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Pressure Dependence of the Propagation Rate Coefficient k_p for Vinyl Acetate Polymerizations in Bulk and in Solution of Fluid CO_2

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ABSTRACT: The propagation kinetics of vinyl acetate (VAc) free-radical homopolymerization in bulk and in solution of 40 wt % CO_2 have been studied by the PLP−SEC method at pressures up to 1500 bar. The molecular weight distributions of the polymer samples show well-resolved pulsed-laser-induced structure with at least two, in most cases even three, distinct inflection points. At the p and T conditions of this work, no difference is seen in propagation rate coefficients, k_p, of VAc in solution of carbon dioxide and in bulk. The activation volume for k_p at 25 °C in both reaction media is $\Delta V^{\#} = -(10.2 \pm 0.9)$ cm^3 mol^{-1}.

Introduction

Supercritical carbon dioxide ($scCO_2$) has been demonstrated to be a promising alternate reaction medium for free-radical polymerization.[1] Thus far, most studies have focused on heterogeneous-phase polymerizations and on the development of new surfactants. Information on free-radical polymerizations in homogeneous-phase $scCO_2$ is scarce. DeSimone and co-workers showed that solution polymerizations of 1,1-dihydroperfluorooctyl acrylate (FOA) and siloxanes can be performed in CO_2.[2] Recently, it was shown that, in acrylate polymerizations, fairly high degrees of monomer conversion (~60%) can be reached in the homogeneous phase because of the cosolvent action of the monomer.[3] Restricting the molecular weights, even styrene polymerizations can be carried out up to considerable monomer conversions (up to 35%).[4,5]

Cloud point measurements by Rindfleisch et al.[6] revealed that poly(vinyl acetate) is remarkably soluble in CO_2. Thus, vinyl acetate (VAc) polymerizations in $scCO_2$ should be feasible up to high degrees of monomer conversion in the homogeneous phase. With respect to solution polymerizations in compressed fluid CO_2, it appeared interesting to investigate the pressure dependence of k_p. For comparison, k_p as a function of pressure has also been measured for polymerizations in the bulk. The temperature dependence of the bulk k_p value at ambient pressure has already been reported by Hutchinson et al.[7]

k_p is determined by the so-called PLP−SEC method, which combines pulsed-laser-initiated polymerization (PLP) with analysis of the resulting polymer by size-exclusion chromatography (SEC).[8] This procedure has been extensively used to determine k_p values for free-radical polymerizations in bulk and in conventional solvents and is recommended as the method of choice by the IUPAC Working Party on Modeling of Polymerisation Kinetics and Processes. Benchmark k_p data sets for styrene,[9] methyl methacrylate,[10] and alkyl methacrylate[11] bulk polymerizations have already been collated.

k_p is derived via eq 1 from the characteristic degree of polymerization, L_i, which is directly obtained from the molecular weight distribution (MWD).

$$L_i = ik_p c_M t_0 \quad i = 1, 2, 3, ... \tag{1}$$

where c_M is the monomer concentration and t_0 is the time between two successive laser pulses. As detailed elsewhere,[9] L_1 is best identified with the position of the inflection point on the low-molecular-weight side of the MWD peak maximum. To obtain reliable k_p values, the existence of a second or even third inflection point at degrees of polymerization around L_2 and L_3 is required. The occurrence of such higher-order inflection points serves as a consistency check of the PLP−SEC method.[9,12]

Experimental Section

Vinyl acetate (Fluka Chemie AG, 99% purity) was distilled over K_2CO_3 under reduced pressure to remove the inhibitor. The photoinitiator benzoin (Fluka Chemie AG, ≥99% purity), carbon dioxide (CO_2; grade 4.5, Messer Griesheim) tetrahydrofuran (THF; Fluka Chemie AG, 99.5% purity), methanol (Fluka Chemie AG, p.a.), and hydroquinone (Merck-Schuchardt, >99% purity) were used as supplied.

The experimental setup for the preparation of the reaction mixture has already been described elsewhere.[3] VAc concentrations for bulk experiments are calculated from the monomer densities, ρ_M, at the reaction conditions, The temperature dependence of ρ_M is reported in ref 13, but the variation of ρ_M with pressure is not known. It has been assumed that the reported compressibility of ethyl acetate[14] might also hold for VAc. Initial VAc concentrations for reaction mixtures with CO_2 at p and T are calculated from the known molar fractions of VAc and CO_2 under the assumption of a negligible excess volume of the mixture. The validity of this procedure has been demonstrated for butyl acrylate/CO_2 systems, where the estimated monomer concentration, c_M, is compared to c_M from quantitative spectroscopic measurements.[15]

The initial monomer concentration of each experiment is included in Table 1. The initial vinyl acetate concentration was around 11 mol L^{-1} for bulk polymerizations and around 7 mol L^{-1} for reactions in CO_2. The benzoin concentrations were between 1×10^{-3} and 5×10^{-3} mol L^{-1}. Benzoin decomposition was induced by excimer laser pulses (LPX 210i, Lambda

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Table 1. Polymerization Parameters and Experimental Results for Vinyl Acetate Polymerizations in Solution of CO_2 and in Bulk[a]

	T (°C)	p (bar)	ρ_M g cm^{-3}	c_M (mol L^{-1})	c_I (mmol L^{-1})	M_1 (g mol^{-1})	M_2 (g mol^{-1})	k_p (L mol^{-1} s^{-1})
bulk	22	1	0.929	10.8	1	31 800	62 800	3430
	22	1	0.929	10.8	1	33 900	67 100	3650
	22	500	0.963	11.2	1	40 100	75 000	4160
	22	1000	0.994	11.6	1	56 600	99 500	5700
	22	1500	1.023	11.9	1	72 800	132 700	7120
	22	1	0.929	10.8	2	32 800	62 800	3530
	22	1	0.929	10.8	2	32 900	62 400	3540
	22	1	0.929	10.8	2	33 400	63 700	3600
	22	500	0.963	11.2	2	42 200	77 400	4380
	22	500	0.963	11.2	2	37 200	69 000	3860
	22	750	0.979	11.4	2	44 800	82 200	4570
	22	750	0.979	11.4	2	44 400	79 600	4530
	22	1000	0.994	11.6	2	57 400	105 900	5770
	22	1000	0.994	11.6	2	50 900	92 000	5120
	22	1500	1.023	11.9	2	68 500	140 000	6700
	22	1500	1.023	11.9	2	66 500	134 000	6510
	22	1	0.929	10.8	5	32 100	73 100	3450
	22	1	0.929	10.8	5	31 300	69 500	3360
	22	500	0.963	11.2	5	39 400	81 700	4100
	22	1000	0.994	11.6	5	54 500	112 700	5480
	22	1000	0.994	11.6	5	55 300	110 400	5570
CO_2	23	1000	0.993	7.29	2	32 000	64 000	5100
	24	1000	0.992	7.28	2	33 500	64 000	5340
	26	200	0.938	6.43	5	22 000	39 600	3980
	27	200	0.936	6.43	5	23 300	39 900	4220
	26	500	0.958	6.88	5	27 500	50 900	4650
	24	500	0.961	6.89	5	26 700	48 400	4510
	26	1000	0.989	7.27	5	34 400	65 800	5490
	28	1500	1.015	7.53	5	45 800	80 900	7070
	24	1500	1.020	7.55	5	40 900	75 500	6300
	26	1500	1.017	7.54	5	44 100	80 900	6790

[a] T, temperature; p, pressure; ρ_M, monomer density (bulk); c_M, monomer concentration; c_I, initiator concentration; M_i ($i = 1, 2$), molecular mass at the first and second inflection points; k_p, propagation rate coefficient calculated from M_1.

Physik) at 351 nm with a laser pulse repetition rate of 100 Hz. The samples were subjected to laser pulsing for times sufficient to convert around 3% of the monomer into polymer. Monomer conversion was monitored by NIR spectroscopy in the region of the first C−H stretching overtones at around 6205 cm^{-1} after application of a sequence of laser pulses. The experimental details are listed in Table 1. After irradiation, the reaction mixture is depressurized, and the monomer/polymer mixture is collected. To prevent further polymerization and to precipitate the polymer, a mixture of hydroquinone and methanol is added.

Molecular weight distributions were determined by means of size-exclusion chromatography using a Waters 515 HPLC pump; Waters 2410 refractive index detector; PSS−SDV columns with nominal pore sizes of 10^5, 10^3, and 10^2 Å; and tetrahydrofuran (THF) at 35 °C as the eluent. The SEC setup was calibrated against polystyrene (PS) standards of narrow polydispersity (MW = 410−2 000 000) provided by Polymer Standards Service. Absolute molecular weights of the poly(vinyl acetate) samples were estimated via the principle of universal calibration[16] using the Mark−Houwink constants $K = 11.4 \times 10^{-5}$ dL mol^{-1} and $a = 0.716$ for PS, as well as $K = 22.4 \times 10^{-5}$ dL mol^{-1} and $a = 0.674$ for poly(vinyl acetate).[7]

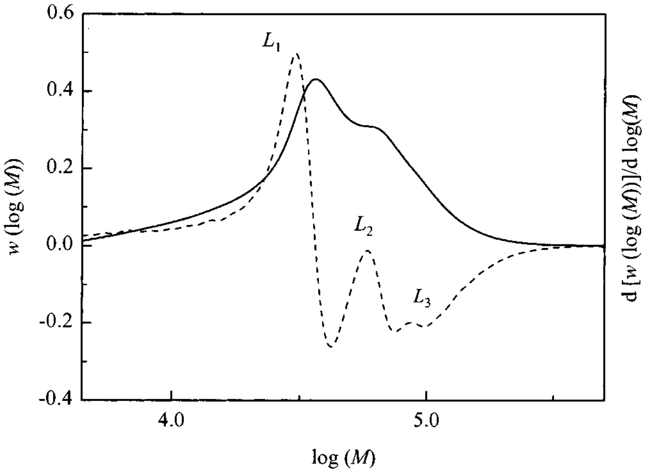

Figure 1. Polymer molecular weight distribution (full line) and associated derivative curve (dashed line) obtained from a VAc polymerization at 23 °C and 1000 bar in the presence of 40 wt % CO_2 ($c_I = 2$ mmol L^{-1}).

Results and Discussion

Figure 1 shows the MWD of poly(VAc) from a polymerization at 23 °C and 1000 bar in the presence of 40 wt % CO_2 (photoinitiator concentration $c_I = 2$ mmol L^{-1}). The dashed line represents the first derivative curve of the MWD, which clearly exhibits three maxima, marked L_1, L_2, and L_3, that correspond to inflection points of the original MWD. These inflection points are located at molecular weights that fulfill the consistency criteria $M_2 \approx 2M_1$ and $M_3 \approx 3M_1$ (see Table 1). The results in Table 1 demonstrate that initiator concentration has no influence on M_1 and thus no influence on k_p.

Via the Arrhenius activation energy, $E_A(k_p) = 20.5$ kJ mol^{-1} reported in ref 7, the k_p values of the present study, which were measured at temperatures between 22 and 28 °C, have been calculated for 25 °C.

According to eq 1, k_p values were calculated from the molecular weights at the first inflection point. The results are given in the last column of Table 1. The pressure dependence of k_p for vinyl acetate polymerizations in CO_2 solution and in the bulk is presented in

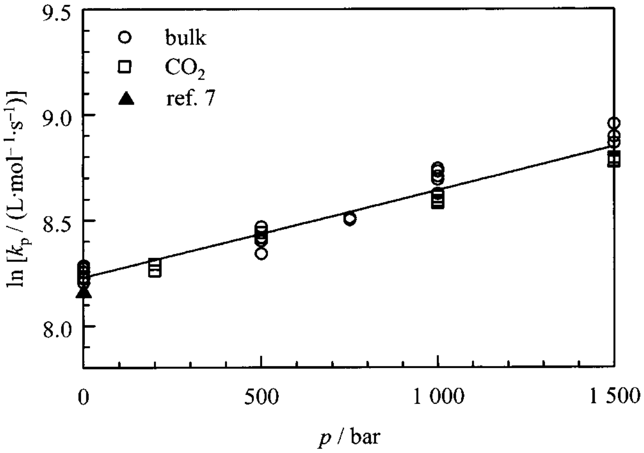

Figure 2. Pressure dependence of k_p for VAc polymerizations in carbon dioxide (squares) and in bulk (circles) at 25 °C. The fitted line (eq 2) is obtained by linear least-squares fitting of the combined data set. The triangle represents the literature value from ref 7.

Figure 2. The two data sets overlap, which indicates that there is no significant influence of CO_2 on the k_p value of VAc. It is gratifying to note that the mean value of k_p at ambient pressure and 22 °C, $\overline{k_p} = 3510$ L mol^{-1} s^{-1}, is in close agreement with the corresponding literature value provided by Hutchinson et al. of $k_p = 3230$ L mol^{-1} s^{-1}, which is considered to be accurate to within ±10%.[7]

The entire set of bulk and solution k_p data is well-represented by a single straight line. Linear least-squares fitting of the data set leads to the following expression for the pressure dependence of k_p at 25 °C

$$\ln k_p/(\mathrm{L\ mol^{-1}\ s^{-1}}) = (8.23 \pm 0.03) + (4.13 \pm 0.36) \times 10^{-4}(p/\mathrm{bar}) \quad (2)$$

$$\text{(25 °C, polymerizations in bulk and in 40 wt \% of CO}_2\text{)}$$

According to the relationship $\partial(\ln k_p)/\partial p = -\Delta V^{\#}/RT$, the activation volume $\Delta V^{\#}$ for k_p is determined to be $\Delta V^{\#}(k_p) = -(10.2 \pm 0.9)$ cm^3 mol^{-1}. This activation volume is close to the activation volumes for styrene, $\Delta V^{\#}(k_p) = -(12.1 \pm 1.1)$ cm^3 mol^{-1},[17] and acrylate polymerizations, $\Delta V^{\#}(k_p) = -(12 \pm 2)$ cm^3 mol^{-1},[18] whereas the activation volume of methacrylate is significantly lower, $\Delta V^{\#}(k_p) = -(16 \pm 2)$ cm^3 mol^{-1}.[19] This finding can be explained by the similarity in sterical demand of the transition states in VAc, styrene, and acrylate propagation. For methacrylates, with an additional CH_3 group at the double bond, a more congested transition state occurs, which is associated with a lower (more negative) activation volume.

In contrast to what is seen for VAc (Figure 2), a significant reduction in the propagation rate coefficient due to the presence of CO_2 has been observed with butyl acrylate (BA) and methyl methacrylate (MMA), amounting to about 40% at 40 wt % CO_2. Equation 1 shows that the experimentally accessible quantities are L_1 and the time t between two successive laser pulses. Thus, the experiment allows only for the determination of the product of k_p and c_M. Changes in k_pc_M might result from variations in k_p, in c_M, or in both of these quantities. Because of the invariance, within experimental accuracy, of the activation energy and activation volume seen for polymerizations in the bulk and in solutions of CO_2,[15] it seems reasonable to assume that the observed change in k_p is not an intrinsic kinetic effect. If it is not the kinetic coefficient that is varied by the presence of CO_2, the observed reduction of k_pc_M should be due to a lowering of local monomer concentrations in the vicinity of the propagating radical, $c_{M,loc}$, with respect to the overall monomer concentration, c_M. The effect on $c_{M,loc}$ is assumed to result from interactions between CO_2 and polar segments of the polymer, which compete with *intra*molecular interactions of polymer segments. Along these lines, the observed influence of CO_2 on the acrylate and methacrylate k_p values can be understood as resulting from stronger *intra*molecular interactions of polar segments as compared to segment−CO_2 interactions. Such an argument also explains why, in polymerizations of styrene, where dipolar *intra*segmental interactions are absent, the k_p values in solution with CO_2 and in bulk are almost identical,[5] although scCO_2 is only a poor solvent for polystyrene.[26]

One might expect that a variation in k_p would occur also for VAc polymerization in a solution of CO_2, as the polymer contains polar groups. The present study, however, shows that k_p for VAc polymerizations in the bulk and in solutions of CO_2 is the same. This result suggests that fluid CO_2 has a solvent quality for poly(vinyl acetate) that is similar to that of VAc. With the *intra*segmental interactions and the interactions between polar segments and monomer/CO_2 species being not too different in the bulk and in solution of CO_2, $c_{M,loc}$ should be similar in both cases, and thus, k_p as deduced from eq 1 should be the same for the two reaction media. The assumption of favorable interactions of poly(vinyl acetate) segments with CO_2 is supported by the phase behavior measurements of Rindfleisch et al.[6] From studies of the solubity of homopolymers in scCO_2, these authors found much higher cloud point pressures for poly(methyl acrylate) than for the remarkably soluble poly(VAc). These data are consistent with the observed difference in the influence of CO_2 on k_p for VAc and for methyl acrylate.[20] Whereas k_p(VAc) is not changed, k_p(MA) is reduced by 40% in the presence of 40 wt % CO_2.

Variations in the local monomer concentration are assumed to occur in systems where strong *intra*segmental interactions are operative and where the solvent quality of CO_2 (or of a conventional solvent) for the polymer differs significantly from the solvent quality of the monomer. To test the validity of this assumption, polymerizations of monomers with different polarities and associated polymers with different solubilities in CO_2 are currently under investigation in our laboratory.

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