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## DIRECT DETERMINATION OF THE RATE CONSTANT OF PROPAGATION BY PSEUDOSTATIONARY POLYMERIZATION TECHNIQUE: SCREENING INVESTIGATION FOR THE (IMPLICIT) PENULTIMATE EFFECT

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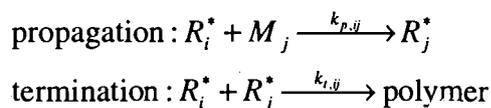
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### SUMMARY

The systems styrene-p-methylstyrene, styrene-p-chlorostyrene, methyl methacrylate-p-methylstyrene and methyl methacrylate-p-chlorostyrene were polymerized under pseudostationary conditions (rotating sector or pulsed laser) at 25°C, 40°C and 50°C. The respective molecular weight distributions measured by GPC were analysed in order to derive directly the phenomenological rate constant of propagation,  $\bar{k}_p$ . Copolymer compositions as a function of monomer feed could be described by the terminal model, whereas the kinetic results could only be interpreted in terms of the restricted penultimate model.

### I. INTRODUCTION

The investigation of copolymer systems can be dated back already to 1941 (1). At the beginning the studies concentrated on copolymer composition and/or polymerization rates. The simple kinetic scheme of chain initiation, propagation and termination was extended to take into account the different nature of the radical site in a polymer chain:



This terminal or Mayo-Lewis (2) model has proven useful to describe the copolymer composition as a function of monomer feed but it cannot explain the observed rate behaviour. The rate of (co)polymerization for a binary system can be written as the sum of four terms:

$$v_p = \sum_{i=1}^2 \sum_{j=1}^2 k_{p,ij} [R_i^*] [M_j] \quad \text{or} \quad v_p = \bar{k}_p [R^*] [M]$$

with

$$\bar{k}_p = \frac{r_1 f_1^2 + 2f_1 f_2 + r_2 f_2^2}{\frac{r_1 f_1}{k_{p,11}} + \frac{r_2 f_2}{k_{p,22}}}, \quad [R^*] = [R_1^*] + [R_2^*] \quad \text{and} \quad [M] = [M_1] + [M_2]$$

$$f_i = \frac{[M_i]}{[M_1] + [M_2]} \quad i = 1, 2 \quad \text{and} \quad r_1 = \frac{k_{p,11}}{k_{p,12}}, \quad r_2 = \frac{k_{p,22}}{k_{p,21}}$$

$r_i$  = (monomer) reactivity ratio

The phenomenologic rate constant of propagation  $\overline{k_p}$  was introduced by Fukuda et al. and was measured for a number of copolymerization systems (3,4,5). Their elaborate measurements very clearly demonstrated that not only the overall rate of polymerization cannot be described by the terminal model but also the overall rate constant of propagation did not follow the given relationship. Copolymer composition, however, could always be described by the terminal model.

To overcome this discrepancy the so called restricted penultimate unit model was introduced:

$$\overline{k_p} = \frac{r_1 f_1^2 + 2f_1 f_2 + r_2 f_2^2}{\frac{r_1 f_1 + f_2 / s_1}{k_{p,111}(1 + f_2 / (r_1 f_1))} + \frac{r_2 f_2 + f_1 / s_2}{k_{p,222}(1 + f_1 / (r_2 f_2))}} \quad \text{with}$$

$$r_1 = \frac{k_{p,111}}{k_{p,112}} = \frac{k_{p,211}}{k_{p,212}}, \quad r_2 = \frac{k_{p,222}}{k_{p,221}} = \frac{k_{p,122}}{k_{p,121}}$$

$$s_1 = \frac{k_{p,211}}{k_{p,111}} = \frac{k_{p,212}}{k_{p,112}}, \quad s_2 = \frac{k_{p,122}}{k_{p,222}} = \frac{k_{p,121}}{k_{p,221}}$$

We were able to confirm qualitatively Fukudas results (5) concerning  $\overline{k_p}$  for the copolymerization system styrene-methyl methacrylate (6). The values of  $\overline{k_p}$  were determined directly by analysing the molecular weight distribution of the copolymers prepared under pseudostationary conditions (rotating sector) at a single sector speed.

## II. PSEUDOSTATIONARY POLYMERIZATION

Contrary to conventional pseudostationary polymerization techniques (i.e. rotating sector – determination of the radical lifetime) pulsed laser polymerization technique (7) and related pseudostationary polymerization techniques (8,9,10) offer the advantage to determine directly the kinetic constants - especially the rate constant of propagation - from a single polymerization experiment. This can be done by carefully analysing the molecular weight distribution of the polymer prepared under pseudostationary conditions. As these conditions imply that the radical concentration is periodically varied between certain limits an increase in radical concentration leads automatically to an increased production of inactive polymer due to the bimolecular termination reaction.

In the simplest case of a  $\delta$ -pulse initiation of polymerization all radicals can be regarded as having almost the same chain length. In the period following this  $\delta$ -pulse the radicals are either capable of adding successively one monomer unit after the other or encounter another radical and yield polymeric products. Due to the statistical nature of chain propagation the chain lengths of those radicals which have survived can be described by a Poisson distribution. With the arrival of the next  $\delta$ -pulse the surviving radicals are now opposed to a drastically increased number of radicals and their probability for bimolecular termination is enhanced. Thus an increased fraction of the radicals is deactivated by the arrival of the first consecutive pulse giving rise to an additional peak in the molecular weight distribution centered around

$$L_0 = k_p [M] t_0$$

$t_0$  = time interval between two successive pulses

For the radicals still active after the second pulse the same reasoning can be applied as before and so on. In all, this leads to a multimodal molecular weight distribution characterized by the appearance of the so-called additional-peaks at  $n \cdot L_0$  ( $n=1,2,3,\dots$ ). The positions of the extra-peaks (characterized by the point of inflection on the low molecular weight side) are determined from the molecular weight distribution measured by gel permeation chromatography and used to calculate the rate constant of propagation.

The relationship given above was confirmed by several working groups (11,12,13) and led to a general recommendation of the (new) pseudostationary polymerization technique to benchmark kinetic data (14,15).

### III. EXPERIMENTAL SET-UP

Prior to polymerization experiments styrene, p-chlorostyrene, p-methylstyrene and methyl methacrylate were distilled in nitrogen atmosphere under reduced pressure and stored in the refrigerator. The copolymerization mixtures were prepared at 25°C; Benzoin ( $4 \cdot 10^{-3}$  mol l<sup>-1</sup>) was added as sensitizer. Oxygen was removed by repeated freeze-pump and thaw cycles.

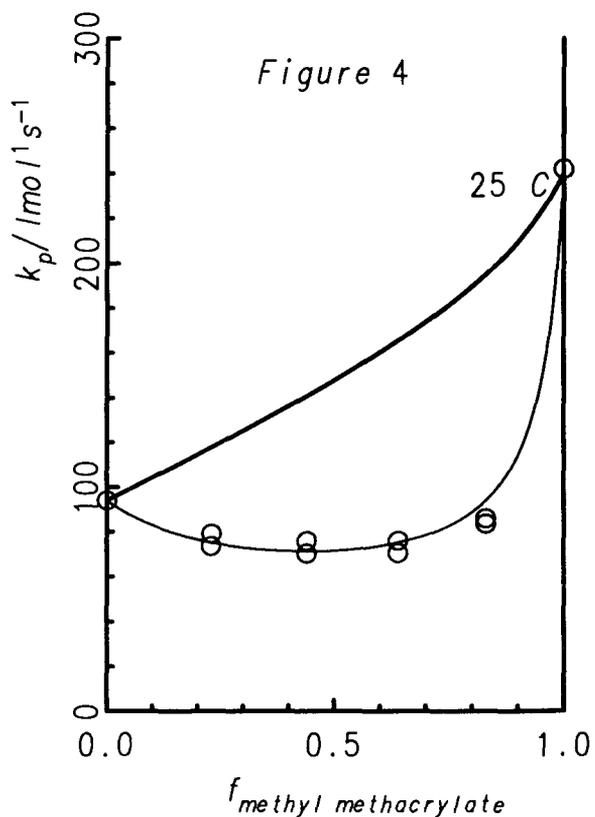
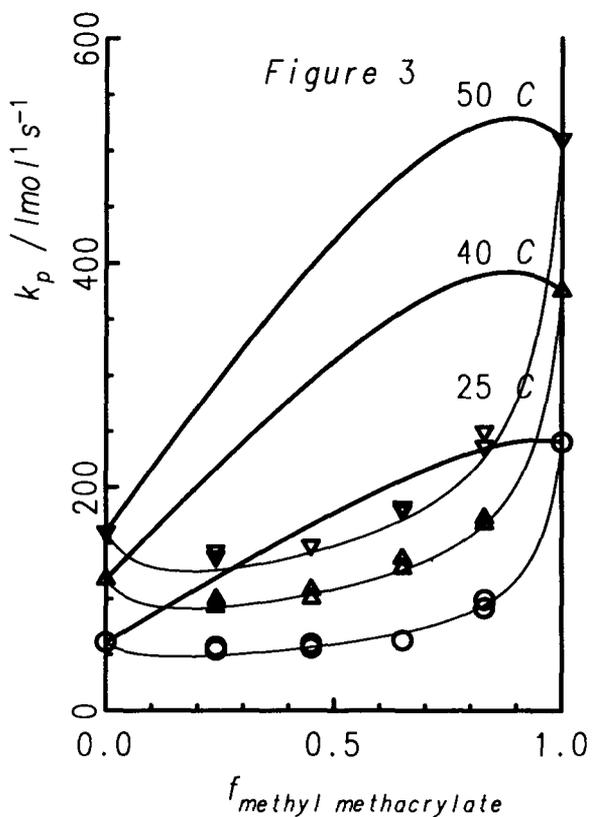
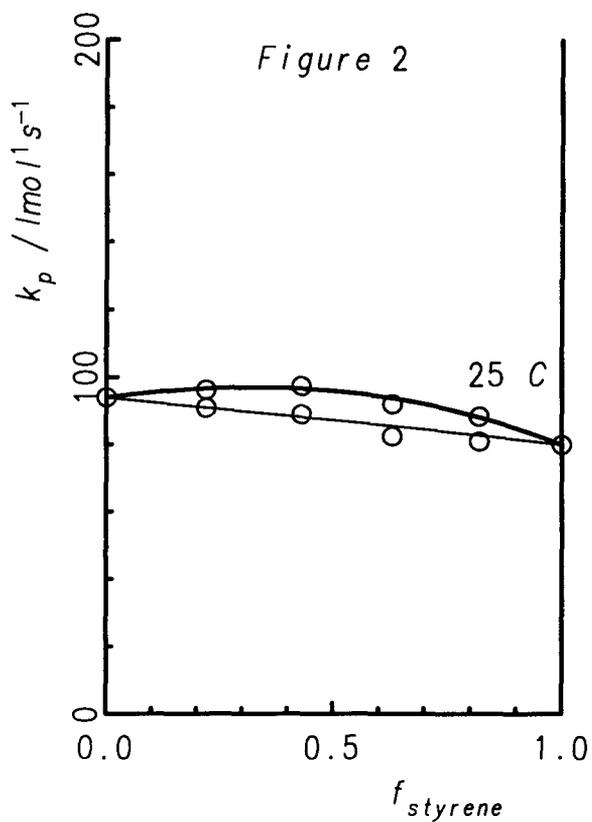
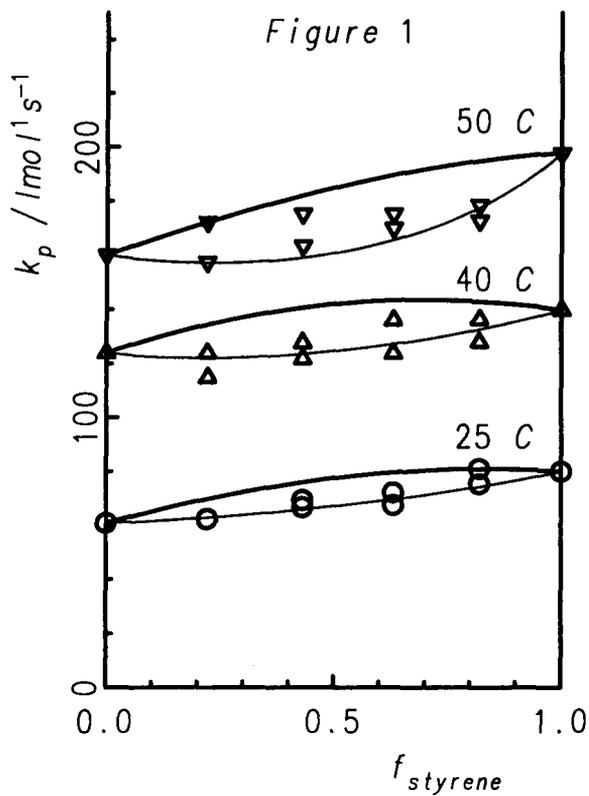
Photopolymerizations were carried out in sealed rectangular Pyrex cells at 25°C. In all cases conversions were kept below 5%. a) Rotating Sector method: The samples were irradiated with filtered light (365 nm) of a mercury high pressure lamp (Spindler and Hoyer, HBO 200 W/2). A rotating sector disc with a light-dark ratio of 1:5 and sector speeds of 1-2 rev/sec was used to ensure intermittent illumination. b) Pulsed-Laser polymerization: An excimer laser (Lambda Physik, EMG 101) was operated at 351 nm (XeF). Pulse frequencies were chosen to conform with those from rotating sector experiments (1-2 Hz). After the polymerization the samples were freeze-dried and dissolved in THF. Copolymer compositions were determined by elemental analysis.

Gel permeation chromatography (GPC): solvent: THF; T=30°C; flow rate: 1.2 ml min<sup>-1</sup>; columns: 500, 10<sup>3</sup>, 10<sup>4</sup> and 10<sup>5</sup> Å; Polymer Standard Service, Germany; differential refractometer (Viscotec); conventional calibration with narrow poly-styrene and poly-(methyl methacrylate) standards.

For p-methylstyrene two samples were polymerized thermally (stationary) and viscosities were measured in toluene and THF at 30°C ( $K=8.86 \cdot 10^{-3}$  ml g<sup>-1</sup>,  $a=0.74$ , toluene (16)) in order to estimate the Mark-Houwink constants ( $K=14.47 \cdot 10^{-3}$  ml g<sup>-1</sup> and  $a=0.704$ ) for this polymer in THF. Comparison of calculated hydrodynamic volumina of p-methylstyrene and styrene for the same degree of polymerization ( $K=16 \cdot 10^{-3}$  ml g<sup>-1</sup>,  $a=0.706$  THF (17)) showed that the first is always bigger than the latter, the deviation remaining almost constant at about 10 % over the complete range. This systematic deviation nevertheless is comparable with the experimental accuracy usually accepted. As there are no data available about Mark-Houwink constants for the copolymerization system styrene-p-methylstyrene calibration was done via universal calibration with the assumption that the hydrodynamic volume of the copolymer can be constructed as a linear combination of the hydrodynamic volumina of the homopolymers according to their copolymer composition.

### IV. RESULTS AND DISCUSSION

The following diagrams show the results for the copolymerization systems styrene-p-methylstyrene (Fig.1), styrene-p-chlorostyrene (Fig.2), methyl methacrylate-p-methylstyrene (Fig.3) and methyl methacrylate-p-chlorostyrene (Fig.4) at different temperatures. In all cases



the terminal model (upper curve for each data-set) fails to describe  $\overline{k_p}$ . The reactivity ratios were determined by the Kelen-Tüdös method from the copolymer composition. They agree favourably well with literature values (20) and are included in table I for comparison. For the determination of the (penultimate) radical reactivity ratios  $s_1$  and  $s_2$  a one parameter fitting procedure based on the identity  $r_1 r_2 = s_1 s_2$  suggested by Fukuda et al (18) was done (using  $s_1=1$  for the systems 1 and 2). In all cases due to the small number of data no extended fitting procedures were applied.

For three copolymer systems (1, 3 and 4) the penultimate effect very clearly demonstrates its existence. With increasing temperature the absolute differences between the two models become more pronounced as was already observed in the system styrene-methyl methacrylate (6). For the system styrene-p-chlorostyrene the situation is not unambiguous. With the given parameter set the difference between the terminal and the penultimate curve is small and is within the experimental accuracy of the GPC-experiments. Comparison with literature values for the homopropagation rate constant for p-chlorostyrene (19) shows that the value listed below is about 40% smaller. Nevertheless, correcting for this deviation and reanalysing the data does not improve the situation. In all, the implicit penultimate effect in this case can neither be excluded nor confirmed with certainty. As with p-methylstyrene the penultimate effect becomes more apparent at 50°C extension of the studies to higher temperatures might help to elucidate the behaviour of this copolymerization system. In the copolymerization systems 3 and 4 the existence of the penultimate effect is out of question. The trend of a more obvious penultimate effect at elevated temperatures is also observed for the system methyl methacrylate-p-methylstyrene as the differences between the two models exceed clearly the experimental accuracy expected from GPC-data.

Table I

| System                                | $k_{p,11}$ | $k_{p,22}$ | $r_1$ | $r_2$ | T/°C             | $s_1$ | $s_2$ |
|---------------------------------------|------------|------------|-------|-------|------------------|-------|-------|
| 1 Styrene-p-methylstyrene             | 80         | 66         | 0.667 | 0.775 | 25               | 1     | 0.665 |
|                                       | 136        | 124        | 0.919 | 0.816 | 40               | 1     | 0.665 |
|                                       | 198        | 160        | 0.847 | 0.965 | 50               | 1     | 0.665 |
|                                       |            |            | 0.891 | 0.993 | 60 <sup>*)</sup> |       |       |
| 2 Styrene-p-chlorostyrene             | 80         | 95         | 0.667 | 1.025 | 25               | 1     | 0.737 |
|                                       |            |            | 0.62  | 1.08  | 30 <sup>*)</sup> |       |       |
| 3 methyl methacrylate-p-methylstyrene | 240        | 66         | 0.366 | 0.382 | 25               | 0.65  | 0.235 |
|                                       | 375        | 117        | 0.379 | 0.403 | 40               | 0.65  | 0.235 |
|                                       | 510        | 160        | 0.399 | 0.41  | 50               | 0.65  | 0.235 |
|                                       |            |            | 0.405 | 0.44  | 60 <sup>*)</sup> |       |       |
| 4 Methyl methacrylate-p-chlorostyrene | 240        | 95         | 0.395 | 0.89  | 25               | 1.2   | 0.293 |
|                                       |            |            | 0.4   | 0.8   | 40 <sup>*)</sup> |       |       |

<sup>\*)</sup> c.f. ref. 20

## V. CONCLUSIONS

A screening investigation on the systems styrene-p-methylstyrene, styrene-p-chlorostyrene, styrene- methyl methacrylate, p-methylstyrene-methyl methacrylate, p-chlorostyrene-methyl methacrylate at different temperatures gives a clear evidence that an implicit penultimate effect is present in the majority of cases.

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