been observed in the initial stage of the reaction. A method is described for studying light-induced polymerizations at high temperatures. It is found that the rate of polymerization and the temperature of the reaction are of more importance than the method of initiation.

INTRODUCTION

Light-induced polymerizations are often thought of yielding products with inferior properties, in comparison with products obtained via conventional methods (DE POORTERE et al. 1978).

It is our aim to make a detailed comparison of thermally and light-induced polymerization reactions of acrylates. Some preliminary results are presented.

EXPERIMENTAL

Materials

Ethyl acrylate (Merck) and methyl methacrylate (Aldrich) were freed of inhibitor, dried and used as such.

GPC and HPLC chromatograms (Waters Ass.) showed that no oligomer or polymer was present and that the inhibitor was removed. Freshly prepared monomers were always used.

2, 2'-azobisisobutyronitrile (AIBN) (Aldrich) was used as received and benzoin methyl ether (BME) (Aldrich) was recrystallized three times from methanol: water 9 : 1.

Procedure

Polymerizations were carried out in modified sample pans of a Perkin-Elmer differential scanning calorimeter (DSC-IB) operated isothermally. The apparatus was installed in a room with yellow light ($\lambda > 500$ nm).

We designed a sample pan suitable for use with light-induced as well as with thermally induced polymerizations. It was made from the standard PE volatile sample pan. A hole was punched in the aluminium lid, and sealed with a thin plastic film, e.g. Mylar (Du Pont), which was bonded to the lid with a heat resistant, non swelling, adhesive, e.g. Araldite AV-8 (Ciba-Geigy). This cover was then sealed onto the

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aluminium pan, similar to the common volatile sample pans. The weight loss of the sample due to evaporation of the monomer during polymerization was less than 0.5%. There was no weight loss at all with the common volatile sample pans. The base line drift during the isothermal polymerization was less than 1% of the full scale deflection (4mcal s^{-1}).

Polymerization was induced using a 200W high pressure mercury lamp (Philips, CS200), a Bausch and Lomb grating monochromator, type 33-86-79, set at 366 nm, with a spectral bandwidth of 20 nm and a ground quartz diffuser in order to ensure homogeneous illumination of the sample. The light intensity in the plane of the sample was measured with a spectroradiometer (EG & G, type 580/585) fitted with a fibre optics probe. It amounted to approximately 10^{-5} W cm^{-2} at 366 nm wavelength. For the thermally induced bulk polymerizations, the DSC temperature was set at the proper value.

All sample solutions were purged with nitrogen before use. The pans were sealed in a dry nitrogen glove box, installed in a room with yellow light.

RESULTS AND DISCUSSION

The more common methods for the detection of the kinetics of polymerization reactions all rely on the measurement of a bulk property of the sample, such as volume, viscosity, weight. With the exception of DSC, they suffer from the disadvantage of not being adequate for the detection of high degrees of conversion, especially if cross-linking occurs. However, measurement of the heat of reaction is a suitable probe only if the polymerization is being dominated by one reaction.

For auto-accelerated reactions, such as the polymerization of methyl methacrylate, asymmetrically peak-shaped exotherms have been observed with dilatometry (SCHULZ and HARBORTH 1947) and DSC (MALAVASIC et al. 1974). However, the shoulder on the asymmetric DSC peak found by HORIE et al. (1968) was neither observed by us, nor by MALAVASIC et al. (1974), nor by BARRETT and THOMAS (1970). Incidentally, however, similar exotherms as reported by HORIE et al. (1968) were found but this was invariably accompanied by a considerable weight loss and base line drift. Using newly designed DSC pans with a light window, as described in the experimental part, we obtained DSC exotherms with the same shape as those measured during thermal polymerizations (Fig. 1).

Unlike methyl methacrylate, the polymerization of ethyl acrylate does not yield similar rate versus time curves for DSC and dilatometry.

Fig. 2 shows DSC exotherms for thermal and light-induced bulk polymerizations of ethyl acrylate.
Since little data of rates of initiation are available we made the following estimation. The initiation efficiency for AIBN radicals ranges from 0.6 to 1.0 for the polymerization of various vinyl monomers (ODIAN 1970). Since two radicals are formed, 1.2 to 2.0 chains are started after each dissociation. According to CARLBLOM and PAPPAS (1977) the quantum efficiency for the formation of polymer molecules is about 0.5 for the BME initiated polymerization of methyl acrylate in benzene solution. Since termination was found to occur mainly by recombination the quantum efficiency for photoinitiation is approximately 1.0, one chain is started for every photon absorbed. This shows that the initiation efficiencies of radicals derived from AIBN and BME are of similar magnitude. Assuming equal reactivities of all initiator fragments, we estimated the rates of initiation at 70°C to be 5.10^{-8} Mole

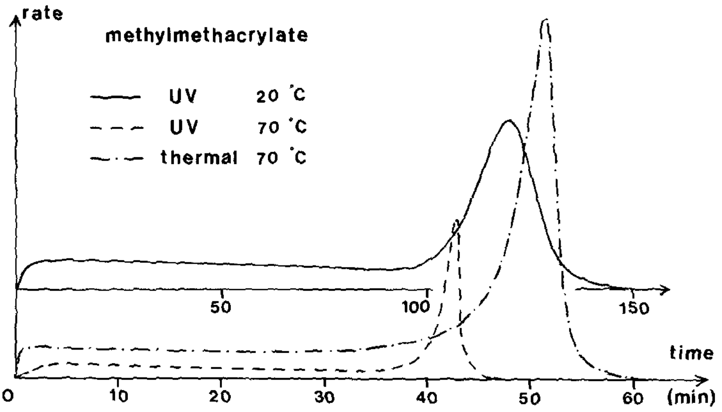

Fig. 1. DSC exotherms for thermally and light-induced polymerizations of methyl methacrylate. Initiator: 5.10^{-2} Mole l^{-1} AIBN; 5.10^{-2} Mole l^{-1} BME.

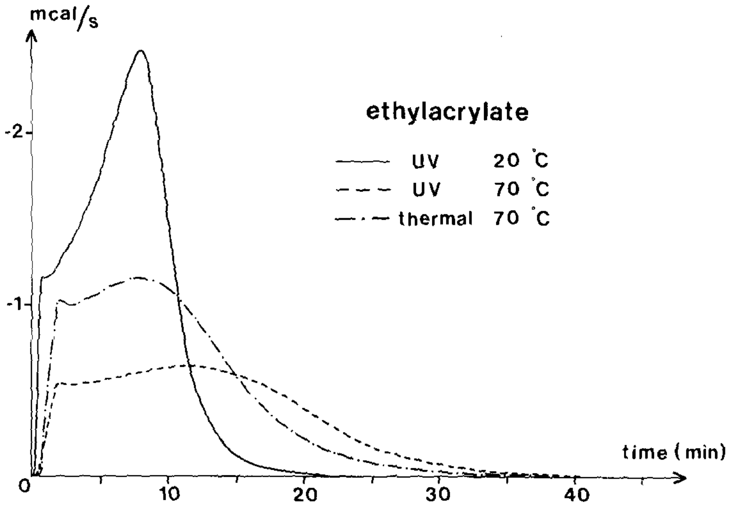

Fig. 2. DSC exotherms for thermally and light-induced polymerizations of ethyl acrylate. Initiator: 5.10^{-3} Mole l^{-1} AIBN; 5.10^{-3} Mole l^{-1} BME (at 20°C a higher UV-light intensity was used).

l^{-1} s^{-1} for the thermally and light-induced polymerization of ethyl acrylate. Although the DSC curves were not exactly identical, comparison shows that the assumption of equal reactivity is not unrealistic. At 20°C a somewhat higher light intensity was used. The DSC curve still exhibited the same general features. The shoulder in the early stages of the reaction was still observed at $-25°C$, just below T_g of the formed polymer. For ethyl acrylate this shoulder was not observed in dilatometric experiments because in a conversion versus time plot these delicate variations are easily obscured (MANGARAJ and PATRA 1967). The same shoulder was observed with DSC for 2-ethylhexyl acrylate and n-dodecylacrylate. The occurrence of the shoulder cannot be explained by the "pre-effect" (BAMFORD and TIPPER 1976), since under our experimental conditions for light-induced polymerization the radical concentration reaches its steady state value within 10 seconds or less.

$$\frac{[R\cdot]}{[R\cdot]_s} = \tanh\,(I.k_t)^{-\frac{1}{2}}t$$

We assume that steady state conditions are reached when $[R\cdot] = 0.99\,[R\cdot]_s$ and that the termination rate constant $k_t \geqslant 10^7$ l Mole^{-1} s^{-1} (BAMFORD, C. and TIPPER, C. 1976, p. 8).

tanh 2.65 = 0.99 yields $t = 2.65 \cdot (I.k_t)^{-\frac{1}{2}} \leqslant 5$ s.

The shoulder shows the occurrence of two distinct periods of acceleration. This can be explained as due to a local and general gel-effect (KLOOSTERBOER and BRESSERS 1980).

Preliminary GPC measurements show that light- and thermally induced polymerizations at 70°C yield molecular weight distributions (MWD) of similar shape. Comparison of light-induced reactions at 70°C and 20°C, with identical rates of initiation, shows that at the lower temperature a polymer with a somewhat lower molecular weight and a narrower distribution is formed. It appears that the rate of initiation and the temperature of reaction are more important for the MWD of the final product than the method of initiation.

Light-induced polymerization should enable a better control of the MWD than thermal polymerization, since a large range of reaction-temperatures is available and, if desired, the light intensity can also be modulated during polymerization.

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