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Determination of Propagation Rate Constants Using a Pulsed Laser Technique

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ABSTRACT: Propagation rate constants (k_p) for the polymerization of methyl methacrylate (MMA) and styrene (STY) were determined by using a recently developed experimental technique. The procedure utilized a pulsed laser UV light source for the polymerization, and gel permeation chromatography (GPC) was used to analyze the products. The average k_p values obtained were 294 ± 9 and 78 ± 6 L mol^{-1} s^{-1} for MMA and STY, respectively at 25 °C. These k_p values were found to be independent of chain length (ν), initiator type, and concentration. The inclusion of methanol, ethylbenzene (to STY), ethyl acetate (to MMA), or poly-STY at 0.5% w/v as additive to the polymerization mixture had no significant effect on k_p.

Introduction

Recently Olaj and co-workers[1-3] have developed a technique which utilizes a pulsed laser light source to evaluate individual kinetic rate constants in free-radical polymerization. The adoption of the laser technique simplifies the kinetic expressions normally associated with nonstationary experimental procedures, e.g., rotating sector and spatially intermittent polymerization.[4]

Olaj, Bitai, and Gleixner[1] have derived the rate expression given by

$$\frac{R_p t_f}{[M]} = \frac{k_p}{k_t} \ln \left\{ 1 + \frac{\rho k_t t_f}{2} \left[1 + \left(1 + \frac{4}{\rho k_t t_f} \right)^{1/2} \right] \right\} \qquad (1)$$

where R_p, k_p, k_t, and [M] have their usual meanings; t_f is the dark time between flashes; and ρ is the radical concentration. This relationship may be used to obtain k_p/k_t values in an analogous procedure to the rotating sector experiment.

In a later publication[2] Olaj et al. describe a technique whereby k_p can be easily determined without reference to k_t or ρ. An analysis of the molecular weight distribution by GPC of the polymer produced by such a polymerization allows calculation of ν_p, the chain length of polymer formed between successive pulses. k_p can then be obtained from

$$\nu_p = k_p[M]t_f \qquad (2)$$

The process is shown schematically in Figure 1. The radical concentration generated by each pulse decays according to a second-order rate law. When the next flash occurs there is a rapid increase in the overall radical concentration and any residual radicals (from the preceding pulse) are subject to a vastly increased probability of termination. Thus formation of polymer of chain length ν_p is favored. Clearly some radicals will survive to produce polymer chains of length $2\nu_p$, $3\nu_p$, etc.

Olaj and co-workers[2] have reported a value of k_p for styrene at 25 °C as 107 L mol^{-1} s^{-1}, measured at a ν_p of 2740. More recently[3] they have amended this value to 80 L mol^{-1} s^{-1} on the basis of a reevaluation of data.

The object of the present paper is to report some experimental results obtained here by this technique, for both STY and methyl methacrylate (MMA) homopolymerizations with particular reference to the existence of any chain length effects. Similar experiments conducted on the copolymerization of STY with MMA have been described elsewhere.[6]

Experimental Section

Materials. STY and MMA were washed with aqueous sodium hydroxide, dried over calcium hydride, and distilled in an atmosphere of nitrogen under reduced pressure. Benzoin (BZ) and azobis(isobutyronitrile) (AIBN) were recrystallized three times from ethanol and methanol, respectively. Ethyl acetate (EA), ethyl benzene (EB), and methanol (MeOH) were distilled prior to use. Tetrahydrofuran (THF) for GPC measurements was refluxed over potassium, distilled, and stabilized with 2,6-di-*tert*-butyl-*p*-cresol. Poly-STY of molecular weight $M_n = 2.75 \times 10^6$ and narrow polydispersity ($M_w/M_n = 1.04$) was used as an additive in several polymerizations.

Polymerizations. The relevant freshly distilled monomer, together with initiator and additive (total volume 2 mL), was charged to Pyrex ampules (square cells 1 cm × 1 cm) and subsequently degassed and sealed.

The experimental setup used to irradiate the cells is indicated in the schematic shown in Figure 2. Each cell was placed in a thermostated cell holder maintained at 25 °C as monitored by a thermocouple.

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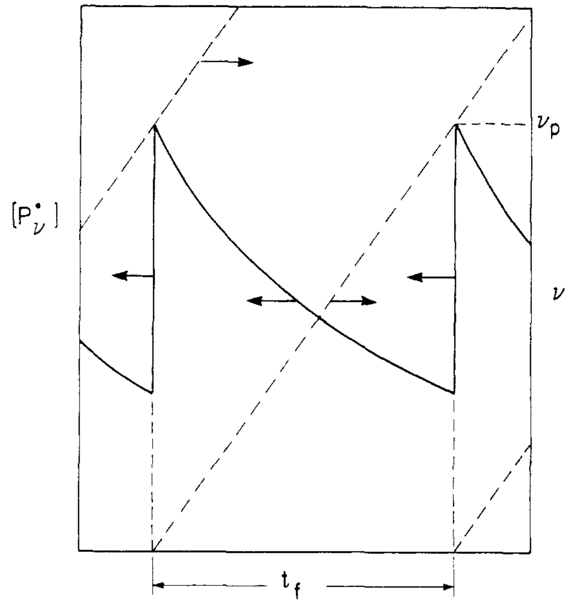

Figure 1. Schematic representation of the polymerization process. Where $[P_\nu{}^\bullet 1]$ = the radical concentration, ν = chain length, and ν_p = chain length generated in the time period between two pulses.

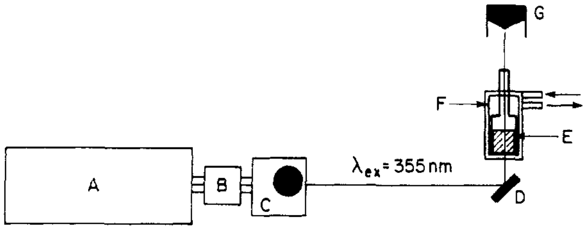

Figure 2. Schematic diagram of the experimental apparatus. A = Nd:YAG laser; B = harmonic generator (1064, 532, and 355/266 nm); C = harmonic separator; D = dielectric mirror; E = sample cell; F = cell holder; G = beam dump; H = circulated water supply.

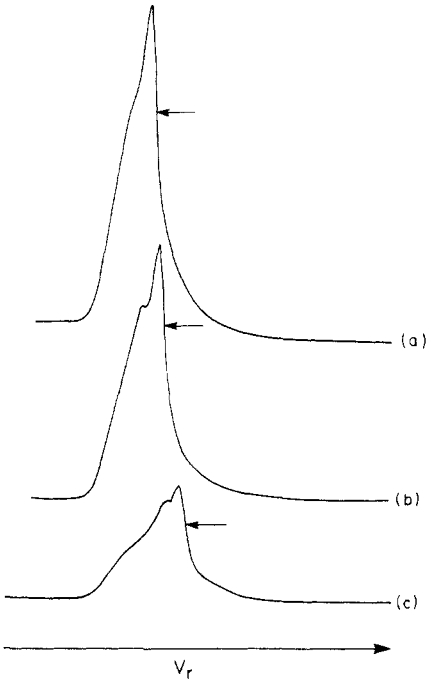

Figure 3. GPC chromatograms of PMMA polymerized by the pulsed laser technique; V_r = retention volume: (a) t_f = 2 s; (b) t_f = 1 s; (c) t_f = 0.33 s.

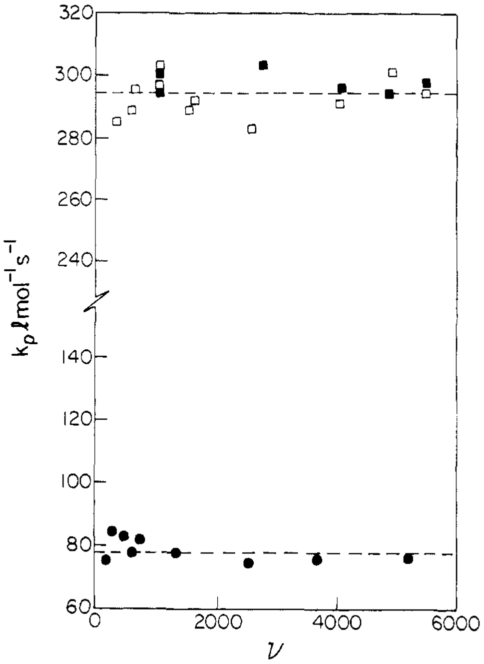

Figure 4. Plot of ν versus k_p for the bulk homopolymerizations of STY initiated with AIBN (●) and MMA initiated with AIBN (□) and BZ (■).

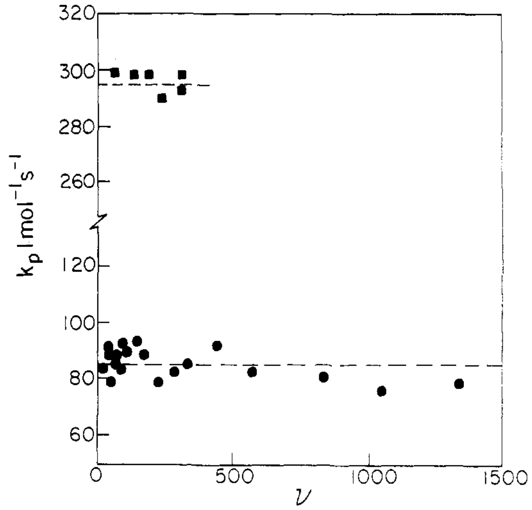

Figure 5. Plot of ν versus k_p for the homopolymerizations of STY diluted with EB (●) and MMA diluted with EA (■).

A Quantaray DCR2 Nd:YAG laser was used to generate light of wavelength 355 nm at a pulse energy of 35 mJ/pulse and a pulse width of 15 ns (at half-height). The beam was directed vertically from the laser, through the bottom of the sample holder and cell. The diameter of the beam was ≈9 mm, thus maximizing the reaction volume. The pulse repetition rate of the laser was triggered externally for a preset number of pulses by an IBM AT compatible computer, allowing t_f to be varied between 0.1 and 10 s.

The estimated radical concentration was 6.5×10^{-7} mol L^{-1} and the number of pulses required to generate 0.5–0.75% conversion was calculated by eq 1. Preliminary experiments gave conversions concurring with this estimate.

Analysis. The samples were analyzed on a Waters GPC-590 fitted with three μ-styragel columns (10^5, 10^3, 10^2 Å), using THF as eluant. The columns were maintained at 25 °C. Detection was by an online differential refractometer. The columns were calibrated by using both poly-STY and poly-MMA standards of narrow polydispersity. Examples of molecular weight distributions produced by the laser flash technique are shown in Figure 3. Radicals surviving the subsequent pulse to their generation contribute to secondary or tertiary peaks in some instances.

Results

Invoking values for ν_p, [M], and t_f into eq 2 leads to corresponding values for k_p. These are plotted in Figures

Table I
Experimental Conditions and Average k_p Values for the Homopolymerizations of STY and MMA

monomer	initiator	additive	[M], mol L^{-1}	t_f, s	ν_p	k_p, L mol^{-1} s^{-1}	Figure
STY	AIBN, 10^{-3} M, 5×10^{-3} M		8.66	0.22–8.02	142–5201	78	4
STY	AIBN, 10^{-2} M	EB	1.73–8.66	0.11	16–88	85	5
STY	AIBN, 10^{-3} M	EB	1.73–8.66	1.98	284–1339	80	5
				0.22	35–169	90	5
STY	AIBN, 5×10^{-3} M	MeOH	6.93–8.66	0.22	137–176	91	6
				0.99–1.21	696–752	84	6
STY	AIBN, 5×10^{-3} M	poly-STY	8.66	0.11–3.02	87–1934	84	6
MMA	AIBN, 10^{-3} M, 5×10^{-3} M		9.39	0.11–1.98	295–4970	292	4
MMA	BZ, 10^{-3} M, 5×10^{-3} M		9.39	0.38–1.98	1084–5507	297	4
MMA	AIBN, 10^{-3} M	EA	1.88–9.39	0.11	62–302	295	5
MMA	AIBN, 5×10^{-3} M	MeOH	7.51–9.39	0.22	510–619	304	6
				0.99–1.21	2623–2817	292	6
MMA	AIBN, 5×10^{-3} M	poly-STY	9.39	0.11–1.76	305–4970	296	6

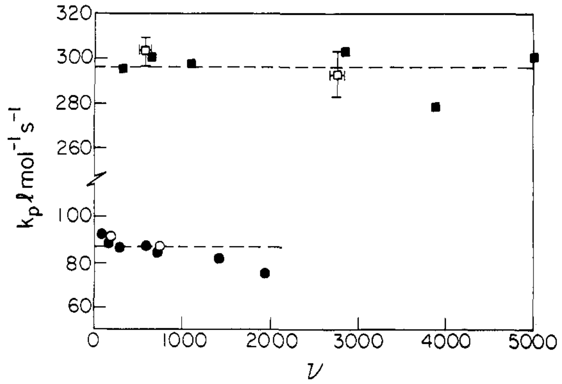

Figure 6. Plot of ν versus k_p for the homopolymerizations of STY in the presence of poly-STY (●) and diluted with MeOH (○) and MMA in the presence of poly-STY (■) and diluted with MeOH (□). See text for further explanation.

4–6 as a function of ν_p. Full details of the experiments are given in Table I.

Here the chain length (ν_p) generated between successive pulses was derived from the inflection point of the low molecular weight peak of the GPC chromatogram. Olaj et al.[2] have shown that the inflection point gives the best estimate of ν_p.

The results plotted in Figure 4 confirm that k_p for both MMA and STY is chain length independent. Moreover altering initiator concentration or type has no effect on the measured k_p.

The chain length independence of k_p is maintained down to low values of ν_p as shown in Figure 5. By use of fast repetition rates and systems diluted with EB and EA for STY and MMA, respectively, chain lengths as low as 16 were generated.

The addition of 0.5% w/v poly-STY of narrow polydispersity had no effect on the polymerization of MMA (Figure 6). However, there is a slight decrease in k_p for STY as chain length increases. This decrease in k_p is within the experimental scatter of the procedure and cannot be regarded as significant.

Diluting the monomers with MeOH (5–20% v/v) likewise had no effect on k_p, the MeOH acting merely as a diluent (Figure 6). These experiments were conducted so as to increase the time between pulses (t_f) to compensate for the dilution effect in order to generate similar chain lengths. For STY all five experiments at each chain length gave virtually identical results and could not be distinguished on the plot, for MMA the scatter is larger and is signified by the scatter bars marked on the plot.

Discussion

A chain length dependence of k_p has been generally dismissed[7] and indeed the constancy of k_p is implicit in many widely adopted models of polymerization and copolymerization. There may be a case for excepting the initial steps of propagation, as the inductive effects of the initiator fragment may interfere with the radical reactivity. The measured k_p values (typically 10^2–10^3 L mol^{-1} s^{-1}) also seem to preclude any diffusion control in the process at low conversions. However, emulsion polymerization studies by Ballard et al.[8] have indicated that k_p does decrease significantly at high weight fractions of polymer.

Despite this, there has been some published work which seems to contradict the chain length independence of k_p at low conversions for MMA[9,10] and more recently for ethylene polymerization[11] (this result may be an artifact of the adopted procedure[12,13]). An argument predicting a decrease in observed k_p with increasing chain length was alluded to by Flory.[14] The contention being that the reactive chain end of a large polymer molecule will be shielded by the coilings of its own chain. This would only be true in very dilute solutions where the chains exist independently. In concentrated solutions where the chains overlap, the environment of a reactive chain end will not alter with its chain size.

The experimental results reported here suggest that k_p is independent of chain length for STY and MMA even in dilute solution (conversions 0.5–0.75%). Inclusion of polymer or a poor solvent (MeOH) had no significant effect on k_p, indicating that neither a coil's dimensions nor its environment affect the radical reactivity.

The average values of k_p obtained here for STY and MMA at 25 °C are 78 ± 6 and 294 ± 9 L mol^{-1} s^{-1}, respectively. These average values are based on the experiments conducted in bulk with varied t_f (those represented in Figure 4). If those values obtained from solution polymerizations are included, then the average k_p values become for STY 84 ± 11 L mol s^{-1} and for MMA 295 ± 12 L mol s^{-1}. These are in excellent agreement with the values reported by Olaj et al. [3,15] at 25 °C of 80 and 299 L mol^{-1} s^{-1} for STY and MMA, respectively, using the same technique and also with the values given by O'Driscoll and Mahabadi[16] of 74 and 315 L mol^{-1} s^{-1} for STY and MMA, respectively, at 25 °C using the SIP reactor. The latter two values have now been established as benchmark values[5] by an IUPAC Working Party.

Regarding the technique itself, the assignment of k_p is sensitive to the GPC calibration. (In the course of this work, for example, it was found that small rounding errors in the calibration equation significantly affected results leading to an initial, erroneous conclusion that there was a chain length dependence of k_p). We find an error of 5–10% is associated with the assignment of ν_p using GPC. Also the external control of t_f is subject to a timer resolution of 0.054 s, thus resulting in larger errors at fast repetition rates. Nonetheless the reproducibility of the procedure indicates that it is an excellent method for determining k_p values.

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Registry No. MMA, 80-62-6; STY, 100-42-5.

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Kinetic Treatment of Sequence Distributions Occurring in Vinyl Polymerization According to Bernoulli and First- and Second-Order Markoff Processes

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ABSTRACT: Sets of kinetic differential equations corresponding to Bernoulli and to first- and second-order Markoff processes employed in the description of vinyl polymerizations are set up and solved, with appropriate initial conditions, in order to obtain expressions for the probabilities of finding various diads, triads, and tetrads in the product sequence structures. Since a non-steady-state stage exists, during which the configurational sequence structures of products change with polymerization parameters, for both first- and second-order Markoff processes, a simple experimental method for distinguishing first- and second-order Markoff processes from Bernoulli processes emerges: A plot of the sequence structures versus any polymerization parameter (such as monomer conversion) is characteristic of a Bernoulli process if it gives a horizontal straight line over the entire reaction process. Otherwise, it should likely be classified as a Markoff process. Experimental results for the polymerization of methyl methacrylate are utilized to illustrate this expectation.

1. Introduction

Sequence distribution and chain configuration in polymers are both of practical importance and theoretical interest. Much work on this problem has been carried out[1–6] since the pioneering paper by Bovey and Tiers[7] on the application of NMR to the study of the configurational sequence in poly(methyl methacrylate). Configuration sequences in polyolefins, however, depend upon their history of generation, with the consequence being that statistical theory can be applied to sequence distributions of vinyl polymers without consideration of the kinetics of the polymerization process only under stationary conditions. A kinetics study of the sequence distribution of vinyl polymers, based upon stationarity, has been carried out by Figni.[8] The same problem has been treated by one of the authors[9] in terms of kinetics without stationarity. Because the method was so complicated, only first-order Markoff processes could be included at that time. Using the simpler non-steady-state kinetics method developed later,[10] we have obtained exact solutions for the same problem from the Bernoulli process to the second-order Markoff process. As these results show that there are non-steady-state stages of Markoff processes of polymerization of vinyl monomer even in the case of instantaneous initiation, and that no such stages occur for Bernoulli processes, a simple method can be proposed for judging the polymerization mechanism.

2. Bernoulli Processes

If the configuration of any placement in vinyl polymers is independent of its previous placement, the polymerization generating these polymer chains is a Bernoulli process. Let m^* and m' represent the "living" and "dead" meso diad, and r^* and r' denote the "living" and "dead" racemic diad, with I and N^* indicating initiator and active monomer adjacent to initiator. The polymerization of vinyl polymers initiated instantaneously can be expressed by Figure 1, where only the living diads formed in the reaction