

Pyrene Fluorescence as a Probe for the Monitoring of Polymerization Processes: Simultaneous DSC and Fluorescence Study

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The polymerization of cyclohexylmethacrylate was monitored, over a wide temperature range, by simultaneous differential scanning calorimetry (DSC) and fluorimetry (FL); the equipment for both being optically coupled. Pyrene was used as a fluorescent probe. There was excellent agreement between the exothermic peak time obtained by DSC and the time at which the maximum gradient was obtained in the fluorescence intensity–time curves, but only for temperatures above 60°C. Activation energies for the gel effect onset were obtained for both, the conversion–time and intensity–time curves being concordant except for data at low temperatures, below 60°C. It was concluded that vitrification occurs at temperatures below 60°C and its presence was demonstrated by fluorimetry, by means of the conversion change associated with the fluorescence intensity jump $\Delta\alpha_{(\text{off-on})}$.

KEY WORDS: Pyrene; probe; polymerization; differential scanning calorimetry; fluorimetry.

INTRODUCTION

Since the early work of Loutfy,⁽¹⁾ fluorescence spectroscopy has been used to monitor polymerization reactions in, among others, acrylics and epoxies⁽²⁾ and for gel point determination in cross-linking reactions.⁽³⁾ Various photophysical phenomena can be used to monitor polymerization reactions: intensity increases,⁽¹⁾ changes in excimer-to-monomer ratios,⁽⁴⁾ fluorescence changes of reactive dye labels employed in condensation cure reactions,⁽⁵⁾ and quenching of fluorescence by electron acceptors.⁽⁶⁾ Excellent reviews of early work in this area are given in Refs. 7 and 8. When pyrene is used as a fluorescent probe, a significant increase in the fluorescence response is observed, which is associated with a

decrease in the rate of nonradiative processes. However, although simple proportionality relations between pyrene luminescence and the degree of conversion are usually assumed, they do not rely on accurate experimental results. In this work accurate relations between stationary steady-state fluorescence and differential scanning calorimetry measurements are presented.

In the presence of free monomer the system can be considered as a thermal bath with a quasi-continuum of states acting as an energy sink for rapid vibrational relaxation processes;⁽³⁾ therefore, at low conversion pyrene fluorescence should be collisionally quenched. As polymerization proceeds the rigidity of the medium increases, reflecting that the energy sink may be shifted through a higher energy and the probability of energy exchange between the excited chromophore and the surrounding medium decreases. Therefore as polymerization proceeds emission of pyrene occurs from excited, less relaxed states. It is common to observe, in the case of forming polymers with a glass transition temperature

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(T_g) higher than the polymerization temperature, that even at moderate conversions when the polymer fraction is relatively low, the fluorescence intensity remains high, meaning that the presence of polymer chains restricts the collisional quenching of the chromophore. On the other hand, it has been observed⁽⁹⁾ that when the formed polymer has a T_g well below the polymerization temperature, that is, when there are no thermal restrictions for conformational rearrangements, pyrene fluorescence intensity also increases with conversion, although the intensity–conversion–time relationship may be quite different. In the former case, the polymer dynamics is thermally restricted and the polymer–monomer system becomes vitrified; therefore, it seems that the energy exchange probability depends mainly on the presence of polymer chains and their conformational properties. In this work we study the intensity–conversion relationships during the polymerization of cyclohexylmethacrylate at temperatures above and below the appearance of vitrification.

EXPERIMENTAL

The bulk polymerization of cyclohexyl methacrylate (CHM) was studied using simultaneous fluorescence spectroscopy and differential scanning calorimetry. Isothermal polymerization processes were run on a Perkin–Elmer LS-50B fluorimeter and on a Perkin–Elmer DSC-7 differential scanning calorimeter. Both apparatuses were optically coupled and details of the optical arrangement are given elsewhere.⁽⁹⁾

The monomer (Sigma: >97%) was vacuum distilled. The initiator, 2,2'-azobisisobutyronitrile (AIBN; Fluka: >98%), was recrystallized twice from methanol. The samples corresponding to the same experimental series were prepared simultaneously and kept in a dark place at -25°C until the experiments were performed. A constant initiator concentration of 1% (w/w) was used.

Pyrene was used as a fluorescence probe; its concentration was kept below 10^{-4} M. Excitation was fixed at 338 nm and the fluorescence intensity at the maximum (393 nm) was collected as a function of the reaction time. For polymerizations at low temperatures (45–60°C), the full emission spectrum was collected. The degree of conversion as a function of time was calculated as the ratio of the isothermal polymerization heat at the given time to the sum of the total isothermal polymerization heat and the residual monomer polymerization heat. The residual heat was measured raising the polymerization temperature to 150°C in a dynamic DSC scan.

RESULTS AND DISCUSSION

In Figs. 1 and 2, the fractional conversion and fluorescence intensity, normalized at their maximum values, are plotted versus the isothermal polymerization time at temperatures ranging from 45 to 90°C. The residual heat was calculated after the isothermal experiment, scanning from the working temperature to 150°C.

At temperatures below 65°C (Fig. 1) conversion initially increases linearly with time up to about 40%, depending on the polymerization temperature; in this time range fluorescence intensity remains essentially constant. Beyond 40%, the polymerization rate suddenly increases, thus causing the gel effect to appear. The associated increase in fluorescence intensity is slightly shifted to higher conversions. At long enough times a plateau in conversion and fluorescence intensity is reached. Above 60°C (Fig. 2) the data obtained by DSC and fluorimetry are closer.

Because of the different time scales of DSC and fluorescence experiments, it is interesting to compare the increase in fluorescence and the corresponding increase in conversion. This is done in Fig. 3, in which an Arrhenius plot of the reciprocal of the exothermic peak time and the reciprocal of the time for maximum fluorescence gradient is presented.⁽²⁾ Excellent agreement between the time parameters is observed, reflecting that they both correspond to the same phenomena. Values of the activation energies for gel formation obtained from DSC and fluorimetry are 18.3 and 19.3 kcal/mol, respectively. Although these two values are very close to each other, it should be noted that the difference of about 1 kcal/mol is due mainly to the contribution of the fluorescence time parameters at low temperatures, i.e., below 60°C. Nevertheless, these values are slightly higher than those obtained for the bulk polymerization (16.1 kcal/mol) and for the cross-linking polymerization of methylmethacrylate in toluene^(2,10) (17.2 kcal/mol). Equivalent Arrhenius plots (not shown) can be determined using as time parameters the time for the onset of the gel effect and the time for the onset of the fluorescence increase; the same coincidence can be found and the activation energies obtained are about 1 kcal/mol higher, being 19.6 kcal/mol for the former and 20.6 kcal/mol for the later.

The polymer formed up to 100% conversion has a T_g value around 92°C (at 20°C/min). Vitrification might occur at polymerization temperatures somewhat below the T_g , but the conversion–time curves do not reveal it. Vitrification is associated with a mobility restriction of the monomer and the gel effect of restriction of polymer

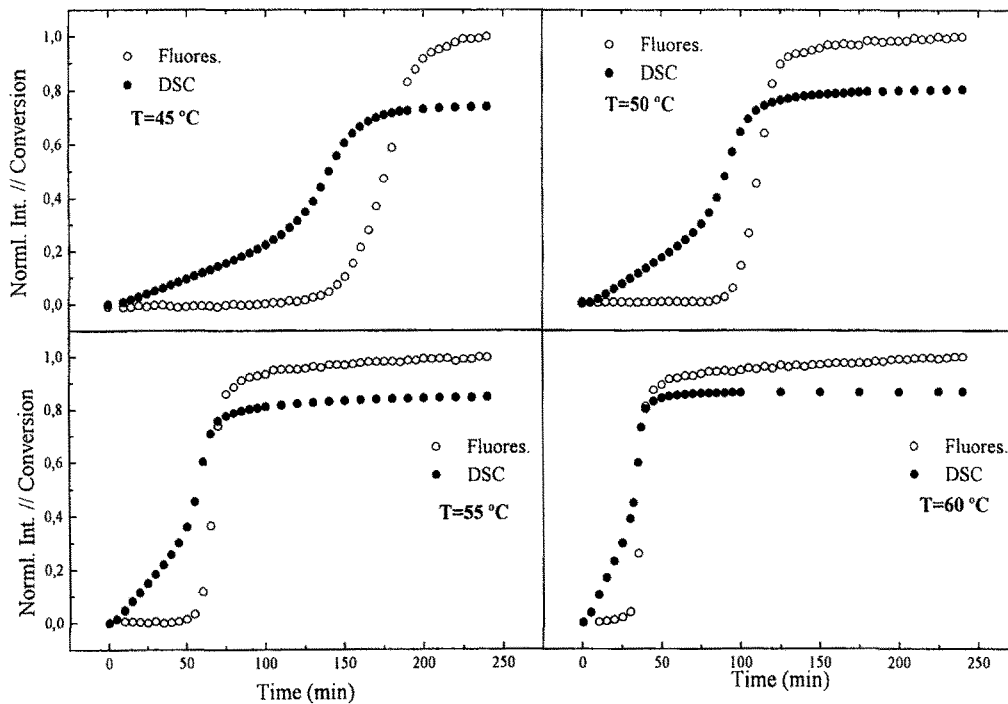


Fig. 1. Conversion (filled circles) and normalized fluorescence intensity (open circles) as a function of polymerization time for cyclohexylmethacrylate at 45, 50, 55, and 60°C. [AIBN] = 1% (w/w); [Py] $\leq 10^{-4}$ M.

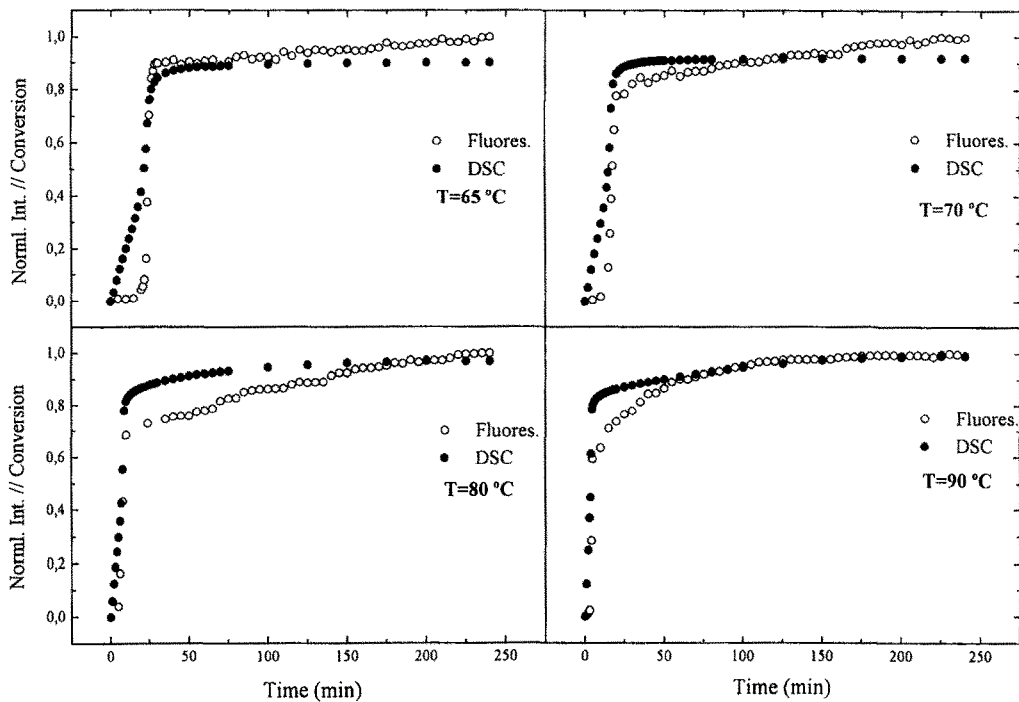


Fig. 2. Conversion (filled circles) and normalized fluorescence intensity (open circles) as a function of polymerization time for cyclohexylmethacrylate at 65, 70, 80, and 90°C. [AIBN] = 1% (w/w); [Py] $\leq 10^{-4}$ M.

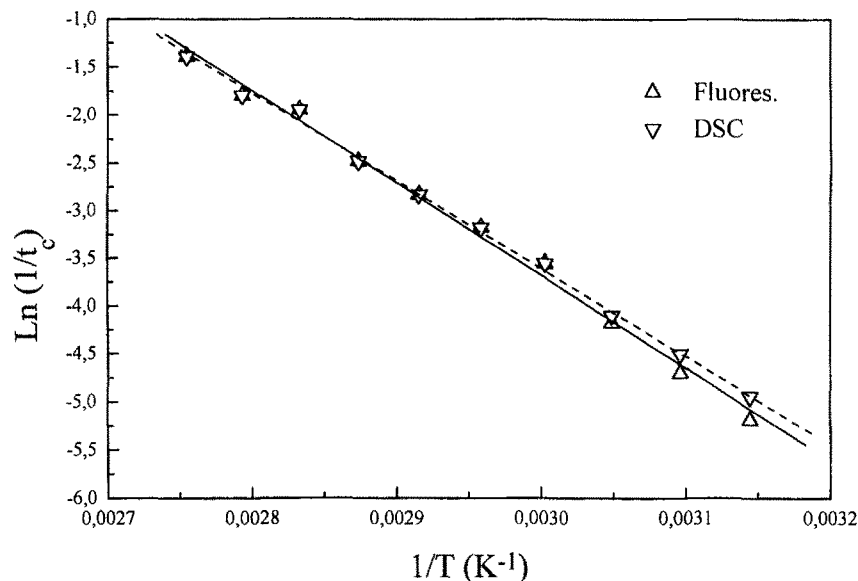


Fig. 3. Arrhenius plot of the reciprocals of the exothermic peak time (down triangles) and maximum intensity gradient time (up triangles)

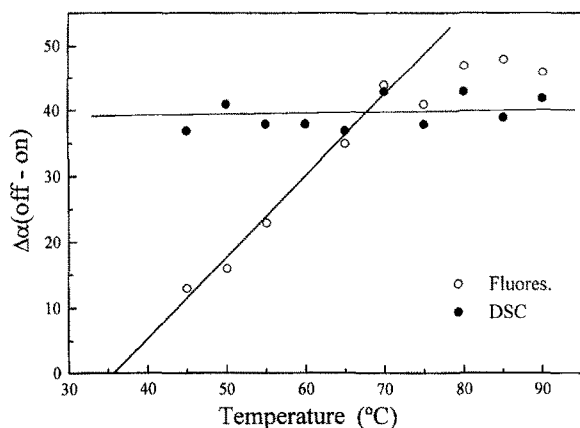


Fig. 4. Conversion change $\Delta\alpha_{(\text{off-on})}$ as a function of polymerization temperature (see text). Filled circles: $\Delta\alpha_{(\text{off-on})}$ for the conversion-time curves. Open circles: $\Delta\alpha_{(\text{off-on})}$ for the intensity-time curves.

diffusion; therefore, due to the small size of the chromophore a different behavior of the intensity profile should be observed when vitrification appears. We found a graphic representation that shows a different behavior for the fluorescence intensity when vitrification occurs and when the gel effect controls the polymerization. Figure 4 shows this plot, in which the difference between the conversion at the onset and that at the offset of the intensity-time profile is presented as a function of the polymerization time. This plot represents the conversion jump associated with the fluorescence intensity jump, $\Delta\alpha_{(\text{off-on})}$ for the different polymerizations. For the pur-

pose of comparison, the values of $\Delta\alpha_{(\text{off-on})}$ obtained from the conversion-time curves are also presented in Fig. 4.

It can be seen that $\Delta\alpha_{(\text{off-on})}$ remains almost-constant around 40%, over the whole range of polymerization temperatures in the case of the data obtained from the conversion-time curves. Values of $\Delta\alpha_{(\text{off-on})}$ corresponding to the intensity-time curves stabilize around 45% only at temperatures above 65°C. At lower temperatures, $\Delta\alpha_{(\text{off-on})}$ decreases in an approximately linear way as the temperature decreases. Extrapolation of $\Delta\alpha_{(\text{off-on})}$ down to its minimum value (zero) leads to a temperature value of 35°C at which it is predicted that a rapid increase in the fluorescence intensity would occur without variation in conversion, this conversion being very close to the limiting conversion of the polymerizing system.

CONCLUSIONS

Two main conclusions can be drawn.

(1) It has been demonstrated experimentally that the exothermic peak time obtained by DSC coincides with the intensity maximum gradient time obtained by fluorimetry above the vitrification temperature.

(2) A method has been proposed for detecting vitrification phenomena which consists of the measurement of the conversion change associated with the fluorescence intensity jump. For a given polymerization temperature, values below 45% suggest the presence of vitrification. For the polymerization of cyclohexylme-

thacrylate, the vitrification temperature has been observed as 60°C.

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